THERMAL AND PHOTOLYTIC ACID-CATALYZED DECOMPOSITION OF TETRAMETHYL-2-TETRAZENE

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Thermal and Photolytic Acid-Catalysed Decomposition of Tetramethyltetrazene.

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ABSTRACT

THERMAL AND PHOTOLYTIC ACID-CATALYZED DECOMPOSITION OF TETRAMETHYL-2-TETRAZENE

Tetramethyl-2-tetrazene (TMT) was decomposed by concentrated sulfuric acid to yield dimethylaminium radicals. In the presence of toluene, this decomposition gave o-, m- and p-N,N-dimethyltoluidines (II-3) in a 15:10:75 ratio. TMT decomposition in trifluoroacetic acid generated a dimethylnitrenium ion which was intercepted by toluene to give o, m, and p II-3 in a 2:0:1 ratio. Irradiation of TMT in dilute acidic solutions was a clean source of $(CH_3)_2NH^{\cdot +}$ radicals which added in good yields to cyclohexene, norbornene, and 1,5-cyclooctadiene (COD) under either nitrogen or oxygen.

Under nitrogen, only a trace of 1,2 addition of $(CH_3)_2NH^{\cdot +}$ was observed. Addition of $(CH_3)_2NH^{\cdot +}$ to an olefin led to a β-dimethylammoniumalkyl radical (III-2). The III-2 radical derived from cyclohexene combined in a 1,2 fashion with a dimethylaminomethyl moiety to form cis and trans-2-dimethylaminomethyl-1-dimethylaminocyclohexane and the one derived from COD combined with this moiety in a transannular fashion to give 6-exo-dimethylaminomethyl-2-exo-dimethylamino-cis-bicyclo[3.3.0]octane. The III-2 radical derived from norbornene resulted in high yields of dimerization. In all three cases, products of hydrogen abstraction at the III-2 radical centre were also observed. Under oxygen, III-2 radicals combined with oxygen and led to hydroperoxides which were reduced to the corresponding β-dimethylaminoalcohols in good yields.

"Leaving Warsaw, the Germans demolished the city completely and subjected the people to mass annihilation... 'We want to have, once and for all, a friendly Poland as our neighbor'
- Stalin, 1945"

G.K. Zhukov
"Memoirs" (1969)

To my parents and
friends in Montreal

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They made it all possible.

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CHAPTER 1

INTRODUCTION

(A) GENERAL

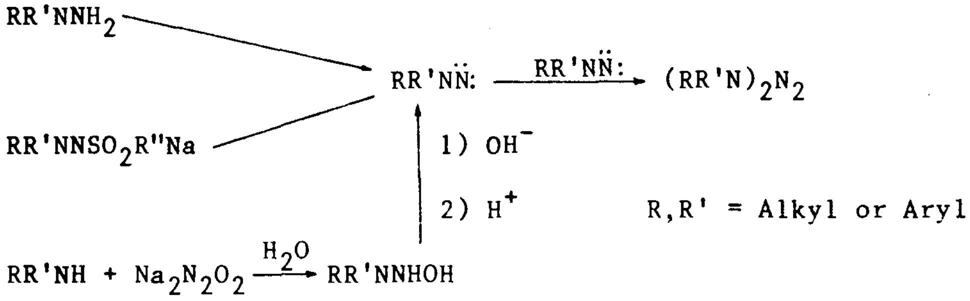
The major part of this work is devoted to the study of the thermal and photochemical decomposition of N,N,N',N'-tetramethyl-2-tetrazene (TMT) under acidic conditions. It was hoped to establish whether this decomposition proceeded via a nitrenium ion or an amino/aminium radical pathway through the reaction patterns with various substrates. Therefore, a brief survey of 2-tetrazene reactions is in order.

(B) CHEMISTRY OF TETRAALKYL-2-TETRAZENES

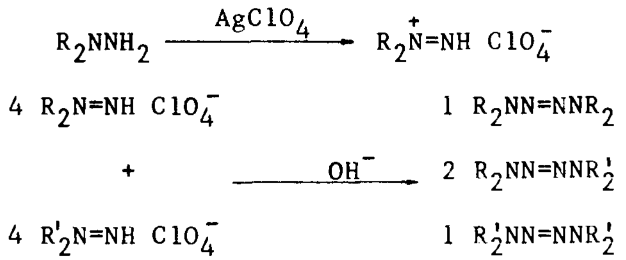
(1) Preparation

Tetrasubstituted-2-tetrazenes are readily prepared by the oxidation of 1,1-disubstituted hydrazines (1-12), decomposition of sulfonylhydrazine salts, or by the reaction of secondary amines with Angeli's salt (10) through a mechanism involving an aminonitrene (1,1-diazene) intermediate (Scheme I-1) (8-11). Perchlorate salts of these aminonitrenes have been isolated in the silver perchlorate oxidation of 1,1-disubstituted hydrazines and a statistical mixture of 2-tetrazenes was obtained when a mixture of two different dialkylaminonitrene salts was basified (Scheme I-2) (8). The aminonitrene intermediate has been further supported by the generation of a diazenium ion (I-9), which could be trapped by olefins (Scheme

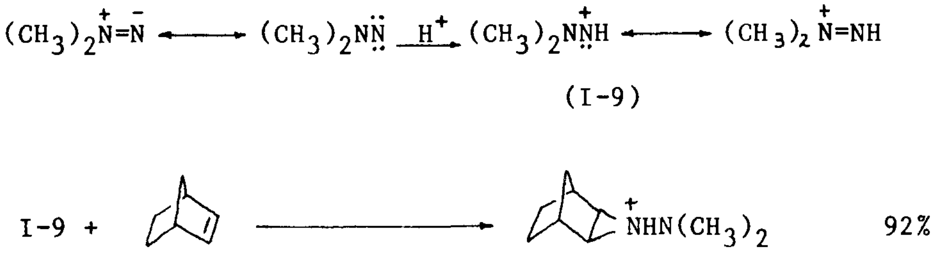
I-3), when the oxidation of 1,1-disubstituted hydrazines was allowed to take place in an acidic medium (9).



Scheme I-1

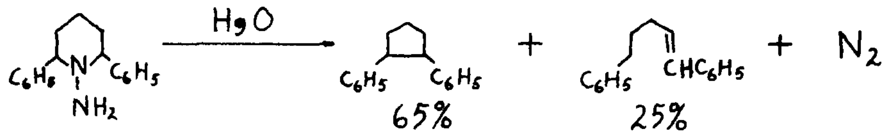


Scheme I-2



Scheme I-3

The stability of the intermediate aminonitrenes should be an important consideration when attempting a 2-tetrazene synthesis since they may react or decompose by completely different routes (Scheme I-4) giving little or no tetrazene (10). However, the best yields of TMT are obtained when 1,1-dimethylhydrazine (DMH) is oxidized under basic conditions with mercuric oxide (12).



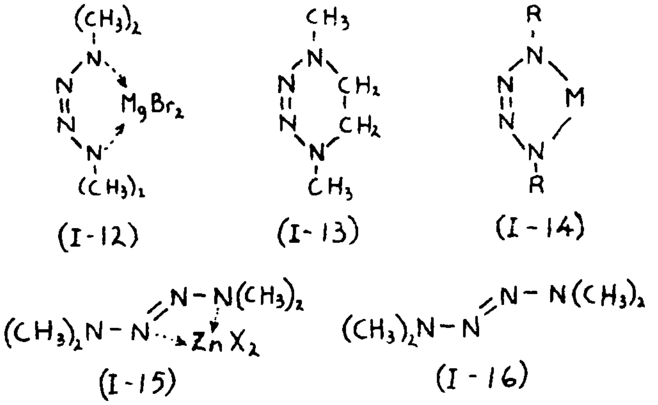
Scheme I-4

(2) Properties

a) Basic Properties: Tetralkyl-2-tetrazenes undergo protonation (2-7,13,14), alkylation and acylation (5,15-19) reactions quite readily as well as forming salts and complexes with a large variety of Lewis acids (1-7,20-23). TMT has a pK_b=7.8 (14,16,24,25,31), a first ionization potential (I.P.) of 7.96 eV (18), and an oxidation potential of $E_{1/2}{}^{o}$=0.42 volts in acetonitrile (16). The pK_2 has never been measured owing to rapid decomposition above pH=0 (13,14,16). However, at pH=0, TMT is still monoprotonated (14,16) and it may be still monoprotonated in solutions of H_o=-3 since no radicals are observed and the plot of decomposition rate versus acidity is linear indicating specific acid catalysis (14). I.r. and

Raman studies have shown a bond order N-N = 1.44 and N=N = 1.72, indicative of a delocalized π-nitrogen bonding (26). This is in agreement with a large π-conjugation along the nitrogen chain in recently synthesized 2-tetrazene ($H_2N-N=N-NH_2$) (27,28).

TMT exists mainly in the _trans_ configuration (6,7,29,30) having C_{2h} symmetry (26) as does 2-tetrazene (27,28). Some other isomer of TMT [probably the _cis_ (29)] with another C symmetry has been observed in trace amounts at room temperature (26). TMT has an u.v. absorption at λ_{max}=277 nm (ϵ=8.2x10^3) in ethanol (6,7,14,30,31) and λ_{max}=237 nm (ϵ=8.0x10^3) in dilute HCl (14,31). A _cis_ tetrazene, 1,4-dimethyl-1,4,5,6-hexahydro-1,2,3,4-tetrazine (I-13), has been shown to have a u.v. absorption at λ_{max}=268 nm (ϵ=6x10^3) in ethanol (30) (Figure I-1). Although X-ray analysis has shown 1,4-di-_para_-fluorophenyl- tetrazenecarbonyl_bis_(triphenylphosphine)-iridium(I) cation to be of _cis_ geometry (32) as in I-14, recent X-ray analysis of _bis_(perfluoro-phenyl) tetramethyltetrazene zinc(II) (I-15) reveals a _trans_ form in the single crystal, but the structure in solution is unclear (33).



(I-12) (I-13) (I-14) (I-15) (I-16)

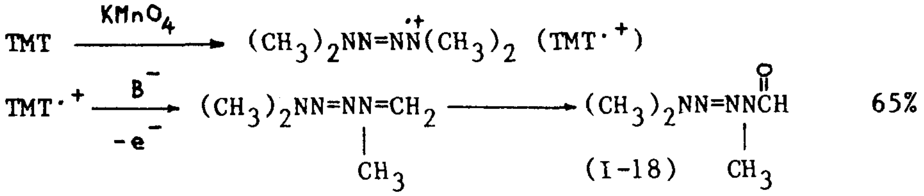
Figure I-1: Possible Configurations of TMT salts.

Low temperature n.m.r. studies of the TMT-HCl salt (I-16) have shown its structure to be in a <u>trans</u> configuration (34). Ingold has proposed that the photolytic decomposition of tetraisopropyl-2-tetrazene is due to the photolytic formation of the <u>cis</u> tetrazene from the <u>trans</u> followed by thermal decomposition of the <u>cis</u> tetrazene (29). Nelsen has pointed out that a conformational change is required prior to bond cleavage in the decomposition of substituted-1,4-diaryl-1,4-dimethyl-2- tetrazenes (35).

b) Oxidation: TMT can be easily oxidized [I.P.=7.96 eV (18)] to the TMT cation radical ($TMT^{\cdot +}$) by electrochemical oxidation (16,18,30,34,36); certain organic acids or acid anhydrides (16,19); oxidizing agents such as cerium(IV), $KMnO_4$, or potassium bromate (36,25); other radicals (18); or tetranitromethane (34,37). Thun and McBride have pointed out that $TMT^{\cdot +}$ would have an even greater

π-conjugation with respect to TMT, strengthening the N-N bond and thus preventing facile elimination of nitrogen (25).

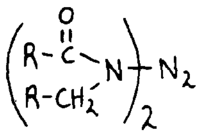
c) Stability: It has been possible to carry out reactions on the substituents of 2-tetrazenes. Permanganate oxidation of TMT, yielding carboxy derivative I-18, is believed to involve TMT$^{\cdot +}$ (Scheme I-5) (25). Further oxidation has made available a large class of compounds having amido moieties (Figure I-2) (25).



$$\text{TMT} \xrightarrow{KMnO_4} (CH_3)_2NN{=}N\overset{\cdot +}{N}(CH_3)_2 \quad (\text{TMT}^{\cdot +})$$

$$\text{TMT}^{\cdot +} \xrightarrow[-e^-]{B^-} (CH_3)_2NN{=}N\underset{CH_3}{N}{=}CH_2 \longrightarrow \underset{(\text{I-18})}{(CH_3)_2NN{=}N\underset{CH_3}{N}\overset{O}{\overset{\|}{C}}H} \quad 65\%$$

Scheme I-5

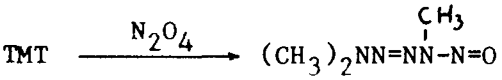


R = H, CH_3, CH_2CH_3, C_6H_5.

Figure I-2: Amido-tetrazenes

The reaction of TMT with dinitrogen tetroxide is suspected of proceeding through a free radical mechanism giving an N-nitroso compound (I-20) (Figure 1-3) (25). However, with

1,4-diphenyl-1,4-dimethyl-2-tetrazene, nitration of the aryl ring occurred (38).

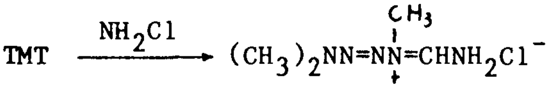


$$\mathrm{TMT} \xrightarrow{N_2O_4} (CH_3)_2NN{=}N\overset{CH_3}{N}{-}N{=}O$$

(I-20)

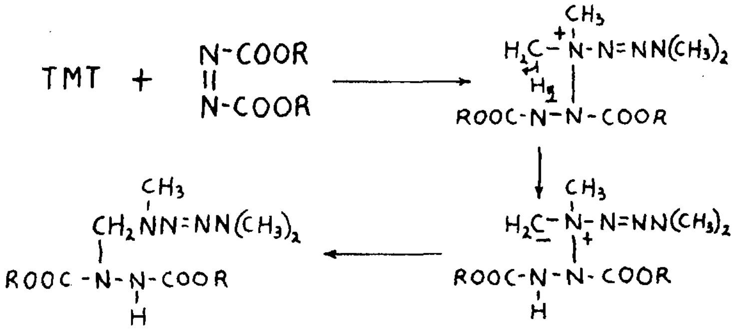
Figure I-3: Nitration of TMT

Reaction on the methyl group of TMT need not proceed via TMT$^{\cdot +}$ as in the case of the reaction of TMT and chloramine (Figure I-4) (39) and the reaction of TMT with azodicarboxylates (Scheme I-6) (40).



$$\mathrm{TMT} \xrightarrow{NH_2Cl} (CH_3)_2NN{=}N\overset{CH_3}{\underset{+}{N}}{=}CHNH_2Cl^-$$

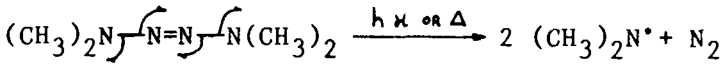
Figure I-4: Reaction of TMT and NH_2Cl.



Scheme I-6

The above reactions indicate the stability of the nitrogen linkage in TMT and TMT$^{\cdot +}$. Attempted Diels-Alder reactions with TMT have been unsuccessful (40,41).

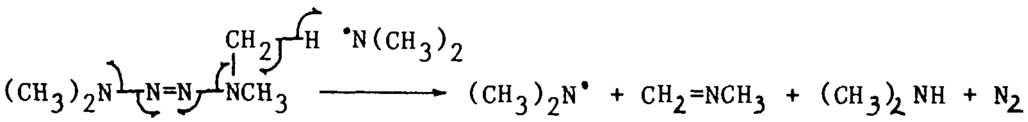
d) Decomposition: TMT has been used as an initiator in styrene and acrylonitrile polymerizations (42-46) but the mechanism may be complex (46). At temperatures above 100° (12,30,41,42,47-55) or during irradiation (29,30,52-57), TMT loses nitrogen homolytically generating two dimethylamino radicals (Scheme I-7). This loss of nitrogen has been proposed to occur, at least in photolysis, from the cis configuration of TMT (29). There is evidence for amino radical induced decomposition of TMT (Scheme I-8) if the concentration of TMT is above 0.2M (53). The fate of these amino radicals will be discussed below.



$$(CH_3)_2N{-}N{=}N{-}N(CH_3)_2 \xrightarrow{h\nu \text{ or } \Delta} 2\ (CH_3)_2N^{\bullet} + N_2$$

TMT (I-23)

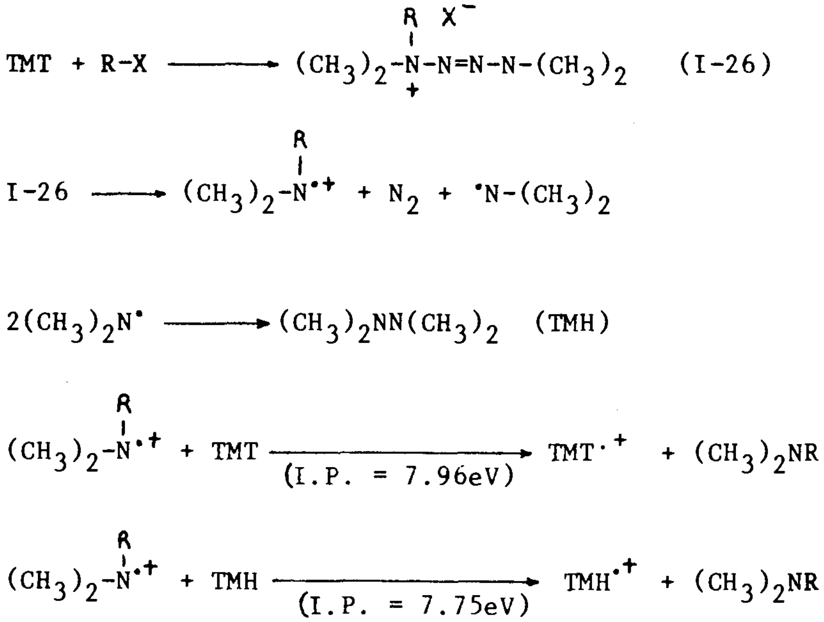
Scheme I-7



$$(CH_3)_2N{-}N{=}N{-}N(CH_3)_2 + {}^{\bullet}N(CH_3)_2 \longrightarrow (CH_3)_2N^{\bullet} + CH_2{=}NCH_3 + (CH_3)_2NH + N_2$$

Scheme I-8

Nitrogen is evolved in the alkylation or acylation of TMT (1-8,15,16,18) along with the generation of $TMT^{\cdot +}$ and tetramethylhydrazine (TMH) cation radical ($TMH^{\cdot +}$) (15,16,18). A general mechanism, involving free radicals, has been proposed for the formation of products arising from these reactions (Scheme I-9) (18).



$$TMT + R\text{-}X \longrightarrow (CH_3)_2\text{-}\overset{R\ X^-}{\underset{+}{N}}\text{-}N{=}N\text{-}N\text{-}(CH_3)_2 \qquad (I\text{-}26)$$

$$I\text{-}26 \longrightarrow (CH_3)_2\text{-}\overset{R}{N}^{\cdot +} + N_2 + {}^{\cdot}N\text{-}(CH_3)_2$$

$$2(CH_3)_2N^{\cdot} \longrightarrow (CH_3)_2NN(CH_3)_2 \quad (TMH)$$

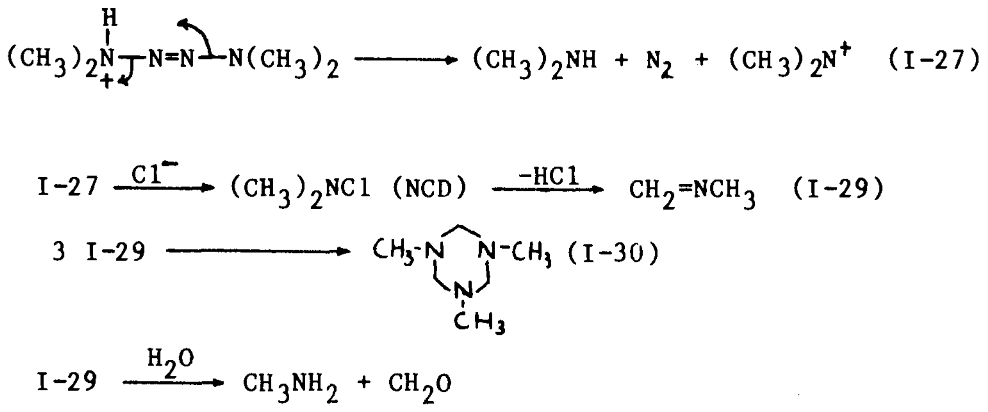
$$(CH_3)_2\text{-}\overset{R}{N}^{\cdot +} + TMT \xrightarrow[(I.P.\ =\ 7.96eV)]{} TMT^{\cdot +} + (CH_3)_2NR$$

$$(CH_3)_2\text{-}\overset{R}{N}^{\cdot +} + TMH \xrightarrow[(I.P.\ =\ 7.75eV)]{} TMH^{\cdot +} + (CH_3)_2NR$$

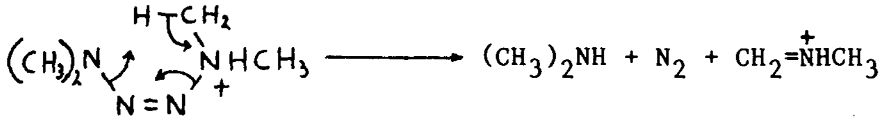
Scheme I-9

The loss of nitrogen in the dilute acid decomposition of TMT is not a free radical process (14). An equimolar ratio of nitrogen, methylamine, dimethylamine, and formaldehyde is produced per mole of TMT decomposed (1-5,13,14,58). The proposed mechanism of decomposition (Scheme I-10) is through an ionic process, possibly generating an intermediate dimethylnitrenium ion (I-27) which may combine with an anion (e.g. Cl^-) (3,4,14,58). The intermediate

N-chlorodimethylamine (NCD) has never been detected in the dilute hydrochloric acid decomposition of TMT (14). The imine I-29 may either form the trimer I-30 or hydrolyze to methylamine and formaldehyde (14). An alternate mechanism has been proposed to account for the lack of choramine formation analogous to the reaction of TMT with azodicarboxylates (Scheme I-11) (40).



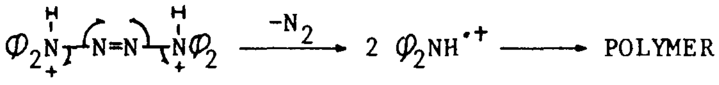
Scheme I-10



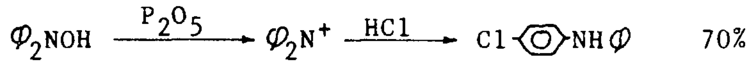
Scheme I-11

If the concentration of TMT in dilute aqueous acids (such as HCl, $HClO_4$, H_2SO_4) is raised above 0.2M, $TMT^{\cdot +}$ is formed (14). No mechanism for the formation of $TMT^{\cdot +}$, under these conditions, has been given.

If strong acids are used (e.g.concentrated H_2SO_4), the decomposition may proceed through a free radical mechanism (13,14). Two diphenylaminium radicals are generated by the homolytic loss of nitrogen from diprotonated tetraphenyl-2-tetrazene (TPT) in concentrated H_2SO_4 to give a polymeric material (Scheme I-12) (59). No polymer was formed when TPT was decomposed in hydrochloric acid; however, the products were not identified (59). It is possible that in weaker acids TPT decomposes via a nitrenium ion such as is formed by the action of P_2O_5 on diphenyl hydroxylamine (Scheme I-13) (59).



Scheme I-12



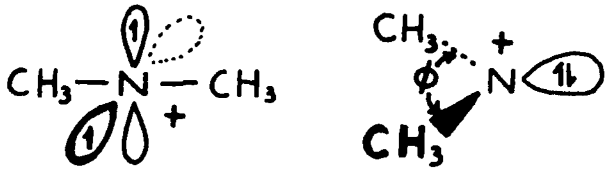
Scheme I-13

The action of concentrated H_2SO_4 on TMT should generate dimethylaminium radicals in an analogous manner to TPT. Dimethylamine is more basic than diphenylamine (60); therefore, TMT would be expected to be diprotonated more efficiently in concentrated H_2SO_4 than TPT. Since TMT is monoprotonated in acidic solutions up to H_o=-3 (14), the question remains whether a dimethylnitrenium ion (I-27) is generated in the weak acid decomposition of TMT.

(C) NITRENIUM IONS

The concept of nitrenium ion intermediates is well documented (11, 61-66). Although the generation of nitrenium ions in the unsaturated N-chloramine intramolecular cyclization reactions has been both supported (61-64,69,70) and discounted (66-68), their possible generation in tetrazene acid decomposition through an ionic mechanism (3-5,13,14,58) has never been substantiated or disproved.

If a dimethylnitrenium ion (I-27, Scheme I-10) is formed in the dilute acid decomposition of TMT, it could exist in either a triplet (I-27a) or a singlet (I-27b) electronic state (Figure I-5) (61,65,66,71,72). INDO calculations on the low lying singlet and triplet electronic states of I-27 indicate the triplet I-27a to be linear and of a lower energy (by 26 kcal mole^{-1}) than the bent singlet I-27b (ϕ = 122°) (71). The energy difference between I-27a and I-27b may be even larger (72).



I-27a I-27b

Figure I-5: The Dimethylnitrenium Ion (I-27)

A singlet nitrenium ion would be expected to react in a similar manner to a singlet carbene (73) or nitrene (74,75), where bond insertion and stereoselective olefin addition predominate (61-66). A triplet nitrenium ion would show similar reactivity to triplet carbenes or nitrenes (mainly hydrogen abstraction) (61-66). One would further expect both species to undergo electrophilic aromatic substitution similar to free nitronium (76-79) or isopropyl cations (80). However, a rapid rearrangement of I-27 to a protonated imine I-29a, similar to the rearrangement in methyl nitrene (82) or isopropyl cation (81), is also expected (Figure I-6).

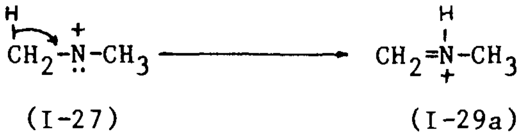


Figure I-6: Rearrangement of I-27

(D) AMINO RADICALS

The products of the intermediate dimethylamino radicals generated in the photolysis or thermolysis of TMT (see above) are TMH [not necessarily arising from geminate pair recombination (55)], imine I-29 or imine trimer I-30, and N,N,N',N'-tetramethylmethylenediamine (12,29,47-52). Dialkylamino radicals can also be produced by irradiation of dialkyl- or trialkylamines (83,85,91-94) or tetraalkylhydrazines (83,85).

These amino radicals are not efficient dehydrogenating agents below 100° (41,48,51-54,84,85) and fail to add intermolecularly to olefins at room temperature (53-55,96). An activation energy of 35-40 kcal/mole has been calculated for the theoretical addition of amino radical $\cdot NH_2$ to ethylene (96). Addition of dimethylamino radicals to ethylene at 127-175° occurs in good yields (48), and some addition to anthracene has been reported (41); however, no addition has been observed to occur with cyclohexene, norbornene (53,54,96), and nonene (48). Products reported as resulting from the addition of amino radicals to α-methylstyrene (42,48) may occur by another route (90, note 14). Electron withdrawing substituents, capable of reducing the nonbonding electron density at the nitrogen, lead to a decrease in the activation energy needed for addition (96); thus, difluoroamino (97) and bistrifluoromethylamino (98) radicals are capable of adding to olefins in good yields.

Although photolysis of di- and trialkylamines in benzene gives amine addition products (91,92), no addition or aromatic substitution occurred when TMT was thermolyzed at 145-150° in the presence of aromatic substrates (51,84).

TMT photolysis at or below room temperature in the presence of olefins is expected to give amino radical combination and disproportionation reactions only (96). However, if amino radicals are protonated (Figure I-7) or complexed with metal ions, they lead to highly reactive species (see below).

$$(CH_3)_2\overset{\bullet+}{N}\text{-}H \rightleftharpoons (CH_3)_2N^{\bullet} + H^{+} \qquad pK_a = 6.5\text{-}7.5 \quad (94,95)$$

Figure I-7: Protonation of $(CH_3)_2N^{\bullet}$

E) AMINIUM RADICALS

The formation and reactions (hydrogen abstraction, electrophilic aromatic substitution, and addition to olefins) of aminium radicals have been investigated and well documented in our group (99-108) and elsewhere (see e.g.: 70,85,109-114). However, it is necessary to elaborate on certain aspects of dimethylaminium radical reactivity pertinent to the results described in this thesis.

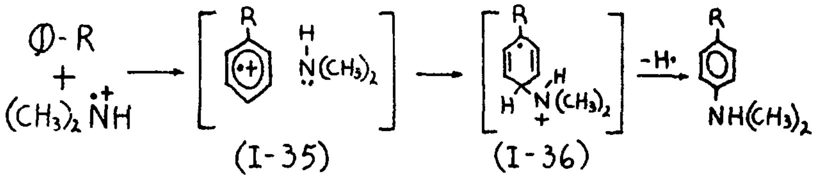
Electrophilic aromatic substitution by aminium radical intermediates generated in strongly acidic media from N-chloramines (109,113-123) has been shown to be complicated by another mechanism. The mechanism proposed by Kovacic (114) involving ionic chloramine addition followed by HCl elimination has been used to explain the high yield of <u>meta</u>-N,N-dimethyltoluidine formed in some reactions by the amination of toluene by NCD under strongly acidic conditions (Table I-1).

Minisci is confident that this mechanism is unlikely to occur in aromatic substitution of toluene by NCD in the ferrous lactate

Table I-1: Toluidine Isomer Ratios From NCD.

No.	Method	T°C	$(CH_3)_2NC_6H_4CH_3$ ortho:meta:para	%Yield	Ref.
1	$AlCl_3/RNO_2$	80	14 : 27 : 59	54	123
2	$h\nu/H_2SO_4$	80	9 : 53 : 38	68	122
3	Na_2SO_4/H_2SO_4	80	9 : 53 : 38	45	121
4	$CuCl/H_2SO_4$	80	21 : 46 : 33	--	121
5	$CuCl/H_2SO_4$	75	17.4:41.8:40.8	--	117
6	$CuCl/H_2SO_4$	40	18 : 13 : 69	--	117
7	$CuCl/H_2SO_4/CH_3COOH$	40	10.9:37.5:57.6	--	117
8	$CuCl/H_2SO_4$	10	18.8: 5.4:75.8	--	117
9	$TiCl_3/H_2SO_4$	40	8.3:36.9:54.7	--	117
10	$FeCl_2/H_2SO_4$	40	9.6:43.6:46.8	--	117
11	$FeCl_2/H_2SO_4$	30	9.6:54.2:36.2	82	116
12	FeII lactate/H_2SO_4/ RNO_2	20	5.6:22.6:71.8	--	115

initiated decomposition in H_2SO_4-nitromethane (No.12, Table I-1) (115). The mechanism of a primary charge transfer (CT) complex (I-35) between $(CH_3)_2NH^{\cdot +}$ and an aromatic substrate followed by a σ-type intermediate (I-36) is invoked to explain the selectivity and reactivity of $(CH_3)_2NH^{\cdot +}$ (Scheme I-14) (115). It is proposed here that a linear energy relationship between the ionization potential (I.P.) of the aromatic substrate (126) and the log of its relative rate of amination is expected if I-35 resembles the transition state (124,125). Indeed, if this is done (Figure I-8, Table I-2), a good correlation is attained in the series benzene, toluene, o-xylene, biphenyl, and anisole. The anomaly of isopropyl- and t-butylbenzene is explained in terms of steric and inductive effects involved in the transition state (115). Both bromo- and chlorobenzene also undergo halogen elimination leading to dimethylaniline (118) (Scheme I-15), accounting for the large deviation of these observed in Figure I-8 because the formation of dimethylaniline was not included in the calculation of the relative rates (118).



Scheme I-14

Table I-2: Ionization potentials (I.P.) and relative rates of amination by $(CH_3)_2NH^{\cdot +}$ of various aromatics.

No.	Aromatic Substrate	I.P. (eV) (126)	Relative Rate	Ref.
1	C_6H_6	9.25	1	115
2	C_6H_5Cl	9.07	ca. 0.1	118
3	C_6H_5Br	8.98	ca. 0.1	118
4	$C_6H_5CH_3$	8.82	11.8	115
5	$C_6H_5CH(CH_3)_2$	8.70	9.3	115
6	$C_6H_5C(CH_3)_3$	8.68	5.3	115
7	o-$C_6H_4(CH_3)_2$	8.56	78.8	115
8	C_6H_5-C_6H_5	8.27	200	115
9	C_6H_5-O-CH_3	8.22	>200	119

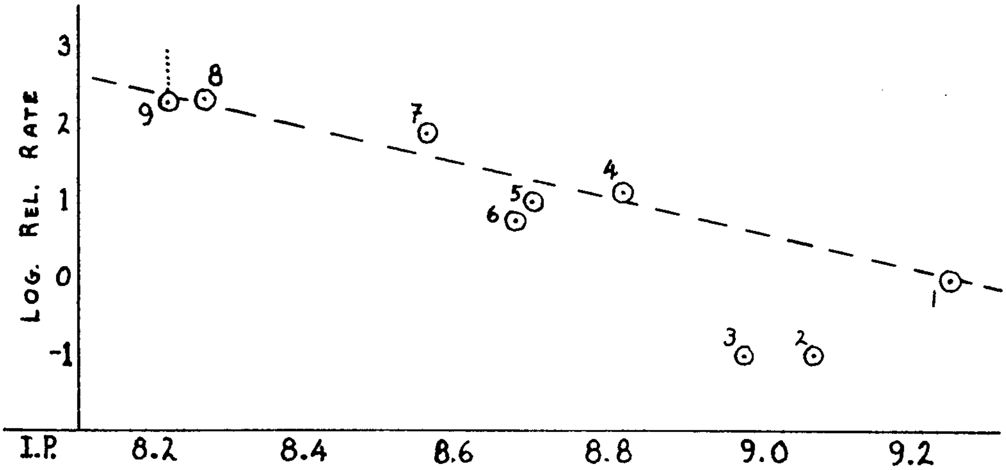
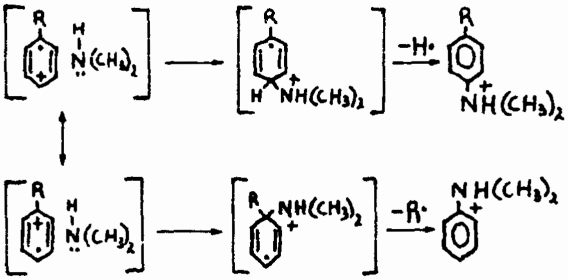


Figure I-8 : Plot of I.P. vs. relative rate of amination.



Scheme I-15

As yet, no satisfactory explanation has been given for the fact that benzylic abstraction increases and ring amination decreases with decreasing acidity from concentrated H_2SO_4 (100% amination) to acetic acid (100% abstraction) (109,116,127). It may be that in less acidic media, no charge transfer occurs. No correlation of I.P. of some substituted toluenes vs. the log of the rate of formation of the corresponding benzyl chlorides from Neale's work (127) could be made. Another explanation may be that the CT complex I-35 eliminates a proton and the reaction between the resulting benzyl radical and an N-chloramine is rate determining in benzyl chloride formation.

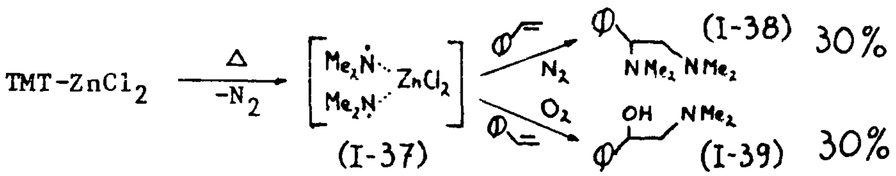
Ingold has proposed the formation of a nitrenium ion from the disproportionation of two aminium radicals (128). However, if a nitrenium ion did participate in the electrophilic substitution of toluene, an ortho:meta:para ratio of toluidines similar to the ratio of nitrotoluenes obtained in toluene nitration by a nitronium ion [2:1, ortho:para, little or no meta (76-79)] or that in the alkylation of toluene by an isopropyl cation [3:1:2, ortho:meta:para (see reference

80, Table 2, no.63)] should be expected because of the formal positive charge on the nitrenium ion (see above). Minisci's mechanism (Scheme I-14), involving direct participation of the aminium radical, is the best explanation of the results in reference 115 to date. Dimethylaminium radicals generated from TMT decomposition should give similar results in the presence of toluene and H_2SO_4.

F) METAL ION COMPLEXES OF AMINO RADICALS

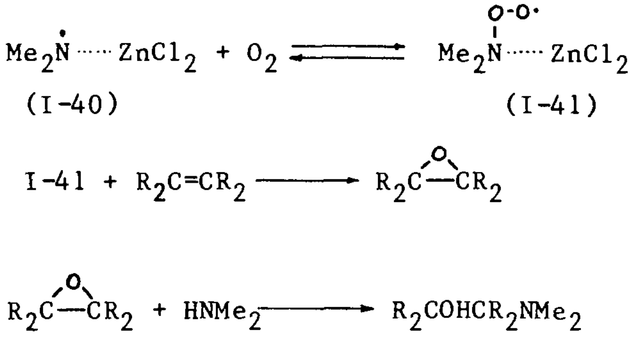
Under neutral conditions, treatment of N-chloramines with metal salts has been proposed to produce complexed amino radicals which undergo similar reactions to aminium radicals but are more selective in hydrogen abstraction and olefin addition reactions (70,110,113).

TMT complexes such as I-12 or I-15 (see above) may produce amino radicals on decomposition (20-23,33,129,130). Michejda and Campbell originally proposed that the decomposition of the zinc chloride-TMT complex gave a bis-dimethylamino diradical (I-37) which could be capable of adding to certain olefins giving diamino compounds (I-38) under nitrogen and amino alcohols (I-39) under oxygen (Scheme I-16) (129). No addition products were obtained with cyclohexene under either gas.



Scheme I-16

The diradical I-37 has been ruled out as a possible intermediate on the basis of recent X-ray analyses (33,130) which show a trans geometry of TMT in I-15. This geometry may account for the formation of methylazide in the TMT-aluminium complex decompositions (20). As a result, a single complexed amino radical (I-40) has been recently proposed as the intermediate leading to I-38 and I-39 (130). The formation of epoxides (5-10% yields) may account for some of product I-39 when TMT-$ZnCl_2$ is decomposed under oxygen (Scheme I-17) (130). Peroxyaminoradicals are highly unstable species, decomposing to nitroxyl radicals quite readily (29,128), and may form epoxides as described (130). TMT decomposition in the presence of metal ions will not be investigated in this thesis as the work is in progress elsewhere (130).



$$Me_2\dot{N}\cdots ZnCl_2 + O_2 \rightleftharpoons Me_2\overset{O-O\cdot}{\overset{|}{N}}\cdots ZnCl_2$$

(I-40) (I-41)

$$I\text{-}41 + R_2C{=}CR_2 \longrightarrow R_2\overset{\;O}{C\text{—}C}R_2$$

$$R_2\overset{\;O}{C\text{—}C}R_2 + HNMe_2 \longrightarrow R_2COHCR_2NMe_2$$

Scheme I-17

CHAPTER II

RESULTS*

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*The yields are based upon one mole TMT giving one mole of products or 1/3 mole of imine trimer I-30.

A) N.M.R. STUDY OF ACID CATALYZED TMT DECOMPOSITION

When TMT was dissolved in concentrated H_2SO_4 at 0^o, it gave a deep yellow color and much gas evolution. The mixture was quickly cooled to -70^o. The n.m.r. recorded at -20^o (Figure II-1a), 30 minutes after mixing, showed the n.m.r. signal at $\tau 7.10$(t) for dimethylammonium and at $\tau 6.27$(dt) and 1.93(m) for N-methyl-methyleneimonium (I-29a) cations in a 1:1 ratio. It also showed a small singlet at $\tau 6.40$. When the solution was warmed to room temperature (Figure II-1b) no detectable increase in either the dimethylamine or imine I-29a signals was observed; however, the singlet at $\tau 6.40$ had increased, and the resolution of all peaks had improved.

The origin of the new signal at $\tau 6.40$ was found to be due to the methyl signals of di-protonated TMH. A solution of TMH in H_2SO_4 at 20^o exhibited a signal at $\tau 6.40$** using $(CH_3)_2NH_2^+$ as an internal standard (Figure II-1d). The TMH-$2H^+$ signal appeared to decrease slightly on standing one day at room temperature (Figure II-1c). This solution, when examined by e.s.r. (see below), showed a poorly resolved series of multiplets for $TMT^{\cdot +}$.

**When this solution was heated at 110^o for one hour, the signal at $\tau 6.40$ was replaced by those of $(CH_3)_2NH_2^+$ and the imine I-29a.

