IMIDYL RADICALS DERIVED FROM N-BROMIDE OF CAGED IMIDO DERIVATIVES

by

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"Imidyl Radicals Derived from N-Bromide of Caged Imido Derivatives"

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ABSTRACT

Photolysis of N-bromosuccinimide in the presence of ethylene oxide and an excess of olefins or benzene has been shown to generate the succinimidyl radical which preferentially attacks the Π-bonds.

To elucidate the electronic configuration of imidyl radicals, their reactivity in intramolecular modes was investigated. For this purpose, model compounds were synthesized by (2+2) photocycloaddition of dichloromaleimide to cyclohexene, cyclopentene, cyclohexadiene, and cyclopentadiene to give (2+2) photoadducts with *cis*,*endo* and *cis*,*exo*-configurations. Only the former photolysis of dichloromaleimide with cyclohexene yielded a *trans*-4,6-adduct. Photoaddition of dichloromaleic anhydride to cyclopentadiene and cyclohexadiene was reinvestigated, and shown to give *cis*,*endo* and *cis*,*exo*-isomers as major products. The structures of the reported *trans*-adducts were revised. The structure and stereochemistry of these photoadducts were determined by 400 MHz NMR spectroscopy. X-ray crystallographic analysis proved the stereochemistry of one of the adducts.

N-Bromo-7,8-dichloro-*cis*-bicyclo[4.2.0]octane-*endo*,*cis*-7,8-dicarboximide and its analog derived from bicyclo[3.2.0]heptane were photolyzed under various conditions. Direct

photolysis and bromine-initiated reactions of these N-bromides demonstrated that two reacting radicals, in addition to bromine atoms, were involved in the formation of brominated and ring-opening products. Product distribution studies showed that both methods led to the generation of imidyl radicals which underwent ring-opening and intermolecular hydrogen abstractions, but did not abstract endo-C_3-H intramolecularly. The Σ-electronic configuration was assigned to these imidyl radicals which are believed to be ground state species since they can also be generated by interaction of bromine atoms with N-bromoimides. The second radical could be generated only by interaction of bromine atoms with N-bromides. It undergoes intramolecular functionalization at the C_3 position but no ring-opening reactions. A radical complex of atomic bromine with the N-bromide is proposed which is in equilibrium with both the N-bromide and the imidyl radical $(Ac_2\dot{N})$, i.e. $Br_2 + (Ac_2N\cdot) \rightleftharpoons Ac_2N\dot{B}rBr \rightleftharpoons Ac_2NBr + \cdot Br$. These equilibria explain the observed product distributions under various reaction conditions. The course of radical reactions depends on the radical concentration and type of substrate. For example, $\Delta^{2,3}$-N-bromides were photolysed to give C_4-brominated olefinic imides.

To my Mother

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Dr. Y.L. Chow for his guidance and genuine interest throughout this work. He also wishes to thank Dr. A.S. Tracey for helpful discussions and general assistance. The collaboration and friendship of fellow members of Dr. Chow's group are gratefully acknowledged. The author also wishes to thank the technical and support staff of Simon Fraser University for their co-operation and assistance. A special thanks to Marion Jacques who endured the typing of the manuscript. Financial assistance from the Department of Chemistry, Simon Fraser University is also acknowledged.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

I-1 Recognition of the Succinimidyl Radical

Nitrogen-centered radicals carrying two acyl groups are referred to as imidyl radicals[1] (I-1); among them the succinimidyl radical (I-2 or S•) is the most discussed and investigated species[1-5]. Although the existence of the succinimidyl radical was proposed some 40 years ago, it has only recently been identified[7]. Since the discovery of N-bromosuccinimide (NBS) as an efficient "allylic" brominating agent[6] in 1942, N-bromoimides have been the favored source for generating imidyl radicals. Inevitably, the progress of imidyl radical chemistry has been complicated by bromine atom reactions and at times has been overshadowed by heightened interest in brominations[4].

$$\underset{\text{(I-1)}}{RCO\dot{N}COR'} \qquad \underset{\text{(I-2 or S•)}}{(CH_2CO)_2N\cdot}$$

Ziegler[6] discovered that a suspension of NBS in boiling CCl_4 could efficiently brominate allylic or benzylic positions. Bromination under Ziegler's condition (heterogeneous phase) has been widely adopted as an efficient and highly selective synthetic tool[5]. The free radical nature of the reaction (e.g., initiated by UV illumination or radical initiators such as azobisisopropionitrile or benzoyl peroxide[8,9]) suggested the succinimidyl radical as a chain propagation species (the Bloomfield mechanism[10], eqs 1 to 3), while the nature of the Ziegler's allylic bromination process under heterogeneous conditions was demonstrated by several groups[11-15] in the early 60's to follow the bromine atom chain process (the Goldfinger mechanism[16], eqs 4 to 8). These groups reached a remarkable agreement in their conclusions. In every case, it was shown that the relative reactivities of bromination of some aralkyl compounds by bromine, NBS and other N-bromoimides[11,14] are nearly identical, as are the Hammett ρ values for the bromination of toluene derivatives by bromine and by NBS (-1.39 at 80°)[11,12,14]. Secondly, the bromination of toluene by bromine or NBS exhibited the same deuterium isotope effects[17]. Finally, the product patterns derived from NBS bromination of certain olefins were essentially the same as those obtained with a low concentration of bromine introduced under controlled conditions[18-20].

The Bloomfield Mechanism

$$(CH_2CO)_2NBr \xrightarrow{h\nu/\Delta} (CH_2CO)_2N\cdot + Br\cdot \qquad (1)$$

$$(CH_2CO)_2N\cdot + CH_2{=}CHCH_2R \longrightarrow (CH_2CO)_2NH + CH_2{=}CH\dot{C}HR \qquad (2)$$

$$CH_2{=}CH\dot{C}HR + (CH_2CO)_2NBr \longrightarrow CH_2{=}CHCHBrR + (CH_2CO)_2N\cdot \qquad (3)$$

The Goldfinger Mechanism

$$Br_2 \overset{h\nu}{\rightleftarrows} 2Br\cdot \qquad (4)$$

$$CH_2{=}CHCH_2R + Br\cdot \rightleftarrows CH_2{=}CH\dot{C}HR + HBr \qquad (5)$$

$$CH_2{=}CHCH_2R + Br\cdot \rightleftarrows BrCH_2\dot{C}HCH_2R \qquad (6)$$

$$(CH_2CO)_2NBr + HBr \longrightarrow (CH_2CO)_2NH + Br_2 \qquad (7)$$

$$CH_2{=}CH\dot{C}HR + Br_2 \longrightarrow CH_2{=}CHCHBrR + Br\cdot \qquad (8)$$

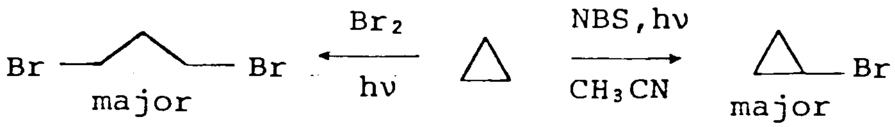
$$CH_2{=}CHCH_2R + Br_2 \longrightarrow CH_2BrCHBrCH_2R \quad \text{(ionic mechanism)} \qquad (9)$$

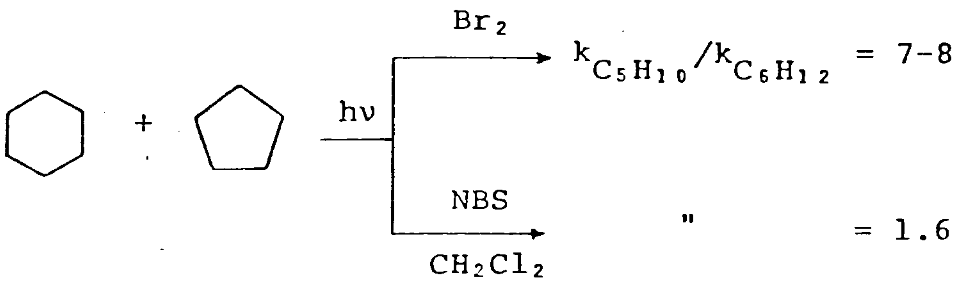
The bromine atom chain mechanism (eqs 4 to 8), in which NBS merely serves as the reservoir for a low concentration of bromine was first suggested by Goldfinger[16] in 1953. Nevertheless, it took another decade of research by various groups to understand the nature of the inter-related reactions and to resolve some ambiguities. The Goldfinger mechanism is believed to operate under Ziegler's heterogeneous conditions in the presence of reactive substrates containing allylic[18,19] and benzylic[11-14] hydrogen and is favored by the following factors. Firstly, the reverse reaction of eq. (6) occurs even at room temperature[18,19], thus forestalling the radical addition reaction. The ionic addition reaction (eq. 9) is limited by the low concentration of bromine. Secondly, NBS is sparingly soluble in CCl_4 (0.006 M) and reacts 10^3 times more slowly than bromine with alkyl radicals[15]. In essence, solubility and reactivity factors conspire together to retard the succinimidyl radical chain (eq. 3) and promote bromine atom chain propagation (eq. 8). Thirdly, HBr is scavenged instantaneously by NBS to maintain a low steady-state concentration of bromine under these conditions[11,21]; thus the reverse reaction of eq. 5 is not important under these conditions though it may become important in certain cases[12,17,20].

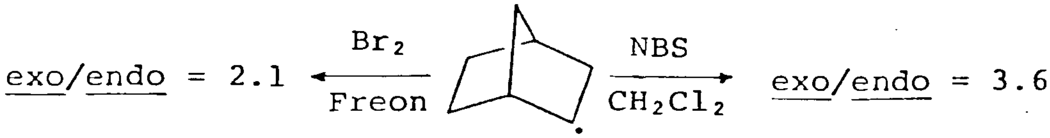
Attempts to observe the succinimidyl radical by ESR spectroscopic techniques in solution were unsuccessful[22,23], although spin trapping with 2-nitroso-2-methylpropane during NBS decomposition gave the corresponding succinimidyl nitroxide[24,25]. Careful examination of the literature suggests that the decomposition of N-bromoimides does not follow a clean bromine atom chain mechanism, but that some imidyl radicals may be generated. Pertinent pieces of evidence are: i) the rearrangement of NBS to β-bromopropionyl isocyanate[14,26,27], as in eq. (10); ii) the addition of NBS across carbon-carbon double bonds[28-33] and iii) the substitution of a benzene hydrogen by the succinimidyl moiety[34]; all these reactions have been found earlier to occur under typical radical reaction conditions.

$$\underset{\text{(NBS)}}{(CH_2CO)_2NBr} \rightarrow S\cdot \rightarrow \underset{(\underline{\text{I-3}},\ \text{PI})}{\cdot CH_2CH_2CONCO} \xrightarrow{\text{NBS}} \underset{(\underline{\text{I-4}},\ \text{BPI})}{BrCH_2CH_2CONCO} + S\cdot \qquad (10)$$

It is interesting to note that events leading to the recognition of the succinimidyl radical in 1972 emerged from the dispute over anchimeric assistance by neighboring bromine in bromine atom attack on the β-hydrogen of alkyl bromides[21,35-38]. Traynham[36] had observed that the product patterns in the bromination of non-activated alkanic C-H bonds (e.g., 1-bromobutane, Table I-1, p.20) are different with bromine and with NBS; therefore the succinimidyl radical must be partially sustaining the chain process. The same group also demonstrated several reactivity differences between the two reagents toward unreactive alkanes, as shown below, and the presence of different bromine transfer processes.



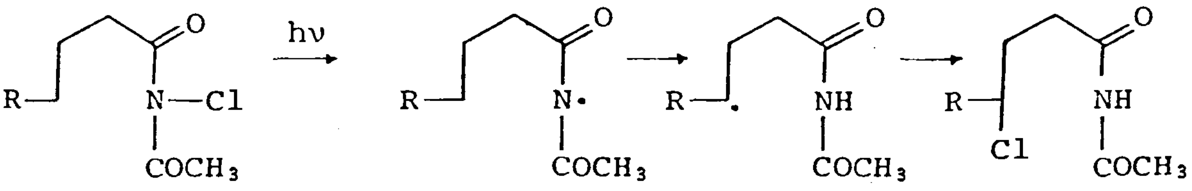




If NBS is used, the succinimidyl radical can be generated only when the bromine chain (Goldfinger mechanism) is effectively rendered inoperative so that the less facile succinimidyl radical chain process can take over (eq. 3) This has been achieved in the following ways:
Firstly, bromine was scavenged with olefins containing no reactive allylic hydrogens[39] (e.g., ethylene, neohexene, 1,1- or 1,2-dichloroethylene) so that the chain sequence of eqs 5, 6 and 8 was stopped. Secondly, NBS concentrations were increased by using relatively inert but more solubilizing solvents[39] such as CH_3CN (0.8 M) and CH_2Cl_2 (0.25 M). Thirdly, HBr was scavenged in order to retard the

bromine formation according to eq. 7; ethylene oxide was shown to react with HBr rapidly[41] in the presence of NBS[40] but its overall effects remained to be established in actual applications. Internal selectivity in the NBS bromination of 1-bromobutane under exemplary conditions (No. 2 and 3 in Table I-1,p. 20) was found to differ considerably from that in the Br_2 bromination (No. 1). The results of experiment No. 3 and 4 (no bromine scavenger was used) should be regarded as the relative reactivities arising mainly (but not purely) from the succinimidyl radical chain process.

In contrast to the extensive use of N-bromo-imide decompositions, only a few alternative methods have been used to generate imidyl radicals[42,44,46]. Photolysis of N-chloro-imides I-4 afforded δ-chloro imides I-6 in moderate yields[42],



I-4 I-5 I-6

obviously via the imidyl radicals I-5 which abstract a δ hydrogen intramolecularly. Benzoyl peroxide or light-initiated NIS oxidation of 1-phenylethanol was shown to be a succinimidyl radical mediated chain reaction giving excellent yields of acetophenone[43]. The yield increases if silver acetate is added to scavenge hydrogen iodide leading to the proposal of Bloomfield-type mechanism.

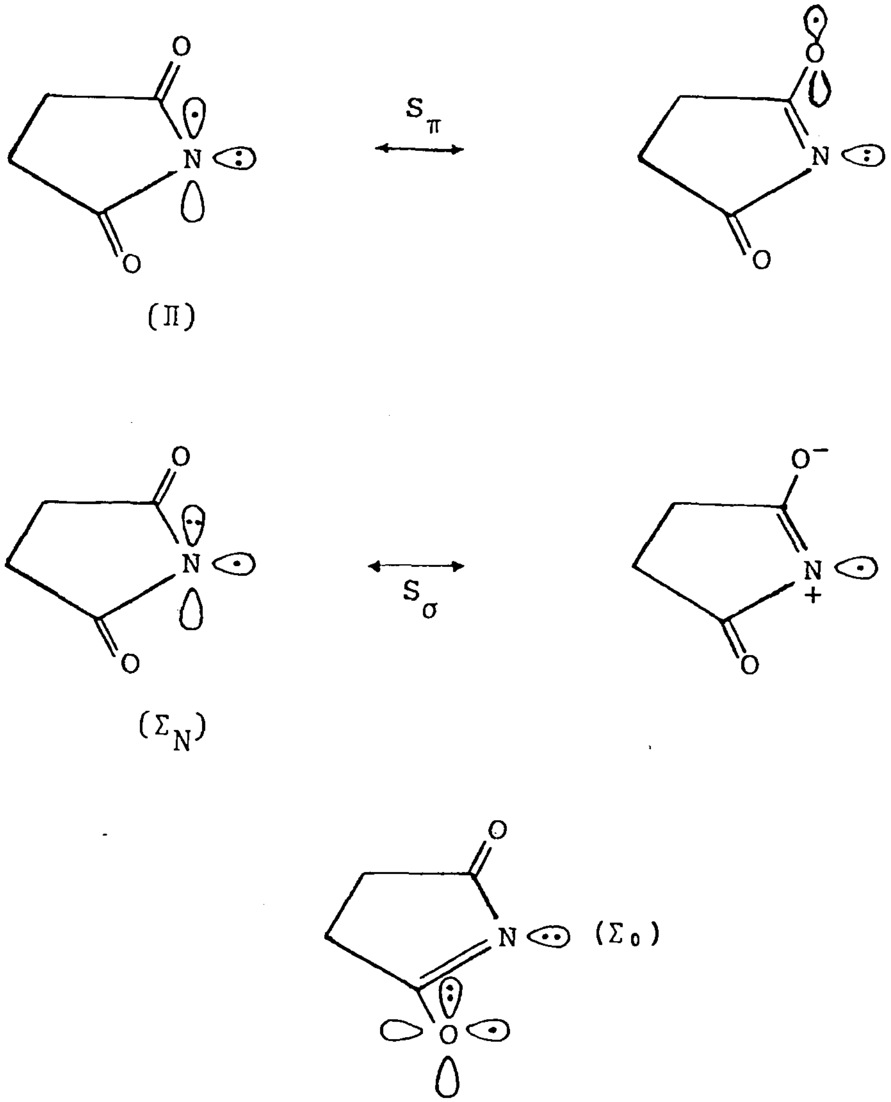
$$\underset{\text{(NIS)}}{(CH_2CO)_2N\text{-}I} + C_6H_5CHOHCH_3 \qquad (CH_2CO)_2NH + C_6H_5CI(OH)CH_3$$

$$C_6H_5COCH_3 + HI$$

$$HI + AgOCOCH_3 \rightarrow AgI + CH_3CO_2H$$

I-2 Electronic Configuration

Simple MO theory predicts that imidyl radicals (e.g., S•) may have Π, Σ_N or Σ_O electronic configurations as shown below if one assumes sp^2 hybridization at the nitrogen center. Since S• adds as a nitrogen centered radical, the Σ_O configuration may be unimportant in solution chemistry.

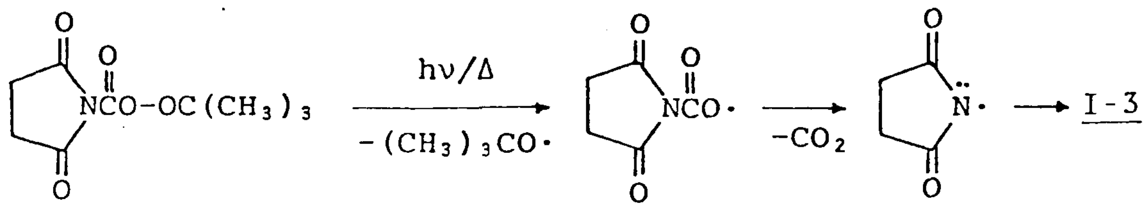


Scheme I-1

After many years of inconclusive arguments based on theoretical calculations[45], direct ESR evidence[48] has confirmed that the related amidyl radicals have the Π configuration. Using MO calculations, Hedaya et al.[44] had predicted the succinimidyl radical to have the S_σ ground state configuration; this group also predicted the S_σ to be more reactive and less selective.

INDO calculations[49], however, indicate that S_π is lower in energy and, therefore, should be the ground state species, while S_σ (Σ_N and/or Σ_O configuration) is the excited state and has the symmetry that correlates with the open-chain radical (I-3 eq. 10). More sophisticated calculations by *ab initio*[50], MINDO[51] and UMINDO[47] methods also indicate that S_π is the ground state and S_σ is the lowest excited state with a Σ-Π energy difference of 15≈25 kcal/mole.

Recently, the succinimidyl radical was generated by single crystal X-irradiation of succinimide[52] at 26°K and was shown to have the Π-electronic configuration with 60% spin density on the nitrogen atom. The open-chain radical (I-3) was not observed in this study. However, Hedaya[44] has presented evidence for the formation of (I-3) during photolysis of *t*-butyl succinimide percarboxylate (I-7) at 77°K.



I-7 I-8 I-2

Skell and coworkers have recently published a series of papers[53-57] describing two reactive radical species, in addition to halogen atoms, formed during the decomposition of NBS and other haloimides. The two reacting species were generated by the propagation steps shown in (eqs. 11 to 13), and it was proposed that they are the ground state (S_π) and the lowest excited state (S_σ) of the succinimidyl radical; noteworthy is the generation of the excited state S_σ by thermal processes[54,55]. It has been claimed that the S_σ radical is as reactive as Cl• and OH• radicals (less selective) in hydrogen abstraction, that it can rearrange rapidly to PI radical <u>I-3</u> (eq. 10)[57], and that it can attack alkenyl and aromatic π-bonds. In comparison, S_π was found to be

$$X\bullet \ + \text{NBS} \rightarrow S_\pi + \text{XBr} \quad -\Delta H = 0 \text{ kcal/mol} \qquad (11)$$

($X\bullet$ = •Br, •CCl_3 or an allylic radical)

$$\bullet R + \text{NBS} \rightarrow S_\sigma + \text{RBr} \quad -\Delta H = 7 \text{ to } 5 \text{ kcal/mol} \qquad (12)$$

(•R = 1° alkyl, 2° alkyl or •$CHCl_2$)

$$\bullet R(3^\circ) + \text{NBS} \rightarrow S_\sigma(95.5\%) + S_\pi(4.5\%) + \text{RBr} \qquad (13)$$

less reactive (more selective) and could add to alkenyl π-bonds, but could neither attack aromatic π-bonds nor rearrange[57] to <u>I-3</u>. The products of both addition and rearrangement have been extensively utilized by Skell's group[53-57] for the identification of the two propagating radical species.

I-3 Reactivity of Imidyl Radicals

(a) Hydrogen Abstraction

The relative reactivities of alkanic substrates (unreactive toward bromine radicals) with NBS under well-defined conditions were used to establish the two reactive species in NBS decomposition[54,56]. For example, in the competitive halogenation of neopentane and CH_2Cl_2 (Table 1-2, p.22) in the presence of olefins containing no allylic hydrogens to scavenge atomic and molecular bromine, S_σ is the sole hydrogen abstracting species (generated by reaction 12) giving a relative reactivity per hydrogen $k_{(CH_3)_4C}/k_{CH_2Cl_2}$* of ca. 17 regardless of the halo-succinimide used. The propagation steps (14) to (15) were proposed for this system.

$$S_\sigma + RH \rightarrow SH + R\bullet \qquad (14)$$

$$R\bullet + NBS \rightarrow RBr + S_\sigma \qquad (15)$$

$$* \quad \frac{k_{(CH_3)_4C}}{k_{CH_2Cl_2}} = \frac{\text{rate constant for H abstraction from } (CH_3)_4C}{\text{rate constant for H abstraction from } CH_2Cl_2}$$

$$= \frac{[C_5H_{11}Br][CH_2Cl_2]}{[C_5H_{12}][BrCHCl_2] \times 6}$$

In the presence of bromine (>10^{-3} M) or $BrCCl_3$ (>3.4 M) at concentrations high enough to intercept all alkyl radicals, S_π was the sole hydrogen abstracting species regenerated by eq.11 to give $k_{(CH_3)_4C}/k_{CH_2Cl_2}$ of nearly one[54-57]. The proposed mechanism for S_π chain propagation is shown in eqs. (16 to 18) in which BrX is Br_2 or $BrCCl_3$, a chain mediator. The extensive formation of halopropionyl isocyanates under the S_σ conditions, but not under the S_π conditions, led the authors[54,56] to assign the S_σ or S_π configuration, respectively, to the chain propagating species, according to the prediction made by Koenig and Wielesek[49].

$$S_\pi + RH \rightarrow SH + R\cdot \qquad (16)$$

$$R\cdot + BrX \rightarrow RBr + X\cdot \qquad (17)$$

$$X\cdot + NBS \rightarrow S_\pi + BrX \qquad (18)$$

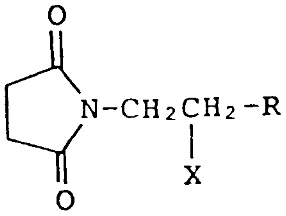
Several other relative reactivity determinations by internal or external competition also showed similar trends[57]. The experimental conditions for generating S_σ and S_π radicals are defined in Table I-1 (p.20). Table I-1 shows that the reactivity of the S_σ radical for the abstraction of hydrogen is comparable to that of Cl•, while the S_π radical reactivity is comparable to that of t-BuO•.

(b) Rearrangement of halo imides

On the basis of the MO correlation of Koenig and Wielesek[49], Skell has proposed[55] that S_σ rearranges to I-3 (eq. 10); therefore the BPI formation is a key indicator for the generation of S_σ. Extensive studies of various halo imide decompositions showed that the rearrangement is facilitated by the formation of stabilized carbon radicals; e.g., the formation of the 3° alkyl radical from the 2,2'-dimethylsuccinimidyl radical was particularly favored[55,56]. The ring opening reaction of S_σ radicals (eq. 10) has been established to be reversible and in competition with other S_σ reactions as shown by deuterium labelling experiments[55]. Thus, low concentrations of NBS yielded less BPI, and NCS, being a poor chlorine donor, failed to give β-chloropropionyl isocyanate.

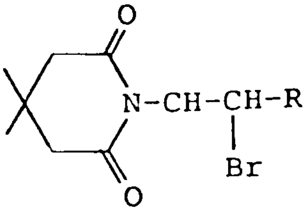
(c) Addition to alkenes

Photoinitiated additions of NBS, NCS and NBDMG (N-bromo-3,3-dimethylglutarimide) to olefins containing no reactive allylic hydrogen typically afford imidyl radical-initiated adducts (I-9) and (I-10) in excellent yields[40,53]; the olefins functioning as bromine scavengers and as substrates. Photodecomposition of NBS in CH_3CN in the presence of cyclohexene gave more complex product patterns; 1- or 3-succinimidyl-cyclohexene were minor products[40]. However, the formation of a substantial quantity of 4-bromocyclohexene



X = Br, Cl; R = H, t-Bu, n-Bu

I - 9

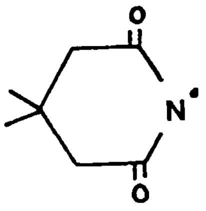


R = t-Bu, C_6H_5

I - 10

was invoked[53,55,56] as an indication of the high reactivity of S_σ, but could not be repeated[40].

Flash photolysis of NBDMG in CCl_4 gave absolute rate constants for addition to double bonds and hydrogen abstractions of the dimethyl glutarimidyl (DMG) radical and its precursor[60]. While the two reacting species were formed by direct excitation and their configurations (Σ vs. Π) were not unequivocally identified, the rate constant ratio for the DMG radical reaction with neohexene and cyclohexane was 2.6×10^3;the precursor, on the other hand, reacted with neohexene 10^8 times faster than with cyclohexane. The former ratio is what would be expected for nitrogen centered radical reactions[60,62,64-70].

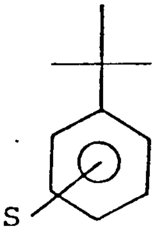


DMG

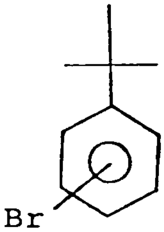
(d) Substitution at aromatic nuclei

It has been stated that S_σ radicals attack benzene derivatives and condensed aromatics efficiently but S_π radicals do not; indeed, benzene could be used as a convenient S_σ scavenger for creating S_π conditions, since the stabilized cyclohexadienyl radicals react with NBS to generate S_π radicals[54,56,57]. The decomposition of NBS in CH_2Cl_2 containing benzene under S_π conditions produced no BPI, and both the yields of N-phenylsuccinimide and $CHBrCl_2$ were small and comparable[56].

The substitution patterns of the products formed from various monosubstituted benzenes in N-bromoimide photolyses[53,61] were typical of free radical reactions. With tert-butylbenzene in acetonitrile containing neohexene(0.12 M), the absolute yields of the products shown below varied only slightly with temperature or on the addition of ethylene epoxide. It has also been shown that benzene adds succinimidyl radical twice as fast as neohexene[53].



o-, 8%
m-, 14%
p-, 11%



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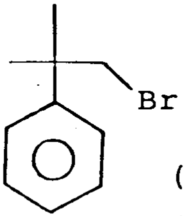


1%

$(CH_3)_3CCHBrCH_2Br$ 98%
$(CH_3)_3COHBrCH_2S$ 1.3%

I-4 Recent Disputes

On the basis of thermochemical calculations on the formation of S_σ and S_π radicals (eqs. 11 to 13) and of the assumption that the activation energy for the latter process is higher than that of the former, Skell[55] estimated the S_σ andS_π energy difference to be ≈15 kcal/mol. The transition state for the S_π radical generation (eq. 11) has been visualized as a radical approach to the N-Br bond from the direction perpendicular to the plane of NBS and that for the S_σ radical generation (eq. 12) as a coaxial radical approach along the axis of the N-Br bond. Both proposals were later supported by theoretical calculations[51]. Even if the rationalizations contain elements of speculation, Skell's experimental data are impressively self-consistent except for a few points. However, more recently other groups[62,63] have carried out similar investigations and obtained experimental data at variance with that reported by Skell's group[57].

1) Walling and co-workers[62] have confirmed the relative reactivity data of the neopentane-CH_2Cl_2 system[54-56] and also the requirement of two radical chain carriers, in addition to the bromine atom, in NBS decompositions. However, their experimental rate constants for the reactions of both radicals were much smaller than Skell's, leading them to argue against the validity of the excited state S_σ reactions. Tanner et al.[63] concluded that in the competitive bromination of cyclopentane-cyclohexane, NBS-Br_2 reagents show essentially the bromine atom chain reactivity while NBS-ethylene reagents show the S• chain reactivity.

2) Contrary to Skell's claims, both Walling[62] and Tanner[63] found that BPI was formed under the S_π conditions.

3) The kinetic isotope effects k_H/k_D measured by Skell[57] and Walling[62] (shown below) are at variance.

		NBS-CH_2CCl_2	NBS-Br_2
Skell's Group[57]	CH_2Cl_2/CD_2Cl_2	1.5	5.8
	$CHCl_3/CDCl_3$	1.4	6.3
Walling's Group[62]	CH_2Cl_2/CD_2Cl_2	10	10

4) Some of the reaction rate constants estimated by Skell[56] and Walling[62] from static product analyses differ by two to three orders of magnitude; e.g., for the ring opening shown in eq. 10 (10^7 and 10^4 sec^{-1}), and for the hydrogen abstraction

from cyclohexane (10^6 vs. 10^4 M^{-1} sec^{-1}), by S• under the S_σ conditions. Walling[62] estimated the rate constants of S• hydrogen abstraction from neopentane and CH_2Cl_2 in the thermally initiated NBS reaction to be 380 and 55 $M^{-1}s^{-1}$ under S_π conditions, and 590 and 5.8 $M^{-1}s^{-1}$ under S_σ conditions. Noting that the rate constants were very close despite the different selectivities observed for the two reacting radicals, and taking the deuterium isotope effects (see above) into account, Walling has stated that the proposal of excited state S_σ reactions is untenable. He argues that the ground state succinimidyl radical is one of the reacting species, and that the other chain carrier might be a radical complex between bromine atom and NBS such as (<u>I-11</u>).

$$\text{NBS} + \text{Br}\bullet \longrightarrow \underset{(\underline{\text{I-11}})}{\text{S-}\overset{\bullet\bullet}{\text{Br}}\text{-Br}} \xrightarrow{\text{RH}} \text{SH} + \text{RBr} + \text{Br}\bullet \qquad (19)$$

Table I-1 Percentage Functionalization of 1-Bromobutane[a]

	Reagents	Radical	CH_3-	CH_2-	CH_2-	CH_2Br	Ref.
1.	Br_2, hν, 25°	Br•	0	14	84	1	35
2.	NBS, CH_2Cl_2, $CH_2=CH_2$, 25°	S•	18	44	31	7	39
3.	NBS, CH_3CN, 60° (5%)[b]		10	57	17	16	36
	(36%)[b]	(S•+Br•)	5	52	28	14	36
	(96%)[b]		2	41	47	10	36
4.	NBS, CH_3CN, 30°	(S•+Br•)[c]	0	61	24	15	37
5.	Cl_2, hν, 60°	Cl•	23	50	22	5	35
6.	*t*-BuOBr, hν, 45°	*t*-BuO•	6	40	30	24	58
7.	NBS, CH_2Cl_2, $CH_2=CCl_2$, 15°	S_σ[d]	20	46	25	9	57
8.	NBS, Br_2, CH_2Cl_2, 15°	$\dot{B}r$[e,f]	0	12	88	0	21
9.	NBS, CH_2Cl_2, $BrCCl_3$, $CH_2=CCl_2$, 15°	S_π[f]	5	27	65	3	57
10.	NBS, CH_2Cl_2, $BrCCl_3$, $CH_2=CCl_2$, 35°	S_π[f]	2	31	61	6	57

[a] Except No. 10 which was initiated by benzoyl peroxide, all reactions were photoinitiated; [b] Percentage decomposition of NBS; [c] After 3 hours (photobromination 12% complete); [d] BPI was formed in 95% yield; [e] $[Br_2] = 0.2$ M.; [f] No BPI was formed.

Table I-2. Relative Reactivities[54,56,57] of Succinimidyl Radicals in CH_2Cl_2 at 15° toward Neopentane and CH_2Cl_2.

Reagents	$k_{(CH_3)_4C}/k_{CH_2Cl_2}$ (per H)[a]	XCH_2CH_2CONCO (%)
NBS,*t*-$BuCH=CH_2$ (0.144 M)[c]	18.0[b]	80
NBS,$CH_2=CCl_2$ (0.06 M)[c]	16.1[b]	93
NCS,$CH_2=CH_2$ (0.1 mmol)	20.8	0
NIS,$CH_2=C=CH_2$ (0.6 mmol)	(>100)[b]	97
NBS,Br_2 (0.01 M)	1.0	0
NBS,$BrCCl_3$ (25.4 mmol), $CH_2=CCl_2$ (0.5 mmol)[c]	1.1	0
NIS,I_2 (0.04 mmol)	1.1	0
Br_2	0.1	

[a] CH_2Cl_2 served as solvent and substrate. The relative rates were calculated from the yields of $C_5H_{11}X$ and $XCHCl_2$ on a per hydrogen basis.

[b] The yields of $C_5H_{11}X$ and $XCHCl_2$ were low; the reviewer calculated the data for the NIS experiment.

[c] $CH_2=CCl_2$ is a bromine scavenger and does not add NBS.

I-5 Research Proposal

The recent reports by Skell[57], Walling[62], and Tanner[63] on NBS decompositions raise the following questions:

i) Does the succinimidyl radical exist in two different electronic states namely Σ (excited state, e.g. II-32) and π (ground state, II-33)?

ii) If so, what is its electronic configuration when generated in the presence of an olefin (which traps bromine)?

iii) What are the structures and configurations of the radical intermediates formed in the presence of bromine?

To answer these questions we decided to synthesize a series of model compounds, namely:

(a) the saturated tricyclic N-bromosuccinimide derivatives II-31 and II-41 as stereoelectronic probes of the model of hydrogen abstraction (intra-vs.-intermolecular), and;

(b) the $\Delta^{2,3}$-unsaturated tricyclic N-bromosuccinimides II-50, II-60, and II-63 as probes for the electronic configuration of imidyl radicals capable of undergoing addition to olefinic double bonds.

It is well known that intramolecular hydrogen transfer from carbon to a radical species occurs efficiently when the C-H bond and the orbital with the unpaired electron are in a radii[108,109] (nitrogen 1.5 Å, hydrogen 1.2 Å)[111]. Examination of Dreiding models of II-31 reveals that the nitrogen and the endo-C_3 hydrogen atom are separated by ca. 2.0 Å with the cyclohexyl moiety in the pseudo-chair conformation [110], and by ca. 1.2 Å in the tucked-in pseudo-boat conformation; in the endo-envelope form of II-41 the corresponding interatomic distance is ca. 2.5 Å which is still below the required maximum of 2.7 Å. Furthermore, the endo C_3-H bond and the nitrogen p-orbital are colinear (or nearly so) in all three cases. In the radical complexes II-34 and II-47, which may also be envisaged as reaction intermediates, the unpaired electron of bromine may occupy one of the three equatorial dsp^3 hybrid orbitals (trigonal bipyramid) which can also reach the endo-C_3 hydrogen. The geometry of the model compounds II-31 and II-41 ensures that intermolecular hydrogen abstraction can occur only from the exo-face of the cis-fused cycloalkyl moiety.

These model studies suggest that intramolecular hydrogen transfer should lead to regiospecific bromination at C_3 if the radical intermediate formed from II-31 or II-41 has the π-electronic configuration (II-33 or II-49) or is a bromine atom complex[112] (II-34 or II-47), while intermolecular hydrogen abstraction (e.g. from the solvent) should be observed if it has the Σ configuration (II-32 or II-48).

The $\Delta^{2,3}$-unsaturated tricyclic N-bromosuccinimide derivatives II-50, II-60, and II-63 were synthesized in order to study the mode of addition of imidyl radicals to double bonds. Dreiding models reveal that the imidyl radicals derived from II-50 and II-60 could add intramolecularly to the double bonds if they have Π-, but not Σ-configurations. In the latter case, the orbital containing the unpaired electron is orthogonal to the ρ-orbitals of the double bond. In II-63 intramolecular reaction is not feasible because the imidyl group is in the exo-position with respect to the cyclopentenyl group.

