PHOTOADDITION OF N-NITROSAMINES TO

CONJUGATED DOUBLE BONDS

by

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ABSTRACT

The photoaddition of N-nitrosamines to conjugated cyclic
and acyclic, dienes has been investigated. The 1:1 photo-
adducts were obtained in which the 1,4-addition mode occurs
preferentially over the 1,2-addition mode. In acyclic dienes,
the 1,4-addition resulted in the trans-orientation of the ole-
finic bond; in the 1,2-addition to unsymmetrical acyclic 1,3-
dienes the addition of nitrosamine did not lead to rearrange-
ment of the remaining unsymmetrical double bond. The photo-
addition to 1-vinylcyclohexene gave only a normal 1,2-adduct
and the "inverse"-1,4-adducts. The result is interpreted in
terms of steric restrictions present in the transition state
leading to product formation.

The attempts at isomerizing cis, cis-1,3-cyclooctadiene,
trans-1,3-pentadiene and cis-1,3-pentadiene by N-nitrosopipe-
ridine photosensitization failed.

The photosensitized addition of N-nitrosopiperidine using
several aromatic compounds as sensitizers led to the conclu-
sion that a singlet energy transfer from an excited aromatic
compound to nitrosamine occured since the quantum yield of
photoaddition can be directly correlated to the sensitizer
of the aromatic compounds. It was also found that a singlet

quencher, such as perylene, could retard the photoaddition of N-nitrosopiperidine to cyclohexene. It was established that naphthalene and other aromatic compounds whose triplet energies lie below 62 Kcal/mole could suppress the photodecomposition of N-nitrosopiperidine.

The photoaddition of N-nitrosamine to anthracene and acenaphthylene gave 1:1 addition products. The other aromatic compounds studied gave products only under forcing conditions but no 1:1 adducts were obtained.

In the photosensitized addition of N-nitrosopiperidine to anthracene, the first singlet of anthracene was capable of photosensitizing the nitrosamine.

To Gisela and the Children.

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Acknowledgement

Introduction

Several years ago it was discovered in our laboratory
that a nitrosamine could undergo photolytic addition to a
carbon-carbon double bond very efficiently in the presence of
an acid (1). Prior to this discovery, it was demonstrated by
Chow (2,3) as well as by Burgess (4) that a nitrosamine under-
goes photodecomposition in the presence of an acid to give
the corresponding α- t-amidoxime. Subsequently these photo-
reactions were extensively studied in this laboratory (5,6,7)
and much information has accumulated concurrent with this
investigation. With respect to the nitrosamine photodecom-
position, various fellow investigators simultaneously found
that a photoexcited nitrosamine reacts with methanol to give
piperidine, formaldehyde, N-piperidinoformamide and, probably,
HNO (5,6,7).

However, the photoaddition to an olefin was a more effi-
cient process than all these photodecompositions since irra-
diation of a nitrosamine in methanolic solution of an olefin
generally gave more of the photoadduct than the photodecompo-
sition products (8). It was proven to be that the amino
moiety attached itself to the least substituted carbon atom
of the double bond and the nitroso group to the most substi-
tuted carbon atom (8). The primary photoadduct was shown to

be a 1-amino-2-nitrosoalkane which dimerized reversibly to the

corresponding trans-dimer or tautomerized to the corresponding

oxime (8). Generally, both the dimer of the C-nitroso com-

pound and the oxime could be isolated in a good yield; the

former could be transformed to the latter under the irradia-

tion conditions. Further, HNO (formed in situ) was shown to

add to a C-nitroso compound leading to N-nitrosophydroxylamine

(5,6). Concurrent work by S.C. Chen of this laboratory

demonstrated that an ionic mechanism was unlikely and that

the trans-addition mode pertained in the photoaddition (5).

He further proposed a free radical mechanism to explain the

photoaddition (8). The pattern of the photoaddition can be

summarized as follows:
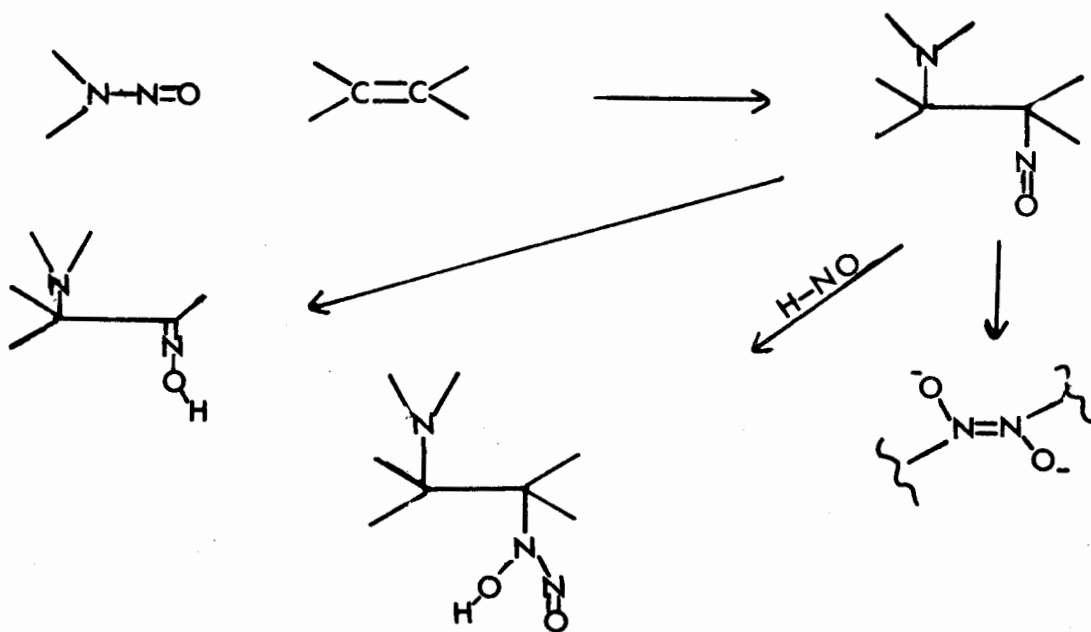
A survey of the literature has revealed that the photo-additions of the various XY addenda across a carbon-carbon double bond to give X-C-C-Y-type compounds generally follow a free radical chain process (9).

Of particular interest to this work is the addition of N-chloramines to olefins (10 - 13). This addition has been postulated to proceed through an aminium free radical intermediate as shown below.

$$>\overset{\oplus\cdot}{N}-H \;+\; >C=C< \;\longrightarrow\; >\overset{\oplus}{\underset{H}{N}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$$

$$>\overset{\oplus}{\underset{H}{N}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \;+\; >\overset{\oplus}{\underset{H}{N}}-Cl \;\longrightarrow\; >\overset{\oplus}{\underset{H}{N}}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Cl$$

$$+$$

$$>\overset{\oplus\cdot}{N}-H$$
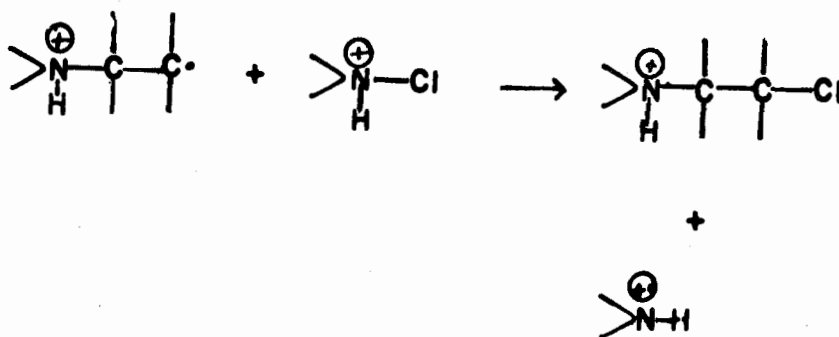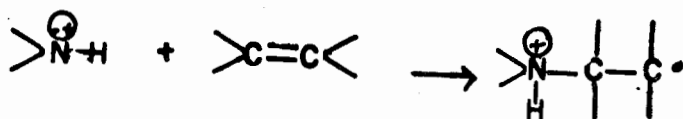
Thus by analogy it could be expected that the N-nitrosamines would photolytically cleave in a similar manner to give an aminium radical and nitric oxide. However, evidence against such a process was found through the study of the photoaddition of hindered nitrosamines to olefins (14). A salient point in this study, was the fact that the supposedly more hindered N-nitroso-2,6-dimethylpiperidine would add to styrene almost quantitatively while the supposedly less hindered N-nitroso-2-methylpiperidine would do so in about 50% yield. A nmr study on the conformation in solution of several N-nitrosamines (15) revealed that the N-nitroso-2,6-dimethylpiperidine had the 2,6-methyl groups axially oriented while in the N-nitroso-2-methylpiperidine, the methyl group is equatorially oriented. The equatorial methyl group hindered the photoaddition while ones at axial positions did not. If an aminium radical was the reactive species generated in solution, it is expected in the N-nitroso-2,6-dimethylpiperidinium radical would have the 2,6-dimethyl groups equatorially oriented. This would be reflected in very low yields of photoaddition product. Thus the N-nitrosamines must add to unsaturated hydrocarbons as a complete entity. In order to unravel the subsequent steps after the initial addition step, it was decided to investigate the nitrosamine photoaddition to conjugated

dienes and to aromatic hydrocarbons. At the same time, the probability of an aromatic hydrocarbon-photosensitized reaction of N-nitrosamine was investigated.

Results

Section I

1. <u>Photolysis</u> <u>of</u> <u>N-nitrosopiperidine</u> <u>in</u> <u>the</u> <u>presence</u> <u>of</u> <u>cyclic</u> <u>1,3-dienes</u>

The photolysis of N-nitrosopiperidine in methanolic solution containing at least one equivalent of mineral acid and in the presence 1,3-cyclooctadiene, proceeded smoothly. The N-nitrosopiperidine absorption band at ca. 350 mu decreased with the expected zero order kinetics. The neutral fraction of the photolysate was shown to contain N-nitrosopiperidine and 1,3-cyclooctadiene by ir and nmr spectral analysis. The basic resin, upon treatment with cyclohexane, gave white crystals as the major product. The major product was shown by elemental analysis to be a 1:1 adduct, <u>syn</u>-4-piperidino-2-cyclooocten-1-one oxime (I-1). The mass spectrum did not show the molecular ion peak, but showed the (M^+ - OH) peak distinctly at m/e 204 (Fig. 1). The ir spectrum showed the typical oximino group absorption in the 1000-900 cm^{-1} region and the C=C absorption at 1615 cm^{-1}. The nmr spectrum of this compound showed the olefinic protons as a part of an ABX system in which H_A appeared as a doublet (J_{AB}=12.5 cps), H_B as a quartet and H_X as a multiplet. The chemical shift for the various protons appear in Table I . The coupling constant

TABLE I

The chemical shifts of the various protons

of the 1:1 adducts to 1,3-dienes

	H_A	H_B	H_X	H_C
I-1	3.54	4.27	6.34	-
I-2	-	-	-	-
I-3	3.98	3.71	6.38	
I-4	3.84	4.18	7.9 - 8.6	6.57
I-5	3.8	4.46		
I-6	3.55	3.92		6.85
I-7				5.92
I-8				6.98
I-9	3.73	3.73	7.47	5.72
I-10	3.43	3.43	7.4	6.09
I-11	3.6	3.6	6.0	
I-15	3.28	4.38		6.90
I-16	3.38	3.93	6.96	
I-17				
I-18				6.68
I-19	3.69	4.2	7.91	6.41
I-20	3.97	4.21	8.23	6.85
I-22	3.96	3.96	8.25	6.65
I-23	3.36	3.36	8.18	6.87
I-24	3.86	3.86	7.0	
I-25	3.96	3.96	8.18	6.57
I-26	3.94	3.18	6.82	
I-27	3.28	3.28	8.12	6.67
I-29				6.62
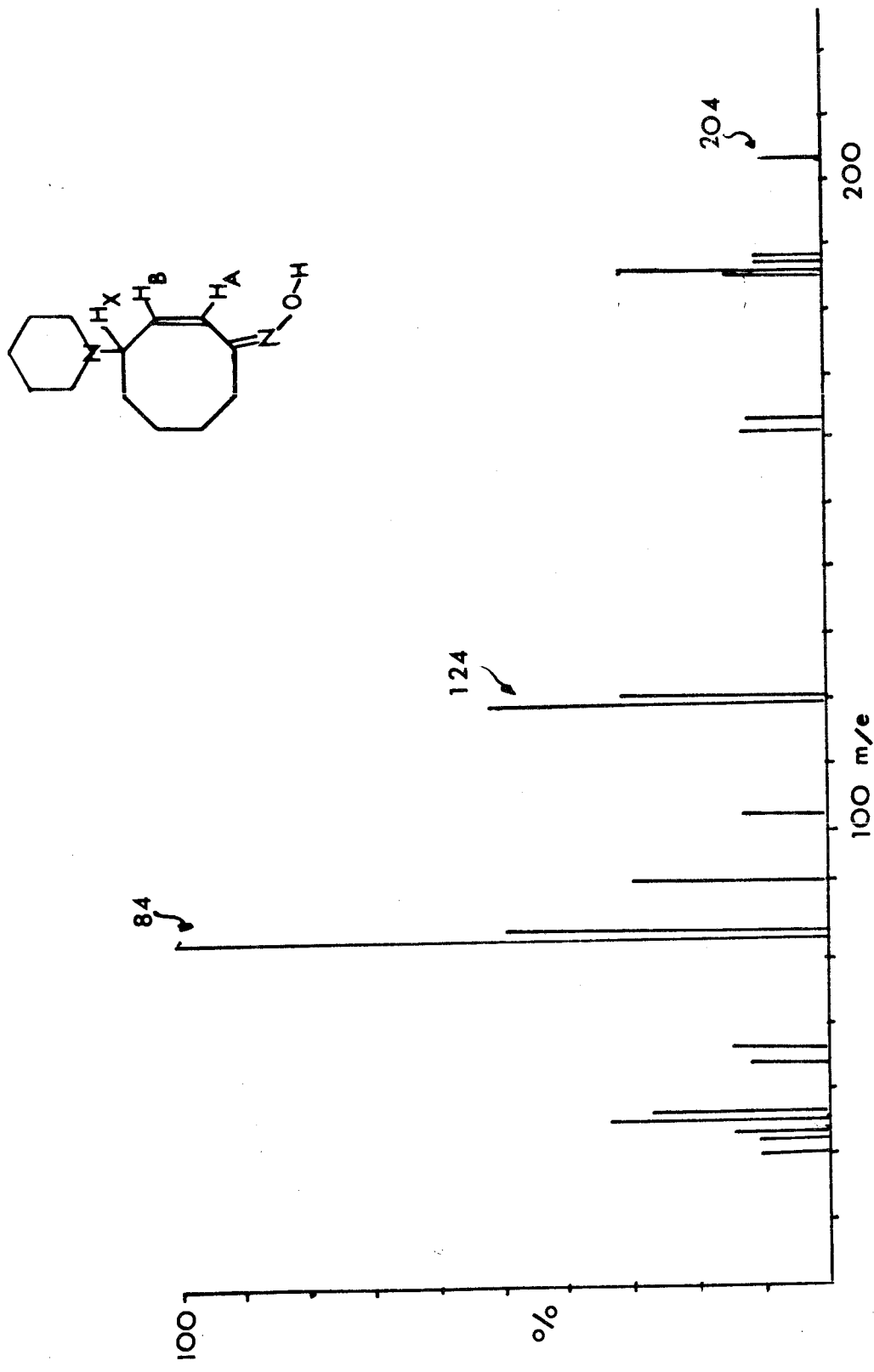
Fig. I. The mass spectrum of I-1 at 80 eV.
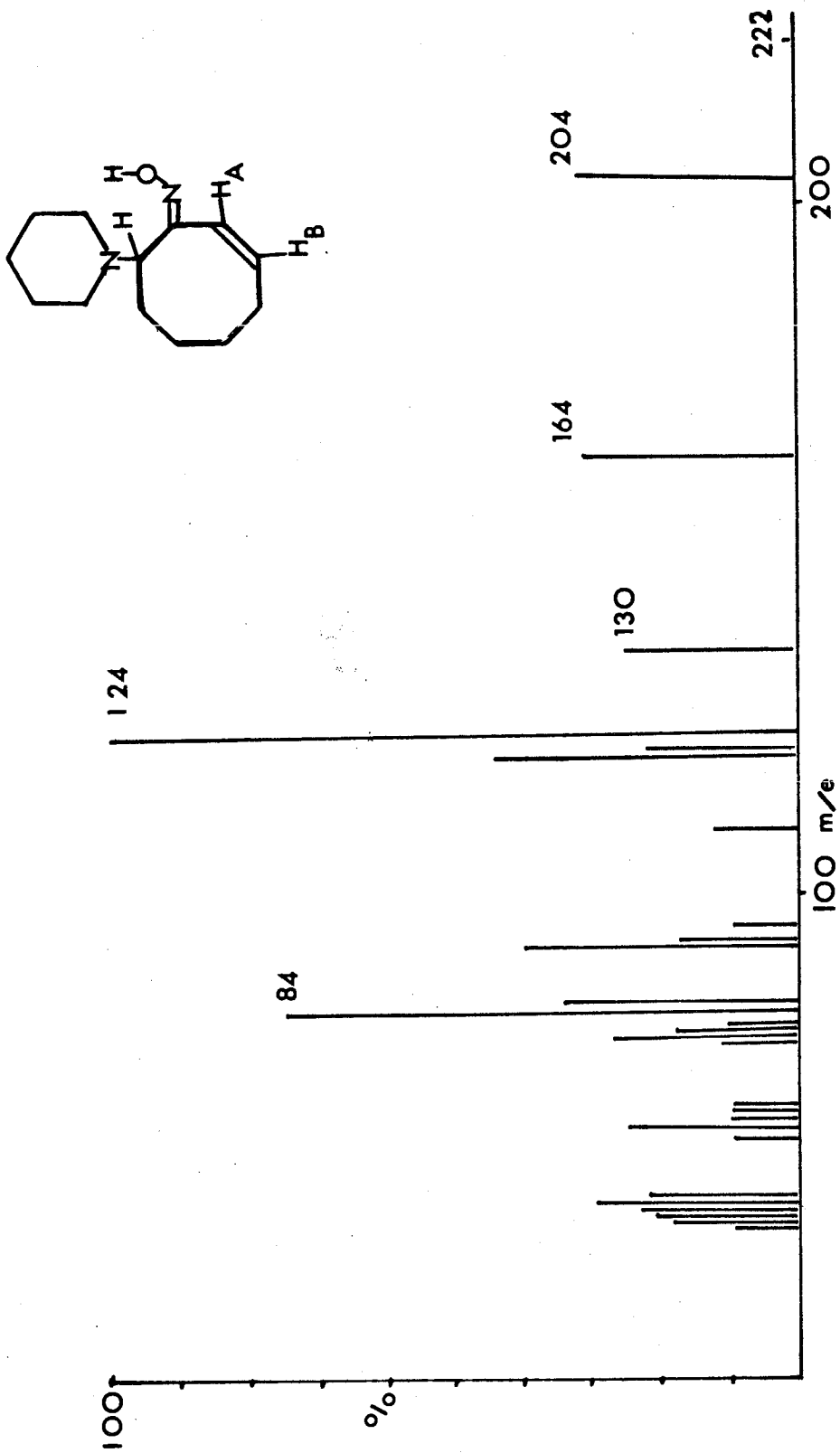
Fig. 2. The mass spectrum of I-2 at 80 eV.

of 12.5 cps clearly indicates the cis configuration for the

double bond and the coupling patterns place the piperidine

ring at the C-4 carbon atom. The spectral evidence also

excludes the alternate structures I-2 and I-4, i.e. the 1,2-

addition products from this diene. The geometry of the oxi-

mino group was assigned as syn* configuration (vide infra).

I-2, I-3, I-4, I-5 were isolated as minor photolysis

products by chromatography of the cyclohexane mother liquor.

The first compound eluted was identified as syn-8-piperidino-

2-cycloöcten-1-one oxime (I-2); mp 111-115°. The mass spec-

trum of I-2 gave the correct M^+ ion (222) for $C_{13}H_{22}N_2O$ and

the readily interpretable fragmentation pattern (Fig. 2)

which is very similar to that of the corresponding anti-isomer

I-4. The syn** configuration was assigned on the basis of

the tlc mobility of I-2 in comparison to that of the corres-

ponding anti-isomer I-4. We had shown (16) that the syn iso-

mers of α-t-amino oximes generally have higher mobility than

the corresponding anti-isomers on tlc analysis. Also the syn

isomer was generally stained light yellow with iodine vapour

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*Syn, in the case of 1,4-addition, is defined as the
isomer having the oxime hydroxyl group on the same side as
the c=c double bond, the anti being the opposite case.

**The syn configuration of α-t-amino substituted oximes
is assigned to the isomer which has the hydroxyl group of the
oximino moiety on the same side as the α-amino substituent.
The anti-isomer is the opposite case.
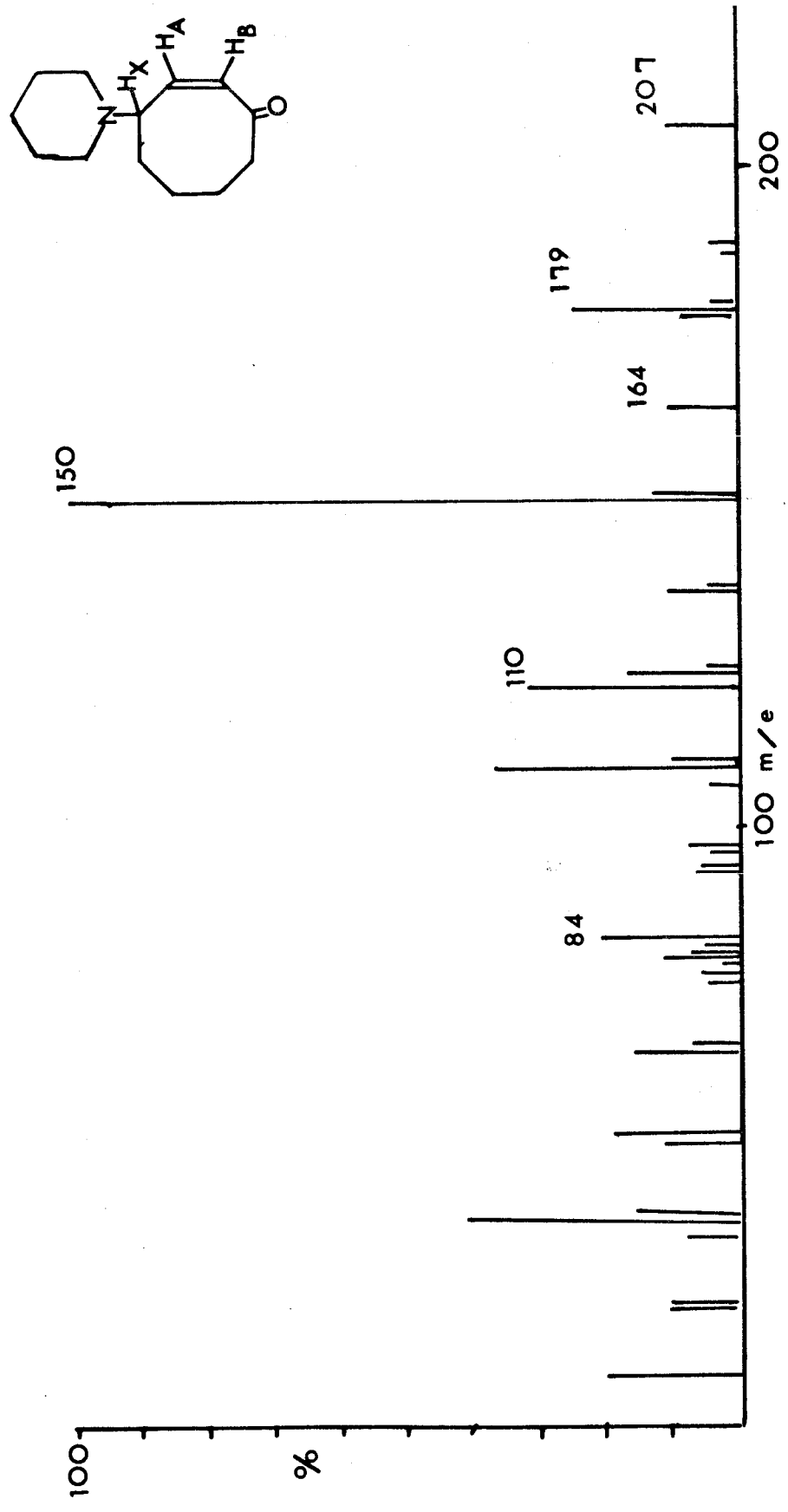
Fig. 3. The mass spectrum of I-3 at 80 eV.
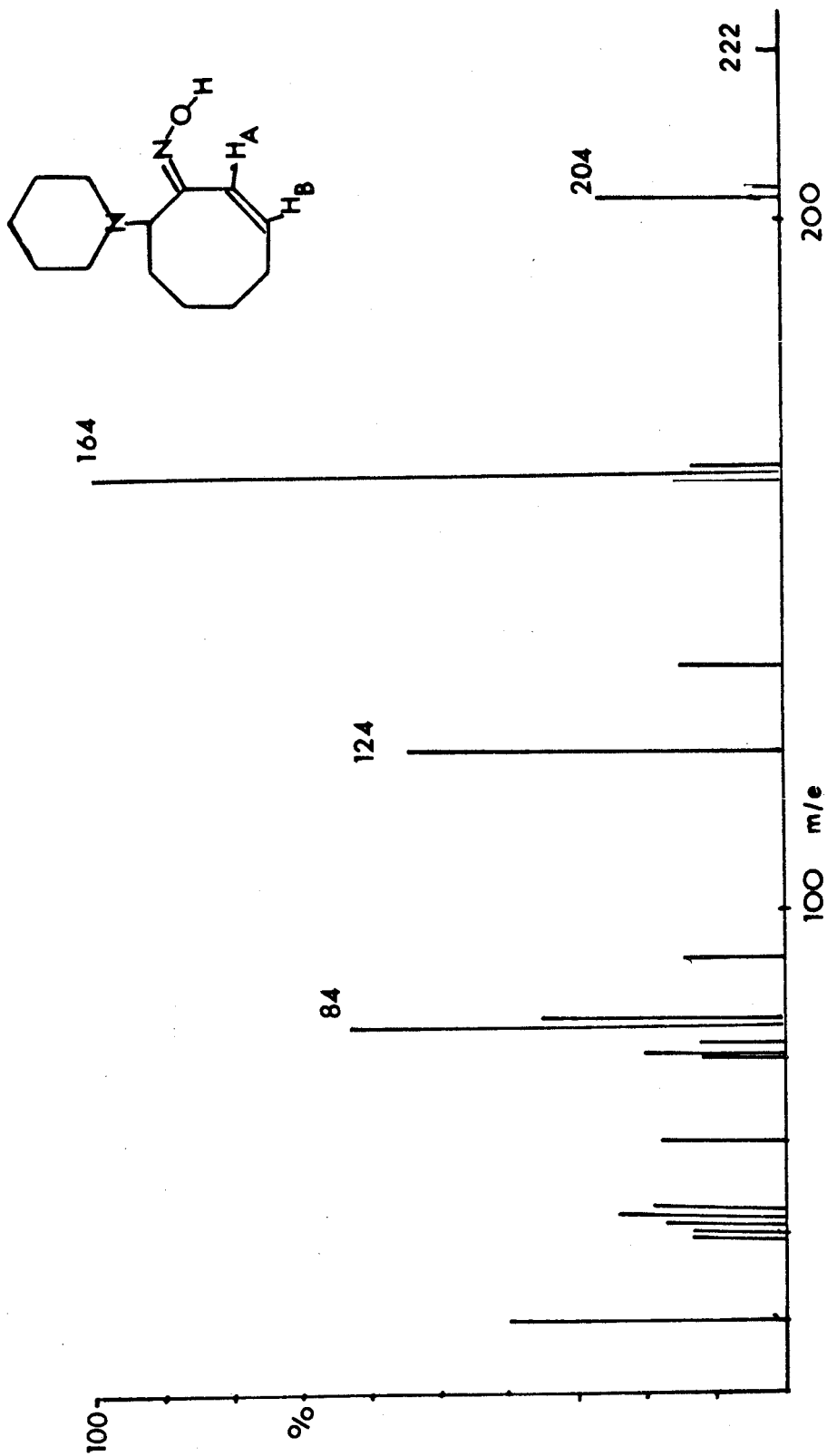
Fig. 4. The mass spectrum of I-4 at 80 eV.

while the anti-isomer stained dark brown.

The next compound eluted was identified as 4-piperidino-2-cyclooöcten-1-one (I-3). This oil showed a strong carbonyl absorption at 1665 cm^{-1}. The nmr spectrum showed the olefinic protons as a part of an ABX system in which H_A proton appeared as a doublet (J_{AB}=10 cps), H_B proton as a double doublet and H_X as a multiplet. This data indicated that I-3 contained a δ-amino-α,β-unsaturated ketone system. The mass spectrum substantiated the molecular formula $C_{13}H_{21}NO$ by showing a distinct M^+ peak at m/e 207 (Fig. 3).

On continued elution, anti-8-piperidino-2-cyclooöcten-1-one oxime (I-4) was obtained. The ir spectra showed absorption at 1660 and 1000-900 cm^{-1} and molecular formula $C_{13}H_{22}N_2O$ was confirmed by M^+ ion peak at 222 (Fig. 4). The nmr spectrum showed the olefinic protons as part of a poorly resolved ABX_2 system. Proton H_A appeared as a doublet (J_{AB}=12 cps) and the proton H_B as a multiplet. The signal for H_X was superimposed on the signals due to the remaining methylene protons (τ 7.9 - τ 8.6). The signals for H_C were a broad multiplet centered at τ 6.57.

The remaining fraction from chromatography was a mixture of the syn-and anti-1,4-adducts. The anti-4-piperidino-2-cyclooöct-2-en-1-one oxime I-5 could not be obtained in pure

state but its presence was indicated by the nmr spectrum of the mixture (Fig. 5). The complex signals in the olefinic region can be resolved into two doublets (due to H_A and H_A') and two double doublets (due to H_B and H_B'). The doublet (H_A) at $\Upsilon 3.26$ and the double doublet at $\Upsilon 4.2$ (H_B) are due to the olefinic proton of syn isomer I-1. The second doublet (H_A') at $\Upsilon 3.8$ and the remaining double doublet at $\Upsilon 4.46$ (H_B') were assigned to the olefinic protons of anti-isomer I-5.
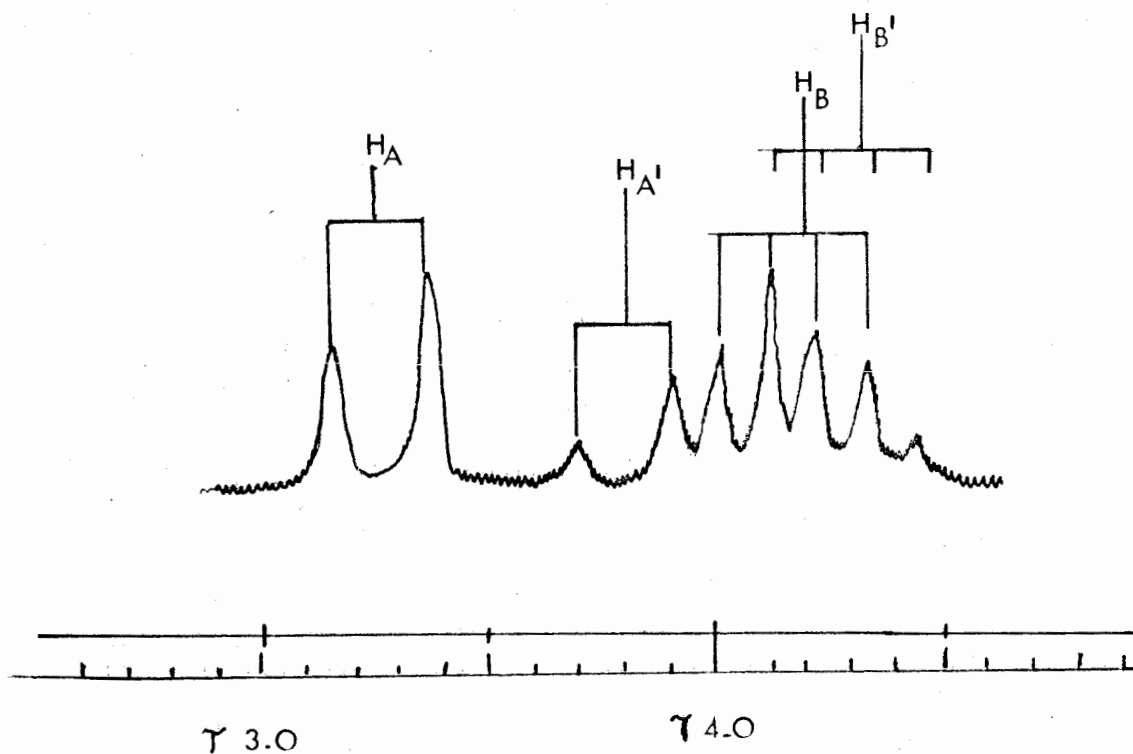
Fig. 5. The coupling pattern of the olefinic protons of a mixture of I-1 and I-5.

H_A and H_B were more deshielded by a long range anisotropic
effect of the syn oximino group.

The photolysis of N-nitrosopiperidine in the presence
of 1,3-cyclohexadiene gave similar results. Evaporation of
the photolysate yielded a salt. A part of this salt was
basified and the product recrystallized to afford anti-4-
piperidino-2-cyclohexen-1-one oxime (I-6). In addition to
the pertinent analysis data and the ir absorption, the nmr
spectrum at 60 Mc (Fig. 6) showed H_A at Υ 3.55 and H_B at
Υ 3.92 as the AB part of an ABX system. Since the pattern
of the multiplet in the region of Υ 6.14-7.0, integrated to
~1.5 protons, remained unchanged at higher temperature
(60°, 80° and 100°C), this signal cannot be due to two slowly
equilibrating chair conformations of I-6. The nmr spectros-
copy at 100 Mc (17) (Fig. 7) revealed that the multiplet
could be resolved into two components: one proton double
triplet H_E (J = 17 and 7 cps) centered at Υ 6.59 and one
proton multiplet at Υ 6.85 for H_C. The low chemical shift
of H_E clearly indicated the anti configuration of I-6 since
Tragger and Huitric (18) found that the equatorial proton
syn to the oximino hydroxyl group resonated at ca. Υ 6.61
in 4-butylcyclohexanone oxime.
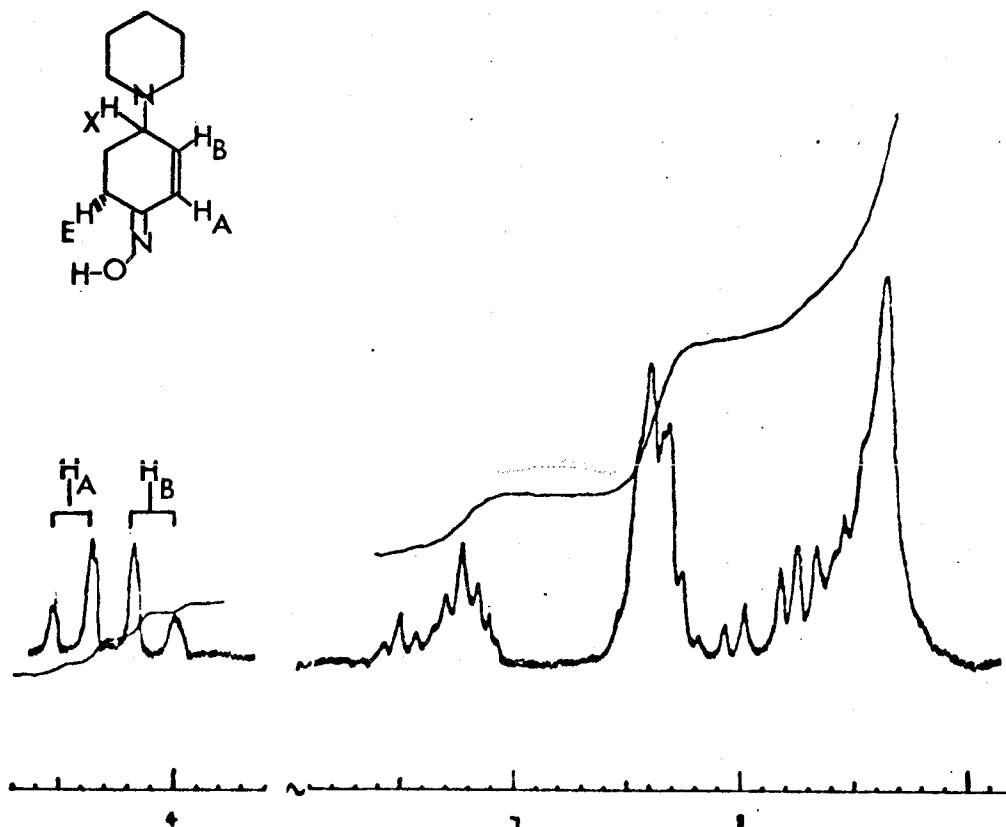
Fig. 6. The nmr spectrum of I-6 at 60 Mc.
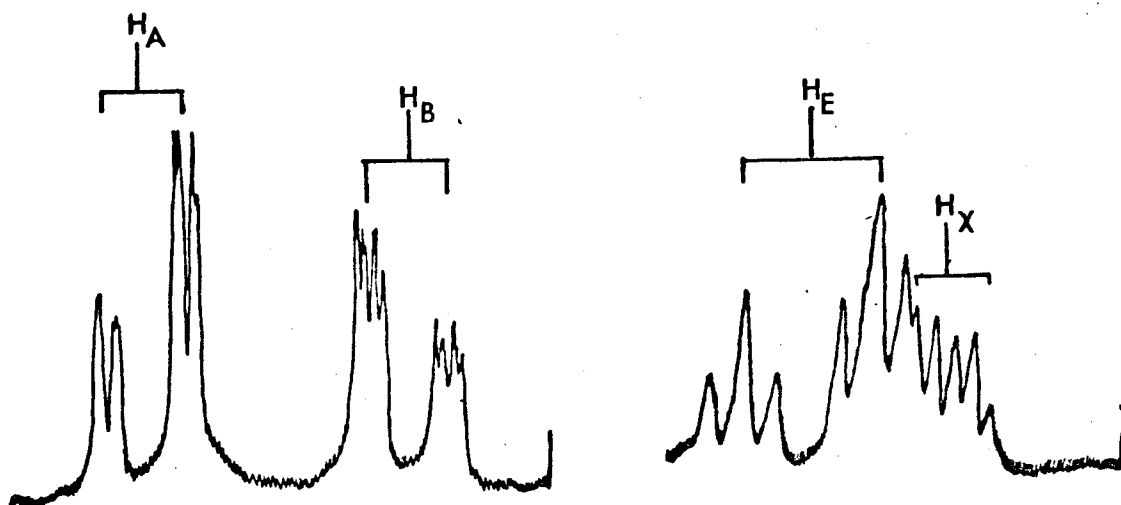
Fig. 7. The H_A, H_B, H_E and H_X signals of I-6 at 100 Mc.

The minor products were syn-6-piperidino-2-cyclohexen-1-one oxime, I-7, and the corresponding anti-isomer I-8. The corresponding syn-1,4-adduct, syn-4-piperidino-2-cyclohexen-1-one oxime, could not be detected among the minor products. The 1,2-adducts I-7 and I-8 showed the expected hydroxyl, olefinic and oximino group stretching absorptions in the ir region. The nmr spectra for these two isomers differed only in the chemical shift of those protons affected by the diamagnetic anisotropic effect of the oximino group. Each isomer showed the signals due to the olefinic protons as the AB part of an ABX_2 system, indicating that the piperidine ring was not located at the C-4 position. The position of the piperidine ring at C-6 was established by the double doublet (J = 5, 3 cps) of the methine proton H_C which indicated that H_C was coupled to equatorial and axial protons of the vicinal methylene group. The syn and anti isomerism of I-7 and I-8 was established by the tlc method (16) and further substantiated by nmr spectral analysis. Isomer I-7 showed the oximino hydroxyl proton at Υ -4.1 in contrast to that of I-8 which appeared at Υ 2.53 under a comparable concentration (0.1M) and indicated a possible intramolecular hydrogen bonding (19) between this proton and the piperidine nitrogen atom. The methine proton H_C (Fig. 8, 9) in I-7 shifted downfield
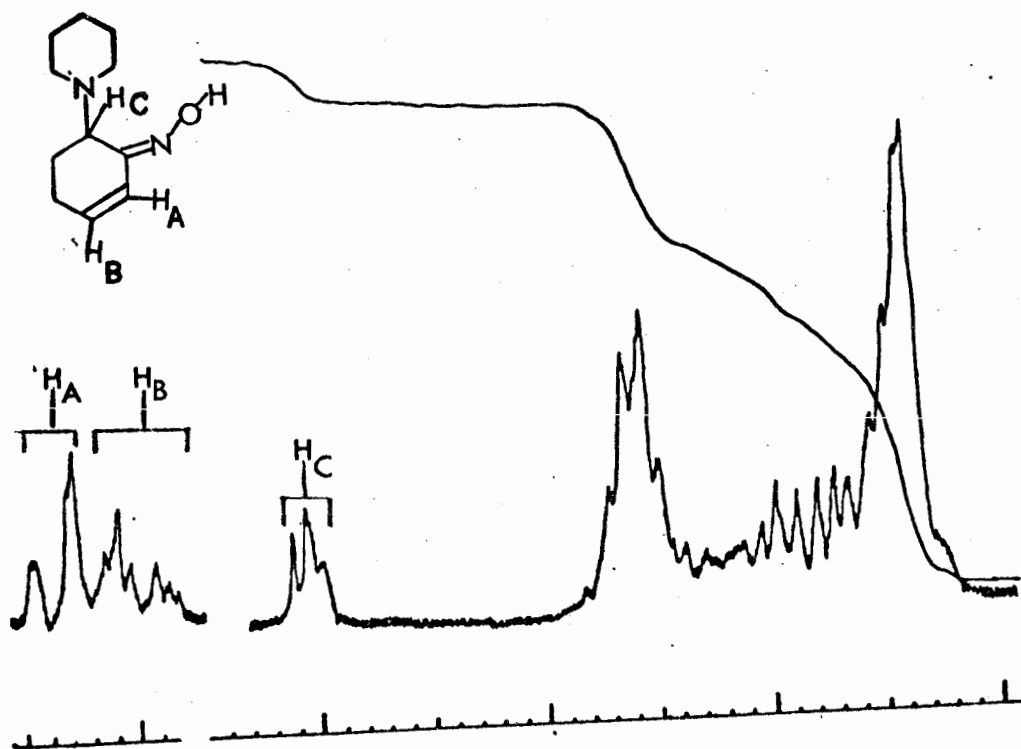
Fig. 8. a) The nmr spectrum of I-7 at 60 Mc.
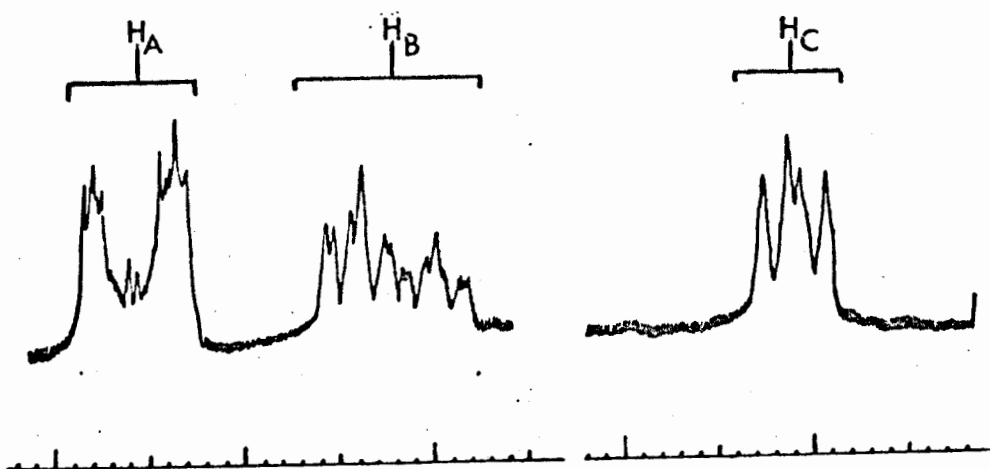
Fig. 9. The H_A, H_B and H_C signals of I-7 at 100 Mc.