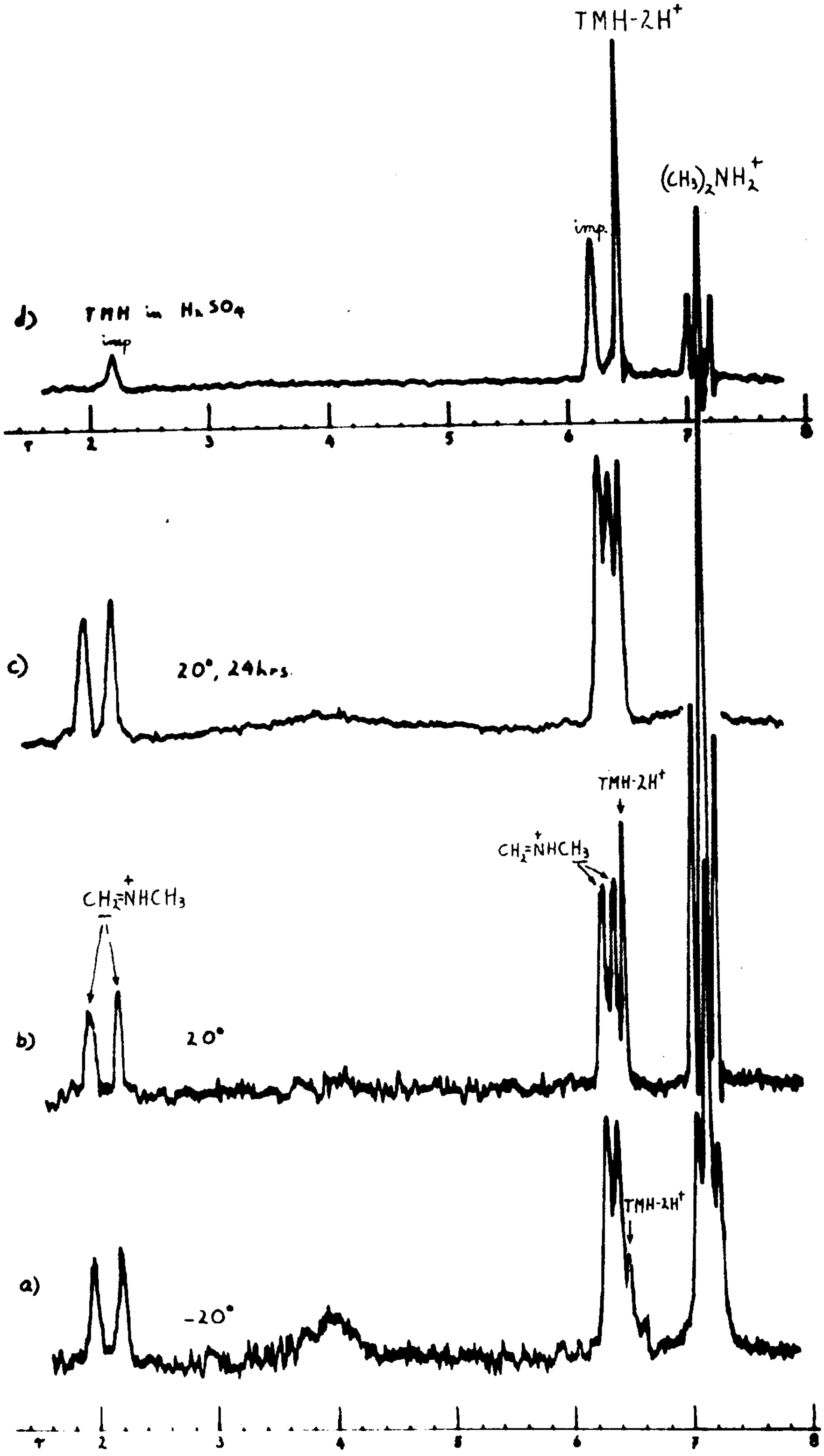


Figure II-1: a-c) N.M.R. study of TMT decomposition in H_2SO_4, d) TMH in H_2SO_4

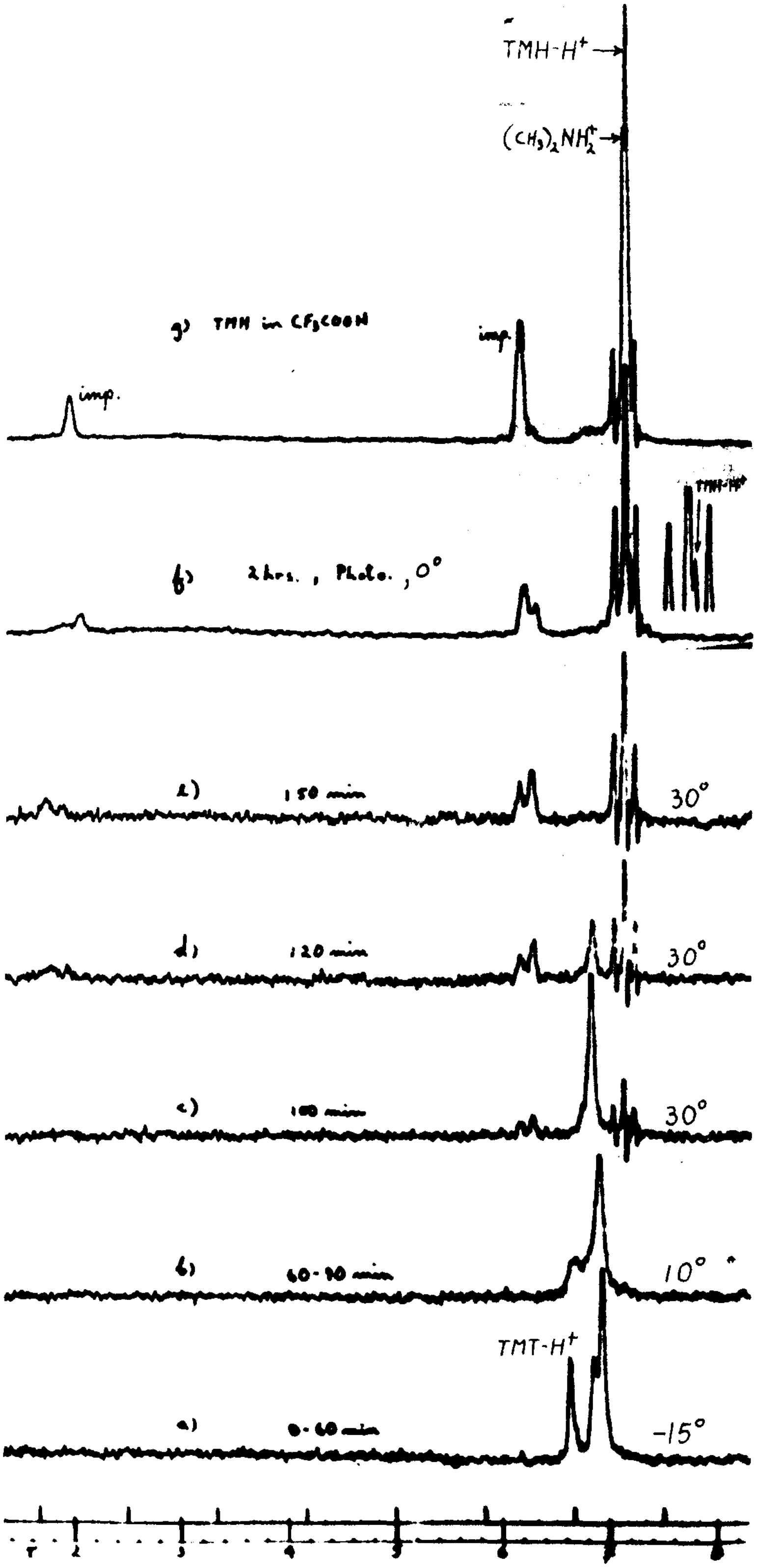


Figure II-2: N.M.R. study of TMT decomposition in CF_3COOH
a-e) thermal, f) photolysis, g) TMH

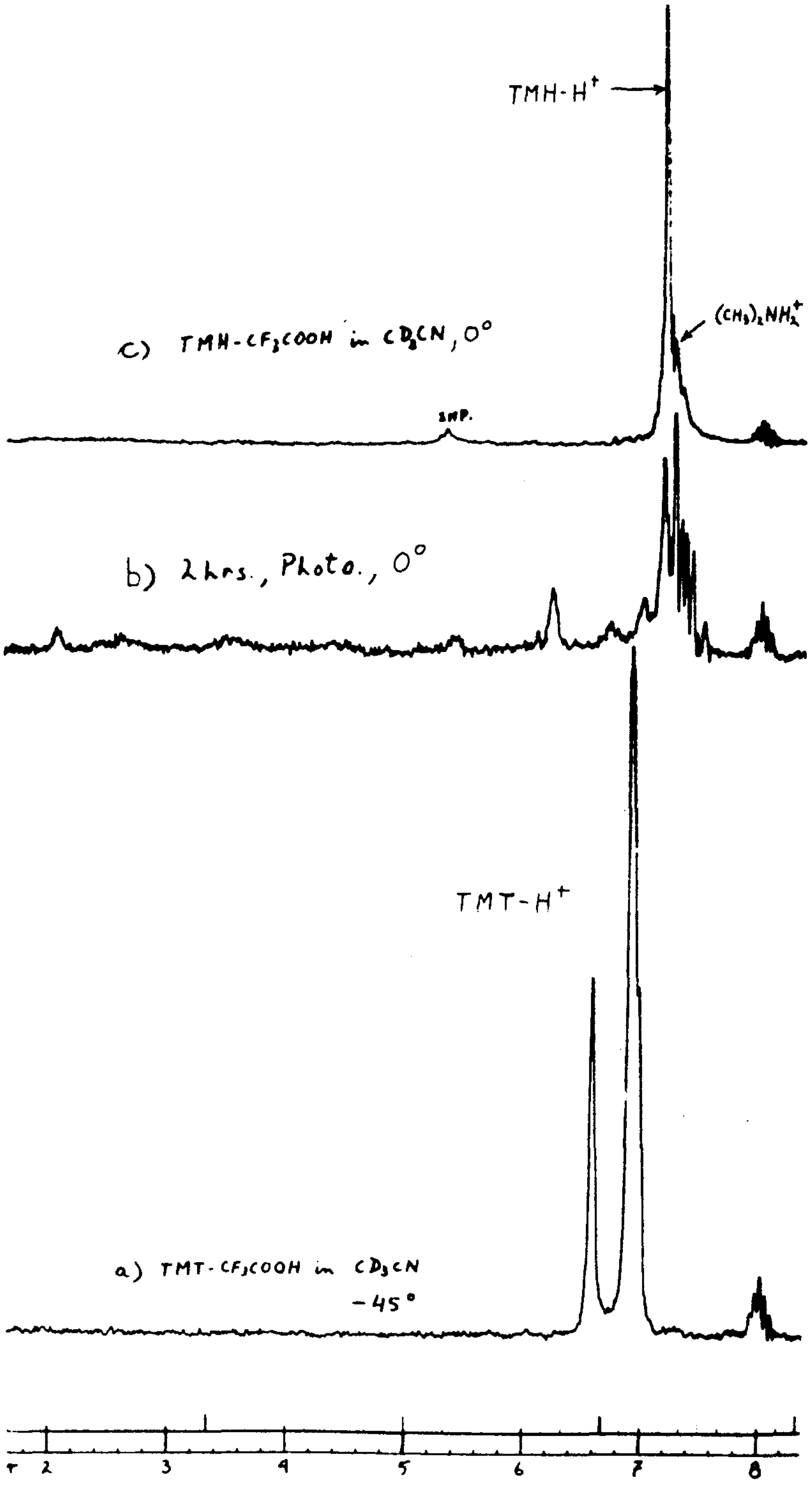


Figure II-3: N.M.R. of TMT in 1M CF_3COOH in CD_3CN, a) before and b) after photolysis, c) TMH

When TMT was dissolved in CF_3COOH at -15°, the N-methyl n.m.r. signals were split into three singlets at τ6.62, 6.82, and 6.92 in a ratio of 1:1:2 (Figure II-2). A similar splitting has been observed for the TMT-HCl salt in $CDCl_3$ and has been assigned to $TMT\text{-}H^+$ <u>trans</u> configuration (34). There was no sign of decay of this $TMT\text{-}H^+$ signal at -15° over one hour (Figure II-1a). Warming the solution to 10° broadened the $TMT\text{-}H^+$ signal, but there was again no sign of decomposition within 30 minutes (Figure II-2b). On warming to 30°, the $TMT\text{-}H^+$ signal coalesced to a singlet at τ6.78 (Figure II-2c) and decayed within 50 minutes to be replaced by the n.m.r. signal at τ7.10(t) for dimethylamine and at τ6.25(m) and 1.90(m) for imine I-29a (Figure II-2e). The signals at τ7.10 and 6.25 were in a 2:1 ratio indicating an equimolar yield of these compounds.

Photolysis of the $TMT\text{-}H^+$ solution in CF_3COOH at 0° (Figure II-2f) showed the n.m.r. signal at τ7.10(t) for $(CH_3)_2NH_2^+$ and at τ6.25 and 2.10 for the imine I-29a. The latter signals were slightly different in shape to that observed above and might be due to a product other than I-29a. The signal for $(CH_3)_2NH_2^+$ was overlapped with that of $TMH\text{-}H^+$ at τ7.14 (see Figure II-2g). The ratio of the $(CH_3)_2NH_2^+$ signal at τ7.10 to that at τ6.25 was about 3.5:1.

When TMT was dissolved into acetonitrile containing CF_3COOH and cooled to -40°, the $TMT\text{-}H^+$ appeared as three singlets at τ6.58, 6.88, and 6.96 in a ratio of 1:2:1 (Figure II-3a). Irradiation of this solution at 0^o gave rise to a complex n.m.r. spectrum (Figure II-3b) which could not be assigned.

B) THE E.S.R. STUDY OF ACID CATALYZED TMT DECOMPOSITION

The e.s.r. signal of $TMT^{\cdot +}$ was generated at room temperature in concentrated H_2SO_4 (Figure II-4). It consisted of a series of poorly resolved bands having a splitting of ca.10G and g-factor of 2.0040 ± 0.0005 for $TMT^{\cdot +}$ (34,37). The signal decayed slowly over several days and no other signal was observed.

A better resolved $TMT^{\cdot +}$ signal could be generated in a CF_3COOH- acetonitrile solution at room temperature (Figure II-5) or at -45^o (see Figure II-8a). The coupling constants of $a_N(2,3N)=1.15$, $a_N(1,4N)=10.85$, $a_H(6H)=10.40$, $a_H(6H)=10.60$ G and the g-factor of 2.0040 ± 0.0005 obtained from these spectra agree favourably with those reported elsewhere for $TMT^{\cdot +}$ (34,37). At -45^o, this signal showed very little decay over several hours but, at room temperture, it decayed over two hours with no appearance of any other signal.

TMT decomposition in a solution of CF_3COOH in benzene formed two liquid phases. The top benzene phase was examined by e.s.r. at room temperaure and showed a $TMT^{\cdot +}$ signal superimposed with another

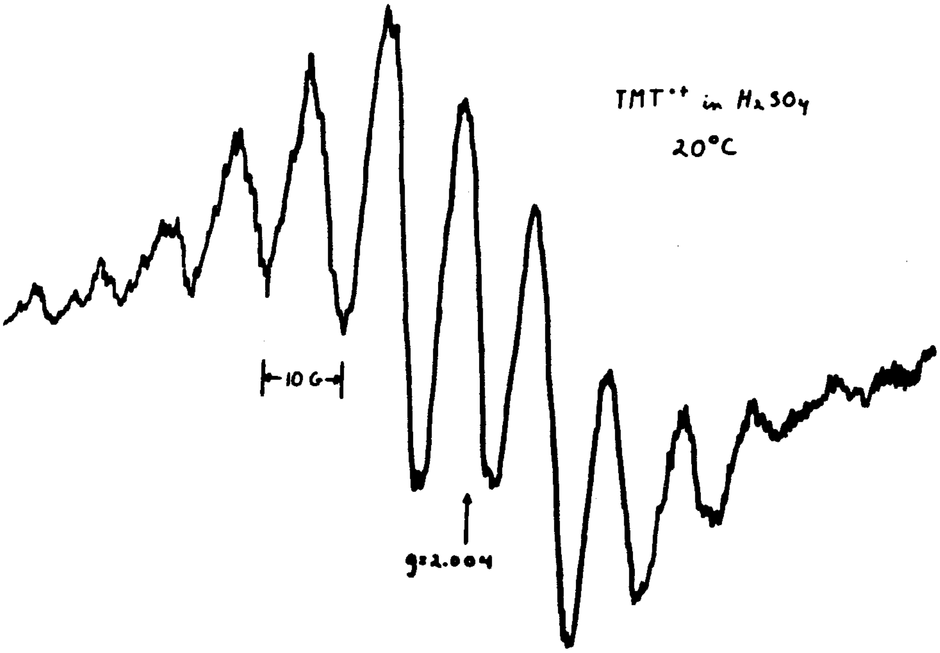


Figure II-4: TMT$^{\cdot +}$ E.S.R. in H_2SO_4 at 20°

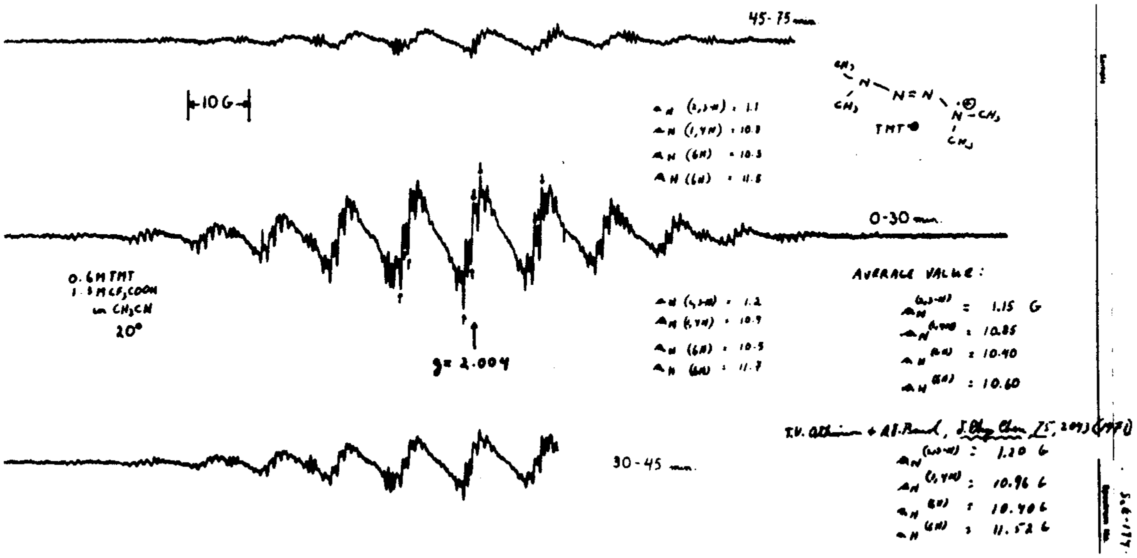
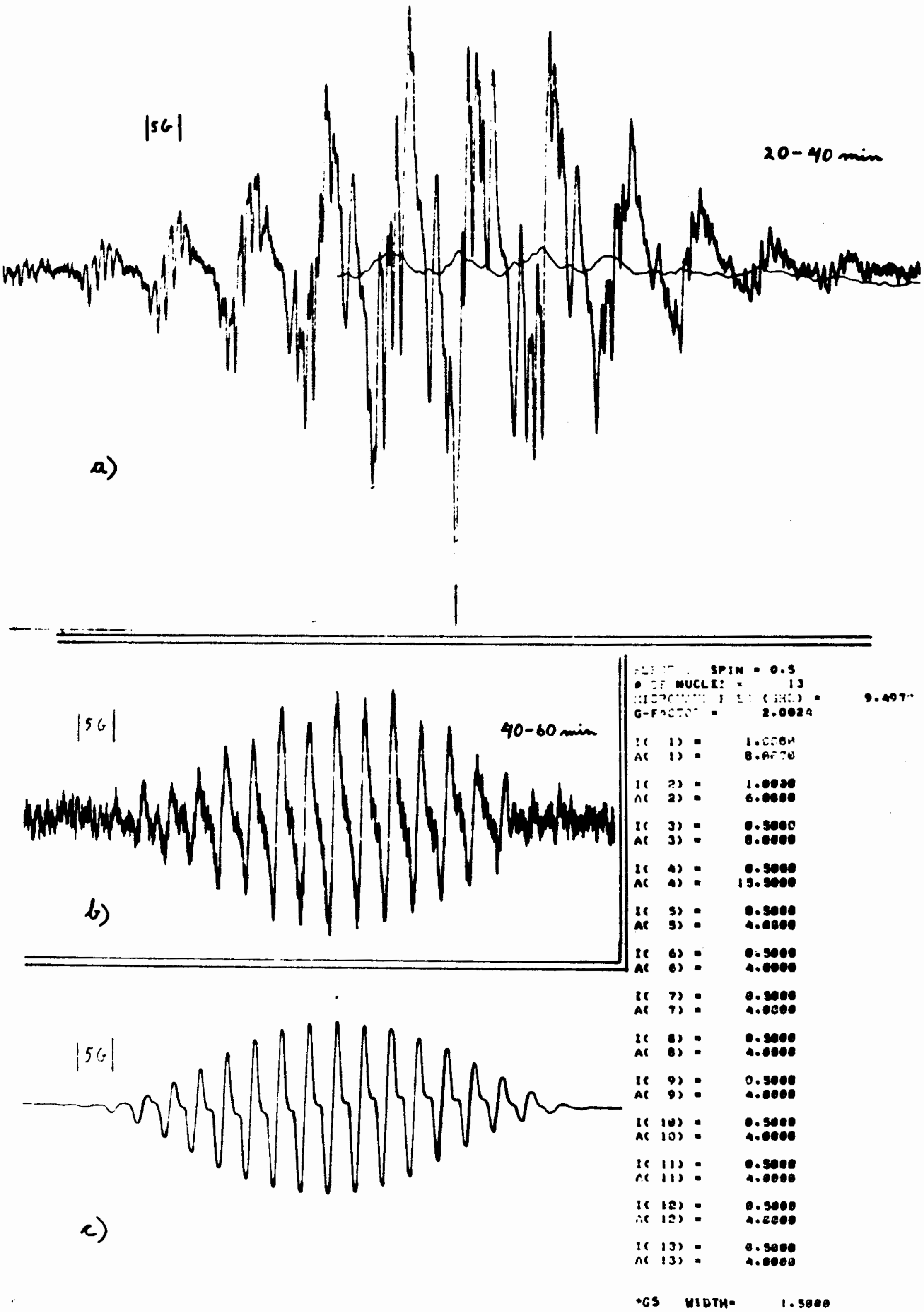


Figure II-5: TMT$^{\cdot +}$ E.S.R. in CF_3COOH-CH_3CN at 20°

unidentified signal (Figure II-6a). This signal was replaced within 30 minutes by another weaker signal at g=2.002±0.001 showing at least 17 major bands 4.2G apart in a ratio (outer to centre) of 12:23:25:35:60:65:73:90:100 (Figure II-6b). In another experiment, TMT was added to a solution of CF_3COOH in 1:1 cyclohexene-acetonitrile. Again, the e.s.r. of the top phase at room temperature showed an ill resolved $TMT^{\cdot +}$ signal (Figure II-7a) which decayed in 45 minutes to be replaced by a weaker signal very similar to that observed previously: g=2.0024±0.0004, 17 major bands 4.2G apart in a ratio of 7:12:20:25:50:60:65:75:100 (Figure II-7b).

Both these new signals decayed in 30 minutes at room temperature. These signals were tentatively assigned to an N,N,N'-trimethyldiaminomethyl radical (II-2) on the basis of the following arguments. The low g-factor of 2.0024 is indicative of a carbon centred radical (131). Comparison of a simulated spectrum (Figure II-6c) using the coupling constants of known α-aminoalkyl radicals (83,93) (Table II-1) with the observed one agrees well with this assignment. Furthermore, the slightly lower g-factor is in agreement with similar results seen in α-alkoxyalkyl radicals where the g-factor decreases with increasing alkoxy substitution at the radical centre (131).

When TMT was added to a solution of CF_3COOH in acetonitrile at -45°, the e.s.r. signal of $TMT^{\cdot +}$ was detected (Figure II-8a).



```
PLOT .   SPIN = 0.5
# OF NUCLEI =      13
MICROWAVE FIELD (GHZ) =      9.497
G-FACTOR =       2.0024

I(  1) =       1.0000
A(  1) =       8.8570

I(  2) =       1.0000
A(  2) =       6.0000

I(  3) =       0.5000
A(  3) =       8.0000

I(  4) =       0.5000
A(  4) =      15.5000

I(  5) =       0.5000
A(  5) =       4.0000

I(  6) =       0.5000
A(  6) =       4.0000

I(  7) =       0.5000
A(  7) =       4.0000

I(  8) =       0.5000
A(  8) =       4.0000

I(  9) =       0.5000
A(  9) =       4.0000

I( 10) =       0.5000
A( 10) =       4.0000

I( 11) =       0.5000
A( 11) =       4.0000

I( 12) =       0.5000
A( 12) =       4.0000

I( 13) =       0.5000
A( 13) =       4.0000

*GS   WIDTH=       1.5000
```

Figure II-6: a) E.S.R. of TMT decomposition at 20° in C_6H_6-CF_3COOH, b) assigned to N,N,N'-trimethylaminomethyl radical (II-2), c) simulated spectrum of II-2

Table II-1: α-Amino alkyl radical coupling constants.

Radical	g-factor	a(Hα)	a(N)	$a(H_N)$	a(Hβ)	a(Hγ)	REF.
$\dot{C}H_2NHCH_3$	2.00280	10.91	5.84	6.35	--	4.21	93
$\dot{C}H_2NH_2$	2.00282	15.30	4.98	4.40	--	--	93
$\dot{C}H_2N(CH_3)_2$	2.00274	11.61	7.03	--	--	4.06	93
$(CH_3CH_2)N\dot{C}HCH_3$	2.0031	13.6	5.2	--	19.6	2.3	132
$CH_3(CH_2)_2\dot{C}HNH_2$	2.0026	14.8	4.8	5.0	14.8	--	132
$CH_3(CH_2)_3\dot{C}HNH_2$	2.0028	15.1	5.0	5.1	15.1	--	132
II-2	g-factor	a(Hα)	a(N)	a(HN)	a(Hγ)	a(N')	a(Hγ')
$(CH_3)_2N'\dot{C}HNHCH_3$	2.0024	15.5	8.0	8.0	4.0	6.0	4.0

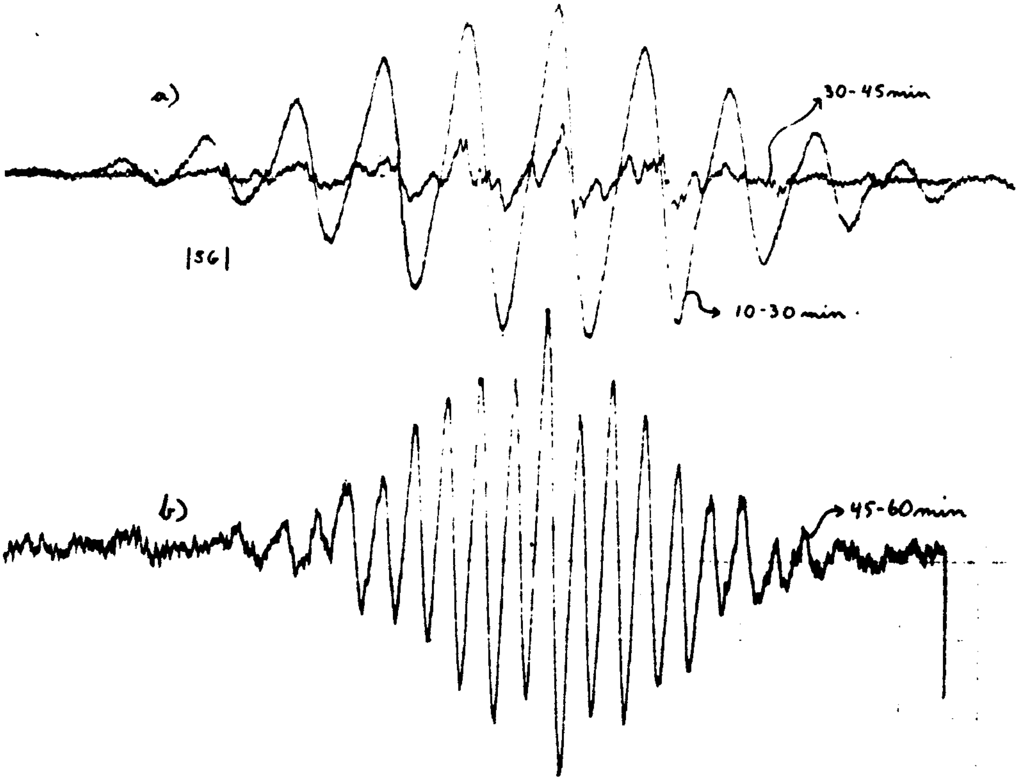


Figure II-7: ESR of TMT decomposition at 20° in CF_3COOH-C_6H_{12}

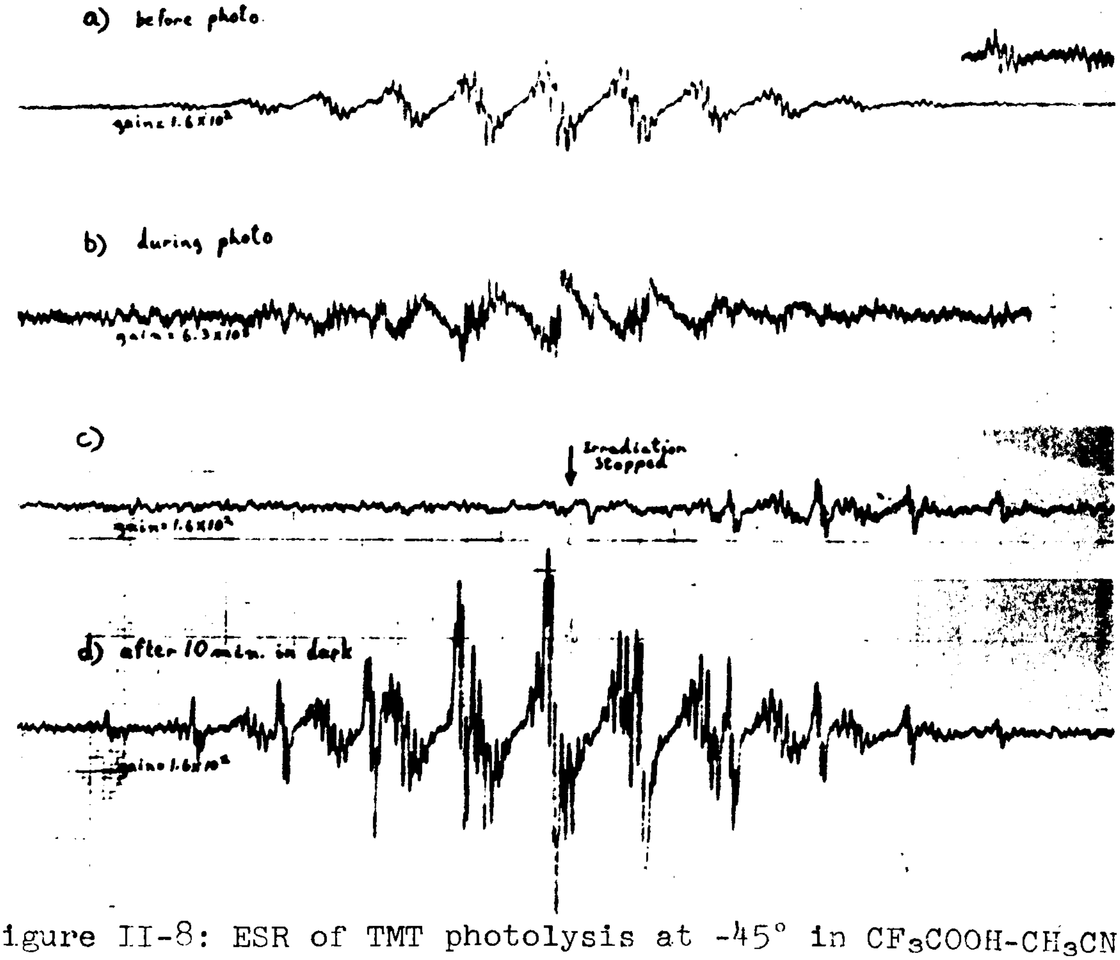


Figure II-8: ESR of TMT photolysis at -45° in CF_3COOH-CH_3CN

Irradiation of this solution at -45° with an unfiltered mercury lamp caused a slight decrease in the $TMT^{\cdot +}$ signal and an appearance of other weak signals (Figure II-8b and c). However, when the photolysis was stopped, a stronger signal of $TMH^{\cdot +}$ appeared (Figure II-8b, centre) and grew to a maximum within three minutes in the dark. The $TMH^{\cdot +}$ signal was superimposed with that of $TMT^{\cdot +}$ which also increased in the dark (Figure II-8d). This $TMH^{\cdot +}$ signal decayed slowly over several hours at -45° but within 30 minutes on warming to room temperature to leave behind the $TMT^{\cdot +}$ e.s.r. signal. Addition of cyclohexene at -45° caused an instantaneous decay of the $TMH^{\cdot +}$ signal (Figure II-9). Addition of cyclohexene to the above solution after warming to room temperature and recooling to -45° produced no change in the $TMT^{\cdot +}$ e.s.r. signal (Figure II-10).

Irradiation of $TMT\text{-}H^+$ solution in acetonitrile at 25°, using CF_3COOH as the acid, caused a build up of $TMH^{\cdot +}$ within 5 minutes after interruption of the photolysis (Figure II-11a) which decayed within one hour. The observed coupling constants for $TMH^{\cdot +}$ of $a(N)=13.2$, $a(H)=12.7G$ and g-factor$=2.0039\pm0.0006$ were similar to that reported by Nelsen (15). A simulated stick diagram for the $TMH^{\cdot +}$ e.s.r. signal, using the above coupling constants, is given in Figure II-11b.

When TMT was dropped into a mixture of $SbCl_5$ and H_2SO_4, a violent reaction occurred and the mixture became red-orange. The

Figure II-9: a) TMH$^{\cdot +}$ at -45°, b) C_6H_{12} added

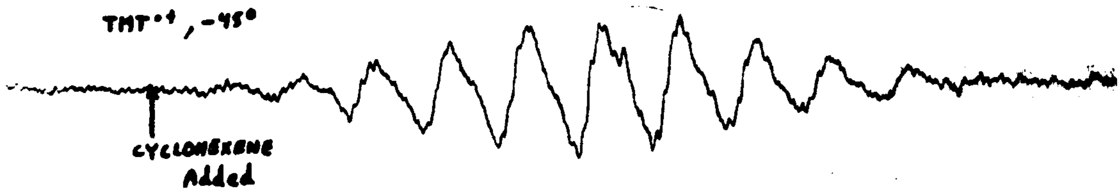


Figure II-10: TMT$^{\cdot +}$ ESR after solution in Figure II-9 warmed to 20° and recooled to -45°, C_6H_{12} added at -45°

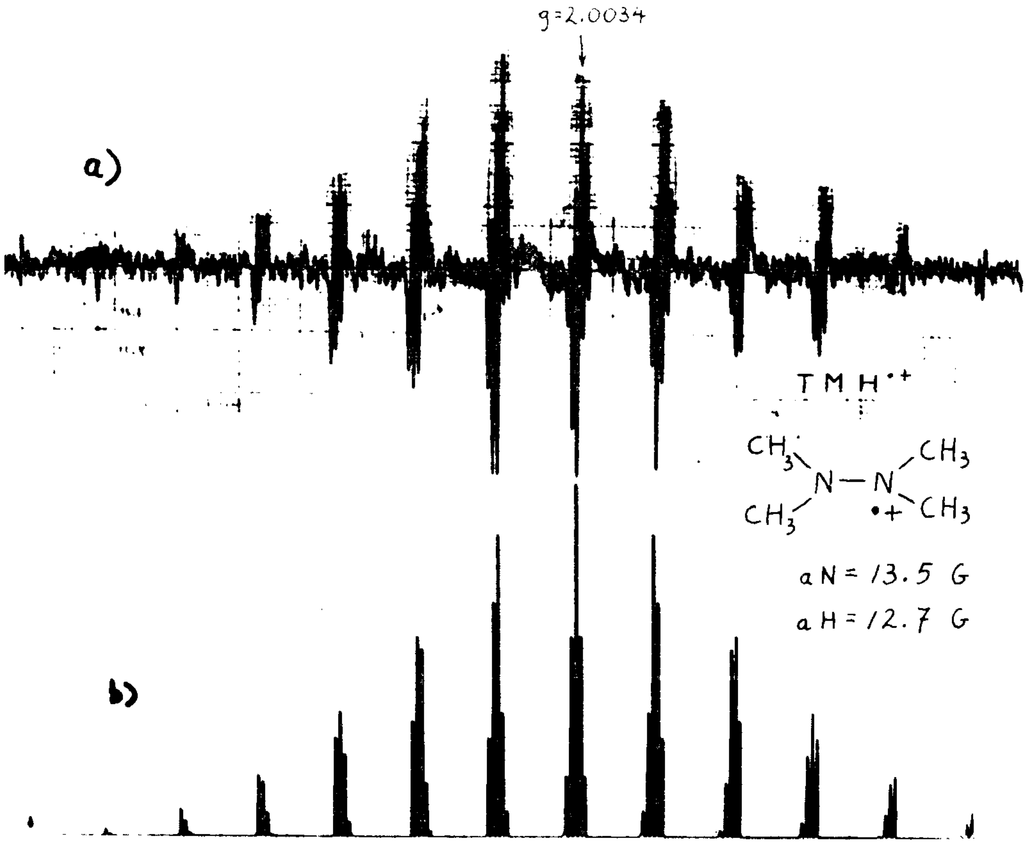


Figure II-11: a) TMH$^{\cdot+}$ ESR signal at 20°, b) simulated spectrum using coupling constants shown

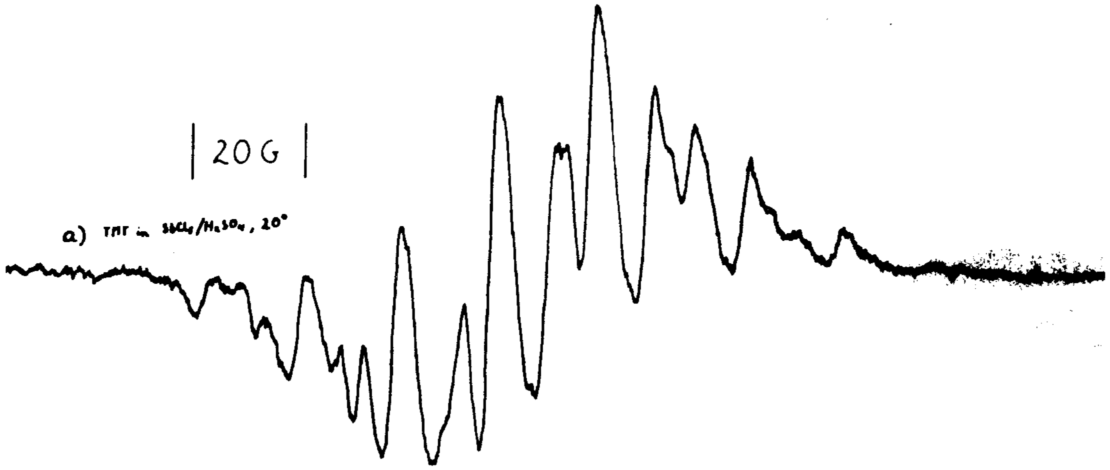


Figure II-12: ESR signal observed when TMT added to $SbCl_5$ H_2SO_4 mixture at 20°

e.s.r. spectrum of this mixture, recorded at room temperature, showed many broad lines (Figure II-12). The spectrum appeared to be caused by several radical species; however, none of these could be identified.

C) ACID CATALYZED TMT DECOMPOSITION IN THE PRESENCE OF TOLUENE

1) In Concentrated H_2SO_4

Since the reaction of TMT, toluene, and concentrated H_2SO_4 consisted of two liquid phases, the concentration of these substrates in either phase could not be determined. The initial molar ratio was kept at about 1:10:5, respectively, which was the ratio found by Bock and Kompa (121) to give optimum yields of amination of toluene with N-chlorodimethylamine (NCD). From the outset it was necessary to establish the optimum conditions, e.g. (i) an efficient quantitative of the products, (ii) the effect of oxygen on the decomposition of TMT, and (iii) the reaction time, since the disappearance of TMT could not be followed directly.

A satisfactory analytical procedure for the basic products, employing g.c. and g.c.-m.s. analyses, as described in Chapter V (Experimental), allowed compilation of the data presented in Tables II-2 and II-3. The g.c. procedure, using chlorobenzene as internal standard, allowed the concentration of the basic products to be determined with less than 5% uncertainty.

Table II-2: H_2SO_4 decomposition of TMT in the presence of toluene

NO.	TEMP. °C	TIME (hrs.)	MOLAR RATIO TMT:ϕCH_3:H_2SO_4	% YIELD[a]								
				II-3[b], o : m : p	II-7[c]	II-6[d]	II-8[e]	II-10[f]	II-9[g]	II-11[h]	II-4[i]	OTHERS
1[j]	90	12	1[j] : 6 : 6	35.0, 9 : 61 : 30	—	—	—	+	+	—	8	3[k], 5
2	0-60	0.75	1 : 4 : 4	4.3[l], 5 : 11 : 84	+	+	1.4[l]	+	—	+	+[m]	5
3	0-20	48	1 : 8 : 4	23.3[l], 10 : 12 : 78	+	+	+	+	+	+	11[m]	5
4	0	3	1 : 17 : 2	5.0, 19 : 5 : 76	+	+	+	+	+	+	4.5	20[n,o]
5[p]	0	10	1 : 17 : 2	6.2, 14 : 10 : 76	+	+	+	+	+	+	2.1[m]	5[n]
6	0	72	1 : 17 : 2	12.1, 15 : 10 : 75	+	+	+	+	+	+	4[m]	5[n]
7	0	3	1 : 11 : 9 : 4[q]	<1, 5 : 10 : 85	+	+ +[r]	+	—	+	+	5	5[n]
8	20	20	1 : 16 : 3	4.2, 13 : 17 : 70	0.22	3.0	+	0.8	+	200 mg	8.3	5
9	-5[s]	20	1 : 10 : 6	10.1, 4 : 12 : 84	0.5	1.2	3.1	0.4	0.3	400 mg	9.4[m]	5
10	50	2	1 : 10 : 6	1.6, 20 : 20 : 60	1.7	24.2	0.7	2.8	+	50 mg	10[m]	3
11	80	0.25	1 : 10 : 6	1.2, 26 : 19 : 55	0.4	29.2	0.3	8.0	—	+	10[m,t]	1

a) all yields are based on one mole TMT giving one mole of products, +: detected but not determined, -: none observed; b) N,N-dimethyltoluidine; c) N,N-dimethylbenzylamine; d) N-methylphenethylamine; e) N-methylindoline; f) N,N-dimethylphenethylamine; g) p-N-methyltoluidine; h) polymeric material in mg/g of starting TMT; i) ortho- and para-benzyltoluenes; j) NCD; k) p-chlorotoluene; l) obtained by column chromatography; m) trace of bibenzyl; n) contains some imine trimer I-30; o) some starting TMT; p) under nitrogen; q) CH_3COOH; r) estimated 10% from nmr; s) temperature spontaneously rose to 27° for 5 min. on appearance of a purple color; t) trace of meta-benzyltoluene.

TABLE II-3: Mass Spectra of major compounds in Table II-2.

	o-II-3[a]	m-II-3	p-II-3	II-7[b]	II-6[c]	II-8[d]	II-10[e]	II-9[f]
m/e	%	%	%	%	%	%	%	%
149							2	
148							2	
135	100	81	78	26	5		-	
134	99	100	100	18	3		2	
133	-	-	-	-	-	74	-	
132	4	-	-	-	-	100	-	
121	-	-	-	-	-	-	-	81
120	78	9	8	-	-	-	-	100
119	12	19	17	-	-	-	-	-
118	31	16	17	-	-	-	-	-
117	-	-	-	-	-	45	-	-
106	-	-	-	-	7	-	-	21
105	-	-	-	-	-	-	4	-
104	21	-	-	-	-	15	-	-
91	47	34	24	49	16	32	7	52
77	15	10	7	4	7	23	7	35
65	23	14	10	18	8	23	4	34
58	-	-	-	100	-	17	100	-
44	13	-	-	13	100	95	-	-
42	10	6	-	80	10	52	10	-

a) N,N-dimethyltoluidine; b) N,N-dimethylbenzylamine; c) N-methylphenethylamine; d) N-methylindoline; e) N,N-dimethylphenethylamine; f) p-N-methyltoluidine.

The reaction of NCD with toluene in H_2SO_4 (no.1, Table II-2) was carried out as described by Bock and Kompa (121) to provide a mixture of o, m, and p-toluidines (II-3) which was used to standardize the g.c. column. The neutral fraction from this reaction contained a mixture of o- and p-benzyltoluenes (II-4), and p-chlorotoluene (II-5) in 8% and 3% yields, respectively, as estimated from n.m.r. and g.c. peak areas; these products were previously unreported (109,121).

N-Methylphenethylamine (II-6), N,N-dimethylbenzylamine (II-7), N-methylindoline (II-8), p-N-methyltoluidine (II-9), as well as toluidines II-3 were identified by g.c. peak matching with the authentic compounds (133) (see Chapter V, Table V-1). The assignments were further confirmed by g.c.-m.s. (Table II-3) and isolation of some of these compounds by column chromatography (see below).

No significant change in the yield or o:m:p ratio of toluidines II-3 was observed when TMT decomposition was carried out under a nitrogen atmosphere (no.5, Table II-2) as compared with that carried out in air (no.4, Table II-2). As a result, no precautions were taken to exclude atmospheric oxygen. The reaction time needed for optimum yields of II-3 was at least two days at 0° (no.3, Table II-2). The general procedure for the TMT decomposition in the reactions in Table II-2 was to terminate a particular reaction by addition of ice when no further gas evolution was observed. Reactions below 30° (nos.2-9, Table II-2) produced a deep purple color together with a sharp rise in temperature and vigorous gas evolution usually in one to five minutes after addition of a TMT-toluene solution to H_2SO_4. These reactions returned to ambient temperature within five minutes and were terminated when the purple color had changed to yellow or brown and gas evolution had subsided. At temperatures above 30° (nos.10 and 11, Table II-2) neither purple color nor rise in temperature was observed; they were terminated when gas evolution had ceased.

Addition of ice liberated a brown polymeric material in all cases. This material was soluble only in concentrated H_2SO_4 and showed an unresolved strong e.s.r. singlet at $g=2.0036\pm0.0004$, $\Delta G_{pp}=8G$ in H_2SO_4. The n.m.r. was poorly resolved but showed aromatic protons at τ2.7-3.6. The i.r. indicated a presence of a monosubstituted benzene ring at 1600(s), 817, 739(s), and 701(s) cm^{-1} and an ammonium sulfate or a sulfonic acid at 3500-2000(b), 1200(s), 1170(s), 1033(s), and 1011(s) cm^{-1}. The m.s. showed peaks up to m/e 600. The peaks at: m/e(%), 135(13), 91(50), 77(12), 44(100) indicated the presence of an N-methylphenethylamino (II-6) moiety.

The neutral fraction was found to contain benzyltoluenes (II-4) as the only major products after distillation of the toluene. Except in reaction no.11 (Table II-2), where the _meta_ isomer (lit. n.m.r. τ6.15(s), $-CH_2-$; i.r. 1090, 1072, 774(s), 757(s) cm^{-1} (134)) constituted ca.5% of the total II-4, only the _ortho_ and _para_ isomers were formed in a 40:60 ratio. Most reactions also showed a trace of bibenzyl (lit. n.m.r. τ7.15(s), $-CH_2-CH_2-$ (134)).

