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Organic mass spectrometry of nitroolefins and structurally related compounds

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ORGANIC MASS SPECTROMETRY OF NITROOLEFINS AND STRUCTURALLY RELATED COMPOUNDS

by

John Gerritt Stam

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DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

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PREFACE

Mass spectroscopy has come of age as a research tool for the organic chemist. It now ranks in importance with infrared spectroscopy and nuclear magnetic resonance for determining the structure of organic molecules. In fact, mass spectroscopy is indispensable in certain areas of modern organic research. Furthermore, it has been shown that mass spectral reactions to a certain extent parallel those of more conventional thermal (1) and photochemical (2) reactions and might serve as a useful model for these reactions.

The spectacular growth of organic mass spectroscopy parallels to a large extent the mechanistic investigations carried out on the fragmentation pathways of various organic functional groups. These studies have allowed the organic chemist to predict with reasonable assurance the expected fragmentations of a molecule in spite of the numerous molecular rearrangements which can occur upon electron impact. Frequently, these rearrangements are characteristic of a particular type of compound, and can be extremely useful in identification, if the rearrangement process is understood. The continued growth and use of mass spectroscopy in organic chemistry will depend on further mechanistic studies on functional groups which have not yet received mass spectral scrutiny.

The intent of this thesis is to present the results of a mechanistic mass spectral study on a number of different but related functional groups common to organic chemistry. The results of labeling experiments employing deuterium and carbon-thirteen are used in deducing the precise fragmentation pathways and in determining the possible structures of gaseous ions formed in the fragmentation process. Finally, where applicable, parallels are drawn between mass spectral reactions and more conventional reactions in organic chemistry.

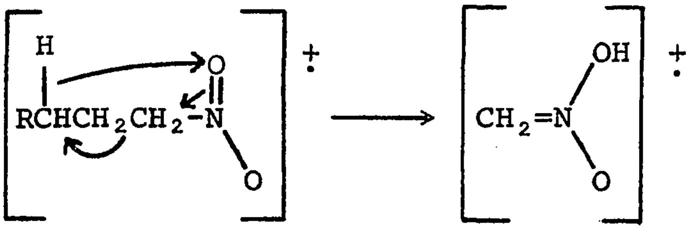
PART I: MASS SPECTRA OF NITROOLEFINS AND RELATED TOPICS

HISTORICAL

The mass spectra of nitroaliphatics and nitroaromatics have been explored extensively. In comparison, the mass spectra of nitroolefins have received scant attention. In fact, the mass spectrum of only one nitroolefin, 2-nitropropene, appears in the chemical literature (3). The mass spectrum of 2-nitropropene was reported for thirty electron volts without mestastables, and no attempt was made at interpreting the spectrum. The mass spectrum exhibits a low intensity molecular ion at m/e 87 (2.8%) under these conditions. The base peak in the spectrum corresponds to the loss of the nitro group from the molecular ion to give an ion at m/e 41. The subsequent loss of one and two hydrogen atoms yields prominent ions at m/e 40 and m/e 39. Low intensity ions at m/e 58 (0.5%) and m/e 57 (1.0%) are of mechanistic interest since they could correspond to the loss of CHO and NO from the molecular ion. The remainder of the mass spectrum is unexceptional.

Due to the limited amount of information on nitroolefins, the work done on nitroaliphatics and nitroaromatics becomes important in the interpretation of nitroolefin spectra. This is especially true since *a priori* one might expect nitroolefins to show characteristics of both types of nitro compounds. Since these compounds are important to an accurate interpretation of the data on nitroolefins, they are discussed briefly below.

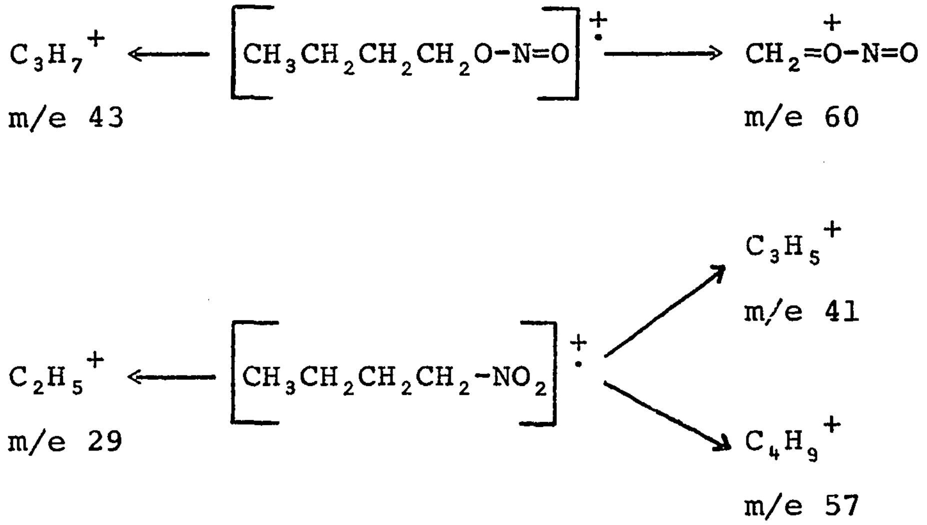
Perhaps the most striking feature of the mass spectra of the aliphatic nitro group is its poor charge stabilizing ability (4, 5). The virtual absence of molecular ions in the spectra of aliphatic nitro compounds much larger than nitromethane is a reflection of this characteristic. The very facile α-cleavage which occurs with charge retention on the alkyl group again reflects the lack of charge stabilization by the nitro group. Unfortunately this α-cleavage reaction cannot be used to characterize the alkyl portion of a nitroalkane, since the alkyl chain from higher molecular weight nitroalkanes generally fragments into more stable C_3 and C_4 fragments. The facile loss of the nitro group also makes it difficult to distinguish between isomers of nitroalkanes except for the relative abundance of certain fragment ions. Another connotation of the lack of charge stabilization by the nitro group is the virtual absence of McLafferty rearrangement ions of the type shown in Scheme 1.



Scheme 1

Although γ-hydrogen rearrangements of a similar nature can occur, they are usually of low abundance, or charge retention is on the alkyl chain.

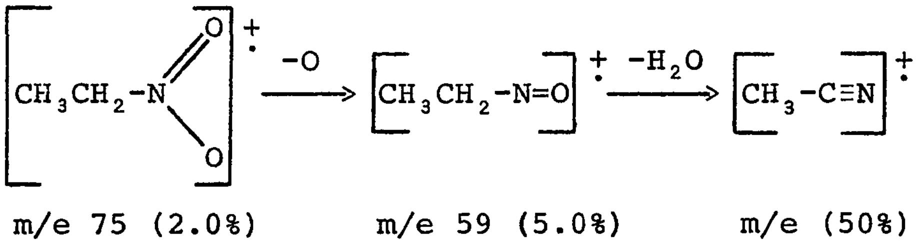
Another characteristic of the mass spectra of nitroalkanes is the lack of a nitro-nitrite rearrangement, a common process in nitroaromatics (4, 5). The lack of rearrangement provides an easy method of distinguishing between the nitro and nitrite compounds by mass spectroscopy as illustrated in Scheme 2 for butylnitrite and nitrobutane. The mass spectrum of butylnitrite shows abundant ions at m/e 43 and m/e 60 which are essentially absent in the mass spectrum of nitrobutane. Nitrobutane gives primarily hydrocarbon ions via α-cleavage of the nitro group. Only two exceptions are known for this lack of nitro-nitrite rearrangement, these are 3-phenyl-1-nitropropane (5, 6) and nitrocyclopropane (5, 7). For 3-phenyl-1-nitropropane the loss of nitric oxide from the molecular ion, which signifies a nitro-nitrite rearrangement, might involve the formation of a



Scheme 2

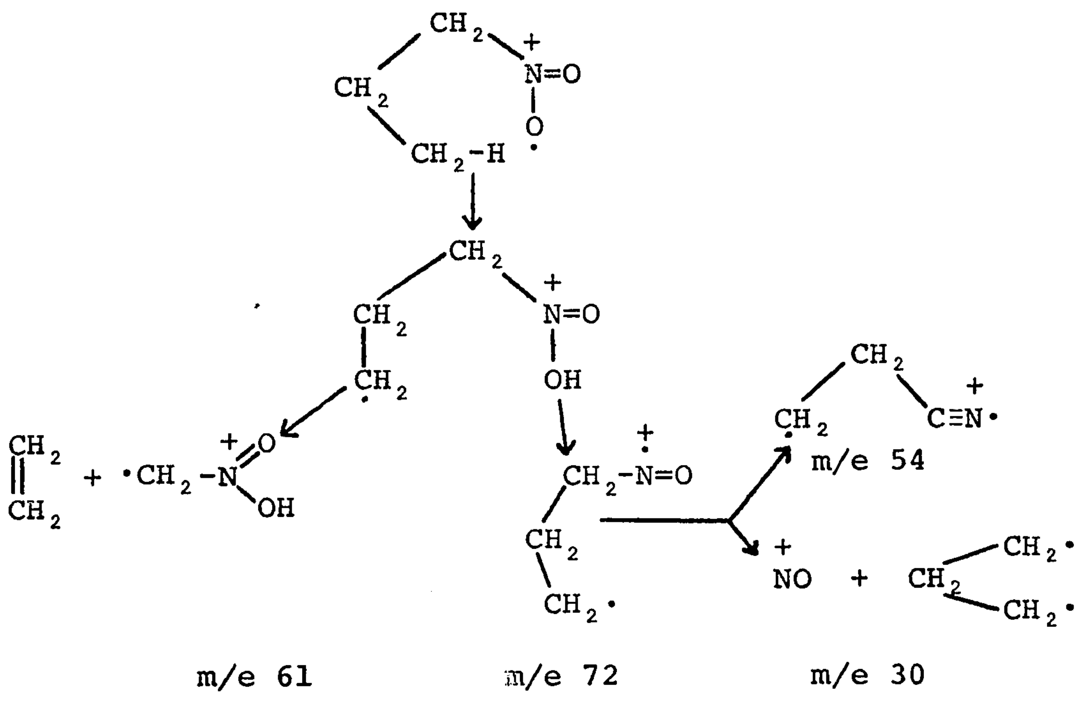
carbon oxygen bond with the aromatic ring, whereas the hybridization of the carbon atoms in the cyclopropane ring are enough like an olefinic system that the rearrangement is thought to be real. The lack of nitro-nitrite rearrangement along with the absence of any other carbon oxygen bond forming reactions precludes the formation of ions containing only carbon, hydrogen, and oxygen as demonstrated by high resolution mass spectroscopy.

One of the more interesting fragmentations of nitroalkanes involves the sequential loss of oxygen followed by the loss of water to give the equivalent of an ionized nitrile as indicated for nitroethane in Scheme 3 (4, 5). The reverse process, loss of water followed by the loss of oxygen, is known for certain nitro compounds (6). The higher molecular weight nitriles formed in this way undergo a subsequent decomposition by loss of ethylene as do nitriles upon electron impact.



Scheme 3

An excellent study has been done on the mass spectrum of 1-nitropropane employing the α, β, and γ deuterium labeled compounds to interpret the modes of fragmentation (8). The basic spectrum of 1-nitropropane is what one might expect from the previous discussion. The presence of γ-hydrogens, however, leads to the formation of some interesting ions by γ-hydrogen abstraction as indicated in Scheme 4. Abstraction of a γ-hydrogen followed by loss of ethylene leads to a low intensity ion having the structure of aci-nitromethane at m/e 61 (1.0%). Loss of a hydroxyl radical after γ-hydrogen abstraction can give rise to an ion at m/e 72 (15.0%). The ion generated at m/e 72 can further decompose by loss of water or nitric oxide as illustrated in Scheme 4.

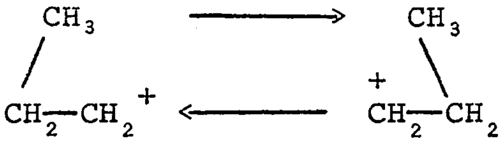


Scheme 4

The main peaks in the spectrum of 1-nitropropane correspond to hydrocarbon ions formed by α-cleavage as expected (8). The α-cleavage reaction yields an ion at m/e 43 which shifts as expected in the spectra of the labeled compounds. The ion at m/e 43 can further decompose by loss of $|H_2|$ to give an allylic cation at m/e 41 as pictured (Scheme 5). It was noticed, though, that the mass spectra of the α and β deuterium labeled compounds were very similar up to m/e 45. Furthermore, both the α and β labeled compounds exhibited loss of $|H_2|$ and $|HD|$ in the reaction shown in Scheme 5. This lead to the suggestion that a 1,2 methyl migration was taking place as depicted in Scheme 6. In agreement with this proposal is the observation that the γ-deuterium labeled compound loses $|HD|$ only.

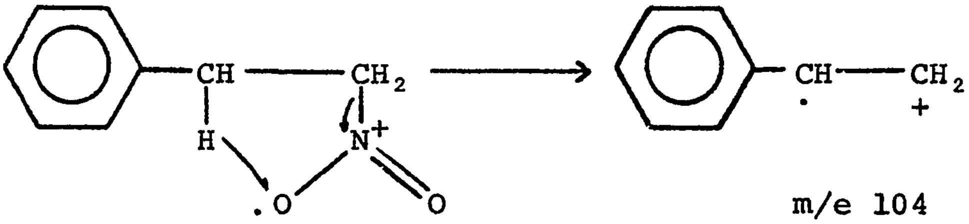
$$\underset{m/e\ 43}{CH_3CH_2CH_2^{+}} \longrightarrow \underset{m/e\ 41}{H_2C{=}CH{-}CH_2^{+}} + H_2$$

Scheme 5



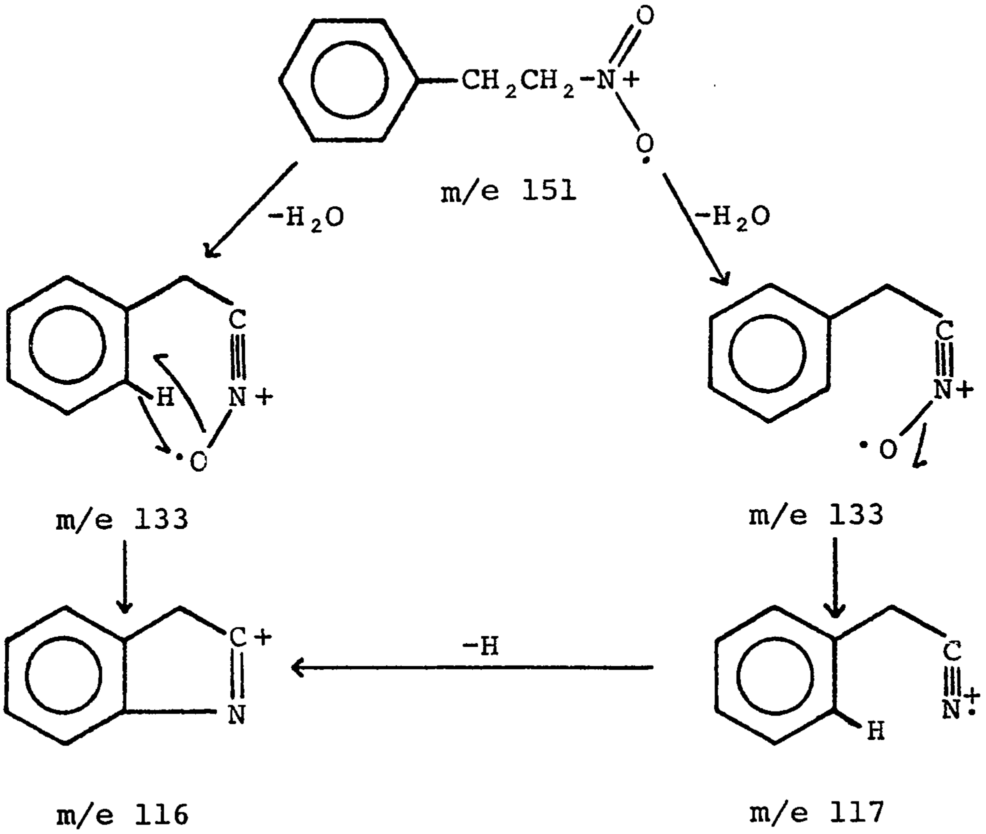
Scheme 6

A couple of excellent studies have been conducted on the mass spectra of arylalkyl nitro compounds (6, 9). In one investigation, the mass spectra of phenylnitromethane, 2-phenyl-1-nitroethane, 3-phenyl-1-nitropropane, and their specifically deuterium labeled side chain analogs were explored (6). In many respects these arylalkyl nitro compounds resemble simple nitroaliphatics since they give essentially no molecular ion, and do give numerous hydrocarbon ions. The base peak in the spectrum of phenylnitromethane corresponds to simple α-cleavage of the nitro group to give the tropylium ion at m/e 91. The base peak in the spectrum of 2-phenyl-1-nitroethane corresponds to the loss of nitrous acid, $|HNO_2|$, to give an ion at m/e 104 as depicted in Scheme 7. The loss of nitrous acid rather than simple cleavage to give a tropylium ion is taken as evidence for ionization on the nitro group instead of the aromatic ring where one would expect the formation of the tropylium ion. The base peak in the spectrum of 3-phenyl-1-nitropropane is the tropylium ion, but the formation of this ion probably occurs by a variety of fragmentation pathways other than just simple cleavage.



Scheme 7

The mass spectra of all three arylalkyl nitro compounds exhibit peaks corresponding to the previously mentioned nitriles (6). These ions occur by dehydration involving the hydrogen atoms α to the nitro group to give a nitrile oxide, which can then lose an oxygen atom to give the nitrile as illustrated for 2-phenyl-1-nitroethane in Scheme 8. The nitrile oxides which form can often undergo other reactions

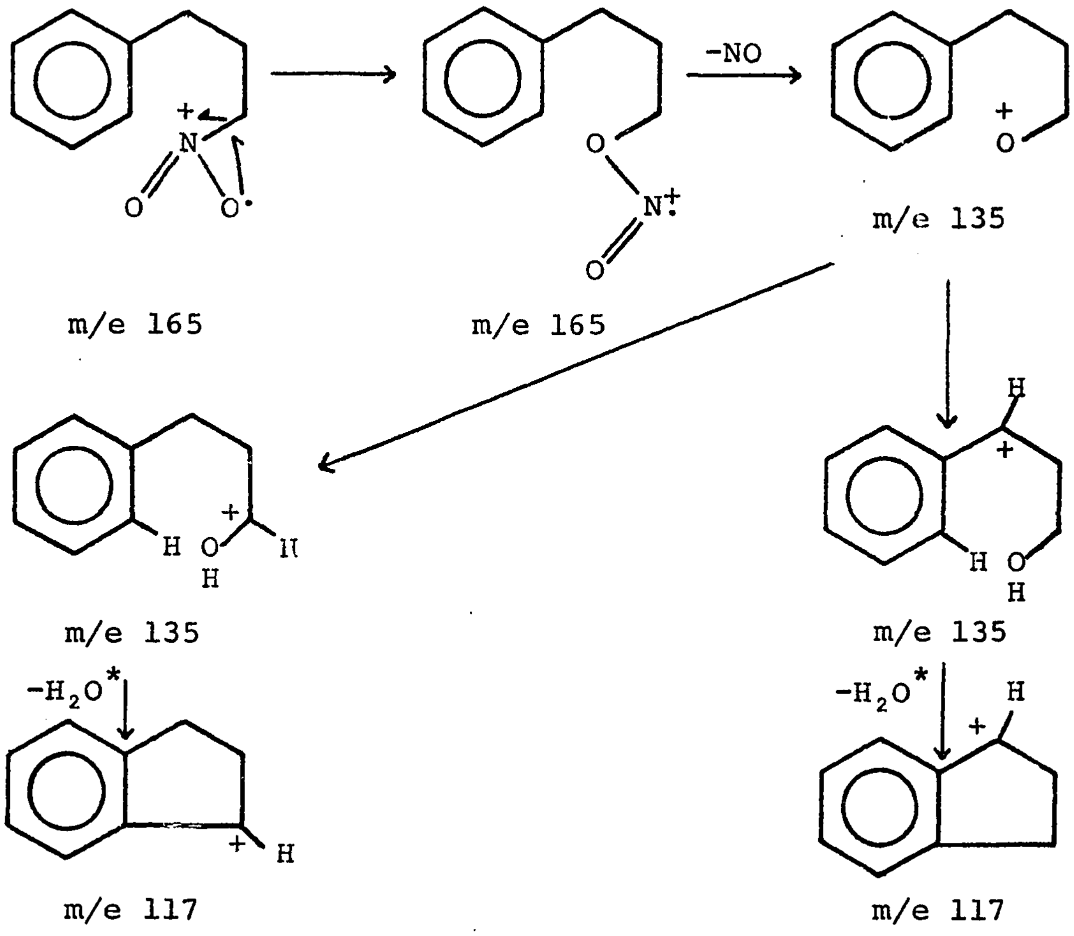


Scheme 8

such as abstraction of an <u>ortho</u> hydrogen, and loss of a hydroxyl radical to form a cyclic ion as illustrated for

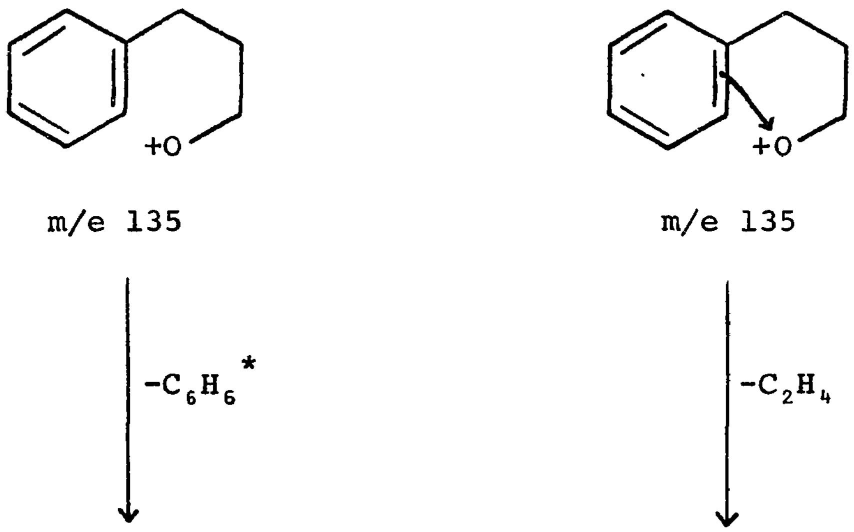
2-phenyl-1-nitroethane (Scheme 8). The previously described process involving loss of an oxygen atom followed by loss of water (4, 5) apparently only occurs from phenynitromethane (6) in this series.

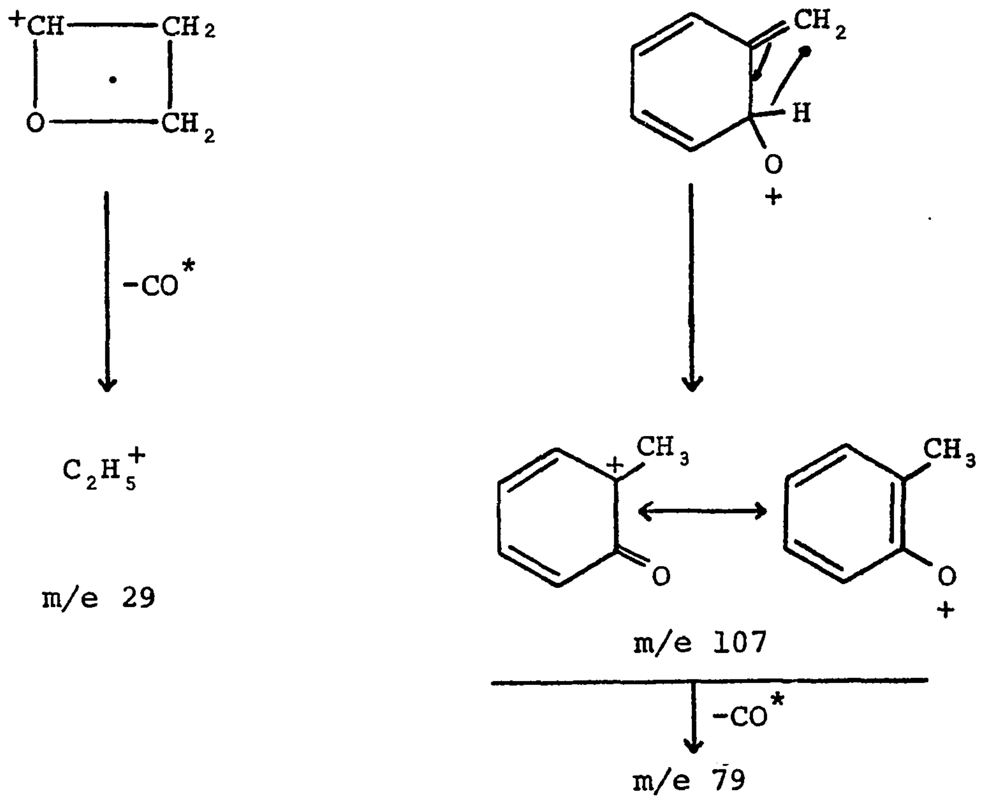
The mass spectrum of 3-phenyl-1-nitropropane is unusual and interesting in a number of respects, and deserves further comment (6). The mass spectrum of 3-phenyl-1-nitropropane exhibits the loss of nitric oxide, |NO|, from the molecular ion



Scheme 9

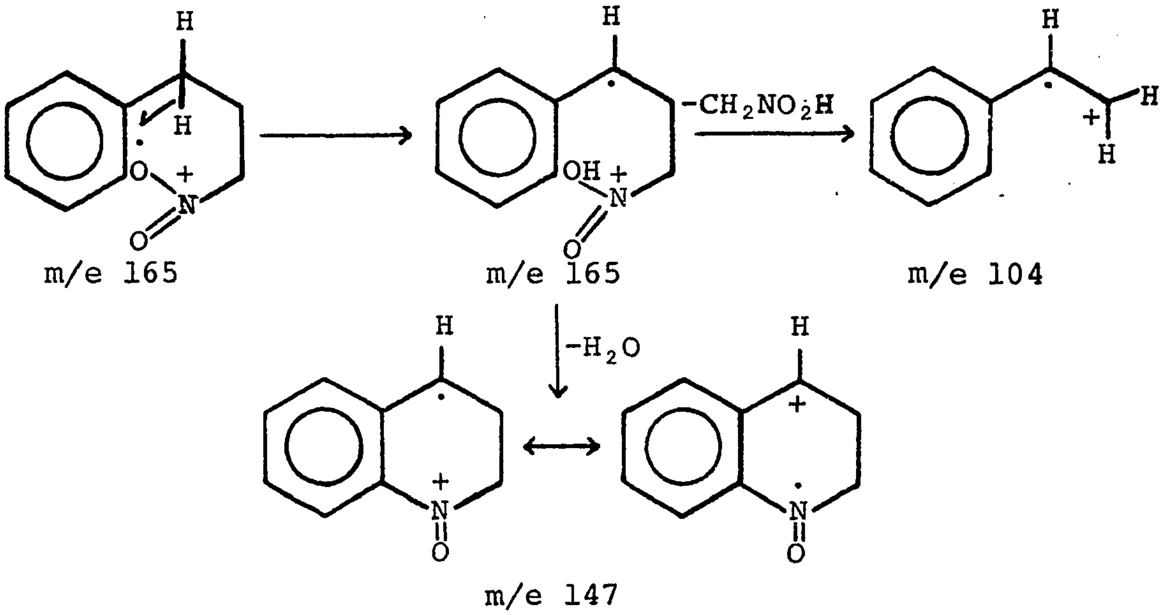
which suggest a nitro-nitrite rearrangement is taking place. The author depicts the process as a simple nitro-nitrite rearrangement with loss of nitric oxide, but the loss might also involve interaction with the phenyl ring as previously described (5). The ion formed by loss of nitric oxide may further fragment by abstraction of an α, or γ hydrogen as shown by deuterium labeling and further abstraction of a hydrogen from the <u>ortho</u> position of the phenyl ring with the eventual expulsion of a molecule of water as depicted in Scheme 9. Labeling data suggests that the m/e 135 ion can also decompose by two other pathways as illustrated in Scheme 10. The m/e 135 ion loses benzene to give an ion at m/e 57 which loses carbon monoxide to give an ion at m/e 29, or alternately the m/e 135 ion can decompose by loss of ethylene to give an ion at m/e 107 which loses carbon monoxide to give an ion at m/e 79.





Scheme 10

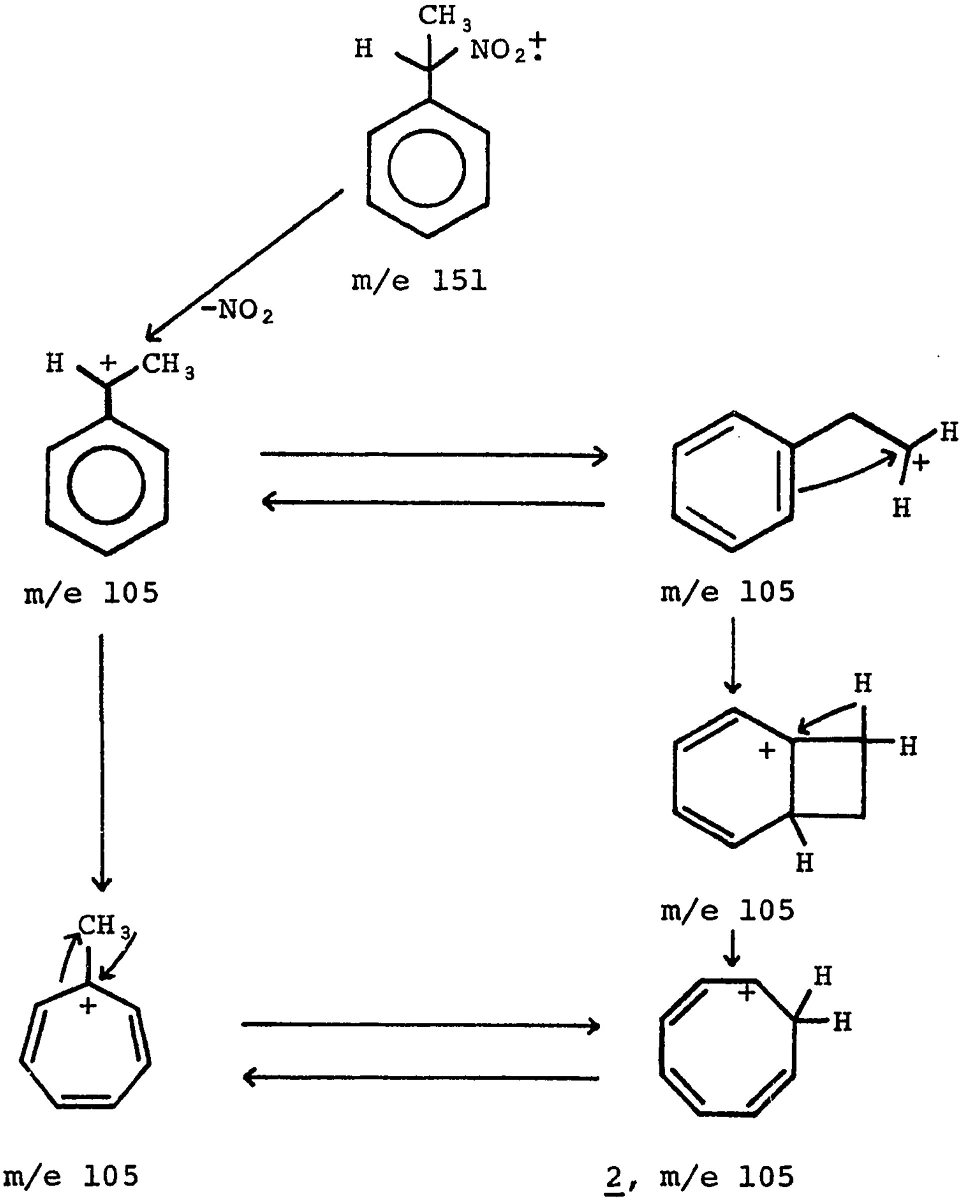
The presence of γ-hydrogens leads to another interesting rearrangement ion (6). Labeling studies indicate that abstraction of a γ-hydrogen by the nitro group followed by loss of the aci form of nitromethane results in the formation of an intense ion at m/e 104 (30.0%) corresponding to the ionized form of styrene as indicated in Scheme 11. The high intensity of this ion may be due in part to the presence of benzylic hydrogens in the γ-position. The γ-hydrogen abstraction process can also result in the formation of an ion at m/e 147 by loss of water as presented in Scheme 11.



Scheme 11

The second investigation of arylalkyl nitro compounds was of 1-phenyl-1-nitroethane, 1-phenyl-1-nitropropane, 1-phenyl-2-nitropropane, and their specifically deuterated side chain analogs (9). The mass spectra of these compounds again are similar to simple nitroalkanes, since no molecular ion is observed, and the nitro group is cleaved readily to yield alkylbenzene ions. The spectrum of 1-phenyl-2-nitropropane is reminiscent of 2-phenyl-1-nitroethane in that loss of nitrous acid is observed. The spectra of these arylalkyl nitro compounds are quite different from the previously discussed arylalkyl nitro compounds (6) in that no ions are observed which indicate the nitro group is playing an important role in decomposition.

The main fragmentation of all three compounds is the loss of the nitro group to generate a $C_8H_9^+$ or $C_9H_{11}^+$ ion (9). The structure of the $C_8H_9^+$ ion has been suggested to be the methyl tropylium ion <u>1</u>, Scheme 12, but the author finds that all of



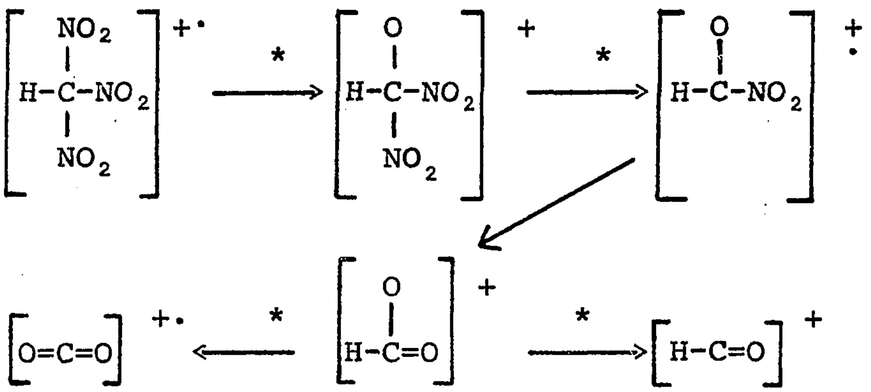
Scheme 12

the hydrogen atoms become equivalent before loss of acetylene even those of the methyl group in 1-phenyl-1-nitroethane as shown by deuterium labeling. The methyl hydrogens are not rearranged in the molecular ion since the methyl group can be lost completely with label from the molecular ion. It was suggested, therefore, that the $C_8H_9^+$ ion at m/e 105 has the eight membered ring structure <u>2</u>, Scheme 12, or may possibly have a homotropylium ion structure. The scrambling in structure <u>2</u> could take place by a series of 1,2 or 1,5 hydrogen shifts. It is, also, suggested that structures <u>1</u> and <u>2</u> might interconvert. The $C_9H_{11}^+$ ion which is formed from the arylalkyl nitropropanes is formulated as the phenylated cyclopropane species. A new fragmentation involving the random transfer of a hydride from the cyclopropane ring to the aromatic ring to generate a $C_3H_5^+$ ion was reported.

The mass spectra of some tertiary nitroalkanes have also been investigated (4). It was reported that the most favorable fragmentation involves loss of nitrous acid to give an olefin. The other ions in the spectrum supposedly come from the subsequent decomposition of the olefin. More recently other workers have reported that the mass spectrum of 2-methyl-2-nitropropane does not lose nitrous acid, but instead simply cleaves the nitro group to give a hydrocarbon ion which undergoes further fragmentation (10). These authors postulate that the previously reported loss of nitrous acid was due to the presence of γ-hydrogens in all of the compounds studied. The loss of nitrous acid, therefore, probably involves a six-membered ring hydrogen abstraction reaction rather than a simple elimination reaction.

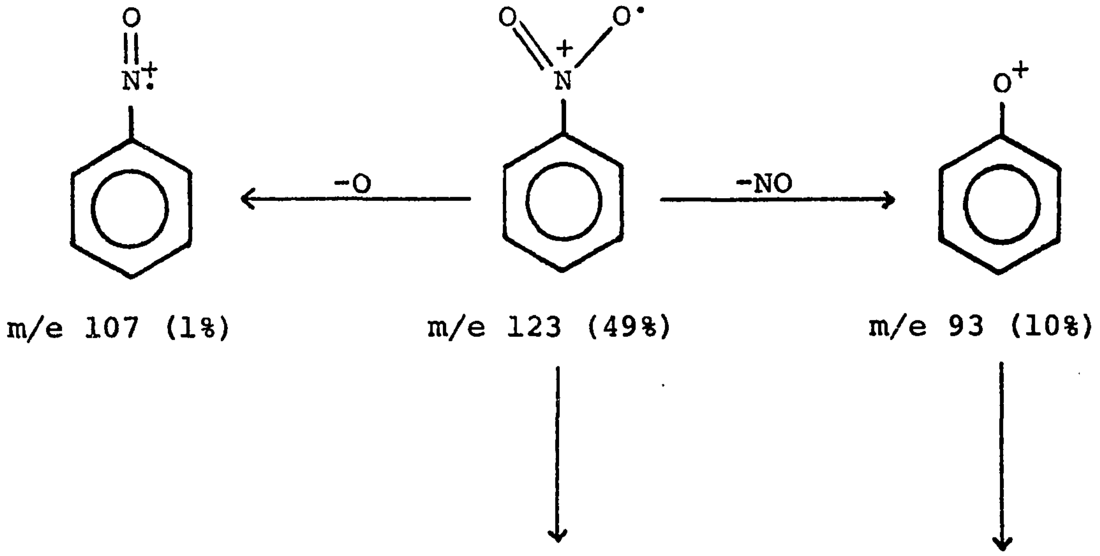
The mass spectra of alicyclic nitro compounds (4) such as nitrocyclohexane and nitrocyclopentane are again dominated by loss of the nitro group, but the mass spectra of nitrocyclopropane and some of its derivatives (7) are more interesting. The parent compound, nitrocyclopropane, shows a weak but discernable molecular ion. Loss of oxygen, and the nitro-nitrite rearrangement occur to give the weak ions $C_3H_5NO^{+\cdot}$ (0.35%) and $C_3H_5O^+$ (0.75%), respectively, but the base peak again corresponds to the simple cleavage of the nitro group.

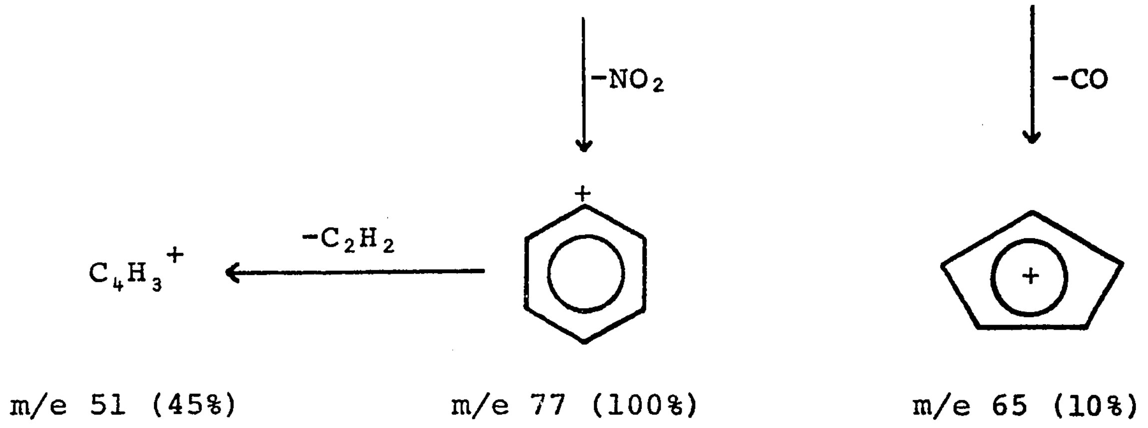
In addition to the mass spectra of simple nitroalkanes, the mass spectra of a number of polynitroalkanes have been discussed (10, 11). The fact that the polynitroalkanes do not give a molecular ion is the only characteristic that they have in common with simple nitroaliphatics. Their spectra are characterized by loss of the nitro group and nitric oxide with charge retention on these groups. The occurrence of nitro-nitrite rearrangements is common giving rise to ions containing only carbon, hydrogen, and oxygen as illustrated for trinitromethane in Scheme 13.