(Υ 5.92) while in I-8 appeared at a higher field (Υ 6.98).

In contrast, the olefinic pattern of I-8 appeared at lower

field (Υ 3.5) relative to that of I-7 (3.9) (Fig. 10, 11).

These patterns of the chemical shifts are in agreement with

the assignments of the syn-configuration to I-7 and the anti

to I-8.

The photoaddition to cyclopentadiene showed quite a dif-

ferent uv profile during the reaction. While the 350 mu band

decreased with zero order kinetics, two new absorption bands

appeared at ca. 300 mu and 407 mu. The 300 mu band reached

the maximum after three quarter hours of irradiation and then

gradually disappeared. The second absorption band at 407 mu

reached a maximum intensity at the end of photolysis (1 hour

and forty minutes). This band gradually disappeared upon

standing in the dark. Though the course of the photoaddition

appeared different, the products were syn-5-piperidino-2-

cyclopenten-1-one oxime (I-9), anti-5-piperidino-2-cyclopen-

ten-1-one oxime (I-10) and 4-piperidino-2-cyclopenten-1-one

oxime (I-11). The 1,4-adduct, I-11, was the major product.

The three adducts showed the characteristic absorptions for

a hydroxyl (3200 cm^{-1}), an olefinic (1625 cm^{-1}) and an oxi-

mino group (1000-900 cm^{-1}) stretching frequencies in their

ir spectrum. The nmr spectrum for I-11 (Fig. 12) showed an
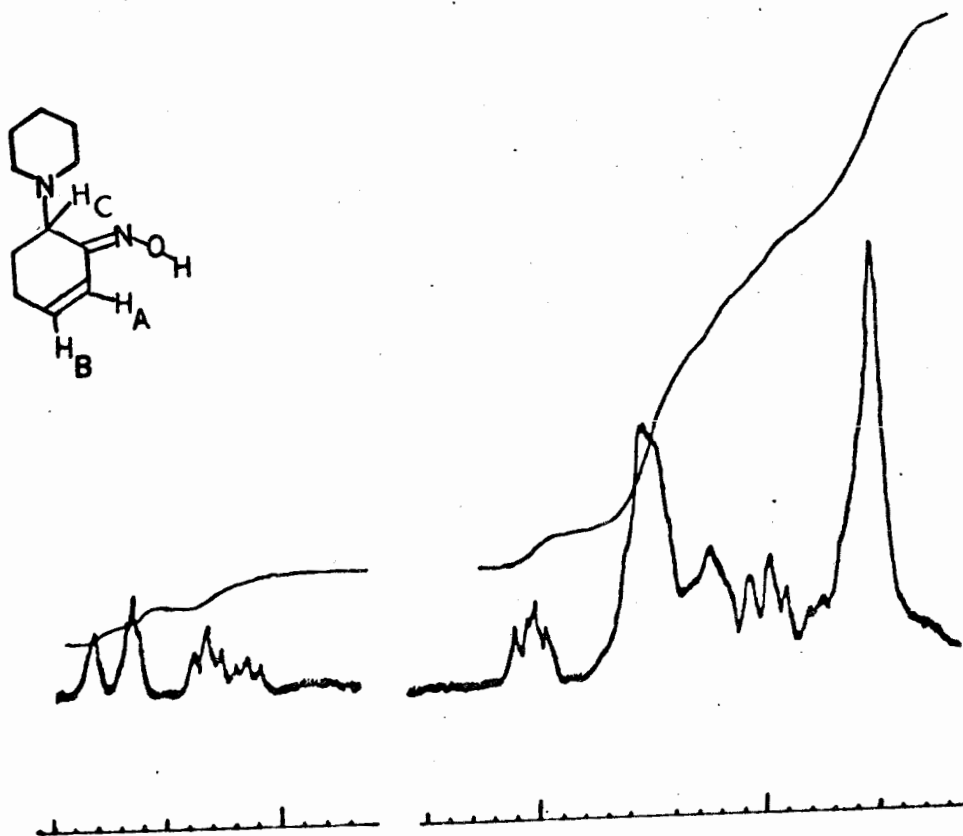
Fig. 10. a) The nmr spectrum of I-8 at 60 Mc.
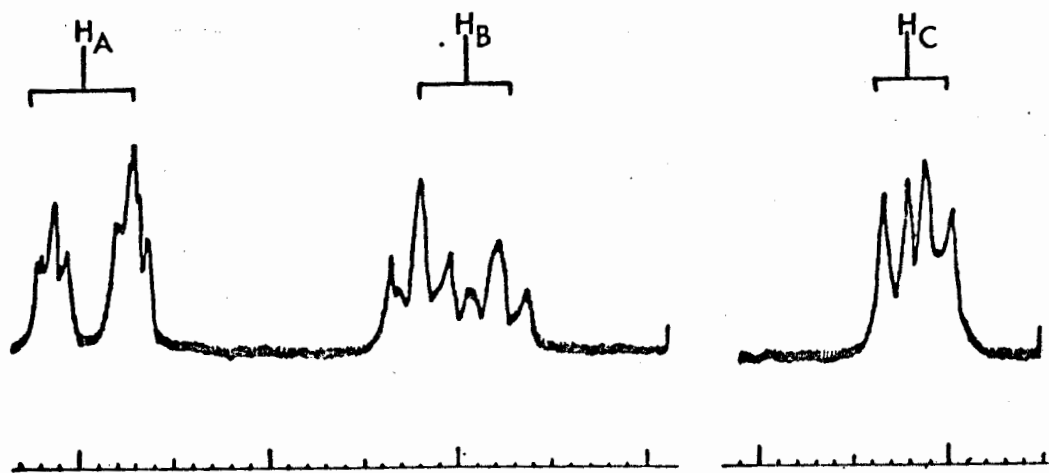
Fig. 11. The H_A, H_B and H_C signals of I-8 at 100 Mc.
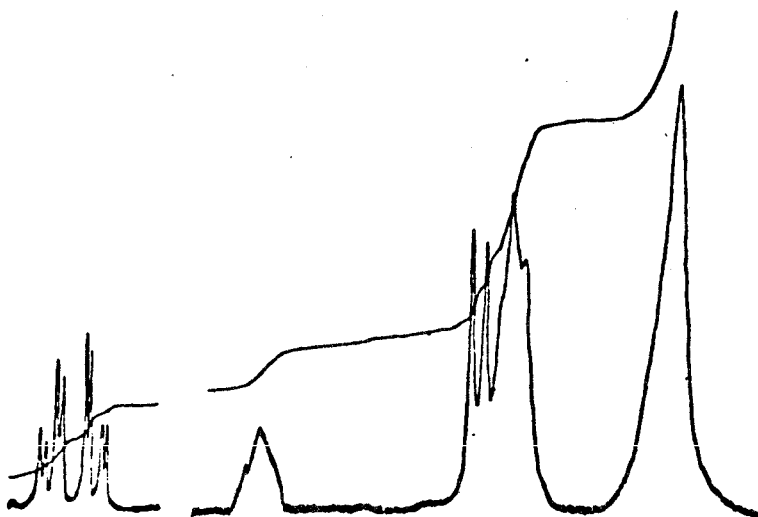
Fig. 12.   The nmr spectrum of I-11 at 60 Mc.

Fig. 13.   The nmr spectrum of I-9 at 60 Mc.
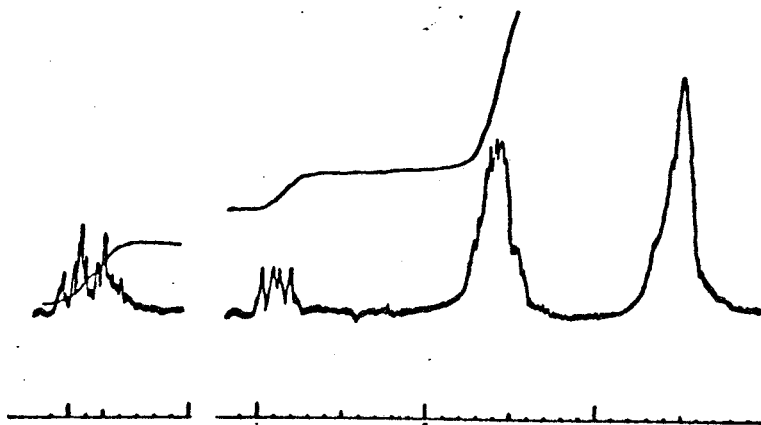
Fig. 14.   The nmr spectrum of I-10 at 60 Mc.

ABX pattern substantiating the assignment of a 1,4-adduct.

The syn-anti isomerism of the 1,2-adducts I-9 and I-10 was

established by the tlc method and by the downfield shift of

those protons on the same side of the oximino hydroxyl group

(Fig. 13, 14).

2. Photolysis of N-nitrosopiperidine in the presence of

acyclic 1,3-dienes

In an attempt to shed more light on the mechanism of

photoaddition, the photoaddition to acyclic 1,3-dienes were

investigated. The photoaddition N-nitrosopiperidine to buta-

diene gave syn and anti-1-piperidino-3-buten-2-one oximes

(I-12, I-13) as the minor products. The ir spectra for these

two isomers showed the characteristic hydroxyl, olefinic and

oximino group stretching absorption. The nmr spectra of these

compounds showed a clean ABX system for the three olefinic

protons. The methylene group of syn isomer I-12, as expec-

ted, appeared at a lower field (Υ 6.56) relative to anti iso-

mer I-13 (Υ 6.82). The major photoadduct was 4-piperidino-2-

butenal oxime (I-14). The ir spectrum of I-14 showed the

expected absorption for the structure. The nmr spectrum showed

the methylene signal at Υ 6.91 which was coupled to the olefi-

nic protons. However, the complex coupling pattern of the

olefinic protons did not allow the determination of the confi-

guration of the double bond. Treatment of aldoxime I-14 with

p-toluenesulfonyl chloride in pyridine (Beckmann dehydration)
converted it to 4-piperidino-trans-2-crotonitrile (I-15)
(Scheme 1) in which the trans-configuration of the double
bond was decided by the coupling constant (16 cps) between
the olefinic protons (Fig. 15c).

Scheme 1:

I-14   I-15
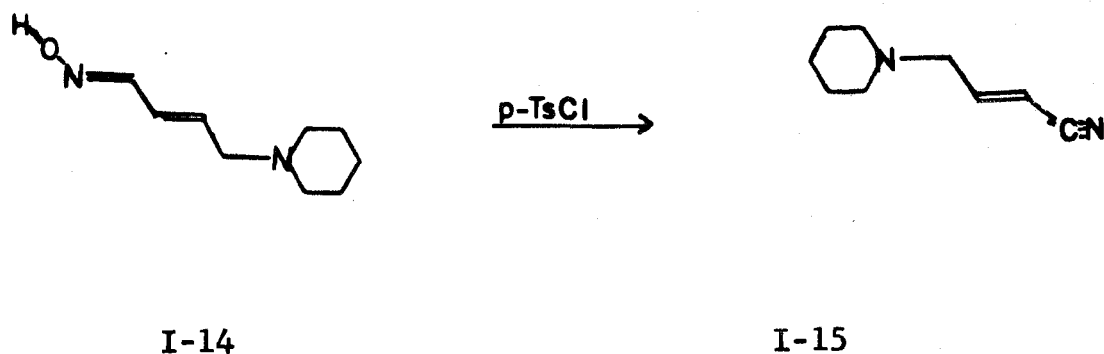
Beckmann dehydration of the crude product yielded a
basic fraction which was shown, without further purification,
to be pure I-15 as indicated by a comparison of the nmr spec-
trum with that of a synthetic mixture of the cis and trans-
4-piperidinocrotonitrile (Fig. 15a and 15b). The analysis
demonstrated the absence of 4-piperidino-cis-2-crotonitrile
in the Beckmann dehydration product and therefore the absence
of 4-piperidino-cis-2-butenal oxime in the crude mixture from
photolysis.

Fig. 15. The nmr spectrum of 4-piperidinocrotonitrile I-15
at 60 Mc, obtained from:
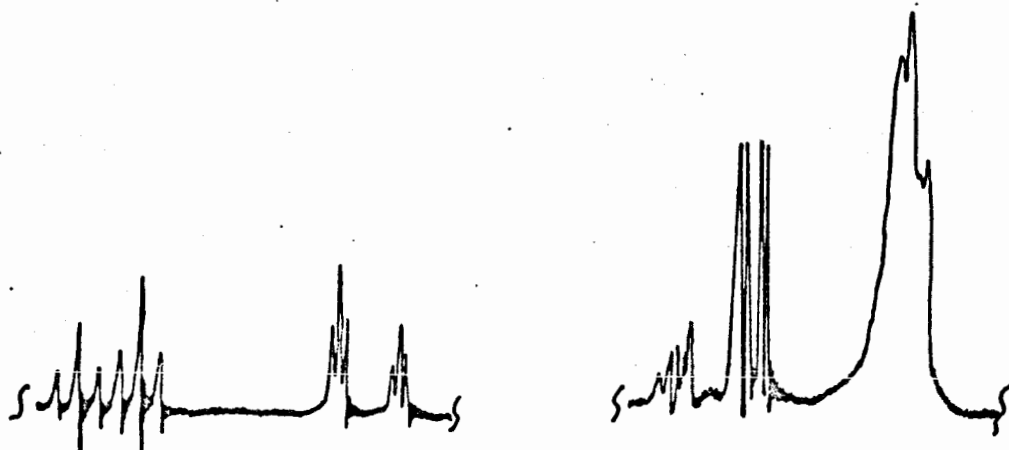
a) the crude photolysate
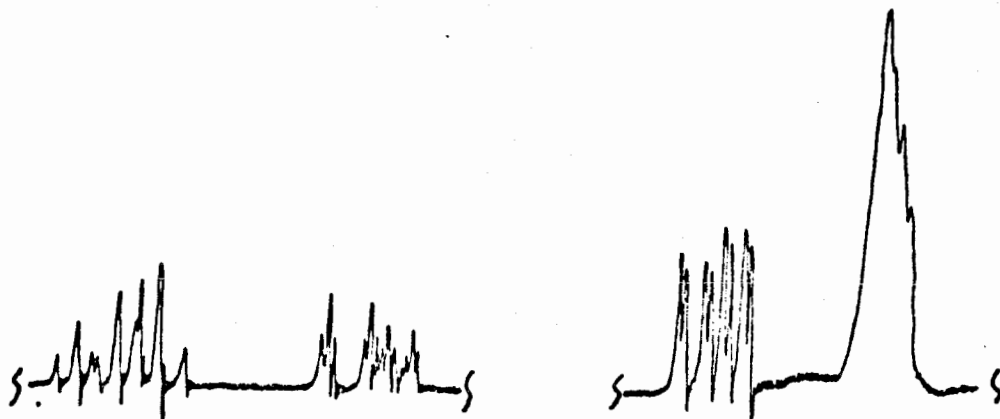
b) synthetic mixture

3

7
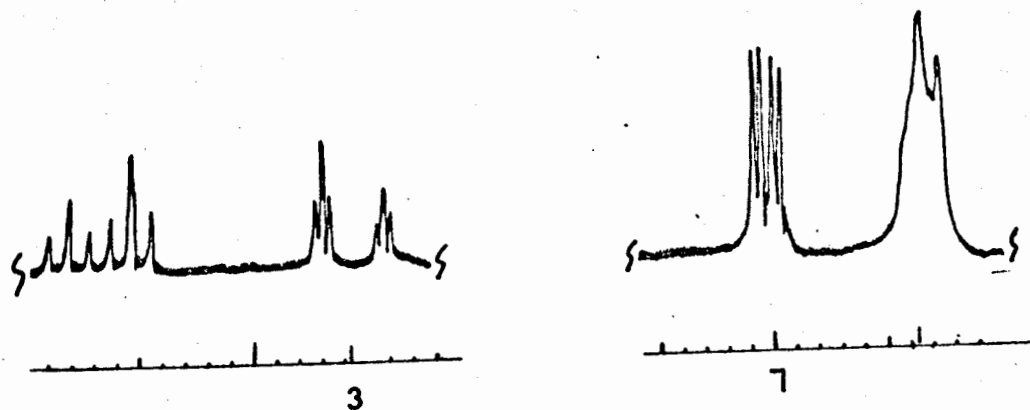
c) I-14

The photoaddition to cis- and trans-1,3-pentadiene gave
a more complex mixture of adducts. Since 1,3-pentadienes are
readily isomerized by photosensitization (20) it was necessary
to examine whether the photoexcited nitrosoamine could sensi-
tize such isomerization. In the absence of an acid, the ratio
of a cis-trans mixture (40:60) of 1,3-pentadiene was not chan-
ged when irradiated in the presence of N-nitrosopiperidine in
a pyrex apparatus (Sect. I, 13). This negative result did
not safeguard that similar results would be obtained under the
conditions in which the photoaddition took place, i.e. in an
acidic media. When the photoaddition to pure cis- or trans-
1,3-pentadiene was terminated at about 80% completion, it was
found that the remaining 1,3-diene was not isomerized at all,
as analysed by vpc (Exp. Sect. I, 14, 15).

The photoaddition of N-nitrosopiperidine to cis-1,3-
pentadiene following the usual experimental procedures gave
5-piperidino-trans-3-penten-2-one oxime (I-16) as the major
product (Scheme 2). I-16 showed the ir absorption at 3200,
1620, 1000-900 cm^{-1}. The nmr spectrum taken in pyridine showed
an ABX$_2$ system with a large J_{AB} coupling (16 cps) indicating
that the double bond had the trans configuration. The methy-
lene hydrogens (H$_X$) resonated at τ 6.96 as a doublet (J_{BX}
6 cps) which confirm the location of the piperidine ring

Scheme 2:

I-16

I-19

I-20

I-17 .

I-21

I-18
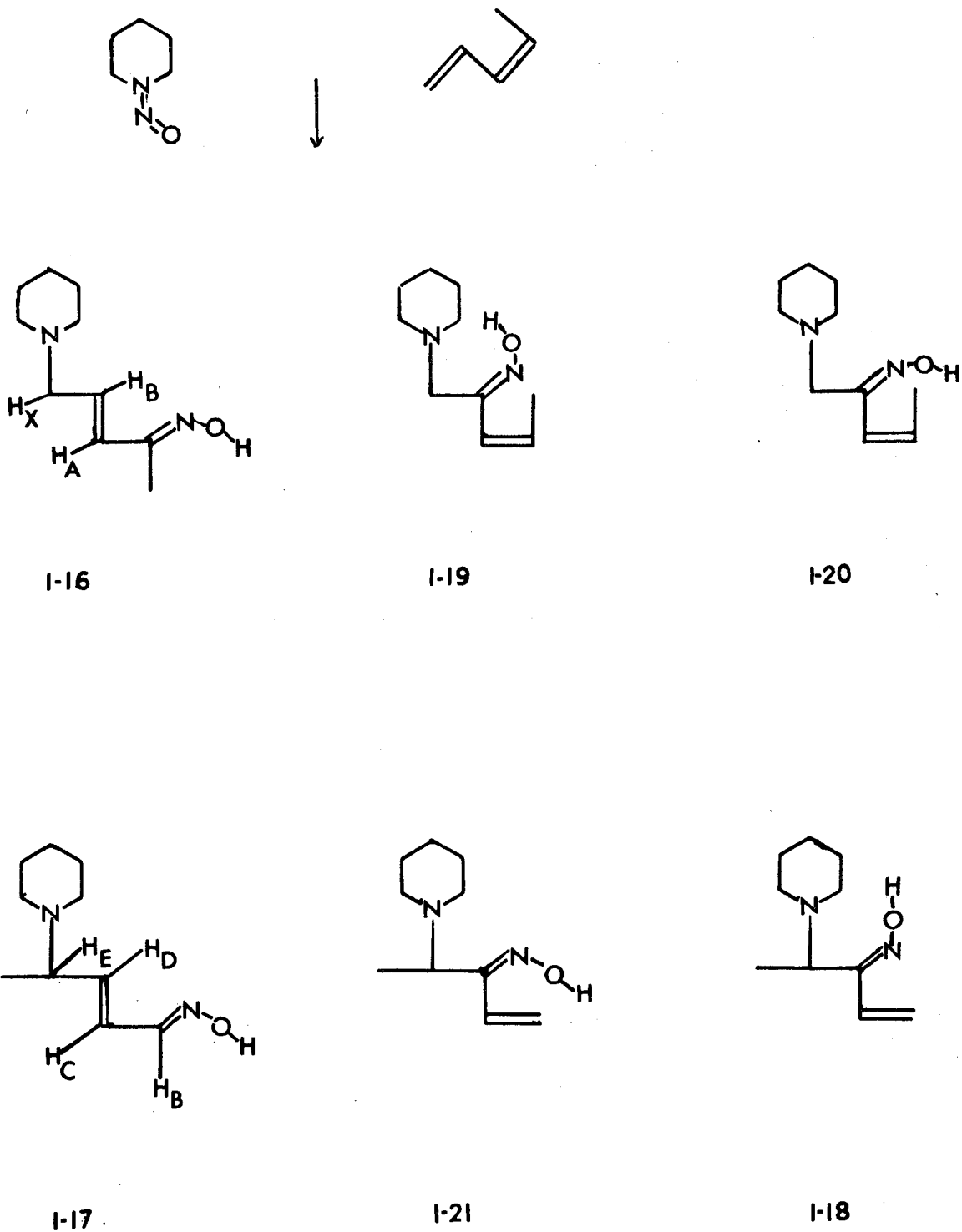
The terminal methyl group appeared as the singlet at Υ 7.87.

The product of the alternative mode of addition, (4,1-addition)

4-piperidino-trans-2-pentenal oxime (I-17), was also observed

in 12% yield. This compound could not be obtained in spectros-

copically pure form since a small amount of I-16 could not be

removed through conventional chromatographic or recrystalliza-

tion techniques. However, the nmr spectrum of a mixture of

I-17, 70% enriched in I-17, showed the signal for H_B as

doublet at Υ 2.3 (J_{BC} = 9 cps). The signals for H_C and H_D

were superimposed with the olefinic proton signals of I-16.

The methyl group at Υ 8.78 was split into a doublet

(J = 6 cps) by H_E.

The 1,2-adducts syn-2-piperidino-4-pentene-3-one oxime

(I-18), syn-1-piperidino-cis-3-penten-2-one oxime (I-19) and

anti-1-piperidino-cis-3-penten-2-one oxime (I-20) were obtai-

ned by chromatography of the crude basic resin and they were

minor products. Compounds I-19 and I-20 are the "normal"

1,2-adducts while compound I-18 is a reverse or 4,3-addition

product to the disubstituted double bond. The corresponding

anti isomer of the 4,3-adduct, anti-2-piperidino-4-penten-3-

one oxime (I-21), could be detected by nmr and tlc but could

not be properly characterized.
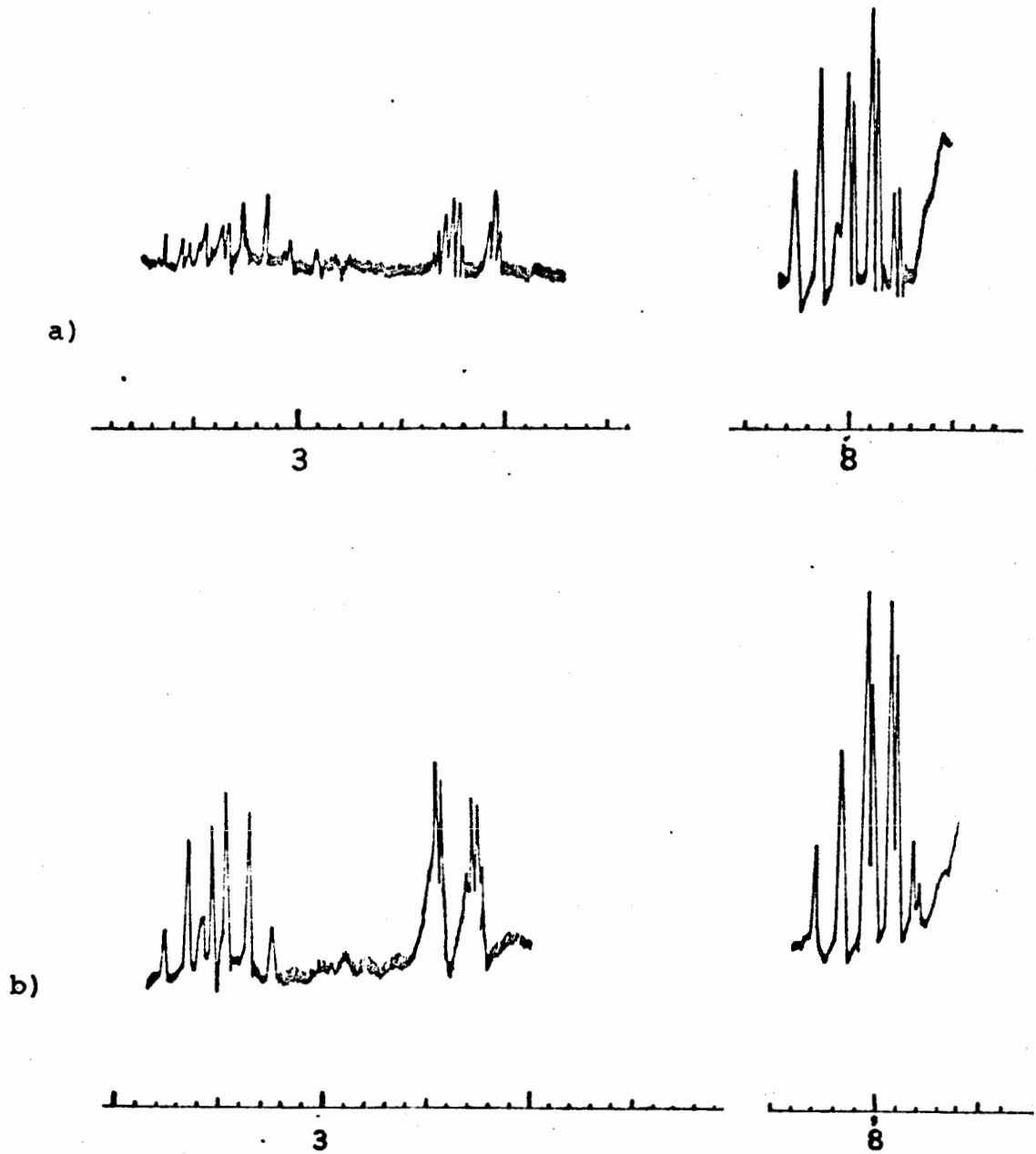
Fig. 16. The nmr spectrum of cis-crotonitrile obtained:

    a) from I-20

    b) crude mixture
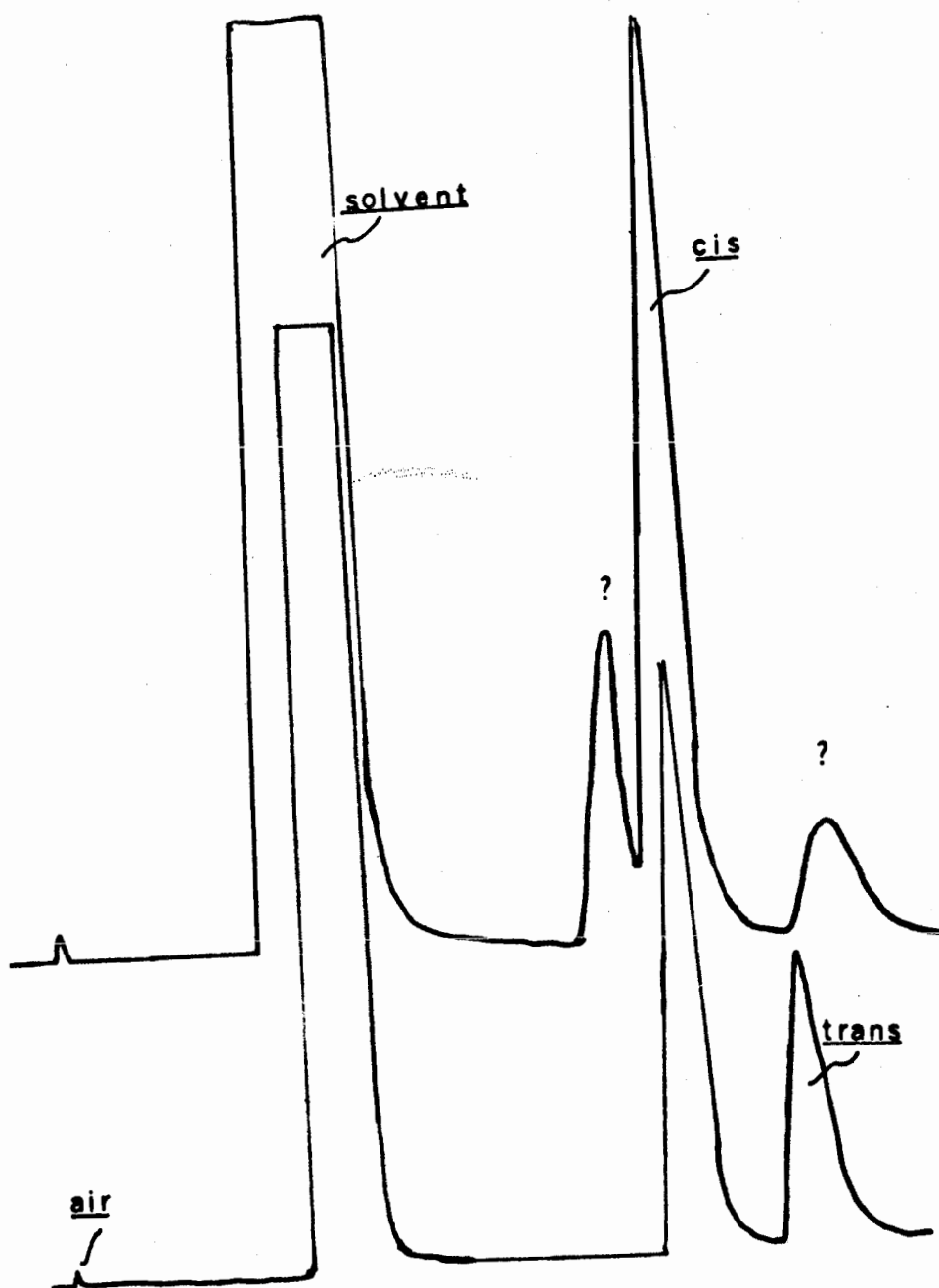
Fig. 17.   The vpc analysis of a)   the products from
                                     Beckmann dehydration of
                                     a mixture of I-19, I-20.

                                 b)   commercial mixture.

The nmr spectra of the 1,2-adducts were very useful for
the determination of the stereochemistry. The coupling cons-
tants for the ABX_3 pattern for the olefinic protons of adducts
I-19 and I-20 were 12.5 and 12 cps respectively, showing that
the double bond had retained the original cis configuration.
This conclusion was further substantiated by Beckmann cleavage
reaction (21) of anti-1,2-adduct I-20 and a crude mixture of
the 1,2-adducts to give cis-crotonitrile exclusively as shown
by the nmr and vpc analyses (Fig. 16, 17, Scheme 3).

Scheme 3:
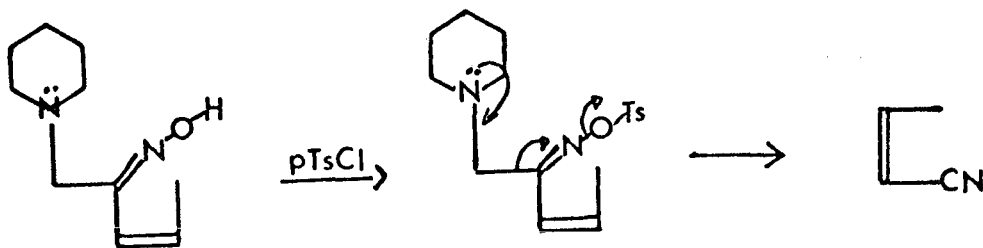
Similar results were obtained from the addition of N-
nitrosopiperidine to trans-1,3-pentadiene. The major product
from photolysis was again the 1,4-adduct, I-16. The inverse
4,1-adduct, I-17 was also present but only in ~ 3% yield.
Careful tlc and nmr analyses of the crude mixture from photo-
lysis showed that the inverse 4,3-adducts, I-18 and I-21 were
present in trace amounts. The normal 1,2-adducts, syn-1-
piperidino-trans-3-penten-2-one oxime (I-22) and anti-1-
piperidino-trans-3-penten-2-one oxime (I-23), were isolated
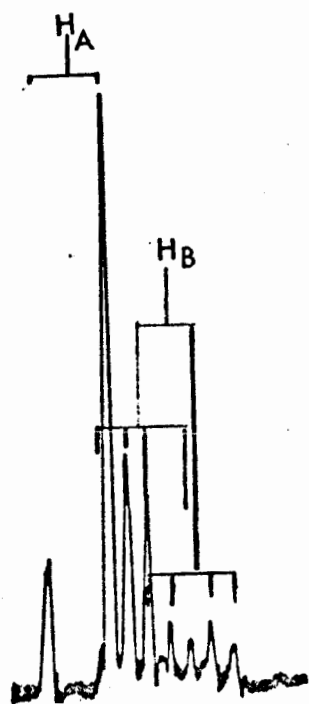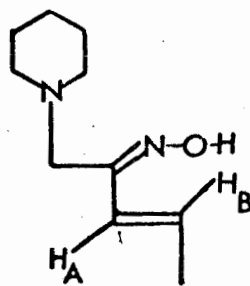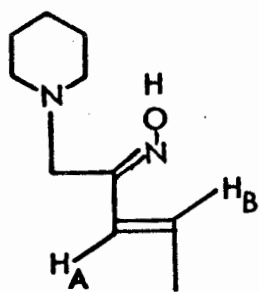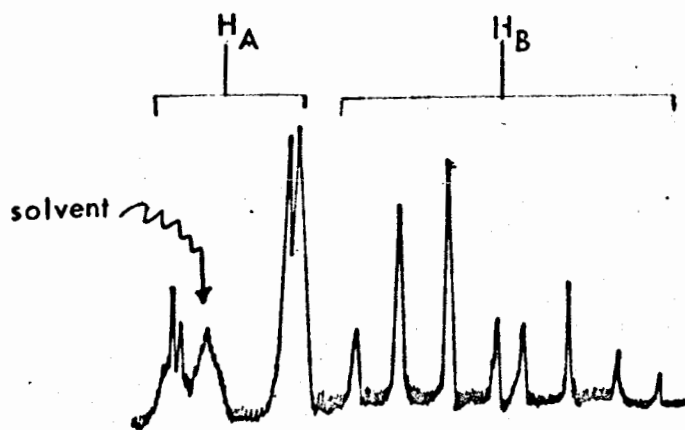
Fig. 18. The olefinic pattern of I-22 (500 cps sweep width) and I-23 (250 cps sweep width) at 60 Mc.
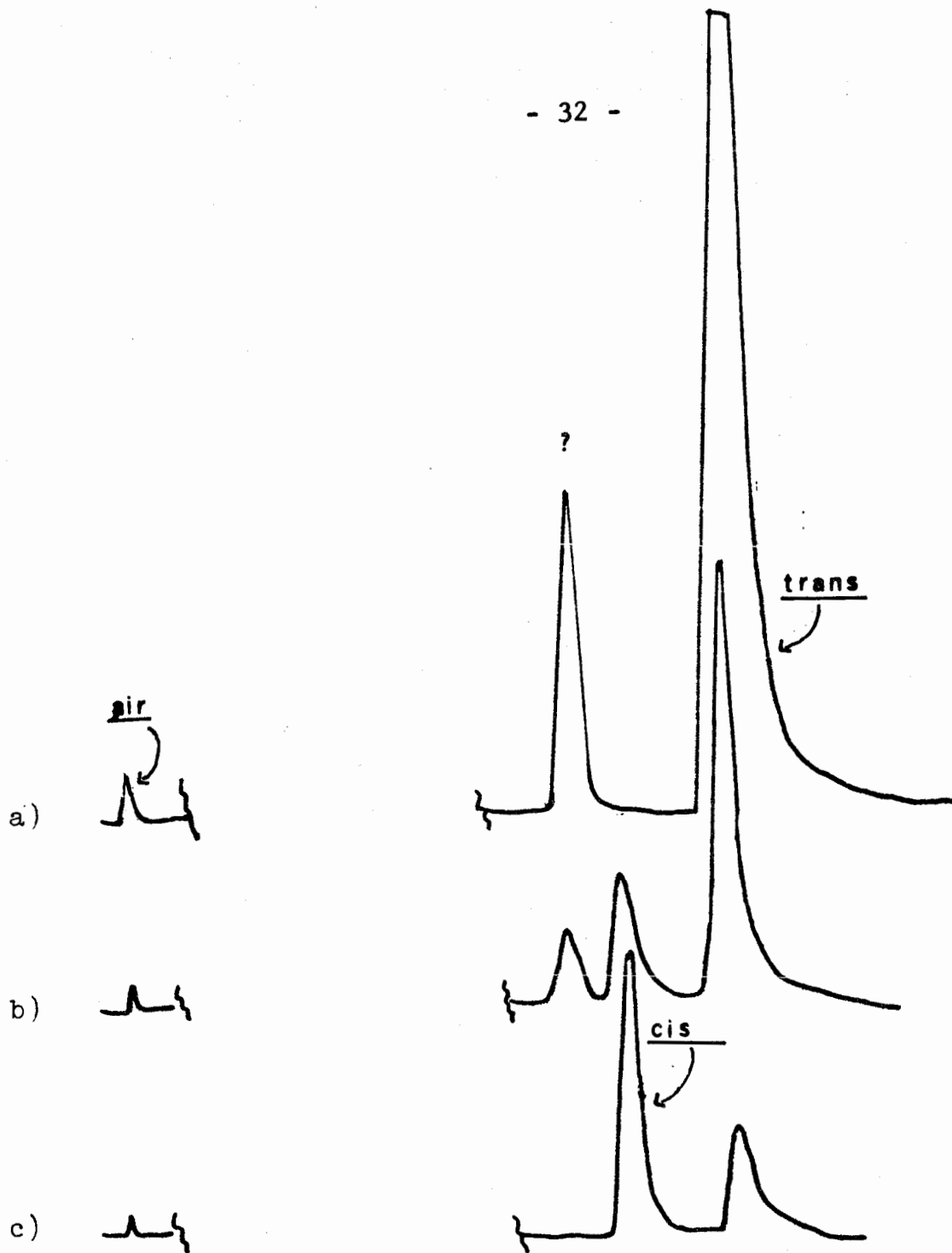
Fig. 19.   The vpc analysis of the crotonitrile obtained from

Beckmann cleavage of a) crude mixture of I-22 and I-23

b) mixed injection of a) and c)

c) commercial mixture of crotoni-

trile
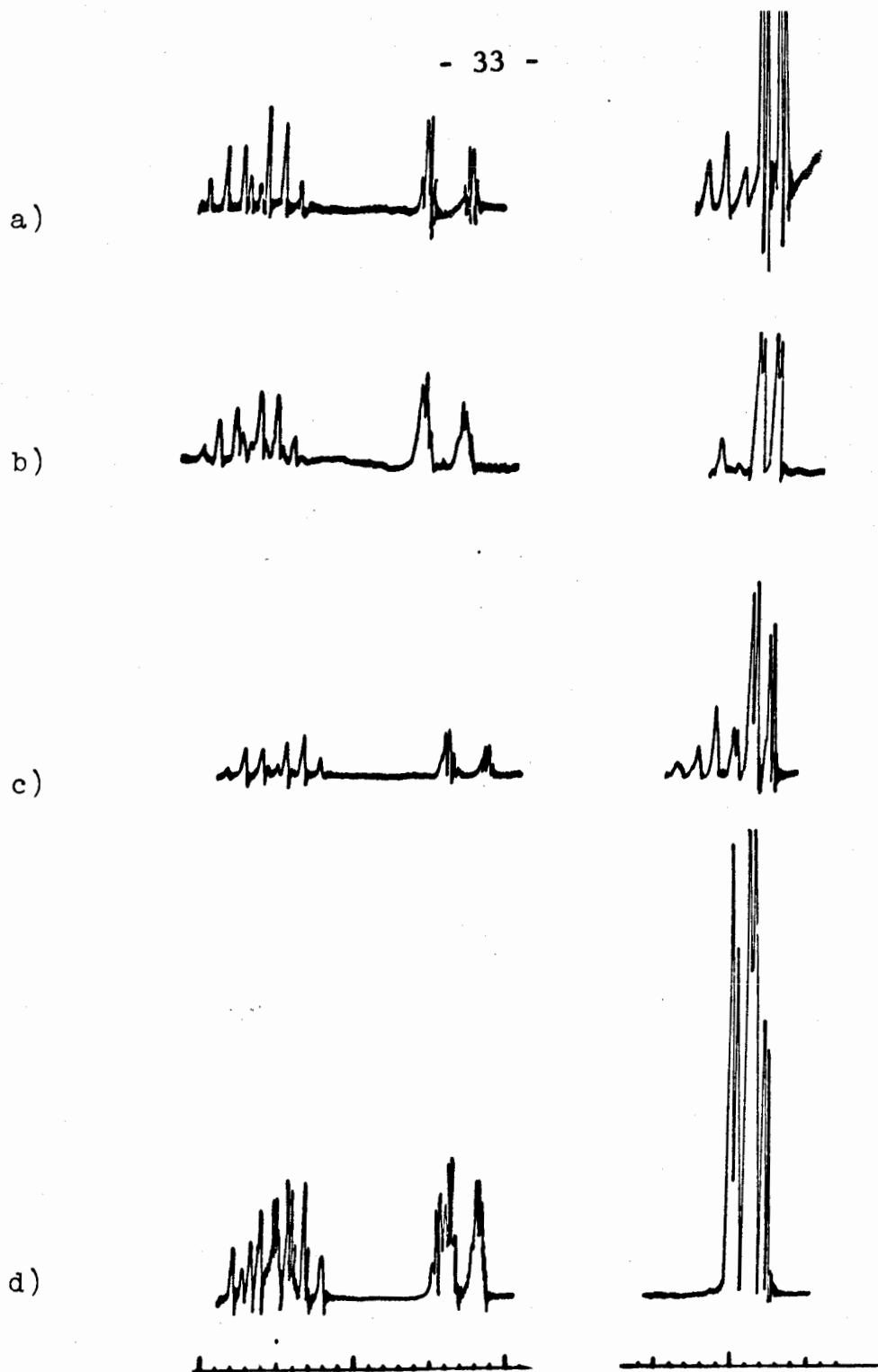
Fig. 20. The nmr spectrum crotonitrile obtained from Beckmann cleavage of a) I-23 b) mixture of I-22 and I-23 c) I-23 in 2% KOH d) commercial mixture of cis-and trans-crotonitrile.

in 10% and 17% yield, respectively. The nmr spectrum in benzene-d_6 (Fig. 18) of syn isomer I-22 showed the olefinic proton H_A as a doublet and H_B as two quartets (J_{AB} = 16 cps). The nmr spectrum of anti isomer I-23 (Fig. 18) showed the olefinic proton H_A as a doublet. Each line of the doublet is further slightly split (1 cps) by the methyl group (H_X) through an allylic coupling. The H_B proton appeared as two quartets with J_{AB} = 16 cps and J_{BX} = 6 cps. The larger olefinic couplings (16 cps) proved these compounds to have the trans configuration. The trans configuration of 1,2-adducts I-22 and I-23 was further substantiated through Beckmann cleavage reaction. The first reaction carried out, using 2% aqueous KOH was inconclusive since a pure sample of trans I-23 gave a mixture of trans:cis crotonitrile (80:20). The isomerization might have happened during cleavage reaction. However when the cleavage reactions were run at low temperatures in pyridine, a pure sample of I-23 afforded pure trans crotonitrile. Under the same conditions a crude mixture of I-22 and I-23 was cleaved to trans-crotonitrile. The vpc and nmr analyses (Fig. 19 and Fig. 20) showed that no cis-crotonitrile was present in the crude reaction mixture. Thus, the addition to the trans 1,3-diene is also a stereospecific addition.

