

1965

# Photocycloaddition reactions of trans-[beta]-nitrostyrene

Edward Dermot Hoganson  
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TRANS- $\beta$ -NITROSTYRENE.

Iowa State University of Science and Technology  
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PHOTOCYCLOADDITION REACTIONS OF

TRANS- $\beta$ -NITROSTYRENE

by

Edward Dermot Hoganson

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
The Requirements for the Degree of  
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

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1965

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## VITA

The author was born in Hibbing, Minnesota to Mr. and Mrs. Edward T. Hoganson. He attended Hibbing Public Schools where he graduated from high school in May, 1956. In September, 1956, he enrolled at Hibbing Junior College, Hibbing, Minnesota graduating with a two-year degree in May, 1958. In September, 1958, he transferred to Gustavus Adolphus College, St. Peter, Minnesota. He was granted the Bachelor of Science degree in May, 1960.

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## INTRODUCTION

The photochemistry of  $\alpha, \beta$ -unsaturated carbonyl compounds has been one of the most productive areas of organic chemistry in recent years. These compounds are known to undergo double-bond migrations, cleavage reactions, valence tautomerizations, gross structural rearrangements, dimerizations, and photoaddition reactions. Recently, photoaddition reactions of  $\alpha, \beta$ -unsaturated carbonyl compounds with olefins have received much attention. In general, these involve the addition of a photoactivated double bond of the unsaturated carbonyl group to an unactivated double bond. There has been no report in the literature of such a reaction between an  $\alpha, \beta$ -unsaturated nitro compound and an ethylenic linkage. This is surprising, since the nitro group is known to undergo  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  excitation analogous to that of carbonyls.

This volume describes a study of the photochemical addition of trans- $\beta$ -nitrostyrene (I) to different olefins and reactions of  $\beta$ -methyl- $\beta$ -nitrostyrene (II).



## HISTORICAL

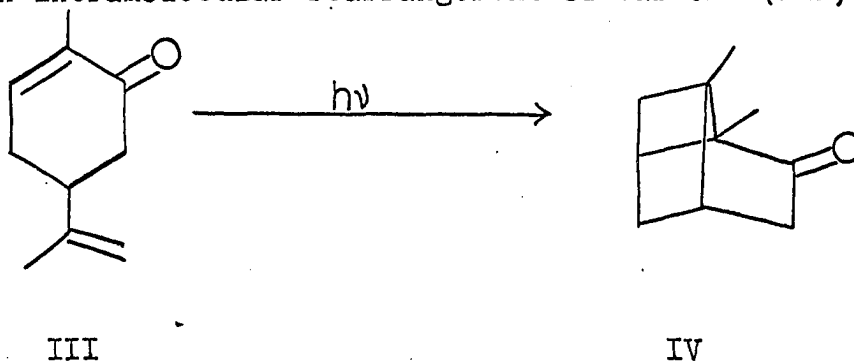
The historical section contains a review of photocycloaddition reactions of  $\alpha, \beta$ -unsaturated carbonyl compounds with alkenes and the photochemistry of nitro compounds.

Photocycloaddition Reactions of  
Unsaturated Carbonyl Compounds

In order for a cycloaddition reaction between an  $\alpha, \beta$ -unsaturated group and an ethylenic linkage to take place, one must have an ethylenic linkage capable of being activated by the light used, and a nearby, but not necessarily activated, double bond. These photocycloaddition reactions are of particular interest to the organic chemist since they lead to strained systems not always available by normal synthetic routes.

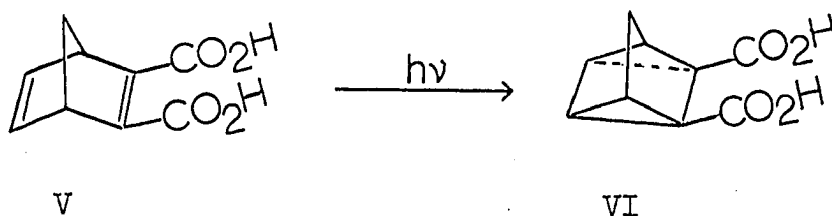
Intramolecular photocycloaddition reactions

One of the first examples of a photocycloaddition reaction is an intramolecular rearrangement of carvone (III) to

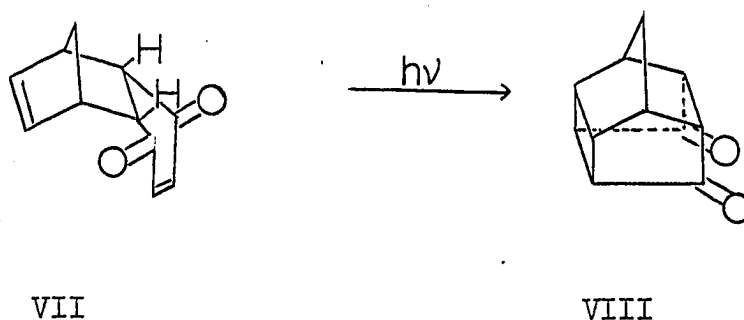


carvone camphor (IV) by Büchi and Gold (1).

An example of such a photochemical transformation in a rigid system is given by Cristol and Snell (2,3) in the irradiation of bicyclo[2.2.1]heptadien-2,3-dicarboxylic acid (V) to photoproduct VI.



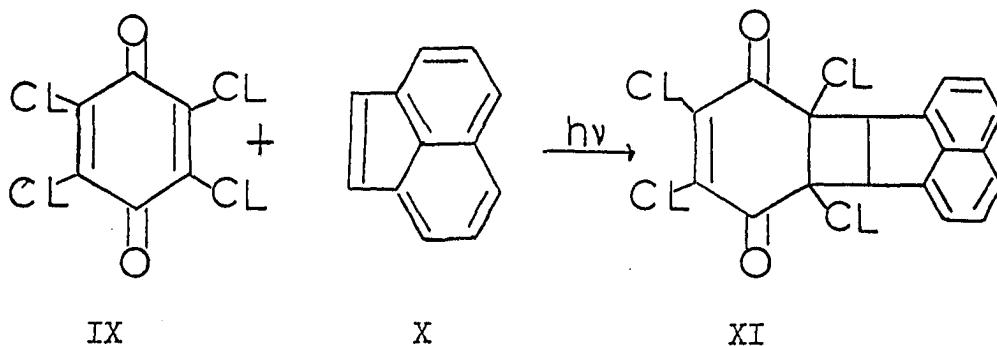
A final example of an intramolecular reaction is provided by Cookson et al. (4) in the irradiation of the Diels-Alder adduct (VII) of cyclopentadiene and benzoquinone into a "cage" photoisomer (VIII).



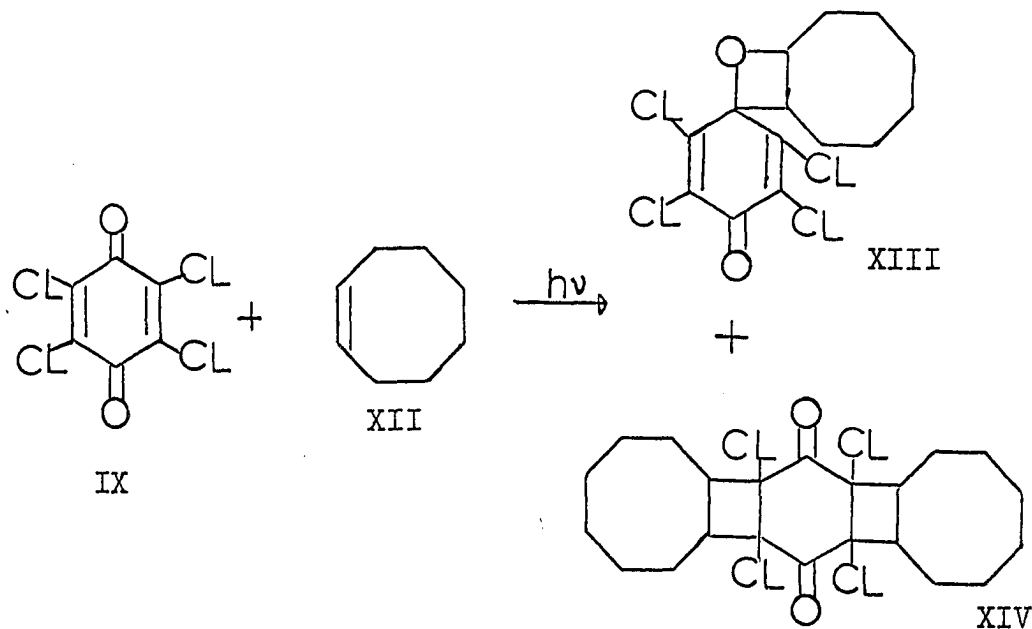
#### Photocycloaddition reactions of substituted benzoquinones

The first example of a photochemical cycloaddition reaction between a benzoquinone and an alkene was provided by Schenck (5) in the addition of chloranil (IX) to acenaphthylene

(X) to give photoaddition product XI.

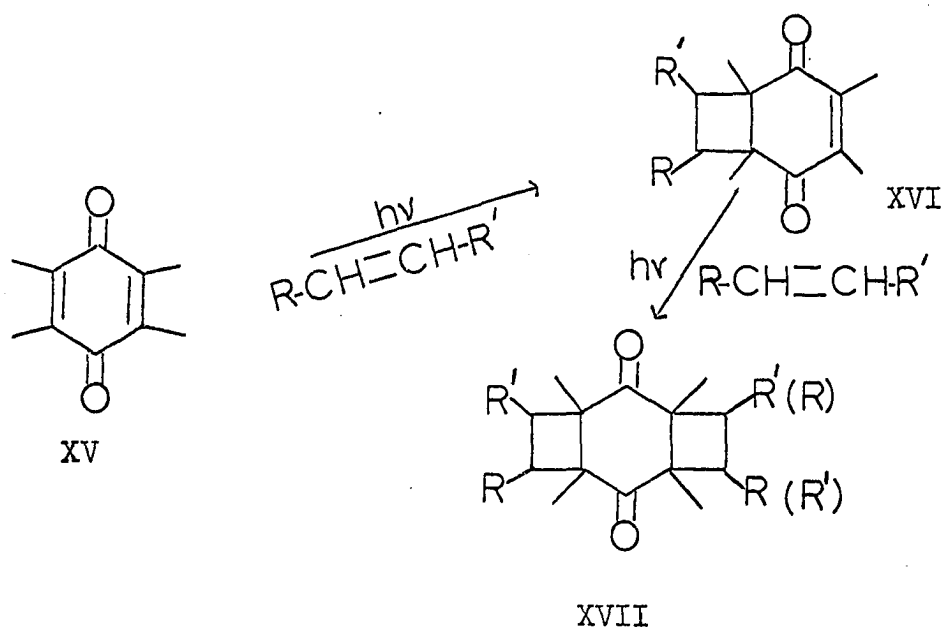


Choranil (IX) has recently been irradiated in excess cyclooctene (XII) by Bryce-Smith and Gilbert (6) to give photo-products XIII and XIV in approximately equal quantities.



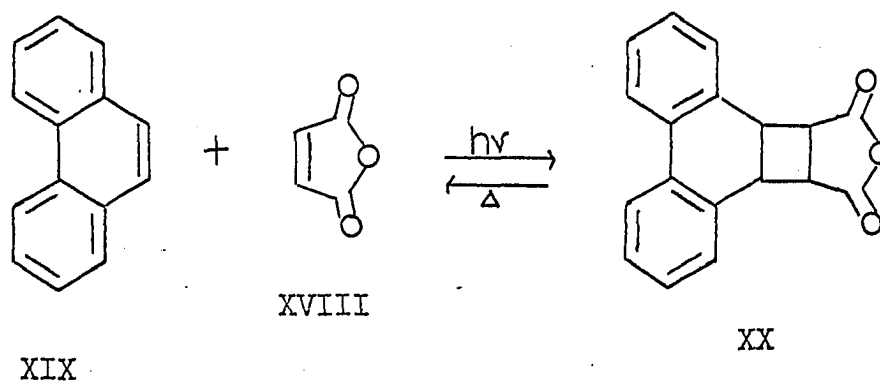
Schenck et al. (7) have irradiated 2,3,5,6-tetramethyl-1,4-benzoquinone (XV) in the presence of different alkenes to give both monoaddition (XVI) and diaddition products (XVII). Examples of alkenes that give monoaddition products (XVI) are acenaphthylene, vinylacetate, and isobutylene, while styrene, vinylacetate, and vinylethylether give diaddition products

(XVII).



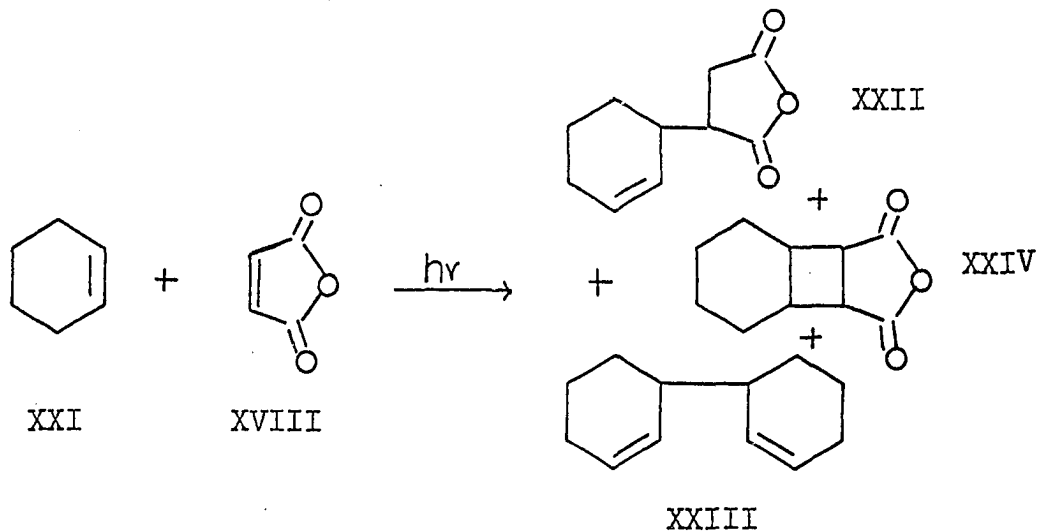
Photocycloaddition reactions of maleic anhydride and dimethyl maleate

The irradiation of maleic anhydride (XVIII) in the presence of phenanthrene (XIX) in hexane solution by Bryce-Smith and Vickery (8) gives photoaddition product XX, which goes back to the starting material after being heated at 300°.

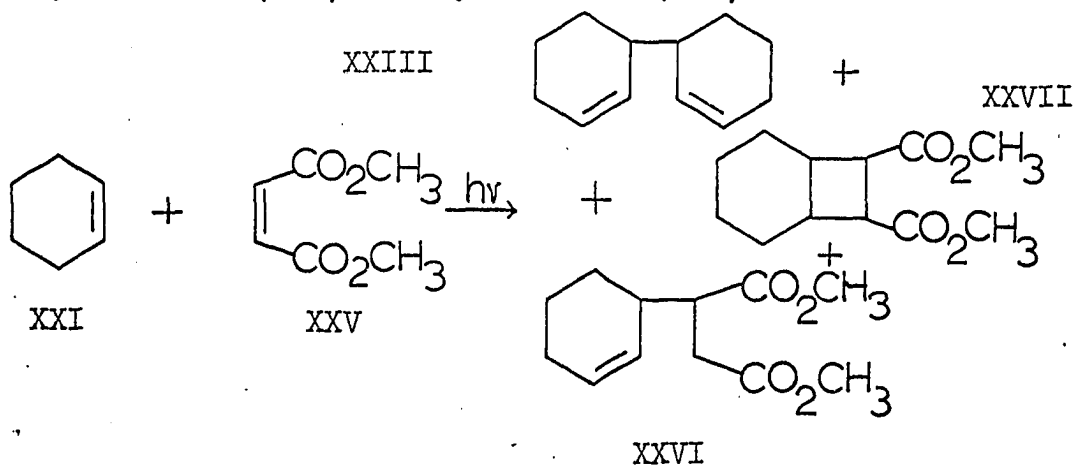


Barltrop and Robson (9) and Robson *et al.* (10) irradiated maleic anhydride (XVIII) and cyclohexene (XXI) to give cyclo-

hex-2-enylmaleic anhydride (XXII), bicyclohex-2-enyl (XXIII), and four isomers of bicyclo[4.2.0]octane-7,8-anhydride (XXIV).



They noted that maleic anhydride (XVIII) in the presence of cyclohexene (XXI) forms a charge transfer complex, whereas fumaronitrile, maleonitrile, and dimethyl maleate do not. Dimethyl maleate (XXV) and cyclohexene (XXI) have been irradiat-

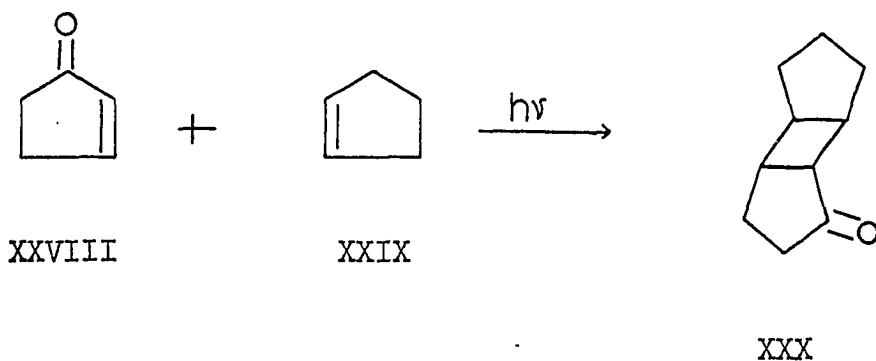


ed by deMayo et al. (11, 12) to give bicyclohex-2-enyl (XXIII), dimethyl cyclohex-2-enylsuccinate (XXVI), and four isomers of dimethyl bicyclo[4.2.0]octane-7,8-dicarboxylate (XXVII).

Photocycloaddition reactions of cyclic

$\alpha, \beta$ -unsaturated ketones

One of the first examples of an intermolecular photocycloaddition reaction of an  $\alpha, \beta$ -unsaturated ketone and an alkene is reported by Eaton (13). He irradiated 2-cyclopentenone (XXVIII) in excess cyclopentene (XXIX) in a Pyrex flask to give photoproduct XXX.

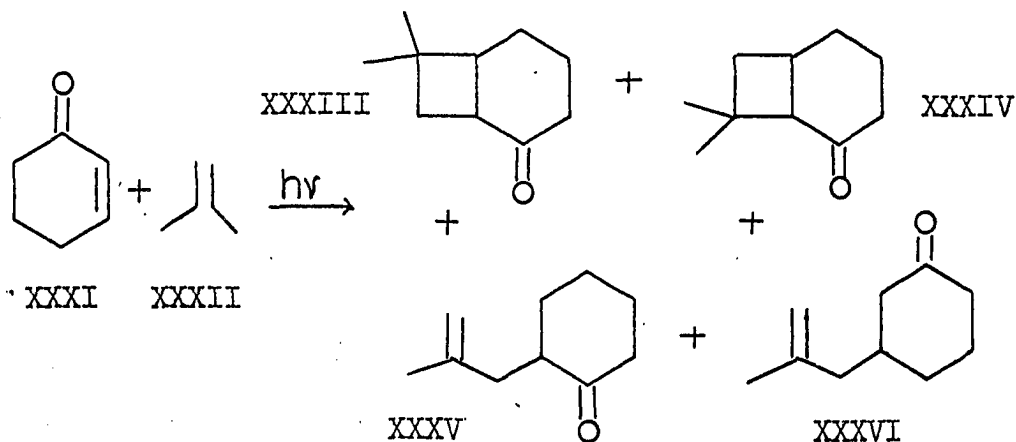


Saltiel (14) suggested that the photocycloaddition of  $\alpha, \beta$ -unsaturated ketones to alkenes is due to an excited triplet state rather than the lowest excited singlet state, since the irradiation of cyclohexenone in the presence of cyclopentadiene yields cyclopentadiene dimers as major products. He believes that the increased yield of cyclopentadiene

dimers is due to the higher triplet excitation energy of the cyclohexenone being transferred to the diene.

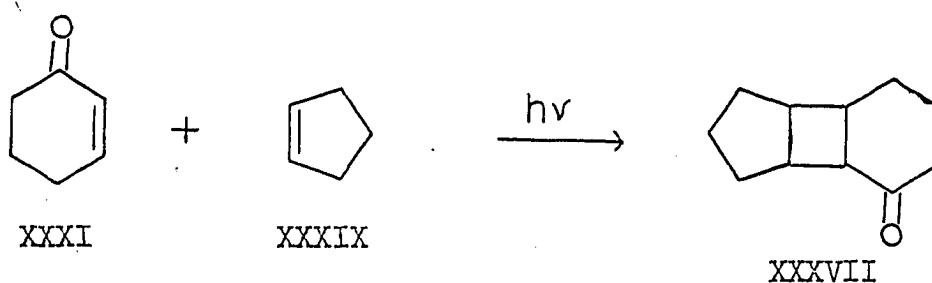
The photochemical reactions of 2-cyclohexenone and other conjugated enones with a variety of unsaturated substances have been investigated by Corey *et al.* (15, 16) to determine the scope, orientation, and stereochemistry of cyclophotoaddition. The occurrence of marked orientational specificity is confirmed, as is the frequent formation of a trans-fused ring system.

One example of this cycloaddition is the irradiation of 2-cyclohexenone (XXXI) and excess isobutylene (XXXII) in a Pyrex container immersed in a Dry Ice-ethanol bath. The photoproducts from this irradiation are trans- and cis-7,7-dimethylbicyclo[4.2.0]octan-2-one (XXXIII), 8,8-dimethylbicyclo[4.2.0]octan-2-one (XXXIV), 2-( $\beta$ -methylallyl)cyclohexanone (XXXV), and 3-( $\beta$ -methylallyl)cyclohexanone (XXXVI). The major product is trans-XXXIII which is formed in 26.5% yield, while the cis-XXXIII is produced in 6.5% yield. The



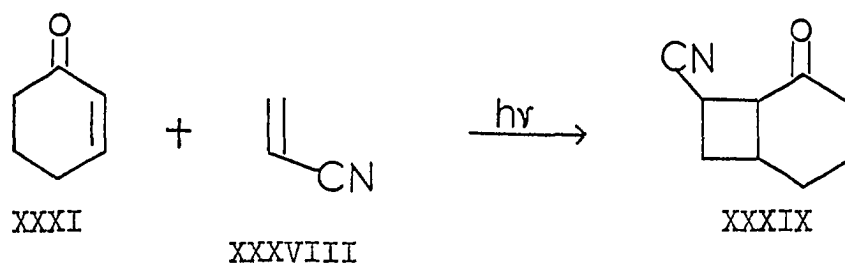
alternate cycloaddition product, 8,8-dimethylbicyclo[4.2.0]octan-2-one (XXXIV) is formed as a minor product (6%).

The photoaddition of 2-cyclohexenone (XXXI) to cyclopentene (XXXIX) by Corey *et al.* (15) gives two stereoisomeric derivatives (XXXVII) which differ in geometry of the 6-4 ring fusion.

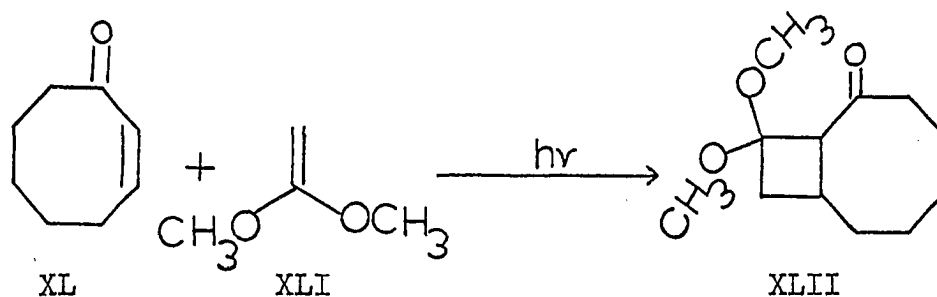


In the case of 2-cyclohexenone it appears that both orientational specificity and ease of reaction can be expected with olefins having electron supplying group(s) at the double bond. The dominant cycloaddition product is that in which the  $\alpha$ -carbon of the enone (electrophilic species) has attached itself to the carbon of the olefin which is most nucleophilic. The susceptibility of a number of olefinic substrates to attack by excited 2-cyclohexenone has been measured by competition experiments which establish the series: 1,1-dimethoxyethylene > methoxyethylene > cyclopentene > isobutylene >> acrylonitrile. Noteworthy features of the irradiation of 2-cyclohexenone (XXXI) with acrylonitrile (XXXVIII) are its relative slowness and the fact that the major product is 8-cyanobicyclo[4.2.0]octan-2-one (XXXIX).

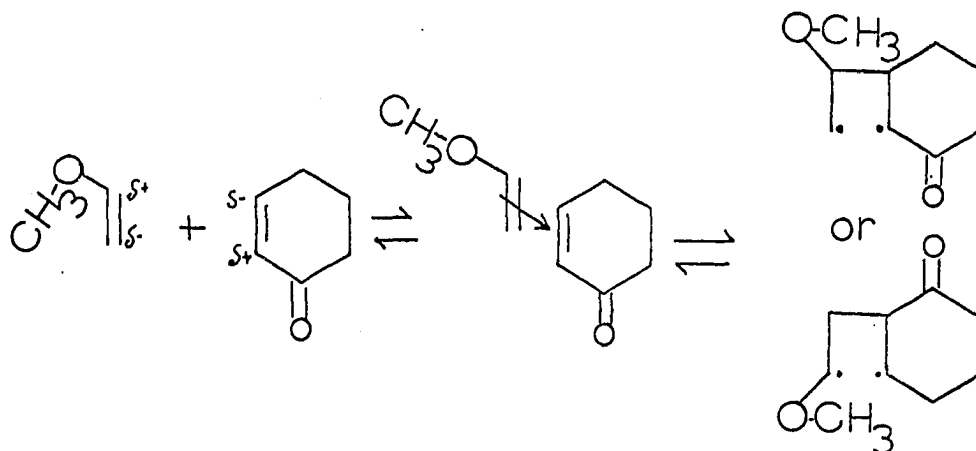
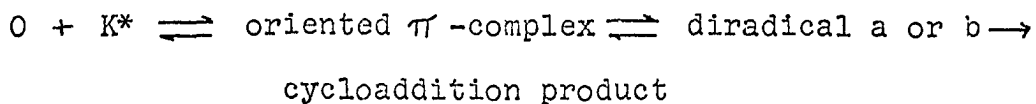




It was found by Corey *et al.* (15) that the irradiation of cis-2-cyclooctenone (XL) and 1,1-dimethoxyethylene (XLI) gave XLII by a different mode of addition. This difference was shown to be caused by a special reaction pathway for 2-cyclooctenone involving prior cis→trans isomerization of the ketone, followed by thermal cycloaddition. The irradiation of cis-2-cycloheptenone and dimethoxyethylene gave no 1:1 adduct, but only self-condensation of the ketone. It has been shown recently by Corey *et al.* (17) and Eaton and Lin (18) that the self-condensation of 2-cycloheptenone was due to prior cis→trans isomerization.

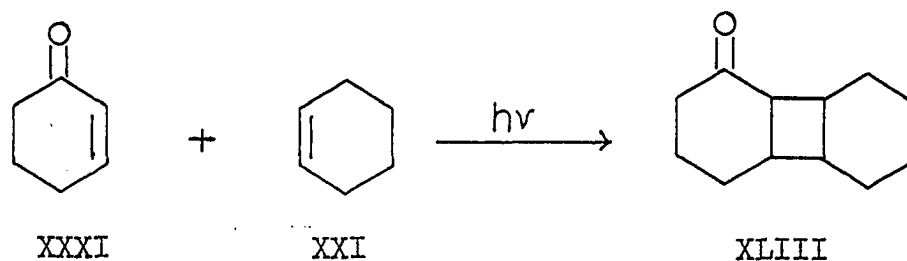


A hypothesis advanced by Corey *et al.* (15) to explain the observed orientational specificity, the stereochemistry of photoaddition, and the relative reactivity of different olefins (0) with the  $n, \pi^*$  excited state of 2-cyclohexenone ( $K^*$ ) is outlined as follows:



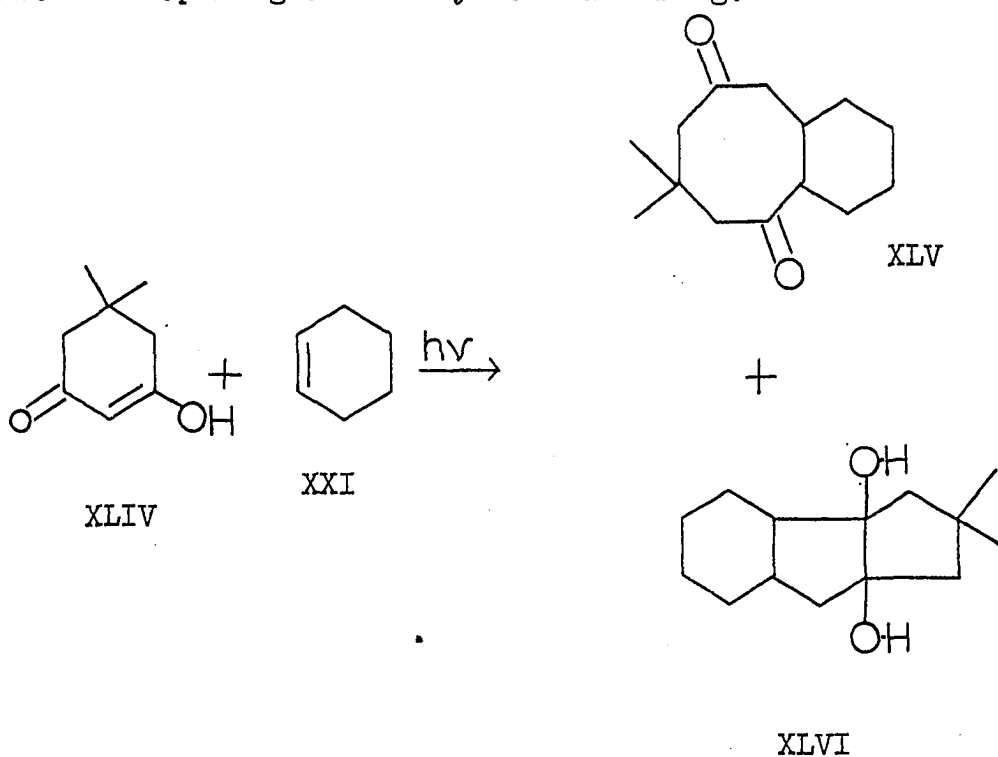
Corey et al. (15) believe that the excited state initially formed from 2-cyclohexenone is the  $n, \pi^*$  singlet, which is immediately transferred into the  $n, \pi^*$  triplet. They found no direct evidence for the formation of the  $n, \pi^*$  triplet.

Valentine et al. (19) irradiated 2-cyclohexenone (XXXI) in the presence of excess cyclohexene (XXI) in a Pyrex container to give a mixture of four isomers of cycloaddition product XLIII.



Photocycloaddition reactions of 1,3-diketones

The photocycloaddition reactions of 1,3-diketones or the enol acetates of 1,3-diketones with olefins by Hikino and deMayo (20) and deMayo *et al.* (21) are similar to the cycloaddition reactions of  $\alpha,\beta$ -unsaturated ketones. One example of the former is the irradiation of dimedone (XLIV) and cyclohexene (XXI) to give photoisomers XLV and XLVI, which result from the opening of the cyclobutane ring.

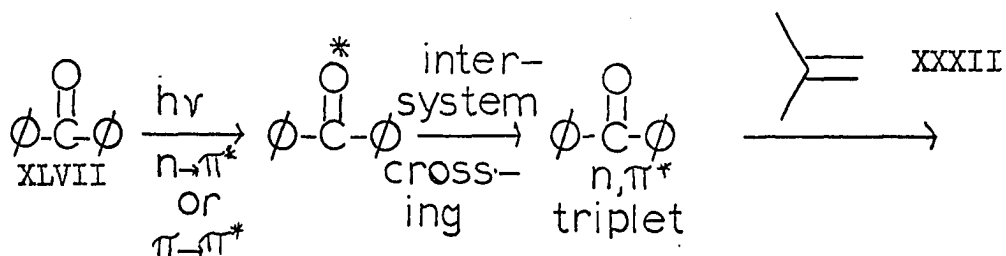


Photochemical dimerizations

Photochemical dimerizations of  $\alpha,\beta$ -unsaturated carbonyl groups have been known for some time (22-28), but they will not be discussed since they are not directly related to this study.

Formation of oxetanes

Oxetanes are formed in the irradiation of saturated ketones with olefins, as was originally reported by Paterno and Chieffi (29). The reaction has recently been reinvestigated by Büchi *et al.* (30). The investigation of the mechanism of oxetane formation, with particular regard to the character of the excited state involved, has more recently been carried out by Arnold *et al.* (31). They found that ketones that are not reduced upon irradiation in isopropyl alcohol do not form oxetanes in the presence of olefins. Observations by Yang (32) indicate that oxetane formation is due to a low-lying  $n, \pi^*$  triplet state of the carbonyl group. Arnold *et al.* (31) found



that when the triplet energy of the olefin is less than that of the carbonyl compound, triplet-triplet transfer can take place to the exclusion of oxetane formation. They feel that the formation of oxetanes will involve the preceding scheme,

as shown by the irradiation of benzophenone (XLVII) in the presence of isobutylene (XXXII) to form oxetane (XLIX). The major product (XLIX) is formed from the most stable diradical intermediate (XLVIII).

#### Summary of photocycloaddition reactions

A few examples have been given of the photocycloaddition reactions of benzoquinones, maleic anhydride, and dimethyl maleate with olefins. However, more pertinent to this study is the report by Eaton (13) of an intermolecular cycloaddition between 2-cyclopentenone (XXVIII) and cyclopentene (XXIX) to give photoproduct XXX. More recently, Corey *et al.* (15) irradiated 2-cyclohexenone (XXXI) in the presence of different alkenes. They conclude that the dominant cycloaddition product is that in which the  $\alpha$ -carbon of 2-cyclohexenone (electrophilic species) has attached itself to the carbon of the olefin which is most nucleophilic. Saltiel (14) suggested that the photocycloaddition of  $\alpha, \beta$ -unsaturated ketones is the result of an excited triplet state, since the irradiation of cyclohexenone (XXXI) in the presence of cyclopentadiene yields cyclopentadiene dimers as major products. Corey *et al.* (15) suggest that the cycloaddition reaction of cyclohexenone is due to an  $n, \pi^*$  triplet, but no evidence is given.

Recently, Hoffmann and Woodward (33) have developed selection rules for predicting thermal and photochemical reactions. Their procedure consists in the construction of cor-

relation diagrams for the molecular orbitals involved in the reaction, classifying the levels with respect to the symmetry elements of the transition state. The correlation diagram for 1,2-addition predicts a photochemical process; however, the selection rules need not apply to multistep cycloaddition reactions.

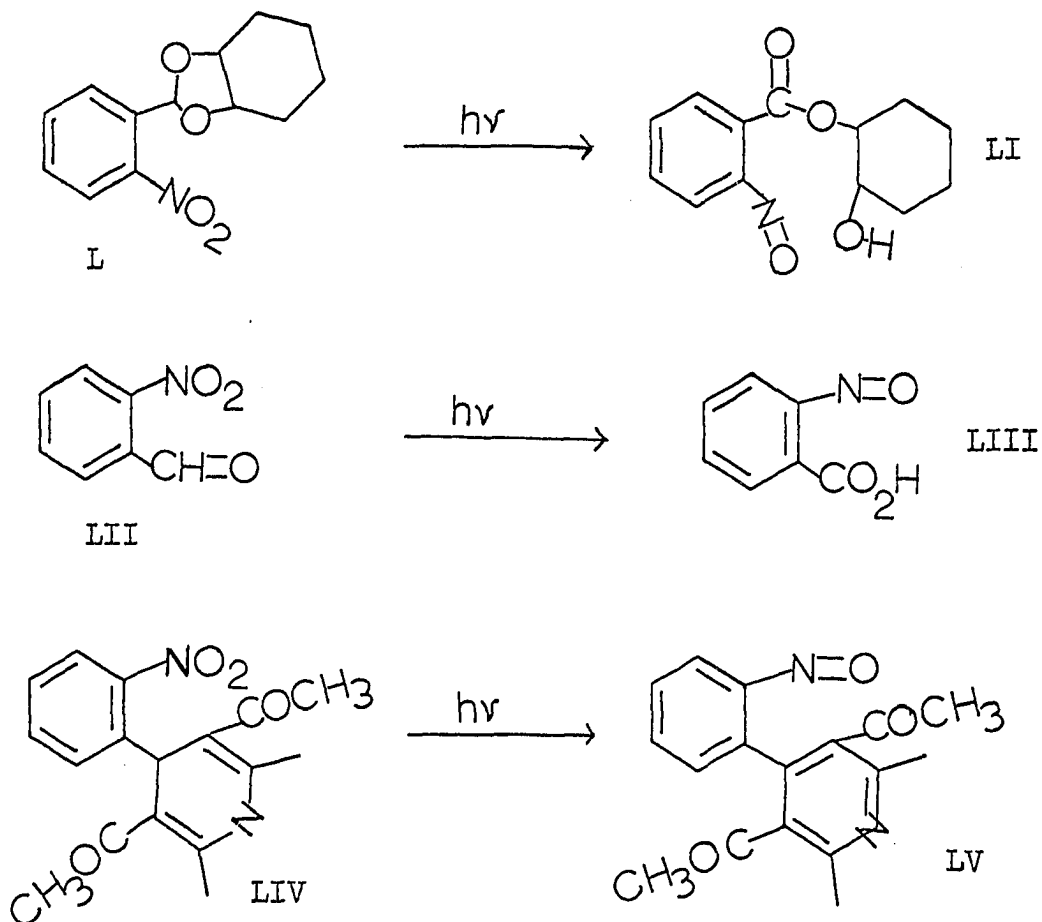
Oxetanes are formed in the irradiation of saturated ketones with alkenes. The major oxetane product is formed from the most stable diradical intermediate, according to Arnold *et al.* (31). They and Yang (32) conclude that the addition of the carbonyl group to an olefin to form an oxetane requires a low-lying  $n, \pi^*$  triplet.

### Photochemistry of Nitro Compounds

#### Irradiation of *o*-nitroaromatic compounds

Much work has been done on the irradiation of *o*-nitro compounds. One example is given by Tanasescu and Ionescu (34) in the irradiation of *o*-nitrobenzylidene-1,2-cyclohexanediol (L) to give photoproduct LI. Another example is given by Leighton and Lucy (35) in the irradiation of *o*-nitrobenzaldehyde (LII) to *o*-nitrosobenzoic acid (LIII). A more recent example of the irradiation of *o*-nitro compounds is given by Berson and Brown (36) in the irradiation of 2,6-dimethyl-3,5-diacetyl-4-(2'-nitrophenyl)-1,4-dihydropyridine (LIV) to 2,6-dimethyl-3,5-diacetyl-4-(2'-nitrosophenyl)pyridine (LV). The

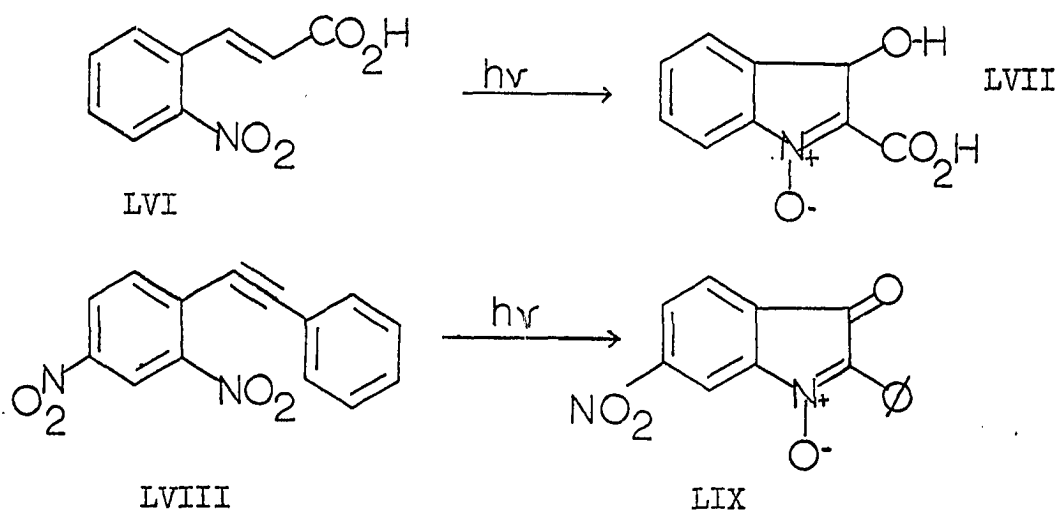
photolysis of each of the preceding o-nitroaromatic compounds involves an intramolecular attack of the nitro group on the ortho substituent, resulting in reduction of the nitro to a nitroso group and oxidation of the ortho substituent.