We decided to re-investigate the photodecomposition of N-bromosuccinimide (NBS) itself under conditions comparable to those reported by Skell and co-workers[53]. The results of our work confirmed Skell's findings and added some further information in this area.

The next section of the thesis describes the synthesis of the model compounds and their structure elucidation, and the results of the mechanistic studies of the photodecomposition of NBS and its tricyclic derivatives.

Following the presentation of the results there is a discussion of the important features of the synthetic work and the conclusions drawn from the mechanistic studies.

The final section of the thesis presents the experimental details of the synthesis, the structural elucidations, and the mechanistic studies.

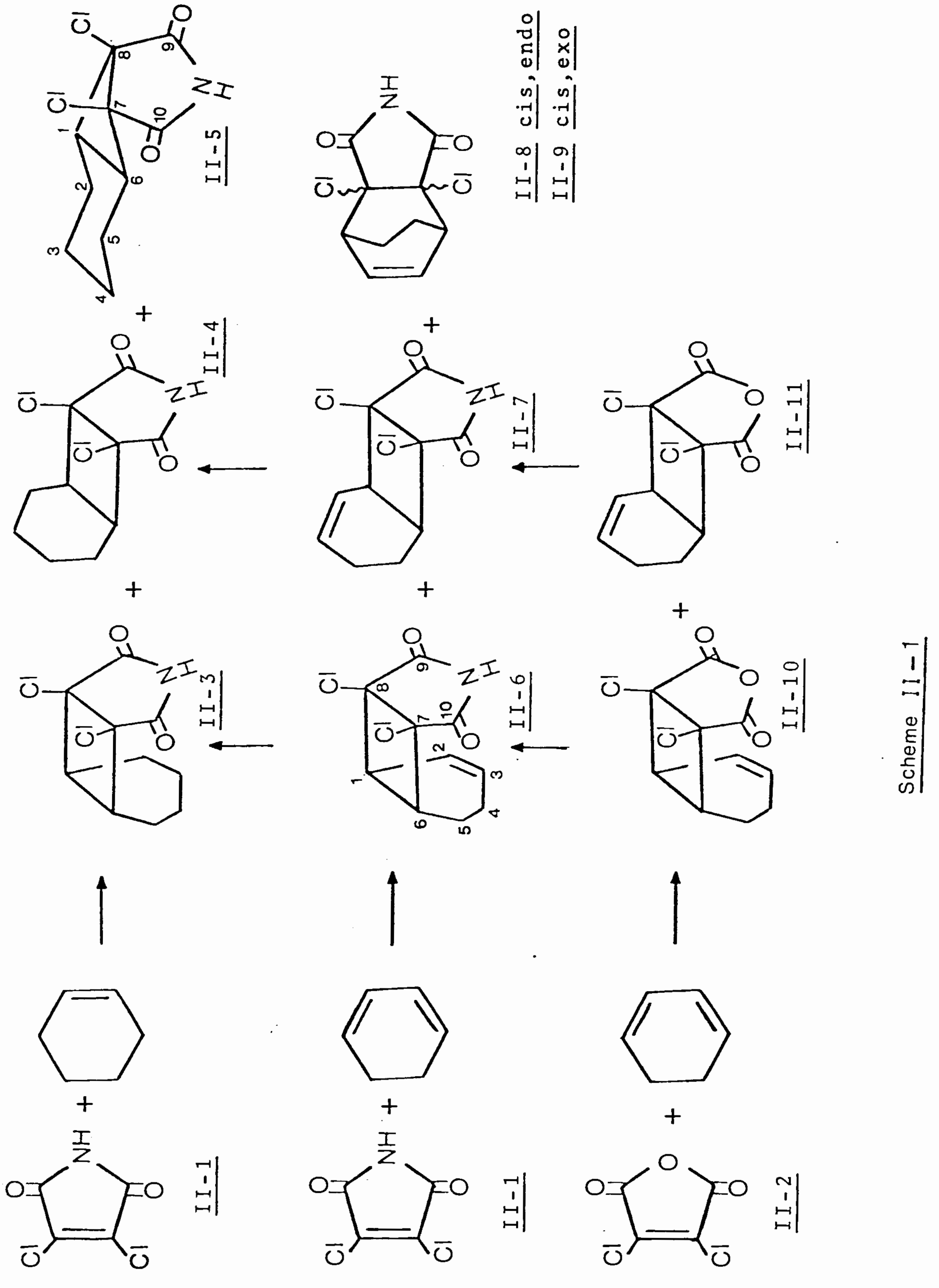
II. RESULTS

II-1 [2+2] Photocycloaddition of Dichloromaleimide and Dichloromaleic Anhydride to Cyclic Olefins

[2+2] Photocycloadditions are very useful methods to construct cyclobutane rings[71,72] and have been extensively studied with wide variations of addenda[73-80]. As model compounds such as II-3, II-6, II-15 and II-17 were required for mechanistic studies, we have investigated the photoaddition of dichloromaleimide and dichloromaleic anhydride to suitable olefins. Maleic anhydride derivatives have been shown to form complexes with olefins exhibiting new bands in the 280 nm region[81-84]. Irradiation of this charge transfer band or sensitization by triplet sensitizers such as benzophenone initiates the [2+2] cycloaddition to give cyclobutane derivatives with all possible stereochemical orientations[83-87]. Photoadditions of maleimides to acyclic dienes are also known[81,84].

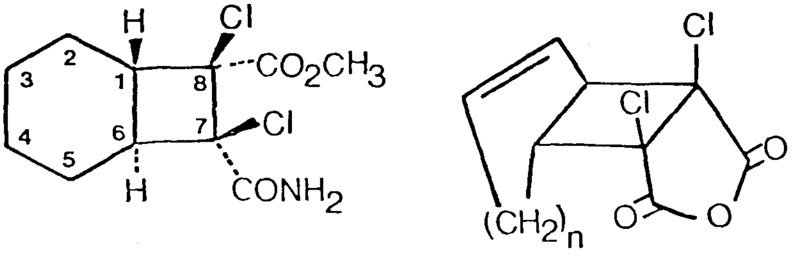
II-1-1 Photoaddition of Dichloromaleimide to 1,3-Cyclohexadiene and Cyclohexene

Irradiation of a solution of dichloromaleimide (II-1) and 1,3-cyclohexadiene in dioxane through a Pyrex filter resulted in the formation of the (2+2) photoadducts (relative yields) 7,8-dichloro-*cis*-bicyclo[4.2.0]oct-2-ene-*endo*,*cis*-7,8-dicarboximide (II-6, 50%) and 7,8-dichloro-*cis*-bicyclo[4.2.0]oct-2-


II-1
II-1
II-2
II-3
II-6
II-10
II-4
II-7
II-11
II-5
II-8 cis,endo
II-9 cis,exo

Scheme II-1

Scheme II-2



II-12

II-14 $n = 1$

II-13 $n = 2$

ene-exo,cis-7,8-dicarboximide (II-7, 43%) along with small amounts of the (4+2) adducts II-8 (5%), and II-9 (2%). Chromatographic separation afforded pure II-6 and II-7. Similar photolysis of a solution of dichloromaleimide and cyclohexene in dioxane led to 7,8-dichloro-cis-bicyclo[4.2.0] octane-endo,cis-7,8-dicarboximide (II-3, 14%),7,8-dichloro-cis-bicyclo[4.2.0] octane-exo,cis-7,8-dicarboximide (II-4, 32%), and 7,8-dichloro-trans-bicyclo[4.2.0]octane-cis-7,8-dicarboximide (II-5, 49%). The treatment of the crude mixture with charcoal in methanol converted II-5 to compound II-12 by solvolysis. Flash chromotographic separation of the mixture gave pure photoadducts (II-3, II-4, II-5) and the amide-ester II-12.

The cyclobutyl compounds II-3 to II-7 showed the expected IR absorptions (Table IV-1), and mass spectral fragments (Table IV-2) and elemental analyses (Table IV-3, see Experimental Section). Structural studieswere primarily concerned with the *cis*-*trans* configuration at the ring junction and with the *endo*-*exo*-orientation of the dicarboximide group with respect to the *cis*-ring fusion of the bicyclic system. For this purpose, high field NMR spectroscopy was extensively used, and X-ray crystallographic analysis[90] proved the structure of one of the adducts.

The ^1H NMR spectral data of II-6 and II-7 are given in Table II-1 (p.39). Decoupling of the olefinic protons had no effect on the signals of H_6 and H_5 thus permitting a distinction between the cyclobutyl protons H_1 and H_6, and between the methylene protons at C-4 and C-5. The assignment of H_2 and H_3 followed from their interactions with the C-4 protons. This was further confirmed by nuclear Overhauser effect experiment[101,102]: irradiation of H_1 resulted in a 12% enhancement of the H_2 signal in II-7. The distinction between H_{5x} and H_{5n} followed from the observation that H_{5x} showed an nOe enhancement (≈ 7%) on decoupling H_6. The conformation of II-6 in the solid state is shown in Figure II-1 and Table II-5 (p.49).

Figure II-1 (a) Perspective view of II-6 from X-ray analysis showing the atom numbering scheme, for clarity the hydrogen atoms have not been labelled. (b) Bond lengths (Å) and angles (°); intermolecular distances less than 3.8 Å: the distance of the C_{10} oxygen to C_4 is 3.553 Å and that of N to C_3 is 3.309 Å.

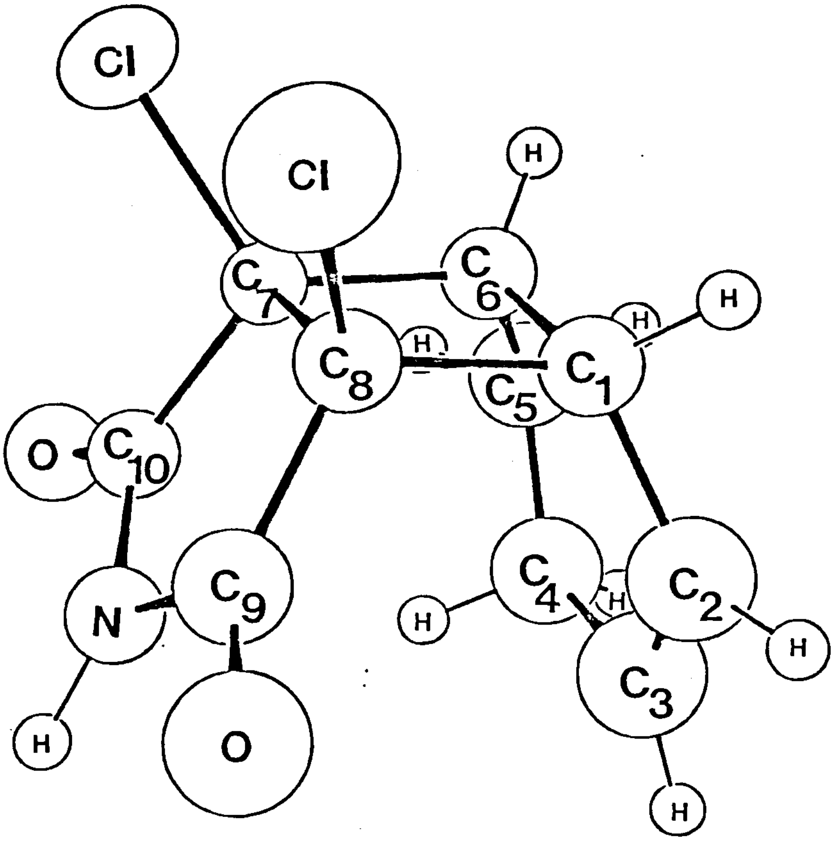


Fig. II-1(a)

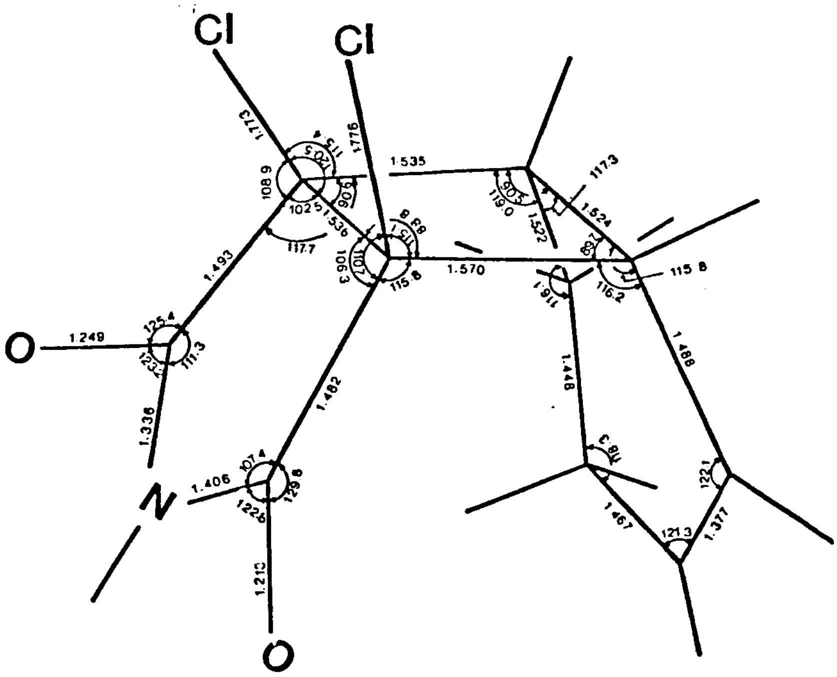


Fig. II-1(b)

The ring junction of the bicyclic system in II-7 was assigned cis-configuration since H_6 showed a 7.4% enhancement on irradiation of H_1. The exo-configuration of the imidyl group with respect to the cis-ring fusion of the bicyclic system in II-4 and II-7 followed from the nOe enhancement found for H_1 and H_6 on decoupling the respective imidyl proton (NH). A similar irradiation of the imidyl proton (NH) in II-3 and II-6 did not cause nOe for H_1 and H_6,therefore the imidyl group was assigned an endo-configuration.

The ^{13}C resonances of II-6 and II-7 are listed in Table II-2 (p.45). The signals were assigned with the aid of selective decouplings[99,100], and the results are summarized in Table II-3.

Catalytic hydrogenation of II-6 and II-7 afforded endo,cis-imide II-3 and exo,cis-imide II-4, respectively, in quantitative yields. Imides II-3 and II-4 exhibited complex ^1H NMR patterns which could not be analyzed precisely. However, irradiation of the H_1 (or H_6) signal changed the pattern of the H_2 (or H_5) signals but not the H_3 (or H_4) signals, and also caused the intensity enhancement of the intensity of the H_{2x} (or H_{5x}) signal.

The ^{13}C proton-decoupled spectra of II-3 and II-4 displayed five lines indicative of a plane of symmetry (Table II-2, p.45). The distinction between the C_2 and C_3 signals in II-3 followed from the off-resonance proton decoupled spectra. When the decoupler frequency was centered at δ 3.85 ppm, the C_2 signal showed smaller residual splittings[99] (J^r = 65 Hz) than C_3 (J^r = 70 and 74 Hz). Also the signal due to C_2 was collapsed to a doublet when the decoupler was set at the H_2 signal. The assignment of the C_2 and C_3 signals in II-4 followed from decoupling at δ 2.35 ppm which resulted in smaller residual splittings (J^r = 17 Hz) for C_2 than for C_3 (J^r = 21 and 22 Hz).

Table II-2 (p.45) also shows that in the endo-isomers II-3 and II-6 the signals of C_5 and imidyl group carbons are shifted upfield, whereas C_1 and C_6 are shifted downfield relative to those of the corresponding carbons in the exo-isomers II-4and II-7, respectively, which is due to the steric compression[99] in endo-isomers.

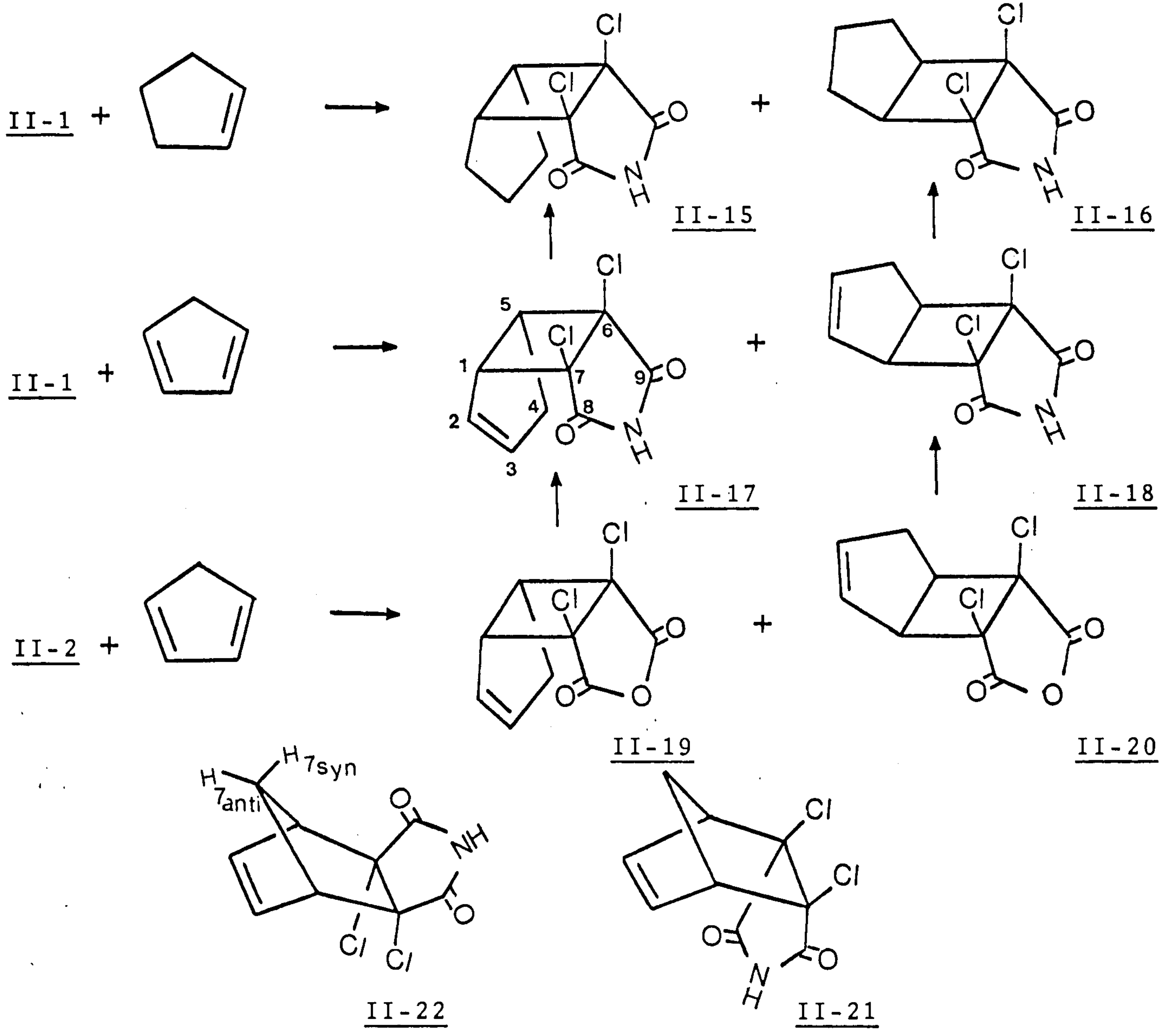
The structure proof of the trans-imide II-5 relied on decoupling experiments. The spectral parameters of II-5 are given in Table II-1 (p.39). The assignment of H_{2e} and H_{2a} followed from decoupling of H_1; and the assignment of H_{3a} and H_{4a} followed from their interactions with H_{2a} and H_{5a}, respectively. The observed coupling constants indicated that the cyclohexane ring is frozen in a chair conformation. The H_6 signal resonates at distinctly higher field (1.45 ppm) than H_1 (δ 2.15 ppm) owing to the anisotropic shielding effect of the imide group[88]. The ten signals in the ^{13}C NMR spectrum (Table II-2) clearly indicate that, in constrast to II-3 and II-4, II-5 does not possess a plane of symmetry. The ^{13}C signal assignments were based on: (a) selective decoupling of H_1 giving rise to a singlet for C_1 and an enhancement in the C_8 and C_9 signals; (b) decoupling of H_{2e} resulting in a doublet for C_2, and (c) the collapse of the C_3 and C_4 signals to doublets on irradiation of the signal at δ 1.54 ppm.

The trans-imide II-5 underwent methanolysis by heating in methanol to give a single stereoisomer which was assigned structure II-12 on the basis of the nucleophilic attack of methanol from the least hindered site at C_9. The structure of the amide-ester II-12 was established on the following basis: Elemental analysis and MS(CI) established the molecular formula as $C_{11}H_{15}Cl_2NO_3$. The infrared spectrum showed characteristic ester bands at 1735, 1170, 1290 cm^{-1}, and amide bands at 3440, 3340, 3210, 1660, and 1610 cm^{-1}. The ^1H NMR spectrum showed a singlet at δ 3.72 (OCH_3). The ^{13}C NMR spectrum displayed the expected 11 lines (Table II-2).

II-1-2 Photoaddition of Dichloromaleimide to Cyclopentadiene and Cyclopentene

Photolysis of *II-1* and cyclopentadiene in dioxane through a Pyrex filter resulted in the formation of the (2+2) adducts (relative yields), 6,7-dichloro-*cis*-bicyclo[3.2.0]hept-2-ene-*endo*,*cis*-6,7-dicarboximide (*II-17*, 47%) and 6,7-dichloro-*cis*-bicyclo[3.2.0]hept-2-ene-*exo*,*cis*-dicarboximide (*II-18*, 43%), and of the (4+2) photoadduct 5,6-dichloro-*cis*-bicyclo[2.2.1] hept-5-ene-*exo*,*cis*- 5,6-dicarboximide (*II-22*, 10%). The (2+2) adducts *II-17* and *II-18* were obtained pure by flash chromatography and characterized by elemental analysis, IR, MS, and NMR spectroscopy (see Experimental Section and Tables *II-1* and *II-2*). The (2+4) photoadduct *II-22* was obtained as a mixture with *II-18*. Similar photolysis of a solution of *II-1* and cyclopentene in dioxane gave 6,7-dichloro-*cis*-bicyclo[3.2.0] heptane-*endo*,*cis*-6,7-dicarboximide (*II-15*) and 6,7-dichloro-*cis*-bicyclo[3.2.0]heptane-*exo*,*cis*-6,7-dicarboximide (*II-16*) in the approximate ratio 1:1; they were separated by flash chromatography.

^1H NMR spectra of the (4+2) photoadduct *II-22* and the thermally derived Diels-Alder adduct *II-21* are distinctly different and indicative of the exo-configuration of the imide group in *II-22*. The ^1H NMR spectrum of *II-22* featured the C-7 protons at δ 1.62 (H_{7syn}) and 1.9 (H_{7anti}), while in *II-21*


II-1
II-1
II-2
II-15
II-16
II-17
II-18
II-19
II-20
II-21
II-22
Cl
O
NH
O
1
2
3
4
5
6
7
8
9
H7syn
H7anti

Scheme II-3

the C-7 protons resonated at δ 2.5 (H_{7syn}) and 2.18 (H_{7anti}). The pronounced upfield shift of H_{7syn} in <u>II-22</u> is ascribed to the anisotropic effect of the imide group[88].

The stereochemistry at the ring fusion and the configuration of the imide group with respect to the bicyclic system in <u>II-17</u> and <u>II-18</u> were deduced from a complete analysis of the respective ^1H and ^{13}C NMR data. The ^1H NMR spectral parameters of <u>II-17</u> and <u>II-18</u> are listed in Table II-1 (p.39). The assignment of H_1 and H_5 followed from the observation that the signals of the vinyl protons H_2 and H_3 collapsed to triplet of doublets on decoupling H_1, while irradiation of H_5 had no effect on the H_2 and H_3 signals. The assignment of H_{4n} and H_{4x} followed from the large coupling ($J_{5,4x}$ = 8.6 Hz) and the small coupling ($J_{5,4n}$ = 1.5 - 1.8 Hz) arising from the dihedral angles, $\phi_{5,4x} \simeq 30°$ and $\phi_{5,4n} \simeq 90°$, respectively, as estimated from Dreiding models. The exact assignment of the vinylic protons followed from the nOe results (Table II-4). Irradiation of H_1 had no effect on the H_3 signal intensity while H_2 showed an enhancement indicating that H_2 is adjacent to H_1. For further confirmation of our assignments, the coupling constants of a closely related compound[91] are listed in Table II-1.

Table II-1 also shows that in <u>II-17</u> the H_{4n} and H_5 signals are shifted upfield and downfield, respectively, relative to those of the corresponding protons in II-18, due to the anisotropic effect of the imide group and indicative of the *exo*- and *endo*-configuration for the imide group in II-17 and II-18 respectively. The anisotropic effects of the imide group on the H_2 and H_3 protons are relatively small in this series. This may imply that in these molecules the imide group and the pentane ring are rigidly held and that the imide group and the ring protons are spaced farther apart than in the 4,6-ring fused system. The *cis*-fusion of C_1 and C_5 in II-17 and II-18 was deduced from nOe experiments (Table II-4). Irradiation of H_1 led to an 8% enhancement of the H_5 signal indicative of a similar orientation for H_1 and H_5 in both isomers.

Mild hydrogenation of II-17 and II-18 gave II-15 and II-16, respectively, whose proton-decoupled ^{13}C-spectra (five signals) were indicative of a plane of symmetry. The ^{13}C shifts of the pertinent compounds are given in Table II-2. The assignments of the different carbons in II-15 and II-16 followed from the signal intensity ratios and multiplicities in the off-resonance proton decoupled spectra. The ^{13}C signal assignments of II-17 and II-18 followed from: (a) selective decoupling of H_1 and H_2 which collapsed the signals of the corresponding carbons C_1 andC_2; (b) the intensity enhancement of the carbonyl C_8 and C_9 signals upon irradiation of H_1 and H_5, respectively; and (c) the signal due to C_7 which showed a broad singlet, while C_6 displayed a multiplet (with small splittings, $J \approx 8$ Hz) in the proton-coupled spectra; irradiating the allylic protons removed some of the splittings.

II-1-3 Photoaddition of Dichloromaleic Anhydride to 1,3-Cyclohexadiene and Cyclopentadiene

Photolysis of dichloromaleic anhydride II-2 and 1,3-cyclohexadiene in dioxane using a Pyrex filter gave (2+2) photoadducts II-10 and II-11 as major components. Preparative GC allowed the isolation of the predominant components II-10 (pure) and II-11 (admixed with II-10; 15%) and a small amount of an unknown compound.

Similar photolysis of dichloromaleic anhydride (II-2) with cyclopentadiene afforded the (2+2) adducts II-19 and II-20 in the approximate 1:1 ratio in addition to a minor component which was not further investigated. Flash chromatography of the crude product afforded pure II-19 and a fraction which was II-20 admixed with II-19 (30%). Due to partial hydrolysis, the recovery of these anhydrides from flash chromatography column was low. The structures of these cyclobutyl anhydrides II-10, II-11, II-19 and II-20 were directly related to imides II-6, II-7, II-17 and II-18, respectively, by their conversion through ammonolysis and cyclization.

TABLE II-1

The ^{1}H NMR Data of Cycloaddition Products[a]

Compound	Chemical Shifts (ppm)	Coupling Constants (Hz)
II-3	1.27(m;H_{3n} and H_{4n}), 1.45 (m;H_{3x} and H_{4x}), 1.57(m;H_{2n} and H_{5n}), 1.83(m;H_{2x} and H_{5x}), 3.11(m;H_1 and H_6), 8.18(N$\underline{H}$)	
II-4	1.38(m;H_{3n} and H_{4n}), 1.75(m;4H), 1.86(m;H_{2x} and H_{5x}), 2.84(m;H_1 and H_6), 8.83(N$\underline{H}$)	
II-5[b]	0.7(m;H_{3a} and H_{4a}), 1.11(dq,3.7,12: H_{2a}), 1.19(ddt,3.7,10.7,12.8;H_{5a}), 1.25(m;H_{3e} and H_{4e}), 1.33(qd,3.7, 12.5;H_{5e}), 1.43(ddd,3.7,10,12;H_6), 1.67(qd,3.5,12.5;H_{2e}), 2.15(ddd,3,12,13;H_1)	$J_{1,2e}$(3), $J_{1,2a}$(13), $J_{1,6}$(12.5), $J_{2e,2a}$(12.5), $J_{2e,3a}$(3.8), $J_{2a,3a}$(12.8), $J_{4e,5a}$(3.8), $J_{4a,5a}$(12.8), $J_{5a,5e}$(12.8), $J_{5e,6}$(3.8), $J_{5a,6}$(10.8)

Table II-1 (Cont'd.)

Compound	Chemical Shifts (ppm)	Coupling Constants (Hz)
II-6	1.72(tdd,6.4,8.6,14.6;H_{5x}), 1.95(tdd,3.9,6.2,14.6;H_{5n}), 2.04(m;H_{4n} and H_{4x}), 3.45(ddd,4,6.4,11;H_6), 3.48(qdd,2,3.6,11;H_1), 5.83(tdd,2,3.8,10;H_2), 6.05(dddd,1.4,3.2,5,10;H_3), 9.05(N<u>H</u>)	$J_{1,2}$(3.8), $J_{1,3}$(1.4), $J_{1,6}$(11), $J_{2,3}$(10), $J_{2,4n}$(2), $J_{2,4x}$(2), $J_{3,4x}$(5), $J_{3,4n}$(3.4), $J_{4x,4n}$(17), $J_{4x,5n}$(3.8), $J_{4n,5x}$(8.8), $J_{4n,5n}$(6.8), $J_{4x,5x}$(6.5), $J_{5x,5n}$(15), $J_{5n,6}$(4), $J_{5x,6}$(6.4)
II-7	1.91(m;H_{5n} and H_{5x}), 2.03(m;H_{4n}), 2.29(dqd,2,5.4,17;H_{4x}), 3.04(td,8,9;H_6), 3.24(dtdd,0.5,2,5,8;H_1), 5.64(tdd,2,4.4,10;H_2), 6.27(dddd,2,3.4,5.2,10;H_3), 8.54(N<u>H</u>)	$J_{1,2}$(4.4), $J_{1,3}$(1.8), $J_{1,6}$(8.8), $J_{2,3}$(9.9), $J_{2,4x}$(1.6), $J_{2,4n}$(2.2), $J_{3,4x}$(5.3), $J_{3,4n}$(3.4), $J_{4n,4x}$(17), $J_{4x,5x}$(5.3), $J_{4x,5n}$(5.1), $J_{4n,5n}$(5.6), $J_{4n,5x}$(9), $J_{5x,5n}$(17.2), $J_{5x,6}$(7.2), $J_{5n,6}$(8).
II-8	1.38(md,8,H_{7anti} and H_{8anti}), 2.21(md,8;H_{7syn} and H_{8syn}), 3.23(m;H_1 and H_4), 6.28(m;H_2 andH_3)	

Table II-1 (Cont'd.)

Compound	Chemical Shifts (ppm)	Coupling Constants (Hz)
II-9	1.45(md,10;H_{7anti} and H_{8anti}), 1.67(md,10;H_{7syn} and H_{8syn}), 3.37(m;H_1 and H_4), 6.48(m;H_2 and H_3)	
II-10[d]	1.77(tdd,6.5,10,15;H_{5x}), 2.05(tdd,3,6.5,15;H_{5n}), 2.1(m;H_{4x}), 2.18(m;H_{4n}) 3.48(m;H_1 and H_6), 5.87(md,10;H_2), 6.15(dtd,1.8,4,10;H_3)	
II-11[d]	1.93(m;H_{5n} and H_{5x}), 2.05(m;H_{4n}), 2.32(qd,4.5,17;H_{4x}), 3.10(td,7,9;H_6), 3.37(m;H_1), 5.65(tdd,1.8,4,10;H_2), 6.28(dddd,2,3,5.5,10;H_3)	
II-12	1.36(m;H_3 and H_4), 1.43(dq,3.5,12;H_{5a}), 1.53(dq,3.5,12;H_{2a}), 1.82(m;H_3,H_4,H_{5e}), 1.92(qd,3,12;H_{2e}), 2.37(ddd,3.5,12,13;H_6), 2.85(ddd,3.5,11,13;H_1), 3.72(s,CH_3), 5.72($N\underline{H}$), 6.55($N\underline{H}$)	$J_{1,6}$(13), $J_{1,2a}$(12), $J_{1,2e}$(3.5), $J_{6,5a}$(12)

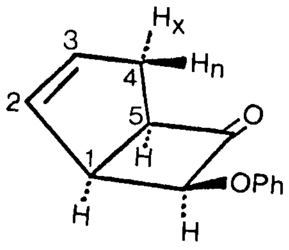
Table II-1 (Cont'd.)

Compound	Chemical Shifts (ppm)	Coupling Constants (Hz)
II-15	1.76(m;3H), 1.82(m;1H), 2.04(m;2H), 3.45(m;H_1 and H_5), 8.75(N$\underline{H}$)	
II-16	1.73(m;2H), 1.83(m;1H), 1.9(m;1H), 2.22(m;2H), 3.18(m;H_1 and H_5), 8.57(N$\underline{H}$)	
II-17	2.62(qdd,2.2,8.8,19;H_{4x}), 2.78(md, 18.6;H_{4n}), 3.62(dt,1.8,9;H_5), 3.92(md,9;H_1), 5.75(qd,2.2,5.8;H_2), 6.02(qd,2,5.6;H_3), 8.58(N$\underline{H}$)	$J_{1,2}$(2.3), $J_{1,3}$(2), $J_{1,4n}$(3), $J_{1,4x}$(2.2), $J_{1,5}$(8.8), $J_{2,3}$(5.6), $J_{2,4n}$(2.3), $J_{2,4x}$(2.3), $J_{3,4n}$(2.4), $J_{3,4x}$(2.2), $J_{4n,4x}$(18.6), $J_{4n,5}$(1.8), $J_{4x,5}$(8.8)
II-18	2.72(tddd,1.8,2.2,8.6,18;H_{4x}), 3.0(md,18;H_{4n}), 3.37(ddd,2,6.4,8;H_5), 3.87(m,H_1), 5.72(qd,2.4,5.6;H_2), 6.08(qd,2.2,5.6;H_3), 8.27(N$\underline{H}$)	$J_{1,2}$(2.6), $J_{1,3}$(2.7), $J_{1,4n}$(1.5), $J_{1,4x}$(2.5), $J_{1,5}$(6.2), $J_{2,3}$(5.7), $J_{2,4n}$(2.4), $J_{3,4x}$(2.0), $J_{3,4n}$(2.3), $J_{3,4x}$(2), $J_{4n,4x}$(18.4), $J_{4n,5}$(1.5), $J_{4x,5}$(8.6)

Table II-1 (Cont'd.)

Compound	Chemical Shifts (ppm)	Coupling Constants (Hz)
II-19[d]	2.67(qdd,2,8,19;H_{4x}), 2.87(md,19;H_{4n}), 3.67(t,8.5;H_5), 3.95(md,8;H_1), 5.83(qd,2,6;H_2), 6.13(m;H_3)	$J_{1,2}$(*ca*.2), $J_{1,4x}$(*ca*.2), $J_{1,5}$(8.5), $J_{2,3}$(6), $J_{2,4x}$(*ca*.2), $J_{3,4x}$(*ca*.2), $J_{4n,4x}$(19), $J_{5,4x}$(8)
II-20[d]	2.8(qdd,2,8,18.5;H_{4x}), 3.05(md,18;H_{4n}), 3.43(t,7.5;H_5), 3.93(m;H_1), 5.77(qd,2,5.5;H_2), 6.13(m;H_3)	$J_{1,2}$(*ca*.2), $J_{1,4x}$(*ca*.2), $J_{1,5}$(7.5), $J_{2,3}$(5.5), $J_{2,4x}$(*ca*.2), $J_{3,4x}$(*ca*.2), $J_{4x,4n}$(18.5), $J_{5,4x}$(8)
II-21	2.18(md,10;H_{7anti}), 2.5(md,10;H_{7syn}), 3.42(m;H_1 and H_4), 6.32(m;H_2 and H_3)	
II-22	1.62(md,11;H_{7syn}), 1.9(md,11;H_{7anti}), 3.53(m;H_1 and H_4), 6.52(m;H_2 and H_3)	

Table II-1 (Cont'd.)