The basic fraction was found to contain (see Tables II-2, II-3, and V-1), in addition to the expected toluidines II-3, varying amounts of phenethylamines II-6 and II-10, benzylamine II-7, indoline II-8, toluidine II-9, some imine trimer I-30, and on one occasion (no.4, Table II-2) some starting TMT. Compound II-10 has been assigned to N,N-dimethylphenethylamine on the basis of the identical m.s. (see Table II-3) to that of an authentic sample.

In addition to g.c. peak matching with the authentic compounds (133) (see Table V-1) and g.c.-m.s. analysis (Table II-3), the following compounds were obtained from the basic fraction of reaction nos.2 and 3 (Table II-2) by column chromatography on silicic acid. p-N,N-Dimethyltoluidine (p-II-3) was obtained in pure form as the major toluidine isomer having identical i.r. and n.m.r. spectra to the authentic (134). A 2:1 mixture of N-methylindoline (II-8) and p-II-3 was also obtained and was identified by comparison of the i.r. and n.m.r. spectra with those of an artificial mixture of authentic II-8 (136) and p-II-3 (134). o- and m-N,N-Dimethyltoluidine were obtained as a 1:1 mixture (134). These mixtures were difficult to separate as all four compounds o-, m-, and p-II-3 and II-8 occurred in one spot on a t.l.c. plate (silicic acid/ether).

Traces of other amines were detected by g.c.-m.s.; among them were a compound having a m.s. m/e(%), 225(M^+,1), 134(90), 91(100), and 77(1) indicating the presence of two benzyl or toluyl groups and a dimethylamino moiety; a compound having a m.s. m/e(%), 178(M^+,1), and 134(100) indicating the presence of two dimethylamino and one toluyl moieties; and a compound having a m.s. m/e(%), 192(M^+,3), 148(2), 134(15), 58(100), and 44(12) indicative of a dimethylaminomethyl moiety at m/e 58(100%) and a dimethylaminotoluidine at m/e M^+-58=134(15%).

2) In CF_3COOH

The decomposition of TMT in CF_3COOH in the presence of toluene was worked up and analysed in a similar manner to that in H_2SO_4; the conditions and results are given in Table II-4. In all cases, the major product obtained (up to 85%) was the trimer I-30. Reaction no. 12 (Table II-4) gave the same pattern of products observed in H_2SO_4 (Table II-2) and also exhibited purple or red-brown colors immediately after the addition of the TMT-toluene solution; however, no perceptible rise in temperature was observed.

When the decompositions were run at higher temperatures (nos.14,15, Table II-4), the reaction solution was pale yellow and gave no polymeric material on addition of ice. The o:m:p ratio of toluidines II-3 changed dramatically in reactions 14 and 15 as

Table II-4: CF$_3$COOH decomposition of TMT in the presence of toluene

NO.	TEMP. °C	TIME (hrs.)	CONCENTRATION [TMT]:[ϕCH_3]:[TFA]	SOLVENT[b]	% YIELD[a]		
					II-3[c], o : m : p	II-7[d]	I-30[e]
12	0	48	0.7 : 7 : 4 : 1[i]	—	2.7, 26 : 15 : 59	+[fgh]	10
13	0	42	0.7 : 7 : 4	—	$\ll 1$, ———	+[fj]	36
14	25	16	0.7 : 7 : 4	—	2.1, 61 : 0 : 39	+[j]	+
15	50	8	0.7 : 7 : 4	—	2.0, 65 : 0[j] : 35	0.4	85
16	40	2	0.26 : 2.6 : 1.54	AN	$<1\times10^{-3}$, 66 : 0 : 34	—	+
17	40	2	0.26 : 2.6 : 1.54	P-70	$\genfrac{}{}{0pt}{}{0.030}{\pm 0.003}$, 64 : 0 : 36	3×10^{-4}	+
18	40	2	0.26 : 2.6 : 1.54	BF	$\genfrac{}{}{0pt}{}{0.052}{\pm 0.004}$, 67 : 0[j] : 33	+	30

a) all yields are based on one mole TMT giving one mole of products or $^1/_3$ mole imine trimer I-30, +: detected but not determined, -: none observed; b) TFA: CF$_3$COOH, AN: CH$_3$CN, P-70: perfluoroalkane-70, BF: CHBr$_3$; c) N,N-dimethyltoluidine; d) N,N-dimethylbenzylamine; e) N-methylmethyleneimine trimer; f) some benzyltoluenes II-4; g) trace N-methylphenethylamine II-6; h) trace N-methylindoline II-8; i) H$_2$SO$_4$; j) trace amount detected by g.c.

compared with reactions 1-12 (Tables II-2 and II-4), showing little or no meta II-3 and an o:p II-3 ratio of approximately 2:1. With the exception of the trimer I-30 and a trace of N,N-dimethylbenzylamine (II-7), no other amines or benzyltoluenes were obtained from reactions 14 and 15. o-N,N-Dimethyltoluidine was isolated from reaction 15 by preparative g.c. as the major II-3 isomer and was identified by comparison of the i.r. with that of an authentic sample (134).

Reactions 16 to 18 (Table II-4) were carried out in solvents in which the imine trimer I-30 was obtained as the major product in addition to low yields of ortho and para II-3 (2:1 ratio) and II-7; little or no meta II-3 was detected.

D) ACID CATALYZED TMT DECOMPOSITION IN THE PRESENCE OF OLEFINS

Acid catalyzed decomposition of TMT has been shown to produce the imine I-29 or imine trimer I-30 in quantitative yields (13,14). No addition products to olefins were obtained when TMT was decomposed in CF_3COOH in the presence of cyclohexene or in a CF_3COOH-acetonitrile solution in the presence of cyclohexene or norbornene. The major product obtained in the basic fractions was I-30. Proton signals typical for a norbornane skeleton were observed in the n.m.r. of the basic fraction obtained from the decomposition in the presence of norbornene; however, there were no $N-CH_3$ signals except that of I-30. Both g.c. and t.l.c. showed at least eight constituents in this basic extract from which I-30 was the only one identified. When TMT was decomposed in dilute HCl in methanol in the presence of cyclohexene, I-30 was obtained in a quantitative yield.

E) PHOTOLYSIS OF TMT IN ACIDIC SOLUTION IN THE PRESENCE OF OLEFINS

1) Cyclohexene

a) In HCl under Nitrogen: When the photolysis of TMT was conducted in the presence of cyclohexene in a dilute HCl solution in acetonitrile under nitrogen at 0^o through a Pyrex filter (u.v. cut-off at 290nm), it took 69 hours fo the TMT-H^+ absorption at 239 nm to disappear. Column chromatography (silica gel) of the basic extract provided the following compounds.

Bis-dimethylaminobicyclohexane (II-15, 0.2%) was identified on the basis of its i.r. and mass spectra. The i.r. showed characteristic Bohlmann bands at 2740, and 2720 to 2680 cm^{-1} (137), and a strong absorption at 1042 cm^{-1} for C-N stretching (138,139); no absorption in the 3500-3000 cm^{-1} region was observed. II-15 showed a h.r.m.s. molecular ion at m/e 252.2541 in agreement with the molecular formula $C_{16}H_{32}N_2$.

Trans-2-chloro-N,N-dimethylcyclohexylamine (II-16, 7.1%) was obtained as an oil (95% pure) by column chromatography. Its n.m.r.

is consistent with the <u>trans</u> configuration by showing a signal at τ6.11 (dt, J=4 and 10Hz; H-2) (140,141). II-16 showed h.r.m.s. molecular ions m/e 163.1011 and 161.0944 in a ratio 39:100 for the chlorine isotope ratio in the molecular formula $C_8H_{16}NCl$. A minor product, believed to be a dimethylaminomethylchlorocyclohexane (II-17), was also identified in the g.c.-m.s. analysis on the basis of its m.s. fragmentation pattern of m/e(%), 177(M^+,3), 175(M^+,8) 140(2), and 58(100). The m/e 177 and 175 peak intensity ratio of 35:100 and the peak at M^+-Cl=m/e 140 is consistent with monochlorinated compounds (135). The intense m/e 58 peak is a commonly observed peak in most of the isolated compounds in the present studies and is indicative of a dimethylaminomethyl moiety (102,103,135).

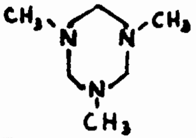
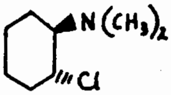
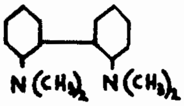
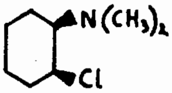
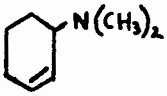
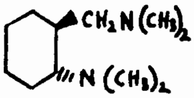
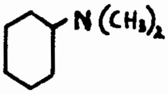
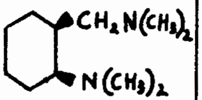
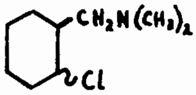
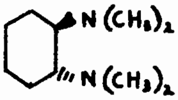
The 98% pure <u>cis</u>-2-chloro-N,N-dimethylcyclohexylamine (II-18, 1.5%) as obtained from column chromatography showed the n.m.r. signal at τ7.67 (s,6H) for the N-methyl groups and a characteristic equatorial proton signal at τ5.43 ($W_{1/2}$=7Hz, H-2) for CHCl (140,141). II-18 had virtually identical m.s. to that of the <u>trans</u> isomer II-16. II-18 decomposed rapidly at room temperature to a dark brown tar. The highly polar trimer I-30 (28%) was obtained as a pale yellow liquid from the later fraction of the chromatography.

By the peak matching method with the now available authentic materials the crude basic extract was also analysed by g.c. (10%

Carbowax 20M, to 200°). This procedure showed trimer I-30 as the major constitutent, along with about equal amounts of 3-dimethylaminocyclohexene (II-19), dimethylaminocyclohexane (II-20), β-chloramines II-16 and II-18 as the minor products. The yields of these minor products must be on the order of 7% since β-chloramine II-16 was obtained in 7.1% yield by column chromatography. As mentioned above, β-chloramine II-18 and II-16 decomposed readily on standing at room temperature and might have decomposed on the silica gel column accounting for the low yield obtained; although not confirmed, cyclohexene II-19 could be a product of this decomposition. It was demonstrated that both authentic cyclohexene II-19 and cyclohexane II-20 could easily be removed on the rotary evaporator (20°/30mm Hg) and might have been lost during the working up.

In silica gel chromatography of the basic fraction, a large portion of highly polar substance was obtained by the eluant of 1N HCl in methanol. This oil showed N-methyl and cyclohexane ring n.m.r. signals and was analyzed by g.c. peak matching with the authentic compounds , synthetically obtained by other routes (see Chapter V-H and V-I). The compounds were trans-1,2-bisdimethylaminocyclohexane (II-21, 2.4%), trans-2-dimethylaminomethyl-1-dimethylaminocyclohexane (II-22, 13%), and cis-2-dimethylaminomethyl-1-dimethylaminocyclohexane (II-23, 1%).

TABLE II-5: PHOTOLYSIS OF TMT IN THE PRESENCE OF CYCLOHEXENE AND HCl UNDER NITROGEN

STRUCTURE	NO.	%YIELD		STRUCTURE	NO.	%YIELD
	I-30	28			II-16	7.1
	II-15	0.2			II-18	7
	II-19	7			II-22	13
	II-20	7			II-23	1
	II-17	0.4			II-21	2.4

The major constituent (trans-aminomethyl II-22) was isolated by preparative g.c. and had identical i.r., n.m.r., and m.s. to that of authentic II-22. The dipicrate (mp 176-177°) gave no melting depression when mixed with the dipicrate prepared from authentic II-22 (see Chapter V-I).

The results are summarized in Table II-5. The yields of β-chloramine II-18, cyclohexene II-19, and cyclohexane II-20 are approximated from the g.c. results.

b) In CF_3COOH under Nitrogen: Photolysis of TMT in the presence of cyclohexene, when carried out under nitrogen using a low pressure mercury lamp and a Vycor filter in acetonitrile containing CF_3COOH as acid, developed a deep yellow color which disappeared slowly over 6 hours of irradiation. The crude basic extract was heated with a Na_2CO_3 solution on a steam bath for two hours in an attempt to hydrolyze any trifluoroacetates to the corresponding β-aminoalcohols since the former may have been formed through an ionic mechanism (see Discussion). Analysis of the basic extract after hydrolysis, using g.c. peak matching with the authentic materials, afforded the results given in Table II-6. Neither trimer I-30 nor any 2-dimethylaminocyclohexanols (II-24) were detected.

However, without the hydrolysis step of the basic fraction, a 60% yield of trimer I-30 was obtained along with the other compounds in

TABLE II-6: PHOTOLYSIS OF TMT IN THE PRESENCE OF CYCLOHEXENE AND CF_3COOH UNDER NITROGEN

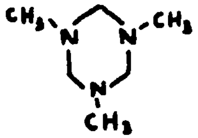
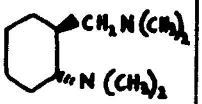
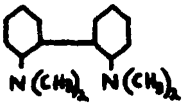
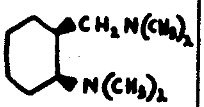
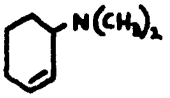
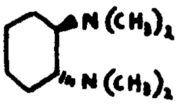
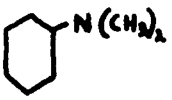
STRUCTURE	NO.	% YIELD	STRUCTURE	NO.	% YIELD
	I-30	60		II-22	15.6
	II-15	1.4		II-23	4.1
	II-19	8.4		II-21	1.2
	II-20	16.9			

TABLE II-7: PHOTOLYSIS OF TMT IN THE PRESENCE OF CYCLOHEXENE AND CF_3COOH UNDER OXYGEN

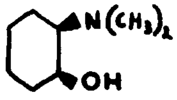
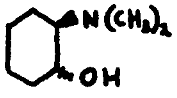
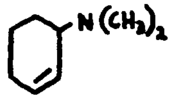
STRUCTURE	NO.	% YIELD
	II-24a	18.3
	II-24b	36.7
	II-19	3.5

Table II-6. Compounds II-19, II-20, II-22, and II-15 were isolated by preparative g.c.: all four showed the identical i.r., n.m.r., or m.s. with those of the authentic compounds synthesized or isolated previously.

c) In CF_3COOH under Oxygen: Photolysis of TMT (0.0172 moles) in the same conditions as used in (b), except under oxygen instead of nitrogen again produced a deep yellow color. Iodometry showed the photolysate to contain 0.005 equivalents of oxidizing material. The photolysate was evaporated and the residue was basified without separation of any neutral or acidic products. The total ether extract obtained from the photolysate gave a negative test to KI-starch paper.

The basic residue was reduced with LAH to afford an oil which showed two g.c. peaks, one corresponding to cyclohexene II-19 (3.5%), the other to a mixture of cis- and trans-2-dimethylaminocyclohexanols (II-24a and b, 55%) as identified by g.c. peak matching with the authentic materials (142). The n.m.r. spectrum of the oil exhibited the signals corresponding to -CH=CH- (II-9) at τ4.26 (m, $W_{1/2}$=35Hz) and an equatorial α-hydroxy proton (II-24a) at τ6.00 (m, $W_{1/2}$=9Hz) and an axial α-hydroxy proton (II-24b) at τ6.69 (dt, J=4.5 and 10Hz) (134,142) in a 1:5:10.5 ratio. Aminoalcohols II-24a and b were isolated as a mixture by preparative g.c. and had an identical i.r. to that of an authentic sample of II-24 prepared by another route by K.S. Pillay (142).

The unreduced basic fraction showed a strong i.r. absorption at 1710 cm^{-1} as well as strong i.r. characteristics for amino alcohols II-24 at 3380, 2780, 1268, 1036, 946, 873, and 847 cm^{-1} (142). Analysis by g.c. showed this oil contained mainly II-24, along with cyclohexene II-19 and an unidentified g.c. peak in the ratio of 80:2:15. Treatment of this portion with hydroxylamine hydrochloride in pyridine gave an oil which could not be crystallized; the oil did not contain the unidentified minor g.c. peak observed above. The n.m.r. of this oil indicated the presence of II-24a [τ5.93(m)] and II-24b [τ6.70(m)] in a 1:2 ratio and showed a weak signal in the olefinic region at τ4.22. The results, based on g.c. areas and n.m.r. ratios, are given in Table II-7.

2) Norbornene

a) In CF_3COOH under Nitrogen: The photolysis of TMT was conducted in the presence of norbornene in a CF_3COOH-acetonitrile solution under nitrogen through a Vycor filter at 0°; the photolysate showed a deep yellow color upon irradiation which disappeared in two hours. The first basic extract showed n.m.r. signals typical of $N-CH_3$ groups and norbornane ring systems. Further extraction provided a second basic fraction consisting mainly of the imine trimer I-30 in a 40% yield as estimated by n.m.r.

Both t.l.c. and g.c. showed the first basic extract to be composed of five major compounds. Three of these compounds were obtained pure and are described below. The yields were obtained from a second photolysis under the same conditions, but employing a different work up (see below) and are presented in Table II-8.

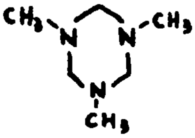
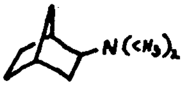
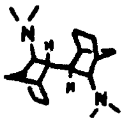
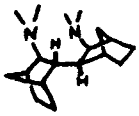
2-Exo-dimethylaminobicyclo[2.2.1]heptane (II-26) was obtained from the first basic fraction by preparative g.c. II-26 showed the correct molecular ion at m/e 139 (38%) and the mass peaks typical for dimethylaminonorbornanes (103) at m/e (%) 124(8), 110(46), 98(38), 84(29), 71(33) and 58(100). The i.r. of II-26 showed characteristic Bohlman bands at 2759(s) cm^{-1} (137), a C-N stretching at 1040(s) cm^{-1} (138,139), and no absorption in the 3500-3000 cm^{-1} region. The absorptions at 1021(s) and 819 cm^{-1} are characteristic for the exo-II-26 isomer (reported 1022(s) and 820 cm^{-1}) (143).

2-Endo-(3'-exo-dimethylaminobicyclo[2.2.1]hept-2'-endo-yl)-3-exo-dimethylaminobicyclo[2.2.1]heptane (II-27) was obtained from column chromatography of the first basic fraction as white prisms, mp 165-171^{o} (sublim.). Analysis and h.r.m.s. agreed with the molecular formula $C_{18}H_{32}N_2$. The i.r. bands at 2775(s) and 1042 cm^{-1} with no absorption in the 3500-3000 cm^{-1} region suggested the presence of a tertiary amine (137-139) and the ^1H n.m.r. showed the presence of two $(CH_3)_2N$ groups at τ7.75 (s,12H). The mass spectrum showed mass peaks typical for dimethylaminonorbornanes (103) at m/e(%)

124(7), 98(10), 84(45), and 58(39). The ^{13}C n.m.r. showed only 8 peaks, among them one at 42.4 ppm (q, $N-CH_3$) nearly twice as high as the rest, for the 18 carbons. The ^{13}C n.m.r., indicated the structure as that of two dimethylaminonorbornane moieties symmetrically joined with a plane of symmetry. The low solubility in methanol and high solubility in hexane, unusual for tertiary amines, indicated II-27 as having a low dipole moment possibly arising from this high symmetry (144).

The structure of II-27 was assigned on the basis of ^{13}C n.m.r. data (Figure II-13 and Table II-9) by comparison with the chemical shift data for substituted norbornanes (145) and the off centre decoupling experiments. The carbons at 35.3 (d; C-1), 46.9 (d; C-4), 28.5 (t; C-5), and 23.2 ppm (t; C-6) were assigned in good agreement with reported ^{13}C chemical shift data (145). The decoupling results also showed the C-3 signal at 74.9 ppm (d) and the C-7 at 37.2 ppm(t). The relatively high field shift of the C-6 carbons at 23.3 ppm indicated an endo orientation at the C-2 or C-3 positions (145). If the $(CH_3)_2$-N groups were endo, the shift at C-5 would be in the order of 20 ppm (145), higher than that observed. Thus, the linkage at C-2 must be endo-endo and the $(CH_3)_2$-N groups exo. This is in general agreement with the fact that a dimethylaminium radical (103,106,146,147) and other bulky radicals (148) attack norbornene preferentially from the exo face.

Table II-8: Photolysis of TMT in the Presence of Norbornene and CF$_3$COOH under Nitrogen

STRUCTURE	NO.	%YIELD		STRUCTURE	NO.	%YIELD
	I-30	40			II-26	5
	II-27	16			II-28	22
UNIDENTIFIED OTHERS	—	15				

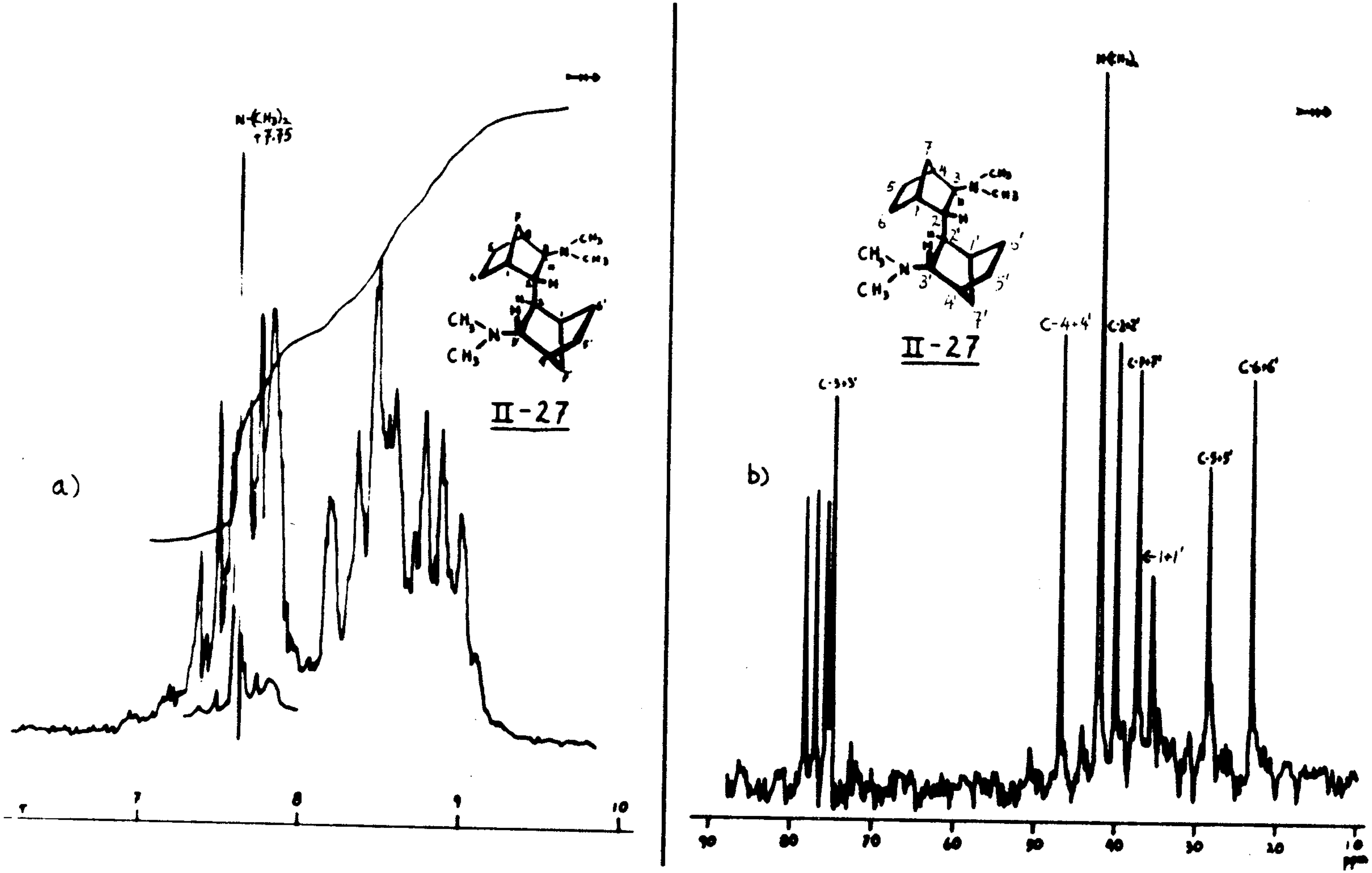


Figure II-13: a) ^{1}H and b) ^{13}C NMR of 2-endo(3'-exo-dimethylaminobicyclo[2.2.1]hept-2'-endo-yl)-3-exo-dimethylaminobicyclo[2.2.1]heptane (II-27)

TABLE II-9: ^{13}C N.M.R. Chemical Shifts for Bis-Norbornanes II-27, II-28, and II-36.

^{13}C	II-27 ppm	II-28 ppm	II-36 ppm
1	35.5	35.0	33.4
2	40.0	40.0	39.9
3	74.9	76.6	77.1
4	46.9	45.5	47.6
5	28.5	28.4	29.2
6	23.2	23.0	22.7
7	37.3	37.2	34.3
1'	35.5	34.2	33.4
2'	40.0	39.0	37.4
3'	74.9	71.9	82.7
4'	46.9	53.2	53.0
5'	28.5	30.3	20.5
6'	23.2	29.2	27.1
7'	37.3	35.0	34.3
$N(CH_3)$	42.4	43.0	44.0
$N'(CH_3)$	42.4	48.8	-

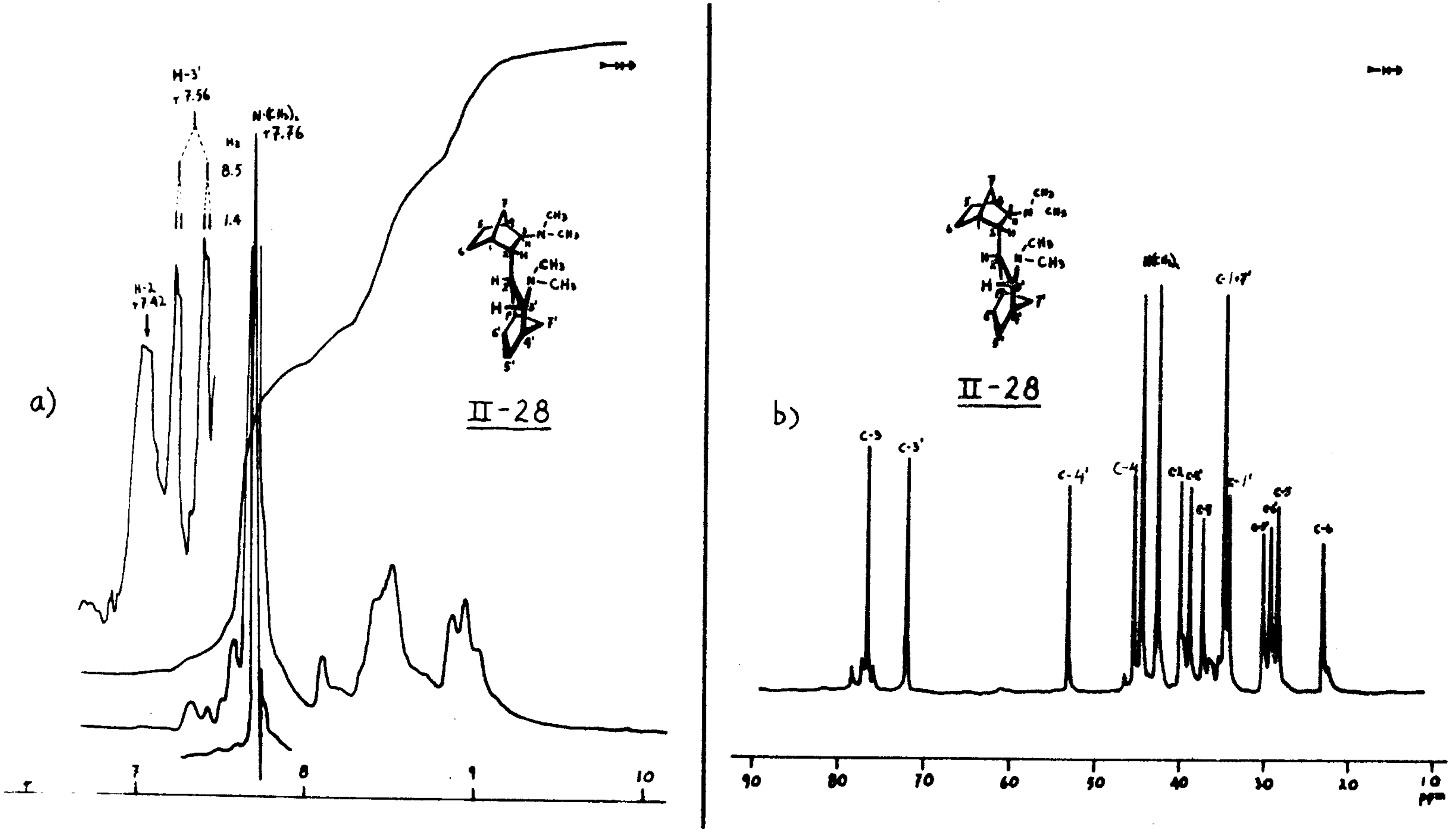


Figure II-14: a) ^{1}H and b) ^{13}C NMR of 2-endo-(3'-exo-dimethylaminobicyclo[2.2.1]hept-2'-exo-yl)-3-exo-dimethylaminobicyclo[2.2.1]heptane (II-28)

2-Endo-(3'-exo-dimethylaminobicyclo[2.2.1]hept-2'-exo-yl)-3-exo-dimethylaminobicyclo[2.2.1]heptane (II-28) was also obtained from column chromatography as white needles (mp 67-72° sublim.) soluble in methanol but insoluble in hexane. Analysis and m.s. agreed with the molecular formula of $C_{18}H_{32}N_2$. As in II-26 and II-27, i.r. and m.s. of II-28 indicated the presence of $(CH_3)_2$-N and norbornane moieties. The ^1H n.m.r. spectrum of II-28 showed 3 downfield protons at τ7.43 (m, $W_{1/2}$=11Hz), 7.55 (dd, J=8.5, 1.4Hz), and 7.72(m), a singlet for the $(CH_3)_2$-N at τ7.76(12H), and an unresolved multiplet for the cycloalkane portion. When 100% "Eu-Resolve" shift reagent was added, the $(CH_3)_2$-N signals were split (3Hz) into 2 singlets. The ^{13}C n.m.r. spectrum (Figure II-14 and Table II-9) showed 15 peaks, 3 of these at 44.8, 43.0, and 35.0 ppm were about twice as high as the rest, indicating a bis-dimethylaminodinorbornane lacking the symmetry of II-27.

Proton off centre decoupling indicated i) two different carbons at 35.0 ppm, a triplet for C-7 and a doublet for another carbon ii) another C-7 carbon at 37.2 ppm(t), and iii) two different $(CH_3)_2$-N groups at 44.8(q) and 43.0 ppm (q) probably joined to carbons at 76.6(d) and 71.9 ppm (d) (145). The assignment of the proton spectrum and verification of the assignment of the ^{13}C spectrum was accomplished by single frequency irradiation of proton signals and observation of the resulting ^{13}C spectra. The ^{13}C signal of a carbon directly bound to the particular irradiated proton would collapse to a singlet due to spin decoupling and increase due to a resulting Nuclear Overhauser Effect (145). The proton chemical shifts and corresponding decoupler frequencies were initially determined by a graphical method outlined by Varian (149) and described by Birdsall et al (150). The result of this decoupling work related the 3'-proton at τ7.56 (dd, J=8.5, 1.4Hz) to the 3'-carbon at 71.9 ppm (d), the 2'-proton at τ7.72(m) to the 2'-carbon at 39.0 ppm (d), and the 2-proton at τ7.42 (m, $W_{1/2}$=11Hz) to the 2-carbon at 40.0 ppm (d). The decoupling further confirmed 2 completely different carbons present at 35.0 ppm (t, C-7'; and d, C-4), thus making assignment of each much more reliable.

The lack of a ^{13}C signal at about 20 ppm indicated both $(CH_3)_2$-N groups must be exo-oriented (145). The highest signal at ppm 23.9(t) is assigned to a C-6 carbon in one norbornane ring and indicated this ring to have an endo-2-alkyl substituent (145). One half of II-28 was therefore assigned to a geometry similar to II-27 (Figure II-13 and Table II-9). On the basis of the ^{13}C signal at 35.0 ppm (t; C-7') and the relatively low field carbons at 30.3 (t; C-5') and 29.2 ppm (t; C-6'), the other half of II-28 was assigned to an exo-exo-2',3'-substituted norbornane (145), in agreement with the coupling constants of the 3'-endo-proton of $J_{3'n,2'n}$=8.5 and $J_{3'n,7'a}$=1.4Hz (140). The remaining carbons at 71.9 (d; C-3'), 34.2 (d; C-1'), 44.8 [q; $(CH_3)_2$-N'], 39.0 (d; C-2'), and 53.2 ppm (d, C-4') were assigned by comparison with II-27 (Table II-9) and reported ^{13}C chemical shifts for substituted norbornanes (145).

A mixture of at least 3 other compounds, showing one major and two minor spots on a t.l.c. plate, was also obtained by column chromatography of the first basic fraction. This mixture showed i.r. at 2875(s), 2822(s), 2770(s), 1052 and 1020(s) cm^{-1} and n.m.r. at τ7.70(s) and 7.6-9.3(bm) characteristic of dimethylamino and norbornane moieties. It also showed m.s. peaks at m/e(%) 290(2), 276(9), 261(100), 192(45), 182(30), and 58(55) indicative of the presence of another dimer analogous to II-27 and II-28 (m/e 276 for M^+), a compound having the M^+ at m/e 290 and another at m/e 182 for M^+. Neither of the latter two m.s. peaks were observed in the m.s. of II-27 or II-28. This mixture proved difficult to separate by column chromatography and was not analyzed further.

About 30% of the first basic fraction was eluted as a dark viscous oil. This oil was believed to consist of reaction products of the dimers with CH_2Cl_2 since it was not obtained when ether was used in the work up. The i.r. absorptions at 3420, 3350, 2795, 1640 and 1012 cm^{-1} are indicative of an ammonium salt and the strong aborption at 732 cm^{-1} could be due to the presence of a C-Cl bond (138,139). The $N\text{-}CH_3$ signal shifted from τ7.7 to τ7.1 and 7.3 clearly indicating ammonium salt formation (140,141). The relatively simple m.s. fragmentation pattern of m/e(%) 276(1), 261(31), 192(5), 58(10) is also indicative of an ammonium salt (103,141) of a dimer analogous to II-27 or II-28. This material was not analyzed further.

Analysis of the first basic fraction by g.c. showed a peak for the monomer II-26 at 25 min. and four peaks in the 135-160 min. region in a ratio of 1:4. The latter four peaks were in a ratio of 43:11:31:16 in which the first and third peaks were identified as dimers II-28 and II-27 by g.c. peak matching.

When the photolysis was repeated under similar conditions, using ether as the solvent in the work up, the first basic fraction showed g.c. peaks at 25 min. (II-26, 5%) and four peaks in the 135-160 min. region in a ratio 1:10. The latter four g.c. peaks were in a ratio of 40 (II-28, 22%):10:30 (II-27, 16%):10.

b) In CF_3COOH under Oxygen: Photolysis of TMT under oxygen, conducted in the presence of norbornene in acetonitrile solution containing CF_3COOH at 0^o through a Vycor produced a deep yellow color which faded over two hours. The photolysate gave a strong positive test to KI-starch paper, indicating the presence of oxidizing agents. It was immediately evaporated to 15 ml, basified, and extracted with ether without isolation of any acidic or neutral products. The ether extract was immediately reduced with $NaBH_4$. The temperature was kept at or below 0^o throughout the entire above work up.

After acidification of the $NaBH_4$ mixture, a small amount (2.2%) of 2,7-dihydroxybicyclo[2.2.1]heptane (II-31) was obtained as an oil and converted to the bis-p-nitrobenzoate (II-31a): mp 164-165°; m.s. M^+ m/e 426. An authentic sample of the diol II-31 was prepared by the known hydrolysis of exo-2,3-epoxynorbornane (II-32) (151,152). The i.r. of the authentic bis-p-nitrobenzoate (mp 159-162°) was superimposable on the one obtained from the oxidative photolysis. No 1,3-bis-hydroxymethylcyclopentane (II-33) (lit. bis-p-nitrobenzoate: mp 117-118°; m.s. M^+ m/e 428 (103)) was detected. II-33 had been obtained in large amounts in the oxidative photolytic addition of nitrosamines to norbornene (103).

The acidified $NaBH_4$ reduction mixture was made basic and extracted with ether to provide an oil. Analysis of this oil by g.c. and g.c.-m.s. showed 3-exo-dimethylamino-2-endo-bicyclo[2.2.1]-heptanol (II-34) as the major product in 57% yield comprising 75% of all g.c. peaks. One of the minor peaks was 5% of the major and was shown to be due to 3-exo-dimethylamino-2-exo-bicyclo[2.2.1]heptanol (II-35). These g.c. peaks were matched with those of a 1:1 mixture of authentic II-34 and II-35 (153).

The amino alcohol II-34 was obtained as an oil by column chromatography of this basic extract and was sublimed to give translucent prisms: mp 67-68°. II-34 had the correct molecular ion at m/e 155 and correct elemental analysis for the molecular formula $C_9H_{17}NO$. The ^1H n.m.r. showed the $(CH_3)_2N$ signal at τ7.74,

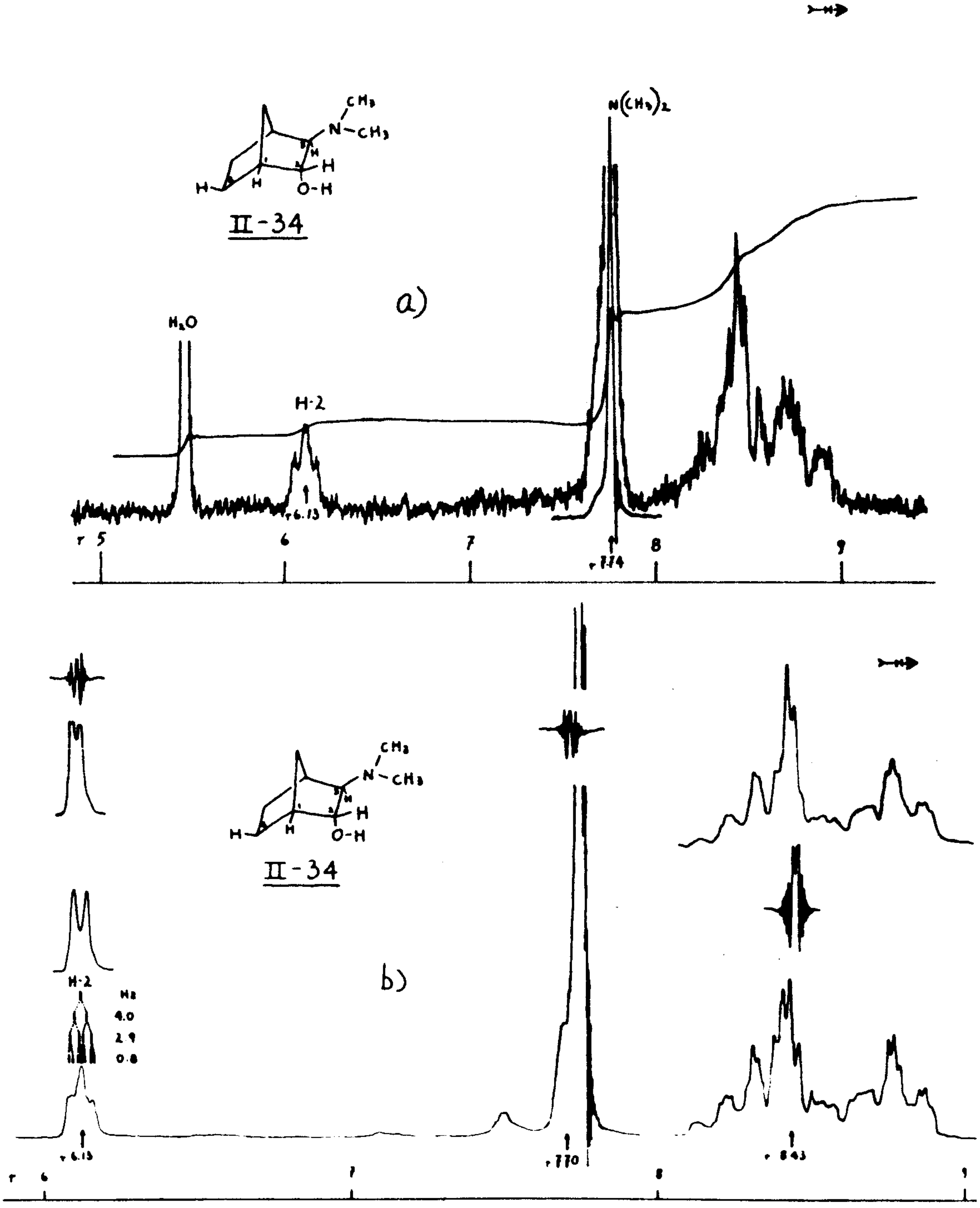


Figure II-15: a) 60 MHz and b) 100 MHz ^{1}H NMR of 3-exo-dimethylamino-2-endo-bicyclo[2.2.1] heptanol (II-34)

Table II-10: 3-*Exo*-dimethylamino-2-*endo*-bicyclo[2.2.1]heptanol (II-34) N.M.R. Data.

	^{13}C (ppm)	$^{1}H(\tau)$	Coupling constants(Hz)
1	42.5	8.45	
2	78.2	6.13	$J_{2x,3n}=4.0$
3	76.6	7.75	
4	39.0		$J_{2x,1}=2.9$
5	28.4	7.66-8.92	
6	19.4		$J_{2x,6x}=0.8$
7	34.3		
N-CH_3	43.6	7.74	
O-H	--	5.85	

the O-H at τ5.85, and the 2-proton signal at τ6.13 (ddd, J=4.0, 2.9, 0.8Hz). The coupling constants of $J_{2x,2n}$=4.0, $J_{2x,1}$=2.9, and $J_{2x,6x}$=0.8Hz were determined by spin decoupling (see Table II-10, Figure II-15) and were in good agreement with reported coupling constants for a 2-exo-proton in norbornanes having a trans-3-exo-2-endo-configuration (103,140,148). The ^{13}C assignments (Table II-10) were made on the basis of the above structure in good agreement with those of dimers II-27-28 and other reported values for substituted norbornanes (145).

A crystalline compound obtained by column chromatography of the reduced extract was believed to be 2-endo-(3'-endo-hydroxy bicyclo-[2.2.1]-hept-2'-exo-yl)-3-exo-dimethylaminobicyclo[2.2.1]-heptane (II-36) on the basis of the following evidence. The molecular ion at m/e 249 and analysis agree with the molecular formula $C_{16}H_{27}NO$. The ^{1}H n.m.r. indicated the $(CH_3)_2N$ signal at τ7.76 (s,6H); the 3'-exo-proton at τ5.54 (ddd, J=4.5, 2.0, 0.5Hz) had coupling constants similar to the 2-exo-proton of II-34 (see Table II-10). The ^{13}C n.m.r. indicated a bisnorbornane skeleton analogous to dimer II-28 (see Figure II-14) with a 2,2'-endo-exo dimer linkage as indicated by the signal at 22.70 ppm for a C-6 carbon. Since a dimethylaminium radical attack on norbornene is exclusively exo (103,106,146,147), the $(CH_3)_2N$ group should be exo-oriented at the C-3 position. The C-5' at 20.52 ppm should, therefore, be due to an endo-hydroxy group at the C-3' position (145). The structure of II-36, along with ^{1}H and ^{13}C results, is given in Figure II-16 and Table II-9.