Irradiation of aromatic nitro compounds containing unsaturated o-substituents

Irradiation of a nitro group, ortho, to an ethylenic linkage gives a different product, as shown by Tanasescu (37) in the irradiation of o-nitrocinnamic acid (LVI) to hydroxyisato-genic acid (LVII). A related photochemical reaction is the photolysis of 2,4-dinitrotolane (LVIII) to 6-nitro-2-phenyl-

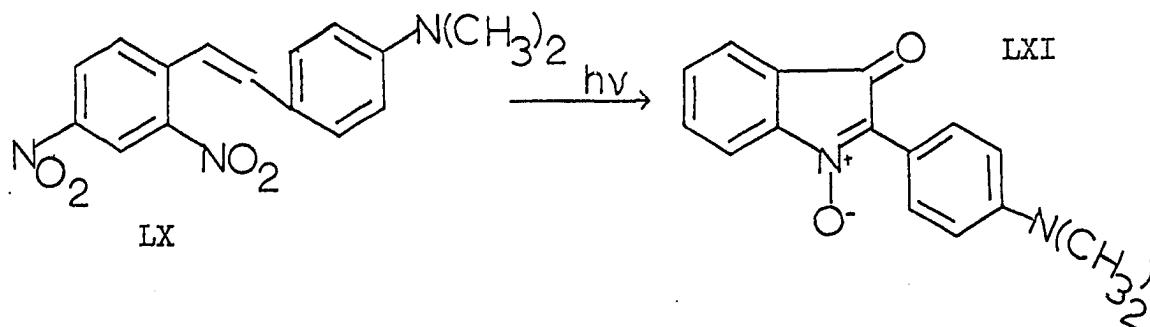
isatogenin (LIX) by Pfeiffer and Kramer (38).



Splitter and Calvin (39) irradiated a number of substituted nitrostilbenes. If the nitro group is placed in the para-position of the stilbene, only trans- to cis- isomerization results, but if the stilbene is substituted in the ortho-position by a nitro group, a new photoproduct results. One example is the photolysis in benzene of 4'-dimethylamino-2,4-dinitrostilbene (LX) to isatogen (LXI). It was suggested by Splitter and Calvin (39) that the photochemical reaction is in two phases. The first phase is the disappearance of the stilbene by the absorption of light, while the second phase is a thermal dark reaction. At least two intermediates are apparent in the spectroscopic study of the dark reaction.

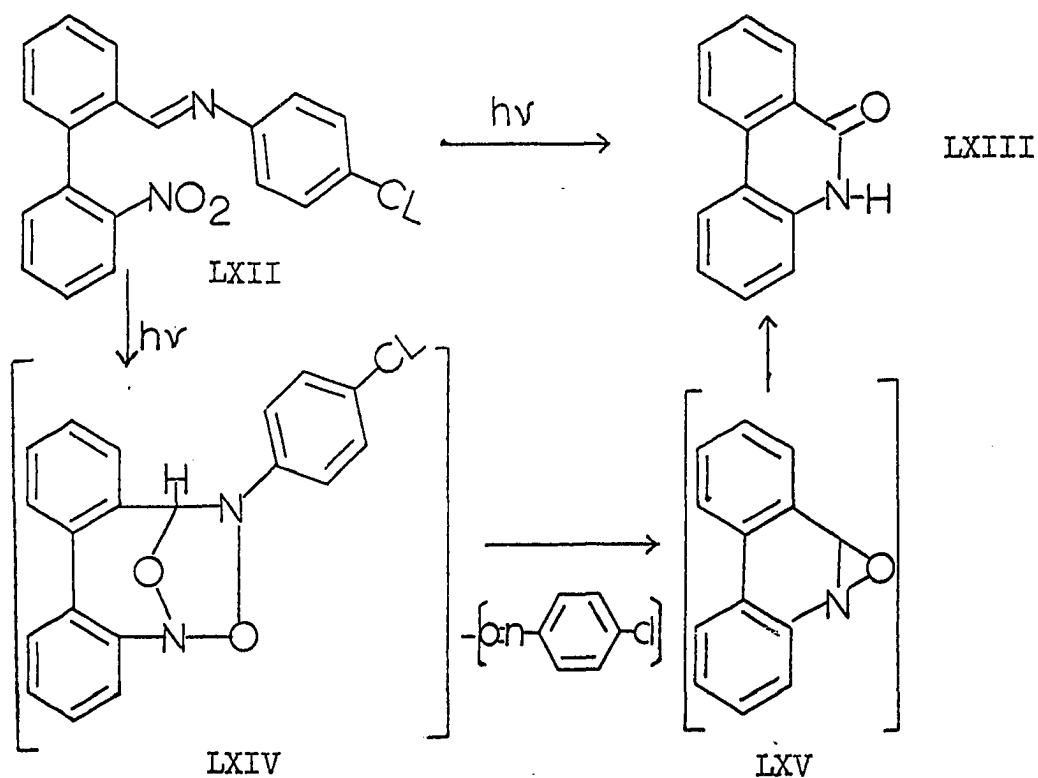
The photolysis of each of the preceding o-nitro compounds involves an attack of the nitro group on the unsaturated group in the ortho position to form an isatogen.





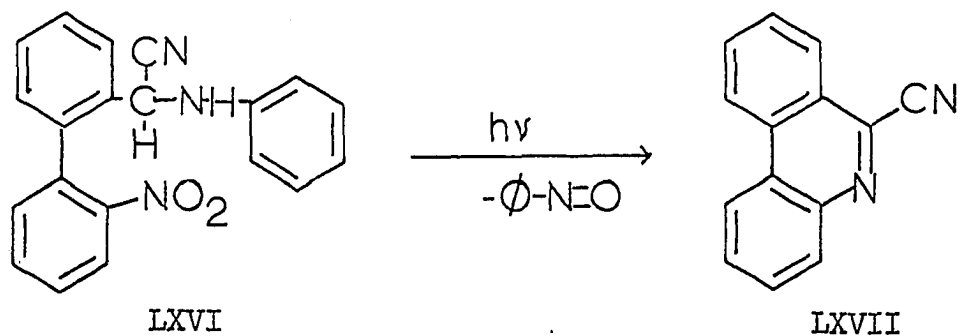
Irradiation of *ortho,ortho'*-disubstituted biphenyls

An example of photochemical interactions in *ortho,ortho'*-disubstituted biphenyls is given by Taylor *et al.* (40). Their irradiation of the *p*-chlorophenylanil of *o*-nitro-*o'*-formylbi-



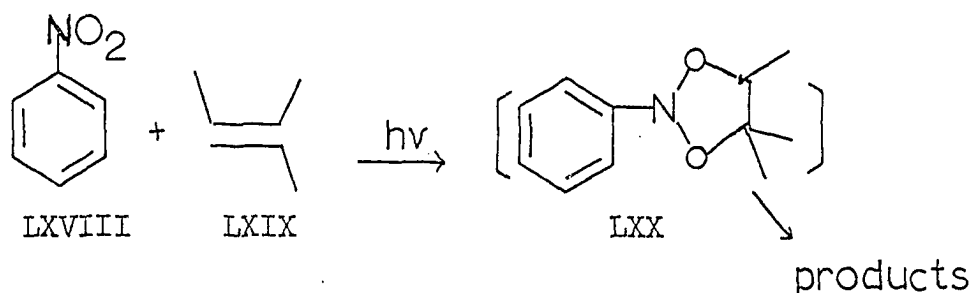
phenyl (LXII) in ethanol solution results in formation of 5(6H)-phenanthridone (LXIII). The favored mechanism is cycloaddition of the nitro group to the anil ( $C=N$ ) bond to give 1,3,2-dioxazolidine (LXIV). Subsequent collapse of this intermediate with loss of p-chloronitrosobenzene could lead to oxaziridine (LXV), which then proceeds to photoproduct LXIII.

Taylor *et al.* (40) also irradiated o-(cyanoanilinomethyl)-o'-nitrobiphenyl (LXVI) to give 6-cyanophenanthridine (LXVII). The conversion is thought to proceed by an initial abstraction of hydrogen, by the nitro group, from the methyl group on the opposite ortho-position of LXVI, followed by electron pairing, dehydration, and elimination of nitrosobenzene. It can be seen from the work of Taylor *et al.* (40) that a group in an ortho'-position of an o-nitrobiphenyl is susceptible to attack, as is the group in the ortho-position of an o-nitroaromatic compound.



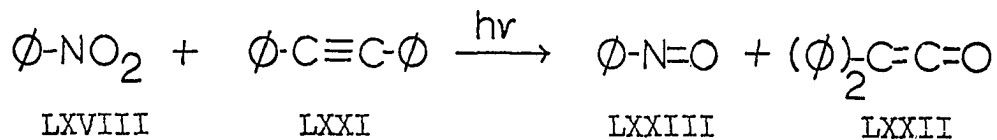
Irradiation of nitrobenzene in the presence of alkenes and alkynes

An example of an intermolecular attack of an aromatic nitro group on an unsaturated group is given by Büchi and Ayer (41) in the irradiation of nitrobenzene (LXVIII) and 2-methylbutene (LXIX) to give azobenzene, N-phenylacetamide, acetone, and acetaldehyde. These products can be rationalized in terms of an intermediate (LXX) that is analogous to the intermediate (LXIV) proposed by Taylor *et al.* (40).

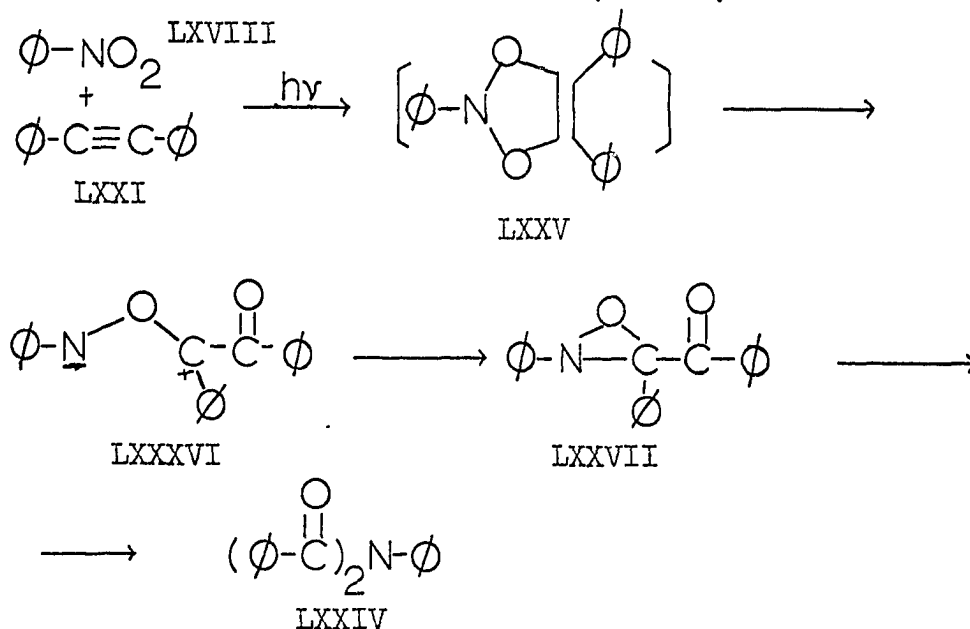


Another example of an irradiation of nitrobenzene with an unsaturated group is given by Scheinbaum (42) in the irradiation of nitrobenzene (LXVIII) in the presence of diphenylacetylene (LXXI). Diphenylketene (LXXII) is postulated as an intermediate in the formation of benzophenone anil, carbon dioxide, and the  $\beta$ -lactam of N-phenyl- $\beta$ -aminotetraphenylpropionic acid. Scheinbaum (42) proposed that the diphenylketene (LXXII) is formed by transfer of an oxygen atom from the nitro group of LXVIII to the acetylenic carbon, followed by cleavage of nitrosobenzene (LXXIII) and migration of a phenyl group. He also postulated that formation of dibenzanilide

(LXXIV) proceeds through an unstable 1,3,2-dioxazole (LXXV), which can cleave at one of the weak O-N bonds to form zwitterion (LXXVI). The unstable LXXV is similar to intermediate

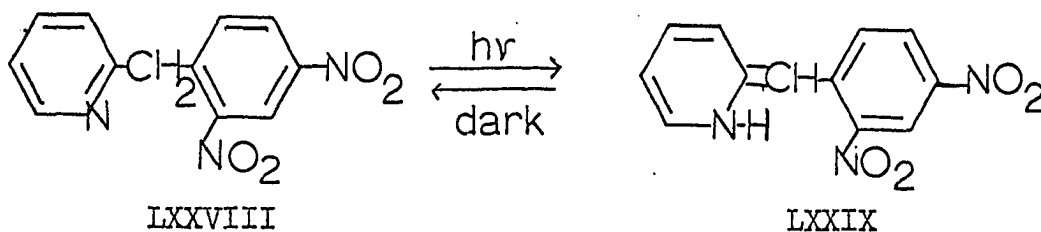


LXX proposed by Büchi and Ayer (41). The zwitterion (LXXVI) is then capable of rearranging to dibenzanilide (LXXIV) through the oxazirone intermediate (LXXVII).



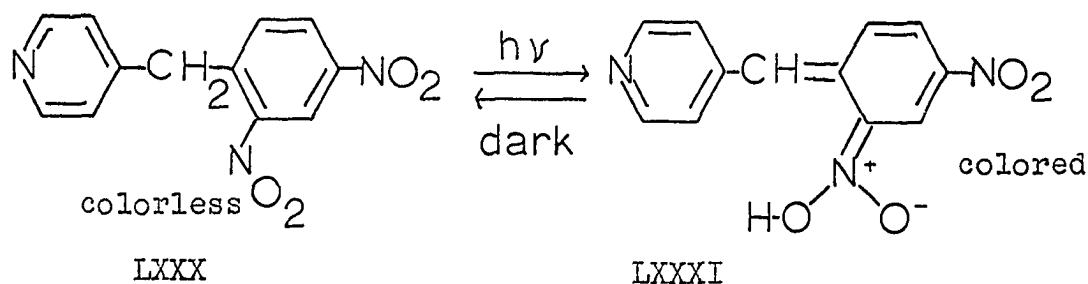
### Photochromism of aromatic nitro compounds

Photochromism of an ortho substituted nitro compound was



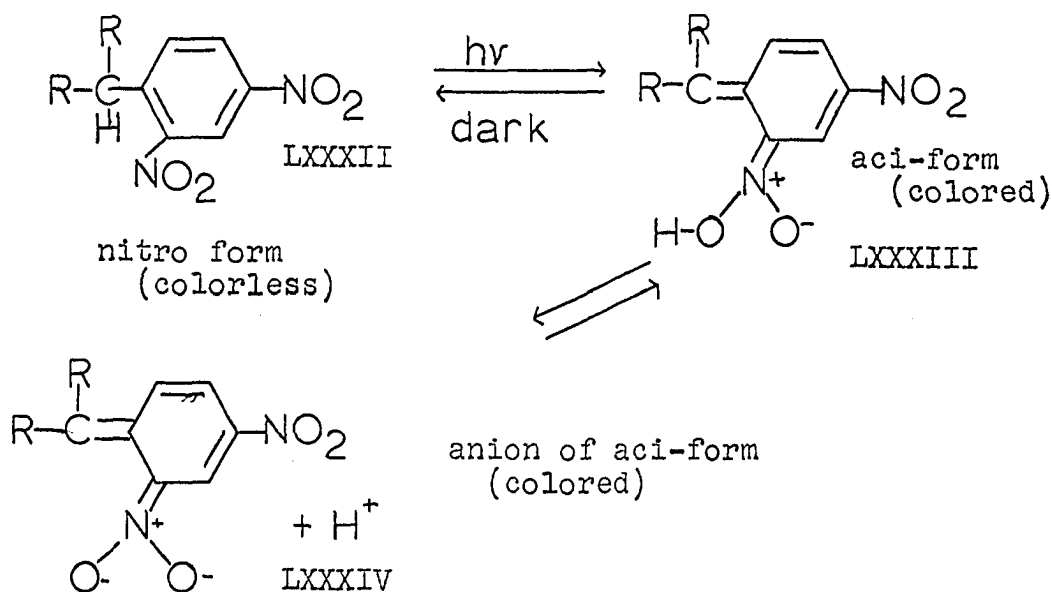
first reported by Tchitchibabine *et al.* (43) for the photo-induced isomerization of crystalline 2-(2',4'-dinitrobenzyl)-pyridine (LXXVIII). They proposed the above tautomeric equilibrium of LXXVIII to LXXIX.

Mosher *et al.* (44) found that 4-(2',4'-dinitrobenzyl)-pyridine (LXXX) undergoes a colorless to deep violet conversion analogous to that of the above isomer (LXXVIII). They postulated the alternative mechanism (LXXX  $\rightarrow$  LXXXI) involving hydrogen transfer from the methylene group to the *o*-nitro group via a six-membered ring.



Recently, Margerum *et al.* (45) investigated a number of nitrobenzyl derivatives (LXXXII) in an attempt to clarify the mechanism of photochromic isomerization. They concluded that a) a pyridyl group was not necessary for photochromic activity in the nitrobenzylpyridine type systems, and b) a nitro group ortho to an acidic hydrogen on a tertiary carbon atom, or a methylene group on the same phenyl, appears to be a key requirement for photochromic activity. Their results are entirely consistent with a hydrogen transfer photochemical mechanism, producing a planar aci-form (LXXXIII) in equilibrium

with its anion (LXXXIV). A more general form for this transformation can be written in which  $R_1$  may be H,  $C_6H_5^-$ , or  $CH_3$ , etc.  $R_2$  may be a substituent which increases the ionizing ability of the C-H group without interfering with the light absorption of the 2,4-dinitrophenyl moiety and which becomes conjugated with the aci form.



Photochemistry of 2,3-dimethyl-1-nitronaphthalene and 9-nitroanthracene

Chapman et al. (46) irradiated a sample of 2,3-dimethyl-1-nitronaphthalene in a solution of acetone or 95% ethanol to give 2,3-dimethyl-1,4-naphthoquinone. Examination of literature for analogous transformations gives reports of photo-oxidation of 9-nitroanthracene (LXXXV) to anthraquinone (LXXXVI) and 9-nitroanthrone (LXXXVII) by Dufraisse and Priou (47) and Battegay et al. (48). It has been suggested by

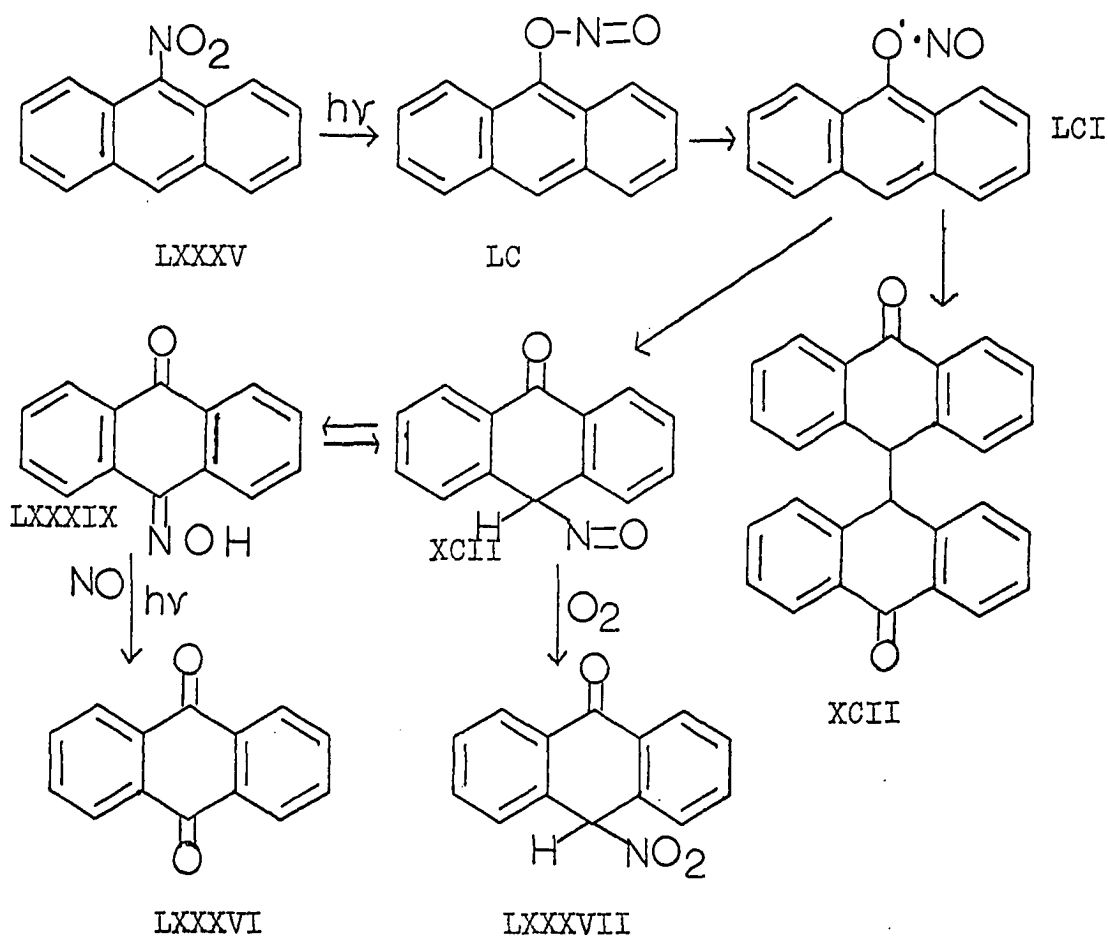
Dufraisse and Priou (47) that a peroxide is an intermediate in the production of LXXXVI and LXXXVII. More recently, it has been reported by Greene (49) that 9-nitroanthracene on irradiation with light of wavelength 420-530  $\mu$  gives the photodimer, while light of 370-410  $\mu$  gives 10,10'-bianthrone (LXXXVIII) and nitrogen (II) oxide.

It was found by Chapman et al. (46) that the photo-oxidation of 2,3-dimethyl-1-nitronaphthalene and 9-nitroanthracene (LXXXV) to 2,3-dimethyl-1,4-naphthoquinone and anthraquinone (LXXXVI) does not require oxygen, but proceeds smoothly in degassed solutions; therefore, a peroxide intermediate can be excluded.

Irradiation of 9-nitroanthracene (LXXXV) for short periods with a continuous nitrogen flush gives nitrogen (II) oxide, anthraquinone (LXXXVI, 13%), 10,10'-bianthrone (LXXXVIII, 48%) and anthraquinone mono-oxime (LXXXIX, 30%). Irradiation of LXXXV, with nitrogen oxide bubbling through the solution, gives a substantially greater yield (77%) of anthraquinone at the expense of 10,10'-bianthrone (9%).

The results can be understood, according to Chapman et al. (46), by the following mechanistic path. Photoisomerization of the nitro compound gives the nitrite ester (XC), which can decompose thermally or photochemically to the 9-anthroxy radical (XCI) and nitrogen (II) oxide. Dimerization of two 9-anthroxy radicals would give 10,10'-bianthrone (LXXXVIII), while addition of nitrogen (II) oxide to XCI

would give nitrosoketone (XCII). Oxidation of XCII (in experiments in which oxygen is present) could give the 9-nitroanthrone (LXXXVII) reported by Dufraisse and Priou (47). Isomerization of the nitrosoketone would give anthraquinone mono-oxime (LXXXIX). Irradiation of LXXXIX gives anthraquinone (LXXXVI).



Evidence for formation of a nitrite ester from a nitro compound is given by Brown and Pimentel (50) in the photolysis of nitromethane in a solid argon matrix. They postulate the primary process to be an isomerization to methyl nitrite,



which undergoes secondary photolysis. More recently, Rebbert and Slagg (51) have irradiated nitromethane and nitroethane in liquid and gaseous phases. The primary process is given as photochemical decomposition of nitromethane to a methyl radical and nitrogen dioxide, followed by recombination of the radicals to form either the starting material or methyl nitrite.

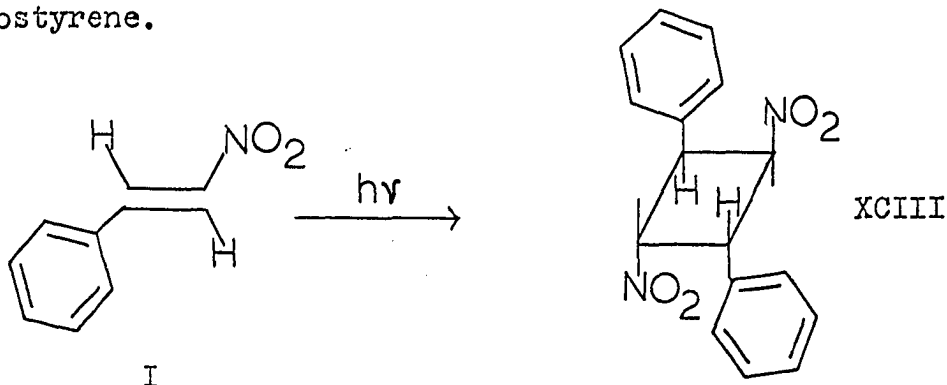
#### Irradiation of $\beta$ -nitrostyrene

Dipole moment studies on crystalline (m.p. 57-58°)  $\beta$ -nitrostyrene (I) by Vasil'eva et al. (52) and Goebel and Wenzke (53) have shown that it is in the trans-form. Ultra-violet studies by Skulski and Plenkiewicz (54) have placed the nitro and phenyl groups trans to each other, both in crystalline  $\beta$ -nitrostyrene and crystalline  $\beta$ -methyl- $\beta$ -nitrostyrene. Nuclear magnetic resonance studies on crystalline  $\beta$ -nitrostyrene by the author have also shown that it is in the trans-form.

Trans- $\beta$ -nitrostyrene has been irradiated in benzene solution in the presence of oxygen by Ried and Wilk (55) to give an amorphous polymer. Dudinskaya et al. (56) irradiated trans- $\beta$ -nitrostyrene to cis- $\beta$ -nitrostyrene. The experimental proof of this conversion centers on two points: 1) the absorption of an infrared band at 945-970  $\text{cm}^{-1}$  is decreased, while a weak band appears at 805  $\text{cm}^{-1}$ , and 2) a 62% yield of 2-nitro-3-phenylbicyclo[2.2.1]hept-5-ene is formed when cyclo-

pentadiene is added to a solution of irradiated trans- $\beta$ -nitrostyrene as soon as the light source is removed. A similar solution of trans- $\beta$ -nitrostyrene that had not been irradiated did not react appreciably in the same length of time. It has been reported by Dudinskaya *et al.* (56) that the cis- $\beta$ -nitrostyrene reverts back to trans- $\beta$ -nitrostyrene in approximately twelve hours; however, the work of Lenz (57) has shown that a mixture of cis- and trans- $\beta$ -nitrostyrene can last a week without substantial change in the ultraviolet spectrum.

More recently, Miller and Shechter (58) have irradiated solid trans- $\beta$ -nitrostyrene (I) to give 1,trans-3-dinitro-cis-2,trans-4-diphenylcyclobutane (XCIII). Their irradiation of trans- $\beta$ -nitrostyrene in solution gives only cis- $\beta$ -nitrostyrene.



No evidence is available on the emission spectra of  $\beta$ -nitrostyrenes, but it is known that aromatic nitro compounds show both phosphorescence and fluorescence. Evidence for phosphorescence of a number of aromatic nitro compounds such as  $\alpha$ -nitronaphthalene,  $\alpha$ -nitrofluorene, and 1,5-dinitronap-

thalene is given by Lewis and Kasha (59) and McClure (60). The phosphorescence of aromatic nitro amines has been studied by Foster et al. (61). Lippert (62, 63) has studied the fluorescence of nitroaromatic compounds.

#### Summary of the photochemistry of nitrocompounds

The photochemistry of the o-nitroaromatic compounds given in the first examples involves an intramolecular attack of the nitro group on the ortho substituent, resulting in reduction of the nitro to a nitroso group and oxidation of the ortho substituent. An example is the photolysis of o-nitrobenzaldehyde (LII) to o-nitrosobenzoic acid (LIII). Irradiation of a nitro group, ortho, to an ethylenic linkage gives a different product, as shown by Splitter and Calvin (39) in the irradiation of 4'-dimethylamino-2,4-dinitrostilbene (LX) to isatogen (LXI). An unsaturated group in an ortho' position of an o-nitrobiphenyl can be attacked by the nearby o-nitro group, as shown by Taylor et al. (40) in the irradiation of the p-chlorophenylanil of o-nitro-o'-formylbiphenyl (LXII) to give 5(6H)-phenanthridone. The favored mechanism is cycloaddition of the nitro group to the anil (C=N) bond to give 1,3,2-dioxazolidine (LXIV).

An example of an intermolecular attack of an aromatic nitro group on an unsaturated group is given by Büchi and Ayer (41) in the irradiation of nitrobenzene (LXVIII) and 2-methylbutene (LXIX). The products can be rationalized in

terms of an intermediate (LXX) which is reminiscent of the intermediate (LXIV) proposed by Taylor *et al.* (40). Nitrobenzene (LXVIII) also reacts with diphenylacetylene (LXXI) to give a number of products (42).

The irradiation of 9-nitroanthracene (LXXXV) to give anthraquinone (LXXXVI), 10,10'-bianthrone (LXXXVIII), and anthraquinone mono-oxime (LXXXIX) is a different type of photoreaction. The products are understood by Chapman *et al.* (46) to result from an initial photoisomerization of the nitro compound to give the nitrite ester (XC). Evidence for formation of a nitrite ester from a nitro compound is given (50, 51) in the photolysis of nitromethane.

Trans- $\beta$ -nitrostyrene has been irradiated in solution by Dudinskaya *et al.* (56) to give a mixture of cis- and trans- $\beta$ -nitrostyrene. More recently, Miller and Shechter (58) have irradiated solid trans- $\beta$ -nitrostyrene to give 1,trans-3-dinitro-cis-2,trans-4-diphenylcyclobutane (XCIII).

## RESULTS

## Irradiations

Methods

The irradiations to be discussed in this thesis were run using a Hanovia Type A 500-watt mercury arc lamp (lamp emission is primarily at 313 and 366  $\mu$  (64)) in a Pyrex immersion well, unless otherwise noted. A drawing of the immersion well is shown in Figure 1, page 32. The Pyrex vessel used cuts off about 90% of the light at 300  $\mu$  and approximately 100% by 290  $\mu$  (65). The irradiations of trans- $\beta$ -nitrostyrene (I) were carried out by dissolving I in either excess olefin or a mixture of olefin and a hydrocarbon solvent such as hexane or pentane. The irradiation solutions were stirred magnetically and cooled with tap water, while a slow stream of nitrogen was bubbled through them.

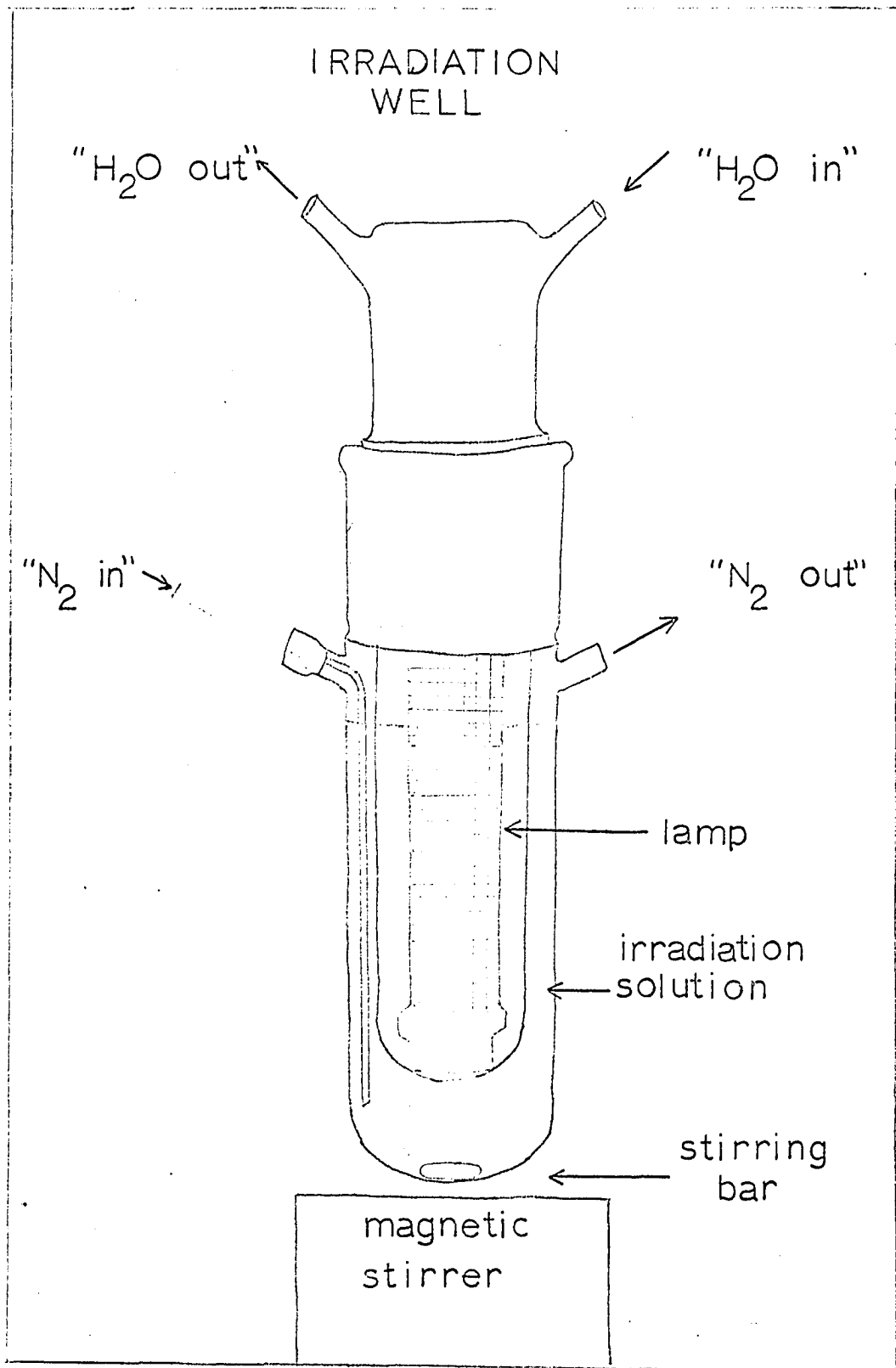
The trans- $\beta$ -nitrostyrene gives an intense ( $\epsilon = 17,700$ ) high wavelength absorption maximum at 298  $\mu$  (cyclohexane), which is a complex absorption made up of  $n-\pi^*$  and either  $\pi-\pi^*$  or charge transfer transitions.

The photoproducts were characterized by loss of the nuclear magnetic resonance absorption between 2.20 and 3.50 p.p.m.<sup>1</sup> for the olefinic protons of cis- and trans- $\beta$ -nitrostyrene and gave new infrared absorptions at approximately

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<sup>1</sup>The nuclear magnetic resonance positions are given in p.p.m. on the  $\tau$  (Tau) unit scale (66). Splitting values given in this discussion are accurate to 0.5 c.p.s.

Figure 1. Immersion well



6.46 and 7.29  $\mu$  which are assigned to the asymmetric and symmetric stretching of a nitro group on a saturated carbon (67, p. 68). The photoproducts showed loss of the intense ultraviolet absorption at 298  $\mu$  for trans- $\beta$ -nitrostyrene and gave absorptions between 250 and 270  $\mu$  ( $\epsilon = 200-2700$ ) typical for a phenyl group on a saturated carbon (67, p. 100). Each photoproduct also gave an acceptable elemental analysis for a 1:1 adduct.

A Nef reaction was run on some of the photocycloaddition products, according to the methods of Hawthorne (68), Noland et al. (69) and Wildman and Wildman (70), to further characterize them. The salts of secondary nitro compounds are hydrolysed to ketones under the conditions of the Nef reaction (71). However, no substituted cyclobutanones were separated from the Nef reactions run on the photoproducts, although the infrared spectra of the crude products shows an absorption near 5.63  $\mu$ , which is characteristic of cyclobutanones (72, p. 42).

Pyrolysis of some of the cycloaddition products was carried out in an attempt to further characterize them. Two photoproducts, 2,3,3-triphenyl-1-nitrocyclobutane (XCIV) and 2,3-diphenyl-1-nitrocyclobutane (XCV), gave  $\beta$ -nitrostyrene on pyrolysis.

The photoproducts were deuterated in order to simplify their nuclear magnetic resonance spectra. The deuterations were carried out by dissolving the photoproduct in deuterio-



methanol in the presence of sodium methoxide. In each case, the nuclear magnetic resonance spectra showed loss of the proton alpha to the nitro group.

All of the photocycloaddition products formed from β-nitrostyrene and olefin which are discussed in this volume were reacted with sodium methoxide in absolute methanol under the same conditions as the deuterations. The nuclear magnetic resonance and infrared spectra of the products from these reactions were always identical to those of the starting materials. Even if the photoproducts contained two isomers, the products from the reaction with base remained the same. In the reaction of sodium methoxide with the photoaddition products, a thermodynamic equilibrium is established which should give the most stable isomer(s) on addition of water to the reaction mixture. Examination of Framework Molecular Models of all the substituted β-phenyl-α-nitrocyclobutanes discussed in this thesis reveals that more steric repulsion will result if the nitro and adjacent phenyl groups are cis. Therefore, the nitro and phenyl groups must be trans in all the substituted β-phenyl-α-nitrocyclobutanes. The large coupling constants between the protons alpha to the nitro and adjacent phenyl groups are in accord with this assignment.

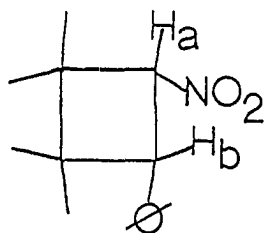
The two isomeric photoproducts from the irradiation of trans-β-nitrostyrene in styrene were completely degraded by Lenz (57). This degradation established the structure and stereochemistry of these isomeric photoproducts.

Additions to symmetrically substituted olefins

Trans- $\beta$ -nitrostyrene was irradiated in tetramethylethylene. The crude irradiation product was chromatographed on silica gel. Elution with 9:1 Skelly B-benzene gave white crystals of "Unknown A" (m.p. 80-81.5°) in a trace amount. The infrared spectrum (KBr) shows absorption at 6.25, 6.70, 6.88, 7.27, 13.17 and 14.32  $\mu$  (Figure 21, page 106). The nuclear magnetic resonance spectrum (Figure 10, page 72) shows absorption signals at 2.93 and 3.02 p.p.m., 4.68 p.p.m. (a very broad triplet), 6.38 p.p.m. (multiplet), and 8.30 to 8.60 p.p.m. (multiplet), which integrate 5:1:1:6. The elemental analysis for "Unknown A" gives carbon (90.66%) and hydrogen (9.29%).

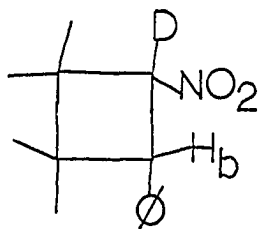
Continued elution with 3:1 Skelly B-benzene gave a colorless liquid, 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI, 58.7%). XCVI shows absorption in the ultraviolet at  $\lambda$   $\begin{matrix} 95\% \text{ EtOH} \\ \text{max} \end{matrix}$  248s (407), 253.5 (398), 259.5 (407), 265 (347) and 269  $\mu$  (295). The infrared spectrum (neat) gives absorption at 6.23, 6.48, 6.66, 7.30, 13.48 and 14.31  $\mu$  (Figure 18, page 100).

The nuclear magnetic resonance spectrum of photoproduct XCVI is shown in Figure 2, page 46. A nine proton triplet at 8.85 p.p.m. is assigned to three methyl groups, while the remaining methyl group is a three proton singlet at 9.37 p.p.m. The methyl group at 9.37 p.p.m. is assigned to one of the methyl groups next to the phenyl group, since an equiv-



XCVI

alent high field methyl appears in the nuclear magnetic resonance spectrum of 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII, Figure 7, page 66). The two small absorptions at 8.17 and 8.43 p.p.m. (0.7 proton) are due to impurities. A one proton doublet centered at 5.19 p.p.m. is assigned to the proton alpha to the nitro group,  $H_a$ , while the proton adjacent to the phenyl group,  $H_b$ , appears as a doublet centered at 6.10 p.p.m. Double resonance studies definitely establish that the proton at 6.10 p.p.m. is benzylic. Protons  $H_a$  and  $H_b$  make up an AB spin system ( $J = 10$  c.p.s.). The five aromatic protons are centered at approximately 2.85 p.p.m.



XCVIII

Deuteration of photoproduct XCVI gives 1,1,2,2-tetra-

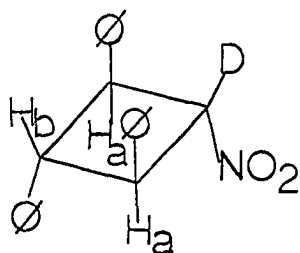
methyl-4-phenyl-3-deuterio-3-nitrocyclobutane (XCVIII; 6.23, 6.50, 6.66 and 7.29  $\mu$ ). The nuclear magnetic resonance spectrum of the deuteration product (XCVIII, Figure 2, page 46) shows weak absorption at 5.19 p.p.m. The proton alpha to the phenyl group is a broad singlet at 6.11 p.p.m. The rest of the spectrum is the same as photoproduct XCVI.

Since the reaction of sodium methoxide in methanol with 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI), under conditions identical to those for deuteration, gives only starting material, the nitro and phenyl groups must be trans.