The experimental results appear to point out that a cis

double bond was more reactive than the trans double bond

towards the photoaddition, since the inverse-4,1-adduct

(I-17) was isolated in amounts four times larger in the for-

mer case. For this reason the addition to cis-trans-2,4-

hexadiene was investigated. Irradiation of N-nitrosopiperi-

dine in the presence of the olefin gave the 1,4-adduct,

namely 5-piperidino-trans-3-hexen-2-one oxime (I-24) as the

major product. The minor products were syn-2-piperidino-

trans-4-hexen-3-one oxime (I-25), 5-piperidino-trans-3-hexen-

2-one (I-26) and the anti-2-piperidino-trans-4-hexen-3-one

oxime (I-27). The trans configuration in I-25 was indicated

by the ABX_3 coupling pattern in the nmr spectrum in which the

coupling constant for the olefinic protons (centered at Υ3.96)

was 16 cps. The methyl group (H_X) appeared as a doublet

(J_{BX} = 6 cps). The nmr spectrum of I-27 showed the olefinic

protons as the part of an ABX_3 system in which H_A and H_B are

centered at Υ3.28 (J_{AB} = 17 and J_{AX} = 7 cps). The syn and

anti configuration was deduced from the chemical shifts of

the double bond as well as from their tlc mobility.

In order to find out the selectivity of addition to the

cis and the trans double bond, the crude 1,2-adducts were

converted to the crotonitrile by Beckmann cleavage reaction. The nmr and vpc analysis of the crude nitrile fraction showed that the ratio of cis-to trans-crotonitrile was 3 to 97.
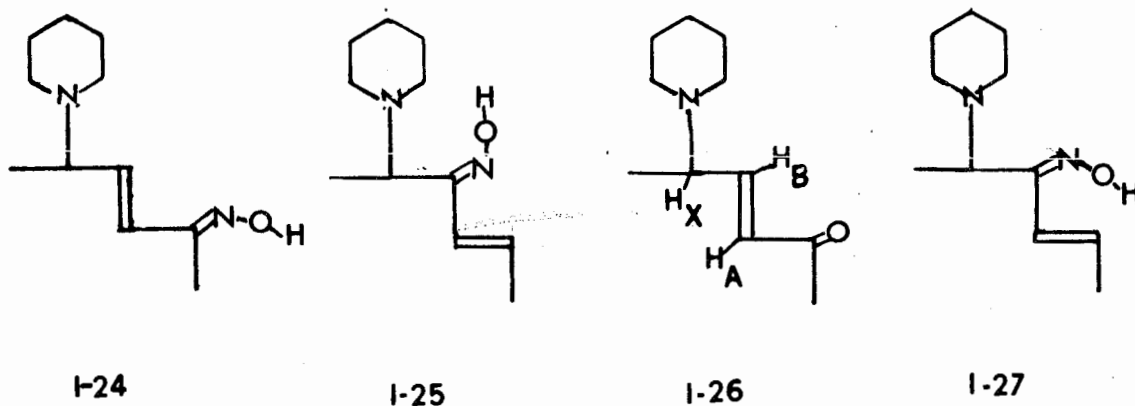
Fig. 21. The 1:1 adducts to cis, trans-2,4-hexadiene.

The third minor product isolated in a small amount was the ketone I-26. This compound was isolated as an oil which showed a carbonyl stretch at 1678 cm^{-1}. The nmr spectrum showed an ABX system for the olefinic protons with H_B at Υ 3.18 as a double doublet (J_{AB} = 17 and J_{AX} = 7 cps) and H_A proton at Υ 3.94 as a doublet. The H_X proton at Υ 6.12 appeared as two quartets (J_{DX} = 7 cps) (Fig. 21). It is assumed that the small amount of ketone isolated comes from hydrolysis of the corresponding oxime during work-up.

The last photoaddition investigated in this sequence was the addition to 1-vinylcyclohexene. This diene was synthesized as described in the literature (22) which consisted of treating cyclohexanone with the potassium salt of acetylene

Scheme 4:
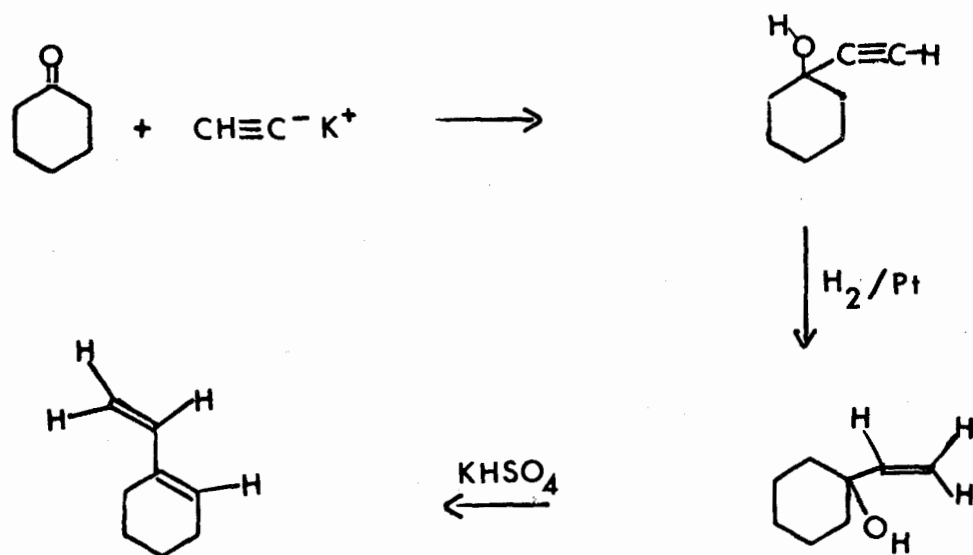
to give 1-acetylene-1-cyclohexanol as the first step. The acetylene derivative was then reduced over platinum to give 1-vinylcyclohexanol and this was then dehydrated over potassium hydrogen sulfate to give 1-vinylcyclohexene (Scheme 4). The product, though it gave the correct boiling point, contained about 5% of I-28 as an impurity, as shown by the nmr analysis. The mixture was used for the photoaddition. The irradiation of N-nitrosopiperidine in the presence of this

diene followed zero order kinetics until the complete disap-

Scheme 5:
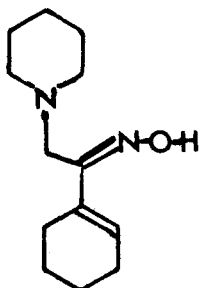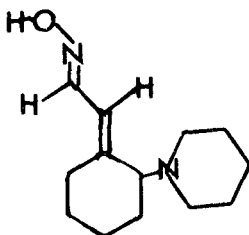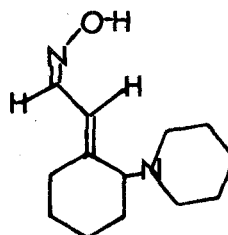
I-29   I-30   I-31

pearance of the 350 mu band. The solution was worked up as

discribed in the experimental section to afford compounds

I-29, I-30 in 13% yield and I-31 in 27% yield. (Scheme 5).

The compound I-29 showed ir absorptions at 3110 cm^{-1},

1680 cm^{-1}, and 1608 cm^{-1}. The typical N-0 stretching modes

appeared in the 1000-900 cm^{-1} region. The nmr spectrum

showed a D_2O exchangeable proton at 0.07, the olefinic proton

at 4.03, and the methylene singlet at 6.62. Microanalysis

and mass spectral analyses of I-29 showed the compound to

have the molecular formula $C_{13}H_{22}N_2O$. This information showed

that the compound was the 1,2-adduct across the vinyl group.

Compounds I-30 and I-31 were the syn and anti isomers result-

ing from the "inverse" 4,1-addition and were obtained as a

mixture. <u>Syn</u> isomer I-30 showed H_A as a doublet at Υ 1.92

(J_{AB} = 10 cps) coupled with the olefinic proton H_B (Υ 3.97).

Scheme 6:

I-30   I-31

pTs Cl
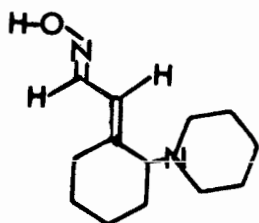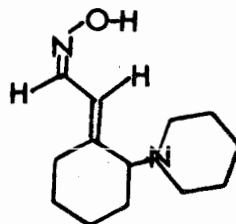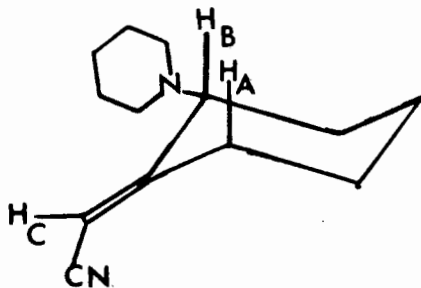
I-32

Anti isomer I-31 showed H_A at a higher field (τ 2.10, J_{AB} = 10 cps) relative to H_A of the syn isomer coupled with the olefinic proton H_B, (τ 3.41). The chemical shift patterns were in full agreement with the long range anisotropic effect of an oximino group (18). A mixture of these isomers was dehydrated (Scheme 6) to give the same nitrile I-32, substantiating the syn and anti-assignments. The 100 Mc nmr spectrum of nitrile I-32 showed the H_C proton as a broad singlet (τ 4.62) which was resolved to a doublet when either H_A (τ 7.73) or H_B (τ 7.21) was decoupled from which the coupling constants were found to be J_{CA} = 1.0 and J_{CB} = 1.4 cps. It has been shown that trans allylic coupling is always smaller than cis coupling by about 0.5 cps (23). Thus, compound I-32 has the piperidine group oriented trans to the nitrile group. Thus the configuration of oximes I-30 and I-31 must have the piperidino and the aldoximino group in the trans relation as shown.

3. Quantum yield determination for the disappearance of N-nitrosopiperidine

The quantum yields were determined using a merry-go-round apparatus. The chemical actinometry described by Parker and Hatchard was used for photon count (24). The plot of the optical density of the actinometer solution com-

CONCENTRATION OF Fe^{2+} x 10^{-8} M
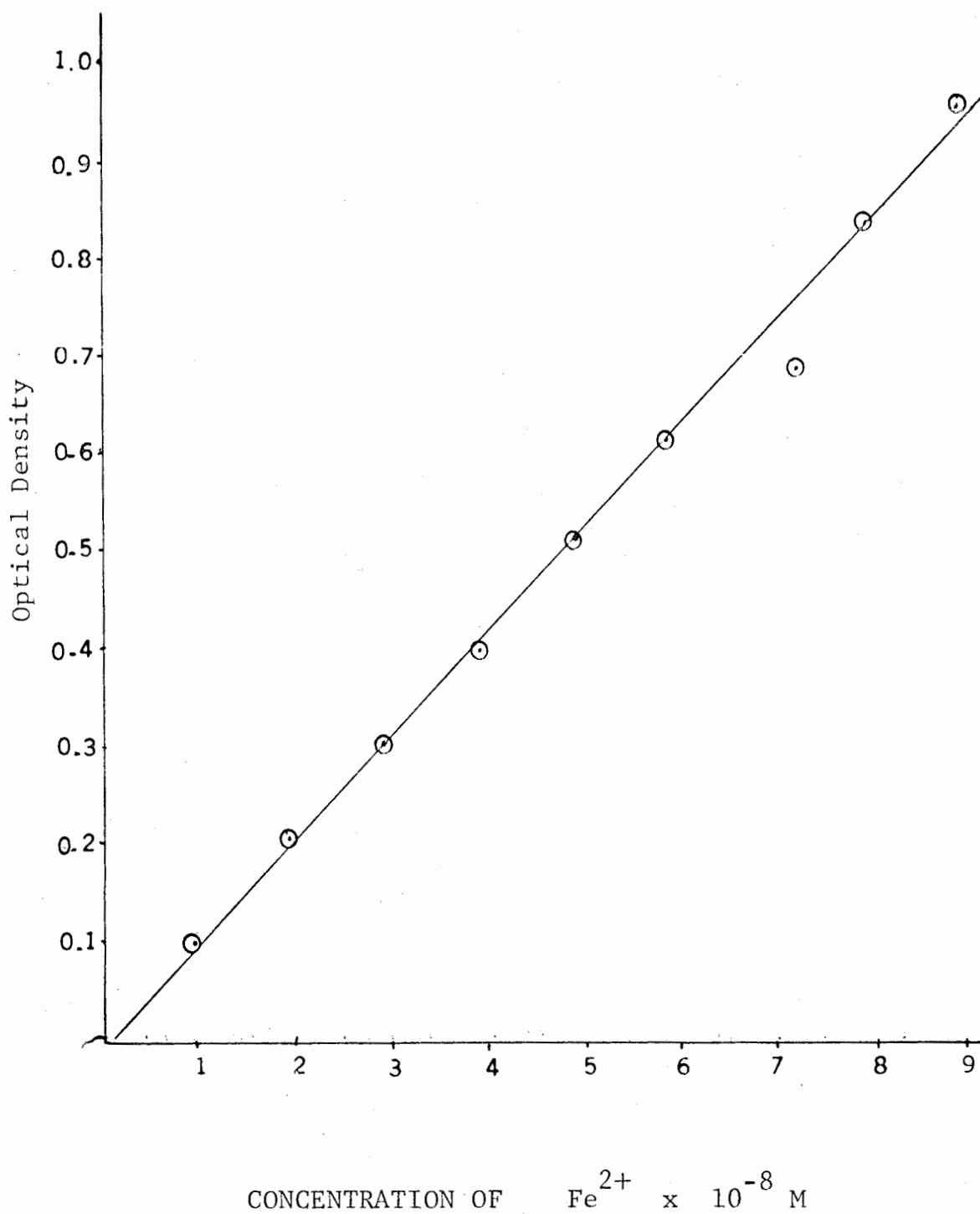
Fig. 22. Plot of Fe^{+2} concentration versus optical density

of actinometer solution complexed with 1,10-phenan-

throline measured at 510 mu.

TABLE II

The variation in quantum yield of the photoaddition of N-nitrosopiperidine
to olefin or diene in 0.06N methanolic HCl solution

olefin	olefin moles	N-nitroso-piperidine moles	optical density 0 min	optical density 20 min	ϕ_B nitrosamine disappear-ance
none	----	2.06×10^{-3}	1.74	1.40	2.56
cyclohexene	2.6×10^{-3}	2.06×10^{-3}	1.74	1.38	2.66
1,3-pentadiene	3.2×10^{-3}	2.06×10^{-3}	1.74	1.38	3.02
trans, trans-2,4-hexadiene	2.4×10^{-3}	2.06×10^{-3}	1.74	1.31	3.23
cis, trans-2,4-hexadiene	2.2×10^{-3}	2.06×10^{-3}	1.74	1.30	3.31

TABLE III

The variation in quantum yield of the photoaddition of N-nitrosopiperidine to olefin or diene in 0.5 N methanolic HCl solution

olefin	olefin moles	N-nitroso-piperidine moles	optical density 0 min	optical density 20 min	ϕ_B for nitrosamine disappearance
none	----	2.05×10^{-3}	1.65	1.30	2.46
cyclohexene	2.0×10^{-3}	2.05×10^{-3}	1.65	1.26	2.74
1,3-pentadiene	2.0×10^{-3}	2.05×10^{-3}	1.65	1.215	3.06
trans, trans-2,4-hexadiene	2.1×10^{-3}	2.05×10^{-3}	1.65	1.216	3.05
cis, trans-2,4-hexadiene	2.3×10^{-3}	2.05×10^{-3}	1.65	1.23	2.95

TABLE IV

Quantum yield determination of the disappearance of N-nitrosopiperidine in 0.5N methanolic HCl solution with varying concentration of olefin

(cycloöctene) M	N-nitroso-piperidine moles	optical density 0 min	optical density 20 min	ϕ_B for nitrosamine disappearance
0.00	2.08×10^{-3}	1.700	1.328	2.89
2.0×10^{-2}	2.08×10^{-3}	1.328	1.235	3.56
4.0×10^{-2}	2.08×10^{-3}	1.680	1.214	3.80
8.0×10^{-2}	2.08×10^{-3}	1.665	1.263	3.26
16.0×10^{-2}	2.08×10^{-3}	1.69	1.200	3.69

plexed with 1,10-phenanthroline versus ferrous ion concentration is shown in Fig. 22.

The quantum yields in the presence of varying cyclooctene concentrations are summarized in Table I V , and were shown to be independent of olefin concentrations within 5% of the average value (3.55). In Table II and III, the quantum yields of the dissapperance of the nitrosamine in the presence of various unsaturated hydrocarbons, determined at two different acid concentrations, are tabulated. The average values are about the same. A comparison shows the quantum yield to be highest in the presence of a 1,3-diene, medium in the presence of an olefin and lowest in the absence of an unsaturated hydrocarbon.

4. Temperature effect in the photoaddition

The rate of the photoaddition process for N-nitrosopiperidine to 1,3-cyclohexadiene at various temperatures was investigated (Table V). The rate of disappearance of the nitrosamine (k,μ moles/minute) is plotted against temperature on Fig. 23. It shows a 14 fold decrease by lowering from room temperatures to 198°K and only a slight increase by elevating the temperatures. The product distribution in each addition did not appear to vary appreciably as shown by nmr and ir spectral analysis and tlc analysis.

TABLE V

The variation of the rate of disappearance of

N-nitrosopiperidine with temperature

Rate k	Temp. K°	1/T°
125 μ moles/min	322°	3.1×10^{-3}
111 μ moles/min	273°	3.7×10^{-3}
8.3 μ moles/min	198°	5.0×10^{-3}
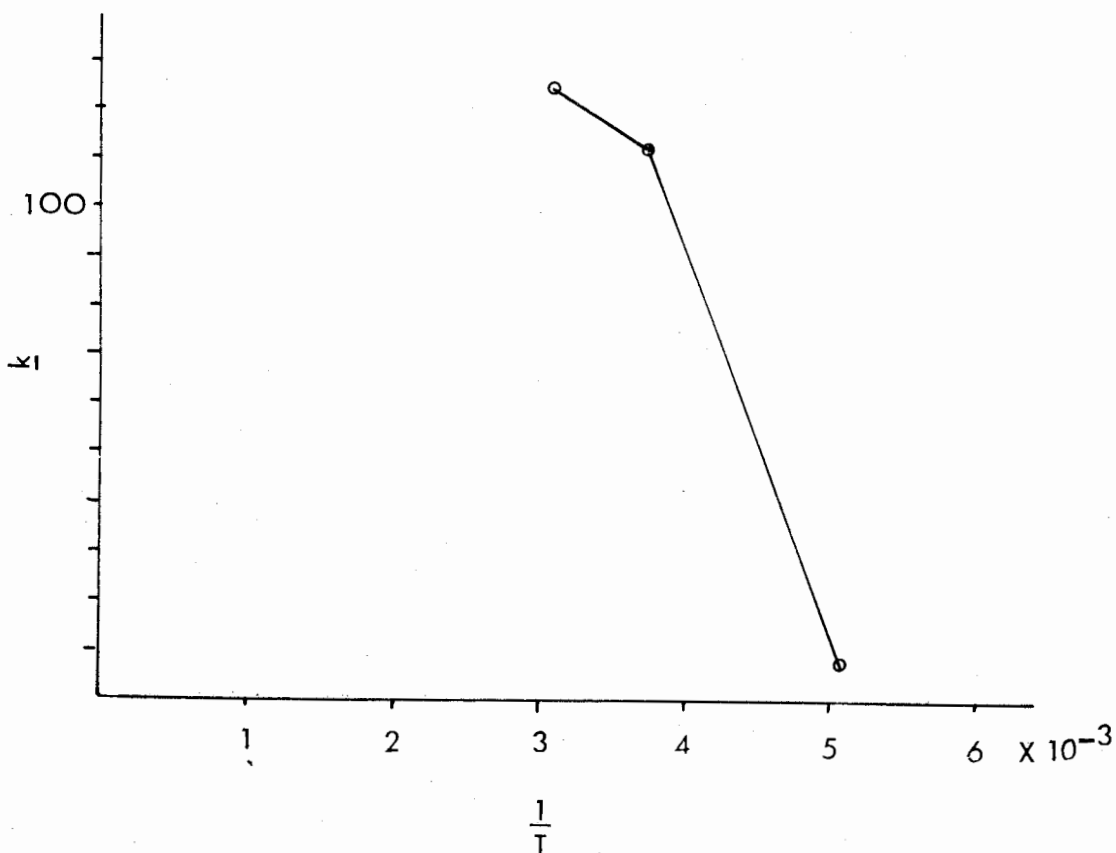
Fig. 23. Plot of temperature versus the rate of disappearance

of N-nitrosopiperidine.

Results

Section II

    1. <u>Sensitization</u> <u>and</u> <u>quenching</u> <u>of</u> <u>the</u> <u>photoaddition</u> <u>of</u>

<u>N</u>-<u>nitrosopiperidine</u> <u>to</u> <u>unsaturated</u> <u>hydrocarbons</u>

    A photosensitized rearrangement of <u>cis</u>, <u>cis</u>-1,3-cyclooc-

tadiene to <u>cis</u>, <u>trans</u>-cyclooctadiene (25) using N-nitrosopipe-

ridine as the sensitizer in both neutral and acidic media, was

found to be totally absent. Neither did <u>trans</u>- or <u>cis</u> -1,3-

pentadiene isomerize under the same conditions.

    In order to establish the energy and the multiplicity of

the excited states of N-nitrosopiperidine, the sensitized photo-

addition of the nitrosamine to cyclohexene, was investigated

(Table VI). The symbols E_{S_1} E_{T_1} and E_{T_1} represent the energies

of the lowest singlet and the second and the first triplet

excited states of the sensitizers, respectively. The symbols

ϕ f, ϕ isc, ϕ p represent the quantum yields of fluorescence,

intersystem crossing and phosphorescence respectively. The

rate of formation, k, for the sensitized addition of the nitro-

samine is given in millimoles per hour, if it can be estimated

by uv analysis or by actual isolation; unless otherwise it is

listed as positive or negative using tlc analysis as the means

of detection. In all determination, caution was taken to keep

TABLE VI

Results of the photosensitized addition of N-nitrosopiperidine to unsaturated hydrocarbon

Sensitizer*	E_{S_1}	E_{T_2}	E_{T_1}	Φ_F	Φ_{isc}	Φ_P	mmoles/hr	olefin
acetophenone	78.6		76.0	0.0	0.99	0.62	(+)	cyclohexene
anthracene	76.4	74.4	42.5	0.27			4.3×10^{-1}	cyclohexene
triphenylene	80.6		66.6	0.08	0.95	0.84	0.75×10^{-1}	cyclohexene
naphthalene (a)	90.8		60.9	0.19	0.39	0.03	2.78×10^{-1}	cyclohexene
" (b)							2.30×10^{-1}	cyclohexene
								benzonitrile
" (c)							(-)	1,3-pentadiene
1,2-benzanthracene	69		47	0.20	0.55	0.001	2.8×10^{-1}	cyclohexene
1,4-dimethylanthra-cene							(-)	cyclohexene
perylene	65			0.98			(-)	cyclohexene

*See ref. (74-76) for energy values.

TABLE VII

The rate of photosensitization of N-nitrosopiperidine with
different sensitizers

Sensitizer*	ϕ_F	ϕ_{ISC}	(k) in mmoles/hr
(a) naphthalene	0.19	0.39	2.78×10^{-1}
(b) naphthalene in presence of benzonitrile	0.19	0.39	2.36×10^{-1}
(c) triphenylene	0.05	0.95	0.75×10^{-1}
(d) 1,2-benzanthra- cene	0.20	0.55	2.8×10^{-1}
(e) 1,4-dimethylan- thracene	-	-	
(f) anthracene	0.3		4.3×10^{-1}
(g) acetophenone	0.0	0.99	0

* See ref. (74-76) for energy values.

the conditions as comparable as possible. Certain reactions were shown to be reproducible (Exp. Sect. II). The rate of photosensitized addition, k, can be correlated directly with the quantum yield of flourescence ϕ_f of the sensitizers (Fig. 24, Table VII) with the exception of perylene, who with a ϕ_f = 0.95, showed negative sensitization.

The direct irradiation of N-nitrosopiperidine in the presence of cis- and trans-1,3-pentadiene was carried out using napthalene as quencher. For a comparison, the same reaction was carried out in the absence of naphthalene. The rate of disappearance for the nitrosamine was 0.005 moles per hour in both cases. It was concluded that naphthalene does not quench the photoaddition.

When perylene was used as the quencher of N-nitrosopiperidine addition to cyclohexene, the uv absorptions of perylene at 400 mu and longer wavelength increased in intensity at first, then gradually decreased and broadened. At the conclusion of the irradiation at 350 mu (9 hrs.), a third of the original N-nitrosopiperidine and almost all of the perylene was recovered. The photoadduct, 2-piperidinocyclohexanone oxime, was isolated in 37% yield and a trace of a purple compound was observed by tlc. As a control, the identical reaction
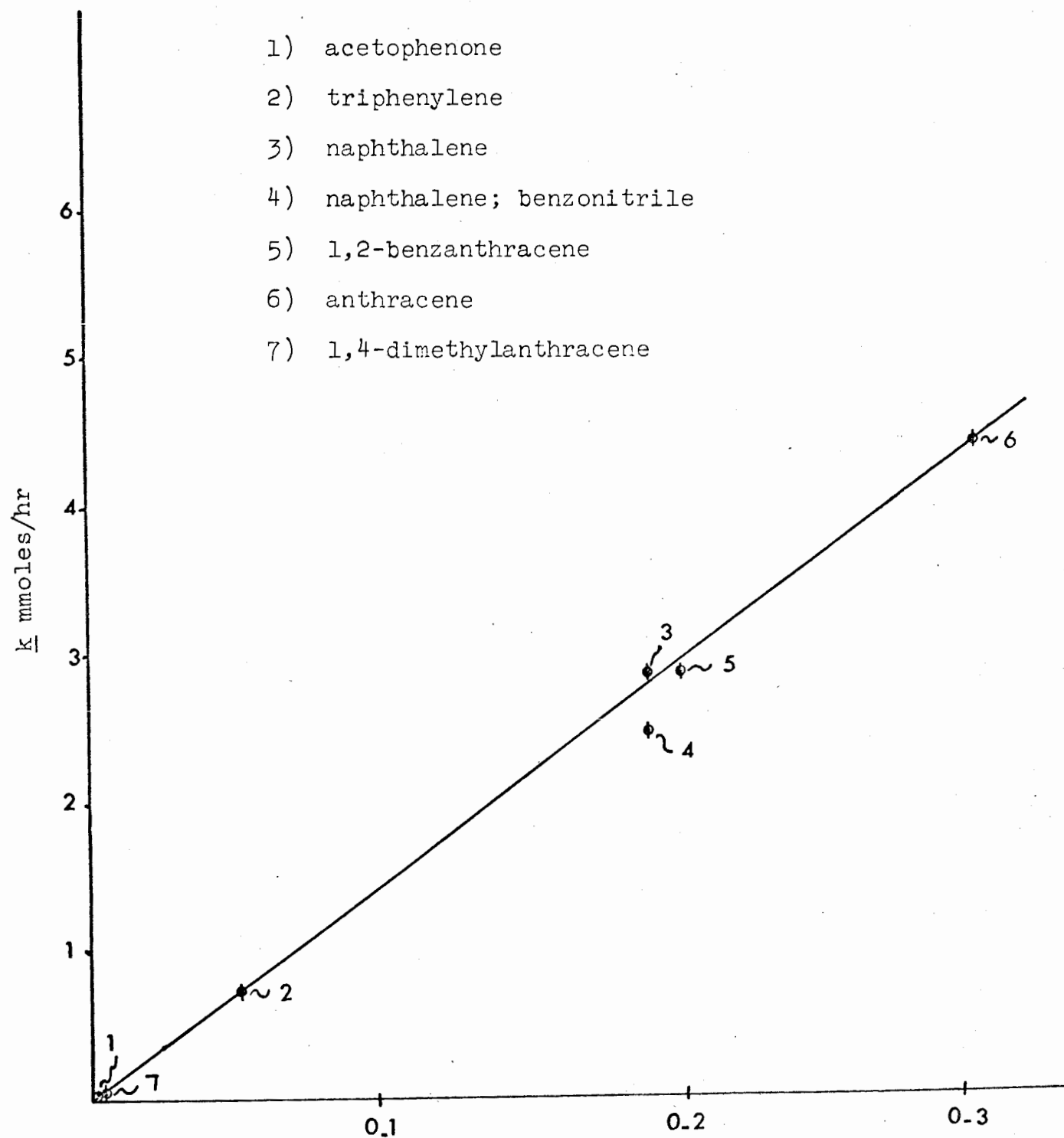
Fig. 24. Plot of the rate of sensitization of N-nitrosopiperidine versus Φ_f.

was performed in the absence of perylene, and yielded 72% of 2-piperidinocyclohexanone oxime.

2. Quenching of the photoreduction process

In ethanol solution, N-nitrosopiperidine photolytically reacted with ethanol to give acetaldehyde, piperidine and N-piperidinoacetamide (Scheme 7); this process is very similar to the photoreduction of carbonyl compounds (26-29). Acetaldehyde and N-piperidinoacetamide were obtained by reaction between ethanol and N-nitrosopiperidine.

The photoreduction of N-nitrosopiperidine in the presence of a triplet quencher was investigated. The photolysis, in the presence of acetophenone (E_{T_1} = 73.6 Kcal/mole) (30), or in the absence of acetophenone, gave the same rate in the disappearance of nitrosamine, as determined by the disappearance of the 350 mu peak, (0.0025 moles per hour). The products obtained were piperidine, as the hydrochloride in almost quantitative amounts, and a trace of N-piperidinoacetamide. Using triphenylene (E_{T_1} = 66.6 Kcal/mole) (30) as the quencher, an identical result was obtained. In this case, acetaldehyde which could not be isolated as the 24-DNPH derivative in the previous case, was identified as the 2,4-dinitrophenylhydrazone (2,4-DNPH) derivative.

Scheme 7:
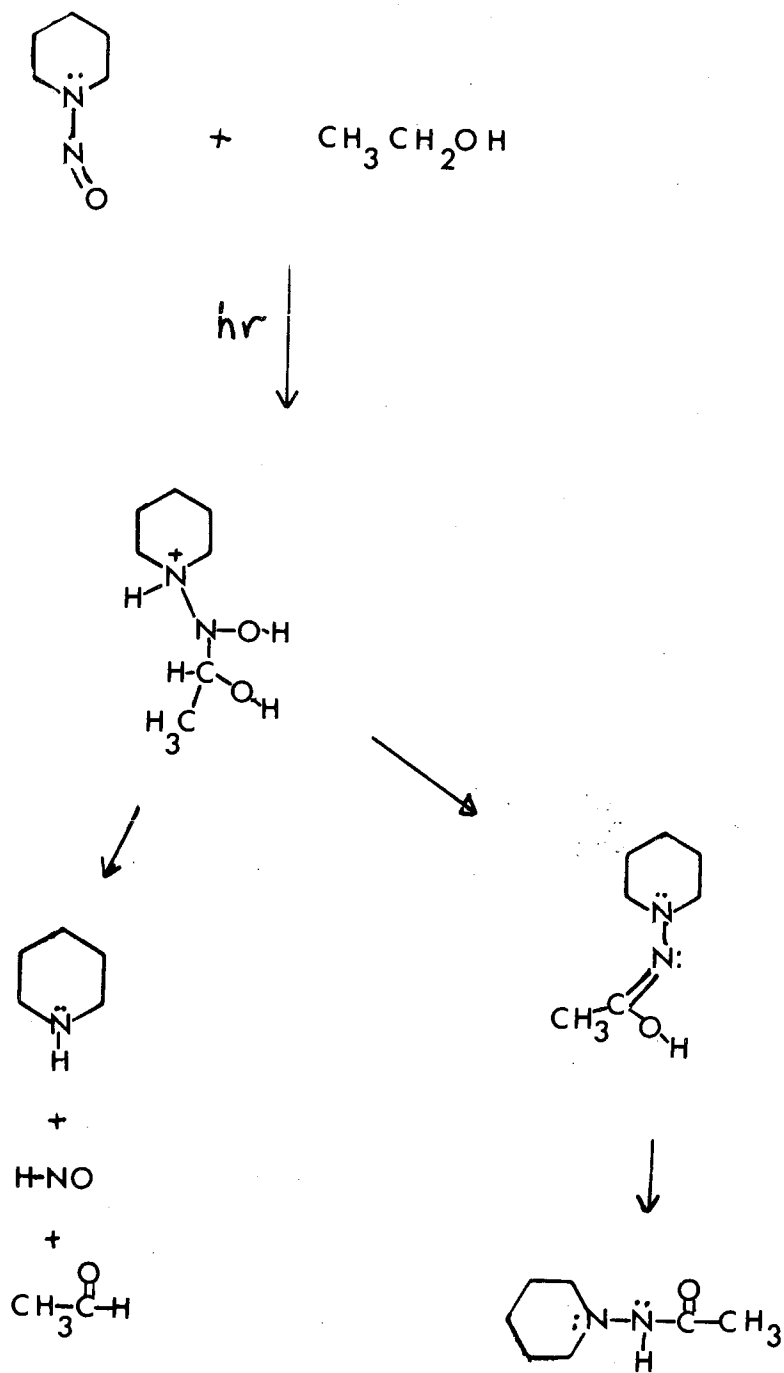
Using naphthalene (E_{T_1} = 60.9 Kcal/mole) (30) as the quencher, the nitrosamine absorption band at 350 mu region did not decrease and the solution turned slowly yellow. On prolonged irradiation, the uv absorption at 350 mu gradually broadened and increased in intensity, and the photolysate turned deep red-brown. Analysis of the photolysate revealed that the nitrosamine had survived, and a trace of red compound was detected by tlc analysis.

Results

Section III

    1. <u>Sensitized photoaddition of N-nitrosoamines to aroma-tic hydrocarbons</u>

During the investigation of the sensitized addition of N-nitrosopiperidine to olefins, it was discovered that some of the aromatic hydrocarbon sensitizers were capable of reacting with the nitrosamine. The aromatic hydrocarbons that underwent addition with an excited nitrosamine were anthracene, acenaphthylene, 1,3-dimethylanthracene (1,3-DMA), 1,4-dimethylanthracene (1,4-DMA), 1,2-benzanthracene, phenanthrene, azulene and pyrene.

Irradiation of anthracene in the presence of N-nitrosopiperidine, in which anthracene absorbed more than 95% of the light, under helium atmosphere, gave 9-piperidinoanthrone oxime (III-1). The compound III-1 showed the ir absorption peaks at 3300, 1500, 1000-900, and 800-700 cm^{-1}. The nmr spectrum (in pyridine d-5) showed multiplets at Υ 0.9 (H$_A$), Υ 1.8 (H$_B$), Υ 2.5(H$_C$) and a singlet at Υ 5.18(H$_D$) (Fig. 25). Since the molecular formula was shown to be $C_{19}H_{20}N_2O$ by elemental analysis, the structure of III-1 was confirmed.

The neutral fraction afforded anthracene dimer (III-2) identified by comparison of its spectrum with that of an authentic sample. From this fraction a small amount of

Fig. 25. The structure of III-I.
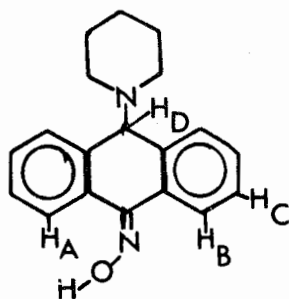
9-ethoxyanthrone oxime (III-3) was also isolated. This compound showed ir absorption bands at 3400, 1000-900 cm^{-1} and 1295 cm^{-1}; the last of which is due to C-0 stretch of ether linkage. The nmr spectrum showed in addition to the signals for the aromatic protons and the methine protons (Υ 2.5 and Υ 4.60), a quartet (Υ 6.44, J_{AB} = 7 cps) and a triplet (Υ 8.76, J_{AB} = 7 cps) indicating the presence of an ethoxy group. Mass spectral analysis confirmed the molecular formula of $C_{16}H_{15}NO_2$ (m/e 253). Compound III-3 probably arises from III-1, since irradiation of III-1 gave III-3 in a small amount (Scheme 8).

Scheme 8:
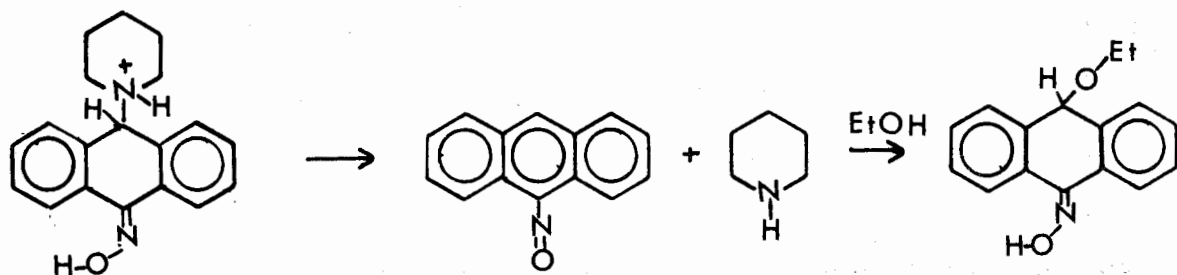
When the irradiation of anthracene was carried out under a nitrogen or oxygen atmosphere other products were obtained in addition to III-1, III-2, III-3. These products were 9-nitroanthracene (III-4) anthraquinone (III-5), cis and trans-9-piperidino-10-ethoxy-9,10-dihydroanthracene (III-6 and III-7) and 9-piperidino-10-hydroxy-9,10-dihydroanthracene (III-8).

Compounds III-4 and III-5 were identified by direct comparisons with those of authentic samples. Compounds III-6 and III-7 showed the ir absorption at 1290 cm^{-1} due to C-O stretching vibration of the ether linkage (31). The methine protons appeared at τ 4.84 and τ 5.39 for III-6 and at τ 4.26 and τ 5.31 for III-7. In addition the ethoxy protons in both compounds showed typical quartet and triplet signals. Mass spectrum and analytical data set the molecular formular for the two isomers at $C_{21}H_{25}NO$. At present definite assignment of cis-trans stereochemistry to these two compounds is not possible.

The ir spectrum of III-8 showed absorptions at 3200 and 1290 cm^{-1} indicating the presence of an alcohol group. The nmr spectrum of III-8 showed a D_2O exchangeable signal at τ 3.86 and singlets at τ 4.76 and τ 6.07 for the methine protons. The major product of photolysis under oxygen atmosphere was III-8.

It was necessary at this point to see the effect of oxygen on the photoaddition. The photoaddition of N-nitrosopiperidine to cyclohexene was carried out in the presence of oxygen, and the cis (III-9) and trans (III-10) isomers of 2-piperidino-1-nitratocyclohexane were isolated as the hydrochlorides in good yield. Compound III-9; III-10 exhibited ir absorption at 1640, 1260, 870 cm^{-1} characteristic of a C-O-NO$_2$ group (31). The H$_A$ for the nitrato compound III-9 appeared at τ 4.47 as a triplet (J = 3 cps) and H$_{A'}$ of III-10 resonated at τ 4.77 as two partially superimposed triplets (J = 6 cps) (Fig. 26).

Fig. 26. The structure of III-9 & III-10.

The smaller coupling constant of 3 cps is characteristic of cis configuration while the larger coupling constant of 6 cps is that of trans configuration (32). Both isomers III-9 and III-10 gave the expected elemental analyses. The nitrato compounds III-9 and III-10 are stable only in the form of their salts. The free base decomposed rapidly to

2-piperidinocyclohexanone which further decomposed to a red
tar. The cyclohexanone compound was oximated to yield
2-piperidinocyclohexanone oxime (III-14). The similar ni-
trato derivatives were obtained in the photoaddition of nitro-
sodimethylamine to cyclohexene and were reduced by sodium
borohydride to give a mixture of cis and trans-2-dimethylami-
nocyclohexanol.

Scheme 9:

III-9   III-10

OH⁻

NH₂OH

O₂→

NaBH₄
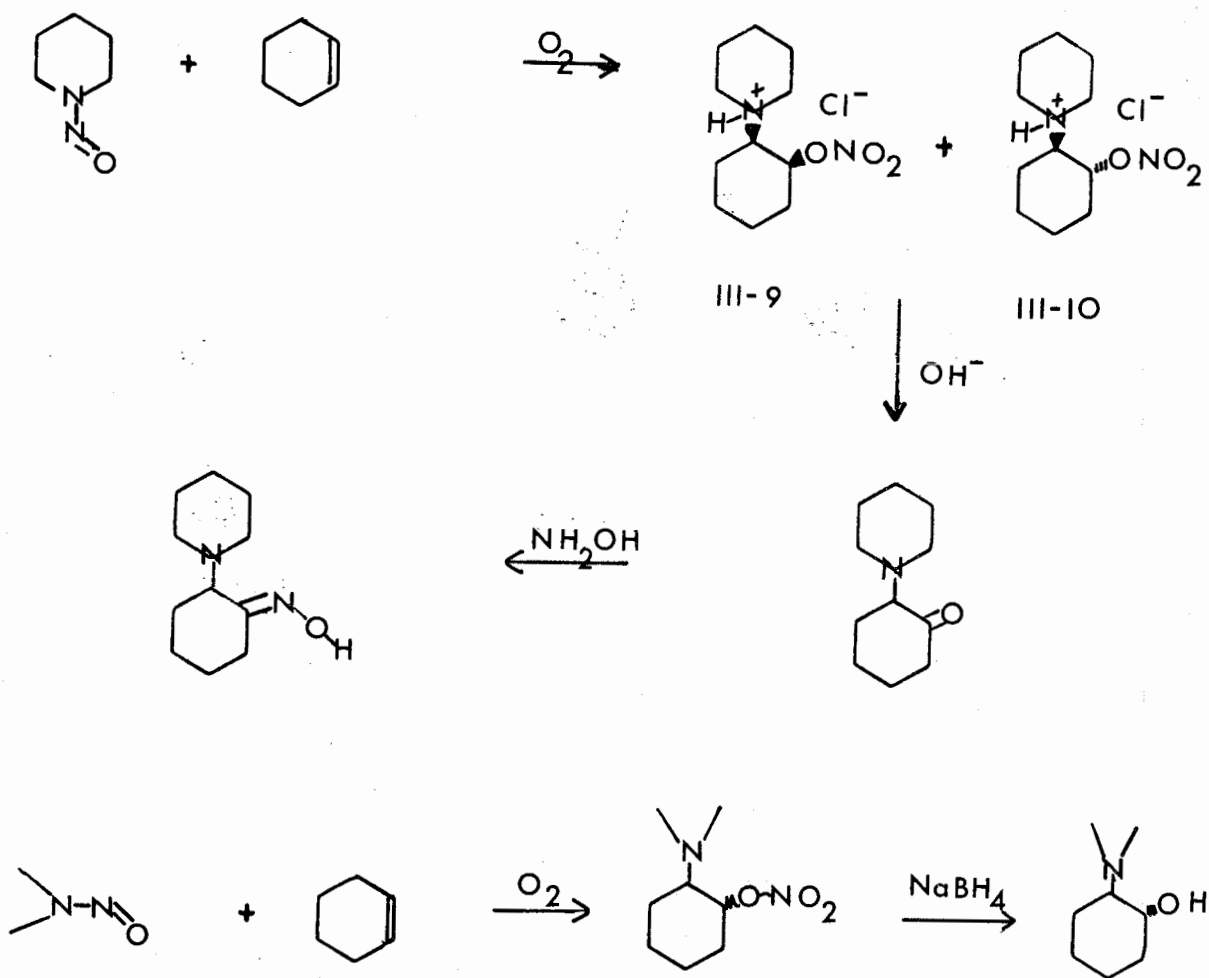
The formation of a nitrato compound in the photolysis led us to suspect that the precursor of the aromatic oxygenated products (III-4, III-5, III-6, III-7, III-8) was a nitrato compound (III-11). This was inferred by the typical nitrato absorptions at 1640, 1260, 870 cm^{-1} shown by the crude residue obtained from a photoaddition to anthracene in the presence of oxygen (31). Many attempts to isolate this intermediate failed. When the crude residue from the photolysate was chromatographed on a silicic acid column, the nitrate of 9-piperidinoanthrone (III-12) was obtained.