Scheme 13

The previous discussion has revealed some interesting facts about the mass spectra of nitroalkanes of various types. The mass spectra of nitroaromatics, however, are more interesting because the nitro group plays a more important role in directing fragmentation. The mass spectrum (12, 13, 14) of the simplest nitroaromatic, nitrobenzene (Scheme 14), reveals some of the characteristics of nitroaromatics.

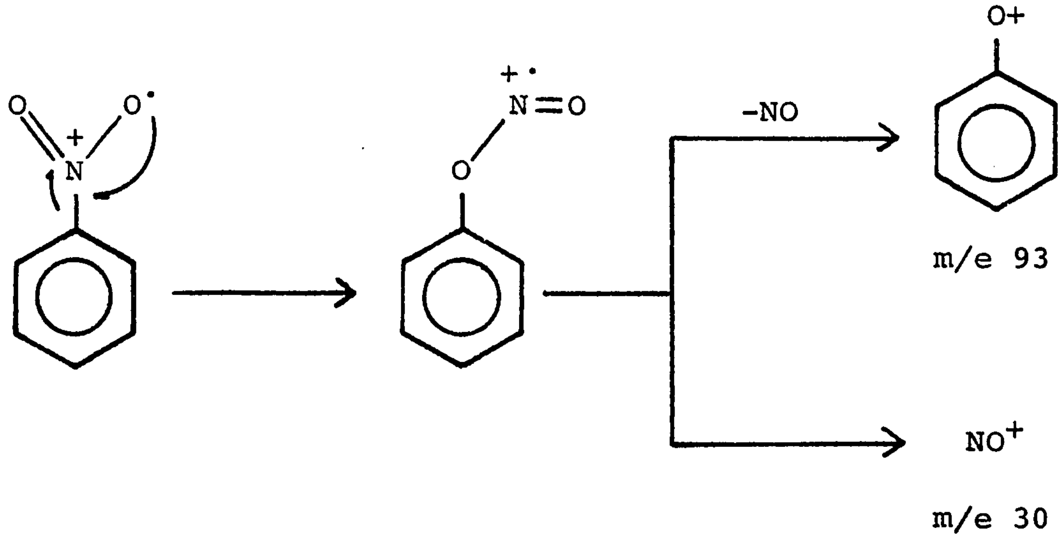




Scheme 14

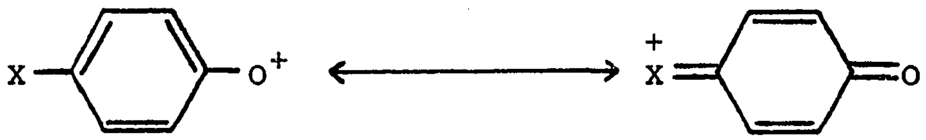
The base peak in the spectrum corresponds to cleavage of the nitro group from the reasonably stable molecular ion (m/e 123, 49%) to give the phenyl cation m/e 77. Perhaps the most interesting fragmentation of nitrobenzene is the metastable loss of nitric oxide from the molecular ion to generate an ion at m/e 93 (10.0%), a process which is believed to occur via a nitro-nitrite rearrangement. The m/e 93 ion can further fragment by loss of carbon monoxide to give a hydrocarbon ion, $C_5H_5^+$, at m/e 65. Charge retention on the nitric oxide moiety gives an ion at m/e 30 as substantiated by an appropriate metastable. The presence of a low intensity ion at m/e 107 (1.0%) indicates that the loss of oxygen from the nitro group occurs to only a limited extent.

The mechanism for loss of nitric oxide via the nitro-nitrite rearrangement shown in Scheme 15 was first proposed by Beynon (13). Evidence in favor of this mechanistic scheme has



Scheme 15

come from several sources. It has been demonstrated, for example, that electron donating substituents in the _para_ position enhances the nitro-nitrite rearrangement, and subsequent loss of nitric oxide, whereas electron withdrawing substituents in the _para_ position, and all _meta_ substituents do not enhance rearrangement (15). The enhancement of the nitro-nitrite rearrangement is believed due to stabilization of the product ion through a quinoid structure of the type _3_ (Scheme 16). For enhancement to occur the oxygen of the nitro group must become attached to the same carbon atom as the nitrogen atom in the original nitro group. Furthermore, it has been shown by



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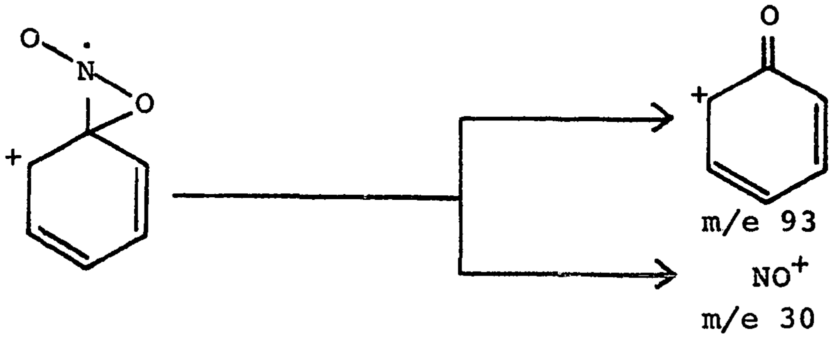
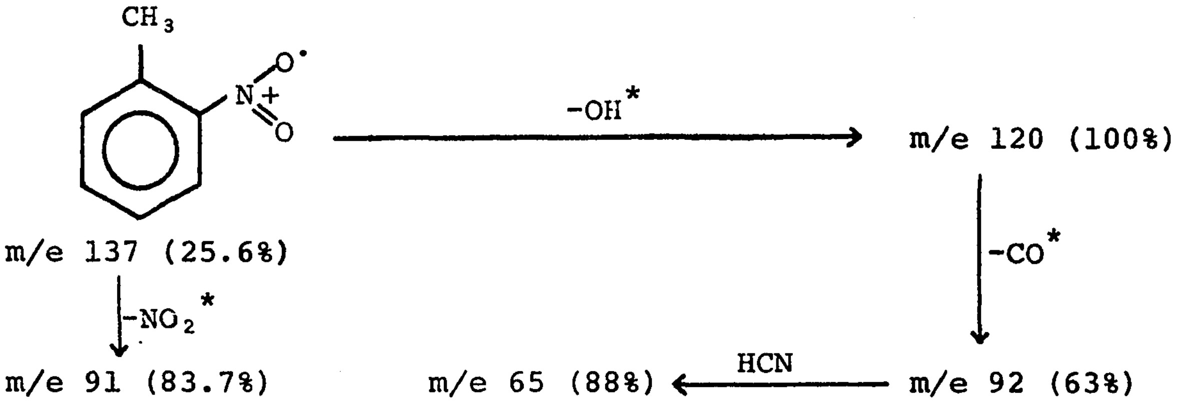
Scheme 16

application of the Hammett equation that the *para* substituted analogs of the m/e 93 ion in Scheme 15 decompose in a manner similar to the same ions being generated from various *para* substituted anisoles by loss of the methyl group (16). Recently it has been demonstrated that steric inhibition of resonance can prevent the aforementioned enhancement of the nitro-nitrite rearrangement (17). Other authors have demonstrated the effects of charge localization (18), and the presence of a charged group in the *para* position (19) on the nitro-nitrite rearrangement. It should be pointed out, however, that the results of the previous discussion could also be explained in terms of a mechanism involving a three membered ring state of the molecular ion as shown in Scheme 17.



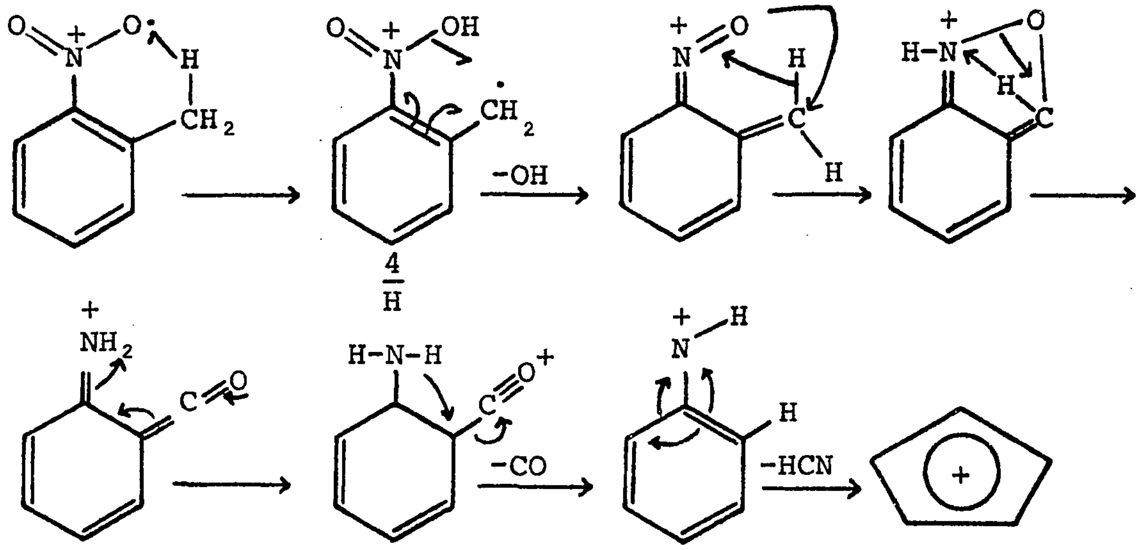
Scheme 17

The mass spectra of simple nitroaromatics with various substituents in the *meta* and *para* positions generally resemble those of nitrobenzene. In sharp contrast, the presence of a substituent in the *ortho* position often leads to quite different spectra due to interaction of the nitro group and the substituent (often called an *ortho*-effect). If the *ortho* substituent has α-hydrogens, abstraction of a hydrogen atom often occurs with subsequent loss of a hydroxyl radical followed by other decompositions (5, 13, 14, 20, 21, 22, 23). The mass spectrum of *ortho*-nitrotoluene (Scheme 18) with a base peak corresponding to OH loss serves to illustrate the effects of *ortho*-substituents (13).



Scheme 18

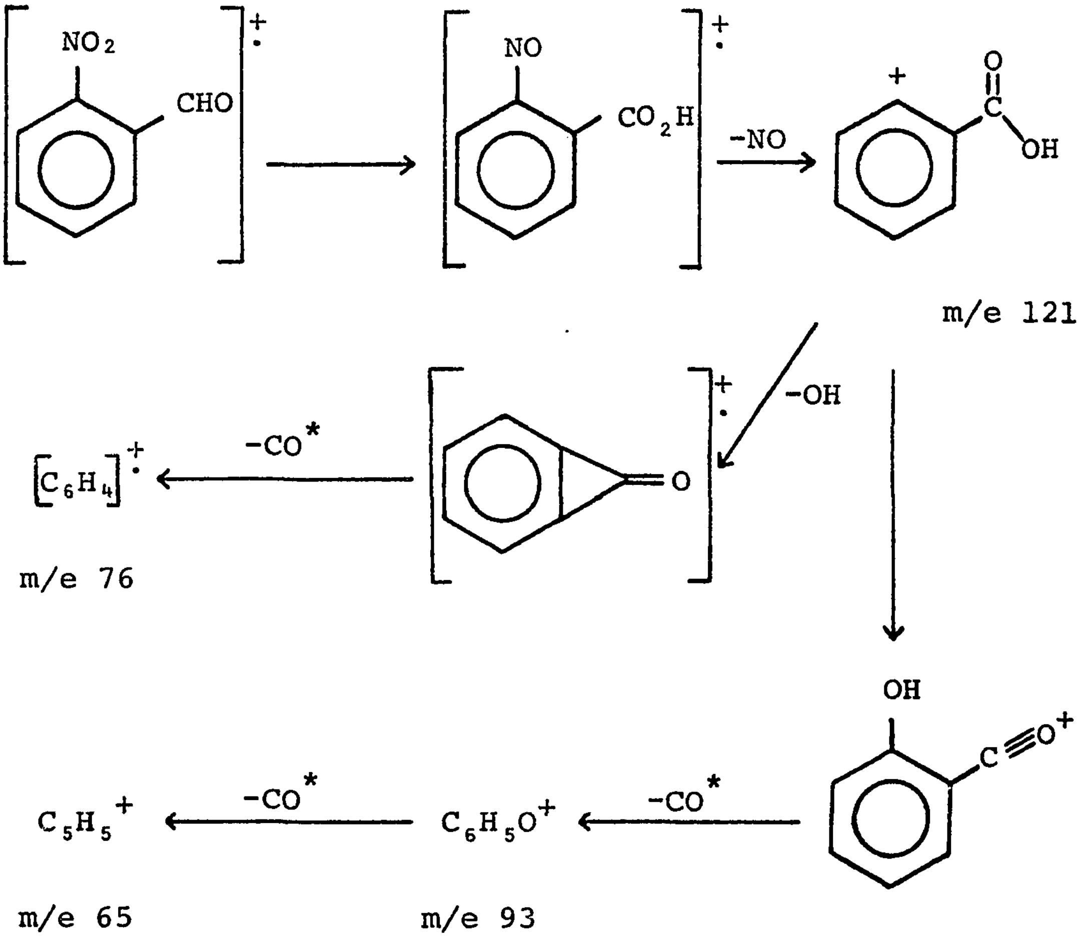
The sequential loss of carbon monoxide and hydrogen cyanide from the $\overset{+\cdot}{M}$-OH ion is of interest since it could possibly occur from the nitro or nitrite form of the molecular ion.



Scheme 19

Carbon thirteen labeling has revealed that the loss of carbon monoxide involves the carbon of the methyl group as opposed to the phenyl ring thus ruling out the nitrite form of the molecule as the precursor (20). Deuterium labeling results substantiate the abstraction of a hydrogen atom from the methyl group with subsequent loss of a hydroxyl radical (22). A large isotope effect for this reaction lead to the suggestion that the carbon hydrogen bond is broken substantially in the transition state and could even involve the discrete intermediate 4 (Scheme 19). Furthermore, the deuterium labeling results indicate that the hydrogen involved in the loss of hydrogen cyanide comes primarily from the methyl group. The mechanistic pathway proposed in Scheme 19 is consistent with these findings.

Ortho effects have also been observed for nitroaromatics with an α-carbonyl containing substituent in the ortho position (21). Such an interaction has been proposed to explain the mass spectrum of ortho-nitrobenzaldehyde. The loss of nitric oxide from the molecular ions of most nitroaromatics with an α-carbonyl containing substituent in the ortho position is minimal, but in the mass spectrum of ortho-nitrobenzaldehyde it is the base peak. Hence, it has been proposed that the loss of nitric oxide is occurring by the rearrangement presented in Scheme 20. The subsequent loss of two molecules of carbon



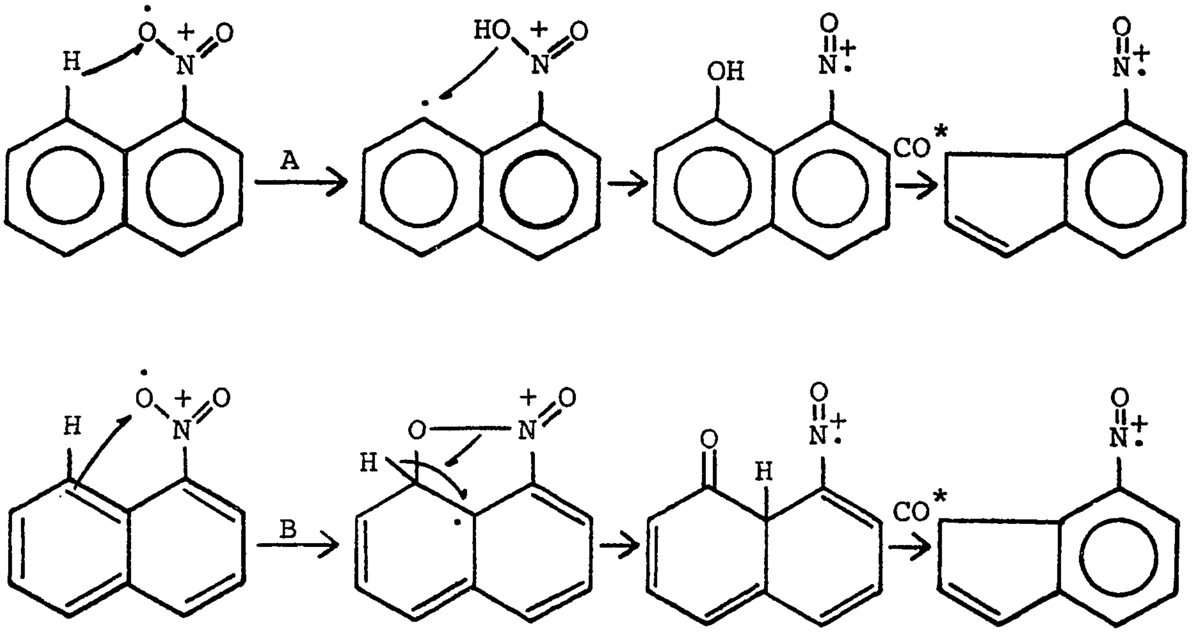
Scheme 20

monoxide or the alternate loss of a hydroxyl radical followed by loss of carbon monoxide supports this hypothesis to a limited extent. The rearrangement of *ortho*-nitrobenzaldehyde to *ortho*-nitrosobenzoic acid is a known photochemical reaction, and it was suggested that the mass spectral fragmentation might parallel the photochemical reaction. Although *ortho*-nitrosobenzoic acid fragments in a similar manner, the intensity of the ions observed are so different that it has been argued by other authors (5, 24) that this loss occurs only by nitro-nitrite rearrangement.

On the basis of the fragmentations observed for simple nitroaromatics, the mass spectral behavior of dinitroaromatics can be predicted quite accurately (13, 14). In the mass spectrum of dinitrobenzene ions are observed corresponding to $M^{+\cdot}$-O, $M^{+\cdot}$-NO, $M^{+\cdot}$-NO_2, $M^{+\cdot}$-NO_2-O, $M^{+\cdot}$-NO_2-NO, and $M^{+\cdot}$-NO_2-NO_2. *Ortho* effects, also occur in the mass spectra of dinitroaromatics. The operation of such an *ortho*-effect is seen in the consecutive loss of two hydroxyl radicals in the mass spectrum of 2, 6-dinitrotoluene. Nitro-nitrite isomerization occurs at several stages in the fragmentation, as evidenced by the loss of NO. An ion at m/e 108 originates by the interesting loss of a nitro group followed by the loss of carbon monoxide.

The mass spectra of various nitronaphthalenes that have been investigated (5, 14, 21, 25) are similar to those of nitrobenzenes in that they give strong molecular ions, and fragment with the metastable loss of nitric oxide and the nitro group. The base peak in the mass spectrum of α- and β- nitronaphthalenes corresponds to the loss of the nitro group from the molecular ion. Two other frequently encountered ions occur at m/e 114 and m/e 115. These ions are believed to have an indenyl structure.

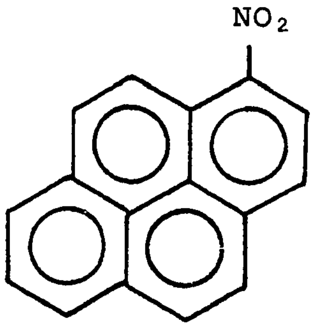
The most interesting fragmentation of certain nitronaphthalenes corresponds to the metastable loss of carbon monoxide in one step from the molecular ion as substantiated by high resolution mass spectroscopy (21, 25). The loss of carbon monoxide occurs only when the nitro group is in the one- or α-position and the eight-position is not occupied by a substituent other than hydrogen or flourine. The stereospecificity of this fragmentation coupled with the absence of an ion corresponding to loss of carbon monoxide from the molecular ion of nitrobenzene or β-nitronaphthalene suggests that the loss of carbon monoxide involves the *peri*-position. Indeed carbon thirteen labeling has confirmed this hypothesis (5). Two mechanisms A and B (Scheme 21) have been proposed for the ejection of carbon monoxide from the molecular ion of α-nitronaphthalenes (25). Mechanism B is favored since 8-fluro-1-nitronaphthalene exhibits loss of carbon monoxide from the molecular ion and it is unlikely that abstraction of flourine by oxygen as required by reaction A would occur (5). The loss of carbon monoxide from the molecular ion can be followed by the subsequent loss of carbon monoxide as shown by high resolution mass spectroscopy (25). The presence of amino or flouro



Scheme 21

substituents when in the two position increases the observed loss of carbon monoxide, but decreases the loss of carbon monoxide when at position six or seven (5). The ejection of carbon monoxide appears to be rather specific since compounds with similar structural features such as 1-nitropyrene <u>5</u> and 1-nitroazulene <u>6</u> show virtually no loss of carbon monoxide.

The mass spectra of a number of nitro compounds that have been documented in the literature are not related here, including: nitroalkanes (26, 27), nitropyridines (28), 2,4-



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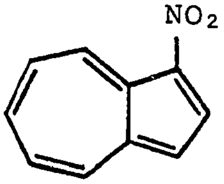

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dinitrophenylhydrazones (29, 30), dinitroaminoalcohols (31), nitroisoxazolizidines (32), and nitroimidazoles (33).

Pyrolysis of Nitroolefins

A literature search on the pyrolysis of nitro compounds reveals an extensive amount of work on nitroalkanes and nitroaromatics. Pyrolysis of nitroalkanes and polynitroalkanes has recently been reviewed (34). Pyrolysis of nitroalkanes generally results in cleavage of the nitroalkyl bond to generate two radicals which lead to the observed products. A typical sequence of reactions is illustrated for nitromethane in Scheme 22.

The pyrolysis of nitroaromatics has received little attention until recently (35). Fields and Meyerson have found that the nitroarene bond in nitrobenzenes and other nitroaromatics breaks above 400°C (36). They have used this reaction to generate various aromatic radicals and have studied their reactions with various substrates (37). More recently, they have investigated the interaction of the nitro group and

$$CH_3NO_2 \xrightarrow{\Delta} CH_3\cdot + \cdot NO_2$$

$$CH_3\cdot + CH_3NO_2 \longrightarrow CH_4 + \cdot CH_2NO_2$$

$$\cdot CH_2NO_2 + \cdot NO_2 \longrightarrow CH_2O + \cdot NO + \cdot NO_2$$

$$CH_2O + \cdot NO_2 \longrightarrow CO + \cdot NO + H_2O$$

$$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6$$

$$\cdot CH_2NO_2 \longrightarrow CH_2O + \cdot NO$$

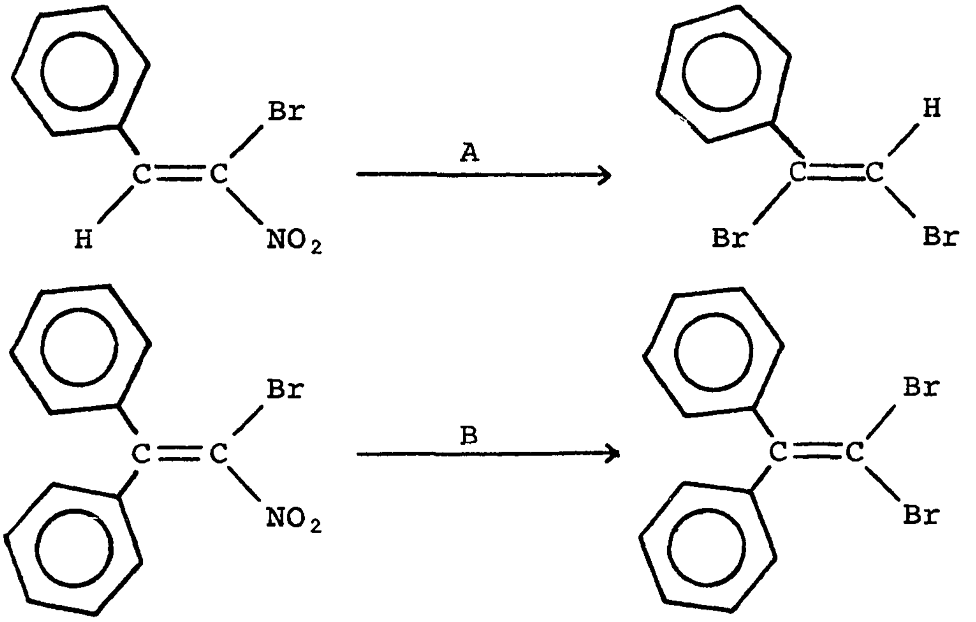
$$CH_3\cdot + \cdot NO \longrightarrow CH_3NO \longrightarrow HCN + H_2O$$

Scheme 22

ortho-substituents under pyrolytic conditions (38). They found, for example, that the pyrolysis of *ortho*-nitrotoluene involves rearrangement to anthranilic acid with subsequent decarboxylation to aniline.

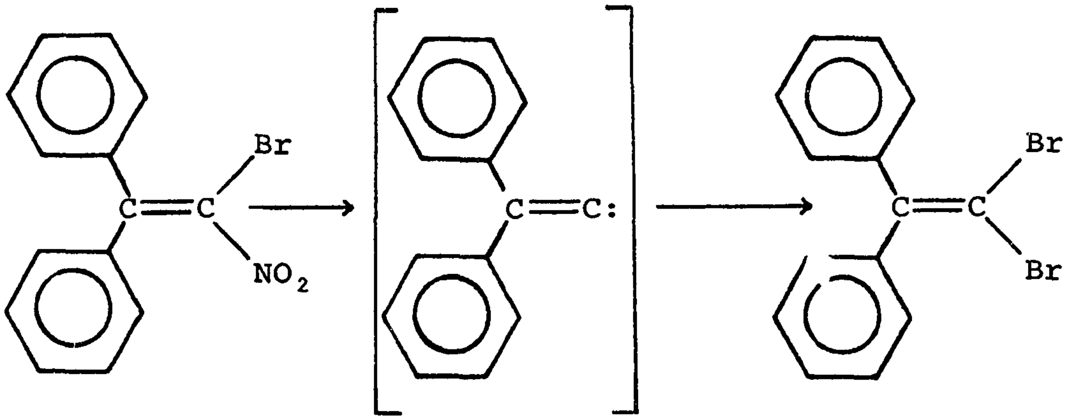
In comparison to the studies on nitroalkanes and nitroaromatics, there is a startling lack of information on the pyrolysis of nitroolefins. Undoubtably, this is due in part to the thermal instability of simple nitroolefins. Attempts at distilling nitroolefins such as 1- or 2-nitropropylene at atmospheric pressure leads to intractable tars (39). Two studies, however, have been reported on the pyrolysis of the more stable nitrostyrenes.

The pyrolysis of a number of bromonitrostyrenes have been investigated by simply heating the compounds in a flask or sealed tube at temperatures in the range of 190-300°C (40). The formation of the α,β- or β,β-dibromostyrenes as indicated in Scheme 23 was explained in terms of a divalent carbon



Scheme 23

intermediate which adds bromine to give the observed products (Scheme 24). A 1,2-hydrogen migration was postulated to



Scheme 24

explain the formation of the α,β-dibromostyrenes shown in reaction A (Scheme 23).

Table 1. Results of Allen and Happ (41)

Compound	Pyrolsis products and ions
β-Nitrostyrene	(149) U.M. (102) Phenylacetylene; (30) NO
2,5-Dimethoxy-β-Nitrostyrene	(209) U.M., (30) NO
β-Methyl-β-nitrostyrene	(233) U.M., (30) NO
β-Bromo-β-nitrostyrene	(262) 1,2-Dibromostyrene, (258) Bromodiphenylethylene, (228) U.M., (30) NO
1,1-Diphenyl-2-nitroethylene	(225) U.M.; (30) NO
1-Phenyl-1-biphenyl-2-nitroethylene	(301) U.M.; (30) NO
1,1-Diphenyl-2-bromo-2-nitroethylene	(338) 2,2-Dibromo-1,1-diphenylethylene, (332) Tetraphenylethylene, (303) U.M., (178) Tolane; (30) NO

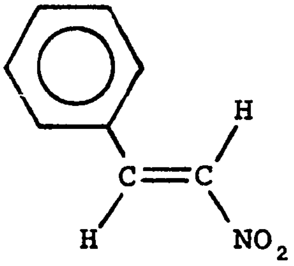
The only other pertinent study was the pyrolysis of some β-nitrostyrenes at 230° C in a glass inlet system of a mass spectrometer (41), with product identification from the mass spectrum. The nitro compounds studied were found to be surprisingly stable to thermolysis as can be seen from the results displayed in Table 1, where U.M. refers to undecomposed molecular ion. The nitric oxide ion observed in most of the mass spectra could arise either as a pyrolysis product, or from the mass spectral fragmentation of the original nitrostyrene.

RESULTS AND DISCUSSION

The lack of mass spectral data concerning nitroolefins, and the synthetic utility of this important class of compounds (42) prompted an investigation of their electron impact chemistry. Since nitroolefins resemble both nitroaromatics and nitroaliphatics in structure, it was felt that interesting parallels in mass spectral behavior might occur as well as fragmentations characteristic of nitroolefins alone. Due to the simplicity of preparation from readily available starting materials, a variety of nitrostyrenes was investigated first.

Mass Spectra of Nitrostyrenes

The investigation was initiated by examination of the mass spectra of the parent compound β-nitrostyrene 7 and β-methyl-β-nitrostyrene 8. The mass spectrum of 7 is displayed in Figure 1 and an outline of the interesting fragmentations appears in Scheme 25, where an asterisk denotes a process supported by the presence of a metastable. A glance at



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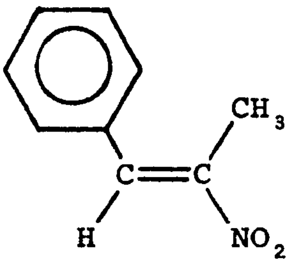

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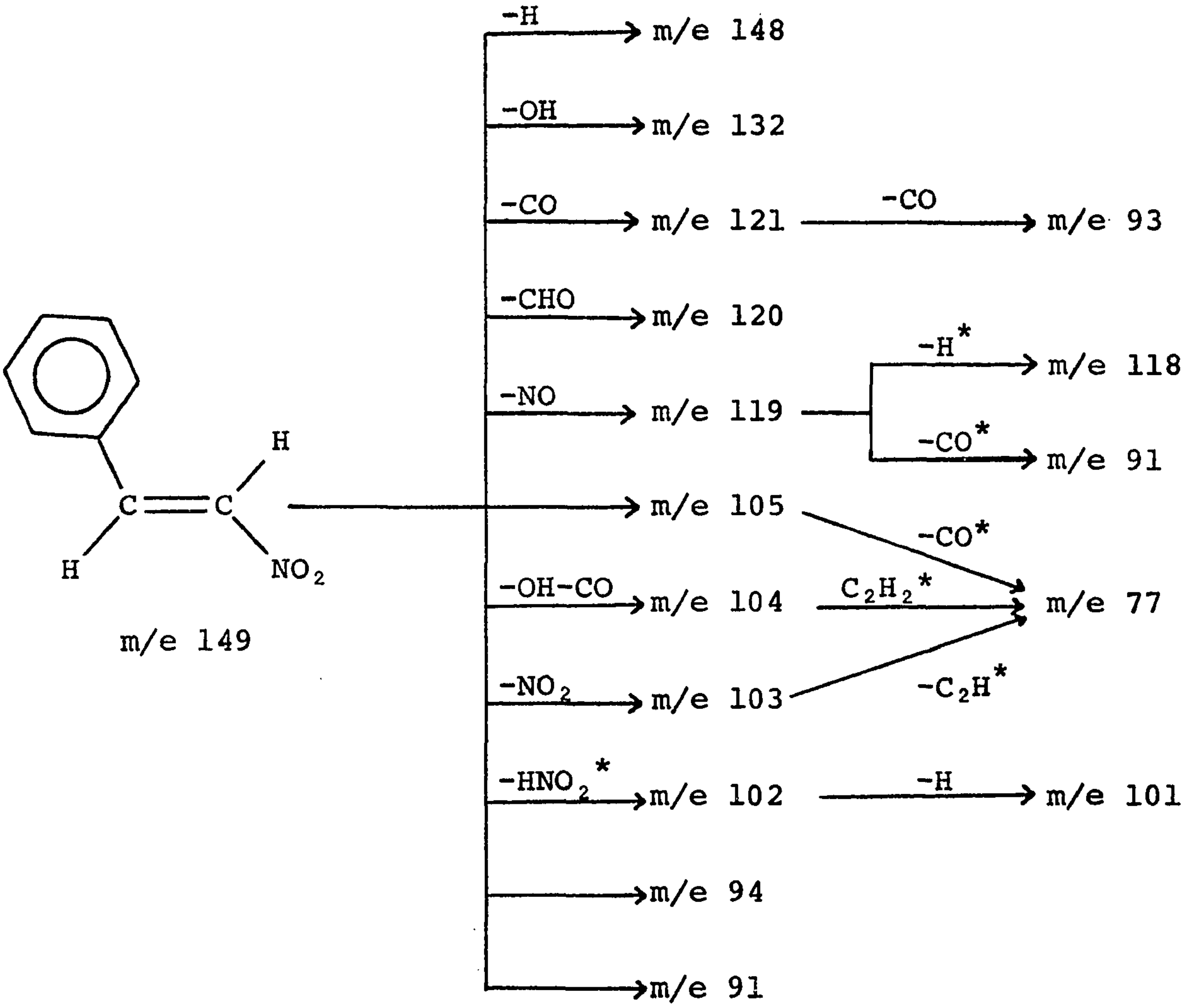


Scheme 25

Scheme 25 reveals a variety of fragmentations some of which must involve extensive rearrangement. The mass spectrum of 8 is presented in Figure 2, and the main fragmentations are sketched in Scheme 26.

It is immediately apparent from a comparison of Schemes 25 and 26 that the fragmentation modes of 7 and 8 are very similar. Due to the similarity of the two spectra, and the

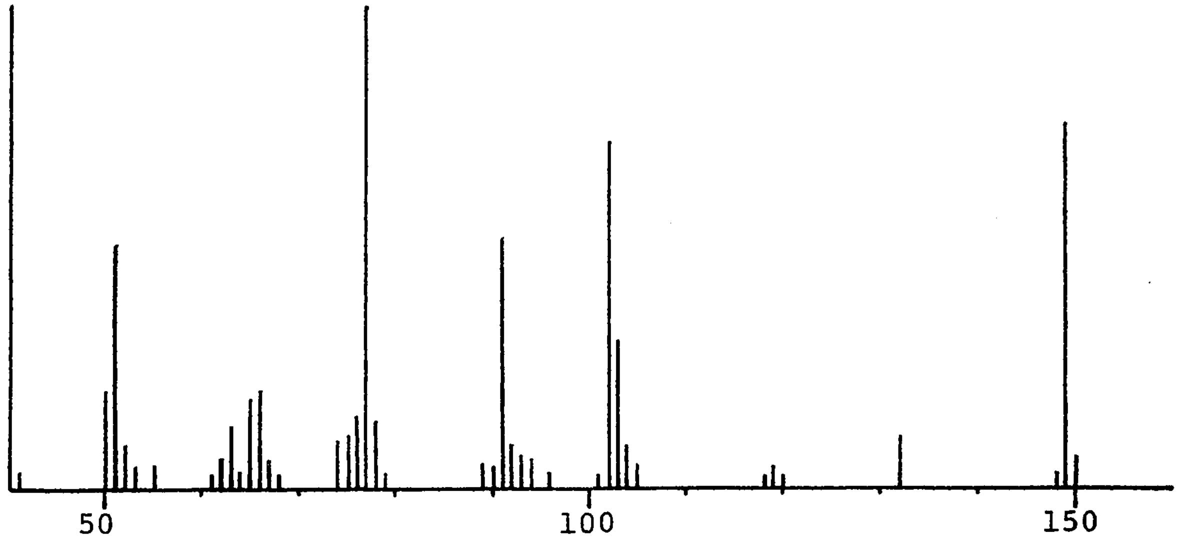


Figure 1. Mass spectrum β-nitrostyrene 7

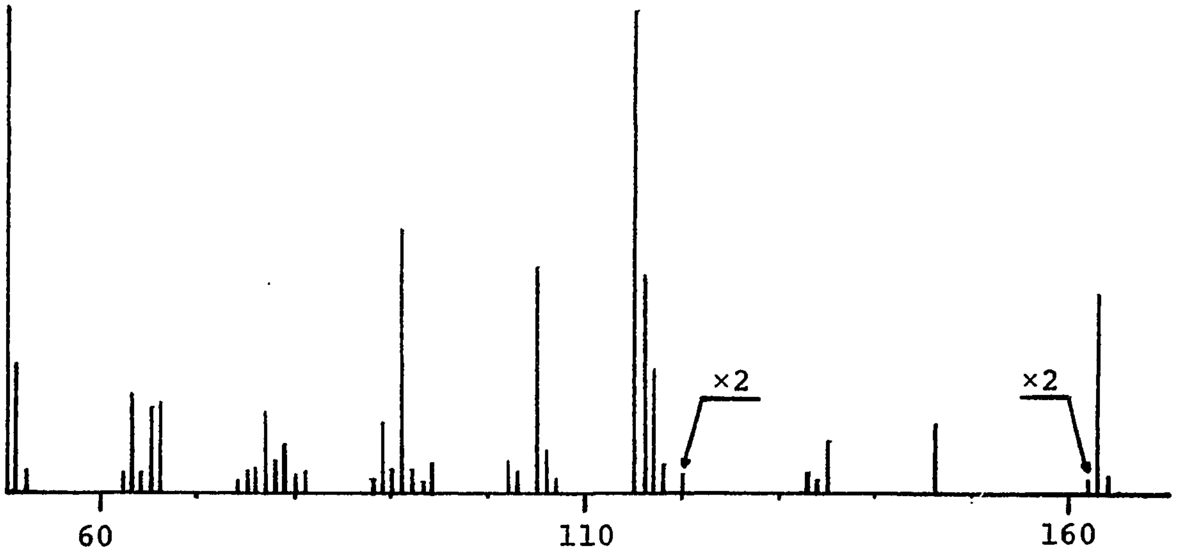
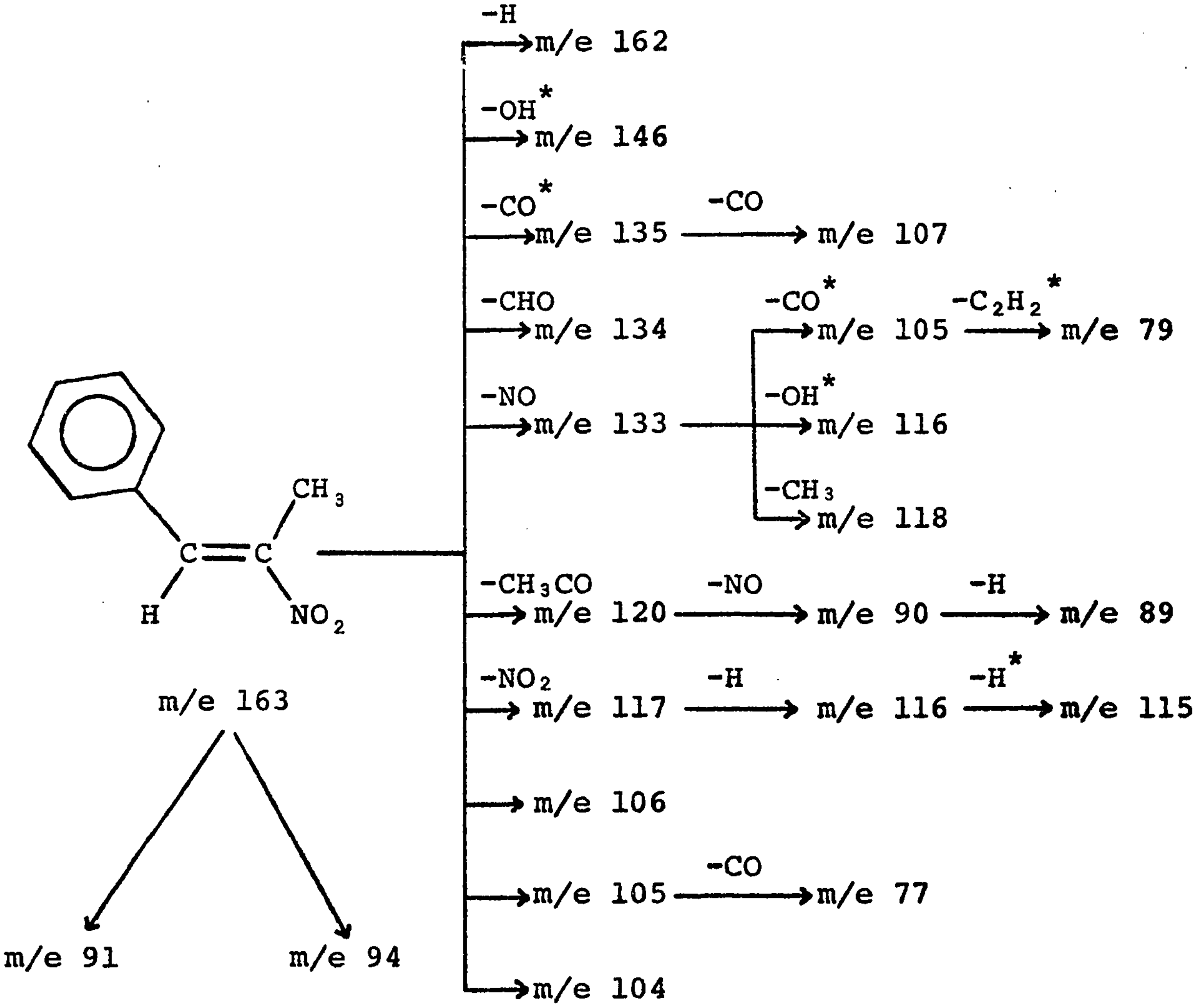


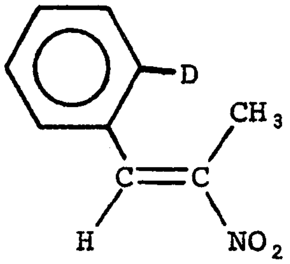
Figure 2. Mass spectrum β-methyl-β-nitrostyrene 8



Scheme 26

easier handling of 8 in the mass spectrometer, it was selected for further labeling work to clarify the observed fragmentations and the labeled compounds 9 - 13 were prepared.