An attempt to oxidize photoproduct XCVI to a substituted cyclobutane (73) by stirring the potassium salt with potassium permanganate gave only starting material. A free radical bromination of the photoproduct was attempted using N-bromosuccinimide, but no reaction took place.

A solution of trans- $\beta$ -nitrostyrene and trans-stilbene was irradiated in absolute ether. The crude irradiation product was chromatographed on florisil. Elution with 20:1 Skelly B-benzene gave cis- and trans-stilbene. Continued elution with 3.3:1 Skelly B-benzene gave white crystals of 2,3,4-triphenyl-1-nitrocyclobutane (XCIX, m.p. 125.5-126.5 $^{\circ}$ , 26.8%). The ultraviolet absorption is at  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  252.5s (2,690), 258 (2,460), 265s (2,000) and 269s  $\mu$  (1,260). The infrared spectrum shows maxima at 6.22, 6.45, 6.66, 6.89 and 7.32  $\mu$  (Figure 22, page 108). Photoproduct XCIX was stirred with sodium methoxide in deuteriomethanol to give 2,3,4-triphenyl-

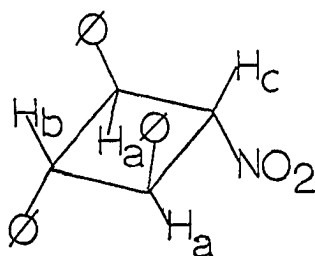
1-deuterio-1-nitrocyclobutane (C; 6.23, 6.50, 6.68 and 7.34 u).



C

The nuclear magnetic resonance spectrum of the deuterated product (C, Figure 3, page 48) gives protons  $H_a$  as a two proton multiplet centered at 5.78 p.p.m., while proton  $H_b$  appears as a multiplet centered at 6.48 p.p.m. The protons  $H_a$  and  $H_b$  analyse as an  $A_2B$  spin-spin system, according to the method given by Pople et al. (74, p. 126). The analysis gives  $J_{ab}$  as 10 c.p.s., and the ratio of coupling constant to chemical shift calculated is 0.25. The  $A_2B$  system indicates that the phenyls alpha to protons  $H_a$  are cis. The fifteen aromatic protons are centered at 2.70 p.p.m. There is a small absorption due to an impurity at 8.74 p.p.m.

The nuclear magnetic resonance spectrum of 2,3,4-triphenyl-1-nitrocyclobutane (XCIX, Figure 3, page 48) gives a two proton multiplet centered at 5.80 p.p.m., which is assigned to the benzylic protons,  $H_a$ . The one proton multiplet centered at 4.92 p.p.m., that is lost on deuteration, is assigned to the proton alpha to the nitro group,  $H_c$ . Proton  $H_b$



XCIX

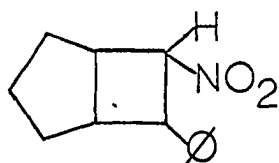
appears as a multiplet centered at 6.46 p.p.m., and its splitting is identical to that of proton  $H_b$  in the spectrum of the deuteration product (C, Figure 3, page 48). Proton  $H_c$  could be treated as the A portion of an  $AB_2$  spin system by a first order approximation, but further coupling of the benzylic protons,  $H_a$ , by proton  $H_b$  makes a complete analysis tedious. The fifteen aromatic protons are centered at 2.70 p.p.m.

Treatment of 2,3,4-triphenyl-1-nitrocyclobutane (XCIX) with sodium methoxide did not cause isomerization. The nitro group thus must be trans to both the adjacent phenyl groups.

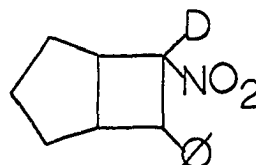
In all the photoaddition products discussed in this thesis, it is shown that  $\beta$ -nitrostyrene has added trans. Therefore, the orientation of the phenyl group alpha to proton  $H_b$  (position 3) is governed by the stilbene during its addition. The most favorable situation would be when stilbene is adding trans, since there would be less steric interaction in the transition state of the photoreaction. From these considerations, one would predict that 2,3,4-triphenyl-1-nitro-

cyclobutane (XCIX) has the substituents alternately trans around the cyclobutane ring. The 10 c.p.s value for  $J_{ab}$  is in accord with this assignment.

Trans- $\beta$ -nitrostyrene (I) in cyclopentene (XXIX) solution when irradiated in a quartz immersion well gave a light yellow liquid, 6-nitro-7-phenylbicyclo[3.2.0]heptane (CI, b.p. 105-107°/0.07 mm., 64% recovered yield). The infrared spectrum (neat) showed peaks at 6.48 and 7.27 (nitro group on a saturated carbon), 6.24, 6.68, 13.48 and 14.34  $\mu$  (aromatic group) (Figure 18, page 100);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  253s (631), 259.5 (562), 265.5s (447) and 269  $\mu$  (363) (aromatic group). The liquid gives two close spots above trans- $\beta$ -nitrostyrene on a thin-layer plate.



CI



CII

The nuclear magnetic resonance spectrum of photoproduct CI (Figure 4, page 50) shows that two isomers are present in approximately a 2:1 ratio (based on relative integrals of the two benzylic proton triplets at 5.65 and 6.21 p.p.m.).

Deuteration of photoproduct CI gave two stereoisomeric 6-deuterio-6-nitro-7-phenylbicyclo[3.2.0]heptanes (CII; 6.53

and 7.30 u (nitro group on a saturated carbon)). The nuclear magnetic resonance spectrum is shown in Figure 4, page 50.

In the reaction of base with 6-nitro-7-phenylbicyclo- $\sqrt{3.2.0}$ /heptane (CI), the ratio of the two isomers remains the same.

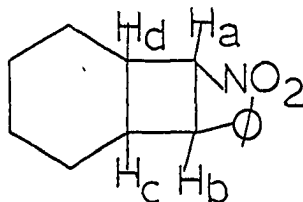
Trans- $\beta$ -nitrostyrene and cyclopentene were irradiated for a short time in a Pyrex immersion well to show that cis- $\beta$ -nitrostyrene is formed under the conditions of the irradiation. A yellow liquid, cis- and trans- $\beta$ -nitrostyrene, was distilled (80°/0.2 mm.). The cis- isomer gives nuclear magnetic resonance absorptions at 3.46, 3.31, 3.21 and 3.03 p.p.m. Photoproduct CI was also separated on distillation.

In order to show that the nitro group is necessary for a photocycloaddition reaction to take place, a solution of styrene was irradiated in excess cyclopentene in an internally cooled Pyrex vessel. The solution was transferred to an internally cooled quartz container and irradiated for a longer period of time, but in both cases there was no change in the ultraviolet spectrum. This experiment establishes that a nitro group on the beta position of styrene is necessary in order for photoaddition to take place.

The infrared spectrum of the crude product from the Nef reaction on photoproduct CI shows unreacted CI, a cyclobutanone (5.65 u), and an unknown product with an absorption at 5.97 u (carbonyl). An attempt to separate these compounds on a silica gel column was not successful.



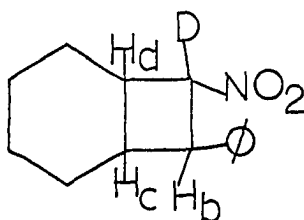
A solution of trans- $\phi$ -nitrostyrene (I) in cyclohexene (XXI) was irradiated to give a light yellow liquid, 7-nitro-8-phenylbicyclo[4.2.0]octane (CIII, b.p. 118-120°/0.1 mm., 58%). This liquid gives two close spots above trans- $\beta$ -nitrostyrene on a thin-layer plate. The infrared absorption spectrum (neat) shows peaks at 6.48 and 7.29 (nitro group on a saturated carbon), 6.24, 6.67, 13.47 and 14.37  $\mu$  (aromatic group) (Figure 18, page 100). CIII shows absorption in the ultraviolet at  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  252s (617), 258 (540), 264.5s (437) and 268s  $\mu$  (355) (aromatic group).



CIII

The nuclear magnetic resonance spectrum of photoproduct CIII (Figure 5, page 52) shows that two isomers are present. A broad ten proton absorption between 6.88 and 9.17 p.p.m. is assigned to the eight methylene protons and to the bridgehead protons,  $H_c$  and  $H_d$ . Proton  $H_b$  appears as a broad multiplet at 5.80 to 6.55 p.p.m. The two triplets (one proton) centered at 5.02 and 5.55 p.p.m. (1:2 ratio, respectively) are assigned to the proton alpha to the nitro group,  $H_a$ , which is coupled to protons  $H_d$  and  $H_b$  in both isomers. The five

aromatic protons are centered at 2.84 p.p.m.



CIV

Deuteration of photoproduct CIII gave two stereoisomeric 7-deuterio-7-nitro-8-phenylbicyclo[4.2.0]octanes (CIV; 6.51 and 7.31 u). The nuclear magnetic resonance spectrum of the deuteration product (CIV, Figure 5, page 52) shows the loss of the proton alpha to the nitro group (proton  $H_a$  from the preceding discussion). The benzylic proton,  $H_b$ , appears as two broad doublets (one proton) centered at 5.98 p.p.m. ( $J=8.5$  c.p.s.), and 6.37 p.p.m. ( $J=9.2$  c.p.s.).<sup>2</sup> Proton  $H_b$  is coupled to the bridgehead proton,  $H_c$ , in both isomers. A broad ten proton absorption between 6.90 and 9.20 p.p.m. is assigned to the eight methylene protons and protons  $H_c$  and  $H_d$ . The five aromatic protons are centered at 2.83 p.p.m.

In the reaction of base with 7-nitro-8-phenylbicyclo[4.2.0]octane (CIII), the ratio of the two isomers remains

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<sup>2</sup>Until a formal analysis of the complex nuclear magnetic resonance spectra in this thesis is completed, one must regard coupling constants ( $J$ ) as  $J$  apparent rather than as true coupling constants.

the same. Examination of the Framework Molecular Model of photoproduct CIII shows that a trans relationship between the nitro and adjacent phenyl groups should result in less steric repulsion in both the 4-6 trans- and cis-fused ring systems.

The infrared of the crude product from the Nef reaction on photoproduct CIII shows unreacted CIII, a cyclobutanone (5.58  $\mu$ ), and an unknown compound with an absorption at 5.92  $\mu$  (carbonyl). An attempt to separate these compounds on a florisil column was unsuccessful.

#### Additions to unsymmetrically substituted olefins

The cycloaddition reactions of trans- $\beta$ -nitrostyrene to unsymmetrically substituted olefins were investigated in order to determine the orientation and stereochemistry of the additions.

Irradiation of a solution of trans- $\beta$ -nitrostyrene in diphenylethylene gave a viscous, reddish brown liquid, 2,3,3-triphenyl-1-nitrocyclobutane (XCIV, 45.5%);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  253s (1585), 259 (1515), 264s (1350) and 270s  $\mu$  (1050). The infrared spectrum ( $\text{CHCl}_3$ ) shows absorption at 6.24, 6.47, 6.69, 7.32 and 7.65  $\mu$  (Figure 22, page 108).

The nuclear magnetic resonance spectrum of photoproduct XCIV (Figure 6, page 64) gives a two proton octet between 6.30 and 7.26 p.p.m. for methylene protons  $\text{H}_a$  and  $\text{H}_b$ . Protons  $\text{H}_a$  and  $\text{H}_b$  could be treated as an AB part ( $J = 12.5$  c.p.s.) of an ABX spin system by a first order approximation, but

Figure 2. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of  
1,1,2,2-tetramethyl-4-phenyl-3-nitro-  
cyclobutane (XCVI)

Bottom: Nuclear magnetic resonance spectrum of  
1,1,2,2-tetramethyl-4-phenyl-3-deuterio-  
3-nitrocyclobutane (XCVIII)

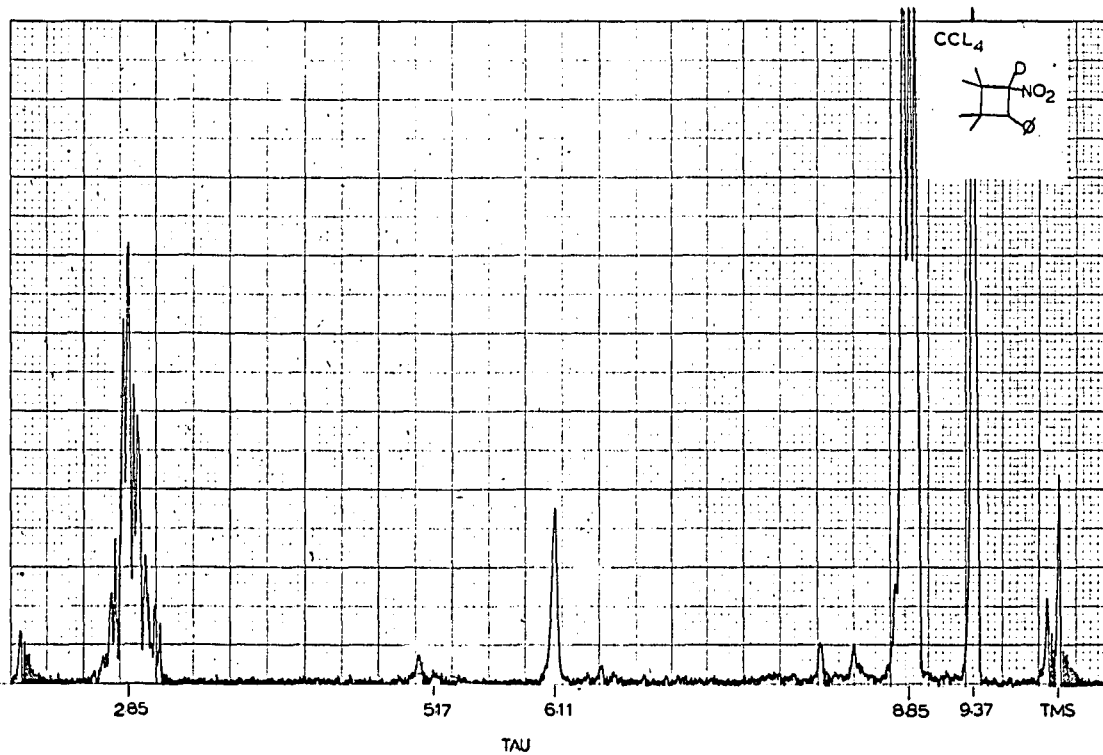
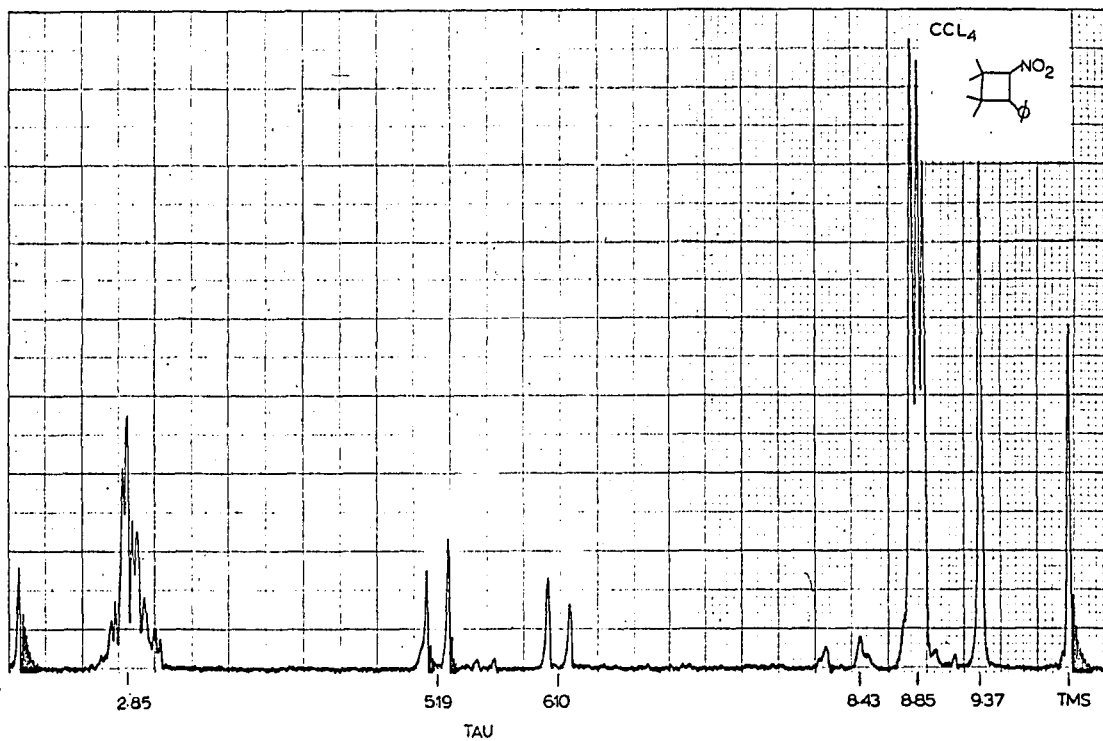


Figure 3. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of  
2,3,4-triphenyl-1-deuterio-1-nitro-  
cyclobutane (C)

Bottom: Nuclear magnetic resonance spectrum of  
2,3,4-triphenyl-1-nitrocyclobutane (XCIX)

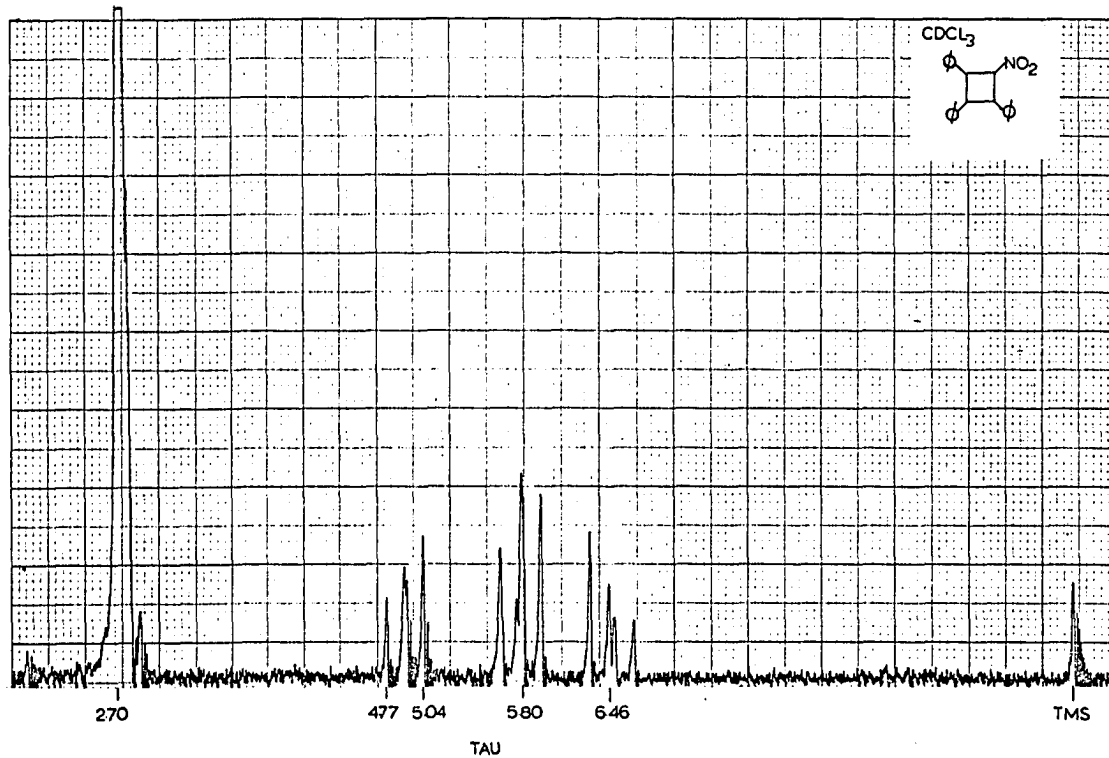
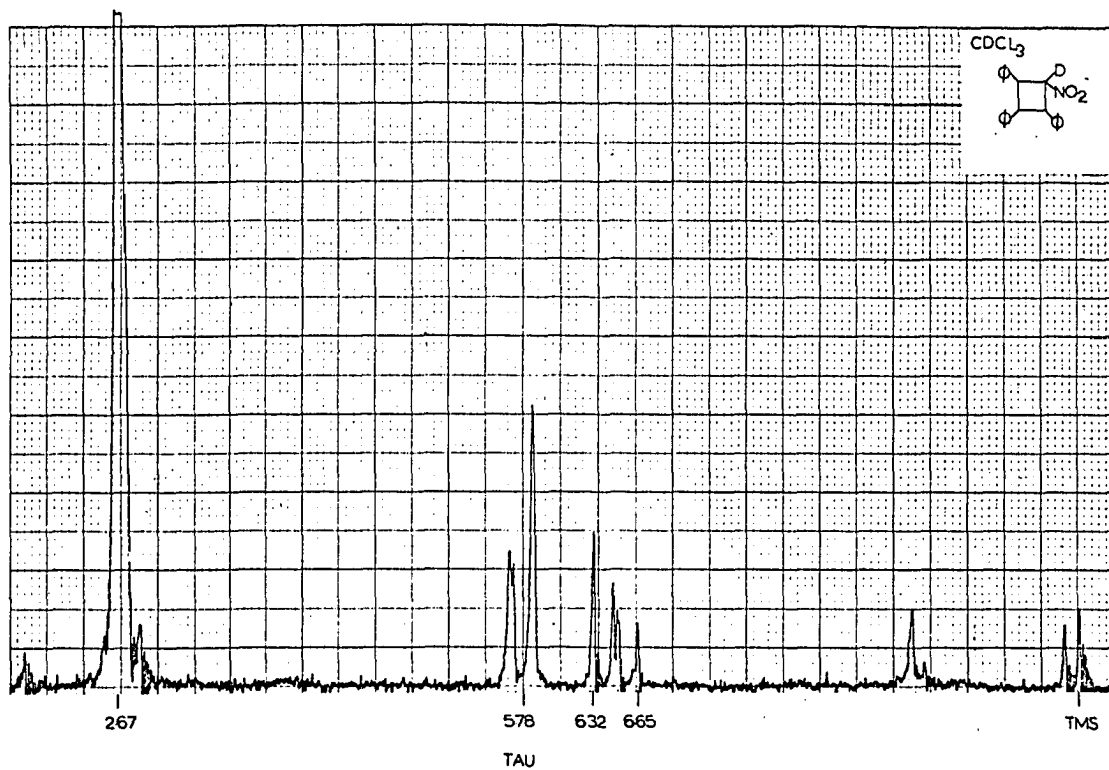


Figure 4. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of  
6-nitro-7-phenylbicyclo[3.2.0]heptane (CI)

Bottom: Nuclear magnetic resonance spectrum of  
6-deuterio-6-nitro-7-phenylbicyclo-  
[3.2.0]heptane (CII)



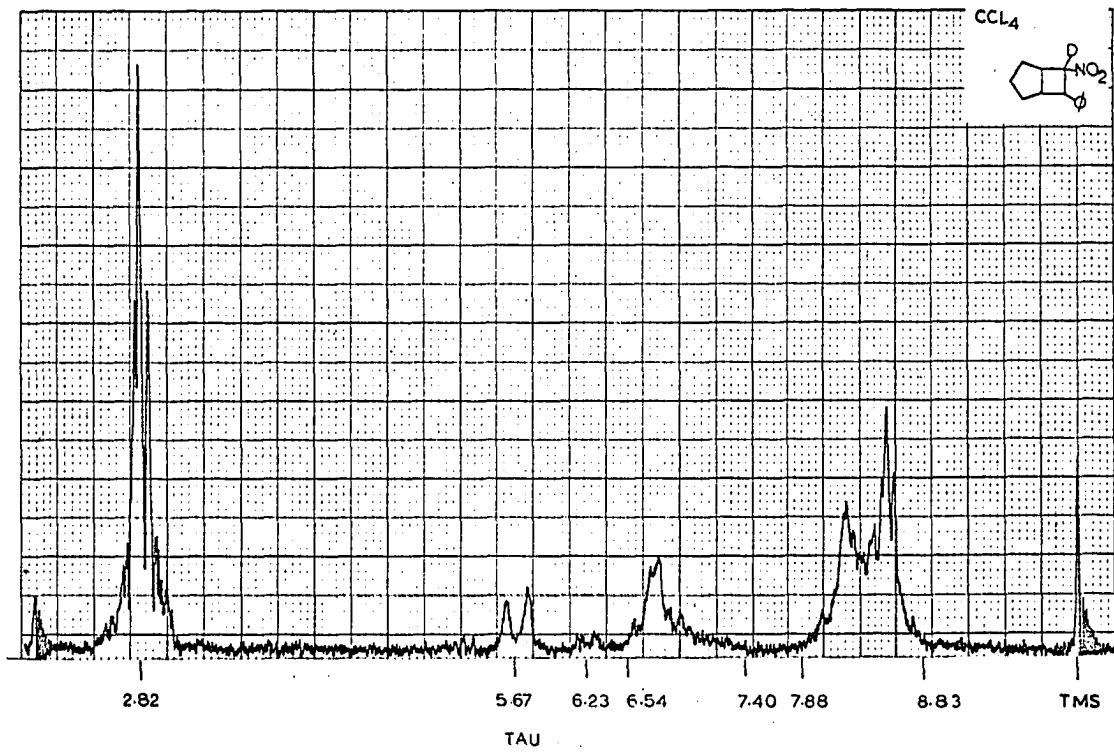
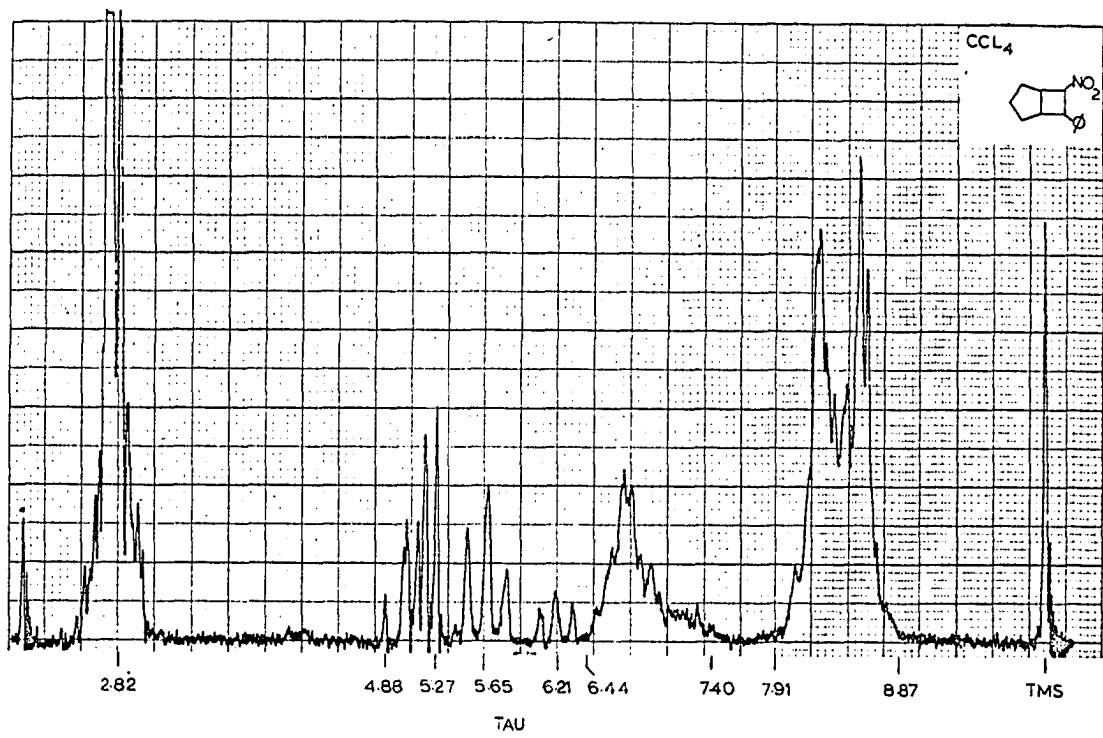
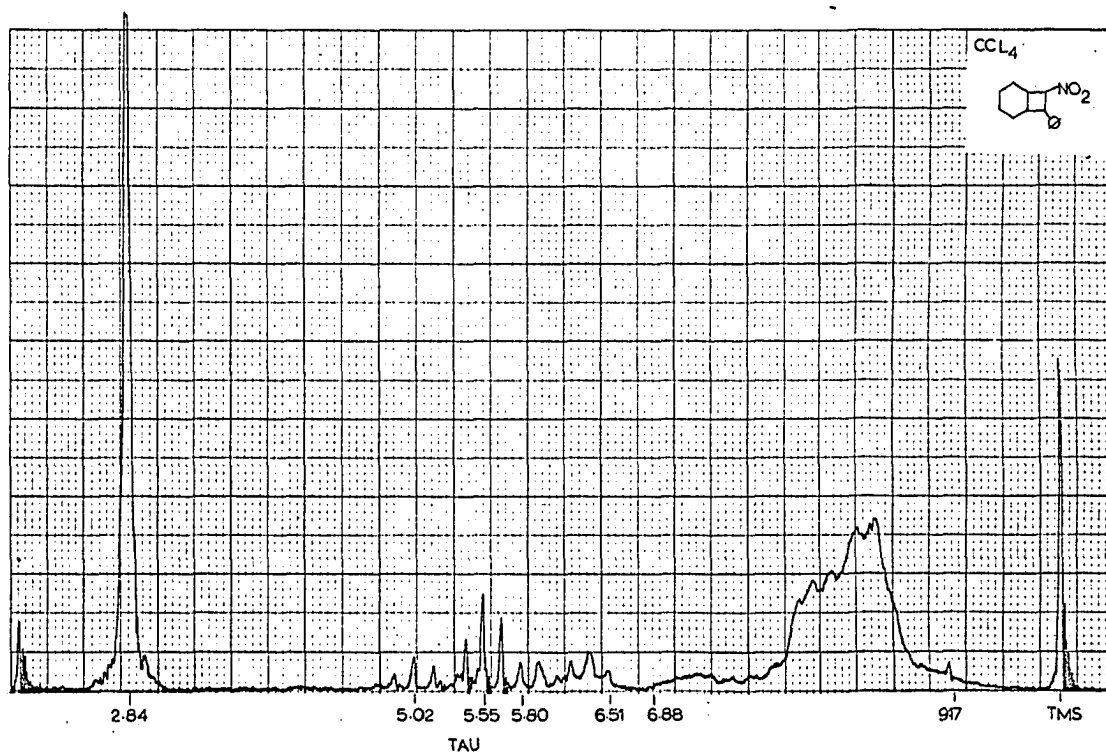
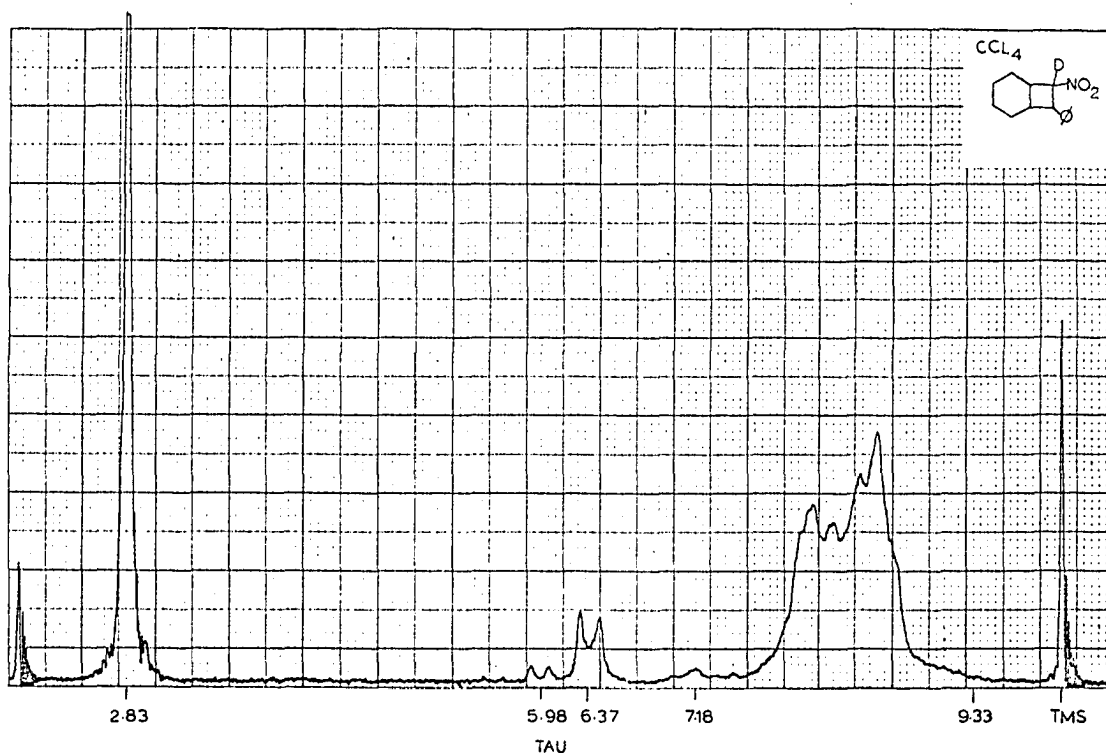
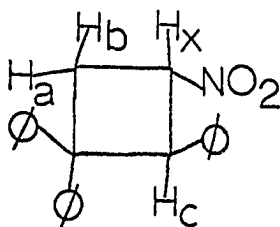


Figure 5. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of  
7-deuterio-7-nitro-8-phenylbicyclo-  
[4.2.0]octane (CIV)

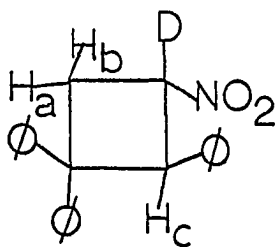
Bottom: Nuclear magnetic resonance spectrum of  
7-nitro-8-phenylbicyclo[4.2.0]octane (CIII)





XCIV

analysis is not possible since proton  $H_x$  is further split. This assignment will be confirmed by the analysis of the nuclear magnetic resonance spectrum of the deuterated photoproduct. A slightly split, broad quartet at 4.55 to 5.00 p.p.m. is assigned to the proton alpha to the nitro group,  $H_x$ , which is coupled to protons  $H_a$ ,  $H_b$  and the benzylic proton,  $H_c$ . Proton  $H_c$  appears as a doublet ( $J = 9.9$  c.p.s.) centered at 5.18 p.p.m., split by proton  $H_x$ . The fifteen aromatic protons are centered at approximately 2.77 and 3.03 p.p.m.



CV

Deuteration of photoproduct XCIV gave 2,3,3-triphenyl-1-deuterio-1-nitrocyclobutane (CV; 6.24, 6.49, 6.68, 7.31 and

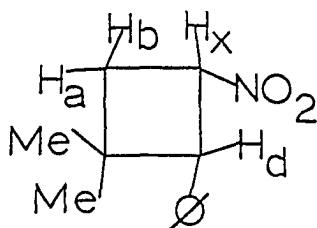
11.26 u). The nuclear magnetic resonance spectrum of the deuterated product (Figure 6, page 64) gives no absorption between 4.55 and 5.00 p.p.m. A broad proton singlet appears at 5.18 p.p.m. for the benzylic proton,  $H_c$ . Methylene protons,  $H_a$  and  $H_b$ , are assigned to a two proton quartet centered at approximately 6.77 p.p.m. Protons  $H_a$  and  $H_b$  constitute an AB system ( $J_{ab} = 12.2$  c.p.s.). The fifteen aromatic protons are centered at approximately 2.82 and 3.07 p.p.m. The absorptions at 8.07 and 8.73 p.p.m. are due to impurities.

The reaction of sodium methoxide with 2,3,3-triphenyl-1-nitrocyclobutane (XCIV) gave only starting material; therefore, the nitro and phenyl groups must be trans.

An attempt to brominate photoproduct XCIV using N-bromosuccinimide gave only starting material. XCIV was pyrolysed (490-510°) back to  $\beta$ -nitrostyrene. Pyrolysis of 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI) and 7-nitro-8-phenylbicyclo[4.2.0]octane (CIII) did not give  $\alpha$ -nitrostyrene under the same conditions.

Trans- $\beta$ -nitrostyrene and isobutylene (XXXII) were irradiated in hexane solution at -12° to -3°. The crude irradiation product was chromatographed on a silica gel column. Elution with 7:3 Skelly B-benzene gave a light yellow liquid, 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII, b.p. 81°/0.2 mm., 77.6%);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  252s (480), 258.5 (426), 265 (331) and 268.5s  $\mu$  (263). The infrared spectrum (neat) shows maxima at 6.23, 6.45, 6.66, 7.30, 13.45 and 14.34 u (Figure 19,

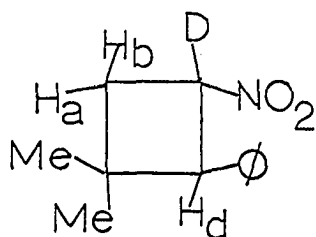
page 102).



XCVII

The nuclear magnetic resonance spectrum of photoproduct XCVII (Figure 7, page 66) shows the two methyl groups as three proton singlets at 8.66 and 9.22 p.p.m. A two proton octet at 7.37 to 7.96 p.p.m. is assigned to the methylene protons,  $H_a$  and  $H_b$ . Protons  $H_a$  and  $H_b$  could be treated as the AB part of an ABX spin system ( $J = 11.6$  c.p.s.) by a first order analysis, but analysis is complicated by the proton  $H_x$  being split further. The nuclear magnetic resonance spectrum of the deuterated photoproduct (CVI) further confirms this assignment (see below). The benzylic proton,  $H_d$ , appears as a doublet centered at 6.21 p.p.m. ( $J = 9.6$  c.p.s.), due to coupling to the proton alpha to the nitro group,  $H_x$ . Proton  $H_x$  is assigned to a one proton quartet between 4.64 and 5.08 p.p.m., since it is coupled to the methylene protons,  $H_a$  and  $H_b$ , and proton  $H_d$ . The five aromatic protons are centered at approximately 2.78 p.p.m. The absorptions at 8.27 and 8.75 p.p.m. are due to small amounts of impurities.

Sodium methoxide was added to a solution of photoproduct



CVI

XCVII in deuteriomethanol to give 3,3-dimethyl-2-phenyl-1-deuterio-1-nitrocyclobutane (CVI; 6.23, 6.50, 6.66, 7.28, 13.50 and 14.33 u). The nuclear magnetic resonance spectrum of the deuterated product (CVI) is shown in Figure 7, page 66. The two methyl groups appear as three proton singlets at 8.67 and 9.25 p.p.m. The methylene protons,  $H_a$  and  $H_b$ , are assigned to a quartet at 7.70 p.p.m. Protons  $H_a$  and  $H_b$  form an AB system ( $J = 11.9$  c.p.s.). The benzylic proton,  $H_d$ , is a broad one proton singlet at 6.22 p.p.m. There is no absorption between 4.64 and 5.08 p.p.m. The five aromatic protons are centered at approximately 2.82 p.p.m.

Treatment of 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII) with sodium methoxide gave only starting material; therefore, the nitro and phenyl groups must be trans.

Continued elution of the silica gel column with 15:85 Skelly B-benzene gave white crystals of Dimer A (m.p. 160-161°, 0.08%) in a trace amount. The infrared spectrum (KBr) shows maxima at 6.24, 6.31, 6.45, 6.67, 6.87, 7.31, 13.36 and 14.33 u (Figure 19, page 102). The nuclear magnetic reso-

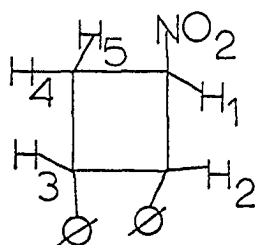
nance spectrum of Dimer A (Figure 10, page 72) shows absorption at 2.70 p.p.m., 4.00 to 4.78 p.p.m. (multiplet) and 4.86 to 5.28 p.p.m. (multiplet), which integrate 10:2:2. Dimer A analyses for  $C_{16}H_{14}N_2O_4$ . The infrared and nuclear magnetic resonance spectra and the elemental analysis suggest that Dimer A is a cyclobutane dimer of  $\beta$ -nitrostyrene. The orientation of the nitro and phenyl groups is not known.

A short duration irradiation of trans- $\beta$ -nitrostyrene and isobutylene in hexane was carried out at  $-12^\circ$  to  $-3^\circ$ . The nuclear magnetic resonance spectrum of the crude irradiation product shows absorption at 3.05, 3.24, 3.33 and 3.50 p.p.m., which correspond to cis- $\beta$ -nitrostyrene. Trans- $\beta$ -nitrostyrene was present, and 3,3-dimethyl-2-phenyl-1-nitrocyclobutane had been formed, according to the nuclear magnetic resonance and infrared spectra.

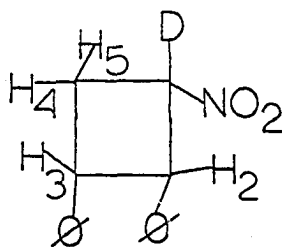
A solution of trans- $\beta$ -nitrostyrene in styrene was irradiated to give a light brown liquid, 2,3-diphenyl-1-nitrocyclobutane (XCV, b.p.  $131-133^\circ/0.08$  mm., 70%). A solid isomer A (XCV<sub>a</sub>, m.p.  $104-105^\circ$ , 17.2%) crystallized out on cooling. Solid isomer A (XCV<sub>a</sub>) shows ultraviolet absorption at  $\lambda_{\max}^{95\% \text{ EtOH}}$  255s (850), 260 (795), 266s (646) and 270s  $\mu$  (500). The infrared spectrum ( $CHCl_3$ ) shows maxima at 6.23, 6.45, 6.67, 6.88 and 7.30  $\mu$  (Figure 20, page 104).