Compound	Chemical Shifts (ppm)	Coupling Constants (Hz)
 II-23		$J_{1,2}$(1.7), $J_{1,3}$(2), $J_{1,4n}$(2.8), $J_{1,4x}$(2.1), $J_{1,5}$(7.3), $J_{2,3}$(5.8), $J_{2,4x}$(1.9), $J_{2,4n}$(2.1), $J_{3,4x}$(2.2), $J_{3,4n}$(2.2), $J_{4x,4n}$(16.9), $J_{5,4x}$(8.7), $J_{5,4n}$(1.4)

a - in $CDCl_3$ at 400 MHz

b - in C_6D_6 at 400 MHz

c - in a mixture of II-18 and II-22

d - Literature[87], in CCl_4 at 60 MHz: II-10 δ 2.1(4H), 3.6(2H), 6.05(2H); II-11 δ 2(4H), 3(1H), 3.8(1H), 5.9(2H); II-19 δ 2.8(2H), 4-3.5(2H), 6.0(2H); and II-20 δ 2.9(2H), 3.5(1H), 3.9(1H), 6(2H).

TABLE II-2

^{13}C NMR Spectral Data of Cycloaddition Products[a]

Compound	
II-3	21.3(t,130:C_3 and C_4), 22.44(t, 130;C_2 and C_5), 42.58(d,145;C_1 and C_6), 69.46(s;C_8 and C_7), 172.44(s:C=0)
II-4	21.32(t,130;C_3 andC_4), 23.09(t,130;C_2 and C_5), 39.6(d,148;C_1 and C_6), 71.47(s;C_8 and C_7), 173.81(s;C=0)
II-5[c]	26.03(t,130;C_4)[b], 26.32(t,130;C_3)[b]. 27.49(t,130;C_2), 29.22(t,130;C_5), 50.20(d,136:C_6), 52.62(d,130:C_1), 68.43(d,8:C_8), 75.75(s;C_7), 171.19(d,8;C_9), 172.28(d,4;C_{10})
II-6	19.75(t,128;C_5), 21.22(tt,3.5,129;C_4), 42.76(d,149:C_1), 43.09(d,143;C_6), 67.88(s,br:C_7), 70.26(d,7;C_8), 122.65(dd,4,162;C_2), 133.50(d,158;C_3), 171.48(s;C_9)[b], 172.68(d,4;C_{10})[b]
II-7	22.38(t,128;C_4), 22.81(t,130;C_5), 39.48(d,146;C_6), 40.09(d,140;C_1), 69.4(s,br;C_7), 72.3(d,8;C_8), 122.53(d,165;C_2), 134.58(d,170;C_3), 173.4(d,3.6;C_9), 173.74(d,3.7;C_{10})

Table II-2 (Cont'd.)

II-12	25.05, 25.61, 26.13, 28.16, 45.73, 52.15, 52.53, 75.15, 76.20, 168.94, 169.28
II-15	27.78(t,130;C_3), 28.43(t,130;C_2 and C_4), 51.34(d,150;C_1 and C_5), 68.21(s;C_6 and C_7), 172.11(s;C=0)
II-16	27.1(t,132:C_3), 30.4(t,133:C_2 and C_4), 47.15(d,147;C_1 and C_5), 69.93(s;C_6 and C_7), 174.40(s;C=0)
II-17	35.15(tt,9,133;C_4), 47.31(md, 151:C_5), 57(md,153;C_1), 68.44(m;C_6), 71.4(br,s;C_7), 128.35(md,168;C_2), 138.52(md,165;C_3), 171.69(s;C_8), 171.97(d,3.9;C_9)
II-18	36.49(tt,9,133;C_4), 44.35(dd,3.4,147:C_5), 54.69(md,147;C_1), 70.52(s;C_7), 72.28(m;C_6), 128.8(md,172;C_2), 137.1(md,165;C_3), 173.68(d,3.2;C_8), 173.8(d,3.8;C_9)

a In acetone-d_6 at 100 MHz; md = multiplet of doublet, br,s = broad singlet.

b The pair of signals is interchangeable.

c In acetone-d_6: δ 1.54 (H_{3a} and H_{4a}), 1.51 (H_{2a}), 1.61 (H_{5a}), 1.82 (3H), 1.93 (H_{2e}), 2.33 (H_6), 2.44 (H_1).

TABLE II-3

Off-Resonance Decoupling of the ^{13}C NMR Spectra of II-6 and II-7

^{13}C NMR Signals	II-6	II-7
C_1 and C_6	C_1 enhanced[a] on decoupling of H_2 and H_3.	C_1 collapsed to a singlet on decoupling H_1.
C_2 and C_3	C_2 collapsed on decoupling of H_2.	C_2 collapsed to a singlet on de-. coupling H_2.
C_4 and C_5	C_5 collapsed to a doublet on decoupling of either H_{5x} or H_{5n}.	C_4 enhanced[a] on decoupling H_2 and H_3.
C_9 and C_{10}	b	C_9 enhanced[a] on decoupling H_1. C_{10} enhanced on decoupling H_6.
C_7 and C_8	C_7 enhanced[a] on decoupling of H_5.	C_8 enhanced[a] on decoupling of H_1. C_7 enhanced on decoupling H_6.

[a] The "enhancement" arises from removal of long range coupling (see Reference 89).

[b] The two signals are overlapped with solvent peaks and cannot be differentiated.

Table II-4[a]

nOe Results for II-17 and II-18

Proton		Percentage Enhancement			
Irradiated	H_2	H_1	H_5	H_{4n}	H_{4x}
II-17; H_1	5.9	--	8.2	--	--
H_5	--	5.7	--	--	4.5
II-18; H_1	5.7	--	8.0	--	--
H_5	--	6.5	--	--	12

[a] Solvent C_6D_6

II-17: δ 1.8(H_{4x}), 2.5(H_{4n}), 3.0(H_5), 3.3(H_1), 5.2(H_2), 5.3(H_3), 7.2(NH).

II-18: δ 2.0(H_{4x}), 2.5(H_5), 2.6(H_{4n}), 3.2(H_1), 5.3(H_2), 5.5(H_3), 6.9(NH).

Table II-5

Torsional Angles in Degrees for II-6 as Determined by X-Ray Analysis

Atom 1	Atom 2	Atom 3	Atom 4	Angle
C_9	N	C_{10}	C_7	0
C_{10}	N	C_9	C_8	-2.3
C_8	C_7	C_{10}	N	1.6
C_6	C_7	C_{10}	N	98.9
C_{10}	C_7	C_8	C_9	-2.8
C_{10}	C_7	C_8	C_1	113.8
C_6	C_7	C_8	C_9	-121.4
C_6	C_7	C_8	C_1	-4.8
C_{10}	C_7	C_6	C_1	-99.5
C_{10}	C_7	C_6	C_5	22.5
C_8	C_7	C_6	C_1	5.0
C_8	C_7	C_6	C_5	127.0
N	C_9	C_8	C_7	3.1
N	C_9	C_8	C_1	-93.6
C_7	C_8	C_1	C_2	-114.0
C_7	C_8	C_1	C_6	4.9
C_9	C_8	C_1	C_2	-6.4
C_9	C_8	C_1	C_6	112.5
C_8	C_1	C_2	C_3	90.2
C_6	C_1	C_2	C_3	-13.2
C_8	C_1	C_6	C_7	-4.9
C_8	C_1	C_6	C_5	-128.3
C_2	C_1	C_6	C_1	114.3
C_2	C_1	C_6	C_5	-9.1
C_1	C_2	C_3	C_4	13.7
C_2	C_3	C_4	C_5	9.7
C_3	C_4	C_5	C_6	-31.3
C_4	C_5	C_6	C_7	-76.6
C_4	C_5	C_6	C_1	30.8

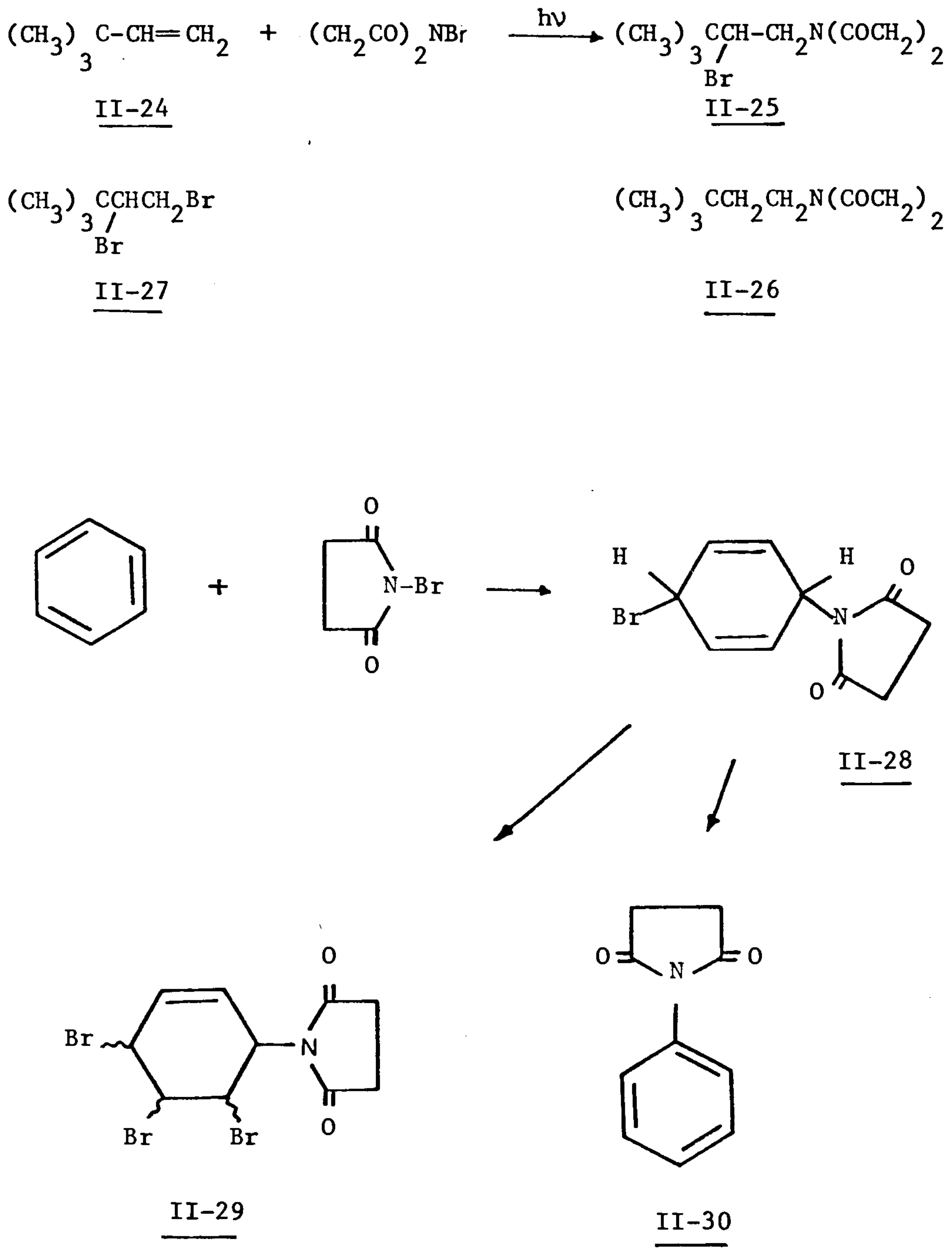
II-2 Photodecomposition of N-Bromosuccinimide (NBS)

The initial stage of my work involved the investigation of NBS photolysis in the presence of benzene and/or an olefin which lacks reactive hydrogens. It has been demonstrated that the succinimidyl radical could be generated by photolysis of NBS by suppressing[39-41] the bromine atom chain (Goldfinger mechanism). Therefore, ethylene oxide was chosen to scavenge HBr and a high concentration of an olefin to scavenge bromine was used. Acetonitrile was employed as solvent owing to its small tendency to donate hydrogen and its reasonably good solubilizing power for NBS. 3,3-Dimethyl-1-butene (neohexene) was the choice of olefin since it lacks reactive hydrogens.

Photolysis of NBS (0.011 mol) in acetonitrile in the presence of neohexene (0.119 mol) and ethylene oxide (0.031 mol) under nitrogen was carried out in a Pyrex apparatus immersed in a cooling bath. The reaction progress was monitored with KI-starch test paper and/or iodometry. A dark reaction was run simultaneously to confirm that thermal reaction occurred to only a small extent (< 5%), or not at all. The photolysate was evaporated to give a crude product which exhibited a clean ^{1}H NMR spectrum essentially similar to that of 1-succinimidyl-2-bromo-3,3-dimethylbutane (II-25). GC analysis of the crude product showed that it contained trace amounts of four minor products (2-3%); the minor components had no succinimide moiety as shown by GC-MS (no peak at m/e 100 for $C_4H_6NO_2^+$). Recrystallization afforded II-25 (65% yield) which showed physical constants and analysis data in agreement with an addition product. Reduction with zinc powder and sodium iodide gave II-26. The ^1H NMR spectrum of the latter exhibited, in addition to two singlets, symmetrical multiplets of type A_2B_2 at δ 1.46 and 3.52.

Photolysis of NBS in benzene in the presence of ethylene oxide was run in a similar manner at 10°C to give II-29 as the major product and a small amount of II-30. The isomeric mixture (40% yield) could not be easily separated by chromatography; the chromatographic fractions showed similar mass spectral patterns but drastically different ^1H NMR patterns, and gave good analyses for $C_{10}H_{10}Br_3NO_2$ arising from the addition of NBS and bromine to benzene. By extensive chromatography and recrystallization, small amounts of pure isomers having m.p. 204-205°C and m.p. 153-157°C were isolated. The complexity of their ^1H NMR spectra did not permit determination of structures.

Scheme II-4


(CH3)3C-CH=CH2
+
(CH2CO)2NBr
hν
(CH3)3CCH-CH2N(COCH2)2
Br
II-24
II-25
(CH3)3CCHCH2Br
Br
II-27
(CH3)3CCH2CH2N(COCH2)2
II-26
O
N-Br
O
H
Br
H
O
N
O
II-28
Br
Br
Br
O
N
O
II-29
O
N
O
II-30

The structure of II-30 was readily proved by direct comparison with an authentic sample[94] prepared by the reaction of succinic anhydride with aniline[95]. It is assumed that both II-29 and II-30 were formed from the primary adducts, such as II-28 or its isomer, by bromine addition and HBr elimination, respectively.

Photolysis of NBS (7.8 mmol) in acetonitrile containing benzene (167 mmol), ethylene oxide (30 mmol), and neohexene (22 mmol) with a 200W lamp through a Pyrex filter resulted in the formation of II-30 (26%), dibromide II-27 (68%), succinimide (49%), and II-25 (≈ 2%). Under similar photolysis conditions, except in the absence of ethylene oxide, the photodecomposition of NBS (7.5 mmol) in the presence of benzene (167 mmol) and neohexene (22 mmol) gave II-30 (39%), II-27 (64%), succinimide (56%), and II-25 (2%).

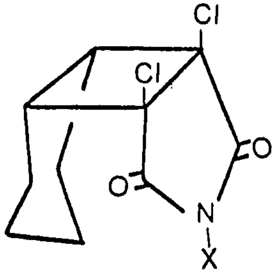
In view of the extensive formation of bromine, as witnessed by the isolation of II-29, in spite of the presence of ethylene oxide, photolysis of bromine in the presence of ethylene oxide *and* NBS in benzene was examined using a GWC filter to cut off the light below 350 nm. The NBS concentration decreased slowly owing partially to interference caused by the precipitated succinimide, but no reaction of NBS with bromine was observed in the dark. From the photolysate was obtained, in addition to a nearly quantitative yield of succinimide, a mixture of polybrominated benzene derivatives none of which contained the succinimide moiety. Photobromination of benzene has been reported to yield hexabromocyclohexane via the bromine radical addition [96,97].

II-3 Photodecomposition of N-Bromo-7,8-Dichloro-cis-Bicyclo [4.2.0]Octane-endo,cis-7,8-Dicarboximide (II-31)

The photodecomposition of II-31 was carried out under various conditions and the products were identified in order to clarify the nature of the radical intermediates involved.

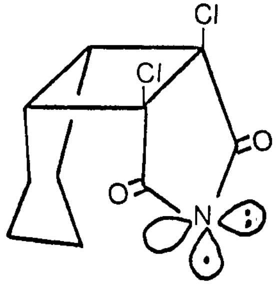
Photolysis of N-bromoimide II-31 in CH_2Cl_2 through a Pyrex filter resulted in the formation of imide II-3, cyclohexyl ring brominated imides II-35(C_1-Br), II-36(C_{2x}-Br), II-37(C_{3x}-Br), II-38(C_{3n}-Br), and two isomeric amides II-39 and II-40. The two amides differed in stereochemistry of the substituents and obviously arose from the ring opening of the imidyl radical followed by facile hydrolysis and decarboxylation during work-up of the crude product, i.e., II-32 (or II-33) → RCON=C=O → $RCONHCO_2H$ → $RCONH_2$ + CO_2. The decomposition of II-31 did not occur in the dark as shown by IR and ^1H NMR spectroscopy, and the crude products were stable when kept at room temperature. GC-MS of some of the crude products ascertained the formation of $BrCHCl_2$.

Scheme II-5

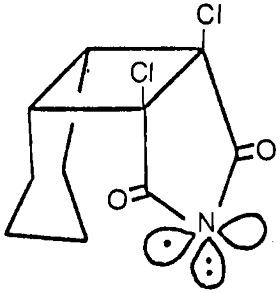


II-3 : X = H

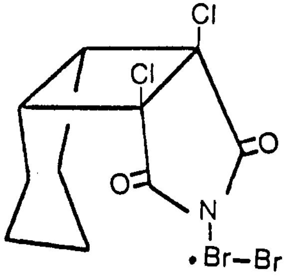
II-31 : X = Br



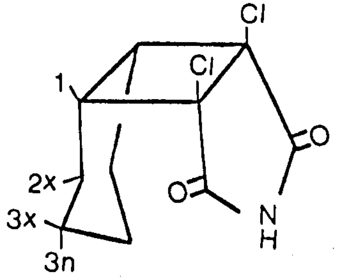
II-32



II-33



II-34

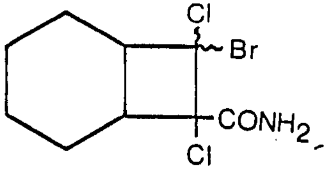


II-35 (C_1-Br)

II-36 (C_{2x}-Br)

II-37 (C_{3x}-Br)

II-38 (C_{3n}-Br)



II-39

II-40

The C-brominated imides II-35 to II-38 were also formed by photobromination of imide II-3 with molecular bromine in which no amides II-39 and II-40 were detected by GC.

Photodecomposition of II-31 in the presence of neohexene and/or 1,1-dichloroethylene led to imide II-3 and amides II-39 and II-40, but no C-brominated imides (II-35 to II-38) were formed (as shown by GC-analysis).

Careful column and thin layer chromatographic separations of the crude products obtained by photodecomposition of II-31 and by photobromination of II-3 afforded II-39 (amide), II-36 (C_{2x}-Br), II-37 (C_{3x}-Br), and II-38 (C_{3n}-Br) as impure samples, while II-40 (amide) and II-35 (C_1-Br) were obtained as mixtures along with II-39(amide) and II-36 (C_{2x}-Br), respectively.

The structure and stereochemistry of II-35 to II-38 were determined by ^{1}H and ^{13}C NMR spectral analysis (Tables II-6, p.70, and II-7, p.73), IR (Table IV-4) and mass spectra (Table IV-5). The positions of bromine substituents in these imides were assigned on the basis of the ^{13}C deshielding effect of a bromo-substituent on the β-carbon by ≈ 10-14 ppm[99,100] relative to the parent imide II-3. The bromine substituent in II-36 (C_{2x}-Br) caused downfield shifts, of ≈ 10 ppm of the methine and methylene carbon signals as compared to the corresponding signals in imide II-3. The bromine in II-38 (C_{3n}-Br)and II-37 (C_{3x}-Br) caused downfield shifts of 10-14 ppm of two methylene carbon signals. Extensive decoupling experiments clarified the coupling patterns of the CHBr and some related protons determining the orientation and position of the bromine substituent. The pertinent arguments in support of the structural assignments are outlined below.

II-37 (C_{3x}-Br): Irradiation of the C_3-H signal (4.23 ppm) caused the H_2 (2.37 ppm) and H_2' (2.05 ppm) signals to collapse to double doublets (J=9,15 and J=8,15 Hz, respectively), but did not affect H_1 and H_6. Irradiation of H_1 (3.38 ppm) caused the H_2 and H_2' multiplets to collapse to double doublets (J=3.7, 15 and J=5.4,15 Hz, respectively). Irradiation of H_6 (3.27 ppm) had no effect on the H_3, H_2 and H_2' signals. nOe experiment showed no enhancement of the H_1 and H_6 signals upon decoupling H_3 indicating an exo-configuration for the bromine substituent at C-3.

II-38 (C_{3n}-Br): Irradiation of H_3 (3.78 ppm) caused the H_2 signal to collapse to a double doublet (J=7.2, 13.6 Hz), but no change in the H_1 and H_6 (3.16 ppm) signals. Irradiation of H_1 caused the H_2 signal to collapse to a double doublet (J=4.4, 14 Hz), but no change in the H_3 signal. Upon low power irradiation of H_3 (3.78 ppm), the H_1 and H_6 intensities were enhanced by 5.7% indicative of an endo-configuration for bromine at C-3.

II-36 (C_{2x}-Br): Irradiation of H_2 (4.22 ppm) caused the H_1 signal to collapse to a doublet (J=12 Hz), and the H_{3n} and and H_{3x} signals to double doublets but no change in the H_6 signal.

II-35 (C_1-Br): Its ^1H NMR displayed only one cyclobutyl proton (δ 3.44 ppm), and no signal characteristic of C<u>H</u>Br (in the low field region).

The two amides gave closely spaced GC peaks, and only one of them was separated in a semi-pure state. GC-MS unambiguously demonstrated the two amides are configurational isomers showing the typical peak pattern of two chlorines and one bromine atom for the molecular ions.

Product Distribution Studies

As the bromine atom mediated bromination is an inevitable side reaction, photobromination of imide II-3 with bromine in CH_2Cl_2 was carried out to determine the product distribution. The percentage yields of C_1-, C_{2x}-, and C_3-brominated products at various bromine concentrationswere obtained by GC, and the results are listed in Table II-9 (p.76). For either series using a Pyrex filter or a GWV filter (cut-off at 380 nm) the C_2 -Br/$_x$$C_1$-Br, C_3-Br/C_1-Br and C_3 -Br/$_x$$C_3$ -Br$_n$ ratios were found to be nearly constant and independent on product yields.

The photolysis of N-bromoimide II-31 (8.4×10^{-3}M) at ≈320 nm ($CoSO_4$ and $NiSO_4$ filter solutions[105c]) was monitored by UV spectroscopy (Figure II-2). During the initial irradiation period (1 to 4 min.), an absorption band at 385-395 nm increased, exhibiting an isosbestic point at 325 nm. After 4 to 12 minutes of irradiation, this band had shifted to 408 nm and slowly decreased in intensity, with a second isosbestic point at 365 nm indicating that another absorbing species was formed. Further irradiation increased the absorbency in the 320 nm region. Similar absorbency (in the 320 nm region) was observed in the photobromination of imide II-3 with bromine (Fig. II-5). The build-up of the band at 385-395 nm and the decrease of the bromine maximum at ≈ 405 nm coincided with the formation of several species, the absorption of which extended to the 320 nm region. The photolysis of II-31 was repeated under similar conditions, and after 5 minutes irradiation the photolysate was quenched with 5% aqueous sodium bisulfite. GC analysis showed the presence of the C-Br isomers II-35 to II-38 and amides II-39 and II-40. Similar photolysis of II-31 (8.4×10^{-3}M) and bromine (4.2×10^{-4}M), with UV monitoring (Fig. II-3), showed a blue shift (≈ 5 nm) of the bromine absorption (at t=0, λ_{max}=408nm) during the initial irradiation period (1 to 5 mins.). As irradiation continued this band shifted to 408 nm and decreased in the same manner as above. Similar results (Fig. II-4) were also obtained by photolysis of II-31 in the presence of added bromine using sodium nitrite - potassium biphthalate solution as a filter[103] (cut-off ≈ 400 nm). The change in the bromine absorption might be due to the formation of complexes similar to those found in NBS photolysis[62]. Visually, the formation of bromine in the photolysis of II-31 in CH_2Cl_2 could be detected by the change from a colorless to a light yellow photolysate in several minutes.

The quantum yields for the disappearance of II-31 in CH_2Cl_2 at various times were measured by iodimetry under the conditions shown in Table II-8 (p.75). Both the complex pattern of the UV absorption (Fig. II- 2) and varying quantum yields (e.g., *ca*. 2 to 1 for 6% and 30% decomposition of II-31, respectively) suggested that photolysis of II-31 changes the reaction pattern as it progresses, most likely, owing to the formation of bromine. In contrast, the quantum yields determined under similar conditions but in the presence of neohexene (a bromine scavenger) were nearly constant at 1.2 + 0.1 for 8% and 24% decomposition of II-31. The low quantum yields of the N-bromoimide II-31 photodecompositions indicate that the imidyl radical is primarily generated by photoexcitation and only to a small extent by thermal propagation processes. In the presence of added bromine, the measured quantum yields for the disappearance of N-bromoimide II-31 using a Pyrex filter ranged from 8 to 5 showing the incursion

Figure II-2*: Photolysis of N-bromoimide II-31 ($8.4 \times 10^{-3}M$) in CH_2Cl_2 at room temperature ($NiSO_4$ and $CoSO_4$ filter solutions; light intensity, $I=3.6 \times 10^{-6}$ Einstein/min.).

Figure II-3*: Photolyusis of II-31 (8.4 ×m $10^{-3}M$) and bromine ($4.2 \times 10^{-4}M$) in CH_2Cl_2 at room temperature ($NiSO_4$ and $CoSO_4$ filter solutions; $I=3.6 \times 10^{-6}$ Einstien/min.). Curve a, II-31 ($8.4 \times 10^{-3}M$) without bromine.

Figure II-4*: Photolysis of II-31 ($1.2 \times 10^{-2}M$) and bromine ($0.78 \times 10^{-3}M$) in CH_2Cl_2 at room temperature (sodium nitrite-potassium-biphthalate filter solution). Curve a, II-31 ($1.2 \times 10^{-2}M$) without bromine.

Figure II-5*: Photobromination of imide II-3 ($2 \times 10^{-2}M$) with bromine ($1.9 \times 10^{-3}M$) in CH_2Cl_2 at room temperature ($NiSO_4$ and $CoSO_4$ filter solutions; $I=2.82 \times 10^{-6}$ Einstein/min.) Curve a, II-3 ($2 \times 10^{-2}M$) and bromine ($1.9 \times 10^{-4}M$); curve b, I-3 ($2 \times 10^{-2}M$) and bromine ($3.8 \times 10^{-4}M$); curve c, II-3 ($2 \times 10^{-2}M$) and bromine ($1.1 \times 10^{-3}M$).

* The numbers on the curves designate irradiation times in minutes. All photolyses were carried out using the optical bench described in the Experimental Section.

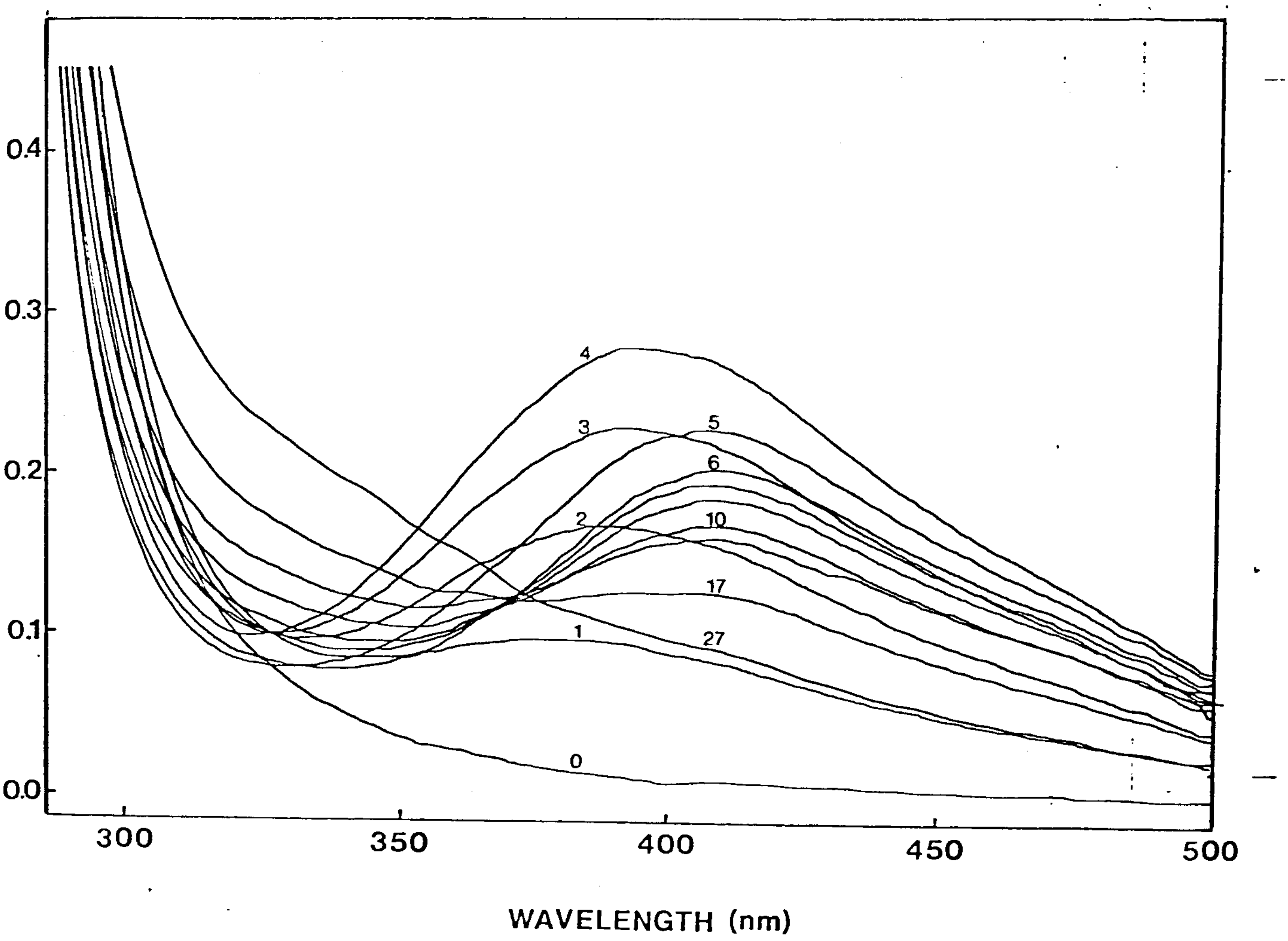

0.4
0.3
0.2
0.1
0.0
300
350
400
450
500
WAVELENGTH (nm)
4
3
5
6
2
10
17
1
27
0

Figure II-2

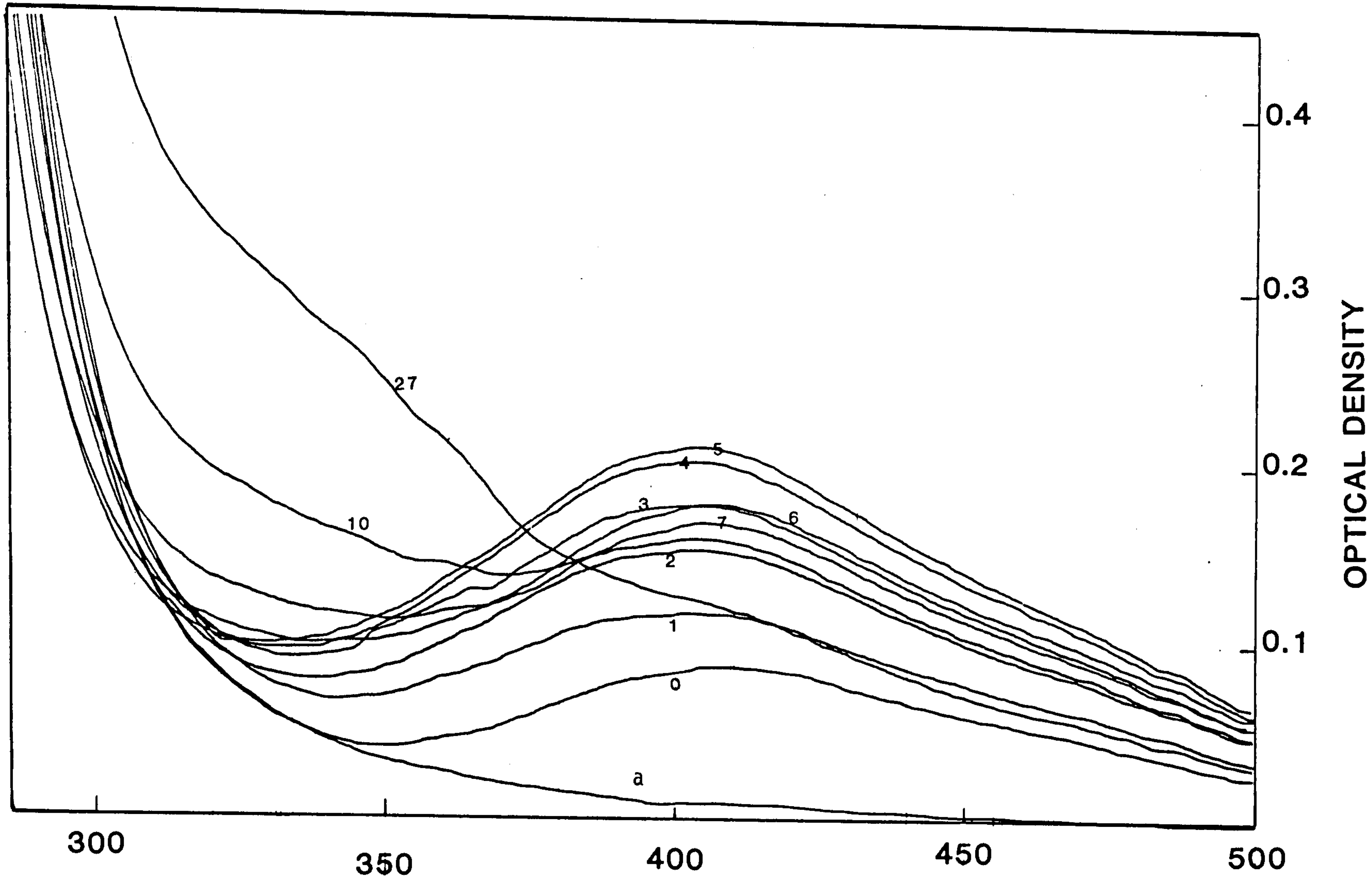

0.4
0.3
0.2
0.1
OPTICAL DENSITY
27
10
5
4
3
7
6
2
1
0
a
300
350
400
450
500
WAVELENGTH (nm)