Both β-nitrostyrene 7 and β-methyl-β-nitrostyrene 8 give strong molecular ions at m/e 149 (76.2%) and m/e 163 (41.2%), respectively. The subsequent loss of a hydrogen atom from the



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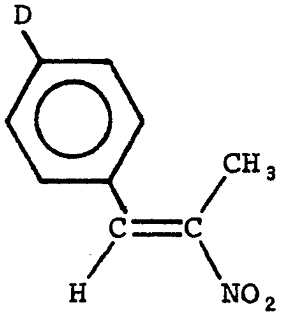

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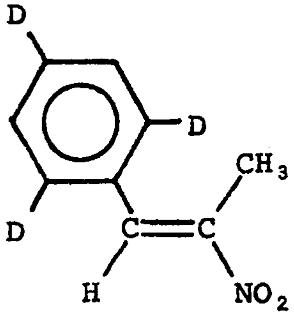
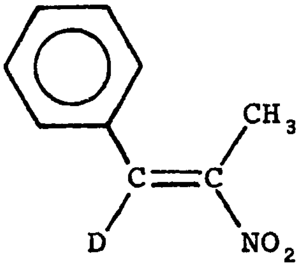


11



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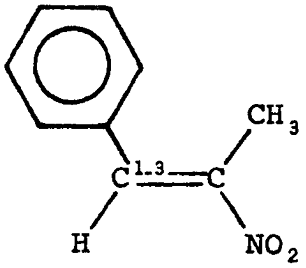


13

molecular ion to generate low intensity ions at m/e 148 (2.55%) and m/e 162 (1.75%) is of some interest, since compound 11 loses both hydrogen and deuterium from the molecular ion (Figure 3). After correcting for carbon-13 and 3.6% D_2 in 11, the calculated losses of hydrogen and deuterium at 70 eV are 32.0% and 68.0% respectively. These percentages demand randomization of hydrogen and deuterium in the phenyl ring prior to expulsion of hydrogen or deuterium as depicted in Scheme 27. On the basis of complete randomization and no deuterium isotope effect, the predicted losses would be 40% hydrogen and 60% deuterium. The differences between the calculated and observed values could be due to incomplete randomization, or errors inherent in the small numbers involved in the calculation.

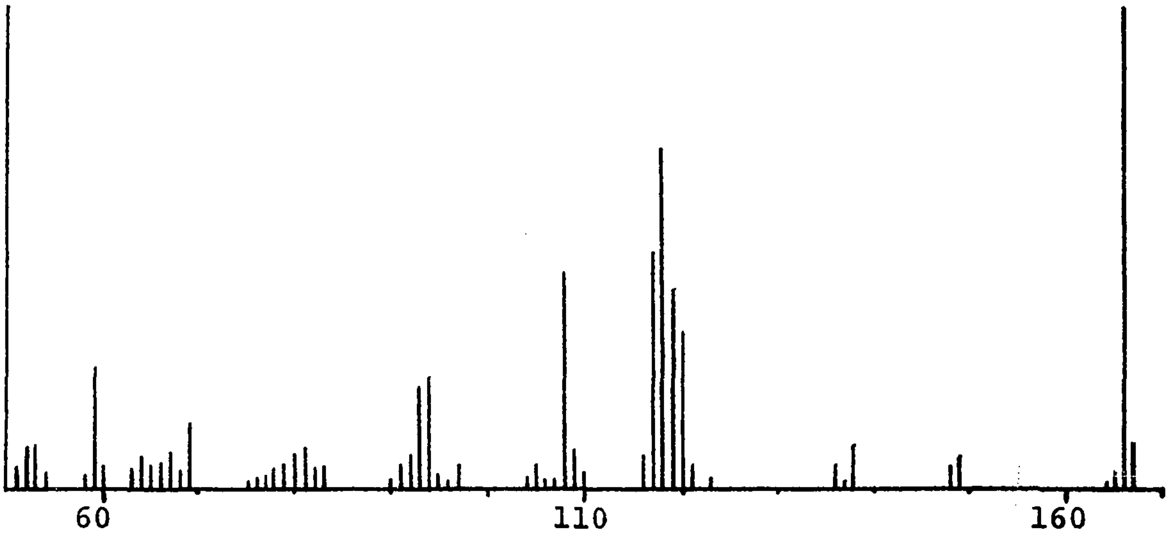


Figure 3. Mass spectrum β-methyl-β-nitrostyrene D_3 11

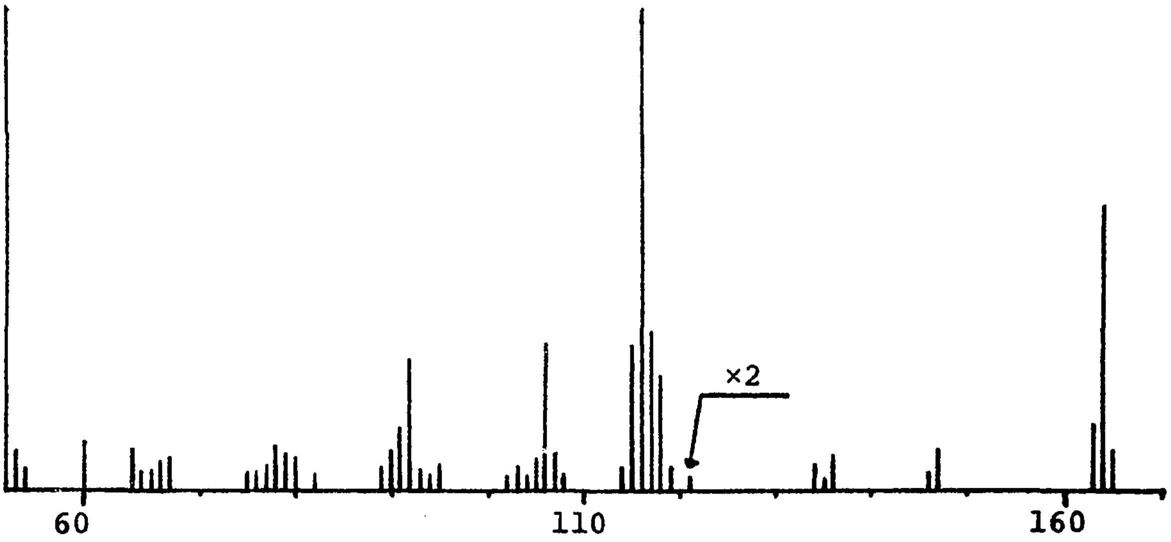
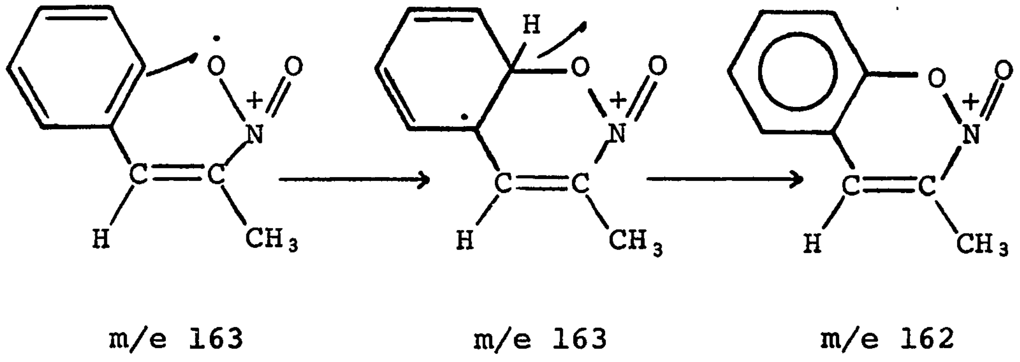


Figure 4. Mass spectrum β-methyl-β-nitrostyrene o-D_1 9



Scheme 27

The loss of both hydrogen and deuterium from the molecular ion of 10 is additional evidence for the randomization mechanism. The absence of an $M^{+\cdot}-2$ ion in the mass spectrum of 12 is again consistent with the proposed mechanism. The intensity of the $M^{+\cdot}-H$ ion is so low at reduced electron energies that it is not feasible to check the extent of hydrogen scrambling under these conditions. The loss of hydrogen from the molecular ion of 7, probably, occurs by a similar mechanism.

The loss of oxygen from the molecular ion does not occur for β-nitrostyrene 7 or β-methyl-β-nitrostyrene 8, but the metastable loss of a hydroxyl radical from the molecular ion is important. Deuterium labeling results (Table 2) indicate that the loss of a hydroxyl radical involves both the phenyl

Table 2. Deuterium labeling results for β-methyl-β-nitrostyrene <u>8</u>

Compound	%D	Observed OD	Observed OH	Predicted OD	Predicted OH
11	96.4% D_3	47.6%	52.4%	60.0%	40.0%
9	84.6% D_1	24.5%	75.5%	20.0%	80.0%
9	84.6% D_1	24.5%	75.5%	13.1%[a]	86.9%
10	93.2% D_1	0.0%	100.0%	20.0%	80.0%
10	93.2% D_1	0.0%	100.0%	13.1%[a]	86.9%
12	98.8% D_1	0.0%	100.0%	0.0%	100.0%

[a] Percentages predicted on the basis of an isotope effect needed to give the observed loss of OH and OD in <u>11</u> for a random process.

ring and the β-methyl group. The calculated losses of OH and OD from <u>11</u> are 52.4% and 47.6% respectively. If loss of a hydroxyl radical involved abstraction of a hydrogen or deuterium atom from the phenyl ring after complete randomization of aromatic deuterium and hydrogen, the predicted loss of OH and OD in the absence of an isotope effect would be 40% and 60%, respectively. The abstraction of a hydrogen atom would have to be favored 1.65 times over deuterium abstraction to obtain the observed values for loss of OH and OD. Although an isotope effect of this magnitude is not unreasonable (43), data from the other labeled compounds (Table 2) excludes a mechanism

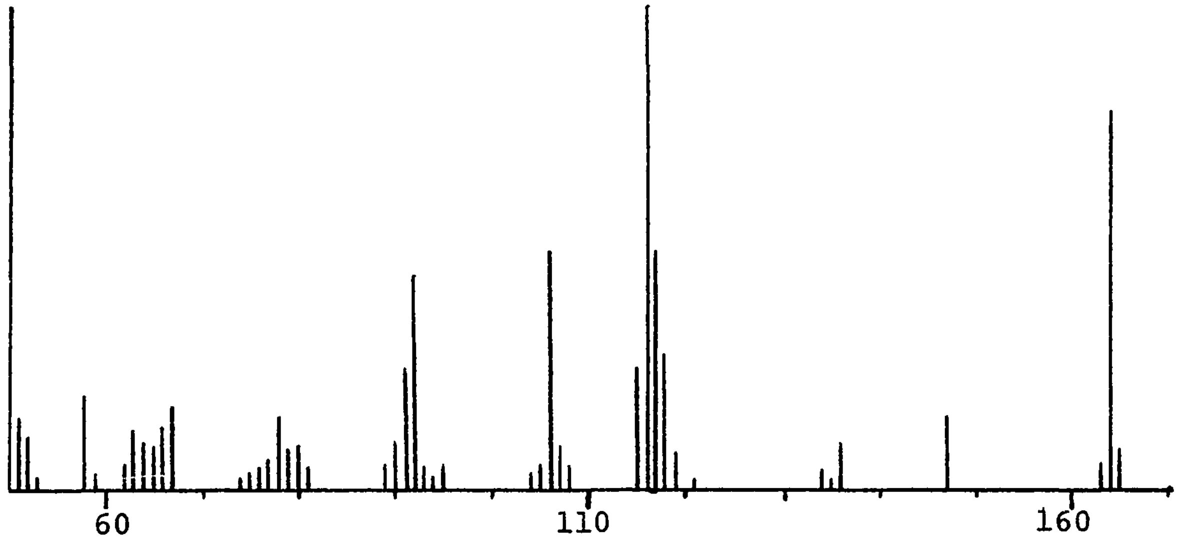


Figure 5. Mass spectrum β-methyl-β-nitrostyrene p-D_1 10

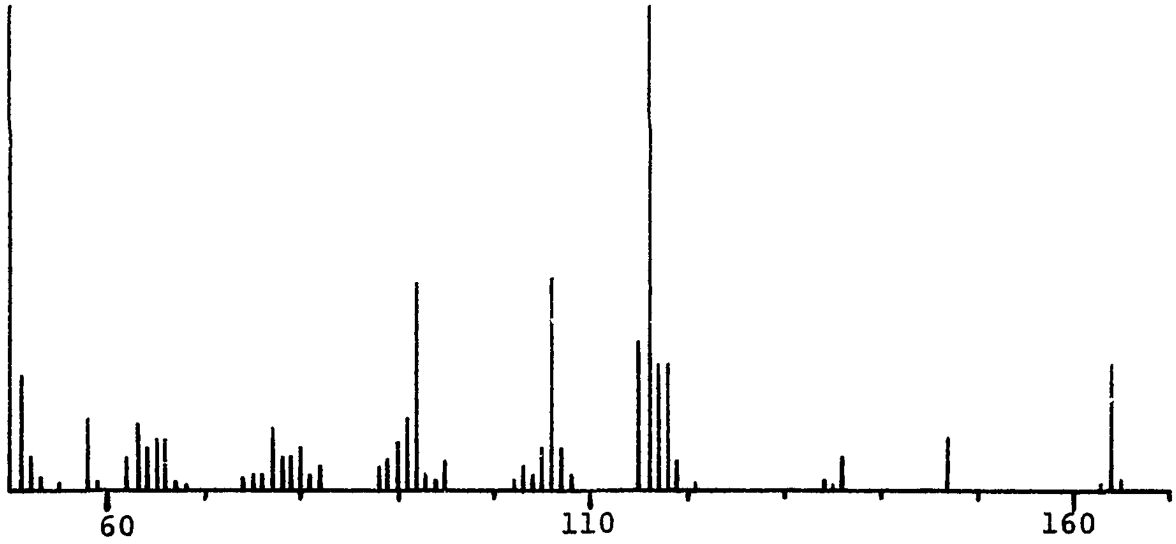
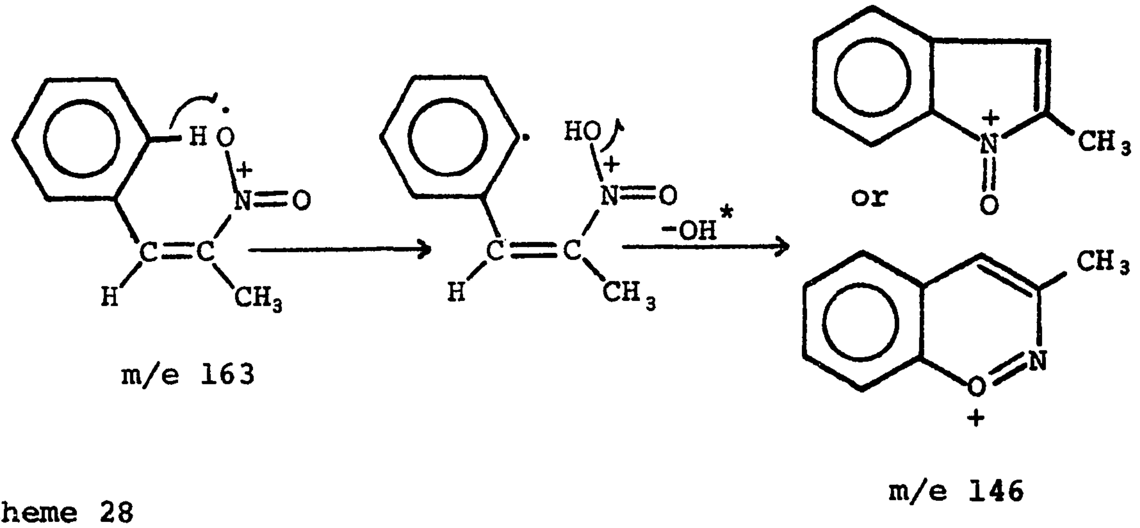


Figure 6. Mass spectrum β-methyl-β-nitrostyrene α-D_1 12

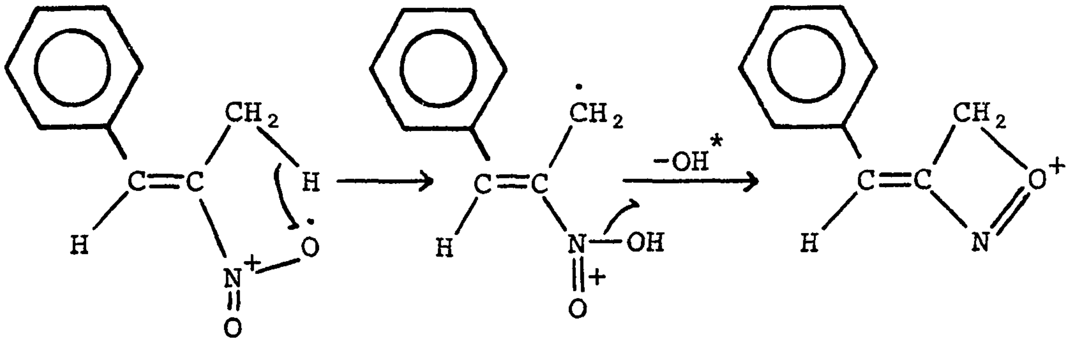
involving randomization.

For example, the calculated losses of OH and OD in compound 9 with a single deuterium in the ortho position are 75.5% and 24.5% each. On the basis of a randomization model with no deuterium isotope effect the predicted losses would be 80% OH and 20% OD. Assuming an isotope effect of the magnitude necessary to give the results observed for 11, the predicted losses would be 86.9% OH and 13.1% OD. Clearly the observed results do not match either possibility. Instead the observed 24.5% loss of OD is almost one-half of the 47.6% observed in 11 suggesting that the loss of OD is a specific process with little or no isotope effect. Confirmation of this idea comes from the mass spectrum of 10 which exhibits no loss of OD. Therefore, approximately fifty percent of the observed loss of a hydroxyl radical involves the specific abstraction of an ortho hydrogen by the nitro group with subsequent loss of a hydroxyl radical as depicted in Scheme 28.



Scheme 28

The other fifty percent loss of a hydroxyl radical must involve hydrogen abstraction from either the meta position of the phenyl ring or from the β-methyl group, since 12 exhibits only loss of OH from the molecular ion. The abstraction of a hydrogen atom from the methyl group as depicted in Scheme 29 is more reasonable on steric grounds. Furthermore, in the mass spectrum (Figure 8) of 2-nitroindene 15, where the nitro group cannot interact with the phenyl ring, the loss of a hydroxyl radical still takes place. The observed percentages for loss of OH and OD in 11 change very little at low electron energies suggesting that both processes leading to loss of a hydroxyl radical are of comparable activiation energy in the absence of a significant isotope effect. For example, at 16 eV they are 55.2% OH loss and 44.8% OD loss. At 12 to 14 eV the fragmentation no longer occurs. The loss of a hydroxyl radical from the



m/e 163

m/e 146

Scheme 29

molecular ion of β-nitrostyrene 7 must involve abstraction of a hydrogen atom from the phenyl ring only in the absence of a β-methyl group.

The loss of a hydroxyl radical involving the specific abstraction of an *ortho* hydrogen atom from the phenyl ring is of considerable interest. The structure of β-nitrostyrene 7 (44) and β-methyl-β-nitrostyrene 8 (45) is such that the phenyl ring and nitro group are *trans* to one another so rotation about the double bond must occur prior to hydrogen abstraction from the phenyl ring. Double bond isomerization has been observed for other mass spectral reactions (46). The absence of a significant isotope effect in the abstraction of a hydrogen atom from the phenyl ring is in sharp contrast to the relatively large isotope effect found by Meyerson, Puskas, and Fields (22) for abstraction of a hydrogen atom from the methyl group in *o*-nitrotoluene. This perhaps implies that the rate controlling step in the fragmentation process involves rotation of the phenyl group about the double bond. This barrier to rotation is generally about 40 to 45 kcal/mole for solution reactions and somewhat lower for conjugated systems (47).

The absence of randomization in the abstraction reaction indicates that ionization or better charge localization is probably occurring on the nitro group as opposed to the phenyl ring. Charge localization on the phenyl ring would be expected to cause randomization in view of other published work (48).

The abstraction reaction, itself, is indicative of unpaired electron character on the nitro group. Indeed, the loss of a hydrogen atom from the molecular ion, and other fragmentations, to be discussed, are best explained in terms of charge localization on the nitro group.

The ion at m/e 135 in the mass spectrum (Figure 2) of β-methyl-β-nitrostyrene <u>8</u> corresponds to the loss of carbon monoxide from the molecular ion. A metastable at m/e 111.8 confirms the formation of this ion in one step from the molecular ion. Consistent with this are the shifts of m/e 135 to m/e 138 in the mass spectrum of <u>11</u> (Figure 3), and the shift of m/e 135 to m/e 136 in the mass spectra of <u>9</u>, <u>10</u>, and <u>12</u> (Figure 4-6). The mass spectrum (Figure 7) of the α-carbon-thirteen labeled β-methyl-β-nitrostyrene <u>13</u> demonstrates that the α-carbon atom is not the source of carbon for loss of carbon monoxide, since ions appear at m/e 135 and m/e 136 in the correct ratio for carbon-thirteen retention. In the absence of further labeling work, it is concluded that loss of carbon monoxide involves the <u>ortho</u> carbon atoms of the phenyl ring as presented in Scheme 30 in analogy to the observed losses of carbon monoxide from <u>o</u>-nitrobiphenyl (22) and α-nitronapthalenes (5, 14, 21, 25). The fact that 2-nitroindene <u>15</u>, where the phenyl and nitro groups cannot interact, does not lose carbon monoxide supports this conclusion. The loss of a second molecule of carbon monoxide to generate the ion at m/e 107 is

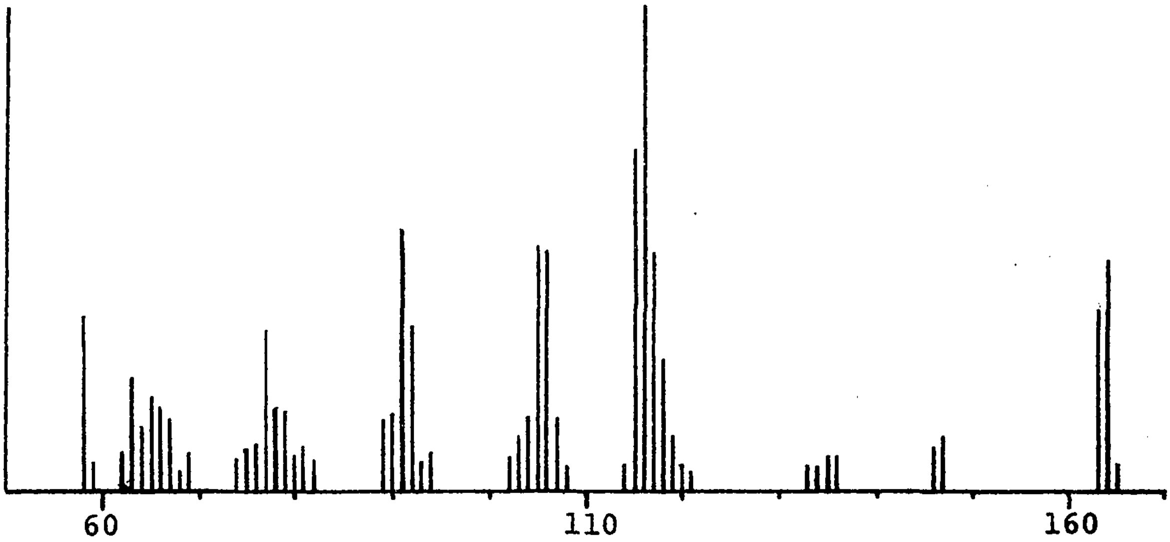


Figure 7. Mass spectrum β-methyl-β-nitrostyrene α-C^{13} 13

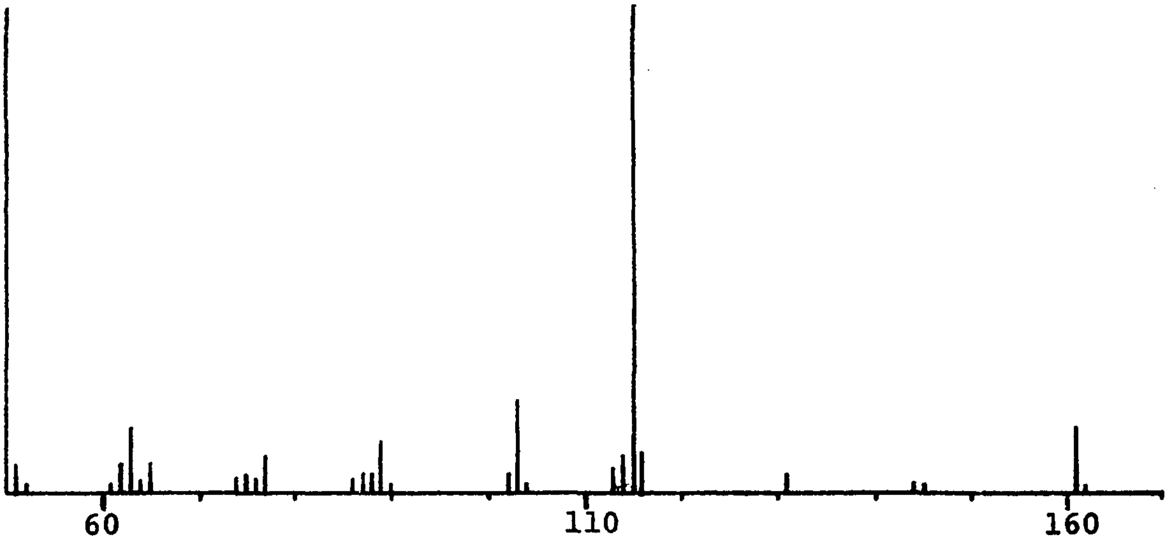
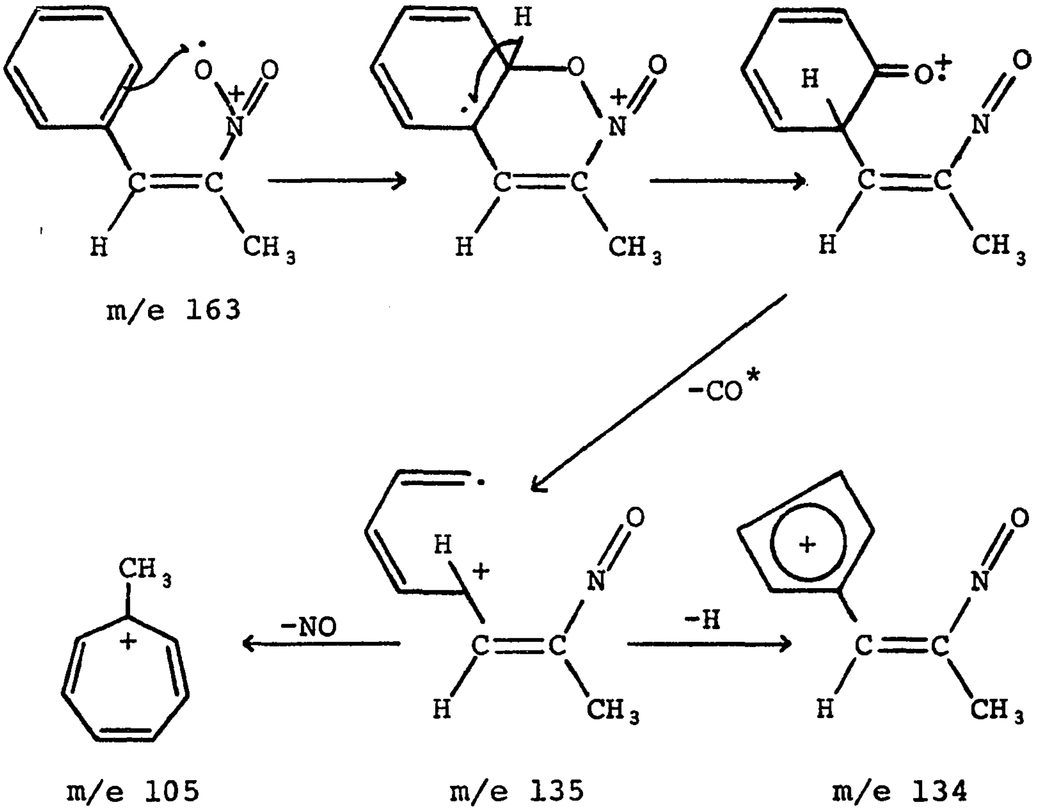


Figure 8. Mass spectrum 2-nitroindene 15

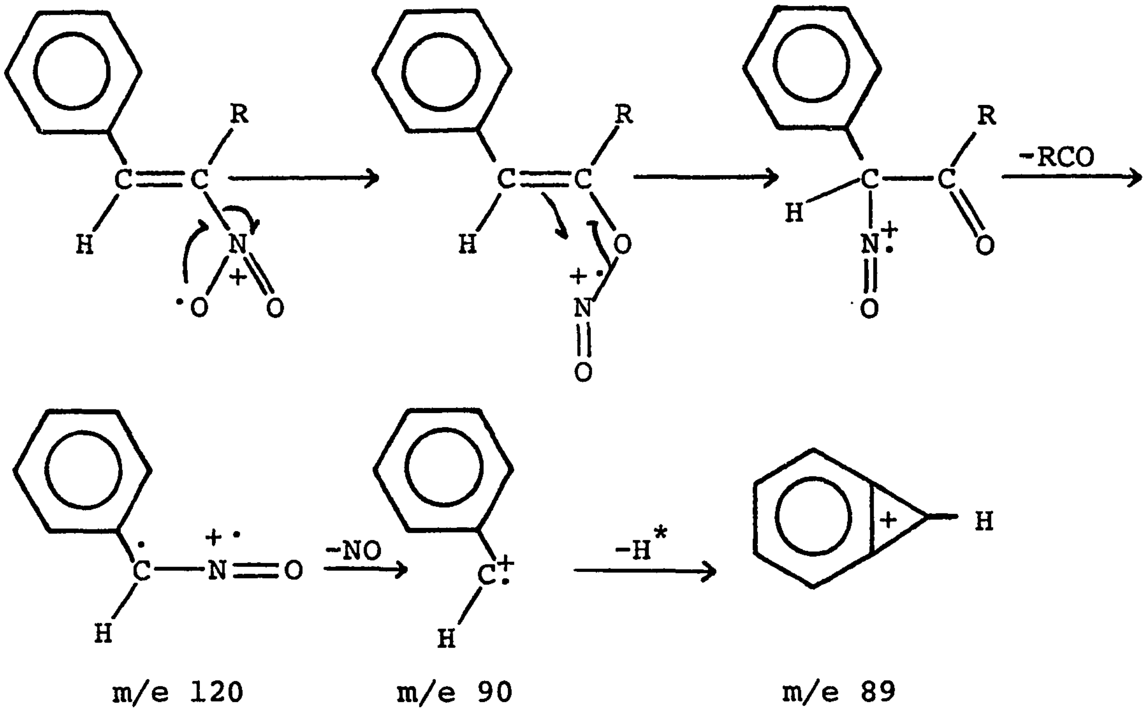


Scheme 30

in agreement with labeling studies, and is reminiscent of the mass spectral fragmentations of α-nitronapthalenes (5, 14, 21, 25).

The subsequent loss of a hydrogen atom from m/e 135 (Scheme 30) apparently gives rise to the low intensity ion at m/e 134 (2.63%), since at low electron energies the m/e 134 ion decreases in intensity relative to m/e 135. Furthermore, this reaction sequence is confirmed for other nitrostyrenes by the presence of a metastable. In the mass spectrum of 11 (Figure 3) this ion appears at m/e 137 and m/e 136 indicating loss of CHO and CDO. The subsequent loss of hydrogen and deuterium implies prior randomization of hydrogen and deuterium, or an indiscriminate loss of hydrogen and deuterium from various sites in the m/e 138 ion. Unfortunately, interference from the $M^{\overset{+}{\cdot}}$-30 ion and incomplete labeling prevent ascertaining the truth of this statement from calculations involving the labeled compounds. However, labeling results are accurate enough to demonstrate that loss of CDO is greater than CHO as would be expected on the basis of randomization in the original phenyl ring. Furthermore, the mass spectrum of 12 is indicative of no DCO loss, again suggesting that the phenyl ring is the source of hydrogen in this fragmentation.

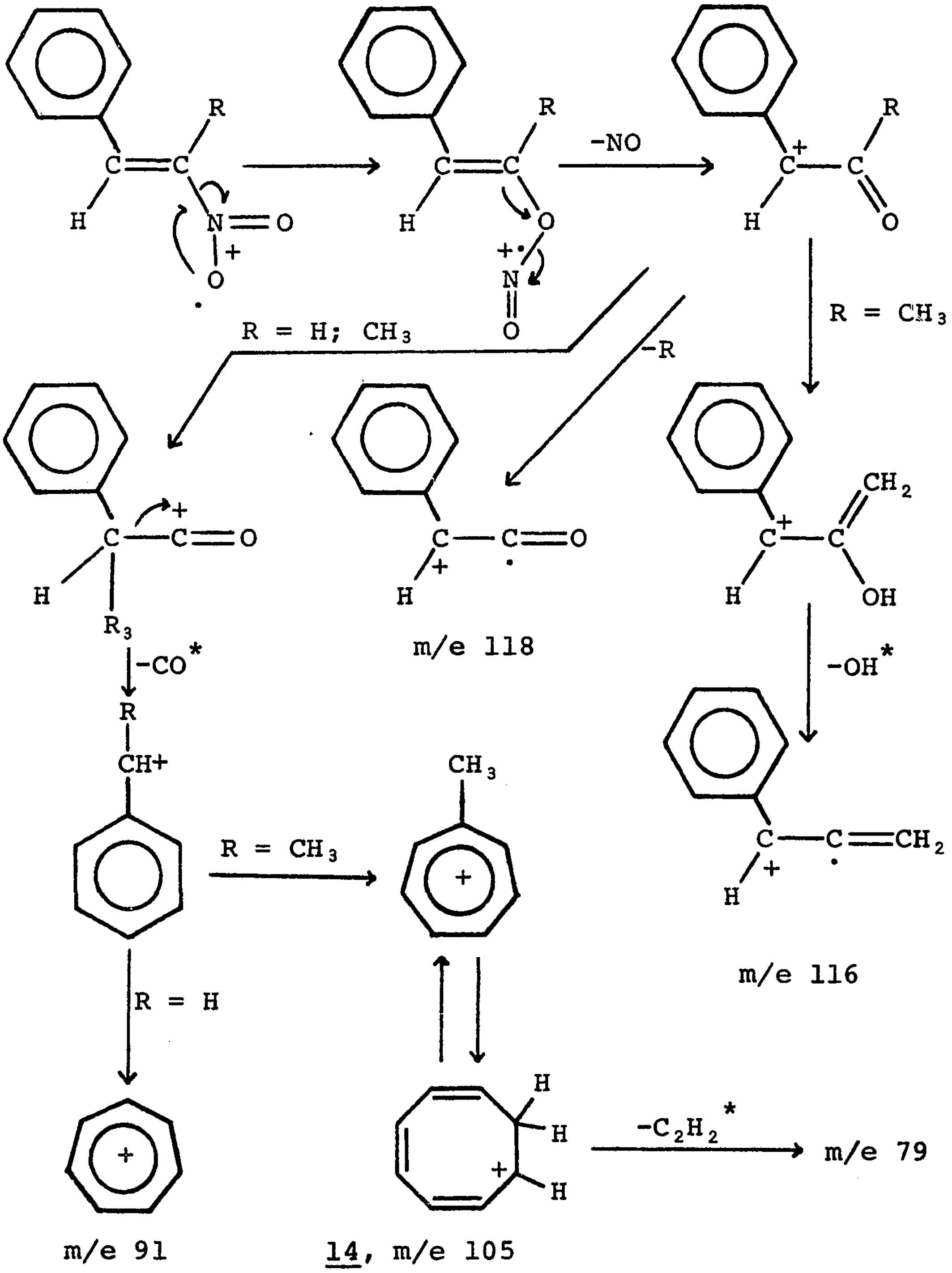
The loss of carbon monoxide from the molecular ion of β-nitrostyrene 7 probably occurs in a manner similar to that depicted for 8 in Scheme 30. The loss of CHO in the mass spectrum of 7 must, also, occur in part from the subsequent loss of a hydrogen atom as described for 8. Nevertheless, the greater intensity of this ion relative to the loss of carbon monoxide indicates the possibility of an additional pathway for the formation of this ion. The observance of a low intensity ion at m/e 120 (2.0%) corresponding to the loss of CH_3CO from the molecular ion of 8, implicates the β-carbon and hydrogen in the loss of CHO. The loss of CH_3CO from the molecular ion of 8 is confirmed by the shift of m/e 120 to m/e 121 in the mass spectra of 9, 10, and 12, and the shift to m/e 123 in the mass spectrum of 11. Although the m/e 120 ion could correspond to stepwise losses of CO and CH_3, metastable evidence from other spectra suggests that CH_3CO is lost as one unit. The observed losses of CH_3CO and CHO must then involve a nitro-nitrite rearrangement with migration of NO as depicted in Scheme 31. The further loss of NO from the m/e 120 ion could account for the hydrocarbon ions observed at m/e 90 and m/e 89 in both spectra.



Scheme 31

Both β-nitrostyrene 7 and β-methyl-β-nitrostyrene 8 undergo a nitro-nitrite rearrangement reaction as evidenced by the loss of thirty mass units from the molecular ion to give ions at m/e 119 and m/e 133 respectively. The nitro-nitrite rearrangement is analogous to that observed for nitroaromatics (5, 13), but is not too surprising since the carbon atoms involved in the rearrangement are both sp^2 hybrids. It is interesting to note, however, that the mass spectral rearrangement has a photochemical analogy in the rearrangement of β-methyl-β-nitrostyrene to 1-phenyl-1-oximinopropane-2-one (49, 50) via a nitro-nitrite rearrangement.

The three major decomposition pathways available to the $M^{+\cdot}$-NO ion are illustrated in Scheme 32. In analogy to the behavior of nitroaromatics (5, 13) metastable expulsion of carbon monoxide following R group migration occurs as indicated in Scheme 32 to give a hydrocarbon ion at m/e 105. The possibility also exists that the m/e 105 ion is formed in part by the sequence $M^{+\cdot}$-CO-NO as illustrated in Scheme 30. Consistent with the hydrocarbon nature of m/e 105 is the shift of this ion to m/e 106 in the mass spectra of 9, 10, and 12, as well as the shift to m/e 108 in the mass spectrum of 11. Recently (9) the eight membered ring structure 14 has been proposed for the m/e 105 ion on the basis of statistical randomization of hydrogen and deuterium prior to the subsequent loss of acetylene. The possibility of an interconversion between 14 and the


R
N
O
+
H
-NO
R = H; CH₃
-R
R = CH₃
R₃
-CO*
CH+
CH₂
OH
-OH*
m/e 118
m/e 116
R = CH₃
R = H
CH₃
-C₂H₂*
m/e 79
m/e 91
14, m/e 105

Scheme 32

methyltropylium ion was also postulated. In our case interference from other ions prevented any attempt at identifying the structure of the m/e 105 ion from labeling results. At electron energies low enough to remove interfering ions, this fragmentation pathway terminates. A similar fragmentation for β-nitrostyrene 7 leads to the m/e 91 ion in Scheme 32.