III-12 exhibited strong absorption at 1678 cm^{-1} due to the carbonyl stretching vibration. The nmr spectrum of III-12 in D_2O showed a singlet at τ 3.98 in addition to the aromatic proton signal at τ 2.2. Further, the elemental analysis confirmed the molecular formula $C_{19}H_{20}N_2O_4$. On standing III-12 gave anthraquinone III-5. This information led us to propose that III-12 and III-5 were formed from the nitrato precursor III-11 by elimination and air oxidations. The formation of III-6, III-7 and III-8 could be interpreted as substitution of the nitrate group in III-11 by solvents (Scheme 10).

During the investigation of this reaction it was found that the product distribution and the yields of the products were highly dependent on reaction conditions. As seen in

Scheme 10:

III-11

ROH

III-6

III-12

O_2
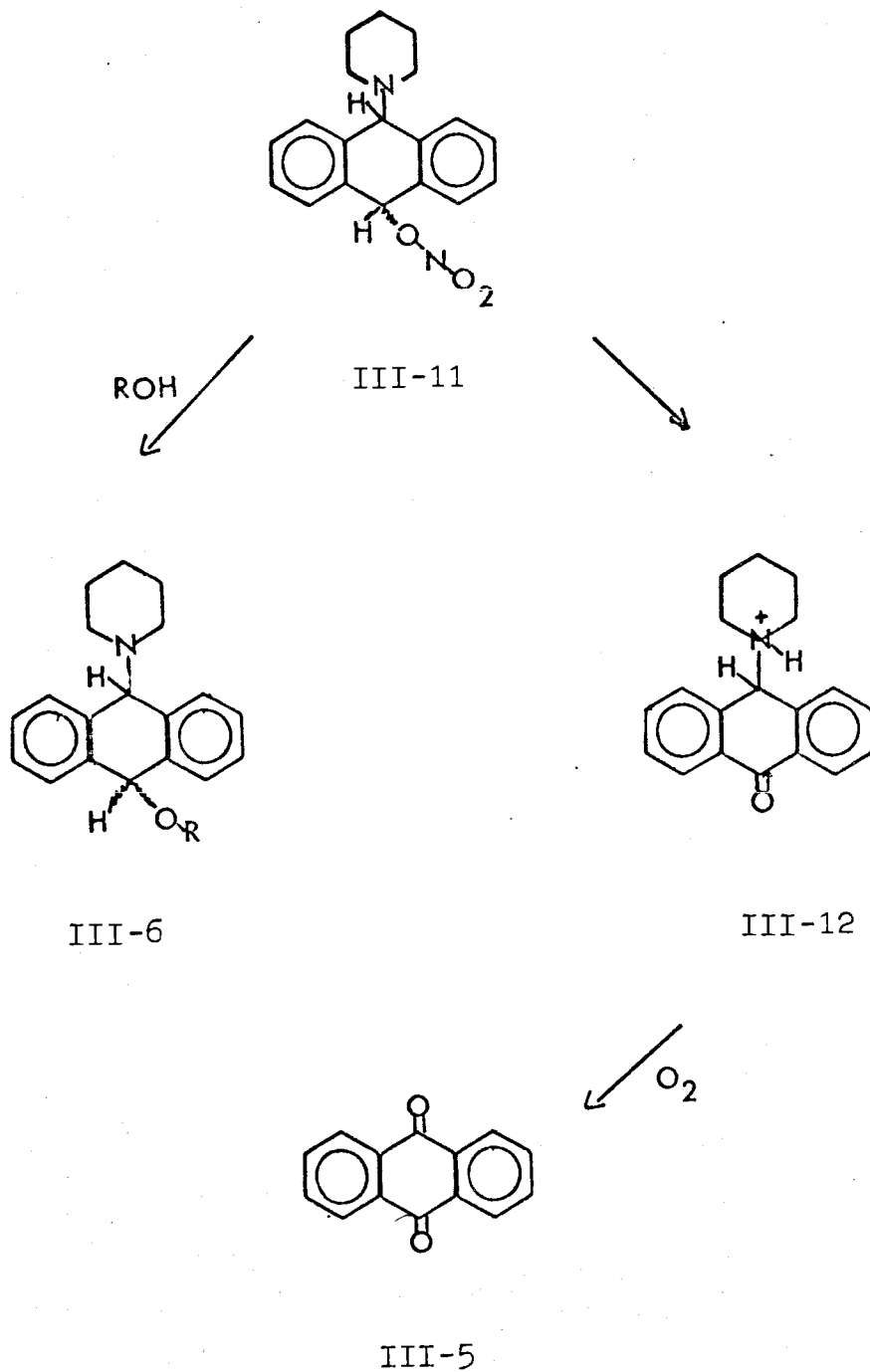
III-5

TABLE VIII

Photosensitization of N-nitrosopiperidine using anthracene

Added reagents		Atmos-phere	Product yields							
			III-1	III-3	III-4	III-5	III-6	III-7	III-8	III-14
a) cyclohexene	0.12 M	N_2	1%	---	2%	18%	4 1/2%	21%	2%	(trace)
b) cyclohexene	0.12 M	He	45%	---	---	---	---	7%	1%	---
c) "	0.6 M	He	34%	6%	---	---	---	---	---	---
d) "	0.12 M	He	---	---	---	---	---	---	1%	---
e) cyclohexene	0.12 M	He	1%	---	---	---	---	5%	1%	---
bromobenzene	0.2 M									
f) none	---	N_2	35%	---	1%	8%	5%	13%	---	---
g) none	---	He	95%	5%	---	---	---	---	---	---
h) none	---	O_2	---	---	---	11%	---	5%	27%	---
i) bromobenzene	0.2 M	He	49%	---	---	---	---	---	---	---
j) "	0.6 M	He	46%	---	---	---	---	---	---	---
k) no hydrochloric acid		He	---	---	---	1%	---	---	---	---
l) cis-4-methyl-2-pentene	0.12 M	He	---	---	---	---	---	---	2%	---
bromobenzene	0.24 M									

All photolyses were run at 350 mu except (d) which was run at 300 mu

The yields of all products were based using the yields of III-1, III-3 in reaction (g) as the 100% standard.

Table VIII, under nitrogen atmosphere, the oxygen containing by-products (III-4 III-8) were obtained in which III-6 and III-7 were the predominant by-products. These products disappeared (g) or became negligibly small under a helium atmosphere (b). That the by-products were formed through an oxidation reaction due to the trace of oxygen in the commercial nitrogen was shown by carrying out the reaction under oxygen atmosphere (h) from which the oxygenated products (III-5-III-8) consisted of the major part of the products; III-5 and III-8 became the dominant ones.

The sensitized nitrosamine photoaddition to anthracene was also sensitive to the presence of bromobenzene, and olefin. Optimum yield of III-1 was obtained when neither of these reagents was present (g). When the reaction was carried out in the presence of 0.12M (b) or 0.6M of cyclohexene (c), the yield of III-1 decreased to ca 50% and 30%, respectively, relative to the yield obtained the absence of cyclohexene. Curiously in these two reactions 2-piperidinocyclohexane oxime (III-14) was obtained in very small amounts. It was also surprising to find that this photoaddition virtually does not take place when the reagents were irradiated with Rayonet 300 mu lamp (d). In the presence of 0.2M (i) and 0.6M (j) of bromobenzene, the yield of III-1, III-1

decreased by ca 50% in both cases. The photoaddition was, however, retarded severely when both cyclohexene (0.13M) and bromobenzene (0.2M) were added; only small amounts of III-1, III-6, III-7, III-14 were obtained. When cyclohexene was substituted by cis-4-methyl-2-pentene in this reaction, however, no such effect was observed as that observed in (i). It was also noticed that this olefin was not isomerized during the photoaddition of N-nitrosopiperidine to anthracene and that scarcely any photoadduct to this olefin was detected. A control reaction showed that neither the yield of III-14 nor the rate of the photoaddition of the N-nitrosopiperidine to cyclohexene was affected by the presence of bromobenzene. Further, it was shown that while bromobenzene could efficiently isomerize cis-4-methyl-2-pentene into the trans isomer when a methanol solution was irradiated through corex filter, N-nitrosopiperidine did not sensitize the isomerization.

The photoaddition of N-nitrosodimethylamine to acenaphthylene gave, as the basic products, anti-2-dimethylamino-acenaphth-1-one oxime (III-15) as the major product and the syn-2-dimethylaminoacenaphth-1-one oxime (III-16) in lesser amount (Scheme 11). Compound III-15 showed hydroxyl absorption at 3100 cm^{-1} and typical oximino absorptions in the 1000-900 cm^{-1} region. The nmr spectrum showed a D_2O exchange-

Scheme 11.
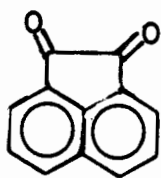
III-18
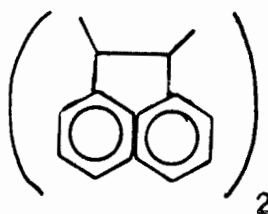
III-17
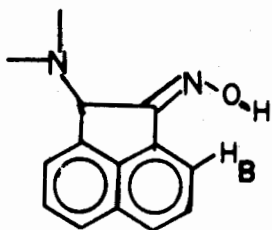
III-15
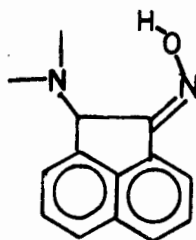
III-16

able proton at Υ -1.0 and a one proton multiplet at Υ 1.6 for

H_B. The signals for the remaining aromatic protons appeared in

the Υ 2.3 region. The methine proton appeared as a singlet at

Υ4.78 and the signals for the dimethylamino group at Υ7.86.

The syn isomer III-16 showed the methine proton and the dime-

thylamino group signals shifted downfield relative to those

of III-15 at Υ4.57 and Υ7.58. The minor products in this

photoaddition were acenaphthylene dimer (III-17) and acenaph-

thoquinone (III-18). The physical data for these compounds

are in agreement with those reported in the literature (33,

34).

The photolysis of 1,3-DMA in the presence of N-nitroso-

piperidine did not proceed readily and gave small amounts of

various products under forcing conditions in glacial acetic

acid solution containing hydrochloric acid. These products

were 1,3-DMA dimer (III-19), 9-chloro-1,3-DMA (III-20

19-chloro-1,3-DMA (III-21), 1,3-dimethyl-9-acetoxyanthrone

III-22 9-piperidino-10-hydroxy -9,10-dihydro-1,3-DMA (III-23)

and 10-piperidino-9-hydroxy-9,10-dihydro-1,3-DMA (III-24).

Due to the small amounts available for investigation, the

structural elucidations were based exclusively on spectral

data (Exp. Sect. III) and the assignments should be regarded

as tentative ones. Other sensitized additions of N-nitroso-

piperidine to aromatic hydrocarbons gave similar results.
The are summarized as follows.

The photolysis of 1,4-DMA in the presence of N-nitroso-
piperidine under nitrogen atmosphere gives minor amount of
1,4-DMA dimer (III-25), 9-piperidino-10-methoxy-9,10-dihydro-
1,4-DMA (III-26) and 9-piperidino-10-hydroxy-9,10-dihydro-1,
4-DMA (III-27) (Scheme 12).

The photolysis of 1,2-benzanthracene in the presence of
N-nitrosodimethylamine proceeded very sluggishly and gave a
darkened solution on prolonged irradiation. The products were
small amounts of 9-methoxy-10-dimethylamino-9,10-dihydro-1,2-
benzanthracene (III-28) and 9-hydroxy-9,10-dihydro-10-dimethyl-
amino-1,2-benzanthracene (III-29). The self sensitized photo-
addition of N-nitrosopiperidine to phenanthrene, azulene and
pyrene gave low yields of compounds containing the amino group.
In the case of pyrene, 1-piperidinopyrene (III-30) was the
only isolable product. The position of the piperidino group
was determined by comparison of the nmr spectrum of III-30
with that of 3-acetamidopyrene which showed a very different
nmr pattern. In the case of azulene, x-piperidino-azulene
(III-31, 15%) was the only isolable product. Only minor
amounts of azulene were recovered and large amount of black
gum was also obtained. The phenanthrene photolysis gave
x-dimethylaminophenanthrene (III-32) in minute yield.

Scheme 12.

III-25   III-26

III-27
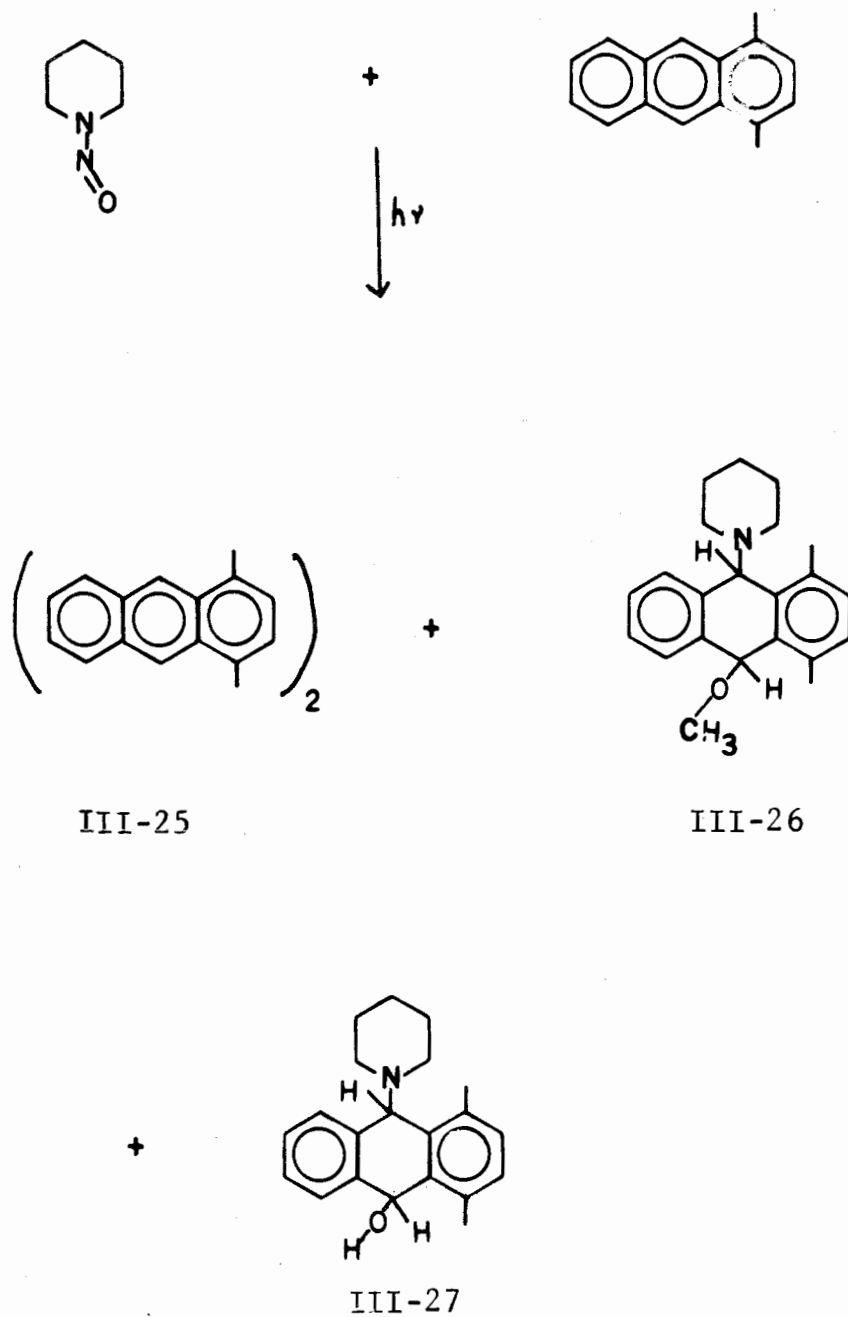
Discussion

Section I

It is generally recognized that a conjugated diene under-
goes addition reaction more readily than does an isolated

double bond (35). In the present case, N-nitrosopiperidine

also shows a remarkable facility to add to a conjugated diene

system similar to the general reactivity pattern. Thus the

reaction exhibits a potential utility for the synthesis of

alpha, beta-unsaturated oximes. The photoaddition is regio-

specific (36) in its orientation in which the piperidino group

always attaches itself to the 1-position of the symmetrical

diene system while the nitroso group goes to either the

2-position or the 4-position. A free radical addition to a

conjugated diene generally gives more 1,4-adducts than 1,2-

adducts (37, 38), while the trend is reversed if a metal ion

is involved during the addition (39, 40). However, there is

no predictable pattern on the mode of addition in an ionic

mechanism (35). Although nitrosopiperidine preferentially

adds to the symmetrical conjugated dienes in 1,4-mode, this

information alone does not allow a decision to be made on

the reaction mechanism.
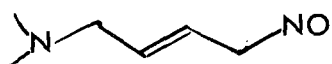
I-33
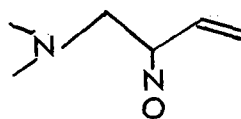
I-34

That the C-nitroso compounds (I-33 and I-34) are the primary photoadducts is shown by the typical blue color developed during the photoaddition to cyclopentadiene. An attempt to trap the C-nitroso compounds I-33 and I-34 as the corresponding dimers (41) by performing the photoaddition at a low temperature gave a dark blue solution which turned to a tar on continuing irradiation. When the photolysis was run at room temperature, the oximes I-9, I-10 and I-11 were obtained in good yields although a pale blue color was still observed during the reaction. At this temperature I-33 and I-34 probably tautomerize very rapidly due to the allylic nature of the migrating hydrogen (8), which may account for the good yields of I-1 ∿ I-11. With a high concentration of I-33 and I-34 at a low temperature and under the photolysis conditions, an unknown secondary reaction of I-33 and I-34, probably photolytic in nature, prevails leading to tar formation.

The tautomerization of the C-nitroso compounds to syn or anti oximes is governed by the energetics of the transition states along the reaction axis to the respective oximes (14) and very much related to conformational problems in alpha, beta-unsaturated oximes. The requirement of coplanarity in the cyclohexenone oxime system in syn I-6 makes the OH group
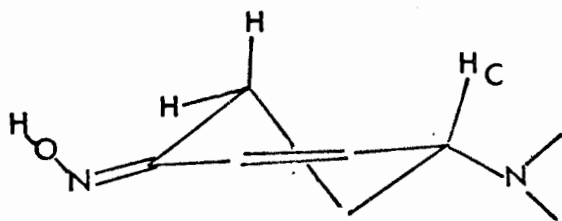
I-6
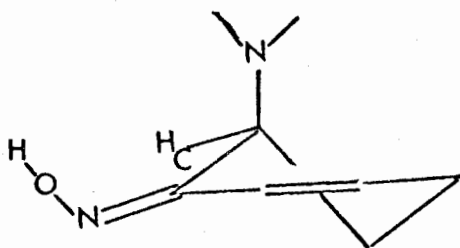
I-7
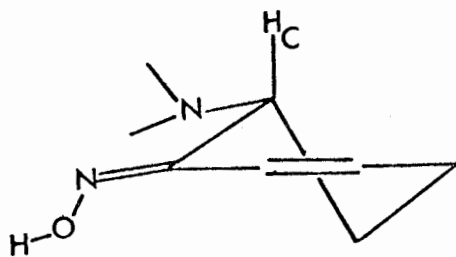
I-8

Fig. 27. The conformation of the 1,2- and 1,4-adducts of
N-nitrosopiperidine to cyclohexene.

experience a severe interaction with the C-2 olefinic proton
(H_A) and thus destabilized the <u>syn</u>-oxime I-6 greatly (15) in
comparison to the <u>anti</u>-oxime. The only 1,4-adduct obtained
is therefore assigned the <u>anti</u>-configuration (I-6). In agre-
ement, the C-6 equatorial proton resonates at Υ 6.78 which is
comparable to the chemical shift of the <u>cis</u>- α -equatorial
proton (Υ 6.61) in t-butylcyclohexanone oxime (18). The sole
1,4-adduct obtained from cyclopentadiene is also assigned the
<u>anti</u>-configuration I-11 for similar but even more severe ste-
ric reasons.

The <u>syn</u>-cyclohexenone oxime I-7 must have the forced con-
formation (Fig. 27), with the axial orientation of the pipe-
ridine ring, since a severe $A^{1,3}$ interaction (15, 42) would
not allow an equatorial orientation of piperidine ring in the
alternative conformation. Since the severe $A^{1,3}$ interaction
no longer exists in <u>anti</u>-oxime I-8, the conformation can be
represented as shown in (Fig. 27) and is supported by the
chemical shift of C-6 axial methine proton* at Υ 6.98 (16).
In this conformation, however, there exists an interaction
between the OH group and C-2 olefinic proton (H_A), though
the magnitude must be less than the interaction between

---

*The corresponding proton in <u>anti</u>-2-piperidinocyclo-
hexanone oxime shows the chemical shift at Υ 7.24.

the OH and an axial piperidine conformation. Due to the un-favourable interactions in both conformations (Fig. 27), the actual shapes of I-7 and I-8 are probably distorted to relieve the strains. The distortion is indicated by the coupling pattern of the C-6 proton in I-8 (6 and 3 cps) and I-7 (5 and 3 cps) which are far from the expected values for axial and equatorial protons.

Finally the coupling constants between H_C and the olefinic protons in I-11 and I-6 merit a discussion in connection with the conformations. If the assignments of the olefinic nmr signals to H_A and H_B are accepted the allylic coupling J_{AC} in I-6 and I-11 (2.5 and 2 cps, respectively) turns out to be equal to or larger than the vicinal coupling constant J_{AB} (2.5 and 1.5 cps, respectively). Such a situation can arise only where the C-H_C bond orients itself perpendicular, or nearly so, to the plane defined by C_2-C_3-C_4 in (Fig. 27). In this case the maximum allylic coupling and the minimum vicinal coupling are achieved (23, 43). An anologous situation is observed in I-11.

The photoaddition to acyclic 1,3-dienes provided a better opportunity for the study of the specificity of the addition. The salient points can be summarised as follows. Firstly, the photoaddition to acyclic dienes is also regiospecific in

which the amino group always attaches itself to the terminal

carbon of the diene system and does so predominantly on the

least substituted carbon if an alternative possibility exists.

The isolation of minor amounts of reverse 4,1-adduct I-17

from the 1,3-pentadienes are the first instance of such re-

verse photoaddition. The reverse addition of a nitrosamine

to a simple olefin has never been observed. This reverse

photoaddition may be due to the increased reactivity of the

diene toward an excited nitrosamine causing a loss in selec-

tivity.

Secondly, the 1,4-(or 4,1-) addition exclusively results

in the formation of trans-configuration on the newly formed

double bond. A survey of the literature indicates that trans-

double bond is exclusively or predominantly formed in 1,4-

additions by a free radical mechanism (37, 38). The 1,4-con-

jugated additions by ionic mechanism do not show a uniform

tendency in this respect (39, 40), but the adduct containing

the cis-double bond can be made the dominant product if the

addition is catalysed by a metal ion.

Thirdly, in the 1,2-photoadducts the original stereoche-

mistry of the remaining double bond is completely retained

as shown in I-18, I-19, I-22 and I-23. This claim is amply

substantiated by converting the crude products to the confi-

gurationally pure crotonitrile in each case by the amino group
assisted Beckmann cleavage reaction (21) which does not dis-
turb the stereochemistry of the double bond under the experi-
mental condition. The retention of the double bond configu-
ration in a generated allyl radical is known to pertain under
special conditions, namely, at a low temperature and/or under
rapid removal of the allyl radical (35). This suggests a very
rapid reaction of the second step in this photoaddition if
it follows a stepwise free radical addition as suggested
before (44).

Fourthly, the photoaddition always gave 1,4-adducts as
the major product and 1,2-adducts the minor. Finally the
addition to cis, trans-2,4-hexadiene appeared to take place
nearly exclusively to the cis-double bond. The possibility
of isomerization during the addition process can be dismissed
in the light of the results from the addition to 1,3-penta-
dienes. A priori, two alternative interpretations can be
considered. First of all, and the simplest, an excited
nitrosamine may preferentially attack at the cis-double bond
over the trans-double bond. Secondly, the initial attack to
the trans-double bond may lead to 1,4-addition exclusively
while the addition to cis-double bond collapses partially to
the 1,2-adducts, I-25 and I-27. Since there is no preferen-

tial addition of a photoexcited N-nitrosopiperidine to cis,
trans-over trans, trans-2,4-hexadiene when the photoaddition
is run in the presence of a mixture (1:1) of the isomers*, the
first explanation is not tenable. The ratio of the isomeric
dienes was shown to be the same after the photoaddition was
terminated at 80% completion. Although extension of an argu-
ment based on intermolecular process to that of an intramole-
cular process requires caution, the initial attack of an exci-
ted nitrosamine to a diene is apparently random, at least in
the intermolecular cases. It, therefore, appears that the
second explanation is more probable.

The photoaddition to 1-vinylcyclohexene does not com-
pletely follow the addition pattern observed in the cyclic
and acyclic dienes series; the 1,2-adducts (I-29) are formed
in less amount than the 1,4-adducts (I-30, I-31) and the
latter adduct follows the reverse addition. The totally dif-
ferent mode of the addition may indicate the importance of
a preferential complexation of the diene with the nitrosamine
prior to the photoaddition step.

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*In agreement we also observed no preferential photo-
addition to cis-1,3-pentadiene over trans-1,3-pentadiene
(Exp. Sect I).
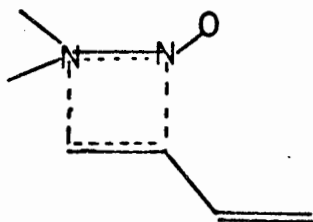
Fig. 28.   Proposed complex leading to the 1,2-addition

of N-nitrosopiperidine to a carbon carbon

double bond
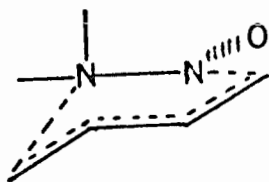
Fig. 29.   Proposed complex leading to 1,4-addition of

N-nitrosopiperidine to a 1,3-diene.

Recent flash photolysis experiments carried out by

M. P. Lau (45) have established that the nitrosamine must be

complexed with the unsaturated hydrocarbon previous to under-

going photoaddition and is also supported by nmr spectroscopy

in which it was shown that the nitrosamine complexes with

π electron cloud systems (46).

The products obtained in the addition to vinylcyclohe-

xene lead us to the assumption that only certain nitrosamine-

diene complexes are formed. The complexes envisaged are shown

in (Figs. 28, 29). The first one (Fig. 28) leads to the 1,2-

adduct I-29; the second one (Fig. 29) leads to the 4,1-adducts

I-30 and I-31. Similar types of complexes have been proposed

for the Cope and Oxy-Cope rearrangements (47). Finally the

quantum yield values for the disappearance of the N-nitrosamine

in the absence and presence of unsaturated hydrocarbons show

values greater than one. Such results indicate that the dis-

appearance of the N-nitrosamine follows a free radical pathway.

This compilation of salient points permits us to sug-

gest a possible mechanism for the photoaddition reaction.

The suggested mechanism follows.

$$\underset{\oplus}{>}\!\!N\text{-NOH} \quad + \quad >\!\!C = C\!\!< \quad \rightleftarrows \quad \left[\; \underset{\oplus}{>}\!\!N - N\!\!=\!\!OH\;\text{---}\; >\!\!C = C\!\!< \right] \quad (1)$$

$$\left[\; \underset{\oplus}{>}\!\!N\text{-NOH}\;\text{----}\; >\!\!C = C\!\!< \right] \quad \rightarrow \quad \begin{array}{c} \underset{\oplus}{>}\!\!N - N\!\!-\!\!OH \\ | \quad\quad | \\ >\!\!C - C\!\!< \end{array} \quad (2)$$

$$\begin{array}{c} \underset{\oplus}{>}\!\!N - N\!\!-\!\!OH \\ | \quad\quad | \\ >\!\!C - \dot{C}\!\!< \end{array} \quad \rightarrow \quad \begin{array}{c} \underset{\oplus}{>}\!\!N\!\!-\!\!-\!\!N\!\!-\!\!OH \\ | \quad\quad | \\ C\;-\;C \end{array} \quad (3)$$

$$\begin{array}{c} \underset{\oplus}{>}\!\!N\!\!-\!\!-\!\!N\!\!-\!\!OH \\ | \quad\quad | \\ >\!\!C - C\!\!< \end{array} \quad \rightarrow \quad \begin{array}{c} >\!\!N\!\!-\!\!H \quad N\!\!=\!\!O \\ \underset{\oplus}{|} \quad\quad | \\ C\;-\;C \end{array} \quad (4)$$

$$(5)$$

$$(6)$$

$$(7)$$
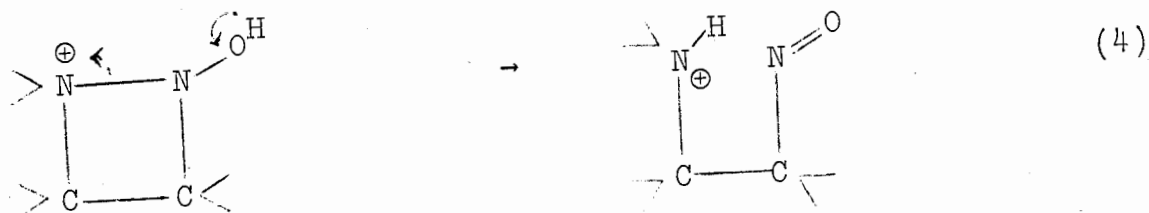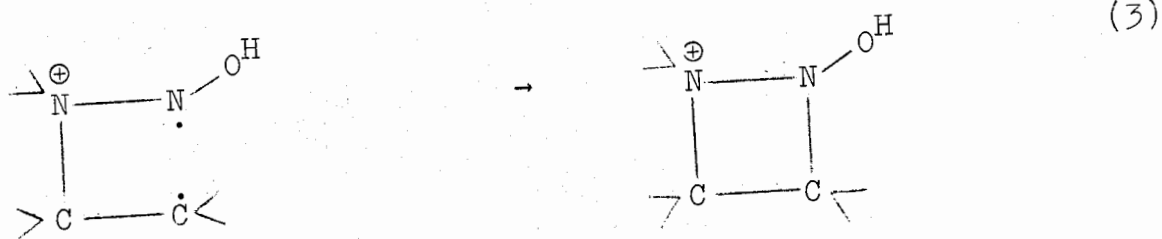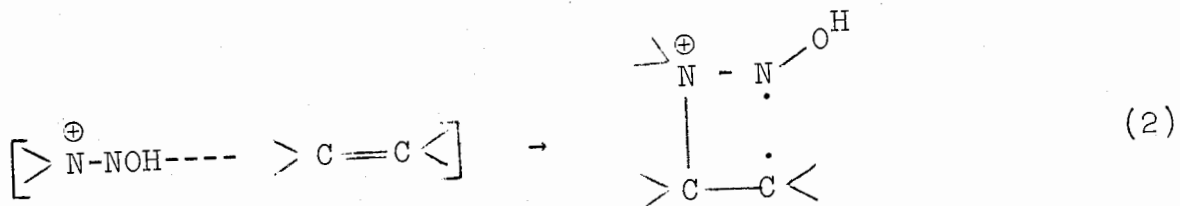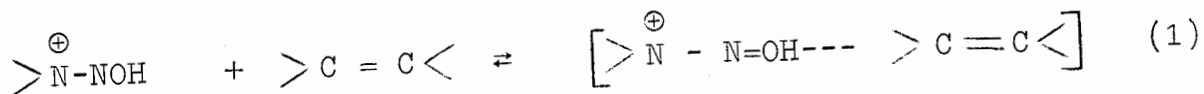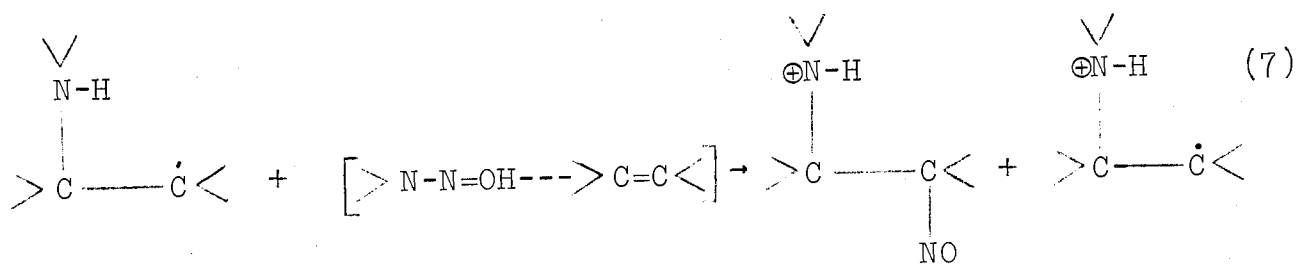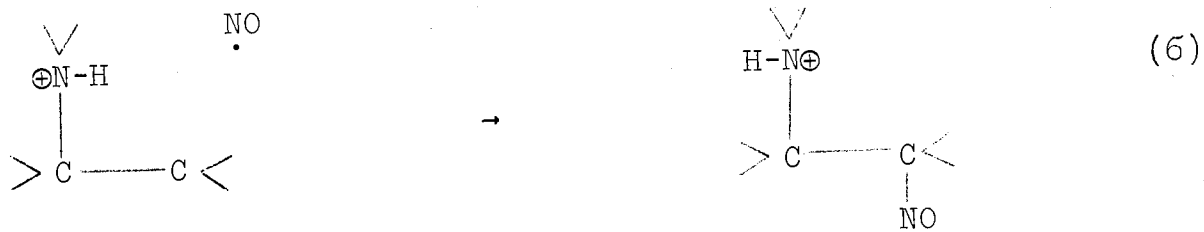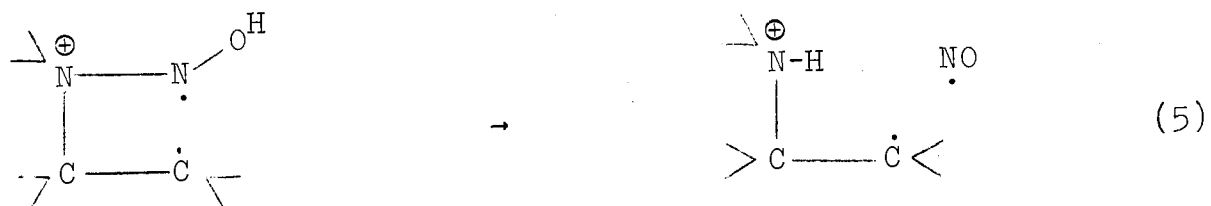
The first step shows the formation of the nitrosamine-olefin complex previous to excitation. The second step is excitation of the complex which leads to a diradical. This diradical may close into a 4 membered ring intermediate, and rearrange to give the c-nitroso intermediate (steps 3, 4), or collapse to give nitric oxide and an alkyl radical (step 5). The alkyl radical and nitric oxide may recombine to give the nitroso compound step (6). The last step involves the abstraction of nitrous oxide from the nitrosamine-olefin complex to give the c-nitroso compound and another alkyl radical which either recombines with nitrous oxide (step 6) or abstracts nitric oxide from the nitrosamine olefin complex (step 7). This step is included in view of the higher than one quantum yield values.

Section II

Although the photoreaction of nitrosamine has been demonstrated, it is still not clear which excited state is responsible for the photoreactions observed. A nitrosamine generally shows a n-π^* band at 340 mu region and a π-π band at 250 mu region; the latter generally tails into the 300 mu region (48). In these photolyses it can be assumed both bands are irradiated. It has been shown by Lau (45) that irradiation of either n-π or π-π^* band does promote the photoaddition reaction. Unfortunately a nitrosamine does not give either fluorescence or phosphorescence. The determination of the lowest singlet and triplet energy therefore must be done by other means.

The failures of N-nitrosopiperidine to isomerise 1,3-pentadiene and cis,cis-1,3-cycloöctadiene are surprising. The reason can be i) that the photoaddition is efficient and rapid from the singlet excited state or ii) that the E_{T_1} and E_{S_1} of nitrosopiperdine are far lower than those of the dienes. The former reason implies that every collision of the excited nitrosamine results in reaction and does so irreversibly.

We have failed to sensitize the photoaddition of N-nitrosopiperidine to a mixture of cis and trans-1,3-penta-

diene with naphthalene. This is not surprising in view of the reported efficiency of the pentadienes to quench the singlet and triplet excited naphthalene molecule (49). However, it was gratifying to find a series of aromatic hydrocarbons that sensitize the photoaddition of nitrosopiperidine to cyclohexene (Table VII). The successful linear correlation of the fluorescence quantum yields with the rate of photosensitization suggests that the photoaddition reaction is related to the singlet state of nitrosopiperidine. Since energy transfer from the singlet state aromatic hydrocarbon to nitrosopiperidine presumably occurs, the E_{S_1} of nitrosopiperidine must be comparable to that of the lowest E_{S_1} of those aromatic hydrocarbons; anthracene has the lowest E_{S_1} (76.4 Kcal/mole). Thus the failure of perylene (E_{S_1} 65 Kcal/mole) (50) to sensitize the photoaddition should be interpreted as the E_{S_1} of nitrosopiperidiene being higher by more than 5 Kcal/mole. It is interesting to point out that perylene quenches the photoaddition of nitrosopiperidine to cyclohexene by 50%, while naphthalene does not quench the photoaddition.

Investigation on photoreduction of N-nitrosopiperidine reveals that acetophenone and triphenylene cannot quench the photoreduction, but naphthalene quenches effectively. Merely from this information it is suspected that E_T of N-nitroso-

piperidine is higher than that of naphthalene (61 Kcal/mole),

if the triplet state of N-nitrosopiperidine is assumed respon-

sible for photoreduction. However on prolongued photolysis

of N-nitrosopiperidine in the presence of naphthalene, it

appears that a reaction is taking place between naphthalene

and N-nitrosopiperidine although the red oil is not characte-

rised. It is therefore premature to conclude that the triplet

state of N-nitrosopiperidine is undergoing photoreduction.

Section III

The photoaddition of N-nitrosopiperidine to anthracene

in ethanol solutions where anthracene absorbed greater than

95% of the incident light should be regarded as a self sensi-

tization by anthracene to give the 1:1 adduct III-1 as the

product. The ability of anthracene to add x-y type addenda

across the 9,10-position such as photodimerization, photo-

cycloaddition of maleic anhydride (51) and photoaddition of

oxygen (52), are well known and extensively investigated. In

the photoaddition of the nitrosamine to anthracene a mineral

acid is required for the photoaddition to take place, indicat-

ing the similarity with the additions of N-nitrosamine to ole-

fins and 1,3-dienes. In this reaction it is also demonstrated

that, in the presence of cyclohexene, the additions of nitroso-

piperidine to both cyclohexene and anthracene take place to

give the 1:1 adducts, III-14 and III-1, suggesting the addi-

tions are triggered by photoexcited nitrosamine. Since in

this photoaddition anthracene absorbs all of the incident

light, it must be concluded that an singlet excited anthracene

molecule transfers its energy to give an excited nitrosamine.

That this energy transfer occurs at the singlet manifold is

discussed in Sect. II.

Scheme 13:

III-1a

III-12

III-11

III-5

III-6
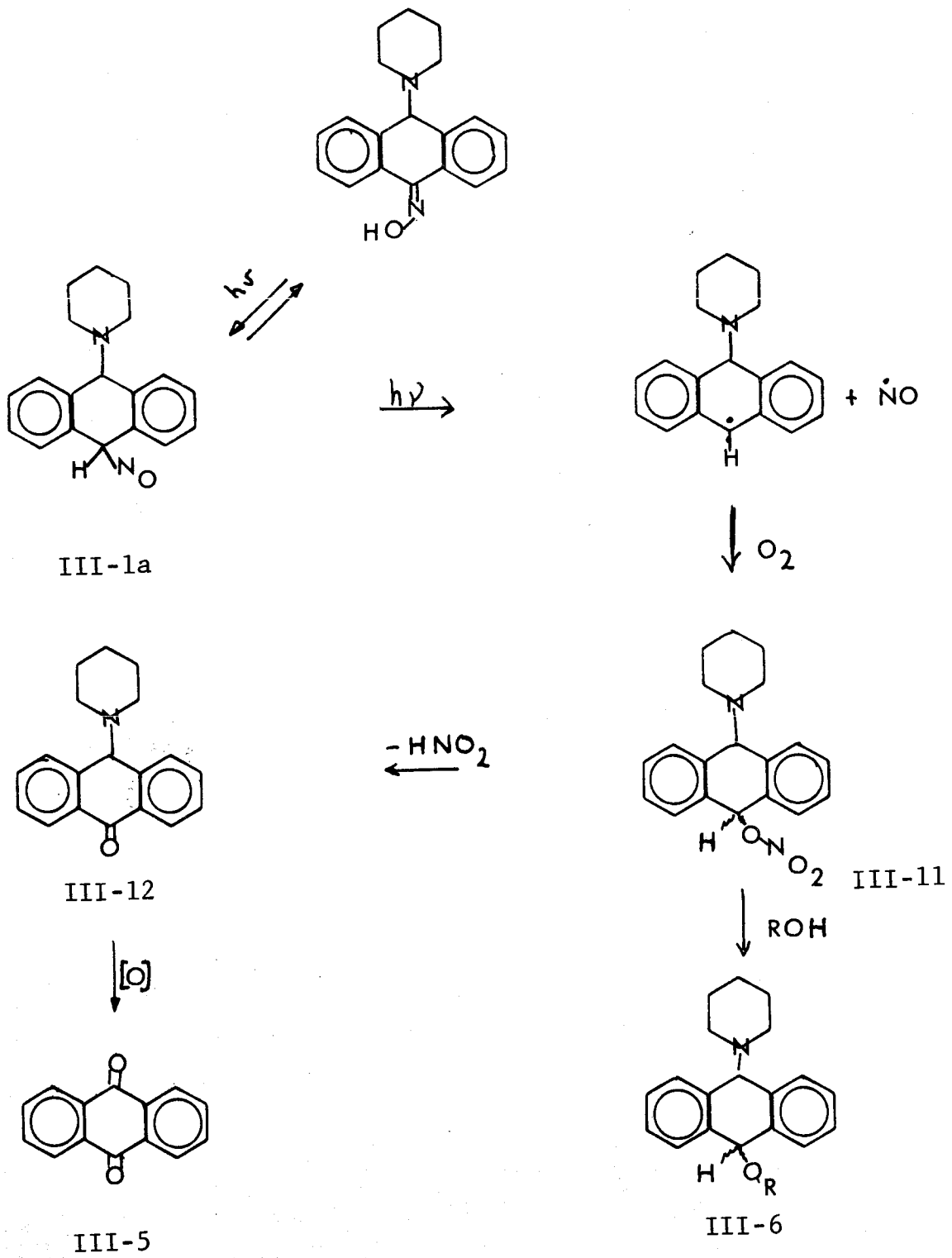
The by-products other than III-3 obtained in the reaction appear to result from secondary reaction of the 1:1 adduct as shown in Scheme 13. It is observed that addition of N-nitrosopiperidine to cyclohexene in the presence of oxygen gives the cis and trans mixture of nitrato compounds III-9, III-10, which indicates that the primary photoadduct, 1-nitroso-2-piperidinocyclohexane is undergoing a photooxidation. Such photooxidation of C-nitroso compounds has been demonstrated in benzene solution (53) and has been proposed to follow the mechanism similar to that shown below.

$$\cdot NO + O_2 \longrightarrow \cdot NO_3$$
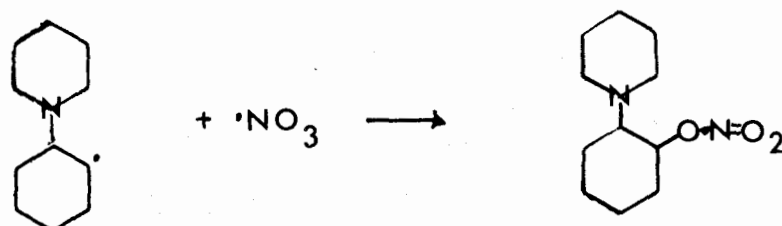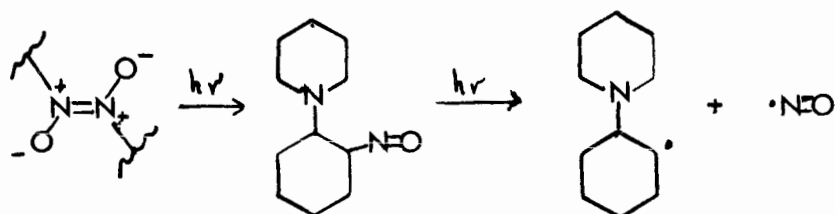
The recombination of nitrogen trioxide and cyclohexane radical
naturally gives the cis and trans compounds (III-9 and III-10).
Thus it is expected that the nitrato intermediate III-11 must
arise from photolysis of the C-nitroso compound III-1a, the
tautomer of III-1, which is oxidized to nitrate III-11 as shown
in Scheme 13. It is assumed that the oxime III-1 and its tau-
tomer III-1a are in equilibrium due to the labile hydrogen in
both structures. Whether the position of the equilibrium is
affected by photoexcitation of the molecules is, however, not
known. The decomposition of III-11 to the ketone III-12 is
similar to the behaviour of III-9, III-10 which give 2-piperi-
dinocyclohexanone upon basification. The oxidation of ketone
III-12 to anthraquinone (III-5) takes place either on standing
or during photolysis, probably caused by air in the former
case or by the nitric oxides present in the photolysate in the
latter case. The formation of III-6, III-7, III-8 may arise
from solvolysis of the nitrato intermediate III-11. It is
worthwhile to comment the formation of these products derived
from the nitrato compound III-11 when the reaction is run
under nitrogen atmosphere. These compounds (III-4 - III-8)
are always obtained even when the commercial nitrogen gas was
carefully scrubbed with either vanadyl sulphate solution
or Fieser's solution. Obviously nitrato compound III-11 is

formed under nitrogen atmosphere. The genesis of this forma-
tion may be attributed to the disproportionation of nitric
oxide when the C-nitroso compound III-1a was homolytically
dissociated. A similar disproportionation has been proposed
(54). However, the fate of the two anthracenyl radicals
remaining from the disproportionation is not known (Scheme 14).