Figure II-3

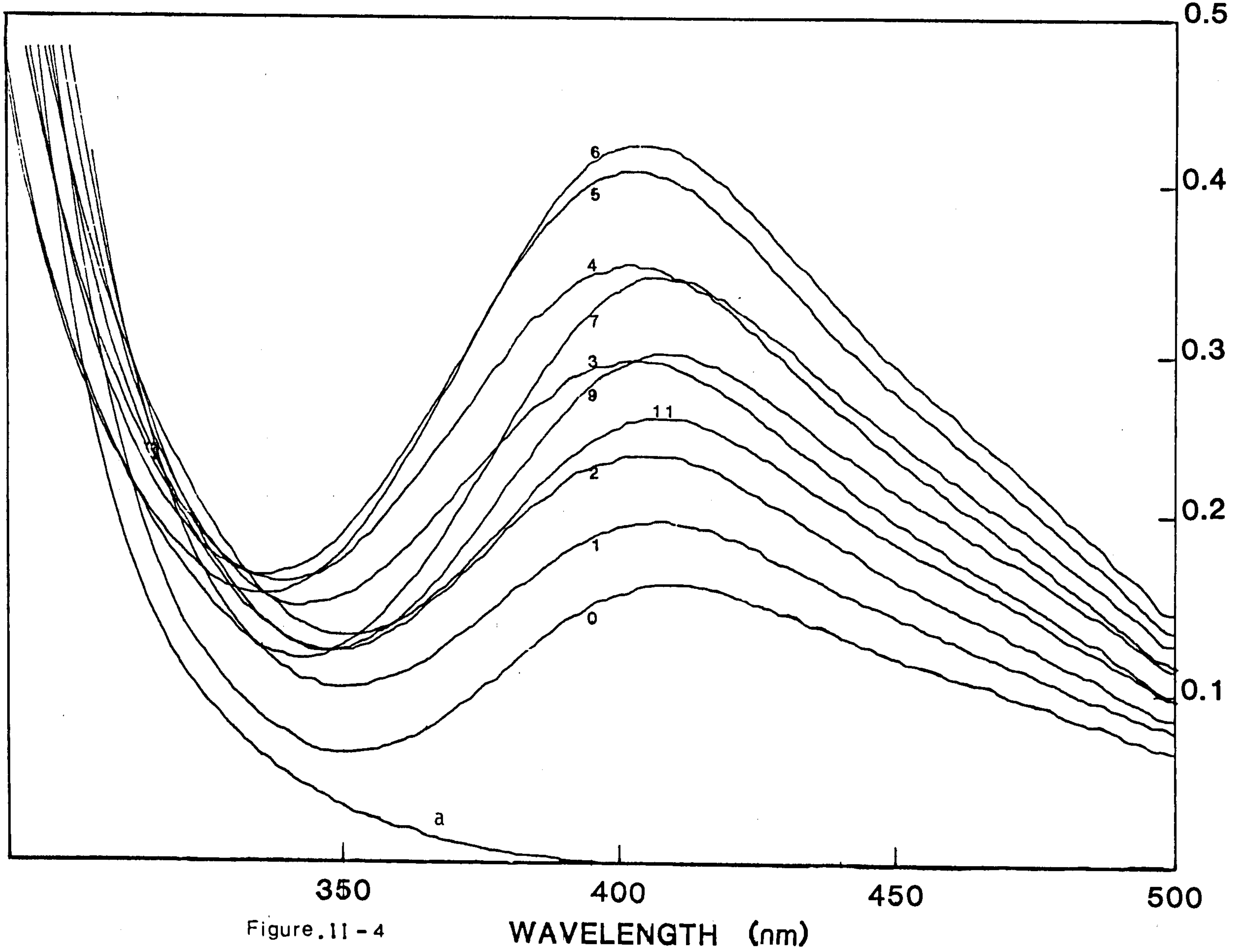

0.5
0.4
0.3
0.2
0.1
OPTICAL DENSITY
350
400
450
500
WAVELENGTH (nm)
6
5
4
7
3
9
11
2
1
0
a
3

Figure.II-4

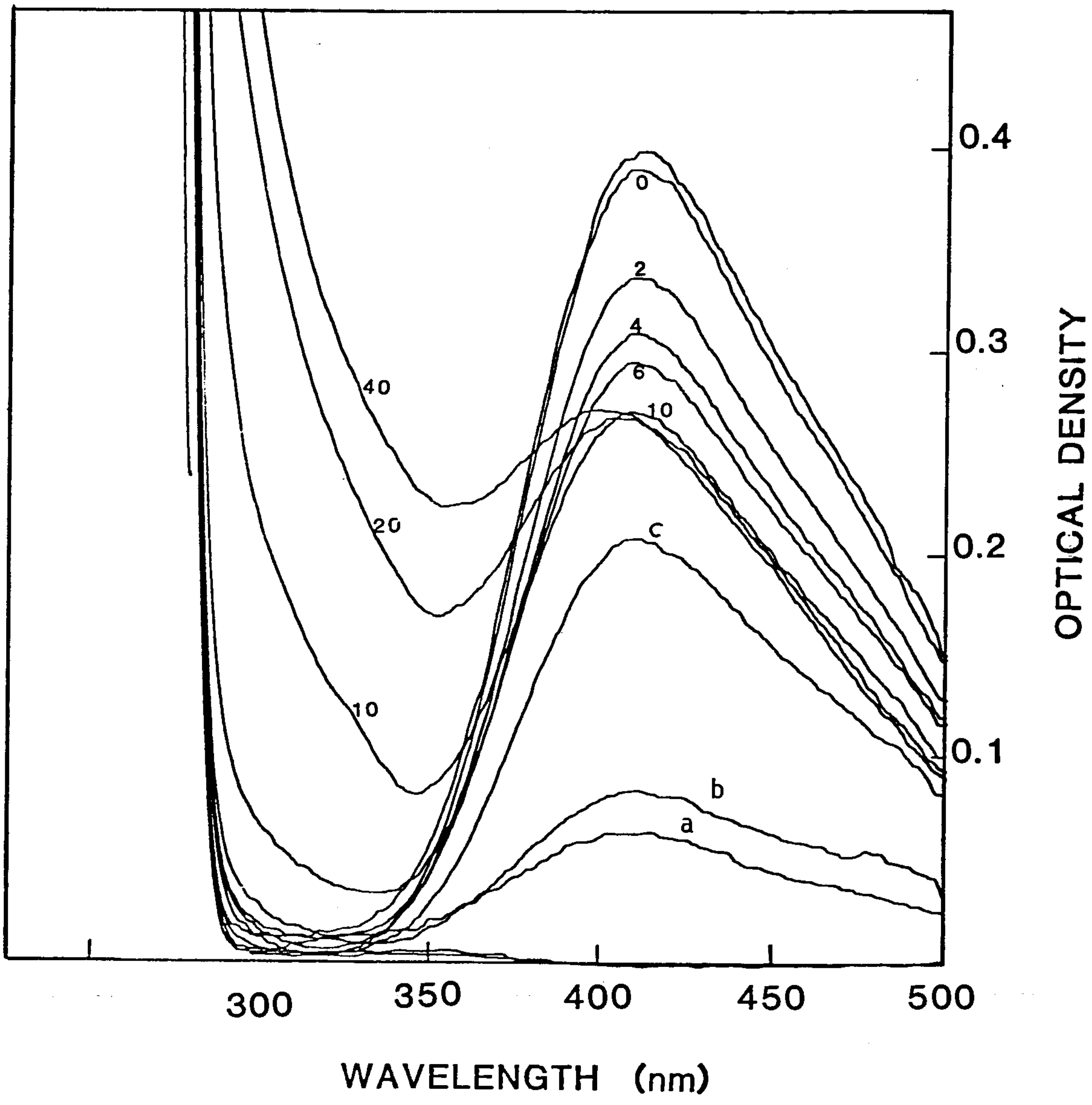

0
2
4
6
10
40
20
10
c
b
a
0.4
0.3
0.2
0.1
OPTICAL DENSITY
300
350
400
450
500
WAVELENGTH (nm)

Figure II-5

of bromine atom in the chain processes. The chain appears to be longer because bromine atom transfers with Br_2 are faster than with N-bromoimide II-31 and in agreement with the fact that the latter is sterically hindered. The quantum yield for the disappearance of II-31 in the presence of Br_2 using a GWV filter is 2.6 for 27% decomposition of II-31 . The quantum yields for the disappearance of bromine, determined by UV spectroscopy in CH_2Cl_2 were low (ca. 0.04).

In view of changing reaction patterns in the photodecomposition of II-31, its product distribution was examined as a function of the duration of irradiation. Two series of experiments were run at different light intensities by adjusting the distance between the lamp and the sample cell. Similar results were obtained, and are given in Table II-10. At low conversion (5-10 minutes irradiation) the C_{2x}-Br/C_1-Br and C_3-Br/C_1-Br ratios were slightly higher and the (C_3-Br)e/amides ratio was lower than those observed after this initial stage. As can be seen from Table II-10 (Series II), the percentage of amides increased gradually between 2 and 15 minutes irradiation and then remained nearly the same. Similarly the percentages of C-Br isomers increased gradually from 2 to 30 minutes irradiation. Throughout the irradiation period, the ratio C_{3x}-Br/C_{3n}-Br was nearly constant at 1.8

± 0.1. Even at low percentage conversions with relatively higher percentage errors, the trend of changing the reaction pattern could be recognized in the early stage. The results imply that attempts to determine kinetic rate constants of this sytem will be futile. However, the good reproducibility of the product ratios permits their use as diagnostic tools for mechanistic evaluation.

In Table II-11 (experiments 1-7), product distributions obtained by photodecomposition of II-31 at 10^{-3} to 10^{-1}M in CH_2Cl_2 through a Pyrex filter are summarized. The reactions were carried out to the complete consumption of II-31. In spite of some scattering, the ratios C_{3x}-Br/C_{3n}-Br and C_3-Br/C_1-Br remained nearly constant. In contrast, the ratio C_{2x}-Br/C_1-Br increased systematically from 2.2, similar to that obtained in the photobromination of imide II-3 (Table II-9), to 2.9 over the twenty-fold change in the concentration of II-31. From the C_3-Br/C_1-Br ratios in Table II-9 and Table II-11, it is clear that more C_3-Br is formed in the photodecomposition of II-31 than in the photobromination of II-3. Assuming that in the former decomposition the bromine atom chain mechanism leads to a C_3-Br/C_1-Br ratio of unity, as shown in Table II-9, the excess C_3-Br listed in Table II-11 can be calculated to be $(C_3\text{-Br})_e = (C_3\text{-Br}) - (C_1\text{-Br})$; it is assumed that $(C_3\text{-Br})_e$ is formed by an intramolecular hydrogen transfer pathway. If one also assumes that C_{2x}-Br is formed by an intermolecular hydrogen transfer process, and that $C_3\text{-Br}/C_{2x}\text{-Br} = 0.48$ (Table II-9), the excess C_3-Br can be calculated, namely $(C_3\text{-Br})_e = (C_3\text{-Br}) - 0.48(C_{2x}\text{-Br})$, and the results are given in Table II-11. The $(C_3\text{-Br})_e$/amides ratios listed in Table II -11 vary slightly, 0.62-0.52, indicating that these two types of compounds are formed by similar mechanisms and presumably originate from radical intermediates that are closely related by a reversible reaction.

The results of the photodecomposition of N-bromide II-31 under other conditions are shown in Table II-11 (experiments 8 to 14). The product distribution and ratio are very similar when using freeze-thaw cycles as the degassing device (expt 8) instead of purified nitrogen gas, and qualitatively indistinguishable when dibromomethane (expt 9) or chloroform (expt 10) are used as the solvent. The most important observation is that in the presence of bromine scavengers, such as neohexene in CH_2Cl_2, or 1,1-dichloroethylene in $CHCl_3$ (degassed by freeze-thaw), the photodecomposition of II-31 produced only imide II-3 and amides II-39 and II-40 but no C-Br compounds (experiments 11 and 12). The presence of the HBr scavenger ethylene oxide (experiment 13) does not affect the $C_2\text{-Br}/C_1\text{-Br}$ ratio but definitely decreases the $C_3\text{-Br}/C_1\text{-Br}$ and $(C_3\text{-Br})_e$/amides ratios. The imidyl radical is obviously not generated efficiently in thermally initiated processes (experiment 14), as shown by the low yields of amides II-39 and II-40.

These results clearly establish that two radical intermediates are involved in the decomposition of N-bromide II-31. One radical is generated by the photoexcitation of II-31 when molecular bromine and bromine atoms are scavenged. As this radical leads to the formation of amides II-39 and II-40, it can be safely assumed to be the imidyl radical. The other radical is generated only in the presence of bromine atoms and/or a small amount of molecular bromine and undergoes intramolecular hydrogen transfer leading to the formation of additional C_3-Br (experiments 2 to 10); it does not lead to amide formation.

Photodecomposition of II-31 in CH_2Cl_2 through a GWV filter (cut-off ≈ 380 nm) was very slow (Table II-12, expt. 1) since it does not absorb appreciably above 360 nm (at 10^{-2}M), and the initiation depends on the presence of a trace amount of bromine in the solution. The product distribution showed a drastic decrease in the amounts of amides II-39 and II-40 and an increase in II-35 to II-38 as compared to experiment 2 in Table II-11, irradiation through a Pyrex filter. Similar photolysis in the presence of added bromine gave results that amplified these observations (Table II-12). As the concentration of added bromine increased, the C_{2x}-Br/C_1-Br ratios remained unchanged, while the C_3-Br/C_1-Br ratio decreased gradually to unity, the ratio obtained in the photobromination of imide <u>II-3</u> by bromine. Three series of similar experiments were carried out and revealed the same trends, (Table II-12). The steady increase in the quantities of C-Br compounds <u>II-35</u> to<u>II-38</u> contrasted to the drastic decrease in the amounts of amides <u>II-39</u> and <u>II-40</u> as the bromine concentration increased, indicating that the bromine atom chain became gradually more important. Yet, the calculated quantity of $(C_3\text{-Br})_e$ also decreased, while the $(C_3\text{-Br})_e$/amides ratio increased rapidly with increasing bromine concentration, indicating that amides <u>II-39</u> and <u>II-40</u> were formed by a different pathway than that responsible for $(C_3\text{-Br})_e$. Therefore, the thermal interaction of bromine with N-bromide <u>II-31</u> generates both the imidyl radical and a second radical intermediate, and the rates of the two radicals are unequal and depend on the concentrations of molecular bromine and/or bromine atoms.

Table II-6. ^1H NMR Parameters of Compounds Obtained by Photodecomposition of N-Bromoimides II-31 and II-41[a]

Compound	Chemical Shifts (ppm)	Coupling Constants (Hz)
C_{2x}-Br (II-36)	1.45(m, 3H), 1.77(dddd, J=4.7, 7.2, 9, 14.4; H_{3x}), 1.88(m;1H), 1.98(tdd, J=5, 7, 14; H_{3n}), 3.30 (td; 8.2, 11.8; H_6), 3.53 (dd, 8.0, 12; H_1), 4.22 (ddd, 4.5, 7.8, 9.0; H_2)	$J_{1,2}$(8.0); $J_{1,6}$(12) $J_{2,3n}$(4.5); $J_{2,3x}$(9); $J_{6,5}$(8.2); $J_{6,5'}$(8.2)
C_1-Br[b] (II-35)	2.33(td, 3.6, 15.1; H_2), 3.44(t, 8.0; H_6)	$J_{6,5}$(8.0); $J_{6,5'}$(8.0); $J_{2,3}$(3.6); $J_{2,3'}$(3.6)
C_{3x}-Br (II-37)	1.67-1.93(m, 3H), 2.05(ddd, 3.6, 8.0, 15, H_2), 2.13(m, 1H), 2.37(ddd, 5.4, 9.0, 15.2; $H_{2'}$), 3.27(ddd, 6.2, 8.6, 11.7; H_6), 3.38(td, 8.4, 12; H_1), 4.32(tt, 3.8, 6.0; H_3), 8.12(NH)	$J_{1,2'}$(9.)); $J_{1,2}$(8.0); $J_{1,6}$(12); $J_{2',3}$(5.4); $J_{2,3}$(3.6); $J_{3,4}$(3.8); $J_{3,4'}$(6.0); $J_{5,6}$(8.6); $J_{5',6}$(6.2)

Table II-6. (Cont'd.)

Compound	Chemical Shifts (ppm)	Coupling Constants
C_{3n}-Br (II-38)	1.78(m; 3H), 2.13(m; 2H), 2.64 (ddd, 4.5, 7.8, 13.6; H_2), 3.16(m; H_1 and H_6), 3.78(tdd, 4.3, 9.0, 11; H_3), 8.23 (NH)	$J_{3,2}(4.5)$; $J_{3,\hat{2}}(11)$; $J_{3,4}(4.3)$; $J_{3,\hat{4}}(9.0)$; $J_{1,2}(7.8)$
Amide (II-39)	0.97(1H), 1.66(4H), 1.88(1H), 2.10(1H), 2.32(1H), 3.01(1H), 3.54(1H), 5.63(NH_2)	
C_{2x}-Br (II-42)	2.03(m; 1H), 2.23(m; 3H), 3.62(dt, 2, 8.5; H_5), 3.83(d, 9; H_1), 4.63(d, 5; H_2), 8.4 (NH)	$J_{1,2}(0)$; $J_{1,5}(8.5)$; $J_{2,3n}(5)$; $J_{2,3x}(0)$; $J_{5,4n}(2)$; $J_{5,4x}(8.5)$
C_{3x}-Br (II-43)	2,28(mddd, 7, 8.5, 15; H_{2x} and H_{4x}), 2.42(mddd, 3, 6.5, 15; H_{2n} and H_{4n}), 3.60(m; H_1 and H_5), 4.35 (tt, 6,7; H_3), 8.5 (NH)	$J_{1,2x}(8.5)$; $J_{1,2n}(3)$; $J_{2x,2n}(15)$; $J_{3,2x}(7)$; $J_{3,2n}(6.5)$

Table II-6. (Cont'd.)

Compound	Chemical Shifts (ppm)	Coupling Constants
C_{3n}-Br (<u>II-44</u>)	1.90(m; 2H), 2.75(m; 2H), 3.35 (m; H_1 and H_5), 3.85(tt, 7, 11.5; H_3), 8.5 (N<u>H</u>)	$J_{3,2x}(7)$; $J_{3,2n}(11.5)$; $J_{2x,2n}(11)$
Amide (<u>II-45</u>)	1.75(m; 3H), 1.97(m;2H), 2.22(m; 1H), 3.50(dt, 2.9, 8.6; H_5), 3.92 (dt, 1.41, 8.6; H_1), 6.01(N<u>H</u>), 6.12 (N<u>H</u>)	$J_{1,5}=J_{1,2x}=J_{5,4x}=8.6$, $J_{1,2n}(1.4)$; $J_{5,4n}(2.9)$

[a] In $CDCl_3$ at 400 MHz.

[b] C_1-Br was obtained as 2:1 mixture with C_{2x}-Br, the higher field signals are overlapped with those of C_{2x}-Br isomer and could not be resolved.

Table II-7. ^{13}C NMR Parameters of Compounds Obtained by Photodecomposition of II-31 and II-41.

Compounds	Chemical Shifts in ppm
C_1-Br + C_{2x}-Br^a (II-35 & II-36)	18.13(?)^c, 18.92(t), 20.04(t), 20.64(?)^c, 29.57(t), 32.00(t), 34.07(t), 43.36(d), 43.79(d), 51.22(d), 56.26(d), 62.95(s), 65.96(s), 67.58(s), 67.75(s), 74.86(s), 169.55 (C=0), 170.05 (C=0), 170.57 (C=0, two overlapped signals).
C_{2x}-Br (II-36)	20.05(t, C_4), 20.88(t, C_5), 32.1(t, C_3), 43.41(d, C_2), 43.76(d, C_6), 51.29(d, C_1), 63, 67.5, 170, 170.5.
C_{3x}-Br (II-37)	19.64(t),30.55(t),31.90(t),39.86(d), 40.77(d), 46.35(d), 67.34(s), 68.05(s), 170.35 (C=0), 170.45 (C=0).
C_{3n}-Br (II-38)	21.64(t), 33.24(t), 35.15(t), 39.74(d), 43.5(d), 46.30(d), 67.19(s), 69.87(s), 171.4 (C=0), 171.3 (C=0).
Imide (II-3)	20.8(t), 21.45(t), 41.69(d), 68.04(s), 171.46 (C=0).
C_{2x}-Br (II-42)	25.37(t, C_4), 38.15 (t, C_3), 48.10(d,C_2), 49.40(d, C_5), 59.23(d, C_1), 65.84(s), 66.88(s), 169.85, 170.15

Table II-7 (Cont'd.)

Compounds	Chemical Shifts in ppm
C_{3n}-Br (<u>II-44</u>)	39.03(t, C_2 and C_4), 43.76(d, C_3), 47.44(d, C_1 and C_5), 66.86 (s, C_6 and C_7), 170.16
C_{3x}-Br (<u>II-43</u>)	39.13 (C_2 and C_4), 47.66 (C_3), 48.94(C_1 and C_5), 66.42 (C_6 and C_9), 169.86
Amide[d] (<u>II-45</u>)	26.84(t), 30.62(t), 31.73(t), 42.86(d), 59.06(d), 169.11
Imide <u>II-15</u>	26.73(C_3), 27.52(C_2.C_4), 50.24 (C_1,C_5), 66.78(C_6,C_7), 171.36(C_8,C_9)

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[a] The underlined figures are due to the signals of the C_{2x}-Br. derivative.

[b] ppm downfield from TMS, in $CDCl_3$.

[c] Multiplicity could not be determined.

Table II-8.

Quantum Yields of Photodecomposition of N-bromide II-31 through Pyrex Filter and GWV filters

Time (min.)	% Decomposition	Φ
Irradiation through Pyrex[a]		
1. N-Bromide II-31 ($\approx 6.3\times10^{3}$ M)		
1	6.0	1.95
3	16.8	1.83
5	18.5	1.21
10	31.1	1.01
20	56.7	0.92
2. In the presence of neohexene (0.013 M)		
2	8.2	1.33
4	14.2	1.16
6	23.9	1.30
3. In the presence of bromine (0.66×10^{-3} M)		
1	23.4	7.64
3	60.5	6.57
5	81.7	5.33
Irradiation through GWV[b]		
4. II-31 (7×10^{-3}M), bromine (1.3×10^{-3})		
10	27	2.6
30	65	1.9

a–The light intensity was measured by benzophenone actinometry[104].

b–The light intensity was measured using potassium ferrioxalate actinometry[105].

Table II-9. Photobromination of Imide II-3 with Bromine[a] in CH_2Cl_2 at 0°C.

	% Yields				$\frac{C_3\text{-Br}}{C_2\text{-Br}}$[e]	$\frac{C_{2x}\text{-Br}}{C_1\text{-Br}}$	$\frac{C_3\text{-Br}}{C_1\text{-Br}}$	$\frac{C_{3x}\text{-Br}}{C_{3n}\text{-Br}}$
$10^3[Br_2]$M	C_1-Br	C_{2x}-Br	C_{3x}-Br	C_{3n}-Br				
2.9[b]	1.53	2.75	0.82	0.51	0.48	1.80	0.92	1.39
5.9[b]	2.38	4.55	1.20	0.91	0.46	1.91	0.89	1.32
12[b]	4.36	8.60	2.30	1.70	0.47	1.97	0.92	1.36
6.7[c]	1.97	4.40	1.36	0.83	0.50	2.23	1.12	1.64
13[c]	3.96	8.02	2.30	1.46	0.47	2.03	0.95	1.58
26[c]	5.27	11.68	3.44	2.18	0.48	2.22	1.07	1.58
8.0[d]	1.33	2.53	1.05	0.71	0.70	1.90	1.32	1.48

[a] The percentages of unreacted II-3 are not given. Each photolysate has been analysed by several GC injections and the average values are given; the calculated percentage of errors of means are mostly <±5% except in a few cases.

[b] [II-3] = 10^{-2}M, Pyrex filter; a minor peak (<0.5%) was observed.
Benzophenone was employed as a standard, absolute yields of imide II-3 were determined and yields of C-Br isomers were relative to II-3.

[c] [II-3] = 2.7×10^{-2}M, GWV filter. Relative yields of C-Br isomers were based on total GC peak areas including imide II-3.

[d] Benzoyl peroxide (1.2×10^{-3}M) initiated thermal bromination at [II-3] = 4.2×10^{-2}M at 40°C. Diels-Alder adduct II-21 was used as a standard.

[e] $(\%C_3\text{-Br}) = (\%C_{3x}\text{-Br}) + (\%C_{3n}\text{-Br})$

Table II-10. Photodecomposition of N-Bromoimide II-31 Monitored at Various Intervals[a].

				Product Distribution (%)								
Time (Minutes)	Imide (II-3)	Amides	C_1-Br	C_{2x}-Br	C_{3x}-Br	C_{3n}-Br	$(C_3\text{-Br})_e$	$\frac{C_{2x}\text{-Br}}{C_1\text{-Br}}$	$\frac{C_3\text{-Br}}{C_1\text{-Br}}$	$\frac{C_{3x}\text{-Br}}{C_{3n}\text{-Br}}$	$\frac{(C_3\text{-Br})_e}{\text{Amides}}$	$\frac{(C\text{-Br})}{\text{Amides}}$
Series I[b]												
0	98	--	--	--	--	--						
10[d]	71	11.3	1.56	5.38	5.38	2.77	6.59	3.45	5.22	1.94	0.58	1.38
20[d]	54	12.8	3.12	9.6	8.77	4.57	10.22	3.08	4.28	1.92	0.80	2.04
60[d]	52	12.7	3.06	9.36	8.03	4.51	9.48	3.06	4.10	1.78	0.75	1.97
120[d]	55	13.5	3.41	10.06	8.67	4.8	10.06	2.95	3.95	1.80	0.75	2.00
Series II[c]												
2	97	--	--	--	--	--						
6	89	4.61	--	--	--	--						
10	91	6.76	(0.48)	(1.82)	(1.30)	(0.63)	1.45	3.79	4.02	2.06	0.21	0.63
15	76	14.38	1.49	4.98	4.35	2.41	5.27	3.34	4.54	1.80	0.37	0.92
30[d]	60	13.81	2.86	8.67	7.62	3.68	8.44	3.03	3.95	2.07	0.61	1.65
60[d]	63	13.81	3.00	9.62	8.29	4.15	9.44	3.21	4.15	2.00	0.68	1.81

[a] Reactions were run in CH_2Cl_2, and irradiated through a Pyrex filter at 0°C. The samples withdrawn at the indicated intervals were quenched with 5% aqueous sodium bisulfite. The percentage errors of average values were calculated from two or more GC injections and were in the range of ± 5%. The numbers in parentheses are too small to be accurate. Product yields were determined by GC employing an inernal standard and were based on N-bromoimide. Absolute yields of imide <u>II-3</u> were determined, and yields of amides and C-brominated isomers were related to <u>II-3</u>.

$(C_3\text{-Br})_e = (C_3\text{-Br}) - (C_1\text{-Br})$; $(C_3\text{-Br}) = (C_{3x}\text{-Br}) + (C_{3n}\text{-Br})$;

$C\text{-Br} = C_1\text{-Br} + C_2\text{-Br} + C_3\text{-Br}$.

[b] N-Bromoimide <u>II-31</u>, 8.8×10^{-2}M.

[c] N-Bromoimide <u>II-31</u>, 5.2×10^{-2}M.

[d] An unidentified minor peak (≈ 0.6%) was detected.

Table II-11. Photodecomposition of N-bromide II-31 Under Various Conditions[a]

			Product Distribution (%)						$\frac{C_{2x}\text{-Br}}{C_1\text{-Br}}$	$\frac{C_3\text{-Br}}{C_1\text{-Br}}$	$\frac{C_{3x}\text{-Br}}{C_{3n}\text{-Br}}$	$\frac{(C_3\text{-Br})_e}{\text{Amides}}$	Remarks
Exp't	10^2[II-31]M	II-3	Amides	C_1-Br	C_{2x}-Br	C_{3x}-Br	C_{3n}-Br	$(C_3\text{-Br})_e$	$(C_3\text{-Br})_{\acute{e}}$					
1	0.47	89	5.15	1.08	2.37	2.71	1.54	3.17	3.11	2.19	3.94	1.76	0.62	b
2	0.95	80	8.25	1.38	3.02	2.99	1.73	3.34	3.27	2.19	3.42	1.73	0.40	b
3	0.95	81	7.29	1.38	3.09	3.12	1.72	3.46	3.36	2.24	3.51	1.81	0.48	b
4	1.0	82	8.63	1.51	3.99	3.69	2.48	4.66	4.25	2.64	4.09	1.49	0.54	b
5	2.4	76	12.13	2.16	5.90	5.42	3.07	6.33	5.66	2.73	3.93	1.77	0.52	b
6	2.4	71	11.16	2.39	6.32	6.00	3.30	6.91	6.27	2.64	3.89	1.82	0.62	b
7	9.6	57	13.70	3.34	9.59	7.13	4.07	7.86	6.6	2.87	3.35	1.75	0.57	b
8	2.5	76	9.39	2.05	5.61	5.07	2.24	5.26		2.74	3.57	2.26	0.56	c
9	1.9	63	7.75	2.20	5.71	5.88	2.88	6.56		2.60	3.98	2.04	0.84	d
10	1.8	81	6.64	1.21	2.25	2.45	1.25	2.49		1.86	3.06	1.96	0.38	e
11	0.95	70	27.0	0	0	0	0	0		-	-	-	-	f
12	1.9	64	27.0	0	0	0	0	0		-	-	-	-	c,e,g
13	2.0	85	11.15	1.81	3.79	1.46	0.98	0.63		2.09	1.35	1.49	0.057	h
14	2.9	94	1.0	1.14	4.20	1.44	0.95	1.25		3.68	2.10	1.52	1.25	c,i

Table II-11 continued

a All solutions were purged with nitrogen and irradiated through a Pyrex filter at 0°C to the complete disappearance of N-bromide II-31, except expt. 14; and were run in CH_2Cl_2 except expts 9, 10 and 12. The percentage errors of average values were calculated from two or more GC injections and were in the range of ±5% except in a few cases.

Absolute yields of imide II-3 were determined employing either benzophenone or Diels-Alder adduct II-21 as a standard and were based on II-31, yields of amides and C-Br isomers were determined relative to imide II-3.

$(C_3\text{-Br})_e = (C_3\text{-Br}) - (C_1\text{-Br})$;

$(C_3\text{-Br}) = (C_{3x}\text{-Br}) + (C_{3n}\text{-Br})$; $(C_3\text{-Br})_{e'} = (C_3\text{-Br}) - 0.48\,(C_{2x}\text{-Br})$.

b A minor peak (≈0.5%) was detected. Three series of experiments were run under identical conditions, namely, series I (expts 1,2), series II (expts 3,6), series III (expts 4, 5,7).

c Degassed by freeze-thaw technique.

d CH_2Br_2 as solvent.

e $CHCl_3$ as solvent; minor peaks (≈0.5%) at 5.49 and 10.21 minutes were detected.

f Neohexene added, 5×10^{-3}M; the GC showed minor peaks (<3%) at 4.3, 6.3, 7.5 and 9.42 minutes, none of which were found to correspond to those of II-34 to II-39; the peak for 1,2-dibromo-3-methylbutane appeared at a retention time of 1.8 minutes.

g $CH_2{=}CCl_2$ added, 6.6×10^{-2}M; GC showed minor peaks (<3%) at 2.3, 2.8, 4.6 and 11.18 minutes, none of which were found to correspond to those of II-34 - II-39.

h Ethylene oxide added, 0.67M.

i Thermally initiated with benzoyl peroxide, 2×10^{-3}M, at 40 ± 2°C; additional GC peaks were observed near the solvent peak.

Table II-12. Photodecomposition of N-Bromoimide II-31 in the Presence of Added Bromine Using a GWV Filter[a].

			Product Distribution (%)						$\frac{C_{2x}\text{-Br}}{C_1\text{-Br}}$	$\frac{C_3\text{-Br}}{C_1\text{-Br}}$	$\frac{C_{3x}\text{-Br}}{C_{3n}\text{-Br}}$	$\frac{(C_3\text{-Br})_e}{\text{Amides}}$
10^3[II-31]M	$10^3[Br_2]$M	II-3	Amides	C_1-Br	C_{2x}-Br	C_{3x}-Br	C_{3n}-Br	$(C_3\text{-Br})_e$				
Series I[b]												
9.2	--	88	4.41	2.27	4.90	2.90	2.21	2.84	2.16	2.25	1.31	0.64
9.7	0.77	81	3.51	2.90	7.00	3.25	2.25	2.6	2.41	1.90	1.44	0.74
9.5	2.3	75	1.40	3.73	8.97	3.35	2.12	1.74	2.40	1.47	1.58	1.24
10	4.6	71	0.80	4.44	10.80	3.99	2.36	1.91	2.43	1.43	1.69	2.39
Series II												
11	3.1	79	1.40	4.54	10.92	4.68	2.76	2.9	2.41	1.64	1.70	2.07
10	6.2	77	0.79	5.45	12.84	5.27	2.99	2.81	2.36	1.52	1.76	3.56
9.4	12	65	0.30	6.77	15.70	4.77	2.80	0.80	2.32	1.12	1.70	2.67
9.5	92	55	0.0	10.30	22.75	7.25	4.07	1.02	2.21	1.10	1.78	--
Series III												
9.5	--	85	5.28	2.31	5.00	3.25	2.13	3.07	2.16	2.33	1.53	0.58
9.7	3.1	75	1.15	4.07	9.31	3.68	2.07	1.68	2.29	1.41	1.78	1.46
9.4	6.2	72	0.61	4.97	11.43	4.29	2.32	1.64	2.30	1.33	1.85	2.69
9.5	12	65	0.27	6.80	15.92	5.73	3.22	2.15	2.34	1.32	1.78	7.96

Table II-12 (Continued)

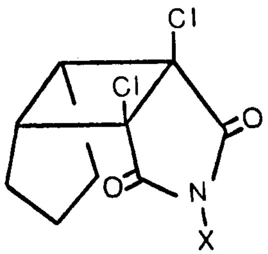
[a] All reactions were carried out in CH_2Cl_2 at 0°C and photoinitiated through a GWV filter. The experiments were run until N-bromoimide had been consumed. The excess bromine was destroyed with 5% aqueous $NaHSO_3$. Benzophenone or Diels-Alder adduct II-21 was used as a standard to determine the percentage yield of imide II-3 (based on N-bromoimide II-31). Yields of amides and C-Br isomers are relative to II-3. The % errors of the mean values of more than two injections were shown to be $\pm$ 5% except in a few cases.

$(C_3\text{-Br}) = (C_{3x}\text{-Br}) + (C_{3n}\text{-Br})$; $(C_3\text{-Br})_e = (C_3\text{-Br}) - (C_1\text{-Br})$

II-4 Photodecomposition of N-Bromo-6,7-Dichloro-cis-Bicyclo [3.2.0]Heptane-endo,cis-6,7-Dicarboximide (II-41)

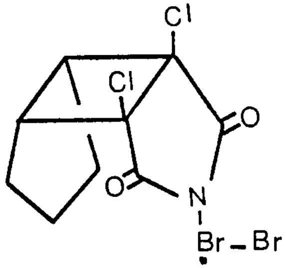
Photolysis of II-41 in CH_2Cl_2 through Pyrex gave imide II-15, the cyclopentyl ring brominated imides II-42 (C_{2x}-Br), II-43 (C_{3x}-Br), II-44 (C_{3n}-Br), and two isomeric amides II-45 and II-46 arising from ring opening of the imidyl radical followed by facile solvolysis and decarboxylation. The bromides II-42 to II-44 were also formed by photobromination of imide II-15 in which no amides II-45 and II-46 were detected by GC analysis. Surprisingly, no C_1-Br isomer was detected in these reactions, presumably owing to steric factors which hinder the attack of bromine atom at the C_1 position. Photolysis of N-bromoimide II-41 in chloroform in the presence of 1,1-dichloroethylene resulted in the formation of imide II-15 and amides II-45 and II-46, but none of the C-Br isomers II-42 to II-44 were detected by GC. The C-Br isomers and one isomer of the two amides were separated by column and thin layer chromatography (ca. 90% pure). The amides displayed two closely spaced GC peaks, and GC-MS showed them to be configurational isomers with the typical peak pattern of two chlorine and one bromine for the molecular ions.

The structure and stereochemistry of the brominated imides

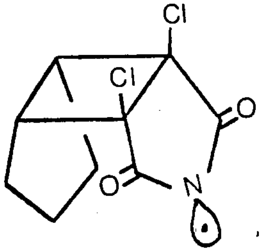


X = H II-15

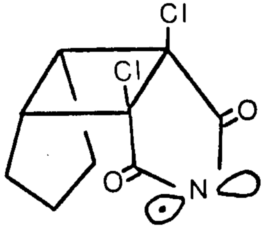
X = Br II-41



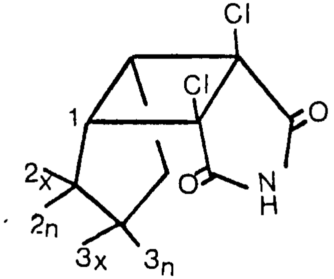
II-47



II-48



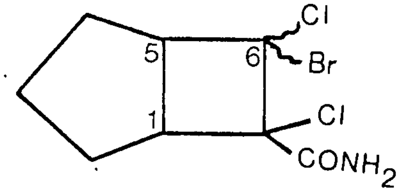
II-49



II-42 C_{2x}–Br

II-43 C_{3x}–Br

II-44 C_{3n}–Br

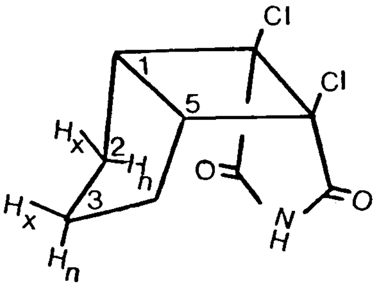


II-45 , II-46

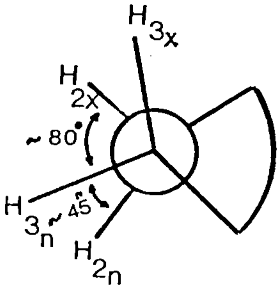
II-42 to II-44 were determined by ^1H and ^{13}C NMR spectral analyses (Tables II- 6 and II-7), IR (Table IV-4), and mass spectra (Table IV-5). The position and configuration of the bromine substituent were deduced from complete analysis of the respective ^1H and ^{13}C NMR spectra, and the pertinent arguments are summarized below.

The ^{13}C NMR spectra of II-43 (C_{3x}-Br) and II-44 (C_{3n}-Br) displayed five signals indicative of a plane of symmetry, while the spectrum of II-42 (C_{2x}-Br) showed nine lines. As can be seen from Table II-7 (p.73), the bromine substitution shifted the β-carbon signals downfield by *ca.* 10 ppm as compared to the corresponding carbons in the parent imide II-15. In II-42 (C_{2x}-Br) the methine and methylene carbon signals are shifted downfield by *ca.* 11 ppm, and in both II-43 (C_{3x}-Br)and II-44 (C_{3n}-Br) the two methylene carbons are deshielded by *ca.* 12 ppm.