Another unique decomposition mode of the $M^{+\cdot}$-NO ion is the subsequent loss of that group attached to the β-carbon atom to form a ketene ion as shown in Scheme 32. Compatible with this assignment is the shift of m/e 118 in the mass spectrum of 8 to m/e 119 for 9, 10, 12, and to m/e 121 for 11. A metastable in the mass spectrum of 7 for m/e 119 $\longrightarrow$ m/e 118 supports the proposed mechanism. The observance of a weak metastable at m/e 84.0 for the formation of the m/e 118 ion in one step from the molecular ion of β-methyl-β-nitrostyrene 8 is probably due to the very rapid loss of CH_3 after initial loss of NO. Metastables are generally indicative of a one step fragmentation, but if consecutive reactions are rapid enough, they can give rise to a metastable (51).

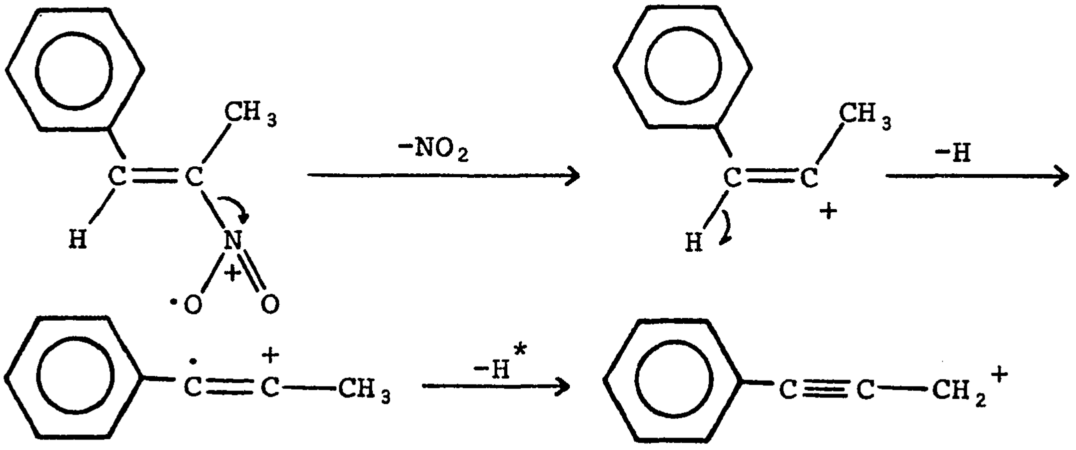
A final fragmentation route of the m/e 133 ion is the loss of a hydroxyl radical to give an ion at m/e 116 with a metastable at m/e 101.2. Metastable shifts in the mass spectra of labeled compounds 9 - 12 suggest the β-methyl group as the source of hydrogen in this fragmentation. A mechanism involving enolization as depicted in Scheme 32 is consistent with the absence of a similar fragmentation for β-nitrostyrene 7.

Moderately intense ions in the mass spectra of β-nitrostyrene 7 and β-methyl-β-nitrostyrene 8 are generated by simple cleavage of the nitro group. The subsequent loss of one and two hydrogen atoms is a favorable fragmentation, and in fact, the loss of H_2NO_2 gives rise to the base peak in the mass spectrum of 8 (Figure 2). The sequential nature of the hydrogen loss is vividly demonstrated in the low electron energy mass spectrum of 8 where the m/e 117 peak grows rapidly at the expense of the m/e 116 and m/e 115 ions. The successive loss of these two hydrogen atoms is a complex process. By assuming (one) that the m/e 146 ion does not decompose by loss of NO, and (two) that the direct loss of HNO_2 by hydrogen abstraction does not occur, two different fragmentation processes leading to the m/e 116 and m/e 115 ions can be delineated.

How valid are these two assumptions? The first assumption is probably true since fragmentation of an even electron ion to an odd electron ion is generally an unfavorable process (52). An assessment of the second assumption is somewhat more difficult, but low electron energy spectra suggest that the loss of HNO_2, and H_2NO_2 occur only by sequential loss of hydrogen after loss of NO_2. Furthermore, metastables occur for the sequential loss of hydrogen, but do not occur for the direct loss of HNO_2. Finally, the calculations, themselves, suggest that the direct loss of HNO_2 is unimportant at 70 eV.

The mass spectrum of compound 12 (Figure 6), particularly the low energy spectrum, clearly shows that loss of the nitro group is followed exclusively by loss of the α-hydrogen atom. Furthermore, calculations based on the mass spectra of compounds 8, 11, and 12 indicate that the second hydrogen lost is largely or exclusively from the methyl group. The reaction sequence illustrated in Scheme 33 is compatible with the above findings. It can be calculated using the mass spectra of compounds 8, 11, and 12, that this reaction sequence contributes 62.5% to the m/e 116 ion, and 33% to the intensity of the m/e 115 ion in the mass spectrum of 8 (Figure 2) after correcting for carbon-13.

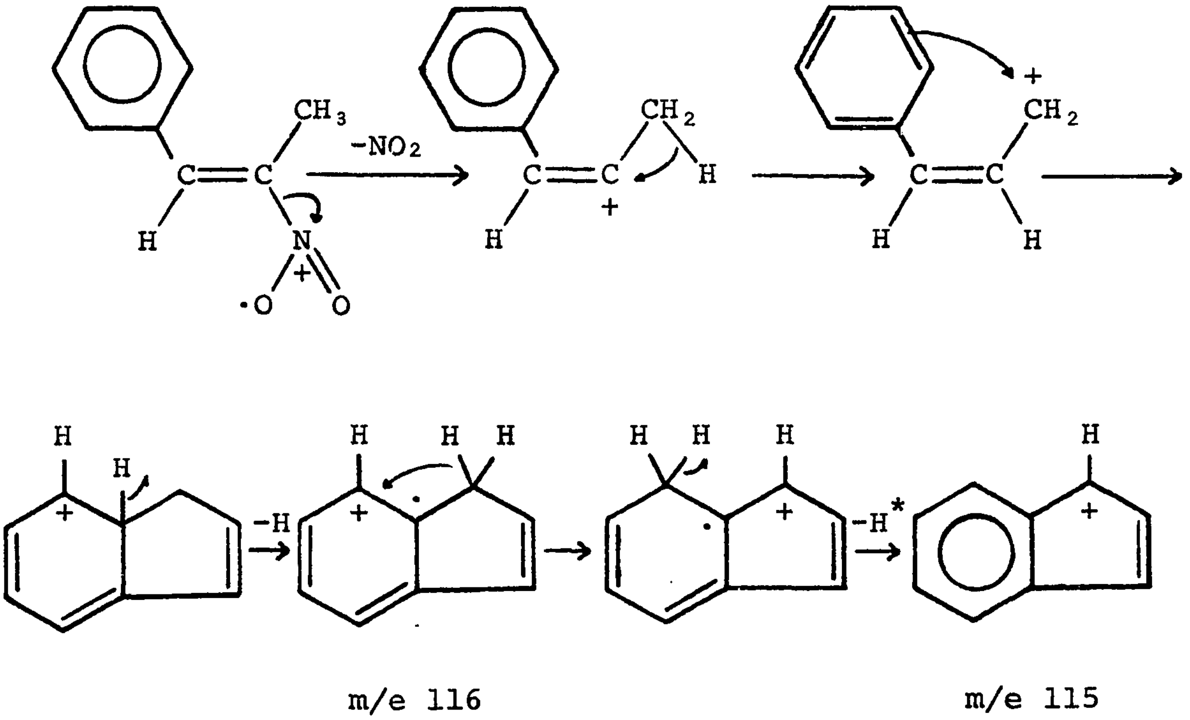
A second sequence of reactions leading to the m/e 116 and m/e 115 ions can be uncovered by subtracting the contribution



m/e 116 m/e 115

Scheme 33

of sequence one (Scheme 33) from the mass spectrum of 11. The actual calculations involve the mass spectra of 8, 11, and 12 (see Appendix A). The second sequence of reactions is of considerable interest, because calculations indicate the initial hydrogen lost in this sequence comes from the phenyl ring with prior randomization of hydrogen and deuterium. The calculated losses of hydrogen and deuterium from 11 are 40.5% and 59.5% respectively, while the predicted values on the basis of randomization are 40% loss of hydrogen, and 60% loss of deuterium. The excellent agreement between the calculated and observed values leaves little doubt that randomization does occur, and that the assumptions involved in the calculation are valid. The loss of the second hydrogen atom is an unusual process, too, and could occur from either m/e 119 or m/e 118 by loss of hydrogen or deuterium in the mass spectrum of 11. Further loss of hydrogen or deuterium from m/e 119 would generate ions at m/e 118 and m/e 117 respectively, while loss of hydrogen or deuterium from m/e 118 would generate ions at m/e 117 and m/e 116 respectively. Assuming the subsequent decompositions to equal 100%, the following percentages were calculated for the intensities of the m/e 116, m/e 117, and m/e 118 ions: m/e 116 (8.5%), m/e 117 (63%), and m/e 118 (28.5%). The observed percentages strongly suggest that the loss of a second hydrogen atom involves randomization of all the remaining hydrogen and deuterium atoms in the m/e 119 and m/e 118 ions. For complete randomization the predicted intensities of the ions would be m/e 116 (15%), m/e 117 (60%), and m/e 118 (25%). The slight discrepancies between the calculated and predicted values imply incomplete randomization, or a slight error in the calculation. The reaction sequence shown in Scheme 34 is consistent with the above observations. This sequence of reactions contributes 37.5% to the intensity of m/e 116 and 67% to the intensity of m/e 115 in the mass spectrum of 8 after correcting for carbon-13. Although the above arguments fit the data and the calculations are internally consistent, it should be understood that many assumptions are involved in the calculations, and the results may be fortuitous.

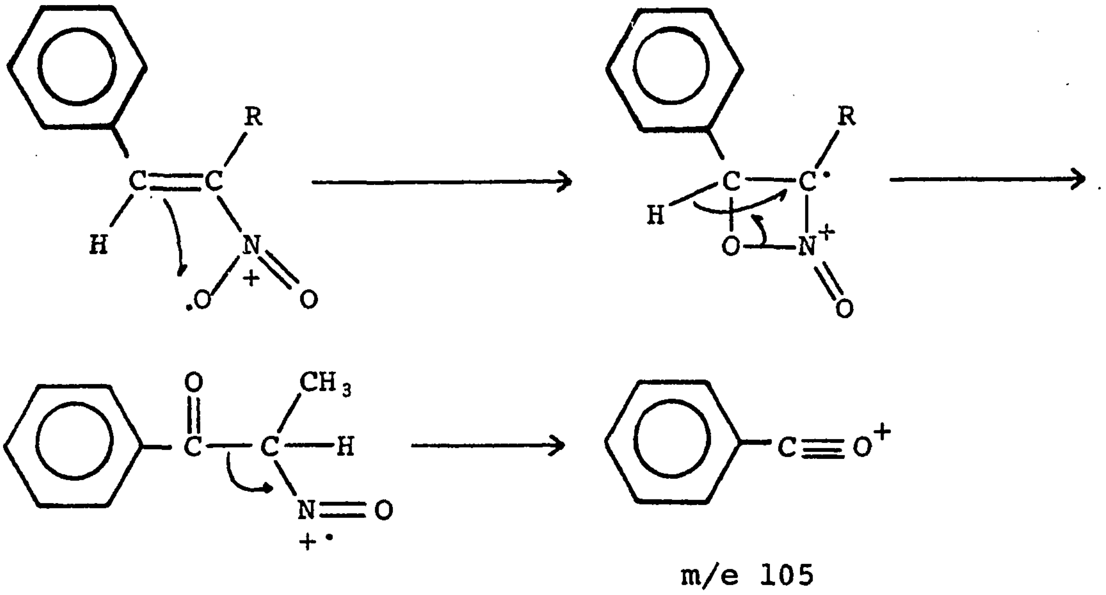


Scheme 34

The mass spectrum of β-nitrostyrene 7 is somewhat different in regard to the loss of NO_2 and subsequent hydrogen atoms, since ions of an indenyl structure are not possible. The main route to the m/e 102 ion probably involves loss of the nitro group and the α-hydrogen atom. The subsequent loss of a hydrogen atom is confirmed by the presence of a metastable for m/e 103 going to m/e 102. In addition, metastable evidence indicates that the direct loss of HNO_2 occurs. The absence of such a direct loss in the mass spectrum of β-methyl-β-nitrostyrene 8 points out the importance of the β-methyl group, and the driving force for formation of the very stable indenyl cation. The ion at m/e 101 is probably formed by the subsequent loss of a hydrogen atom from m/e 102.

Although the m/e 105 ion discussed previously in regard to the mass spectrum of β-methyl-β-nitrostyrene 8 is primarily hydrocarbon in nature, labeled compound 12 indicates that 15% of this ion must have a different structure, because the m/e 105 ion does not shift totally to m/e 106. The metastable loss of twenty-eight mass units, carbon monoxide, from this ion leads to the conclusion that it has the benzoyl cation structure, and is formed as shown in Scheme 35. The identity of this ion is confirmed by its presence in the mass spectrum of β-nitrostyrene 7 (Figure 1).

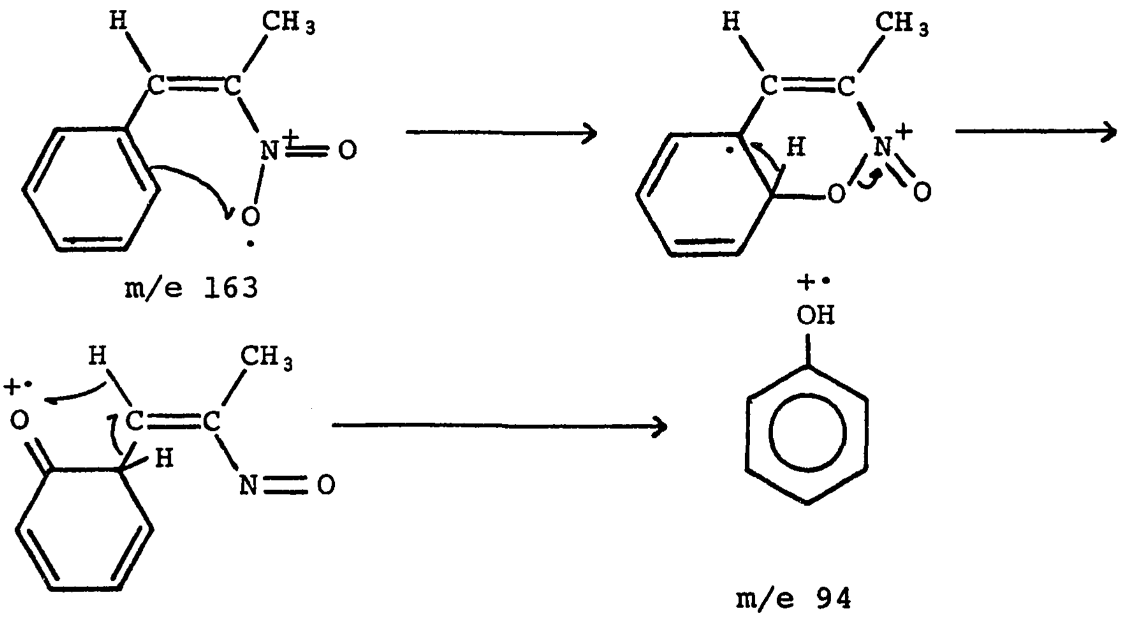
The structure and mode of formation of one more intriguing ion remains to be clarified. The mass spectra of β-nitrostyrene



Scheme 35

$\underline{7}$ and β-methyl-β-nitrostyrene $\underline{8}$ exhibit an ion of low intensity at m/e 94. This ion shifts cleanly to m/e 95 in the mass spectra of $\underline{9}$, $\underline{10}$, or $\underline{12}$, and shifts cleanly to m/e 97 in the mass spectrum of $\underline{11}$. These ion shifts, particularly in the spectrum of $\underline{12}$, suggest that the ion at m/e 94 has a phenolic structure as depicted in Scheme 36.

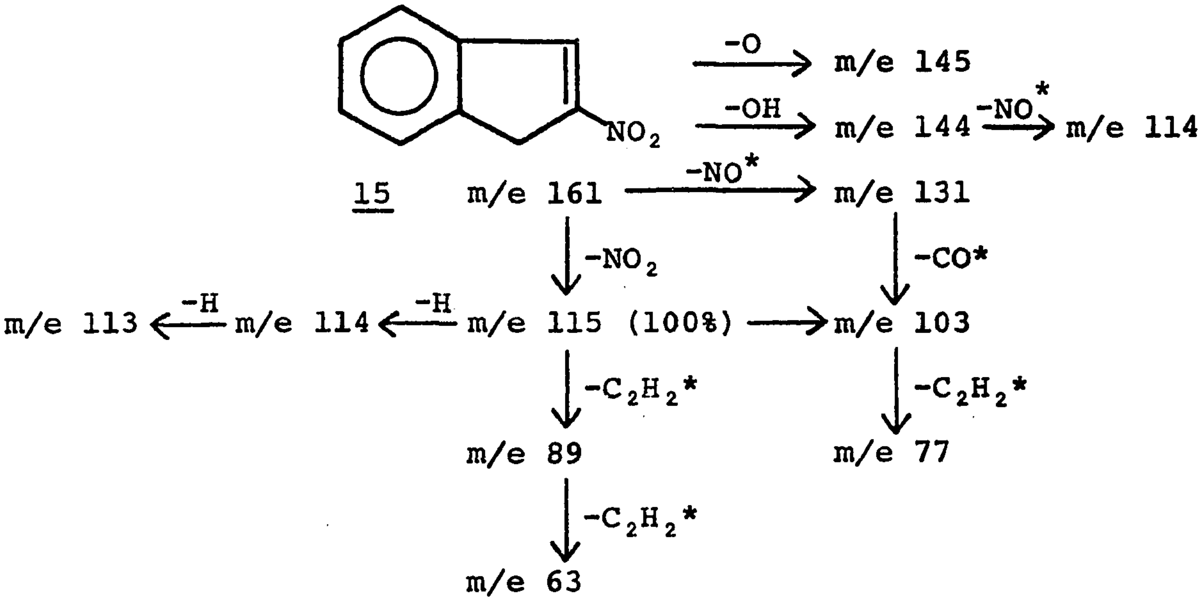
In the above study on the mass spectra of β-nitrostyrene $\underline{7}$ and β-methyl-β-nitrostyrene $\underline{8}$, it was pointed out that many of the fragmentations involved randomization of hydrogen. The subject of hydrogen scrambling has recently been reviewed (48), and is currently a topic of considerable interest. Therefore, it is considered worthwhile to discuss the above reactions in



Scheme 36

more detail. The observed hydrogen scrambling in the $M^{+\cdot}$-H and $M^{+\cdot}$-HCO ions (Schemes 27 and 30) probably occurs by a mechanism similar to that proposed by Ronayne, Williams, and Bowie for chalcones (46), since the initial step in each fragmentation pathway is the attack of an oxygen radical on an aromatic ring to generate a new radical site in the phenyl ring. Presumably the presence of a radical site in the phenyl ring causes rapid interchange of hydrogen with the result being randomization prior to expulsion of hydrogen. Similar randomization reactions involving a cation and a cation radical might be envisioned in the formation of the $M^{+\cdot}-HNO_2$ and $M^{+\cdot}-H_2NO_2$ ions in 8. The specificity of the hydroxyl radical loss involving the phenyl ring (Scheme 28) suggests that simple abstraction of a hydrogen atom from a phenyl ring will not cause randomization of hydrogen, but attack on the carbon skeleton of the phenyl ring will. The specific loss of a hydrogen atom from a phenyl ring has been reported previously for other mass spectral reactions of a slightly different nature (48).

The fragmentations modes postulated for β-nitrostyrene 7 and β-methyl-β-nitrostyrene 8 are supported by fragmentation patterns and metastables observed for other nitroolefins in this series. In this regard the mass spectrum of 2-nitroindene 15 (Figure 8) is of some interest. The main features of the mass spectrum are outlined in Scheme 37. The molecular ion at m/e 161 (13.5%) is of moderate intensity. In contrast to 7 and 8, the loss of oxygen from 15 is observed to generate a low intensity ion at m/e 145 (1.2%). As already mentioned the loss of a hydroxyl radical from the molecular ion in the absence of any readily available aromatic hydrogen atoms supports the previously postulated mechanism of hydrogen abstraction from the methyl group with subsequent loss of a hydroxyl radical for 8. The greater difficulty of this fragmentation in a fused ring system is reflected in the low intensity of the m/e 144 ion (1.6%). As indicated previously the absence of



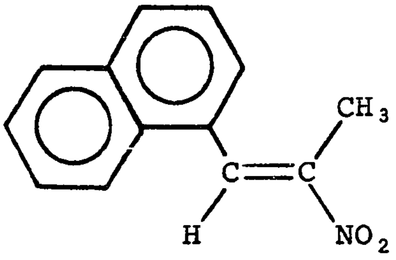
Scheme 37

ions corresponding to loss of CO or CHO from the molecular ion supports the proposed mechanism for formation of these ions in 7 and 8.

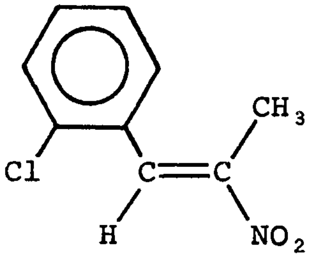
The loss of nitric oxide occurs to give an ion at m/e 131 (3.6%). The m/e 131 ion in analogy to 7 and 8 undergoes the metastable loss of carbon monoxide to give a hydrocarbon ion at m/e 103. A metastable indicates that the subsequent loss of acetylene yields the m/e 77 ion. The base peak in the mass spectrum of 15 corresponds to loss of the nitro group, probably with rearrangement to the indenyl cation. Metastables indicate that the indenyl cation can decompose by two consecutive losses of acetylene to generate ions at m/e 89 and m/e 63.

The mass spectra of 1-(α-naphthyl)-2-nitropropene 16

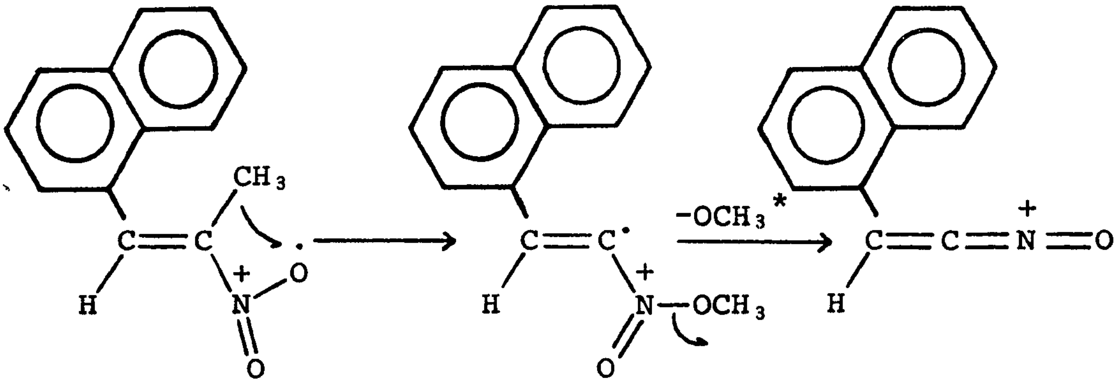
(Figure 9) and o-chloro-β-methyl-β-nitrostyrene 17 (Figure 10) are similar in many respects to those of 7 and 8, although some interesting differences are observed. The loss of a methyl group from the molecular ion of 16 to give an ion at m/e 198 implies possible steric crowding by the naphthalene ring. The observation of a metastable loss of CH_3O from the molecular ion of 16 is additional evidence of steric strain. Apparently the naphthalene ring forces the methyl group close enough to the



16



17



m/e 213

m/e 182

Scheme 38

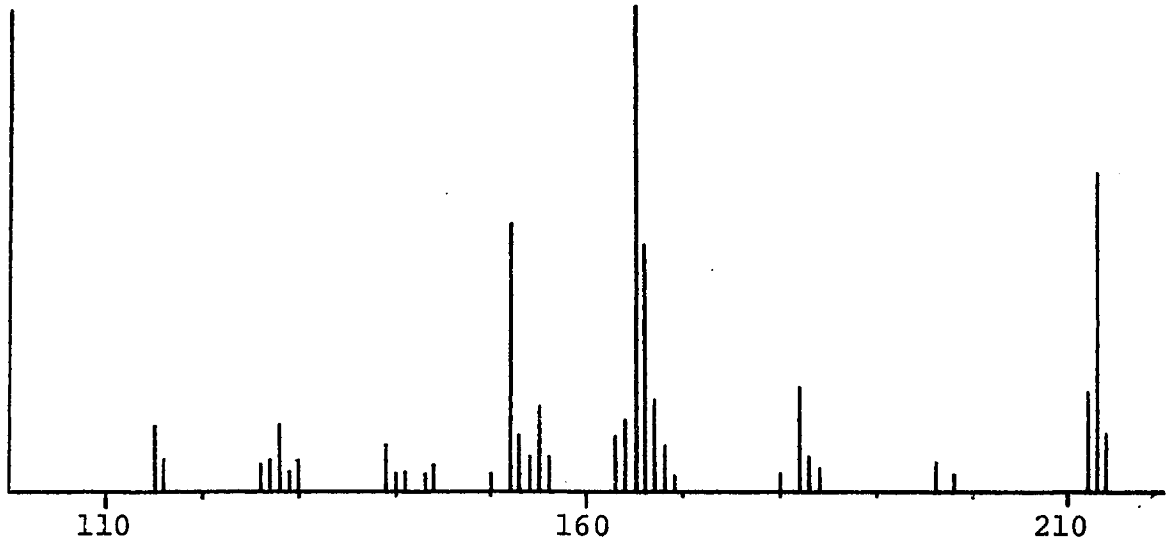


Figure 9. Mass spectrum 1-(α-naphthyl)-2-nitropropene 16

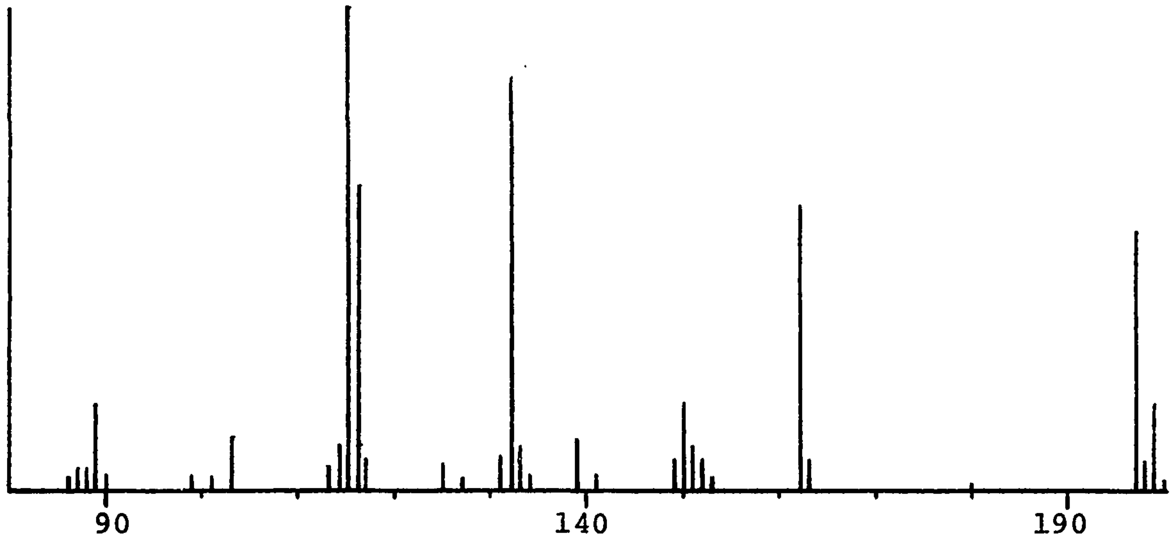
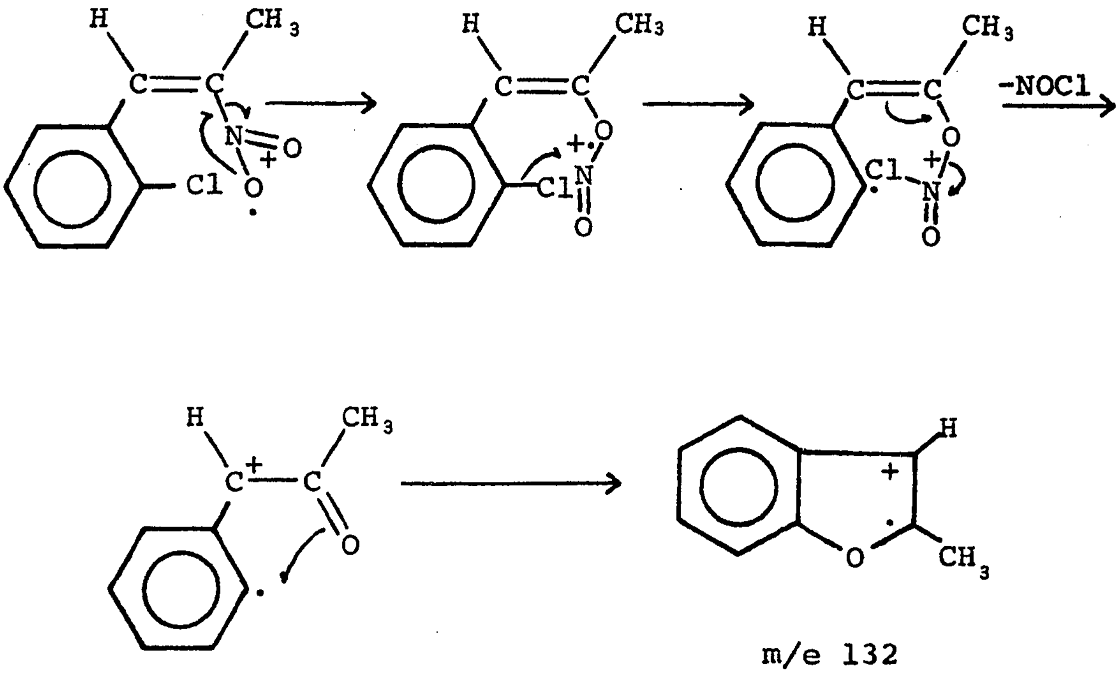


Figure 10. Mass spectrum o-chloro-β-methyl-β-nitrostyrene 17

nitro group for abstraction to occur with the subsequent loss of CH_3O as depicted in Scheme 38. The ion thus formed at m/e 182 fragments by loss of HCN to form an ion at m/e 155 accompanied by a broad metastable centered at m/e 132.1, and probably loses NO as well to form the ion at m/e 152. Other differences in the mass spectrum of 16 compared to 8 are the absence of an ion corresponding to the loss of CH_3CO from the molecular ion, and the preferential loss of CHO over CO from the molecular ion.

The presence in 17 of a chlorine atom in the ortho position also has a decided effect on the mass spectrum. The losses of OH, CO, CHO, and NO from the molecular ion are negligible at 70 eV, but do occur with the exception of $M^{+\cdot}$-CHO at lower electron energies. The base peak in the mass spectrum of 17 corresponds to the indenyl cation at m/e 115. Other important ions are formed at m/e 162 and m/e 132 by the consecutive losses of Cl and NO from the molecular ion. An intense metastable at m/e 88.5 indicates that the direct loss of nitrosyl chloride (NOCl) can also occur from the molecular ion. The reaction sequence shown in Scheme 39 is proposed for the direct loss of NOCl. The driving force for the reaction must be formation of the stable 2-methylbenzofuran ion 18, since NOCl is not a very stable neutral molecule (53). Many of the ions common to 8 are observed after the initial loss of chlorine from 17.



m/e 132

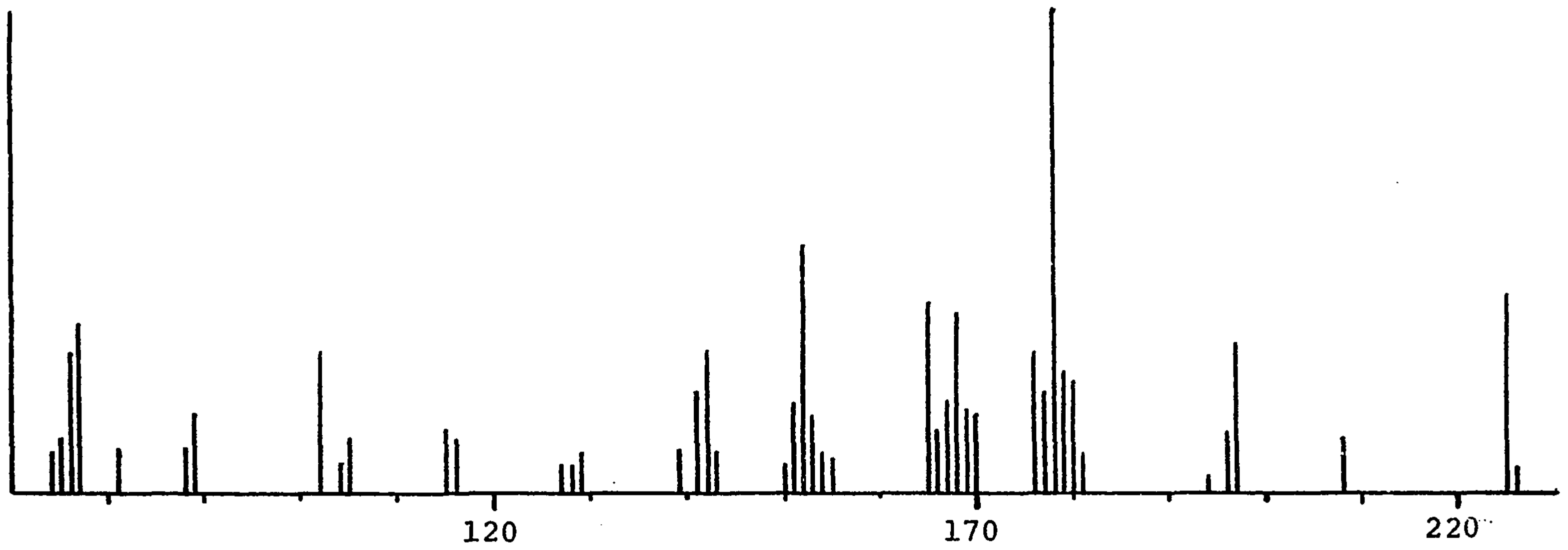
18

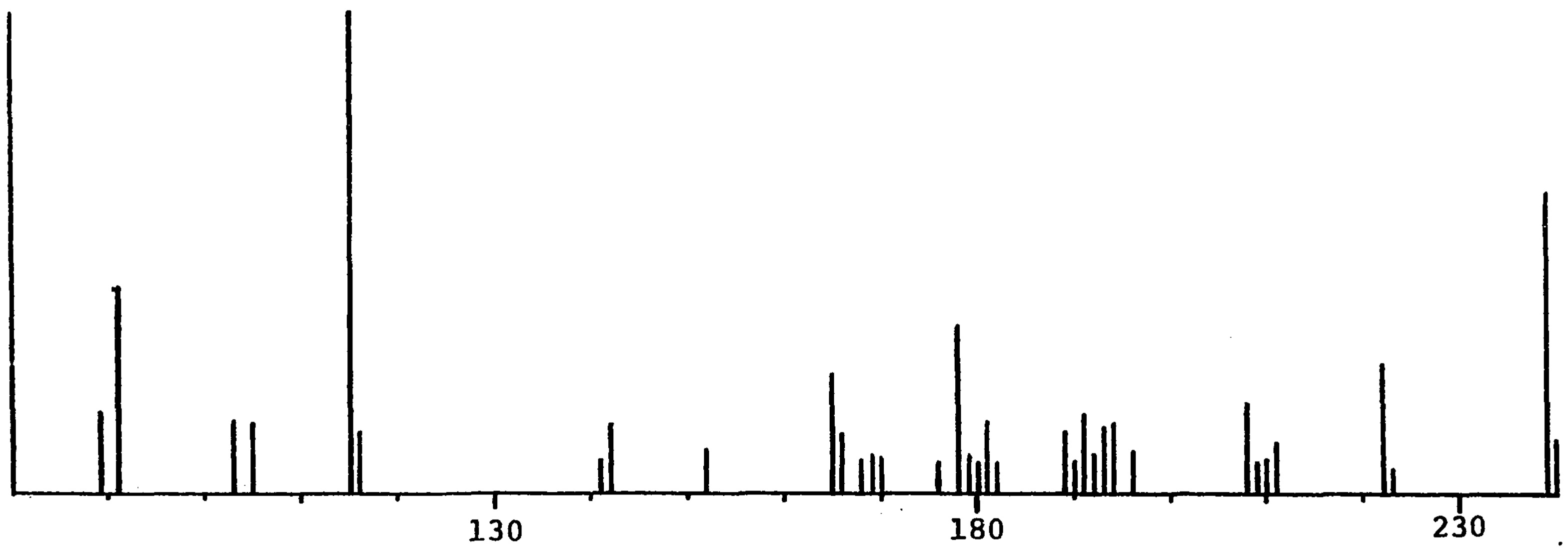
Scheme 39

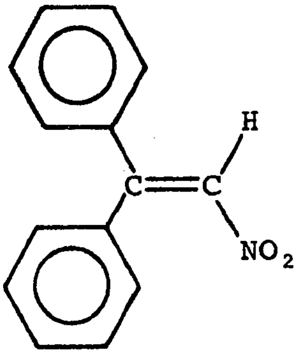
The mass spectra of 1,1-diphenyl-2-nitroethylene 19 (Figure 11) and 1,1-diphenyl-2-nitropropene 20 (Figure 12) were investigated to determine the effect of a second phenyl ring on the α-carbon atom. Their spectra were very similar to those of 7 and 8, respectively, showing very little change due to the additional phenyl ring. However, the occurrence of some new fragmentations, and the existence of an inordinate number of metastables makes a discussion of certain aspects of the mass

Figure 11. Mass spectrum 1,1-diphenyl-2-nitroethylene <u>19</u> (top)

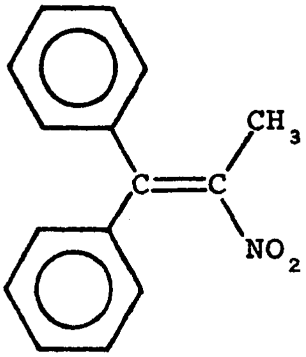
Figure 12. Mass spectrum 1,1-diphenyl-2-nitropropene <u>20</u> (bottom)


120
170
220


130
180
230



19



20

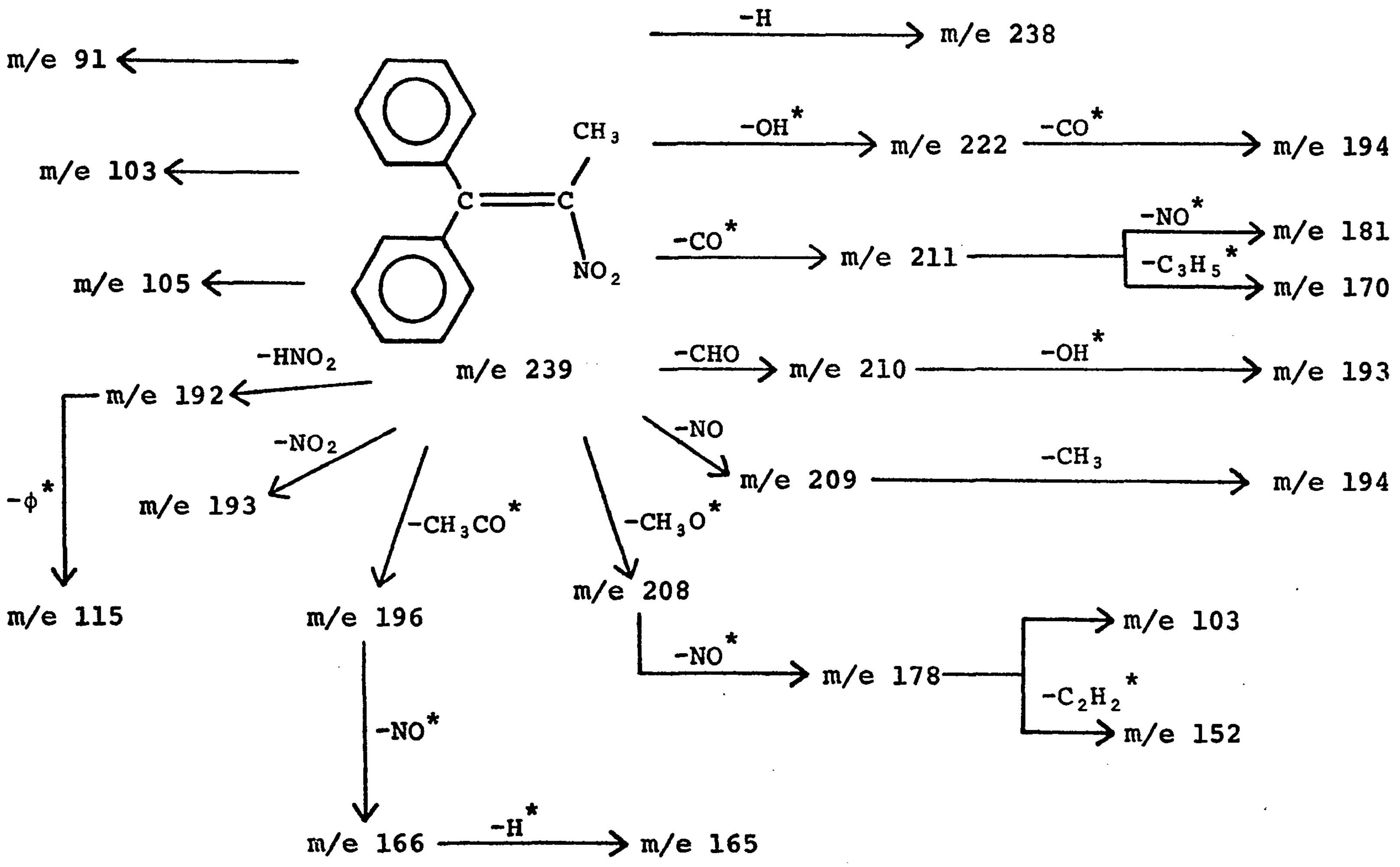
spectra worthwhile.