The nuclear magnetic resonance spectrum of solid isomer A (XCV<sub>a</sub>, Figure 8, page 68) shows an eleven peak multiplet for the methylene protons,  $H_4$  and  $H_5$ , at 6.63 to 7.47 p.p.m. The



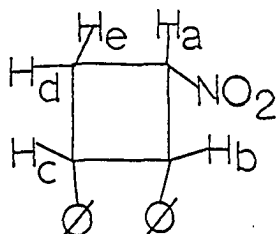
XCV<sub>a</sub>

one proton sextet centered at 6.06 p.p.m. is assigned to a benzylic proton, H<sub>3</sub>, that is coupled to protons H<sub>2</sub>, H<sub>4</sub> and H<sub>5</sub>. The benzylic proton, H<sub>2</sub> appears as a broad triplet centered at 5.45 p.p.m., split by protons H<sub>1</sub> and H<sub>3</sub>. The proton alpha to the nitro group is assigned to a quartet between 4.22 and 4.75 p.p.m. ( $J = 8.8$  c.p.s.), due to coupling by the methylene protons, H<sub>4</sub> and H<sub>5</sub>, and the benzylic proton, H<sub>2</sub>. The ten aromatic protons are centered at approximately 3.00 p.p.m. The weak absorption at 8.59 p.p.m. is due to an impurity.

CVII<sub>a</sub>

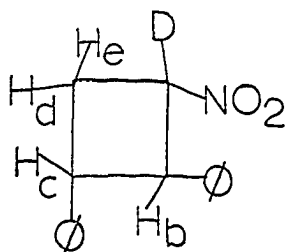
Solid isomer A (XCV<sub>a</sub>) was stirred with base in deuterio-methanol to give solid 2,3-diphenyl-1-deuterio-1-nitrocyclo-

butane (CVII<sub>a</sub>; 6.23, 6.50, 6.66, 6.88 and 7.30 u). The nuclear magnetic resonance spectrum of the deuteration product of solid isomer A (CVII<sub>a</sub>, Figure 8, page 68) gives no absorption between 4.22 and 4.75 p.p.m. The benzylic proton, H<sub>2</sub>, appears as a broad doublet ( $J = 10$  c.p.s.) centered at 5.45 p.p.m., coupled to proton H<sub>3</sub>. Proton H<sub>3</sub> is a sextet centered at 6.03 p.p.m., and is identical to the equivalent proton, H<sub>3</sub>, in the nuclear magnetic resonance spectrum of the undeuterated solid isomer A. The methylene protons, H<sub>4</sub> and H<sub>5</sub>, appear as a broad two proton multiplet between 6.44 and 7.40 p.p.m. The five aromatic protons are centered at approximately 2.96 p.p.m. The absorption at 8.77 p.p.m. is due to an impurity.

XCV<sub>b</sub>

The light brown liquid left after removal of solid isomer A was a second isomer B, contaminated with a very small amount of solid isomer A. The infrared spectrum (CHCl<sub>3</sub>) of liquid isomer B of 2,3-diphenyl-1-nitrocyclobutane (XCV<sub>b</sub>) shows maxima at 6.23, 6.45, 6.67, 6.89 and 7.32 u (Figure 20, page 104). XCV<sub>b</sub> shows ultraviolet absorption at  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  254s (1585),

260s (1380), 266s (1070) and 270s mu (795). The nuclear magnetic resonance spectrum (XCV<sub>b</sub>, Figure 9, page 70) shows a sextet at 7.00 to 7.40 p.p.m. for the methylene protons, H<sub>d</sub> and H<sub>e</sub>. The one proton sextet between 6.38 and 6.83 is assigned to the benzylic proton, H<sub>c</sub>, that is coupled to the methylene protons, H<sub>d</sub> and H<sub>e</sub>, and proton H<sub>b</sub>. Proton H<sub>b</sub> appears as a triplet centered at 5.92 p.p.m. (J = 9.1 c.p.s.), split by protons H<sub>c</sub> and H<sub>a</sub>. The proton alpha to the nitro group, H<sub>a</sub>, appears as a quartet between 4.82 and 5.23 p.p.m. (J = 8.5 c.p.s.), due to coupling to the methylene protons, H<sub>e</sub> and H<sub>d</sub>, and benzylic proton H<sub>b</sub>. The ten aromatic protons are centered at approximately 2.73 p.p.m. The weak absorptions at 4.43, 4.58, 5.40 and 5.57 are due to a small amount of solid isomer A present as an impurity.

CVII<sub>b</sub>

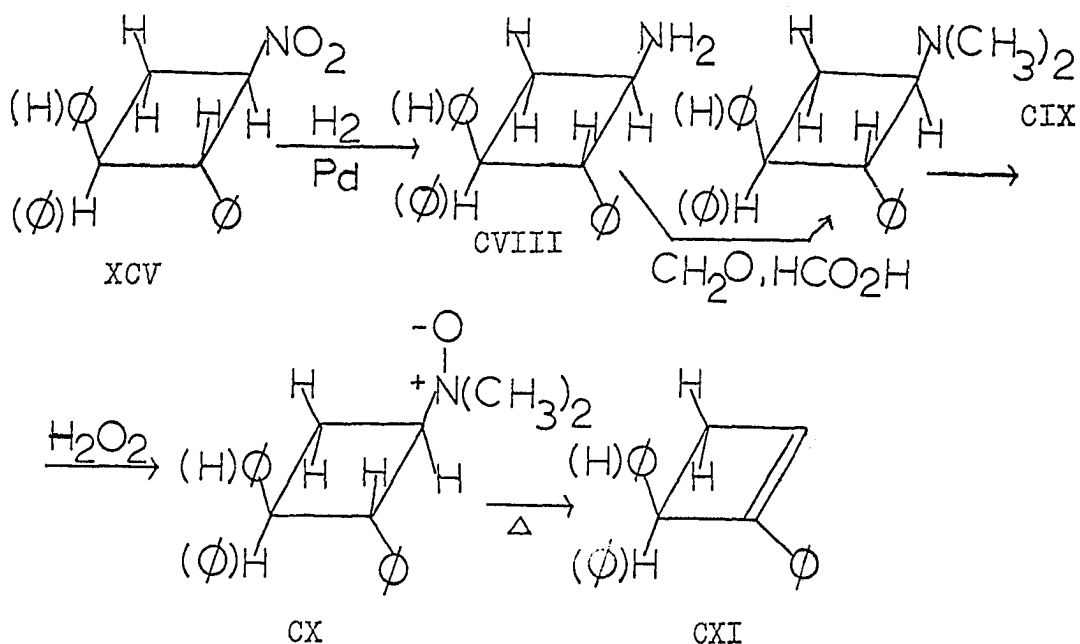
Deuteration of liquid isomer B (XCV<sub>b</sub>) gave 2,3-diphenyl-1-deuterio-1-nitrocyclobutane (CVII<sub>b</sub>; 6.24, 6.50, 6.68, 6.90 and 7.32 u). The nuclear magnetic resonance spectrum of deuterated liquid isomer B (CVII<sub>b</sub>, Figure 9, page 70) gives no absorption between 4.82 and 5.23 p.p.m. The benzylic proton,

$H_b$ , appears as a doublet centered at 5.90 p.p.m. ( $J = 9.5$  c.p.s.), since it is coupled to the benzylic proton,  $H_c$ . Proton  $H_c$  is a sextet centered between 6.43 and 6.88 p.p.m. and is identical to an equivalent proton  $H_c$  in the spectrum of the undeuterated liquid isomer B ( $XCV_b$ ). The methylene protons,  $H_e$  and  $H_d$ , appear as a two proton triplet at 7.15 to 7.35 p.p.m. The ten aromatic protons are centered at 2.75 p.p.m.

The reaction of sodium methoxide with both solid isomer A and liquid isomer B of 2,3-diphenyl-1-nitrocyclobutane (XCV) gave back only the original isomer in each case. This shows that the nitro and adjacent phenyl groups are trans in both isomers. Formation of the two isomers must be due to the phenyl group at position 3 being either cis or trans to the phenyl group at position 2 in XCV.

The stereochemistry of solid isomer A and liquid isomer B is further confirmed by the work of Lenz (57). Lenz catalytically reduced both isomers of XCV to the corresponding amines (CVIII). Methylation of CVIII with formaldehyde and formic acid gave the dimethylamines (CIX) which were oxidized with hydrogen peroxide to the amine oxides (CX). The pyrolysis of the amine oxides gave the same product, 1,4-diphenylcyclobutene (CXI). The formation of CXI from the amine oxides (CX) from both isomers of 2,3-diphenyl-1-nitrocyclobutane establishes that the nitro and adjacent phenyl groups are trans, since pyrolysis of an amine oxide proceeds by a cis

elimination (75).



#### Additions to 1,3-dienes

The photoadditions of trans-β-nitrostyrene to 1,3-dienes were investigated, since both 1,2- and 1,4-addition products are possible. Formation of a 1,4-addition product would be indicative of a diradical intermediate. The additions were also studied to determine the orientation and stereochemistry of cycloaddition.

A solution of trans-β-nitrostyrene and 2,3-dimethyl-1,3-butadiene was irradiated to give a yellow orange liquid, 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII, b.p. 102-104°/0.32 mm., 70%). The liquid gives only one spot on a silica gel thin-layer plate, but vapor phase chromatography shows that two isomers are present. The infrared spectrum (neat) shows maxima at 6.11 (double bond), 6.44 and 7.28

Figure 6. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of  
2,3,3-triphenyl-1-nitrocyclobutane (XCIV)

Bottom: Nuclear magnetic resonance spectrum of  
2,3,3-triphenyl-1-deuterio-1-nitrocyclo-  
butane (CV)

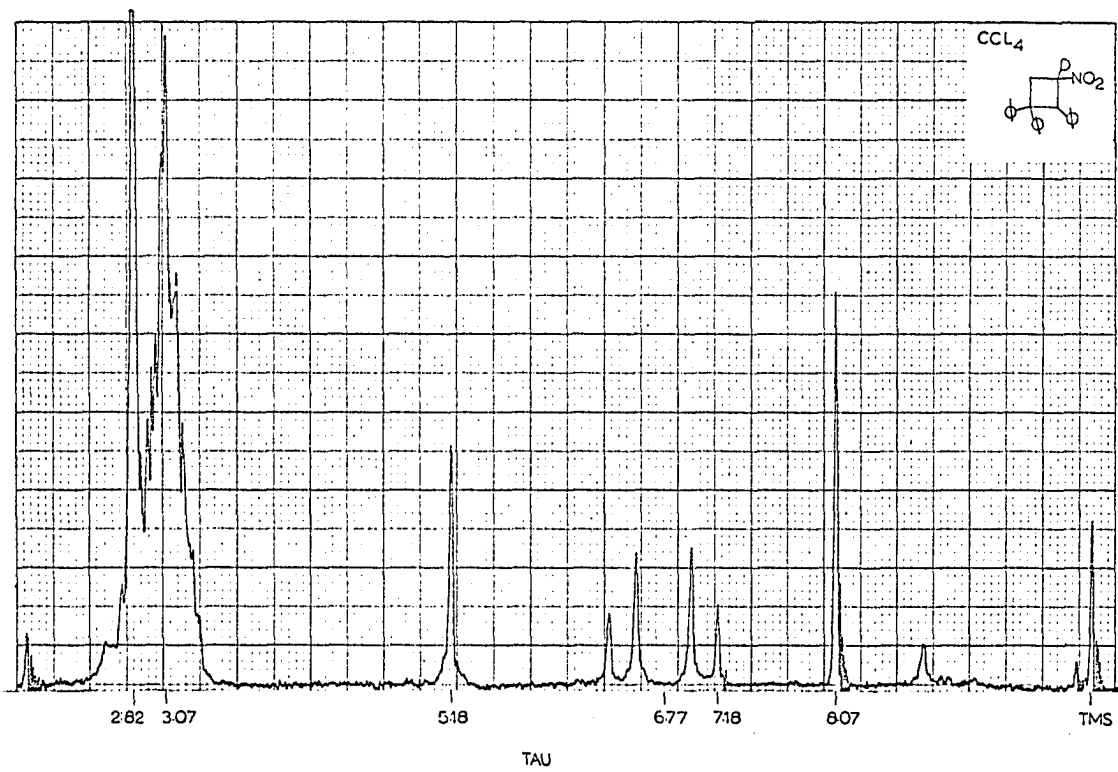
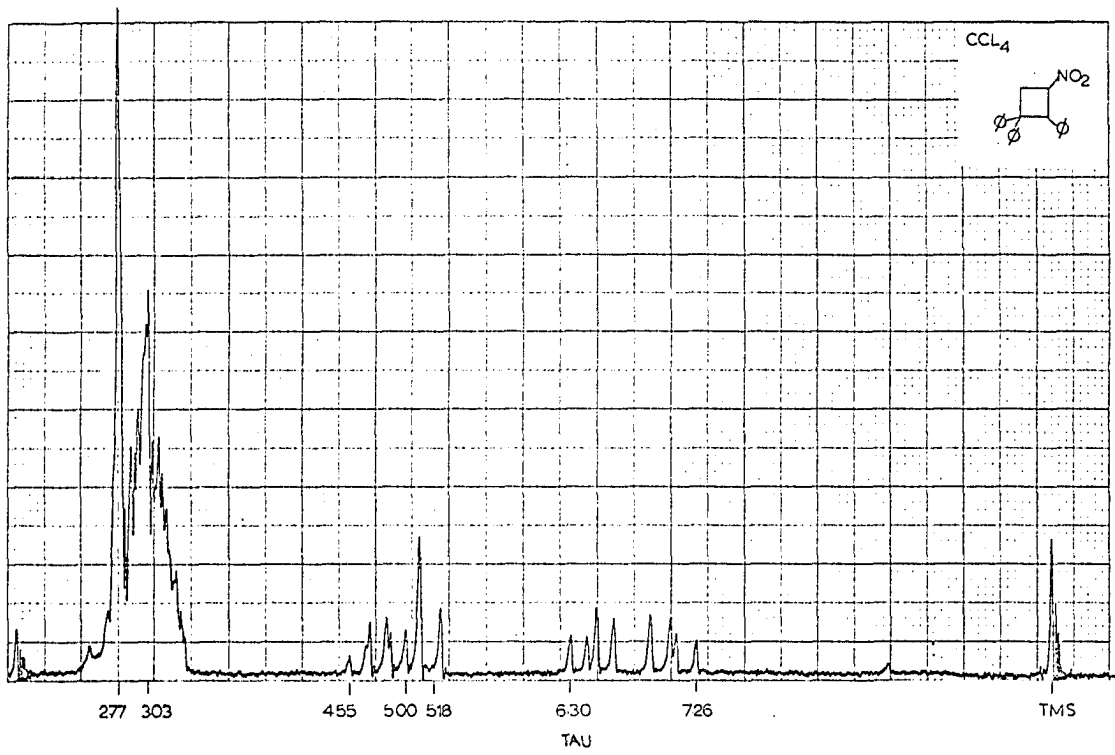


Figure 7. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of  
3,3-dimethyl-2-phenyl-1-nitrocyclo-  
butane (XCVII)

Bottom: Nuclear magnetic resonance spectrum of  
3,3-dimethyl-2-phenyl-1-deuterio-1-  
nitrocyclobutane (CVI)



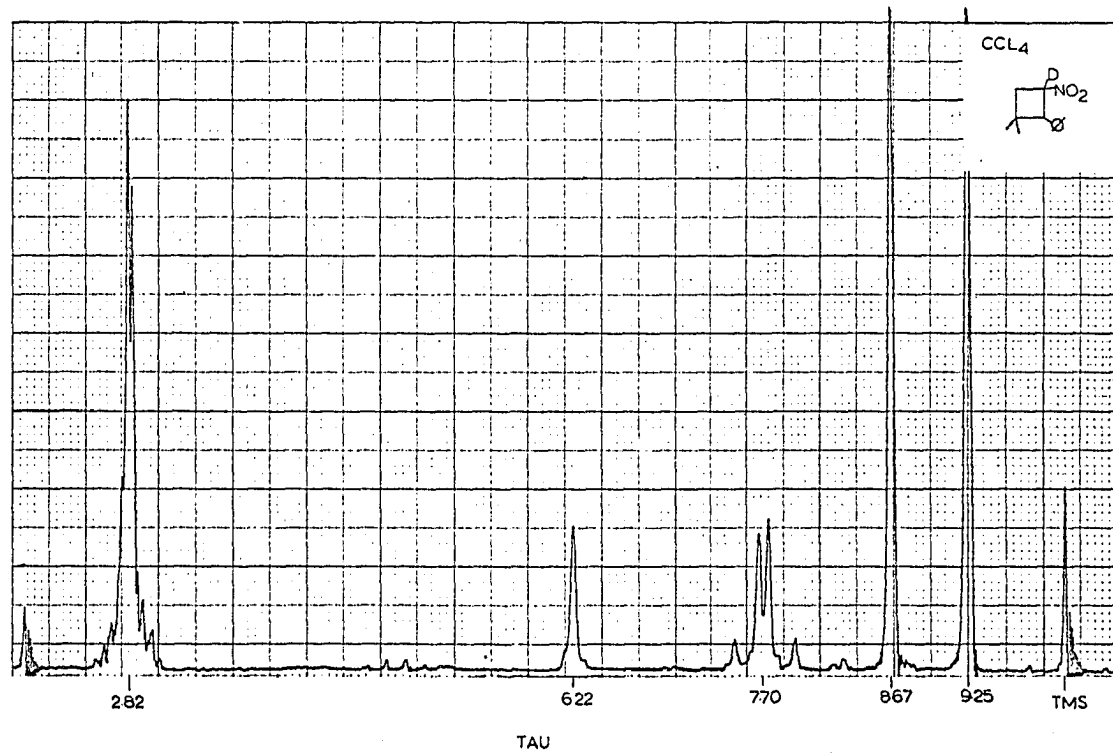
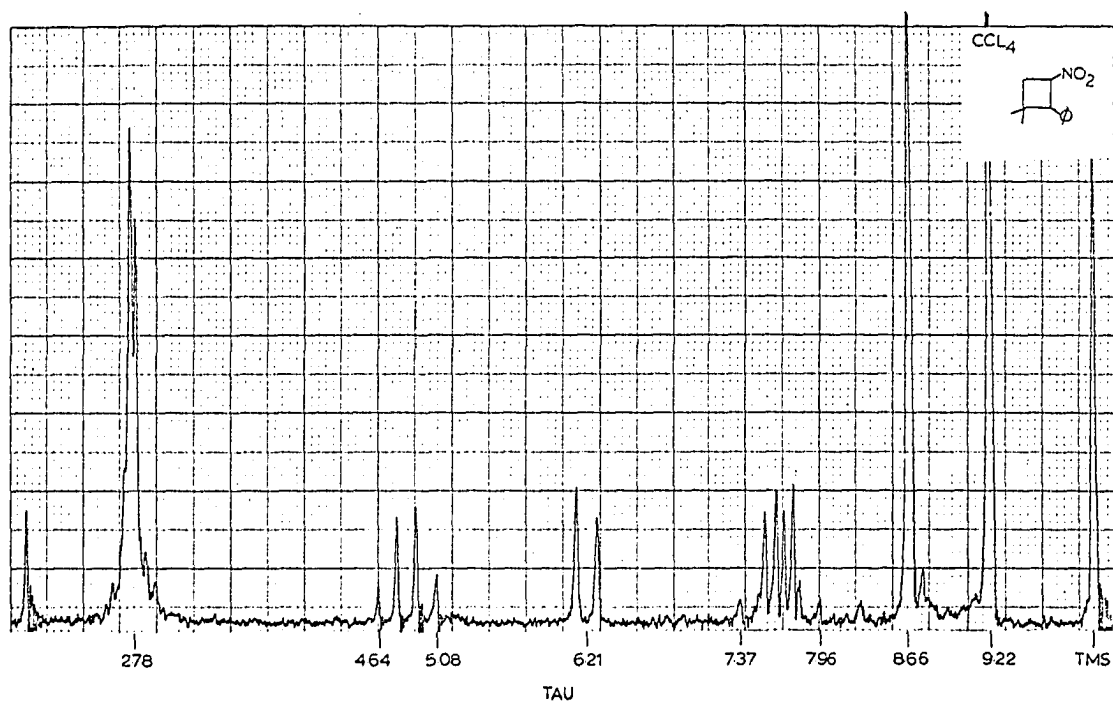


Figure 8. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of solid isomer A of 2,3-diphenyl-1-nitrocyclobutane (XCV<sub>a</sub>)

Bottom: Nuclear magnetic resonance spectrum of solid isomer A of 2,3-diphenyl-1-deuterio-1-nitrocyclobutane (CVII<sub>a</sub>)

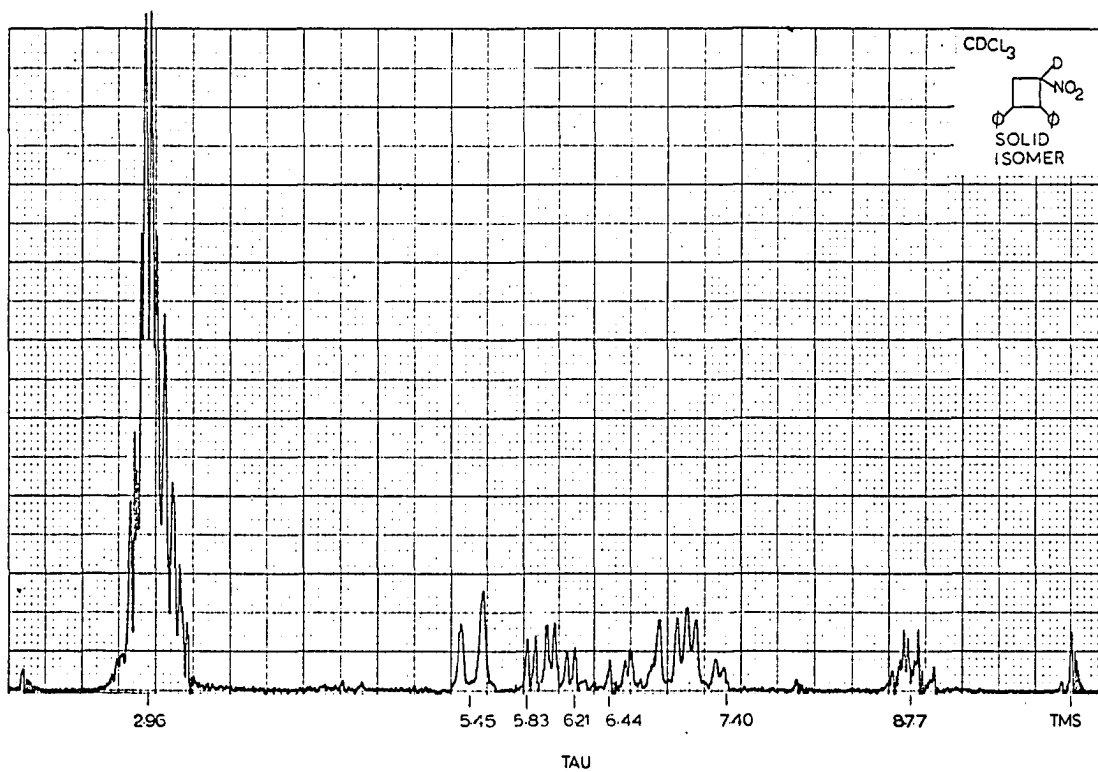
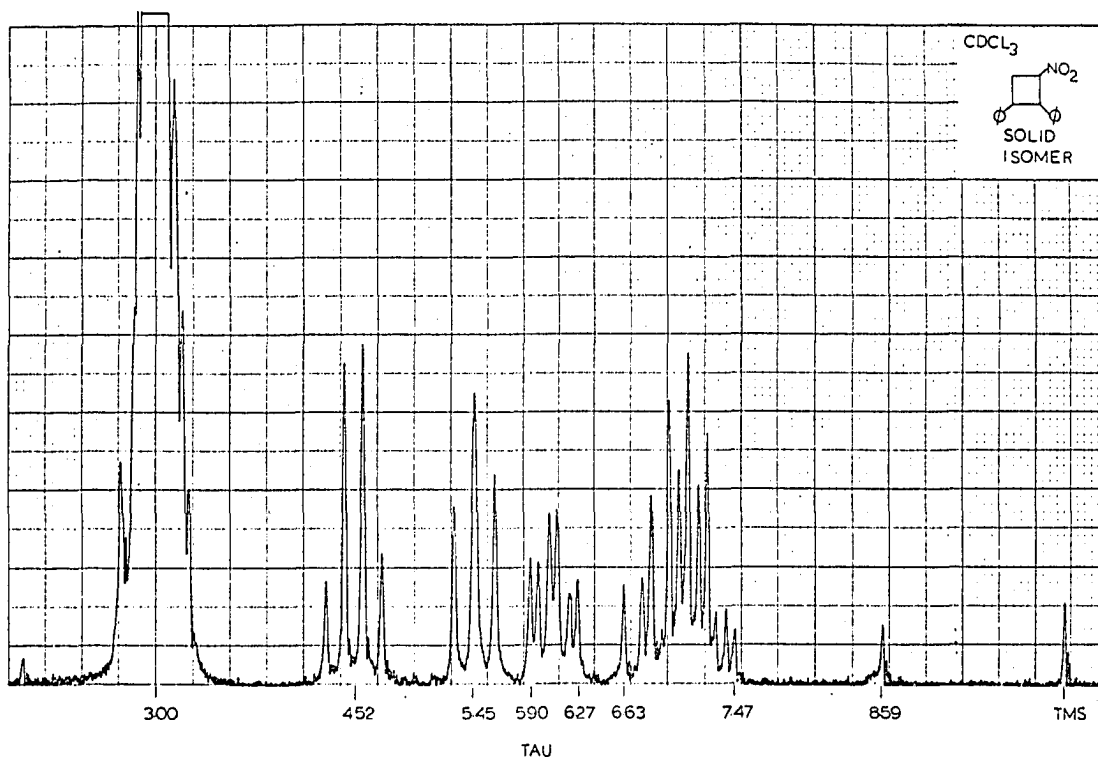


Figure 9. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of liquid isomer B of 2,3-diphenyl-1-nitrocyclobutane (XCV<sub>b</sub>)

Bottom: Nuclear magnetic resonance spectrum of liquid isomer B of 2,3-diphenyl-1-deuterio-1-nitrocyclobutane (CVII<sub>b</sub>)

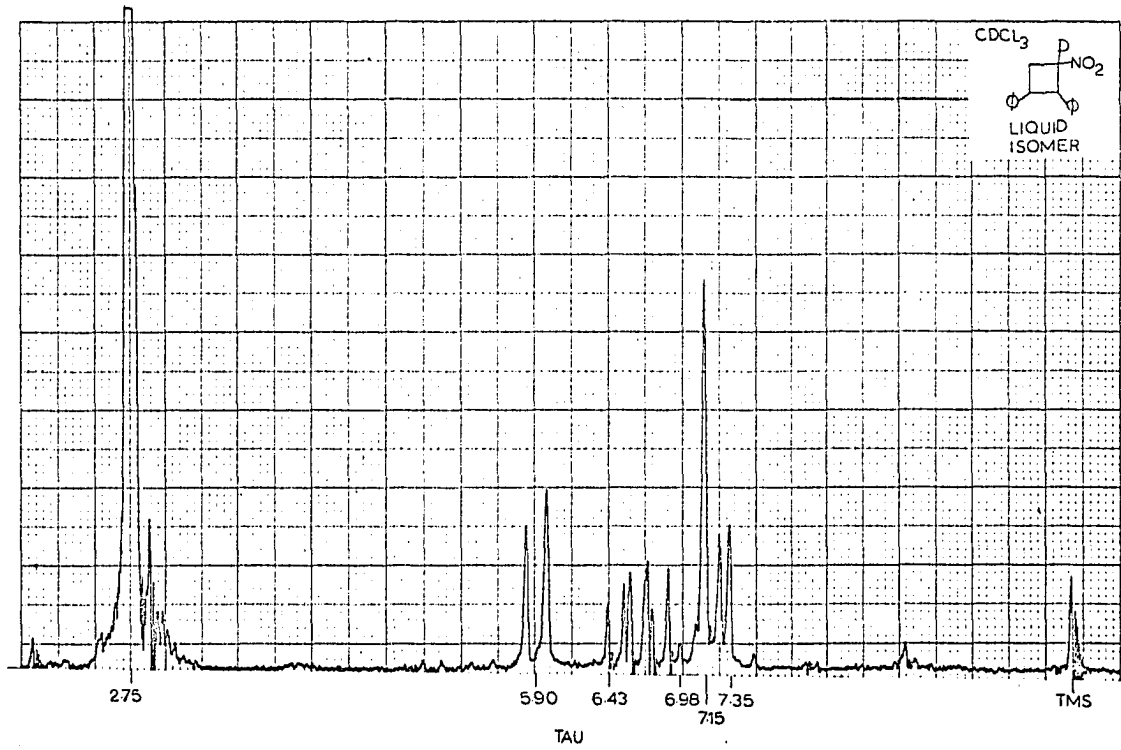
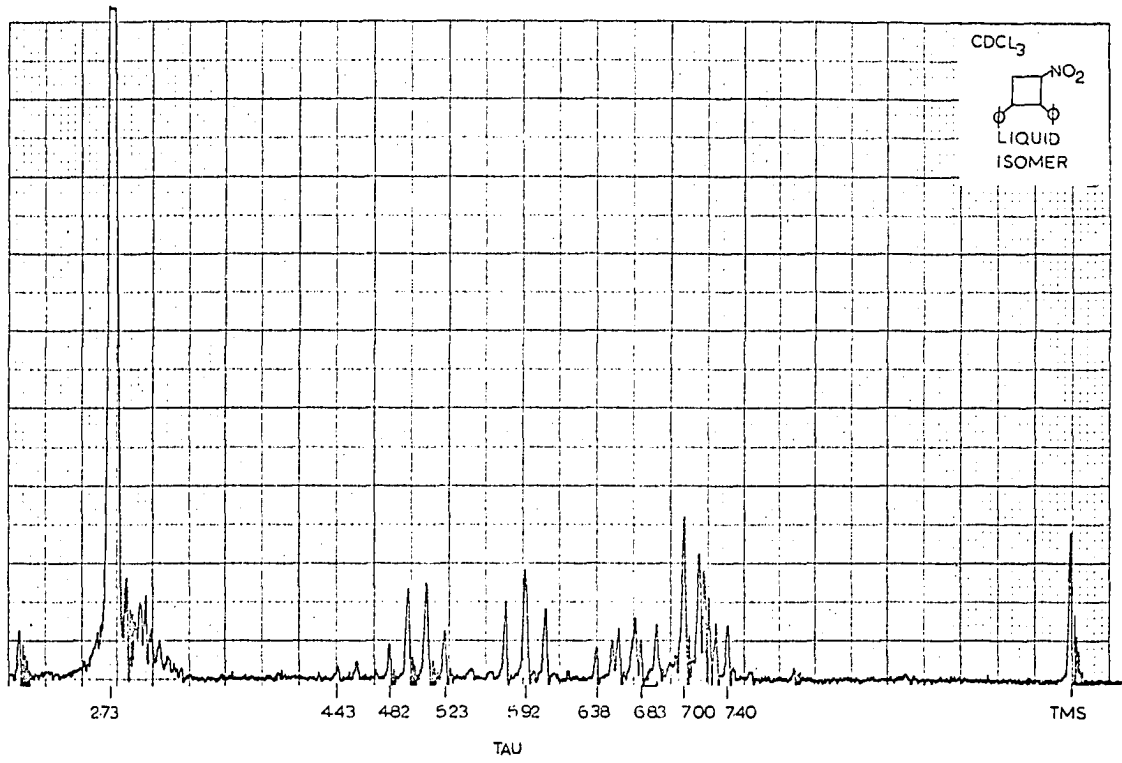
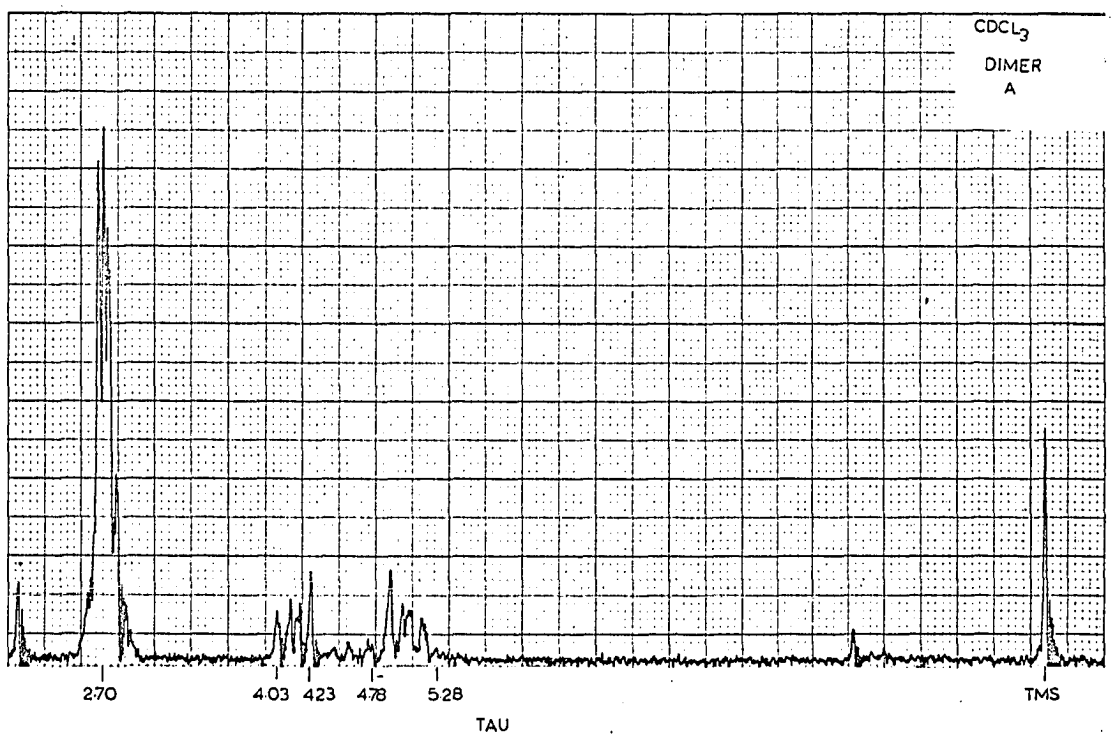
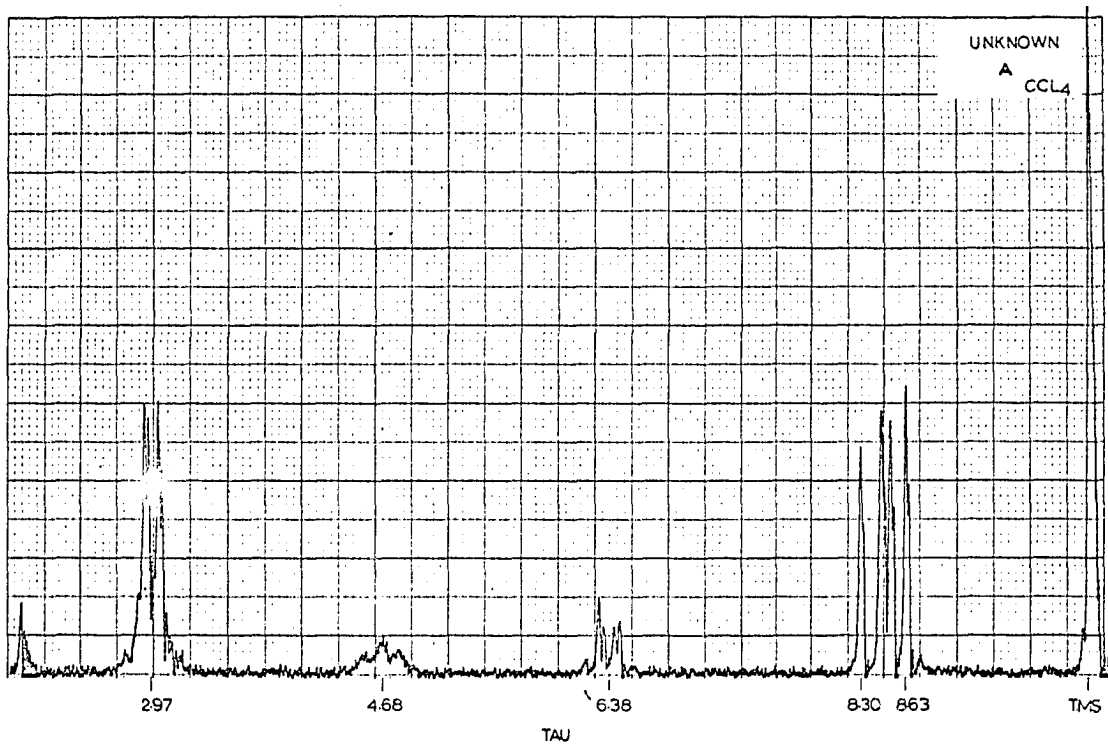


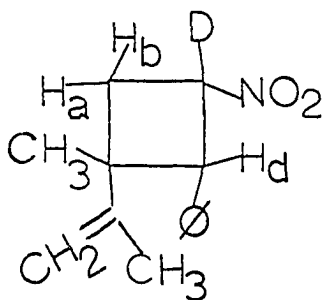
Figure 10. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of  
"Unknown A"

Bottom: Nuclear magnetic resonance spectrum of  
Dimer A



(nitro group on a saturated carbon), 6.24, 6.66, 13.40 and 14.35  $\mu$  (Figure 19, page 102). CXII gives ultraviolet absorption at  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  254s (955), 259.5s (870) and 265.5s  $\mu$  (725).

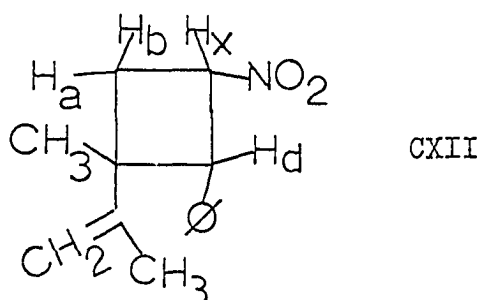


CXIII

The nuclear magnetic resonance spectrum of the deuteration product, 1-methyl-1-isopropenyl-2-phenyl-3-deuterio-3-nitrocyclobutane (CXIII, two isomers, Figure 11, page 81) will be discussed first, since it is less complex than that of photoproduct CXII. The six proton quartet between 8.20 and 9.10 p.p.m. is assigned to the two methyl groups of the two isomers. Expansion of the spectrum shows that the peaks at 8.26 and 8.96 p.p.m. are triplets, while the peaks at 8.55 and 9.06 p.p.m. are singlets. The peaks at 8.26 and 8.96 p.p.m. can be assigned to the methyl on the isopropenyl group of the two isomers, since it would be slightly split by the methylene protons on the double bond. The methylene protons,  $H_a$  and  $H_b$ , appear as a two proton multiplet at 7.08 to 7.86 p.p.m. Protons  $H_a$  and  $H_b$  could be treated as two overlapping AB systems ( $J = 11.3$  and  $12$  c.p.s., respectively) by a first



order approximation. The two singlets at 5.83 and 6.19 p.p.m. integrate for one proton. They are assigned to the benzylic protons,  $H_d$ , of the two isomers that are present in approximately a 1:1 ratio, respectively. The methylene protons on the double bond in both isomers are centered at 5.13 p.p.m., while there is no absorption between 4.64 and 5.04 p.p.m. The five aromatic protons are centered at 2.80 p.p.m.

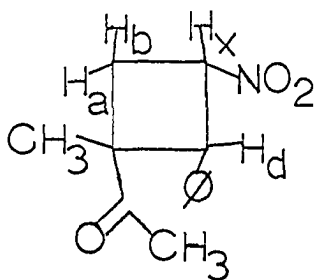


The nuclear magnetic resonance spectrum of 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII, Figure 11, page 81) shows a two proton multiplet between 7.00 and 7.90 p.p.m. for the methylene protons,  $H_a$  and  $H_b$ . The pair of doublets at 5.83 and 6.21 p.p.m. is assigned to proton  $H_d$  of the two isomers, which is coupled to proton  $H_x$  to give a doublet for each isomer ( $J = 9.23$  c.p.s.). The isomers are present in approximately a 1:1 ratio. The proton alpha to the nitro group appears as a multiplet between 4.64 and 5.04 p.p.m. The rest of the spectrum is the same as deuteration product CXIII (Figure 11, page 81).

The nuclear magnetic resonance spectrum of the liquid

obtained from the reaction of photoproduct CXII with sodium methoxide at room temperature is about the same as the starting material, although there is a very small change in the intensities of some of the peaks. CXII was stirred with base at 75° to see if any further change would occur, but none did. Therefore, the nitro and adjacent phenyl groups are trans. The formation of two isomers is due to the isopropenyl group being either cis or trans to the adjacent phenyl group.