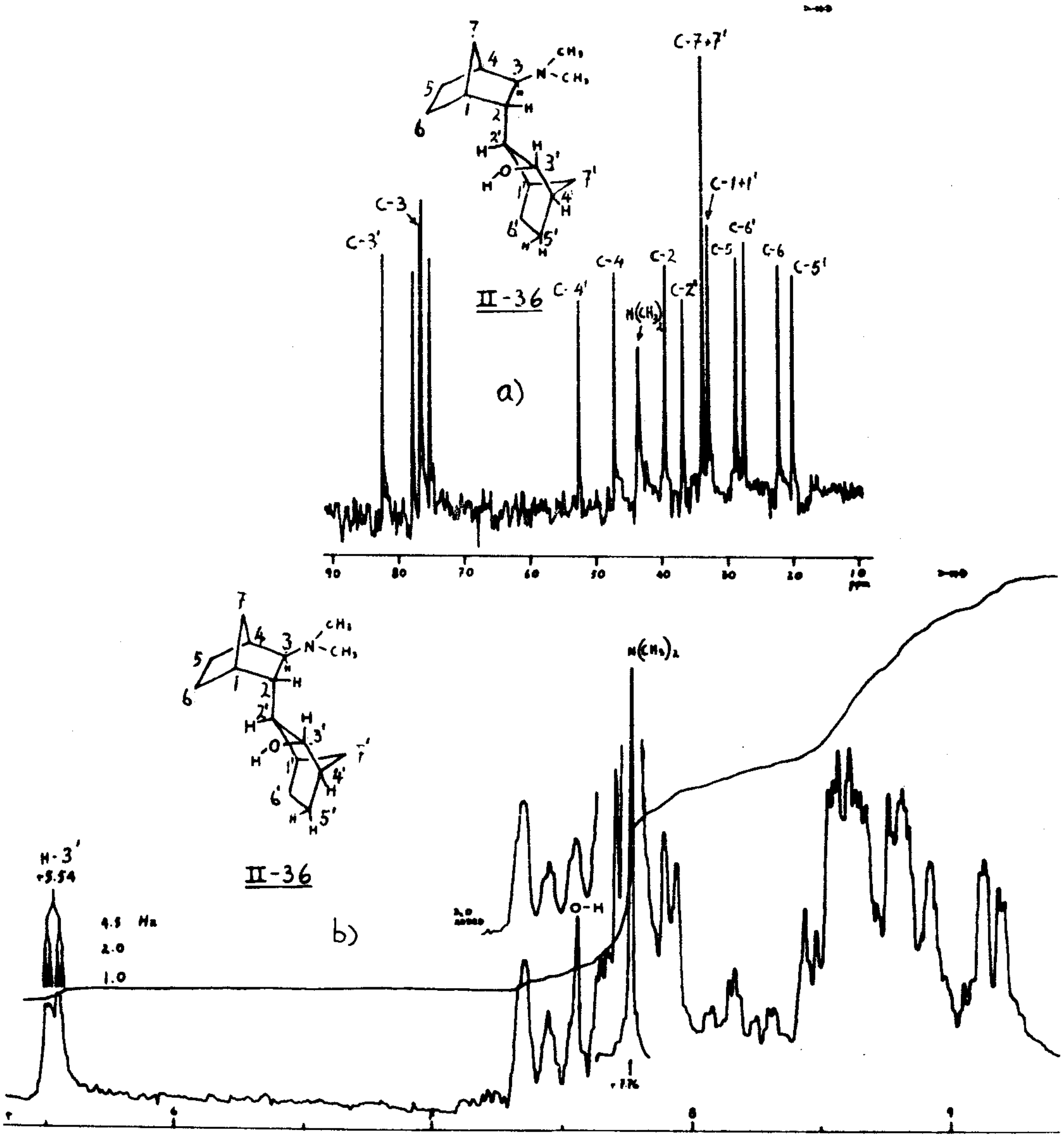
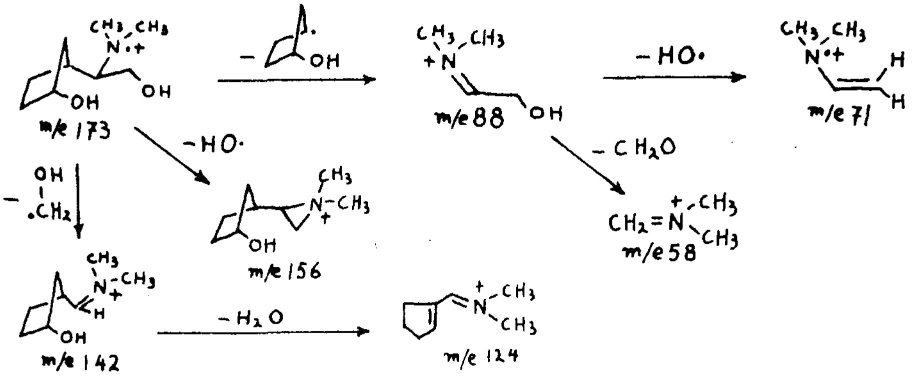


Figure II-16: a) ^{13}C and b) ^{1}H NMR of 2-*endo*-(3'-*endo*-hydroxybicyclo[2.2.1] hept-2'-*exo*-yl)-3-*exo*-dimethylaminobicyclo[2.2.1] heptane (II-36)

Another compound obtained as an oil from the reduced extract was tentatively assigned to 3-cis-(1'-dimethylamino-2'-hydroxyethyl)-cyclopentanol (II-37). It showed i.r. characteristics of a $(CH_3)_2N$ moiety at 2868, 2834, and 2786 cm^{-1} (138) and of an alcohol at 3340 (sb) and 1035(sb) cm^{-1} (138,139). The n.m.r. indicated the $(CH_3)_2N$ signal at τ7.70 (s; 6H) and two D_2O exchangeable protons at τ6.30. High resolution m.s. provided the molecular ion at m/e 173.1413 in agreement with the molecular formula $C_9H_{19}NO_2$. The possible m.s. fragmentation pattern shown in Scheme II-1 was indicated by the peaks at m/e(%) 173(6, $C_9H_{19}NO_2$), 156(4, $C_9H_{18}NO$), 142 (26, $C_8H_{16}NO$), 124(6, $C_8H_{14}N$), 88(26), 71(11), and 58(100).



Scheme II-1: M.s. fragmentation of II-37.

TABLE II-11: PHOTOLYSIS OF TMT IN THE PRESENCE OF NORBORNENE AND CF_3COOH UNDER OXYGEN AFTER REDUCTION

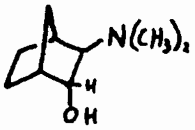
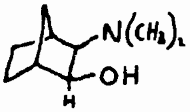
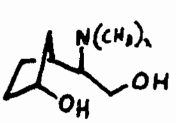
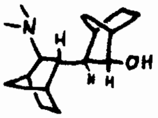
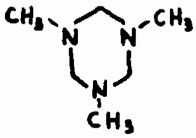
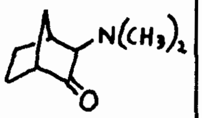
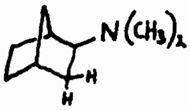
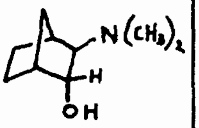
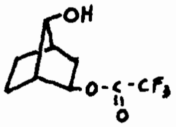
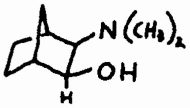
STRUCTURE	NO.	%YIELD		STRUCTURE	NO.	%YIELD
	II-34	57			II-35	4
	II-37	6			II-36	5

TABLE II-12: PHOTOLYSIS OF TMT IN THE PRESENCE OF NORBORNENE AND CF_3COOH UNDER OXYGEN BEFORE REDUCTION

STRUCTURE	NO.	%YIELD		STRUCTURE	NO.	%YIELD
	I-30	55			II-39	40
	II-26	TRACE			II-34	7
	II-38	2.5			II-35	10

The results of this first photolysis are summarized in Table II-11.

In a separate photolysis a solution of TMT (0.069 moles), norbornene and CF_3COOH in acetonitrile was irradiated under oxygen at 0^o through Vycor for 5 hours. After 4 hours a new absorption at λ_{max} 270 nm was observed. Iodometry indicated 0.045 equivalents of oxidizing agents present in the photolysate.

The photolysate was evaporated and extracted with ether to give a brown semi-solid (505mg). This extract did not contain any expoxide II-32 at 760(s) cm^{-1} when the i.r. was compared with that of authentic II-32. However, the i.r. of this acidic and neutral fraction showed absorptions at 1779(s), 1219, and 1170 cm^{-1} indicative of trifluoroacetates (154) and at 3350(sb) and 1065(b) cm^{-1} characteristic of alcohols. G.c. showed one major peak about 80% in area of all peaks. This was tentatively assigned to 7-hydroxylbicyclo[2.2.1]hept-2-yltrifluoroacetate (II-38). The g.c.-m.s. of II-38 lacks the M^+ peak at m/e 224, which is not unusual for esters (135), but shows a strong peak at M^+-CF_3COOH = m/e 110 and weak ones at M^+-OH = m/e 207 and M^+-H_2O = m/e 206. It is possible that II-31, observed in the previous photolysis, was formed by $NaBH_4$ reduction of II-38. The yield of II-38, based on one mole TMT, was estimated from g.c. peak areas to be 2.5%.

An authentic sample of the trifluoroacetate II-38 was prepared by stirring the epoxide II-32 in a 1M CF_3COOH solution in CH_2Cl_2 to give the rearranged product analogous to that obtained in the reaction of II-32 and formic acid (152). This gave an oil which showed i.r. 3400(sb), 1777(s), 1352(s), 1220, 1165(sb), and 1080(b) cm^{-1}. When the trifluoroacetate II-38 was stirred overnight in 40% aqueous dimethylamine solution, some exo-alcohol II-35 was detected by g.c.; however, no endo-alcohol II-34 was observed.

The remainder of the photolysate was basified and extracted with ether at room temperature. This extract showed one major g.c. peak at 6.9 min. and two minor ones at 7.5 and 8.1 min. in a ratio of 6:1.5:1 on an SE-30 column. The peaks at 7.5 and 8.1 min. were matched with II-34 and II-35, respectively (153). The major g.c. peak was identified as exo-3-dimethylaminobicyclo[2.2.1]heptan-2-one (II-39, 40%) by g.c. peak matching with an authentic sample (155).

The aminoketone II-39 was obtained as an oil by preparative g.c. and showed i.r. absorptions at 2822, 2778(s), 1746(s) and 1040(s) cm^{-1} (lit. i.r. 2815, 2770, 1742 and 1045 cm^{-1} (106)). The m.s. of II-39 showed M^+ at m/e 153 and a base peak at m/e 58. LAH reduction of the ketone II-39 gave the exo-alcohol II-35 and the endo-alcohol II-34 in a 90:10 ratio. $NaBH_4$ reduction of II-39 gave II-35 and II-34 in equal ratios. Both II-35 and II-34 were obtained by preparative g.c. from the $NaBH_4$ reduction and their i.r., n.m.r,

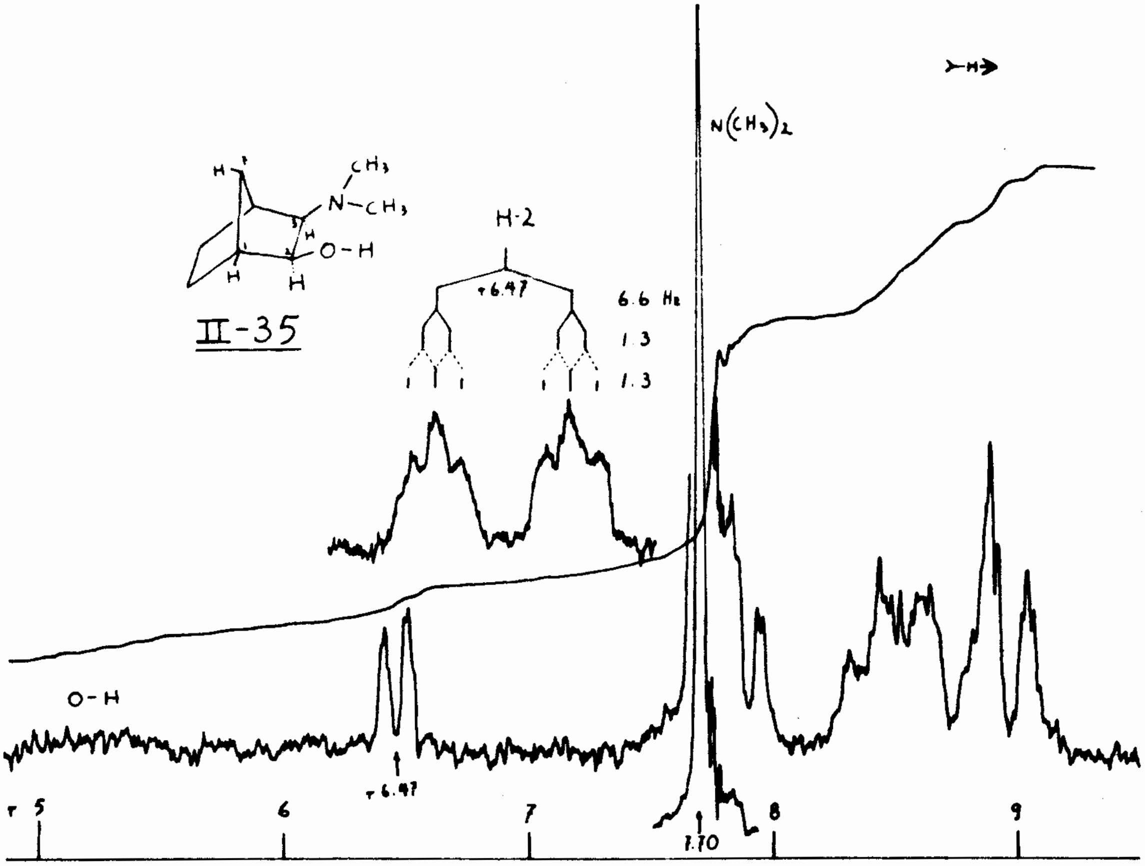


Figure II-17: 60 MHz ^{1}H NMR of 3-*exo*-dimethylamino-2*exo*-bicyclo[2.2.1] heptanol (II-35)

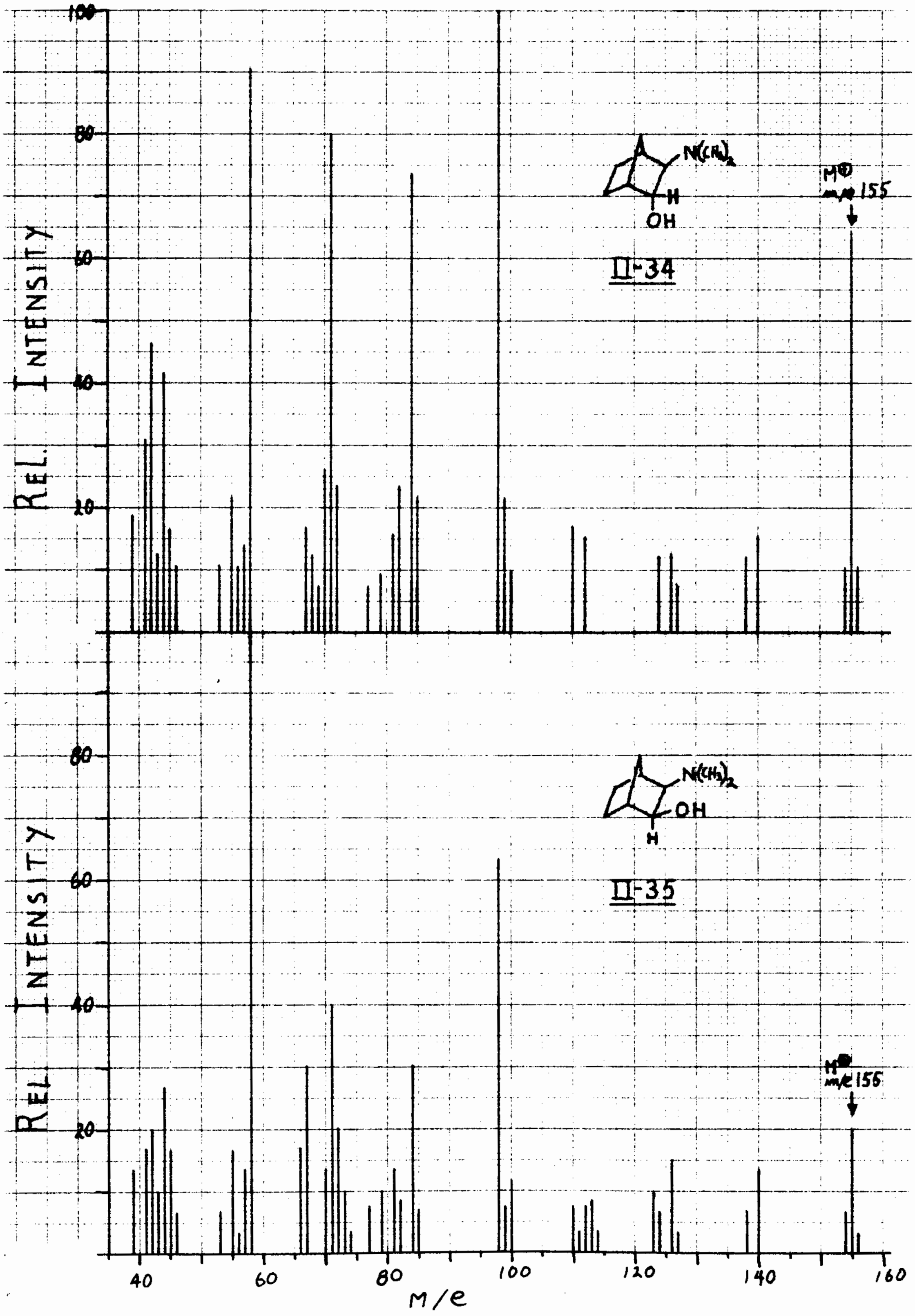


Figure II-18: Mass spectra of amino alcohols II-34 and II-35 and m.s. spectra were superimposable on those of the authentic compounds (103,153).

Further extraction of the basified photolysate provided a second basic fraction mainly consisting of the trimer I-30 in a 55% yield. The m.s. of aminoalcohols II-34 and II-35 are given in Figure II-18 for comparison.

c) Neutral conditions under Oxygen: When an acetonitrile solution of TMT (0.069 moles) and norbornene was irradiated through Vycor at 0^o under oxygen, it took 6 hours for the TMT absorption and λ_{max} 280 nm to disappear. The photolysate gave a negative test to a KI-starch-CH_3COOH solution. No yellow color was observed in the photolysate as had been seen in acidic solutions.

Addition of CF_3COOH to the photolysate and evaporation of the solvent provided 354 mg of a neutral fraction. This fraction showed at least 8 g.c. peaks of almost equal areas. One of the peaks was matched with the trifluoroacetate II-38 but the others could not be identified. Only a trace amount of the epoxide II-32 was detected by g.c. and t.l.c.

The basic fraction consisted mainly of the trimer I-30 (90% yield)without a trace of addition products by g.c. or n.m.r. examinations; however, some TMH (4%) was also identified.

3) 1,5-Cyclooctadiene (COD)

a) In CF_3COOH under Nitrogen: The photolysis of TMT in the presence of COD and CF_3COOH in acetonitrile under nitrogen at 0° produced a yellow color which disappeared within 2 hours. No products could be obtained from the neutral and acidic extract.

Two compounds, 5-dimethylaminocyclooctene (II-40, 32%) and 6-exo-dimethylaminomethyl-2-exo-dimethylamino-cis-bicyclo[3.3.0]octane (II-41, 12%), were obtained from the basic fraction by column chromatography. These two compounds were in a 1.9:1 ratio as observed by gas chromatography. No change in yield or product distribution was observed when a portion of the photolysate was treated with $NaBH_4$ before being made basic (see Experimental).

The aminooctene II-40 was identified on the basis of its spectra. The i.r. absorptions at 3020 and 727 cm^{-1} indicated the presence of a cis-olefin (138) and at 2862, 2828, 2779, and 1035 cm^{-1} suggested a dimethylamino moiety. Proton n.m.r. of II-40 showed the olefinic protons at $\tau 4.48$ (m, $W_{1/2}$=35Hz; 2H) and the $(CH_3)_2$-N group at $\tau 7.92$ (s; 6H). The molecular ion at m/e 153 and analysis agreed with the molecular formula $C_{10}H_{19}N$. The picrate, mp 153-167°, gave the correct analysis for $C_{16}H_{22}N_4O_7$.

The bicyclooctane II-41 was obtained by column chromatography as an oil. Its i.r. indicated the presence of a dimethylamino group at 2863, 2818, 2770, and 1040 cm^{-1} but no olefin at ca. 3020 and 720 cm^{-1}. The proton n.m.r. showed the presence of two different $(CH_3)_2N$ signals at τ7.74 and 7.78, but no protons downfield from τ7.72. The signal of the ring protons was not resolved, showing a broad multiplet τ7.7 to 9.0. The molecular ion at m/e 210 and analysis agreed with the molecular formula $C_{13}H_{26}N_2$. The intense m.s. fragment at m/e 58 suggested the presence of a dimethylaminomethyl moiety. Analysis of its dipicrate II-41a, mp 217-221° (decomp.), agreed with the formula $C_{25}H_{32}N_8O_{14}$ and showed h.r.m.s. peaks at m/e 228.9971 (calcd. for $C_6H_3N_3O_7$, picric acid: 228.9971) and 210.2090 (calcd. for $C_{13}H_{26}N_2$, II-41: 210.2096). The di-methiodide II-41b, mp 155-190° (decomp.), had a molecular formula $C_{15}H_{32}N_2I_2$ by analysis and had intense m.s. fragments at m/e 210, 142, 127, and 58. The structure of II-41b was confirmed by proton n.m.r. decoupling (Figure II-19 and Table II-13).

The analytical and spectral data indicated II-41 to be a bicyclooctane derivative having dimethylamino and dimethylaminomethyl substituents. Both bicyclo[4.2.0]octane and trans-bicyclo[3.3.0]octane systems have higher strain energies than cis-bicyclo[3.3.0]octanes (156). The latter is formed exclusively in transannular free radical cyclization of COD (156,157). Furthermore,

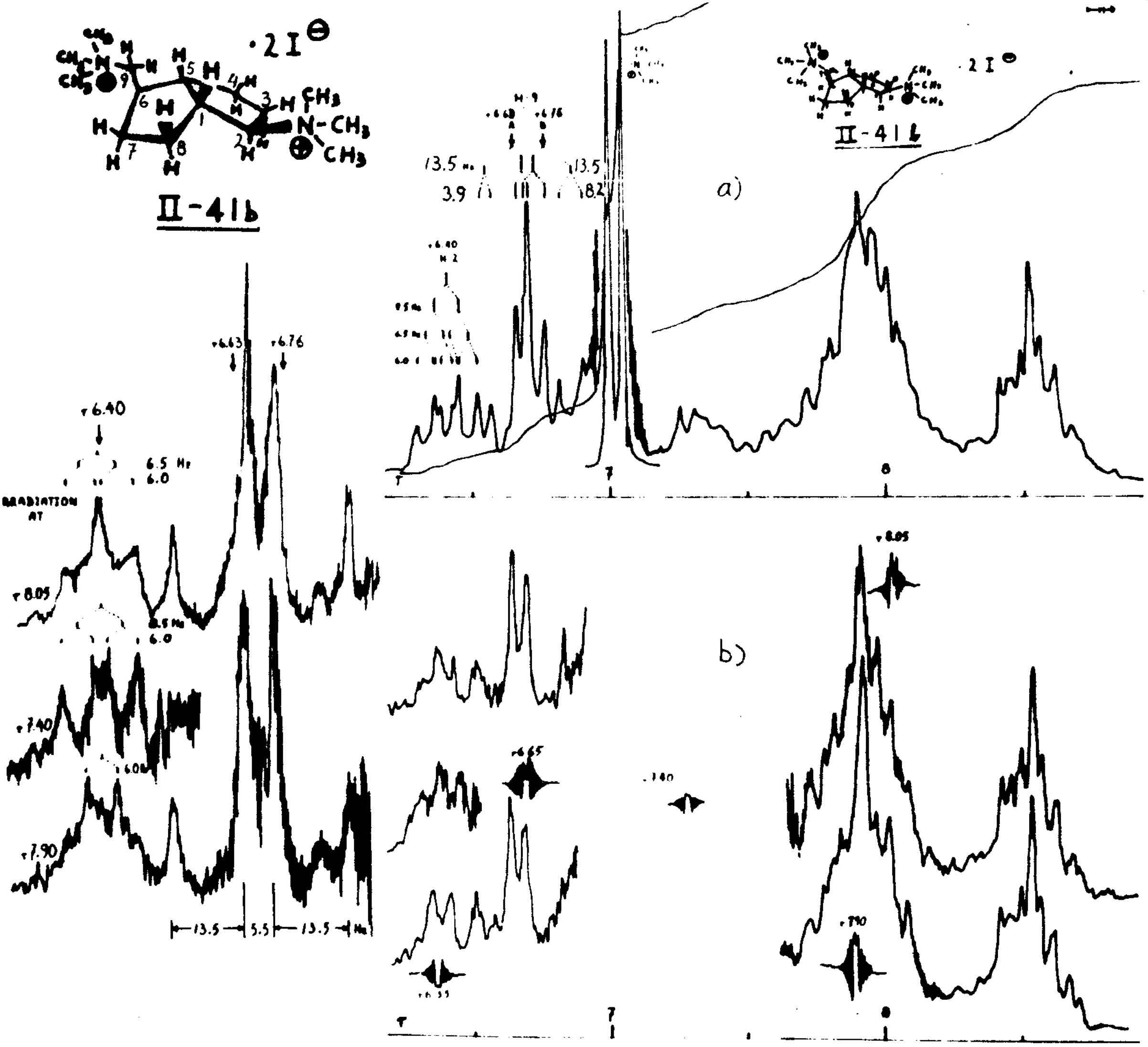


Figure II-19: ^{1}H NMR decoupling of 6-exo-dimethylaminomethyl-2-exo-dimethylamino-cis-bicyclo[3.3.0]octane dimethiodide (II-41b)

Table II-13: Chemical shifts and coupling constants for II-41b.

Chemical shift (τ)

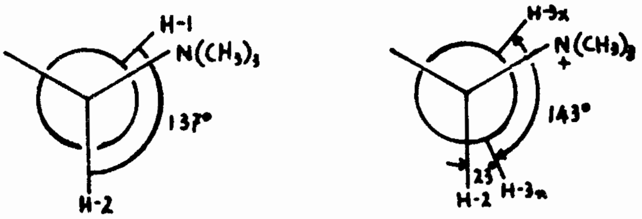
H	τ
1	7.32
2	6.40
3x	7.80
3n	8.00
6	7.93
9A	6.63
9B	6.76
N-CH_3	6.99 and 7.04

^1H-^1H coupling constants (Hz)

J	Hz
$J_{2,1}$	6.5
$J_{2,3x}$	6.0
$J_{2,3n}$	8.5
$J_{9(AB)}$	13.5
$J_{9A,6}$	8.2
$J_{9B,6}$	3.9

the initial radical attack on COD occurs in such a manner as to orient the incoming radical into the exo-2-position of the cis-bicyclo[3.3.0]octane ring system (157). Therefore, a dimethylaminium radical was expected to attack COD in a similar manner to generate an intermediate 2-exo-dimethylamino-cis-bicyclo[3.3.0]oct-6-yl radical (II-42). II-42 might combine with a dimethylaminomethyl moiety from the less crowded (156) exo side to produce the observed product II-41.

An examination of Dreiding molecular models of II-4b suggested a W (envelope) conformation to lead to the least amount of interactions (see reference 158). Newman projections for this model of C-2 on C-1 or C-3 (Figure II-20) showed the following dihedral angles: $\phi 1\text{-}2=137^{o}$, $\phi 2\text{-}3_{x}=143^{o}$, and $\phi 2\text{-}3_{n}=23^{o}$. Using the respective observed coupling constants (Table II-13) and the above angles, values of $J^{o}=10.0$Hz, $J^{180}=11.5$Hz, were calculated for the Karplus relationship (140). The magnitude of J^{180} is in the range for protonated or acylated cyclohexylamines ($J_{aa}=11\text{-}12$Hz (159)). On examination of other molecular models, the observed coupling constants (Table II-13) could not be made to fit either an endo-2-substituted cis-bicyclo[3.3.0]octane or a rearranged bicyclo[3.2.1]octane system.



C-2 on C-1 C-2 on C-3

Figure II-20: Dihedral angles in II-41b.

b) In CF_3COOH under Oxygen: The photolysis of TMT (4g) under oxygen, in the presence of COD in acetonitrile containing CF_3COOH, developed a deep yellow color which disappeared within two hours. The photolysate gave a strong positive test to KI-starch paper indicating the presence of oxidizing agents. The solvent was evaporated and the residue immediately treated with $NaBH_4$. The basic extract (3g) from the $NaBH_4$ mixture was found to contain the following compounds.

Trans-2-dimethylaminocyclooct-5-en-1-ol (II-44, 27%) was obtained as a colorless oil by preparative g.c., and was identified by peak matching with an authentic sample (160): i.r., n.m.r., and m.s. were identical to that of an authentic sample of II-44 prepared by Dr. K.S. Pillay (103, 161). The n.m.r. (Figure II-21) and m.s. (Figure II-22) are included as a comparison with the *cis* isomer II-45.

Cis-2-dimethylaminocyclooct-5-en-1-ol (II-45, 46%) was obtained by preparative g.c. as white prisms, mp 72-76°. It had the correct molecular ion at m/e 169. The i.r. of II-45 indicated the presence of a cis-olefin at 3020, 721 cm^{-1}, a hydroxy group at 3130(sb), 1120(sb) cm^{-1}, and a dimethylamino moiety at 2874(s), 2840(s), 2794(s), and 1023(s) cm^{-1}. The assignment of the structure to II-45 was confirmed by n.m.r. decoupling experiments (Figure II-23 and Table II-14).

A Dreiding molecular model of amino alcohol II-45 indicated that the least interactions occurred if the $(CH_3)_2N$ moiety was in a pseudo-equatorial orientation. The H-1 would then be oriented at ca. 90° to H-2, in accordance with the low coupling constant observed ($J_{1,2}$=1.2Hz), and about in the middle of H-8c and H-8t ($J_{1-8c}=J_{1-8t}$=4.0Hz). The pseudo-equatorial position of H-1 was indicated by the two W-Plan couplings between this proton and H-3c and H-7t ($J_{1,3c}$=0.8; J_{1-7t}=1.0Hz). These W-Plan couplings could not be measured directly but were approximated to account for the broadening observed in the H-1 signal. The pseudo-axial orientation of H-2 was indicated by a large axial-axial coupling with H-3t (J_{2-3t}=10.7Hz). The conformation of II-45 was identical to that speculated for its nitrate ester (103). The oxygen of II-45 was in close proximity to the double bond and might cause the downfield shift (ca. 0.3 ppm) observed for H-5 and H-6 relative to II-44 (see Figure II-21).

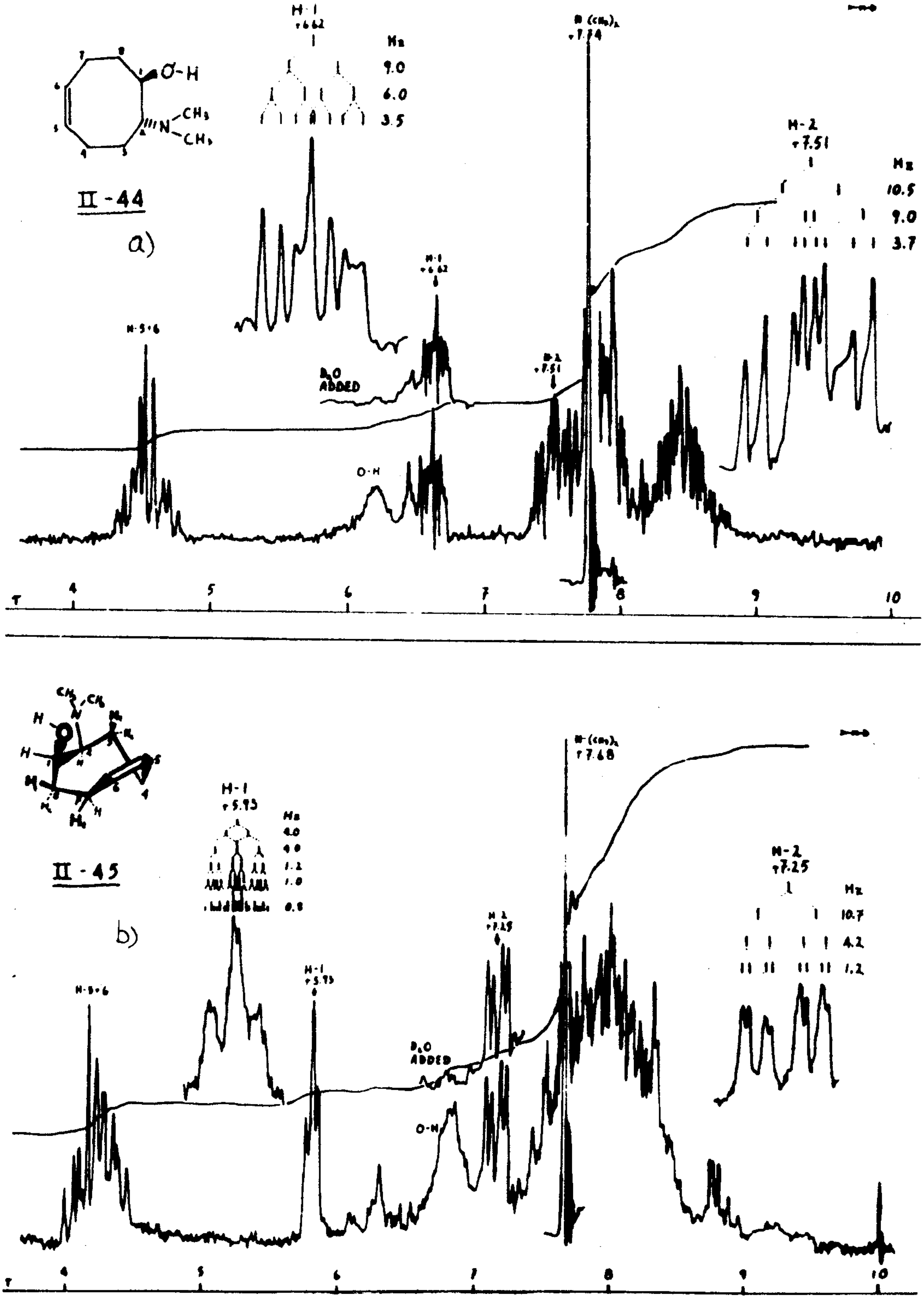


Figure II-21: ^{1}H NMR of a) trans-(II-44) and b) cis-(II-45)-2-dimethylaminocyclooct-5-en-1-ols

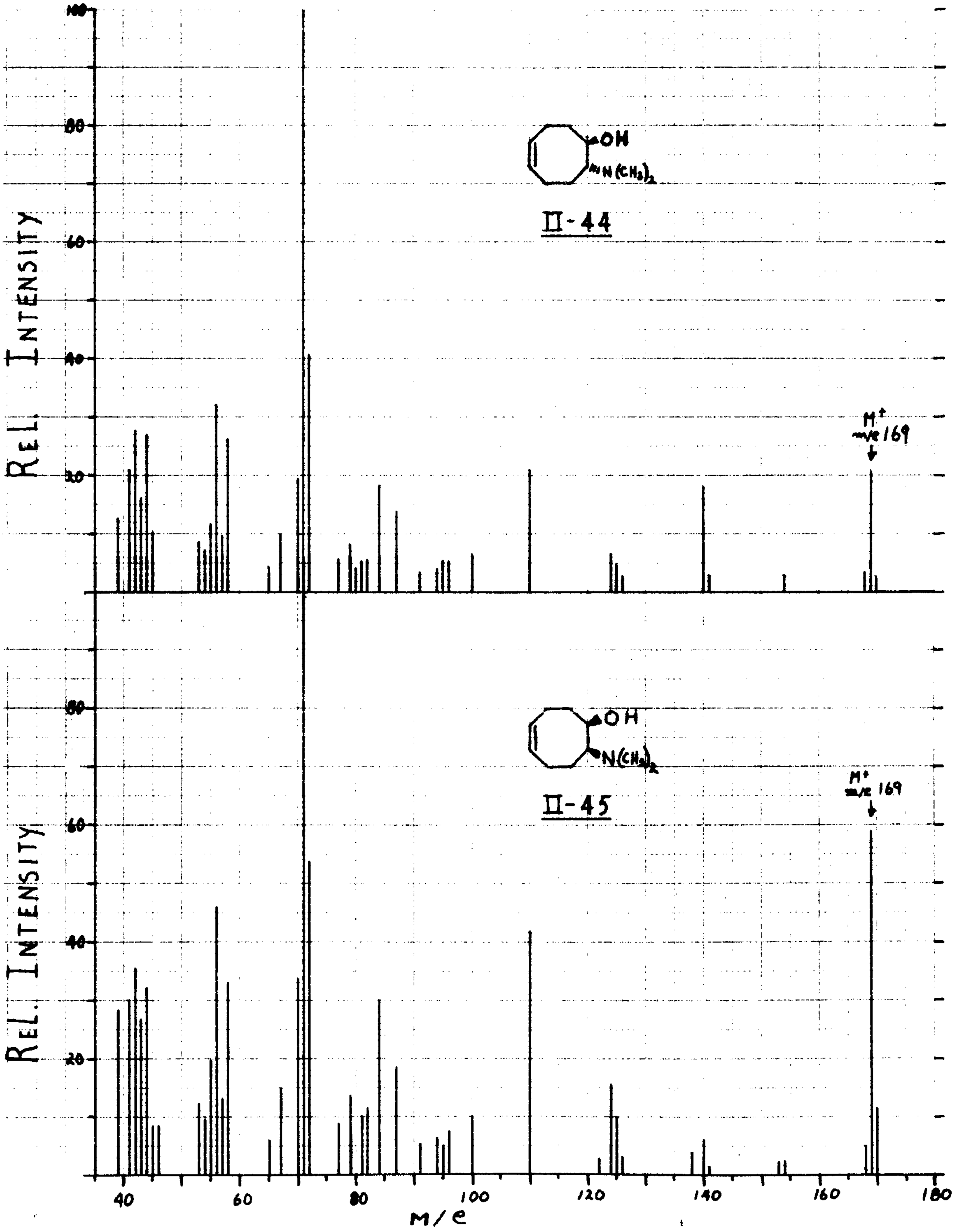


Figure II-22: Mass spectra of amino alcohols II-44 and II-45

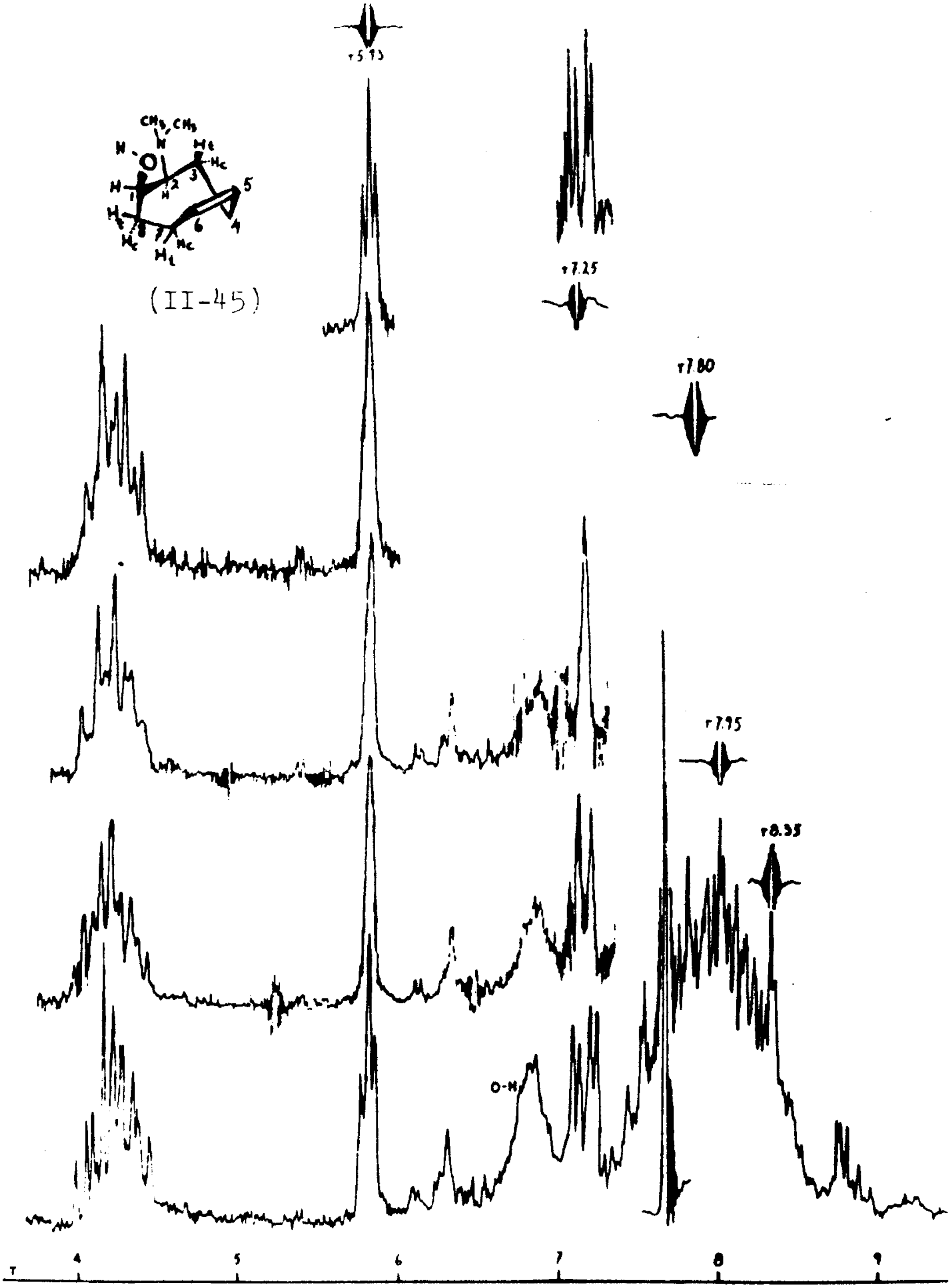


Figure II-23: ^{1}H NMR decoupling of amino alcohol II-45

Table II-14: Cis-2-dimethylaminocyclooct-5-en-1-ol (II-45)

^1H chemical shift (τ)

^1H	τ
1	5.93
2	7.25
3c	8.0
3t	8.35
5,6	4.25
7t	8.35
8c	8.2
8t	8.2
N-CH_3	7.68
O-H	6.90

^1H-^1H coupling constants (Hz)

J	Hz
1,2	1.2
1,3c	ca. 0.8
1,7t	ca. 1.0
1,8c	4.0
1,8t	4.0
2,3c	4.2
2,3t	10.7

In addition to amino alcohols II-44 and II-45, a small amount of aminooctene II-40 was detected by g.c. peak matching.

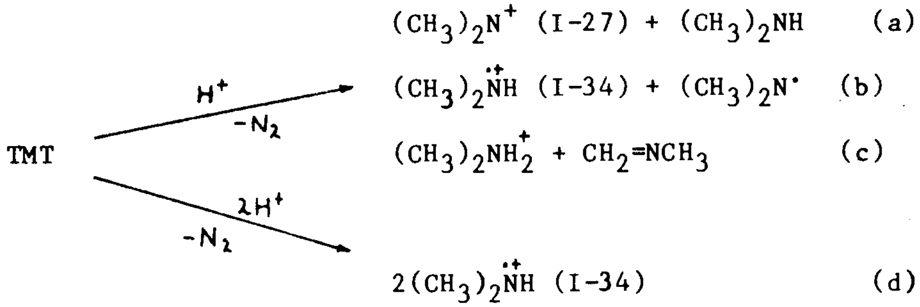
Further extraction of the basified $NaBH_4$ mixture provided a highly polar tar which could not be separated by t.l.c. but showed at least 3 g.c. peaks at long retention times (over 1 hour). The n.m.r. of this tar exhibited four strong singlets in the $(CH_3)_2N$ region (τ7.6-7.8), a broad cycloalkane absorption in the region τ7.8-8.7, and signals probably arising from α-hydroxy protons in the region τ6.0-6.5. The olefinic proton signals at τ4.0-4.5 were very weak. The i.r. of this tar indicated the presence of a hydroxy group at 3300(sb) and 1050(sb) cm^{-1} and a dimethylamino moiety at 2830 and 2785 cm^{-1}. The very weak n.m.r. olefinic proton signals indicated the possible presence of a bicyclic compound which could not be isolated.