In the mass spectrum of 19 the usual loss of carbon monoxide from the molecular ion is followed by the interesting metastable loss of a hydroxyl radical to form the ion at m/e 180. A metastable at m/e 195.1 indicates that the loss of CHO from the molecular ion occurs by loss of a hydrogen atom after loss of carbon monoxide as previously postulated for 7 and 8. The direct loss of CHO from the molecular ion postulated for 7 (Scheme 34) also occurs as proven by the subsequent decomposition of the M-CHO ion at m/e 196. The m/e 196 ion fragments by the consecutive losses of NO, and H to generate ions at m/e 166 and m/e 165 as evidenced by metastables. In addition, the m/e 196 ion loses HNO in a metastable process.

At 70 eV 19 does not lose nitric oxide from the molecular ion, but at 30 eV the fragmentation does occur to give an ion at m/e 195, probably indicating a rapid decomposition of this ion at 70 eV. Replacing the α-hydrogen atom with a phenyl ring causes the loss of the nitro group to be followed by loss of a phenyl radical to form the m/e 102 ion. The observed loss of HNO_2 from the molecular ion probably occurs by a hydrogen abstraction mechanism.

The mass spectrum of 20 is especially worthy of attention, since metastables occur in its mass spectrum which support analogous processes for 8 which were proposed on the basis of labeling data. The basic fragmentations of this molecule are sketched in Scheme 40. The previously proposed carbon-oxygen bonded structure shown for the m/e 146 ion in the mass spectrum of 8 (Scheme 28) is supported by the metastable loss of carbon monoxide after initial loss of a hydroxyl radical from the molecular ion of 20. Furthermore, the subsequent fragmentations of the $M^{+\cdot}$-CO and $M^{+\cdot}$-HCO ions from 20 (Scheme 40), as demonstrated by metastables, are in accord with the proposed mode of formation of these ions in the mass spectrum of 8.

The metastable loss of thirty-one mass units from the molecular ion of 20 to give the m/e 208 ion must correspond to the loss of CH_3O rather than HNO, since the subsequent decomposition of the m/e 208 ion by loss of NO is substantiated by a metastable. This fragmentation is similar to that observed in the mass spectrum of 16, and steric factors again are probably an important element in the observation of this fragmentation. Having a phenyl ring on the same side as the nitro group probably forces it close enough to the methyl group for insertion


m/e 91
m/e 103
m/e 105
CH3
C
C
NO2
m/e 239
-H
m/e 238
-OH*
m/e 222
-CO*
m/e 194
-CO*
m/e 211
-NO*
m/e 181
-C3H5*
m/e 170
-CHO
m/e 210
-OH*
m/e 193
-NO
m/e 209
-CH3
m/e 194
-HNO2
m/e 192
-φ*
m/e 115
-NO2
m/e 193
-CH3CO*
m/e 196
-NO*
m/e 166
-H*
m/e 165
-CH3O*
m/e 208
-NO*
m/e 178
m/e 103
-C2H2*
m/e 152

Scheme 40

to occur with the subsequent loss of CH_3O. The phenyl-nitro interaction forces the nitro group out of the plane of the double bond, and is the main reason that the phenyl and nitro groups are trans to each other in 8 (45).

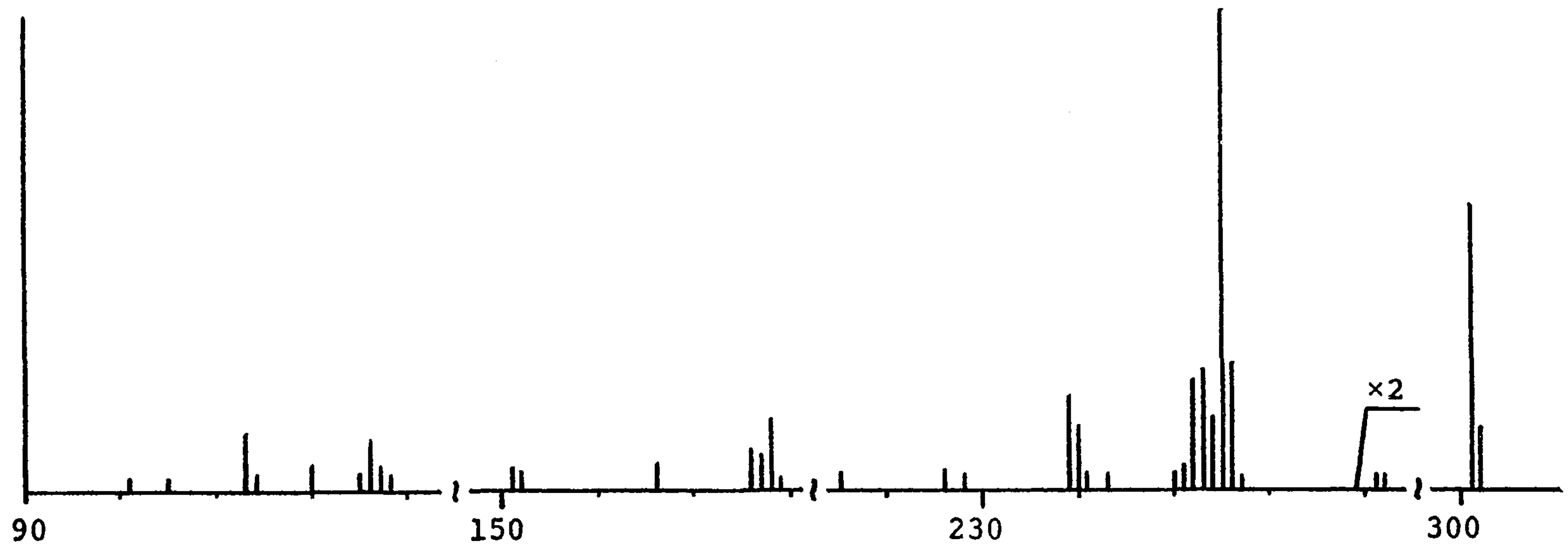
A metastable at m/e 160.5 for the direct loss of CH_3CO from the molecular ion of 20 is evidence for the concerted nature of this fragmentation in the mass spectrum of 8 (Scheme 31). Metastables indicate that the subsequent decompositions of the m/e 196 ion so formed from 20 are in agreement with the mechanism of formation for the analogous ion in the mass spectrum of 8. The other fragmentations are very similar to those observed for 8.

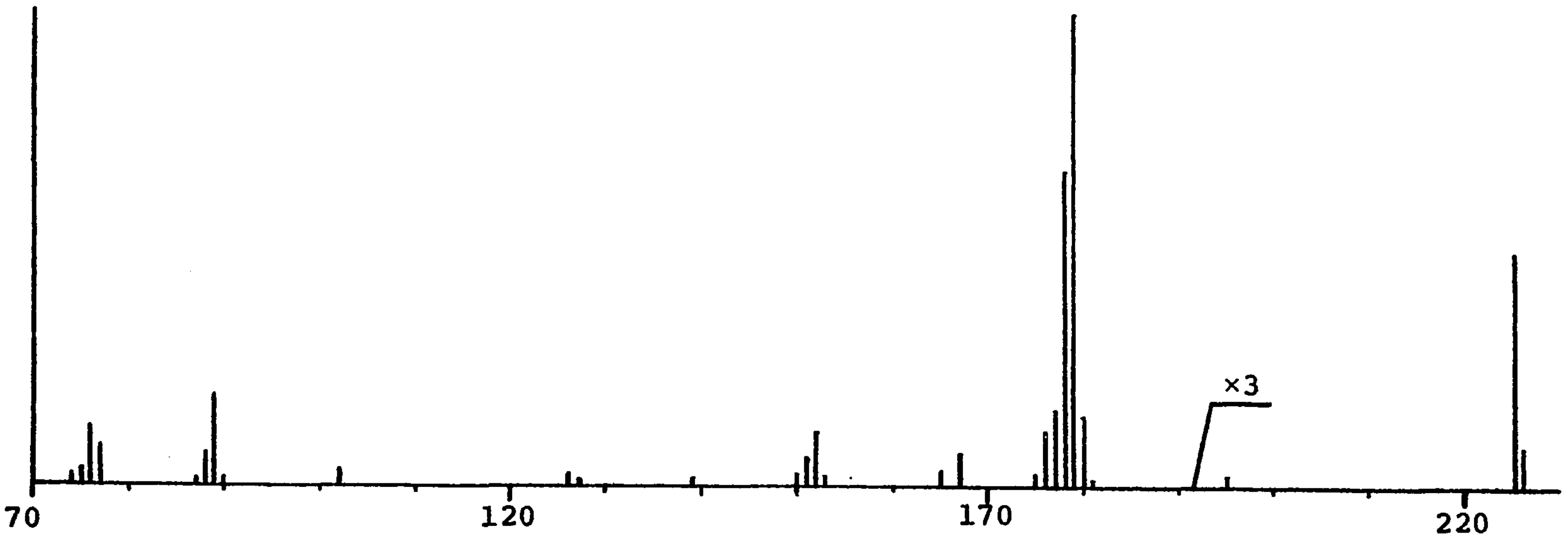
Although an additional phenyl ring on the α-carbon atom has little effect on the mass spectrum, substituting a phenyl ring on the β-carbon atom alters the mass spectra drastically. The effect clearly seen in the mass spectra of nitrotriphenylethylene 21 (Figure 13) and nitrostilbene 22 (Figure 14), is to cause a large acceleration in the cleavage of the nitro group to give a hydrocarbon ion which is the base peak in mass spectra of 21 and 22. Preferential cleavage of the nitro group diminishes or eliminates many of the previous fragmentations. Other ions observed in the spectra are due to subsequent fragmentation of the hydrocarbon ion formed by cleavage of the nitro group.

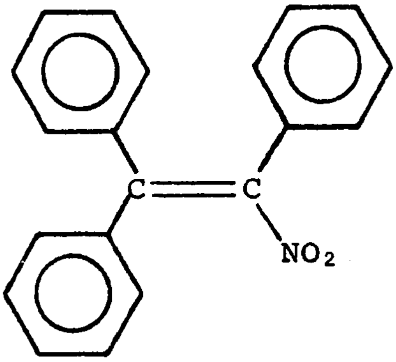
The subsequent decomposition of the m/e 255 ion formed in

Figure 13. Mass spectrum nitrotriphenylethylene <u>21</u> (top)

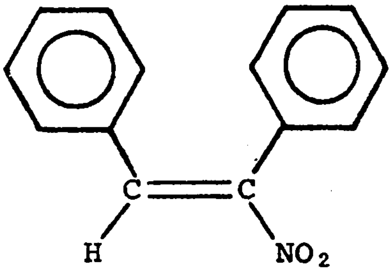
Figure 14. Mass spectrum nitrostillbene <u>22</u> (bottom)


×2
90
150
230
300


×3
70
120
170
220

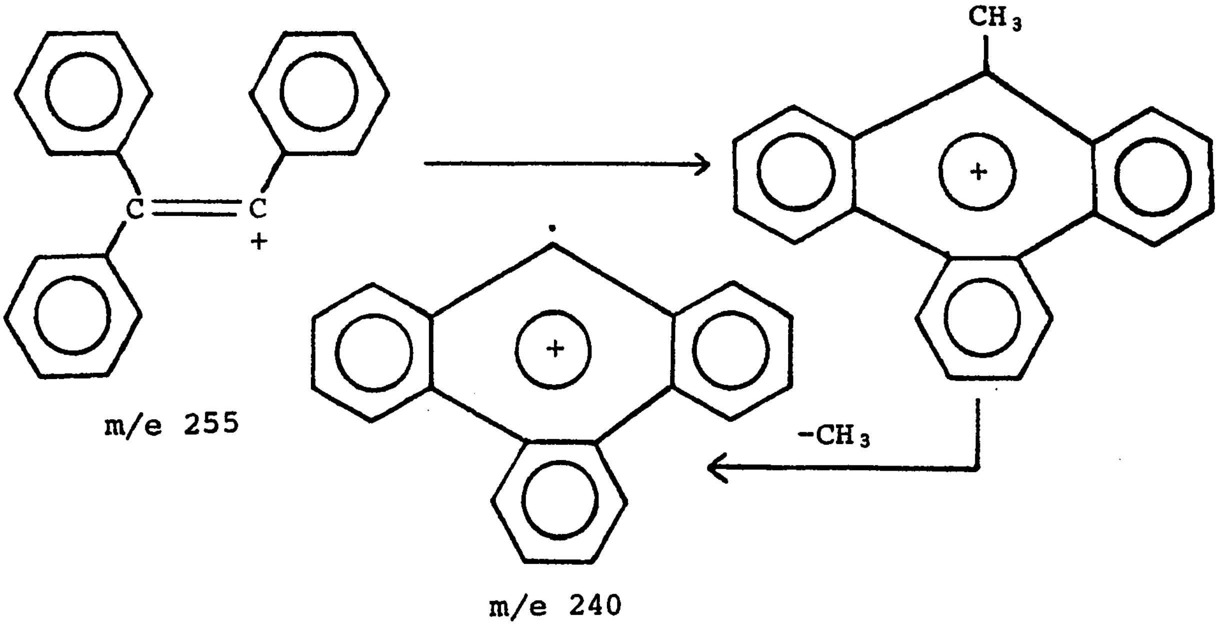


21



22

the mass spectrum of 21 by cleavage of the nitro group is of special interest. The m/e 225 ion decomposes further by the metastable loss of a methyl group, although no such grouping of atoms exists in the original molecule. The reaction sequence shown in Scheme 41 is proposed for this fragmentation. This loss of a methyl group is similar to that observed for stillbene (54) and triarylethylenes (55). The fragmentation in this

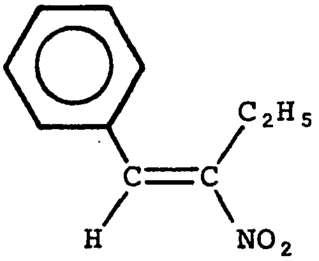


Scheme 41

case is somewhat more unusual, though, since there are no hydrogen atoms on the β-carbon, and the fragmentation corresponds to an even electron ion going to an odd electron ion.

Thermal Effects on the Mass Spectra of Nitrostyrenes

The mass spectra of the nitrostyrenes discussed above were obtained using a direct inlet system under conditions in which thermal effects would be minimal. On the other hand, the mass spectrum of β-ethyl-β-nitrostyrene 23 (Figure 15), an oily liquid, was run using a heated stainless steel inlet system maintained at 150° C with a source temperature of 200° C. The mass spectrum of 23 obtained under these conditions is different in a number of respects from the mass spectra reported previously.



23

Although the fragmentations reported earlier are found in the mass spectrum of 23, a number of additional fragmentations occur as well. For example, ions are observed for the losses of O_2, O_2H, and O_2H_2 from the molecular ion. At low electron energies the loss of O_2 from the molecular ion becomes the most intense ion in the mass spectrum. Furthermore, at low electron energies ions corresponding to losses of O, OH, and OH_2 from the molecular ion increase in importance. Another change in the spectrum is the presence of an intense ion at m/e 106 corresponding to benzaldehyde. Ions of this type were minute if not totally absent in the previously reported spectra. The ion at m/e 105 must come in part from the m/e 106 ion, since this is a known fragmentation of benzaldehyde.

The changes observed in the mass spectrum of 23 prompted an investigation into thermal effects on the mass spectra of some of the following compounds: β-nitrostyrene 7, 1,1-diphenyl-2-nitroethylene 19, and 1,1-diphenyl-2-nitropropene 20. The spectra were obtained on a high temperature inlet system maintained at 180-210° C with an ion source temperature of 220° C.

In general the mass spectra obtained under these conditions gave the same ions as obtained by the direct inlet system, but the relative intensity of the ions changed dramatically. In addition, new ions arising from thermal effects were observed. An appreciation of the changes observed in the spectra can be acquired by comparing the heated inlet spectra of 7, 19, and 20 (Figures 16-18) with their direct inlet spectra (Figures 1, 11, and 12).

The losses of O_2 and O_2H from the molecular ion are observed in all of the spectra examined. At low electron

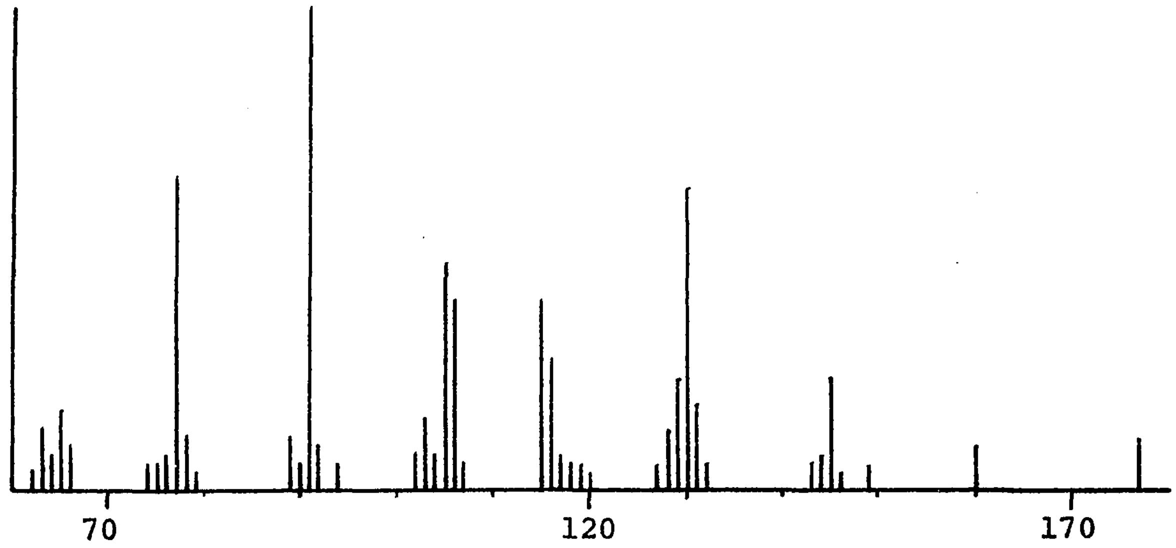


Figure 15. Mass spectrum, heated inlet, β-ethyl-β-nitrostyrene 23

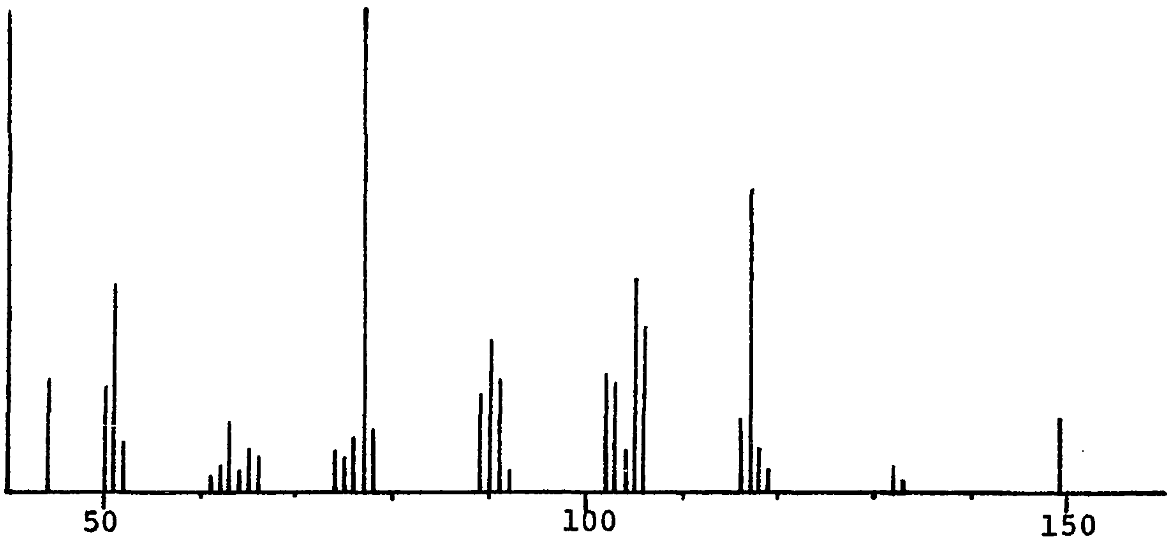
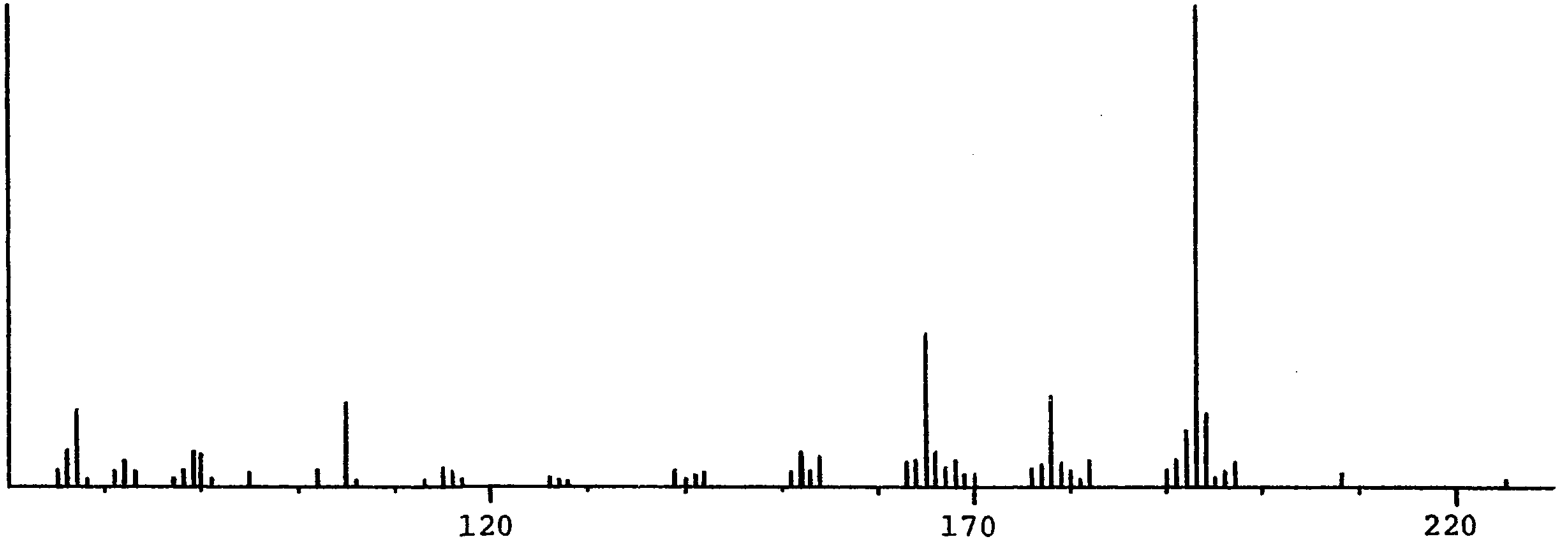
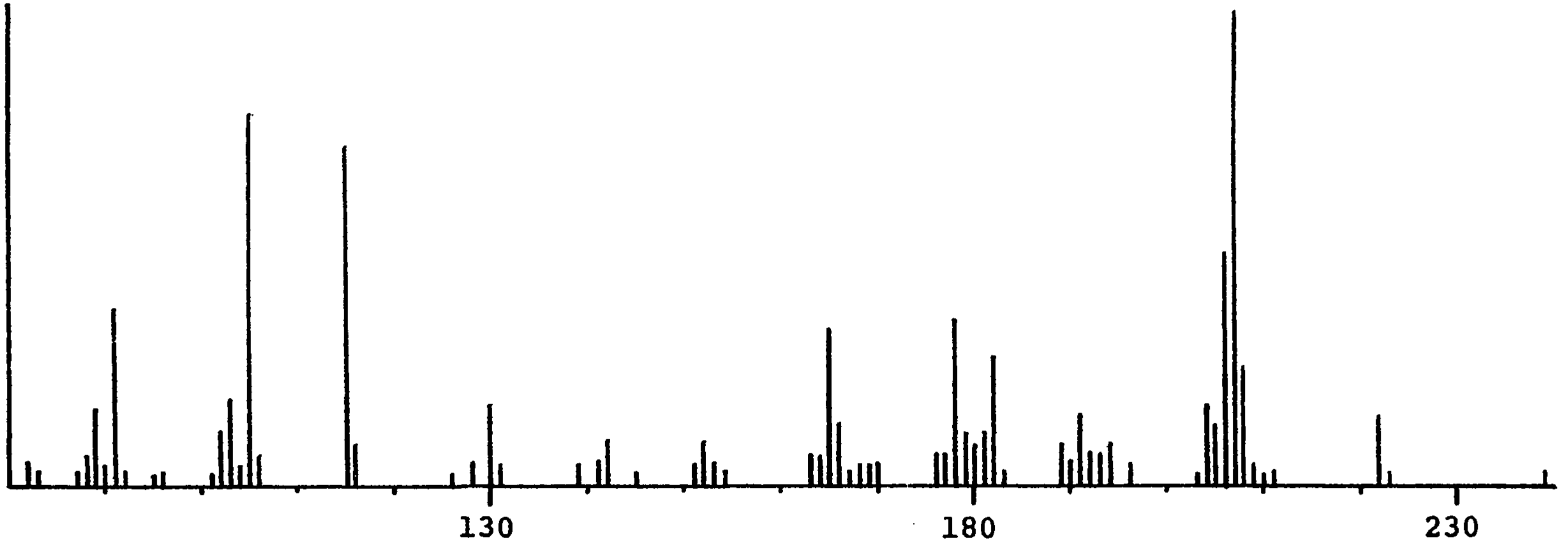


Figure 16. Mass spectrum, heated inlet, β-nitrostyrene 7

Figure 17. Mass spectrum, heated inlet, 1,1-diphenyl-2-nitroethylene <u>19</u> (top)

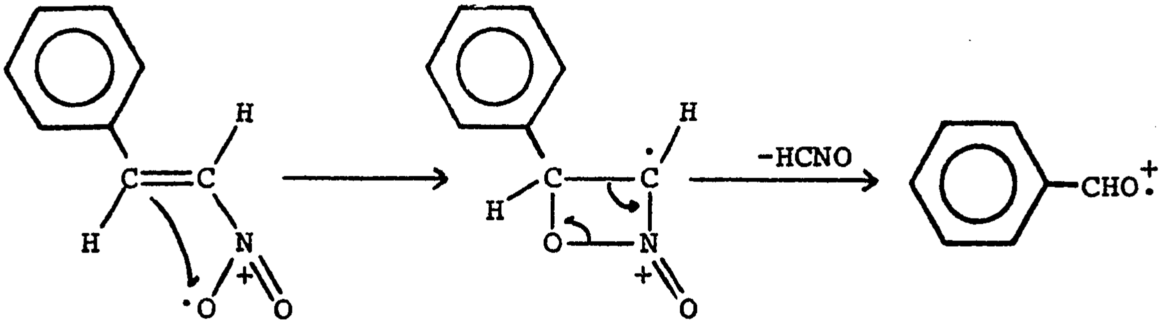
Figure 18. Mass spectrum, heated inlet, 1,1-diphenyl-2-nitropropene <u>20</u> (bottom)


120
170
220


130
180
230

energies the loss of two oxygen atoms from the molecular ion comprises the base peak in the mass spectra. Subsequent losses of HCN and H occur from the m/e 117 ion in the mass spectrum of <u>7</u>.

Thermal effects are also seen in the genesis of a benzaldehyde ion at m/e 106 in the mass spectrum of <u>7</u> and a benzophenone ion at m/e 182 in the spectra of <u>19</u> and <u>20</u>. At low electron energies these ions comprise the second most intense ion in their respective spectra. These ions could arise as shown in Scheme 42 for <u>7</u>, or they could correspond to an ionized molecular ion from pyrolysis in the inlet system.



m/e 149 m/e 106

Scheme 42

The observed thermal effects could be due to a thermal reaction of the samples in the inlet system, or could be the result of simply increasing the thermal energy of the molecules prior to ionization thereby giving a different distribution of energy among the precursor ions (56). The later effect is probably responsible for most of the observed changes, since many of the same fragmentations are observed with different relative intensities. The possibility that benzaldehyde and benzophenone are formed by a thermal reaction has been ruled out since compounds 7, 19, and 20 are stable below 400° C in vacuum pyrolysis experiments (see later section) and molecular ions corresponding to the other expected products of pyrolysis are not observed. This conclusion is in agreement with the work of Allen and Happ (41), who found nitrostyrenes to be surprisingly stable when pyrolyzed in the heated inlet of a mass spectrometer.

Mass Spectra of Heteroaromatic Nitroolefins

To test the generality of the fragmentations observed for nitrostyrenes, the heteroaromatic substituted nitroolefins 24-28 were investigated using a direct inlet system to minimize thermal effects. The mass spectrum of 1-(3-pyridyl)-2-nitropropene 24 (Figure 19), in which both pseudo-*ortho* positions are occupied by carbon, is very similar to that of β-methyl-β-nitrostyrene 8. Only ions analogous to $M^{+\cdot}$-CO, $M^{+\cdot}$-CH_3CO, and $M^{+\cdot}$-CO-CO do not occur. The observation of an additional low intensity ion corresponding to loss of HCN from the molecular ion is not surprising. The loss of CHO from the molecular ion is preferred over loss of CO.

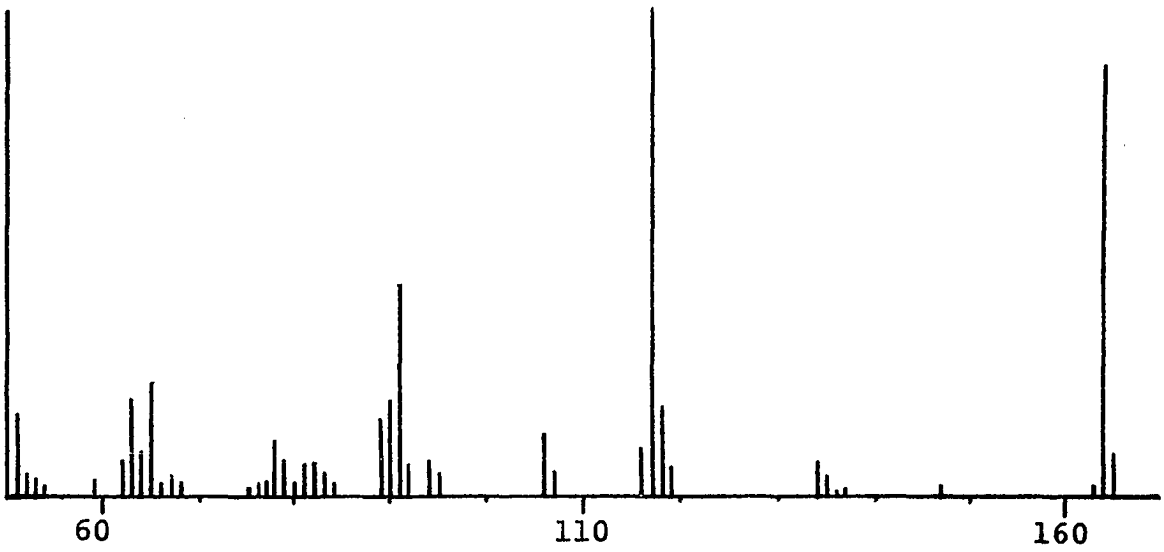


Figure 19. Mass spectrum 1-(3-pyridyl)-2-nitropropene 24

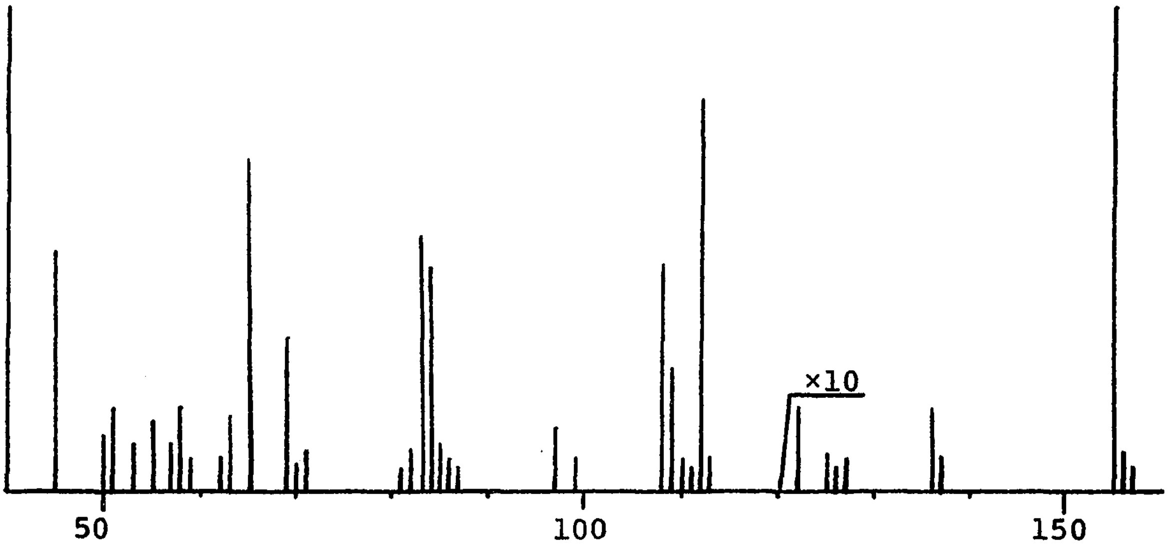
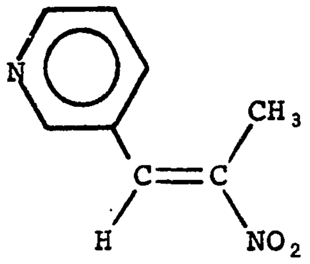
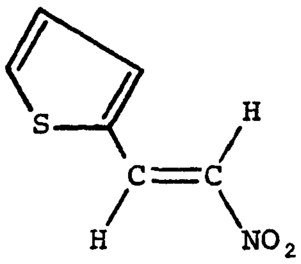


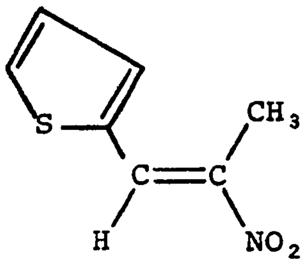
Figure 20. Mass spectrum 1-(2-thienyl)-2-nitroethylene 25



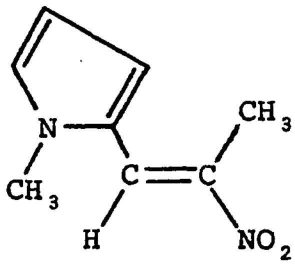
24



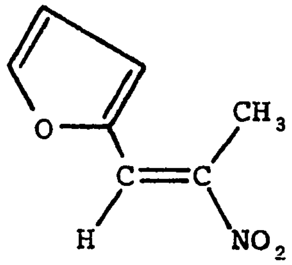
25



26



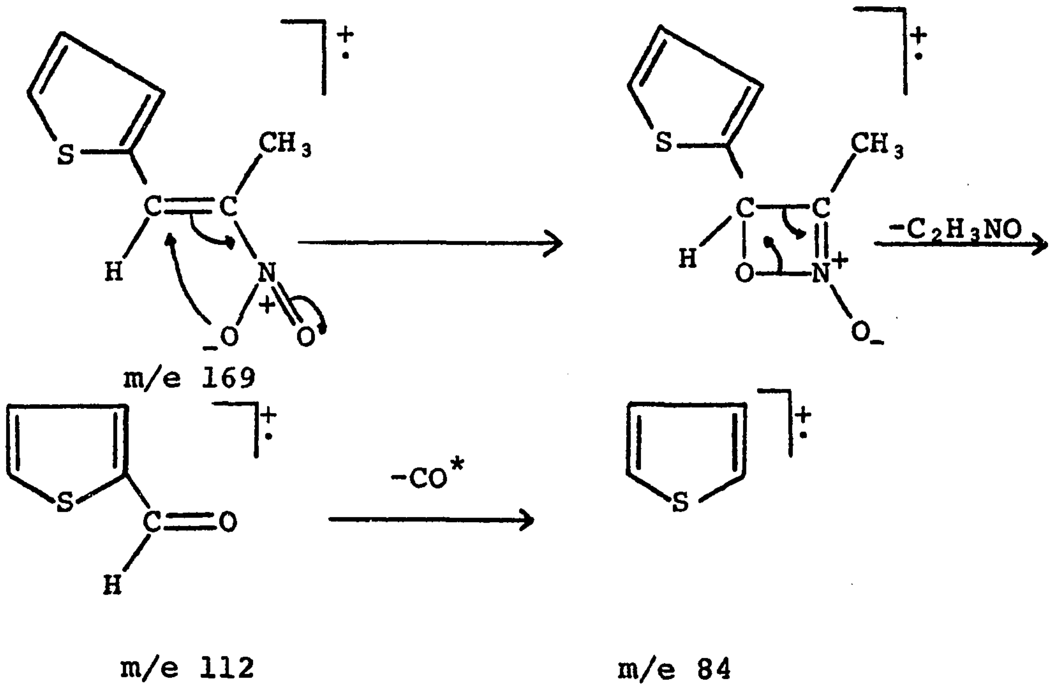
27



28

The presence of a heteroatom in one of the pseudo-ortho positions in compounds 25-28 causes many changes in the mass spectra. For example, those fragmentations proposed to involve attack on the ortho positions, such as $M^{+\cdot}$-H, $M^{+\cdot}$-CO, $M^{+\cdot}$-CHO, and the phenolic ion m/e 94, are of negligible intensity in the mass spectra of 25-28 (Figures 20-23) and the loss of a hydroxyl radical from the molecular ion is somewhat reduced in intensity. The loss of nitric oxide from the molecular ion is of diminished intensity, however, ions corresponding to the subsequent decomposition of the $M^{+\cdot}$-NO ion are observed in all of the spectra. The observed changes are due in part to a heteroatom in one of the pseudo-*ortho* positions, but the degree of change suggests that competition between the heteroatom and the nitro group for charge localization is, also, an important contributing factor.

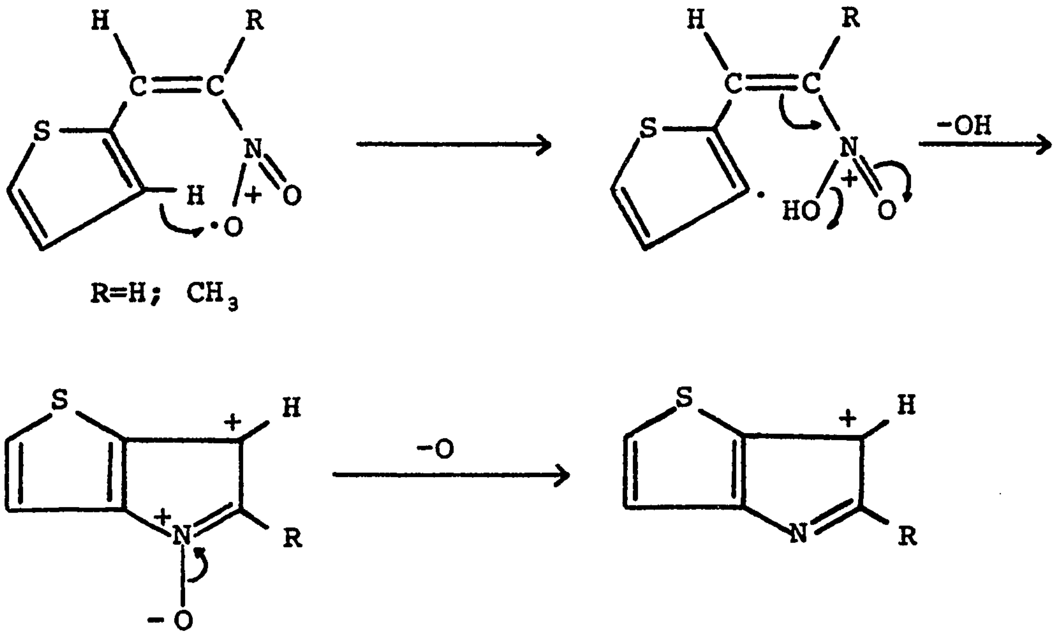
The mass spectra of compounds **25**-**28** all show intense ions corresponding to the heteroaromatic aldehydes. In fact this ion comprises the base peak in the spectra of **26** and **27**. Aldehyde or ketone ions are generally of low intensity in the mass spectra of nitrostyrenes unless thermal effects are operative. Metastables indicate these ions are formed in one step from the molecular ion, possibly via the reaction sequence illustrated in Scheme 43 for **26**. The aldehyde ion formed in



Scheme 43

this manner usually fragments by the metastable loss of carbon monoxide to give an ion corresponding to the heteroaromatic ring system.