Photoproduct CXII was further characterized by ozonization to give white crystals of 1-acetyl-1-methyl-2-phenyl-3-nitrocyclobutane (CXIV, m.p. 73-75°, 13.5%);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  253s (295), 260 (276), 266 (251) and 270.5s  $\mu$  (209). The infrared spectrum (KBr) shows absorption at 5.92 (carbonyl), 6.48 and 7.24 (nitro group on a saturated carbon), 6.25, 6.31, 6.65, 13.32 and 14.20  $\mu$  (Figure 21, page 106).

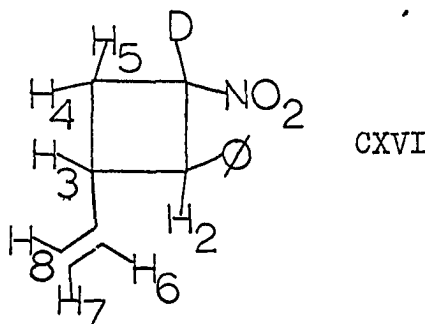


CXIV

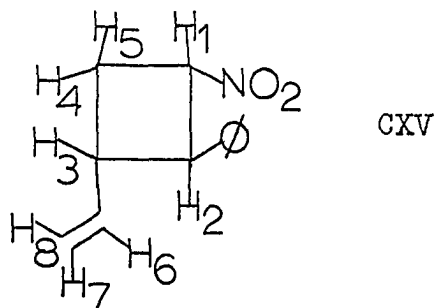
The nuclear magnetic resonance spectrum (Figure 12, page 83) of the ozonolysis product (CXIV) gives a three proton singlet at 8.47 p.p.m. for the methyl on a cyclobutane ring, while the three proton singlet at 8.32 p.p.m. is due to the

acetyl methyl group. The methylene protons,  $H_a$  and  $H_b$ , appear as two quartets centered at 6.80 and 7.80 p.p.m. Protons  $H_a$  and  $H_b$  could be treated as an AB part of an ABX spin system ( $J = 11.7$  c.p.s.) by a first order approximation, but the analysis is complicated since proton  $H_x$  is further split by proton  $H_d$ . The benzylic proton,  $H_d$ , is a doublet at 6.00 p.p.m. ( $J = 9.25$  c.p.s.). The proton alpha to the nitro group,  $H_x$ , is a quartet at 4.43 to 4.86 p.p.m., due to coupling to protons  $H_a$ ,  $H_b$  and  $H_d$ . The five aromatic protons are centered at 2.72 p.p.m. The nuclear magnetic resonance spectrum shows that the ozonolysis product (CXIV) consists of a single isomer.

Trans- $\beta$ -nitrostyrene and 1,3-butadiene were irradiated at  $-15^\circ$  to  $-3^\circ$  in hexane solution to give a light yellow liquid, 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV, b.p.  $82-84^\circ/0.25$  mm., 75.5%). The liquid gives only one spot on a thin-layer plate, but vapor phase chromatography shows that two isomers are present. The infrared spectrum (neat) shows maxima at 6.09 (double bond), 6.23, 6.45, 6.66, 13.46 and 14.35  $\mu$  (Figure 21, page 106).



The nuclear magnetic resonance spectrum of the deuteration product, 3-vinyl-2-phenyl-1-deuterio-1-nitrocyclobutane (CXVI, two isomers, Figure 13, page 85) will be discussed first, since it is not as complex as that of photoproduct CXV. The five aromatic protons are centered at 2.80 p.p.m.: The one proton multiplet between 3.75 and 4.65 p.p.m. is assigned to proton H<sub>6</sub> of the two isomers. The complex multiplet (two protons) at 4.71 to 5.22 p.p.m. is assigned to the methylene protons, H<sub>7</sub> and H<sub>8</sub>. The benzylic protons, H<sub>2</sub>, of the two isomers appear as two broad doublets centered at 5.75 p.p.m. ( $J = 9.6$  c.p.s.) and 6.21 p.p.m. ( $J = 8.5$  c.p.s.). The two doublets are due to proton H<sub>2</sub> being coupled to the allylic proton, H<sub>3</sub>, in both isomers. Integration of these doublets (one proton) shows the isomers to be in a 1:2 ratio, respectively. The methylene protons, H<sub>4</sub> and H<sub>5</sub>, and proton H<sub>3</sub> are assigned to the complex absorption between 6.52 and 7.82 p.p.m.



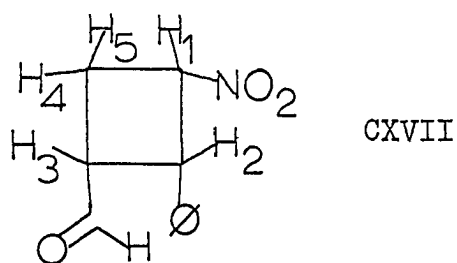
The nuclear magnetic resonance spectrum of 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV, Figure 13, page 85) is very

complicated, due to the existence of two isomers. The aromatic protons are centered at 2.78 p.p.m., while the one proton multiplet between 3.78 and 4.70 p.p.m. is assigned to proton H<sub>6</sub>. The methylene protons, H<sub>7</sub> and H<sub>8</sub>, and the proton alpha to the nitro group of the two isomers appear as a complex multiplet at 4.75 to 5.48 p.p.m. The two broad triplets centered at 5.74 and 6.21 p.p.m. (one proton) are assigned to the benzylic proton, H<sub>2</sub>. The two triplets are the result of proton H<sub>2</sub> being coupled to protons H<sub>1</sub> and H<sub>3</sub> in each isomer. A three proton multiplet between 6.52 and 7.80 p.p.m. is assigned to the methylene protons, H<sub>4</sub> and H<sub>5</sub>, and to the allylic proton, H<sub>3</sub>.

Since the reaction of base with photoproduct CXV gives back only the starting mixture unchanged, the nitro and the adjacent phenyl groups must be trans. The formation of two isomers is the result of the vinyl group being either cis or trans to the adjacent phenyl group.

Photoproduct CXV was further characterized by ozonization to give a liquid, 3-formyl-2-phenyl-1-nitrocyclobutane (CXVII, b.p. 134-136°/0.18 mm., 31.3%);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  253s (537), 258 (468), 264.5s (372) and 268s  $\mu$  (302). The infrared spectrum (neat) gives maxima at 3.55 and 3.68 (aldehyde proton), 5.82 (carbonyl), 6.24, 6.48, 6.66, 7.28, 13.40 and 14.33  $\mu$  (Figure 21, page 106).

The nuclear magnetic resonance spectrum of the ozonolysis product (CXVII, Figure 12, page 83) is difficult to interpret,



due to the presence of more than one isomer. The presence of two isomers is shown by the two doublets (one proton) at 0.14 and 0.44 p.p.m. ( $J = 1-2$  c.p.s.) for the aldehyde protons, which are in a 3:1 ratio, respectively. The five aromatic protons are centered at 2.63 p.p.m. The proton alpha to the nitro group,  $H_1$ , appears as a multiplet between 4.50 and 5.25 p.p.m., while the benzylic proton,  $H_2$ , is a quartet between 5.40 and 5.85 p.p.m. The methylene protons,  $H_4$  and  $H_5$ , and the proton alpha to the formyl group,  $H_3$ , of the two isomers are assigned to a multiplet at 6.60 to 7.45 p.p.m.

#### Search for ground state complexes

Complex formation between solute and solvent or an aggregate of solute molecules can sometimes be detected by measuring the absorption of light as a function of concentration. According to Beer's law, the absorbency at a given wavelength is directly dependent on concentration. A deviation from Beer's law, with increasing concentration, may be indicative of complex formation or aggregation (76, p. 3).

Figure 11. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of  
1-methyl-1-isopropenyl-2-phenyl-3-  
nitrocyclobutane (CXII)

Bottom: Nuclear magnetic resonance spectrum of  
1-methyl-1-isopropenyl-2-phenyl-3-  
deuterio-3-nitrocyclobutane (CXIII)

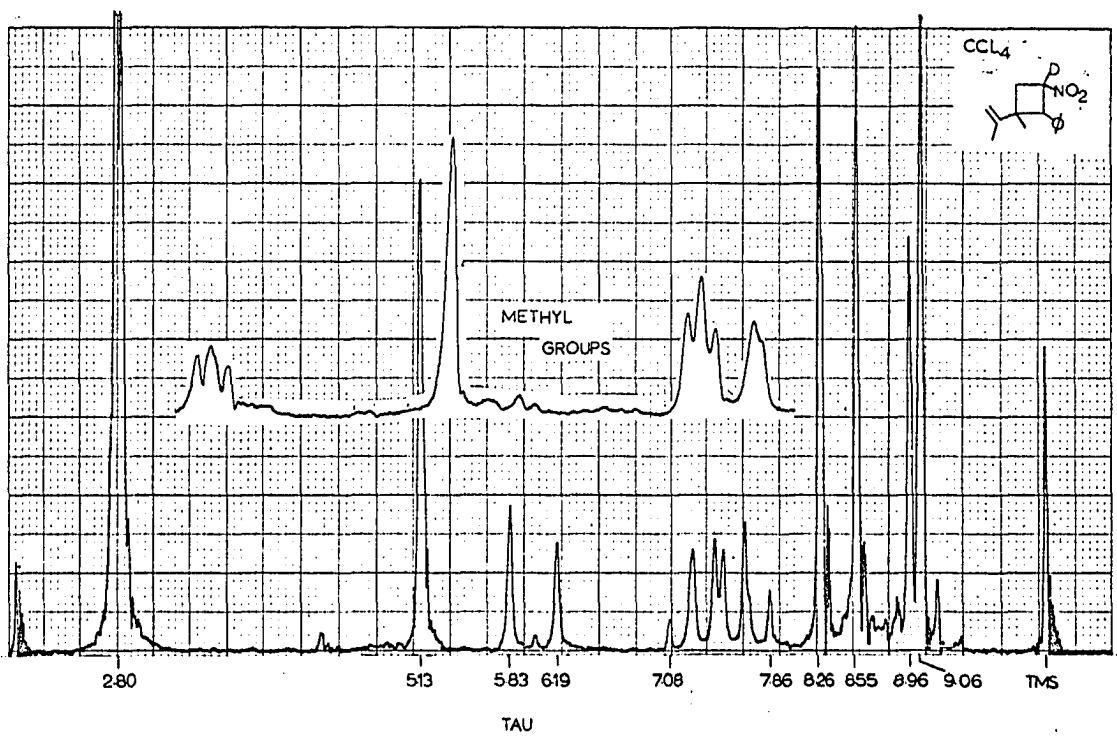
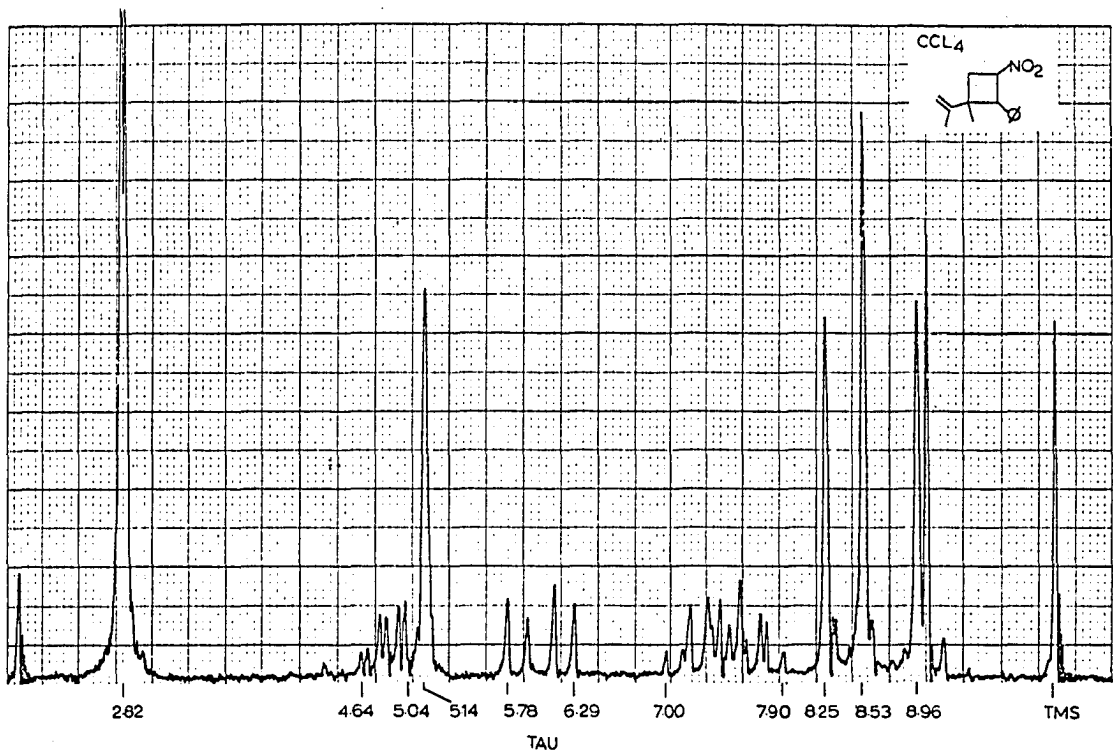




Figure 12. Nuclear magnetic resonance spectra

- Top: Nuclear magnetic resonance spectrum of  
1-acetyl-1-methyl-2-phenyl-3-nitrocyclo-  
butane (CXIV)
- Bottom: Nuclear magnetic resonance spectrum of  
3-formyl-2-phenyl-1-nitrocyclobutane (CXVII)

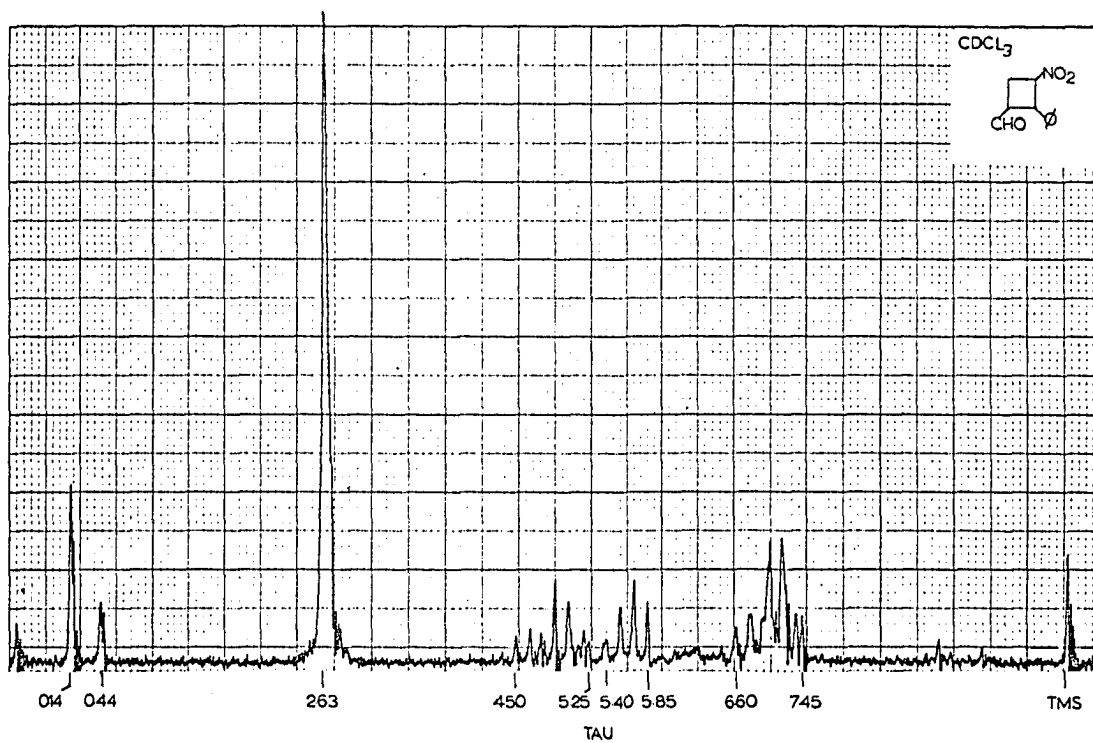
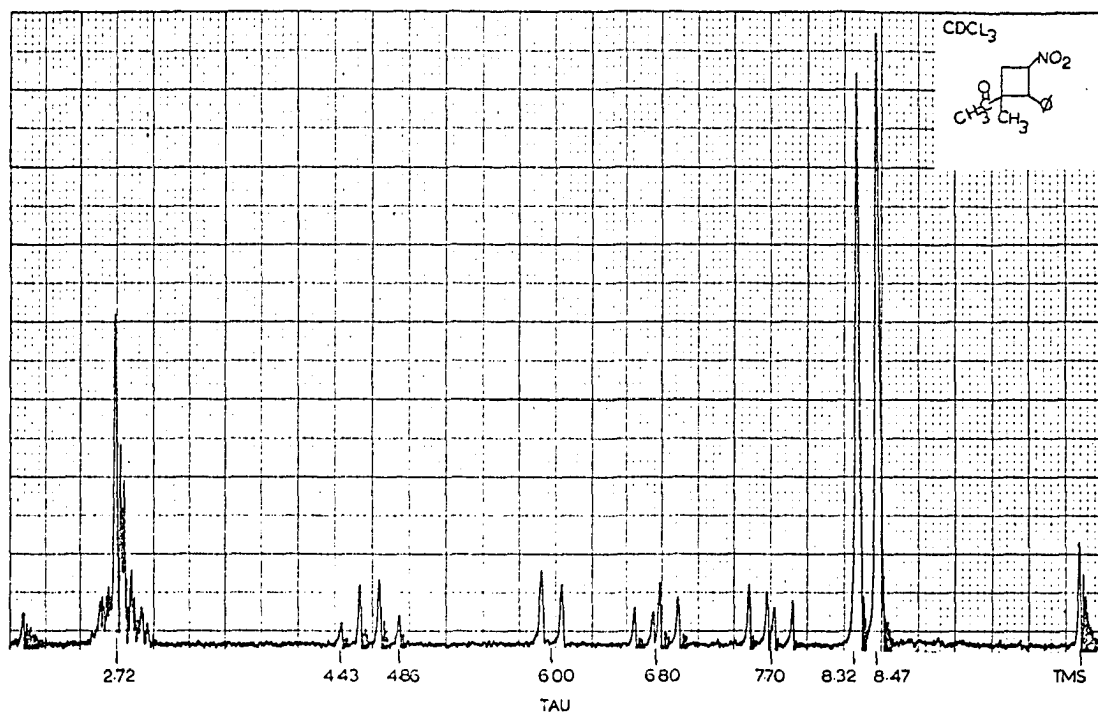
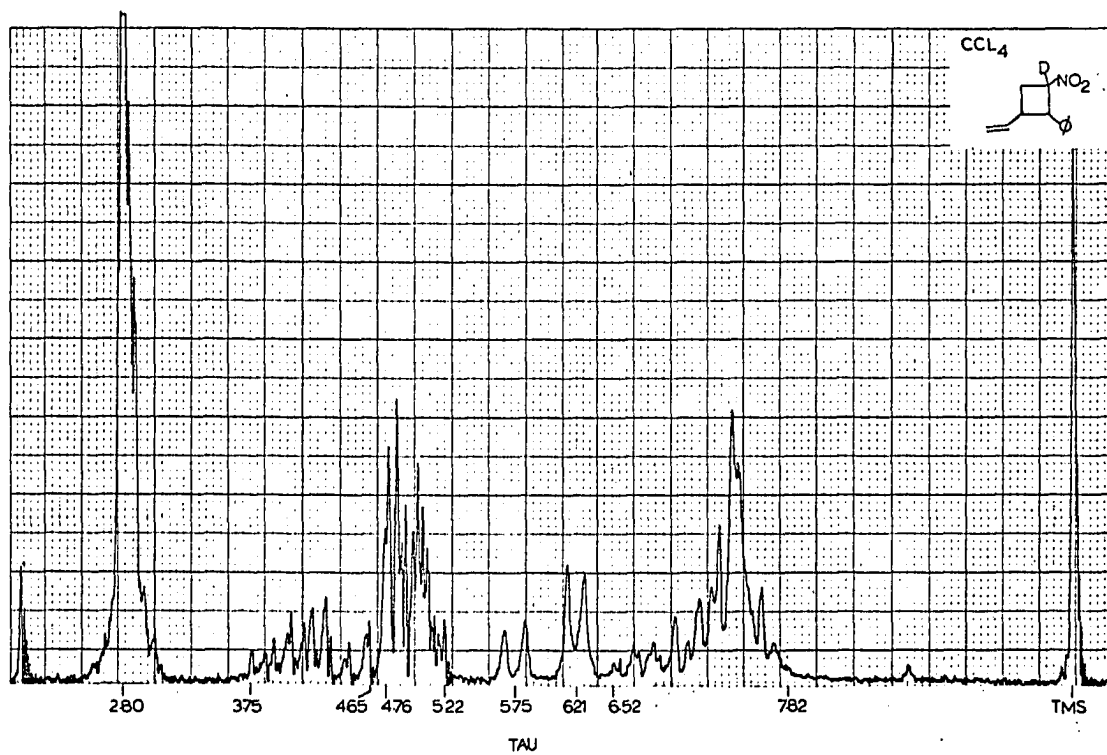
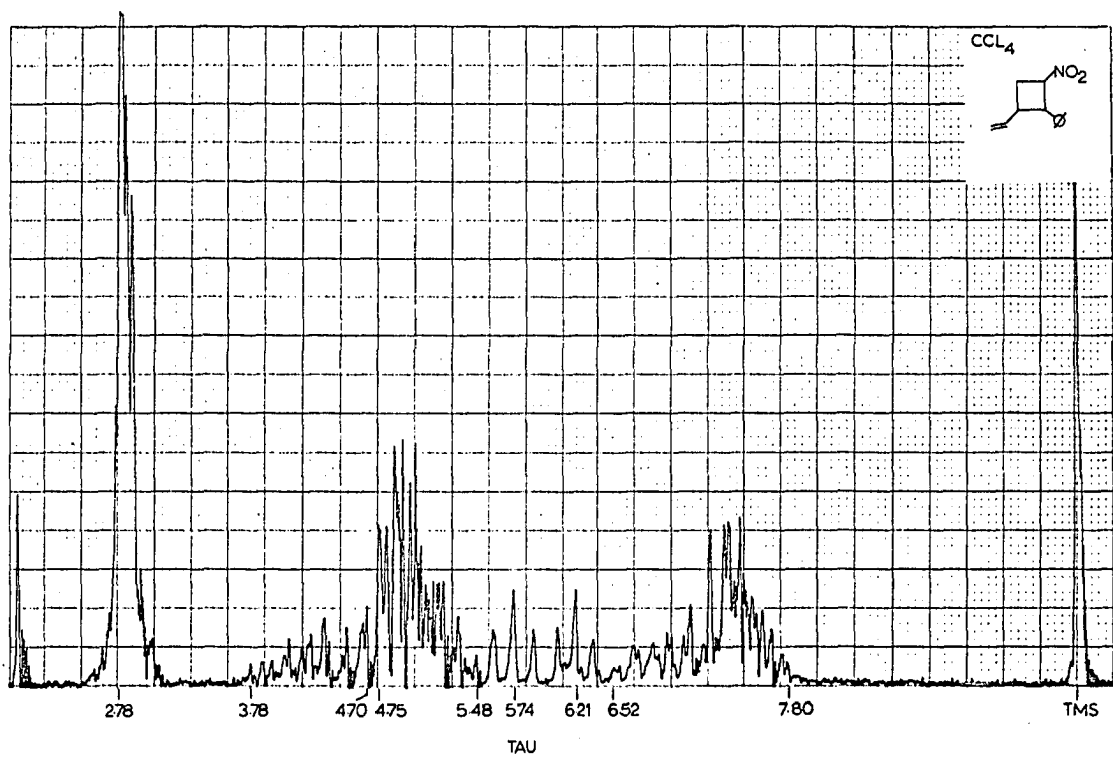


Figure 13. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of  
3-vinyl-2-phenyl-1-nitrocyclobutane (CXV)

Bottom: Nuclear magnetic resonance spectrum of  
3-vinyl-2-phenyl-1-deuterio-1-nitrocyclo-  
butane (CXVI)



The absorption of trans- $\beta$ -nitrostyrene (I) was measured as a function of concentration at 300 m $\mu$  in cyclohexene solution. A plot of absorbency against concentration of I is shown in Figure 14, page 88, using both 0.1 cm. and 1 cm. cells. Within experimental error, no deviation from Beer's law was noted. The absorption of I was measured as a function of concentration at 297.7 m $\mu$  in cyclohexane solution using 5 cm., 1 cm., and 0.1 cm. cells to give a broader concentration range. A plot of absorbency against concentration of I is shown in Figure 15, page 90. No deviation from Beer's law was noted. Cyclohexene was added to I in cyclohexane solution, but no change either in intensity or wavelength of the absorption peak at 297.7 m $\mu$  took place.

The ultraviolet spectrum of trans- $\beta$ -nitrostyrene and of some of the different olefins used in the irradiations were run in 95% ethanol in order to get some idea of the amount of light absorbed by each. The molar concentration ratio of olefin over I was equal to that used during the irradiations. If more than one irradiation was carried out with an olefin, the value from the irradiation with the greatest molar concentration of olefin over I was used. The absorbency of trans- $\beta$ -nitrostyrene was compared to the absorbency of the olefins at 300 m $\mu$ , since most of the irradiations were carried out in a Pyrex immersion well (Figure 16, page 92). The Pyrex immersion well transmits less than 10% of the light at 300 m $\mu$  (65). The comparison of the absorbency of trans- $\beta$ -nitrostyrene to

Figure 14. Beer's law plot of trans-4-nitrostyrene (I)  
in cyclohexene

Top: Beer's law plot run in 1 cm. cells

Bottom: Beer's law plot run in 0.1 cm. cells

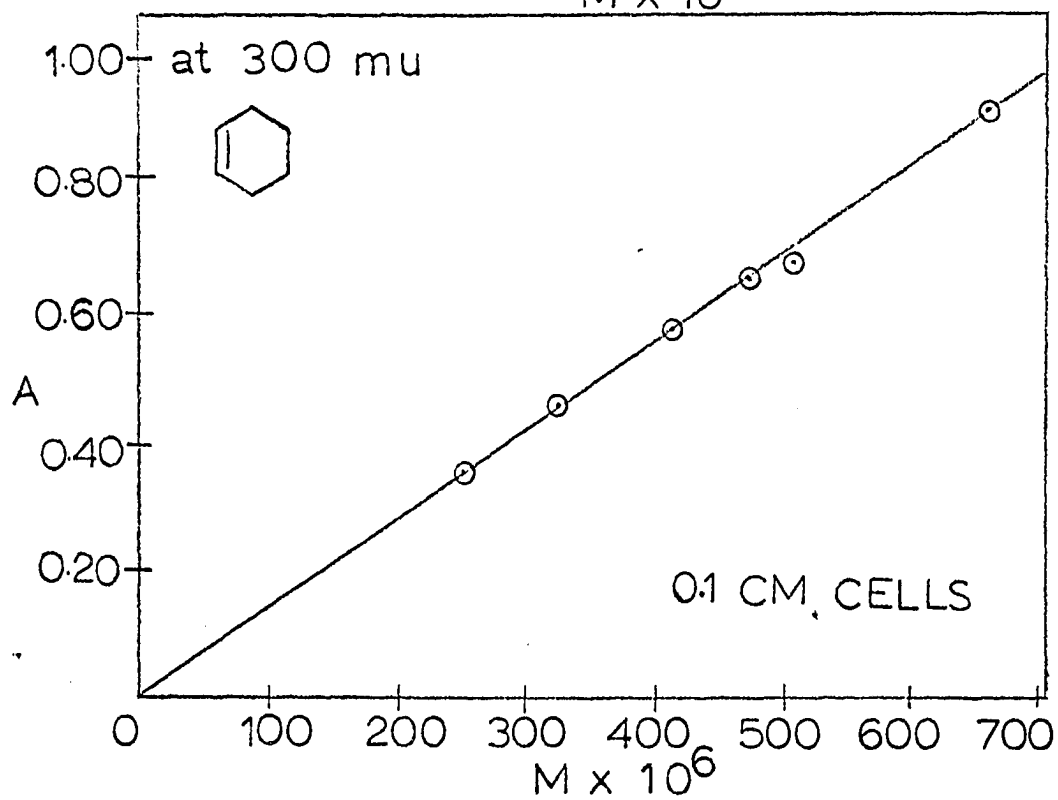
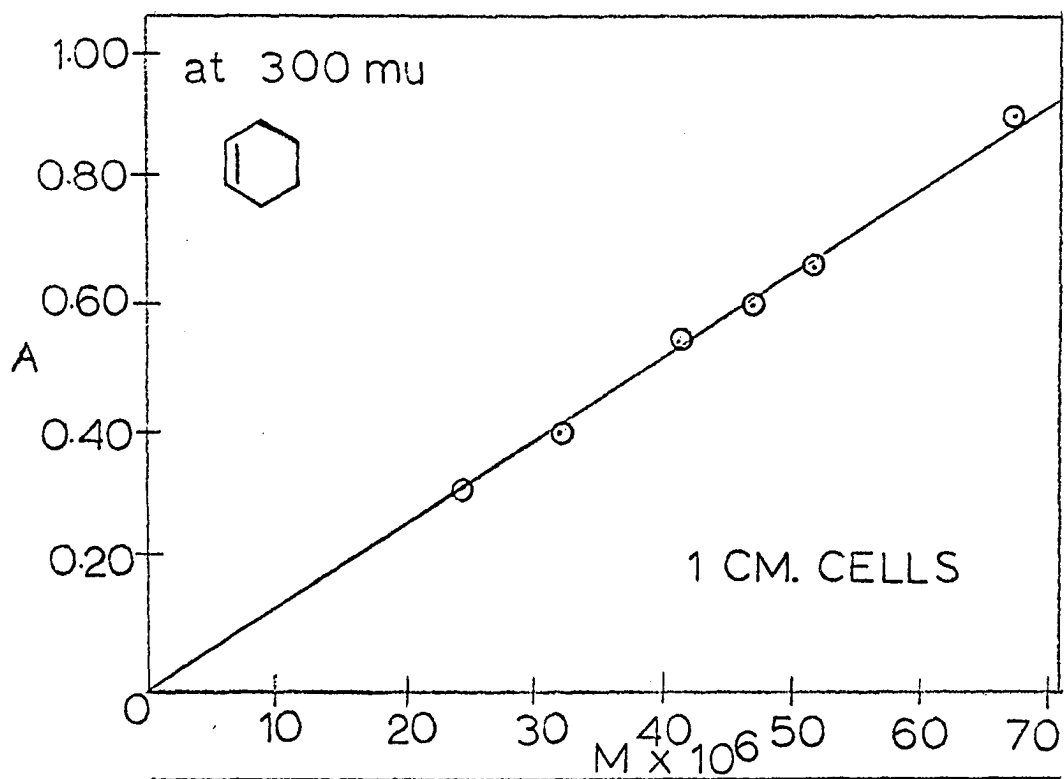


Figure 15. Beer's law plot of trans-β-nitrostyrene (I)  
in cyclohexane

Top: Beer's law plot run in 1 cm. cells

Bottom: Beer's law plot run in 0.1 cm. cells



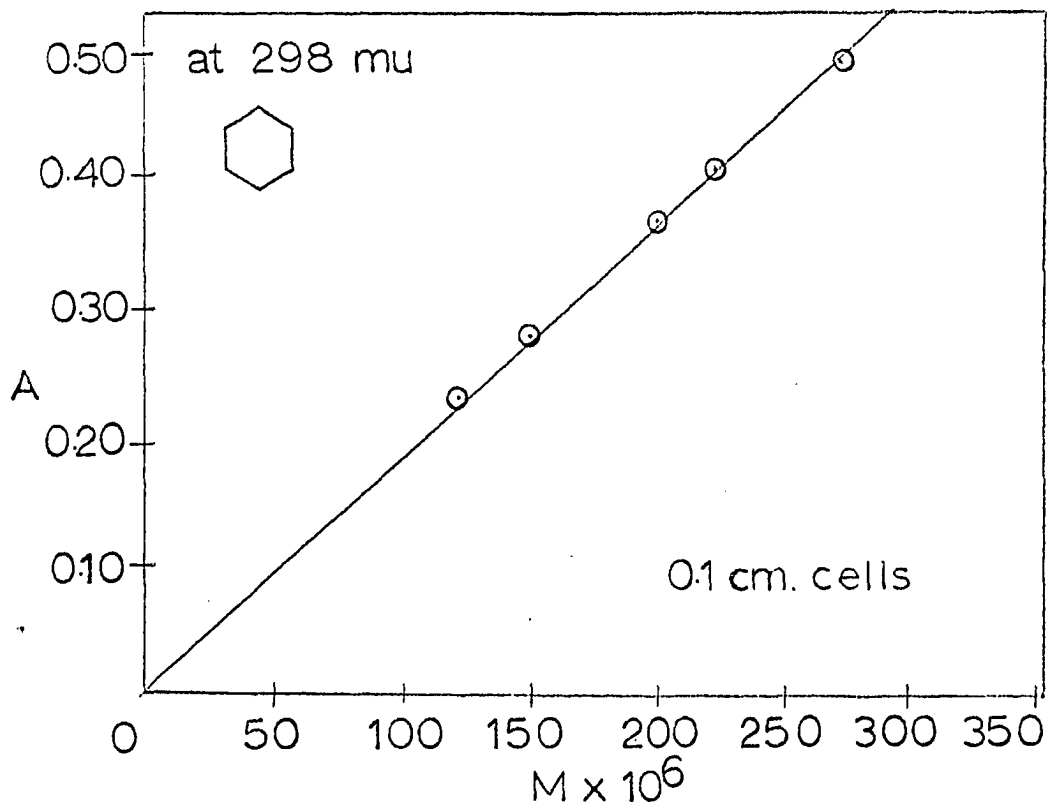
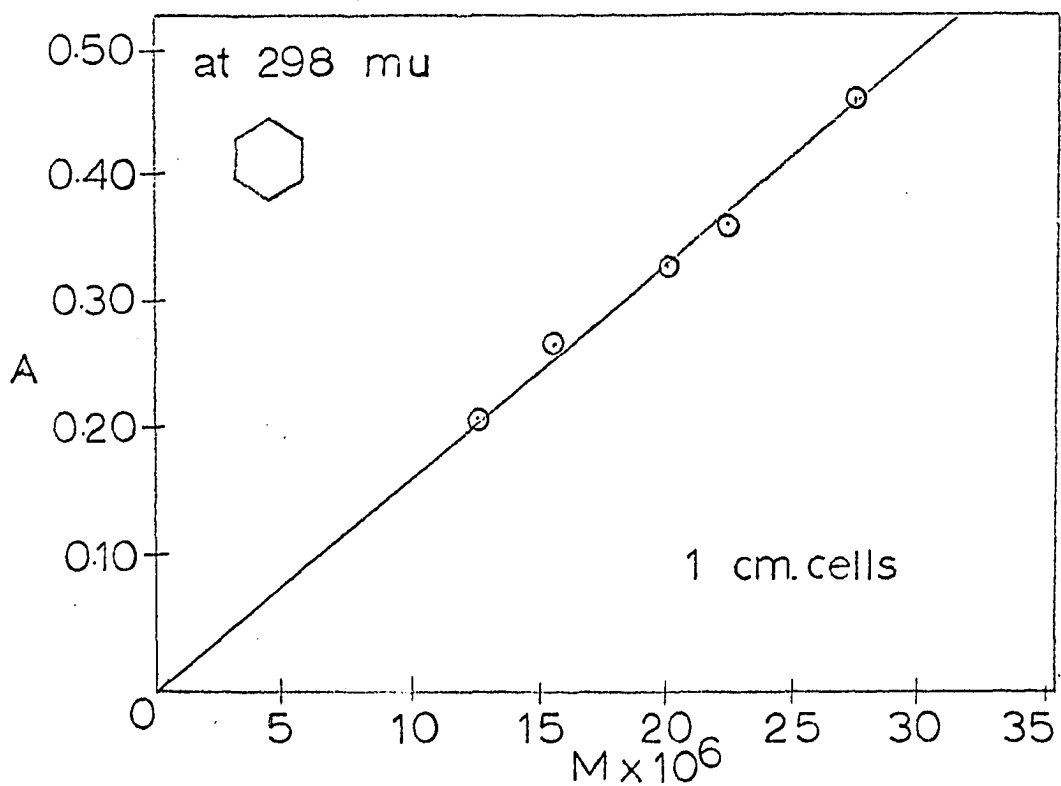
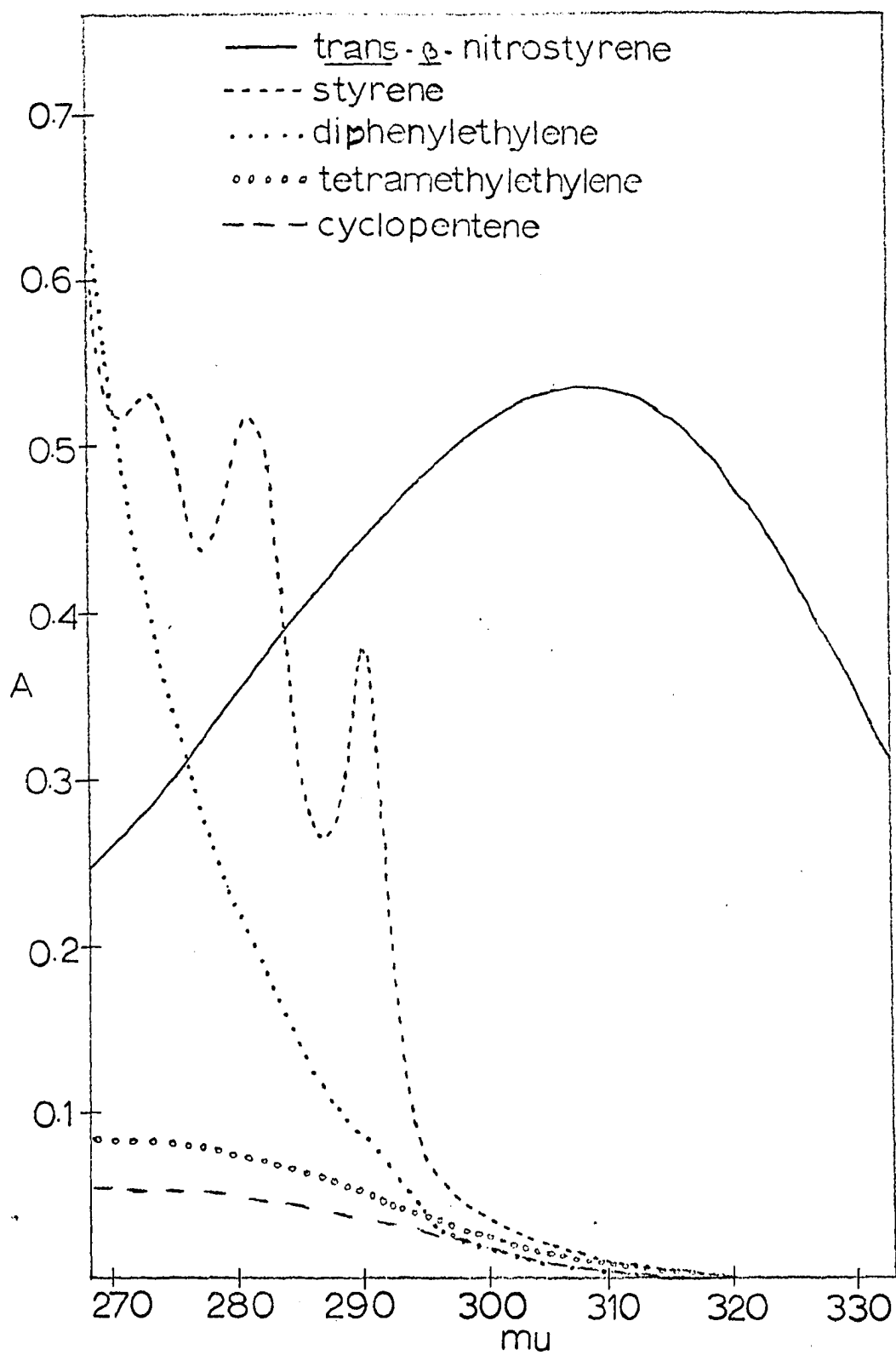


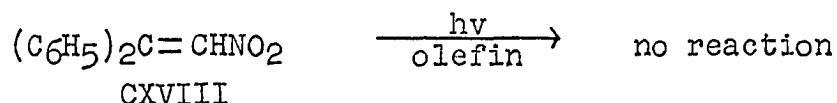
Figure 16. Ultraviolet absorption plot of trans- $\beta$ -nitrostyrene and different olefins



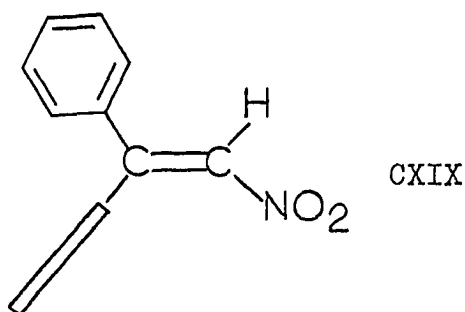
the different olefins shows that I always absorbs greater than 90% of the light at 300 mu. The values for the concentration and the absorbency of the olefins are given in Table 3, page 158.