CHAPTER III

DISCUSSION

A) THERMAL TMT DECOMPOSITION

The present results allow a differentiation on the mode of TMT decomposition under acidic conditions. Other workers have found that, in dilute aqueous acidic solutions up to H_o=-3, TMT decomposition may take place from the first conjugate acid of TMT (13,14,16) via ionic intermediates (4,14,58,59); however, in concentrated H_2SO_4 it has been proposed that 2-tetrazenes may lose nitrogen from the second conjugate acid to form two aminium radicals (14,59). Thus, we have found it convenient to study TMT decomposition in CF_3COOH and in H_2SO_4 which have $-H_o$=3.03 and 11, respectively (128). It has been proposed that TMT decomposition through mono-protonation in CF_3COOH or di-protonation in H_2SO_4 might generate a dimethylaminium radical (I-34), a dimethylnitrenium ion (I-27), or elimination products as shown in Scheme III-1.



Scheme III-1

1) In H_2SO_4: If the decomposition of tetraphenyltetrazene (TPT) in H_2SO_4, where the decomposition is proposed to occur through TPT-$2H^+$ to generate diphenylaminium radicals (59), can be taken as an analogy, TMT in H_2SO_4 may decompose to give two dimethylaminium radicals via TMT-$2H^+$ (14). From studies on aminium radicals generated from the chloramine decompositions in H_2SO_4, Ingold (128) has suggested that the bimolecular self reaction of dimethylaminium radicals may proceed through combination and disproportionation as shown in reactions 1 and 2. For aminium radicals such as the 2,2,6,6-tetramethyl- piperidinium radical, where 1 and 2 cannot operate, Ingold (128) has further considered the formation of a nitrenium ion as shown in reaction 3.

$$2(CH_3)_2NH^{\cdot +} \rightleftharpoons (CH_3)_2\overset{+}{N}H\overset{+}{N}H(CH_3)_2 \quad (\text{TMH-}2H^+) \qquad [1]$$

$$2(CH_3)_2NH^{\cdot +} \longrightarrow (CH_3)_2NH_2^+ + CH_2{=}\overset{+}{N}HCH_3 \qquad [2]$$

$$2R_2NH^{\cdot +} \longrightarrow R_2NH_2^+ + R_2N^+ \qquad [3]$$

Reactions 1 and 2 appear to occur since the corresponding products are observed by n.m.r. in H_2SO_4 (Figure II-1). However, no e.s.r. signal for the dimethylaminium radical could be detected at -20° or higher in these solutions. Since vigorous gas evolution occurs on mixing in H_2SO_4, it appears that TMT-$2H^+$ decomposition is too rapid to be detected. Nevertheless, the formation of toluidines II-3 in the TMT decomposition in H_2SO_4 in the presence of toluene suggests the intermediacy of the dimethylaminium radical in analogy to the postulated chloramine decomposition (115).

The amination of toluene by dimethylaminium radicals has been reviewed in the Introduction section. The formation of a primary charge transfer (CT) complex (I-35) between a dimethylaminium radical and toluene, as proposed by Minisci (115), is attractive in view of the toluidine II-3 isomer ratios obtained in the present work (Table II-2). The π-electron spin densities of the toluene cation radical have been reported to be o=0.081, m=0.035, and p=0.335 (124,162) having the o:m:p ratio of 18:7:75. This ratio is reasonably close to the toluidine II-3 isomer ratio obtained.

Although the mechanism leading to high yields of meta toluidine II-3 is proposed by Kovacic (114) to involve ionic addition of the chloramine to toluene followed by HCl elimination, Minisci and coworkers (115) have taken special care to avoid such an ionic mechanism in their amination of toluene in the dimethylchloramine decomposition. However, their toluidine II-3 o:m:p ratio of 7:22:71 suggests concurrence of an ionic reaction leading to the meta isomer with that of an aminium radical reaction leading to the para isomer. Since such an ionic mechanism cannot occur during TMT decomposition in H_2SO_4, the present toluidine II-3 ratio of 15:10:75 (No.6, Table II-2) probably represents more accurately the isomer ratios resulting from a dimethylaminium radical attack on the toluene nucleus. The reaction of the dimethylaminium radical with toluene under these conditions are proposed in Scheme III-2.

The CT complex I-35 may rapidly collapse to a σ-complex (I-36, Scheme I-16) (115) with an <u>ortho</u>, <u>meta</u>, and <u>para</u> distribution as represented in the observed toluidine II-3 ratios. Alternatively, the CT complex I-35 may dissociate as shown in 5 to give the toluene cation radical. The toluene cation radical may eliminate a proton to generate a benzyl radical by reaction 6 (163-165). A benzyl radical may also be formed by hydrogen atom abstraction from toluene by a dimethylaminium (127) or other radical species present in solution. The benzyl radical may combine with a dimethylaminium radical to give the observed N,N-dimethylbenzylamine in trace amounts. Trace amounts of bibenzyl are also obtained from most reactions in H_2SO_4 supporting the presence of benzyl radicals.

$$\phi CH_3 + (CH_3)_2NH^{\cdot +} \longrightarrow [\phi CH_3^{\cdot +}\quad HN(CH_3)_2]\quad (I\text{-}35) \qquad [4]$$

$$[\phi CH_3^{\cdot +}\quad HN(CH_3)_2] \xrightarrow{H_2SO_4} \phi CH_3^{\cdot +} + (CH_3)_2NH_2^{+} \qquad [5]$$

$$\phi CH_3^{\cdot +} \rightleftharpoons \phi CH_2^{\cdot} + H^{+} \qquad [6]$$

$$\phi CH_3 + (CH_3)_2NH^{\cdot +} \longrightarrow \phi CH_2^{\cdot} + (CH_3)_2NH_2^{+} \qquad [7]$$

$$\phi CH_2^{\cdot} + (CH_3)_2NH^{\cdot +} \longrightarrow \phi CH_2NH(CH_3)_2^{+} \qquad [8]$$

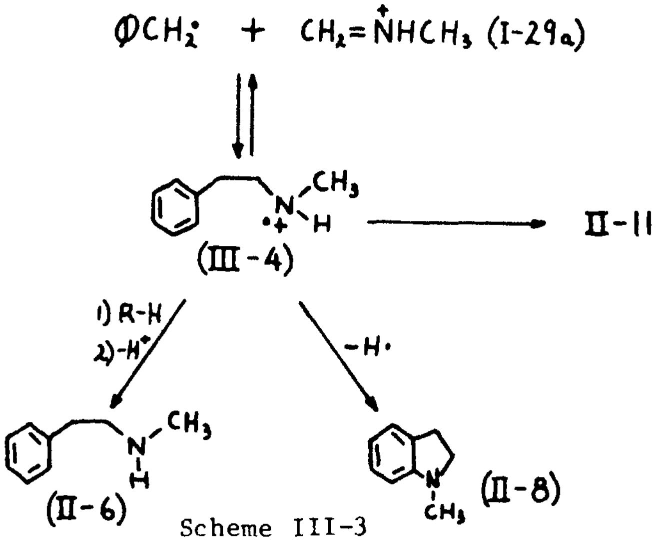
$$\phi CH_2^{\cdot} + (CH_3)_2NH^{\cdot +} \longrightarrow \phi CH_2^{+} + (CH_3)_2NH \qquad [9]$$

$$\phi CH_2^{+} + \phi CH_3 \longrightarrow \phi CH_2\phi CH_3 + H^{+} \qquad [10]$$

Scheme III-2

Although no precedence is known, a benzyl radical attack on the protonated imine (I-29a) would result in the formation of an

N-methylphenethylaminium radical (III-1, Scheme III-3). The cyclization to N-methylindoline (II-8), and H atom abstraction to N-methylphenethylamine (II-6) are reported (102,109).



Scheme III-3

The intervention of a benzyl carbonium ion is required to account for the formation of *o*- and *p*-benzyltoluenes in a 4:6 ratio. The latter are clearly derived from an ionic benzylation reaction on toluene. Such a reaction has been shown to give an *o*:*p* ratio of 4:5 with only a trace of the *meta* isomer (76,168). The *meta* isomer is formed as the major product in the presence of Lewis acid catalysts where isomerization cannot be avoided (168,169). It may be significant that a 4:5 ratio of *o*- and *p*-benzyltoluenes is obtained whether the N-chloramine (No.1, Table II-2) or TMT (Nos.2-12, Table II-2) is decomposed in H_2SO_4. Bock and Kompa (120,121) did not report this product in their dimethylchloramine decomposition in H_2SO_4 and toluene. Although the mechanism leading to the formation of the benzyl carbonium ion is uncertain, a possible oxidation of the benzyl radical may occur (164,165) as shown in reaction 9.

The possibility exists that the benzyl carbonium ion is generated from toluene by a dimethylnitrenium ion hydride abstraction. Edwards (66) has considered such a mechanism for nitrenium ions. Although Ingold (128) suggests that dimethylaminium radicals disproportionate through reaction 2, he does not discount the formation of a nitrenium ion through reaction 3. The formation of nitrenium ions in TMT decomposition in H_2SO_4 cannot be unequivocally discounted. However, as will be discussed below, a nitrenium attack on the toluene nucleus may result in a different toluidine isomer ratio than observed in H_2SO_4.

Since the n.m.r. results show that TMT is decomposed within 30 minutes at -20° in concentrated H_2SO_4, the extended times required to obtain an optimum yield of toluidines II-3 (Table II-2, Nos.3 and 6) suggest that there is another source, probably diprotonated TMH, for the dimethylaminium radicals. As demonstrated in the n.m.r. investigation, TMH-$2H^+$ is formed when TMT is dissolved in H_2SO_4 and decomposes slightly in this solution during one day at room temperature*. In analogy to the ready dissociation of

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*An authentic sample of TMH in H_2SO_4 showed no decrease of the TMH-$2H^+$ n.m.r. signal at τ6.40 after standing at 20° for two weeks. This signal however disappeared within one hour when the solution was heated at 110° to be replaced by the n.m.r. signals of the protonated imine I-29a and $(CH_3)_2NH_2^+$ in about an equimolar ratio.

diprotonated tetraphenylhydrazine in H_2SO_4 to generate diphenylaminium radicals (59,83), $TMH\text{-}2H^+$ may decompose slowly to release diemthylaminium radicals, the reverse process of reaction 1. This slow release could account for the slow formation of toluidine II-3. Thus, the measure of N_2 gas evolution cannot be used to indicate the rate of toluidine formation.

It is not surprising that no $TMH^{\cdot +}$ e.s.r. signal is detected when TMT is dissolved in H_2SO_4 since $TMH\text{-}2H^+$ is resistant to oxidation. However, it is not clear how $TMT^{\cdot +}$ is formed in H_2SO_4. The latter could have been present in the starting TMT since neat TMT is seen to display a weak $TMT^{\cdot +}$ e.s.r. signal. Thermal decomposition of $TMT^{\cdot +}$ can be discounted as a source for the dimethylaminium radical because of its high stability (25) as observed over several days in H_2SO_4 at room temperature, its low concentration ($<10^{-4}$M), and its failure to react with cyclohexene.

2) In CF_3COOH: The thermal decomposition of TMT in CF_3COOH takes a somewhat different course from that in H_2SO_4 as revealed in n.m.r. and product patterns. Although a weak $TMT^{\cdot +}$ e.s.r. signal is also observed in CF_3COOH, the product pattern from the TMT decomposition in CF_3COOH at -15 to 30^o strongly suggests that

ionic reactions are the major decomposition route. In agreement with the structure of the previously reported TMT-HCl salt (34), TMT in CF_3COOH at -15^o exhibits three strong singlets at $\tau 6.62$, 6.82, and 6.92 in a ratio of 1:1:2 corresponding to $TMT\text{-}H^+$ in the trans-configuration. This species shows no evidence of decomposition at this temperature, but at 30^o, it decomposes with first order kinetics where $k=6.5\pm1x10^{-4}sec^{-1}$ can be estimated from a half life of about 20 minutes (Figure II-2). McBride and Thun (14) have observed a large temperature dependence of $TMT\text{-}H^+$ decomposition rate, having found $k=1x10^{-4}sec^{-1}$ in perchloric acid solutions of $H_o=-3$ at 25^o. They have proposed an ionic mechanism to account for the clean formation of N-methylmethyleneimine and dimethylamine in an equimolar ratio (14). The ionic process for the decomposition of $TMT\text{-}H^+$ has also been favored by other workers (4,58,59).

In the present study of TMT decomposition in CF_3COOH-toluene solvent systems, the observed results are contrary to the intermediacy of the dimethylaminium radical but are more compatible with that of the dimethylnitrenium ion. Aminium radicals generated from chloramines in CF_3COOH or in acidic solutions of a similar $-H_o$ range of 2-4 (128) exclusively abstract benzylic hydrogens (116,127) without attacking the toluene nucleus (116) but add efficiently to olefins (88). In thermal $TMT\text{-}H^+$ decomposition in CF_3COOH, the absence of addition products to olefins, the lack of benzylic abstraction products such as bibenzyl except the trace of

N,N-dimethylbenzylamine, the small yield of amination product toluidine II-3, and the lack of TMH formation, all these preclude the intermediacy of dimethylaminium radicals. Furthermore, the toluidine II-3 o:p ratio of 2:1 with only a trace of the meta isomer obtained in this decomposition (Table II-4) is significantly different from the ratio obtained in H_2SO_4 (Table II-2) and suggests that an aminating species different from the dimethylaminium radical is involved. Aminium radicals have been shown to give a low toluidine II-3 o:p ratio (115). The observed high toluidine II-3 o:p ratio in CF_3COOH suggests a species such as the dimethylnitrenium ion attacking the π-electrons of toluene since highly electrophilic species such as nitronium ions or isopropyl cations, having approximately the same size as the proposed nitrenium ion, give nitrotoluenes in an o:p ratio of 2:1 with only a trace of meta (76) and isopropyltoluenes in an o:m:p ratio of 3:1:2 (80, Table 2, No.63).

The nitrenium ion intermediacy in CF_3COOH is further supported by the formation of trace amounts of N,N-dimethylbenzylamine. This compound may, in principle, have been formed by the combination of benzyl and dimethylaminium radicals. However, no other product suggests the presence of these radicals under the conditions. Because of the high yield of imine trimer I-30, a benzyl radical would undoubtedly undergo reactions, as observed in H_2SO_4 and shown above in Scheme III-3, leading to a fair amount of N-methylphenethylamine. Since no trace of the latter is detected in the CF_3COOH decomposition, a benzyl radical is not likely. The formation of N,N-dimethylbenzylamine might be considered to occur through bond insertion into a toluene benzylic position by the singlet electronic state of the nitrenium ion (61,65).

Attempts to get a high yield of amination by stabilizing the nitrenium ion or using a more reactive aromatic substrate were not very successful. A yield of 5-10% amination of anisole did occur in TMT decomposition in CF_3COOH (Appendix B) giving a 2:1 o:p ratio of anisidines. This compares with only 2% yield of toluene amination under the same conditions but the yield of anisidines are nevertheless disappointingly low. In a hoped-for stabilization of the nitrenium ion by non-bonding electrons, CH_3CN, $CHBr_3$, and perfluoroalkane-70 are used as solvent (Nos. 16-18, Table II-4), but the expected stabilization is not observed. The presence of bromine may facilitate the nitrenium ion singlet-triplet intersystem crossing (61,65); however, there is no evidence for the triplet reacting with toluene in $CHBr_3$. Trapping of the proposed nitrenium ion with CO (170) has also been unsuccessful. It is likely that the dimethylnitrenium ion rapidly decomposes to the imine $CH_2{=}NHCH_3^+$ to account for the high yield of imine trimer I-30 and low yield of amination found in TMT decomposition in CF_3COOH. Such a reaction might find analogies in the rapid rearrangement of methylnitrene (82) and isopropyl cation (81).

The nitrenium ion derived from piperidine is believed to react exclusively through the triplet state (62,71). No toluene amination products are detected in the decomposition of 1,4-bis-pentamethylene-2- tetrazene (BPMT) in CF_3COOH at 50° (31 and Appendix A). However, a 3% yield of benzyltoluenes is obtained in the neutral fraction indicating the formation of a benzyl carbonium ion. Since no products derived from toluene have been obtained in the basic fraction, a benzyl radical is probaby not formed. Unlike TMT decomposition in CF_3COOH, where no benzyltoluenes are detected, it appears that if a nitrenium ion is formed from BPMT decomposition, it can react with toluene exclusively by hydride abstraction. Such a reaction pathway for nitrenium ions has been proposed by Edwards (66); however, this is not compatible with the triplet state of the nitrenium ion structure.

The formation of the N,N,N'-trimethyldiaminomethyl radical II-2 in the benzene or cyclohexene layer when TMT is dissolved in $CF_3COOH-C_6H_6$ or CF_3COOH-cyclohexene may be derived from a reaction sequence outlined in Scheme III-4. Attack of a dimethylaminium radical on the imine followed by a rearrangement in the hydrocarbon solvent may explain its formation. Alternatively, II-2 may be formed by a hydrogen abstraction from a molecule such as N,N,N'-trimethylmethylenediamine. The latter is particularly attractive since it could lead to a dimethylaminomethyl moiety found when TMT is photolyzed in $CF_3COOH-CH_3CN$ solutions containing olefins.

$$(CH_3)_2NH^{\cdot +} + CH_2{=}NHCH_3^{+} \longrightarrow (CH_3)_2NCH_2\overset{\cdot +}{N}HCH_3 + H^{+} \qquad [11]$$

$$(CH_3)_2NCH_2\overset{\cdot +}{N}HCH_3 \longrightarrow (CH_3)_2N\dot{C}HNHCH_3(II\text{-}2) + H^{+} \qquad [12]$$

$$(CH_3)_2NCH_2NCH_3 \xrightarrow{R\cdot} (CH_3)_2N\dot{C}HNHCH_3(II\text{-}2) \qquad [13]$$

$$(CH_3)_2NCH_2NHCH_3 \xrightarrow{H^{+}} (CH_3)_2N{=}CH_2^{+} + NH_2CH_3 \qquad [14]$$

Scheme III-4

Although the formation of radicals under these conditions contradicts previous observations in CF_3COOH, a photoinduced decomposition of TMT by the fluorescent lighting may operate. As will be discussed below, when solutions of TMT, CF_3COOH-CH_3CN, and olefins are left to decompose in the dark, aminium radicals are not formed. However, when these solutions are irradiated, products of dimethylaminium radical addition to olefins are formed in abundance. Since α-aminoalkyl radicals are protonated in solutions of pH<6 (93), it is not clear why the II-2 radical is not protonated in the benzene or cyclohexene layer containing CF_3COOH.

Nelsen (16) has observed radical formation in the methylation or acylation of TMT and has stated that in non-polar solvents such as CCl_4 or C_6H_6, acetic or formic acid decomposition of TMT produces a 6% yield of radical species. In addition to $TMT^{\cdot +}$ and $TMH^{\cdot +}$, one of the radicals observed by Nelsen (16) has a (N)=12.6, a (3H)=11.75, a (2H)=6.3G and a g-factor of 2.0059. Although the structure of the latter is uncertain, the relatively high g-factor suggests a nitroxyl radical (131). The coupling with five adjacent hydrogens further suggest that this species may be derived from one of the radicals shown in Scheme III-4 reacting with oxygen.

B) PHOTOLYTIC TMT DECOMPOSITION

The results show that distinction can be made between the photolytic and thermal modes of TMT-H^+ decomposition under dilute acidic conditions (pH=0-2). Since at 0^o, the irradiated solutions show TMT-H^+ decomposition complete within a few hours whereas those kept in the dark show little or no decomposition during this time, the primary mechanisms for these decompositions should be different. As demonstrated above, the thermal decomposition ($0-60^o$) proceeds by a heterolytic pathway a̲ or c̲ shown in Scheme III-1. However, it will be shown below that irradiation of these TMT-H^+ solutions can divert the decomposition to a homolytic path b̲. This is clearly exemplified by the products obtained when either decomposition is conducted in the presence of olefins. Although there is no evidence for a dimethylamino group incorporation into the olefin in the thermal decomposition, it is judged from the products containing this group when these TMT-olefin solutions are irradiated under acidic conditions that a dimethylaminium radical addition to the olefin has occurred.

The detection of the n.m.r. signal for TMH-H^+ and the e.s.r. signal for $TMH^{\cdot +}$ after photolysis of TMT-H^+ in neat CF_3COOH or in $CF_3COOH-CH_3CN$ gives further support to the homolytic pathway b shown in Scheme III-1. The formation of $TMH-H^+$ can best be explained by a combination of dimethylamino and dimethylaminium radicals. Since, dimethylamino radicals are protonated in solutions of pH<6 (94,95), the formation of $TMH-H^+$ can also occur through a combination of aminium radicals, as shown above in reaction 1, followed by loss of a proton. The oxidation of $TMH-H^+$, presumably by a dimethylaminium radical (18), can account for the formation of $TMH^{\cdot +}$.

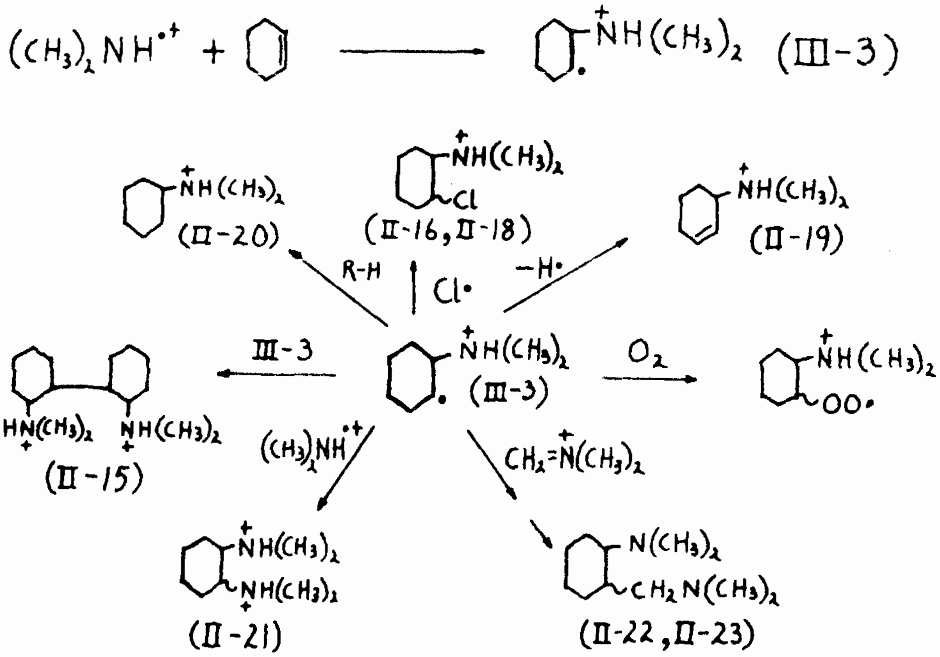
Since the original weak $TMT^{\cdot +}$ e.s.r. signal decreases during irradiation at -45°, $TMT^{\cdot +}$ is probably undergoing photolysis. It is possible that $TMH^{\cdot +}$ is also undergoing a photochemical reaction so that its signal appears only after interruption of the irradiation. The steady build up of both these signals to a maximum in about 10 minutes after the irradiation is stopped suggests the presence of a species capable of abstracting a hydrogen atom from $TMT-H^+$ and $TMH-H^+$. Although this species is most likely the dimethylaminium radical, its e.s.r. signal cannot be seen. It may be that a low steady state concentration of these aminium radicals is generated in the dark from a thermally unstable intermediate which has been formed during the $TMT-H^+$ photolysis. Ingold (29) has proposed that a neutral 2-tetrazene in the starting trans configuration may be transformed photolytically to a thermally unstable cis-tetrazene which then may decompose to generate amino radicals. A similar process in the photolysis of trans-TMT-H^+, where the thermal decomposition of an intermediate cis-TMT-H^+ may generate aminium radicals, can be invoked to explain the increase of $TMT^{\cdot +}$ and $TMH^{\cdot +}$ signals in the dark after irradiation.

Although thermal trans-TMT-H^+ decomposition in CF_3COOH shows a clean formation of dimethylamine and the imine I-29 without any sign of either TMH-H^+ or $TMH^{\cdot +}$, the n.m.r. results of the irradiated solutions show that, along with the formation of TMH-H^+, dimethylamine is formed in greater amounts to the imine I-29 and that other unidentified products are also present. This suggests that aminium radicals in addition to combination and disproportionation reactions 1 and 2, may also react with the imine through a sequence similar to that in Scheme III-4. The isolation of compounds having a dimethylaminomethyl group in TMH-H^+ photolyses in the presence of olefins is a futher indication of such a possible reaction.

Judging from the addition products containing dimethylamino groups, an aminium radical addition has occurred to the olefins described below. The additions of aminium radicals to olefins have been well documented and are reviewed elsewhere (85,99,113,114). The subsequent products of the β-ammoniumalkyl radicals (III-2) formed by this addition allow such a mechanism to be inferred which in turn indicates that the photolysis of TMT-H^+ in dilute acidic solutions (pH=0-2) generates dimethylaminium radicals.

Since TMT-H$^+$ appears not to be a good radical donor, the alkyl radical III-2 must seek other compounds in the reaction system during its lifetime. Since there are no good radical donors or scavengers when the photolysis is carried out under nitrogen, a variety of compounds is formed. However, under oxygen, the reactions of III-2 are cleanly diverted to the formation of alkyl hydroperoxides. The reaction pathways of alkyl radicals III-2 formed by dimethylaminium radical addition to cyclohexene, norbornene, or 1,5-cyclooctadiene (COD) are discussed below.

1) Cyclohexene: The intermediate β-dimethylammoniumcyclohexyl radical (III-3), formed by dimethylaminium radical addition to cyclohexene, undergoes further reactions which are summarized in Scheme III-5. Chances of combination with another aminium radical to give the diaminocyclohexane II-21 are rather low because the concentration of aminimum radicals is low at any given time during photolysis. In this system the hydrogen donor is probably cyclohexene itself which may lead to the formation of the cyclohexylamine II-20 and a cyclohexenyl radical. Various pathways for the formation of the cyclohexene II-19 are conceivable, among them, hydrogen elimination from the intermediate III-3 is the simplest one.



Scheme III-5

A combination of two III-3 radicals could lead to the dimer II-15. Since neither bicyclohexyl derivatives having a single dimethylamino substituent nor any having a dimethylaminomethyl substituent are obtained, a stepwise addition of III-3 to cyclohexene followed by further radical reactions is unlikely. The formation of the aminomethylcyclohexylamines II-22 and II-23 is tentatively explained as a radical attack of III-3 on $CH_2{=}N(CH_3)_2{}^+$ since no reasonable ionic route to introduce the dimethylaminomethyl moiety in II-22 and II-23 can be formulated (see Discussion on COD).

An oxidation of a chloride ion (electron affinity of $Cl^{\cdot}$ = 3.72 eV (171)) by a dimethylaminium radical (ionization potential of dimethylamine = 8.27 eV (126)) may give a chlorine atom which can be scavenged by III-3 radicals to give the β-chloramines II-16 and II-18. It is interesting to note that in nitrosamine photolytic addition to cyclohexene in the presence of HCl, some β-chloramines II-16 and II-18 have been detected (141,172). Dimethylnitramine photolysis in the presence of COD, using HCl as acid, has given a small yield of 5-dimethylamino-6-chlorocyclooctene (172).

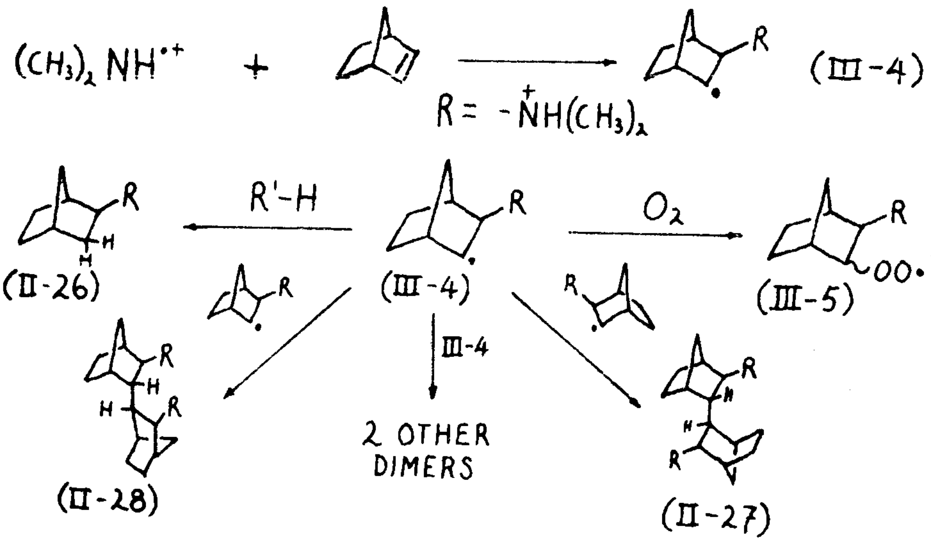
The alternate mechanism leading to the β-chloramines II-16 and II-18 by an ionic route involving the nitrenium ion can be discounted since such a pathway is likely to stereospecifically yield only trans II-16 (173) via the aziridinium intermediate (9). The lack of the amino alcohol II-24 formation in TMT-H^+ photolysis in the presence of cylcohexene, using CF_3COOH as acid, also supports that the aziridinium intermediate is not involved.

Under oxygen, III-3 radicals are efficiently scavenged by oxygen to give β-peroxyamino radicals and eventually hydroperoxides (see below). The latter are easily reduced to the corresponding cis- and trans-amino alcohols II-24a,b.

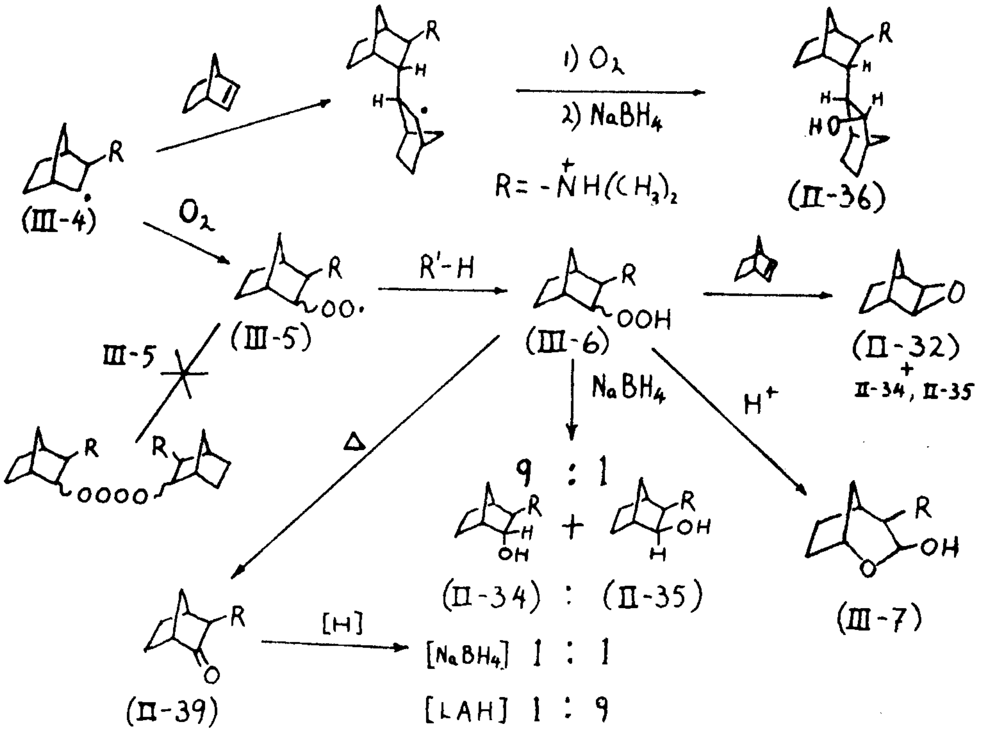
2) Norbornene: Attack of a dimethylaminium radical on norbornene occurs exclusively from the exo side (103,106,146,147) to form the intermediate exo-3-dimethylammonium-2-norbornyl radical (III-4). The subsequent reactions of this norbornyl III-4 radical formed when TMT-H^+ is photolyzed in the presence of norbornene are summarized in

Scheme III-6. For the most part, III-4 appears to undergo hydrogen abstraction or dimerization under nitrogen or formation of an exo-3-dimethylammoniumnorbornyl-2- peroxy radical (III-5) under oxygen.

Under nitrogen, the major products of dimers II-27 and II-28 may be formed by combination of norbornyl III-4 radicals rather than through a stepwise addition of III-4 to norbornene followed by radical combination with a dimethylaminium radical. First of all, the stepwise mechanism would incorporate a dimethylaminomethyl group, as found in additions to cyclohexene and COD, rather than a dimethylamino group. Secondly, for the steric reasons described by Osborn and coworkers (148), the major dimer II-28 would have the second $(CH_3)_2N$ group in the endo-orientation in the stepwise process rather than the observed exo. Thirdly, the dimer II-27, having an endo-endo dimer linkage could not possibly be formed through a stepwise mechanism since a bulky radical such as III-4 would attack norbornene exclusively from the exo side (148,176,177). Products from such a stepwise pathway under nitrogen have not been isolated but may be present in trace amounts. This may account for several unidentified minor products. The combination of norbornyl III-4 radicals means that they must have sizable concentration in the reaction system. This, in turn, means that III-4 has some stability, probably due to the bicyclic structure. The dimethylaminium radical generated in the photolysis probably adds very efficiently to norbornene to give this high concentration of III-4 radicals.



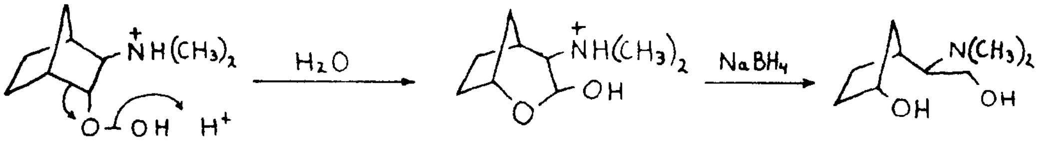
Scheme III-6



Scheme III-7

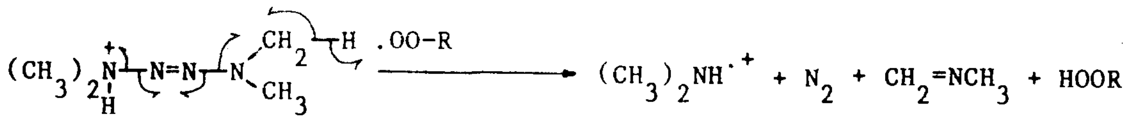
The formation of II-27 and II-28 as the major dimer products represents steric control during the combination of norbornyl III-4 radicals. Although two other dimers of undetermined stereochemistry are also observed, they are formed in lesser amounts. Since a "racemic" mixture of III-4 radicals is formed, dimerization of III-4 can, in principle, occur in 8 different endo/exo combinations to give a total of 6 dinorbornyl diastereomers. However, an examination of Dreiding molecular models shows that the least interactions occur in the approach of two different III-4 radical "enantiomers" during the formation of an endo-endo dimer linkage (i.e. II-27). Similarly, the least hindered combination of like III-4 "enantiomers" leads to the dimer II-28. The two minor dimers are probably formed through more sterically hindered combinations of III-4.

Under oxygen, the norbornyl III-4 radical is expected to be trapped by oxygen to give the peroxy radical III-5 which should lead to the norbornylhydroperoxide III-6. The subsequent reactions of III-6 are summarized in Scheme III-7. That a peroxide has been formed during the photolytic addition of dimethylaminium radicals is indicated by the presence of a sizable amount of oxidizing product and the isolation of the amino diol II-37. An acid catalyzed rearrangement of hydroperoxide III-6 to III-7 has precedent examples in other cycloalkylhydroperoxides (174,175); $NaBH_4$ reduction of III-7 gives amino diol II-37. Furthermore, the isolation of ketone II-39 as the major product in the room temperature work up of the oxidative photolysate also suggests the precursor to be hydroperoxide III-6 since such a decomposition pathway is well known to alkylhydroperoxides (174,175). Moreover, the latter observation also indicates that the peroxy III-5 radical has not dimerized to a tetroxide as tetroxides are expected to decompose thermally to the corresponding ketones and alcohols in equimolar ratios (179).



(III-6) (III-7) (II-37)

A stepwise reaction of an attack of the norbornyl III-4 radical on norbornene followed by oxygen incorporation is indicated as occurring to a small extent by the isolatin of 2.5% of the amino alcohol II-36. As discussed above in the photolysis under nitrogen, this stepwise mechanism plays a minor role in III-4 reaction. Although it appears that under nitrogen, III-4 radicals do not abstract hydrogens to any great extent, the proposed formation of hydroperoxide III-6 from a peroxy III-5 radical requires a hydrogen donor. It is uncertain that norbornene is the hydrogen donor; however, by analogy to the proposed induced decomposition of TMT under neutral conditions (53), $TMT\text{-}H^+$ may provide a hydrogen atom and itself undergo decomposition as indicated. If such a pathway is available to the peroxy III-5 radical under oxygen, it again indicates the stability of the norbornyl III-4 radical under nitrogen since the latter yields combination products as the major and hydrogen abstraction product III-26 as the minor.

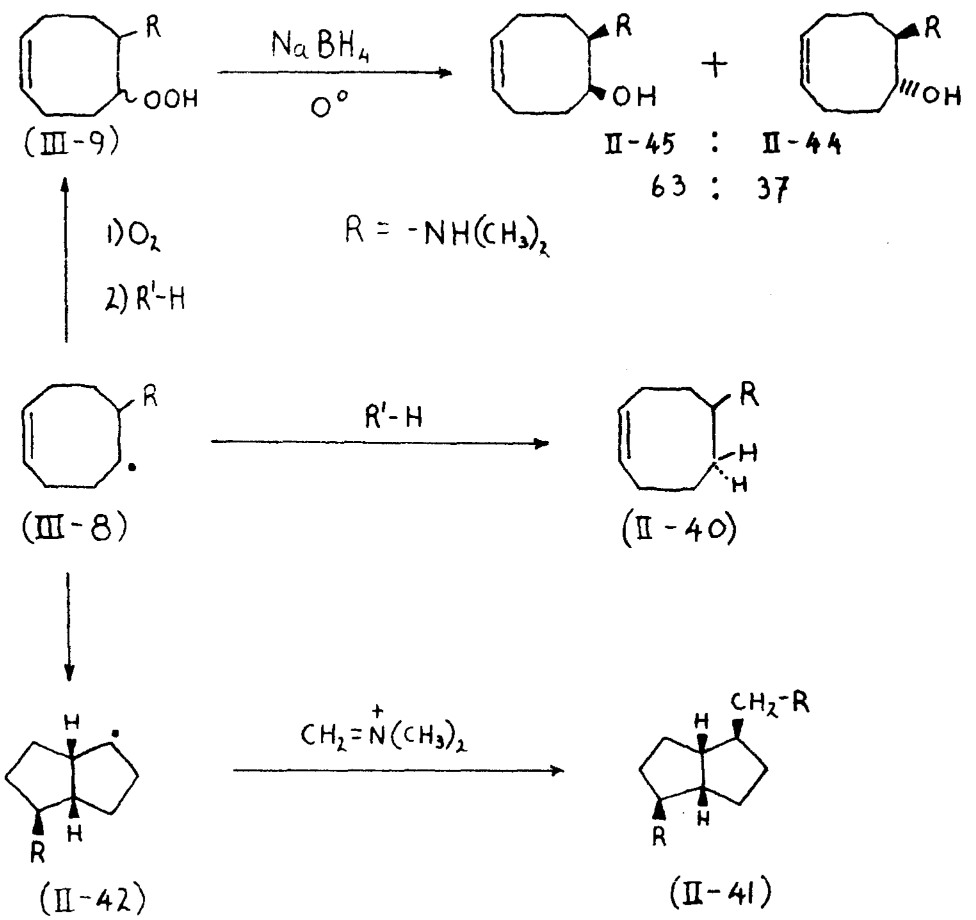


$$(CH_3)_2\underset{H}{\overset{+}{N}}-N=N-N(CH_3)-CH_2-H \;\; \cdot OO\text{-}R \longrightarrow (CH_3)_2NH^{\cdot +} + N_2 + CH_2=NCH_3 + HOOR$$

The interesting question about the hydroperoxide III-6 is its stereochemistry, namely, the stereochemical course of radical addition to norbornene. The bulky dimethylaminium radical approaches norbornene from the exo face, as has been observed in nitrosamine photoaddition (103,106,146,147), to form the norbornyl III-4 radical. The subsequent approach of an oxygen molecule may come from the exo or endo face of III-4 in which the latter approach generally predominates in various other radical additions to norbornene (148,176,177). The 9:1 ratio of endo- and exo-amino alcohols II-34 and II-35 obtained when the oxidative photolysate is worked up and reduced at 0^{o} is regarded, on the basis of the following arguments, to approximate the ratio of endo- and exo-peroxide III-6; in other words, the approach of oxygen to the norbornyl II-4 radical occurs predominantly from the endo face. Firstly, the crude product shows only a weak carbonyl absorption at 1746 cm^{-1}; hence, this oil is not decomposed to the ketone II-39 under the isolation conditions. Secondly, in support of our claim, it is shown that reduction of ketone II-39 gives endo- and exo-amino alcohols in a 1:1 ratio with $NaBH_4$ and in a 1:9 ratio with LAH. The low yield of the exo-amino alcohol II-35 in the low temperature isolation means that the ketone II-39 is responsible for very little if any of the amino alcohols.

In view of Michejda's (130) claim that an epoxide is the precursor to amino alcohols in his $ZnCl_2$-TMT-O_2 decomposition system in the presence of an olefin, the possible role played by the epoxide II-32 should be discussed. That II-32 is not the precursor to amino alcohols II-34 and II-35 is established by the fact that treatment of this epoxide with 1M CF_3COOH in CH_2Cl_2 readily forms the rearranged trifluoroacetate II-38; thus, it is unlikely that any epoxide would survive under our acidic photolysis conditions. The epoxide II-32 is probably formed in small amounts as judged by the isolation of the trifluoroacetate II-38 or the diol II-31 in 2-3%; the latter is derived from the $NaBH_4$ reduction of II-38. The trifluoroacetate II-38 is not the precursor to the amino alcohols since treatment of II-38 with aqueous dimethylamine gave a norbornyldiol as the major product and a trace of the exo-amino alcohol II-35 but no endo-II-34. Even in TMT photolysis under neutral conditions and oxygen, where no amino alcohols were detected, less than 2% of epoxide II-32 or epoxide derived products are found. It is speculated that the hydroperoxide III-6 may act as the oxidizing agent on norbornene to give II-32 (163). If the amine dioxy radical, as proposed by Michejda (130), is formed in our system, it may play a very minor role in the reaction.

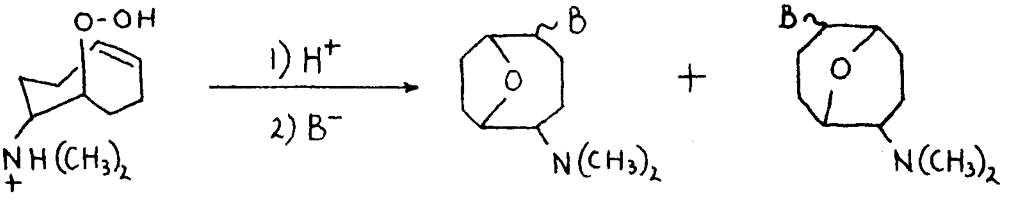
3) 1,5-Cyclooctadiene (COD): The reactions of the intermediate 6-dimethylammonium-5-cyclooctenyl radical (III-8), formed by addition of the dimethylaminium radical to COD, are summarized in Scheme III-8. Under nitrogen, the intermediate III-8 radical undergoes two major pathways, i.e., the abstraction from a hydrogen atom donor to give the aminocyclooctene II-40 and a radical transannular cyclization followed by a termination to give the bicyclooctane II-41. In view of the extensive transannular reactions reported (156,157) in radical addition to COD, it is surprizing that the transannular formation of II-41 operates to a lesser extent than the abstraction pathway leading to II-40. It is also surprizing that no bicyclic product of hydrogen atom abstraction by the intermediate bicyclooctyl II-42 radical could be found. The hydrogen donor in this reaction may be COD itself. Alternatively, as discussed above, TMT-H$^+$ may provide a hydrogen atom.