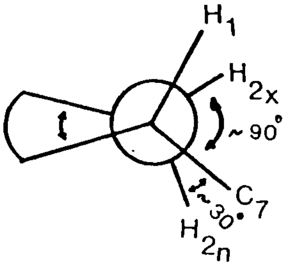
^1H NMR spectra and decoupling experiments also demonstrated the presence of bromine at C-3 in the II-43 (Table II-6, p.70) (C_{3x}-Br) and II-44 (C_{3n}-Br) isomers. There are two configurations (*exo*-



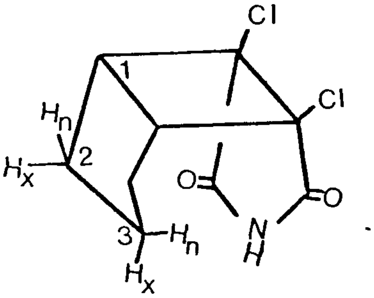
Exo-envelope



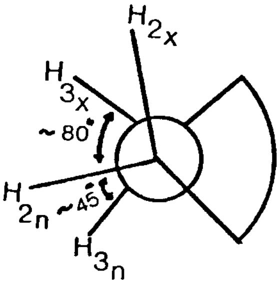
Bond C_3-C_2

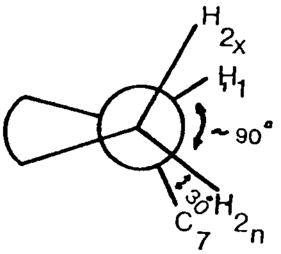


Bond C_1-C_2



Endo-envelope





and endo-) for bromine at C-3; each can adopt either the endo-envelope conformation or the exo-envelope conformation* (Scheme II-7). For steric reasons, II-44 (C_{3n}-Br) can only adopt exo-conformation in which the dihedral angles $\phi_{3x,2x} \approx \phi_{3x,4x} \approx 45°$, and $\phi_{3x,2n} \approx \phi_{3x,4n} \approx 170$ in accordance with the observed couplings (triplet of triplet, J = 7, 11.5 Hz). The ^{1}H NMR spectrum of II-43 (C_{3x}-Br) exhibited a triplet of triplets (J=6 and 7 Hz) for the CHBr proton indicative of the exo-envelope conformation in which the dihedral angles† $\phi_{3n,2n} \simeq 50°$ and $\phi_{3n,2x} \simeq 70°$.

Product Distribution Studies

Photobromination of imide II-15 with bromine in CH_2Cl_2 was carried out with various ratios of bromine to imide II-15 and the results are given in Table II-13 (p.91). The C_3-Br/C_{2x}-Br and C_{3x}-Br/C_{3n}-Br ratios are nearly constant,0.18 ± 0.01 and 2.7 ± 0.22, respectively, regardless of the extent of bromination.

Table II-14 (p.92) shows the effect of varying N-bromoimide II-41 concentrations on product distributions. Solutions of II-41 in CH_2Cl_2 at various concentrations were irradiated through a

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* For a similar proposal of endo- and exo-envelope conformation in bicyclo[3.2.0]heptane systems see reference 106. The estimated dihedral angles were adopted from reference 107.

† The effect of a bromine substituent on the dihedral angles and proton-proton coupling constants was not considered. For the later, see reference 115.

Pyrex filter to the complete consumption of II-41. As can be seen, the C_3-Br/C_{2x}-Br and C_{3x}-Br/C_{3n}-Br ratios remained constant. The former (ca. 0.5) is higher than that obtained from photobromination of imide II-15 with bromine (0.18) indicating that excess C_3-Br might have been formed by an intramolecular hydrogen abstraction pathway. On the assumption that C_{2x}-Br is formed primarily by intermolecular process,the excess C_3-Br formed in the photodecomposition of II-41 can be calculated: $(C_3\text{-Br})_e = (C_3\text{-Br}) - 0.18(C_2\text{-Br})$, (Table II-14). As the concentration of II-41 increases (from 0.01 to 0.74M), both the amides and $(C_3\text{-Br})_e$ increase within experimental error, but the $(C_3\text{-Br})_e$/amides ratio increases from 0.2 at 1.2×10^{-2}M to 0.5 at 4.5×10^{-2}M and then remains constant. Therefore, at concentrations of II-41 higher than 0.045M the proportion of amides and $(C_3\text{-Br})_e$ is nearly the same.

Photodecomposition of II-41 in CH_2Cl_2 using a GWV filter (Table II-15, p.93) yielded smaller amounts of amides (II-45 and II-46) and $(C_3\text{-Br})_e$ and a larger $(C_3\text{-Br})_e$/amides ratio (expt 2) than those obtained by using a Pyrex filter (expt 1). Similar trends were observed in the presence of added bromine and irradiation through a GWV filter (expts 8 and 9). On the other hand, decomposition of II-41 in the presence of added bromine through Pyrex did not give reproducible results presumably due to irradiation of both N-bromoimide II-41 and bromine which obscures bromine atom initiated processes.

It should be mentioned that, at ≈ 10^{-2}M, decomposition of II-41 resulted in a smaller amount of $(C_3\text{-Br})_e$ (0.63 constituting 17% of total C-Br isomers; Table II-14, expt 1, p.92) than that obtained by decomposition of II-31 (4.66 constituting 40% of total C-Br isomers; Table II-11, expt 4, p.80). These results suggest that the inefficient intramolecular pathway in II-41 is due to its rigid structure.

Photodecomposition of II-41 in chloroform in the presence of 1,1-dichloroethylene resulted in the formation of imide II-15 and amides II-45 and II-45, but no C-Br compounds (Table II-14, expt 7, p.92).

Table II-13

Photobromination of Imide II-15 with Bromine[a] in CH_2Cl_2 at 0°C

		% Yields[b]			
$10^2[Br_2]M$	C_{2x}-Br	C_{3x}-Br	C_{3n}-Br	$\frac{C_3\text{-Br}}{C_{2x}\text{-Br}}$	$\frac{C_{3x}\text{-Br}}{C_{3n}\text{-Br}}$
1.8	2.29	0.29	0.10	0.170	2.9
3.7	4.26	0.56	0.20	0.178	2.8
7.6	11.1	1.58	0.67	0.203	2.4

[a] [II-15] = 1.7 × 10^{-2}M, Pyrex filter. The percentage yields of recovered II-15 are not included. Each experiment was analysed by 2 to 3 GC injections and the average values are given; the calculated percentage deviations from the mean were mostly ± 10% except in a few cases.

[b] Absolute yields of imide II-15 were first determined employing exo,cis-imide II-7 as internal standard, and yields of C-Br isomers are relative to II-15.

Table II-14. Effect of Varying Concentration of N-Bromoimide II-41 on Product Distribution[a]

			Product Distribution (%)							
Expt.	10^2[II-41]M	II-15	Amides	C_{2x}-Br	C_{3x}-Br	C_{3n}-Br	$(C_3\text{-Br})_e$	$\frac{C_3\text{-Br}}{C_{2x}\text{-Br}}$	$\frac{C_{3x}\text{-Br}}{C_{3n}\text{-Br}}$	$\frac{(C_3\text{-Br})_e}{\text{Amides}}$
1	1.24	87	3.58	2.63	0.73	0.37	0.63	0.42	1.97	0.18
2	2.9	82	6.04	5.18	1.94	0.91	1.92	0.55	2.13	0.32
3	3	83	5.59	6.05	2.25	0.96	2.12	0.53	2.34	0.38
4	4.5	75	5.50	8.56	3.00	1.32	2.78	0.50	2.27	0.51
5	15	68	7.67	12.42	3.90	1.88	3.54	0.46	2.07	0.46
6	74	51	10.81	20.95	5.67	2.97	4.87	0.41	1.91	0.45
7[b]	8.4	68	23	0	0	0	—	—	—	—

[a] All reactions were run in CH_2Cl_2 at 0°C through a Pyrex filter, and carried out to the complete disappearance of N-bromoimide II-41. Absolute yields of imide II-15 were determined employing exo,cis-imide II-7 as a standard. Yields of amides and C-Br isomers were determined relative to imide II-15. The % errors of the mean values of more than two injections were shown to be ± 10% except in a few cases. $(C_3\text{-Br}) = (C_{3x}\text{-Br}) + (C_{3n}\text{-Br})$; $(C_3\text{-Br})_e = (C_3\text{-Br}) - 0.18(C_{2x}\text{-Br})$

[b] $Cl_2C{=}CH_2$ added

Table II-15. Effect of Added Bromine on Photodecomposition of N-Bromoimide II-41[a]

				Product Distribution (%)							
Expt.	10^2[II-41]M	$10^3[Br_2]$M	II-15	Amides	C_{2x}-Br	C_{3x}-Br	C_{3n}-Br	$(C_3\text{-Br})_e$	$\frac{C_3\text{-Br}}{C_{2x}\text{-Br}}$	$\frac{C_{3x}\text{-Br}}{C_{3n}\text{-Br}}$	$\frac{(C_3\text{-Br})_e}{\text{Amides}}$
1	1.6	--	88	3.72	2.62	0.77	0.50	0.8	0.48	1.54	0.21
2	1.6	--	94	2.04	1.68	0.62	0.39	0.71	0.60	1.59	0.35
3	1.6	2.5	95	0.61	2.32	0.70	0.24	0.52	0.41	2.92	0.86
4	1.7	5	92	0.41	4.52	1.20	0.36	0.75	0.35	3.33	1.82
5	1.8	10	94	0.32	3.14	0.70	0.23	0.36	0.30	3.04	1.14
6	1.6	20	95	0.24	3.48	0.56	0.23	0.16	0.23	2.43	0.68
7	2.2	--	85	5.59	5.54	2.18	0.77	1.95	0.53	2.83	0.35
8	2.5	4	84	2.93	7.79	2.46	0.67	1.73	0.40	3.67	0.59
9	2.4	8	83	1.91	8.88	2.33	0.64	1.37	0.33	3.64	0.72

Table II-15 (Continued)

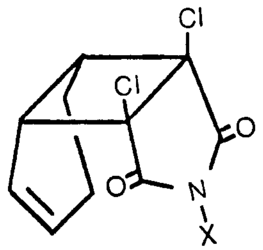
[a] All reactions were carried out to the complete consumption of II-41 in CH_2Cl_2 and irradiated at 0°C through a Pyrex filter, except expts 2, 8, and 9 for which a GWV filter was used. Yields of products listed in expts 1-6 are relative and based on total GC peak areas. In expts 7 to 9, absolute yields of imide II-15 were determined using exo,cis-imide II-7 as a standard and were based on N-bromoimide II-41, yields of other products were relative to that of II-15.

$(C_3\text{-}Br) = (C_{3x}\text{-}Br) + (C_{3n}\text{-}Br)$, $(C_3\text{-}Br)_e = (C_3\text{-}Br) - 0.18\,(C_{2x}\text{-}Br)$.

II-5 Photodecomposition of N-Bromo-7,8-Dichloro-cis-Bicyclo [4.2.0]Oct-2-ene-endo,cis-7,8-Dicarboximide (II-50)

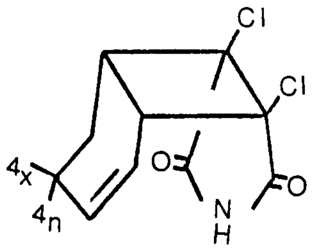
The photolysis of N-bromoimide II-50 (0.06 mmol) in CH_2Cl_2 (5 ml) was run at 0°C through Pyrex, and its progress was followed by the KI-starch test. GC-MS of the photolysate showed the presence of imide II-6, allylic bromide II-51, and a peak tentatively identified as diene II-54. The ^1H NMR spectrum of the crude product showed the major component to be allylic bromide II-51; some weak signals could be due to isomeric allylic bromides (Scheme II-8); none of these signals corresponded to the dibromide II-55. The weak signals in the olefinic region of the ^1H NMR spectrum showed diene II-54 to be a minor compound which is nevertheless formed in substantial amounts probably by the dehydrobromination of allylic bromide II-51 during GC-MS of the crude product. The IR spectrum showed no isocyanate absorption. A sample of II-50 in CH_2Cl_2 kept in the dark showed no decomposition (by IR).

In an attempt to separate the components giving rise to weak signals at δ 1.68, 1.93, 2.77, 3.5, 3.9, 4.63, 5.1, 5.9, 6.1 and 6.3 ppm in the ^1H NMR spectrum of the crude product, N-bromoimide II-50 (0.29 g) in CH_2Cl_2 was photolysed to completion. Flash chromatography of the crude product with monitoring by HPLC gave a fraction containing all minor peaks



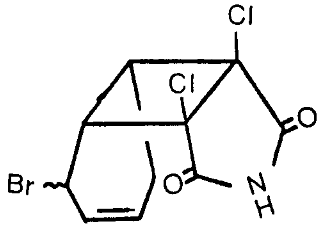
<u>II-6</u> X = H

<u>II-50</u> X = Br

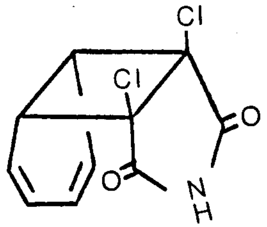


<u>II-51</u> 4x = Br, 4n = H

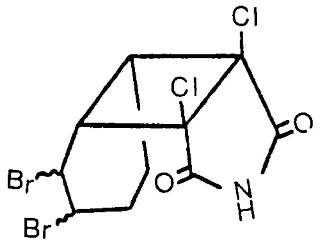
<u>II-52</u> 4x = H, 4n = Br



<u>II-53</u>

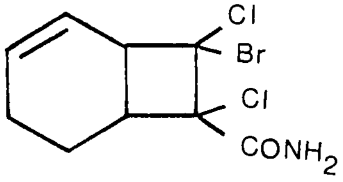


<u>II-54</u>



<u>II-55</u>

(one isomer is formed)



<u>II-56</u>

which showed a complex ^{1}H NMR spectrum indicative of decomposition on the column. The second fraction gave the allylic bromide II-51 (0.14g, solid) which was recrystallized and characterized by IR, ^{1}H NMR, and MS spectra (Experimental Section).

Photobromination of imide II-6 and bromine in CH_2Cl_2 was carried out at 0°C through a GWV filter until the bromine color had disappeared. The solvent was removed and a white solid was obtained whose ^{1}H NMR spectrum (at 400 MHz) displayed signals of II-51 and (II-6).

A solution of imide II-6 and bromine in CH_2Cl_2 was kept at 0°C in the dark for 1/2 hour. The solvent was removed and an oil was obtained. The ^{1}H NMR spectrum (at 100 MHz, $CDCl_3$) showed the presence of imide II-6 and dibromide II-55 (δ4.1) (6:1 ratio), in addition to weak signals of the allylic bromide II-51 (δ 4.6). The crude product was recrystallized several times from chloroform to afford pure dibromide II-55. Its structure was established by IR, ^{1}H NMR and MS spectral data (Experimental Section).

The results obtained by photodecomposition of N-bromoimides II-50 or II-60 in the presence of an olefin are admittedly less clear cut owing to difficulties in product isolation. However, the reactions yielded the parent imide in substantial amounts and the respective allylic bromides were not observed by ^{1}H NMR (absence of CHBr signal, δ 4.83 and 5.25 ppm for II-51 and II-61, respectively, characteristic of the allylic bromide) and GC analysis. GC showed the formation of the 1:1-adducts (as shown by GC-MS analysis) as minor components. The IR spectra of the crude products showed the isocyanate absorptions, at ≈ 2300 cm^{-1}. Owing to the complexity and the predominance of the parent imide, the isolation of minor components (ring opening products and 1:1-adducts) was not successful.

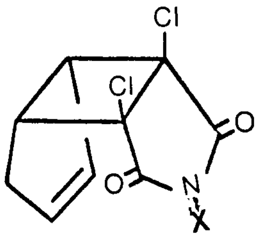
II-6 Photodecomposition of N-Bromo-6,7-Dichloro-cis-Bicyclo [3.2.0]Hept-2-ene-endo,cis-6,7-Dicarboximide (II-60)

Photolysis of N-bromoimide II-60 (0.3 mmol) in acetonitrile (7 ml) was carried out at 0°C through a Pyrex filter, and its progress was monitored by the KI-starch paper test. The photolysate was found to contain (relative yields by GC) imide II-17 (9%) and allylic bromide II-61 (90%). Recrystallization of the crude product afforded pure allylic bromide II-61 which gave spectral data in agreement with the assigned structure. The *exo*-configuration of bromine at C-4 in II-61 followed from a complete analysis of its ^{1}H NMR spectrum (at 400 MHz). The H_5 signal (δ 3.88 ppm) showed a small coupling (J=0.5 Hz, $\phi_{5,4n} \approx 90°$) with the C$\underline{H}$Br signal (δ 5.25 ppm).

Under similar photolysis conditions. photodecomposition of II-60 in CH_2Cl_2 resulted in the formation of imide II-17 (14%) and allylic bromide II-61 (86%) as shown by GC. Similar photolysis of II-60 in carbon tetrachloride resulted in a white solid (89%) which showed on GC one peak corresponding to II-61 (no imide II-17 was detected), and its IR spectrum was identical with that of II-61. The IR spectra of the crude products from the above photolyses were void of isocyanate absorptions (≈ 2300 cm^{-1}). The IR and ^1H NMR spectra of zero hour samples kept in the dark at 0°C showed no decomposition products.

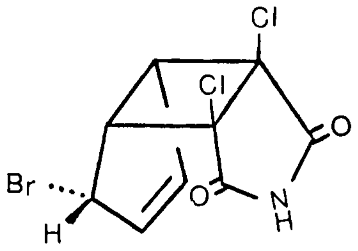
Photolysis of II-60 (0.16 mmol) in CH_2Cl_2 (6 ml) in the presence of bromine (0.01 mmol) through a GWV filter gave a white solid shown by IR and ^1H NMR to be identical with those of II-61.

Photobromination of imide II-17 with bromine in CH_2Cl_2 through Pyrex resulted in a white solid which was shown by IR and ^1H NMR spectra to be II-61. GC-analysis (relative yields) of the crude product showed peaks for II-61 (rt 4.6 min., 91%), imide II-17 (rt 3.3 min., 3%), and an unidentified component (rt 6.7 min., 5%). A sample of imide II-17 and bromine in CH_2Cl_2 kept in the dark showed no reaction (as shown by ^1H NMR).

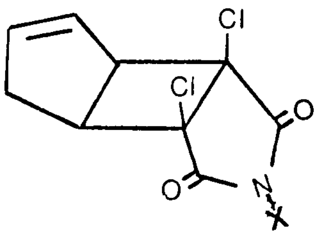


X = N II-17

X = Br II-60

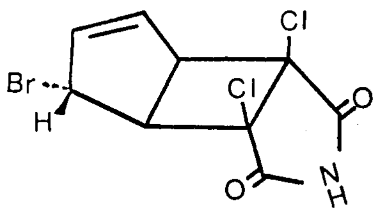


II-61

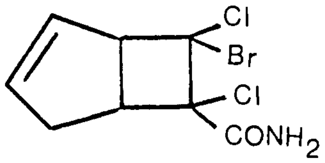


X = H II-18

X = Br II-63



II-64



II-62

II-7 Photodecomposition of N-Bromo-6,7-Dichloro-cisBicyclo [3.2.0]Hept-2-ene-exo,cis-6,7-Dicarboximide (II-63)

A solution of N-bromoimide II-63 in CH_2Cl_2 was photolysed at 0° through Pyrex until the KI-starch test was negative. The photolysate showed on GC (relative yields) imide II-18 (32%), allylic bromide II-64 (62%) and an unknown compound (6%). The IR spectrum showed no isocyanate absorptions (2250-2300 cm^{-1}). The zero hour sample kept in the dark showed no decomposition. Flash chromatography of the crude product afforded pure allylic bromide II-64. Its structure was determined by IR, ^1H NMR, ^{13}C NMR, and elemental analysis (Experimental Section). The stereochemistry of bromine at C-4 followed from the observation that the H_5 signal (δ 3.63 ppm) is weakly coupled with the H_4-proton (J=0.5 Hz) indicating a dihedral angle of ≈ 90°.

III. DISCUSSION

III-1 Synthesis of the Model Compounds: [2+2] Photocyloaddition of Dichloromaleimide and Dichloromaleic Anhydride to Cyclic Olefins

In the synthesis of the model compounds used in the mechanistic studies, a number of interesting observations were made, and these will now be discussed.

Direct photolysis of CH_2Cl_2 (II-1) with cyclohexene or cyclohexadiene gave cyclobutane derivatives II-3 to II-7 as the major products. The formation of imide II-5 (with *trans*-ring fusion) as major product indicates that cycloaddition follows a stepwise mechanism as suggested previously[82,83]. The lower yield of *endo*,*cis*-imide II-3 relative to that of *exo*,*cis*-imide II-4 (1:2 ratio) suggests that the reaction is significantly controlled by steric repulsion. Irradiation of solutions of dichloromaleimide in the presence of either cyclopentadiene or cyclopentene afforded (2+2) adducts II-15 to II-18. The pertinent arguments in support of the structural assignments of the cyclobutyl imides are summarized below.

1. The ^{13}C NMR spectra of *endo*,*cis*-cyclohexyl II-3, *exo*,*cis*-cyclohexyl II-4, *endo*,*cis*-cyclopentyl II-15 and *exo*,*cis*-cyclopentyl imides showed only five signals indicating

molecular symmetry with respect to the plane bissecting the molecules through the nitrogen atom.

2. The isomers II-6 (endo,cis-cyclohexenyl), II-7 (exo,cis-cyclohexenyl), II-17 (endo,cis-cyclopentenyl), II-18 (exo, cis-cyclopentenyl) were converted to II-3 (endo,cis-cyclohexyl), II-4 (exo,cis-cyclohexyl), II-15 (endo,cis-cyclopentyl), II-16 (exo,cis-cyclopentyl), respectively, by mild hydrogenation.

3. Irradiation of H_1 resulted in a 7.4% n.O.e. of the H_6 signal in II-7 and a ca. 8% nOe. of H_5 in II-17 and II-18.

4. Irradiation of an NH proton caused signal enhancement (nOe.) of H_1, H_6 in II-4, II-7 and H_1, H_5 in II-16. Similar irradiations in II-3, II-6 and II-15 did not cause nOe. of the respective cyclobutyl protons.

5. The ^{1}H NMR signals of the cyclobutyl protons in II-4, II-7, II-16 and II-18 are shifted to higher fields relative to the corresponding signals in II-3, II-6, II-15, and II-17, respectively, as a result of the anisotropic effect of the dicarboximide group.

Observations (1) - (3) are indicative of a *cis*-ring fusion. Observations (4) - (5) ascertain the structural assignment of the carboximide group (*endo* vs. *exo*). Finally the structure of compound *II-6* was determined by X-ray crystallographic analysis[90] (see Figure II-1).

The coupling constants of the various protons of the *trans*-imide *II-5* clearly indicate that the cyclohexane ring has a chair conformation with diequatorial fusion to the cyclobutane ring. The molecular strain due to *trans*-fusion between the four- and six-membered rings is clearly manifested by the facile methanolysis of the imide ring whereby the strain is partially relieved.

The precursors *II-3*, *II-6*, *II-15*, *II-17*, and *II-18* were converted into the corresponding N-bromoimides *II-31*, *II-50*, *II-41*, *II-60*, and *II-63*, respectively, by treatment with tert-butylhypobromite.

Photocyloaddition of dichloromaleic anhydride (*II-2*) to cyclohexadiene has been reported by Scharf[87] to give *II-10* (*endo*,*cis*-cyclohexenyl) and *II-13* (*trans*-cyclohexenyl). The latter is a trans-4,6-fused bicyclic compound with reported m.p. 158°. In our hands, photocycloaddition of *II-2* to cyclohexadiene gave *endo*,*cis*-cyclohexenyl anhydride *II-10* and a fraction with physical constants corresponding to those reported for trans-cyclohexenyl anhydride II-13. This fraction was found to be a mixture containing II-10 (30%) and a second component (70%) which were readily converted to II-6 (endo,cis-cyclohexenyl imide) and II-7 (exo,cis-cyclohexenyl imide), respectively, by ammonolysis followed by cyclization; the major component is therefore 7,8-dichloro-cis-bicyclo[4.2.0]oct-2-ene-endo,cis-7,8-dicarboxylic acid anhydride II-11 and not II-13. Olefinic products of trans-4,6-fusion with a carbon-carbon double bond, such as II-13, are relatively difficult to form owing to ring strains (we were not able to isolate any II-13), but have been isolated in the photoaddition of dimethylmaleic anhydride to cyclohexadienes[85,86]. Their ring strains are shown by the facile hydrolysis of the imide ring of II-5.

Benzophenone-sensitized photoaddition of dichloromaleic anhydride (II-2) to cyclopentadiene in dioxane gave the endo,cis-isomer II-19 and its exo,cis-isomer II-20 as major products. The structures of II-19 and II-20 were directly correlated with those of II-17 (endo,cis-cyclopentenyl) and II-18 (exo,cis-cyclopentenyl imide), respectively, by ammonolysis and cyclization. The same photoaddition has been reported by Scharf[87] to give as major products the endo,cis-isomer II-19 (m.p. 90°) whose structure was proven by a series of chemical reactions, and its trans-4,5-fused isomer II-14 (m.p. 122°, higher GC retention time). Our second major products. The structures of II-19 and II-20 were directly correlated with those of II-17 and II-18, respectively, by ammonolysis and cyclization. The same photoaddition has been reported by Scharf[87] to give as major products the *cis*,*endo*-isomer II-19 (m.p. 90°) whose structure was proven by a series of chemical reactions, and its *trans*-4,5-fused isomer II-14 (m.p. 122°, higher GC retention time). Our second major product, though not obtained in a pure state, exhibited a proton NMR pattern (at 60 MHz) identical with that of Scharf's sample[87] but was directly correlated to *exo*,*cis*-isomer II-18 by ammonolysis and cyclization. In view of this evidence, the analysis of the 400 MHz NMR spectrum and of the strain present in *trans*-4,5-ring fusion products containing a carbon-carbon double bond, it is concluded that II-20, rather than Scharf's II-14, is the correct structure of the second major product.

III-2 Photodecomposition of N-Bromosuccinimide

As noted earlier, we investigated first the photodecomposition of NBS. While this work was in progress, Skell[53] reported data on this reaction which are relevant to our conclusions presented below.

The orientation of the NBS photoaddition to 3,3-dimethyl-1-butene (II-24, neohexene) and the failure of the dark reaction indicate that the succinimidyl radical initiates the attack on the π-bond which is followed by bromine transfer with NBS (see equations 20 and 21). The excellent yield of the 1:1 adduct (II-25) indicates that the abstraction of hydrogen by the succinimidyl radical from the tertiary butyl group does not compete to any significant extent. Analogous results have subsequently been reported[60] for the flash photolysis of N-bromo-3,3-dimethyl-glutarimide.

$$(CH_3)_3CCH{=}CH_2 + (CH_2CO)_2N^{\bullet} \rightarrow (CH_2CO)_{22}NCH_2\overset{\bullet}{C}HC(CH_3)_3 \qquad (20)$$

II-24

$$(CH_2CO)_2NCH_2\overset{\bullet}{C}HC(CH_3)_3 + NBS \rightarrow (CH_2CO)_2NCH_2CHBrC(CH_3)_3$$

II-25

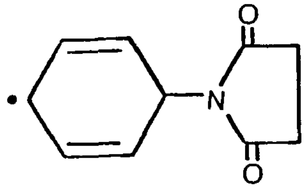
$$+ (CH_2CO)_2N^{\bullet} \qquad (21)$$

If the succinimidyl radical is generated by photolysis of NBS in benzene in the presence of ethylene oxide, the benzene ring is attacked efficiently to give the 1,4-adduct (II-28) and/or 1,2-adduct as primary products followed by addition of bromine or elimination of HBr to yield tribromo adducts (II-29, 40%) and N-phenyl-succinimide (II-30, 8%), respectively. The surprisingly high yield of the former in spite of fairly efficient scavenging of HBr by ethylene oxide indicates that reaction (22) rather than reaction (7) constitutes the major pathway for the formation of bromine.

$$(CH_2CO)2NBr + Br^{\bullet} \quad (CH_2CO)_2N^{\bullet} + Br_2 \tag{22}$$

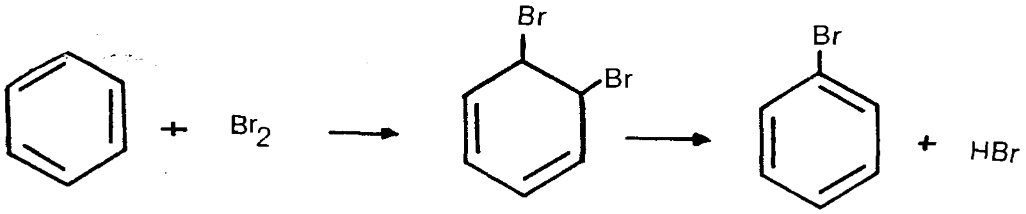
$$(CH_2CO)_2NBr + HBr \rightarrow (CH_2CO)_2NH + Br_2 \tag{7}$$

Photolysis of NBS in acetonitrile containing benzene and a small amount of neohexene (to scavenge bromine) gives <u>II-30</u> in <u>ca</u>. 30% yield in the presence, and in a slightly higher yield in the absence of ethylene oxide. This indicates that ethylene oxide is not very effective in promoting the succinimidyl radical addition. No dimerization products of the cyclohexadienyl radical, similar to those obtained in homolytic additions of phenyl radicals to arenes[98], have been detected, probably owing to the rapid reaction of <u>III-1</u> with bromine donors to give <u>II-28</u> (or its 1,2-isomer).



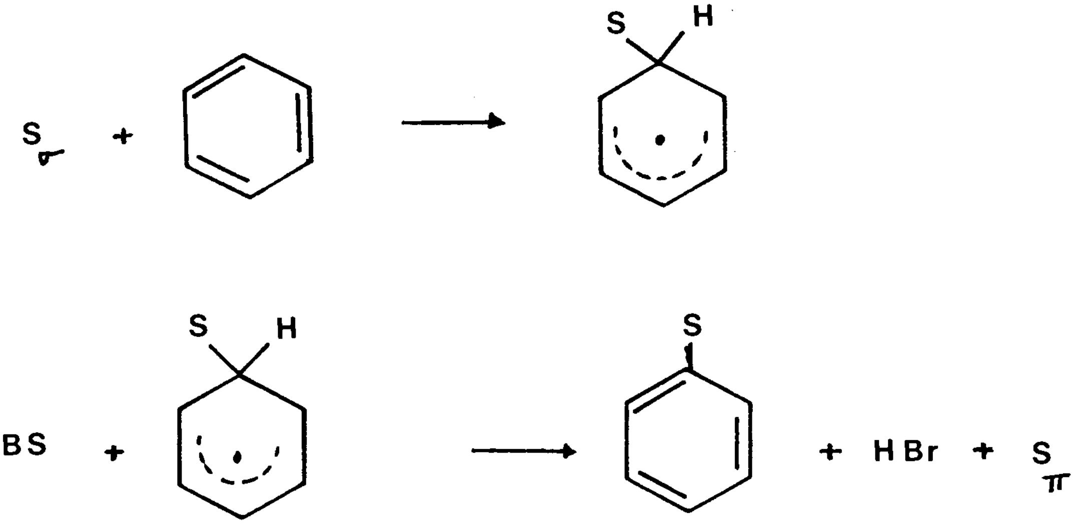
<u>III-1</u>

Photolysis of bromine in the presence of NBS in benzene resulted only in the bromination of benzene but not in the formation of tribromo adducts II-29 or II-30 N-phenyl-succinimide. Under these conditions, the succinimidyl radical is most likely not generated owing to the consumption of NBS via its reaction with HBr as shown below.



In summary, the overwhelming tendency of the succinimidyl radical to add to olefinic and benzene π-bonds suggests that it is highly electrophilic and that it has the Σ rather than the Π electronic configuration. It is known that a carbon radical having the unpaired electron in an sp^2 orbital is generally more electrophilic than one with the electron in a p or sp^3 orbital. In analogy with this general correlation, the Σ electronic configuration of the succinimidyl radical is expected to be more electrophilic than its Π electronic configuration.

Skell[53] has claimed that interaction of cyclohexadienylic radical III-1 with NBS generates s_π, and that only S_σ but not S_π adds to benzene. To continue the chain, CH_2Cl_2 was used as an intermediary to generate S_σ, as shown below. In our hands, we found that the succinimidyl radical adds efficiently to benzene (using benzene as a solvent and substrate) precluding the requirement of an intermediary to regenerate S_σ.



$$S_\pi + CH_2Cl_2 \rightarrow \dot{C}HCl_2 + \text{succinimide}$$

$$\dot{C}HCl_2 + NBS \rightarrow BrCHCl_2 + S_\sigma$$

III-3 Photodecomposition of N-Bromoimides II-31 and II-41

While both Skell[53-57] and Walling[62] agree that two radical species, (in addition to bromine atoms), must be postulated to explain the different results obtained in NBS reactions performed under different sets of conditions, the identity of these two species has been the focus of disagreement.

The results obtained for the photodecompositions of N-bromoimides II-31 or II-41 also clearly demonstrate the presence of two different radicals (in addition to bromine atoms). One of these radicals is identified as the imidyl radical II-32 or II-48 which undergoes ring opening to give amides II-39/II-40 or II-45/II-46, respectively, and abstracts hydrogen from the solvent intermolecularly. Since it is generated not only by photoexcitation as judged by low quantum yields for the disappearance of N-bromoimide II-31 in the presence of neohexene, but also by bromine-atom or benzoyl-peroxide initiated decomposition of II-31, it is more likely to be in the ground state than in the lowest excited state. Also, as the reactions of bromine atoms with N-bromoimides are known to be thermoneutral[113], there is not enough energy to raise imidyl radicals to the excited state if one assumes the energy gap between the two states to be 15-20 kcal/mole[55].

The results listed in Table II-10 (p.78) show that the $(C\text{-}Br)_e$/amides ratio is a function of the extent of conversion of the N-bromoimide *II-31*. At low conversion of *II-31*, the imidyl radical is the dominant species, but as the reaction proceeds and the concentration of bromine increases, the $(C_3\text{-}Br)_e$/amides ratio changes to resemble those listed in Table II-11 (p.80, expts 1-7). The formation of Br_2 is also shown by monitoring the photodecomposition by UV spectroscopy (Fig. II-2). The change in mechanism might be due to the transfer reaction between the imidyl radical and molecular bromine ($Ac_2N\cdot + Br_2 \rightleftharpoons Ac_2NBr + \overset{\bullet}{B}r$); a similar assumption has been reported by Tanner[63] to explain the change in the product distribution observed for the NBS bromination of 1-bromobutane[36] (Table I-1, p.21, entry 3). Alternatively, since the quantum yields for the disappearance of N-bromoimide *II-31* are low, most of the ring opening products may be formed via initial photoexcitation of *II-31* as suggested by Walling[62]. Either interpretation could account for the low C-Br/amides ratio at low conversion of *II-31*.

In N-bromoimide-olefin systems no C-Br products were detected. This result indicates that the ground state imidyl radical must have the Σ-electronic configuration (*II-32* or *II-48*) which cannot intramolecularly abstract the *endo* C_3-hydrogen and that Σ and Π-imidyl radicals do not interconvert.

Skell[55] has claimed that in the NBS/$Cl_2C=CH_2$/$CHCl_3$ system, the stabilized $\cdot CCl_3$ radical reacts with NBS to generate exclusively S_π as shown by the failure to detect ring opening product (isocyanates). In contrast, Walling[62] reported an 80% yield of isocyanates in the same system precluding the requirement that the transfer of bromine from NBS to $\dot{C}Cl_3$ generates exclusively a S_π (whose reactions do not correlated with a ring opening process). In our hands, photodecomposition of $CHCl_3$ solutions of N-bromoimide II-31 and $Cl_2C=CH_2$ (degassed by freeze-thaw cycles) and of II-41 and $CCl_2=CH_2$ (degassed with nitrogen) led to ring-opening (amides II-39/II-40, and II-45/II-46, respectively). These results indicate that $\cdot CCl_3$ generates from II-31 or II-41 the same imidyl radical as does $\cdot CHCl_2$ having the same Σ-configuration.

Discussion of the nature of the second radical involved in the decomposition of both II-31 and II-41 must take into account the following observations (see Results section): (i) it is generated by the thermal interaction of a bromine atom with N-bromoimide II-31 or II-41 in which imidyl radicals are also formed albeit inefficiently; (ii) it is not formed by direct photolysis of II-31 or II-41 in the presence of bromine scavengers; (iii) it is responsible for the formation of $(C_3\text{-}Br)_e$ by intramolecular hydrogen transfer; and (iv) it fails to open the imide ring to give amides.