A new low intensity $M^{+\cdot}-33$ ion occurs in the mass spectra of 25 and 26. A metastable at m/e 107.9 in the mass spectra of 25 indicates that the ion is formed by loss of a hydroxyl radical followed by an oxygen atom as depicted in Scheme 44. This fragmentation is of negligible importance for the other heteroaromatic nitroolefins investigated.



Scheme 44

Although the mass spectra of compounds 25-28 are significantly different when compared with the nitrostyrenes, they do have several features in common with them. For example, a clearly discernable molecular ion occurs in the mass spectra of compounds 25-28 in analogy to nitrostyrenes. Cleavage of the nitro group from the molecular ion with further losses of hydrogen is another common feature. Although the phenolic ion is absent in the mass spectra of compounds 25-28, the analog of the ion containing one less hydrogen atom is present. In fact the greater relative intensity of this ion suggests that the heteroatom is important in stabilizing the positive charge in the ion as indicated in Scheme 45. The identity of this ion is supported by the metastable loss of carbon monoxide as observed

X = N, O; S

Scheme 45

for 26. Finally, many of the other fragmentations are observed even if they are of diminished intensity.

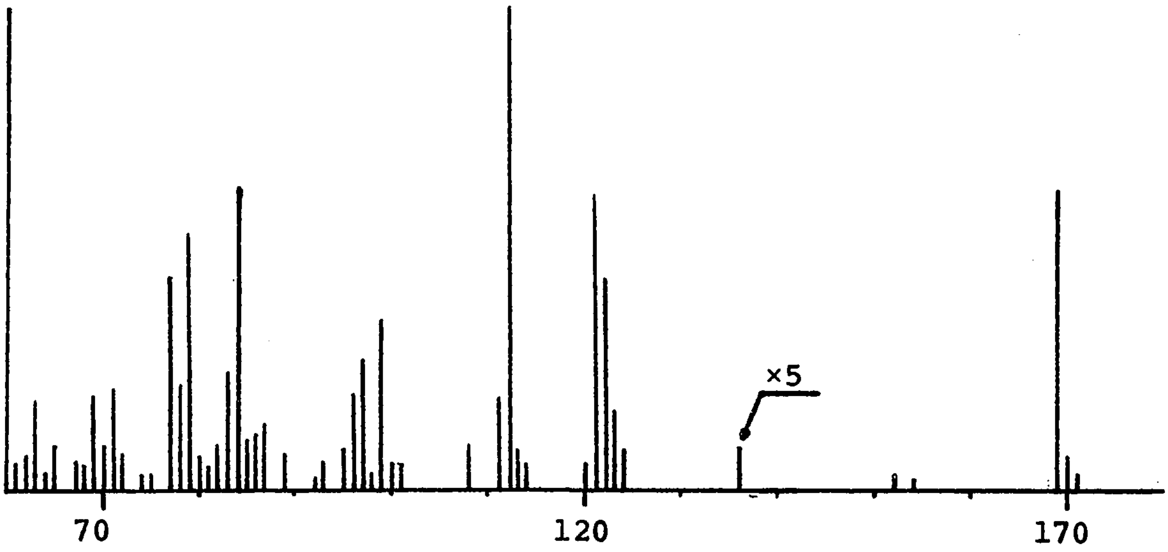


Figure 21. Mass spectrum 1-(2-thienyl)-2-nitropropene 26

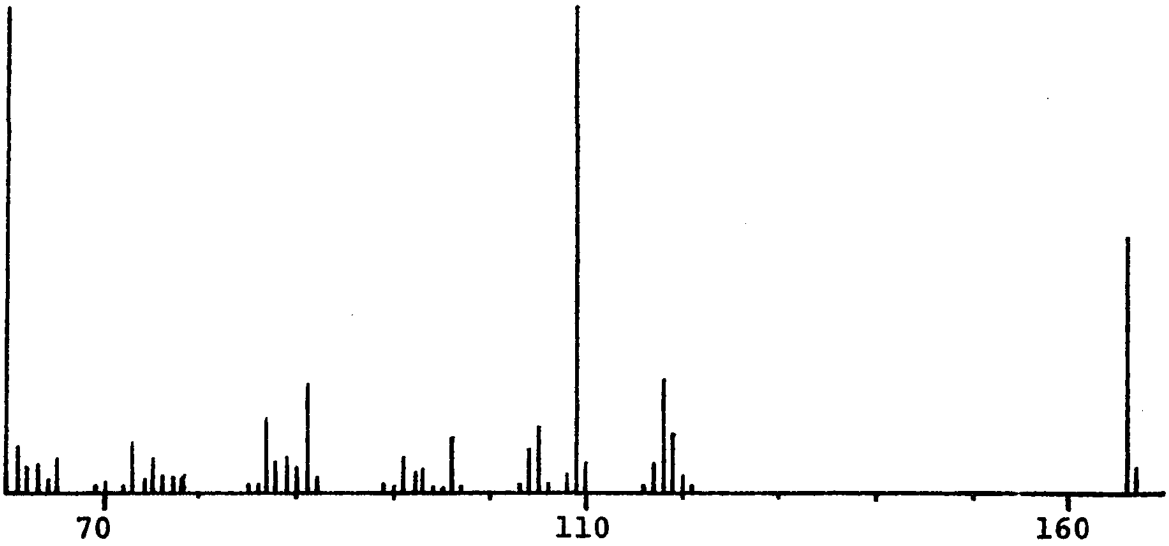
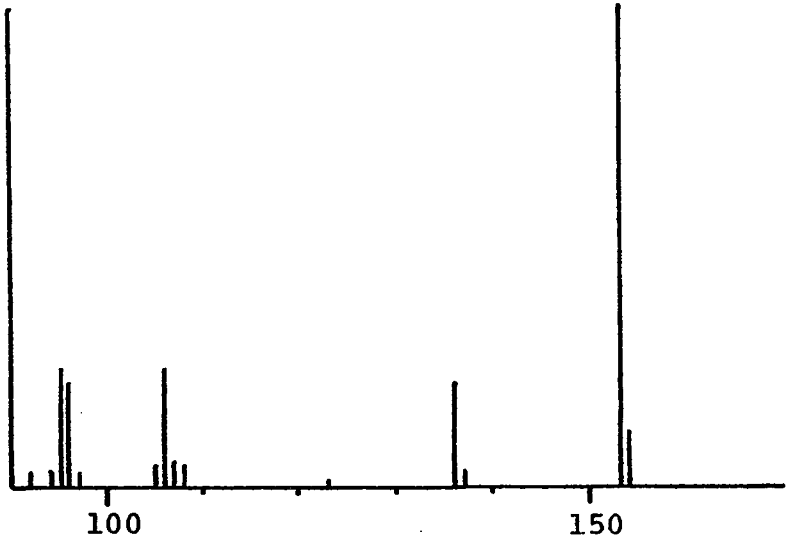
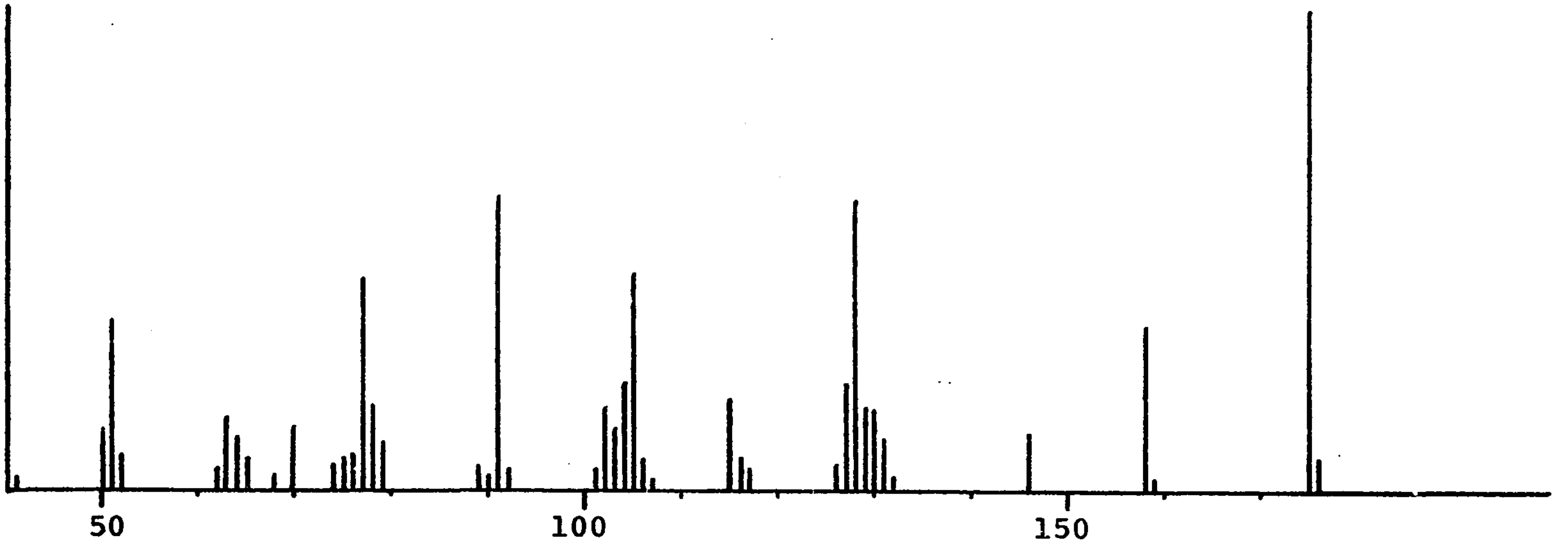


Figure 22. Mass spectrum 1-(2-N-methylpyrrole)-2-nitropropene 27

Figure 23. Mass spectrum 1-(2-furyl)-2-nitropropene <u>28</u> (top)

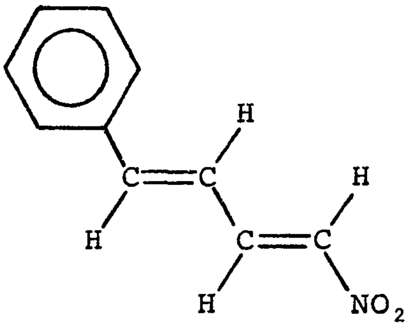
Figure 24. Mass spectrum 1-nitro-4-phenylbutadiene <u>29</u> (bottom)

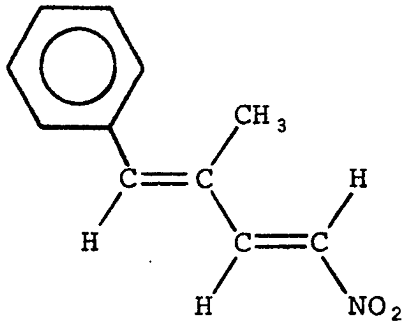

100
150

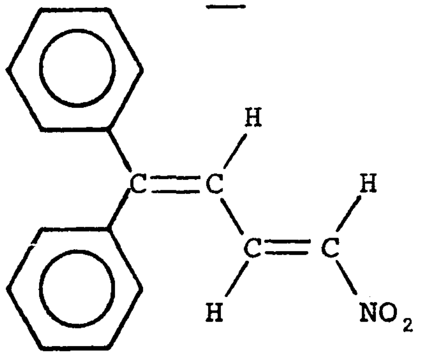

50
100
150

Mass Spectra of Nitrodienes

The mass spectra of some nitrodienes were investigated to determine the effect of extended conjugation on the mass spectra of nitroolefins, and to further test the generality of the fragmentations observed for nitrostyrenes and heteroaromatic nitroolefins. The mass spectra of compounds 29-32 (Figures 24-27) were investigated in this regard. An abundant molecular ion was observed in all cases, and surprisingly enough, many of the fragmentations were analogous to those reported for nitrostyrenes and heteroaromatic nitroolefins. The main fragmentations of the parent nitrodiene, 1-nitro-4-phenylbutadiene 29, are outlined in Scheme 46. Since most of the


29


30


31

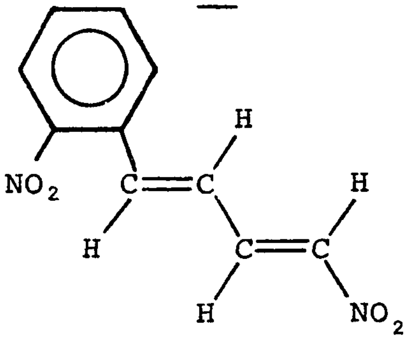
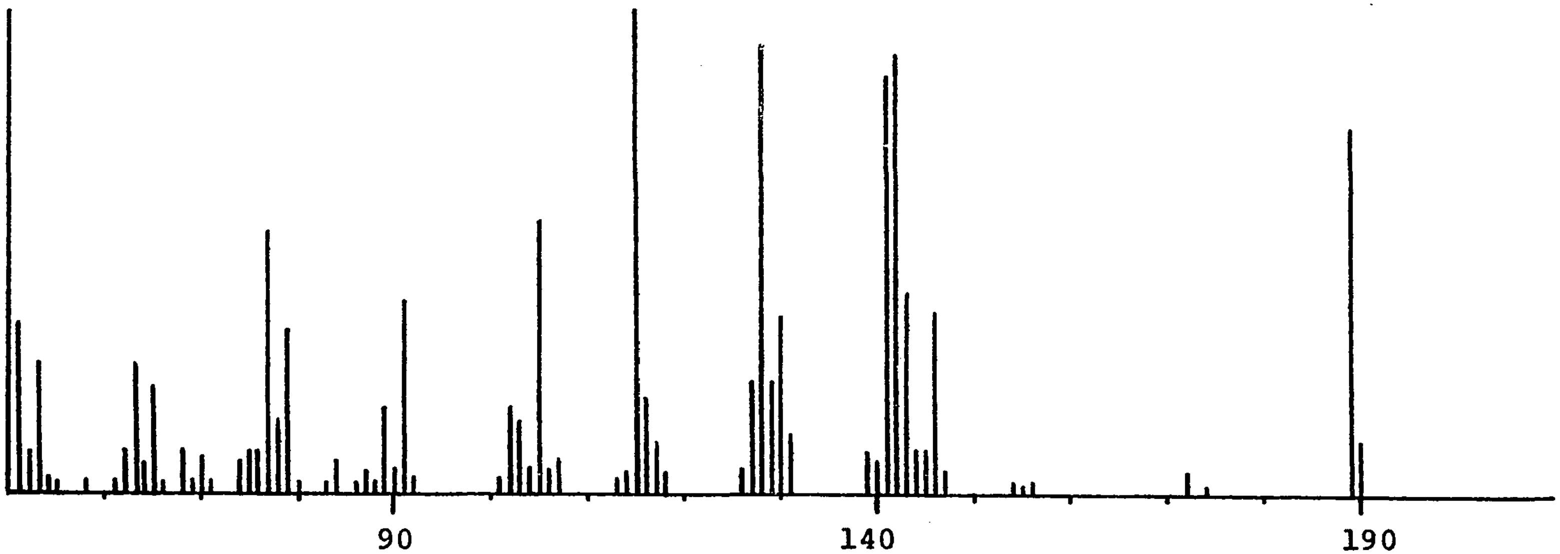

32

Figure 25. Mass spectrum 3-methyl-1-nitro-4-phenylbutadiene 30 (top)

Figure 26. Mass spectrum 1,1-diphenyl-4-nitrobutadiene 31 (bottom)


90
140
190

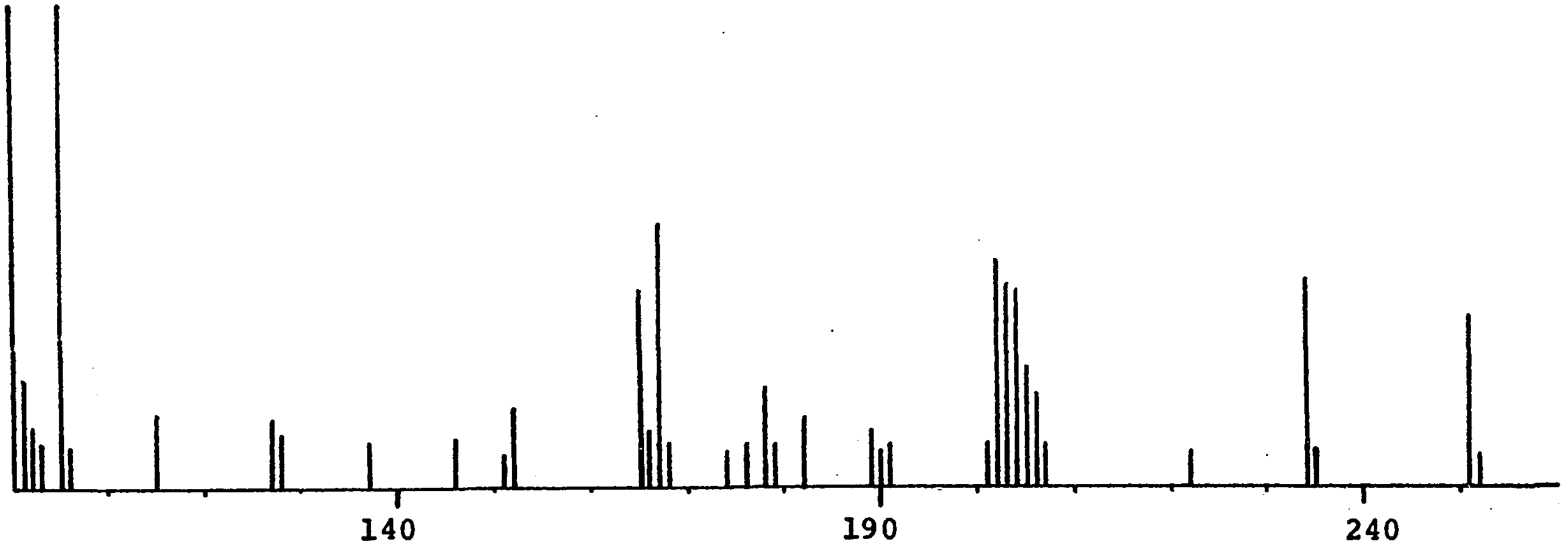
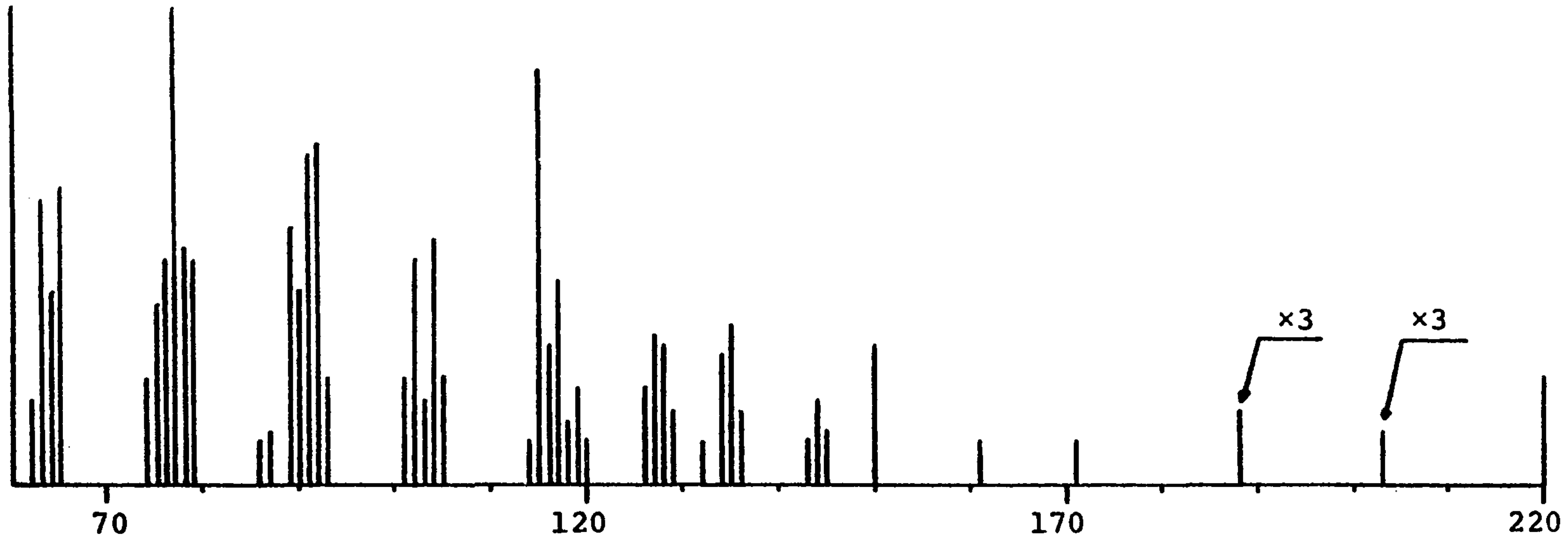

140
190
240

Figure 27. Mass spectrum 1-nitro-4-(o-nitrophenyl)-butadiene 32 (top)

Figure 28. Mass spectrum α-deuterio-1-nitro-4-phenylbutadiene 33 (bottom)


×3
×3
70
120
170
220

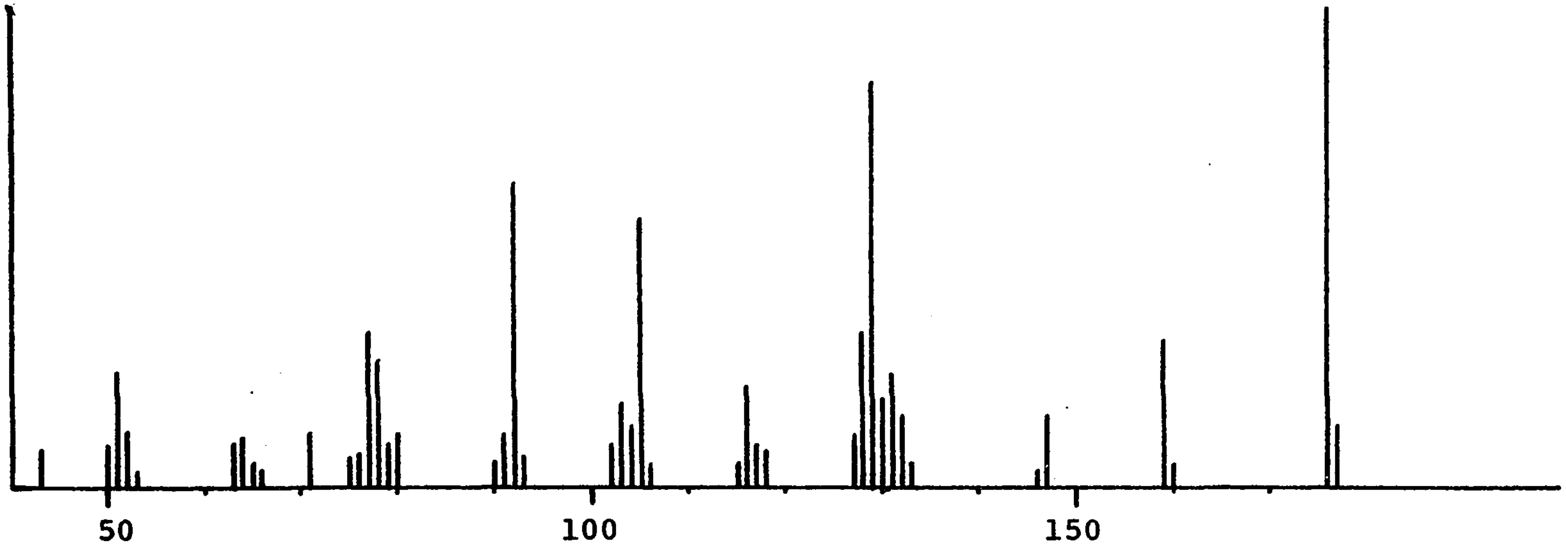
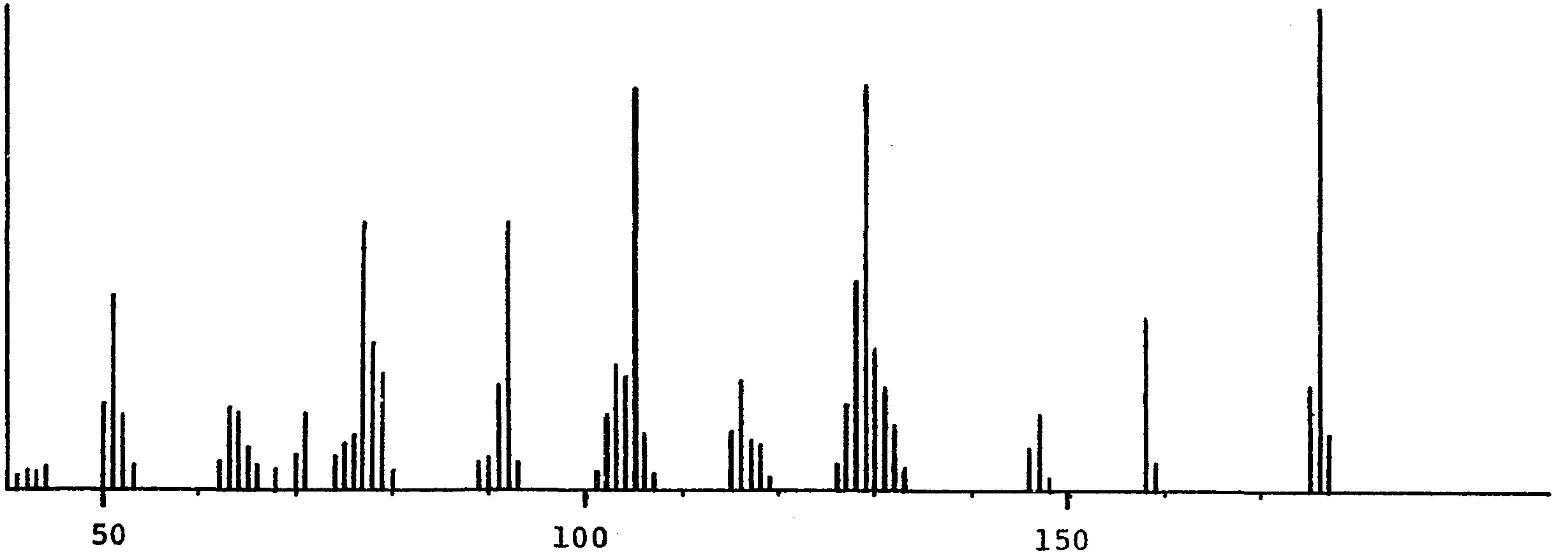
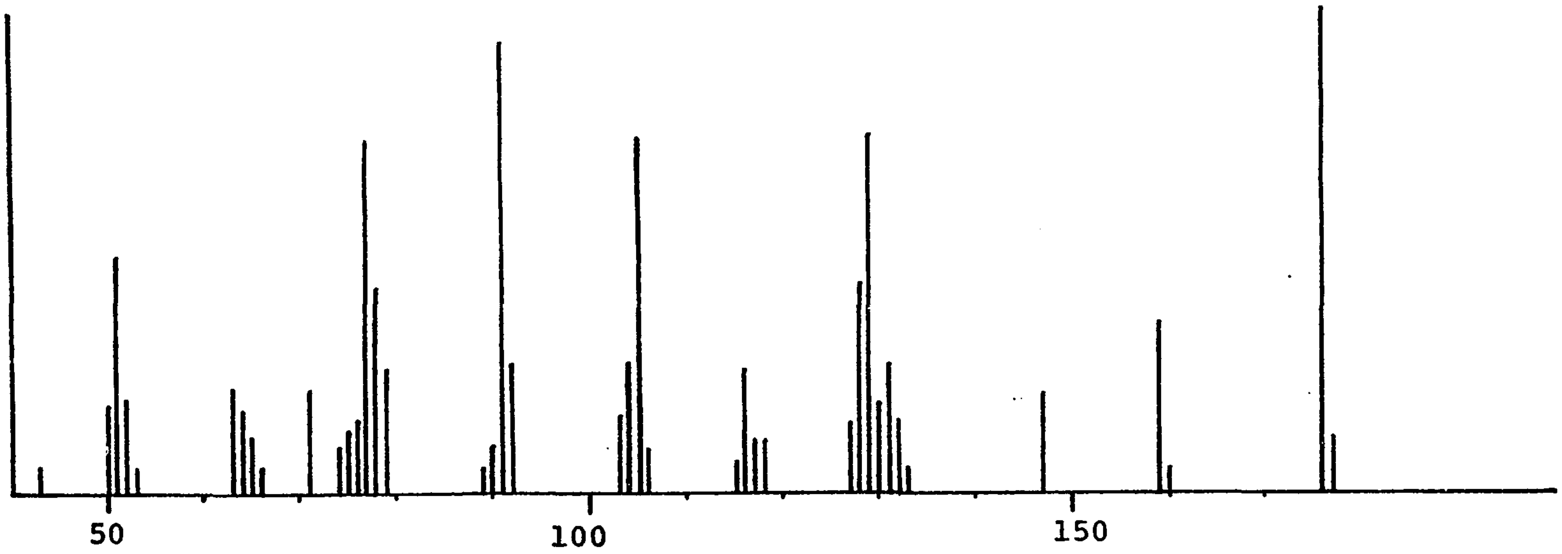
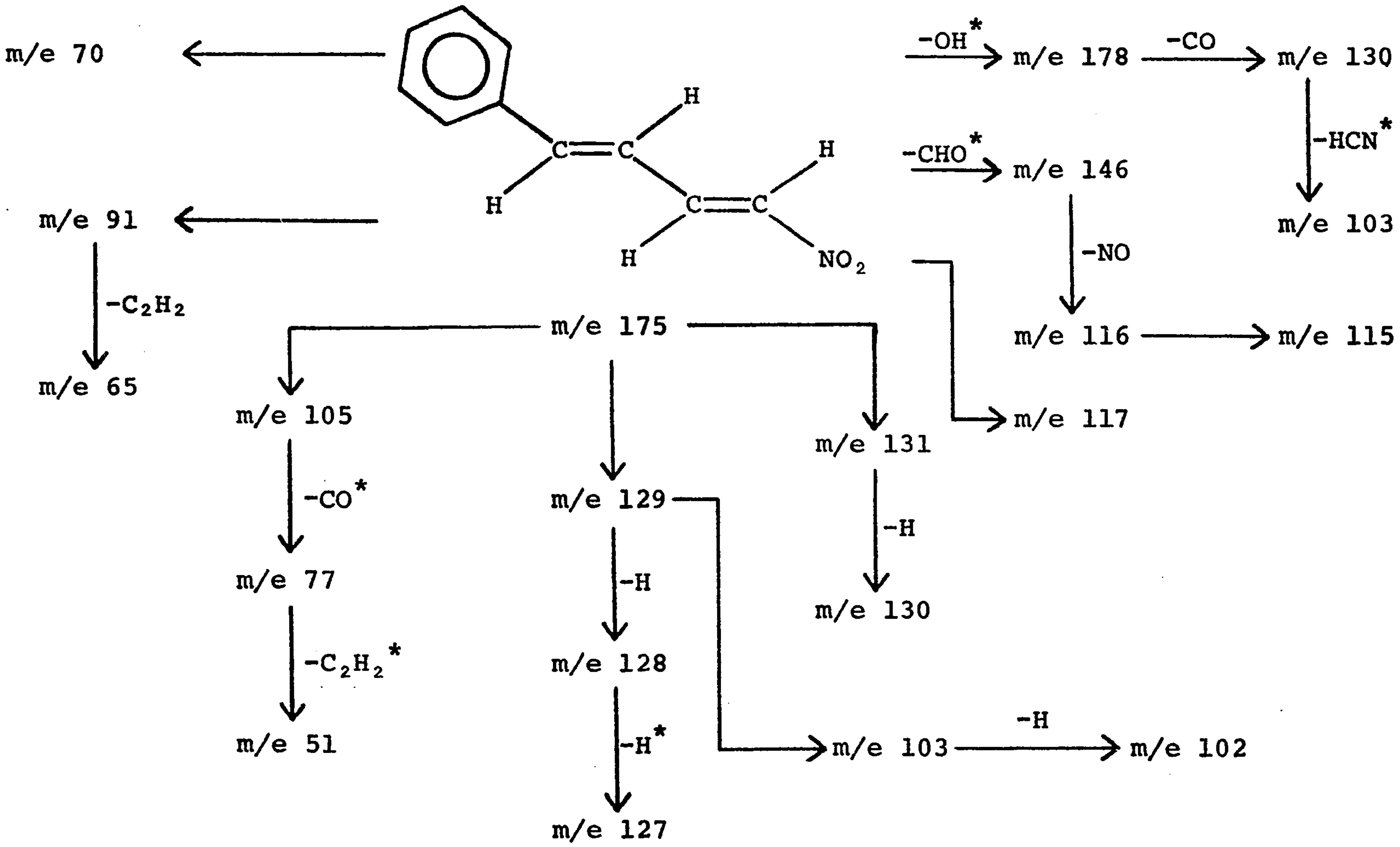

50
100
150

Figure 29. Mass spectrum β-deuterio-1-nitro-4-phenylbutadiene <u>34</u> (top)

Figure 30. Mass spectrum γ-deuterio-1-nitro-4-phenylbutadiene <u>35</u> (bottom)

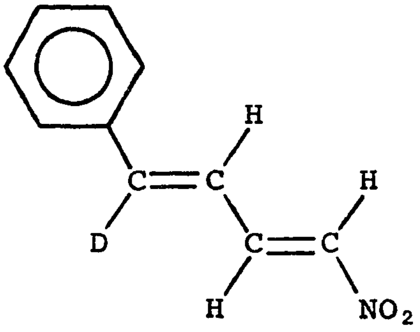

50
100
150


50
100
150

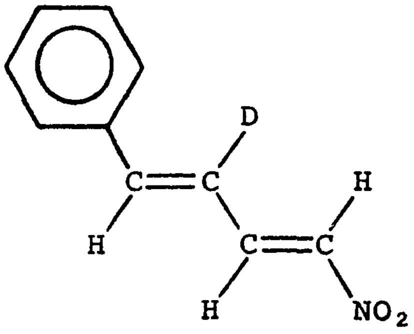

m/e 70
m/e 91
-C_2H_2
m/e 65
H
H
H
H
NO_2
-OH*
m/e 178
-CO
m/e 130
-HCN*
m/e 103
-CHO*
m/e 146
-NO
m/e 116
m/e 115
m/e 117
m/e 175
m/e 105
-CO*
m/e 77
-C_2H_2*
m/e 51
m/e 129
-H
m/e 128
-H*
m/e 127
m/e 131
-H
m/e 130
m/e 103
-H
m/e 102

Scheme 46

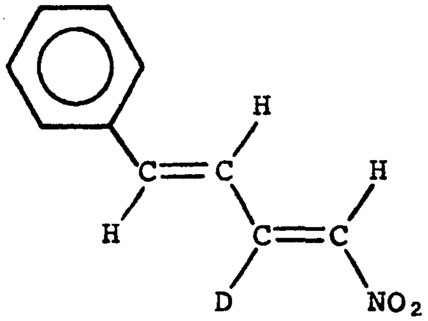
fragmentations observed for 29 are common to the other nitrodienes investigated, some deuterium labeled derivatives (33-35) of 29 were prepared and studied in an effort to determine more exactly their fragmentation mechanisms.



33

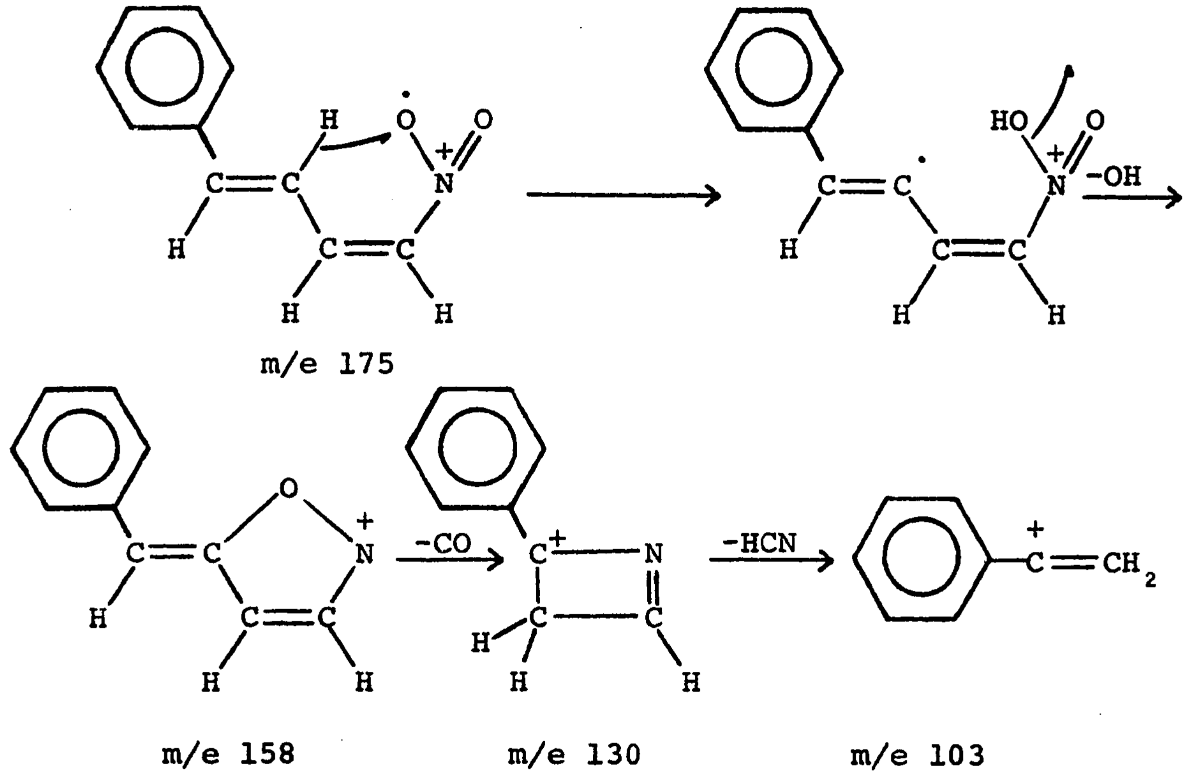


34



35

Results from 34 demonstrate that the loss of a hydroxyl radical from the molecular ion of 29 to give the m/e 158 ion involves the specific abstraction of a hydrogen atom from the β-carbon as illustrated in Scheme 47. The specificity of this process is confirmed by the loss of OH only in the mass spectra of 33 and 35. The loss of a hydroxyl radical from the



Scheme 47

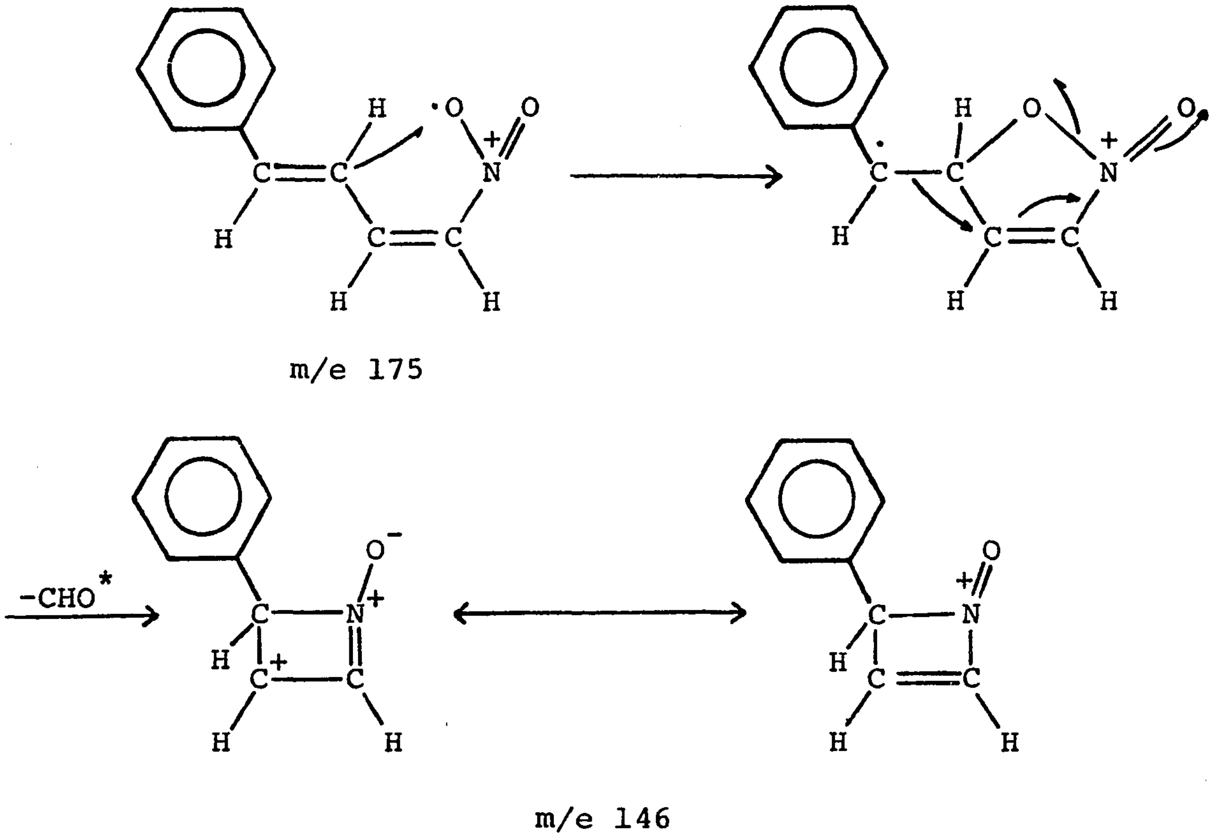
molecular ions of the other nitrodienes must occur in a similar manner. In 30, where a methyl group is substituted for the hydrogen atom of the β-carbon, the corresponding fragmentation is of much lower intensity (Figure 25) and must involve hydrogen abstraction from another site, perhaps the methyl group.