Scheme III-8

A major question arising from the addition under nitrogen is the source of the dimethylaminomethyl moiety in II-41 or in II-22 and II-23 obtained when either COD or cyclohexene are used as olefins. At the present, the most likely candidates to donate this moiety during the reaction are $(CH_3)_2\overset{+}{N}HCH_2NHCH_3$ and $(CH_3)_2\overset{+}{N}=CH_2$, both of which could be derived from the imine I-29. In the former case, a radical substitution and in the latter case addition is involved. There are certainly other compounds containing this moiety that have not been isolated from the reaction systems. The dimethylaminomethyl radical, if found in reasonably high concentration in our reaction systems, may also serve as a source to yield II-41. The combination of this radical and a dimethylamino radical has been proposed to acount for the formation of N,N,N',N'-tetramethylmethylenediamine in photolysis of TMT in the gas phase or in neat liquid (12).

The addition under oxygen is considerably simplified since the intermediate III-8 radical is efficiently scavenged by oxygen followed by hydrogen atom transfer to yield a hydroperoxide III-9. The trapping of the III-8 radical appears to be efficient so that the amino alcohols II-45 and II-44 are obtained in high yields after reduction with very little contamination by side products. Since the ratio of the cis- and trans-amino alcohols II-45 and II-44 isolated after a low temperature work up is 63:37, this ratio may represent the stereochemistry of the hydroperoxide III-9 and in turn that of oxygen incorporation into III-8. If the intermediate hydroperoxide III-9 is formed, the one corresponding to the cis alcohol II-45 may undergo an ionic catalysed cyclization as indicated. Such a mechanism would be similar to that observed in the oxidative photoaddition of nitrosamines to COD (103).



CHAPTER IV

CONCLUSIONS
AND
RESEARCH PROPOSALS

A) CONCLUSIONS

Acid catalyzed thermal (0-60^o) decomposition of TMT in CF_3COOH is proposed, on the basis of the results described above, to go through an ionic pathway via TMT-H^+ to generate a short-lived dimethylnitrenium ion intermediate. The latter can be intercepted by toluene to give low yields (2%) of o- and p-N,N-dimethyltoulidines in a 2:1 ratio through ring amination and a trace of N,N-dimethylbenzylamine through an insertion reaction. The major reaction pathway of the proposed nitrenium ion in the presence of toluene appears to be a rapid rearrangement to the imine I-29 which is obtained as the trimer I-30 in an 85% yield. In the absence of toluene, the yield of the imine I-29 is quantitative. The yields of amination are slightly better in the presence of anisole (5-10%), but no amination of cyclohexene or norbornene is observed in CF_3COOH.

The thermal (0-80^o) decomposition of TMT in concentrated H_2SO_4 is found to produce dimethylaminium radicals which can combine to form TMH-$2H^+$ or disproportionate to the imine I-29a and $(CH_3)_2NH_2^+$. The generation of aminium radicals probably occurs through TMT-$2H^+$ by analogy to the decomposition of TPT-$2H^+$ in H_2SO_4 (59). When the TMT-$2H^+$ decomposition is carried out in the presence of toluene, amination by dimethylaminium radicals gives a 15:10:75 ratio of o:m:p toluidines II-3 in 5-25% yields. A considerable amount of side reaction products is also obtained. The

N-methylphenethylamine (2-30%) and N-methylindoline (1-3%) are probably formed by a benzyl radical attack on the protonated imine I-29a. The o- and p-benzyltoluenes (10%) in a 4:6 ratio are formed through a benzyl carbonium ion attack on toluene.

Although relative rate studies of aminium radical amination have not been carried out in this work, the results obtained by Minisci (115, and Introduction section), using the N-chloramine decomposition in H_2SO_4, have allowed him to propose a CT complex between an aminium radical and the aromatic substrate as the slow step in the amination. The present work supports such a CT complex between a dimethylaminium radical and toluene since the toluidines II-3 isomer ratios obtained when TMT is decomposed in H_2SO_4 approximate the unpaired electron spin density of the toluene cation radical. It is believed that in addition to TMT-$2H^+$, TMH-$2H^+$, which is formed during TMT-$2H^+$ decomposition in H_2SO_4, may act as a secondary source for dimethylaminium radicals by analogy to the ready decomposition of TPH in H_2SO_4 (59).

Photolysis of TMT under neutral conditions has been shown by other workers to produce dimethylamino radicals (12,29,47-55); however, these amino radicals do not generally add to olefins below 100^o (96). In the present work, photolysis of TMT in dilute acidic solutions (pH 0-2) is a clean source of dimethylaminium radicals which add efficiently to olefins such as cyclohexene, norbornene, and COD to form β-dimethylammoniumalkyl radicals (III-2). These III-2 radicals are efficiently scavenged by oxygen to lead to hydroperoxides which are reduced to the corresponding β-amino alcohols II-24, II-34, II-35, II-44 and II-45 (45-74%) or are thermally decomposed to the corresponding ketones such as II-39 (40%).

Under nitrogen, the intermediate III-2 radical must seek other reaction pathways since there are no radical scavengers or good radicals donors in this system. As a result, a variety of compounds is formed. Combination of the III-2 radical with another dimethylaminium radical to give diamines such as II-21 (2%) is unlikely because the concentration of aminium radicals is low at any given time during the photolysis. Products such as aminoalkanes II-20, II-26 and II-40 (5-32%) are formed by the intermediate III-2 radical hydrogen abstraction. Conceivably, TMT-H^+ may act as the hydrogen atom donor through a III-2 radical induced decomposition pathway, regenerating an aminium radical. However, the hydrogen atom abstraction pathway is not too efficient since the intermediate III-2 radical forms products by other routes in higher yields. The III-2 radicals derived from norbornene (III-4) mainly undergo a bimolecular combination to form dimers such as II-27 and II-28 (53%). Since only a trace of dimer II-15 (0.2%) is obtained when cyclohexene is used as the olefin and no dimers are observed in the case of COD, the high yield of bis-norbornanes II-27 and II-28 suggests that the norbornyl III-4 radical has some stability, possibly because of its bicyclic structure.

With cyclohexene as the olefin and HCl as the acid, a combination of the intermediate β-dimethylammoniumcyclohexyl radical (III-3) with Cl· leads to the formation of β-chloramines II-16 and II-18 (14%). The formation of Cl· in this system is considered to take place by the $(CH_3)_2NH^{\cdot +}$ oxidation of Cl^-. The formation of compounds II-22 and II-23 (14-20%), containing an unexpected methylene group, is unclear but an attack of the intermediate III-3 radical on $(CH_3)_2N{=}CH_2^+$ is proposed. In the case of COD, the intermediate cyclooctenyl III-8 radical undergoes transannular cyclization to a bicyclo[3.3.0]octyl radical II-42 before incorporation of the dimethylaminomethyl moiety to give the bicyclic II-41 (12%). In view of the extensive reported transannular radical cyclizations of COD (156,157), it is not clear why such large yield of the uncyclized III-8 radical hydrogen abstraction product II-40 (32%) is obtained but products of hydrogen atom abstraction by the bicyclic II-42 radical are not observed.

B) RESEARCH PROPOSALS

It is hoped that this work can be extended into several areas as described below.

1) Decomposition of 2-Tetrazenes under Acidic Conditions

a) Photolysis: On the basis of this work with TMT, photolysis of other 2-tetrazenes in dilute acidic solutions (pH 0-2) is expected to be a good source for aminium radicals. Since additions of aminium radicals to olefins are efficiently attained through the photolysis of chloramines (85) or nitrosamines (99), the synthetic use of 2-tetrazenes would have limited appeal, especially in photoadditions under nitrogen where a variety of compounds may be produced. However, the additions of aminium radicals, formed during the photolysis of 2-tetrazenes under acidic conditions, may be synthetically useful when radical scavengers are introduced to the reaction system. As demonstrated in this work, if the photoaddition is performed under oxygen, good yields of hydroperoxides are produced. The chemistry of the latter (174) allows for the selective formation of alcohols, ketones, or rearranged products depending upon the chosen experimental conditions.

As shown in Figure II-2, the photolysis of TMT in CF_3COOH apparently produces products other than $CH_2{=}NHCH_3^+$ and $(CH_3)_2NH_2^+$ observed in the thermal decomposition. It would be useful to investigate the formation of these photoproducts in the absence of substrates since they may play a role in the reaction system. One of these products is believed to be $(CH_3)_2N{=}CH_2^+$ which could be responsible for the dimethylaminomethyl moieties found in photoadditions to COD and cyclohexene. This proposal could be easily tested by introducing $(CH_3)_2NH$ and CH_2O forming $(CH_3)_2N{=}CH_2^+$ (183) in the TMT-acid-olefin system before irradiation under nitrogen. If such a procedure increases the yield of compounds containing the $(CH_3)_2NCH_2$ moiety, this photoaddition may provide a convenient route to compounds having 1-dimethylaminomethyl-2-dimethylamino substituents. The latter class of compounds are potential alkali metal chelates (190).

It would be useful to investigate the photolysis of TMT and other 2-tetrazenes in the presence of olefins in buffered solutions of pH 3-5 where the concentrations of the 2-tetrazenes and their conjugate acids are about equal (7,14,31). Besides the advantage of a milder acidity range over that used in this work (pH 0-2), the irradiation of the unprotonated 2-tetrazene band at λ_{max} ca. 280nm as compared with the first conjugate acid band at ca. 235nm (14) may protect photolabile olefin substrates by use of an appropriate filter. Irradiation of a 2-tetrazene band at ca. 280nm produces a high yield of amino radicals (29,53,56) which generally do not add to olefins (96); however, amino radicals are rapidly protonated in solutions of $pH<6$ to the corresponding aminium radicals (94,95) which add efficiently to olefins (99).

A preliminary investigation of the above has been carried out in this work (Appendix C). Photolysis of TMT in the presence of cyclohexene through a Corex filtr (u.v. cut off at 270 nm) in methanol containing CH_3COOH-CH_3COONa (pH5) gave a large amount of basic material. The latter showed n.m.r. signals for cycloalkyl ring protons and about seven $(CH_3)_2N$ groups. No attempt however has been made to isolate and identify the compounds in this mixture.

b) Decomposition of mono-protonated 2-tetrazenes: On the basis of this work, the formation of $(CH_3)_2N^+$ is proposed to occur through TMT-H^+ decomposition in CF_3COOH. However, $(CH_3)_2N^+$ appears to be short lived species probably because of a rapid rearrangement to the imine $CH_2{=}NHCH_3{}^+$ analogous to that observed in $CH_3\ddot{N}$: to give $CH_2{=}NH$ (82) and in $(CH_3)_2CH^+$ to give $CH_3CH_2CH_2{}^+$ (81). If a starting 2-tetrazene can be chosen to yield a nitrenium ion where such a rearrangement is retarded or where the positive charge is stabilized, nitrenium ions with longer lifetimes than $(CH_3)_2N^+$ could be generated in high concentration.

Acid catalyzed decomposition of the appropriate 2-tetrazenes through mono-protonation in the presence of substrates such as aromatics or olefins may give higher yields of amination than observed during TMT decomposition in CF_3COOH. Since nitrenium ions have a triplet ground state (71,72), the ones with sufficient stability to be generated in high concentration may be observed by e.s.r. or other spectroscopic means. 2-Tetrazenes such as tetra-_t_-butyl or _tetrakis_-trifluoromethyl may be a convenient route to stable nitrenium ions. The formation of nitrenium ions $[(CH_3)_3C]_2N^+$ in the former and

$(CF_3)_2N^+$ in the latter would both retard the rate of rearrangement to the corresponding imines relative to $(CH_3)_2N^+$ and stabilize the positive charge because of an inductive effect.

c) Decomposition of di-protonated 2-tetrazenes: Aminium radical formation during the decomposition of 2-tetrazenes in H_2SO_4 through di-protonation (59) may be used to further confirm the intermediate CT complex during aminium radical amination of aromatic hydrocarbons proposed by Minisci (115). As described in the Introduction section, a plot of the log of the relative rate of amination versus the ionization potential of various aromatic substrates should be linear if the CT complex is the rate determining step (124-125). The relative rates can be derived from a competitive reaction where mixtures of aromatic substrates are used (115). Furthermore, if a CT complex formation is the slow step in amination, the isomer distribution obtained should approximate the unpaired spin density of the aromatic cation radicals (124). Such a study would allow one to predict the rates and products in aromatic amination by aminium radicals. Although this generalization cannot be made on the basis of this work, the amination of toluene during the acid catalyzed TMT decomposition in H_2SO_4 did give a toluidine II-3 isomer ratio very close to that of the toluene cation radical unpaired spin density distribution.

2) Synthesis of Phenethylamines and Indolines

The observed side reaction in H_2SO_4 of a benzyl radical attack on $CH_2{=}NHCH_3^+$ to give N-methylphenethylamine and N-methylindoline might be extended to provide a convenient route to compounds of this class. Such compounds have potential medical utility. As an example, β-phenylisopropylamines are finding applications in psychotherapy (166); however, their syntheses from the starting toluenes are often laborious (166,167). New possible routes to the simplest homologue, amphetamine, are described below.

A solution of ethylamine in CH_3COOH when oxidized by cobalt (III) acetate would form the imine $CH_3CH{=}NH_2^+$ (178). If toluene is then added to this mixture, the benzyl radical formed by Co(III) oxidation (163) should follow the reaction sequence outlined in reactions 1-5 to give amphetamine and 2-methylindoline. Alternatively, $CH_3CH{=}NH_2^+$ may be formed by a condensation of CH_3CHO and $NH_4^+Cl^-$ (178). Introduction of toluene and a radical initiator such as benzoylperoxide or _t_-butylperoxide (131) into this system would again lead to reactions 3-5. An interesting system which could be investigated might be the irradiation of toluene and ethylamine in the presence of a ketone such as acetone or benzophenone. Triplet ketones both oxidize amines to imines (125) and abstract benzylic positions (131); thus, reactions 3-5 may be attained using a triplet ketone as the initiator.

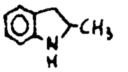
$$CH_3CH_2NH_2 \xrightarrow{Co\,III} CH_3CH{=}NH_2^{+} \qquad [1]$$

$$\phi\text{-}CH_3 \xrightarrow{Co\,III} \phi\text{-}CH_2^{\bullet} \qquad [2]$$

$$\phi\text{-}CH_2^{\bullet} + CH_3CH{=}NH_2^{+} \longrightarrow \phi\text{-}CH_2CHCH_3NH_2^{\bullet +} \qquad [3]$$

$$\phi\text{-}CH_2CHCH_3NH_2^{\bullet +} + \phi\text{-}CH_3 \longrightarrow \phi\text{-}CH_2CHCH_3NH_3^{+} + \phi CH_2^{\bullet} \qquad [4]$$

$$\phi\text{-}CH_2CHCH_3NH_2^{\bullet +} \longrightarrow \quad \longrightarrow$$



[5]

3) Reactions of TMH and TMH$^{\cdot +}$

It has been proposed in this work that TMH-2H$^+$ decomposition might lead to $(CH_3)_2NH^{\cdot +}$ radicals by analogy to TPH decomposition in H_2SO_4 (59). When a solution of TMH in H_2SO_4 is heated to 110^o, TMH-2H$^+$ decomposes to $(CH_3)_2NH_2^{\ +}$ and $CH_2{=}NHCH_3^{\ +}$. The latter products could be derived from a disproportionation of $(CH_3)_2NH^{\cdot +}$ radicals (128). Although the n.m.r. signal of TMH-2H$^+$, formed in the decomposition of TMT in H_2SO_4, decreases slightly after one day at 20^o (Figure II-1), no decomposition is observed in a standard sample of TMH in H_2SO_4 at room temperature, even in the presence of toluene. It would nevertheless be of interest to study tetrasubstituted hydrazine decompositions in H_2SO_4 at various temperatures in order to confirm the possible formation of aminium radicals.

The $TMH^{\cdot +}$ e.s.r. signal, but not that of $TMT^{\cdot +}$, is quenched by cyclohexene. It is unclear whether cyclohexene is reacting with $TMH^{\cdot +}$ or its precursors. TMH may be readily oxidized electrochemically to generate $TMH^{\cdot +}$ (15) which then may react with olefins.

CHAPTER V

EXPERIMENTAL

A) GENERAL

Unless otherwise specified, the following conditions were used. Infrared (i.r.) spectra were recorded on a Perkin-Elmer 457 spectrophotometer using a neat liquid film or a nujol mull of the samples. The absorption bands (cm^{-1}) are designated as s (strong), w (weak), and b (broad); undesignated bands are considered to be medium. Ultraviolet (u.v.) spectra were recorded on either a Cary 14 or a Unicam SP8000 spectrophotometer. Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian A 56/60 or on a Varian XL-100 equipped with a Nicolet 1080 Instrument computer using carbontetrachloride (CCl_4) or deuterochloroform ($CDCl_3$) as solvents with tetramethylsilane (TMS) as the internal standard. The chemical shifts are reported in or ppm from TMS, coupling constants (J) in hertz (Hz). The splitting patterns are designated as s (singlet), d (doublet), dd (double doublet), ddd (double dd), t (triplet), dt (double triplet), q (quartet), m (multiplet), and b (broad). The half-height width of a signal is given in hertz as $W_{1/2}$, D_2O exchangeable protons are indicated by D_2O exch., and the number of protons in a corresponding signal are given by multiples of H. The decoupling experiments were performed by Mr. Arthur Brooke or by the author on the XL-100 spectrometer.

Electron spin resonance (e.s.r.) spectra were taken on a Varian E-4EPR spectrometer using a flat quartz Varian E-248 or E-248-1 aqueous solution sample cell. The coupling constants (a) are given in gauss (G) and the g-factor was calculated using diphenylpicrylhydrazyl radical (DPPH) as external standard. Simulations of the e.s.r. spectra were done on a Nicolet 1080 computer using a Nicolet User's Society 420 "EPRCAL" program kindly supplied by Dr. R.J. Cushley. Mass spectra (m.s.) and gas chromatographic-mass spectra (g.c.-m.s.) were obtained on a Hitachi-Perkin-Elmer RMU-6E mass spectrometer by Mr. Gregory Owen. High resolution mass spectra (h.r.m.s.) were performed at the University of British Columbia Mass Spectrometric Services. Elemental analyses were performed at Simon Fraser University by Mr. M.K. Yang using a Perkin-Elmer 240 Microanalyzer.

The gas chromatographic (g.c.) analyses were obtained on an F&M Model 810-19 Dual Flame Analytical Gas Chromatograph using a Varian Aerograph Model 20 strip chart recorder equipped with a Model 224 disc chart integrator or on a Varian Aerograph Series 1700 Thermal Conductivity Preparative Gas Chromatograph. Retention times (r.t.) are given in minutes (min.). Column chromatographic separations were performed on neutral or basic alumina (Brockmann Activity I, Fisher Scientific Co., 80-200 mesh), silica gel (Baker or Fisher Scientific, 60-200 mesh), or silica acid (Mallinckrodt analytical reagent, 100 mesh).

The solvents (reagent grade) were distilled before use. Ether was distilled from lithium aluminum hydride (LAH, 97%, Wilshire Chemical Co.) and not used after one week owing to rapid peroxide formation. Benzene and toluene were stored over sodium, anhydrous methanol over molecular sieve

3A. Acetonitrile (A.C.S. certified, Fisher Scientific Co.), bromoform (Eastman Organic Chemicals), and Perfluoroalkane-70 (Pierce Chemical Co.) were passed through alumina immediately before use. The commercially available olefins (norbornene and 1,5-cyclooctadiene were supplied by Aldrich Chemical Co., cyclohexene by Fisher Scientific Co.) were of sufficient purity, better than 98%, to be used directly without further purificiation. Concentrated sulfuric (H_2SO_4, 98%) and hydrochloric (HCl, 38%) acids were supplied by Fisher Scientific Co., trifluoroacetic acid (CF_3COOH) by Matheson Coleman and Bell, and acetic acid (CH_3COOH, glacial) by the McArthur Chemical Company.

Oxygen (industrial grade) and hydrogen were supplied by Liquid Carbonic, nitrogen and helium were supplied by Union Carbide (Linde), and the gaseous reagents (monomethylamine, dimethylamine, nitrosylchloride, carbonmonoxide, and carbondioxide) were supplied by the Matheson Gas Company. Nitrogen was purified by scrubbing through a Fieser solution (188) followed by concentrated H_2SO_4 and then through potassium hydroxide pellets (KOH, Fisher Scientific Co.).

The photolyses were carried out in a previously described (100-108) Pyrex photolysis vessel using a quartz cold finger and an appropriate filter (Figure V-1). The photolysate was bubbled with the appropriate gas while being irradiated with a 200W medium pressure Hanovia mercury lamp. The photolyses in an e.s.r. cavity were performed with a HBO 200W mercury lamp, Wild Heerbrugg Limited.

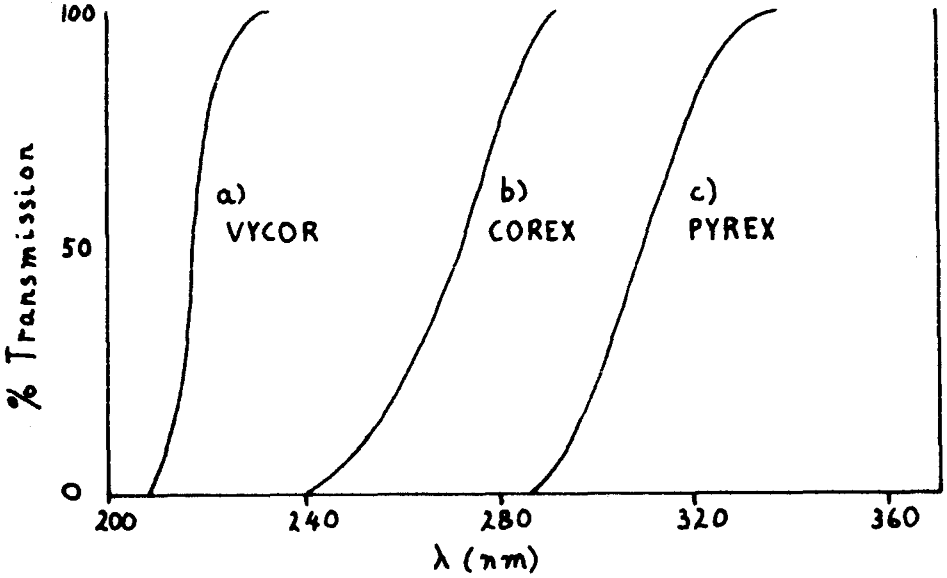


Figure V-1: Filters

Sodium borohydride ($NaBH_4$, 98%), mercuric oxide (HgO, red powder), potassium permanganate ($KMnO_4$), potassium carbonate (K_2CO_3, anhydrous), and magnesium sulfate ($MgSO_4$, anhydrous) were supplied by Fisher Scientific. Catalytic reductions using platinum oxide (Matheson, Coleman and Bell) were performed in a Parr hydrogenation apparatus. Reactions above room temperature were carried out in a Lauda water bath ($\pm 0.1^{\circ}$). Distillation of products were performed on a Nester/Faust spinning band column and flash evaporations on a Buchi Rotovapor. Melting points (mp, uncorrected) were determined either on a Fisher-Johns hot stage or a Gallenkamp heating block apparatus. All temperatures are reported in degrees Celcius (°).

B) PREPARATION OF TMT AND TMH

1) HgO Oxidation of DMH

The procedure of Watson (12) was slightly modified to give better yields. HgO (158.86g, 0.74 moles) was added slowly over two hours to a stirred solution of DMH (50.4 ml, 40g, 0.66 moles, Fisher Sci. Co.) in ether (400 ml) at -5^o. Solid K_2CO_3 (10 g) was then added and the mixture stirred for two more hours at -5^o, then two hours at room temperature. The mixture was filtered, the residue washed with saturated K_2CO_3 solution (30 ml) followed by ether (200 ml). The ether phases were combined, dried over K_2CO_3, and evaporated (20^o/40mm Hg) to yield a yellow liquid (34.14g). This liquid was distilled to give TMT as a pale yellow liquid (29.35g, 32.0ml, 77%): bp $42\text{-}46^o$/28-32mm Hg; i.r. 3000(w), 2962(s), 2858(s), 2780, 1469(s), 1276, 1241, 1141, 1037, 1002(s), 879, and 822 cm^{-1}; n.m.r. τ7.19(s); u.v. λ^{EtOH}_{max}=277nm (ϵ=8.0x10^3), (lit. λ^{EtOH}_{max}=277nm, ϵ=8.3x10^3 (7)). The mercury was collected, washed with water (10x100ml), then acetone (2x50ml), and dried (106.86g, 0.536moles, 81%).

2) $KMnO_4$ Oxidation of DMH

A solution of $KMnO_4$ (160g, 1.08 moles) in dilute KOH (2% aqueous, 31) was added slowly over one hour with rapid stirring to a solution of DMH (120g, 2.0moles) in ice-water (11) and KOH solution (40% aqueous, 200ml).

During the addition of the $KMnO_4$ solution, ice (2kg) was added to keep the temperature below 5°. There was no sign of gas evolution. The reaction was allowed to reach room temperature, benzene (0.51) was added and the mixture stirred rapidly for 22 hours. The benzene phase was removed into a 41 suction flask and the aqueous phase extracted with more benzene (2x0.51). The benzene layer was separated, dried over K_2CO_3, and evaporated to 80ml (15°/40mm Hg) This residue was distilled and the fraction boiling at 42-44°/30mm Hg collected (TMT, 17.5g, 19%). The spectra were identical to the above TMT prepared by HgO oxidation.

3) TMH from TMT

TMH was prepared from TMT by the procedure of Watson (12). TMT (1g) was irradiated with a low pressure PCQ immersion lamp (Ultra Violet Products, Inc.) in a distillation apparatus for 20 hours at 110°. The volatile components (300mg) were collected into a cooled flask. A portion of this colorless distillate containing TMH (lit. bp=73° (12)), dimethylamine and some trace impurities, was dissolved in CF_3COOH: n.m.r. (see Figure II-2g) τ7.10 (t, J=6Hz; $(CH_3)_2NH_2^+$) and 7.14 (s; TMH-H^+). Another portion of the distillate was dissolved in H_2SO_4: n.m.r. (Figure II-1d) τ7.10 (t, J=6Hz; $(CH_3)_2NH_2^+$) and 6.40 (s; TMH-$2H^+$). TMH may also be obtined in good yields by another route described in reference 189.

C) N.M.R. STUDY OF TMT DECOMPOSITION

1) In H_2SO_4

TMT (0.5ml) was dropped slowly into concentrated H_2SO_4 (5ml) with rapid stirring in a 25ml flask at 0 to -10^o. There was much gas evolution and the solution turned a bright yellow. After the addition was complete, this solution was transferred with a cold pipet into an n.m.r. tube cooled in dry ice/acetone. The n.m.r. spectra were recorded within 15 minutes at -20 and then within 30 minutes at 20^o, keeping all other machine parameters constant, and are shown in Figure II-2 (see Results). The molar ratio of the protonated imine (I-29a) at τ1.93 (m,2H), 6.53 (m,3H) to protonated dimethylamine at τ7.10 (t,6H) was equal at -20^o and 20^o. The weak signal at τ6.27 disappeared when the temperature was raised, but the singlet at τ6.40 increased. There was no change in the n.m.r. when the temperature was raised to 40^o from 20^o. However, the signal at τ6.40 decreased slightly after one day at room temperature. This signal was identified as TMH-2H$^+$ by comparison with an authentic sample (see above). When TMH (100 mg) was dissolved in H_2SO_4 (3ml) and heated at 110^o for one hour, the n.m.r. showed that the starting TMH-2H$^+$ signal at τ6.40 decayed cleanly to form the immonium I-29a at τ1.93 (m,2H) and 6.53(m,3H) and dimethylammonium ion at τ7.10(t,6H) in about an equimolar ratio. No change of the TMH-2H$^+$ signal was observed when this H_2SO_4 solution was kept at 20^o for two weeks. The dimethylammonium ion was identified by dissolving the hydrochloride in H_2SO_4. The immonium ion I-29a was identified by dissolving the trimer I-30 in H_2SO_4 (see below).

2) In CF_3COOH

CF_3COOH (0.5ml), cooled to 0°, was added dropwise over 2 minutes to TMT (100mg) in a 25ml flask with rapid swirling at -10°. The solution was transferred into an n.m.r. tube kept in a dry ice/acetone bath. The n.m.r. was recorded from one to three hours at -15, 10 and 30° and is shown in Figure II-2. This solution was pale yellow throughout the three hours. At 30°, a plot of the log of the inverse of $TMT\text{-}H^+$ n.m.r. signal area at $\tau 6.78$(s) vs. time was linear indicating decomposition by first order kinetics. The $k = 6.5 \pm 1 \times 10^{-4}$ was calculated from the half life of this signal of about 20 minutes.

In a separate experiment identical amounts were used but the solution was irradiated in a quartz n.m.r. tube with a 200W Hanovia lamp through a Vycor filter under continuous bubbling of nitrogen. After two hours, the n.m.r. of the deep yellow photolysate was recorded at 30° and is shown in Figure II-2f.

3) In CD_3CN

CF_3COOH (100mg), cooled to 0°, was added dropwise to a solution of TMT (50mg) in CD_3CN (0.5ml) at -10°. The n.m.r. of half this solution was taken at -45° immediately after mixing and at 30° after 3 hours at 40°. The other half was irradiated, as above at 0° and the n.m.r. recorded at 30° after 3 hours. The photolysate was a deeper yellow than that kept in the dark at 40°. The n.m.r. spectra are shown in Figure II-3.

D) E.S.R. STUDY OF TMT DECOMPOSITION

1) In H_2SO_4

When TMT (0.5ml) was added slowly to concentrated H_2SO_4 (3ml) with rapid stirring in a 10ml flask at 0^o, there was much gas evolution and a deep yellow color was observed. The H_2SO_4 was used directly as supplied without futher purification since it showed no e.s.r. signal. The solution was transferred to a flat e.s.r. cell, purged with nitrogen for 2 minutes and the e.s.r. spectrum recorded at room temperature (Figure II-4). This signal is believed to be that of $TMT^{\cdot +}$ (34,36): 13 broad bands, peak to peak separation (ΔG_{pp})=10G, $g=2.004\pm0.0005$. This signal decayed over two days without showing any new signals. The initial signal was strong relative to the Varian weak pitch sample No.904450-02.

2) In CF_3COOH

a)In Acetonitrile: A solution of TMT in acetonitrile (06M, 2ml) was slowly dropped to a stirred solution of CF_3COOH in acetonitrile (1.3M, 2ml) in a 10ml flask at 0^o. A steady evolution of gas was observed as the solution became yellow-orange. This solution was placed in a flat e.s.r. cell, purged with nitrogen for two minutes, and the e.s.r. spectrum of $TMT^{\cdot +}$ recorded at room temperature: $a_N(2,3N)=1.15$, $a_N(1,4N)=10.85$, $a_H(6H)=10.40$, $a_H(6H)=11.60G$, $g=2.0040\pm0.0005$, (lit. $a_N(2,3N)=1.20$, $a_N(1,4N)=10.96G$, $a_H(6H)=10.40$, $a_H(6H)=11.52G$, g=2.0036 (34,36)) (Figure II-5). This signal decayed slowly over several hours and was not replaced by a new signal. The initial signal was strong relative to the Varian weak pitch sample No.904450-02.

This solution was photolyzed in the e.s.r. cavity at room temperature with a 200W unfiltered Wild mercury lamp for 5 minutes. When the e.s.r. spectrum was recorded 5 minutes after photolysis, a new stronger signal of $TMH^{\cdot +}$ was obtained: $a_N(2N)=13.5$, $a_H(12H)=12.7G$, $g=2.0034 \pm 0.0004$ (Figure II-11a); (lit. $a_N(2N)=13.5$, $a_H(12H)=12.7G$, $g=2.0035$ (15)). This signal decayed over one hour but was strong initially relative to the Varian strong pitch sample No.904450.01. This signal was simulated by the EPRCAL program using the observed coupling constants (Figure II-11b).

In a separate experiment (Figure II-8), a solution of 0.17M TMT, 1.1M CF_3COOH in acetonitrile showed an e.s.r. signal of $TMT^{\cdot +}$ at -45^o (Figure II-8a). During photolysis at -45^o with a 200W Wild lamp, the only e.s.r. signal observed was that of $TMT^{\cdot +}$ (Figure II-8c). The receiver gain of the e.s.r. machine was turned down and when the photolysis was stopped, there was an immediate build up of $TMH^{\cdot +}$ (Figure II-8b). The $TMH^{\cdot +}$ signal at -45^o reached a maximum within 10 minutes [Figure II-8d, $a_N(2N)=13.2$, $a_H(12H)=12.7G$, $g=2.0039 \pm 0.0006$]. The $TMH^{\cdot +}$ signal decayed slowly over several hours at -45^o or within 30 minutes on warming to room temperature to be replaced by that of $TMT^{\cdot +}$. When this solution containing $TMT^{\cdot +}$ was recooled to -45^o and cyclohexene added, there was no change in the $TMT^{\cdot +}$ signal (Figure

II-10). When the solution at -45^{o} containing TMH$^{\cdot +}$ was treated with cyclohexene (ca. 0.2ml), the TMH$^{\cdot +}$ signal decreased (Figure II-9) immediately.

b) In Benzene: A solution of TMT (0.1M) and CF_3COOH (1.3M) in benzene showed steady gas evolution and a deep yellow color at room temperature. Two phases appeared about one minute after mixing. The top phase was put into a flat e.s.r. cell and the e.s.r. spectrum recorded 30 minutes after mixing (Figure II-6b). The spectrum showed TMT$^{\cdot +}$, identified by the series of outer bands, and another signal superimposed. After 30 more minutes, this was replaced by a weak signal showing 17 major bands 4.2G apart in an intensity ratio (outer to centre) of 12:23:25:35:60:65:73:90:100 at $g=2.002\pm0.001$ (Figure II-6b). This signal is believed to be due to an N,N,N'-trimethyldiaminomethyl radical II-2. The signal for II-2 was simulated (EPRCAL) using $a_N(N)=8$, $a_N(N')=6$, $a_H(N\text{-}H)=8$, $a_H(\alpha H)=15.5$, $a_H(9H)=4G$ with a gaussian line broadening of 1.5G. (Figure II-6c). This signal disappeared within 30 minutes.

c) In 1:1 Cyclohexene-Acetonitrile: A mixture of TMT (0.25M) and CF_3COOH (0.65M) in 1:1 acetonitrile-cyclohexene was made up by dropping a solution of TMT (0.5M, 2ml) in cyclohexenene to a solution of CF_3COOH (1.3M, 2ml) in acetonitrile at 20^{o}. The mixture (2 phases) showed slow gas evolution and a yellow color. The top phase of this mixture was placed in a flat e.s.r. cell and the spectrum recorded. The broad signal of TMT$^{\cdot +}$ (Figure I-7a) disappeared within 45 minutes to be replaced by a weak signal similar to that in Figure II-6b showing at least 17 bands 4.2G apart in a ratio (outer to centre) of 7:12:20:25:50:60:63:75:100, $g=2.0024\pm0.0004$ (Figure II-7b). This signal disappeared within thirty minutes.

E) DECOMPOSITION OF TMT IN H_2SO_4 IN THE PRESENCE OF TOLUENE

1) General Procedure

The decomposition of TMT was carried out at various temperatures in the range of -10 to 80° in a mixture of toluene and concentrated H_2SO_4. A solution of TMT (1-3M) in toluene (4-20ml) was added dropwise over a period of 15 minutes to a vigorously stirred mixture of concentrated H_2SO_4 (1.5-9ml) and toluene (4-20ml) at a particular temperature. the reaction mixture was stirred a minimum of 15 minutes after gas evolution had ceased. During the addition, the reaction usually turned to a deep purple color. At higher temperatures (50 and 80°), the reaction mixture became brown or yellow. Ice (ca. 20g) was added and the reaction mixture was extracted with ether (25ml). The ether extract was washed with dilute acid (1N HCl, 2x15ml), followed by water (2x15ml), and dried over K_2CO_3. The solvent was removed (20°/30mm Hg) and the residue distilled to remove toluene (to 110°). The residue was then analyzed by g.c., i.r., n.m.r., m.s., and g.c.-m.s. for non-basic products.

Addition of ice usually produced a precipitate of dark tarry material. After the non-basic products were extracted with ether, this material was collected by scraping it of the sides of the flask. It was washed with 10% aqueous KOH solution followed by water and then ether, dried and analyzed for products by i.r., n.m.r., and mass spectra. It usually constituted a large amount of the products (100-600mg/g starting TMT).

The aqueous washings from above were combined with the major aqueous portion. This was basified with 40% aqueous KOH at 0-5^o and extracted with ether (2x25ml). The ether solution was washed with saturated aqueous NaCl (1x15ml), dried over K_2CO_3 and evaporated (20^o/30mm Hg) to give a pale yellow oil. This oil was analyzed by n.m.r., i.r., g.c., m.s., and g.c.-m.s. for products, some of which were isolated by column chromatography. The conditions and results are summarized in Table II-2 (see Results).

2) Isolation and Identification of Products

A solution of TMT (0.9g, 0.0077 moles) in toluene (4.1ml) was added dropwise over 30 minutes to a rapidly stirred mixture of toluene (4.0ml, total 0.077 moles) and concentrated H_2SO_4 (2.5ml, 4.3g, 0.045moles) at -5^o. It is necessary to specify the molar ratio (in this case TMT:toluene:H_2SO_4 = 1:10:6, Reaction 9, Table II-2) since the reaction consisted of two liquid phases. Half way through the addition, much gas evolution was observed, the temperature rose rapidly to 27°* (at temperatures above 20°, no temperature increase was observed), and the mixture became deep purple. The temperature dropped quickly in five minutes to below 0°. The reaction was kept at -5 to 0° for 20 hours, at which time the reaction mixture became a deep brown color, and was worked up as described above.

The acid and neutral fraction was obtained as a pale yellow oil (142mg): i.r. 3028(s), 2920, 1604, 1516, 1497(s), 1456(s), 1031, 791(w), 769(w), 746, 729(s), 698(s), and 600(w) cm^{-1}. The n.m.r. showed the oil to contain toluene and benzyltoluenes (II-4) (identified as <u>ortho</u> and <u>para</u> by comparison of the i.r. and n.m.r. spectra with those of the authentic (134)) in a 6:94 ratio: τ2.81(s) and 7.71(s) (toluene); τ2.75-3.00 (m,9H); 6.05 (s; o-II-4, CH_2) and 6.10 (s, p-II-4, CH_2) (2H, ratio 37:63); 7.15 (weak singlet assigned to bibenzyl (134)); 7.71 (s; p-II-4, CH_3) and 7.79 (s; o-II-4, CH_3) (3H, ratio 63:37 after toluene signal at τ7.71 subtracted). The benzyltoluenes amounted to a 9.4% yield based on starting TMT but could not be separated by preparative g.c. (r.t.=20min., 25% SE-30 on Chromasorb W 60/80, 12'x1/4" aluminum column, 180°, He inlet press. 20psi): m.s. m/e(%), 182 (M^+, 92), 167(100), 165(38), 152(15), 141(4), 128(6), 115(6), 104(36), 91(19), 77(10), 65(8), and 51(6).

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*Note: In two separate experiments, the conditions were kept constant and the temperature monitored in each case, the temperature rose rapidly from -5° to above 20° when the purple color appeared and gas evolution started, but quickly dropped to below 0°.

The polymeric material isolated (ca. 400mg) was completely soluble in concentrated H_2SO_4; slightly soluble in CH_2Cl_2, $CHCl_3$ or CH_3COOH; and insoluble in CCl_4, ether, acetone, methanol, water, or 40% aqueous KOH: i.r. 3500-2000(b), 3420(bs), 2408(w), 1600(s), 1510, 1494, 1220(s), 1170(s), 1033(s), 1011(s), 817, 739(s), and 701(s) cm^{-1}; n.m.r. ($CDCl_3$ after filtration) τ2.80(s), 2.70-3.60(bm), 5.9-6.3(bm), 6.9-7.8(bm), and 7.63(s); n.m.r. (H_2SO_4, poor resolution) τ2.0-3.0(bm), and 6.5-7.6(bm); e.s.r. (H_2SO_4) singlet, ΔG_{pp}=8G, g=2.0036$\pm$0.0004, strong signal relative to Varian weak pitch sample; m.s. (280°) peaks m/e>600, major peaks: m/e(%), 229(2), 224(2), 172(26), 148(9), 135(13), 134(20), 121(7), 120(13), 91(50), 90(26), 77(12), 58(26), and 44(100).

The basic fraction was obtained as a yellow oil (238mg) and showed: i.r. 3100-3000(w), 2940(s), 2800(s), 1605, 1040(s), 808, 748(s), and 700(s) cm^{-1}; n.m.r. τ2.81(s), 2.75-3.66(bm), 6.30-7.10(bm), 7.10-7.35(m), and 7.50-7.80(m). Chlorobenzene (V-1) (0.1ml, 0.197M) was added to the basic fraction and diluted with CCl_4 to 5ml. This was analyzed on a 10% Carbowax 20M on Chromasorb W 100/120, 10'x1/16" stainless steel column, from 100 to 200° at 2°/min., N_2 carrier gas inlet pressure 30psi, and a H_2 flame detector at 23psi, 250°. Yields were calculated by the following formula (see reference 53):

$[\text{V-1}]/1.19 \times A_{\text{II-3}}/A_{\text{V-1}} \times \text{V/TMT}$ = %yield II-3 where [V-1] is the concentration of V-1, $A_{\text{II-3}}$ and $A_{\text{V-1}}$ are the g.c. peak areas of p-II-3 and V-1 (determined with a disc integrator, corrected for baseline drift), 1.19 is a predetermined ratio of the g.c. peak areas of one mole p-II-3 to one mole V-1, V is the volume (5ml), and TMT is the starting amount of TMT in moles. The yields of the other products were calculated assuming the ratio 1.19 to be constant. the g.c. peak areas were checked for a linear response to various concentrations of standard V-1 solutions (0.1 to 0.3M) and various range (1 to 100) and attenuation (32 to 256) settings on the F&M gas chromatograph. The response was linear, except for a setting of range = 1 and attenuation = 64, 128, or 256. As a result, the latter settings were not used.

Table V-1: Gas Chromatographic Analysis of the Basic Fraction from Reaction 9 (Table II-2).

Compound	r.t. (min.)	Area	% Yield
I-30	4.6	-	-
V-1	6.0	2624	Standard
II-7	9.2	120	0.5
o-II-3	10.2	92	0.4
II-10	15.0	94	0.4
II-6	18.6	250	1.2
p-II-3	19.4	1900	8.5
m-II-3	20.2	260	1.2
II-8	23.0	708	3.1
II-9	26.0	70	0.3
Others	>35	-	ca. 5

This procedure showed the oil to contain the compound given in Table V-1. All major peaks, except for II-10 the structure of which was deduced from its m.s. fragmentation pattern, were identified by g.c. peak matching with the authentic compounds (133) and were further confirmed by g.c.-m.s. (5% Carbowax 20M on Chromasorb W 60/80, 6'x1/4" glass column, 150^{o}). The g.c.-m.s. results are given in Table II-3 (Results). Traces of other amines were detected by g.c.-m.s.: m.s. m/e(%), 225(M^+,1), 134(90), 91(100), 77(1); m.s. m/e(%), 178(M^+,1), 134(100); m.s. m/e(%), 192(M^+,3), 148(2), 134(15), 58(100), 44(12). The structure of these could not be determined accurately.

Chromatography on a silicic acid column of the basic extracts from reactions 2 and 3 (see Results, Table II-2) afforded: (i) a mixture of toluidines *o*-II-3 and *m*-II-3 with a trace of *p*-II-3 showing one spot on a t.l.c. plate (silicic acid/ether): i.r. 3010(w), 2965(s), 2930, 2875, 1491(s), 1260, 809(s), 750(s) and 7.30 cm^{-1}; n.m.r. τ2.9-3.6(bm), 7.15(s), 7.35(s), and 7.70(bs); (ii) *p*-II-3 as the major isomer: i.r. 3005(w), 2920(s), 2855, 2800, 1610, 1518(s), 1341(s), 946(s), 805(s), and 744 cm^{-1}; n.m.r. τ2.9-3.6(bm,4H), 7.13(s,6H), and 7.78(s,3H); and (iii) a 2:1 mixture of II-8 and *p*-II-3 showing one spot on a t.l.c. plate: i.r. 3030(w), 2950(s), 2920(s), 2855(s), 2805(s), 1607(s), 1540, 1490(s), 1378, 1340(b), 1274(s), 1219, 1163, 1115, 1021, 990, 948, 868, 807(s), 748(s), and 718 cm^{-1}; n.m.r. τ2.95-3.80(bm), 6.60-7.10(bm; II-8, CH_2CH_2), 7.13(s; *p*-II-3, $N(CH_3)_2$), 7.30(s; II-8, NCH_3), and 7.78(s; *p*-II-3, ϕ-CH_3) ratio of singlet τ7.30 to singlet τ7.78=2:1. The above compounds were identified by comparison of the i.r. and n.m.r. spectra to the authentic materials (134,136).