In our opinion, the Π-configuration (II-33 or II-49) can be excluded on the basis of the following arguments:

(a) The ground state imidyl radical is assigned the Σ-configuration leaving the Π imidyl radical as an excited state. However, this proposal is not compatible with observations (i) and (ii); for example, one would expect an electronically excited radical to be obtained from photoexcitation processes rather than from thermal ones.

(b) If atomic bromine reacts with N-bromoimide to generate a Π-imidyl radical, one would expect a rapid increase in $(C_3\text{-Br})_e$, at least in the low concentration range of added bromine, which is in contrast to the results listed in Tables II-12 (p.82) and II-15 (p.93).

Therefore, we believe that the second radical is an N-bromoimide-Br• complex (II-34 or II-47) similar to that suggested by Walling[62]. This complex agrees with all our experimental observations and does not require the assumption of excited state radicals. It is proposed that the reacting radicals (imidyl, atomic bromine, and bromine atom complex) are related by a series of reversible equilibria, and that the course of the radical reactions depends on the radical concentration and the type of substrates. If the substrate contains allylic hydrogen e.g., N-bromoimides II-50 (endo,cis-cyclohexenyl), II-60 (endo,cis-cyclopentenyl) and II-63 (exo,cis-cyclopentenyl), the bromine atom chain process dominates and the equilibrium shifts to the left.

$$Br\cdot + Ac_2N\text{-}Br \rightleftharpoons \underset{\text{(bromine atom complex)}}{Ac_2N\text{-}\dot{B}r\text{-}Br} \rightleftharpoons \underset{\text{(imidyl radical)}}{Br_2 + Ac_2N\cdot}$$

These radical equilibria can satisfactorily explain the $(C_3\text{-}Br)_e$/amides ratios listed in Tables II-12 (p.82) and II-15 (p.93). At low concentrations of bromine, the imidyl radical $Ac_2N\cdot$ is still generated by bromine atoms. As the concentration increases, the imidyl radical is trapped by bromine and the equilbrium shifts to the left, which increases the $(C_3\text{-}Br)_e$/amides ratio. The radicals equilibrate as shown above and react in nearly the same proportion regardless of the concentration of N-bromoimides to give almost constant values for the $(C_3\text{-}Br)_e$/amides, $C_3\text{-}Br/C_1\text{-}Br$ (Table II-11 (p.80); expts 1-7), $C_3\text{-}Br/C_{2x}\text{-}Br$ and $(C_3\text{-}Br)_e$/amides (Table II-14, p.92) ratios except the latter is low at low concentrations of II-41. Naturally, when bromine is scavenged, the equilibrium shifts to the far right, and only imidyl radical reactions are observed.

Since both $C_{3x}\text{-}Br$ and $C_{3n}\text{-}Br$ are derived from the reaction of the C_3-radical with bromine tranfer agents, the near constancy of their ratio in decompositions of N-bromoimides and photobrominations of their respective parent imides with Br_2 is indicative of bromine probably acting as trapping agent in both systems.

The systematic increase in the C_{2x}-Br/C_1-Br ratio (Table II-14, p.92) above that observed in the photobromination of imide II-3 is dependent on the concentration of II-31. At this stage it is proposed that the extra C_{2x}-Br is formed by inter-molecular hydrogen abstraction by the radical complex II-34. Since II-34 is a sterically hindered radical, it should abstract a hydrogen selectively from relatively unhindered sites. Yet we cannot provide a satisfactory rationalization as to why the C_2-H should be preferentially abstracted by II-34.

III-4 Photodecomposition of N-Bromoimides II-50, II-60, and II-63

In the absence of an olefin the photodecomposition of N-bromoimides II-50, II-60, and II-63 resulted in the formation of the corresponding allylic bromides II-51, II-61, and II-64, respectively. As mentioned before, Skell ;has proposed that in the presence of Br_2 the decomposition of NBS proceeds exclusively via the π-succinimidyl radical. We, therefore, synthesized model compounds II-50 and II-60 in order to study if the corresponding imidyl radicals generated in the presence of Br_2 add intramolecularly to the double bond. However, we found that due to the presence of allylic hydrogens these compounds give the corresponding allylic bromides via the bromine-atom chain mechanism. Thus this part of the study did not provide the desired information on the chemical reactivity of imidyl radicals toward olefinic double bonds.

The results obtained for the photodecomposition of II-50 and II-60 in the presence of an olefin[95] bromine scavenger were not conclusive. Nevertheless, the formation of the corresponding imides II-6 and II-17, and the formation of isocyanates are indicative of Σ-imidyl radical intermediates which undergo ring opening reactions and abstract hydrogen intermolecularly from the solvent.

III-5 Conclusion

Photolytic decomposition of N-bromoimides II-31 and II-41 has been shown to proceed via two reacting radicals and bromine atoms. These observations are in agreement with the conclusions of Walling[62], but not those of Skell[53-57] or Tanner et al.[63]. The two radicals (A and B) were found to have the following characteristics.

Radical A:

(a) It undergoes a ring opening reaction; and it must be an imidyl radical.

(b) In the presence of bromine scavengers, it abstracts hydrogen only by an intermolecular process; therefore it is assigned a Σ electronic configuration.

(c) This radical can be generated either by direct photolysis or by a bromine atom initiated reaction. Therefore, it is assumed to be a ground state species.

Radical B:

(a) This radical can only be generated by the interaction of bromine atoms with N-bromoimides. It undergoes intramolecular functionalization at the C_3 position, but no ring opening reaction.

(b) On the basis of the arguments presented before (p. 110), it is assigned to be a bromine atom complex with the N-bromo-imide which is in equilibrium with both the N-bromoimide and the imidyl radical (radical A).

The course of radical reactions depends on their concentration and type of substrate. If the substrate contains a reactive hydrogen, e.g. N-bromoimides II-50, II-60, and II-63, the rection proceeds by bromine atom mechanism.

The current status of the nature of the chain carriers involved in the N-bromoimide-olefin and N-bromoimide-Br_2 systems can be summarized as:

N-Bromoimide-olefin system

Skell[53-57] assigned an excited state Σ-succinimidyl radical, Walling[62] and Tanner[63] proposed a ground state succinimidyl radical, and we assigned a Σ-configuration for the imidyl radicals $AC_2\dot{N}$ which are believed to be in the ground state. The discrepancy between our conclusion and that of Skell[53-57] may have arisen from structural differences between the imidyl radicals II-32 and II-48 and the succinimidyl radical.

N-Bromoimide-Br_2 system

In this system Skell[53] assigned a ground state π-succinimidyl as the chain carrier, while Tanner concluded that atomic bromine was involved. Our conclusion that a bromine atom complex is the chain carrier is in agreement with Walling[62].

IV. EXPERIMENTAL

IV-1 General Conditions and Chemicals

Unless specified otherwise, the following experimental conditions were used. Melting points were determined on a Fisher-Johns apparatus and were uncorrected. Infrared spectra were recorded on a Perkin-Elmer 599B spectrometer using Nujol mulls. Ultraviolet spectra were obtained on a Unicam SP800 spectrometer. Mass spectra and gas chromatography-mas spectra were taken on a Hewlett-Packard 5985 mass spectrometer using a SE-30 capillary column. High resolution mass spectra (hrms) were performed at the University of British Columbia mass spectrometric services. Elemental analyses were performed by Mr. M.A. Yang on a Perkin-Elmer 240 spectrometer. Gas chromatographic (gc) analyses were performed on a Varian 1400 (FID) with a SE-30 capillary column (J & W, 13.7 m × 0.28 mm) or a Hewlett-Packard 5792 A with a OV-1 capillary column (HP, 12.5 m × 0.20 mm) coupled with HP 3390 integrator. Preparative GC used a Varian 1700 (thermal conductivity detector) on a 10% SE-30 (3 m × 6.4 mm) column. High pressure liquid chromatographic (HPLC) analyses were performed on a LDC Model 711 solvent delivery system, a Rheodyne Model 7120 syringe loading sample injector, a Partisil pxs 10/25 Whatman analytical column and a LDC Model 1203 UV monitor (254 nm).

Separations by column chromatography were carried out using Silica Gel (Baker, 60-200 mesh). Flash chromatographic separations were carried out as described by Still[92] using silica gel (230-400 mesh).

Nuclear magnetic resonance spectra were recorded at 400 MHz on a Bruker WH400 spectrometer in the FT mode, and an internal lock (deuterium) was used. The chemical shifts in ^{1}H NMR spectra were referred to the solvent signals (δ 7.24, 7.15 and 2.04 ppm for $CDCl_3$, C_6D_6, and acetone-d_6, respectively). The peak positions of ^{13}C signals were measured relative to the solvent signals at δ77.0, 128.0 and 30.2 for $CDCl_3$, C_6D_6 and acetone-d_6, respectively.

The coupling patterns of nmr signals ware presented as s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), m (multiplet) and br (broad). In ^{13}C NMR spectra the splitting patterns from off-resonance decoupling (ord) are indicated in parentheses.

The NOE experiments were performed at 400 MHz, using difference spectroscopy, on degassed solutions containing *ca*. 5 mg of a sample in 0.5 mL of solvent.

Dichloromaleic anhydride (Aldrich) was sublimed before use. 1,3-Cyclohexadiene (Aldrich), cyclohexene (Eastman

Kodak), and cyclopentene (Merck) were distilled prior to use. 1,4-Dioxane (Fisher) was distilled over sodium-benzophenone.

N-Bromosuccinimide was recrystallized from water to give white crystals, mp 181-183°C, and was kept in a dark desicator.

Dichloromethane (Fisher, spectroanalyzed grade) was purified by either distillation over P_2O_5 or successive extraction with concentrated H_2SO_4, distilled water, and 5% aqueous sodium bicarbonate, drying over anhydrous calcium chloride, and distillation over P_2O_5. GC analysis showed dichloromethane, purified by either method, to be 99.9% and contained a trace of carbon tetrachloride. Dibromomethane (Eastman Kodak) and chloroform (Burdick and Jackson) and acetonitrile (Fisher) were distilled over P_2O_5 when they were needed. GC analysis showed them to be 99.8% pure. Bromine (Fisher) was used as supplied; 3,3-dimethyl-1-butene (Aldrich), and 1,1-dichloroethylene were distilled prior to experiments. Commercial nitrogen (Union Carbide Linde, 99.997%) was scrubbed with a train of Fieser's solution, concentrated H_2SO_4 and KOH pellets.

Potassium ferrioxalate used as an actinometer was prepared according to the literature[105a], and purified by recrystallization from hot water.

IV-2 [2+2] Photocycloaddition of Dichloromaleimide and Dichloromaleic anhydride to Cyclic Olefins

IV-2-1 Preparation of Dichloromaleimide (II-1)[93]

A mixture of dichloromaleic anhydride II-2 (19.4 g, 0.12 mol), urea (7.4 g, 0.12 mol) and sodium chloride (24.2 g, 0.41 mol) was placed in a round-bottomed flask fitted with an oil trap. The mixture melted at ≈90° and reacted vigorously at about 120°. The mixture was stirred at 120° for 20 minutes, and then water (50 ml) was added at 100°. The precipitate from the cold mixture was collected and recrystallized from methanol-water (2:1 v/v) to give dichloromaleimide (II-1) (11.5 g, 58%); m.p. 174-77° (lit.[81] m.p. 178-180°); λ_{max} 235 nm, ε 7.2×10^4; IR 3200(s), 1730(s,br), 1610(s), 1050(s), and 850(s) cm^{-1}.

IV-2-2 The Procedure of Photolysis

Irradiation of a dioxane solution containing olefins and II-1 and/or II-2 was carried out in an immersion type Pyrex apparatus using a 450-Watt Hanovia medium pressure Hg lamp. The whole apparatus was cooled externally with a water bath at 10-15°. The solution was magnetically stirred and purged with a stream of nitrogen. The progress of the reaction was monitored by GC at suitable intervals to follow the decrease of

II-1 and/or II-2. The photolysate was evaporated under reduced pressure and the crude product was separated by chromatography using GC to monitor the separation.

The spectral data IR, MS, ^{1}H NMR, and ^{13}C NMR of the pertinent compounds are listed in Tables IV-1, IV-2, II-1 and II-2, respectively. Elemental analyses are given in Table IV-3.

IV-2-3 Photoaddition of Dichloromaleimide to 1,3-Cyclohexadiene

A solution of II-1 (4 g, 0.024 mol) and 1,3-cyclohexadiene (2.1 g, 0.026 mol) in anhydrous dioxane (350 mL) was irradiated for 1.5 hours. The crude residue showed GC peaks (10% SE-30, 150-220°C at 10°C/min.; rt, relative yields) corresponding to endo,cis-imide II-6 (r.t. 4.5 min., 50%), exo,cis-imide II-7 (5.3 min., 43%), II-8 (4.8 min., 5%) and II-9 (5.0 min., 2%). Flash chromatography, using ether-pet. ether (1:2) as the eluent, gave four fractions: The first fraction was II-6 (1.3 g, 23%) which was recrystallized from CH_2Cl_2-cyclohexane as white crystals; m.p. 160-162°. The second fraction (0.32 g) consisted of II-6 and II-8 with the GC peak ratio of 1:1. Its ^{1}H NMR spectrum showed, in addition to signals due to II-6, signals at δ 1.38(md,J=8 Hz, 2H), 2.20(md,J=8 Hz, 2H), 3.2(m,2H), 6.28(m,2H) ascribed to II-8. The third fraction

(0.73 g) was a mixture of all four compounds [II-6(35%), II-7(30%), II-8(20%), II-9(15%)] and showed ^{1}H NMR signals at δ 1.45(md,J=10Hz,2H), 1.67(md,J=10Hz,2H), 3.37(m,2H) and 6.48(m,2H) attributed to II-9. The fourth fraction (1.4 g, 24%) was recrystallized from CH_2Cl_2-cyclohexane to give white crystals of II-7; m.p. 173-179°.

IV-2-4 Hydrogenation of Imides II-6 and II-7

A methanol solution of II-6 (96 mg) containing 5% palladium-charcoal (10 mg) was stirred under hydrogen at one atmosphere and room temperature for 3 hours. The solution was filtered and evaporated to give a solid (89 mg), recrystallization from CH_2Cl_2-cyclohexane gave white crystals of II-3; m.p. 169-171°C.

Similar hydrogenation of II-7 (86 mg) under similar conditions gave II-4 (73 mg); m.p. 176-181°.

IV-2-5 Photoaddition of Dichloromaleimide to Cyclohexene

A solution of II-1 (0.93 g, 5.6 mmol) and cyclohexene (1.62 g, 19.7 mmol) in anhydrous dioxane (150 mL) was irradiated for four hours. The photolysate showed three GC peaks corresponding to *trans*-imide II-5 (5.77 min., 49%), *endo,cis*-imide II-3 (6.13 min., 14%) and *exo,cis*-imide II-4 (7.84 min., 32%) in addition to other minor peaks. The crude product was taken up in hot methanol; the solution showed a new

GC peak for trans-amide ester II-12 in addition to those of II-3 and II-4 and the much decreased II-5. Flash chromatography (ethylacetate-pet. ether 1:2) of the crude product gave four fractions. The first (110 mg, 7%) and third (200 mg, 14%) fractions were recrystallized from CH_2Cl_2-cyclohexane to give II-3 and II-4, respectively. The compounds were identified by mixture melting point and comparison of the IR and NMR spectra with those obtained from hydrogenation of II-6 and II-7, respectively. The second fraction (340 mg, 24%) was recrystallized from CH_2Cl_2-cyclohexane to give white crystals of II-5; m.p. 189-192°. The last fraction (90 mg) was recrystallized from chloroform to give white crystals of the ester II-12; m.p. 161-167°. A methanol solution of II-5 was refluxed with a small amount of charcoal; the solution gave II-12 (56%) by GC analysis.

IV-2-6 Photoaddition of Dichloromaleic Anhydride to 1,3-Cyclohexadiene

A solution of dichloromaleic anhydride (3 g, 18 mmol) and 1,3-cyclohexadiene (3.4g, 43 mmol) in anhydrous dioxane (350 ml) was irradiated at room temperature for 17 hours. The crude product showed two major GC peaks (10% SE-30, 100-220° at 10°C/min.) at rt 5.2 and 5.8 minutes in the ratio of 1.5:1 in addition to four minor peaks (< 5%). This was separated by preparative GC (SE-30, 3m × 6.4mm, at 200°C) to give endo,cis-anhydride II-10 (rt 16 min.) and a fraction containing exo,cis-anhydride II-11 (20 min.). II-10 was recrystallized from CCl_4 as white crystals; m.p. 106-109° (lit.[87] 108°). The other fraction was recrystallized from CCl_4 to give white solid m.p. 141-152° containing (relative GC peak areas) II-11 (70%), II-10 (15%) and an unknown (10%); In reference 87, this solid was assigned a different structure (i.e. II-13).

IV-2-7 Conversion of Anhydrides II-10 and II-11 to the Corresponding Imides II-6 and II-7

Ammonia was bubbled through a solution containing II-10 (100 mg) in dry dioxane (3 ml) for ten minutes at room temperature. The white precipitate (132 mg) was filtered off: IR 3400(m), 3200(m), 1675(s), and 1600(s)cm^{-1}. The precipitate (100 mg) was refluxed in acetic anhydride (3 ml) for 3 hours. The solution was evaporated under reduced pressure to give a crude product. Its GC analysis showed peaks corresponding to anhydride II-10 (70%), endo,cis-imide II-6 (15%) by peak matching with known samples, in addition to an unknown compound (15%) which gave by GC-MS(CI,CH_4): m/e (%) 208(5), 206(12), 196(10), 194(27), 168(53), and 166(100). The crude product was taken up in methylene chloride to yield a solid (28 mg): m.p. 142-61°; IR 3300-2500(m,br), 1720(s), 1285(s), 1270(s), 1230(m), 1135(m), and 945(m) cm^{-1}. This solid was not further investigated. The methylene chloride solution was evaporated to afford an oil which was chromatographed (silica gel, 5% CH_3OH-CH_2Cl_2) twice to give II-6; IR and ^1H NMR spectra were superimposable with those of the authentic sample obtained by photoaddition of II-1 to cyclohexadiene.

The semi-pure fraction containing II-11 was treated in a similar manner as above to give a crude product which showed the GC peaks (relative peak areas) of imide II-7 (rt 4.7, 34%), anhydride II-11 (rt 2.4, 50%) and two minor peaks at rt 0.8 (10%) and rt 1.5 (6%). Preparative TLC (silica gel, 5% CH_3OH-CH_2Cl_2) gave imide II-7; the IR and NMR spectra were superimposable with those of the authentic sample obtained by photoaddition of II-1 to 1,3-cyclohexadiene.

IV-2-8 Photoaddition of Dichloromaleimide to Cyclopentadiene

A solution of II-1 (0.52 g, 3 mmol) and cyclopentadiene (0.25 g, 4 mmol) in anhydrous dioxane (300 ml) was irradiated for 1/2 hour. The crude product showed three GC (10% SE-30) peaks at rt 8.7 (47%), 9.1 (10%) and 9.7 minutes (43%) corresponding to II-17, II-22 and II-18. The product was purified by chromatography using a silica gel column (2% CH_3OH-CH_2Cl_2). A white solid which was recrystallized from methanol-water and shown to be endo-cis-imide II-17 (42 mg); m.p. 195-8°. Elution with 2% and 5% CH_3OH-CH_2Cl_2 gave a mixture of isomers; rechromatography gave II-17 (95 mg), and exo,cis-imide II-18 (189 mg) which was recrystallized from methanol-water as white crystals; m.p. 202-207°.

When the above reaction was repeated on a large scale it was possible to separate a fraction enriched in (2+4) adduct II-22 admixed with II-18. The ^1H NMR spectrum showed, in addition to II-18, signals at δ 1.62(md, J=11 Hz, 1H), 1.9(md, J=11 Hz, 1H), 3.53(m, 2H), and 6.52(m, 2H) assigned to II-22.

IV-2-9 Bromination of a Mixture Containing II-17, II-18 and II-22

A mixture (102 mg, 0.42 mmol) comprised of II-17 (rt 2.7, 46%), II-18 (rt 3.3, 36%) and II-22 (rt 2.9 min., 18%), as shown by GC (10% SE-30, 150-220° at 10°C/min.), was treated with bromine (0.12 mmol) in CH_2Cl_2 at room temperature, in the dark, with stirring for approximately 12 hours. GC analysis of the resulting mixture showed that the amount of II-22 had decreased and that an additional peak (rt 8.2 min.) was observed which was identified as the dibromide of II-22 by GC-MS, m/e (%) 397(0.4), 395(3.1), 393(8.6), 391(8.2), 389(3.9, M^+), 360(1.0), 358(4.5), 356(6.1), 354(3.2, $M^+-{}^{35}Cl$), 360(1.0), 358(4.5), 356(6.1), 316(2.0), 314(11.2), 312(21.9), 310(14.7, $M^+-{}^{79}Br$), 288(1.3), 286(11.8), 284(22.9), 282(15.7), 278(4.4), 276(15.5), 274(13.0), and 66(100).

The above reaction was utilized to improve the separation of isomers II-17 and II-18 from the crude product of the photolysate.

IV-2-10 Thermal Addition of Dichloromaleimide to Cyclopentadiene

A solution of II-1 (18 mg) and cyclopentadiene (15 mg) in dimethoxyethane was stirred overnight at room temperature The crude product was recrystallized from methanol-water to give II-21 (30 mg) as white needles; m.p. 196-213° (decomposition).

IV-2-11 Hydrogenation of Imides II-17 and II-18

Imide II-17 (110 mg) was hydrogenated as above in methanol to give a crude product (90 mg), recrystallization from CH_2Cl_2-cyclohexane gave II-15; m.p. 154 -155°.

Similarly, imide II-18 (102 mg) was hydrogenated and recrystallized to give II-16; m.p. 209-213°.

IV-2-12 Photoaddition of Dichloromaleimide to Cyclopentene

A dioxane solution (300 mL) containing II-1 (3 g, 18 mmol) and cyclopentene (3.1 g, 45 mmol) was irradiated for four hours at room temperature. The photolysate showed two GC (OV-1,160° iso.) peaks at rt 4.9 (45%) and 6.47 minutes (57%) corresponding to endo,cis-imide II-15, and exo,cis-imide II-16. Flash chromatography (ethyl acetate-pet. ether, 1:5 ratio) gave a fraction (1.6 g, 38%) which was recrystallized from CH_2Cl_2-cyclohexane to afford II-15; m.p. 156-8°. The second fraction (2.1 g, 49%) was recrystallized from CH_2Cl_2-cyclohexane to afford II-16; m.p. 209-212°. These samples showed identical IR and NMR spectra with those obtained from the above hydrogenation.

IV-2-13 Photoaddition of Dichloromaleic Anhydride to Cyclopentadiene

A solution of II-2 (3.5 g, 20 mmol) cyclopentadiene (4 g, 60 mmol) and benzophenone (0.49 g, 2.7 mmol) in dioxane (350 ml) was irradiated for 10 hours. The photolysate showed two major peaks (by GC, OV-1, 160°C iso., relative yields based on total peak area) at rt 1.88 (45%) and 2.15 minutes (42%) and a minor peak at 2.82 minutes (10%). Flash chromatography (ethyl acetate-pet. ether, 1:2 ratio) gave two fractions. The first (0.69 g) was recrystallized from carbon tetrachloride to give endo,cis-anhydride II-19 as white crystals: m.p. 88-90° (lit.[87] m.p. 93°). The second fraction was recrystallized from carbon tetrachloride to afford exo,cis-anhydride II-20 admixed with II-19 (ca. 34%); the ^{1}H NMR spectrum showed, in addition to signals of II-19, signals at 2.8(qdd,J=2,8,18.5 Hz), 3.05(md,J=18 Hz), 3.43(t,J=7.5 Hz), 3.93(m), 5.77(m) and 6.13(m), each of which were equivalent to one proton.

The recovery of the products from the column chromatography was low due to hydrolysis of the anhydrides to dicarboxylic acids[87] which were not investigated further.

IV-2-14 Conversion of Anhydrides II-19 and II-20 to the Corresponding Imides II-17 and II-18

The anhydride II-19 (20 mg) was treated with ammonia in dry dioxane to give a precipitate which was refluxed in acetic anhydride for three hours to give a crude product. The crude product exhibited the GC peak of II-17 as the major component (peak matching) and other minor peaks. Preparative TLC of the crude product on silica gel (1:2 EtOAc-pet.ether as the eluent) gave II-17 (7 mg) which exhibited m.p., IR and NMR spectra identical to those of the sample obtained by photoaddition of II-1 to cyclopentadiene.

Similarly, a mixture of II-19 and II-20 (3:7 ratio, 20 mg) was treated as above to give a mixture which showed GC peaks corresponding to II-17 and II-18 by peak matching. Preparative TLC (silica gel, EtOAc-pet.ether 1:2) gave both II-17 and II-18 as pure samples as compared by their mixture m.p., IR and ^{1}H NMR spectra with the known samples.

TABLE IV-1

IR Absorption Data of Cycloaddition Products[a]

Compound	ν_{max} in cm^{-1}
II-3	3220(m,br), 3090(w), 1800(m), 1715(s), 1330(m), 1260(w), 1190(m), 1110(m), 960(w)
II-4	3190(m), 3080(m), 1785(m), 1720(s), 1330(m), 1250(m), 1210(s), 1190(w), 1130(w), 1080(w), 1005(m), 960(w), 730(m)
II-5	3220(m), 3100(m), 1795(m), 1790(m), 1755(s), 1720(s), 1340(m), 1325(m), 1250(w), 1210(m), 1150(m), 1120(m), 1015(m), 970(m), 780(m,br)
II-6	3260(m), 3160(m), 3100(m), 1790(m), 1730(s), 1330(m), 1280(w), 1245(w), 1165(m), 1125(w), 1070(m), 1020(m), 950(w), 790(w), 770(w), 745(w), 720(w), 690(w)
II-7	3180(m), 3080(m), 1790(m), 1730(s), 1335(m), 1215(m), 1190(m), 1070(m), 1000(w), 955(w), 765(w), 740(w), 725(w), 700(w)
II-10	1860(m), 1800(s), 1600(m,br), 1270(s), 950(m)
II-11	1870(w), 1860(w), 1795(s), 1600(w,br), 1230(m), 940(s)

Table IV-1 (Cont'd.)

II-12	3440(s), 3340(s), 3210(m), 1735(s), 1700(w), 1660(s), 1615(s), 1290(s), 1260(w), 1235(m), 1210(m), 1200(m), 1170(m), 1090(m), 1005(m), 760(m)
II-15	3280(m), 3180(m), 3080(m), 1790(m), 1715(s), 1335(m), 1320(m), 1210(m), 1140(s), 1060(w), 1030(m), 980(m), 825(m), 750(m)
II-16	3190(m), 3090(m), 1800(m), 1725(s), 1340(m), 1330(m), 1230(m), 1140(m), 1070(m), 965(w), 900(m), 835(m), 750(w)
II-17	3180(m), 3080(m), 1790(m), 1730(s), 1330(m), 1290(w), 1260(w), 1240(w), 1190(w), 1155(m), 1065(m), 1050(w), 970(w), 920(w), 850(w), 820(m), 770(m), 740(w)
II-18	3200(m), 3090(m), 1790(m), 1720(s), 1330(m), 1225(m), 1210(m), 1055(m), 990(w), 945(w), 905(w), 755(m), 730(m)
II-19	1865(m), 1795(s), 1605(w,br), 1210(m), 960(s)
II-21	3210(m), 3100(m), 1800(m), 1710(s), 1350(m), 1320(w), 1265(w), 1255(w), 1235(m), 1070(m), 960(w), 885(m), 770(w), 750(m)

[a] Spectra were taken in Nujol mulls

TABLE IV-2

Mass Spectral Data of Cycloaddition Products[a]

Compound	m/e(%)
II-3	214(37), 212(100, M^+-Cl), 176(10), 169(22), 167(23), 81(30), 77(28), 67(39), 45(24), 41(22) CI (CH_4) 252(10), 250(68), 248(100,M^++H), 216(5), 214(30), 212(44), 178(12)
II-4	CI (CH_4) 252(10), 250(68), 248(100,M^++H), 214(31), 212(46), 178(12)
II-5	214(37), 212(100,M^+-Cl), 176(12), 170(16), 169(18), 158(13), 81(12), 77(10), 67(12), 55(10) CI (iso-C_4H_{10}) 252(10), 250(65), 248(100,M^++H), 216(9), 214(29), 178(24)
II-6[d]	212(5), 210(18,M^+-Cl), 169(18), 167(23), 80(92), 79(100), 77(43), 51(39) CI CH_4) 250(10), 248(61), 246(100,M+H), 212(15), 210(40), 170(20), 168(35)
II-7[d]	212(6), 210(24,M^+-Cl), 167(5), 169(3), 80(100), 79(53), 77(33), 51(34) CI (CH_4) 250(10), 248(60), 246(100,M^++H), 212(12), 210(30), 105(20)

Table IV-2 (Cont'd.)

II-8[d]	212(30), 210(100,M^+-Cl), 169(9), 167(14), 148(12), 146(13), 141(6), 139(18), 80(35)
II-9[d]	212(6), 210(22,M^+-Cl), 169(18), 167(26), 148(8), 146(13), 141(8), 139(22), 80(100), 79(41)
II-10[b]	CI (CH_4) 251(3), 249(15), 247(22,M^++H), 221(12), 219(17), 213(37), 211(100), 185(10), 183(20)
II-11[b]	CI (CH_4) 251(10), 249(42), 247(54,M^++H), 221(25), 219(40), 213(49), 211(100), 185(17), 183(38)
II-12	283(11), 281(6), 279(13,M^+), 246(35), 244(100,M^+-Cl), 229(18), 227(50), 214(38), 212(100), 195(67) CI (iso-C_4H_{10}) 284(10), 282(67), 280(100,M^++H), 250(20), 248(27), 210(43)
II-15	200(30), 198(100,M^+-Cl), 169(12), 167(15), 162(17), 155(20), 154(20), 134(12), 127(13), 91(46), 68(44), 67(48), 65(23), 63(20) CI (CH_4) 238(10), 236(61), 234(100,M^++H), 200(13), 198(32)

Table IV-2 (Cont'd.)

II-16	200(30), 198(100,M^+-Cl), 164(8), 162(20), 157(8), 155(2), 127(13), 91(42), 68(30), 67(32), 65(20), 63(18) CI (CH_4) 238(15), 236(61), 234(100,M^++H), 200(7), 198(10), 157(7), 155(18)
II-17	198(33), 196(96,M^+-Cl), 127(11), 125(35), 89(21), 66(100) CI (iso-C_4H_{10}) 236(11), 234(75), 232(100,M^+ H), 198(10), 196(7)
II-18	198(32), 196(89,M^+-Cl), 127(8), 125(24), 89(16), 66(100) CI (CH_4) 236(15), 234(84), 232(100,M^++H), 198(28), 196(38), 168(12), 166(20), 162(15)
II-22[c]	198(30), 196(83,M^+-Cl), 127(15), 125(40), 89(32), 66(100)
II-21	198(13), 196(37,M^+-Cl), 66(100) CI (iso-C_4H_{10}) 236(12), 234(70), 232(100,M^++H), 200(7), 148(20), 162(18)

Table IV-2 (Cont'd.)

a Unless otherwise specified, the mass spectra (EI and CI) were obtained for pure compounds.

d MS (EI) of II-6, II-7, II-8 and II-9 were obtained from GC-MS (SE-30, iso-200°) of a mixture containing II-6 (rt 4.0), II-7 (rt 4.6), II-8 (rt 4.2) and II-9 (rt 4.4 min.)

b GC-MS of the photolysate (SE-30, 100-200°), II-10 (rt 5.8) and II-11 (rt 6.5 min.)

c GC-MS (SE-30, 160-240°) of the crude product: II-17 (rt 12), II-18 (rt 13.4) and II-22 (rt 12.5 min.)

TABLE IV-3

Elemental Analysis of Cycloaddition Products

Compound	Calculated			Found			
Mol. Formula	C	H	N		C	H	N
$C_{10}H_{11}O_2NCl_2$	48.39	4.44	5.65	II-3	48.61	4.56	5.73
				II-4	48.68	4.55	5.77
				II-5	48.38	4.41	5.46
$C_{10}H_9O_2NCl_2$	48.78	3.66	5.69	II-6	48.98	3.87	5.66
				II-7	48.87	3.73	5.69
$C_{11}H_{15}O_3NCl_2$	47.14	5.36	5.0	II-12	47.12	5.28	4.84
$C_9H_9O_2NCl_2$	46.15	3.85	5.98	II-15	46.02	3.93	5.98
				II-16	45.89	3.86	5.98
$C_9H_7O_2NCl_2$	46.55	3.02	6.03	II-17	46.24	3.19	6.13
				II-18	46.88	3.20	6.16
				II-21	46.56	2.96	6.06

IV-3 Photodecomposition of N-Bromosuccinimide

IV-3-1 Preparation of Authentic Samples

(a) N-Phenylsuccinimide

N-Phenylsuccinimide (II-30) was prepared by the method described by Cava et al.[95] In a 100 ml three-necked round bottomed flask, fitted with a condenser and a dropping funnel, was placed succinic anhydride (2g, 0.02 mol) in tetrahydrofuran (THF)(25 ml). Aniline (1.8 ml, 0.02 mol) in THF (5 ml) was added in one portion, through the funnel, to the stirred solution of succinic anhydride, stirred for 1 hour at room temperature, and then the solvent was removed in vacuo to yield an acid-amide as a pale yellow powder (4.2 g): IR 3300(s), 3000(br,m), 1700(s), 1660(s), 1600(s), and 1550(s). The acid-amide (4 g) was added to acetic anhydride (15 ml) and anhydrous sodium acetate (1 g) and heated on a steam bath for 30 min., cooled to room temperature, and then poured into cold water. The resulting precipitate was filtered, washed with water, and dried to give 1.2 g of a white solid, recrystallization from cyclohexane afforded (II-30) as white needles: m.p. 154-155°C (lit.[94] m.p. 155.2 - 155.7°C); IR 1780(w), 1710(s), 1595(w), 1500(w), 1445(m), 1395(m), 1190(s), 700(m), 600(m)cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.85(s,4H), and 7.35 (m,5H); ^{13}C NMR ($CDCl_3$) δ 27.9(t), 126.1(d), 128.1(d), 128.7(d), 131.6(s), and 175.9(s); MS m/e (%): 175(100), 120(34), 119(45), and 93(28).

(b) 1,2-Dibromo-3,3-Dimethybutane

Addition of bromine to neohexene gave a colorless oil of 1,2-dibromo-3,3-dimethylbutane (II-27) which darkens on storage. The distilled oil showed IR: 1380(s), 1320(m), 1260(m), 1230(m), 900(m), 875(m)cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15(s,9H), 3.55(dd,J=11 and 9.5Hz, 1H), and 4.1(m,2H); MS m/e (%) 246(0.2), 244(0.6), 242(0.3), 231(1.8), 229(3.4), 227(1.8), 165(29), 163(31), 147(9.3), 149(9.7), 83(32), 57(100), 56(10), 55(22).

IV-3-2 Photodecomposition of NBS in the Presence of Neohexene

A solution of NBS (2 g, 0.011 mol), neohexene (10 g, 0.119 mol), and ethylene oxide (2 ml, 0.031 mol) in acetonitrile (70 ml) was purged with nitrogen for a few minutes and irradiated with a Hanovia lamp (200W) at -10°C for 3.5 hours. At intervals, small samples were withdrawn for iodimetric tests to follow the progress of the reaction. A sample kept at -10°C in the dark showed no decomposition after 4 hours as shown by titration. The photolysate was evaporated to afford a white solid (2.72 g) which showed a ^{1}H NMR spectrum essentially that of adduct II-25 in addition to small signals at δ 1.00, 2.26, and 3.23 ppm and a GC (10% SE) showed one major and four minor peaks (2-3% yields based on total GC peaks). By quantitative peak matching the major peak was shown to correspond to II-25 (85% yield). GC-MS analysis (SE-30, 80-220°C at 6°C/min.) showed that the first two minor components contain no bromine atom and showed strong m/e at 57. The first component showed m/e (%) 152(5), 149(5), 137(2), 135(3), 83(11), 57(100), 56(41), 55(18); and the second component gave me (%) 166(6), 165(7), 152(3), 149(2), 123(1), 121(2), 119(1), 83(12), 69(4), 67(7), 57(100), 56(4), 55(10). The third component could not be detected by GC-MS. The fourth component gave m/e (%) 208 (0.2), 206(0.7), 204(0.4), 182(4), 167(5), 126(100), 57(29), 55(12), the strong peak at m/e 126 is probably derived from $(CH_3)_3CCH(OCH_2CH_2Br)CH_2Br$. Recrystallization of the solid (1.56 g) from petroleum ether gave 1-succinimido-2-bromo-3,3-dimethylbutane <u>II-25</u> (65%): m.p. 85-87°C; IR 1700 and 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15(s,9H), 2.75(s,4H), and 3.5 to 4.4(m,3H); ^{13}C NMR ($CDCl_3$) δ 26.9(q), 27.6(t), 34.6(s), 41.5(t), 63.9(t), 176.2(s); MS m/e (%) 263(25), 261(25), 248(10) 246(10), 207(92), 205(93), 183(17), 182(100), 166(38), 149(6), 127(11), 126(90), 112(65), 100(92), 84(49), 83(78), 82(18), 57(69), 56(32), 55(69). Anal.calcd for $C_{10}H_{16}NO_2Br$: C 45.81, H 6.15, N 5.34; found: C 46.04, H 6.16, N 5.26.