Scheme 14:
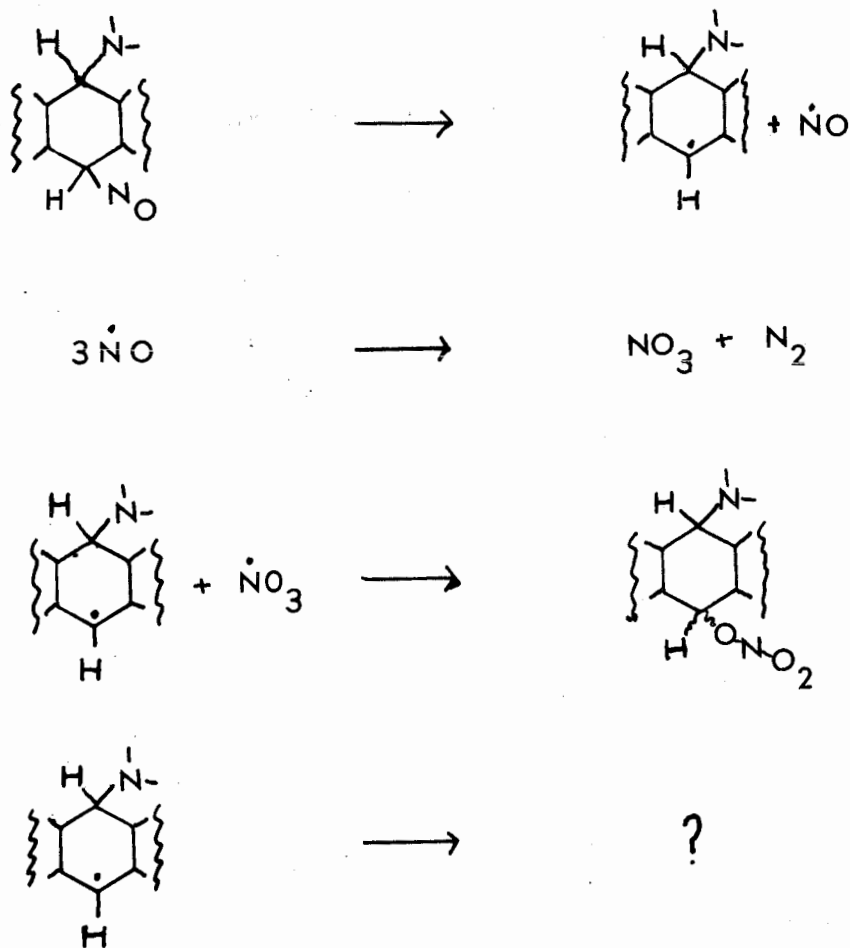
Mechanistically, three excited states of anthracene can be responsible for the photosensitization, namely the S_1 state (76.4 Kcal/mole), the T_2 state (74.4 Kcal/mole) and the T_1 state (42.5 Kcal/mole) (55). The T_1 state may be excluded since the nitrosamine triplet energy appears to be around 58 Kcal/mole (6). The T_2 state of anthracene has been shown to be capable of transfering its energy (55) to olefins. However, since acetophenone (E_T 73.6 Kcal/mole) is unable to sensitize the nitrosamine photoaddition, it can also be disregarded.

The remaining possibility, the singlet energy transfer from anthracene to the nitrosamine was corroborated by carrying the reaction in the presence of bromobenzene. Bromobenzene has been shown to quench the flourescense of anthracene (56, 57). That bromobenzene is not promoted to an excited state in the process, was shown by the lack of isomerization of cis-4-methyl-2-pentene when the latter was included in the reaction mixture. In this connection we have ascertained that photoexcited bromobenzene readily isomerizes cis - 4 - methyl-2-pentene to the trans isomer. The photoreactions carried out in 0.2M and 0.6M bromobenzene solutions showed ca 50% decrease in the formation of III-1, showing that the

singlet excited anthracene molecules are being demoted to the ground state by bromobenzene.

The photoaddition of N-nitrosopiperidine to anthracene in (0.2M) bromobenzene solution containing cyclohexene shows a further drastic reduction in the yield of III-1 but no concurrent increase in the yield of III-14 was observed. When cis-4-methyl-2-pentene is used, however, no such decrease in the yield of III-1 is observed. At present, no definite interpretation can be offered concerning this phenomenon.

With respect to the other aromatic compounds investigated, only acenaphthylene gave the 1:1 adducts III-15 and III-16. Acenaphthaquinone III-18 was obtained as a by-product and most likely arose via the corresponding C-nitrato compound which decomposed in an analogous manner as that proposed for the formation of III-11.

The 1,3-DMA, 1,4-DMA and 1,2-benzanthracene photolyses gave poor yields of basic products, primarily the amino ethers or amino alcohols. The lack of formation of oxime derivatives is ascribed to steric restrictions imposed by flanking methyl or aromatic group in the transition state. Alternatively the same steric effect may prevent the C-nitroso intermediate from tautomerizing to the more stable oxime. The formation of the ethers (III-26, III-28) and alcohols

(III-23 III-24, III-27, III-28) probably follows the same mechanism as proposed for the anthracene case. The low yield of basic products may be due to the formation of red coloration during photolysis which acted as an internal filter.

With regard to pyrene, azulene and phenanthrene, forcing condition had to be used to obtain small yields of basic products. It is quite likely that this is due to the poor reactivity of the aromatic compound to undergo addition reactions.

Experimental

Section I

Microanalyses were performed by Dr. A. Bernhardt, West
Germany. Melting points were determined on a Gallenkamp appa-
ratus and were not corrected. The infrared spectra were recor-
ded as nujol mulls for solid samples and as film for a liquid
sample with either a Unicam SP-200 or a Perkin Elmer model 457.
The ultraviolet spectra were recorded with either a Cary
Model 14 or a Unicam SP-800 recording spectrophotometer. The
nmr spectra were obtained with a Varian A 56/60 instrument
and were reported in (γ) values. Unless otherwise stated,
the nmr spectra were recorded in $CDCl_3$ solution, using tetra-
methylsilane as the internal standard; coupling constants (J)
are given in cycles per second (cps); s, d, d-d, t, 2t, qt,
bm, m, o, designated singlet, doublet, doublet of doublet,
triplet, two triplets, quartet, broad multiplet, multiplet
and octet respectively. Decoupling experiments were perfor-
med with a Varian HA-100 spectrometer. The mass spectral
analyses were performed using a Hitachi-Perkin Elmer model
RMU-6E or an MS-9. The vapour phase chromatographic analyses
were performed on an Aereograph autoprep model 700 using a
(20 ft x 3/8 in., 30% SE-30, chrom W) column, or with a
Varian Aereograph (series 1200) using a (12 ft. x 1/8 in.,

on firebrick) column, or a (6 ft. x 1/8 in., 20% tris-cyano-
ethoxypropane (TCEP), on chrom W) column. The separations by
column chromatography were performed using basic alumina
Brockman, Activity I (80-200 mesh) or silicic acid Mallinckrodt,
analytical reagent (100 mesh). Thin layer chromatography (tlc)
analyses were performed on (20 cm x 5 cm) plates (0.3mm thick)
using Camag Aluminiumoxid DS-5.

Material

The CP olefins were used as supplied without further puri-
fication. Cyclopentadiene (bp 42°) was distilled before use.
Cyclooctadiene was also distilled and the fraction of bp 82-83°
was used for the experiment. The cis-1,3-pentadiene was
obtained by treating a mixture of cis-and trans-1,3-pentadiene
with 1.2 equivalents of maleic anhydride. The cis-1,3-
pentadiene was recovered by distillation and the fraction of
bp 40° was used. The purity of this fraction was established
by vpc (20 ft. x 3/8 in., 30% SE-30, chrom W, 88 ml of He/min,
22°C) to be 99.99% pure cis 1,3-pentadiene.

The 1-vinylcyclohexene was prepared according to the pro-
cedure described (20) and distilled:bp 143-144, lit (20)
144-145° . The nmr spectrum showed signals at Υ 9.0 (t) due
to the presence of x-ethylcyclohexene. This minor component
was present in 8-10% by nmr analysis.

The analytical reagent grade solvents were used without further purification. For chromatography on silicic acid, Shawnigan, reagent grade, $CHCl_3$ (0.75% EtOH) or "Macco" $CHCl_3$ (0.75% EtOH) were used.

The nitrosamines were prepared according to the procedure described previously (2) and distilled. The naphthalene, (reagent grade, Allied Chemical) was sublimed before use: mp 79-80°. Anthracene (reagent grade, Matheson, Coleman and Bell) was sublimed: mp 215-217°, Acetophenone (BDH, reagent grade) was distilled at reduced pressure (18 mm Hg) and the fraction of 96-97° was used for the experiments.

1,4-Dimethylanthracene was prepared by reacting phthalic anhydride with p-xylene to give o-xyloylbenzoic acid. This acid was then cyclized with concentrated sulphuric acid to the 1,4 dimethylanthraquinone (58). The anthraquinone was then reduced to the 1,4-dimethylanthracene with zinc and KOH (59). The 1,4-dimethylanthracene was recrystalized three times from methanol and the crystals melting at 68-70° were used. The 1,3-dimethylanthracene was prepared from phthalic anhydride and m-xylene in an analogous manner, and recrystallized three times from methanol: mp 74.5-76°.

Perylene: mp 276-278°, (Aldrich, puriss.) was used as supplied without further purification. Triphenylene was chro-

matographed on alumina (30g). Elution with petroleum ether

afford white, sharp melting crystals: mp 193.5-195°

lit (60) 199° . 1,2-Benzanthracene (Aldrich, reagent) was

recrystalized once and sublimed to give pale yellow crystals:

mp 158-159° lit (61) 162° . Bromobenzene (Matheson, Coleman

and Bell, reagent) was distilled and the fraction of 156-157°

was collected. Benzonitrile (Eastman Kodak, reagent, aniline

free) was used as supplied. Zinc powder (Allied Chemical,

technical) was activated with 2% $CuSO_4$ solution before use.

Lamp sources

The solutions were irradiated with an RPR 3000Å, or

RPR 3500Å, or 200 watt Hanovia source (type 654A36) or a

450 watt Hanovia (type 679A36) source. For the quantum yield

measurements a PEK (model 911-Q) 100 watt lamp whose emission

was filtered through a corning filter #5030, maximum trans-

mittance at 366 mu, was used.

General Procedure for the Photolysis of N-nitrosopiperi-

dine in the presence of a 1,3-diene.

The photolyses were carried out in specially made pyrex

vessels (Figure 30). The vessels were equipped with a con-

denser at the upper end and an inlet at the lower end of the

cell to introduce the inert gas. The photocell was then

cold water
inlet

water outlet

gas
inlet

Hanovia
654A36
lamp

photolysate

cold
finger

magnet bar

magnetic
stirrer
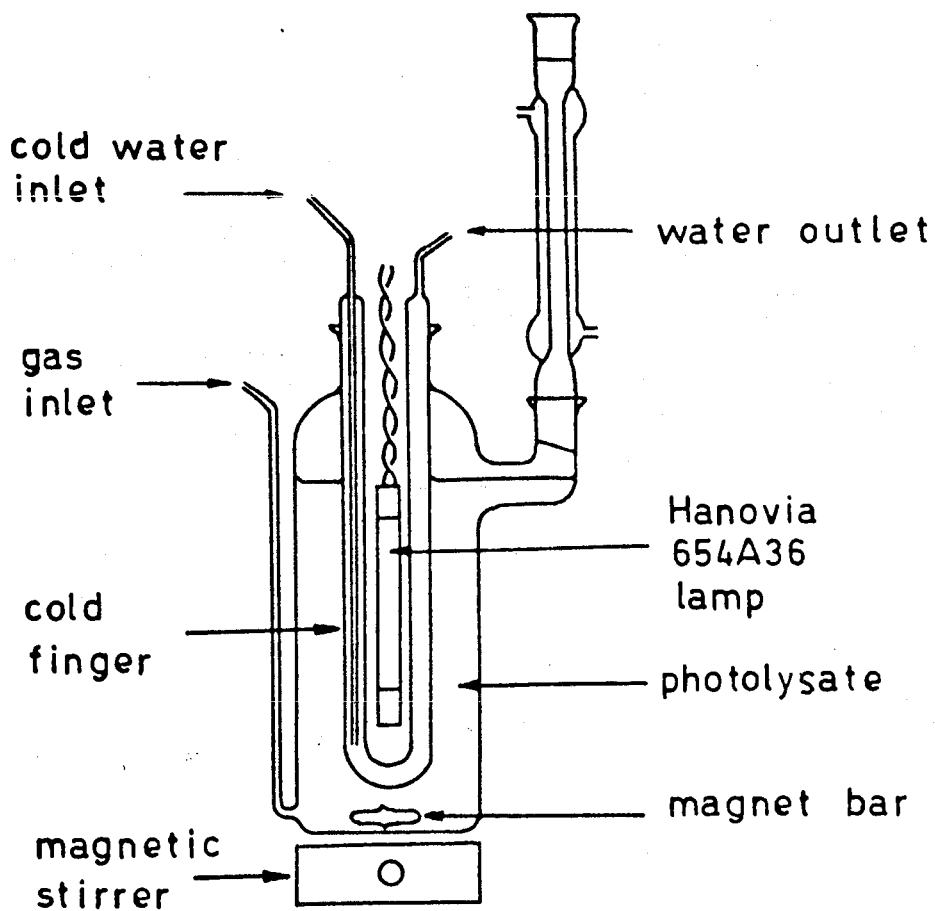
Fig.30. The photolysis apparatus

immersed in an ice bath, and the cell was filled to about
three quarters of its volume with methanol. The solution
was stirred while a stream of nitrogen was introduced. After
about fifteen minutes, the stirring and the flow of nitrogen
were reduced to a moderate rate and the reagents for the reac-
tion were then introduced. The photocell was then filled to
its full volume.

Any traces of oxygen or hydrogen sulphide which could
be present in the nitrogen gas were removed by scrubbing the
inert gas through Fieser's solution followed by (5%) lead
acetate solution. The gas was then dried by passing through
concentrated sulfuric acid before being allowed to enter the
photocell. The solutions were then irradiated by placing a
light source in the hole of the photocell. The optical den-
sity of the nitrosamine was measured at 350 mu by pipetting
out an aliquot portion of the photolysate at suitable inter-
vals. This aliquot was properly diluted (usually 1/10 dilu-
tion) for spectroscopic measurement in the 250-400 mu region.
The decrease in this absorption maximum (350 mu) showed zero
order kinetics and the solution was irradiated until this
absorption had disappeared. The solvent of the photolysate
was then removed under vacuum using a rotary evaporator and
the residue was diluted with water. This acidic aqueous

TABLE IX

Reagents, quantities and conditions used in the photolyses of N-nitrosopiperidine
in the presence of 1,3-dienes

olefin	moles	N-nitrosopiperidine moles			Methanol mls	lamp*	Irrad. time min.
butadiene	5.8 (0.1)	5.70 (0.05)	(5 mls,	0.06)	200	-2-	105
cis-1,3-pentadiene	4.0 (0.06)	5.70 (0.05)	(5 mls,	0.06)	200	-3-	50
trans-1,3-pentadiene	3.74 (0.055)	5.70 (0.05)	(5 mls,	0.06)	200	-3-	70
cis,trans-2,4-hexadiene	4.1 (0.06)	4.56 (0.04)	(4 mls,	0.048)	200	-2-	100
cyclopentadiene	6.64 (0.1)	5.70 (0.05)	(5 mls,	0.06)	300	-2-	100
1,3-cyclohexadiene	8.0 (0.1)	5.70 (0.05)	(5 mls,	0.06)	200	-3-	45
1,3-cyclooctadiene	10.8 (0.1)	5.70 (0.05)	(5 mls,	0.06)	200	-2-	120
1-vinylcyclohexene	2.5 (0.02)	2.3 (0.02)	(2 mls,	0.024)	200	-1-	480

*lamp 1, RPR 3500Å

lamp 2, Hanovia 200 watt

lamp 3, Hanovia 450 watt

TABLE X

Products obtained from the photolyses of N-nitrosopiperidine in the presence of the various 1,3-dienes

olefin	1,2-syn (%)	1,2-anti (%)	1,4-adduct (%)	4,3-syn	4,3-anti	4,1-adduct	ketone
butadiene	10%	16%	57%	-	-	-	-
cis-1,3-pentadiene	2-3%	7-8%	72%	(trace)	(trace)	12%	-
trans-1,3-pentadiene	10%	14-17%	60%	(trace)	(trace)	4.5%	-
cis, trans-2,4-hexadiene	3%	6-8%	85%	-	-	-	2%
cyclopentadiene	7%	18%	56%	-	-	-	-
1,3-cyclohexadiene	2%	2%	61%	-	-	-	-
1,3-cyclöoctadiene	(trace)	(trace)	-	-	-	-	-
1-vinylcyclohexene	-	13%	-	-	-	27%	-

solution was then extracted with an organic solvent (50 ml x 3)

to give a neutral fraction. The aqueous solution was then

basified to pH 9-10 with a saturated K_2CO_3 solution and extrac-

ted again with an organic solvent to afford a basic fraction.

The organic extracts were washed with water (20 ml x 3), dried

($MgSO_4$) and evaporated under vacuum. The residues were then

examined by thin layer chromatography (tlc), nmr, and ir spec-

troscopy. The separation of its components was done by chro-

matography on basic alumina or on silicic acid column. The

reaction conditions and yields of products are summarized in

Tables I X, X.

1. Photoaddition of N-nitrosopiperidine to 1,3-dienes.

A. To 1,3-cyclooctadiene.

N-nitrosopiperidine (5.70g, 0.05 moles), cis,cis-1,3-

cyclooctadiene (18.8g, 0.1 moles) and concentrated hydroch-

loric acid (5 ml, 0.06 moles) were dissolved in methanol

(200 ml). This solution was photolyzed as described with a

200 watt Hanovia lamp for 120 minutes until the absorption

maxima at 350 mu had completely disappeared. The decrease

in the optical density of the nitrosamine showed zero order

kinetics up to 85% completion. The solvent was then removed

under vacuum and the residue was treated with water (50 ml).

The aqueous solution was extracted with ether (50 ml x 3).

The ether extract was washed with water and dried ($MgSO_4$).

Evaporation of the ether under vacuum gave an oil (114 mg)

which contained N-nitrosopiperidine and cycloöctadiene by

ir and nmr spectral analysis. The aqueous acidic layer was

basified with a saturated K_2CO_3 solution to pH 9-10 and extrac-

ted with ether (50 ml x 3). The ether was removed under vacuum

to give a mixture of oil and crystals (13.3g). This residue

was treated with cyclohexane (25 ml) and the mixture filtered

to give white crystals (5.4g): mp 130-140°. These crystals

were recrystallized from 2-propanol three times and further

sublimed to give an analytical sample of syn-4-piperidino-2-

cycloöcten-1-one oxime (I-1): mp 153-156°; ir 3080, 1615,

1100, 1000-900, 870, 755; nmr (pyridine) Υ 3.54 (d, 1H,

J=12.5cps), Υ 4.27 (d-d), 1H, J=12.5cps, J=7cps), Υ 6.34

(m,1H), Υ 7.61 (m,4H), Υ 8.58 (m,14H); mass spectrum (80eV)

m/e (rel intensity) 204 (9), 186 (32), 119 (53), 84 (100);

Anal. Calcd for $C_{13}H_{22}N_2O$: C,70.23; H,9.97; N,12.60. Found:

C,70.33; H,10.08; N,12.75.

The cyclohexane mother liquor was evaporated to dryness

to give a resin (4.76g), a part of which (1.5g) was chromato-

graphed on silicic acid (40g). The first compound was eluted

with 2% methanol in $CHCl_3$ as an oil (23 mg). This oil showed

as a single spot on a tlc plate and could be crystallized from

2-propanol to give white crystals (5 mg) of <u>syn</u>-8-piperidino-2-cycloöcten-1-one oxime (I-2): mp 111-115°; ir 3200, 1620, 1100, 1090, 980, 960, 940, 760, 740, 710; mass spectrum 80 (eV) <u>m/e</u> (rel intensity) 222 (0.5), 204 (31), 164 (30), 124 (100).

The next compound was eluted with 3% methanol in $CHCl_3$ as an oil (50 mg). This oil was contaminated by I-2 and was rechromatographed again on silicic acid (2g) to afford pure 4-piperidino-2-cycloöcten-1-one (I-3, 15 mg) as an oil (tlc single spot): ir 3000, 1665, 1460, 1100, 760; nmr Υ3.71 (d-d, 1H, J=10cps, J=5cps), Υ 3.98 (d, 1H, J=10cps), Υ 6.38 (m, 1H, J=5cps), Υ 7.5 (m, 6H), Υ 8.50 (m, 12H); mass spectrum (80eV) <u>m/e</u> (rel intensity) 207 (10), 178 (25), 150 (100).

The next fraction (362 mg), eluted with 3% methanol in $CHCl_3$ was rechromatographed on silicic acid to afford a fraction (125 mg, tlc one spot) which was crystallized from 2-propanol to give white crystals (35 mg) of <u>anti</u>-8-piperidino-2-cycloöcten-1-one oxime (I-4): mp 162-164°; ir 3080, 1660, 1620, 1080, 980, 960, 940, 870, 858, 760, 750, 730; nmr (pyridine) Υ3.84 (d, 1H, J=12cps), Υ4.18 (m, 1H), Υ6.57 (m, 1H), Υ 7.5 (m, 4H), Υ 7.9-8.6 (bm, 14H); mass spectrum (80eV) <u>m/e</u> (rel intensity) 222 (1), 204 (22), 164 (100).

The syn and anti mixture of I-1 and I-5 (1.2g) was elu-
ted with 4-10% methanol in CHCl$_3$. The syn and anti mixture
of these 1,4 adducts, ir 3300, 1630, 1100, 1000-900 could not
be separated by rechromatography or recrystallization. The
nmr of this mixture showed two different ABX patterns; the
signals due to the syn isomer I-1 at 𝜏 3.25 (d, 1H, J=12cps)
𝜏 4.28 (qt, 1H, J=13cps, J=6cps), 𝜏 6.5 (m, 1H) and those due
to the anti isomer I-5 at 𝜏 3.79 (d, 1H, J=12.5 cps), 𝜏 4.12
(qt, 1H, J=12.5cps, J=6cps), 𝜏 6.5 (m, 1H). In addition the
signals at 𝜏 7.5 (m, 4H), 𝜏 8.5 (m, 12H) were also observed.

B. To 1,3-cyclohexadiene

The nitrosamine (5.70g, 0.05 moles), 1,3-cyclohexadiene
(8.0g, 0.1 moles) and concentrated hydrochloric acid (5 ml,
0.06 moles) were dissolved in methanol (200 ml). The solu-
tion was irradiated with the 450 watt Hanovia lamp until the
nitrosamine absorption at 350 mu had disappeared (45 min).
Upon evaporation of the methanol to a small volume, crystals
appeared which were filtered (4.5g). These crystals (2g)
were dissolved in water and the solution was basified with a
saturated K$_2$CO$_3$ solution to pH 9-10. The solution was then
extracted with CHCl$_3$ (50 ml x 3) to give an oil (1.6g). This
oil when treated with 2-propanol gave white powdery crystals
of 4-piperidino-2-cyclohexen-1-one oxime (1.2g, I-6): mp

129-132°. The crystals were recrystallized 5 times from
2-propanol to afford an analytical sample (single spot on
tlc): mp 139-140°; ir 3150, 1618, 1166, 1120, 1050-880 mul-
tiple peaks, 815, 740, 730; nmr (pyridine) Υ3.55 A part of
AB qt (d, 1H, J=10cps), Υ3.92 B part of AB qt (d, 1H,
J=10cps), Υ6.50-6.78 (m, 2H), Υ7.60 (m, 4H), Υ7.96-8.25
(m, 3H), Υ8.61 (m, 6H); nmr 100 Mc (pyridine) Υ3.55 (o, 1H,
J=10cps, 2.5 cps and 1 cps) Υ3.80-3.86 (o, 1H, J=10 cps,
= 2.5 cps and 4 cps), multiplet at Υ6.50-6.78 (d of t, 1H,
J=17 and 4 cps); Anal. Calcd for $C_{11}H_{18}N_2O$:C, 68.01; H,
9.34; N, 14.42. Found: C, 68.13; H, 9.12; N, 14.01.

The acidic aqueous layer from photolysis was basified
with a saturated K_2CO_3 solution to pH 9-10 and extracted
with $CHCl_3$ (50 ml x 3) to give a resin (2.56g). This resin,
and the mother liquour which gave the crystals of I-6 were
combined and treated with 2-propanol to give white crystals
(1.26g) which by tlc analysis were shown to be identical
with the analytical sample of I-6. The mother liquour was
evaporated to dryness to give a resin (2.0g). This resin
was chromatographed on silicic acid (35g). The first fraction
(310 mg) was eluted with $CHCl_3$ and was shown to contain a 1:1
mixture of the nitrosamine and syn-6-piperidino-2- cyclohexen-
1-one oxime (I-7). This fraction was treated with petroleum

ether to give pale yellow crystals of I-7 (35 mg): mp
108-111°, which showed a single spot on tlc. They were
sublimed (90°/0.1 mm Hg) to give white crystals: mp 111.5-
113.5°; ir 3130, 1635, 1095, 998, 970, 958, 943, 920, 870,
790, 754; nmr Υ -4.1 (D_2O exchangeable) (b, 1H), Υ 3.9 (m, 2H),
Υ 5.95 (m, 1H), Υ 7.3 (m, 4H), Υ 7.9 (bm, 4H), Υ 8.4 (m, 6H);
nmr (pyridine) 100 Mc (15) Υ 3.63 (d, 1H, J=10 cps), Υ 3.98
(2t, 1H, J=10 cps, J=4.5 cps), Υ 5.92 (d-d, 1H, J=5 cps,
J=3.2 cps).

Continued elution with 1-4% methanol in $CHCl_3$ gave crude
anti-6-piperidino-2-cyclohexen-1-one oxime (I-8, 200 mg) con-
taminated with I-7 by tlc analysis. This mixture was rechro-
matographed on silicic acid (3 g) to afford a pure fraction
of I-8 (39 mg, tlc single spot) which was sublimed (100°/0.1
mm Hg) to give white crystals: mp 132-134°; ir 3290, 1638,
1100, 985, 978, 937, 778; nmr Υ 2.53 (b, 1H, D_2O exchangeable),
Υ 3.28 (d, 1H, J=10 cps), Υ 3.77 (2t, 1H, J=10 cps, J=4 cps),
Υ 6.98 (d-d, 1H, J=5.5 cps, J=4 cps), Υ 7.49 (m, 4H), Υ 7.77-
8.03 (m, 4H), Υ 8.48 (m, 6H); nmr 100 Mc (pyridine) Υ 3.29 (qt,
1H, J=10.5 cps, J=3.5 cps), Υ 3.77 (2t, 1H, J=10.5 cps,
J=4 cps), Υ 6.95 (d-d, 1H, J=5.5 cps, J=3.5 cps).

C. To cyclopentadiene.

N-Nitrosopiperidine (5.70 g, 0.05 moles), freshly dis-
tilled cyclopentadiene (6.64 g, 0.1 moles) and concentrated
hydrochloric acid (5 ml, 0.06 moles) were dissolved in metha-
nol (300 ml). This solution was photolyzed as described with
a 200 watt Hanovia lamp under a nitrogen atmosphere for one
hour and forty minutes. A new absorption at 300 mu reached
a maximum absorption after 3/4 of an hour of irradiation and
gradually disappeared after 1/2 hour of irradiation. The
407 mu absorption reached a maximum height at the end of the
irradiation but gradually disappeared upon leaving the solu-
tion in the dark. The methanol was then removed under vacuum
and treated with water (50 ml). The neutral fraction (114 mg)
was extracted with ether (50 ml x 3) and was shown to contain
N-nitrosopiperidine and cyclopentadiene by ir and nmr spectral
analysis. The aqueous solution was basified with K_2CO_3 and
extracted with CH_2Cl_2 (50 ml x 4) and was worked up in the
usual manner to give a thick oil (9.37 g). One gram of this
oil was chromatographed on alumina (30 g) with benzene as
eluant. The fraction eluted with 50% benzene in $CHCl_3$ gave a
solid (80 mg) which was recrystallized from cyclohexane twice
to give syn-5-piperidino-2-cyclopenten-1-one oxime (I-9):
mp 103-105°; ir 3200, 1000-905 (multiple peaks), 878, 750,

738, nmr Υ 0.34 (b, 1H, D_2O exchangeable), Υ 3.73 (m, 2H),

Υ 5.72 (d-d, 1H, J=7 cps, J=4 cps), Υ 7.47 (m, 6H), Υ 8.46

(m, 6H). Further elution showed no separation and the com-

pounds were stripped off from the column with methanol.

Another gram of the basic crude mixture was chromatographed

on silicic acid (30 g). Fifty ml fractions were collected

in succession. The fractions 5 and 6 eluted with 3% methanol

in $CHCl_3$ gave I-9 (38 mg) as shown by tlc analysis. Fraction

7 gave an oil (71 mg) which was crystallized from 2-propanol

to give white crystals of anti-5-piperidino-2-cyclopentene-1-

one oxime (I-10): mp 130-132°; ir 3200, 1630, 1100-918 (mul-

tiple peaks), 870, 750, 720, 658; nmr Υ 0.97 (b, 1H, D_2O

exchangeable), Υ 3.43 (qt, 2H, J=5 cps), Υ 6.09 (d-d, 1H,

J=6 cps, J=4 cps), Υ 7.4 (bm, 6H), Υ 8.48 (bm, 6H).

The following fractions eluted with 4% methanol in $CHCl_3$

gave a solid (800 mg) which was recrystallized from a solution

of benzene-petroleum ether to give 4-piperidino-2-cyclopenten-

1-one oxime (I-11, tlc single spot): mp 101-104°; ir 3200,

1648, 1000, 960, 950, 800; nmr Υ 1.6 (b, 1H, D_2O exchangeable),

Υ 3.6 (m, 2H, J=5 cps, J=1.5 cps), Υ 6.0 (m, 1H), Υ 7.36

(d, 2H, J=5 cps), Υ 7.56 (m, 4H), Υ 8.54 (m, 6H); Anal. Calcd

for $C_{10}H_{16}N_2O$:C, 66.62; H, 8.95; N, 15.55. Found: C, 66.52;

H, 8.98; N, 15.41.

D. To cis-1,3-pentadiene.

The nitrosamine (5.70 g, 0.05 moles), cis-1,3-pentadiene
(4.0 g, 0.06 moles) and concentrated hydrochloric acid (5 ml,
0.06 moles) were dissolved in methanol (200 ml). This solu-
tion was irradiated with 450 watt Hanovia lamp (70 min). The
solvent was removed under vacuum at a water bath temperature
of 40°. The usual work up gave a neutral fraction from ether
which contained, N-nitrosopiperidine (116 mg) as shown by ir
and nmr analysis. The basic fraction was extracted with $CHCl_3$
(50 ml x 3) to give a mixture of crystals and oil (9.7 g). To
this mixture was added some ether and the mixture was cooled.
Filtration of the mixture gave nice white crystals (3.73 g):
mp 132-136°. These crystals were recrystallized from a mixture
of benzene-skelly solve B three times to afford 5-piperidino-
trans-3-penten-2-one oxime (I-16): mp 141-142°; ir 3200, 1620,
1092, 1010-895 (multiple peaks), 763; nmr Ƭ 0.0 (b, 1H, D_2O
exchangeable), Ƭ 3.82 (m, 2H), Ƭ 6.92 (m, 2H), Ƭ 7.59 (m, 4H),
Ƭ 8.05 (s, 3H), Ƭ 8.50 (m, 6H); nmr (pyridine) ABX_2 pattern)
Ƭ 3.38 (d, 1H, J=16 cps), Ƭ 3.93 (2t, 1H, J=16 cps, J=6 cps),
Ƭ 6.96 (d, 2H, J=6 cps), Ƭ 7.66 (m, 4H), Ƭ 7.87 (s, 3H), Ƭ 8.58
(m, 6H); Anal. Calcd for $C_{10}H_{18}N_2O$: C, 65.90; H, 9.95;
N, 15.37. Found: C, 65.62; H, 9.85; N, 15.68.

The mother liquour was evaporated to dryness to give a mixture of crystals and oil (5.95 g). This mixture was chromatographed on silicic acid (60 g). The first six fractions eluted with 0-3% methanol in $CHCl_3$ (600 ml) gave Fraction A as an oil (360 mg). Next six fractions eluted with 4% methanol in $CHCl_3$ gave the only fraction B, (580 mg). Eluting with 6% methanol in $CHCl_3$ gave fraction C as a resin (908 mg). With 8% methanol in $CHCl_3$ an oil (442 mg) and fraction D with 20% methanol in $CHCl_3$ were eluted.

Fraction A showed one predominant spot at Rf 0.3 and two smaller spots at Rf 0.6. The oil was rechromatographed on silicic acid (5 g) giving an oil (109 mg) as the first fraction eluted with $CHCl_3$. The nmr spectrum showed this oil to be mostly N-nitrosopiperidine and another compound. This oil was then distilled (110°/0.1 mm Hg) to remove the more volatile nitrosamine giving a colorless resinous liquid (30 mg) of syn-4-piperidino-1-penten-3-one oxime (I-18): ir 3300, 1660, 1280, 1260, 1100, 995, 940; nmr Υ 3.74 (qt, 1H, J=17 cps, J=11 cps), Υ 4.70 (qt, 1H, J=17 cps, J=8 cps), Υ 4.8 (d, 1H, J=11 cps), Υ 6.68 (qt, 1H, J=7 cps), Υ 8.72 (d, 3H, J=7 cps); mass spectrum (80eV) m/e (rel intensity) 182 (6.2), 112 (88), 98 (90), 84 (100), 41 (92). The third fraction from this chromatograph gave an oil (27 mg) which showed a single spot

on a tlc plate. This oil was distilled (100°/0.1 mm Hg) to afford a colorless oil identified as syn-1-piperidino-cis-3-penten-2-one oxime (I-19): ir 3300, 1640, 1110, 1000-900 (multiple peaks); nmr Υ 3.69 (d-d, 1H, J=12.5 cps, J=1 cps), Υ 4.2 (d-d, 1H, J=12.5 cps, J=7 cps), Υ 6.41 (s, 2H), Υ 7.54 (m, 4H), Υ 7.91 (d-d, 3H, J=7 cps, J=1 cps); mass spectrum (80eV) m/e (rel intensity) 195 (44), 182 (3), 98 (100).

Fraction B consisted predominantly of a new compound as shown by tlc, and was rechromatographed on silicic acid (10g). On eluting with 1% methanol in $CHCl_3$ an oil (230 mg tlc single spot) was obtained which was distilled in small scale (90°/0.2 mm Hg) to give anti-1-piperidino-cis-3-penten-2-one oxime (I-20): ir 3350, 1643, 1459, 1370, 1300, 1270, 1110, 1008, 985, 940, 860, 760; nmr Υ 0.9 (b, 1H, D_2O exchangeable), Υ 3.97 (d, 1H), Υ 4.21 (qt, 1H), Υ 6.85 (s, 2H), Υ 7.61 (m, 4H), Υ 8.23 (d, 3H), Υ 8.53 (m, 6H); nmr (pyridine) Υ 3.48 (d-d, 1H, J=12 cps, J=1 cps), Υ 4.17 (d-d, 1H, J=12 cps, J=7 cps), Υ 6.70 (s, 2H), Υ 7.61 (m, 4H), Υ 7.12 (d-d, 3H, J=7 cps, J-1 cps), Υ 7.64 (m, 6H); mass spectrum (20eV) m/e (rel intensity 182 (2), 164 (26), 98 (100).

Fraction C showed one predominant spot on tlc analysis which corresponded to the 1,4-adduct I-16: nmr Υ 3.9 (m, 2H), Υ 6.9 (m, 2H), Υ 7.6 (m, 4H), Υ 8.0 (s, 2H), Υ 8.5 (m, 6H). In

addition another minor spot could be detected by tlc which ran slightly ahead but superimposed on the spot of the 1,4-adduct. This spot contributed signals at Υ3.55 (qt, J=16 cps, J=7 cps), Υ4.1 (d, J=7 cps), Υ8.7 (d, J=6 cps) to the nmr spectrum of the mixture. This minor compound is probably <u>anti</u>-2-piperidino-4-penten-3-one oxime (I-21).

Fraction <u>D</u> consisted of a mixture of I-16 and another compound which on the tlc showed an additional spot beside the spot of I-16. The nmr of this mixture showed in addition to the signals typical of I-16 at Υ4.0 (m), Υ7.5 (m, 4H), Υ8.03 (s, 3H), Υ8.5 (m), signals at Υ2.3 (d, 1H, J=9 cps), Υ4.0 (m, superimposed with the olefinic proton signals of I-12), and Υ8.78 (d, 3H). The ratio of the integration for the signals at Υ8.03 and Υ8.78 was 15:38, respectively, which indicated that this compound is about 70% (38:53) of the total mixture. This fraction was recrystallized from 2-propanol and the crystals were examined by nmr. The same ratio for the signals at Υ8.03 and Υ8.78 was observed (15:38). On the basis of nmr spectral evidence this new compound is assigned to be 4-piperidino-<u>trans</u>-2-pentenal oxime (I-17). The % yield of compound I-17 was estimated by nmr analysis to be 12%.

E. To trans-1,3-pentadiene.

The photolysis was carried out as previously described.
The quantities of starting materials appear in Table IX. .
The reaction was worked up in the usual manner. The acidic
ether extract gave a crude oil (36 mg) which was not investi-
gated further. The basic extract was obtained by extracting
with CHCl$_3$ (50 ml x 3) which upon evaporation of the solvent
gave a resin (9.3 g). This resin was treated with ether to
give crystals (8.6 g); superimposable ir and nmr with those
of I-16. The mother liquour was evaporated down to give a
resin (5.29 g) which was chromatographed on silicic acid
(60 g). The first compound eluted with CHCl$_3$ (100 ml) was
a solid (670 mg) which showed to be a single spot by tlc
analysis and was recrystalized from cyclohexane to give syn-
1-piperidino-trans-3-penten-2-one oxime (I-22, 360 mg):
mp 96-97.5; ir 3180, 1650, 1009, 1005-900 (multiple peaks),
863, 790; nmr Υ-0.9 (b, 1H), Υ3.96 (m, 2H), Υ 6.65 (s, 2H),
Υ 7.60 (m, 4H), Υ 8.25, (d, 3H, J=5 cps), Υ 8.54 (m, 6H);
nmr (benzene-d$_6$) ABX$_3$ pattern Υ 3.63 (d, 1H, J=16 cps), Υ 4.0
(2 qt, 1H, J=16 cps, J=6 cps), Υ 8.38 (d, 3H, J=6 cps); Anal.
Calcd for C$_{10}$H$_{18}$N$_2$O: C, 65.90; H, 9.95; N, 15.37. Found: C,
65.90; H, 9.73; N, 15.19.

The next fraction eluted with 2% methanol in $CHCl_3$ was

an oil (1.4 g) which could be crystallized from petroleum ether

to give white crystals (350 mg, tlc single spot): mp 72-73.5°.

They were sublimed (70°/0.2mm Hg) to give <u>anti</u>-1-piperidino-

<u>trans</u>-3-penten-2-one oxime (I-23): mp 72-73.5°; ir 3250, 1640,

1113, 1118, 1000-940 (multiple peaks), 760; nmr 𝜏0.9 (b, 1H,

D_2O exchangeable), 𝜏3.36 (m, 2H), 𝜏6.87 (s, 2H), 𝜏7.65 (m, 4H)

𝜏8.18 (d, 3H, J=6 cps), 𝜏8.57 (m, 6H); nmr (benzene-d_6) ABX_3

pattern 𝜏3.0 (d-d, 1H, J=16 cps, J=1 cps), 𝜏3.5 (2 qt, 1H,

J=16 cps, J=6 cps), 𝜏8.42 (qt, 3H, J=6 cps, J=1 cps). The

mother liquour from the recrystallizations were combined to

give a residue. This residue was slightly contaminated by

I-22 showing signals at 𝜏2.8 and 𝜏6.6. This residue was sub-

jected to the amino group assisted cleavage.

Continued elution with 2% methanol in $CHCl_3$ gave com-

pound I-16 (1.3 g); ir 3200, 1620, 1010-895; nmr 𝜏3.82

(m, 2H), 𝜏6.92 (m, 2H), 𝜏7.59 (m, 4H), 𝜏8.05 (s, 3H),

𝜏8.50 (m, 6H). In the last fraction from this chromatogra-

phy, compound I-19 appeared admixed with compound I-16 as

shown by a doublet at 𝜏2.34 and 𝜏8.78, the rest of the sig-

nals being superimposed with those of I-16.

F. To cis, trans-2,4-hexadiene.

The reaction was carried in the same manner as described. The conditions are described on Table IX, X. The compounds isolated and the yields appear on Table X. The acidic extract (60 mg) showed several unidentified compounds. The $CHCl_3$ extraction (50 ml x 3) of the basic aqueous solution afforded a light yellow oil (10.0 g) which was chromatographed on silicic acid (60 g).

The first fraction A eluted with $CHCl_3$ was an oil (516 mg) and on a tlc plate showed 2 predominant spots, Rf 0.42 and 0.29. Continued elution with $CHCl_3$ gave fraction B which was a mixture of 2 compounds showing spots on the Rf 0.16 and 0.08. The remaining fraction C was eluted with 1-20% methanol in $CHCl_3$ to give predominantly the last compound showing Rf of 0.08 (6.48 g) on tlc.