F) DECOMPOSITION OF TMT IN CF_3COOH IN THE PRESENCE OF TOLUENE

1) Neat

The general procedure was similar to the above TMT decomposition in H_2SO_4. The results are presented in Table II-4 (see Results). A solution of TMT (0.9g, 0.0077moles) in toluene (4.0ml) was added dropwise over 15 minutes at a particular temperature with rapid stirring to a solution of CF_3COOH (5.25g, 0.0462moles) in toluene (4.1ml, total 0.077moles). During the course of addition, a gas was evolved and two liquid phases appeared, the lower being yellow. The reactions were terminated by addition of ice (25g) and worked up and analyzed as described above. Neither purple color nor polymeric material was observed, except where noted in Table II-4.

o-II-3 was isolated by preparative g.c. (25% Carbowax 20 PTAT) as the major isomer in reaction 15 (Table II-4): i.r. 2940(s), 2870, 2835(s), 2780, 1600(s), 1494(s), 945(s), 805, 762(s), and 725(s) cm^{-1}. The trimer I-30 was separated from the mixture by sublimation (30°/20mm Hg): i.r. 3400(wb), 2946(s), 2790(s), 1660(wb), 1470, 1449, 1389, 1263, 1238, 1160, 1125(s), 1003, 915(s), and $860cm^{-1}$; n.m.r. τ 6.80(s,6H) and 7.80 (s,9H).

2) In Solvent

A solution of CF_3COOH (5.25g, 0.0462moles) in 20ml of a solvent (acetonitrile, perfluoroalkane-70, or bromoform) was added all at once to a solution of TMT (0.9g, 0.0077moles) in toluene (8.1ml, 7.2g, 0.0077moles) with rapid stirring at 40°. The mixture became yellow and slow gas evolution was observed. Two liquid phases were observed in the case of perfluoroalkane-70 and bromoform, but only one in the case of acetonitrile. After 2 hours, the mixture was evaporated to 10ml (15°/30mm Hg) and dilute HCl (3N, 10ml, 0.03moles) added. The reactions were then worked up and analyzed as above. Neither purple color, polymeric material, nor any rise in temperature was observed.

G) PHOTOLYSIS OF TMT IN THE PRESENCE OF HCl AND CYCLOHEXENE

A solution TMT (3g, 0.025moles, 0.125M), cyclohexene (20ml, 16.5g, 0.2moles, 1M), and concentrated HCl (15ml, 0.2moles, 1M) in acetonitrile (200ml) was placed in a photolysis vessel and purged with nitrogen for 10 minutes at -5 to 0° (ice/salt bath). The solution was then irradiated for 69 hours with a medium pressure 200W Hanovia lamp at 0° under nitrogen through a Pyrex* filter until aliquots (5μl dissolved in 5ml methanol) showed no u.v. absorption maximum at 239mm.

The photolysate was evaporated to 20ml (20°/30mm Hg) and extracted with ether (2x30ml). The ether phase was washed with water (20ml), dried over K_2CO_3, and evaporated (20°/30mm Hg) to yield an oily residue (22.5mg). The n.m.r. of this residue showed no $N\text{-}CH_3$ signal and t.l.c. (alumina/CH_2Cl_2) showed at least four spots.

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*Note: It was originally planned to use a Vycor filter. This filter was erroneously labelled "Vycor" but found later to be Pyrex.

The aqueous solution was basified with NaOH solution (20% aqueous, 120ml) at 0-5° and continuously extracted with ether (200ml, overnight). The ether solution was dried over $MgSO_4$ and evaporated (20°/30mm Hg) to give a pale yellow oil (2.52g): n.m.r. τ 4.30(m), 5.45(m), 6.35(m), 6.75(s), 7.60-7.90 (ca. 7 singlets), and 7.90-8.10(bm).

This crude basic fraction showed seven spots on a t.l.c. plate (alumina/ether). This mixture (2.50g) was chromatographed on a silica gel column (70g) and gave, on elution with ether, a fraction (10mg, 0.2%) which showed one spot on a t.l.c. plate and was tentatively identified as a bis-dimethylaminobicyclohexane (II-15): i.r. 2930(s), 2860, 2780, 1450, 1261, 1185(w), 1153, 1042(sb), 872, and 805(b) cm^{-1}; h.r.m.s. (90°) m/e(%), 252.2541 (M^+, 8; calcd. for $C_{16}H_{32}N_2$: 252.2565), 237.2307 (12; calcd. for $C_{15}H_{29}N_2$: 237.2330), 208.2044 (14; calcd. for $C_{14}H_{26}N$: 208.2065), 207.1966 (22; calcd. for $C_{14}H_{25}N$: 207.1987), 192.1724 (12; calcd. for $C_{13}H_{22}N$: 192.1752), 167.0839 (20; calcd. for $C_{13}H_{11}$: 167.0861), 149.1061 (24; calcd. for $C_9H_{13}N_2$: 149.1079), 140.1415 (24; calcd. for $C_9H_{18}N$: 140.1439), 125.1201 (36; calcd. for $C_8H_{15}N$: 125.1206), 84(100), 71(46), and 58(54).

Continued elution with ether gave a pale yellow oil (285mg, 7.1%) identified by its spectral characteristics as trans-2-chloro-N,N-dimethylcyclohexylamine (II-16): n.m.r. τ 6.11 (dt; J=4 and 10Hz; 1H), 7.65(m,1H), 7.67(s,6H), and 8.0-9.0(m,8H). The g.c.-m.s. (10% SE-30, 100-200° at 10°/min) indicated II-16 to be

95% pure showing two peaks at 1.9min., m/e(%), 163(M^+,14), 161(M^+,33), 126(31), 118(11), 84(100), 71(36), 58(14), 44(14), and 42(17); and 1.3min., m/e(%), 177(M^+,3), 175(M^+,8), 140(2), 96(4), 95(3), 84(6), and 58(100). The ratio of the peak at 1.9 min. to that at 1.3 min. was 95:5. The impurity in II-16 is believed to be a dimethylaminomethylchlorocyclohexane (II-17) on the basis of its m.s. fragmentation pattern. This oil slowly decomposed on standing, turning to a brown tar within several days. It was sublimed (40°/0.05mm Hg) to give ca.10mg of a yellow liquid which was immediately sent out for h.r.m.s.: m/e, 163.1011 (calcd. for $C_8H_{16}N^{37}Cl$: 163.0942), 161.0944 (calcd. for $C_8H_{16}N^{35}Cl$: 161.0972), 126.1280 (calcd. for $C_8H_{16}N$: 126.1282).

Elution with 10% CH_2Cl_2 in ether gave a yellow oil (59mg, 1.5%) identified from spectral data as cis-2-chloro-N,N-dimethylcyclohexylamine (II-18). It was shown to be over 95% pure by g.c. analysis (10% SE-30); n.m.r. τ 5.43(m, $W_{1/2}$=7Hz, 1H), 7.67(s,6H), 7.75(m,1H), and 8.0-9.0(m,8H). The g.c.-m.s. (10% SE-30, 100-200° at 10°/min) showed the major peak at 2.4min. (the m.s. pattern identical to the trans-isomer II-16), and an unidentified peak at 1.3 min. in a ratio of 98:2. This oil quickly decomposed at room temperature to give a dark brown tar.

Elution with 20% methanol in CH_2Cl_2 gave a pale yellow liquid which consisted mainly of imine trimer I-30 (292mg, 28%): i.r. 2946(s), 2790(s), 1660(wb), 1470, 1449, 1389, 1263, 1238, 1160, 1115(s), 1003, 915(s), and 860cm^{-1}; n.m.r. τ6.83(s,6H) and 7.84(s,9H).

The crude basic extract was analyzed by g.c. peak matching (10% Carbowax 20M, 100-200^{o} at 2^{o}/min.). This showed the trimer I-30 as the major constitutent at 1.1 min. along with: 3-dimethylaminocyclohexene (II-19, 2.2min.), dimethylaminocyclohexane (II-20, 6.1min.), II-16 (8.0min.), and II-18(9.0min.) in equal g.c. peak areas. II-20 was obtained from methylation of cyclohexylamine and II-19 from a reaction of 3-bromocyclohexene and dimethylamine.

The silica gel column was washed with dilute HCl (1N, 500ml methanol). The majority of the solvent was evaporated after filtration, the residue was basified and extracted with CH_2Cl_2. The CH_2Cl_2 phase was dried over $MgSO_4$ and evaporated to yield a colorless oil (725mg): i.r. 2920(s), 2860(s), 2822(s), 2772(s), 1450(s), 1373, 1270, 1260, 1194, 1154, 1036(s), 868, 848, and 812(w) cm^{-1}; n.m.r. τ7.45 (part of dt, J=12 and 3Hz), 7.75(s), 7.79(s), 7.81(s), and 7.9-9.0(bm). This residue showed three components on a preparative g.c. column (20% Dowfax 9N9, 10% TEP on Chromasorb P 60/80, 8'x1/4" copper, 150-200^{o} at 2^{o}/min., He inlet pressure at 18psi, and a thermal conductivity detection). The following compounds were identified by peak matching with the authentic (see syntheses below) and the yields are approximated from g.c. peak areas as no other compounds were observed. The g.c. showed this residue to contain: trans-1,2-bis- dimethylaminocyclohexane (II-21, 26min., 2.4%), trans-2-dimethylaminomethyl-1- dimethylaminocyclohexane (II-22, 28min., 13%), and cis-2-dimethylaminomethyl-1- dimethylaminocyclohexane (II-23, 33min., 1%) in a g.c. peak area ratio of 15:80:5, respectively.

The major component was isolated by preparative g.c. and shown to be pure II-22: it had identical i.r., n.m.r., and m.s. to the authentic material synthesized by another route (see below). The dipicrate (ca. 10mg) was recrystallized from ethanol as yellow needles, mp 176-177°, authentic dipicrate of II-22 mp 176-179° (see below), mixed mp 176-177°.

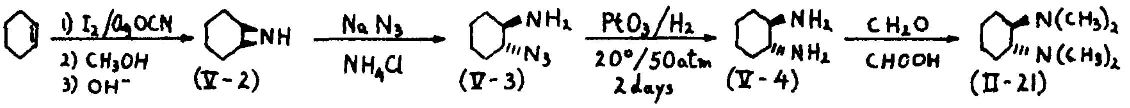
h.r.m.s. M^+ m/e calcd. for $C_{11}H_{24}N_2$: 184.1939

M^+ m/e found : 184.1941.

H) SYNTHESIS OF Trans-1,2-BisDIMETHYLAMINOCYCLOHEXANE (II-21)

1) Preparation of Trans-1,2-cyclohexanediamine (V-4)

V-4 was prepared by the method of G. Swift (173) as outlined in Scheme V-1.



Scheme V-1

7-Azobicyclo[4.1.0]heptane (V-2) was obtained crude from a reaction of cyclohexene (8.2g, 0.1moles), iodine (25.4g, 0.1moles) and freshly prepared silver cyanate (180) (15g, 0.1moles) in dry ether. The ether phase was evaporated after filtration, dry methanol (150ml) was added to the residue and the solution refluxed for 5 hours. To this was then added a solution of KOH (30g in 60ml H_2O) and refluxed an additional 5 hours. V-2 was obtained as a crude oil (7.63g, 79%): i.r. 3280(b), 3001, 2938(s), 2862, 1645, 1443, 1252, 962, 879, 836(s), and 775(s) cm^{-1}; n.m.r. τ7.21(bs, D_2O exch., 1H), 7.78-7.85(m,2H), 8.03-8.37(bm, 4H), and 8.42-8.92(bm,4H).

The azide V-3 was prepared from crude V-2 by a reaction with NaN_3 (19.5g, 0.3moles) and NH_4Cl (16.0g, 0.3moles) in ethanol-water (3:1, 400ml). This gave crude V-3 as an oil (3.39g, 31%, 24% overall): i.r. 3300(sb), 1590(s), 2090(s), and 1258(s) cm^{-1}.

V-4 was obtained by catalytic reduction of crude V-3 over Adam's catalyst (PtO_2, 200mg) for 2 days at 20° and 800psi hydrogen. V-4 was obtained as a colorless oil (2.63g, 96%, 23% overall): i.r. 3280(b), 1578(b), 1450(s), 1377, 1085, 1052(s), and 960-840(b) cm^{-1}; n.m.r. τ 7.60-7.90(bm,2H), 8.06(bs,D_2O exch., 4H), and 8.0-8.9(bm,8H).

2) Preparation of II-21

II-21 was prepared from V-4 by an Eschweiler-Clark methylation as outlined by F. Winternitz et al. (181) for the methylation of a mixture of V-4 and the cis isomer. V-4 (2.5g, crude) was refluxed for 12 hours in a solution of formic acid (90% aqueous, Fisher Scientific Co., 30ml, 0.6moles) and formaldehyde (37% aqueous, Mallinckrodt; 60ml, 0.75moles) to give II-21 as a pale yellow oil (2.59g, 66%, 15% overall from cyclohexene). This oil showed one major component (ca. 90% of all g.c. peaks) on a preparative g.c. column at 22 min. (20% Dowfax 9N9, 10% TEP on Chromabsorb P 60/80, 8'x1/4" copper, 180°) and several other g.c. peaks at higher retention times. II-21 was isolated by preparative g.c.: i.r. 2928(s), 2862(s), 2830(s), 2781(s), 1452(s), 1172(s), 1065, 1047(s), 1026(s), 950, and 878 cm^{-1}; n.m.r. τ 7.71(s,12H), 7.45-7.75(bm,2H), 8.00-8.45(bm,4H), and 8.6-9.1(bm, 4H); m.s. (80°) m/e(%), 170(M^+,100), 155(6), 125(27), 124(29), 110(25), 97(53), 84(100), 71(84), and 58(65). The dipicrate of II-21 was recrystallized from ethanol as yellow plates mp 209-211° (lit. mp 204° (181)).

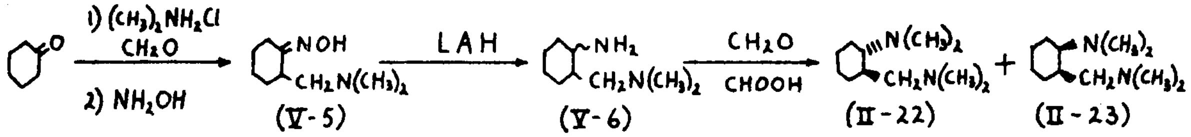
Anal. Calcd. for $C_{22}H_{28}N_8O_{14}$: C, 42.04; H, 4.49; N, 17.83

found : C, 42.16; H, 4.47; N, 17.97

I) SYNTHESIS OF Cis- and Trans-2-DIMETHYLAMINOMETHYL-1-DIMETHYLAMINOCYCLOHEXANE, II-23 and II-22.

1) Preparation of Cis- and Trans-2-dimethylaminomethylcyclohexylamine (V-6)

V-6 was prepared by a method outlined by J. Hine and W.-S. Li (182) and given in Scheme V-2.



Scheme V-2

2-Dimethylaminomethylcyclohexanone oxime V-5 was prepared by a Mannich reaction (183). Cyclohexanone (50g, 0.5moles), dimethylamine hydrochloride (9g, 0.11moles) and formaldehyde (37% aqueous, 10ml, 0.12moles) were warmed to reflux for 30 minutes. The mixture was cooled, water (50ml) was added, the unreacted cyclohexanone was separated, and the aqueous portion evaporated to a paste. This paste was dissolved in dilute NaOH (20% aqueous, 20ml, 0.1moles), hydroxylamine hydrochloride (11g, 0.15moles) was added, and the solution heated at 80° for 15 minutes. Cooling and addition of cold NaOH solution (50% aqueous, 30ml) produced an immediate precipitate (19.33g): mp 105-111°. This precipitate was recrystallized from aqueous ethanol to yield V-5 as white needles (8.28g, 49%): mp

113-116°, (lit. mp 110-120° (184)); i.r. 3300-2500(b), 1642, 1174, 1023, 1002, 938(s), 891, 871, 850, 822, 797, and 660cm^{-1}; n.m.r. τ0.09(bs, D_2O exch., 1H), 7.30-7.65(bm,5H), 7.75(s,6H), and 8.2-8.5(bm,6H).

The recrystallized oxime V-5 (4.34g, 0.025moles) was reduced with LAH (4g, 0.105moles) in refluxing dry ether for seven hours. The usual work up provided crude V-6 as a colorless oil (2.32g, 60%): i.r. 3350(b), 2930(s), 2860(s), 2820(s), 2770(s), 1595(b), 1450(s), 1381, 1261, 1185, 1156, 1041, and 849(b)cm^{-1}; n.m.r. τ 7.40-7.80(m,2H), 7.83 and 7.87 (two singlets in a ratio 1:3, 6H), 8.08(s, D_2O exch., 2H), and 8.1-9.1(bm,8H).

2) Preparation and Separation of II-22 and II-23.

The above crude V-6 (2.15g, 0.0137moles) was refluxed with formic acid (90% aqueous, 30ml, 0.6moles) and formaldehyde (37% aqueous, 40ml, 0.5moles) for 20hours. Dilute HCl (1N,20ml) was added and the solution evaporation to 20ml (35°/10mm Hg). This residue was basified with KOH solution (40% aqueous, 100ml) at 0°, and extracted with ether (2x50ml). The ether phase was dried over a colorless oil containing crude II-22 and II-23 (2.32g, 94%, 28% overall from cyclohexanone): i.r. 2928(s), 2860(s), 2820(s), 2770(s), 1460(s), 1453(s), 1374, 1261, 1194, 1184, 1153, 1037(s), 887, 870, and 849 cm^{-1}; n.m.r. τ 7.82-7.88 (4 singlets,12H), and 7.46-9.10(bm,12H).

II-22 and II-23 were separated by preparative g.c. (20% Dowfax 9N9, 10%TEP on Chromasorb P 60/80, 8'x1/4" copper, 170°, He inlet pressure at 20psi). II-23 was obtained as an oil: r.t.=41min.; i.r. 2925(s), 2855(s), 2818(s), 2763(s), 1451(s), 1372, 1270, 1260, 1193, 1152, 1061, 1036(s), 1018, 870, 849 and 813cm^{-1}; ^{1}H n.m.r. τ 7.58(dt, J=3,12Hz,1H), 7.81(s,8H), 7.87(s,6H), and 7.9-9.2(bm,9H); ^{13}C n.m.r. ppm 17.3, 21.3, 21.7, 30.6, 37.9 (C-2), 39.9 ($CH-N-(CH_3)_2$) 46.0 ($-CH_2-N-(CH_3)_2$), 62.8 (CH_2-N), and 66.2 (C-1); m.s. (80°) m/e(%), 184(M$^+$,27), 140(34), 139(66), 138(21), 126(14), 124(34), 111(36), 110(51), 84(59), 71(48), 58(100), 44(36), 42(36).

Anal. Calcd. for $C_{11}H_{24}N_2$: C, 71.68; H, 13.12; N, 15.20
found : C, 71.34; H, 13.22; N, 15.35

The dipicrate of II-23 was recrystallized from ethanol: mp 176-179° (decomp.).

Anal. Calcd. for $C_{23}H_{30}N_8O_{14}$: C, 42.99; H, 4.71; N, 17.44
found : C, 42.80; H, 4.71; N, 17.34

The *cis* isomer II-22 was isolated as an oil: r.t.=51min.; i.r. 2930(s), 2860, 2818, 2764(s), 1465(s), 1452(s), 1374, 1261, 1183, 1035(s), 887, and 856cm^{-1}; n.m.r. τ7.80(m, $W_{1/2}$=7Hz,1H), 7.85(bs,14H), and 7.90-9.00(m,9H); the m.s. was identical to the above *trans* isomer II-23. The g.c. peak area ratio of II-23 to II-22 was 6:4, respectively.

J) DECOMPOSITION OF TMT IN HCl IN THE PRESENCE OF CYCLOHEXENE

A solution of TMT (3g, 0.026moles), cyclohexene (20ml, 16.4g, 0.2moles), and concentrated HCl (15ml, 0.2moles) in methanol (200ml) was stirred in the dark at 4° for 120 hours. At this time, the reaction had reached one third completion as indicated by the decrease of the 237 nm u.v. absorption. The solution was then stirred for 24 hours at room temperature, at which time no absorption maximum was observed at 237 nm.

The solution was evaporated to 20ml (20°/10mm Hg) and the residue extracted with ether. No products were obtained on evaporation of the ether. The aqueous methanol solution was basified with NaOH solution (20% aqueous, 100ml) at 0-5° and extracted with CH_2Cl_2 (2x50ml). The CH_2Cl_2 phase was washed with saturated NaCl solution (20ml), dried over $MgSO_4$, and evaporated (steam bath) to yield a pale yellow liquid (1.76g) consisting of CH_2Cl_2 and the imine trimer I-30 in a 5:6 molar ratio, respectively, as approximated by n.m.r.: τ4.60(s;CH_2Cl_2), 6.83(s; I-30, CH_2), and 7.84(s;I-30, CH_3); the ratio of the singlets at τ4.60 and τ6.83 was 1:4. The yield of I-30 was quantitative.

The above yellow liquid was further evaporated to remove CH_2Cl_2: i.r. 2945(s), 2780(s), 2638, 1675(w), 1470, 1445, 1388, 1263(s), 1236(s), 1160, 1115(s), 1004, 915(s), and 860cm^{-1}; n.m.r. (H_2SO_4) ppm (from H_2SO_4) -7.57(dt, J=6,1.5Hz,3H), -3.38(m,1H), -3.15(m,1H), and -3.70(bs,1H); m.s. (20°) m/e(%) 43(62), 42(100).

K) DECOMPOSITION OF TMT IN CF_3COOH IN THE PRESENCE OF CYCLOHEXENE AND CARBON MONOXIDE

A solution of TMT (1g, 0.0088moles) and cyclohexene (7.25g, 0.088moles) was added dropwise over two minutes to CF_3COOH (8g, 0.071moles) with rapid stirring under a continuous stream of carbon monoxide (CO) at room temperature. A reddish purple color developed immediately in the lower of the two liquid phases which were formed. After 15 minutes, the CO flow was momentarily interrupted and gas evolution was observed to come from the lower purple phase. After 30 minutes, the purple color had disappeared, the lower phase became pale yellow, and no gas evolution was observed. An aliquot (5µl in 25ml methanol) showed no u.v. absorption at λ_{max} 237 or 277 nm, but a strong absorption at 260nm. The reaction was stirred an additional 90 minutes. Water (50ml) was added and the mixture continuously extracted with 1:1 ether-pentane (100ml, overnight) to avoid extraction of CF_3COOH (i.r. 1823 and 1203cm^{-1} (154)). The ether-pentane phase was washed with dilute acid (3N HCl, 10ml), dried over $MgSO_4$ and evaporated (25°/30mm Hg) to give a liquid (283mg): i.r. 1782(s), 1640, 1220(s), 1170(s), and 700cm^{-1}; n.m.r. τ-1.40(s), 1.01(bs), and 7.20-9.00(bm), no $N-CH_3$ signal was seen. When this liquid was dissolved in water (5ml) and slowly basified with K_2CO_3 solution, gas was evolved. The ether extracts from this basic solution gave no products.

The aqueous portions were combined and slowly basified with dilute K_2CO_3 (10% aqueous) to pH=3.5-4 and continuously extracted with 4:1 ether-pentane (100ml, 70 hours). The ether-pentane phase was dried over $MgSO_4$ and evaporated (0°/50mm Hg) to give a liquid residue (160mg): i.r. 1780(s), 1640(s), 1215(s), 1170(s), and 700cm^{-1}; n.m.r. τ-1.40(s), -0.55(bs), 2.90(m,$W_{1/2}$=8Hz), 6.90(s), 7.02(s), 7.40 (bm,$W_{1/2}$=18Hz), and 8.0(bm, $W_{1/2}$=35Hz), no N-CH_3 signal was seen.

The aqueous portions were combined, basified with KOH (40% aqueous, 50ml), and were continuously extracted with ether (100ml, 50hours). The ether phase was dried over $MgSO_4$ and evaporated (15°/30mm Hg) to yield a liquid consisting mainly of the imine trimer I-30 (180mg, 47% yield): i.r. 2945(s), 2780(s), 2638(w), 1470, 1447, 1388, 1262(s), 1236(s), 1159, 1114(s), 916(s), and 860cm^{-1}; n.m.r. τ6.91(s,6H) and 7.78(s,9H), no cyclohexane signal was seen.

The two acid fractions from above were not analyzed farther since no $(CH_3)_2N$ moiety was observed in their spectra.

L) PHOTOLYSIS OF TMT IN THE PRESENCE OF CF_3COOH AND CYCLOHEXENE

A solution of TMT (6g, 0.05moles), cyclohexene (25ml, 20.2g, 0.25moles), and CF_3COOH (26ml, 40g, 0.35moles) in acetonitrile (400ml) was made up at 0°. Most of this solution (325ml, 81%) was placed in a photolysis vessel, purged with nitrogen for 10min., and irradiated with a low pressure mercury lamp (Ultra Violet Products, Inc., 100W PCQ lamp) under nitrogen through a Vycor filter at 0^{o} for 6 hours until the u.v. absorption at 236 nm of an aliquot (5μl in 10ml methanol) disappeared. After one hour, the nitrogen flow was interrupted and gas evolution was observed in the photolysate. After two hours, the photolysate became yellow. The remainder of the original solution (75ml, 19%) was kept in the dark under nitrogen at 0^{o}. It showed no sign of gas evolution, little decay (ca. 10%) of the 236 nm absorption, and remainded colorless throughout the 6 hours. The photolysate was distilled to 20ml on a water bath, the solution turning brown. This residue was cooled to 0^{o}, taken up in dilute HCl (1N, 50ml), and the aqueous solution extracted with ether (2x50ml). No products were obtained when the ether was evaporated.

The aqueous portion was basified to pH=10 with saturated $NaCO_3$ solution and heated on a steam bath for two hours in an attempt to hydrolyze any ester products. It was continuously extracted with ether (150ml, overnight), the ether phase was dried over $MgSO_4$ and evaporated over a water bath to yield a thick brown oily residue (2.87g): i.r. 3300(wb), 2925(s), 2860(s), 2825(s), 2775(s), 1670, 1450(s), 1268, 1038(s), 868, and $848cm^{-1}$; n.m.r. τ 4.28(m), 7.75-7.82(6 strong singlets), 8.0-9.1(bm).

This basic residue showed five major spots on a t.l.c. plate (alumina, 20% methanol in ether), of which three matched with authentic compounds: II-19, r.f. (retention factor)=0.63; II-20, r.f.=0.50; and an unresolved mixture of II-22 and II-23, r.f.=0.21. The following compounds were identified by g.c. peak matching with the authentic compounds on a 20% Dowfax 9N9, 10% TEP on Chromasorb P 60/80, 8'x1/4" copper column, 150-200° at 2°/min., He inlet pressure at 18psi, and a thermal conductivity detector. They were described in the order of the elution, r.t., relative area, and % yield approximated from g.c. areas: II-20, 13min., 30, 16.9%; II-19, 14.5min., 15, 8.4%; II-21, 26min., 2, 1.2%; II-22, 29min., 40, 15.6%; II-23, 32 min., 8, 4.1%; and a peak believed to be II-15, 40 min., 5, 1.4%.

The four major components were isolated by preparative g.c. (20% Dowfax 9N9, 10% TEP; as above). II-20 had i.r. and n.m.r. identical to that of the authentic (134); II-19 had identical i.r. to that of the authentic (134) and showed a poorly resolved n.m.r. τ 4.3(m,2H), 6.9(m,1H), 7.7(s,6H), and 7.9-9.0(bm,6H); II-22 had identical i.r., n.m.r., and m.s. to the material synthesized above; and II-15: i.r. 2930(s), 2860, 2780, 1450(s), 1260(s), 1185, 1154, 1044(sb), 874, and 805cm^{-1}; m.s. (20°) m/e(%), 252(M^+,6), 237(13), 208(13), 207(10), 192(9), 167(44), 125(49), 110(34), 84(84), and 58(100). Compound II-22 gave a dipicrate which was recrystallized from ethanol as yellow needles: mp 167-175° (decomp.), authentic II-22 dipicrate mp 176-179° (decomp.).

The remainder of the original solution (75ml, 19%) was kept in the refrigerator in the dark at 0-4° for one month, at which time it had become yellow and showed no u.v. absorption maximum at 236 nm. It was worked up in a similar manner to the photolysate yielding a semi-solid (0.31g) basic fraction: i.r. 3400(sb), 3260, 2950, 2860(w), 2795, 2450(w), 1680(sb), 1635(b), 1470(b), 1200, 1175, and 1130(b) cm^{-1}; n.m.r. τ6.77(s), 7.30(m), 7.69(s), and 7.99(s); ratio of singlets at τ6.77 to 7.69 was 1:3, respectively; no cyclohexane signal was observed in the n.m.r. The signals at τ6.77 and 7.69 and i.r. at 2860, 2795, 1175, and 1130 cm^{-1} are due to imine trimer I-30; the signal at τ7.79 and i.r. 3400, 3260, 1680 and 1635 cm^{-1} are due to acetamide probably formed by hydrolysis of acetonitrile.

In a separate photolysis, the same conditions were adopted but hydrolysis was omitted, i.e. the aqueous phase was basified at 0-5^{o} and extracted immediately with ether. The n.m.r. of the crude basic fraction showed signals at τ6.80(s), 7.80(s), ca.7.75 (a number of weak singlets), and 7.9-9.1(m, weak cyclohexyl group). Comparison with the imine trimer I-30 n.m.r. showed the presence of this compound in about 60% yield.

The crude basic extract was analyzed by g.c. (20% Dowfax, as above) and g.c.-m.s. (28% Penwalt 223 on Gas Chrom R 80/100, 6'x1/4" glass, 140-190^{o} at 2^{o}/min.). This showed the following peaks which were described in the order of elution (M^{+}, m/e), r.t., area, % yield approximated from g.c. peak areas: II-20 (M^{+}, 127), 13 min., 3.1, 13%; II-19 (M^{+},125), 14.5min., 1.6, 6%; I-30 (M^{+},43), 19min., 9, 50%; II-21(M^{+},170), 42min., 0.2, 0.6%; II-22 (M^{+},184), 44min., 3.8, 10%;

II-23(M^+,184), 49min., 0.3, 1%. Owing to the large amount of column bleeding, only M^+ m/e's are given. Compounds II-20 II-19, I-30, II-22, and II-21 were identified by peak matching with the authentic samples.

M) PHOTOLYSIS OF TMT IN THE PRESENCE OF CF_3COOH AND CYCLOHEXENE UNDER OXYGEN

A solution of TMT (2g, 0.0172 moles, containing some benzene impurity) and cyclohexene (2g, 0.025 moles) in acetonitrile (50ml) was added to a solution of CF_3COOH (10.4g, 0.9 moles) in acetonitrile (50ml) in a 100ml quartz photovessel at 0^o and was purged with oxygen for 10 minutes. This solution was irradiated with a 200W Hanovia lamp through a Vycor filter at 0^o under oxygen for 90 minutes, at which time an aliquot (5µl in 10ml acetonitrile) showed no u.v. absorption maximum at 235nm. The photolysate did show a u.v. absorption at λ_{max} 255nm (believed to be benzene impurity) and a weak band at 325nm. The photolysate had turned to a bright yellow color. An aliquot (5ml) of the photolysate was treated with KI/CH_3COOH solution and the liberated iodine titrated with thiosulfate (9.27×10^{-2}M, 2.6ml) indicating 0.005 equivalents of an oxidizing agent present in the photolysate.

The remainder of the photolysate was evaporated to 10ml (10^o/10mm Hg), basified with KOH (40% aqueous) to pH>14 (ice-salt bath), and extracted with ether (4x25ml). The ether phase was dried over K_2CO_3; it gave a negative test to KI/starch paper. No attempt was made to isolate any acidic or neutral products.

Half the ether phase was evaporated to yield a pale yellow oil (677mg): i.r. 3380(sb), 2780(s), 1710(s), 1665(b), 1450(s), 1268(s), 1060, 1036(s), 946, 874, and 847cm^{-1}. Analysis of this oil by g.c. (20% Dowfax 9N9, 10%TEP on Chromasorb P 60/80, 8'x1/4" copper, 210^{o}, He at 20psi, and a thermal conductivity detector) showed one major and two minor g.c. peaks: 3.7min. for an unidentified compund; 5.4min. for II-19; 9.4min. for a mixture of cis- and trans-2-dimethylaminocyclohexanols (II-24a and II-24b). The g.c. peak area ratio was 15:2:80. The latter two peaks were identified by peak matching with authentic samples (142).

This oil was treated with hydroxylamine hydrochloride (1.5g) in pyridine (20ml) at 100^{o} for 10 minutes. Addition of ice-water (30g) produced no precipitate. The solution was basified with solid K_2CO_3 (5g) and extracted with ether (4x25ml). The ether phase was dried over K_2CO_3 and evaporated to yield an oil (ca.1g) containing about 30% pyridine as indicated by n.m.r. (134): τ1.40(m) and 2.55(m) for pyridine, 4.22(m), 4.83(bs, D_2O exch.), 5.93(m, $W_{1/2}$=8Hz), 6.70(m, $W_{1/2}$=30Hz), 7.71(s), 7.75(s, strong), and 7.50-9.00(bm); i.r. 3300(sb), 2780(s), 1645(b), 1580(w), 1440(s), 1268, 1058, 1033, 935, 872, 846, 748, and 704cm^{-1}. The area of multiplets at τ4.22, 5.93, 6.70 was in a 1:6:12 ratio. Analysis of this oil by g.c. showed the peak at 3.7min. to have disappeared and a new peak of the pyridine impurity (2.8min.). The major g.c. peak after treatment with hydroxylamine hydrochloride at r.t. 9.4min. was isolated on the above column and shown to be a II-24a and b mixture by comparison of the i.r. with an authentic sample (142): 3420(sb), 2780(s), 1630(wb), 1448(s), 1400, 1299, 1268(s), 1182, 1113, 1074, 1058, 1032(s), 946, 873(s), and 847cm^{-1}.

The remaining half of the ether phase was added to a mixture of LAH (1g) in ether (50ml) and refluxed with stirring for four hours. The mixture was treated with KOH (40% aqueous, 3ml) and water (5ml) at 0°, refluxed an additional 10 minutes, cooled and filtered. The remaining white solid was washed with a 1:1 methanol/ether solution (4x25ml) in an attempt to recover any more product. This methanol/ether solution was evaporated to 10ml on a water bath, basified with KOH (40% aqueous, 20ml) and extracted with ether (4x25ml). The ether phases were combined, dried over K_2CO_3, and evaporated on a water bath to yield a pale yellow oil (700mg): n.m.r. τ 4.26(m, $W_{1/2}$=35Hz), 6.00(m, $W_{1/2}$=9Hz), 6.11(bs, D_2O exch.), 6.69(dt, J=4.5,10Hz), 7.69(s, strong N-CH_3), and 7.60-9.00(bm), the area ratio of the multiplets at τ 4.26, 6.00, and 6.69 was 1:2.5:5.2.

Analysis by g.c. (20% Dowfax, as above, 210°) showed one major and one minor peak; II-19 at 5.3min. was estimated to be 3.5% yield; the mixture of II-24a and b at 9.5min. was estimated to be 55%. The g.c. peak area ratio of the two was 1:18. The two peaks were identified by peak matching with the authentic materials (142). No g.c. peak at 3.7min. was observed in this reduced fraction.

N) PHOTOLYSIS OF TMT IN THE PRESENCE OF CF_3COOH AND NORBORNENE

A solution of TMT (3g, 0.025moles) in acetonitrile (100ml) was added to a solution of norbornene (6.85g, 0.073moles) and CF_3COOH (22.8g, 0.2moles) in acetonitrile (100ml) at 0^o in a 200ml photolysis vessel and purged with nitrogen for 10 minutes. This solution was irradiated with a 200W Hanovia lamp through a Vycor filter under nitrogen at 0^o for 2 hours until the u.v. absorption at λ_{max}=235nm of an aliquot (5μl in 10ml methanol) disappeared. The photolysate turned to a deep yellow color after 15 minutes of irradiation but faded to pale yellow after 2 hours. An aliquot of the original solution (2ml), which was stored in the dark at 0^o, showed no decrease in the absorption at 235nm and remained colorless during the 2 hours.

The photolysate was evaporated to 5ml (15^o/35mm Hg) and the residue basified with 10% aqueous KOH solution (50ml) at 0-5^o without extraction of any neutral or acidic material. This mixture was continuously extracted with CH_2Cl_2 (200ml, 35hours). The CH_2Cl_2 phase was dried over K_2CO_3 and evaporated (15^o/20mm Hg) to give a pale yellow semi-solid (2.68g): i.r. 2940(s), 2872(s), 2820, 2775(s), and 1040(sb)cm^{-1}; n.m.r. τ 7.60-7.90(7 singlets) and 8.20-9.20(bm).

Further continuous extraction of the aqueous solution with CH_2Cl_2 (200ml, 35hours) provided a second basic fraction on evaporation of most of the solvent as a yellow liquid (740mg). This liquid consisted of CH_2Cl_2 (n.m.r τ4.65) and trimer I-30 (n.m.r. τ6.78 and 7.79) in a molar ratio of 2:1. The yield of I-30 was approximately 40%.

The first basic fraction showed five major spots on a t.l.c. plate (alumina, 5% methanol in CH_2Cl_2) and five g.c. peaks (20% Dowfax 9N9, 10% TEP on Chromasorb P 60/80, 8'x1/4" copper, 120-200° at 2°/min) as shown in the order of r.t. and relative area: 25min., 22; 134min., 35; 143min., 9; 150min., 25; and 158min., 13. The latter four peaks were in a ratio of 43:11:31:16. The first g.c. peak (25min.) was isolated as an oil and is 2-exo-dimethylaminobicyclo[2.2.1]heptane (II-26) on the basis of its m.s. and i.r. (see below) spectra: m.s. m/e(%), 139(M^+,38), 124(8), 110(46), 98(38), 84(29), 71(33), and 58(100).

This first basic fraction (2.58g) was chromatographed on a basic alumina column (160g) and gave, on elution with CH_2Cl_2, a white solid (440mg, 7%) showing one spot on a t.l.c. plate (r.f.=0.9, alumina, petroleum ether). It was sublimed (50°/0.05mm Hg) to give 2-endo-(3'-exo-dimethylaminobicyclo[2.2.1]hept-2'-endo-yl)-3-exo-dimethylaminobicyclo[2.2.1]hetpane (II-27) as white prisms: mp 165-171° (sublim.); i.r. 2870(s), 2822, 2775(s), 1290, 1268, 1179, 1169, 1060, 1042, 1013, 850, and 764cm^{-1}; ^1H n.m.r. τ7.75(s,12H), 7.7-7.9(m,2H), 8.06(m, $W_{1/2}$=4Hz, 2H), and 8.2-9.2(bm,16H); ^{13}C n.m.r. ppm (off centre decoupling) 74.9(d), 46.9(d), 42.4(q, N-CH_3), 40.0(d), 37.3(t), 35.3(d), 28.5(t), and 23.2(t); h.r.m.s. (80°) m/e(%) 276.2561(M^+, 10; calcd. for $C_{18}H_{32}N_2$: 276.2565), 261.2322(100; calcd. for $C_{17}H_{29}N_2$: 261.2331), 232.2063(10; calcd. for $C_{16}H_{26}N$: 232.2065), 218.1908(10; calcd. for $C_{15}H_{25}N$: 218.1908), 192.1749(51; calcd. for $C_{13}H_{22}N$: 192.1753), 150.1267(9; calcd. for $C_{10}H_{16}N$: 150.1282), 138.1279(9; calcd. for $C_9H_{16}N$: 138.1282), 137.1197(9; calcd. for $C_9H_{15}N$: 137.1205), 124.1126(7; calcd. for $C_8H_{14}N$: 124.1127), 98.0968(10; calcd. for $C_6H_{12}N$: 98.0970), 84(45) and 58(39).

Anal. Calcd. for $C_{18}H_{32}N_2$: C, 78.20; H, 11.67; N, 10.13
Found : C, 78.25; H, 11.58; N, 10.13

Elution with 1% methanol in CH_2Cl_2 gave a colorless oil (282mg) which showed one major and two minor spots on a t.l.c. plate: i.r. 2875(s), 2822(s), 2770(s), 1750(w), 1460(s), 1294, 1261, 1175, 1145, 1052, 1037, 1020(s), 948, 886, 859, 841, and 759cm^{-1}; n.m.r. τ 7.20(m, $W_{1/2}$=6Hz, ca. 1H), 7.43(m, $W_{1/2}$=11Hz, ca.1H), 7.70(s, ca.12H), 7.6-8.1(bm, ca. 2H), and 8.2-9.3(bm, ca.16H); m.s. (80°) m/e(%) 290(M^+,2; impurity?), 276(9), 261(100), 192(45), 182(30), and 58(55). This material solidified to a pale yellow semi-solid on standing, but was not analyzed any farther.

Elution with 2% methanol in CH_2Cl_2 gave a pale yellow solid (798mg, 12%) which showed one spot on a t.l.c. plate and was sublimed (20°/0.05mm Hg) to give 2-endo-(3'-exo-dimethylaminobicyclo[2.2.1]hept-

2'-exo-yl)-3-exo-dimethylaminobicyclo[2.2.1]heptane (II-28) as white needles: mp 67-72° (sublim.); i.r. 2878(s), 2824, 2777(s), 1680(wb), 1292, 1270, 1260, 1174, 1091, 1056, 1025(s), 1012, 942, 888, 848, and 760cm^{-1}; ^{1}H n.m.r. (100MHz) τ7.42(m, $W_{1/2}$=10Hz, 1H), 7.56(d, J=8Hz,1H), 7.76(s,12H), 7.7-7.9(m,ca.2H), and 8.16-9.22(bm,16H); ^{13}C n.m.r. ppm (off centre decoupling) 76.6(d), 71.9(d), 53.2(d), 45.5(d), 44.8(q,N-CH_3), 43.0(q, N-CH_3), 40.0(d), 39.0(d), 37.2(t), 35.0(d and t), 34.2(d), 30.3(t), 29.2(t), 28.4(t), and 23.0(t); m.s. (80°) m/e(%) 276(M^+,8), 261(100), 232(17), 218(17), 192(53), 152(26), 98(22), 84(53), and 58(43). When 20% Europium shift reagent ("Eu-Resolve", Europium(III)-2,2,6,6,-tetramethylheptanedionate; supplied by Alfa Products, Ventron Corp.) was added, two low field protons could be seen clearly in the ^{1}H n.m.r. at τ7.43(m, $W_{1/2}$=11Hz) and 7.55(dd, J=8.5, 1.4Hz). When 100% of the shift reagent was added, two singlets, 3Hz apart, appeared fo the N-CH_3 protons. Single frequency irradiation (bandwidth <10Hz) of the proton spectrum and observation of the ^{13}C n.m.r. gave the following singlets in ppm with the corresponding proton chemical shifts in τ values and decoupler offset frequency in Hz in brackets: 40.0 (7.42, 45065); 71.9(7.56, 45055); 39.0(7.72, 45045); 44.8 and 43.0(7.76, 45034); 34.2(7.85, 45034); 76.6 and 35.0(ca. 8.10, 45001); 45.5(ca. 8.25, 44985); 53.2(ca. 8.50, 44961); 30.3, 29.2, 28.4, and 23.0(ca. 8.80, 44931); and 37.2 and 35.0(ca. 9.20, 44891).

Anal. Calcd. for $C_{18}H_{32}N_2$: C, 78.20; H, 11.67; N, 10.13
Found : C, 77.54; H, 11.72; N, 10.65

Further elution with 25% methanol in CH_2Cl_2 gave a viscous oil (1.06g): i.r. 3420(s), 3350, 3260, 2960(s), 2880, 2795(w), 1640, 1468(s), 1037(s), 1012(sb), and 732(s)cm^{-1}; n.m.r. τ 4.48(s), 6.60-6.75(bm), 7.10-7.30(2 strong singlets), and 7.40-8.90(bm); m.s. (100°) m/e(%) 276(1), 261(31), 192(5), 87(11), 86(47), 85(61), 84(75), 83(100), and 58(10). This material was not analyzed farther.