Irradiation of 1,1-diphenyl-2-nitroethylene (CXVIII)

In order to simplify the stereochemical problem, 1,1-diphenyl-2-nitroethylene (CXVIII) was irradiated in both tetramethylethylene and styrene under the same conditions as those used in the irradiation of trans- $\beta$ -nitrostyrene with different olefins, but no reaction took place. The lack of reactivity of CXVIII may be due to steric interference with the addi-



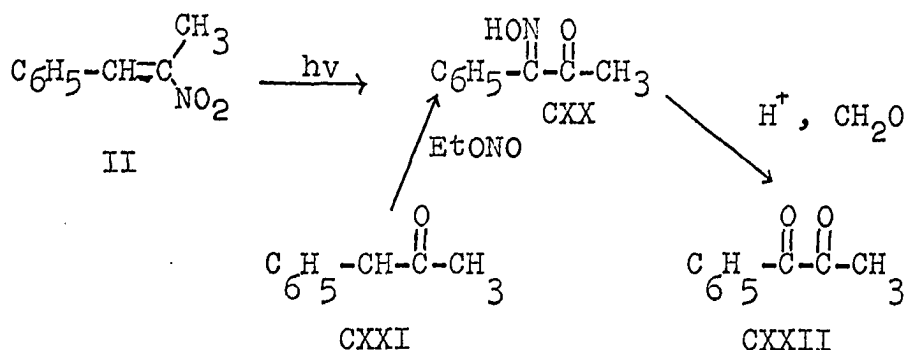
tion by a nonplanar aromatic group (CXIX).



Photochemical rearrangement

$\beta$ -methyl- $\beta$ -nitrostyrene (II) was irradiated in order to evaluate the effect of the methyl substituent on the reactivi-

ty of  $\beta$ -nitrostyrene. II was irradiated in both tetramethylethylene and styrene. The infrared spectrum of the crude



product shows that no cycloaddition product had been formed. Addition of carbon tetrachloride to the crude irradiation product gave white crystals of isomer A of 1-oximino-1-phenylpropan-2-one (CXX<sub>a</sub>). Confirmation of this structure will be given in the following discussion.

$\beta$ -methyl- $\beta$ -nitrostyrene (II) was irradiated in acetone solution to show that the presence of an olefin was not necessary for the new rearrangement product to be formed. The crude irradiation product was chromatographed to give an 81.7% yield of both isomers of 1-oximino-1-phenylpropan-2-one (CXX), but crystallization of the product gave only stable isomer A (CXX<sub>a</sub>, m.p. 161.5-162.5°). The infrared spectrum (CHCl<sub>3</sub>) of isomer A (CXX<sub>a</sub>) gives absorption at 2.80 and 3.07  $\mu$  (free and hydrogen bonded -OH stretching), 5.92 (carbonyl) and 6.24  $\mu$  (Figure 22, page 108). The nuclear magnetic resonance spectrum (CDCl<sub>3</sub>) of isomer A (Figure 17, page 98) shows five aromatic protons at 2.63 and 2.75 p.p.m. The methyl group

appears as a singlet at 7.49 p.p.m. The hydroxyl proton is not visible, since the compound is in such low concentration; however, it can be assigned to a broad peak at -2.55 p.p.m. (one proton) in dimethylsulfoxide. The 1-oximino-1-phenylpropan-2-one (CXX) that was prepared from 1-phenylpropan-2-one (CXXI) by the method of Ferris (77) gives no melting point depression upon admixture with photoisomer A (CXX<sub>a</sub>). The infrared (Figure 22, page 108) and nuclear magnetic resonance spectra of CXX, prepared by the method of Ferris, are identical to that of isomer A. Isomer A was hydrolysed in the presence of formaldehyde to give 1-phenylpropan-1,2-dione (CXXII, 50-51°/0.3 mm.). The infrared spectrum of CXXII gives maxima at 5.85 and 5.98 (carbonyls), 6.25, 6.33, 12.73 and 14.25 u. The nuclear magnetic resonance spectrum shows maxima at 2.13 p.p.m. (multiplet), 2.61 p.p.m. (multiplet) and 7.60 p.p.m. (singlet), which integrate 2:3:3. 1-phenylpropan-1,2-dione which was obtained from Eastman Chemical Company gives identical nuclear magnetic resonance and infrared spectra.

The unstable isomer B of 1-oximino-1-phenylpropan-2-one (CXX<sub>b</sub>) shows infrared (CHCl<sub>3</sub>) maxima at 2.78 and 3.04 (-OH stretching), 5.86 (carbonyl), 6.24 and 6.68 u. Attempted crystallization of photoisomer B (CXX<sub>b</sub>) gave only photoisomer A. The nuclear magnetic resonance spectrum of isomer B in dimethylsulfoxide gives two sharp peaks for the -OH proton at -2.6 and -1.9 p.p.m. (one proton). Removal of the dimethyl-

sulfoxide under reduced pressure gave only isomer A ( $CXX_a$ ). These results suggest that isomer B equilibrates to give isomer A in dimethylsulfoxide. It was previously shown that pure isomer A gives an absorption at -2.55 p.p.m. for the -OH proton in dimethylsulfoxide solution.

Figure 17. Nuclear magnetic resonance spectra

Top: Nuclear magnetic resonance spectrum of  
unknown oxime

Bottom: Nuclear magnetic resonance spectrum of  
photoisomer A of 1-oximino-1-phenylpropan-  
2-one (CXX<sub>a</sub>)



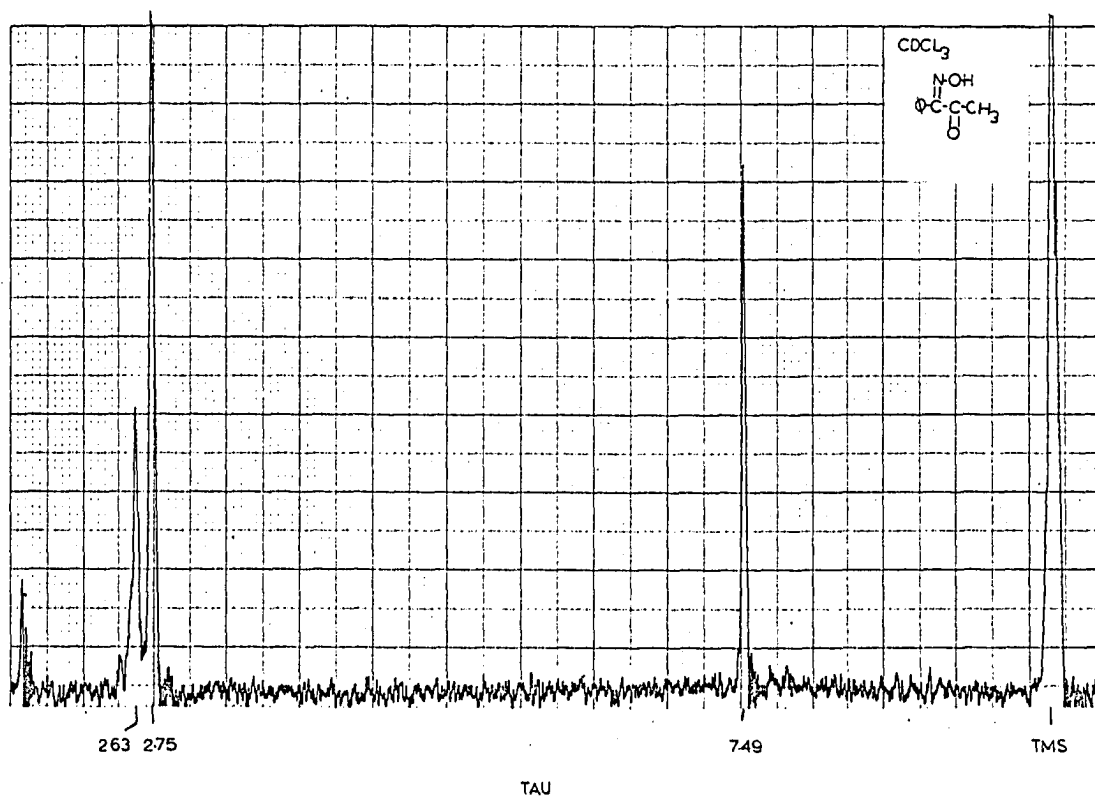
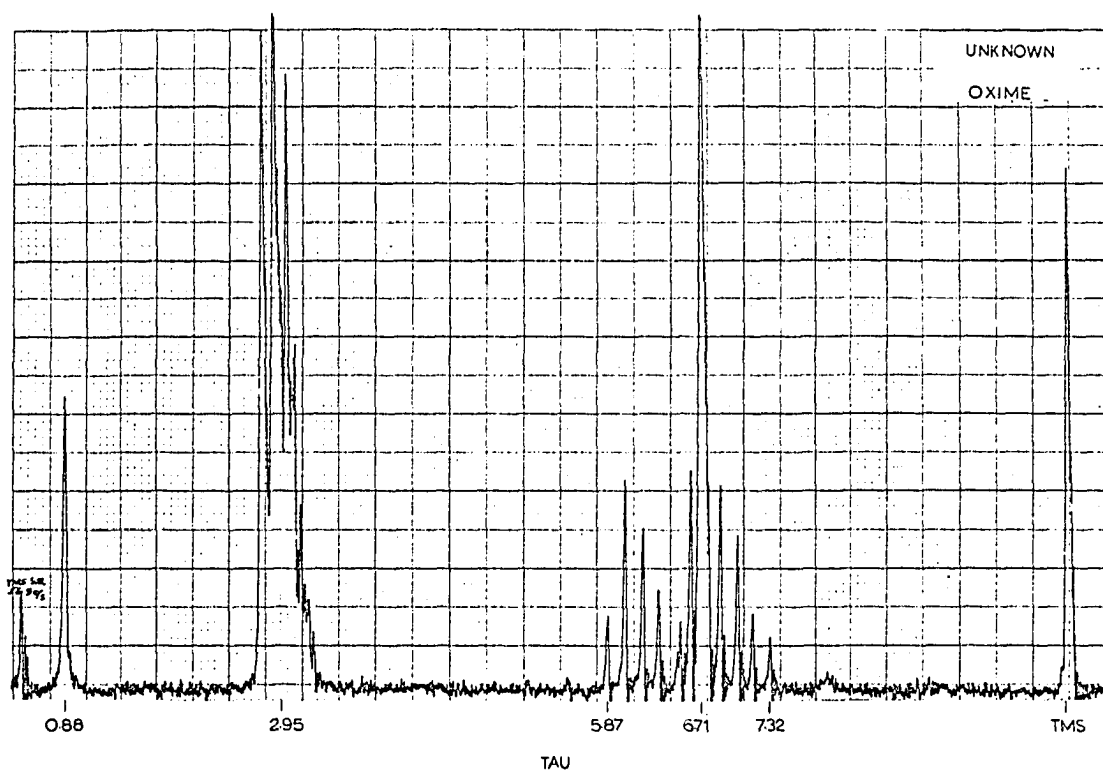


Figure 18. Infrared spectra

- Top: Infrared spectrum of 6-nitro-7-phenyl-  
bicyclo[3.2.0]heptane (CI)
- Middle: Infrared spectrum of 7-nitro-8-phenyl-  
bicyclo[4.2.0]octane (CIII)
- Bottom: Infrared spectrum of 1,1,2,2-tetramethyl-  
4-phenyl-3-nitrocyclobutane (XCVI)

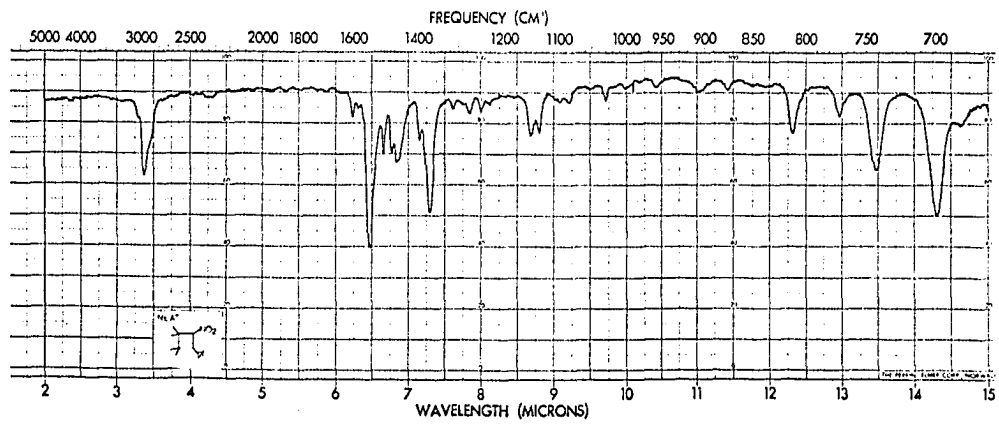
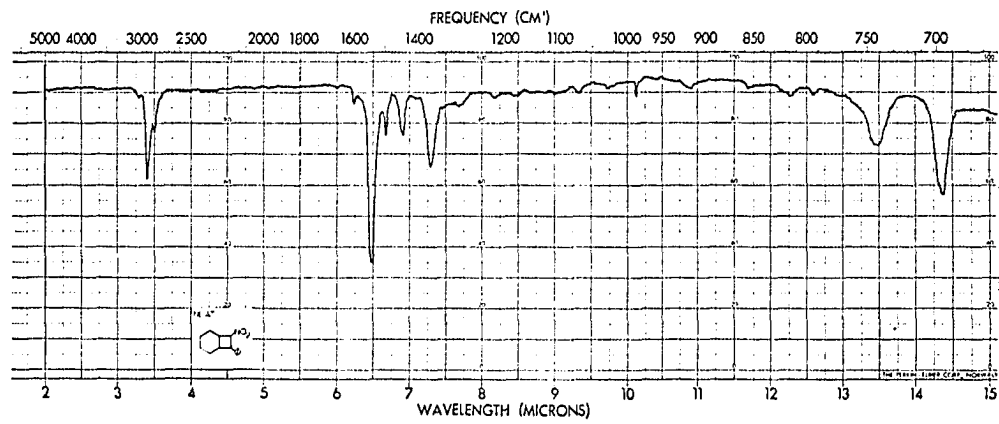
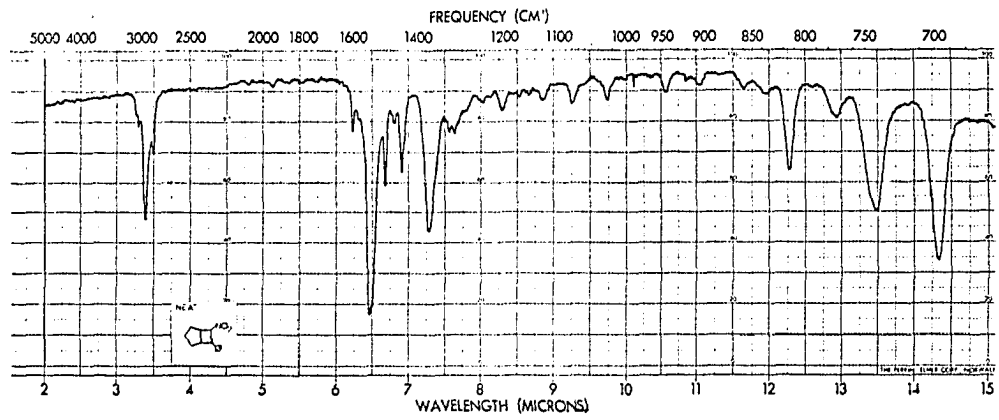


Figure 19. Infrared spectra

Top: Infrared spectrum of 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII)

Middle: Infrared spectrum of Dimer A

Bottom: Infrared spectrum of 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII)

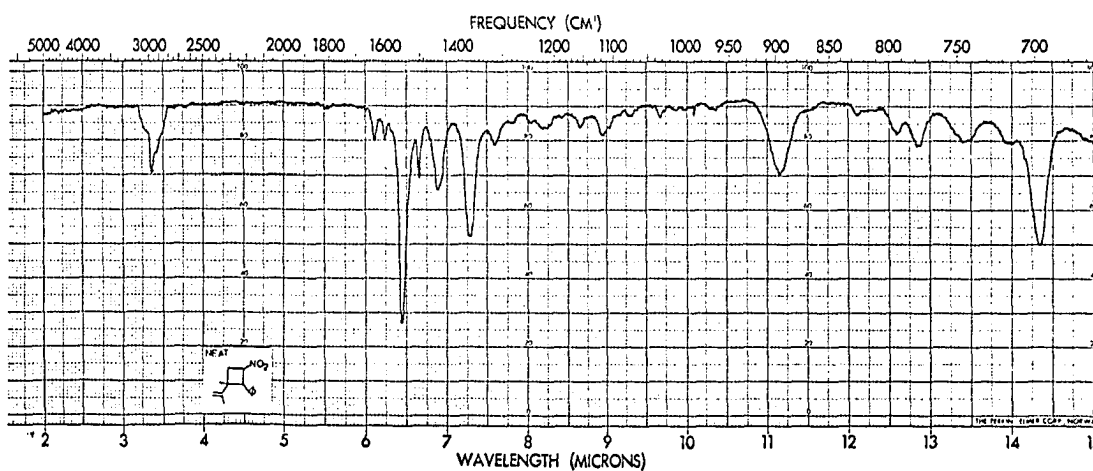
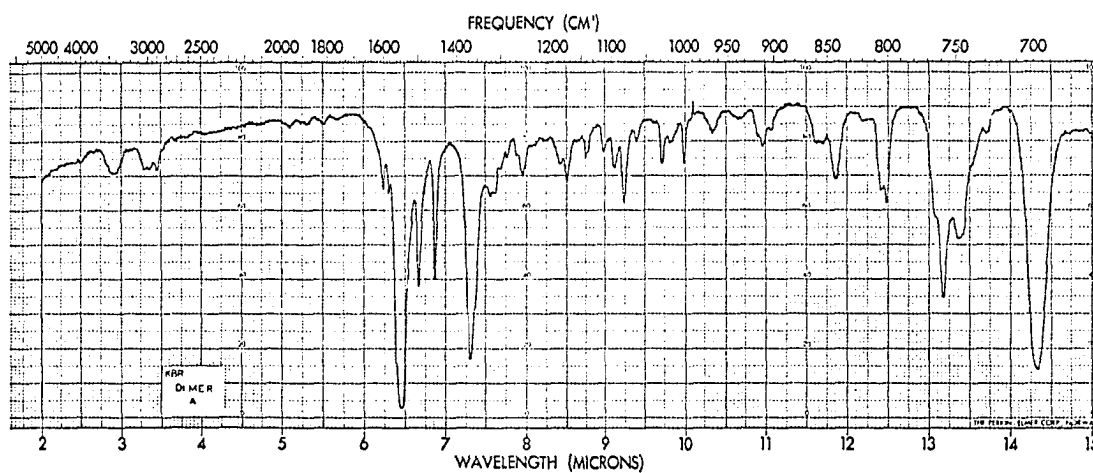
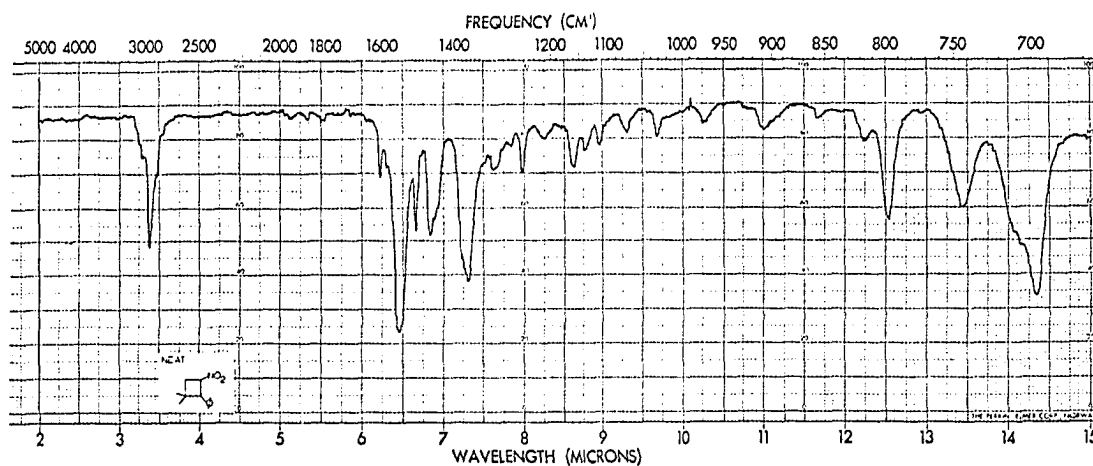


Figure 20. Infrared spectra

Top: Infrared spectrum of 1-acetyl-1-methyl-2-phenyl-3-nitrocyclobutane (CXIV)

Middle: Infrared spectrum of 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV)

Bottom: Infrared spectrum of 3-formyl-2-phenyl-1-nitrocyclobutane (CXVII)

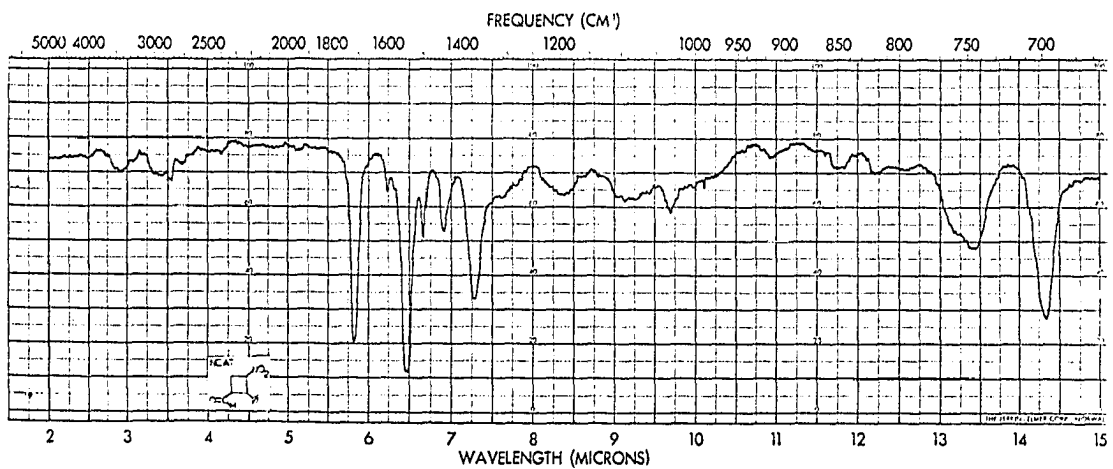
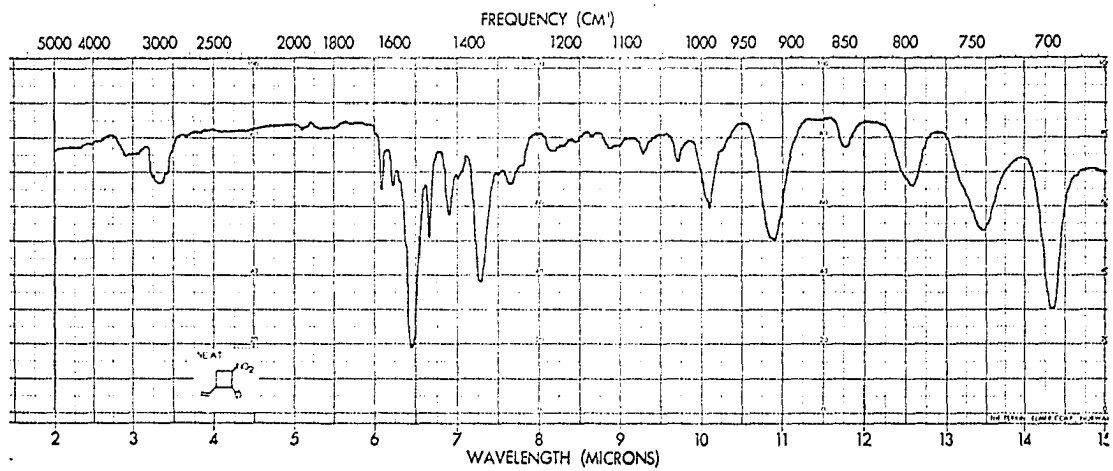
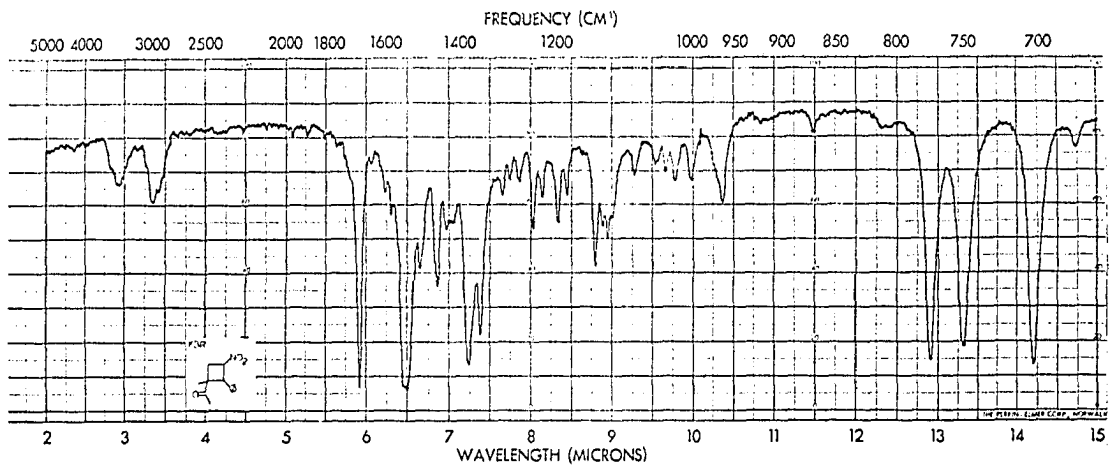


Figure 21. Infrared spectra

- Top: Infrared spectrum of "Unknown A"
  - Middle: Infrared spectrum of unknown oxime
  - Bottom: Infrared spectrum of 2,3-diphenyl-1-nitrocyclobutane (XCV)
- 
- Top: Solid isomer A of 2,3-diphenyl-1-nitrocyclobutane (XCV<sub>a</sub>)
  - Bottom: Liquid isomer B of 2,3-diphenyl-1-nitrocyclobutane (XCV<sub>b</sub>)



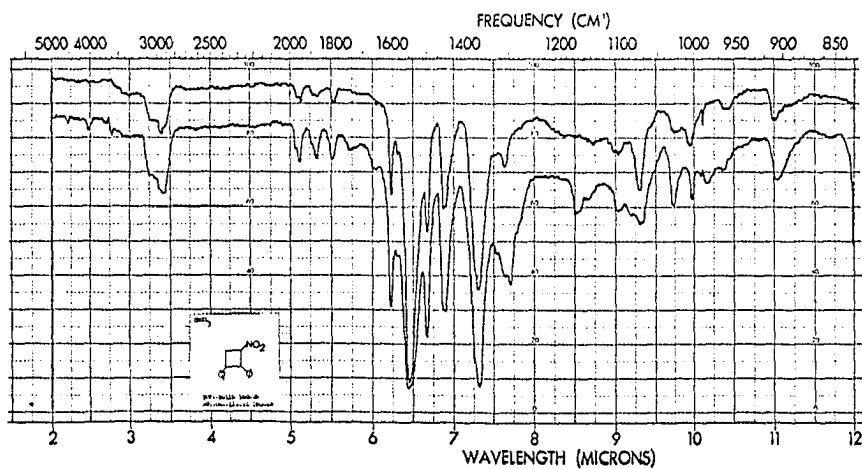
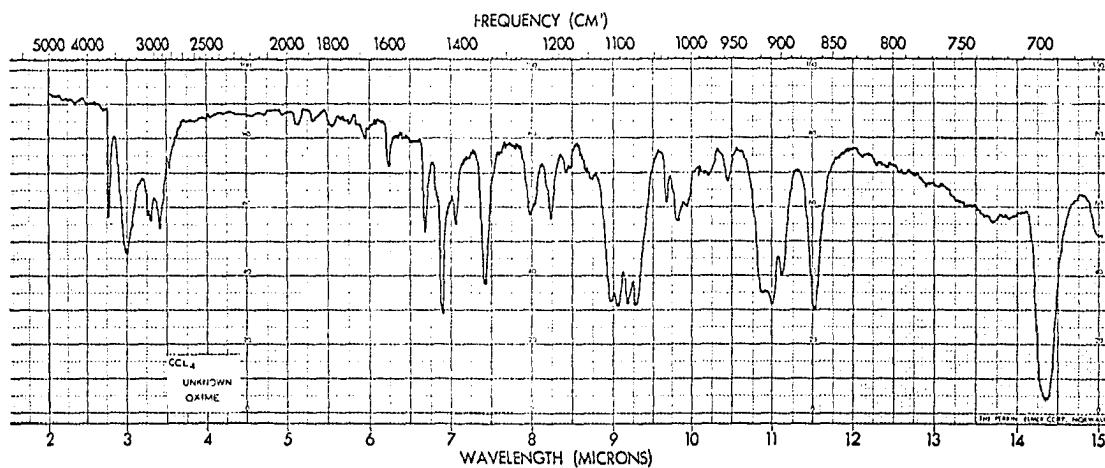
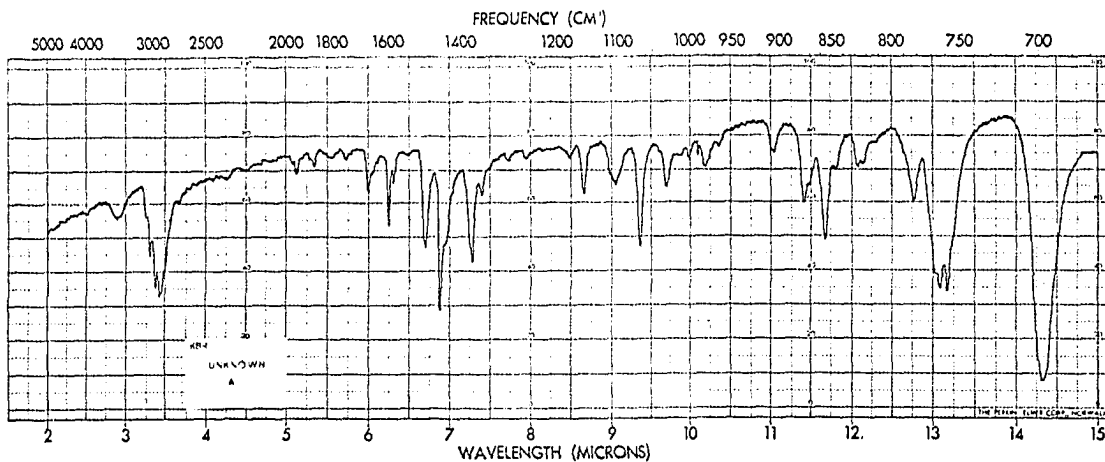


Figure 22. Infrared spectra

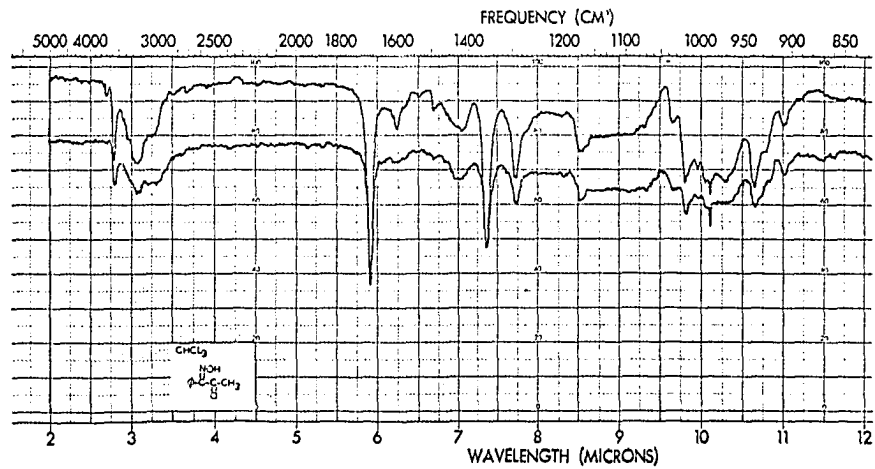
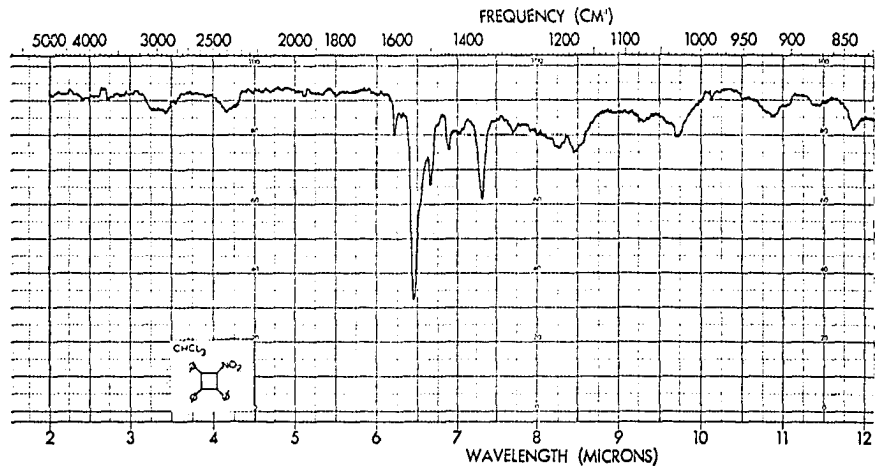
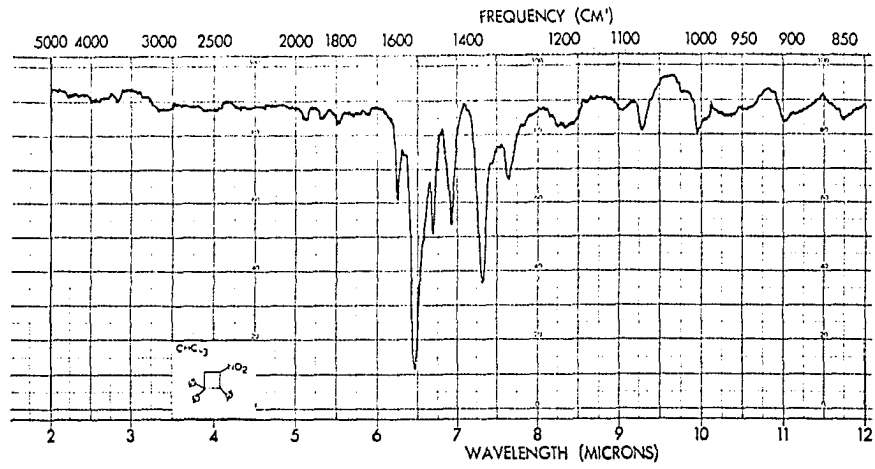
Top: Infrared spectrum of 2,3,3-triphenyl-1-nitrocyclobutane (XCIV)

Middle: Infrared spectrum of 2,3,4-triphenyl-1-nitrocyclobutane (XCIX)

Bottom: Infrared spectrum of 1-oximino-1-phenylpropan-2-one (CXX)

Top: Isomer A of 1-oximino-1-phenylpropan-2-one (CXX<sub>a</sub>)

Bottom: 1-oximino-1-phenylpropan-2-one prepared by the method of Ferris (77)



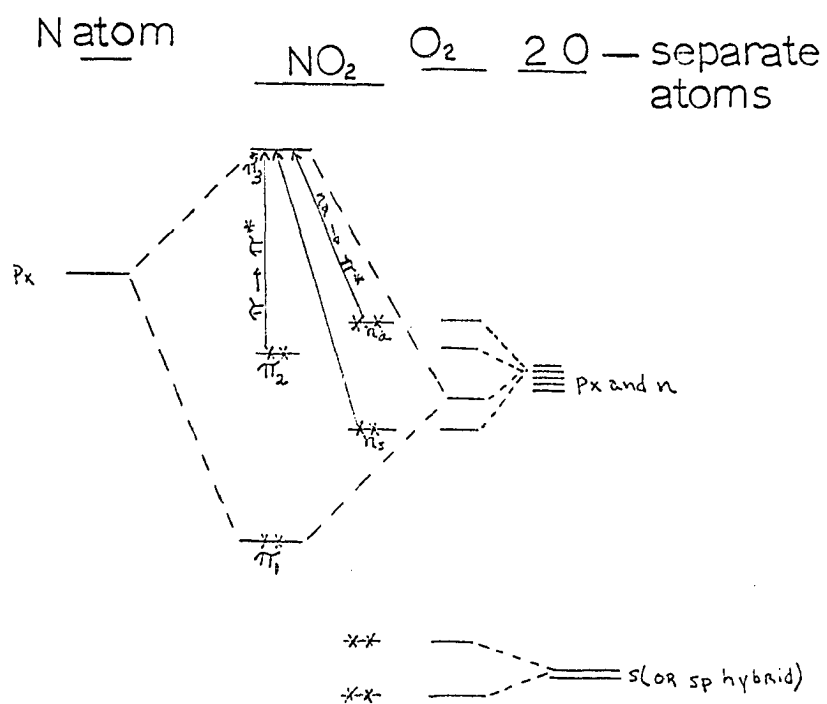
## DISCUSSION

The nitro group on a saturated carbon is known to undergo  $n-\pi^*$  and  $\pi-\pi^*$  excitation analogous to ketones. An energy level diagram for the nitro group is shown in Figure 23, page 111 (78, p. 183). It would be of interest to learn something about which excited state of  $\beta$ -nitrostyrene is involved in the formation of products. In most cases, the first excited state formed in the irradiation of a compound is an excited singlet state; the absorption of light promotes one electron to a vacant orbital, but the two electrons remain spin-paired. Since the singlet-singlet transition is allowed, the lifetime of the excited singlet state is very short (about  $10^{-7}$  to  $10^{-8}$  second).

The excited-singlet intermediate can undergo intersystem crossing to a second excited state, a triplet; one electron inverts its spin and is no longer paired. The triplet-state intermediate has a relatively longer lifetime (greater than  $10^{-4}$  second) than an excited-singlet state. Therefore, the triplet state is the most likely candidate to be involved in an intermolecular reaction (79).

The involvement of a short-lived excited singlet state in an intermolecular reaction would be more credible if evidence could be found for the existence of a ground state complex between trans- $\beta$ -nitrostyrene and olefin. Such a complex could be excited by the irradiating light to give a photoaddi-

Figure 23. Energy level diagram for the nitro group



"Energy levels of the  
nitro group"

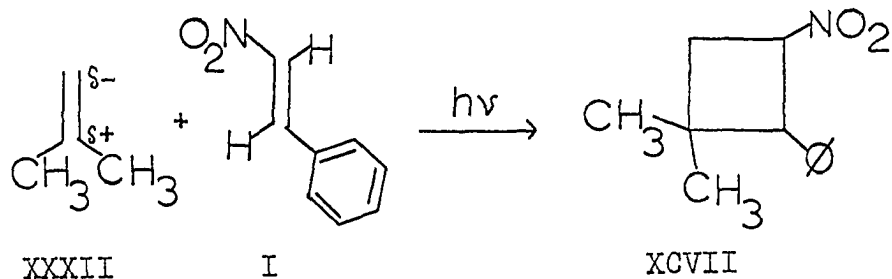
- $\pi_3^*$  - antibonding MO
- $\pi_2$  - nonbonding MO
- $\pi_1$  - bonding MO
- $n_2$  - antisymmetric n orbital

tion product, offering an alternative in which the excited molecule collides with another molecule. Beer's law experiments were carried out to determine whether a ground state complex might exist in the solutions; however, a straight line was obtained when trans- $\beta$ -nitrostyrene was plotted against absorbency in both cyclohexene and cyclohexane solutions.

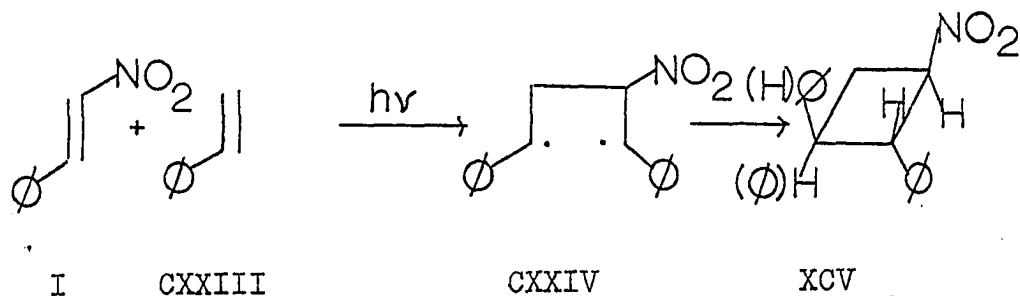
It has been shown (80) that  $n, \pi^*$  singlets and  $n, \pi^*$  triplets of  $\alpha, \beta$ -unsaturated ketones are more electron rich at the beta carbon relative to the alpha carbon than in the ground state. Corey et al. (15) find in the case of 2-cyclohexenone (XXXI) that both orientational specificity and ease of reaction can be expected of olefins having electron supplying group(s) on the double bond. The dominant cycloaddition reaction is that in which the alpha carbon of the excited enone (electrophilic species) has attached itself to the carbon of the olefin which is most nucleophilic.