Fraction A was rechromatographed on silicic acid (15 g). Elution with $CHCl_3$ gave four consecutive fractions which showed a single spot on a tlc plate. These fractions were combined (200 mg) and distilled to give a colorless oil (170 mg) of syn-2-piperidino-trans-4-hexen-3-one oxime (I-25); ir 3350, 1660, 1620, 1590, 1390, 1340, 1150, 1110, 990, 940; nmr Υ-1.25 (b, 1H, D_2O exchangeable), Υ3.96 (m, 2H), Υ6.57 (qt, 1H, J=7 cps), Υ7.5 (m, 4H), Υ8.18 (d, 3H, J=5 cps),

Υ8.47 (m, 6H), Υ8.67 (d, 3H, J=7 cps); nmr (pyridine) ABX$_3$

pattern Υ3.3 (2 qt, 1H, J=16 cps), Υ3.74 (d, 1H, J=16 cps),

Υ8.23 (d, 3H, J=6 cps); mass spectrum (80 eV) m/e (rel

intensity) 196 (1), 111 (32), 84 (53), 41 (100). Continued

elution with 1% methanol in CHCl$_3$ gave a fraction which on

the plate showed a single spot. This oil was distilled on

a small scale (110°/0.2 mm Hg) to give a colorless sample

(40 mg) of 5-piperidino-trans-3-hexen-2-one (I-26): ir 2950,

2800, 1678, 1630, 1450, 1360, 1258, 1110; 990; nmr Υ3.18

(d-d, 1H, J=17 cps, J=7 cps), Υ3.94 (d, 1H, J=17 cps),

Υ6.82 (2 qt, 1H, J=7 cps, J=7 cps), Υ7.5 (m, 4H), Υ7.71

(s, 3H), Υ8.46 (m, 6H), Υ8.76 (d, 3H, J=7 cps); mass spec-

trum (20 eV), m/e (rel intensity) 181 (4), 111 (46), 84

(100).

Fraction B was rechromatographed on silicic acid (15 g).

Eluting with up to 1% methanol in CHCl$_3$ gave 4 fractions

which were predominantly a new compound contaminated slightly

by I-26 and I-27. Continued elution with 2% methanol in

CHCl$_3$ gave an oil (28 mg) which showed a single spot on a

tlc plate. This oil was distilled to afford an analytical

sample of anti-2-piperidino-trans-4-hexen-3-one oxime (I-27):

ir 3350, 2995, 1650, 1638, 1458, 1383, 1120, 963, 940; nmr

Υ0.9 (b, 1H, D$_2$O exchangeable), Υ3.28 (m, 2H, J=17 cps),

Υ6.67 (qt, 1H, J=7 cps), Υ7.50 (m, 4H), Υ8.12 (d, 3H, J=6 cps) Υ8.50 (m, 6H), Υ8.73 (d, 3H, J=7 cps): mass spectrum (80 eV) $\underline{m/e}$ (rel intensity) 196 (1.8), 179 (5.4), 84 (8), 41 (100); Anal. Calcd for $C_{11}H_{20}N_2O$: C, 67.31; H, 10.27; N, 14.27. Found: C, 67.20; H, 10.26; N, 14.47.

One of the fractions from fraction $\underline{C}$ (single spot on tlc, 300 mg) crystallized from petroleum ether: mp 83-85°. These crystals were recrystallized three times from petroleum ether and then sublimed (90°/0.2 mm Hg) to give white crystals of 5-piperidino-$\underline{trans}$-3-hexen-2-one oxime (I-24): mp 88-89°; ir 3000, 1630, 1145, 1110, 1060, 980-900 (multiple peaks), 870, 840, 780, 675; nmr Υ-1.00 (b, 1H, D_2O exchangeable), Υ3.86 (m, 2H), Υ7.0 (m, 1H), Υ7.52 (m, 4H), Υ8.04 (s, 3H), Υ8.52 (m, 6H), Υ8.81 (d, 3H, J=6.5 cps); nmr (pyridine) Υ3.5 (d, 1H, J=16 cps), Υ3.98 (d-d, J=16 cps, J=7 cps); Anal. Calcd for $C_{11}H_{20}N_2O$; C, 67.31; H, 10.27; N, 14.27. Found: C, 67.25; H, 10.14; N, 14.40.

G. To 1-vinylcyclohexene.

The photolysis was carried out in a similar manner as shown in 1A. The conditions and yields are described in Table IX and X. The acidic ether extract gave an oil (50 mg) which contained N-nitrosopiperidine and other minor unidentified products. The basic $CHCl_3$ extract (50 ml x 3)

gave an oil (4.14 g). This oil was chromatographed on sili-
cic acid (60 g). Six fractions (<u>A</u>) were eluted with $CHCl_3$
and were shown to be predominantly one compound (700 mg).
Continued elution with 2% methanol in $CHCl_3$ afforded frac-
tion <u>B</u> (1.2 g).

Fraction <u>A</u> was chromatographed on alumina (15 g) using
cyclohexane and benzene as eluent. Four fractions were elu-
ted with benzene and up to 60% $CHCl_3$ in benzene to give a
solid (200 mg) which was sublimed (85°/0.2 mm Hg) to give
white crystals of I-29 (13%): mp 98-99°; ir 3110, 1680, 1608,
1100, 1043, 1000, 980, 968, 928, 785; nmr τ 0.07 (b, 1H, D_2O
exchangeable), τ 4.03 (m, 1H), τ 6.62 (s, 2H), τ 7.61 (m, 8H),
τ 8.46 (m, 12H); mass spectrum (15 eV) <u>m/e</u> (rel intensity)
222 (18), 205 (15), 98 (100) 84 (16); Anal. Calcd for
$C_{13}H_{22}N_2O$: C, 70.23; H, 9.97; N, 1260. Found: C, 70.13; H,
9.79; N, 12.46.

Fraction B showed a single spot on tlc but the nmr spec-
trum showed it to be a mixture of the <u>syn</u> and <u>anti</u> isomers,
I-30 and I-31 (27%) showing two sets of quartets centered at
τ 2.94 and τ 2.75. The mixture was chromatographed an alu-
mina (15 g). Two fractions eluted with $CHCl_3$ (300 mg) were
combined and distilled in small scale to give a colorless
oil: ir 3350, 1650, 1260, 1200, 1000-900 (multiple peaks)

760; nmr τ1.00 (b, 1H, $D_2$0 exchangeable), τ1.92 (d, 1H,

J=10 cps), τ3.97 (d, 1H, J=10 cps for the syn isomer), τ2.10

(d, 1H, J=10 cps), τ3.41 (d, 1H, J=10 cps for the anti isomer),

τ7.5 (m, 7H), τ8.5 (m, 12H); mass spectrum (25 eV) m/e (rel

intensity) 222 (38), 162 (56), 59 (100): Anal. Calcd for

$C_{13}H_{22}N_2$0: C, 70.23; H, 9.97; N, 12.60. Found: C, 70.41;

H, 10.01; N, 12.62.

The aqueous basic solution was continuously extracted

with $CHCl_3$. The $CHCl_3$ was evaporated to give a light oil

which smelled strongly of piperidine. This oil was dissolved

in ether and treated with HCl gas to give a white precipitate

(17 mg). The nmr and ir spectra of this solid was identical

to those of an authentic sample of piperidine hydrochloride.

H. To butadiene.

N-nitrosopiperidine (5.70 g, 0.05 moles) and concentra-

ted hydrochloric acid (15 ml) were dissolved in methanol

(190 ml). The photocell was immersed in an ice-salt water

bath and the solution cooled down to -8°. Butadiene was con-

densed in a U-tube at liquid nitrogen temperature until a

suitable amount had liquified (5.8 g). The U-tube was con-

nected to the inlet tube of the photocell and the butadiene

was allowed to evaporate into the cold solution at a moderate

rate. After 1/2 hour of irradiation more butadiene (5.8 g)

was charged into the solution in the same manner. The solu-
tion was irradiated with the 200 watt Hanovia lamp for
105 min. The photolysate was worked up by the usual proce-
dure. The acidic extract gave an oil (234 mg) which contained
N-nitrosopiperidine and some minor unidentified non-basic com-
ponents. The basic $CHCl_3$ extract gave a light oil (7.1 g).
This oil was treated with cyclohexane to give white crystals
(1.25 g, tlc single spot): mp 91-93°. These crystals (120 mg)
were sublimed to give crystals of 4-piperidino-trans-2-butenal
oxime (I-14): mp 97-99°; ir 3200, 1620, 1150, 1118, 1108,
1046, 990, 960, 910, 870, 778; nmr Υ-1.0 (b, 1H, D_2O exchan-
geable), Υ 2.28 (d, 1H, J=9 cps), Υ3.89 (m, 2H), Υ6.91 (d, 2H,
J=5 cps), Υ7.54 (m, 4H), Υ8.47 (m, 6H); Anal. Calcd for
$C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.65. Found: C, 64.35; H,
9.60; N, 16.84.

The mother liquour from the crystallization was evapora-
ted to give an oil (5.85 g), a part of which (1.0 g) was chro-
matographed on silicic acid (30 g). The following compounds
were identified in their order of elution from the column.
With 4% methanol in $CHCl_3$ an oil (47 mg, tlc single spot) was
eluted and then distilled (70/0.1 mm Hg) to give white crys-
tals of syn-1-piperidino-3-buten-2-one oxime (I-12, 40 mg):
mp 87-90°; ir 3150, 1630, 1320, 1258, 1110, 1040, 1010, 985,

925, 908, 890, 790, 720; nmr τ -1.8 (b, 1H, J=17 cps),

τ 4.72 (d, 1H, J=11 cps), τ 6.56 (s, 2H), τ 7.52 (m, 4H),

τ 8.48 (m, 6H).

With 5% methanol in $CHCl_3$ an oil (87 mg) was eluted

which showed a single spot on a tlc plate. It gave the

picrate with poorly defined melting point: mp 70-80°. The

tlc shows this compound to have a lower Rf (0.18) than I-14

(0.24) on the plate. This oil is assigned to be anti-1-

piperidino-3-buten-2-one oxime (I-13): ir 3300, 1610, 1305,

1280, 1120, 1040, 1020, 995, 950, 918, 870, 795; nmr τ 2.0

(b, 1H, D_2O exchangeable), τ 3.02 (qt, 1H, J=18cps, J=11 cps),

τ 4.02 (qt, 1H, J=18 cps, J=1.5 cps), τ 4.50 (qt, 1H, J=11

cps, J=1.5 cps), τ 6.82 (s, 2H), τ 7.60 (m, 4H), τ 8.53 (m, 6H).

Further elution with 8% methanol in $CHCl_3$ gave I-14 as

identified by ir, nmr and tlc analysis.

2. Beckmann dehydration of crude 4-piperidino-2-butenal

oxime (I-14).

The crude resin (1.59 g, 0.0088 moles) obtained from the

photoaddition of the nitrosamine to butadiene without further

purification, was dissolved in pyridine (30 ml). To this

solution was added p-toluenesulfonyl chloride (3.0 g, 0.015

moles) as a finely ground powder. The solution was stirred

at room temperature for 24 hours. At this time, the pyridine

was removed under vacuum leaving a dark black oil. This oil

was treated with saturated K_2CO_3 solution and stirred for one

hour at room temperature. This solution was then extracted

with ether (20 ml x 3). The ether extract was re-extracted

with a 2N hydrochloric acid solution (20 ml x 3). The acidic

washings were combined and basified with a saturated K_2CO_3

solution and extracted with $CHCl_3$ (50 ml x 3). The solvent

was evaporated giving a brown-black oil (860 mg). The oil

was then distilled by bulb distillation at a vacuum of

0.2 mm Hg. The forerun collected distilled at a chamber

temperature of 70-76° and the main distillate was collected

at a temperature range of 76 to 88°. Both the forerun and

the main fraction showed nmr signals at τ 3.28 (2t, 1H,

J=16 cps, J=5.5 cps), τ 4.38 (2t, 1H, J=16 cps, J=2 cps),

τ 6.90 (d-d, 2H, J=5.5 cps, J=2 cps), τ 7.61 (m, 4H), τ 8.50

(m, 6H) and ir at 2225, 1640, 1108 which were superimposable

with that of trans-4-piperidinocrotonitrile (I-15).

   3. Synthesis of 4-piperidinocrotonitrile.

   N-bromosuccinimide (17.8 g, 0.11 moles) and 10 g of a

40:60 cis, trans mixture of crotonotrile were refluxed in

CCl_4 for 15 hours. At this time, the succinimide had crys-

talized as a top layer in the CCl_4 solution and was filtered.

To the CCl_4 filtrate was then added piperidine (20 g, 0.24

moles). Upon standing at room temperature piperidine hydro-
bromide (15.5 g, 0.095 moles) precipitated and was filtered.
The filtrate was then refulxed for one hour. The CCl_4 was
then removed under vacuum to give a brown oil which was dis-
solved in ether and the ether solution washed with water
(50 ml x 3), dried ($MgSO_4$) and evaporated to give a crude
oil (11.4 g): ir 2225, 1640, 1108. This oil was distilled
to give a main fraction (76-82°/1.5 mm Hg): ir 2225, 1640,
1108; nmr τ 2.5 (m, 1H), τ 2.6 (m, 1H), τ 6.8 (m, 2H), τ 7.6
(m, 4H), τ 8.5 (m, 6H).

4. <u>Beckmann</u> <u>cleavage</u> <u>of</u> <u>anti-1-piperidino-cis-3-penten-
2-one</u> <u>oxime</u> (<u>I-20</u>).

In a round bottom flask (50 ml) equipped with a conden-
ser, I-20 (244 mg, 0.0013 moles) was dissolved in pyridine
(10 ml). The top of the condenser was closed with a stopper.
To the solution was added p-toluenesulfonyl chloride (600 mg,
0.003 moles) and the resulting solution was stirred for
18 hours. It was then treated with ether. The ether layer
was washed with 2N hydrochloric acid solution (30 ml x 3),
and then with a saturated K_2CO_3 solution and lastly with
water. The ether extract was then dried ($MgSO_4$) and filtered.
The ether solution was concentrated to a small volume (10 ml)
in a distillation apparatus equipped with a vigoreaux column

(50 mm). This residual ether (10 ml) was examined by vpc and

nmr. The vpc analysis (20 ft. x 3/8 in., 30% SE-30, chrom W,

100 ml of He/min, 120°) showed that no trans-crotonitrile was

present. The nmr showed signals at τ3.5 (2 qt, 1H, J=11

cps, J=7 cps), τ4.66 (2qt, 1H, J=11 cps, J=1.5 cps), τ8.0

(qt, 3H, J=7 cps, J=1.5 cps).

5. Beckmann cleavage of crude mixture of I-19 and I-20.

A second photolysis was run in an identical manner as

that described in 1-D. The crude product obtained from the

basic extract was chromatographed on silicic acid (60 g).

The fractions obtained were examined by tlc and those frac-

tions containing the minor products other than I-12 were com-

bined. This crude material (1.73 g, 0.0095 moles) was dis-

solved in pyridine and cooled in an ice bath to 3° with cons-

tant stirring. To this solution was added finely powdered

p-toluenesulfonyl chloride (3.8 g, 0.02 moles) and the re-

sulting solution was stirred overnight. The temperature rose

gradually to 22° after stirring for 18 hours. The solution

was diluted with ether (50 ml). The ether was washed with

2N hydrochloric acid solution, followed by washing with a

saturated K_2CO_3 solution. The ether was then washed with

water and dried ($MgSO_4$) and filtered. The ether solution

was then carefully distilled to small volume (10 ml). The

nmr and vpc analysis in the same manner (135 ml/min, 100°)

showed only cis-crotonitrile.

6. Beckmann cleavage of anti-1-piperidino-trans-3-
penten-2-one oxime.

I-23, (300 mg, 0.0016 moles) as finely ground crystals,

was disolved in pyridine (15 ml). p-Toluenesulfonyl chloride

(960 mg, 0.002 moles) was added and this solution was stirred

for 16 hours. The reaction was worked up as previously des-

cribed. A vpc analysis (150 ml of He/min, 123°) and nmr

spectrum of the concentrated ether solution showed it to

contain only trans-crotonitrile.

An analogous reaction was carried out in an aqueous

2% KOH solution. The recovered crotonitrile was analysed to

contain about 20% cis and 80% trans isomer by vpc analysis

(125 ml of He/min, 85°). The commercially available cis and

trans crotonitrile mixture was stirred for 20 hours in an

aqueous 2% KOH solution. The cis to trans ratio was found

to be unchanged.

7. Beckmann cleavage of a crude mixture of I-22 and
I-23.

A second photolysis was carried out as described in 1-E.

The basic crude mixture from photolysis was chromatographed

on silicic acid (60 g). All the fractions which showed the

presence of the minor components other than I-16 by tlc analy-
sis were combined (2.124 g, 0.0118 moles). The oil was treated
with p-toluenesulfonyl chloride (4.85 g, 0.025 moles) in
pyridine (20 ml) the solution was stirred for 16 hours. The
solution was then worked up in the usual manner. The concen-
trated ether extract was examined by vpc (120 ml of He/min,
126°) and nmr and was shown to contain only trans-crotonitrile.

8. Beckmann cleavage of the crude mixture of I-25 and
I-27.

A second photolysis was carried out as described in 1-F.
The basic fraction was chromatographed and all the fractions
which showed the presence of minor components other than I-24
were combined to give a crude mixture (560 mg, 0.0029 moles).
This crude mixture was treated with p-toluenesulfonyl chloride
(1.3 g, 0.0065 moles) in pyridine (20 ml) for 22 hours at room
temperature and the solution was worked up in usual way. The
ether extract was examined by vpc analysis (30% SE-30 on
chrom W, 150 ml of He/min, 80°) and shown to contain cis- and
trans-crotonitrile in a ratio of 3 to 97 by mixed injection.
The retention times for the trans-crotonitrile was 8 min. and
for the cis isomer 9.5 min.

9. Beckmann dehydration of the mixture of I-30 and I-31.

The crude mixture of I-30 and I-31 (895 mg), obtained
from the chromatography of the basic fraction was treated

with p-toluenesulfonyl chloride (1.4 g, 0.010 moles) in pyri-

dine (30 ml) for 36 hours at room temperature. The reaction

mixture was worked up in the same manner as described in 2

to afford a basic fraction (250 mg) as an oil. This oil was

distilled (120°/0.2 mm Hg) twice to give a colorless oil of

I-32: ir 3050, 3000, 2700, 2220, 1673, 1625, 1165, 1118, 1101;

nmr τ4.62 (s, 1H), τ7.26 (m, 3H), τ7.65 (m, 4H), τ8.51

(m, 12H). Decoupling experiments of I-32 at 100 Mc showed

that irradiation of H_A at τ7.73 resolves H_C at τ4.62 into

a doublet, J=1.4 cps; irradiation of H_B at τ7.21 resolves

H_C into a doublet, J=1.0 cps.

10. Isomerization of cis, cis-1,3-cyclooctadiene (COD)

using acetophenone as sensitizer.

The isomerization and identification of the products for-

med was carried out according to procedure described by R.S.

Liu (23). A solution of cis, cis-1,3-cyclooctadiene (20 g,

0.2 moles) and acetophenone (2.0 g, 0.016 moles) in pentane

was irradiated with the 200 watt Hanovia lamp for 20 hours.

The isomerization of cis, cis-1,3-COD was followed by vpc

(6 ft x 3/8 in., 20% TCEP, chrom W, 80 ml of He/min, 85°).

The increase in a peak of retention time of 9.8 min. was fol-

lowed. After 20 hours of irradiation this peak appeared in

a ratio of 1:2 relative to cis, cis-1,3-COD whose retention

time was 8 min. under the conditions employed.

11. Attempted isomerization of cis, cis-1,3-COD using
N-nitrosopiperidine.

A mixture of cis, cis-1,3-COD (10.0 g, 0.1 moles) and
N-nitrosopiperidine (4.0 g, 0.035 moles) in pentane (200 ml)
was irradiated for 20 hours with the 200 watt Hanovia lamp.
The vpc analysis of the solution during the irradiation revea-
led no new peak having a retention time of the cis, trans-
1,3-COD (9.8 min.).

12. Attempted isomerization of cis, cis-1,3-COD using
N-nitrosopiperidine in the presence of acid.

A photoaddition was carried in the same manner as des-
cribed in 1-A using a mixture of N-nitrosopiperidine (2.4 g,
0.02 moles), cis, cis-1,3-COD (10.0 g, 0.1 moles) and concen-
trated hydrochloric acid (2 ml, 0.024 moles) in methanol
(200 ml). This solution was irradiated with the 200 watt
Hanovia lamp until the nitrosamine absorption had completely
disappeared (2 hr.). During the irradiation the solution was
examined by vpc (20% TCEP, in chrom W, 80 ml of He/min, 85°).
While the one hour and the two hour sample (2 ul) showed a
decrease in the concentration of cis, cis-1,3-cyclooctadiene
by 20%, no new peaks or peaks having a retention time of 9.8
min. appeared during the irradiation.

13. Attempts to isomerize 1,3 pentadiene using N-nitrosopiperidine in neutral conditions.

The nitrosamine (4.0 g, 0.035 moles) and a mixture of cis and trans-1,3-pentadiene (40:60) in cyclohexane (360 ml) was irradiated for 18 hours with a 200 watt Hanovia lamp. The photolysis solution was analyzed by vpc (20 ft. x 3/8 in., 30% SE-30, chrom W, 86 ml of He/min, 85°). The 0 hr. sample showed the trans:cis ratio of 60:40; the one hr. sample 58.5:41.5; the 3 hr, 59.5:40.5; the 18 hr, 59.5:40.5. The retention time for trans-1,3-pentadiene was 16.5 min. and for the cis-1,3-pentadiene, 17.5 min. under the conditions employed.

14. Attempts to isomerize cis-1,3-pentadiene in acidic media.

N-Nitrosopiperidine (2.3 g, 0.02 moles) cis-1,3-pentadiene (2.2 g, 0.032 moles) and concentrated hydrochloric acid (2 ml, 0.024 moles) in methanol (1.41.) was irradiated with a RPR 3500Å lamp to about 80% completion (4 hr). To this solution was added water (50 ml) followed by sodium bicarbonate (pH 7-8). The photolysate solution was partially distilled to collect 25 ml of distillate (bp 64-65°) while the receiver was cooled with acetone-CO_2. This distillate was examined by vpc to show the peak for cis-1,3-pentadiene with

a retention time of 13.4 min. No other peak having a reten-
tion time of trans-1,3-pentadiene (11.2 min.) was present.

15. Attempts to isomerize trans-1,3-pentadiene in acidic
media.

N-Nitrosopiperidine (3.42 g, 0.03 moles), trans-1,3-
pentadiene (3.40 g, 0.05 moles) and concentrated hydrochloric
acid (3 ml, 0.036 moles) in methanol (360 ml) was photolyzed
for 5 hours with a RPR 3500Å lamp to completion. The remain-
ing diene was examined by vpc in the usual manner to show the
peak of trans-1,3-pentadiene at 13 min. but no peak at 14.2
min. cis-1,3-pentadiene.

16. Photolysis of N-nitrosopiperidine in the presence
of cis and trans-1,3-pentadiene.

A solution of N-nitrosopiperidine (2.3 g, 0.02 moles),
concentrated hydrochloric acid (2 ml, 0.024 moles) and a
(60:40) cis and trans mixture of 1,3-pentadiene (2.72 g, 0.04
moles) in methanol (380 ml) was irradiated for 5 hours and
was worked up in the same manner as 14 to afford the forerun
(20 ml). The forerun was examined by vpc (60 ml of He/min,
70°) to show that the cis:trans ratio of the 1,3-pentadiene
was 60:40, having identical ratio as the 0 hr. sample 6:40.
Under the conditions employed trans-1,3-pentadiene had a
retention time of 19 min., the cis isomer, 20.4 min.

17. Photolysis of N-nitrosopiperidine in the presence of cis, trans-and trans, trans-2,4-hexadiene.

A solution of N-nitrosopiperidine (2.51 g, 0.022 moles), concentrated hydrochloric acid (3 ml, 0.036 moles) and cis, trans-2,4-hexadiene (1.64 g, 0.02 moles) and trans, trans-2,4-hexadiene (1.64 g, 0.02 moles) in methanol (200 ml) was irradiated in the same manner as 14 for 7 hrs. The photolysate was analyzed by vpc (20 ft. x 3/8 in., 30% SE-30, chrom W, 120 ml of He/min, 90°). The cis, trans isomer had a retention time of 16 min. and the trans, trans isomer of 18.2 min. At the zero hour the ratio of cis, trans to trans, trans isomer was 1:1 and at the end of photolysis the corresponding ratio is again 1:1.

18. Photolysis of N-nitrosopiperidine in the presence of 1,3-cyclohexadiene.

A. At - 75°

A solution of the nitrosamine (1.14 g, 0.01 moles), 1,3-cyclohexadiene (1.64 g, 0.02 moles) and methanolic hydrochloric acid (5 ml, 0.01 moles) in methanol (200 ml) was cooled to -75° by immersing in an acetone-dry ice mixture. The solution was irradiated with the 450 watt Hanovia lamp which was cooled by passing a fast stream of air directly

into the sleeve. After 16 hours of irradiation, the nitrosa-
mine absorption had decreased, from 0.86 at 0 hour; to 0.26.
A plot of optical density against time showed that 20 hours
were required to effect 100% disappearance of the nitrosamine.
As the clear solution starts to warm up to room temperature
it turned light green in color. The color faded to light
yellow after a while. The solvent was removed under vacuum
to a small volume at a water bath temperature of 15°. The
products were isolated in the usual manner. The acidic ether
extract gave an oil (50 mg) whose ir spectrum was superimpos-
able with that of authentic N-nitrosopiperidine. The basic
extract gave upon evaporation, an oil (1.0 g) whose ir, nmr
and tlc were identical to the basic crude extract described
in section I-B.

B. At 49°

The same quantities of reactants as described in 1-A
were used. The solution was warmed to 49° by passing a
stream of water which was maintained at 49° through the cold
finger of the photocell. The optical density of the nitro-
samine was measured to be 0.82 and did not change after 20 min.
under this condition. The solution was irradiated for 20 min.
with the 450 watt Hanovia lamp. After 8 min. of irradiation
the optical density had decreased to 0.32 (61%) but tappered

off; at 10 min., 0.32; 13 min., 0.27; 16 min., 0.20; 19 min.,

0.28. The irradiation was discontinued and the photolysate

was worked up in the usual manner. The neutral extract gave

a crude product (1.11 g) whose ir, nmr and tlc behaviour were

identical to that of the crude product described in section

I-B.

19.   Quantum yield determinations for the disappearance

of N-nitrosopiperidine.

A.   With varying concentration of cyclooctene

A stock solution of N-nitrosopiperidine (232 mg, 0.002

moles) in freshly distilled methanol (100 ml) containing con-

centrated hydrochloric acid (4.2 ml, 0.05 moles, 0.5 M) was

prepared.

In five separate volumetric flasks (10 ml), the appro-

priate amounts of freshly distilled cyclooctene: bp 149° were

introduced (see Table IV). The flasks were then filled

with the stock solution (0.5M HCl, 0.02M nitrosamine). The

optical density at 350 mu was measured for each flask. These

solutions (5 ml) were placed in 5 separate tubes respectively

and each tube was degassed by the freeze-pump-thaw cycle

three times under a vacuum of 5u. In the sixth tube, the

ferrioxalate solution (5 ml) (22) was placed. The samples

$$\Phi_B = \frac{N_b \quad \Phi_{Fe}^{+2} \quad (366 \text{ mu})}{N_{Fe}^{+2} \quad (5 \text{ ml})} \quad \text{(i)}$$

where

$$\Phi_B = \text{quantum yield for the disappearance}$$
of N-nitrosopiperidine

$$\Phi_{Fe}^{+2} = 1.21 = \text{quantum yield of the actinometer}$$
solution at 366 mu

$$N_{Fe}^{+2}(5 \text{ ml}) = \text{moles of } Fe^{+2} \text{ produced upon irradiation}$$

and

$$N_{Fe}^{+2}(5 \text{ ml}) = \left[Fe^{+2} \right] \cdot \frac{V_1 \quad V_3}{V_2} \quad \text{(ii)}$$

where $\left[Fe^{+2} \right]$ = determined using the measured optical
density of the actinometer solution at
510 mu and extrapolating that value using
the graph (Fig. 22).

V_1 = volume of actinometer solution irradiated

V_2 = volume of irradiated actinometer solution
taken for analysis

$$V_3 = \text{final volume to which the aliquot } V_2 \text{ is}$$
diluted

and

$$N_b = \text{(moles of N-nitrosopiperidine)}$$

$$\frac{V_4}{V_5} \cdot \cdot \frac{O.D._{min.} - O.D._{20 \text{ min.}}}{O.D._{min.}} \qquad \text{(iii)}$$

where

V_4 = volume of aliquot irradiated from stock solution

V_5 = total volume of stock solution

$O.D._{min.}$ = optical density of the aliquot taken of stock solution at 0 min.

$O.D._{20min.}$ = optical density of the aliquot V_4 after being irradiated for 20 min.

The quantum yields for the disappearance of N-nitrosopiperidine with different olefins in the range of 0.5N and 0.06N methanolic hydrochloric acid solution were carried out in an identical manner as described in the above determination. All the pertinent data appears in Tables II and III, respectively. In addition the determination of the lamp intensity used for the quantum yield determinations was calculated through equation (IV) to be ~3 x 10^{11} quanta/sec.

$$I_o^i = \frac{N_{Fe}^{+2} (5 \text{ ml})}{Fe^{+2} \, t \, (1-10^{e \, A \, 1})} \qquad (iv)$$

where

N_{Fe}^{+2} (5 ml) = same value as in equation (ii)

Fe^{+2} = 1.21

t = 20 min. x 60

e = 1.11×10^4 lit/mole-cm (Fig. 22)

A = 0.4×10^{-6} moles/liter

1 = cell path length, 1cm

I_o^i = incident light intensity

Experimental

Section II

1. <u>Photolysis</u> <u>of</u> <u>N-nitrosopiperidine</u> <u>in</u> <u>the</u> <u>presence</u>
<u>of</u> <u>1,3-pentadiene</u> <u>and</u> <u>Naphthalene</u>.

In the photolysis apparatus, N-nitrosopiperidine (3.42 g,
0.03 moles), 1,3-pentadiene (<u>cis</u>:<u>trans</u>; 60:40), concentrated
hydrochloric acid (3 ml, 0.036 moles) and naphthalene (5.12 g,
0.04 moles) in methanol (400 ml) was irradiated. The experi-
ment was followed by measuring the decrease of the optical
density of the nitrosamine at 350 mu. This was done by pipet-
ting out an aliquot (2 ml) and diluting to the appropriate
volume (10 ml) for spectroscopic measurement. A plot of opti-
cal density against time gave a straight line up to 80% com-
pletion. The solution was irradiated to completion with the
RPR 3500Å lamp (6 hrs.). The rate of disappearance of the
nitrosamine was calculated from the slope to be 0.005 moles
per hour. An identical reaction was carried out in the
absence of naphthalene. The rate of disappearance of the
nitrosamine was determined in the same way to be 0.005 moles
per hour. The photolysate was evaporated to a small volume
(40 ml) and was diluted with water (50 ml). The precipitated
naphthalene was filtered. The acidic aqueous solution was
extracted with $CHCl_3$ (50 ml x 3) which was washed with water,

dried (MgS04) and evaporated to give a residue (500 mg). The residue contained nitrosamine and naphthalene as shown by ir and nmr analysis. The acidic aqueous layer was basified to pH 9-10 with a saturated K_2CO_3 solution and extracted with $CHCl_3$ (50 ml x 3). The $CHCl_3$ extract was washed with water, dried (MgSO4), filtered and evaporated to give a resin (6 g). The resin was treated with ether and cooled to give crystals (4.3 g, 79%). The crystals were identified as I-16 by ir and nmr and tlc analysis with those of an authentic sample.

2. <u>Naphthalene sensitized photoaddition of N-nitroso-piperidine to 1,3-pentadiene.</u>

A homogeneous solution containing N-nitrosopiperidine (3.42 g, 0.03 moles), 1,3-pentadiene (<u>cis</u>:<u>trans</u>); 60:40, 3.40 g, 0.05 moles), concentrated hydrochloric acid (3 ml, 0.036 moles) and naphthalene (10.2 g, 0.08 moles, 0.2M) was prepared in methanol (400 ml). At 300 mu the optical density of this solution was 0.68 (1/100 dilution). A filter solution of N-nitrosodimethylamine (0.18M) in methanol which exhibited an optical density of 0.4 at 300 mu and 1.82 at 345 mu was circulated through the cold finger. The solution was irradiated with a RPR 3000Å lamp. The optical density at 350 mu after 3 hours of irradiation changed to 1.52 from that of 1.51 at zero hour. More naphthalene (6 g) was added

to make a saturated solution. The solution was again irradiated with the RPR 3000Å. After 8 hours of irradiation the optical density at 350 mu changed to 1.43 and after 15 hours to 1.47 from that of 1.45 at starting point. The filter solution was removed and the solution was irradiated at 300 mu for 1 hour. The optical density of the nitrosamine decreased 6% in this time interval. The reaction was not investigated further.

3. Naphthalene sensitized photoaddition of N-nitroso-piperidine to cyclohexene

N-Nitrosopiperidine (3.42 g, 0.03 moles), cyclohexene (24.6 g, 0.3 moles), concentrated hydrochloric acid (3 ml, 0.036 moles) and naphthalene (15.4 g, 0.12 moles) were dissolved in methanol (400 ml). The optical density of the solution without naphthalene was 0.04 (1/10 dilution) at 300 mu and 1.43 at 350 mu. The solution with naphthalene showed an optical density of 0.68 (1/100 dilution) at 300 mu. The cold finger of the photocell was filled with a filter solution of N-nitrosodimethylamine (0.21M). The filter solution had an optical density of 2.0 from 348 mu to 335 mu and 0.3 at 300 mu. The filter solution was not circulated since the RPR 3000Å or the RPR 3500Å do not generate sufficient heat during irradiation to require external cooling. The temperature of the photolysate at equilibrium state was

27-28°. The solution was irradiated with the RPR 3000Å.

After 4 hours irradiation the optical density decreased to

1.37, after 28 hours to 1.05 at 350 mu, equivalent to 26%

decomposition. The methanol was evaporated to a small volume,

water was added and the precepitated naphthalene was filtered.

The aqueous filtrate was extracted with ether (50 ml x 3) to

give a mixture of N-nitrosopiperidine and naphthalene as shown

by ir and nmr analysis. The basic extract gave a light oil

(1.77 g) which showed on tlc analysis one major spot with

Rf 0.22 and 3 minor spots with Rf of 0.42, 0.70 and 0.75 res-

pectively. The major spot had an identical tlc mobility with

that of authentic 2-piperidinocyclohexanone oxime (Rf 0.22).

The crude product was chromatographed on silicic acid (30 g).

The first five fractions (150 mg) eluted with $CHCl_3$, and up

to 4% methanol in $CHCl_3$, were shown to contain the 3 minor

products by tlc analysis. The rest of the fractions eluted

with 6 to 10% methanol in $CHCl_3$ contained 2-piperidinocyclo-

hexanone oxime (700 mg) identified by comparison of the ir

and nmr and tlc analysis with those of an authentic sample.

The mixture was rechromatographed on silicic acid (1.0 g).

The spots which on tlc showed Rf's of 0.70 and 0.75 could

not be separated from one another. The third component of

Rf 0.45 was obtained pure (6 mg) showing a single spot on

tlc. It was sublimed to give a white solid which was identified as 2-piperidinocyclohexanol: ir 3400, 1640, 1400-1300 (multiple peaks) 1078; mass spectrum (15 eV) $\underline{m/e}$ (rel intensity) 183 (30), 124 (57), 85 (100), 88 (83).

4. <u>Naphthalene photosensitized addition of N-nitrosopiperidine to cyclohexene in the presence of benzonitrile</u>

A solution of N-nitrosopiperidine (3.42 g, 0.03 moles), cyclohexene (24.6 g, 0.3 moles), benzonitrile (25 g, 0.24 moles, 0.6M) and concentrated hydrochloric acid (3 ml, 0.036 moles) in ethanol (400 ml) exhibited an optical density of 0.63 at 350 mu and 0.04 at 300 mu with 1/10 dilution. Naphthalene was then dissolved. The optical density at 300 mu was 0.68 with 1/100 dilution. The cold finger of the photocell was filled with a filter solution of N-nitrosodimethylamine (0.028M) in methanol whose optical density was 2.0 from 360 mu to 330 mu and 0.26 at 300 mu. The photocell was immersed in a water bath and was irradiated with the RPR 3000Å for 28 hours. The temperature of the photolysate was 27° at this time. The optical density at 350 mu had decreased from 0.68 to 0.54 during this period. Evaporation of the ethanol afforded an oil which was dissolved in $CHCl_3$ and extracted with 2N hydrochloric acid solution (50 ml x 3). The $CHCl_3$ layer was washed with water, dried ($MgSO_4$) and evaporated under

vacuum to afford the nitrosamine, naphthalene and benzoni-
trile by ir and nmr analysis. The aqueous acidic extract
was basified with a saturated K_2CO_3 solution. The basic
fraction obtained in an usual manner afforded an oil (900 mg).
This oil was shown by nmr and tlc analysis to contain benzo-
nitrile and 2-piperidinocyclohexanone oxime in a 1:1 ratio.
The crude oil was chromatographed on silicic acid (15 g).
The later fractions eluted with 4 to 10% methanol in $CHCl_3$
gave 2-piperidinocyclohexanone oxime (516 mg) identified by
the ir and tlc comparison with those of an authentic sample.

5. Attempted perylene photosensitized addition of
N-nitrosopiperidine to cyclohexene

A solution of the nitrosamine (2.3 g, 0.02 moles), cyclo-
hexene (16.4 g, 0.2 moles) and hydrochloric acid (2 ml, 0.024
moles) in ethanol (400 ml) exhibited an optical density of
0.5 at 350 mu with 1/10 dilution. To this solution was added
perylene (400 mg) which did not dissolve completely. The
solution exhibited absorptions at 438 mu, 408 mu and 378 mu
with optical densities corresponding to 1.58, 1.24 and 0.72,
respectively with 1/100 dilution. A filter solution contain-
ing sodium nitrate (62), and sodium phthalate which absorbed
100% of the light below 400 mu, was circulated through the
cold finger. The solution was irradiated with the 200 watt

Hanovia lamp for 6 hours. The optical density at 350 mu after

1 hour of irradiation was 0.58, after 3 1/2 hours, 0.59 and

after 6 hours 0.62. At this time, the irradiation was discon-

tinued and the filter solution was replaced by a soft glass

filter which absorbs 100% of the light at 300 mu, 50% of the

light at 320 mu and is fully transparent at 350 mu. The solu-

tion was irradiated with the RPR 3500Å lamp for 9 hours. The

photolysate turned red in color and the optical density

increased to a value greater than 2 at 438, 2.0 at 408 and

1.16 at 378 mu after 5 hours of irradiation. After this point

the absorption maxima of the perylene decreased gradually and

broadened. The solution was worked up in the usual manner.

The neutral $CHCl_3$ extract was treated with methanol to afford

perylene (300 mg): mp 267-270°   lit (63) 276-278° . The mother

liquour from these crystals was evaporated to dryness giving

a mixture (562 mg) of N-nitrosopiperidine and perylene and a

trace (by tlc) of a purple colored compound. The basic frac-

tion gave a brown oil (1.45 g) which was dissolved in petro-

leum ether to give crystals (600 mg): mp 86-106°. The nmr

and ir spectra were identical with those of an authentic sam-

ple of 2-piperidinocyclohexanone oxime.

6. Attempted triphenylene sensitized photoaddition of
N-nitrosopiperidine to cyclohexene

A solution of the nitrosamine (640 mg, 0.0057 moles),
cyclohexene (16.4 g, 0.2 moles) and concentrated hydrochloric
acid (1 ml, 0.012 moles) in ethanol (400 ml) showed an opti-
cal density of 0.10 at 300 mu with 1/10 dilution. The tri-
phenylene (1.0 g) was added to give a heterogeneous solution.
The optical density at 300 mu was measured to be 1.34 with
1/10 dilution. The cold finger of the photocell was filled
with N-nitrosodimethylamine (0.028M) in methanol solution.
The solution was irradiated with the RPR 3000Å lamp for
28 hours. The photolysate was worked up in the usual manner
to afford solid triphenylene (870 mg), an acidic (244 mg)
and a basic extract (422 mg). By nmr and ir and tlc analy-
sis the acidic fraction was shown to be N-nitrosopiperidine
and triphenylene. The basic fraction was a mixture of oil
and solid which by ir and nmr spectra and tlc analysis was
shown to be 2-piperidino cyclohexanone oxime. Two more
minor components were detected by tlc analysis.

7. 1,2-Benzanthracene sensitized addition of N-nitroso-
piperidine to cyclohexene

A solution of the nitrosamine (2.38 g, 0.02 moles), cyclo-
hexene (16.4 g, 0.2 moles) and concentrated hydrochloric acid

(2 ml, 0.024 moles) in ethanol (1.4 1.) showed the optical

density of 0.015 at 350 mu with 1/100 dilution. The optical

density of 1,2-benzanthracene was shown to be 0.34 with 1/100

dilution. The hetereogeneous solution was irradiated with

the RPR 3500Å lamp for 14 hours. At this time the solution

was greenish in color. The solution was then filtered to

give 1,2-benzanthracene (1.0 g). The filtrate was evapora-

ted to a small volume and extracted with CH_2Cl_2 (100 ml).

The CH_2Cl_2 solution was then extracted with 2N hydrochloric

acid solution (50 ml x 3). The CH_2Cl_2 was washed with water,

dried $(MgSO_4)$ and evaporated to give a solid (5.15 g) which

by ir and nmr comparison with those of an authentic sample

was shown to be 1,2-benzanthracene and a minor amount of

N-nitrosopiperidine. The acidic aqueous layer was worked up

in the usual manner to give a crude basic resin (776 mg)

which was shown by ir and nmr spectral analysis to be mainly

2-piperidinocyclohexanone oxime. This crude resin was chro-

matographed on silicic acid (15 g). The second fraction

(61 mg) eluted with $CHCl_3$ showed a strong ir peak at 1680 cm^{-1}.

Continued elution with 2 to 10% methanol in $CHCl_3$ gave 2-pipe-

ridinocyclohexanone oxime (306 mg) by ir and nmr spectral com-

parison with those of an authentic sample. The fraction

(ir 1680 cm^{-1}) was rechromatographed on alumina (2 g). Elu-

tion with benzene gave an oil (10 mg) which showed a single spot on tlc: ir 1680, 1640, 1620, 1280, 1118, 1000, 940, 760 cm^{-1}. The compound decomposed in attempted distillation. A tlc comparison against the minor products obtained by direct photolysis of the nitrosamine in the presence of cyclohexene showed that this compound is not one of the minor components obtained from direct irradiation since it showed an Rf different from the minor products.

8. Attempted 1,4-dimethylanthracene sensitized photo-addition of N-nitrosopiperidine to cyclohexene

The nitrosamine (2.3 g, 0.02 moles), cyclohexene (3.28 g, 0.04 moles) and hydrochloric acid (2 ml, 0.024 moles) were dissolved in ethanol (1.4 l.). The optical density at 350 mu was 0.33 with 1/5 dilution. The 1,4-dimethylanthracene was added (6.4 g, 0.02 moles) and the optical density at 350 mu was measured to be 0.72 with 1/100 dilution. The homogeneous solution was irradiated with the RPR 3500Å source for 16 hours. The solution was worked up in the usual manner to give acidic aqueous solution. This acidic solution was extracted with CH_2Cl_2. The acidic CH_2Cl_2 extract (6.9 g) gave 1,4-dimethylanthracene as shown by ir, nmr, and tlc analysis. This acidic aqueous solution was basified with Na_2CO_3 and then extracted with CH_2Cl_2. The basic CH_2Cl_2 extract gave

a solid (185 mg). A careful tlc and nmr analysis revealed

that the crude solid was mostly 1,4-dimethyl-9-piperidino-

10-hydroxy-9, 10-dihydroanthracene (III-27), a small amount

of N-nitrosopiperidine and a minor compound but that no

2-piperidinocyclohexanone oxime was present.