Adduct <u>II-25</u> (156 mg) was stirred in 80% acetic acid (3 ml) with sodium iodide (150 mg) and zinc powder (900 mg) for 48 hr. The solvent was removed in vacuo to yield a colorless oil which was dissolved in chloroform, washed with water, and dried over anhydrous Na_2SO_4. Chloroform was evaporated to give a solid (59 mg), recrystallization from cyclohexane afforded II-26 as a white crystals: m.p. 96-99°C; IR 1760(w), 1695(s), 1405(s), 1355(s), 1305(w), 1235(s), and 1150(s); ^1H NMR ($CDCl_3$) δ 0.92(s,9H), 1.46(m,2H), 2.68(s,4H), 3.52(m,2H); ^{13}C NMR ($CDCl_3$) δ 27.5(t), 28.4(q), 29.1(s), 34.7(t), 40.2(t), and 176.4(s).

IV-3-4 Photolysis of NBS in the Presence of Benzene

(a) In the absence of neohexene

A benzene (350 ml) solution containing NBS (1.5 g) and ethylene oxide (5 ml) was irradiated with a Hanovia lamp (200W) in a Pyrex vessel under nitrogen at 5-10°C for 12 hours until the photolysate gave a negative KI-starch test. The solvent was evaporated, and the residue (2.2g) was chromatographed on a silica gel column using CH_2Cl_2 containing 0-5% methanol as eluent. The first four fractions (455 mg) gave similar MS and IR but different ^1H NMR patterns. The semi-solids showed major mass spectral peaks at m/e 338, 336, 334, 257, 256, 254, 238, 236, 234, 176, 175, 158, 156, 120, 119, 100, and 93, and major IR absorptions at about 1710(s,b), 1150, 1180, 770 cm^{-1}, and their ^1H MNR spectra displayed a singlet at $\delta \approx 2.9$ and multiplets in the 4.5 to 6.2 ppm region. The first fraction was recrystallized from methanol to afford a white solid of II-29 (24 mg): m.p. 153-157°C, IR 1770(w), 1710(s), 1180(s), 1150(m), 770(m); ^1H MNR δ 2.88 (s,4H), 4.6 to 5.2(m,3H), 5.5(m,1H), 6.1(m,2H); MS m/e (%) 338(6), 336(11), 334(7), 257(6), 256(50), 255(7), 254(58), 238(19), 236(37), 234(17), 176(9), 175(17), 158(16), 156(17), 120(12), 119(12), 100(100), 93(10). The fifth and the sixth fractions were rechromatographed to afford a similar semi-solid (81 mg) as above and a crystalline compound (120 mg) identified as II-30 by comparison of IR, ^{1}H NMR, and MS spectra with those of the authentic sample. Elution with 5% CH_3OH-CH_2Cl_2 gave succinimide.

The semi-solid fractions were combined and chromatographed on an alumina column to afford many fractions, one of which (60 mg) was recrystallized from CH_3OH-CH_2Cl_2 to afford white crystals of II-29: m.p. 204-207°C; IR 1700, 1185, 1165, and 780 cm^{-1}; ^{1}H NMR δ 2.86(s,4H), 4.8 to 5.17(m,3H), 5.34 to 5.62(m,1H), and 6.00(m,2H); MS m/e (%) 419(0.2), 417(0.5), 415(0.5), 413(0.2), 338(23), 336(47), 334(27), 256(81), 254(82), 238(23), 236(47), 234(27), 176(30), 175(50), 158(56), 156(56), 120(41), 119(39), 100(100), and 93(29). Anal.calcd for $C_{10}H_{10}NBr_3O_2$:C 28.85, H 2.40, N 3.37; found: C 29.20, H 2.45, N 3.15.

(b) In the Presence of Added Bromine

A solution of NBS (3.55 g), bromine (880 mg), and ethylene oxide (6 ml) in benzene (130 ml) was photolysed through a G.W.C. filter (cut off at 334 nm) at about 10°C. Aliquots withdrawn at intervals were treated with a drop of cyclohexene and tested with KI-starch paper. The zero hour sample kept for

40 hours in the dark was similarly treated wth cyclohexene and titrated iodometrically to show no decomposition. It took 35 hours for NBS to disappear during which white solid precipitated. The solid (1.13 g) was shown to be succinimide by IR and ^{1}H NMR spectral data. The filtrate was evaporated to give an oil. Rechromatography on silica gel (using CH_2Cl_2 as eluent) gave a mixture of polybromobenzenes (1.93 g) and a small amount of succinimide. Rechromatography of the former (silica gel, pentane as eluent) gave four fractions. Fraction A (0.4 g): GC-MS (SE-30) showed dibromobenzene m/e (%) 238(11), 236(20), 238(11), 157(27), 155(28), 50(100), and tribromobenzene m/e (%) 318(4), 316(10), 314(11), 312(4); IR (neat) 3050(w), 2980(m), 1620(w), 1560(s), 1455 (s), 1450(s), 1350(m), 1255(m), 1245(m), 1200(s), 1155(s), 1075(m), 1050(m), 1010(s), 950(s), 900(s), 850(s), 770(s), 725(s), 685(m), 670(s); ^{1}H NMR ($CDCl_3$) δ 7.4 (multiplet). Fraction B (0.25 g): GC-MS showed dibromobenzene m/e (%) 238(35), 236(74), 234(36), 157(51), 155(57), 75(100); IR and ^{1}H NMR were similar to those of fraction A. Fraction C (0.34 g): GC-MS showed bromobenzene m/e (%) 158(17), 156(19), 77(100), tetrabromabiphenyl m/e (%) 237(43), 235(84), 233(46), 156(65), 154(64), 74(100), tribromobenzene m/e (%) 318(19), 316(52), 314(55), 312(19), 74(100), tetrabromocyclohexadiene m/e (%) 400(1), 398(4), 396(5), 394(3), 392(1.0), 319(5), 317(14), 315(15), 313(6), 238(15), 236(30), 234(17), 158(32), 156(35), 77(100), and unidentified peak m/e (%) 321(3), 319(11), 317(9), 315(3), 239(26), 235(24), 158(40), 156(39),

77(100), 51(52), 50(35); its IR spectrum was similar to that of fraction A; ^{1}H NMR displayed multiplets at δ 7.4, 4.7 and minor signals at δ 6.4 and 6.0. Fraction D (0.35 g): GC-MS showed bromobenzene, dibromobenzene, and unidentified component m/e (%) 319(2), 317(2), 315(1), 239(10), 237(19), 235(10), 158(19), 156(21), 78(68), 77(100), 51(92), 50(60); IR(neat) 3060(w), 2980(w), 2940(w), 1620(w), 1560(s), 1460(m), 1450(s), 1350(w), 1250(w), 1200(m), 1150(s), 1075(w), 1060(w), 1010(s), 950(s), 900(m), 870(w), 850(m), 770(s), 720(s), 670(s), 685(m); ^{1}H NMR δ 6.4, 6 and 4.7 ppm

(c) In the Presence of neohexene

A solution of NBS (599 mg, 3.3 mmol), benzene (2.6 ml, 29 mmol), ethylene oxide (1.5 ml, 23 mmol), and neohexene (0.3 ml, 2 mmol) in acetonitrite (100 ml) was irradiated with a 450W Hanovia lamp through a Corex filter for 20 min. at 0°C under nitrogen. The solution was evaporated to afford a brown oil (769 mg). The oil (384 mg) was chromatographed on silica gel using MeOH-CH_2Cl_2 as eluent. The first fraction (53 mg) was II-27 in addition to an unknown and was not further investigated. The fractions (144 mg) collected with 0.1 - 0.2% MeOH-CH_2Cl_2 were mixtures containing II-25, II-29, and II-30. The fractions (191 mg) eluted with 0.5 - 1% MeOH were crystallized from cyclohexane to give II-30; the IR, ^{1}H NMR, and mass spectra were superimposable with those of the authentic sample.

In a separate experiment, a solution of benzene (15 ml, 167 mmol), NBS (1.39 g, 7.81 mmol), neohexene (2.8 ml, 22 mmol), and ethylene oxide (1.5 ml, 30 mmol) in acetonitrite (140 ml) was irradiated in a Pyrex vessel with a 200W Hanovia lamp at 0°C for 10 hrs. IR of the crude mixture was void of isocyanate absorption (2260 cm^{-1}). Absolute yields (by GC using biphenyl as an internal standard) of products: <u>II-30</u> (26%), <u>II-27</u> (68%), succinimide (49%), <u>II-25</u> (1.5%).

In another experiment, a solution of benzene (15 ml), NBS (1.34 g, 7.5 mmol), neohexene (2.8 ml) in acetonitrite (140 ml) was irradiated in a Pyrex cell with a 200W lamp at 0°C for 12 hrs. Absolute yields (by GC) of products: <u>II-30</u> (39%), dibromide <u>II-27</u> (67%), succinimide (56%), 1:1 adduct <u>II-25</u> (2%).

IV-4 Photodecomposition of N-Bromoimides

IV-4-1 General Procedure for Preparation of N-Bromoimides

Tert-butylhypobromite* in CCl_4 (1 to 1.2 mole equiv.) was added to a stirred CH_2Cl_2 solution (CH_3CN was used for imide II-17) of the appropriate imide kept at *ca*. -15°C. After 45 minutes the solvents were removed under *vacuo*. The resulting white solid was washed with cyclohexane and dried over P_2O_5 under vacuum. The purity of N-bromoimides used in the photolyses was assumed to be ≈ 95% since no parent imide was detected by ^{1}HNMR and IR spectroscopy. Iodometric titration, with 2×10^{-3}N sodium thiosulfate, showed the N-bromoimide II-31 to be 97% pure. The N-bromoimides were kept in a dark dessicator over P_2O_5.

(a) N-Bromo-6,8-Dichloro-cis-Bicyclo[4.2.0]Octane-endo,cis-7,8-Dicarboximide (II-31): 82%; m.p. 128-129°C, λ 260 nm(ε 240 tailing to 360 nm) in CH_2Cl_2; IR 1740(s), 1300(m), 1190(s), 1135(s), 950(w), 875(m), 810(m), and 710(m) cm^{-1}; ^{1}HNMR ($CDCl_3$ at 60 MHz) δ 1.2 to 2.1(m,8H), 3.15(m,2H).

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* Concentration of tert-butylhypobromite ≈ 0.6 M, λ_{max}280nm (ε = 120)[114]

(b) <u>N-Bromo-7,8-Dichloro-cis-Bicyclo[4.2.0]Oct-2-ene-endo,cis-7,8-Dicarboximide (II-50)</u>: 74%; m.p. 94-97°C; IR 1795(w), 1730(s), 1160(m), 1100(m), 880(m), 745(m) , and 680(m) cm^{-1}; ^1H NMR ($CDCl_3$ at 60 MHz) δ 1.9(m,4H), 3.5(m,2H), 6.1(md, J = 11 Hz, 1H), and 6.3 (md, J = 11 Hz, 1H).

(c) <u>N-Bromo-6,7-Dichloro-cis-Bicyclo[3.2.0]Heptane-endo,cis-6,7-Dicarboximide (II-41)</u>: 72%; m.p. 139 - 40°C; IR 1800(w), 1725(s), 1300(m), 1260(m), 1210(m), 1150(s), 900(m), 830(m), 740(m), and 705(m) cm^{-1}; ^1H NMR ($CDCl_3$ at 60 MHz) δ 1.3 to 2.2(m,6H), 2.3 (m,2H).

(d) <u>N-Bromo-6,7-Dichloro-cis-Bicyclo[3.2.0]Hept-2-ene-endo, cis-6,7-Dicarboximide (II-60)</u>: 78%; m.p. 123-25°C, UV λ 270(ε250), 261nm ($\varepsilon \approx 378$) in CH_3CN; IR 1720(s), 1290(m), 1160(s), 1090(m), 1035(w), 865(m), and 690(m) cm^{-1}; ^1H NMR ($CDCl_3$ at 60 MHz) δ 2.7(m,2H), 3.8(m,2H), 5.7(m,1H), and 6.0(m,1H).

(e) <u>N-Bromo-6,7-Dichloro-cis-Bicyclo[3.2.0]Hept-2-ene-exo, cis-6,7-Dicarboximide (II-63)</u>: 67%; m.p. 126-32°; IR 1790(w), 1735(s), 1200(m), 1160(m), 1100(m), 800(m), 740(m) cm^{-1}; ^1H NMR ($CDCl_3$ at 60 MHz) δ 2.86(m,2H), 3.35(m,1H), 3.9(m,1H), 5.75(m,1H), and 6.08(m,1H).

IV-4-2 General Procedure of Photodecomposition of N-Bromoimides

Unless specified otherwise, the following experimental conditions were used. In a Pyrex photocell of either ca. 8 or 40 ml capacity, an appropriate solution of the N-bromoimide was placed and purged with purified nitrogen for a few minutes. The photocell was kept in an ice-cooled water bath and about 2 inches away from the light source. The latter was either a 450W medium pressure mercury lamp without a filter or a 200W lamp placed in a GWV filter (cut off at 380 nm). At intervals, small samples were withdrawn for KI-starch tests. Reactions carried out to 100% completion were photolyzed until KI-starch tests showed negative. The photolysates were left overnight and a suitable standard was added, and then passed through a short pad of silica gel which was washed several times with methylene chloride containing 5% methanol. This solution was analyzed by GC. Some of the photolysates were evaporated and the crude products were examined by IR spectroscopy to show isocyanate absorptions at 2280(s) and 2350(m) cm^{-1}.

GC-MS of the photolysates always showed a $CHBrCl_2$ peak (r.t. $\approx$ 0.6 minutes; OV-1, 60°iso.) after the methylene chloride peak: m/e(%) 168(0.4), 166(1.4), 164(3), 162(2), 131(8), 129(35), 127(21), 8.5(68) and 83(100).

The reactions carried out to less than 100% decomposition of N-bromoimide were successively treated wth 5% aqueous sodium bisulfite, 5% aqueous sodium bicarbonate. The aqueous solutions were further extracted twice with methylene chloride. The combined organic extracts were dried over anhydrous sodium sulfate, and a suitable standard was added before GC-analysis.

Two types of controls were carried out. A pre-analyzed photolysate [area ratio of peaks: standard II-21 (40.00), imide II-3 (50.36), amides II-39 and II-40 (4.42), C_1-Br II-35 (0.95), C_{2x}-Br II-36 (2.22), C_{3x}-Br II-37 (2.24), C_{3n}-Br II-38 (1.20)] was irradiated further for 3 hours. The GC analysis showed that the product distributions were identical [standard (40.01), II-3 (49.94), II-39 and II-40 (4.31), II-35 (0.81), II-36 (2.15), II-37(2.27), II-38 (1.20)]. Secondly, the above photolysate was washed successively with 5% aqueous $NaHSO_3$, 5% aqueous $NaHCO_3$ and dried over anhydrous Na_2SO_4, and then passed through a short pad of silica gel; the GC analysis [standard (39.34), II-3 (49.14), II-39 and II-40 (4.23), II-35 (0.90), II-36 (2.14), II-37 (2.29), II-38 (1.25)] gave identical product ratios.

GC-analyses were carried out with a Hewlett-Packard 5792A equipped with a HP3990 integrator and a OV-1 capillary column (HP 12.5 × 0.20 mm). The correction factors (F) of the parent imide and the standard were established, and were also used to calculate the mole ratio of the brominated imides and amides, as shown below.

$$\text{correction factor } (F) = \frac{(A/M)\ \text{standard}}{(A/M)\ \text{imide}}$$

A = peak area, M = mmol

F was pre-determined

mmol of imide in the photolysate, $M_{imide} = F \times M_{standard} \times \dfrac{A_{amide}}{A_{standard}}$

$M_{standard}$ = mmols of the standard added to the photolysate

$$\%\ \text{yield of imides} = \frac{M_{imide}}{M_{N\text{-}bromide}} \times 100$$

Similarly,

$$\%\ \text{yield of amides} = F \times M_{standard} \times \frac{A_{amides}}{A_{standard}} \times \frac{100}{M_{N\text{-}bromide}}$$

Percentage yields were calculated based on mmols of N-bromoimide used. In each analysis, more than two GC injections were made on each sample.

The yields of the unidentified components were based on total peak areas, except that of the standard.

Irradiation of N-bromoimide in the presence of bromine was carried out with a 200W Hanovia lamp filtered through a GWV filter. The sample was treated with a small amount of neohexene and/or cyclohexene to discharge the color and tested with KI-starch paper. The solutions were acidic to a litmus paper. The workup (washing with 5% $NaHSO_3$, 5% $NaHCO_3$, and drying over Na_2SO_4) and analysis were the same as that shown above.

IV-4-3 Photodecomposition of N-Bromo-7,8-Dichloro-cis-Bicyclo [4.2.0]Octane-endo,cis-7,8-Dicarboximide (II-31)

(a) Photolysis of II-31 in CH_2Cl_2

A solution of II-31 (20 mg, 0.062 mmol) in CH_2Cl_2 (6.5 ml) was irradiated with a 450W lamp until KI-starch test was negative (1.5 hr). A faint color of bromine was developed after *ca*. 10 minutes, and then disappeared towards the end of the reaction. The photolysate was worked up as described in the general procedure. Products yields from GC (190°C, isothermal, 8 psi) gave: II-3 (rt 8.2, 0.050 mmol), II-39 and II-40 (rt 8.5 and 8.7 min., total yield 4.5×10^{-3} mmol), II-35 (rt 14.77, 0.86×10^{-3} mmol), II-36 (rt 16.25, 1.92×10^{-3} mmol), II-37 (rt 17.82, 1.93×10^{-3} mmol) and II-38 (rt 18.17 min., 1.07×10^{-3} mmol). Products were identified by comparison of GC retention times with those isolated and characterized. GC-MS of the photolysate showed the formation of bromodichloromethane (rt ≈ 0.6 min. at 60°C).

A CH_2Cl_2 solution of N-bromoimide II-31 kept at 0°C in the dark showed no change in the IR and ^1H NMR spectra.

In a separate experiment, a solution of II-31 (12.3 mg, 0.038 mmol) in CH_2Cl_2 (1.5 ml) was introduced into a 5 ml capacity Pyrex photocell sealed with a Teflon needle valve. The solution was degassed by freezing (liquid nitrogen), evacuating (10^{-4} - 10^{-5} mm Hg), and thawing at ambient temperature three times, and then sealed. The sealed photocell was irradiated with a 450W lamp for two hours. The photolysate was treated successively with 5% aqueous $NaHSO_3$, 5% aqueous $NaHCO_3$, dried over Na_2SO_4, internal standard (II-21) was added, and analyzed by GC. Products yields: II-3 (0.029 mmol), II-39 and II-40 (3.57×10^{-3} mmol), II-35 (0.78×10^{-3} mmol), II-36 (2.13×10^{-3} mmol), II-37 (1.93×10^{-3} mmol), II-38 (0.85×10^{-3} mmol). GC-analysis showed some minor peaks, ≈ 2% each.

N-Bromoimide II-31 (51.2 mg, 0.158 mmol) in CH_2Cl_2 (3 ml) was irradiated with a 200W lamp. The latter was *ca.* 5 inches away from the photocell. At various intervals, samples (0.2 ml each) were withdrawn, quenched with 5% aqueous sodium bisulfite, and worked-up as described in the general procedure. The product yields were determined by GC, and the results are given in Table II-10.

(b) Benzoyl Peroxide Initiated Decomposition of II-31 in CH_2Cl_2

The methylene chloride (1.5 ml) solution of benzoyl peroxide ($2 \chi 10^{-3}$M) and II-31 (14.1 mg, 0.043 mmol) was degassed by three freeze-thaw cycles. The sealed tube was kept at 40 ± 2°C for 24 hours in a dark place. The solution, which showed positive KI-starch test, was washed successively with 5% sodium bisulfite, 5% sodium bicarbonate and water. Work-up in the usual manner gave (by GC): II-3 (0.041 mmol), II-39 and II-40 (0.43×10^{-3} mmol), II-35 (0.49×10^{-3} mmol), II-36 (1.81×10^{-3} mmol), II-37 (0.62×10^{-3} mmol), II-38 (0.41×10^{-3} mmol). GC-analysis showed some peaks, unidentified, close to the solvent peak.

(c) Photolysis of II-31 in the Presence of 1,1-Dichloroethylene in Chloroform

A solution of II-31 (9.4 mg, 2.9×10^{-2} mmol) and freshly distilled 1,1-dichloroethylene (8 μl, 9.9×10^{-2} mmol) in chloroform (1.5 ml) was degassed by three freeze-thaw cycles, and irradiated for 1.5 hr (KI-starch test showed negative). The usual work-up and GC-analysis (isothermal at 200° at 12 psi He) gave II-3 (r.t. 5.66 min., 1.8×10^{-2} mmol), II-39 and II-40 (r.t. 6.11 and 6.30 min., 7.5×10^{-3} mmol) in addition to unidentified minor peaks (relative yields) at 0.5 min. (1.5%), 2.3 (3%), 2.8 (1%), 4.6 (1%) and 11.18 (3%). Under the same GC conditions, the retention times of a product mixture were II-3 (5.63 min.), II-39 and II-40 (5.95 and 6.27), II-35 (10.91), II-36 (12.11), II-37 (13.38), and II-38 (13.63). The crude product showed the characteristic IR absorptions of isocyanates at 2280 and 2350 cm^{-1}.

(d) Photolysis of II-31 in the Presence of Neohexene in CH_2Cl_2

N-Bromoimide II-31 (20 mg, 0.062 mmol) and neohexene (4 µl, 0.031 mmol) in CH_2Cl_2 (6.5 ml) were irradiated to the complete consumption of II-31 (0.5 hr.). IR (neat) showed isocyanates absorptions at 2280(s) and 2350(m). Work-up in the usual manner gave (byGC, 160°C isothermal): II-3 (rt 12.1, 0.046 mmol), II-39 and II-40 (rt 13 and 13.5 min., total 0.013 mmol), 1,2-dibromo-3,3-dimethyl-butene (rt 1.8 min.) identified by peak matching with an authentic sample and GC-MS, in addition to peaks (unidentified) at rt (relative yields): 4.3 (4%), 6.3 (2%), 7.5 (1%) and 9.42 min. (2%). GC-analysis conducted at 190°C for 20 minutes (II-3, rt 6.6; II-39, rt 7.14; II-40 rt 7.36) showed no further peaks indicating no C-Br isomers and 1:1-adduct were formed.

(e) Photolysis of II-31 in the Presence of Ethylene Oxide

To a degassed solution of N-Bromoimide (19.8 mg, 0.61 mmol) in CH_2Cl_2 (2 ml) was added 1 ml of ethylene oxide (1.98M) in CH_2Cl_2. The solution was irradiated until KI-starch test was negative (45 min.). The usual work-up and GC-analysis gave II-3 (0.052 mmol), II-39 and II-40 (6.8×10^{-3} mmol), II-35 (1.1×10^{-3} mmol), II-36 (2.31×10^{-3} mmol), II-37 (0.89×10^{-3} mmol), and II-38 (0.6×10^{-3} mmol).

(f) Photolysis of II-31 in the Presence of Added Bromine

A solution of N-bromoimide II-31 (20.6 mg, 0.063 mmol) in CH_2Cl_2 (5.5 ml) and a 1 ml of bromine solution (2×10^{-2}M) in CH_2Cl_2 was irradiated through a GWV filter until II-31 had been consumed (2 hr.). Work-up in the usual manner and GC-analysis gave II-3 (0.047 mmol), II-39 and II-40 (0.73×10^{-3} mmol), II-35 (2.57×10^{-3} mmol), II-36 (5.86×10^{-3} mmol), II-37 (2.33×10^{-3} mmol), II-38 (1.31×10^{-3} mmol).

(g) Photobromination of Imide II-3 with Molecular Bromine

A 1 ml solution of bromine (2×10^{-2}M) in CH_2Cl_2 was transferred to a solution of II-3 (16.1 mg, 0.065 mmol) in CH_2Cl_2 (5.5 ml) and irradiated until the bromine color had disappeared (0.5 hr.). The usual work-up and GC-analysis gave II-3 (0.063 mmol), II-35 (0.99×10^{-3} mmol), II-36 (1.79×10^{-3} mmol), II-37 (0.53×10^{-3} mmol), and II-38 (0.38×10^{-3} mmol). The results reported in Table II-9 were obtained in a similar manner. No amides II-39 and II-40 were detected by GC.

(h) Product Isolation

Photobromination of Imide II-3

Imide II-3 (230 mg, 0.9 mmol) and bromine (1.4 mmol) in CH_2Cl_2 (20 mL) were irradiated with a 450W lamp at 0°C for 6 hours. More bromine (1.8 mmol in 5 ml CH_2Cl_2) was added and irradiation continued for another 4 hours. The photolysate was washed with 5% sodium bisulfite and 5% sodium bicarbonate. The usual work-up of the organic layer gave an oil, which was chromatographed on silica gel. Elution with 5% EtOAc in hexane gave a fraction (7.7 mg) which was recrystallized from methylene chloroide to afford II-38 (C_{3n}-Br)contaminated with a small amount of II-3. Elution with 10% EtOAc in hexane afforded II-3 (62 mg). Elution with 20% EtAOc in hexane gave a fraction (47 mg) which was purified by preparative TLC to give a mixture of II-35 (C_1-Br) and II-36 (C_{2x}-Br) in 1:1 ratio.

Photolysis of N-Bromide II-31

A solution of II-31 (340 mg, 1.05 mmol) in methylene chloride (40 mL) was irradiated until KI-starch paper test was negative and worked-up as described before. The oil was chromatographed on silica gel. Elution with 10% ether in pet. ether gave II-3 (imide) (164 mg) contaminated with C_{3n}-Br II-38. Elution with 10-20% ether in pet. ether gave fractions A (28 mg), B (59 mg) and C (31 mg). Fraction A was recrystallized to give the slower moving amide (8 mg) (≈ 90%) contaminated by the other amide. Fraction B, by preparative TLC on silica gel and EtOAc-pet. ether, afforded a solid which was recrystallized from methylene chloride to give II-36 (C_{2x}-Br) (7 mg) contaminated by II-3 (8%) and II-35 (5%) as shown by GC-analysis. Fraction C was recrystallized from methylene chloride several times to give II-37 (C_{3x}-Br)(4 mg) contaminated with II-3 (9%) and II-35 as shown by GC analysis. These semi-pure samples were used to record the ^1H (4%) and ^{13}C NMR (Table II-6 and II-7), IR (Table IV-4) and mass spectral data (Table IV-5).

(1) Quantum Yield Determinations

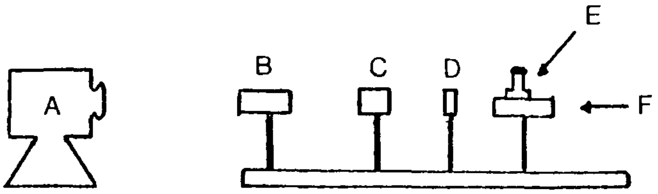
Pyrex test tubes (12 mm diameter × 100 mm length) carrying appropriate solutions were placed in a merry-go-round which was immersed in a water bath kept at 18 ± 2°C. The light source was a 450W lamp housed in a Pyrex cooling jacket. The light intensity (5.63×10^{-7} einstein/minutes) was determined with benzophenone-benzhydrol actinometry ($\Phi = 0.74$ in benzene) as described before.

A stock-solution of II-31 (102.2 mg, 0.314 mmol) in CH_2Cl_2 (50 ml, 6.3×10^{-3}M) was prepared. To each phototube, 3 ml aliquots were charged and degassed with argon for *ca.* 5 minutes. In the absence of additives, irradiation of II-31 solution developed a light yellow color in about 10 minutes. At suitable intervals, an irradiated tube was removed. To the solution, one drop of neohexene was added, to trap bromine. The solution was added to 10 ml of KI solution (5 g KI in 250 ml of water and 150 ml of glacial acetic acid). This mixture was analysed by iodometry using $Na_2S_2O_3$ solution (2×10^{-3}N) for titration. Blank experiments were also carried out to make corrections on the titrations.

In a separate series of experiments, the N-bromide II-31 stock solution (3 ml) and a bromine solution (0.05 ml, 0.04 M) were added to the sample tubes. These solutions were purged with argon for 5 minutes at 0°C, and irradiated. The treatment of the solutions and analysis followed the same procedures as that shown above.

In separate experiments, to each tube charged with 3 ml of the stock solution of <u>II-31</u>, neohexene (5 μl, 0.04 mmol) was added. These tubes were irradiated and analysed as above, except that neohexene was not added after photolysis.

The quantum yield for photobromination of CH_2Cl_2 was determined using an optical bench as shown below.



A	light source (200W PEK 212 high pressure mercury lamp)
B	5 Cm pathlength quartz cell filled with aqueous $CoSO_4$ (24 g/lit.)
C	1 Cm pathlength quartz cell contained aqueous $NiSO_4$ (25 g/50 ml)
D	Pyrex filter
E	1 Cm quartz cuvette (sample cell)
F	Sample holder

A stock solution of bromine (3.8×10^{-2}M) in CH_2Cl_2 was freshly prepared. A 0.1 ml aliquot of the bromine solution was introduced with a glass pipette to a 1 cm quartz cuvette containing CH_2Cl_2 (2.5 ml). The cuvette was chilled to 0°C, degassed with nitrogen (using Teflon tubing) for ca. 3 minutes, sealed with a rubber septum lined with Teflon tape, and placed in the sample holder of the optical bench. The bromine concentration at zero time (1.6×10^{-3}M) was determined spectrophotometrically (Cary 17) assuming $\varepsilon = 205 M^{-1}cm^{-1}$ at λ_{max} 410 nm. The light intensity (2.82×10^{-6} einstein/minutes) was determined with benzophenone-benzhydrol actinometry. The photobromination of CH_2Cl_2 was monitored by withdrawing the cuvette at various intervals and examined spectrophotometrically after thorough agitation. UV absorbencies at λ_{410}(time,min.;ϕ): 0.33(0,0), 0.31(2, ϕ=0.04), 0.27(5, ϕ=0.05), 0.22(10, ϕ=0.05), 0.15(20, ϕ=0.04), and 0.075(45 min., ϕ=0.03). GC-MS of the photolysate, after the usual work-up, ascertained the formation of $BrCHCl_2$.

For quantum yield determinations of II-31 decompositions in the presence of added bromine and irradiation through a GWV filter, the light intensity ($I = 2.34 \times 10^{-7}$ Einstein/min.) was measured using potassium ferrioxalate actinometer as described by Hatchard and Parker[105].

The actinometer solution was prepared by dissolving 1.86g of $K_3Fe\ (C_2O_4)_3$ in 20 ml of H_2O and 2.5 ml of 1·0N H_2SO_4 was added, and the solution was diluted to 25 ml and mixed.

The actinometer solution (3 ml) was added to the sample cell, placed in a merry-go-round, and irradiated through a GWV filter with a 200W lamp for 25 minutes at room temperature. The irradiated solution was thoroughly mixed and a 1 ml aliquot was pipetted into a 10 ml volumetric flask, 4 ml of a 0.1% (by weight) of 1.10 phenanthroline in H_2O, and a 1 ml of buffer solution (8 g NaOAc, 1 ml conc. H_2SO_4, and diluted to 100 ml H_2O) were added, diluted to the mark with H_2O, mixed, and left in the dark for one hour. The UV absorption (0.26) of this solution was measured at 510 nm in a 0.1 cm cell. A blank solution (1 ml) of a nonirradiated actinometer solution gave a 0.01 absorption

$$\text{Light intensity,} \quad I = \frac{AV_2V_3}{\varepsilon\phi t V_1 l}$$

A = corrected absorbance of irradiated actinometer solution (0.25)

V_1 = mls of irradiated actinometer solution withdrawn (1 ml)

V_2 = volume of actinometer irradiated (3 ml)

V_3 = volume used for dilution (10 ml)

ε = $1.11 \times 10^4\ L\ mol^{-1}cm^{-1}$, adopted from reference 105

ϕ ≈ 1.14 was assumed[105]

t = irradiation time

l = path length of the UV cell (0.1 cm)

A stock solution of II-31 (24.1 mg., 0.074 mmol) in CH_2Cl_2 (10 ml) was prepared. To each phototube, 3 ml aliquots were charged. A 0.1 ml of bromine solution (0.04 M) in CH_2Cl_2 was added, chilled to 0°C, purged with argon, placed in the merry-go-round and irradiated through a GWV filter. The treatment and iodometric analysis followed the same procedure as described above.

IV-4-4 Photodecomposition of N-Bromo-6,7-Dichloro-cis-Bicyclo [3.2.0]Heptane-endo,cis-6,7-Dicarboximide (II-41)

(a) Photolysis of II-41 in CH_2Cl_2

N-Bromoimide II-41 (44.7 mg, 0.14 mmol) in CH_2Cl_2 (5 ml) was irradiated to the complete disappearance of II-41 (2.5 hr) as shown by KI-starch paper test. The usual work-up and GC-analysis (170°, isothermal) gave: II-15 (imide) (rt 3.6, 0.115 mmol), II-45 and II-46 (amides) (rt 3.7 and 3.9 min., total yield 8.45×10^{-3} mmol), II-42 (C_{2x}-Br) (rt 8.1, 7.26×10^{-3} mmol), II-43 (C_{3x}-Br) (rt 9.6, 2.72×10^{-3} mmol), II-44 (C_{3n}-Br) (rt 10.1 min., 1.28×10^{-3} mmol), in addition to some other peaks at rt (relative yields based on total peak areas, except that of the standard): 1 (2%), 1.7 (0.4%), 1.9 (1.3%), 4.4 (0.1%), 4.6 (0.1%), 5.5 (1.4%), 7.8 (0.4%), 8.4 (0.3%), 8.7 (0.2%), for GC-MS of the minor components, see below. The relative yields of these peaks were not reproducible.Also, some of these peaks were not observed in imide II-15 and Br_2 reactions, and reactions carried out in the presence of an olefin.

(b) Photolysis of II-41 in the Presence of 1,1-Dichloroethylene

A solution of N-bromoimide II-41 (39 mg, 0.125 mmol) and 1,1-dichloroethylene (20 µl, 0.248 mmol) in chloroform (1.5 ml) was irradiated to the complete consumption of II-41 (1.5 hr). The usual work-up and GC-analysis gave: II-15 (0.085 mmol), II-45 and II-46 (0.029 mmol). No C-Br isomers were detected by GC. GC-analysis showed several peaks close to the solvent peak. IR of the crude product showed isocyanates absorptions at 2330(w) and 2250(s) cm^{-1}.

(c) Photolysis of II-41 in the Presence of Added Bromine

To a solution of II-41 (37.2 mg, 0.12 mmol) in CH_2Cl_2 (4 ml) was added 1 ml of bromine solution (3.8×10^{-2}M) in CH_2Cl_2. The mixture was irradiated through a GWV filter to the complete disappearance of II-41 (2 hr) The usual work-up and GC-analysis gave: II-15 (0.10 mmol), II-45 and II-46 (2.29×10^{-3} mmol), II-42 (1.1×10^{-2} mmol), II-43 (2.8×10^{-3} mmol), and II-44 (0.8×10^{-3} mmol).

(d) Isolation of Products

A solution of II-41 (1.1 g, 3.5 ml) in CH_2Cl_2 (4 ml) was irradiated with a 450W lamp for 13 hr. at 0°C. GC-analysis (160° iso.; rt, yields based on relative areas of all GC peaks): II-15 (3.55, 51%), II-45 (3.71, 4.5%) and II-46 (3.97, 6.3%), II-42 (8.07, 22%), II-43 (9.58, 5.9%), II-44 (10.1 min., 3%), in addition to unidentified peaks at rt 1.0 (1.5%), rt 2.04 (1%), rt 4.51 (1%), rt 4.68 (1.3%), and rt 5.6 min. (2%). The mass spectral data, obtained by GC-MS (CI, iso. C_4H_{10}) of the photolysate of the latter peaks are summarized below:

rt, min.	m/e (%)
1	175.0 (3), 174.0 (34), 172.1 (100)
2.04	253.8 (26), 251.9 (100), 249.8 (82), 174 (10), 172 (30).
4.51	331.8 (3.4), 329.8 (4.7), 327.8 (1), 288.7 (48)2, 286.8 (100), 284.7 (62), 255 (4), 253 (13), 251 (10), 173 (15), 171 (22).
4.68	288.8 (45), 286.8 (100), 284.7 (62), 243 (9), 241 (6), 209 (8), 207 (13), 173 (4), 171 (6).
5.60	335 (3), 333.7 (18), 331.8 (25), 330 (10), 174 (23), 172 (100).