The dimers II-27 and II-28 were found to match with the g.c. peaks (see above) at 150 and 134 min., respectively.

In a separate photolysis, identical conditions and amounts of reagents were used. Again, the yellow color appeared within 15 minutes of irradiation and the 235 nm absorption disappeared after 2 hours.

The photolysate was evaporated to 5 ml (15°/30mm Hg), dissolved in dilute acid (3N HCl, 20ml), and extracted with ether (2x25ml). The ether phase was washed with dilute acid (1N HCl, 10ml), saturated NaCl solution (10ml), then KOH solution (10% aqueous, 10ml), dried over K_2CO_3 and evaporated (water bath) to give a yellow semi-solid (1.04g): i.r. 3300(wb), 2935(s), 2860(s), 2805, 2758(s), 1655(b), 1450(s), 1290, 1258, 1143, 1050, 1033(sb), 935, 880, 838, and 760cm^{-1}; n.m.r. τ 7.7-7.8 (4 singlets), and 7.8-9.1(bm). Analysis by g.c. (20% Dowfax, as above) showed II-26 at 25 min. and four other peaks at 134-158 minutes in the region for dimers II-27 and II-28 and two others. The ratio of II-26 to the dimers at 134-158 minutes was 8:100. The ratio of the latter four peaks was 40:10:28:15, similar to the above reaction.

The aqueous phase was basified with aqueous KOH (40%,100ml) and extracted with ether (4x50ml). The ether phase was dried over K_2CO_3 and evaporated to give a basic fraction (2.46g) which had identical i.r. and n.m.r. to the first basic fraction above. Analysis by g.c. showed the monomer to dimer ratio of 1:10 and the four dimers in a ratio of 40:10:30:10. The monomer II-26 was separated by preparative g.c. (25min., 20% Dowfax as above): i.r. 2862(s), 2809, 2759(s), 1454(s), 1357, 1159, 1147(b), 1072(s), 1040(s), 1021(s), 930, 897, and 819cm^{-1} (lit. i.r. 1022(s) and 820cm^{-1} for exo II-26; 795(s)cm^{-1} for endo II-26 (143)).

0) PHOTOLYSIS OF TMT UNDER OXYGEN IN THE PRESENCE OF NORBORNENE

1) In CF_3COOH

a) Workup below 0°: A cold solution of TMT (3.0g, 0.025moles) in acetonitrile (100ml) was added to a solution of norbornene (7.5g, 0.08moles) and trifuoroacetic acid (22.8g, 0.2moles) in acetonitrile (100ml) at 0° in a photolysis vessel. The solution was purged with oxygen for 10 minutes and was irradiated with a 200W Hanovia lamp through a Vycor filter under oxygen at 0° for two hours until the u.v. peak of an aliquot (5 1 in 10ml methanol) at λ_{max} 235nm disappeared. The photolysate turned to a bright yellow color within 10 minutes and gave a strong positive test to KI/starch paper. No change occurred in an aliquot (2ml) stored in the dark at 0° under oxygen.

The photolysate was evaporated to 15ml (0°/10mm Hg) and immediately basified at 0° to pH 14 (40% aqueous KOH), the basic aqueous phase turning brown. The latter was extracted with ether (4x50ml) and the majority of the ether was evaporated (0°/20mm Hg, no drying). The residue was dissolved in ethanol (50ml) at 0° and a solution of Na_2BH_4 (2g, 0.05moles) in water (50ml) was added slowly. After stirring for 24 hrs at 20°, the $NaBH_4$ solution was acidified (3N HCl, 50ml), and evaporated to 100ml (30°/10mm Hg).

The acidified aqueous portion of the $NaBH_4$ solution was extracted with ether (3x25ml). The ether phase was washed with dilute HCl (1N, 3x25ml), then with water (2x25ml), dried over K_2CO_3, and evaporated on a water bath to give a brown oil (71mg): i.r. 3320(sb), 2940(s), 2880, 1658, 1626, 1446(s), 1279, 1168, 1126(b), 1045(sb), 857, 842, and 802cm^{-1}; n.m.r. τ5.90-6.50(bm) and 7.7-8.9(bm). This oil was treated with p-nitrobenzoyl chloride (200mg) in pyridine (1ml) at 100° for 30 minutes. Addition of ice (10g) liberated a brown paste (ca.100mg). This paste was washed with saturated Na_2CO_3 solution (5x10ml) and recrystallized 4 times from hot ethanol (3ml) to give the bis-p-nitrobenzoate of 2,7-dihydroxylbicyclo[2.2.1]heptane (II-31) as pale yellow needles (ca.20mg): mp 164-165° (decomp.); i.r. was identical to a sample prepared by another route (see below); n.m.r. (acetone-D_6) τ2.05-2.58(bm,8H), 5.00(m, $W_{1/2}$=20Hz,2H), and 7.15-8.80(bm,8H); m.s. (210°) m/e(%) 426(M^+,1), 410(1), 396(1), 300(2), 276(4), 259(16), 213(5), 150(100), 134(20), 120(17), 110(37), 104(52), 92(64), 76(30), and 66(35).

Treatment of norbornene with m-chloroperbenzoic acid provided 2,3-exo-epoxybicyclo[2.2.1]heptane (II-32) (152). The epoxide II-32 was refluxed with formic acid for 2 hours. the formic acid solution was then basified with aqueous KOH and refluxed for 5 hrs to give the crude 1,7-diol II-31 (151) as an oil. This crude product was treated with p-nitrobenzoyl chloride to give a solid which was recrystallized 2 times from propanol to give the bis-p-nitrobenzoate of II-31 as pale yellow needles: mp 159-163 i.r. 3120(w), 3060(w), 1720(s), 1605, 1522(s), 1458, 1353, 1320, 1302, 1286(s), 1122, 1105, 1019, and 721(s)cm^{-1}.

The acidified aqueous portion of the $NaBH_4$ solution was basified with aqueous KOH (40%) at 0-5° to pH>14 and extracted with ether (4x75ml). The ether phase was dried over K_2CO_3 and evaporated on a water bath to give a brown viscous oil (2.91g): i.r. 3330(sb), 2879, 2835, 2787, 1648, 1455(s), 1155, 1048(sb), and 876cm^{-1}; n.m.r. τ5.30(s, D_2O exch.), 5.70-6.15(bm), 6.3-6.7(bm), 7.55-7.85 (at least 2 strong singlets), and 8.0-8.9(bm).

This crude basic fraction showed one major and three minor spots on a t.l.c. plate (alumina, 5% methanol in ether) and one major g.c. peak at 5.8 minutes (10% SE-30 on Chromasorb S 80/100, 6'x1/8" stainless steel column, 120-250^{o} at 10^{o}/min., N_2 at 20psi, and a hydrogen flame detector). The g.c. peak at 5.8 min. was matched with that of 3-exo-dimethylamino-2-endo-bicyclo[2.2.1]heptanol (II-34); the authentic sample was a 1:1 mixture of endo (II-34, r.t.=5.8min.) and exo (II-35, r.t.=6.2mn.) alcohols (153).

The basic fraction was analyzed by g.c.-m.s. (10% SE-30, 120-250^{o} at 10^{o}/min.) to give the following peaks that were described in the order of r.t., relative area, % yield based on g.c. peak area: 5.2min., 3, 3%; 5.6min., 90, 57%; 6.5min., 5, 4%; 7.8min., 10, 6%; 11.1min., 10, 6%; 13.2min., 6, 5%. These peaks showed the corresponding m.s. peaks at the following m/e(% intensity): 5.2min., 110(M^+, 50), 95(21), 92(28), 81(86), 79(76), 67(72), 66(84), and 58(100); 5.6min., II-34, 155(M^+,65), 140(20), 138(12), 126(28), 98(100), 84(84), 71(91), and 58(95); 6.5min., II-35, 155(M^+,17), 138(20), 126(9), 100(21), 98(22), 84(40), 71(64), and 58(100); 7.8min., 173(M^+,6), 88(40), and 58(100); 11.1min., 169(M^+,9), 151(14), 126(9), 110(29), 92(60), 86(66), 60(100), and 43(86); 13.2min., 247(M^+?,16), 232(2), 218(19), 206(14), 124(31), 98(45), 84(100), 71(28), and 58(38). Both II-34 and II-35 were identified by g.c. peak matching with the authentic samples (153).

This crude basic fraction (2.2g) was chromatographed on a neutral alumina column (150g) and gave on elution with 1% methanol in ether a yellow liquid (114mg, 2.5%) which showed one spot on a t.l.c. plate and one major g.c. peak at 13.5min. and a minor one at 5.6min. (10% SE-30, as above). This liquid was sublimed (20°/0.05mm Hg) to give 2-*endo*-(3'-*endo*-hydroxybicyclo[2.2.1]hept-2'-*exo*-yl)-3-*exo*-dimethylaminobicyclo-[2.2.1]heptane (II-36) as a white solid: mp 73-75°; i.r. 3400(wb), 2780, 1650(wb), 1380, 1042, 1016, 993(s), 972(s), 947, and 919cm^{-1}; ^{1}H n.m.r. τ5.54(ddd, J=4.5, 2.5, 0.5Hz; 1H), 7.35(m, $W_{1/2}$=7Hz; 1H), 7.50(bd, J=9.5Hz, $W_{1/2}$ of one of the signals = 5Hz; 1H), 7.56(s, D_2O exch.; 1H), 7.76(s,6H), 7.65-7.95(bm,3H), and 8.00-9.25(bm,14H); ^{13}C n.m.r. ppm (off centre decoupling) 82.72(d), 77.05(d), 52.96(d), 47.59(d), 44.00(q; N-CH_3), 39.94(d), 37.35(d), 34.31(t), 33.41(d), 29.20(t), 27.13(t), 22.70(t), and 20.52(t); m.s. (90°) m/e(%) 249(M^+,1), 248(18), 247(71), 218(18), 206(62), 202(13), 193(13), 192(10), 180(10), 152(16), 150(15), 136(16), 124(66), 98(70), 84(100), 71(43), and 58(36).

Anal. Calcd. for $C_{16}H_{27}NO$: C, 77.06; H, 10.91; N, 5.62
Found : C, 76.72; H, 10.36; N, 5.78

Elution with 3% methanol in ether provided a yellow liquid (712mg, 26%) which showed one spot on a t.l.c. plate and one g.c. peak at 5.6min. (10% SE-30, as above). It was sublimed (20°/0.05mm Hg) to give II-34 as translucent prisms: mp 67-68°; i.r. (melt) 3360(b), 2956(s), 2878, 2832, 2785, 1660(wb), 1464(s), 1156, 1075, 1050(s), 1022, 942(w), 867, 769(w), and 741(w) cm^{-1}; ^{1}H n.m.r. τ5.85(s, D_2O exch.; 1H), 6.13(ddd, J=4.0,2.9,0.8Hz; 1H), 7.74(s;6H), 7.66-7.82(bm;2H), and 8.10-8.92(bm;7H); ^{13}C n.m.r. (off centre decoupling) in ppm 78.6(d), 78.2(d), 43.6(q; N-CH_3), 42.5(d), 39.0(d), 34.3(t), 29.4(t), and 19.4(t); m.s.(90^o) m/e(%) 155(M$^+$,65), 140(14), 138(14), 126(12), 124(12), 112(14), 110(17), 98(100), 84(72), 71(86), and 58(89). Irradiation of the signal (see Figure II-15 and Table II-10) at τ7.75 collapsed the doublet of double doublets at τ6.13 to a double doublet (J=2.9,0.8Hz); irradiation at τ8.45 collapsed the same signal to a doublet (J=4.0Hz).

Anal. Calcd. for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02
Found : C, 69.90; H, 11.10; N, 9.00

Elution with increased methanol (up to 50%) in ether gave a brown viscous oil (1.01g) which showed three spots on a t.l.c. plate and one major (5.6min.) and two minor (7.6 and 10.8 min.) g.c. peaks (10% SE-30, as above): i.r. 3280(sb), 2940(s), 2880, 2790, 1632(s), 1547, 1448(s), 1345, 1160, 1048(sb), and 840(w) cm^{-1}; n.m.r. τ6.00-6.65(bm), 7.70 and 7.80 (2 strong singlets), and 8.0-9.1(bm). II-34 (g.c. peak at 5.6min.) was removed by sublimation (20^o/0.05mm Hg) for one week.

Further sublimation (70^o/0.05mm Hg) provided a pale yellow oil (ca. 100mg) which showed one spot on a t.l.c. plate and one major (7.5min.) and one minor (10.9min.) g.c. peaks (10% SE-30, as above) in a ratio of 18:1.

This oil showed: i.r. 3340(sb), 2950(s), 2868, 2834, 2786, 1640(b), 1458(s), 1340(b), 1262, 1035(sb), and 858cm^{-1}; n.m.r. τ5.65-6.00 (m;ca.1H), 6.20-6.60(m;ca.2H), 6.30(s, D_2O exch.; ca.2H), 7.70(s, ca.6H), 7.55-7.85(bm, poor resolution), and 7.90-8.85(bm, poor resolution); h.r.m.s. (80^o) m/e(%) 173.1413(M^+,6; calcd. for $C_9H_{19}NO_2$: 173.1415), 159.1268 (3; calcd. for $C_8H_{17}NO_2$: 159.1259), 156.1384(2; calcd. for $C_9H_{18}NO$: 156.1389), 142.1251(13; calcd. for $C_8H_{16}NO$: 142.1261), 128.1076(3; calcd. for $C_7H_{14}NO$: 128.1075), 124.1132(3; calcd. for $C_8H_{14}N$: 124.1126), 110.0975(3; calcd. for $C_7H_{12}N$: 110.0970), 110.0732(4; calcd. for $C_7H_{10}O$: 110.0732), 100.0752(8; calcd. for $C_5H_{10}NO$: 100.0762), 98.0980(10; calcd. for $C_6H_{12}N$: 98.0970), 88(26), 84(16), 71(11), 67(14), and 58(100). No ester could be obtained when this oil was treated with p-nitrobenzoyl chloride in tetrahydrofuran by the method of Ikegami et al. for β-amino alcohols (185). This material has been tentatively assigned 3-cis-(1'dimethylamino-2'-hydroxyethyl)cyclopentanol (II-37) on the basis of its mass spectrum.

b) Workup at 25^o: In a separate photolysis a solution of TMT (8g, 0.069 moles), norbornene (11g, 0.11moles) and CF_3COOH (25g, 0.245 moles) in acetonitrile (200ml) was irradiated with a 200W Hanovia lamp through a Vycor filter at 0^o under oxygen for 5 hours until the absorption at λ_{max} 237nm of an aliquot (1:4000 dilution in methanol) disappeared. The photolysate became deep yellow after 10 minutes. After 4 hours, a new absorption, about 1/10 of the starting one at 237nm, appeared at λ_{max} 270nm with a weak tail at λ_{max} ca.310nm. An aliquot of the photolysate (5ml) was treated with KI (1g) in water (5ml) and CH_3COOH (5ml) and the liberated iodine was titrated with thiosulfate solution (1.2ml, $9.27x10^{-2}N$) indicating the presence of 0.045 equivalents of oxidizing agents present in the photolysate.

The photolysate was evaporated to 5ml (15^o/10mm Hg) and the residue diluted with HCl (0.1N, 50ml) at 0^o. This aqueous solution was extracted with ether (5x20ml). The ether was washed with saturated salt solution (3x20ml), then with saturated Na_2CO_3 solution (1x20ml), dried over $MgSO_4$, and evaporated on a water bath to give a brown semi-solid (505mg): i.r. 3350(sb), 2950(s), 2875, 1779(s), 1672(b), 1447(b), 1392(w), 1350(s), 1219, 1202, 1170(sb), 1065(b), 869(w), 840(w), and 721cm^{-1}; n.m.r. τ5.7-6.3(bm) and 7.6-9.0(bm).

Analysis of this acidic and neutral fraction by g.c. (10% SE-30 on Chromasorb S 80/100, 6'x1/8" stainless steel, 100-250^o at 6^o/min., He at 18psi, and a H_2 flame detector) showed one major peak at 9.0 min. and at least 14 minor ones. This major peak at 9.0 min. showed the following g.c.-m.s. m/e% 207(1), 206(2), 169(6), 153(6), 125(5), 115(10), 110(94), 95(76), 92(88), 81(100), 79(92), 69(78), 67(86), 66(78), and 57(78). This major g.c. peak is believed to be due to 7-hydroxybicyclo[2.2.1]hept-2-yl trifluoroacetate (II-38). II-38 was prepared (see reference 152) by stirring the expoxide II-32 (100mg) in a CH_2Cl_2 (2ml) solution containing CF_3COOH (100mg) for 5 minutes at 20^o. The CH_2Cl_2 phase was washed with dilute K_2CO_3

solution at 0^o, dried by passing through an alumina column (2g), and evaporated to yield a colorless oil (ca.150mg): i.r. 3400(sb), 2956(s), 2879, 1777(s), 1445(b), 1393, 1352(s), 1220, 1165(sb), 1080(b), 865(w), 848(w), $720cm^{-1}$. This oil showed a major g.c. peak at 8.5 min. (SE-30, as above) and at least 10 minor g.c. peaks at higher retention times. The major peak at 8.5 min. was matched with the major g.c. peak observed in the above acidic and neutral fraction. The yield of the trifluoroacetate II-38 from the photolysate was approximated from the g.c. peak areas as 2.5%. No epoxide II-32 could be detected in the above acidic and neutral fraction by either g.c., t.l.c., or i.r.

The acidic aqueous solution from this second photolysis was basified with solid K_2CO_3 to pH 12 and extracted with ether (5x40ml). The ether phase was dried over K_2CO_3 and evporated to yield a brown oil (4.6g): i.r. 3400(wb), 2875(s), 2825, 2780(s), 1747(s), 1716(wb), 1453(s), 1177, 1155, and 1042(sb) cm^{-1}; n.m.r. τ 6.02(bm), 6.50(bm), 7.20(m), 7.67(strong singlet), 7.71(s), 7.79(s), and 7.5-9.0(bm). The ratio of the singlets at τ7.67, 7.71, and 7.79 was in the order of 3:1:1.

This basic fraction showed three major g.c. peaks (10% SE-30 on Chromasorb S 80/100, 6'x1/8" stainless steel, 100-250^o at 6^o/min., He inlet pressure 18psi, and a hydrogen flame detector) at 6.9, 7.5, and 8.1 min. in a g.c. peak area ratio of 6:1.5:1 and a minor peak at 3.9 minutes. The three major peaks were matched with the following authentic compounds (153,155): 6.9min., 3-exo-dimethylamino-2-bicyclo[2.2.1]-heptanone (II-39); 7.5min., exo-alcohol II-35; and 8.1min., endo-alcohol II-34. G.c.-m.s. showed the minor peak at 3.9 min. to be II-26: m.s. was identical to that of II-26 obtained above in the photolysis under nitrogen, and the major peak at 6.9min. (II-39): m.s. m/e(%) 153(8), 152(3), 139(3), 135(3), 125(3), 124(3), 122(3), 94(6), 84(3), 79(5), 70(10), 67(12), and 58(100). Separation of this major peak by preparative g.c. (20% Dowfax 9N9, 10% TEP, on Chromasorb P 60/80, 8'x1/4" copper, 220°, He inlet pressure at 20psi) provided II-39 as a colorless oil: r.t. 7.2min.; i.r. 2820, 2778(s), 1746(s), and 1440(sb) cm^{-1} (lit. i.r. 2815, 2770. 1742, and $1045cm^{-1}$ (106)).

Further extraction of the basified aqueous phase with ether (200ml, 14hr.) provided a yellow oil (1.63g) which consisted mainly of the trimer I-30 (55% yield): n.m.r. τ6.77(s;6H) and 7.80(s;9H).

c) Reduction of Ketone II-39: A portion of the above basic fraction (1.42g) containing mainly ketone II-39 was refluxed with LAH (0.75g) in ether (150ml) for 4 hours. The usual work up provided a pale yellow oil (1.20g) which showed 2 g.c. peaks in a ratio of 5:1 at 7.9min. (II-35) and 11.0 min. (II-34), that were matched with the authentic compounds on a 20% Dowfax column (as above). Using the ratio of ketone II-39 to the two alcohols II-34 and II-35 of 6:1.5:1 observed before reduction, it was calculated that reduction of the ketone II-39 by LAH gave the exo-alcohol II-35 as the major product and the endo-alcohol II-34 as the minor product in a 90:10 ratio.

Another portion of this basic extract (500mg) was stirred with a solution of $NaBH_4$ (800mg) in 1:1 ethanol-water (8ml) at 0-5° for 8 hours. The usual work up provided a pale yellow oil (ca.400mg) which was analyzed by g.c. as above and showed II-35 (7.9min.) and II-34 (11.0min.) in a ratio of 1.4:1. It was calculated, as above, that reduction of the ketone II-39 by $NaBH_4$ gave the exo-alcohol II-35 and the endo-alcohol II-34 in equal ratios.

The two peaks were isolated by preparative g.c. (as above) from the $NaBH_4$ reduction. II-35 was obtained as a colorless oil: r.t. 7.9min., i.r. 3300(b), 2870(s), 2830, 2780(s), 1462, 1450, 1396(b), 1139, 1078, 1050(s), 1035(s), 899, 822(w), and 768(s) cm^{-1} (lit. i.r. 3300(m), 2785, 1050(s), and 1035(s) cm^{-1} (103)); n.m.r. τ 5.30(bs, D_2O exch.; 1H), 6.47(dt, J=6.6, 1.3, 1.3Hz; 1H), 7.70(s;6H), 7.75-8.05(bm;3H), and 8.2-9.2(bm;6H); m.s. (80°) m/e(%) 155(M^+,20), 140(14), 126(16), 98(62), 84(37), 71(55), and 58(100). II-34 was obtained as a semi-solid: r.t. 11.0min.; i.r., n.m.r., and m.s. were identical to that of II-34 obtained above in the first photolysis.

d) Reaction of II-38 with dimethylamine: the trifluoroacetate II-38 (ca.150mg) obtained above from the epoxy ring opening of II-32 by CF_3COOH was stirred overnight with a 40% aqueous dimethylamine solution (5ml) at 20°. This mixture was treated with solid K_2CO_3 (1g) and extracted with ether (1x5ml). The ether phase was passed through alumina (2g) and evaporated to give a colorless oil (ca.100mg). This oil showed one peak at 7.9min. on a preparative g.c. column (20% Dowfax, as above) which was matched with the exo-alcohol II-35 and a large peak at 40min. which was not identified. The peak at 7.9min. was isolated and shown to be II-35: i.r. identical to that of II-35 isolated above.

e) Attempted preparation of the ketone II-39: The endo-alcohol II-34 (130mg) obtained from the above first photolysis was treated with acetic anhydride (2ml) in dimethylsulfoxide (Fisher Scientific Co., DMSO; 5ml) for 36 hours according to a procedure of Albright and Goldman for oxidation of hindered secondary alcohols in alkaloids (186). Ice (20g) was added and the mixture was extracted with ether (2x10ml). The ether solution was washed with dilute K_2CO_3 (20% aqueous, 10x10ml), and dried by passing through an alumina column (2g). The ether was evaporated to yield a colorless oil (ca.300mg) which showed 2 g.c. peaks at 6.0 and 9.0min. in equal ratios on a preparative g.c. column (20% Dowfax, as above). The g.c. peak at 6.0min. was matched with authentic DMSO and the one at 9.0min. was isolated to give the endo II-34 acetate as a viscous colorless oil: i.r. 2875(s), 2820, 2770(s), 1733(s), 1445, 1373(s), 1240(sb), 1152, 1037(s), and 860(s) cm^{-1}; n.m.r. τ 5.15 (ddd, J=4.4,4.0,1.2Hz; 1H), 7.62(m;1H), 7.77(s;6H), 7.93(s;3H), 7.7-8.0(bm;1H), and 8.0-9.0(bm;7H). Only a trace amount of the expected ketone II-39 was observed at 7.2 min. and none of the starting endo alcohol II-34 was observed at 11.0 minutes.

Another oxidation of II-34 was attempted by a method of Wuonola and Woodward (187) using chromic anhydride (2.5g) in a solution of pyridine (30ml) and water (4ml). The work up gave a brown tar which showed no starting alcohol II-34 at 11.0min. and only a trace of ketone II-39 at 7.2min. on the 20% Dowfax 9N9 g.c. column. This tar was not analyzed farther.

2) Neutral

The same conditions and amounts were used as (1b) but CF_3COOH was omitted. It took 6 hours for the TMT absorption at λ_{max} 280nm to disappear. At this time the photolysate gave a negative test to KI-starch paper. No yellow color was observed throughout the 6 hours. At this point, CF_3COOH (25g) was added and the photolysate was worked up as in (1b).

The neutral fraction was obtained as a semi solid (354mg): i.r.. 3380(sb), 1670(sb), 1204(s), 1180, 1135(sb), and 1080(b) cm^{-1}; n.m.r. τ4.9(bs, D_2O exch.) and 7.5-9.1(bm). The g.c. of this fraction (see above for conditions) showed 8 peaks, of which the one at 7.6min. was identified as II-38 by g.c. peak matching with an authentic sample. The epoxide II-32 was identified by t.l.c. as a small spot matching with that of an authentic sample. The yield of II-38 was estimated to be below 1%.

The first basic ether extract consisted of a pale yellow liquid (2.5g): i.r. was identical to that of the imine trimer I-30; n.m.r. showed ether at τ6.5(q) and 8.8(t), I-30 at 6.8(s) and 7.7(s), and a small singlet at τ7.78 which was identified as TMH by comparison with that of an authentic sample. The ratio of ether:I-30:TMH was 4:5:1.

Continuous ether extraction provided a second basic fraction as a pale yellow liquid (1.3g): i.r. was identical to that of I-30; n.m.r. showed ether an I-30 in a 3:7 ratio. From the above n.m.r.'s the yield of I-30 was approximated to be 90% and that of TMH about 4%. No basic addition products to norbornene were observed by g.c. or in the above spectra.

P) DECOMPOSITION OF TMT IN THE PRESENCE OF CF_3COOH AND NORBORNENE

A solution of TMT (1g, 0.0088moles) and norbornene (8.3g, 0.088moles) in acetonitrile (10ml) was added dropwise with stirring over 2 minutes to neat CF_3COOH (8g, 0.071moles) at room temperature. The solution turned a pale brown color and slow gas evolution was observed. The absorption at 235nm disappeared in 5 hours. The usual work up provided 250mg of a basic extract: i.r. 3290(s), 2780(s), 1648(s), 1545, 1262(s), 1111(s), and 925(s) cm^{-1}; n.m.r. τ6.78(s) and 7.70(s) (2:3; imine trimer I-30), 6.15(m, $W_{1/2}$=15Hz), ca.7.7 (6 weak singlets), and 8.0-9.1(bm). This fraction showed at least 7 spots on a t.l.c. plate and was not analyzed farther. The yield of I-30 was estimated from the n.m.r. to be 30%.

Q) PHOTOLYSIS OF TMT IN THE PRESENCE OF COD AND CF_3COOH

A solution of TMT (4g, 0.0345moles) and COD (4g, 0.037moles) in acetonitrile (100ml) was added to a solution of CF_3COOH (25g, 0.245moles) in acetonitrile (100ml) at 0^o in a photovessel and was purged with nitrogen for 10 minutes. This solution was irradiated with a 200W Hanovia lamp through a Vycor filter under nitrogen at 0^o for 2 hours until an aliquot (5μl in 10ml methanol) showed no u.v. maximum at 237nm. The photolysate turned bright yellow within 10 minutes of irradiation and gas evolution was observed when the nitrogen flow was interrupted.

One quarter of this photolysate was evaporated to 5ml (20^o/10mm Hg) and 12ml 3N HCl was added. The residue was washed with ether (2x25ml). The ether phase was separated, washed with dilute HCl (0.1N, 2x10ml), and discarded. The aqueous phases were combined, evaporated to a semi solid (20^o/10mm Hg), and treated with 2,4-dinitrophenyldhyrazine hydrochloride (2g) in ethanol (50ml). No precipitate was formed when this solution was diluted with water (50ml). No precipitate was detected when this aqueous ethanol solution was neutralized with aqueous K_2CO_3. This quarter of the photolysate was not analyzed farther.

Another quarter of the photolysate was evaporated to a semi solid as described above. This residue was taken up in water (10ml) and slowly neutralized with a dilute K_2CO_3 solution. A $NaBH_4$ solution in ethanol (2g in 50ml) was added slowly to the above mixture and stirred for

3 hours at 20°. This mixture was acidified and evaporated to a paste (30°/10ml Hg). This paste was basified to pH 14 (40% aqueous KOH) and extracted with ether (4x25ml). The ether phase was dried over $MgSO_4$ and evaporate (steam bath) to yield a pale brown oil (695mg): i.r. 3370(wb), 3015(w), 2820, 2770(s), 1675(b), 1353, 1264, 1040(s), and 726(s) cm^{-1}; n.m.r. τ 4.45(m), 7.8-7.9 (3 strong singlets), and 8.1-9.0(bm).

This crude basic extract showed two spots on t.l.c. plate and two g.c. peaks at r.t. 6.8 and 14.3min. in a ratio of 1.7:1 (25% Carbowax 20 PTAT on Chromasorb A 60/80, 10'x1/4" stainless steel, 240°, He press.=20psi, thermal conductivity detector). The two peaks were separated by preparative g.c.: 6.8min. (II-40); i.r. 3020, 2828, 2779(s), 1688(w), 1458(s), 1264, 1177, 1154, 1043, 1032, 994, and 727(s) cm^{-1}; m.s. m/e(%), 153(M^+,25), 138(5), 136(5), 125(18), 124(18), 110(25), 84(66), and 71(100); 14.3min. (II-41); i.r. 2818, 2770(s), 1458(s), 1351, 1259, 1040(s), 866, and 844 cm^{-1}; m.s. m/e(%), 210(M^+,30), 195(2), 166(22), 165(15), 152(10), 150(6), 137(7), 136(6), 126(23), 124(18), 110(11), 84(49), 71(32), and 58(100).

The remaining half of the photolysate was worked up to give a semi solid as described above. This residue was basified with 40% aqueous KOH to pH 14 and extracted with ether (4x25ml). The ether phase was dried over $MgSO_4$ and evaporated (steam bath) to yield a pale brown oil (1.64g). The i.r. and n.m.r. were identical to the crude basic extract obtained above. This basic extract showed two spots on a t.l.c. plate and two g.c. peaks (25% Carbowax, as above) at 6.8 and 14.3min. in a 1.9:1 ratio.

This oil (1.48g) was chromatographed on a neutral alumina column (75g). Elution with 50% petroleum ether (30/60) in ether gave a colorless oil (565mg) which showed one spot on a t.l.c. plate and one g.c. peak at 6.6min. (25% Carbowax, as above). It was sublimed (10°/0.05mm Hg) to yield a colorless oil identified as 5-dimethylaminocyclooctene (II-40): i.r. and m.s. were identical to the above material obtained by preparative g.c. at 6.8 min.; n.m.r. τ 4.48 (m, $W_{1/2}$=35Hz, 2H), 7.92(s; NCH_3) and 7.8-8.1(m,11H), and 8.15-9.05(bm,6H).

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.37; H, 12.50; N, 9.14
Found : C, 78.15; H, 12.36; N, 9.49

The picrate was recrystallized from ethanol: mp 153-167° (decomp.).

Anal. Calcd. for $C_{16}H_{22}N_4O_7$: C, 50.26; H, 5.80; N, 14.65
Found : C, 50.76; H, 5.97; N, 14.70

Further elution gave an oil (122mg) which showed 2 g.c. peaks at 6.6 and 14.2min. (25% Carbowax, as above).

Elution with 100% ether gave a colorless oil (266mg) which showed one spot on a t.l.c. plate and one g.c. peak at 14.2min. (25% Carbowax, as above). It was sublimed (20°/0.05mm Hg) to give a colorless oil of 6-exo-dimethylaminomethyl-2-exo-dimethylamino-cis-bicyclo[3.3.0]octane

(II-41): i.r. and m.s. were identical to the material obtained previouly by preparative g.c. at 14.3min.; n.m.r. (100MHz) τ7.74(s; N-$(CH_3)_2$), 7.78 (s; N-$(CH_3)_2$) and 7.72-7.82(bm) (18H), and 7.90-8.35(bm,4H).

Anal. Calcd. for $C_{13}H_{26}N_2$: C, 74.23; H, 12.46; N, 13.36
Found : C, 74.18; H, 12.43; N, 13.42

The dipicrate of II-41 was recrystallized three times from ethanol: mp 217-221° (decomp.); h.r.m.s. m/e(%) 228.9971 (2, calcd. for $C_6H_3N_3O_7$: 228.9971), 210.2090 (2, calcd. for $C_{13}H_{26}N_2$: 210.2096), 166.1588 (4, calcd. for $C_{11}H_{20}N$: 166.1595), 165.1518 (4, calcd. for $C_{11}H_{19}N$: 165.1518), 126.1282 (5, calcd. for $C_8H_{16}N$: 126.1282), 124.1124 (3, calcd. for $C_8H_{14}H$: 124.1126), 110.0969 (2, calcd. for $C_7H_{12}N$: 110.0969), 84.0817 (11, calcd. for $C_5H_{10}N$: 84.0813), and 58(100).

Anal. Calcd. for $C_{25}H_{32}N_8O_{14}$: C, 44.91; H, 4.82; N, 16.76
Found : C, 44.78; H, 4.84; N, 16.60

The bis-methiodide of II-41 was recrystallized twice from ethanol: mp 155-190° (decomp.); m.s. m/e(%), 210(4), 142(59), 127(18), 84(17), and 58(100); n.m.r. (60MHz, D_2O) τ6.39(m, $W_{1/2}$=22Hz, 1H), 6.68(m, $W_{1/2}$=18Hz,2H), 6.97(s,9H), 7.02(s,9H), 7.48(m, $W_{1/2}$=30Hz,1H), and 7.7-8.8 (bm,10H); n.m.r. (100MHz, D_2O) τ6.40 (ddd, J=8.5,6.5,6.0Hz, 1H), 6.63 and 6.76 (the AB of an ABX, J_{AB}=13.5, J_{AX}=8.9, J_{BX}=3.9Hz, 2H), 6.99(s,9H), 7.04(s,9H), 7.32(bm, $W_{1/2}$=30Hz,1H), 7.75-8.25(bm,7H), and 8.30-8.83(bm,3H). Irradiation (see Figure II-19) at τ7.90 collapsed the ABX at ca.6.70 to an AB quartet ($\Delta\delta$=0.133ppm, J_{AB}=13.5Hz). Irradiation at τ7.40 collapsed the signal at τ6.40 to a double doublet (J=8.5,6.0Hz); irradiation at τ8.05 collapsed this signal to a double doublet (J=6.5,6.0Hz); and irradiation at τ7.90 collapsed this signal to a doublet (J=6.0Hz).

Anal. Calcd. for $C_{15}H_{32}N_2I_2$: C, 36.45; H, 6.53; N, 5.67

Found : C, 36.48; H, 6.64; N, 5.58

R) PHOTOLYSIS OF TMT IN THE PRESENCE OF COD AND CF_3COOH UNDER OXYGEN

A solution of TMT (3g, 0.025moles) and COD (4g, 0.037moles) in acetonitrile (100ml) was added to a solution of CF_3COOH (23g, 0.2moles) in acetonitrile (100ml) in a photovessel at 0°. This solution was purged with oxygen for 10 minutes and was irradiated for 2 hours at which time an aliquot showed no u.v. maximum at 235nm. After 5 minutes of irradiation the photolysate turned to bright yellow but slowly became light brown over 2 hours. A drop of the photolysate showed a very strong positive test to KI-starch paper. An aliquot (2ml) of the solution stored in the dark under oxygen at 0° showed no change in the absorption at λ_{max} 235nm.

The photolysate was evaporated to 15ml (10^o/10mm Hg). Without washing with ether, the residue was cooled to -30^o (dry-ice/acetone) and dissolved in ethanol (50ml). A cold KOH solution (15ml 40% aqueous KOH in 50ml ethanol) was slowly added followed by slow addition of a $NaBH_4$ solution (4g, 0.1moles, in 50ml 50% aqueous ethanol) at -30^o. The light brown mixture was allowed to come to room temperature and was stirred for 12 hours. The mixture was acidified with dilute acid (3N HCl, 75ml) at 0^o and the volume was reduced to 50ml (20^o/15mm Hg).

This residue was basified with 40% aqueous KOH until pH 14 and extracted with ether (4x75ml). The ether phase was dried over $MgSO_4$ and evaporated (steam bath) to give a light yellow oil (3.08g): i.r. 3360(sb), 3010, 2875, 2780(s), 1650(wb), 1460(s), 1262, 1165(b), 1030(sb), and 723(s) cm^{-1}; n.m.r. τ 4.1-4.7(bm), 6.02(bt, $W_{1/2}$=11Hz), 6.30(bs, D_2O exch.), 6.60(bm, $W_{1/2}$=20Hz), 7.77(s) and 7.81(s) (strong, 2:3), and 7.30-8.75(bm).

This basic extract showed two spots on a t.l.c. plate (alumina, 2% methanol in ether). One with r.f. of 0.72 superimposed on authentic trans-2-dimethylaminocyclooct-5-en-1-ol (II-44) (160,161), and the other with r.f. 0.40 was the larger of the two spots. This oil showed one g.c. peak at r.t. 5.0min. (10% SE-30 on Chromasorb S 60/80, 6'x1/8" stainless steel, $150-300^o$ at 5^o/min., N_2 inlet pressure at 18psi, and a H_2 flame detector) which was superimposable on authentic II-44. But the oil showed two g.c. peaks at 37 and 48min. in a ratio of 1:1.7 and a minor peak (ca.1% of the other two) at 12min. on a different column (20% Dowfax 9N9/10% TEP on Chromasorb P 60/80, 8'x1/" copper, 210°, He press.=18psi, and a thermal conductivity detector). By the peak matching technique, the minor peak at 12min. was shown to be 5-dimethylaminocyclooctene (II-40) and the peak at 37min. to be the *trans* alcohol II-44. The two major peaks were separated and isolated by preparative g.c. on the Dowfax column and the yields were estimated from the g.c. peak areas. II-44 was obtained as a colorless oil (27%); i.r., n.m.r., and m.s. were superimposable with those of the authentic sample (160).

Cis-2-dimethylaminocyclooct-5-en-1-ol (II-45) was obtained as white prisms (46%): mp 72-76°; r.t. 48min.; i.r. (melt) 3130(sb), 3020, 2794, 1635(wb), 1456(s), 1370, 1290, 1260, 1173(s), 1120(sb), 1023(s), 982, 874, 831, 822, 775, and 721(s) cm^{-1}; n.m.r. (100MHz) τ4.0-4.5(m,2H), 5.93(bdt, J=1.2,4.0Hz,1H), 6.90(bs, D_2O exch., 1H), 7.25(ddd, J=10.7, 4.2, and 1Hz, 1H), 7.68(s,6H), and 7.40-8.55(bm,8H); m.s. m/e(%), 169(M^+,19), 154(3), 140(17), 124(5), 110(19), 87(13), 84(17), 71(100). Irradiation (see Figure II-23 and Table II-14) at τ's 7.95 and 8.35 collapsed the broad double triplet at τ5.93 to broad singlets ($W_{1/2}$=6.5Hz) and ($W_{1/2}$=4.0Hz), irradiation at τ7.25 sharpened this signal slightly. Irradiation at τ5.93 collapsed the double dd at τ7.25 to a double doublet (J=10.7 and 4.2Hz); irradiation at τ8.35 collapsed this ddd to a broad doublet (J=4.5Hz, $W_{1/2}$ of one peak =3Hz).

The aqueous phase was further extracted with ether (100ml, 49 hours) to provide a second basic fraction as a viscous brown oil (400mg): i.r. 3600(sb), 2780, 1650(b), 1150(sb), and 1040(sb) cm^{-1}; n.m.r. τ 5.42(bs, D_2O exch.), 6.1-6.6(bm), 7.5-7.8(4 strong singlets), 7.9-8.6(bm), and a very weak signal in the τ4.1-4.7 region. This tar showed a broad streak on a t.l.c. plate and 3 major g.c. peaks with retention times higher than 80min. on the Dowfax column. This second fraction was not analyzed farther.

APPENDICES

APPENDIX A: CF_3COOH Decomposition of 1,4-*Bis*-pentamethylene-2-tetrazene (BPMT) in the Presence of Toluene

1) Results: No products derived from toluene were observed in the basic fraction since the n.m.r. showed no signal for protons in the aromatic region (τ1.5-3). By comparison of then n.m.r. with that of previously isolated benzyltoluenes, the neutral fraction showed *ortho* (τ6.05) and *para* (τ6.10) benzyltoluenes (3% in a 4:6 ratio).

2) Experimental: BPMT (1.5g, 0.0077moles) in toluene (15ml, 0.15moles) was added with stirring to CF_3COOH (6ml, 0.05moles) at 0°.

The yellow mixture, showing gas evolution, was then warmed to 40° for 5 hours, at which time ice (25g) was added. The mixture was worked up as described above for TMT decomposition in H_2SO_4. No polymeric material was observed.

The acidic and neutral products were obtained as a colourless liquid (50mg) having a characteristic odour of benzyltoluenes: n.m.r. τ2.75- 3.00 (bm, 9H); 6.05 (s) and 6.10 (s) (2H, ratio 4:6); 7.71 (s) and 7.77 (s) (3H, ratio 6:4). The basic extract consisted of a viscous brown oil (270mg): n.m.r. τ6.50 (m), 7.20 (m), and 8.40 (m).

APPENDIX B: CF_3COOH Decomposition of TMT in the Presence of Anisole

1) Results: The basic fraction from this reaction contained ortho (τ6.22 (s) and 7.30 (s)) and para (τ6.32 (s) and 7.21 (s)) N,N-dimethylanisidines in a 2:1 ratio. The yield of these anisidines was approximated from the n.m.r. as 7.4%.

2) Experimental: TMT (1.2g, 0.01 moles) in anisole (10.8g, 0.1 moles) was added to CF_3COOH (7g, 0.06 moles) at 50^o. The solution was stirred at 50^o for 2 hours and then worked up as described above for the decomposition of TMT in CF_3COOH. The neutral fraction was not analyzed for products. The basic fraction consisted of a brown oil (280mg): n.m.r. τ2.5-3.5 (bm), 6.22 (s), 6.30 (s), 6.32 (s), 6.93 (s), 7.21 (s), 7.30 (s), and 7.81 (s). The singlets at τ6.93 and 7.81 (2:3 ratio) were assigned to the imine trimer I-30 (30%) by comparison with that of previously isolated I-30, the singlet at τ6.30 was assigned to anisole (134), the singlets at τ6.22 and 7.30 (1:2 ratio) were assigned to o-N,N-dimethylanisidine, and the singlets at τ6.32 and 7.21 (1:2 ratio) were assigned to p-N,N-dimethylanisidine by comparison with those of the authentic (134). The n.m.r. indicated that the ortho- and para-anisidines were in a 2:1 ratio and that the anisidines, anisole, and trimer I-30 were in about equimolar ratios. Thus the yield of anisidines was calculated to be 7.4% and that of I-30 to be about 30%.

APPENDIX C: Photolysis of TMT in the Presence of Cyclohexene at pH5 under Nitrogen

1) Results: The basic fraction from this photolysis contained a large amount of material showing cycloalkyl ring n.m.r. signals at τ7.9 - 9.2 and at least 7 strong singlets in the $N(CH_3)$ region at τ7.6 - 7.8. No attempt was made to isolate the components of this mixture.

2) Experimental: TMT (3g, 0.026 moles) and cyclohexene (24g, 0.3 moles) were dissolved in a solution of methanol (150ml), acetic acid (30ml, 0.5 moles), and sodium acetate (7.3g, 0.5 moles) at 0°. The solution, when tested with pH paper, was shown to be pH5. It was irradiated at 0° under nitrogen with a 200W Hanovia lamp through a Corex filter for 2 hours until an aliquot showed no absorption at 277 nm.

The solution was worked up in the usual manner to provide a basic extract as a viscous oil (2.38g): n.m.r. τ4.2 (bm), 6.2-6.7 (bm), 7.6-7.8 (ca. 7 strong singlets) and 7.9-9.2 (bm).

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