Labeling data and the metastable loss of HCN from m/e 130 to give the ion at m/e 103 suggest that the m/e 130 ion may be formed in part by the loss of carbon monoxide from m/e 158 as depicted in Scheme 47. A similar fragmentation is supported by the presence of a metastable in the mass spectrum of 31. The increased importance of m/e 130 at low election energies is again in agreement with such a proposal. A subsequent fragmentation of this type for the $M^{+\cdot}$-OH ion is important only for 29 and 31. Although the ion at m/e 131 could correspond to the loss of HCN from m/e 158, labeling data from 34 indicates that such a process is not important. Instead the m/e 131 ion probably corresponds to the cinnamoyl cation or an equivalent ion formed in one step from the molecular ion or by the loss of hydrogen from the cinnamaldehyde ion at m/e 132, which itself is formed in one step from the molecular ion. Formation of the cinnamaldehyde ion in one step from the molecular ion parallels a reaction observed for other nitroolefins.

The next fragmentation of interest is the metastable loss of CHO from the molecular ion of 29. Deuterium labeling results indicate this fragmentation is a complicated process. The following losses of CDO are observed for 33, 34, and 35, respectively: 17.5%, 19.3%, and 0%. Two mechanistic pathways can be envisioned to fit this data. One, the possibility exists that the remaining 63.2% loss of CHO involves the δ carbon and hydrogen atoms in a process similar to that proposed for β-nitrostyrene 7 (Scheme 31). The loss of CHO would then occur from the α, β, and δ carbon atoms in a multi-site fragmentation. Although there is evidence from other fragmentations for attack on both the α and β carbon atoms by the nitro group, little or no evidence exists for the nitro-nitrite rearrangement required for loss of CHO involving the δ carbon atom.

A more likely mechanism involves attack by the nitro group on either the α or β carbon atoms with partial randomization of the hydrogen atoms on the phenyl ring and the α and β carbon atoms prior to loss of CHO from the molecular ion. Attack on the β carbon atom seems certain since compound 30 fragments by the metastable loss of CH_3CO from the molecular ion instead of CHO. Loss of CHO from the molecular ion of 31 agrees with attack on the β carbon as well. Then too, initial attack on the β-carbon atom as depicted in Scheme 48 could account for the slightly greater loss of CDO from 34 when compared to 33. Since the radical site generated in this manner is not conjugated with the other double bond, the hydrogen atoms on the γ and δ carbon atoms would not be expected to participate in any randomization reaction. Indeed, no loss of CDO is observed for 35. Only partial randomization can be proposed, because complete randomization would lead to 14.3% loss of CDO in 33 and 34 in the absence of an isotope effect. At lower electron energies the loss of CDO does not change appreciably for 33 or 34. This mechanism, which provides yet another example of attack on a carbon skeleton leading to randomization (48), could be validated by labeling the phenyl ring with deuterium.

As mentioned previously there is little or no evidence for



Scheme 48

nitro-nitrite rearrangement in the mass spectrum of these nitrodienes (no $M^{+\cdot}$-NO ions). The ion at m/e 117 could be formed in the sequence $M^{+\cdot}$-NO-CO, but other pathways can also be envisioned. Apparently the double bond bearing the nitro group must be directly conjugated with a phenyl ring for the nitro-nitrite rearrangement and subsequent decompositions to occur.

Cleavage of the nitro group with subsequent loss of hydrogen, as observed for nitrostyrenes and heteroaromatic nitroolefins, represents an important fragmentation mode for nitrodienes. Deuterium labeling results presented in Table 3 suggest that the hydrogen atom is lost in two different ways. Partial shift of the $M^{+\cdot}-NO_2$ ion at m/e 129 to m/e 128 in the spectrum of <u>35</u> by loss of DNO_2 indicates a 20% loss of the γ-hydrogen (Scheme 49). In a related fragmentation, the loss of

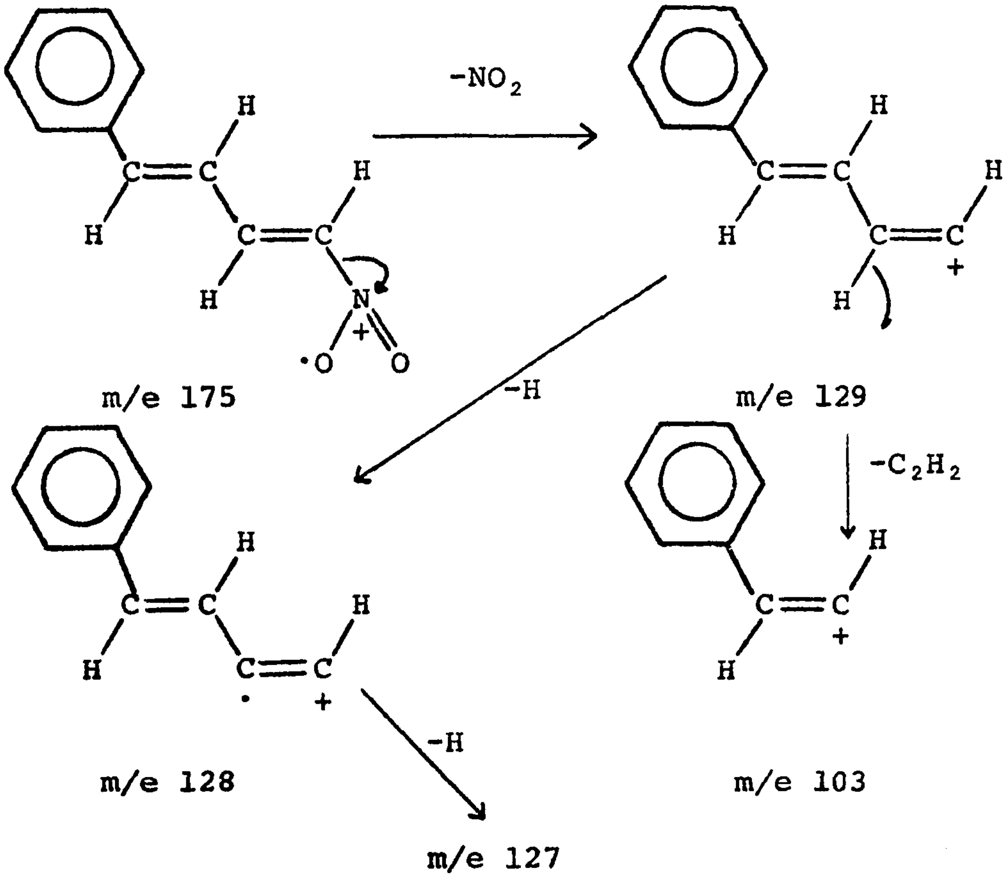
Table 3. Labeling results for $M^{+\cdot}-HNO_2$ in the mass spectrum of 1-nitro-4-phenylbutadiene <u>29</u>[a]

	Compound			
	<u>29</u>	<u>33</u>	<u>34</u>[b]	<u>35</u>
m/e 126	4.75%	1.50%	1.58%	2.06%
m/e 127	18.60%	6.10%	5.96%	7.63%
m/e 128	48.80%	18.40%	17.20%	23.50%
m/e 129	5.22%	45.20%	48.40%	38.40%
m/e 130	13.00%	6.20%	8.90%	5.68%
m/e 131	7.50%	13.30%	9.78%	13.80%
m/e 132	2.13%	7.05%	6.19%	7.20%
m/e 133	0.00%	2.25%	1.97%	1.73%

[a] Expressed as % Σ m/e 126-133 after correcting for carbon thirteen.

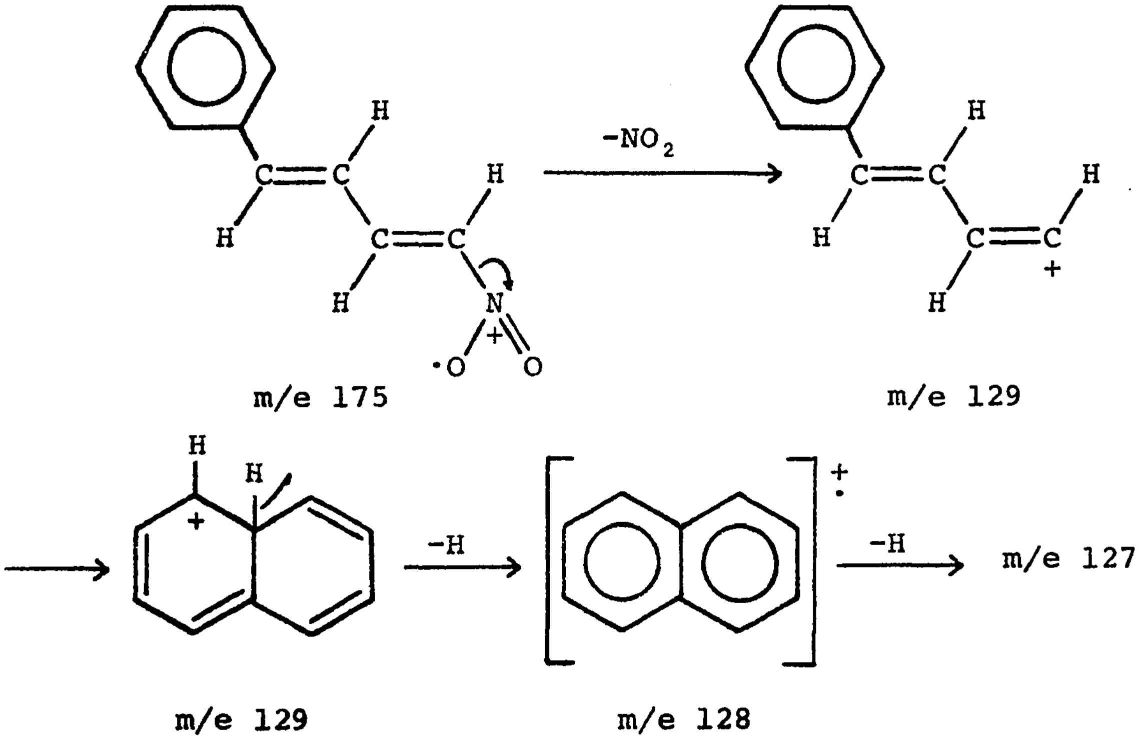
[b] Corrected for 19% d_0.

acetylene from m/e 129 in the spectrum of 29 could account in part for formation of the m/e 103 ion (Scheme 49).



Scheme 49

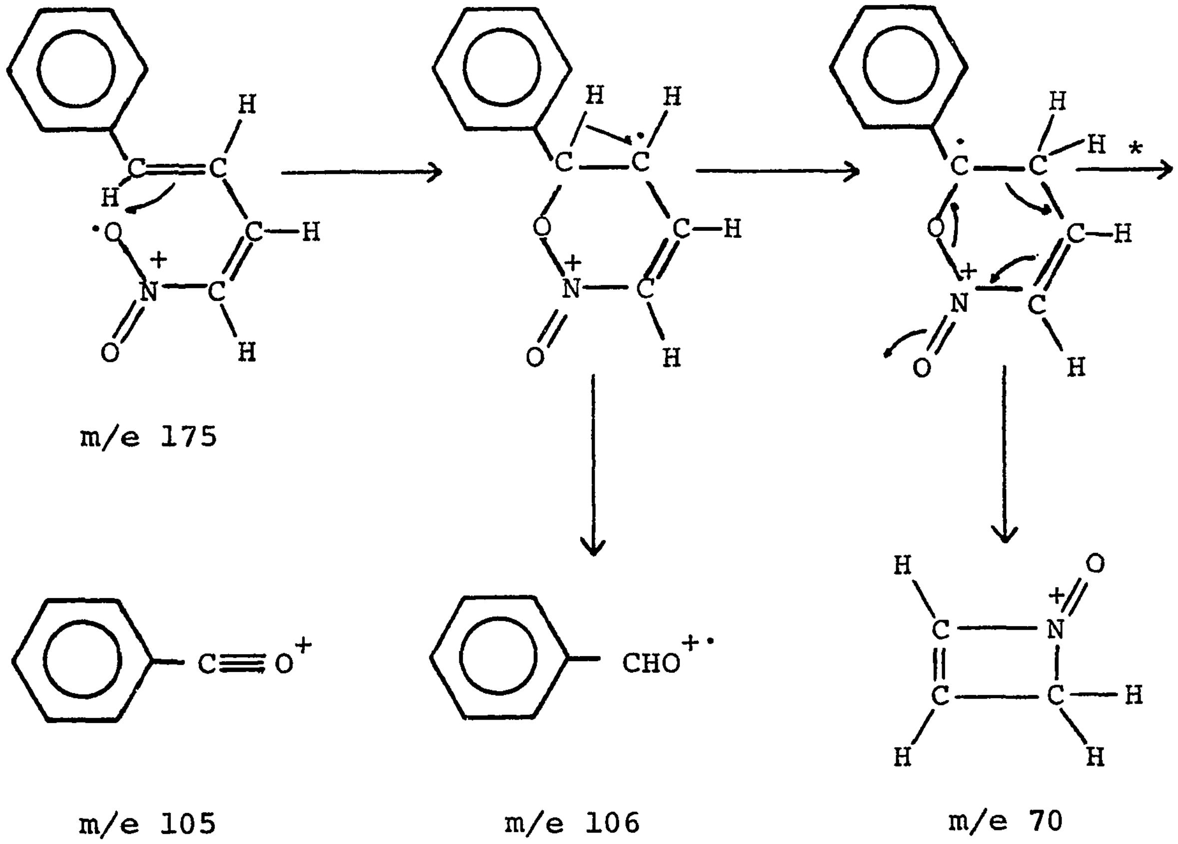
No loss of DNO_2 occurs from the molecular ions of the other labeled compounds (Table 3). Since hydrogen loss from the δ carbon is unlikely, ring closure and loss of a hydrogen atom to give an ionized napththalene ring is proposed (Scheme 50). The cyclization reaction probably causes randomization



Scheme 50

of the hydrogen atoms in the phenyl ring prior to expulsion of hydrogen in analogy to the results for β-methyl-β-nitrostyrene 8. This fragmentation pathway accounts for 80% of the observed loss of HNO_2 from the molecular ion of 29. The further loss of hydrogen from the $M^{+\cdot}-HNO_2$ ion is a complicated process and cannot be adequately defined from the labeling work done.

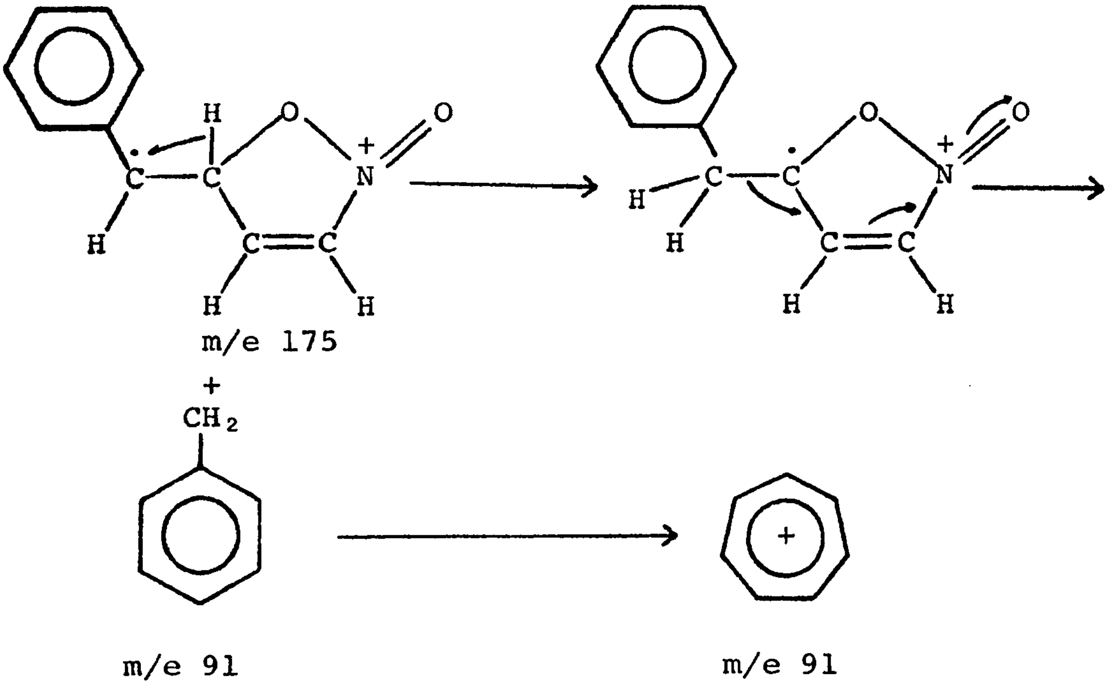
The ion at m/e 105 in the mass spectra of nitrodienes 29-32 corresponds for the most part to the benzoyl cation, as evidenced by no shifts of this ion in the spectra of 33-35, and the observation of a metastable at m/e 56.5 for the loss of carbon monoxide from m/e 105 to give the phenyl cation at m/e 77. The m/e 105 ion is probably formed by attack of the nitro group on the α-carbon atom with hydrogen migration and then fragmentation as portrayed in Scheme 51. Fragmentation prior to hydrogen migration could account for the low intensity benzaldehyde ion observed in the mass spectrum of 29. Loss of a benzoyl radical would account for the m/e 70 ion in the mass



Scheme 51

spectrum of 29. This ion, as expected, shifts cleanly to m/e 71 in the mass spectra of 33-35. With the exception of the aldehyde ion, similar ions are formed in the mass spectra of nitrodienes 30-32. The ions which occur just below m/e 105 are primarily hydrocarbon in nature.

Attack on the β-carbon atom by the nitro group leads not only to the loss of CHO from the molecular ion of 29, but also to formation of the m/e 91 ion as depicted in Scheme 52. Appropriate mass shifts of m/e 91 to m/e 92 in the spectra of 33 and 34 and no mass shift in the spectrum of 35 support this mechanism. The ions at m/e 105 and m/e 167 in the mass spectra



Scheme 52

of 30 and 31 respectively must be formed in an analogous manner. An analog of these ions is not observed in the mass spectrum of 32.

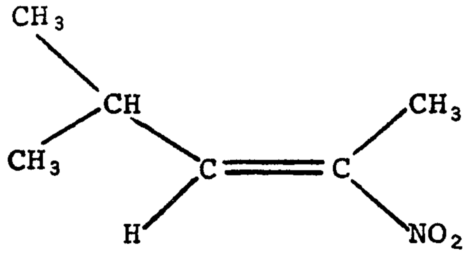
Although the mass spectra of nitrodienes 30-32 resemble 29 in their fragmentations, they demonstrate several fragmentations peculiar to themselves. For example, the loss of CHO in the mass spectrum of 29 becomes the loss of CH_3CO from 30 as pointed out earlier. An intense ion at m/e 128 in the mass spectrum of 30 is formed by the consecutive losses of NO_2 and $CH_3\cdot$ as shown by metastables. The resulting ion may have a naphthalene structure. The m/e 105 ion in the mass spectrum of 30 is a doublet, consisting of $C_7H_5O^+$ and $C_7H_9{}^+$ as demonstrated by the subsequent metastable losses of CO and C_2H_2, respectively, and is formed in fragmentations similar to those depicted in Schemes 51 and 52.

The mass spectrum of 31 is of special interest, too. Initial cleavage of the nitro group is followed by the subsequent loss of three hydrogen atoms to generate an intense ion at m/e 202 which probably has a stable polycyclic structure. The analog of the m/e 91 ion in the spectrum of 29, in the spectrum of 31, is the cation at m/e 167 which fragments by the metastable loss of a methyl radical as expected (57). Attack on the β-carbon atom by the nitro group followed by cleavage prior to hydrogen migration gives the ion at m/e 166 which loses a hydrogen atom.

Finally, the mass spectrum of 32 is interesting due to the diversity of fragmentation observed for this compound. The presence of two nitro groups in the same molecule causes an abundance of fragmentation. Unfortunately, many of the ions formed are of low intensity and cannot be definitely assigned without high resolution mass spectrometry.

Mass Spectrum of 4-Methyl-2-Nitropent-2-ene

The mass spectrum of 4-methyl-2-nitropent-2-ene 36 (Figure 31) was investigated to determine the effect of replacing the phenyl ring of 8 with an alkyl group. Although 36 is an oily liquid, the mass spectrum was obtained using a direct inlet system with the sample absorbed on silica gel to avoid thermal effects. Under these conditions a clearly discernable molecular ion is observed.



36

The branched nature of the alkyl group is reflected in the loss of fifteen mass units from the molecular ion to give an important ion at m/e 114. The loss of a hydroxyl radical occurs to give an ion of low intensity at m/e 112. The absence

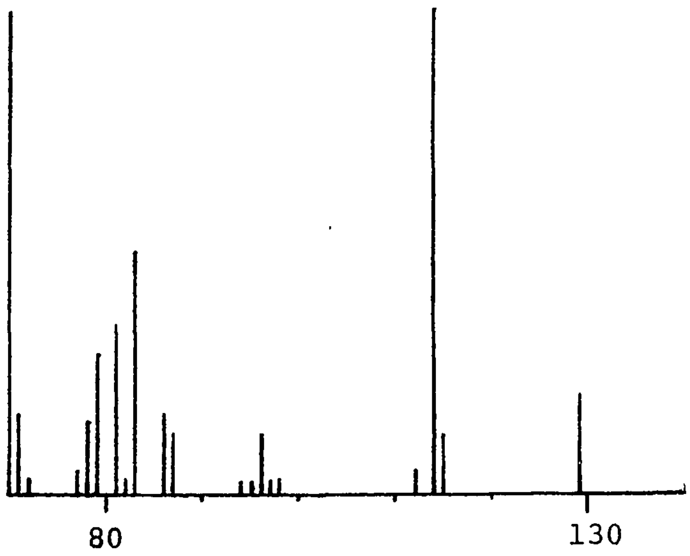


Figure 31. Mass spectrum 4-methyl-2-nitropent-2-ene <u>36</u>

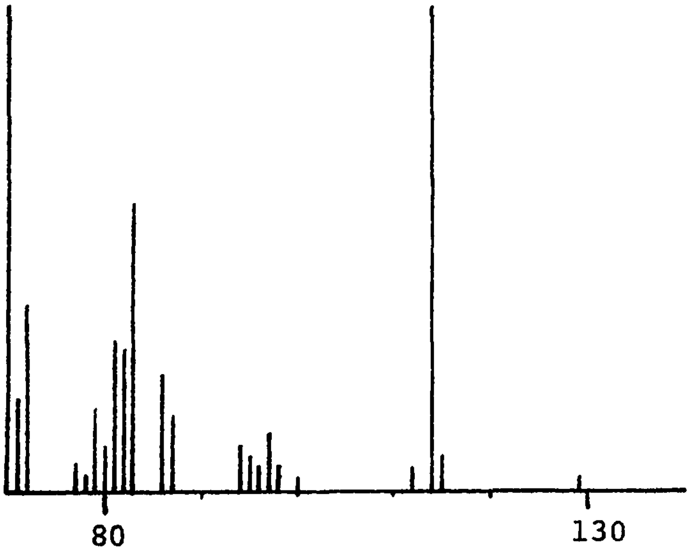


Figure 32. Mass spectrum, heated inlet, 4-methyl-2-nitropent-2-ene <u>36</u>

of a phenyl ring precludes the loss of CO or CHO from the molecular ion of 36 as well as the formation of a phenolic ion. The loss of nitric oxide from the molecular ion of 36 is not observed, which again demonstrates the importance of having a phenyl ring conjugated directly with the double bond bearing the nitro group to observe a nitro-nitrite rearrangement. Apparently sp^2 hybridization of the carbon atom bearing the nitro group is not the only prerequisite for observation of a nitro-nitrite rearrangement.

Cleavage of the nitro group and the subsequent loss of two hydrogen atoms generates ions at m/e 83 and m/e 81, respectively. The ions observed at m/e 72 and m/e 71 are probably dimethylacetaldehyde and the dimethylacylium ion, respectively, formed by processes similar to those proposed for analogous ions in the mass spectra of other nitroolefins. Thus, except for reactions involving the phenyl ring and nitro-nitrite rearrangement, the mass spectrum of 36 resembles that of β-methyl-β-nitrostyrene 8.

The mass spectrum of 36 obtained with a heated inlet system (Figure 32) is changed in accord with predictions from the thermal effects found for several nitrostyrenes.

Summary

Although the nitroolefins investigated vary widely in structure, several common features were found in all their mass spectra. First of all, regardless of structure all nitroolefins gave strong molecular ions in behavior reminiscent of nitroaromatics. Furthermore, carbon-oxygen bond forming reactions and hydrogen abstraction reactions were found to occur in all instances. It was discovered that nitro-nitrite rearrangement is not a universal reaction, but occurs only for nitrostyrenes and certain heteroaromatic nitroolefins. Finally, expulsion of the nitro group with or followed by the loss of one or two hydrogen atoms is an important fragmentation for all nitroolefins investigated.

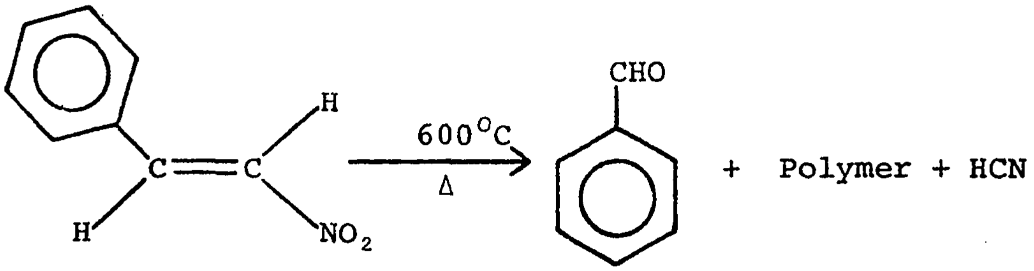
The mass spectra of nitroolefins are sufficiently characteristic to be of use in structural analysis. Nitroolefins can be distinguished from nitroaliphatics by their intense molecular ions and the existence of ions containing only carbon, hydrogen, and oxygen (4), while the loss of the nitro group along with one or two hydrogen atoms serves to distinguish nitroolefins from nitroaromatics.

Vacuum Pyrolysis of Nitrostyrenes

The observation of thermal effects in the mass spectra of certain nitrostyrenes prompted an investigation of their behavior in vacuum pyrolysis experiments. Interesting parallels between mass spectral fragmentations and thermal decomposition reactions have been noted previously (1), and it was felt that a comparison of the mass spectral and pyrolytic behavior of nitrostyrenes might be of interest. Contrary to the behavior of nitroaliphatics (34) and nitroaromatics (36) pyrolysis of nitrostyrenes does not simply cleave the nitro group to give a carbon radical which leads to the observed products, but instead an intramolecular reaction occurs. The nitrostyrenes investigated are indicated in Table 4 along with the experimental conditions and identified products. Vapor phase chromatography, nuclear magnetic resonance, infra-red, and mass spectral techniques were used to identify products and to compare them with authentic materials when possible. Details, including a description of the apparatus used, are given in the experimental section.

The pyrolysis experiments were generally conducted at pressures in the range of 0.001 to 0.005 mm of Hg, but occasionally higher pressures were employed as indicated in Table 4. The nitrostyrenes are thermally stable (41) and did not decompose at temperatures less than 400°C, while even at 500°C the pyrolysis reactions were often incomplete. At temperatures equal to or in excess of 600°C the pyrolysis of nitrostyrenes was complete to give the products designated in Table 4. Generally 0.1 to 0.4 grams of material was pyrolyzed during an 8 to 12 hour period. The yield of products from the pyrolysis reactions was 60-70% with the remainder being volatile or carbonaceous materials.

The pyrolysis of β-nitrostyrene $\underline{7}$ at 600°C resulted in the formation of benzaldehyde, a white polymeric material, and probably hydrogen cyanide as indicated in Scheme 53. The polymeric material changed to a red-brown color upon prolonged exposure to air, and could not be recrystallized from a variety of solvents. The pyrolysis of 1,1-diphenyl-2-nitroethylene 19 under similar conditions gave benzophenone, the same polymeric material, and probably hydrogen cyanide. The formation of the same polymeric material in the pyrolysis of 7 and 19 implicates the β-carbon atom of the nitrostyrenes in its formation. It was postulated that placing an alkyl group on the β-carbon atom might lead to more stable pyrolysis products.



Scheme 53

Indeed, this was proven by the absence of any polymeric products in the pyrolysis of β-methyl-β-nitrostyrene 8, which yielded acetonitrile, benzaldehyde, benzene, methylisocyanate, methylphenylacetylene and an unidentified material (less than 3.5% of total products) as indicated in Scheme 54. If the head temperature was increased above that indicated in Table 4 other unidentified products were formed, probably by intermolecular reactions. The pyrolysis of 1-(α-naphthyl)-2-nitropropene 16 and 1,1-diphenyl-2-nitropropene 20 under similar conditions gave analogous products to those shown in Table 4.

Table 4. Results[a] from the vacuum pyrolysis of nitrostyrenes

Compound	Head temp. °C	Column temp. °C	Pressure mm/Hg	Products
β-Nitrostyrene 7	50-52	400	0.001	SM[b]
"	50-55	600	0.005	Benzaldehyde; polymer
1,1-Diphenyl-2-nitroethylene 19	78-80	700	0.002	Benzophenone; polymer
"	75-78	600	0.001	Benzophenone; polymer
β-Methyl-β-nitrostyrene 8	65-70	400	0.100	SM[b]
"	60-70	500	0.250	SM[b], acetonitrile, benzaldehyde, benzene, methylisocyanate, methylphenylacetylene; UP[c]

---

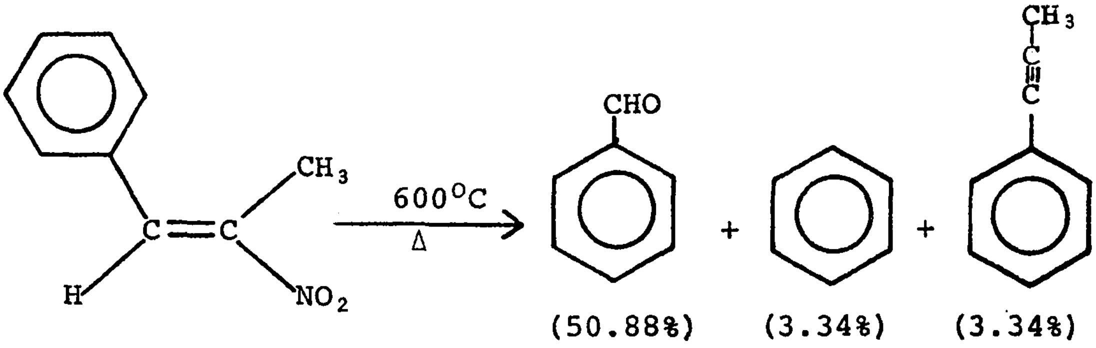
[a] Reproducible as evidenced by several repeated experiments.

[b] SM--starting material.

Table 4 (Continued)

Compound	Head temp. °C	Column temp. °C	Pressure mm/Hg	Products
β-Methyl-β-nitrostyrene 8	50-55	600	0.001	Acetonitrile, benzaldehyde, benzene methylisocyanate, methylphenyl-acetylene; UP[c]
1-(α-Naphthyl)-2-nitropropene 16	52-53	600	0.001	Acetonitrile, methylisocyanate, methyl-α-naphthylacetylene, 1-naphthaldehyde, naphthalene; UP[c]
1,1-Diphenyl-2-nitropropene 20	50-51	700	0.001	Acetonilrile, benzene, benzophenone, methylisocyanate; UP[c]
Nitrotriphenylethylene 21	101-105	600	0.001	Benzene, benzonitrile, benzophenone, phenylisocyanate, 2,3-diphenylbenzofuran; $C_{20}H_{14}$ hydrocarbon

[c] UP--unidentified products (generally less than 10% total).



+ $CH_3C{\equiv}N$ + $CH_3{-}N{=}C{=}O$ + UP

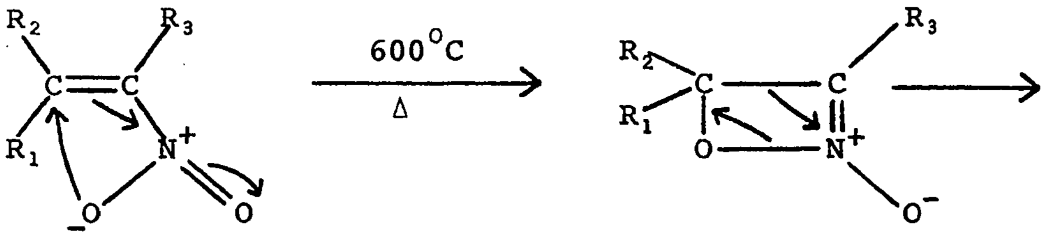
(24.6%) (14.5%) (3.34%)

Scheme 54

The formation of methylphenylacetylene (3.34%) among the pyrolysis products of β-methyl-β-nitrostyrene 8 can be explained simply by the elimination of nitrous acid. The formation of methyl-α-naphthylacetylene in the pyrolysis of 16 must occur in a similar manner. Apparently, β-nitrostyrene 7 does not decompose in this manner, since no phenylacetylene was detected among the pyrolysis products. Cleavage of the nitro group to give a vinyl radical is reminiscent of the pyrolytic behavior of nitroaliphatics (34) and nitroaromatics (36), but it constitutes only a minor decomposition pathway for nitrostyrenes.

The formation of benzene (3.34%) in the pyrolysis of β-methyl-β-nitrostyrene 8 can be explained in terms of a very similar mechanism. Instead of eliminating a nitro group and a hydrogen atom to give methylphenylacetylene, the elimination of the nitro group is followed by loss of a phenyl radical with the concurrent abstraction of a hydrogen atom. On the other hand, the hydrogen abstraction may occur between a phenyl radical and propyne absorbed on the surface of the glass beads used in packing the pyrolysis column. The new radical generated by hydrogen abstraction must decompose to carbon and tar, or react further to give the unidentified product in the pyrolysis of 8. No propyne is observed among the pyrolysis products of 8. A similar reaction sequence can be envisioned for formation of benzene and naphthalene in other pyrolysis reactions. The absence of benzene in the pyrolysis of β-nitrostyrene 7, and the presence of benzene in the pyrolysis of 1,1-diphenyl-2-nitropropene 20 demonstrates that benzene is not being formed by decarbonylation of benzaldehyde. Furthermore, benzaldehyde is not converted to benzene under the pyrolysis conditions.

The major products observed in the pyrolysis of 7, 8, 16, 19, and 20 are somewhat easier to explain. The isolation of carbonyl containing products (Table 4) clearly suggests that one of the oxygen atoms of the nitro group is acting as a nucleophile in an addition to the α-carbon atom of the nitrostyrenes as depicted in Scheme 55. In agreement with this proposal is the well known propensity of nitroolefins to undergo addition reactions with a variety of nucleophiles (42). The subsequent decomposition of the cyclic structure 37 formed in



37

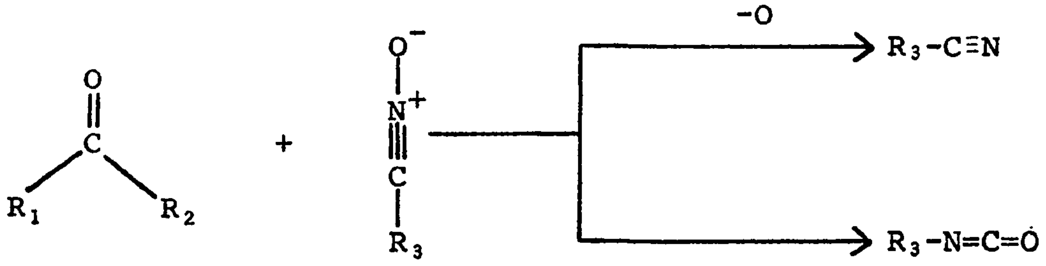
7 $R_1 = R_3 = H;\ R_2 = C_6H_5$

8 $R_1 = H_1R_2 = C_6H_5;\ R_3 = CH_3$

16 $R_1 = H_1R_2 = C_{10}H_7;\ R_3 = CH_3$

19 $R_1 = R_2 = C_6H_5;\ R_3 = H$

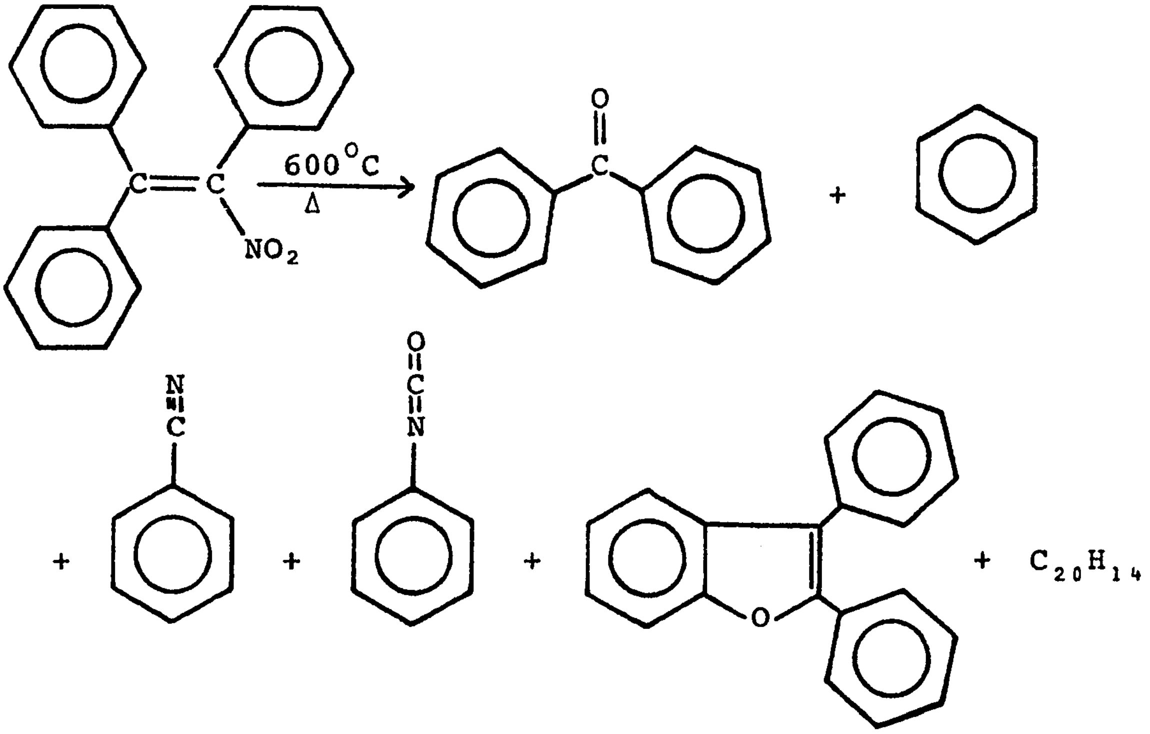
20 $R_1 = R_2 = C_6H_5;\ R_3 = CH_3$



Scheme 55

this way would give carbonyl compounds and nitrile oxides. Since nitrile oxides are known to rearrange thermally to isocyanates (58), the origin of these products is easily explained. The nitriles observed as products in the pyrolysis reactions are probably formed by the thermal loss of oxygen from the nitrile oxides. Although this is not a known reaction of nitrile oxides, chemical removal of oxygen is known to occur easily (59). The polymer formed in the pyrolysis of β-nitrostyrene 7 and 1,1-diphenyl-2-nitroethylene 19 can be explained readily by the presence of HNCO which is known to polymerize spontaneously (60).