Flash chromatography, using ethyl-acetate-pet. ether (1:9) as the eluent, of the crude product gave: fraction A (5 mg) contained II-44 (C_{3n}-Br) (94% by GC) and II-42 (6%).

Fraction B (20 mg) was a mixture of II-42 (C_{2x}-Br) and II-44 (C_{3n}-Br) in 1:3 ratio. Fraction C (52 mg) was shown to be mainly II-42 in addition to II-15 and II-44. Recrystallization (twice) from CH_2Cl_2-cyclohexane afforded a pure sample of II-42 (C_{2x}-Br) (95% by GC). Fractions D (59 mg), E (129 mg), and F (97 mg) were mixtures of II-42 and II-15, in 3:1, 1:1, and 1:3 ratios, respectively. Fraction G (233 mg) was II-15. Fraction H (59 mg) was a complex mixture. Fraction I (89 mg) contained the amide II-46 (rt 3.97 min.) as a major component (ca. 50%). The last fraction (43 mg) was a mixture.

Fraction I was rechromatographed to afford a fraction (6 mg) contained amide II-46 (80% by GC), II-43 (10%), and an unknown; and another fraction (7 mg) contained II-43 (C_{3x}-Br) (70%) in addition to amide II-45 (20%) and unknown (10%). This fraction was recrystallized from CH_2Cl_2-cyclohexane to give II-43 (ca. 80%).

The spectral data of the pertinent compounds are listed in Tables II-6, II-7, IV-4, and IV-5.

Table IV-4 . IR Absorptions in cm^{-1} of Products Obtained by Photodecomposition of N-Bromoimide II-31 and II-41.

C_{2x}-Br (II-36)	(Nujol) 3240(m), 3100(w), 1795(m), 1735(s), 1260(w), 1160(m), 1150(m), 1080(m), 985(m), 740(m), 690(w).
C_{3n}-Br (II-38)	(Nujol) 3200(m), 3090(w), 1790(m), 1735(s), 1200(m), 1160(m), 1080(m), 970(m), 890(w), 740(m).
C_{3x}-Br (II-37)	(Nujol) 3350(m,br), 1790(m), 1730(s), 1330(m), 1260(w), 1200(w), 1080(m), 745(m).
Amide (II-39)	(CH_2Cl_2): 3510(m), 3400(m), 1750(m), 1710(s), 1590(m), 1365(m), 1180(w), 880(w), 830(w).

C_{2x}-Br (II-42)	(CH_2Cl_2): 3360(m), 1795(m), 1745(s), 1310(m), 1130(m), 1065(m), 985(m).
C_{3x}-Br (II-43)	(CH_2Cl_2): 3360(m), 1800(m), 1745(s), 1320(m), 1230(w), 1140(w), 995(w).
Amide (II-45)	(CH_2Cl_2): 3510(m), 3400(m), 1705(s), 1580(m), 1345(m).

Table IV-5. Mass Spectral Data of Compounds Obtained by Photodecomposition of N-Bromoimide II-31 and II-41.

Compound	m/e(%)
C_1-Br (II-35)	(EI): 294(7), 292(28), 290(22), 212(38), 210(93), 81(100).
	(CI, CH_4): 332(6), 330(46), 328(100), 326(65), 294(3), 292(10), 290(8), 250(14), 248(50), 246(63),214(20), 212(68), 210(42), 205(27), 203(39), 178(20), 176(25), 170(24), 168(54), 166(38).
C_{2x}-Br (II-36)	(EI): 294(2), 292(8), 290(6), 212(38), 210(100), 171(6), 169(27), 167(39), 81(26), 80(18), 79(23), 77(18).
	(CI, CH_4): 332(6), 330(45), 328(99), 326(62), 294(3), 292(6), 290(4), 250(9), 248(46), 246(74), 214(27), 212(100), 210(66), 178(8), 176(16), 170(33), 168(51).
C_{3x}-Br (II-37)	(EI): 294(6), 292(20), 290(16), 248(7), 246(10), 212(33), 210(100), 171(3), 169(22), 167(32), 142(5), 140(14), 81(17), 80(38), 79(33), 77(15).
	(CI, CH_4): 332(6), 330(47) 328(100), 326(65), 294(6), 292(11), 290(6), 250(13), 248(66), 246(96) 212(19), 210(83), 170(31), 168(50).

Table IV-5 (Cont'd.)

Compound	m/e(%)
C_{3n}-Br (II-38)	(EI): 294(2), 292(10), 290(16), 250(2), 248(20), 246(26), 212(36), 210(100), 170(14), 169(20), 168(24), 167(34), 166(12), 141(9), 139(14), 80(26), 79(34). (CI, iso-C_4H_{10}): 332(8), 330(45), 328(100), 326(64), 250(6), 248(22), 246(30).
Amide (II-39)	(EI): 268(10), 266(40), 264(30), 230(8), 228(8), 224(6), 222(44), 220(71), 186(14), 184(32), 178(23), 176(30), 105(100), 77(98), 79(60), 44(52). (CI, CH_4): 306(0.8), 304(6), 302(14), 300(9, M^++H), 268(2), 266(8), 264(6), 216(6), 214(19), 188(30), 186(100), 150(15).
Amide (II-40)	(EI): 268(9), 266(40), 264(28), 224(10), 222(65), 220(99), 186(30), 184(81), 148(42), 134(34), 132(100), 105(66), 44(10). (CI, isoC_4H_{10}): 306(7), 304(46), 302(100), 300(62, M^++H), 188(12), 186(40).

Table IV-5 (Cont'd.)

Compound	m/e(%)
C_{2x}-Br (II-42)	(EI), m/e(%): 280(5), 278(18), 276(14), 199(10), 198(79), 197(32), 196(100), 127(18), 125(56), 91(20), 89(22), 67(91), 66(33), 65(34), 63(26), 62(24).
	(CI, isoC_4H_{10}), m/e(%): 316(41), 314(93), 312(58), 282(3), 280(13), 278(15), 276(6), 244(11), 242(10), 234(14), 232(17), 200(27), 198(100), 196(32).
C_{3x}-Br (II-43)	(EI), m/e(%): 280(4), 278(14), 276(10), 234(28), 232(40), 198(24), 196(71), 127(23), 125(70), 91(22), 89(22), 67(100), 66(77), 65(38), 63(32), 62(31).
	(CI, iso.C_4H_{10}), m/e(%): 316(47), 314(100), 312(61), 282(5), 280(17), 278(17), 276(6), 246(4), 244(17), 247(15), 236(8), 234(30), 232(32), 200(18), 198(41), 196(24).
C_{3n}-Br (II-44)	(EI), m/e(%): 280(5), 278(18), 276(13), 272(4), 270(9), 268(5), 244(6), 242(16), 240(10), 222(29), 198(30), 196(100), 127(28), 125(98), 91(23), 89(25), 67(64), 66(77), 65(32), 63(31), 62(29).

Table IV-5 (Cont'd.)

Compound	m/e(%)
	(CI, iso.C_4H_{10}), m/e(%): 316(39), 314(100), 312(55), 282(4), 280(11), 278(13), 276(4), 244(8), 242(9), 236(6), 234(26), 232(28), 200(5), 198(20), 196(20).
Amide (II-45)	(EI), m/e(%): 208(6), 206(10), 170(21), 134(18), 132(14), 121(35), 119(100), 91(18).
	(CI, iso.C_4H_{10}), m/e(%): 290(20), 288(45), 286(28), 174(35), 172(100).
Amide (II-46)	(EI), m/e(%): 216(7), 214(6), 208(19), 206(13), 178(16), 176(15), 170(14), 165(100), 163(97), 91(69), 67(46), 65(46), 51(28).
	(CI, iso.C_4H_{10}), m/e(%): 290(19), 288(42), 286(28), 174(35), 172(100).

IV-4-5 Photodecomposition of N-Bromo-7,8-Dichloro-cis-Bicyclo[4.2.0]Oct-2-ene-endo,cis-7,8-Dicarboximide (II-50)

(a) In the Absence of Additives

N-Bromoimide II-50 (19.2 mg, 0.06 mmol) in CH_2Cl_2 (5 ml) was irradiated through a Pyrex filter with a 450W lamp until KI-test showed negative (45 min.), the solution remained colorless throughout the photolysis. The solvent was evaporated to yield a yellow solid (17.4 mg). ^1H NMR spectrum (acetone-d_6, at 400 MHz) showed the allylic bromide II-51 as the major component, in addition to weak signals at δ 1.68, 1.93, 2.77, 3.5, 3.9, 4.63, 5.1, 5.9, 6.1 and 6.23 ppm. No dibromo-derivative II-55 was detected by ^1H NMR. GC-MS (160-230° at 10°C/min.; CI, iso.C_4H_{10}) showed: compound X (rt 3.9) me(%) 248(6), 246(50), 244(71, $M^+ + H$), 174(46), 170(10), 168(65), 166(100); II-6 (rt 4.1) me(%) 250 (11), 218(64), 246(100, $M^+ + H$), II-51 (rt 6.2 min.) me(%) 330(5), 328(21), 326(49), 324(30, $M^+ + H$), 248(5), 246(16), 244(14), 212(33), 210(100). GC-MS spectrum showed that the compound X in substantial amounts. The MS pattern of compound X suggests that it can be the diene II-50 formed probably by decomposition of II-51 on GC. IR spectrum of the crude product showed no isocyanate absorption. A sample of II-50 in CH_2Cl_2 kept in the dark at 0°C for one hour showed no decomposition as shown by IR.

Similar photolysis of N-bromoimide II-50 (0.29 g, 0.9 mmol) in CH_2Cl_2 (20 ml) and analysis of the photolysate by HPLC (1% iso-propanol-hexane, 500 psi; relative yields based on total peak areas) gave: II-51 (rt 5, 79%), in addition to minor peaks at rt 1.1 (2%), 1.8(4%), 3.5(5%), 3.9(2%), 4.2(4%), and 4.5 min. (6%). Flash chromatography (1:3 EtOAc-pet.ether as eluent) of the crude product gave: fraction A (24 mg) shown by HPLC to be a complex mixture containing all of the above minor components and II-51. Fraction B (137 mg) contained mainly allylic bromide II-51; recrystallization from CH_2Cl_2 afforded a white solid: mp 166-71°; IR 3450(m), 3220(m), 1790(m), 1730(s), 1230(m), 1170(m), 1070(m), 950(m), 780(m), 720(m) cm^{-1}; ^1H NMR (acetone-d_6) δ 2.22(ddd, J=4.5, 8, 15 Hz; H_5), 2.39 (ddd, J=5, 7.5, 15 Hz; H_5), 3.65 (td, J=8, 11.5; H_6), 3.81 (td, J=3, 12; H_1), 4.83 (q, J=5 Hz; H_4), 5.97 (dd, J=3, 10; H_2), 6.28 (ddd, J=2.5, 5, 10 Hz; H_3) [coupling constants (Hz): $J_{1,2}$(3), $J_{1,3}$(2.5), $J_{1,6}$(11.5), $J_{2,3}$(10), $J_{2,4}$(0), $J_{3,4}$(5), $J_{4,5x}$(*ca.* 5), $J_{4,5n}$(*ca.* 5), $J_{6,5n}$(*ca.* 8), $J_{6,5x}$(8), $J_{5n,5x}$(15)]; ^{13}C NMR (acetone-d_6) δ 31.25(t), 41.21(d), 41.37(d), 41.62(d), 68.32(s), 68.96(s), 125.70(d), 134.17(d), 171.2(s), 172.2(s); MS (CI, CH_4) m/e(%) 330(6), 328(42), 326(98), 324(59), 292(3), 290(8), 288(6), 248(13), 246(47), 244(53), 212(18), 210(79), 208(69), 170(21), 168(76), 166(100). The ^1H NMR spectrum also showed weak signals at 1.70, 1.92, 2.75, 3.48, 4.6, 5.87, 6.20 which could be due to the isomeric allylic bromide. Fraction C (4 mg) contained allylic bromide and unidentified compound as shown by HPLC. Fraction D (1.8 mg) was the unidentified compound whose ^1H NMR spectrum showed a complex pattern and could not be analysed.

(b) In the Presence of Neohexene

A solution of II-50 (36 mg, 0.11 mmol) and neohexene (0.15 ml, 1.2 mmol) in CH_2Cl_2 was irradiated through Pyrex with a 450W lamp until KI-starch test showed negative (1.5 hr). The solvent was evaporated and the crude product showed IR absorptions of isocyanates at 2260 and 2340 cm^{-1}. ^1H NMR (acetone-d_6, 400 MHz) showed imide II-6 as the major component, and was void of the allylic bromide II-51 (no CHBr signal at δ 4.8 ppm). GC-MS (CI, iso.C_4H_{10} , relative yields) showed II-6 (rt 3.3, 97%), 1:1-adduct (rt 12.4 min., 3%) m/e(%) 414 (7), 412 (42), 410 (100), 408 (58), in addition to unidentified minor peaks. Preparative TLC (silica gel, ethyl acetate-pet.ether 1:2) afforded three fractions. The first fraction (4 mg) showed a complex ^1H NMR pattern and was not analysed. GC-MS showed the very major peak to be 1:1-adduct. The second and third fractions (22 mg,81%) showed ^1H NMR spectra essentially of II-6 and their GC-MS showed one peak corresponding to II-6.

II-4-6 Photobromination of Imide II-6 with Bromine

Imide II-6 (21.3 mg, 0.09 mmol) in CH_2Cl_2 (3 ml) and 4 ml of bromine solution (1.6×10^{-3}M) in CH_2Cl_2 were irradiated through a GWV filter with a 200W lamp for 0.5 hr; the photolysate became colorless. The solvent was evaporated to give a white solid (22 mg) whose ^1H NMR spectrum (400 MHz, acetone-d_6) displayed, in addition to imide II-6, signals at δ 2.22, 2.39, 3.65, 3.81, 4.88, 5.97, 6.28 ppm characteristic of II-51.

A solution of II-6 (0.108 g, 0.44 mmol) in CH_2Cl_2 (5 ml) and 2.2 ml of bromine solution (0.2M) in CH_2Cl_2 was kept in the dark at 0°C for 1/2 hr. The solvent was evaporated to yield an oil (0.13 g) which was shown by ^1H NMR (100 MHz) to contain unreacted imide II-6 (≈ 85%), dibromo-derivative II-55 (≈ 15%), in addition to weak signals of II-51*. The crude mixture was recrystallized several times from $CHCl_3$ to afford white crystals (9 mg) of II-55: mp 180-83; IR 3300(s), 1790(m), 1735(s), 1170(m), 1165(m), 1070(m), 980(m), 750(m), and 690(m);

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* The above crude product ($CDCl_3$, 100 MHz) δ 1.5 to 2.6(m), 3.1 to 3.8(m), 4.1(m), 4.6(q), 5.8(m), 6.1(m).
II-51 ($CDCl_3$, 100 MHz) δ 2.3, 3.7, 4.6(q), 6.0 and 6.3.
II-55 ($CDCl_3$, 100 MHz) δ 1.6 to 2.5(m), 3.1 to 3.8(m), 4.1(m).

^{1}H NMR (400 MHz, acetone-d_6) δ 2.0 (m; 3H), 2.45(qd, J=5, 15; 1H), 3.52 (ddd, J=6, 7, 12 Hz; H_6), 3.78 (dd, J=10, 12 Hz; H_2), 4.16 (t, J=11.5 Hz; H_1), 4.28 (ddd, J=5.5, 8, 10 Hz; H_3) [coupling constants (Hz): $J_{1,2}$(12), $J_{1,6}$(12), $J_{2,3}$(10), $J_{3,4}$(5), $J_{3,4}$ (8), $J_{6,5}$(7), $J_{6,5}$ (6)]; MS (CI, CH_4) m/e(%) 411(3), 409(23), 407(62), 405(73), 403(28, M^+ + H), 329(6), 327(43), 325(100), 323(61), 291(3), 289(8), 287(7), 249(9), 247(48), 245(80), 243(9), 212(16), 210(61), 208(50), 170(31), 168(56).

II-4-7 Photodecomposition of N-Bromo-6,7-Dichloro-cis-Bicyclo[3.2.0]Hept-2-ene-endo,cis-Dicarboximide (II-60)

(a) Photolysis of II-60 in the Absence of Additives

A solution of N-bromoimide II-60 (96 mg, 0.3 mmol) in acetronile (7 ml) was irradiated through Pyrex with a 450W lamp for one hour (negative KI-starch test), the solution remained coloress throughout the photolysis. The photolysate showed by GC (SE-30, 100-220° at 10°C/min., relative yields based on total peak area) imide II-17 (rt 7.2, 9%), allylic bromide II-61 (rt 9.5, 90%) and an unknown (rt 8.6 min., 1%). The solvent was removed in vacuo to yield a yellow solid (76 mg) which was shown by IR and ^{1}H NMR (100 MHz, acetone-d_6) to be essentially the II-61. The crude product was recrystallized from methanol to afford a white solid (63mg) of II-61: m.p. 219-221°C; IR 3200(m), 3080(w), 1780(m), 1730(s), 1160(m), 1070(m), 1035(m), 975(w), 800(m), 780(w), 740(m), 700(m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.88 (dd, J=0.5, 7.4 Hz; H_5), 4.17 (dtd, J=1.8, 7.4Hz; H_1), 5.25(m;H_{4n}), 5.97 (tdd, J=0.6, 2.6, 5.6 Hz; H_2), 6.25 (dtd, J=1.8, 2, 5.6 Hz; H_3), 8.12 (NH) [coupling constants (Hz): $J_{1,2}$(2.4), $J_{1,3}$(2), $J_{1,4n}$(2.6), $J_{1,5}$(7.4), $J_{2,3}$(5.6), $J_{2,4n}$(0.6), $J_{2,5}$(0.6), $J_{3,4n}$(2.4), $J_{3,5}$(0.5), $J_{3,4n}$(2.4), $J_{3,5}$(0.5), $J_{5,4n}$(0.6)]; ^{13}C NMR (acetone-d_6) δ 50.71(d), 55.82(d), 66.22(s), 69.15(s), 132.27(d), 140.35(d), 170.45(s), 170.73(s); MS(EI)m/e(%) 278(14), 276(48), 274(40), 232(12), 230(19), 159(22), 146(43), 144(41), 89(44), 65(100); HRMS, m/e(%) 312.8917(0.15; calcd for $C_9H_6NO_2Cl^{35}Cl^{37}Br^{81}$: 312.8910), 310.8946(0.31; calcd for $C_9H_6NO_2Cl_2{}^{35}Br^{81}$: 310.8940), 308.8966 (0.19; calcd for $C_9H_6NO_2Cl_2{}^{35}Br^{79}$: 308.8960).

Anal. Calcd for $C_9H_6NO_2Cl_2Br$: C, 34.47; H, 193; N, 4.50
Found: C, 34.24; H, 1.98; N, 4.46

N-Bromoimide II-60 (95 mg, 0.3 mmol) in CH_2Cl_2(7 ml) was irradiated until KI-test showed negative, 1 1/4 hr. The photolysate showed on GC (relative yields): imide II-17 (14%), and allylic bromide II-61 (86%). The solvent was evaporated to give a yellow solid (73 mg) which was shown by IR and ^1H NMR to be mainly II-61.

N-Bromoimide II-60 (96.5 mg, 0.3 mmol) in CCl_4 (7 ml) was irradiated until KI-starch paper showed negative (2 hrs.), and a white solid was precipitated. The solvent was removed to give a white solid (74 mg): m.p. 214-7°. Its IR spectrum was identical with that of II-61, and GC of the photolysate showed one peak corresponding to II-61.

IR and/or ^1H NMR spectra of a zero hour sample (2 ml) of N-bromoimide II-60 in CH_3CN, CH_2Cl_2, CCl_4 kept in the dark at 0°C showed no decomposition.

(b) Photodecomposition of II-60 in the Presence of Added Bromine

N-Bromoimide II-60 (50 mg, 0.16 mmol) in CH_2Cl_2 (6 ml) and a 1 ml of bromine solution (10^{-2}M) in CH_2Cl_2 were irradiated through a GWV filter with a 200W lamp, until N-bromoimide II-60 had disappeared (1.5 hr). The solvent was evaporated to give a white solid (47 mg) which showed IR and ^1H NMR spectra identical with those of allylic bromide II-61. GC analysis of the crude product showed one peak corresponding to II-61.

(c) Photodecomposition of N-Bromoimide II-60 in the Presence of Ethylene

A solution of N-bromoimide II-60 (127.6 mg, 0.4 mmol) in CH_2Cl_2 (6 ml) was irradiated, at 0°C, through a Pyrex filter under a slow stream of ethylene until KI-test showed negative (4 hrs.). The solvent was evaporated to yield an oil (95 mg): IR 3480(w), 3400(w), 3190(m), 3080(m), 2800(w), 2340(2), 2260(m), 1790(s), 1735(s), 1340(m), 1290(w), 1270(s), 1240(w), 1190(m), 1160(m), 1090(w), 1070(m), 740(s), 710(m); ^1H NMR ($CDCl_2$) δ 2.75(m), 3.6(s, $BrCH_2CH_2Br$), 3.75(m), 5.9(m), 9.4(NH). GC-analysis (SE-30) of the crude product showed it to be mainly imide II-17; no allylic bromide II-61 was detected. The crude product was chromatographed (silica gel, CH_3OH-CH_2Cl_2 as eluent) to yield fraction A (10 mg) which showed several peaks by GC (> 10 peaks) and was not further investigated.

Fraction B (7 mg) was amide II-62 (rt 8.4) and unknown (rt 10.5) in 1:1.5 ratio. GC-MS (EI) of fraction B gave: amide(rt 8.4) m/e(%) 289(1), 287(7), 285(18), 283(8, M^+), 251(4), 429(15), 247(17), 245(5), 205(36), 203(47), 145(35), 143(100), and unknown (rt 10.5 min.) m/e(%) 3.5(7), 314(7), 313(18), 312(13), 311(12), 310(9), 279(14), 277(52), 275(35), 217(100), 215(90). Fraction C (37 mg) was shown to be imide II-17 by peak matching and GC-MS.

A sample of N-bromoimide II-60 in CH_2Cl_2 kept at 0°C under a small stream of ethylene for 3 hrs. in the dark showed, by IR and ^{1}H NMR, no decomposition.

II-4-8 Photobromination of Imide II-17 with Bromine

Imide II-17 (20 mg, 0.09 mmol) in CH_2Cl_2 (2 ml) and 0.5 ml of bromine in CH_2Cl_2 (0.2 M) were irradiated at 0°C through a Pyrex filter with a 450W lamp for 1 hr. The solvent was removed to yield a white solid (26 mg) which by GC-analysis (SE-30, 150-220° at 10°C/min.; rt, relative yields) showed: imide II-17 (rt 3.3, 3%), allylic bromide II-61 (rt 4.6, 91%), unidentified components at rt 4.0 (1%), and rt 6.7 min. (5%). The white solid also showed IR and ^1H NMR spectra similar to those of II-61.

II-4-9 Photodecomposition of N-Bromo-6,7-Dichloro-cis-Bicyclo [3.2.0]Hept-2-ene-exo,cis-6,7-Dicarboximide (II-63)

N-Bromoimide II-63 (106 mg, 0.34 mmol) in CH_2Cl_2 (6.5 ml) was irradiated with a 450W lamp until KI-starch test showed negative (1 hr.). The photolysate showed by GC (SE-30, 100-220°C at 10°C/min.; rt, relative yields): imide II-17 (7.9, 32%), allylic bromide II-64 (10.2, 62%) and an unknown (7.3 min., 6%).

The above photolysis was repeated using 70 mg of N-bromoimide II-63. The crude products from these photolyses were combined and flash chromatographed (1:3 ethylacetate-pet.-ether as eluent) to give a fraction (72 mg), recrystallization from CH_2Cl_2 afforded a white solid (63 mg) of II-64: m.p. 179-181°; IR 3200(m), 3090(m), 1805(m), 1715(s), 1270(w), 1225(m), 1210(m), 1170(w), 1105(w), 1070(m), 1030(w), 960(w), 935(w), 900(w), 790(m), 735(m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.63 (dd; H_5), 4.15 (dtd; H_1), 5.33(t;H_{4n}), 6.0 (tdd; H_2), 6.35 (td; H_3), 8.73 (NH) [coupling constants (Hz): $J_{1,2}$(2.5), $J_{1,3}$(1.6), $J_{1,4n}$(2.5), $J_{1,5}$(5.5), $J_{2,3}$(5.5), $J_{2,4n}$(0.5), $J_{2,5}$(0.5), $J_{3,4n}$(2.5), $J_{3,5}$(0.5), $J_{5,4n}$(0.5)]; ^{13}C NMR (acetone-d_6) δ 52.59(d), 53.68(d), 54.34(d), 68.35(s), 70.48(s), 133.13(d), 139.01(d), 171.92(s), 172.43(s); MS(EI) m/e(%) 278(27), 276(100), 274(82), 234(7), 232(36), 230(58), 197(12), 196(18), 195(30), 194(50), 146(43), 144(40), 89(39), 65(42).

Anal. Calcd for $C_9H_6NO_2Cl_2Br$: C, 34.47; H, 1.93; N, 4.50

Found: C, 34.09; H, 1.94; N, 4.87

A sample of N-bromoimide II-63 in CH_2Cl_2 kept in the dark for 2 hrs. showed no decomposition as shown by IR.

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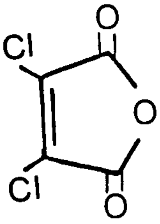
APPENDIX



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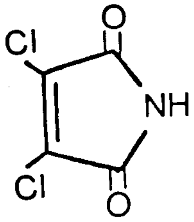

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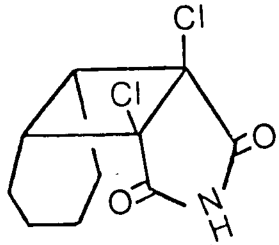

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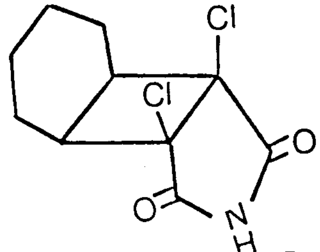

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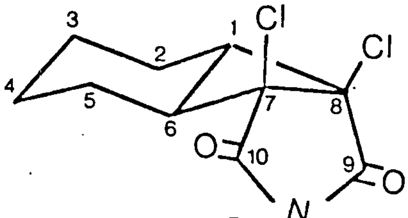

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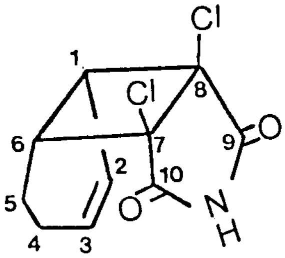

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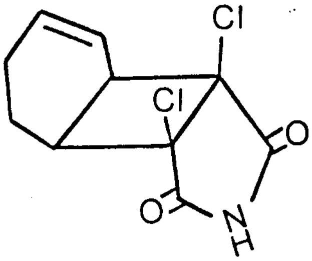

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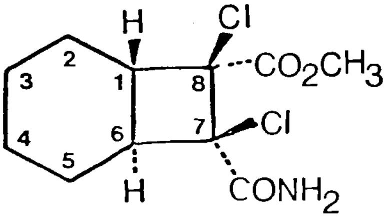

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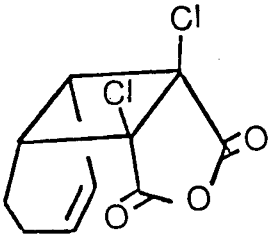

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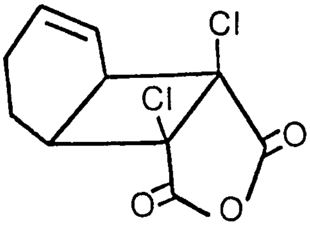

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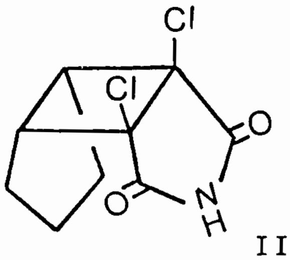

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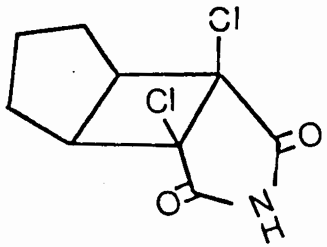

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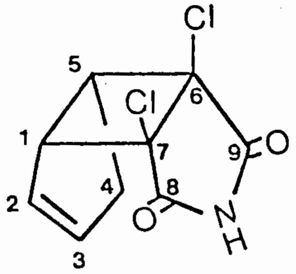

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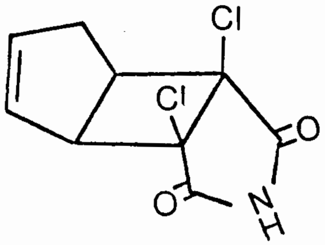

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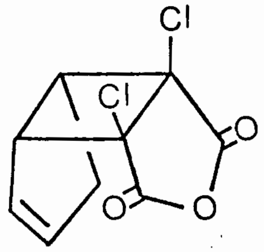

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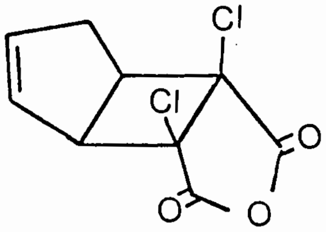

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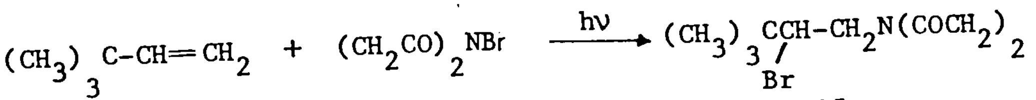
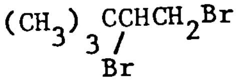


$$(CH_3)_3C{-}CH{=}CH_2 + (CH_2CO)_2NBr \xrightarrow{h\nu} (CH_3)_3C\underset{\text{Br}}{C}H{-}CH_2N(COCH_2)_2$$

II-24

II-25

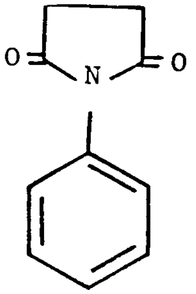


$$(CH_3)_3C\underset{\text{Br}}{C}HCH_2Br$$

II-27

$$(CH_3)_3CCH_2CH_2N(COCH_2)_2$$

II-26



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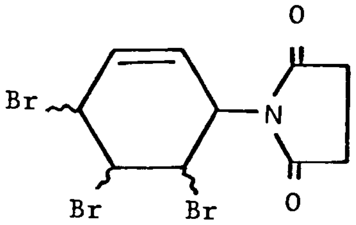

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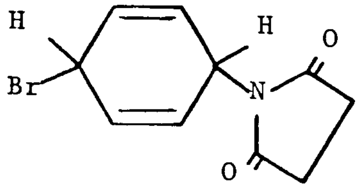

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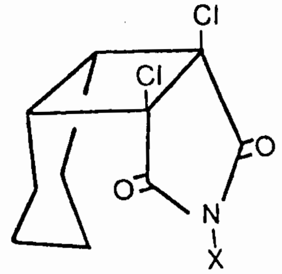
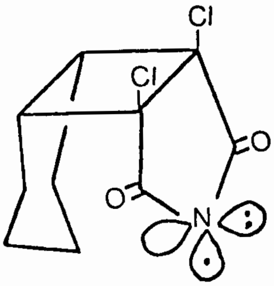


II-3 : X=H

II-31 : X=Br



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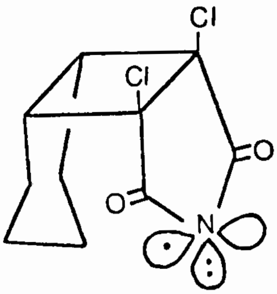

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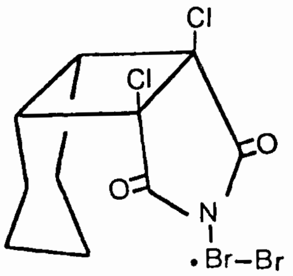

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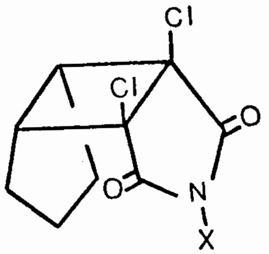
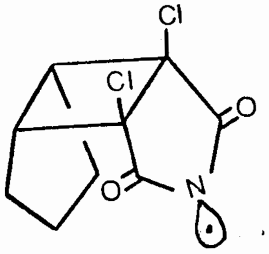


X = H II-15

X = Br II-41



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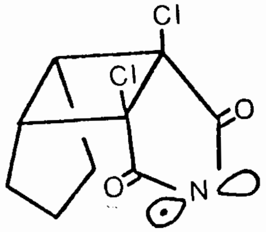

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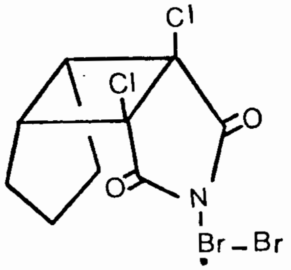

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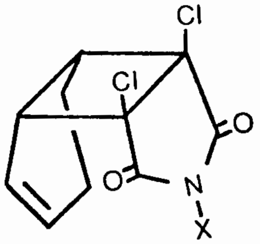
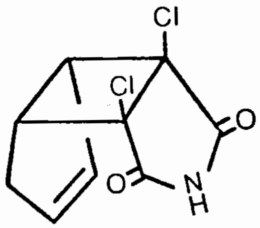


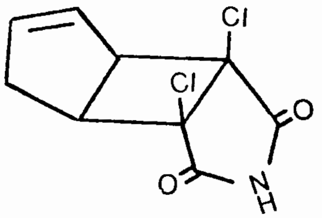
II-6 X = H

II-50 X = Br



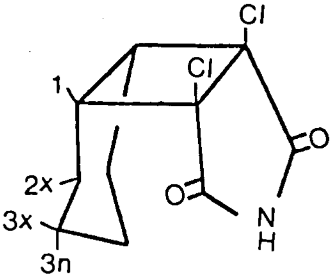
X = N II-17

X = Br II-60

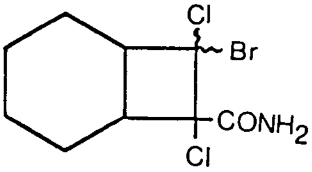


X = H II-18

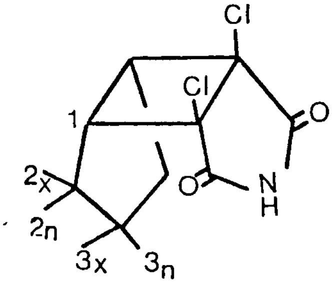
X = Br II-63



II-35 (C_1-Br)
II-36 (C_{2x}-Br)
II-37 (C_{3x}-Br)
II-38 (C_{3n}-Br)



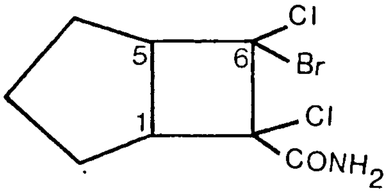
II-39
II-40



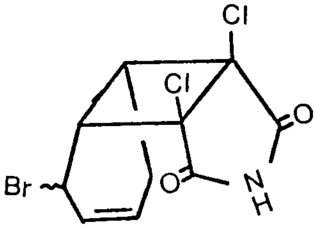
II-42 C_{2x}-Br

II-43 C_{3x}-Br

II-44 C_{3n}-Br



II-45 , II-46



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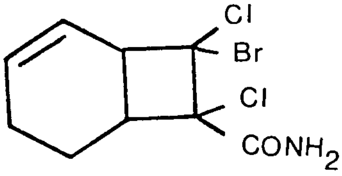

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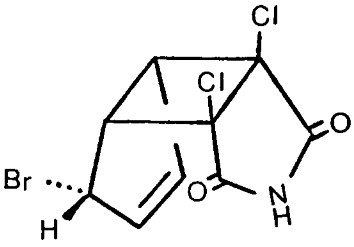

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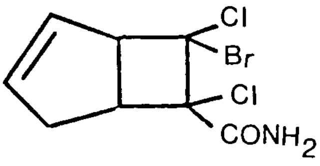

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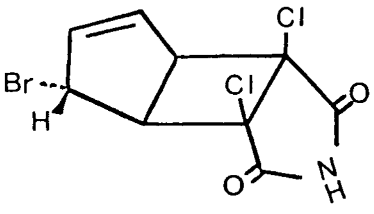

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