9. <u>Anthracene</u> <u>sensitized</u> <u>photoaddition</u> <u>to</u> <u>cyclohexene</u>

A solution of the nitrosamine (2.3 g, 0.02 moles), cyclo-

hexene (16.4 g, 0.02 moles) and hydrochloric acid (2 ml,

0.024 moles) in ethanol (1.4 1.) had an optical density of

0.142 at 350 mu with 1/10 dilution. Anthracene was then

added (5.2 g) and the hetereogeneous solution was vigorously

stirred. The optical density was shown to be 0.30 at 350 mu

with 1/100 dilution. The solution was irradiated for 14

hours with the RPR 3500Å source. At this time the ethanol

was evaporated to a small volume and the precipitated anthra-

cene was filtered: mp 200-208°. The filtrate was worked up

in the usual manner to give an acidic fraction (1.2 g) which

was shown to be a mixture of anthracene and N-nitrosopiperi-

dine by ir and nmr spectral analysis. Analysis by tlc of

this crude mixture showed a trace of an unidentified compound

(Rf 0.15). The acidic aqueous solution was basified with a

saturated K_2CO_3 solution to pH 9-10 to give a precipitate

(1.3 g). The precipitate was filtered and worked up in the

same manner as described on page , to give pure III-1: mp

176-179° dec. The aqueous layer was extracted with CH_2Cl_2

(30 ml x 3) to give a mixture of an oil and solid (607 mg).

The mixture was treated with $CHCl_3$ to give crystals of III-1

(96 mg). The mother liquor was evaporated to dryness and

chromatographed on silicic acid (10 g). The first fraction

eluted with $CHCl_3$ and up to 4% methanol in $CHCl_3$ (200ml com-

bined volume), gave III-8 (69 mg), III-1 (125 mg) and small

amounts of N-nitrosopiperidine. The last fractions eluted

with 6% and up to 10% methanol in $CHCl_3$ were 2-piperidinocy-

clohexanone oxime (125 mg) as shown by comparison of their

nmr spectra and tlc behaviour against those of an authentic

sample.

   10.   Attempted acetophenone photosensitized addition

of N-nitrosopiperidine to cyclohexene

   A solution of the nitrosamine (2.3 g, 0.02 moles),

cyclohexene (16.4 g, 0.2 moles) and hydrochloric acid (2 ml,

0.024 moles) in methanol (400 ml) showed an optical density

of 0.5 at 350 mu and 0.06 at 300 mu with 1/10 dilution.

Acetophenone (14.4 g, 0.12 moles, 0.3M) was then added.

The optical density was measured to be 2.0 at 300 mu and

1.94 at 310 mu with 1/10 dilution. The cold finger of the

photocell was filled with N-nitrosodimethylamine (0.020M)

as filter solution. The solution was irradiated at 300 mu
with the RPR 3000Å source for 20 hours. The uv curve showed
a slight decrease (1%) between the 310 to 355 mu region. The
solution turned slightly yellow at the end of the photolysis.
The solution was worked up in the usual manner. The acidic
CH_2Cl_2 extract gave an oil (15 g) which was shown to be mostly
acetophenone by ir and nmr analysis. The vpc analysis (10 ft.,
1/8 in., 30% SE-30, chrom W, 30 ml of N_2 / min., 200°C) showed
the presence of an unidentified minor component (1%) which
ran slightly behind the acetophenone peak. The basic CH_2Cl_2
extract gave an oil (485 mg) which was chromatographed on
silicic acid (5 g). Elution with $CHCl_3$ gave acetophenone
(73 mg) identified by ir and nmr spectra comparison. Further
elution with 1 to 6% methanol in $CHCl_3$ gave an oil (62 mg,
two spots on tlc, Rf 0.75) whose nmr spectrum showed only
aliphatic protons from τ 6 to τ 8.5. Elution with 6 to 10%
methanol in $CHCl_3$ gave a mixture (140 mg, tlc two spots)
whose Rf values (0.52 and 0.18) were close to two of the basic
products (Rf's 0.42 and 0.23 respectively) obtained from the
direct photolysis. The characterization of these compounds
was not pursued further.

11. <u>Acetophenone sensitized addition of N-nitrosopipe-ridine to cyclohexene</u>

The same quantities of reagents as described in No. 10 were used except that t-butanol was used instead of methanol. The reaction was carried out in an identical manner as No. 10 and the same isolation procedure was followed. The neutral fraction contained acetophenone as the major component. The ir spectra was identical as that of an authentic sample except for two extra peaks of small to medium intensity at 1090 and 985 cm^{-1}. The nmr spectrum of this oil showed that the weak signals at $\tau 6.14$, $\tau 6.5$ and $\tau 8.6$ were due to N-nitrosopiperi-dine. The basic extract gave an oil (600 mg) which by ir and nmr analysis consisted mainly of acetophenone. The tlc analy-sis of this oil showed a spot (Rf 0.22) equivalent to that of authentic 2-piperidinocyclohexanone oxime on the same plate.

12. <u>Quenching of the photolysis of N-nitrosopiperidine</u>

A. <u>In presence of naphthalene</u>

A solution of the nitrosamine (2.4 g, 0.02 moles) and naphthalene (3.45 g, 0.027 moles) and concentrated hydrochlo-ric acid (2 ml, 0.024 moles) in methanol (200 ml) was irra-diated with an RPR 3500Å source. The optical density at 350 mu increased from 1.08 at 0 hour, to 1.25 after 1/2 hour irradiation; to 1.28 after 1 hour; to 1.43 after 2 hours; to

2.0 after 12 hours. The photolysate had turned deep red-brown at this time. The solution was then worked up in the usual manner. The acidic $CHCl_3$ extract gave a red solid (3.5 g) which was chromatographed on alumina (60 g). Elution with cyclohexane gave naphthalene (1.4 g): mp 72-79. Further elution with benzene gave N-nitrosopiperidine (308 mg). Elution with $CHCl_3$ and up to 10% methanol in $CHCl_3$ did not yield any other products. The basic $CHCl_3$ extract gave a crude oil (140 mg) which contained mostly naphthalene (A_2B_2 system at τ2.48) N-nitrosopiperidine and a trace of a basic compound (broad signal at τ7.44).

In a separate experiment, the nitrosamine (4.56 g, 0.04 moles), naphthalene (2.56 g, 0.02 moles) and concentrated hydrochloric acid (5 ml, 0.06 moles) were dissolved in methanol (400 ml) and irradiated with the 450 watt Hanovia lamp. After 110 minutes of irradiation a 50 ml aliquot was taken and worked up in the usual manner. The neutral fraction (864 mg) was shown to contain only nitrosamine and naphthalene and traces of a red colored compound by tlc analysis. The basic portion gave N-nitrosopiperidine (241 mg) and was shown to contain traces of a red colored compound by tlc analysis. The irradiation was continued for another 2 hours and worked up in the usual manner. The neutral CH_2Cl_2

extract gave a residue (2.56 g) which by ir and nmr and tlc

analysis was shown to contain naphthalene and N-nitrosopipe-

ridine. The aqueous layer was basified with Na_2CO_3 to pH

10-11 and extracted with CH_2Cl_2. Evaporation of the CH_2Cl_2

gave a crude resin (536 mg). Analysis by tlc showed the pre-

sence of naphthalene (A_2B_2 at τ 2.48), N-nitrosopiperidine,

and a trace of the red colored compound.

B. In presence of acetophenone

A solution of the nitrosamine (2.3 g, 0.02 moles), con-

centrated hydrochloric acid (2 ml, 0.024 moles) and acetophe-

none (4.7 g, 0.039 moles) in ethanol (400 ml) was irradiated

with the RPR 3500$\overset{o}{A}$ lamp through a soft glass filter. The dis-

appearance of the 350 mu absorption was complete after 8 hours

of irradiation. The solvent was evaporated under vacuum at

40° to give a mixture of oil and solid. This crude product

was treated with ether and filtered to give crystals of pipe-

ridine hydrochloride (2.17 g): mp 210-215°; nmr and ir spectra

superimposable with an authentic sample of piperidine hydro-

chloride. The ether mother liquour was evaporated to give an

oil which was identified as acetophenone.

C. In presence of triphenylene

The nitrosamine (2.3 g, 0.02 moles) and concentrated

hydrochloric acid (2 ml, 0.024 moles) were dissolved in etha-

nol (400 ml). The optical density at 350 mu was 0.56. After

triphenylene (750 mg) was added the optical density at 350 mu

was shown to be 0.58. The solution was irradiated for 8 hours

with the RPR 3500Å lamp through a soft glass filter. At this

time the absorption at 350 mu disappeared. The photolysate

was evaporated to a small volume and the triphenylene (690 mg)

was filtered. The solution was evaporated further. A trace

of triphenylene was removed by extracting with benzene

(20 ml x 3). The syrupy ethanolic aqueous layer was dissol-

ved in $CHCl_3$ and was diluted with ether to give a mixture of

crystals and oil. The crystals (135 mg; mp 215-219°) were fil-

tered and identified as piperidine hydrochloride. The mother

liquor was treated with benzene and the benzene was distilled

under vacuum. The process was repeated until all the water

had been removed giving a white solid (1.2 g) which was iden-

tified to be piperidine hydrochloride. In addition the nmr

showed a small singlet peak at Τ 7.9 which is probably due to

the presence of N-piperidinoacetamide.

D. In ethanol

The same photolysis as described in 12-C was repeated

excluding triphenylene. The solution was irradiated for

8 hours. The rate of disappearance of nitrosamine was found

to be 0.0025 moles per hour which was the same with that of

12-B and 12-C. The solvent was evaporated down to a small

volume under vacuum. The distilled ethanol was recovered

and a small portion (25 ml) was treated with 2,4-dinitrophe-

nylhydrazine to give yellow crystals of a 2,4-dinitrophenyl-

hydrazone of acetaldehyde: mp 140-143°   lit (64) 147°   ; ir

superimposable with an authentic sample. The residue left

after evaporation of the photolysate was recrystallized from

$CHCl_3$-ether solution to give white crystals of piperidine

hydrochloride (1.9 g): mp 190-205°.

Experimental

Section III

General procedure

In a photocell, N-nitrosopiperidine (2.3 g, 0.02 moles),
concentrated hydrochloric acid (2 ml, 0.024 moles) were dis-
solved in ethanol (1.4 l.). The optical density of the undi-
luted solution at 350 mu was measured to be 1.42. To this
solution was then added the aromatic compound (4-5 g, 0.025-
0.03 moles) to give a hetereogeneous solution. The optical
density was then measured again at 350 mu with 1/100 dilution.
The ratio of the incipient light absorbed by the aromatic com-
pound and the nitrosamine was calculated (see specific exam-
ples). The aromatic compound usually absorbed 95% or better
of the incident light. In the water jacketed inner sleeve
one of the following lamps was placed; RPR 3500A, RPR 3000A,
200 watt Hanovia or the 450 watt Hanovia lamp. The solutions
were kept under inert gas atmosphere. Nitrogen was scrubbed
with either a Fieser's solution (65) or a vanadyl sulfate (66)
solution. Helium gas was used directly from a bottle without
purification. The solution was then irradiated for periods
of 14-18 hours. To ensure that the concentration of the aro-
matic compound remained constant in the solution, an aliquot
(0.1 ml) was pipetted out at suitable intervals and was pro-

perly diluted (10 ml) for spectroscopic measurement. The optical density above 300 mu stayed nearly constant during the irradiation eg., the optical density at 350 mu at 0 hour was 0.30, after 3 hours 0.36, at 14 hours 0.41 with 1/100 dilution which corresponded to 95.3%, 96% and 96.5% of the light been absorbed by the aromatic compound.

On completion of the photolysis, the major part of the solvent was removed under vacuum at a bath temperature lower than 40°. The aromatic compound usually precipitated and was filtered. The filtrate was concentrated further and then treated with water (50-100 ml). This acidic aqueous layer was then extracted (50 ml x 3) with ether, $CHCl_3$ or CH_2Cl_2 to give a neutral fraction. The aqueous solution was then basified to pH 10-11 with a saturated K_2CO_3 solution. In some cases the basic product precipitated and was filtered. The filtrate was further extracted with an organic solvent. The crude products were chromatographed and/or recrystallized in order to effect purification. Generally a small sample was further recrystallized from a suitable solvent followed by sublimation to afford an analytical sample.

1. <u>Anthracene sensitized photoaddition of N-nitroso-piperidine in the presence of cyclohexene</u>.

A. <u>Under a nitrogen atmosphere</u>

In a photocell, N-nitrosopiperidine (2.3 g, 0.02 moles)

and cyclohexene (16.4 g, 0.2 moles) and concentrated hydro-

chloric acid (2 ml, 0.024 moles), ethanol (1.4 1.) were char-

ged. The optical density of the undiluted solution at 350 mu

was recorded to be 1.42. To this solution anthracene (5.4 g,

0.03 moles) was added. The suspension was vigorously stirred

for 1/2 hour under nitrogen atmosphere. A sample of the

supernatant solution showed the optical density 0.30 at 350 mu

with 1/100 dilution. The ratio of the optical density shows

that 95% of the incident light at 350 mu is absorbed by the

anthracene. While the hetereogeneous mixture was agitated

with a magnetic stirrer and a stream of nitrogen the solution

was irradiated with a RPR 3500Å lamp for 14 hours. At the

4 and 14 hour periods, the photolysate of the same dilution

(1/100) showed optical densities of 0.36 and 0.41 which indi-

cated that greater than 95% of the incident light is absorbed

by anthracene throughout the reaction. The photolysate was

worked up as described. Anthracene (3.3 g), which precipita-

ted upon the evaporation of the methanol, had mp 198-203°

lit (67) 218°. The acidic ether extract was evaporated to

give a mixture of an oil and crystals (1.0 g) which was shown

to contain N-nitrosopiperidine contaminated with anthracene:

ir 1280, 1180, 1098, 985, 1600, 1500, 860, 720; nmr Υ5.82 (m),

$\Upsilon 6.3$(m), $\Upsilon 8.35$(m), $\Upsilon 2.5$(m). The basic portion was evaporated to afford crystals (760 mg : mp 158-159°) which were recrystallized from 2-propanol twice followed by sublimation to give white crystals of 9-piperidino-10-ethoxy-9,10-dihydroanthracene III-7: mp 170-171°; ir 1317, 1290, 1250, 1178, 1115, 1080, 1065, 1038, 983, 880, 805, 748, 735; nmr Υ 2.45 (m), 2H), Υ 2.78 (m, 6H), Υ 4.26 (s, 1H), Υ 5.31 (s, 1H), Υ 6.17 (qt, 2H, J=7 cps), Υ 7.73 (m, 4H), Υ 8.60 (t, 3H, J=7 cps), Υ 8.63 (m, 6H); Anal. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C, 82.19; H, 8.27; N, 4.70.

The remaining basic extract, after removal of III-7, was chromatographed on silicic acid (30 g). A solid (69 mg) was eluted with pure $CHCl_3$ and was recrystallized from $CHCl_3$ to give needles of 9-nitroanthracene (III-4): mp 141-144° lit (68) 146°; ir 900, 875, 946, 780, 730; nmr 1.60 (s, 1H), 2.34 (m, 8H). The ir and nmr were superimposable with those of an authentic sample of III-4. The following fractions eluted with $CHCl_3$ gave a solid (372 mg) which was recrystallized from a 2-propanol-$CHCl_3$ mixture to give pale pink crystals of anthraquinone (III-5): mp 264-269° lit (69) 274° ; ir 1670, 1338, 1280, 1165, 940, 811, 698; nmr (trifluoroacetic acid) Υ 1.83 (A_2B_2. The ir and nmr spectra were superimposable with those of an authentic sample of III-5. The next 3 frac-

tions eluted with 1-4% methanol in $CHCl_3$, gave a mixture of

3 compounds (300 mg) in a ratio of (4:2:1) by nmr analysis.

The minor component was identified to be III-7 by nmr and

tlc comparison. The second minor component was N-nitrosopi-

peridine by comparison of the nmr spectra of the mixture with

that of authentic N-nitrosopiperidine. The major component

was identified as 9-piperidino-10-hydroxy-9,10-dihydroanthra-

cene (III-8) by nmr and tlc analysis. The nmr spectrum of

the mixture exhibited signals at τ2.78 (m, 8H), τ4.76

(s, 1H), τ6.07 (s, 1H), τ7.58 (m, 4H), τ8.62 (m, 6H).

Continued elution with 6% methanol in $CHCl_3$ gave a mix-

ture (900 mg). This mixture was rechromatographed on silicic

acid (16 g). With pure $CHCl_3$, III-7 (300 mg) was eluted. Elu-

tion with 2% methanol in $CHCl_3$ gave a fraction which was shown

to be 9-piperidino-10-anthrone oxime (III-1, 37 mg) by tlc

and ir comparison. Elution with 2-6% methanol in $CHCl_3$ gave

a fraction (332 mg) which was shown by tlc analysis to con-

tain a small amount of III-1 as the impurity. The impurity,

III-1, was easily removed by preferentially dissolving this

fraction in petroleum ether and filtering the solution. The

petroleum ether was then concentrated further to give crys-

tals of the other isomer of 9-piperidino-10-ethoxy-9,10-

dihydroanthracene (III-6, 150 mg): mp 77-80°; ir 1310, 1280,

1155, 1118, 1078, 998, 763; nmr Υ 2.70 (m, 8H), Υ 4.84 (s, 1H),

Υ 5.39 (s, 1H), Υ 6.43 (qt, 2H, J=7 cps), Υ 7.5 (m, 4H), Υ 7.65

(m, 6H), Υ 7.87 (t, 3H, J=7 cps); mass spectrum (80 eV) m/e

(rel intensity) 307 (2), 222 (12), 195 (48), 178 (100), 83

(77).

A tlc analysis of the basic crude product prior to puri-

fication, showed the presence of a faint new spot. This spot

had an identical Rf(0.30) as that of an authentic sample of

2-piperidinocyclohexanone oxime (III-14). The compound how-

ever could not be isolated in column chromatography.

B. Under helium atmosphere

The same quantities as those described in 1-A were photo-

lyzed in the same manner except that a helium atmosphere was

used. The irradiation was done with a RPR 3500Å source for

14 hours. Following the same isolation procedure anthracene

(3 g) and a residue (1.2 g) from $CHCl_3$ extraction of the

aqueous solution were obtained. The ir and nmr spectra of

the latter fraction showed it to be a 2:1 mixture of N-nitro-

sopiperidine and anthracene. The aqueous layer was then basi-

fied and a white solid (1.3 g, mp 176°dec) precipitated. The

solid (0.3 g) was crystallized twice from 2-propanol to give

9-piperidinoanthrone oxime (III-1, 100 mg): mp 182-184° (de-

composition with evolution of gas); ir 3300, 2400, 1500, 1325,

1193, 1165, 1144, 1118, 1098, 1072, 1060, 1038, 1000, 978, 962,

953, 940, 930, 894, 878, 850, 782, 758, 740, 719, 660; nmr

(pyridine-d$_5$) τ 0.9 (m, 1H), τ 1.8 (m, 1H), τ 2.5 (m, 6H),

τ 5.18 (s, 1H), τ 7.54 (m, 4H), τ 8.75 (m, 6H); Anal. Calcd

for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.90; N, 9.58. Found: C, 77.73;

H, 7.00; N, 9.49.

The filtrate was extracted with CH_2Cl_2 (50 ml x 3) to

give a mixture of oil and solid (607 mg). The mixture was

treated with $CHCl_3$ to afford crystals of III-1 (95 mg). The

mother liquor was evaporated to dryness and was chromatogra-

phed on silicic acid (10 g) to afford on elution with up to

2% methanol in $CHCl_3$, III-8 (69 mg), with 3-4% methanol in

$CHCl_3$, III-1 (125 mg), with 6-10% methanol in $CHCl_3$, a resin

(125 mg). This last resin was identified as 2-piperidinocy-

clohexanone oxime (III-14) by ir and nmr spectra and tlc com-

parison with those of an authentic sample.

C. <u>In the presence of 0.6 M cyclohexene</u>

The same experiment as 1-B except the quantity of cyclo-

hexene was 69 g (0.84 moles) was repeated. The optical den-

sity measurement at 350 mu before (1.44 no dilution) and

after (0.29 at 1/100 dilution) the addition of anthracene

showed that 95% of the incident light at 350 mu was absorbed

by anthracene. The solution was irradiated for 14 hours.

The ethanol was filtered to give white crystals which were identified as anthracene dimer (III-2, 1.29 g): mp 252-262° lit(70) 265 ; ir 1290, 1218, 1167, 1000, 943, 818, 860, 680. The ethanol was evaporated to a small volume (30 ml) and treated with $CHCl_3$ (100 ml). The $CHCl_3$ solution was extracted with a 2N hydrochloric acid solution (75 ml x 4). The $CHCl_3$ layer was evaporated to give a resinous solid. This solid was recrystallized from methanol to give anthracene (700 mg) identified by ir spectral comparison with that of an authentic sample. The mother liquor was evaporated to dryness to give an oil (400 mg) whose nmr spectrum showed it to be an equal mixture of N-nitrosopiperidine and 9-ethoxyanthrone oxime (III-3) by comparison of the nmr spectrum with those of authentic samples.

The basic $CHCl_3$ extract was obtained and worked up in a usual manner to give a solid which was crystallized from $CHCl_3$ to give white crystals of III-1 (700 mg): mp 180-183° decomposition with evolution of gas). The mother liquour was concentrated to give a second crop of III-1 (200 mg): mp 173-178°. The mother liquour was then evaporated to dryness to give a resin (468 mg) which by ir, nmr and tlc analysis was shown to contain mostly 2-piperidinocyclohexanone oxime (III-14) a trace of N-nitrosopiperidine and small amounts of III-1.

D. Irradiation at 300 mu under helium atmosphere

The nitrosamine (640 mg, 0.0057 moles), cyclohexene

(16.4 g, 0.02 moles), hydrochloric acid (2 mg, 0.024 moles)

and ethanol (1.4 l.) were placed in a photocell. The optical

density of the undiluted solution was 0.03 at 300 mu. Anthra-

cene (2.5 g, 0.014 moles) were suspended in the solution. This

solution showed optical density of 1.60 at 300 mu with 1/100

dilution. The ratio of the optical densities shows that anth-

racene absorbs greater than 99% of the light at 300 mu. The

cold finger of the photocell was filled with a solution of

N-nitrosodimethylamine (0.024M) in methanol which absorbs

100% of the light between 360 and 325 mu and showed an opti-

cal density of 0.36 and 300 mu. The solution was irradiated

with the RPR 3000Å for 14 hours. The solvent was evaporated

to a small volume and filtered to give anthracene (1.8 g).

The filtrate was treated with water and extracted with $CHCl_3$

(30 ml x 3) to give a mixture of oil and solid (600 mg),

which by nmr was shown to consist of N-nitrosopiperidine and

anthracene. The acidic aqueous layer was basified and extrac-

ted with $CHCl_3$ (30 ml x 3). The $CHCl_3$ was washed with water,

dried ($MgSO_4$) and evaporated to give a solid (29 mg) whose

nmr was superimposable with that of III-8.

E.   In the presence of 0.2 M bromobenzene

The same quantities of nitrosamine, cyclohexene, anthracene and hydrochloric acid as described in 1-A were dissolved in ethanol (1.4 1.).   In addition bromobenzene (44.0 g, 0.28 moles, 0.2M solution) was also included.   The solution was irradiated at 350 mu (14 hrs.) under a helium atmosphere. The photolysate was concentrated to about 50 ml and treated with 2 N hydrochloric acid (50 ml).   The usual work-up procedure gave III-2 (450 mg); mp 270-275° as the precipitate and a neutral $CHCl_3$ extract.   This extract was then treated with methanol and the crystals filtered to give anthracene (500 mg). The filtrate was evaporated to give a residue which was chromatographed on silicic acid (60 g).   Anthracene (1 g) bromobenzene (1 g) and N-nitrosopiperidine (0.5 g) were eluted out first.   The 4 fractions eluted with 3-6% methanol in $CHCl_3$ gave a solid.   Comparisons of the nmr spectra of these fractions indicated that these were mixture of the hydrochlorides of III-6 and III-7 in variable ratios.   Free bases of each fraction were liberated.   The first of the four fractions is nearly pure III-6 as shown by the signals at $\Upsilon 4.2$, $\Upsilon 5.7$ and $\Upsilon 7.12$.   The content of III-7 increased in the following fractions since the intensity of the signals at $\Upsilon 4.85$ (s), $\Upsilon 5.38$ (s), $\Upsilon 6.4$ (qt) increased.

The acidic aqueous layer was then basified to pH-10 and extracted with $CHCl_3$ (30 ml x 3). The $CHCl_3$ was washed with water, dried ($MgSO_4$) and evaporated to give a resin (330 mg). The nmr and ir spectra of this resin showed typical absorption of 2-piperidinocyclohexanone oxime (III-14) and in addition showed a small singlet at $\tau 5.3$ for III-1. The resin was dissolved in $CHCl_3$ to give crystals of III-1 (17 mg), superimposable ir spectrum.

2. Photoaddition of N-nitrosopiperidine to anthracene

A. Under a nitrogen atmosphere

The nitroso compound (2.3 g, 0.02 moles) concentrated hydrochloric acid (2 ml, 0.024 moles) in ethanol (1.4 1.) exhibited an optical density of 1.40 at 350 mu. Anthracene (5.4 g, 0.03 moles) was added and vigorously stirred for 1/2 hour. The supernatant liquid exhibited optical density of 0.34 at 350 mu with 1/100 dilution. The heterogeneous solution was irradiated for 14 hours with an RPR 3500Å source. The photolysate was concentrated to 60 ml and diluted with water. The precipitated anthracene (2.68 g) was filtered. The acidic aqueous layer was extracted with CH_2Cl_2 (50 ml x 3). The CH_2Cl_2 extract was washed with water, dried ($MgSO_4$) and evaporated to give a resin (2.0 g) which was chromatographed on silicic acid (60 g). Eluting with $CHCl_3$ gave crystals

(13 mg) which were identified as 9-nitroanthracene III-4:

mp 138-143° lit (68) 146° . The following fraction gave a

mixture of an oil and a solid (665 mg). The crystals were

filtered and identified as anthraquinone (III-5, 200 mg):

mp 270° (sublimation). The mother liquour was shown to be

N-nitrosopiperidine by nmr analysis. Eluting with 2-20%

methanol in $CHCl_3$ gave a mixture of hydrochlorides of III-6

and III-7 (800 mg). The mixture was dissolved in $CHCl_3$ and

washed with a K_2CO_3 solution, $CHCl_3$ was washed with water,

dried ($MgSO_4$) and evaporated to afford a mixture of III-6

and III-7 in about a 3:1 ratio by nmr spectral comparison

with those of authentic samples.

The acidic aqueous layer was then basified to pH-10

with a saturated K_2CO_3 solution to give pure crystals of

III-1 (1.25 g): mp 183-4° (decomposition).

B. Under a helium atmosphere

The same quantities as described in 2-A were used. The

solution was kept under a helium atmosphere and irradiated

with a RPR 3500Å lamp for 17 hours. The usual isolation pro-

cedure was followed. The recovered anthracene (2.8 g) was

contaminated with a small amount of anthracene dimer III-2:

ir 820, 770, 680 cm^{-1}. The neutral extract gave a resin

(1.5 g) which was chromatographed on silicic acid (40 g).

Eluting with $CHCl_3$ gave anthracene (76 mg). The following fractions gave N-nitrosopiperidine (500 mg). Eluting with 2% methanol in $CHCl_3$ gave a solid which was sublimed to give crystals of 9-ethoxyanthrone oxime (III-3, 200 mg): mp 155-158°; ir 3400, 1680, 1320, 1295, 1000, 980, 950, 800, 780, 715, 693; nmr τ1.5 (m, 1H), τ2.05 (m, 1H), τ2.53 (m, 6H), τ4.60 (s, 1H), τ6.44 (qt, 2H, J=7 cps), τ8.76 (t, 3H, J=7 cps); mass spectrum (15 eV) $\underline{m/e}$ (rel intensity) 253 (89), 208 (100). The following fractions eluted with 8-32% methanol in $CHCl_3$ gave III-3 (160 mg). The last fraction (38 mg) was green in color but the color faded gradually. A tlc analysis showed the presence of III-3 and two spots of higher Rf in this mixture.

The aqueous layer was basified with a saturated K_2CO_3 solution to give a white precipitate (3.3 g) of nearly pure III-1: mp 182-184°; ir superimposable with the analytical sample. The aqueous filtrate was extracted with CH_2Cl_2 (50 ml x 3) to afford a mixture (50 mg) which by tlc analysis showed 6 spots. The characterization of the compounds in this mixture was not pursued.

C. Under an oxygen atmosphere

The same quantities of starting materials as those described in 2-A were used. The procedure was the same except

that oxygen gas was used instead of nitrogen. The solution
was irradiated for 17 hours with a RPR 3500Å source. The pre-
cipitate (2.0 g) upon evaporation of the solvent was identi-
fied as a mixture of anthracene and anthraquinone: ir peaks
at 1680, 900, 740 cm^{-1} and mp 185-258°. The CH_2Cl_2 neutral
extract (1.0 g) gave a mixture of an oil and solid which was
shown to be N-nitrosopiperidine and anthracene by ir and nmr
analysis.

The aqueous solution, on basification with a saturated
K_2CO_3 solution turned pink and afforded a red basic resin
upon the usual work-up. The resin upon treatment with etha-
nol gave crystals of III-5 (285 mg: mp 274-277°, sublimation);
ir 1680, 840, 820, 700 cm^{-1}. The mother liquour was evapora-
ted to a smaller volume to give a second crop of crystalline
crude III-8 (533 mg, 155-158°) which were contaminated by a
trace of anthraquinone nmr, (γ 2.1 (m); ir 1680 cm^{-1}). The
mother liquour was evaporated to dryness (680 mg) and chroma-
tographed on silicic acid (15 g). Eluting with benzene gave
a mixture of anthracene and anthraquinone (28 mg): nmr A_2B_2
systems at γ 2.0 and γ 2.5. The following fractions eluted
with benzene and up to 4% methanol in $CHCl_3$ gave III-8
(single spot on tlc, 300 mg). One of these fractions (154 mg)
was sublimed but turned yellowish in the process. The subli-

mate was recrystallized twice from ethanol to give diamond-

like crystals of III-8: mp 168-170°; ir 3200, 1275, 1000, 900,

760; nmr τ 2.78 (m, 8H), τ 3.86 (bm, 1H, D_2O exchangeable).

τ 4.76 (s, 1H), τ 6.07 (s, 1H), τ 7.58 (m, 4H), τ 8.62 (m, 6H);

Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found:

C, 81.62; H, 7.64; N, 5.11.

Elution with 8-20% methanol gave a mixture of the hydro-

chlorides of III-6 and III-7 (200 mg). The mixture of the

bases of III-6 and III-7 was liberated with K_2CO_3 solution:

nmr τ 4.82 (s), τ 4.85 (s), τ 5.7 (s), τ 5.88 (s), τ 6.12 (qt),

τ 6.4 (qt).

In a second experiment the same reaction was repeated.

The photolysate was concentrated to give crude anthracene

(2.3 g) which contained some anthraquinone: mp 185-190; ir

1680 cm^{-1} . The filtrate was evaporated further to give a

second crop (150 mg) of anthraquinone: mp 274-279°.

The methanol was removed and the residue was chromato-

graphed on silicic acid (60 g). Eluting with $CHCl_3$ gave

anthracene, followed by N-nitrosopiperidine. Continued elu-

tion with $CHCl_3$ and 2-12% methanol in $CHCl_3$ gave an oil which

decomposed on heating. One of the fractions was dissolved

in $CHCl_3$. Addition of ether afforded crystals (400 mg); mp

100° (decomposition). Continued heating of the melting point

sample up to 270° gave a yellow sublimate. This crop of crys-
tals were recrystallized three times from $CHCl_3$-ether and is
tentatively assigned as the nitrate salt of 9-piperidino-
anthrone (III-12): mp 158.5-160° (decomposition); 2800, 2200,
1678, 1600, 1580, 1300, 940, 720, 700; nmr τ2.2 (m, 8H),
τ3.98 (s, 1H), τ6.60 (bm, 4H), τ8.18 (bm, 6H); Anal. Calcd
for $C_{19}H_{20}N_2O_4$: C, 67.05; H, 5.92; N, 8.23. Found: c, 67.34;
H, 5.89; N, 8.29.

Upon standing for 6 months the mother liquour from these
crystals was dissolved in $CHCl_3$. The $CHCl_3$ extract was washed
with base and then with water. The $CHCl_3$ was then dried and
evaporated to give a resin (624 mg) whose ir showed it to be
mostly anthraquinone: ir 1680, 1280, 948, 820, 700 cm^{-1}.

D. In the presence of 0.2M bromobenzene

A solution of the nitrosamine (638 mg, 0.0056 moles),
bromobenzene (12.56 g, 0.08 moles, 0.2M) and concentrated
hydrochloric acid (2 ml, 0.024 moles) in methanol (400 ml)
showed an optical density of 0.14 at 350 mu with 1/10 dilu-
tion. Anthracene (1.99 g, 0.0084 moles) was added and stir-
red. The supernatant liquid showed an optical density of
0.24 at 350 mu with 1/100 dilution. The ratio of the optical
densities showed that anthracene absorbs 94% of the incident
light at 350 mu. While the solution was kept under a helium

atmosphere it was irradiated (RPR 3500Å lamp) for 12 hours.

The photolysate was concentrated down to about 30 ml and CH$_2$Cl$_2$ (100 ml) was added. The CH$_2$Cl$_2$ was extracted with 2N hydrochloric acid solution (30 ml x 3) washed with water, dried (MgSO$_4$), filtered and evaporated to give a mixture of solid and oil (5.4 g). The nmr spectrum of this crude product indicate the presence of bromobenzene, anthracene and a small amount of N-nitrosopiperidine. This fraction was not investigated further. The acidic aqueous layer was basified to pH-10 and extracted with CH$_2$Cl$_2$ (30 ml x 3). The CH$_2$Cl$_2$ extract was washed with water, dried (MgSO$_4$) and evaporated to give a solid (420 mg) which was crystallized from CHCl$_3$ to give III-1: mp 176-179° (dec, gas).

E. In the presence of 0.6M bromobenzene

The same solution of 2-B carrying bromobenzene (132 g, 0.84 moles, 0.6M) and anthracene (3.2 g, 0.018 moles) in ethanol (1.4l.) was photolysed for 14 hrs. under helium atmosphere with a RPR 3500Å lamp. White crystals of anthracene dimer III-2 (660 mg) were filtered off from the photolysate: mp 256-262°. The filtrate was evaporated to a small volume and CHCl$_3$ was added (100 ml) to give a crystalline precipitate. This precipitate was dissolved in water and the solution was basified to pH-10 to give white crystals of III-1 (0.81 g)

whose ir was superimposable with that of an authentic sample.
The acidic $CHCl_3$ extract was washed, dried ($MgSO_4$) and evapo-
rated to give a mixture of oil and solid which was filtered
to give a solid (460 mg): mp 210-216°; ir superimposable with
that of anthracene. The mother liquour contained bromoben-
zene and N-nitrosopiperidine by ir and nmr analysis. The
acid aqueous solution was basified to give crystals of III-1
(0.82 g) whose ir was identical with that of an authentic
sample of III-1.

F. In the absence of hydrochloric acid

The same solution as 2A containing the nitrosamine
(2.3 g, 0.02 moles) and anthracene (3.7 g) but no hydrochlo-
ric acid was irradiated with a RPR 3500Å lamp for 15 hours
under helium atmosphere. At the end of the photolysis,
hydrochloric acid (3 ml, 0.036 moles) was added and the solu-
tion was evaporated to a small volume (100 ml). The precipi-
tate was filtered (1.85 g, mp 208-260°) which by ir (960,
820, 770, 730, 680), was shown to be a 1:1 mixture of anth-
racene and anthracene dimer III-2. The filtrate was separa-
ted into an neutral (1 g) and a basic (171 mg) fraction in
the usual manner. The neutral fraction contained anthracene
and N-nitrosopiperidine as shown by ir which showed peaks at
1200, 1100, 1000 and 890. The basic fraction, upon treatment

with methanol gave anthraquinone (III-5, 20 mg, ir 1680, 1280,

948, 820, 700). The mother liquour was evaporated to dryness

and chromatographed on silicic acid (4 g) to afford N-nitroso-

piperidine (30 mg) and a solid (100 mg). The solid showed ir

3200, 100, 750; nmr τ2.8 (m, 8H), τ4.8 (s, 1H); τ6.1

(s, 1H), τ7.63 (m, 4H), τ8.6 (m, 6H) that were superimpo-

sable with authentic sample of III-8.

3. Bromobenzene sensitized isomerization of cis-4-
methyl-2-pentene

The cis-4-methyl-2-pentene (2.8 g, 0.03 moles, 0.2M) and

bromobenzene (13.3 g, 0.12 moles, 0.6M) were dissolved in etha-

nol (140 ml). This solution was irradiated with the 200 watt

Hanovia lamp whose emission was filtered through a Corex fil-

ter: 100% absorption at 2580Å, 50% absorption at 2700Å, and

0% absorption at 3000Å. The isomerization was followed by

vpc (12 ft. x 1/8 in., 30% $AgNO_3$- TEG (1:3) on firebrick,

35 ml of N_2/min., 22°). After 3 hours of irradiation, 88% of

the cis-olefin was isomerized to the trans isomer. The trans

isomer had a retention time of 6 min., the cis isomer 8 min.

4. Anthracene sensitized photoaddition in the presence
of bromobenzene and cis-4-methyl-2-pentene

The nitrosamine (2.3 g, 0.02 moles), cis-4-methyl-2-

pentene (16.4 g, 0.2 moles), bromobenzene (44. g, 0.36 moles)

and concentrated hydrochloric acid in ethanol (1.4 1.) showed

optical density of 0.72 at 350 mu. To the solution was added

anthracene (4. g, 0.02 moles) and the measured optical den-

sity was 0.85 at 350 mu with 1/50 dilution. The optical den-

sity ratio showed 97% of the incident light is absorbed by

anthracene. The solution was irradiated with RPR 3500Å lamp

through a soft glass filter for 22 hours. After 15 and 22

hours of irradiation, the vpc analysis of the olefin showed

that no isomerization of the olefin had occurred. The depo-

sited white crystals (685 mg) were filtered to give anthra-

cene dimer III-2: ir 820, 770, 680 cm^{-1} .

The solution was worked up in the usual manner to give

the neutral and basic fraction. The neutral fraction contai-

ned bromobenzene, anthracene and N-nitrosopiperidine as iden-

tified by ir and nmr spectral analysis. The basic fraction

gave crystals of III-1 (1.44 g; ir 100, 900, 780, 758) and

a resin which by ir and nmr spectral comparison with authen-

tic samples was shown to be a (1:1) mixture of N-nitrosopipe-

ridine and III-1: nmr τ 2.1 (m, 1H), τ 4.7 (s, 1H), τ 5.9

(m, 2H), τ 6.3 (m, 2H).

5. <u>Irradiation of anthracene in the presence of bromo-</u>
<u>benzene and cis-4-methyl-2-pentene</u>

Bromobenzene (37.9 g, 0.24 moles) and <u>cis</u>-4-methyl-2-

pentene (6.72 g, 0.082 moles, 0.2M) were dissolved in ethanol

(400 ml). To this solution was added anthracene (1.6 g, 0.009 moles) and the heterogeneous solution was stirred vigorously under helium atmosphere. The solution was irradiated with the RPR 3500Å lamp filtered through soft glass. The solution was examined by the same vpc analysis which showed that the olefin was not isomerized as witnessed by the absence of a peak with the retention time (6 min) corresponding to trans-4-methyl-2-pentene.

The solution was then filtered to give white crystals (1.0 g): mp 263-268°; ir 820, 770, 680 superimposable with authentic III-2.

6. Irradiation of N-nitrosopiperidine in the presence of bromobenzene and cis-4-methyl-2-pentene

N-nitrosopiperidine (2.3 g, 0.02 moles), bromobenzene (13.3 g, 0.084 moles) and cis-4-methyl-2-pentene (2.5 g, 0.033 moles) were dissolved in ethanol (140 ml). The solution was irradiated through soft glass with a RPR 3500Å source for 24 hours. At this time the vpc analysis showed 2% isomerization by the appearance of the new vpc peak corresponding to the retention time of trans-4-methyl-2-pentene (6 min.).

7. Attempted isomerization of cis-4-methyl-2-pentene
by N-nitrosopiperidine

A solution of nitrosamine (2.3 g, 0.02 moles) and cis-4-methyl-2-pentene (2.5 g, 0.033 moles) in ethanol (140 ml) was irradiated through soft glass with a RPR 3500Å source for 24 hours. During the irradiation, the vpc analysis of the solution showed no new peaks having the retention time of the trans-4-methyl-2-pentene.

8. Photolysis of N-nitrosopiperidine in the presence
of bromobenzene and cyclohexene

The nitrosamine (2.3 g, 0.02 moles), cyclohexene (4.1 g, 0.005 moles), bromobenzene (12.56 g, 0.08 moles) and concentrated hydrochloric acid (2 ml, 0.024 moles) were dissolved in methanol (400 ml). The solution was irradiated to completion of reaction (6 hrs.) with a RPR 3500Å lamp. The basic extract contained the crude addition product to cyclohexene III-14 (2.55 g) as shown by ir and nmr spectral comparison with authentic sample.

An identical reaction was repeated except that bromobenzene was omitted in the reaction mixture. The rate of disappearance of the nitrosamine was 0.0033 moles per hour which was the same as in the presence of bromobenzene. The basic extract (2.62 g) gave off a resin whose ir and nmr

spectral analysis showed it to be the cyclohexene adduct

III-14. A comparison of the two crude basic extracts on a

tlc plate showed them indistinguishable from one another.

The crude extract showed spots with Rf of 0.54, 0.22, 0.14,

0.09. The last of which corresponded to III-14. The three

upper spots are the minor unidentified products.

9. Photoaddition of N-nitrosopiperidine to cyclohexene

in the presence of oxygen

A solution of N-nitrosopiperidine (2.3 g, 0.02 moles),

cyclohexene (2.56, 0.03 moles) and concentrated hydrochloric

acid (2 ml, 0.024 moles) in methanol (140 ml) was prepared

and irradiated with the 200 watt Hanovia lamp for 80 minutes

while oxygen gas was bubbled at a moderate rate through the

solution. The methanol was evaporated to a small volume

under vacuum at a water bath temperature of 10° (if heated,

the solution darkens). The methanol was cooled to 0° and

then ether was added gradually to produce slight cloudiness.

Crystals (1.1 g) appeared upon standing at 0°: mp 159-161°

(decomposition). They were recrystallized three times from

2-propanol to give the hydrochloride salt of cis-1-nitrato-

2-piperidinocyclohexane (III-9); mp 169-170°; ir 2500, 1640,

1266, 870; nmr (D$_2$O) τ4.47 (m, 1H), τ6.76 (bm, 3H),

τ7.12 (bm, 2H), τ8.33 (bm, 14H); Anal. Calcd for

$C_{11}H_{21}N_2O_3Cl \cdot H_2O$: C, 47.05; H, 7.48; N, 9.98; Cl, 1265.

Found: C, 46.82; H, 7.89; N, 10.12; Cl, 12.56.

The mother liquour from the first crop of crystals was cooled for another 3 months at -10° to give a second crop of crystals (300 mg) which showed in the nmr spectra a broad multiplet at $\tau 4.77$. These crystals were recrystallized three times from a mixture of 2-propanol-ether to afford the hydrochloride salt of <u>trans</u>-1-nitrato-2-piperidinocyclohexane (III-10): mp 134-137°; ir 3250, 2650, 2530, 1630, 1270, 880; nmr (D_2O) τ 4.77 (bm, 1H), τ 6.65 (b, 5H), $\tau 8.15$ (bm, 14H); Anal. Calcd for $C_{11}H_{21}N_2O_3Cl$: C, 49.90; H, 7.95; N, 10.58; Cl, 13.40. Found: C, 50.10; H, 7.76; N, 10.42; Cl, 13.27.

The presence of 2-piperidinocyclohexanone hydrochloric acid salt (III-13) could be detected by ir (1680 cm^{-1}).