The same type of specificity is found in the reactions of trans- $\beta$ -nitrostyrene with olefins. An example is the irradiation of I in isobutylene (XXXII) to give 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII). It is important to note that the most nucleophilic carbon has attached itself to I at the alpha position. Similar products are obtained in the irradiation of trans- $\beta$ -nitrostyrene in either styrene or 1,1-diphenylethylene to give, respectively, 2,3-diphenyl-1-nitrocyclobutane (XCV) and 2,3,3-triphenyl-1-nitrocyclobutane

(XCIV). This suggests that the  $n, \pi^*$  excited state of trans- $\beta$ -nitrostyrene results in formation of an alpha carbon which is less electron rich relative (more electrophilic) to the beta carbon than in the ground state.



The irradiation of trans- $\beta$ -nitrostyrene (I) in styrene (CXXIII) gave two isomers of 2,3-diphenyl-1-nitrocyclobutane (XCV). In each isomer, the nitro group and the adjacent phenyl group are trans. Formation of the two isomers is due to the phenyl group at position 3 being either cis or trans to the adjacent phenyl group (position 2). This formation could be due to a triplet biradical intermediate (CXXIV) formed from an inactivated olefin and the excited  $n, \pi^*$  triplet state of I.



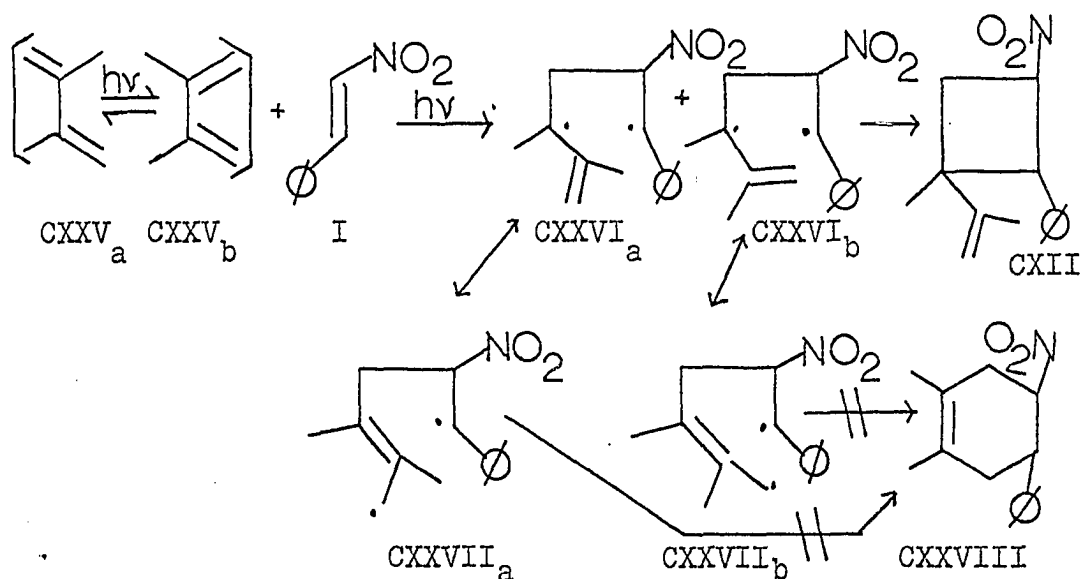
A biradical intermediate may be expected to give an isomer in which the nitro and adjacent phenyl group are cis,



since both phenyl groups should have an opportunity to rotate. However, it may be possible that each time the nitro and adjacent phenyl groups become cis in the biradical intermediate (CXXIV), bond breakage results due to repulsion between the two groups. It is known that cis- $\beta$ -nitrostyrene is formed under the conditions of the irradiations.

The irradiation of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene (CXXV) with trans- $\beta$ -nitrostyrene gave two isomers of both 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV) and 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII), respectively. Under the conditions of the irradiation, both the s-cis and s-trans conformers of the dienes should be present. Srinivasan (81) has shown that 32% of the cis isomer of 1,3-pentadiene is formed on irradiation of the s-trans isomer. The irradiation of 2,3-dimethyl-1,3-butadiene (CXXV) would be expected to give a greater amount of the cis isomer (CXXV<sub>b</sub>), since the steric repulsion between the two methyl groups make the trans isomer (CXXV<sub>a</sub>) less stable. The two isomers (CXXV<sub>a</sub>, CXXV<sub>b</sub>) should give the two biradical intermediates CXXVI<sub>a</sub> and CXXVI<sub>b</sub>. These biradical intermediates (CXXVI<sub>a</sub>, CXXVI<sub>b</sub>) could have other resonance forms (CXXVII<sub>a</sub> and CXXVII<sub>b</sub>) due to delocalization of electrons over the allylic system. The biradical intermediates (CXXVI<sub>a</sub>, CXXVI<sub>b</sub>) might be expected to be able to cyclize to give the substituted cyclohexene (CXXVIII). No substituted cyclohexene was formed on irradiation of either 1,3-butadiene or 2,3-dimethyl-

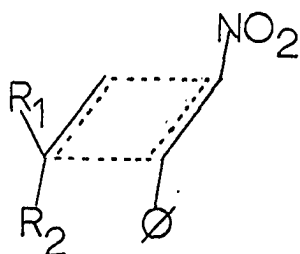
1,3-butadiene. However, it is possible that the biradicals will not form a cyclohexene derivative because they are not sterically suited for cyclization. Evidence for this is given by Hammond and Liu (82) in the irradiation of butadiene in the presence of sensitizers. They found that the s-trans diene will give biradicals which are not well-disposed to cyclize to cyclohexene derivatives, but the s-cis triplets products add to s-trans diene molecules to give biradicals which are sterically well-suited for cyclization with formation of a six-membered ring. In the case of 2,3-dimethyl-1,3-butadiene, a major amount of the s-cis isomer should be present during the irradiation; therefore, the substituted cyclohexene (CXXVIII) would be expected to be formed.



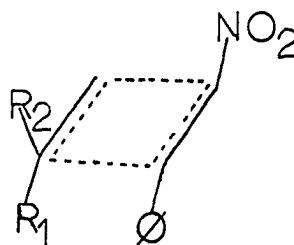
The irradiation of 2-cyclohexenone in the presence of cyclopentadiene yields only cyclopentadiene dimers as major products. Saltiel (14, p. 304) suggested that the triplet

excitation energy of 2-cyclohexenone is transferred to the cyclopentadiene, which then undergoes dimerization. The fact that trans- $\beta$ -nitrostyrene does form 1,2-addition products with 1,3-dienes suggests that it has a lower energy triplet than the corresponding dienes.

A second mechanism that could account for product formation is a concerted addition of trans- $\beta$ -nitrostyrene (I) in an excited singlet state to olefin or diene. The olefin or diene could be added to I in two ways in a concerted reaction, as shown in CXXIX and CXXX. Each photocycloaddition product discussed in this thesis has the nitro and adjacent phenyl groups trans, which suggests that  $\beta$ -nitrostyrene may be adding in a trans manner.



CXXIX



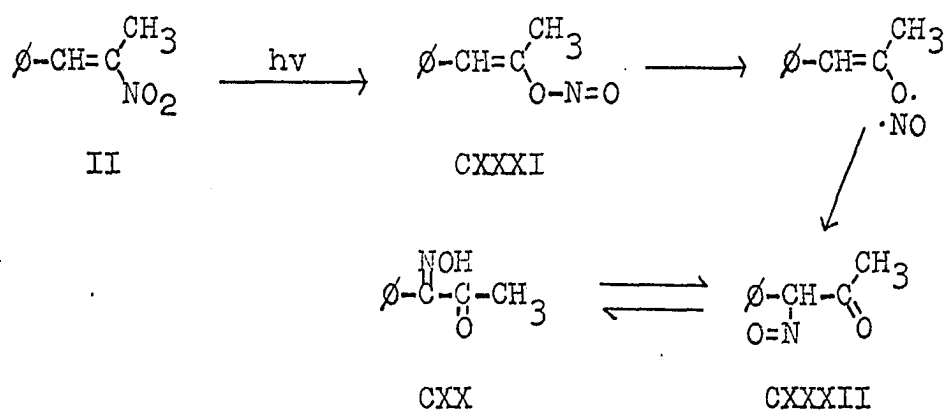
CXXX

Lenz (57) found that the irradiation of a mixture of cis- and trans- $\beta$ -nitrostyrene in styrene gave the same two isomers that were obtained using pure trans- $\beta$ -nitrostyrene. This result also suggests that the trans isomer may be adding selectively.

Recently, Hoffmann and Woodward (33) have developed selection rules for concerted cycloaddition reactions. They

postulate that 1,4-additions will be characteristic of thermal reactions, while 1,2-additions will be favored photochemically. Since 1,2-addition products are obtained from the photo-reactions of trans-β-nitrostyrene with both dienes and olefins, one might predict that these reactions are due to a concerted photocycloaddition.

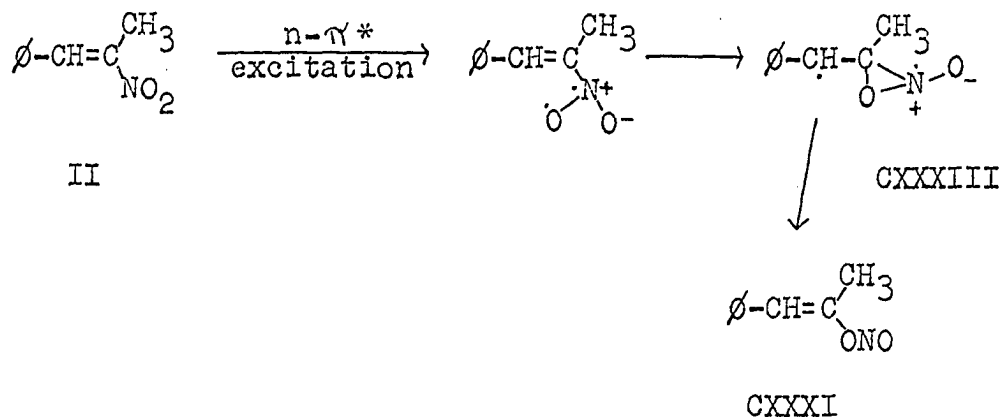
The irradiation of β-methyl-β-nitrostyrene (II) in styrene, tetramethylethylene, and acetone gives 1-oximino-1-phenylpropan-2-one (CXX) as a major product. The mechanism can be rationalized as initial photoisomerization of the nitro group to give the nitrite (CXXXI), which is analogous to the mechanism postulated by Chapman et al. (46) for the formation of products from the irradiation of 9-nitroanthracene. Photochemical or thermal cleavage of the nitrite, followed by re-addition of nitrogen (II) oxide at the alpha carbon, would



give nitrosoketone (CXXXII), which could isomerize to the keto-oxime (CXX).

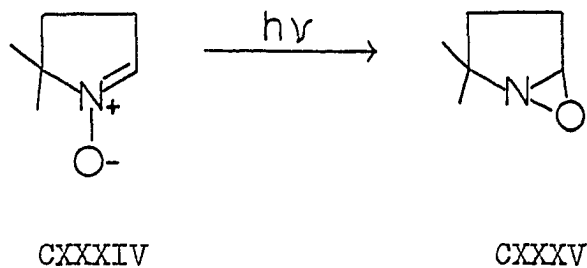
Two mechanisms could be considered for isomerization of the nitro group to a nitrite. The first is direct cleavage of

the C-N bond to form a radical pair that could recombine to form a nitrite. This process is analogous to that proposed by Rebert and Slagg (51) for the photoisomerization of nitromethane to methyl nitrite. The second is formation of an oxazirane intermediate (CXXXIII), which could then rearrange to form the nitrite (CXXXI).



An analogy for the formation of an oxazirane intermediate (CXXXIII) is found in the irradiation of 5,5-dimethyl-1-pyrrolidine-1-oxide (CXXXIV) to give oxazirane (CXXXV). Other examples of this type of reaction are given by Chapman (83, p. 410). The difference in the photoreactions of trans- $\beta$ -nitrostyrene and  $\beta$ -methyl- $\beta$ -nitrostyrene could be the result of the nitro group of II being forced by the adjacent methyl and phenyl groups into a better position to form an oxazirane type intermediate.

Previously, unattainable substituted nitrocyclobutanes have been prepared in greater than 50% yield by the irradiation of trans- $\beta$ -nitrostyrene in the presence of olefins and



dienes. All the photoaddition products formed are the result of 1,2-additions. The photoproduct obtained from the irradiation of I with asymmetrical olefins has the most nucleophilic carbon of the alkene attaching itself to the alpha position of the beta-nitrostyrene, which suggests that the beta-nitrostyrene is acting as an electrophilic species. Each photocycloaddition product discussed in this thesis has the nitro and adjacent phenyl groups trans. This implies that beta-nitrostyrene may be adding in a trans manner. A Beer's law study was carried out to determine if a ground state complex might exist, but no complex formation was noted.

If a methyl group is placed on the beta-position of beta-nitrostyrene, irradiation gives a new photoproduct, 1-oximino-1-phenylpropan-2-one (CXX), rather than a cycloaddition product. This can be rationalized as being due to an initial photoisomerization of the nitro group to a nitrite (CXXXI).

## EXPERIMENTAL

## Instruments and Methods

The ultraviolet spectra were obtained in 95% ethanol solution unless otherwise noted. The spectra and absorbency measurements were recorded on a Beckman Model DK-2A spectrophotometer made available by a grant (NSF-G14916) from the National Science Foundation.

The infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer.

The nuclear magnetic resonance spectra were run in deuteriochloroform or carbon tetrachloride unless otherwise indicated. The spectra were measured on a Varian Associates Model HR-60 spectrometer operating at 60 Mc. Spectra were calibrated by the side band technique using tetramethylsilane as internal standard. Chemical shifts are reported as p.p.m. on the tau-scale (66).

The analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York, unless otherwise noted.

Experimental for the Irradiation  
of Trans- $\beta$ -nitrostyrene (I)

Preparation of 7-nitro-8-phenylbicyclo/4.2.0/octane (CIII)

A solution of 12 g. (0.08 mole) of trans- $\beta$ -nitrostyrene (84) in 210 ml. of freshly distilled cyclohexene (XXI) was irradiated with a Hanovia Type A 550-watt medium pressure mercury arc lamp in a Pyrex immersion well. The solution was stirred magnetically and cooled with tap water while a slow stream of nitrogen was continually run through it. The progress of the reaction was followed by removing aliquots and measuring the ultraviolet absorption. After 4 hours, the absorbency at 308  $\mu$  had disappeared, but the irradiation was continued for 6 more hours. The excess cyclohexene was removed by distillation under reduced pressure. A light yellow liquid, 7-nitro-8-phenylbicyclo/4.2.0/octane (CIII, 13.24 g., 58%), was distilled (118-120°/0.1 mm.);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  252s (617), 258 (540), 264.5s (437) and 268s  $\mu$  (355). The liquid gave two close spots above trans- $\beta$ -nitrostyrene (I) on a silica gel thin-layer plate developed in benzene. The infrared spectrum (neat) showed maxima at 3.41, 6.24, 6.48, 6.67, 6.90, 7.29, 13.47 and 14.37  $\mu$  (Figure 18, page 100). The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 5, page 52.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{17}\text{NO}_2$ : C, 72.70; H, 7.41; N, 6.08. Found: C, 72.95; H, 7.61; N, 6.21.



Deuteration of 7-nitro-8-phenylbicyclo/4.2.0/octane (CIII)

Sodium methoxide (0.027 g., 0.0005 mole) was added to a solution of 7-nitro-8-phenylbicyclo/4.2.0/octane (CIII, 0.27 g., 0.001 mole) in deuteriomethanol (5 ml.). The mixture was stirred at room temperature for 22 hours, and 20 ml. of deuterium oxide was added quickly to the solution. The solution was extracted with anhydrous ether, and the ether was dried over anhydrous magnesium sulfate. The ether was evaporated to give 0.11 g. of a light yellow liquid, 7-deuterio-7-nitro-8-phenylbicyclo/4.2.0/octane (CIV). The infrared spectrum (neat) showed maxima at 3.42, 6.24, 6.51, 6.67, 6.91, 7.31, 13.48 and 14.38  $\mu$ . The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 5, page 52.

Reaction of sodium methoxide with 7-nitro-8-phenylbicyclo/4.2.0/octane (CIII)

Sodium methoxide (0.027 g., 0.0005 mole) was added to a solution of 7-nitro-8-phenylbicyclo/4.2.0/octane (CIII, 0.27 g., 0.001 mole) in absolute methanol (5 ml.). The mixture was stirred at room temperature for 22 hours, and 20 ml. of distilled water was added quickly to the solution. The solution was extracted with ether, and the ether was dried over anhydrous magnesium sulfate to give 0.12 g. of a light yellow liquid. The nuclear magnetic resonance and infrared spectra of this liquid were exactly the same as those of 7-nitro-8-phenylbicyclo/4.2.0/octane (CIII).

Nef reaction on 7-nitro-8-phenylbicyclo/4.2.0/octane (CIII)

Following the procedure of Hawthorne (68), 1 g. of 7-nitro-8-phenylbicyclo/4.2.0/octane (CIII) was dissolved in 18 ml. of 2.5 N sodium hydroxide in 40 ml. of 80% methanol at room temperature under a nitrogen atmosphere. After 30 minutes, 40 ml. of 80% methanol was added, and the solution was stirred for 13 hours. The solution was cooled to 0°, and 12 ml. of 12 N hydrochloric acid was slowly added with stirring. The solution was warmed to room temperature and then diluted with 125 ml. of distilled water. The mixture was extracted with ether, and the ether was dried over sodium sulfate. The ether was evaporated under reduced pressure on a rotatory evaporator. The crude reaction product showed infrared maxima (CCl<sub>4</sub>) at 3.05, 3.40, 5.58, 5.92, 6.48, 6.70, 6.90, 7.33 and 14.35 u. The infrared spectrum showed that the reaction mixture consisted of unreacted photoproduct (CIII), a cyclobutanone (5.58 u), and an unknown compound with an absorption at 5.92 u. An attempt to separate these compounds on a florisil column was unsuccessful.

Preparation of 6-nitro-7-phenylbicyclo/3.2.0/heptane (CI)

Preparation A A solution of 15 g. (0.10 mole) of trans-β-nitrostyrene (84) in 154 g. (2.26 mole) of cyclopentene (XXIX) was irradiated in a quartz immersion well with a Hanovia Type A medium pressure mercury arc lamp. The solution was stirred magnetically and cooled with tap water while a

slow stream of nitrogen was continually run through it. The progress of the reaction was followed by removing aliquots and measuring the ultraviolet absorption. After 27 hours of irradiation, the absorbency at 308  $\mu$  had disappeared. This is not the effective irradiation time since during the last part of the irradiation the immersion well was coated with a polymeric material. The excess cyclopentene was removed by evaporation on a rotatory evaporator under diminished pressure. A light yellow liquid, 6-nitro-7-phenylbicyclo[3.2.0]heptane (CI, 13.1 g., 64% recovered yield), was distilled (105-107°/0.07 mm.);  $\lambda_{\max}^{95\% \text{ EtOH}}$  253s (631), 259.5 (562), 265.5s (447) and 269  $\mu$  (363). The liquid gave two close spots above trans-6-nitrostyrene on a silica gel thin-layer plate developed in benzene. The infrared spectrum (neat) showed maxima at 3.39, 3.50, 6.24, 6.48, 6.68, 6.90, 7.28, 12.27, 13.48 and 14.34  $\mu$  (Figure 18, page 100). The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 4, page 50.

Anal. Calcd. for  $\text{C}_{13}\text{H}_{15}\text{NO}_2$ : C, 71.87; H, 6.96.

Found: C, 71.62; H, 7.12.

Preparation B A solution of 5 g. (0.0366 mole) of trans-6-nitrostyrene (I) dissolved in 62 g. (0.912 mole) of cyclopentene was irradiated in a quartz container, with internal coils through which tap water was circulated. The light source consisted of a Hanovia Type A medium pressure mercury arc lamp mounted approximately 6 inches from the con-

tainer. After 60 hours of irradiation, the excess cyclopentene was removed by distillation on a rotatory evaporator under diminished pressure. A light yellow liquid, 6-nitro-7-phenylbicyclo[3.2.0]heptane (CI, 3.60 g., 49.2%), was distilled (105-107°/0.07 mm.). The liquid gave two close spots above trans-β-nitrostyrene on a silica gel thin-layer plate developed in benzene. The infrared and nuclear magnetic resonance spectra were identical to those of the light yellow liquid (CI) obtained from the preceding irradiation.

Preparation C A solution of 7 g. (0.047 mole) of trans-β-nitrostyrene in 35 g. (0.515 mole) of cyclopentene was irradiated with a Hanovia Type A 550-watt medium pressure mercury arc lamp in a Pyrex immersion well for 7 hours. The solution was stirred magnetically and cooled with tap water while a slow stream of nitrogen was continually run through it. The excess cyclopentene was removed at reduced pressure. A yellow liquid, cis- and trans-β-nitrostyrene, distilled (80°/0.2 mm.). It has been shown by Lenz (57) that trans-β-nitrostyrene is stable under the conditions of the distillation. The infrared spectrum (CHCl<sub>3</sub>) showed maxima at 3.30, 6.12, 6.24, 6.33, 6.68, 6.90, 7.45 and 10.36 u. The nuclear magnetic resonance spectrum (CCl<sub>4</sub>) showed absorption at 2.00, 2.23 and 2.46 p.p.m. (trans-β-nitrostyrene) and 3.03, 3.21, 3.31 and 3.46 p.p.m. (cis-β-nitrostyrene). The absorption values given for cis-β-nitrostyrene agree with the results of Lenz (57).

A light yellow liquid, 6-nitro-7-phenylbicyclo[3.2.0]heptane (CI), was distilled (120°/0.15 mm.). The infrared and nuclear magnetic resonance spectra were identical to those of the light yellow liquid (CI) obtained from the first irradiation.

Irradiation of styrene in excess cyclopentene

A solution of 6 g. (0.0586 mole) of styrene in 100 ml. of cyclopentene was irradiated for a total of 19 hours in an internally cooled Pyrex vessel with a medium pressure mercury arc lamp placed 7 inches away from the Pyrex container. The progress of the reaction was followed by removing aliquots and measuring the ultraviolet absorption. There was no change in the ultraviolet spectrum after 19 hours of irradiation. The solution was placed in an internally cooled quartz container and irradiated for 40 hours more with no detectable change in the 308 mu absorbency.

Deuteration of 6-nitro-7-phenylbicyclo[3.2.0]heptane (CI)

Sodium methoxide (0.031 g., 0.000575 mole) was added to a solution of 6-nitro-7-phenylbicyclo[3.2.0]heptane (CI, 0.250 g., 0.00115 mole) in deuteriomethanol (4 ml.). The mixture was stirred at room temperature for 18 hours, and 14 ml. of deuterium oxide was added quickly to the solution. The solution was extracted with anhydrous ether, and the ether was dried over anhydrous magnesium sulfate. The ether was evapo-

rated to give 0.14 g. of a light yellow liquid, 6-deuterio-6-nitro-7-phenylbicyclo[3.2.0]heptane (CII). The infrared spectrum (neat) showed maxima at 3.40, 6.25, 6.53, 6.68, 6.92, 7.30, 9.27, 9.73, 12.62, 13.55 and 14.35  $\mu$ . The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 4, page 50.

Reaction of sodium methoxide with 6-nitro-7-phenylbicyclo[3.2.0]heptane (CI)

Sodium methoxide (0.031 g., 0.000575 mole) was added to a solution of 6-nitro-7-phenylbicyclo[3.2.0]heptane (CI, 0.250 g., 0.00115 mole) in absolute methanol (4 ml.). The mixture was stirred at room temperature for 18 hours, and 14 ml. of water was added quickly to the solution. The solution was extracted with ether, and the ether was dried over anhydrous magnesium sulfate. The ether was evaporated to give 0.16 g. of a light yellow liquid. The nuclear magnetic resonance and infrared spectra of this liquid were identical to those of photoproduct (CI).

Nef reaction on 6-nitro-7-phenylbicyclo[3.2.0]heptane (CI)

Following the method of Wildman and Wildman (70), a solution of sodium ethoxide (0.2 g. of sodium in 4 ml. of ethanol) was added with stirring to a solution of 0.51 g. of 6-nitro-7-phenylbicyclo[3.2.0]heptane (CI) in 10 ml. of absolute ethanol and allowed to stir for 80 minutes under a nitrogen atmosphere. This ethanolic solution was added to a well-

stirred solution of 3 ml. of concentrated hydrochloric acid in 30 ml. of water and 25 ml. of ethanol at 0° in a nitrogen atmosphere. This solution was stirred at 0° for 30 minutes and then diluted with water and extracted with ether. The ether solution was evaporated on a rotatory evaporator. The crude reaction mixture showed infrared maxima at 3.50, 5.65, 5.97, 6.47, 6.90 and 7.28 u. The infrared spectrum showed that the reaction mixture consisted of unreacted photoproduct CI, a cyclobutanone (5.65 u), and an unknown compound with an absorption at 5.97 u. An attempt to separate these compounds on a silica gel column was not successful.

Irradiation of *trans*- $\beta$ -nitrostyrene in tetramethylethylene

Irradiation A      A solution of 8 g. (0.0537 mole) of *trans*- $\beta$ -nitrostyrene (I) in 85 g. (1.01 mole) of tetramethylethylene was irradiated with a Hanovia medium pressure mercury arc lamp in a Pyrex immersion well for 8 hours and 20 minutes. The solution was stirred magnetically and cooled with tap water while a stream of nitrogen was slowly bubbled through it. The excess tetramethylethylene was evaporated at reduced pressure, and the crude irradiation product was chromatographed on 375 g. of silica gel. Elution of the column with 1.5 l. of 9:1 Skelly B-benzene gave 0.025 g. of a white solid. The white solid was recrystallized from 95% ethanol to give white crystals of Unknown A (0.013 g., m.p. 80-81.5°) in a trace amount. The infrared spectrum (KBr) showed maxima

at 2.90, 3.29, 3.37, 3.43, 6.00, 6.25, 6.70, 6.88, 7.27, 8.65, 9.05, 9.35, 9.70, 10.19, 11.03, 11.41, 11.67, 12.10, 12.77, 13.09, 13.17 and 14.32  $\mu$  (Figure 20, page 104). The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) showed absorption at 2.93 and 3.02 p.p.m., 4.68 p.p.m. (a very broad triplet), 6.38 p.p.m. (multiplet), and 8.30 to 8.60 p.p.m. (multiplet) which integrated 5:1:1:6 (Figure 10, page 72).

Anal. Found: C, 90.66; H, 9.29.

Elution with 1.5 l. of 3:1 Skelly B-benzene gave a colorless liquid, 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI, 7.33 g., 58.7%);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  248s (407), 253.5 (398), 259.5 (407), 265 (347) and 269  $\mu$  (295). The liquid gave one spot above trans- $\beta$ -nitrostyrene on a silica gel thin-layer plate developed in 1:3 Skelly B-benzene. The infrared spectrum (neat) showed maxima at 3.37, 6.23, 6.48, 6.66, 6.77, 6.84, 7.15, 7.30, 8.70, 8.80, 12.31, 12.96, 13.48 and 14.31  $\mu$  (Figure 18, page 100). The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) of the combined fractions from the chromatography is shown in Figure 2, page 46, and is identical to the nuclear magnetic resonance spectrum of these fractions after they had been carefully distilled.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{19}\text{NO}_2$ : C, 72.08; H, 8.21; N, 6.00. Found: C, 72.37; H, 8.04; N, 6.19.

Irradiation B A solution of 5.75 g. (0.0386 mole) of trans- $\beta$ -nitrostyrene dissolved in 100 g. (0.43 mole) of tetramethylethylene was irradiated in a Pyrex container, with



internal cooling coils through which tap water was circulated. The light source consisted of a Hanovia Type A medium pressure mercury arc lamp mounted approximately 6 inches from the container. After 50 hours of irradiation, the excess tetramethylethylene was removed at reduced pressure. A liquid (5.38 g., 60% crude yield) was distilled at (100-102°/0.15 mm.). The liquid gave two spots above trans- $\beta$ -nitrostyrene on a silica gel thin-layer plate developed in 1:3 Skelly B-benzene. The liquid (3.36 g.) was chromatographed on 170 g. of silica gel. Elution with 3:1 Skelly B-benzene gave 2.19 g. of a colorless liquid, 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI). The liquid gave one spot above trans- $\beta$ -nitrostyrene on a silica gel thin-layer plate developed in 1:3 Skelly B-benzene. The infrared and nuclear magnetic resonance spectra of this colorless liquid were identical to those of liquid (XCVI) obtained from the previous irradiation.

Deuteration of 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI)

Sodium methoxide (0.035 g., 0.00065 mole) was added to a solution of 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI, 0.30 g., 0.0013 mole) in deuteriomethanol (6 ml.). The solution was stirred magnetically for 24 hours at room temperature, and 20 ml. of deuterium oxide was added quickly to it. The mixture was extracted with anhydrous ether and was dried

over anhydrous magnesium sulfate. The ether was evaporated to give 0.120 g. of a colorless liquid, 1,1,2,2-tetramethyl-4-phenyl-3-deuterio-3-nitrocyclobutane (XCVIII). The infrared spectrum (neat) showed maxima at 3.37, 6.23, 6.50, 6.66, 6.77, 6.88, 7.16, 7.29, 7.95, 8.65, 8.80, 8.93, 12.37, 13.55, 14.33 and 14.76  $\mu$ . The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 2, page 46.

Reaction of sodium methoxide with 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI)

Sodium methoxide (0.035 g., 0.00065 mole) was added to a solution of 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI, 0.30 g., 0.0013 mole) in absolute methanol (6 ml.). The solution was magnetically stirred for 24 hours at room temperature, and 20 ml. of distilled water was added to it. The mixture was extracted with anhydrous ether and was dried over anhydrous magnesium sulfate. The ether was evaporated to give 0.130 g. of a colorless liquid. The nuclear magnetic resonance and infrared spectra of this liquid were exactly the same as those of photoproduct XCVI.

Attempted bromination of 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI)

A solution of photoproduct XCVI (0.87 g., 0.00373 mole) and 0.700 g. (0.00394 mole) of N-bromosuccinimide in 50 ml. of carbon tetrachloride was refluxed at 130° for 3 hours. During

the period of refluxing, small amounts of benzoyl peroxide were added in an attempt to start the reaction. The reaction mixture was cooled, and the solids were filtered off. The carbon tetrachloride solution was evaporated at diminished pressure on a rotatory evaporator. The residue was dissolved in ether, and the ether was dried over anhydrous magnesium sulfate. The ether was evaporated to give 0.820 g. of a yellow residue that did not give a test for bromine. The residue was chromatographed on 20 g. of silica gel. The only compounds isolated from the chromatography fractions were photoproduct XCVI and benzoic acid.

Attempted oxidation of 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI)

According to the method of Shechter and Williams (73), 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI, 4.6 g., 0.0198 mole) was placed in a solution of 1 l. of 0.1 N potassium hydroxide and 120 ml. of 2 N magnesium sulfate. A solution of 2.84 g. (0.018 mole) of potassium permanganate was added slowly to this solution, but no color change took place. This solution was extracted with ether, and the ether solution was dried over anhydrous magnesium sulfate. The ether was evaporated to give 3.53 g. of a liquid which had an infrared identical to that of photoproduct XCVI.

Formation of 2,3,4-triphenyl-1-nitrocyclobutane (XCIX)

A solution of 5 g. (0.0336 mole) of trans- $\beta$ -nitrostyrene and 15 g. (0.084 mole) of trans-stilbene in 400 ml. of absolute ether was irradiated in a Pyrex immersion well for 43 hours with a medium pressure mercury arc lamp. The solution was stirred magnetically and cooled with tap water while nitrogen was bubbled through it. The ether was evaporated on a rotatory evaporator at reduced pressure, and the crude reaction product was chromatographed on 600 g. of florisil. The column was first eluted with 1 l. of Skelly B. Further elution with 6 l. of 19:1 Skelly B-benzene gave 13.4 g. of cis- and trans-stilbene. The first fractions from the elution with 19:1 Skelly B-benzene contained a colorless liquid that was distilled (70°/0.45 mm.). The infrared and nuclear magnetic resonance absorption of the cis-stilbene from the distillation of the first fractions were identical to those of a pure sample of cis-stilbene. Trans-stilbene did not isomerize to cis-stilbene under the same distillation conditions. The last fractions from the continued elution with 19:1 Skelly B-benzene gave a white solid which was recrystallized to give white crystals; m.p. 124-125°. The infrared and nuclear magnetic resonance absorptions of the white crystals were identical to those of a sample of pure trans-stilbene.

Elution with 5 l. of 3.3:1 Skelly B-benzene gave white crystals of 2,3,4-triphenyl-1-nitrocyclobutane (XCIX, 0.725 g., 26.8% yield based on recovered stilbene ); m.p. 125.5-

126.5°;  $\lambda$   $\overset{95\% \text{ EtOH}}{\text{max}}$  252.5s (2,690), 258 (2,460), 265s (2,000) and 269s  $\mu$  (1,260). The infrared spectrum ( $\text{CHCl}_3$ ) showed maxima at 6.22, 6.45, 6.66, 6.89, 7.32, 8.45 and 9.72  $\mu$  (Figure 22, page 108). The nuclear magnetic resonance spectrum ( $\text{CDCl}_3$ ) is shown in Figure 3, page 48.

Anal. Calcd. for  $\text{C}_{22}\text{H}_{19}\text{NO}_2$ : C, 80.22; H, 5.81; N, 4.22. Found: C, 80.26; H, 5.85; N, 4.40.

Elution with 2 l. of benzene gave a crude material which was recrystallized from benzene to give 0.10 g. of white crystals. The crystals softened at 238-241° and melted at 242-243°. These white crystals were not soluble enough in chloroform, dimethylsulfoxide, or acetone to permit a nuclear magnetic resonance spectrum to be run. The infrared spectrum (KBr) showed absorption at 3.43, 6.11, 6.30, 6.45, 6.68, 6.87, 6.95, 7.26, 7.37, 10.97, 12.68, 13.08, 13.50 and 14.28  $\mu$ .

Anal. Found: C, 63.11; H, 5.41.

#### Deuteration of 2,3,4-triphenyl-1-nitrocyclobutane (XCIX)

Sodium methoxide (0.015 g., 0.00028 mole) was added to a solution of 2,3,4-triphenyl-1-nitrocyclobutane (XCIX, 0.184 g., 0.00056 mole) in deuteriomethanol (5 ml.). The solution was stirred for 15 hours at 60°. The solution was first cooled to room temperature and then added to 20 ml. of deuterium oxide. The solution was extracted with absolute ether, and the ether was dried over anhydrous magnesium sulfate. The

ether was evaporated on a rotatory evaporator to give a white solid, 2,3,4-triphenyl-1-deuterio-1-nitrocyclobutane (C). The infrared spectrum ( $\text{CHCl}_3$ ) showed maxima at 6.23, 6.50, 6.68, 6.90, 7.34 and 9.07  $\mu$ . The nuclear magnetic resonance spectrum ( $\text{CDCl}_3$ ) is shown in Figure 3, page 48.

Reaction of sodium methoxide with 2,3,4-triphenyl-1-nitrocyclobutane (XCIX)

Sodium methoxide (0.015 g., 0.00028 mole) was added to a solution of 2,3,4-triphenyl-1-nitrocyclobutane (XCIX, 0.184 g., 0.00056 mole) in absolute methanol (5 ml.). The solution was stirred at 60° for 15 hours, cooled to room temperature, and added to 20 ml. of distilled water. The solution was extracted with ether, and the ether was dried over anhydrous magnesium sulfate. The ether was evaporated on a rotatory evaporator to give 0.140 g. of a white solid. The nuclear magnetic resonance and infrared spectra of the white solid were exactly the same as those of photoproduct XCIX.

Formation of 2,3,3-triphenyl-1-nitrocyclobutane (XCIV)

A solution of 10 g. (0.067 mole) of trans- $\beta$ -nitrostyrene in 52 g. (0.289 mole) of diphenylethylene was irradiated in a Pyrex immersion well in the presence of a Hanovia Type A 550-watt medium pressure mercury arc lamp for 8 hours. The solution was stirred magnetically, and a slow stream of nitrogen was passed through it. The excess diphenylethylene was dis-

tilled at 0.13 mm. The crude irradiation residue was placed on a column of 600 g. of silica gel and chromatographed. Elution with 3 l. of 1:1 Skelly B-benzene gave a very viscous, reddish brown liquid, 2,3,3-triphenyl-1-nitrocyclobutane (XCIV, 10.1 g., 45.5%);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  253s (1,585), 259 (1,515), 264s (1,350) and 270s  $\mu$  (1,050). These combined fractions were rechromatographed on 290 g. of silica gel in order to obtain pure material for spectral and elemental analysis. The infrared spectrum ( $\text{CHCl}_3$ ) showed maxima at 6.24, 6.47, 6.69, 6.92, 7.32 and 7.65  $\mu$  (Figure 22, page 108). The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 6, page 64.

Anal. Calcd. for  $\text{C}_{22}\text{H}_{19}\text{NO}_2$ : C, 80.22; H, 5.81; N, 4.25. Found: C, 80.18; H, 5.97; N, 4.19.

#### Deuteration of 2,3,3-triphenyl-1-nitrocyclobutane (XCIV)

Sodium methoxide (0.041 g., 0.00076 mole) was added to a solution of 2,3,3-triphenyl-1-nitrocyclobutane (XCIV, 0.5 g., 0.0015 mole) in deuterated methanol ( $\text{CH}_3\text{OD}$ , 7 ml.). The mixture was first stirred at room temperature for 12 hours and then added quickly to 20 ml. of deuterium oxide. The solution was extracted with absolute ether, and the ether was dried over anhydrous magnesium sulfate. The ether was evaporated to give a viscous, reddish brown liquid, 2,3,3-triphenyl-1-deuterio-1-nitrocyclobutane (CV). The infrared spectrum ( $\text{CHCl}_3$ ) showed maxima at 6.24, 6.49, 6.68, 6.91, 7.31, 8.35, 9.03,

9.29, 9.80, 9.98, 11.02 and 11.26 u. The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 6, page 64. The small absorption at 8.05 p.p.m. is due to an impurity.

Reaction of sodium methoxide with 2,3,3-triphenyl-1-nitrocyclobutane (XCIV)

Sodium methoxide (0.041 g., 0.00076 mole) was added to a solution of 2,3,3-triphenyl-1-nitrocyclobutane (XCIV, 0.5 g., 0.0015 mole) in absolute methanol (7 ml.). The mixture was stirred at room temperature for 12 hours, and 20 ml. of water was added quickly to the solution. The solution was extracted with ether, and the ether was dried over anhydrous magnesium sulfate. The ether was evaporated to give 0.219 g. of a viscous, reddish brown liquid. The nuclear magnetic resonance and infrared spectra of this liquid were identical to those of photoproduct XCIV.

Attempted bromination of 2,3,3-triphenyl-1-nitrocyclobutane (XCIV)

A solution of 2,3,3-triphenyl-1-nitrocyclobutane (XCIV, 0.21 g., 0.00064 mole) and 0.120 g. (0.000674 mole) of N-bromosuccinimide in 20 ml. of carbon tetrachloride was refluxed for 4 hours under a nitrogen atmosphere. As the solution was refluxed, small amounts of benzoyl peroxide were added in an attempt to initiate the reaction. After removal of the solids by filtration, the carbon tetrachloride solution



was evaporated at reduced pressure. The residue was dissolved in ether, and the ether solution was shaken with water. The water solution was removed, and the ether was dried over anhydrous magnesium sulfate. The ether was evaporated on a rotatory evaporator to give a brown residue that gave a negative test for bromine.

Preparation of 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII)

Preparation A A solution of 8 g. (0.0537 mole) of trans- $\beta$ -nitrostyrene and 60 ml. of isobutylene (XXXII) in 440 ml. of hexane was irradiated for 7 hours with a Hanovia Type A 550-watt medium pressure mercury arc lamp in a Pyrex immersion well. The irradiation solution was kept at  $-12^{\circ}$  to  $-3^{\circ}$  by placing the immersion well in a mixture of acetone and ice. The excess isobutylene and hexane were removed by distillation at reduced pressure. The crude irradiation product was chromatographed on 300 g. of silica gel. The column was eluted with 1 l. of 19:1 Skelly B-benzene followed by elution with 2 l. of 9:1 Skelly B-benzene. Further elution with 3 l. of 7:3 Skelly B-benzene gave a light yellow liquid, slightly impure 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII, 8.55 g., 77.6%). The yellow liquid (XCVII) gave a single spot on a silica gel thin-layer plate developed in 6:4 Skelly B-benzene; however, it contained an impurity shown by the nuclear magnetic resonance absorption at 5.22 p.p.m.

(broad single peak) and 8.31 p.p.m. Elution with 400 ml. of 15:85 Skelly B-benzene gave 0.20 g. of a white solid of Dimer A that was recrystallized from heptane-benzene to give white crystals in a trace amount; m.p. 160-161° in a closed tube. The infrared spectrum (KBr) showed maxima at 3.30, 3.45, 6.24, 6.31, 6.45, 6.67, 6.87, 7.31, 13.17, 13.36 and 14.33  $\mu$  (Figure 19, page 102). The nuclear magnetic resonance spectrum ( $\text{CDCl}_3$ ) showed absorption at 2.70 p.p.m., 4.00 to 4.78 p.p.m. (multiplet), and 4.86 to 5.28 p.p.m. (multiplet) which integrated 10:2:2 (Figure 10, page 72).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$ : C, 64.30; H, 4.72; N, 9.38. Found: C, 64.10; H, 4.69; N, 9.49.

The nuclear magnetic resonance spectrum, infrared spectrum, and elemental analysis of Dimer A show that it is a cyclobutane dimer of  $\beta$ -nitrostyrene.

The light yellow liquid, slightly impure 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII) was distilled (81°/0.2 mm.), but the distillate still contained an impurity. A second chromatography was run using 2 g. of the distillate on 100 g. of silica gel. The column was eluted with 400 ml. of 9:1 Skelly B-benzene followed by elution with 400 ml. of 8:2 Skelly B-benzene. Further elution with 1 l. of 6:4 Skelly B-benzene gave XCVII. The last fractions from the elution with 8:2 Skelly B-benzene were shown to contain pure 3,3-dimethyl-2-phenyl-1-nitrocyclobutane;  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  252s (480), 258.5 (426), 265 (331) and 268.5s  $\mu$  (263). The infrared

spectrum (neat) showed maxima at 3.37, 6.23, 6.45, 6.66, 6.84, 7.30, 12.54, 13.45 and 14.34  $\mu$  (Figure 19, page 102). The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 7, page 66.

Anal. Calcd. for  $\text{C}_{12}\text{H}_{15}\text{NO}_2$ : C, 70.23; H, 7.37; N, 6.82. Found: C, 70.53; H, 7.42; N, 7.10.

Preparation B A solution of 1.5 g. (0.01 mole) of trans- $\beta$ -nitrostyrene and 50 ml. of isobutylene in 210 ml. of hexane was irradiated for 1 hour with a Hanovia Type A 550-watt medium pressure mercury arc lamp in a Pyrex immersion well. The irradiation was kept at  $-12^\circ$  to  $-3^\circ$  by placing the immersion well in a mixture of acetone and ice. The excess isobutylene and hexane were removed by distillation at reduced pressure. The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) of the crude irradiation product showed absorption at 3.05, 3.24, 3.33 and 3.50 p.p.m. (cis- $\beta$ -nitrostyrene), and 2.20 and 2.45 p.p.m. (trans- $\beta$ -nitrostyrene). The remaining absorptions were identical to the impure 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII) obtained from the preceding irradiation.

Deuteration of 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII)

Sodium methoxide (0.050 g., 0.00092 mole) was added to a solution of 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII, 0.38 g., 0.00185 mole) in 3 ml. of deuteriomethanol. The solution was stirred for 7 hours at room temperature, and

15 ml. of deuterium oxide was added quickly to it. The solution was extracted with anhydrous ether and dried over anhydrous magnesium sulfate. The ether was evaporated under reduced pressure to give 0.21 g. of a light yellow liquid, 3,3-dimethyl-2-phenyl-1-deuterio-1-nitrocyclobutane (CVI). The infrared spectrum (neat) showed maxima at 3.37, 6.23, 6.50, 6.66, 6.84, 7.28, 12.56, 13.50 and 14.33  $\mu$ . The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 7, page 66.

Reaction of sodium methoxide with 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII)

Sodium methoxide (0.050 g., 0.00092 mole) was added to a solution of 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII, 0.38 g., 0.00185 mole) in absolute methanol (3 ml.). The solution was stirred for 7 hours at room temperature, and 15 ml. of water was added quickly to it. The solution was extracted with ether and dried over anhydrous magnesium sulfate. The ether was evaporated under reduced pressure to give 0.20 g. of a light yellow liquid. The nuclear magnetic resonance and infrared spectra of this liquid were exactly the same as those of 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII).

Irradiation of *trans*- $\beta$ -nitrostyrene  
in 1,1-dimethoxyethylene (XLI)

A solution of 10 g. (0.067 mole) of *trans*- $\beta$ -nitrostyrene and 21.5 g. (0.244 mole) of dimethoxyethylene (prepared by the method of Corey *et al.* (15)) in 450 ml. of pentane was irradiated for 8 hours with a Hanovia Type A 550-watt medium pressure mercury arc lamp in a Pyrex immersion well. The excess dimethoxyethylene and pentane were removed by distillation at reduced pressure to give a dark brown, viscous liquid. The infrared spectrum ( $\text{CHCl}_3$ ) of this liquid showed absorption at 5.77, 5.85, 5.99, 6.16, 6.25 and 6.45  $\mu$  (weak). This crude irradiation material was distilled at reduced pressure. Examination of the first five distillation fractions (total of 2 g.) showed infrared absorptions characteristic of carbonyls at 5.85 (medium) and 5.99  $\mu$  (strong), but these fractions showed no absorption characteristic of a nitro group on a saturated carbon. The last two fractions (total of 0.30 g.) distilled at 89-93°/0.35 mm. These fractions showed infrared absorption at 5.77 (strong), 6.45 (medium) and 7.32  $\mu$  (weak). The infrared absorptions at 6.45 and 7.32  $\mu$  are characteristic of a nitro group on a saturated carbon. The last fractions contained such a small amount of material that no further work was carried out on them. The major amount of material remained as a very dark brown residue in the distillation pot.

Formation of 2,3-diphenyl-1-nitrocyclobutane (XCV)

A solution of 11.75 g. (0.0789 mole) of trans- $\beta$ -nitrostyrene in 162 g. (1.55 mole) of styrene was irradiated in a Pyrex immersion well for 20 hours with a medium pressure mercury arc lamp. The solution was magnetically stirred and cooled with tap water while a slow stream of nitrogen was passed through it. The excess styrene was removed by distillation at 10 mm. The crude photoproduct was distilled (131-133°/0.08 mm.) to give a light brown liquid, 2,3-diphenyl-1-nitrocyclobutane (XCV, 14 g., 0.055 mole, 70%). A solid isomer A (XCV<sub>a</sub>, 4.4 g., 17.2%) precipitated out of the liquid on cooling. The solid was collected on a filter and recrystallized from cyclohexane to give white crystals of isomer A; m.p. 104-105°;  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  255s (850), 260 (795), 266s (646) and 270s  $\mu$  (500). The infrared spectrum (CHCl<sub>3</sub>) of isomer A showed maxima at 3.38, 6.23, 6.45, 6.67, 6.88, 7.30, 7.63, 9.30, 9.95 and 11.00  $\mu$  (Figure 20, page 104). The nuclear magnetic resonance spectrum (CDCl<sub>3</sub>) is shown in Figure 8, page 68.

Anal. Calcd. for C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>: C, 75.86; H, 5.97; N, 5.53. Found: C, 75.62; H, 6.10; N, 5.66.

The light brown liquid left after removal of the solid was a second isomer B (XCV<sub>b</sub>) contaminated with a small amount of solid isomer A.

The infrared spectrum (CHCl<sub>3</sub>) of the liquid isomer B of 2,3-diphenyl-1-nitrocyclobutane (XCV<sub>b</sub>) showed maxima at 3.26,

3.41, 6.23, 6.45, 6.67, 6.89, 7.32, 7.70, 8.51, 9.02, 9.30, 9.73 and 11.05  $\mu$  (Figure 20, page 104);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  254s (1,585), 260s (1,380), 266s (1,070) and 270s  $\mu$  (795). The nuclear magnetic resonance spectrum ( $\text{CDCl}_3$ ) of the liquid isomer B shown in Figure 9, page 70, contains a very small amount of isomer A as an impurity.

Anal. Calcd. for  $\text{C}_{16}\text{H}_{15}\text{NO}_2$ : C, 75.86; H, 5.97; N, 5.53. Found: C, 76.06; H, 5.84; N, 5.44.

#### Deuteration of 2,3-diphenyl-1-nitrocyclobutane (XCV)

Deuteration of solid isomer A Sodium methoxide (0.038 g., 0.00069 mole) was added to a solution of solid isomer A of 2,3-diphenyl-1-nitrocyclobutane ( $\text{XCV}_a$ , 0.350 g., 0.00138 mole) in deuteriomethanol (5 ml.). The solution was first stirred at room temperature for 4 hours and then added rapidly to 20 ml. of deuterium oxide. The solution was extracted with anhydrous ether, and the ether solution was dried with anhydrous magnesium sulfate and then evaporated at diminished pressure on a rotatory evaporator to give 0.250 g. of a white solid, 2,3-diphenyl-1-deuterio-1-nitrocyclobutane ( $\text{CVII}_a$ ). The infrared spectrum ( $\text{CHCl}_3$ ) of solid ( $\text{CVII}_a$ ) showed maxima at 3.45, 6.23, 6.50, 6.66, 6.88, 7.30, 9.28 and 9.92  $\mu$ . The nuclear magnetic resonance spectrum ( $\text{CDCl}_3$ ) is shown in Figure 8, page 68.

Deuteration of liquid isomer B Sodium methoxide (0.038 g., 0.00069 mole) was added to a solution of liquid

isomer B of 2,3-diphenyl-1-nitrocyclobutane ( $XCV_b$ , 0.350 g., 0.00138 mole) in deuteriomethanol (5 ml.). The solution was stirred at room temperature for 4 hours. The solution was first added to 25 ml. of deuterium oxide and then extracted with anhydrous ether. The ether was evaporated to give 0.230 g. of a light brown liquid, 2,3-diphenyl-1-deuterio-1-nitrocyclobutane ( $CVII_b$ ). The deuterated liquid isomer B ( $CVII_b$ ) gave infrared absorption at 3.45, 6.24, 6.50, 6.68, 6.90, 7.32, 9.05, 9.55 and 11.24  $\mu$ . The nuclear magnetic resonance spectrum ( $CDCl_3$ ) is shown in Figure 9, page 70.

Reaction of sodium methoxide with 2,3-diphenyl-1-nitrocyclobutane ( $XCV$ )

Reaction of sodium methoxide with solid isomer A      So-  
dium methoxide (0.038 g., 0.00069 mole) was added to a solution of solid isomer A of 2,3-diphenyl-1-nitrocyclobutane ( $XCV_a$ , 0.350 g., 0.00138 mole) in absolute methanol (5 ml.). The solution was first stirred at room temperature for 5 hours and then added rapidly to 20 ml. of distilled water. The solution was extracted with ether, and the ether solution was dried over anhydrous magnesium sulfate. The ether was evaporated on a rotatory evaporator to give 0.260 g. of a solid. The nuclear magnetic resonance and infrared spectra were the same as those of the solid isomer A ( $XCV_a$ ).

Reaction of sodium methoxide with liquid isomer B      So-  
dium methoxide (0.038 g., 0.0007 mole) was added to a solution



of liquid isomer B of 2,3-diphenyl-1-nitrocyclobutane (XCV<sub>b</sub>, 0.350 g., 0.00138 mole) in absolute methanol (5 ml.). The solution was first stirred at room temperature for 4 hours and then added quickly to 20 ml. of distilled water. The solution was extracted with ether, and the ether was dried over anhydrous magnesium sulfate. The ether was removed at reduced pressure to give 0.270 g. of a light brown liquid. The nuclear magnetic resonance and infrared spectra of the light brown liquid were exactly the same as those of liquid isomer B (XCV<sub>b</sub>).

Nef reaction on 2,3-diphenyl-1-nitrocyclobutane (XCV)

Nef reaction A Following the method of Noland et al. (69), 2,3-diphenyl-1-nitrocyclobutane (XCV, 3.5 g., 0.0138 mole, a mixture of two isomers) was added to a solution of saturated (70 g.) potassium hydroxide and 80 ml. of methanol. The solution was first stirred for 90 minutes under a nitrogen atmosphere, and then 50 ml. of saturated potassium hydroxide and 150 ml. of methanol were added. The solution was cooled to 0°, and an ice-cold solution of 150 g. of concentrated sulfuric acid in 130 ml. of water was slowly added with stirring. During the addition of the sulfuric acid, 200 ml. of ether was added slowly to the reaction mixture. To this solution was added 800 ml. of water. The water solution was extracted with ether, and the ether was separated. The ether solution was washed with a potassium hydroxide solution,

separated, and dried over anhydrous magnesium sulfate. The ether solution was evaporated to give a residue that showed infrared absorption at 2.77, 3.05, 3.45, 5.60, 5.73, 5.95, 6.23 and 6.45  $\mu$ . The crude material was chromatographed on a florisil column. Elution with 1:20 ether-benzene gave 0.060 g. of a solid that was recrystallized from benzene-heptane to give white crystals of unknown oxime in a trace amount; m.p. 132-133°. The infrared spectrum ( $\text{CCl}_4$ ) of the white crystals showed maxima at 2.77, 3.00, 3.27, 3.40, 3.53, 6.24, 6.68, 6.90, 7.06, 7.42, 11.52 and 14.35  $\mu$  (Figure 20, page 104). The nuclear magnetic resonance spectrum ( $\text{CDCl}_3$ ) is shown in Figure 17, page 98. The nuclear magnetic resonance spectrum showed a loss of absorption at 0.88 p.p.m. after shaking the deuteriochloroform solution with deuterium oxide. A possible structure for the unknown oxime is the oxime of 2-methoxy-2,3-diphenyl-1-cyclobutanone; however, this does not agree with the elemental analysis.

Anal. Found A: C, 74.81; H, 6.36. Found B: C, 75.07; H, 5.70; N, 6.10.

Nef reaction B Following the method of Noland et al. (69), solid isomer A of 2,3-diphenyl-1-nitrocyclobutane ( $\text{XCV}_a$ , 2.9 g., 0.0115 mole) was added to a saturated solution of 91 g. of potassium hydroxide and 200 ml. of methanol. The solution was stirred slowly at 10° for 30 minutes, and 340 g. of concentrated sulfuric acid in 240 ml. of water was added slowly while keeping the temperature below 12°. During the

addition of the sulfuric acid solution, 480 ml. of ether was added slowly to the reaction mixture. The ether was separated and dried over anhydrous magnesium sulfate. The ether was evaporated on a rotatory evaporator to give 2.82 g. of a light brown solid which showed infrared maxima at 3.42, 5.62, 5.72, 5.94, 6.25, 6.47, 6.90 and 7.41  $\mu$ . The crude reaction product was chromatographed on 120 g. of florisil. Examination of the chromatography fractions by both infrared and thin-layer showed that no separation had taken place. It must be noted that the white solid formed in the preceding reaction, with infrared absorption at 2.77 and 3.00  $\mu$ , was not present in this reaction.

Formation of 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII)

A solution of 4 g. (0.0268 mole) of trans- $\beta$ -nitrostyrene and 12.3 g. (0.15 mole) of 2,3-dimethyl-1,3-butadiene (CXXV) in 240 ml. of hexane was irradiated for 10 hours in a Pyrex immersion well in the presence of a medium pressure mercury arc lamp. The solution was stirred magnetically, and nitrogen was bubbled through it. The hexane and 2,3-dimethyl-1,3-butadiene were removed by distillation at partial pressure. The crude reaction material was distilled (102-104<sup>o</sup>/0.32 mm.) to give 4.32 g. of a yellow orange liquid, 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII, 70%);  $\lambda$ :  $\begin{matrix} 95\% \text{ EtOH} \\ \text{max} \end{matrix}$  254s (955), 259.5s (870) and 265.5s  $\mu$  (725). The liquid

gave one spot on a silica gel thin-layer plate developed in benzene, but vapor phase chromatography showed that two isomers are present in approximately a 1:1 ratio. The infrared spectrum (neat) showed maxima at 3.36, 6.11, 6.24, 6.44, 6.66, 6.88, 7.28, 7.60, 8.95, 11.16, 12.60, 12.85, 13.40 and 14.35  $\mu$  (Figure 19, page 102). The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 11, page 81.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{17}\text{NO}_2$ : C, 72.71; H, 7.42; N, 6.06. Found: C, 73.04; H, 7.65; N, 6.14.

Ozonization of 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII)

A solution of 2.2 g. (0.0095 mole) of 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII) in 150 ml. of absolute ethanol in a bubbler tube was immersed in a Dry Ice-acetone bath. An excess of ozone was bubbled through the solution. Three ml. of 30% hydrogen peroxide was added to the ozonolysis mixture, and the resulting solution was stirred magnetically for 15 hours at room temperature. The excess ethanol was removed by distillation on a rotatory evaporator, and 25 ml. of water was added to the residue. The water solution was extracted with ether, and the ether solution was dried over anhydrous magnesium sulfate. The ether was removed by distillation on a rotatory evaporator under reduced pressure to give 1.8 g. of crude material. The crude reaction material was recrystallized from hexane to give white crystals

of 1-acetyl-1-methyl-2-phenyl-3-nitrocyclobutane (CXIV, 0.3 g., 13.5%); m.p. 73-75°;  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  253s (295), 260 (276), 266 (251) and 270.5s  $\mu$  (209). The infrared spectrum (KBr) showed absorption at 3.35, 5.92, 6.23, 6.31, 6.48, 6.65, 6.86, 7.24, 7.38, 12.90, 13.32 and 14.20  $\mu$  (Figure 21, page 106). The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 12, page 83.

Anal. Calcd. for  $\text{C}_{13}\text{H}_{15}\text{NO}_3$ : C, 66.94; H, 6.48; N, 6.00. Found: C, 67.14; H, 6.39; N, 6.22.

Deuteration of 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII)

Sodium methoxide (0.0334 g., 0.00062 mole) was added to a solution of 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII, 0.290 g., 0.00125 mole) in deuteriomethanol (8 ml.). The solution was stirred for 4 hours at room temperature and then added rapidly to 20 ml. of deuterium oxide. The solution was extracted with anhydrous ether, and the ether was dried over anhydrous magnesium sulfate. The light yellow orange residue (0.19 g.), 1-methyl-1-isopropenyl-2-phenyl-3-deuterio-3-nitrocyclobutane (CXIII), gave infrared absorption (neat) at 3.36, 6.10, 6.23, 6.50, 6.67, 6.89, 7.29, 8.10, 9.03, 9.71, 11.18, 12.80, 13.01, 13.50 and 14.35  $\mu$ . The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 11, page 81.

Reaction of sodium methoxide with 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII)

Sodium methoxide (0.0334 g., 0.00062 mole) was added to a solution of 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII, 0.290 g., 0.00125 mole) in absolute methanol (9 ml.). The solution was first stirred at room temperature for 4 hours and then added rapidly to 20 ml. of distilled water. The solution was extracted with ether and dried over anhydrous magnesium sulfate. The infrared spectrum of the light yellow orange liquid (0.120 g.) was identical to that of photoproduct CXII. The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) was approximately equal to that of photoproduct CXII, although there were very small differences in the intensities of the absorptions.

The above procedure was repeated, but this time the solution was heated at  $75^\circ$  for 4 hours. The liquid product gave the same nuclear magnetic resonance spectrum as the product from the reaction with sodium methoxide at room temperature.

Formation of 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV)

A solution of 4 g. (0.0269 mole) of trans- $\beta$ -nitrostyrene and excess 1,3-butadiene in 350 ml. of hexane was irradiated with a Hanovia Type A medium pressure mercury arc lamp in a Pyrex immersion well for  $6\frac{1}{2}$  hours. The solution was magnetically stirred, and tap water was run rapidly through the cooling jacket. The outside of the irradiation flask was kept at

$-15^{\circ}$  to  $-3^{\circ}$  by an ice-acetone solution. The solvent was carefully evaporated on a rotatory evaporator at reduced pressure. The crude photoproduct was distilled ( $82-84^{\circ}/0.25$  mm.) to give a light yellow liquid, 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV, 3.6 g., 75.5%);  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  253s (1,120), 257.5s (1,000), 265s (832) and 269s  $\mu$  (691). The liquid gave only one spot on a silica gel thin-layer plate developed in 2:3 Skelly B-benzene, but vapor phase chromatography showed that two isomers are present in approximately a 1:3 ratio. The infrared spectrum (neat) showed maxima at 3.25, 3.32, 6.09, 6.23, 6.45, 6.66, 6.90, 7.28, 11.77, 12.57, 13.46 and 14.35  $\mu$  (Figure 21, page 106). The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 13, page 85.

Anal. Calcd. for  $\text{C}_{12}\text{H}_{13}\text{NO}_2$ : C, 70.92; H, 6.45; N, 6.89. Found: C, 71.12; H, 6.23; N, 6.89.

#### Ozonization of 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV)

A solution of 2.38 g. (0.0117 mole) of 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV) in 150 ml. of absolute ethanol in a bubbler tube was immersed in a Dry Ice-acetone bath. An excess of ozone was bubbled through the solution. The solution was placed in a beaker, and 6 ml. of water and 1.75 ml. of glacial acetic acid were added. The solution was stirred vigorously while a total of 1.17 g. of zinc was added slowly. The excess ethanol was distilled under reduced pressure, and 25 g. of water was added to the residue. The water solution

was extracted with ether, and the ether solution was dried over anhydrous magnesium sulfate. The ether was removed by distillation on a rotatory evaporator under reduced pressure. The crude product was chromatographed on 70 g. of silica gel. The column was eluted with 1 l. of 1:1 Skelly B-benzene followed by elution with 500 ml. of benzene. Further elution with 1 l. of 1:4 chloroform-benzene gave a liquid, 3-formyl-2-phenyl-1-nitrocyclobutane (CXVII, 0.75 g., 31.3%). The product (CXVII) was distilled (134-136°/0.18 mm.) to obtain pure material for analysis;  $\lambda_{\text{max}}^{95\% \text{ EtOH}}$  253s (537), 258 (468), 264.5s (372) and 268s  $\mu$  (302). The infrared spectrum (neat) showed absorption at 3.35, 3.55, 3.68, 5.82, 6.24, 6.48, 6.66, 6.90, 7.28, 13.40 and 14.33  $\mu$  (Figure 21, page 106). The nuclear magnetic resonance spectrum ( $\text{CDCl}_3$ ) is shown in Figure 12, page 83.

Anal. Calcd. for  $\text{C}_{11}\text{H}_{11}\text{NO}_3$ : C, 64.37; H, 5.40; N, 6.81. Found: C, 64.12; H, 5.55; N, 6.51.

#### Deuteration of 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV)

Sodium methoxide (0.033 g., 0.00062 mole) was added to a solution of 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV, 0.250 g., 0.00123 mole) in deuteriomethanol (6 ml.). The solution was first stirred at room temperature for 6 hours and then added quickly to 22 ml. of deuterium oxide. The solution was extracted with ether, dried, and evaporated at partial pressure to give a yellow liquid, 3-vinyl-2-phenyl-1-deuterio-1-



nitrocyclobutane (CXVI, 0.155 g.). The infrared spectrum (neat) showed maxima at 3.32, 6.10, 6.23, 6.50, 6.66, 6.90, 7.01, 7.28, 9.31, 9.72, 10.09, 10.90, 13.40 and 14.35  $\mu$ . The nuclear magnetic resonance spectrum ( $\text{CCl}_4$ ) is shown in Figure 13, page 85.

Reaction of sodium methoxide with 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV)

Sodium methoxide (0.033 g., 0.00062 mole) was added to a solution of 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV, 0.250 g., 0.00123 mole) in absolute methanol (6 ml.). The solution was stirred at room temperature for 6 hours and added quickly to 20 ml. of water. The solution was extracted with ether, dried, and evaporated at partial pressure to give 0.150 g. of a yellow liquid. The nuclear magnetic resonance and infrared spectra of the yellow liquid were identical with those of photoproduct CXV.

Irradiation of phenylacetylene in the presence of trans- $\beta$ -nitrostyrene (I)

Irradiation of phenylacetylene and trans- $\beta$ -nitrostyrene in a quartz immersion well A solution of 3 g. (0.02 mole) of trans- $\beta$ -nitrostyrene and 20 g. (0.196 mole) of phenylacetylene in 180 ml. of hexane was flushed with nitrogen and irradiated with a Hanovia Type A immersion lamp in a quartz well. The solution was irradiated for a total of 30 hours

with only a small change in the absorption at 308  $\mu$  in the ultraviolet spectrum. The excess hexane was removed at reduced pressure on a rotatory evaporator. The crude material showed a weak absorption at 6.47  $\mu$  in the infrared spectrum, which is indicative of a nitro group on a saturated carbon. Distillation of the crude irradiation material at reduced pressure gave only phenylacetylene and trans- $\beta$ -nitrostyrene.

Irradiation of phenylacetylene and trans- $\beta$ -nitrostyrene in a Pyrex immersion well A solution of 3 g. (0.02 mole) of trans- $\beta$ -nitrostyrene and 10 g. (0.098 mole) of phenylacetylene in 180 ml. of heptane was irradiated in a Pyrex immersion well with a Hanovia Type A lamp for a total of 44 hours. During the irradiation period, the solution was stirred magnetically, and a slow stream of nitrogen was bubbled through it. After evaporation of the excess heptane at reduced pressure, 2.55 g. of the crude material was chromatographed on 90 g. of florisil. Analyses of the chromatography fractions by infrared showed that no cycloaddition product had been formed.

Beer's law plot of trans- $\beta$ -nitrostyrene (I)

The absorbency of trans- $\beta$ -nitrostyrene (I) in the ultraviolet region (200-360  $\mu$ ) was measured as a function of concentration in cyclohexane and cyclohexene solutions. The 5 cm., 1 cm. and 0.1 cm. cells were used for the cyclohexane solutions (Figure 15, page 90), while 1 cm. and 0.1 cm. cells

Table 1. Absorbency of trans- $\beta$ -nitrostyrene (I)  
in cyclohexene solution

Concentration		<u>300 mu</u>
$M \times 10^6$	A	$\underline{\epsilon} \times 10^{-4}$
1 centimeter cells		
25.0	0.323	1.29
32.2	0.410	1.27
40.9	0.556	1.36
47.0	0.611	1.30
51.7	0.650	1.26
66.4	0.903	1.36
0.1 centimeter cells		
250	0.350	1.40
322	0.453	1.41
409	0.590	1.44
470	0.647	1.38
517	0.693	1.34
664	0.910	1.37

were used for the cyclohexene solutions (Figure 14, page 88). The different size cells were used in order to cover a larger concentration range. The absorbency was plotted against concentration at the maxima. The calculated  $\underline{\epsilon}$ -values are shown in Table 1 and Table 2, page 157. Within experimental error, no deviation from Beer's law was observed. The cyclohexene gave absorption maxima at 213 mu (64) and 258s mu (2.7).

Table 2. Absorbency of trans- $\beta$ -nitrostyrene (I) in cyclohexane solution

Concentration M x 10 <sup>6</sup>	A	<u>298 mu</u> $\epsilon$ x 10 <sup>-4</sup>
5 centimeter cells		
2.42	0.214	1.77
3.10	0.268	1.73
3.90	0.341	1.75
4.42	0.350	1.58
5.36	0.424	1.58
1 centimeter cells		
12.1	0.214	1.77
15.5	0.270	1.74
19.5	0.332	1.70
22.1	0.356	1.61
26.9	0.465	1.73
0.1 centimeter cells		
121	0.231	1.91
155	0.284	1.83
195	0.366	1.87
221	0.407	1.84
269	0.473	1.76

Comparison of the absorbency of trans- $\beta$ -nitrostyrene (I) to different olefins

The ultraviolet spectrum of trans- $\beta$ -nitrostyrene (I) and of some of the different olefins that formed cycloaddition products were run in 95% ethanol in order to get some idea of the amount of light absorbed by each. The molar concentration ratio of olefin over trans- $\beta$ -nitrostyrene was equal to that

Table 3. Comparison of the absorbency of trans- $\beta$ -nitrostyrene (I) to different olefins

Olefin	Concentration of olefin (M x 10 <sup>6</sup> )	Absorbency of olefin (300 mu)	$\frac{\text{Absorbency of olefin}}{\text{Absorbency of } \beta\text{-nitrostyrene}}$ x 100
Styrene	6.09	0.033	6.4
Diphenylethylene	1.33	0.017	3.3
Cyclopentene	7.11	0.017	3.3
Tetramethylethylene	5.75	0.023	4.5

used during the irradiations. If more than one irradiation had been carried out with an olefin, the value from the irradiation with the greatest molar concentration ratio of olefin over trans- $\alpha$ -nitrostyrene was used. The absorbency of the olefins was compared to the absorbency of trans- $\beta$ -nitrostyrene at 300 mu, since most of the irradiations were carried out in a Pyrex immersion well (Figure 16, p. 92). The Pyrex immersion well transmits less than 10% of the light at 300 mu (65). The concentration of trans- $\alpha$ -nitrostyrene used was  $0.31 \times 10^{-4}$  moles/liter, and its absorbency was 0.513 at 300 mu (Table 3, page 158).

#### Pyrolysis of cycloaddition products

The following cycloaddition products were dissolved in cyclohexane and slowly dropped into a vertical, 6 inch by 3/4 inch, Pyrex helices packed pyrolysis column at 490° to 510° (85). The column was swept with a stream of oxygen-free nitrogen. Pyrolysate was collected in a tube immersed in a Dry Ice-acetone bath. After cooling, the column and the collection tube were washed with acetone.

Pyrolysis of 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI) Pyrolysis of 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI) gave a dark brown liquid that had the same infrared spectrum as the beginning material except for a broad band of medium intensity at 5.83 to 5.90 u.

Pyrolysis of 7-nitro-8-phenylbicyclo/4.2.0/octane (CIII)

Pyrolysis of 7-nitro-8-phenylbicyclo[4.2.0]octane (CIII) gave a dark liquid that had the same infrared spectrum as the beginning material except for an absorption at 5.90  $\mu$ .

Pyrolysis of 2,3,3-triphenyl-1-nitrocyclobutane (XCIV)  
Pyrolysis of 2,3,3-triphenyl-1-nitrocyclobutane (XCIV) gave a brown liquid that gave an infrared spectrum with maxima at 6.58 and 7.45  $\mu$ , corresponding to trans- $\phi$ -nitrostyrene.

Pyrolysis of 2,3-diphenyl-1-nitrocyclobutane (XCV)  
Pyrolysis of 2,3-diphenyl-1-nitrocyclobutane (XCV) gave a brown liquid that showed infrared maxima at 6.58 and 7.45  $\mu$ , corresponding to trans- $\phi$ -nitrostyrene. A silica gel thin-layer plate developed in benzene gave a spot with the same  $R_f$  value as trans- $\phi$ -nitrostyrene.

Experimental for the Irradiation of  
1,1-diphenyl-2-nitroethylene (CXVIII)

Irradiation of 1,1-diphenyl-2-nitroethylene (CXVIII)

Irradiation of 1,1-diphenyl-2-nitroethylene in tetramethylethylene A solution of 2.8 g. (0.0124 mole) of 1,1-diphenyl-2-nitroethylene prepared by the method of Bordwell and Garbisch (86) was irradiated for 22 hours in 100 ml. of tetramethylethylene with a medium pressure mercury arc lamp in a Pyrex immersion well. The ultraviolet spectrum showed no change. The solution was placed in a quartz flask that was internally cooled and irradiated for 20 hours with a

mercury arc lamp that was placed 7 inches away from the quartz container. There was a small decrease in the ultraviolet absorption at 305  $\mu$ . Tetramethylethylene was removed at reduced pressure, but the infrared spectrum of the residue showed only the starting material.

Irradiation of 1,1-diphenyl-2-nitroethylene in styrene

A solution of 2.3 g. of 1,1-diphenyl-2-nitroethylene (CXVIII) prepared by the method of Bordwell and Garbisch (86) in 200 ml. of styrene was placed in a quartz immersion well, flushed with nitrogen, and irradiated with a Hanovia Type A immersion lamp for 14 hours. The styrene was distilled off at 0.4 mm., and the infrared spectrum of the residue showed no absorption characteristic of a nitro group on a saturated carbon.

Experimental for the Irradiation  
of o-methyl-o-nitrostyrene (II)

Preparation of 1-oximino-1-phenylpropan-2-one (CXX)

A solution of 8 g. (0.049 mole) of o-methyl-o-nitrostyrene (87) in 250 ml. of reagent grade acetone was irradiated with a Hanovia Type A 550-watt medium pressure mercury arc lamp for 8 hours. The solution was stirred magnetically and cooled with tap water. A rapid stream of pre-purified nitrogen was bubbled through the solution through a teflon tube that extended to the bottom of the irradiation well. The progress of the irradiation was followed by removing



aliquots and measuring the ultraviolet absorption. The absorbency at 302  $\mu$  was lost during the irradiation, and two new absorptions appeared at 254 and 260  $\mu$ . The intensity of these absorptions alternated during the course of the irradiation. The intensity of one absorption increased at the expense of the other; the absorption at 260  $\mu$  was always of higher intensity. During the course of the irradiation, the nitrogen that had passed through the irradiation solution was directed through two Dry Ice traps to a series of two containers of ferrous sulfate in an attempt to trap nitric oxide, but the ferrous sulfate showed no color change. The acetone was carefully removed on a rotatory evaporator at partial pressure. The crude residue showed infrared maxima ( $\text{CHCl}_3$ ) at 2.80, 3.07, 5.86, 5.93, 6.25, 7.00, 7.38 and 7.75  $\mu$ .

On addition of benzene to the crude irradiation mixture, 3.60 g. of a white solid, isomer A of 1-oximino-1-phenylpropan-2-one ( $\text{CXX}_a$ ), precipitated out of the solution. The white solid was recrystallized from water to give white crystals of isomer A of 1-oximino-1-phenylpropan-2-one ( $\text{CXX}_a$ ); m.p. 161-162.5° in a closed tube. The infrared spectrum showed maxima ( $\text{CHCl}_3$ ) at 2.80, 3.07, 5.92, 6.24, 7.00 and 7.37  $\mu$  (Figure 22, page 108). The nuclear magnetic resonance spectrum ( $\text{CDCl}_3$ ) is shown in Figure 17, page 98. The nuclear magnetic resonance spectrum in dimethylsulfoxide gave a broad peak at -2.55 p.p.m. (one proton). The 1-oximino-1-phenylpropan-2-one that was prepared from 1-phenylpropan-2-one ( $\text{CXXI}$ ) by the method

of Ferris (77) gave m.p. 161-163° (closed tube) and showed no melting point depression upon admixture with photoisomer A (CXX<sub>a</sub>). The infrared spectrum of the 1-oximino-1-phenylpropan-2-one prepared by the method of Ferris (77) is shown in Figure 22, page 108. The nuclear magnetic resonance spectrum (CHCl<sub>3</sub>) is exactly the same as that of photoisomer A (CXX<sub>a</sub>) shown in Figure 17, page 98.

The remaining crude photomixture was chromatographed on 200 g. of silica gel. Elution with the first 500 ml. of 1:20 ether-benzene gave 1.56 g. of white crystals of crude isomer B of 1-oximino-1-phenylpropan-2-one (CXX<sub>b</sub>) that showed infrared maxima (CHCl<sub>3</sub>) at 2.78, 3.04, 5.86, 6.24, 6.68, 6.93 and 7.38 u. Attempted recrystallization of photoisomer B (CXX<sub>b</sub>) from benzene or chloroform gave only photoisomer A. The nuclear magnetic resonance spectrum (CDCl<sub>3</sub>) of photoisomer B (CXX<sub>b</sub>) is exactly the same as that of isomer A (CXX<sub>a</sub>). The nuclear magnetic resonance spectrum of photoisomer B in dimethylsulfoxide gave two sharp peaks at -2.6 and -1.9 p.p.m. which integrated for one proton. Removal of the dimethylsulfoxide at reduced pressure gave only photoisomer A (CXX<sub>a</sub>).

The next 200 ml. of 1:20 ether-benzene contained a very small amount of a mixture of the two photoisomers. Elution with the last 500 ml. of 1:20 ether-benzene gave 1.37 g. of photoisomer A. The total amount of 1-oximino-1-phenylpropan-2-one (CXX) from this irradiation was 6.53 g. (81.7%).

Anal. Calcd. for C<sub>9</sub>H<sub>9</sub>NO<sub>2</sub>: C, 66.25; H, 5.56;

N, 8.58. Found: C, 66.27; H, 5.77; N, 8.83.

Hydrolysis of isomer A of 1-oximino-1-phenylpropan-2-one (CXX<sub>a</sub>)

A solution of 1.8 g. of photoisomer A (CXX<sub>a</sub>) in 15 ml. of formaldehyde and 5 ml. of 5% hydrochloric acid was heated at 80-110° for 1 hour with stirring. The solution was diluted with water and extracted with ether. The ether solution was dried over anhydrous magnesium sulfate and evaporated on a rotatory evaporator. The crude product was distilled (50-51°/0.3 mm.) to give 1-phenylpropan-1,2-dione (CXXII). The infrared spectrum (neat) showed absorption at 3.25, 5.85, 5.98, 6.25, 6.33, 6.89, 7.05, 7.38, 7.60, 7.78, 8.60, 11.13, 12.73, 14.25 and 14.62  $\mu$ , which compared exactly to that of a pure sample of 1-phenylpropan-1,2-dione from Eastman Chemical Company. The nuclear magnetic resonance spectrum showed maxima at 2.13 p.p.m. (multiplet), 2.61 p.p.m. (multiplet), and 7.6 p.p.m. (singlet) which integrated 2:3:3. The sample that was obtained from Eastman Chemical Company gave an identical nuclear magnetic resonance spectrum.

Irradiation of  $\beta$ -methyl- $\beta$ -nitrostyrene in tetramethylethylene

A solution of 3 g. (0.0184 mole) of  $\beta$ -methyl- $\beta$ -nitrostyrene (II) in 100 ml. of tetramethylethylene was irradiated with a medium pressure mercury arc lamp that was placed 7

inches away from an internally cooled Pyrex flask. The irradiation was followed by removing aliquots and measuring the ultraviolet spectra. After 19 hours, the irradiation was discontinued since the absorbency at 308  $\mu$  had disappeared. The solvent was removed at diminished pressure. The crude irradiation mixture gave infrared maxima ( $\text{CHCl}_3$ ) at 2.80, 3.05, 3.42, 5.92, 6.60, 7.37 and 7.55  $\mu$ . There was no infrared absorption near 6.45 and 7.28  $\mu$ , which is indicative of a nitro group on a saturated carbon. Addition of carbon tetrachloride to the crude irradiation mixture gave 1 g. (33%) of white crystals of isomer A of 1-oximino-1-phenylpropan-2-one ( $\text{CXX}_a$ ); however, no attempt was made to isolate all of the product.

Irradiation of  $\beta$ -methyl- $\beta$ -nitrostyrene in styrene

A solution of 6.2 g. (0.038 mole) of  $\beta$ -methyl- $\beta$ -nitrostyrene in 100 ml. of styrene was irradiated with a medium pressure mercury arc lamp that was placed 7 inches away from an internally cooled Pyrex flask. After 19 hours, the irradiation was discontinued since the absorbency at 308  $\mu$  had disappeared. The excess styrene was removed (50°/0.15 mm.). The crude irradiation material gave infrared maxima ( $\text{CHCl}_3$ ) at 2.80, 3.03, 3.44, 5.92, 6.25, 6.60, 7.37 and 7.55  $\mu$ . There was no infrared absorption near 6.45 and 7.28  $\mu$ , which is indicative of a nitro group on a saturated carbon. Addition of carbon tetrachloride gave 0.72 g. (11.6%) of a white solid, isomer A of 1-oximino-1-phenylpropan-2-one ( $\text{CXX}_a$ ); however, no attempt was made to isolate all of the product.

## SUMMARY

Previously unattainable substituted nitrocyclobutanes have been prepared in greater than 50% yield by the irradiation of trans- $\beta$ -nitrostyrene in the presence of olefins and dienes.

The nitrocyclobutanes that have been prepared by this method are 1,1,2,2-tetramethyl-4-phenyl-3-nitrocyclobutane (XCVI), 2,3,3-triphenyl-1-nitrocyclobutane (XCIV), two isomers of 2,3-diphenyl-1-nitrocyclobutane (XCV), 2,3,4-triphenyl-1-nitrocyclobutane (CIX), 6-nitro-7-phenylbicyclo[3.2.0]heptane (CI), 7-nitro-8-phenylbicyclo[4.2.0]octane (CIII), 3,3-dimethyl-2-phenyl-1-nitrocyclobutane (XCVII), 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII), and 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV). The two isomers of 2,3-diphenyl-1-nitrocyclobutane (XCV) were completely degraded by Lenz (57). This degradation established the structure and stereochemistry of these isomeric photoproducts. The structures of 1-methyl-1-isopropenyl-2-phenyl-3-nitrocyclobutane (CXII) and 3-vinyl-2-phenyl-1-nitrocyclobutane (CXV) were established by ozonolysis. The ozonolyses gave 1-acetyl-1-methyl-2-phenyl-3-nitrocyclobutane (CXIV) and 3-formyl-2-phenyl-1-nitrocyclobutane (CXVII), respectively.

All the photoaddition products formed are the result of 1,2-additions. The photoproduct obtained from the irradiation of I with asymmetrical olefins has the most nucleophilic

carbon of the alkene attaching itself to the alpha position of the β-nitrostyrene, which suggests that the β-nitrostyrene is acting as an electrophilic species. Each photocycloaddition product discussed in this thesis has the nitro and adjacent phenyl groups trans. This implies that β-nitrostyrene may be adding in a trans manner. A Beer's law study was carried out to determine if a ground state complex might exist, but no complex formation was noted.

1,1-diphenyl-2-nitroethylene (CXVIII) was irradiated in both tetramethylethylene and styrene under the same conditions as those used in the photolysis of trans-β-nitrostyrene with different olefins, but no reaction took place.

If a methyl group is placed on the β-position of β-nitrostyrene, irradiation gives a new photoproduct, 1-oximino-1-phenylpropan-2-one (CXX), rather than a cycloaddition product. This can be rationalized as being due to an initial photoisomerization of the nitro group to a nitrite (CXXXI).

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