10. <u>Photolysis</u> <u>of</u> <u>9-piperidino-10-anthrone</u> <u>oxime</u> <u>(III-1)</u>

Compound III-1 (1.0 g, 0.003 moles) and concentrated hydrochloric acid (2 ml, 0.024 moles) were dissolved in ethanol (400 ml). The optical density at 310 mu was 2 with 1/10 dilution. The solution was irradiated with a RPR 3000Å source for 13 hours. The solvent was removed under vacuum to a small volume (30 ml) to afford a green solution. The solution was treated with water (50 ml) and the mixture extracted with $CHCl_3$ (30 ml x 3). The green color passes into the organic

layer. Upon washing the CHCl$_3$ extract with water the green color disappears. The CHCl$_3$ was dried (MgSO$_4$) and evaporated to give a solid (288 mg). The solid was suspended in a small amount of CHCl$_3$ and filtered to give III-1 (256 mg): mp 178-180° (decomposition). The mother liquour was evaporated to dryness to give a crude resin (32 mg) whose nmr spectra showed it to contain mostly III-3: nmr Υ4.3 (s, 1H), Υ6.4 (qt, 2H), Υ8.7 (t, 3H). The acidic aqueous layer was basified to pH 9-10 and was worked to give III-1 (641 mg): mp 182-184° dec.

11. **Irradiation of 1,4-dimethylanthracene in presence of N-nitrosopiperidine**

The nitrosamine (3.05 g, 0.03 moles) concentrated hydrochloric acid (17.5 ml) and 1,4-dimethylanthracene (1,4-DMA, 3.24 g, 0.014 moles) were dissolved in methanol (400 ml). The solution was irradiated under nitrogen with the 200 watt Hanovia lamp for 6 hours. The deposited crystals were filtered to give 1,4-DMA dimer III-25 (335 mg): mp 242-250; ir 1160, 1030, 938, 807, 760, 750, 660; nmr Υ3.16 (m, 8H), Υ3.56 (s, 4H), Υ5.27 (s, 4H), Υ7.74 (s, 12H). The filtrate was worked up in the usual manner to give the syrupy neutral (5.3 g) and the basic fraction (930 mg). This crude neutral resin (1.0 g) was chromatographed on silicic acid (50 g). Elution with CHCl$_3$ gave N-nitrosopiperidine (100 mg).

Elution with $CHCl_3$ and up to 5% methanol in $CHCl_3$ gave several fractions of a resin which consisted of mostly of the hydrochloride of III-26 (400 mg); ir 3450, 2490, 1600, 1500, 1250, 900, 820, 750; nmr τ 1.75 (m, 2H), τ 2.52 (m, 4H), τ 3.37 (s, 1H), τ 4.50 (s, 1H), τ 6.44 (s, 3H), τ 6.56 (b, 4H), τ 7.31 (s, 3H), τ 7.48 (s, 3H), τ 8.30 (m, 6H). One of these fractions (153 mg) was treated with a saturated K_2CO_3 solution to give a crude resin (100 mg) whose nmr and ir spectra were identical with those of authentic III-25: nmr τ 4.77 (s), τ 5.70 (s), τ 6.52 (s).

The basic syrup was treated with 2-propanol to give crystals (155 mg) which were recrystallized 4 times and sublimed (115°, 0.2 mm Hg) to afford an analytical sample of 1,4-dimethyl-9-piperidino-10-methoxy-9, 10-dihydroanthracene (III-26); mp 145-146°; ir 1612, 1585, 1078, 935, 825, 810, 760, 740; nmr τ 2.60 (s, 4H), τ 2.87 (s, 2H), τ 4.77 (s, 1H), τ 5.70 (s, 1H), τ 6.52 (s, 3H), τ 7.1-8.0 (m, 4H), τ 7.48 (s, 3H), τ 7.52 (s, 3H), τ 8.65 (m, 6H); Anal. Calcd for $C_{22}H_{27}NO$; C, 82.84; H, 8.41; N, 4.36. Found C, 82.16; H, 8.34; N, 4.51. The mother liquour was evaporated to dryness (384 mg) and chromatographed on alumina (40 g). Eluting with 20% $CHCl_3$ in CH_2Cl_2 gave a resin (90 mg) identified as III-26 by ir spectral comparison. The following 3 fractions (30 mg) gave a solid which was crystallized from methanol to

give 1,4-dimethyl-9-piperidino-10-hydroxy-9,10-dihydroanthra-

cene III-27: mp 206-207°; ir 3300, 1600, 1500, 1108, 1070,

1039, 980, 970, 950, 828, 820, 750; nmr τ2.76 (m, 4H),

τ3.00 (s, 2H), τ4.38 (s, 1H), τ5.63 (s, 1H), τ7.50 (s, 3H),

τ7.60 (s, 3H), τ7.50-7.60 (m, 4H), τ8.61 (m, 6H); mass spec-

trum (1,7 kV) $\underline{m/e}$ (rel intensity) 307 (81), 224 (100), 204

(80); (M+) Calcd for $C_{21}H_{25}NO$;307.1936. Found 307.1932.

12. Preparation of 1,4-dimethylanthracene

A similar procedure as that described by Feiser (58) was

used. Phthalic anhydride (75 g, 0.5 moles) was dissolved in

p-xylene (350 ml). To this solution was added $AlCl_3$(134 g)

and mixture was cooled in an ice water bath. After the evolu-

tion of heat had subsided the reaction was heated in a steam

bath for 45 min. The red vat was worked up in the usual manner

to give the crystalline o-xyloylbenzoic acid (110 g): mp 95-111°.

The solid was then poured into cold 0° concentrated sulfuric

acid (600 ml). After all the solid had gone into solution

another 300 ml of sulfuric acid were added and the solution

was warmed on the steam bath at 65-68° for 20 min. The solu-

tion was cooled to 10° and poured into ice. The solid was

then dissolved in CH_2Cl_2 (1 l.) and the solution washed with

a saturated K_2CO_3 solution (300 ml x 3). The CH_2Cl_2 solution

was then washed with water and dried ($MgSO_4$) and concentrated

to a smaller volume (400 ml) to give crystals of 1,4-dimethyl-anthraquinone: mp 134-137° lit (71) 140-141° .

A modification of the Clemmensen reduction (59) was used for the reduction of the anthraquinone. To a solution of the anthraquinone (20 g, 0.085 moles) in xylene (200 ml) water was added (200 ml) followed by zinc (41. g, 0.64 moles) and KOH (51 g, 128 moles). The solution was refluxed with stirring for 90 hours until the red color disappeared. The xylene layer was worked up and then evaporated under vacuum to a small volume (60 ml). Treatment with methanol to cloudiness gave crystals of 1,4-DMA (16 g): mp 68-70° lit (72) 72° .

13. Photolysis of 1,3-dimethylanthracene

N-nitrosopiperidine (1.14 g, 0.01 moles), 1,3-dimethylan-thracene (1,3-DMA, 1.17 g, 0.005 moles) and concentrated hydrochloric acid (10 ml, 0.120 moles) were placed in glacial acetic acid. The resulting hetereogeneous solution was irra-diated with the 450 watt Hanovia lamp for 8 hours. At this time the solution was filtered to give crude crystals of 1,3-DMA dimer (III-19, 125 mg): mp 230-234°: ir 1610, 1585, 1030, 860, 848, 760, 660; nmr τ 3.14 (m, 10H), τ 7.68 (s, 3H), τ 7.76 (s, 3H), τ 7.87 (s, 3H), τ 7.95 (s, 3H). To the gla-cial acetic acid solution was added Na_2CO_3 (7.2 g) and the acetic acid was removed under vacuum to a small volume. The

residue was diluted with water (50 ml) and the water was extrac-
ted with ether. The ether was then washed with a solution of
K_2CO_3 (100 ml x 3) and then with water. The resin (1.1 g)
obtained from ether fraction was chromatographed on silicic
acid (45 g). Elution with $CHCl_3$ gave fraction A (423 mg) which
was a mixture of several compounds by tlc analysis. On conti-
nued elution, a second fraction B gave a resin (136 mg) which
on inspection by tlc showed one predominant spot. Continued
elution with $CHCl_3$ and up to 10% methanol in $CHCl_3$, gave frac-
tion C (450 mg) which consisted of a mixture of 2 compounds by
nmr and tlc analysis.

Fraction A was dissolved in methanol to afford crystals
of 1,3-DMA dimer (III-19, 28 mg): mp 203-215°; ir 1610, 1585,
1030, 860, 848, 760, 660. The mother liquour from these crys-
tals was evaporated to dryness (400 mg) and was chromatographed
on alumina (12 g). Elution with cyclohexane gave 6 fractions
(175 mg) which contained two predominant compounds as shown
by tlc with Rf 0.87 and 0.81 respectively. The first fraction
obtained from cyclohexane (95 mg) was recrystallized from
2-propanol to give 1,3-dimethyl-9-chloroanthracene. (III-20,
20 mg): mp 177-180°; ir 1613, 1591, 896, 883, 868, 855, 790,
765, 733, 685, nmr τ 2.63 (m, 1H), τ 3.18 (m, 4H), τ 3.52
(m, 1H), τ 4.89 (s, 1H), τ 7.70 (s, 3H), τ 7.96 (s, 3H); mass

spectrum (1.5 kV) m/e (rel intensity) 242 (100), 225 (4), 206 (32); (M^+) calcd for $C_{16}H_{13}Cl^{35}$; $C_{16}H_{13}Cl^{37}$; $C_{15}{}^{12}C^{13}H_{13}Cl^{37}$: 240.0710; 242.0674; 243.0706. Found: 240.0706; 242.0676; 243.0710. The other chlorosubstituted 1,3-DMA (III-21) could not be separated from III-20 but the compound exhibited a similar nmr: Υ 2.63-3.52 (m, 6H), Υ 4.95 (s, 1H), Υ 7.78 (s, 3H), Υ 7.96 (s, 3H). Continued elution with benzene and up to 25% $CHCl_3$ in benzene gave the anthraquinone (40 mg); superimposable ir spectrum.

Fraction B was predominantly one compound contaminated by an impurity (Υ 7.73). The resin was dissolved in a mixture of methanol-water to afford crystals (55 mg, mp 130-134°) which were recrystallized from 2-propanol twice to afford an analytical sample of 1,3-dimethyl-9-acetoxyanthrone (III-22): mp, 134-138°; ir 1740, 1660, 1340, 1210, 1100; nmr Υ 1.85 (m, 1H), Υ 2.11 (m, 1H), Υ 2.44 (m, 3H), Υ 2.78 (m, 2H), Υ 7.58 (s, 3H), Υ 7.63 (s, 3H), Υ 7.99 (s, 3H); mass spectrum (1.5 kV) m/e (rel intensity) 280 (16), 238 (40), 221 (100); (M^+) calcd for $C_{18}H_{16}O_3$: 280.1099. Found: 280.1098.

Fraction C consisted of a mixture (450 mg) of 1,3-dimethyl-9,10-dihydro-9-piperidino-10-hydroxy anthracene (III-23) and 1,3-dimethyl-9,10-dihydro-9-hydroxy-10-piperidinoanthracene (III-24). The mixture was rechromatographed on silicic

acid (20 g) but could not be separated. The physical data of
the mixture was: ir 3400, 1660, 1610, 1595, 1000-900, 738;
nmr τ2.74 (m, 4H), τ3.07 (s, 2H), τ3.83 (b, 1H, D_2O
exchangeable), τ4.46 (s, 7/12H), τ4.81 (s, 5/12H), τ5.70
(s, 5/12H), τ6.14 (s, 7/12H), τ7.53-7.74 (m, 10H), τ8.59
(m, 6H)..

14. Preparation of 1,3-dimethylanthracene

The same procedure as described in 12 was used. The
phthalic anhydride (75 g, 0.5 moles) was dissolved in m-xylene
(200 ml) and treated with $AlCl_3$ (155 g). The vat was cooled
until the heat had subsided and then heated on the steam bath
for 1/2 hour. The red paste was worked up to give crystals
of o-xyloylbenzoic acid: mp 123-218°. These crystals were
then treated with concentrated sulfuric acid (900 ml) on a
hot plate at 105° for 5 min. to give crystals of 1,3-dimethyl-
anthraquinone (50 g): mp 154-156° lit (73) 162° . The 1,3-
dimethylanthraquinone (20 g) was reduced with aqueous KOH
(44 g) and a zinc (51 g) suspension in xylene (280 ml) to
afford pale yellow crystals of 1,3-DMA (16 g): mp 74-76°
 lit (73) 79-80° .

15. Photolysis of 1,2-benzanthracene

N-nitrosodimethylamine (1.45 g, 0.02 moles) and concen-
trated hydrochloric acid (1.75 ml, 0.02 moles) were dissolved

in glacial acetic acid (300 ml). To the solution was added
1,2-benzanthracene (1.15 g, 0.005 moles) and the hetereoge-
neous solution was irradiated with a 450 watt Hanovia lamp
for 135 minutes. The photolysate was transferred to a round
bottom flask and the photocell washed with methanol and the
washings were combined with the acetic acid solution. The
photolysate was worked up to give the neutral (1.27 g) and
the basic (534 mg) fraction. The neutral fraction was a mix-
ture (1.27 g) of 1,2-benzanthracene and N-nitrosodimethyla-
mine contaminated by small amounts of the basic products
III-29 and III-28 by nmr analysis, Υ 6.48 (s), Υ 7.38 (s),
Υ 7.46 (s). The basic fraction was chromatographed on alu-
mina (15 g). Elution with benzene gave a compound which was
identified as 9-methoxy-10-dimethylamino-9,10-dihydro-1,2-
benzanthracene (III-28, 90 mg): nmr Υ 1.75 - 2.87 (m, 10H),
Υ 4.24 (s, 1H), Υ 5.20 (s, 1H), Υ 6.57 (s, 3H), Υ 7.72 (s, 6H).
Continued elution with 10-20% $CHCl_3$ in benzene afforded a
solid (170 mg), which was crystallized from 2-propanol twice
and sublimed to give crystals of 9-hydroxy-10-dimethylamino-
9,10-dihydro-1,2-benzanthracene (III-29): mp 170-172°; ir
3200, 1162, 1141, 984, 955, 868, 818, 762, 746, 737; nmr
Υ 2.16-300 (m, 10H), Υ 3.66 (b, 1H), D_2O exchangeable), Υ 3.84
(s, 1H), Υ 6.10 (s, 1H), Υ 7.88 (s, 6H); mass spectrum

(1.7 kV) $\underline{m/e}$ (rel intensity) 289 (65), 245 (100), 229 (85).

(M^+) calcd for $C_{20}H_{19}NO$: 289.1467. Found: 289.1476.

16. Irradiation of Acenaphthylene in presence of N-nitrosodimethylamine.

A solution of the nitrosamine (3.70 g, 0.05 moles) concentrated hydrochloric acid (7.5 ml, 0.09 moles) and acenaphthylene (9.10 g, 0.06 moles) in methanol (400 ml) was irradiated with the 200 watt Hanovia lamp for 8 hours. The solution was then filtered to give crystals of acenaphthylene dimer (III-17, 603 mg): mp 227-229°   lit (31) 234 ; ir 3030, 1600, 1800, 860, 770; nmr τ 2.89 (m, 3H), τ 5.2 (s, 1H); Anal. Calcd for $C_{24}H_{16}$: C, 94.74; H, 5.26. Found: C, 94.44; H, 5.40.

The solution was evaporated to a volume of 40 ml and cooled to give crystals (800 mg, mp 230-235° dec) which were crystallized from 2-propanol three times to give acenaphthaquinone (III-18): mp 252-255°   lit (32) 261° ; ir 1720, 1260; Anal Calcd for $C_{12}H_6O_2$: C, 79.12; H, 3.31. Found: C, 78.82; H, 3.45.

The concentrated photolysate solution was worked up in the usual manner to give a neutral (3.7 g) and a basic (5.9 g) fraction. The neutral fraction contained acenaphthylene and N-nitrosodimethylamine by ir and nmr spectral analysis. The

basic fraction was treated with benzene to afford crystals

(1.05 g): mp 80-87° of the anti isomer. These crystals were

recrystallized five times from benzene to afford an analyti-

cal sample of anti-2-dimethylaminoacenaphth-1-one oxime

(III-15); mp 123-125°; ir 3100, 970, 930, 858, 850, 800,

785; nmr τ -1.0 (b, 1H, D_2O exchangeable), τ 1.6 (qt, 1H,

J=7 cps), τ 2.3 (m, 5H), τ 4.78 (s, 1H), τ 7.86 (s, 6H).

The presence of syn-2-dimethylaminoacenaphth-1-one

oxime (III-16) could be detected in the crude basic extract

by a second set of signals at τ 4.57 (s) for the methine pro-

ton alpha to the dimethylamino group, and at τ 7.58 for the

dimethylamino group. The syn isomer, III-16, accounted for

approximately 30% of the syn-anti mixture by nmr analysis.

Attempts to isolate this isomer were not pursued.

17. Photolysis of N-nitrosodimethylamine in presence

of phenanthrene

A solution of the nitrosamine (1.8 g, 0.025 moles) con-

centrated hydrochloric acid (7.5 ml, 0.090 moles) and phe-

nanthrene (4.5 g, 0.025 moles) in methanol (500 ml) was irra-

diated with the 200 watt Hanovia lamp for 2 hours. At this

time the solvent was removed to a small volume (100 ml) and

the precipitated phenanthrene (2.7 g) was filtered. The fil-

trate was worked up in the usual manner to afford a neutral

solid fraction (1.13 g: mp 85-92°), whose ir and nmr spectra were superimposable with those of phenanthrene, and a basic fraction (514 mg). This latter fraction was treated with hexane to give crystals of the hydrochloride of x-dimethy-laminophenanthrene (III-32) (79 mg: mp 171-175° dec.) ir 1000 940, 790, 750, 730; nmr τ 2.70 (m, 7H), τ 7.1 (s), τ 7.69 (s), τ 7.87 (s). This compound could not be identified. The mother liquor was evaporated to dryness to give a residue (40 mg) and which was not investigated further.

18. **Irradiation of pyrene in the presence of N-nitroso-piperidine**

A heterogeneous solution of N-nitrosopiperidine (2.3 g, 0.02 moles), concentrated hydrochloric acid (2 ml, 0.024 moles) and pyrene (2.1 g, 10.01 moles) in methanol (300 ml) was irradiated under nitrogen with 450 watt Hanovia lamp for 3 hours. At this time the solution had turned black in color. The photolysate was evaporated to 100 ml and filtered to give crystals of pyrene (502 mg): mp 110-118°, the ir and nmr spectra were identical to those of pyrene. The photolysate was worked up in the usual manner to give neutral (2.53 g) and the basic (58 mg) fractions. The neutral oil (1.5 g) was chromatographed on alumina (45 g). Eluting with 20% benzene in petroleum ether gave the major component as a solid (700 mg). The com-

pound was recrystallized 3 times from benzene-2-propanol solution to give 1-piperidinopyrene (III-30): mp 90-91.5°; ir 1600, 1590, 1513, 1226, 840; nmr τ 2.00 (m, 9H); τ 6.9 (m, 4H), τ 8.25 (m, 6H); Anal. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91. Found: C, 88.00; H, 6.82; N, 5.00. Compound III-30 is unstable in $CHCl_3$ solution, the solution turning brown-purple after a while.

Continued elution with 75% benzene in petroleum ether gave N-nitrosopiperidine (100 mg). Elution with 1% methanol in benzene gave a mixture of 3 compounds (200 mg) showing Rf values on tlc of 0.8, 0.44 and 0.27 respectively. The ir of this mixture showed peaks of 3400, 2400, 1678, 1620, 1600, 1175, 1090, 980, 838, 755, 715. The components in this mixture were not identified. The basic fraction (54 mg) whose nmr showed mostly aliphatic protons from τ 6-8.85 was not investigated further.

19. <u>Irradiation</u> <u>of</u> <u>azulene</u> <u>in</u> <u>presence</u> <u>of</u> <u>N-nitrosopiperidine</u>

A homogeneous solution of N-nitrosopiperidine (913 mg, 0.008 moles), azulene (552 mg, 0.004 moles) and concentrated hydrochloric acid (0.7 ml, 0.0084 moles) in methanol (200 ml), was irradiated for 40 min. with the 450 watt Hanovia lamp. The blue color of azulene disappeared quite readily (10 min.).

The methanol was evaporated to a small volume (10 ml) to give

a black residue which was treated with water (50 ml). Addi-

tion of ether to the aqueous solution resulted in an emulsion.

Treatment of this emulsion with sodium chloride followed by

K_2CO_3 saturated solution produced no improvement. The emul-

sion was then extracted with CH_2Cl_2 (100 ml x 4) and concen-

trated to give a blue oil (440 mg) which on tlc analysis sho-

wed 3 spots (Rf 0.68, 0.52 and 0.42). The oil was chromato-

graphed on alumina (15 g). Elution with benzene gave two con-

secutive fractions containing a basic compound (150 mg) as an

oil. The oil was distilled (75-100°/0.04 mm Hg) to afford a

green oil of x-piperidinoazulene (III-31): ir 3000, 1580,

1510, 1400, 1035, 998, 900, 763, 740; nmr τ 1.89 (t, 2H,

J=9.5 cps), τ 2.43 (d, 1H, J=4 cps), τ 2.67 (s, 0.5H), τ 2.85

(d, 1.5H, J=4 cps), τ 3.23 (t, 2H, J=9.5 cps), τ 7.0 (m, 4H),

τ 8.3 (m, 6H); impurity at τ 8.72 (s) and τ 9.1 (bm). Con-

tinued elution with benzene gave N-nitrosopiperidine (155 mg);

superimposable ir spectrum. Further elution with $CHCl_3$ and

up to 20% methanol in $CHCl_3$ gave trace amounts of unidentified

product (s) (26 mg).

20. <u>Photolysis</u> <u>of</u> <u>N-nitrosodimethylamine</u> <u>in</u> <u>the</u> <u>presence</u>
<u>of</u> <u>cyclohexene</u> <u>and</u> <u>oxygen</u>

The N-nitrosodimethylamine (1.48 g, 0.02 moles) and cyclo-
hexene (3.28 g, 0.04 moles) and concentrated hydrochloric acid
(2 ml) were dissolved in methanol (130 ml).

While under oxygen atmosphere, the solution was irradia-
ted with the Hanovia 200 watt lamp for one and one half hours.
The usual work up afforded the hydrochlorides of <u>cis</u> and <u>trans</u>
2-dimethylamino-1-nitratocyclohexane III-33:mp darken 109°,
decomposition 119-122° with evolution of gas; ir 1640, 1280,
870; nmr (D_2O) τ 4.3 (m, 1H), τ 4.7 (bm, 1H), τ 6.5 (bm, 1H),
τ 7.1-7.2 (2s, 6H), τ 7.5-9 (bm, 8H); Anal. Calcd; C, 42.76;
H, 7.57; N, 12.47; Cl, 1581. Found: C, 42.87; H, 7.47; N,
12.35; Cl, 15.70.

The mother liquour of III-33 was evaporated to give a
syrup which was dissolved in methanol (50 ml). The solution
was treated with $NaBH_4$ (1.54g, 0.04 moles) added in small por-
tions while stirring. After 12 hours the solution was treated
with concentrated hydrochloric acid (20 ml) and then with
water (40 ml). Basification of the solution and extraction
with CH_2Cl_2 afforded upon evaporation of the CH_2Cl_2 an oil
(2.2g) of the <u>cis</u> and <u>trans</u> mixture of 2-dimethylaminocyclo-

hexanol III-34: ir 3450, 1270, 980, 960, 880; nmr τ 6.0 (m, 1.5H); τ 7.0 (bm, 1H), τ 7.8 (s, 6H), τ 7.8-9.2 (bm, 8H).

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17. We thank Dr. Karl Kopecky of the University of Alberta for providing the spectrum.

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A proposal for further research

The photoaddition of N-nitrosopiperidine to the 1,3-dienes
has been shown to be a general reaction. However, the results
obtained in the addition to 1-vinylcyclohexene suggest that a
steric hindrance is imposed on the approaching nitrosamine
molecule at some point in the reaction axis leading to product
formation. The magnitude of this steric impediment should be
assesed in order to ascertain the limitations and further
synthetic possibilities of the nitrosamine photochemistry.
It is proposed that a study be conducted, using as model seve-
ral 1,2-disubstituted and 2,3-disubstituted 1,3-dienes. The
subtituents in these 1,3-dienes should be the usual methyl,
ethyl, isopropyl and t-butyl groups, which should enable a
good assesment of the magnitude of the steric interactions
involved. Having this information available one could extend
safely into the natural product field. There are several
terpenes which have a 1,3-diene system. Some of them are
dehydroergostenol, vitamin B_3, 22-dehydroergosterol, $\Delta^{9,11}$-
ergosterol and abeitic acid. The corresponding structures
are shown below.

Another project which can be fruitfully exploited is
the extension of the photoaddition of N-nitrosamines to

Dehydroergostenol
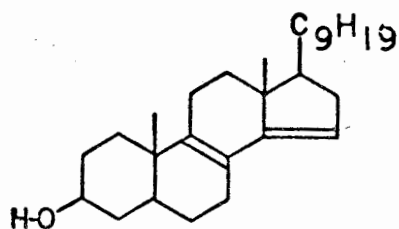
Vitamin - B_3
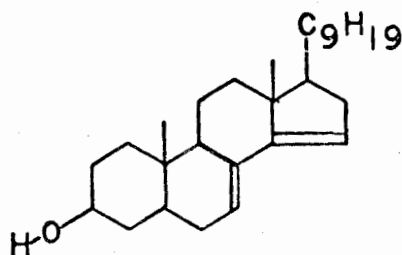
22-Dehydroergosterol
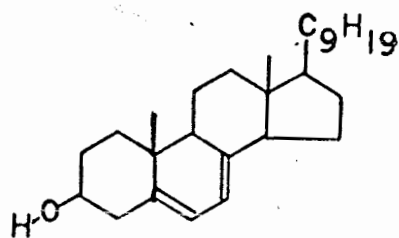
$\Delta^{9,11}$ - Ergosterol
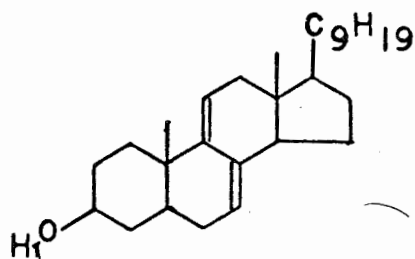
Abeitic acid
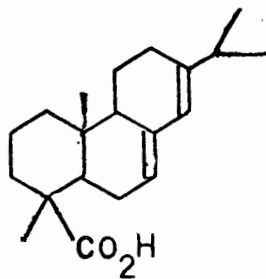
olefins in the presence of oxygen into the 1,3-diene field.
The expected products (shown below) could either be a
1-nitrato-4-amino-2-alkene or its decomposition product, a
dieneamine.
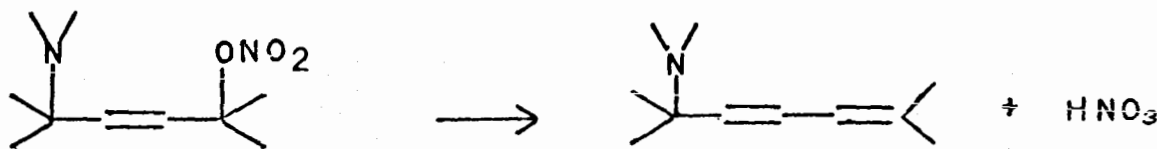
Such a reaction enables the simultaneous introduction of
nitrogen and oxygen substituents at the 1,4-positions in a
carbon chain. This could make this reaction a very useful
synthetic tool.

As a last project, the photo-addition of N-nitrosamines
to unsaturated hydrocarbons in the presence of acetyl or
benzoyl chloride instead of a mineral acid, could be attemp-
ted. The reason for this change is the following. It has
been proposed in this thesis (page 77) that a cyclic inter-
mediate may exist in the transition state. This cyclic inter-
mediate eventually leads to the primary photoadduct, the
c-nitroso compound (see page 79, equation 4). Thus as shown
below acetylation or benzoylation of the nitrosamino oxygen
would prevent the rearrangement of the cyclic intermediate
into the c-nitroso compound.
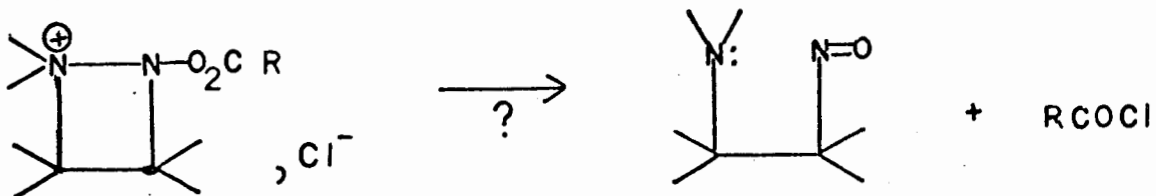
R = Me, Ph.

However, acetylation of the nit rosamine oxygen does not pre-
vent the formation of the corresponding oxime acetate shown
below.
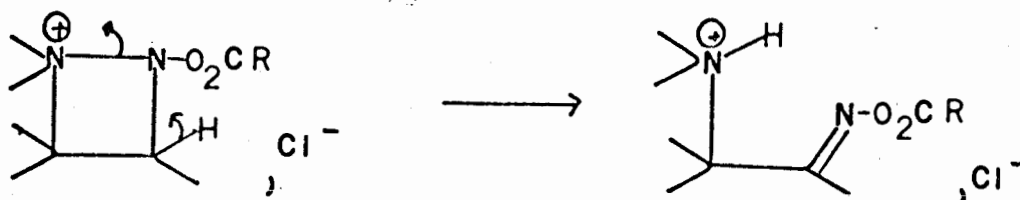
An alternative way of approaching this problem is through
the c-nitroso dimer. Acetylation or benzoylation of the
c-nitroso dimer followed by photolysis may produce the
desired intermediate. This is shown below.
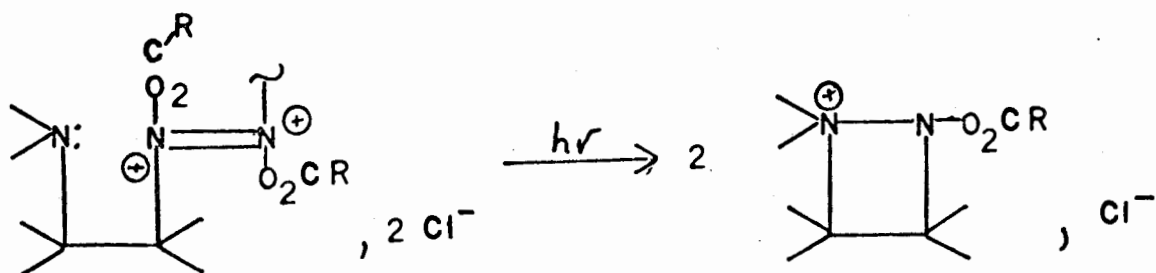
Proof of the existence of the 4-membered ring intermediate would certainly settle some of the most important mechanistic aspects of the photoaddition reaction.
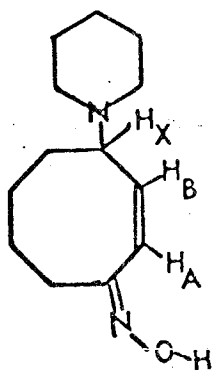
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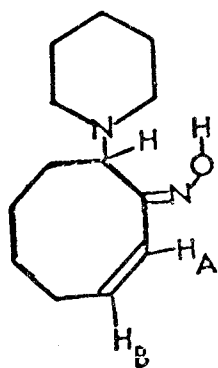
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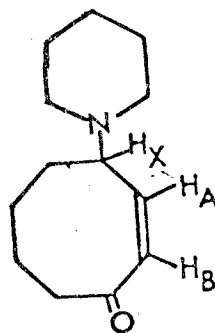
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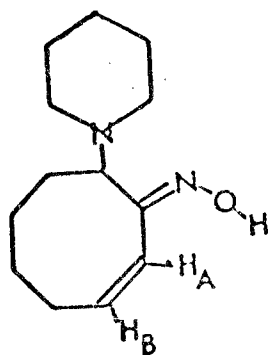
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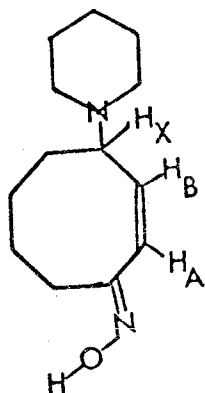
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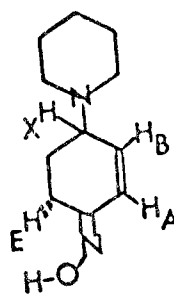
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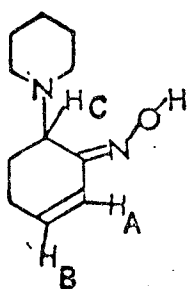
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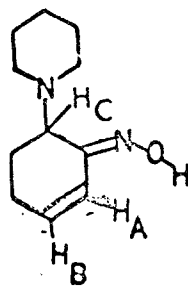
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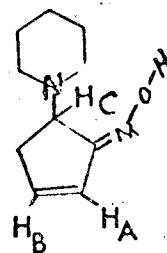
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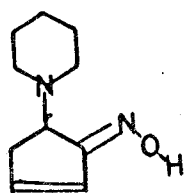
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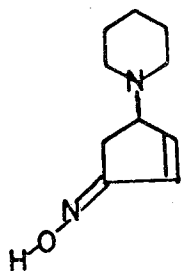
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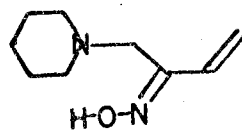
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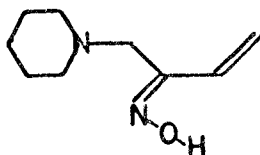
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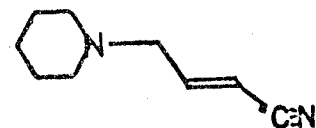
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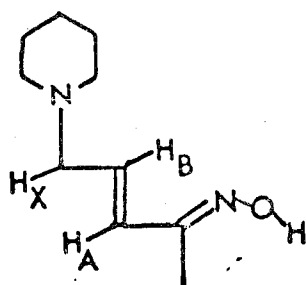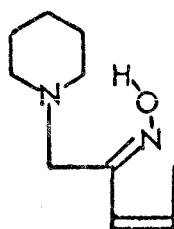
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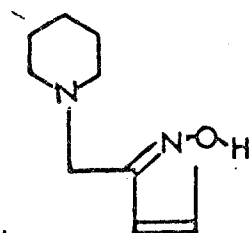
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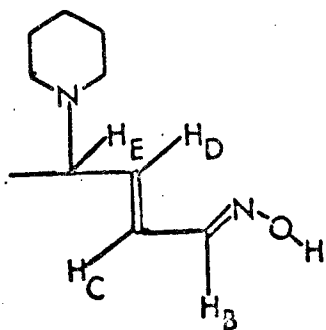
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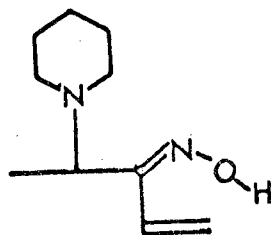
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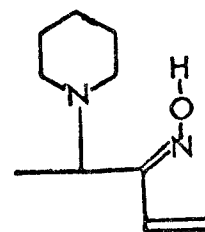
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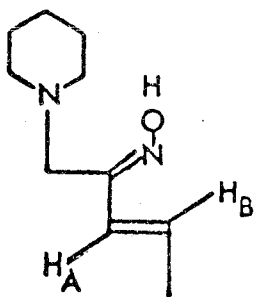
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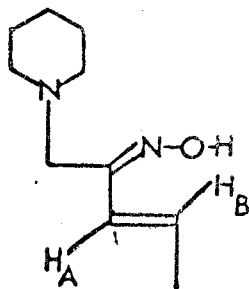
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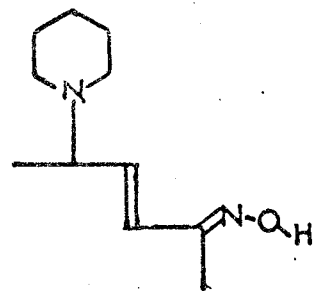
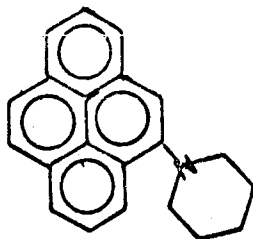I-24
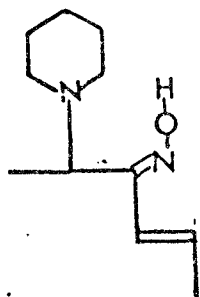
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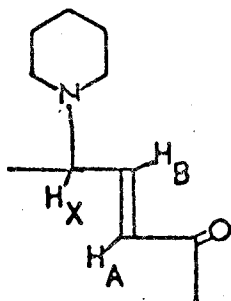
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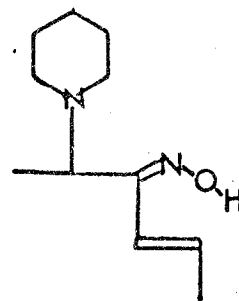
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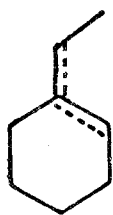
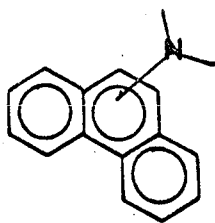I-28
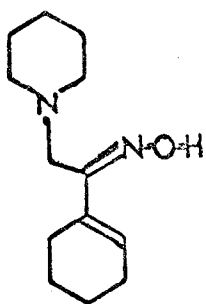
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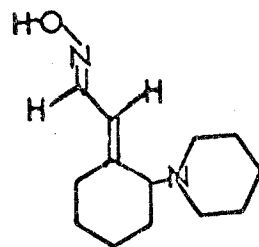
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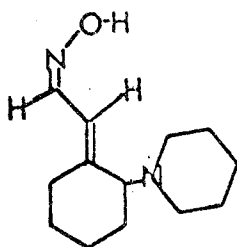
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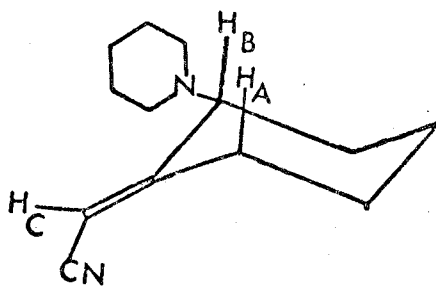
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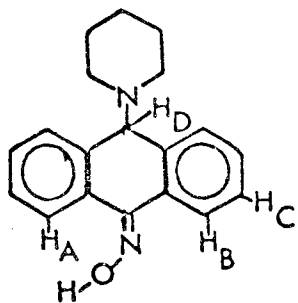
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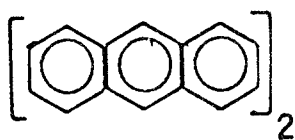
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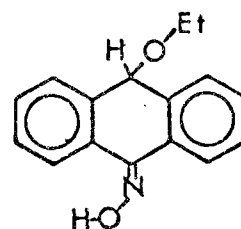
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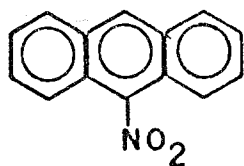
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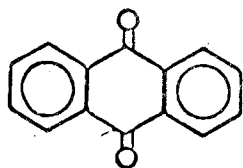
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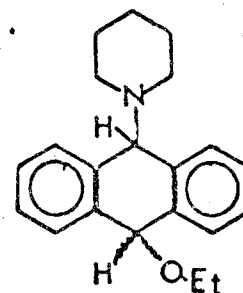
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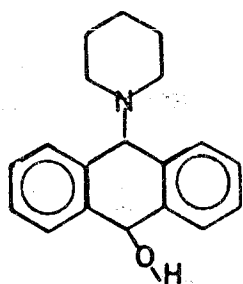
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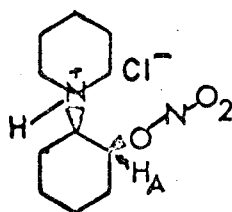
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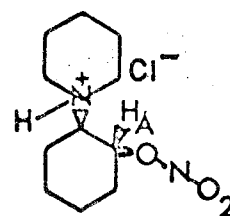
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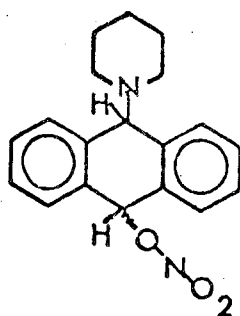
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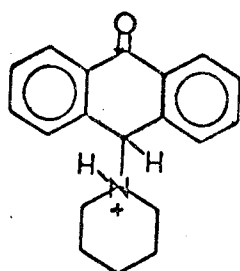
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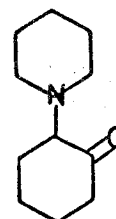
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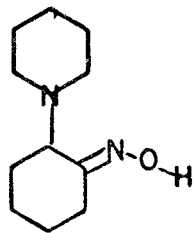
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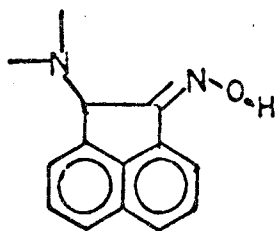
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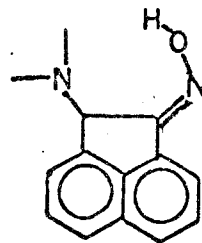
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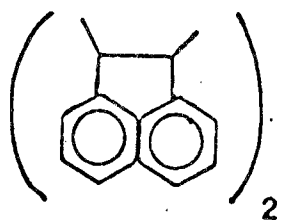
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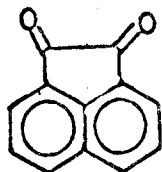
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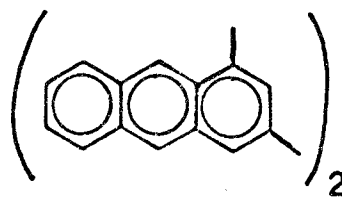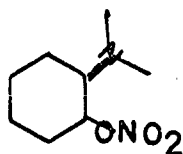
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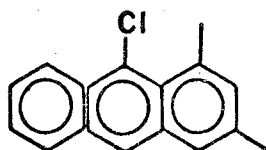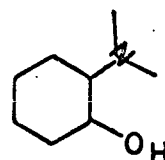
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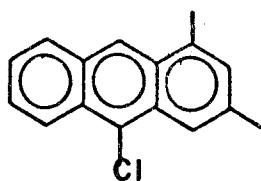
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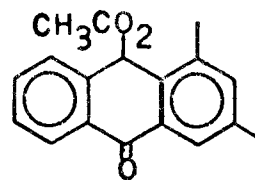
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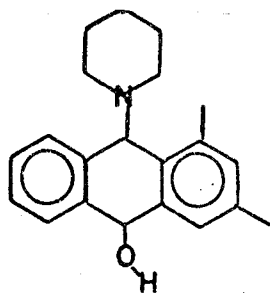
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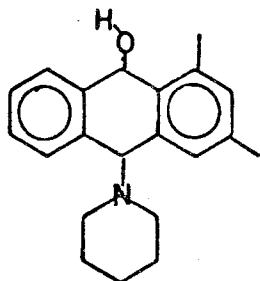
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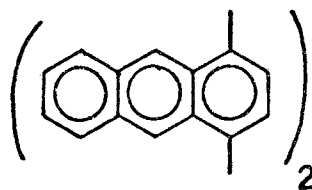
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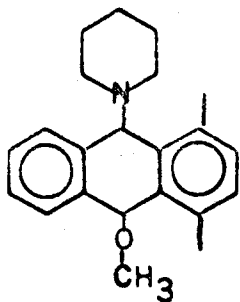
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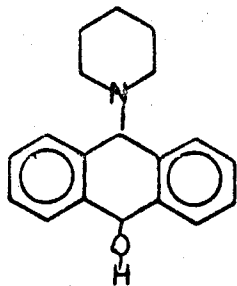
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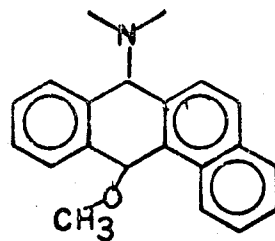
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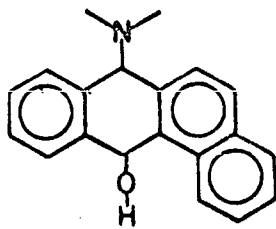
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