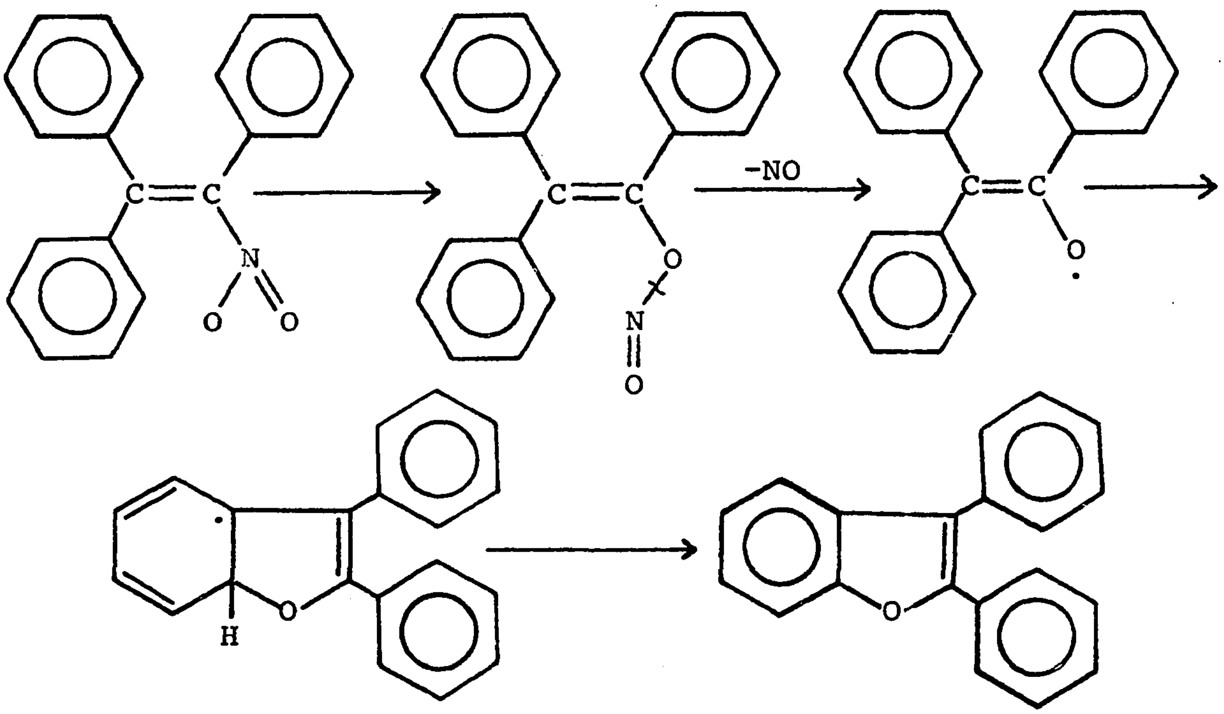
The effect of substituting a phenyl ring on the β-carbon was investigated by pyrolyzing nitrotriphenyethylene 21. The products were identified as benzene, benzonitrile, benzophenone, 2,3 diphenylbenzofuran, phenylisocyanate and a $C_{20}H_{14}$ hydrocarbon of undetermined structure as illustrated in Scheme 56.



Scheme 56

The isolation of benzene, benzophenone, benzonitrile, and phenylisocyanate indicates that mechanisms already discussed are still operative. The initial step in the formation of the $C_{20}H_{14}$ hydrocarbon is probably loss of the nitro group to form a vinyl radical. The vinyl radical can then rearrange with expulsion of a hydrogen atom to give the observed product.

The formation of 2,3-diphenylbenzofuran as a pyrolysis product from 21 is the result of a new decomposition mode. The first step in its formation must be a thermally induced nitro-nitrite rearrangement. A similar rearrangement has been proposed to explain some of the products from the thermal decomposition of nitrobenzene (36). The formation of a radical by breaking the nitrogen-oxygen bond of the nitrite results in attack on a phenyl ring with expulsion of a hydrogen atom to give 2,3-diphenylbenzofuran as indicated in Scheme 57.



Scheme 57

There appears to be a number of correlations between the mass spectral fragmentations of nitrostyrenes and their thermal decomposition, for example, the loss of nitrous acid from 8, and the formation of carbonyl products. Such fragmentations are, admittedly, relatively unimportant for nitrostyrenes unless thermal effects are operative. Finally, the nitro-nitrite rearrangement observed in the pyrolysis of 21 has a correlation with its mass spectral fragmentation.

EXPERIMENTAL

Instruments and Methods

All mass spectra were obtained on an Atlas MAT model CH 4 single focusing mass spectrometer operating at 70 electron volts, 3,000 volts accelerating potential, and a total ionizing current in the range 15-20 μ A. Most samples were also run at lower electron energies. Infrared spectra (ir) were recorded on a Perkin-Elmer Model 21 spectrometer. All nuclear magnetic resonance (nmr) spectra were taken on a Varian Associates Model A-60 spectrometer at 60 MHz. Chemical shift values are reported in parts per million (ppm), δ units, relative to tetramethylsilane as internal standard.

Melting points were obtained on a Fisher-Johns melting point apparatus. All melting points, boiling points and pyrolysis temperatures are uncorrected and reported in degrees centigrade. All pressures are expressed in millimeters of mercury. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan or Chemalytics, Inc., Tempe, Arizona.

All vapor phase chromatography (vpc) work was done on an F & M Scientific Corporation Model 500 gas chromatograph. Separations and analyses were carried out on a butane diol succinate column unless otherwise stated.

All vacuum pyrolysis experiments were performed using a pyrolysis tube (12 in. × 1 in.) made from vycor glass and filled with vycor chips. The pyrolysis tube was heated with a Sola Basic Industries Linberg Hevi-Duty Model 55035-A tube furnace, and the pyrolysis temperatures reported are those recorded by the Platinel II thermocouple. The temperature being read is that between the pyrolysis tube and the heating element, thus the actual temperature inside the pyrolysis tube is probably slightly lower. The vacuum for the pyrolysis apparatus was created by a Consolidated Vacuum Corporation Type VMF oil diffusion pump backed by a Welch Duo-Seal vacuum pump. The samples were sublimed through the pyrolysis tube by placing the tube containing the sample inside an aluminum oven wrapped with a Glas-Col heating tape. Oven temperatures were recorded on a 150° Fisher thermometer inserted in a hole drilled in the wall of the oven. Pyrolysis products were trapped in a U-tube cooled in liquid nitrogen.

Preparations

β-Nitrostyrene (7)

The procedure of Worral (61) was used to prepare β-nitrostyrene 7: mp $55\text{-}56^\circ$ (lit. (61) mp $57\text{-}58^\circ$).

β-Methyl-β-nitrostyrene (8)

An adaptation of the Heinzelman procedure (62) was used to prepare β-methyl-β-nitrostyrene 8 by the n-butylamine catalyzed condensation of benzaldehyde and nitroethane in toluene using a Dean and Stark apparatus to remove water: mp 64° (lit. (63)

mp 65°).

o-Deuterio-β-methyl-β-nitrostyrene (9)

The Grignard reagent prepared from 100 g o-bromotoluene, and 15.2 g magnesium in anhydrous ethyl ether was hydrolyzed with 25 ml of deuterium oxide according to the procedure of Weldon and Wilson (64) to give 6.15 g of o-deuteriotoluene: bp 110°/760 mm. Etard oxidation of 6.15 g o-deuteriotoluene according to the procedure of Wheeler (65) gave 0.84 g o-deuteriobenzaldehyde: bp 25°/1 mm. The condensation of 0.84 g o-deuteriobenzaldehyde and 1.2 g nitroethane was effected by the procedure of Heinzelman (62) as previously described to give 0.93 g of o-deuterio-β-methyl-β-nitrostyrene 9: mp 63-63.5°; ir (CCl_4) 6.0 μ (C=C), 6.55 μ (NO_2) and 7.55 μ (NO_2). Low voltage mass spectrometry showed the material to be: 15.4% d_0 and 84.6% d_1.

p-Deuterio-β-methyl-β-nitrostyrene (10)

The procedure described for the preparation of 9 was utilized in the preparation of p-deuterio-β-methyl-β-nitrostyrene 10. The condensation of 1.27 g p-deuteriobenzaldehyde and 1.20 g nitroethane gave 1.27 g of the desired compound: mp 64°; ir (CCl_4) 6.02 μ (C=C), 6.57 μ (NO_2) and 7.55 μ (NO_2). Low voltage mass spectrometry indicated the following deuterium incorporation: 6.75% d_0 and 93.25% d_1.

2,4,6-Trideuterio-β-methyl-β-nitrostyrene (11)

The procedure of Ronayne, Williams, and Bowie (66) was used to prepare 0.64 g of 2,4,6-trideuteriobenzaldehyde which was condensed with 1.0 g of nitroethane according to the procedure of Heinzelman (62) to give 0.25 g of 2,4,6-trideuterio-β-methyl-β-nitrostyrene 11: mp 62.5°; ir (CCl_4) 6.02 μ (C=C), 6.57 μ (NO_2), and 7.55 μ (NO_2). Low voltage mass spectrometry indicated the following deuterium incorporation: 3.6% d_2 and 96.4% d_3.

α-Deuterio-β-methyl-β-nitrostyrene (12)

The method of Wiberg (67) was used to prepare 1.25 g of α-deuteriobenzaldehyde which was condensed with 1.5 g nitroethane using the procedure of Heinzelman (62) to yield 0.97 g of α-deuterio-β-methyl-β-nitrostyrene 12: mp 63.5-64°; ir (CCl_4) 6.02 μ (C=C), 6.57 μ (NO_2) and 7.55 μ (NO_2). Low voltage mass spectrometry showed the following deuterium incorporation: 1.2% d_0 and 98.8% d_1.

α-C^{13}-β-methyl-β-nitrostyrene (13)

Labeled α-carbon-13 benzoic acid (100 mg) was reduced with lithium aluminum hydride in the conventional manner to give 91.7 mg of benzyl alcohol which was oxidized to benzaldehyde by heating for 10 minutes with a solution of 520 mg of cerric ammonium nitrate in 4 ml of 50% acetic acid according to the procedure of Trahanovsky and Young (68). The resulting solution was extracted with 35 ml of ether and the ether solution was washed with 1.5 N potassium hydroxide until neutral. The separated ether solution was dried over anhydrous magnesium sulfate, filtered, and concentrated at reduced pressure to give crude α-C^{13}-benzaldehyde. The benzaldehyde was distilled (25°/1 mm), and washed from the receiver with 1.5 ml of toluene. The toluene solution of benzaldehyde was allowed to react with 130 mg of freshly distilled nitroethane according to the procedure of Heinzelman (62). The toluene was evaporated from the resulting solution at reduced pressure to give a red oil. Ir (CCl_4) absorptions at 6.02 μ (C=C), 6.57 μ (NO_2) and 7.55 μ (NO_2) were indicative of the desired compound. The compound was separated on an alumina thin layer plate developed with ethyl alcohol. The band containing the α-C^{13}-β-methyl-β-nitrostyrene 13 was scraped from the thin layer plate, and was used as such to obtain a mass spectrum. Low voltage mass spectrometry indicated the following label incorporation: 49% C^{12} and 51% C^{13}.

2-Nitroindene (15)

This compound was prepared according to the procedure of Wallach and Beschke (69). The steam distilled product was recrystallized from glacial acetic acid to give light yellow needles: mp 144° (lit. (69) mp 141°).

1-(α-Naphthyl)-2-nitropropene (16)

The desired compound was prepared by a modification of the McCarthy and Kahl (70) procedure. A solution of 31.2 g 1-napthaldehyde (Aldrich), 15.0 g nitroethane, 1 ml n-butylamine and 20 ml of absolute ethyl alcohol was kept in the dark at room temperature for two weeks. The red bottom layer was then separated and concentrated at reduced pressure to give a red oil. Dissolution of the oil in ethyl alcohol and cooling gave dark brown crystals. These crystals were taken up in 200 ml of hot ethyl alcohol and treated with charcoal to give light yellow needles. Several more recrystallizations from ethanol gave 28.7 g of these light yellow needles: mp 65-67^0; ir (CCl_4) 6.02 μ (C=C), 6.6 μ (NO_2), and 7.55 μ (NO_2); nmr (CCl_4) δ 2.3 (d, 3, CH_3), 7.3-7.9 (m, 7, H-C=C and $C_{10}H_6$), and 8.5 (s, 1, peri H).

Anal. Calcd for $C_{13}H_{11}NO_2$: C, 72.90; H, 5.21; N, 6.58. Found: C, 72.88; H, 5.30; N, 6.64.

o-Chloro-β-methyl-β-nitrostyrene (17)

The procedure of Gilsdorf and Nord (71) was used to prepare o-chloro-β-methyl-β-nitrostyrene 17: mp 44^0 (lit. (71) mp 45^0).

1,1-Diphenyl-2-nitroethylene (19)

This compound was prepared from 1,1-diphenylethylene (Aldrich) according to the procedure of Govindachari, Pai, and

Rao (72). Light yellow needles were obtained after recrystallization: mp 86.5° (lit. (72) mp 87°).

1,1-Diphenylpropene

The procedure of Adkins and Zartman (73) for the preparation of triphenylethylene was adapted to the preparation of 1,1-diphenylethylene from benzophenone and bromoethane. After dehydration of the diphenylethylcarbinol, the resulting olefin was distilled at aspirator pressure: bp 150-160°. The olefin was recrystallized from ethanol to give colorless crystals: mp 48° (lit. (74) mp 52°).

1,1-Diphenyl-2-nitropropene (20)

The desired compound was prepared from 1,1-diphenylpropene using the procedure for 1,1-diphenyl-2-nitroethylene (72). The oil resulting from decomposition of 5.1 g of nitrosite was vacuum distilled (139-142°/1 mm) to give 1.85 g of thick yellow oil. The oil was dissolved in ethanol and cooled in an acetone/dry-ice bath to yield light yellow crystals. Several subsequent recrystallizations from ethanol gave light yellow crystals: mp 49-50°; ir (CCl_4) 6.01 μ (C=C), 6.60 μ (NO_2), and 7.4 μ (NO_2); nmr (CCl_4) δ 2.3 (s, CH_3) and 7.0-7.4 (m, C_6H_5).

Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.32; H, 5.44; N, 5.86. Found: C, 75.39 H, 5.47; N, 5.79

Triphenylethylene

The procedure of Adkins and Zartman (73) was used to prepare triphenylethylene. After vacuum distillation of the product (168-178°/1 mm) and recrystallization of the resulting solid from ethanol, colorless crystals were obtained: mp 68-69° (lit. (73) mp 68-69°).

Nitrotriphenylethylene (21)

This compound was prepared from triphenylethylene according to the procedure of Govindachari, Pai, and Rao (72). The product obtained by decomposition of the nitrosite was recrystallized from ethanol to give light yellow needles: mp 176-177° (lit (73) mp 178°).

α-Nitrotoluene

The impure compound (1.16 g) was prepared from 12.0 g of benzyl chloride and 17.0 g of silver nitrite according to the procedure of Hollemann (75). The crude yellow oil used in subsequent reactions had the following spectral properties: ir (CCl_4) 6.45 μ (NO_2), and 7.3 μ (NO_2); nmr (CCl_4) δ 5.25 (s, 2, CH_2), and 7.3-7.4 (s, 5, C_6H_5).

Nitrostillbene (22)

The desired compound was prepared by condensation of 1.16 g α-nitrotoluene and 1.06 g benzaldehyde according to the procedure of Heinzelman (62). The red oil obtained from this reaction was dissolved in ethanol and cooled in an ice bath to give dark brown crystals. These crystals were filtered and recrystallized several times from ethanol to give 0.15 g light yellow needles: mp 73.5-75^{0} (lit. (76) mp 75^{0}).

β-Ethyl-β-nitrostyrene (23)

The procedure of Hass, Susie and Heider (63) was used to prepare β-ethyl-β-nitrostyrene 23 by condensation of benzaldehyde and 1-nitropropane (Aldrich). The product was distilled at 156-160^{0}/20 mm to give a yellow oil. Redistillation gave a light yellow oil: bp 124-126^{0}/1 mm (lit. (63) bp 125-129^{0}/10 mm); ir (CCl_4) 6.04 μ (C=C), 6.67 μ (NO_2), and 7.55 μ (NO_2).

1-(3-Pyridyl)-2-nitropropene (24)

The method of Burger, Stein, and Clements (77) was used to prepare 1-(3-pyridyl)-2-nitropropene from nicotinaldehyde (Aldrich) and nitroethane. The compound after recrystallization from ethanol gave light yellow crystals: mp 66.5-67.5^{0} (lit. (77) mp 67.5-68^{0}).

1-(2-Thienyl)-2-nitroethylene (25)

The procedure of King and Nord (78) was used to prepare 1-(2-thienyl)-2-nitroethylene 25 from 2-thiophenecarboxaldehyde (Aldrich) and nitromethane. The product recrystallized from ethanol to give light yellow crystals: mp 79-80^{0} (lit. (78) mp 79-80^{0}).

1-(2-Thienyl)-2-nitropropene (26)

The method of King and Nord (78) was used to prepare 1-(2-thienyl)-2-nitropropene 26 from 2-thiophenecarboxaldehyde (Aldrich) and nitroethane. The product recrystallized from ethanol to give yellow crystals: mp 67-68^{0} (lit. (78) mp 68.5^{0}).

1-(2-N-Methylpyrrole)-2-nitropropene (27)

The desired compound was prepared from 10 g N-methylpyrrole-2-carboxaldehyde (Aldrich), 7.5 g nitroethane, 2 ml of n-butylamine, and 10 ml of toluene using the procedure of Heinzelman (62). The reaction was allowed to proceed for 10 hours, and then the toluene was evaporated at reduced pressure to give a dark oil. Dissolution of the oil in ethanol, and cooling in an acetone/dry-ice bath induced crystallization. The crystals were filtered and recrystallized from ethanol to give 3.5 g of 1-(2-N-methylpyrrole)-2-nitropropene 27 as bright yellow crystals: mp 68.5-69.5^{0}; ir (CCl_4) 6.08 μ (C=C), 6.65 μ (NO_2) and 7.75 μ (NO_2); nmr (CCl_4) δ 2.4 (s, 3, C-CH_3), 3.8 (s, 3, N-CH_3), 6.1-6.9 (3m, 3, C_4H_3N), and 8.0 (s, 1, H-C=C).

Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.83; H, 6.02; N, 16.86. Found: C, 57.93; H, 6.05; N, 16.72.

1-(2-Furyl)-2-nitropropene (28)

This compound was prepared from furfural and nitroethane according to the procedure of McCarthy and Kahl (70). The product after recrystallization from ethanol was light yellow needles: mp 49-50^{0} (lit. (70) mp 50-51^{0}).

1-Nitro-4-phenylbutadiene (29)

The procedure of Kochetkov, and Dudykina (79) was used to prepare this compound from cinnamaldehyde (Eastman Kodak) and nitromethane. The product was recrystallized from methanol to give light yellow crystals: mp 45-46^{0} (lit. (79) mp 45-46^{0}).

3-Methyl-1-nitro-4-phenylbutadiene (30)

The procedure of Kochetkov and Dudykina (79) for 29 was adapted to the preparation of this compound. The condensation of 22.0 g α-methylcinnamaldehyde (Aldrich) and 9.3 g nitromethane gave 0.65 g of the desired compound. The product recrystallized from methanol as light yellow needles: mp 85-86^{0}; ir (CCl_4) 6.17 μ (C=C), 6.62 μ (NO_2) and 7.48 μ (NO_2): nmr (CCl_4) δ 2.1 (d, 3, CH_3), 7.3 (s, 5, C_6H_5), and 6.95-7.9 (3m, 3, H-C=C).

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.84; H, 5.81; N, 7.41. Found: C, 69.82; H, 5.69; N, 7.34.

1,1-Diphenyl-4-nitrobutadiene (31)

To a solution of 5.0 g 3,3-diphenylacrolein (Eastman Kodak), 1.46 g nitromethane and 21 ml of absolute methanol at 0^{0} was added slowly 1.02 g sodium hydroxide in 10 ml of absolute methanol while holding the reaction temperature below 5^{0}. This reaction mixture was kept at 0^{0} for one hour, poured onto

100 g of ice in 300 ml of water and 2.04 ml of concentrated hydrochloric acid was added with stirring. After addition of another 250 ml of water, the resulting solution was extracted twice with 250 ml portions of ethyl ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated at reduced pressure to give a yellow oil. Dissolution of the oil in ethanol caused crystallization. The crystals were filtered, and recrystallized from ethanol to give 1.6 g of yellow crystals: mp 85-86°; ir ($CHCl_3$) 6.20 μ (C=C), 6.79 μ (NO_2), and 7.55 μ (NO_2); nmr ($CDCl_3$) δ 6.65-6.90 (d, 1), and 7.1-7.9 (m, 12).

Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48, H, 5.23. Found: C, 76.48; H, 5.17.

4-Methyl-2-nitropent-2-ene (36)

This compound was prepared from butyraldehyde and nitroethane according to the procedure of Hass, Susie, and Heider (63). The product was vacuum distilled to give a light yellow oil: bp 26-27°/0.8 mm (lit. (63) bp 64°/10 mm); ir (CCl_4) 5.97 μ (C=C), 6.6 μ (NO_2), and 7.50 μ (NO_2); nmr (CCl_4) δ 1.15 (d, 6, $(CH_3)_2CH-$), 2.2 (d, 3, $CH_3-C=C$), 2.4-2.8 (m, 1, $(CH_3)_2CH-$), and 6.9 (d, 1, H-C=C).

1-Nitro-4-(o-nitrophenyl)-butadiene (32)

The procedure described for 31 was used in the preparation of 1-nitro-4-(o-nitrophenyl)-butadiene 32. The condensation of

13.5 g o-nitrocinnamaldehyde (Aldrich) and 4.65 g nitromethane gave 1.8 g of light yellow crystals: mp 104-105°; ir ($CHCl_3$) 6.12 μ (C=C), 6.58 μ (NO_2), and 7.45 μ (NO_2); nmr ($CDCl_3$) δ 6.5-8.2 (m, 8).

Anal. Calcd for $C_{10}H_8N_2O_4$: C, 54.55; H, 3.66. Found: C, 54.52; H, 3.66.

α-Deuterio-1-nitro-4-phenylbutadiene (33)

The procedure of Wiberg (67) was used to prepare 5.58 g of α-deuteriobenzaldehyde. The α-deuteriobenzaldehyde was allowed to react with 6.27 g of malonic acid according to the procedure described by Murray and Williams (80) to give 5.0 g of α-deuteriocinnamic acid: mp 133°. The acid chloride was prepared by heating 3.22 ml of thionyl chloride and the α-deuteriocinnamic acid at reflux for 1/2 hour. The reaction mixture was vacuum distilled to give 5.1 g of acid chloride (bp 76°/0.3 mm), which was reduced to α-deuteriocinnamaldehyde with tritertiary-butoxy lithium aluminum hydride according to the procedure of Brown, and Rao (81). Distillation gave 2.1 g of α-deuteriocinnamaldehyde: bp 80°/0.8 mm. The procedure of Kochetkov, and Dudykina (79) was used to prepare 0.15 g of α-deuterio-1-nitro-4-phenylbutadiene 33 by the condensation of 0.884 g nitromethane and 1.9 g α-deuteriocinnamaldehyde. The product recrystallized from ethanol gave light yellow crystals: mp 43-44°. Low voltage mass spectrometry indicated the following label incorporation: 2.5% d_0 and 97.5% d_1.

β-Deuterio-1-nitro-4-phenylbutadiene (34)

The procedure of Shriner and Smith (82) was used to prepare 10.0 g of malonic acid d_4. The malonic acid was reacted with 8.6 g of benzaldehyde according to the procedure of Murray and Williams (80) to give 7.8 g of β-deuteriocinnamic acid: mp 133°. The labeled cinnamic acid was converted to 1.88 g of β-deuteriocinnamaldehyde by the same sequence of reactions described in the preparation of 33. The procedure of Kochetkov and Dudykina (79) was used to prepare β-deuterio-1-nitro-4-phenylbutadiene 34 from 1.68 g of β-deuteriocinnamaldehyde and 0.78 g nitromethane. The yellow oil from this reaction was chromatographed on a silica gel (Baker) column with (1:1) ethyl acetate/petroleum ether as the eluting solvent. Evaporation of solvent at reduced pressure gave a light yellow oil which crystallized upon dissolution in ethanol and cooling. The crystals were filtered and recrystallized from ethanol to give 0.041 g of product: mp 45-45.5°. Low voltage mass spectrometry indicated the following label incorporation: 17.95% d_0, 81.0% d_1, 0.73% d_2, and 0.32% d_3.

Tritertiary-butoxy lithium aluminum deuteride

This compound was prepared from lithium aluminum deuteride and tertiary-butyl alcohol according to the procedure of Brown and Rao (81).

γ-Deuterio-1-nitro-4-phenylbutadiene (35)

A solution of 7.0 g of cinnamic acid (Matheson Coleman & Bell) and 4.5 ml of thionyl chloride was heated at reflux for 1/2 hour. The reaction mixture was then vacuum distilled to give 5.65 g of cinnamoyl chloride: bp 76-78°/0.6 mm. The acid chloride was reduced to γ-deuteriocinnamaldehyde with tri-teritary-butoxy lithium aluminum deuteride by the procedure of Brown and Rao (81). Distillation gave 1.56 g of the labeled aldehyde (bp 78-82°/0.8 mm), 1.38 g of which was reacted with 0.643 g of nitromethane according to the procedure of Kochetkov and Dudykina (79) to give γ-deuterio-1-nitro-4-phenylbutadiene 35. The yellow oil from this reaction was treated as described for 34 to give 0.06 g of light yellow crystals: mp 43-44°. Low voltage mass spectrometry indicated the following label incorporation: 2.58% d_0, 96.3% d_1, 0.86% d_2, and 0.26% d_3.

Pyrolysis of β-nitrostyrene (7)

The pyrolysis of β-nitrostyrene 7 at 400°/0.001 mm with a head temperature of 50-52° resulted in the recovery of starting material as shown by nmr. The pyrolysate of 7 at 600°/0.005 mm with a head temperature of 50-55° was washed from the cold trap with several ml of carbon tetrachloride. This solution became warm and then hot as a white amorphous precipitate formed. The precipitate isolated by filtration exhibited characteristics of a polymer, and turned dark red upon prolonged exposure to air. Nmr analysis of the filtrate revealed the presence of benzaldehyde: nmr (CCl_4) δ 7.2-7.8 (m, 5, C_6H_5), and 9.92 (s, 1, HCO); 2,4-DNP mp 237° (lit. (83) mp 237°).

Pyrolysis of 1,1-diphenyl-2-nitroethylene (19)

The pyrolysis of 1,1-diphenyl-2-nitroethylene 19 was effected at 600°/0.001 mm with a head temperature of 75-78°. The pyrolysate was washed from the cold trap with carbon tetrachloride and gave the same white precipitate observed for 7. Nmr analysis of the filtrate revealed the presence of benzophenone: nmr (CCl_4) δ 7.2-7.8 (m, C_6H_5). The pyrolysate obtained from the pyrolysis of 19 at 700°/0.002 mm with a head temperature of 78-80° was identical with that at 600°.

Pyrolysis of β-methyl-β-nitrostyrene (8)

The pyrolysis of β-methyl-β-nitrostyrene was effected at 600°/0.001 mm with a head temperature of 50-55°. Analysis of the pyrolysate by vpc indicated the presence of at least six components, and the following peaks were observed in the mass spectrum: (70 ev) *m/e* 106, 105, 78, 77, 76, 57, 52, 51, 50, 41, and 39. The pyrolysate was shown to consist of acetonitrile, benzaldehyde, benzene, methylisocyanate, and methylphenylacetylene by comparison of vpc retention times and spectral data with authentic samples. The following spectral data was recorded for the pyrolysate: ir (CCl_4) 4.25 μ -4.55 μ (broad band), and 5.85 μ (CO); nmr (CCl_4) δ 1.9 (s, CH_3-CN), 2.02 (s, $C_6H_5CCCH_3$), 2.1 (s, unknown), 3.0 (s, CH_3NCO), 7.15-

7.3 (m, $C_6H_5CCCH_3$), 7.27 (s, C_6H_6), 7.4-7.8 (m, C_6H_5CHO), and 9.92 (s, C_6H_5CHO). A sixth minor product was not identified. The product ratios were determined by nmr. The pyrolysis of <u>8</u> at 500°/0.250 mm with a head temperature of 60-70° was shown to give starting material and the aforementioned products by nmr. Nmr analysis of the pyrolysate of <u>8</u> at 400°/0.100 mm with a head temperature of 65-70° revealed the presence of starting material only.

<u>Pyrolysis of 1-(α-naphthyl)-2-nitropropene</u> (<u>16</u>)

The pyrolysis of 1-(α-naphthyl)-2-nitropropene <u>16</u> was accomplished at 600°/0.001 mm with a head temperature of 52-53°. Nmr analysis of the pyrolysate indicated the presence of acetonitrile, methylisocyanate, and naphthaldehyde. Vpc analysis of the pyrolysate (BDS/175°) established the presence of naphthalene. Vpc data also suggested the presence of methyl-α-naphthylacetylene which was confirmed by an ir absorption at 4.5 μ (C≡C) in the absence of acetonitrile, and methylisocyanate. A minor component of the pyrolysate was not identified. The following nmr data was obtained for the pyrolysate: nmr (CCl_4) δ 1.9 (s, CH_3CN), 2.15 (s, $C_{10}H_7CCCH_3$) 2.2 (s, unknown), 7.2-8.2 (m, $C_{10}H_7CHO$ and $C_{10}H_8$), and 10.33 (s, $C_{10}H_7CHO$).

<u>Pyrolysis of 1,1-diphenyl-2-nitropropene</u> (<u>20</u>)

The pyrolysis of 1,1-diphenyl-2-nitropropene <u>20</u> was carried out at 700°/0.001 mm with a head temperature of 50-51°.

Nmr analysis of the pyrolysate indicated the presence of acetonitrile, benzene, benzophenone, methylisocyanate, and an unidentified product: nmr (CCl_4) δ 1.9 (s, CH_3CN), 2.1 (s, unknown), 3.0 (s, CH_3NCO), 7.28 (s, C_6H_6), and 7.2-7.9 (m, $(C_5H_6)_2CO$).

Pyrolysis of nitrotriphenylethylene (21)

The pyrolysis of nitrotriphenylethylene was accomplished at 600°/0.001 mm with a head temperature of 101-105°. Vpc analysis of the pyrolysate demonstrated the presence of benzene, benzonitrile, benzophenone, and phenylisocyanate. The presence of benzonitrile, phenylisocyanate, and benzophenone was further confirmed by ir data: ir (CCl_4) 4.35 μ - 4.60 μ (nitrile; isocyanate), and 6.02 μ (CO). A considerable portion of the pyrolysate condensed out before reaching the cold trap. Analysis of this material by mass spectrometry revealed the presence of 2,3-diphenylbenzofuran (m/e 270) and a $C_{20}H_{14}$ hydrocarbon (m/e 254). Although the m/e 254 ion can arise in part by the loss of oxygen from 2,3-diphenylbenzofuran, comparison with the mass spectrum of authentic 2,3-diphenylbenzofuran indicates that the m/e 254 ion is too intense to be formed solely in the manner.

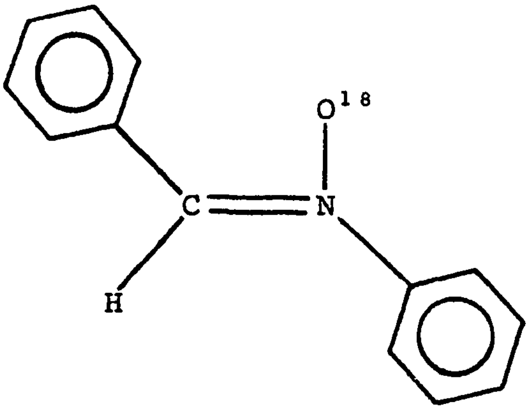
2,3-Diphenylbenzofuran

The procedure of Wacek and Daubner (84) was used to prepare 2,3-diphenylbenzofuran. The product was purified by chromatography on silica gel (Baker) with petroleum ether as the eluting solvent. Evaporation of the petroleum ether at reduced pressure gave light white crystals: mp 123-124^{o} (lit. (84) mp 122-124^{o}).

PART II: MASS SPECTRA OF NITRONES

HISTORICAL

The mass spectra of many compounds structurally related to nitrones have been investigated including: pyridine N-oxides (85), quinoline N-oxides (86, 87, 88), phenazine N-oxides (89), and aromatic azoxy compounds (90, 91). Nitrones, however, have received little attention until quite recently. The first report on the mass spectra of nitrones was published by Russian workers (92), who examined the mass spectra of five diaryl and arylalkylnitrones. From data obtained from α,N-diphenylnitrone 38 labeled with oxygen-eighteen, it was proposed that nitrones rearrange to oxaziridines under mass spectrometric conditions in analogy to the known photochemical reaction. The oxaziridine intermediate was postulated to



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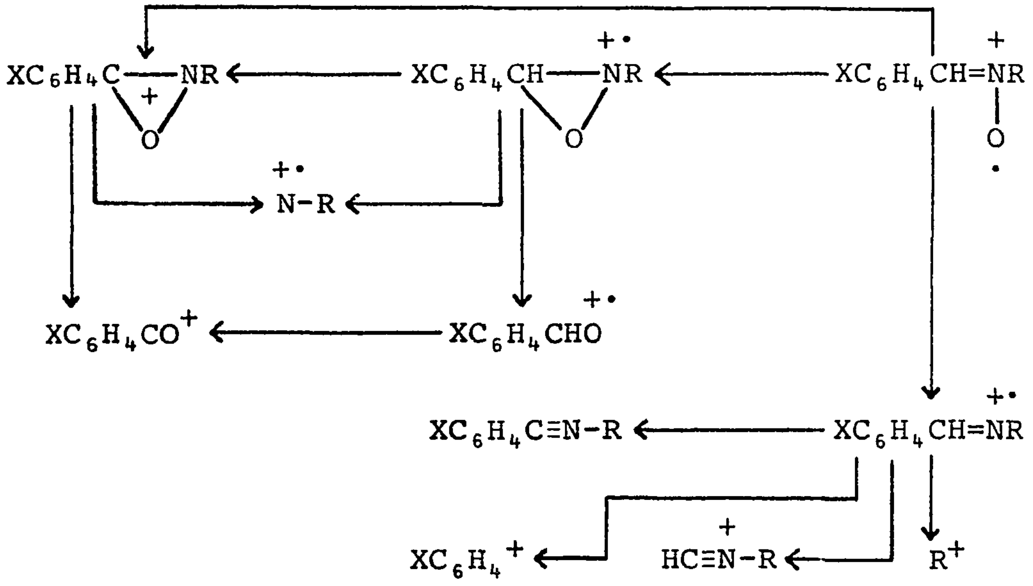
fragment as depicted in Scheme 58 to give many of the intense ions observed in the mass spectra of nitrones. The high intensity (base peak) of the $RN^{+\cdot}$ ion, when R is phenyl, led the authors to propose a ring expansion to an azatropylium ion radical. Comparison with the mass spectrum of benzanilide suggested that the oxaziridine does not rearrange to an aroylamide ion prior to fragmentation. Other reported fragmentations, such as the loss of oxygen from the molecular ion, are indicated in Scheme 58.

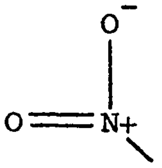


Scheme 58

The main contribution of this work was evidence that nitrones rearrange to oxaziridines under mass spectrometric conditions. Unfortunately, the authors ignored a number of interesting skeletal rearrangement processes and many of the postulated fragmentation pathways in Scheme 58 have been refuted by more recent publications (93, 94, 95, 96). In this regard our work (93, 94) and that of Cooks *et al*. (95, 96) on α,N-diarylnitrones is of considerable importance. Due to the similarity of results and the simultaneous publication dates the work of Cooks *et al*. will not be discussed here, but will be alluded to in a discussion of our own work. Recently a report on the negative ion mass spectra of nitrones has been published (97).

RESULTS AND DISCUSSION

The interesting mass spectral rearrangements observed for nitroolefins prompted an investigation of other isoelectric functional groups in an attempt to determine whether parallels in fragmentation exist. Of the several functional groups isoelectric with the nitro group 39, the azoxy 40 and nitrone 41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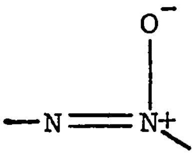
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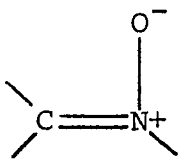
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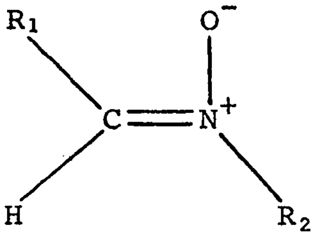
functions are most amenable to study. The nitrone functional group was selected for study since the spectra of aromatic azoxy compounds (90, 91) had already been studied and shown to undergo several skeletal rearrangements, one of which lead to the loss of CO from the molecular ion.

Mass Spectra of Diaryl
and Arylheteroaromatic Nitrones

The nitrones 42-56 were prepared and their mass spectra recorded. The nitrones all gave clearly discernable molecular ions as well as intense M^+-1 ions. The mass spectrum of the parent compound, α,N-diphenylnitrone 42, is shown in Figure 33



	R_1	R_2
42	C_6H_5	C_6H_5
43	p-(CN)C_6H_4	C_6H_5
44	p-$CH_3OC_6H_4$	C_6H_5
45	p-HOC_6H_4	C_6H_5
46	p-(NO_2)C_6H_4	C_6H_5
47	o-HOC_6H_4	C_6H_5
48	Mesityl	C_6H_5
49	C_6F_5	C_6H_5
50	C_6H_5	o-$CH_3C_6H_4$
51	C_6H_5	p-$CH_3C_6H_4$
52	1-Naphthyl	C_6H_5
53	1-Naphthyl	o-$CH_3C_6H_4$
54	9-Anthryl	C_6H_5
55	2-Thienyl	C_6H_5
56	Ferrocenyl	C_6H_5

and the main fragmentations are outlined in Scheme 59. Other nitrones fragment in a similar manner as indicated in Table 5. Several of the ions observed for 42, namely m/e 169, 168, 105,

Table 5. Mass spectra of diarylnitrones with peak heights expressed as percent of base peak

Compound	$M^{+\cdot}$	$M^{+\cdot}$-H	$M^{+\cdot}$-O	$M^{+\cdot}$-OH	$M^{+\cdot}$-CO	$M^{+\cdot}$-CHO	XC_6H_4CO	104	94	91
<u>42</u>	27.8	16.0	3.46	4.95	2.97	5.20	14.5	7.05	7.40	100
<u>43</u>	21.6	3.22	1.12	1.15	0.30	0.67	1.20	1.87	6.39	100
<u>44</u>	56.6	15.7	7.40	9.25	7.40	16.6	28.6	3.70	4.62	100
<u>45</u>	30.0	15.2	8.60	9.55	8.70	9.05	10.5	2.86	6.20	100
<u>46</u>	13.9	0.98	0.85	0.61	0.07	0.06	1.34	3.18	9.28	100
<u>47</u>	71.3	4.92	7.12	40.5	7.12	8.20	7.67	7.12	7.67	100
<u>48</u>[a]	76.5	9.17	5.43	26.1	----	----	3.48	4.78	----	17.6
<u>49</u>	72.8	4.72[b]	5.65	5.65	2.82	10.5[b]	3.77[b]	37.8	11.3	100

---

[a] Base peak corresponds to $M^{+\cdot}-CH_3$.

[b] Hydrogen has been replaced by flourine in these ions.

Table 5 (Continued)

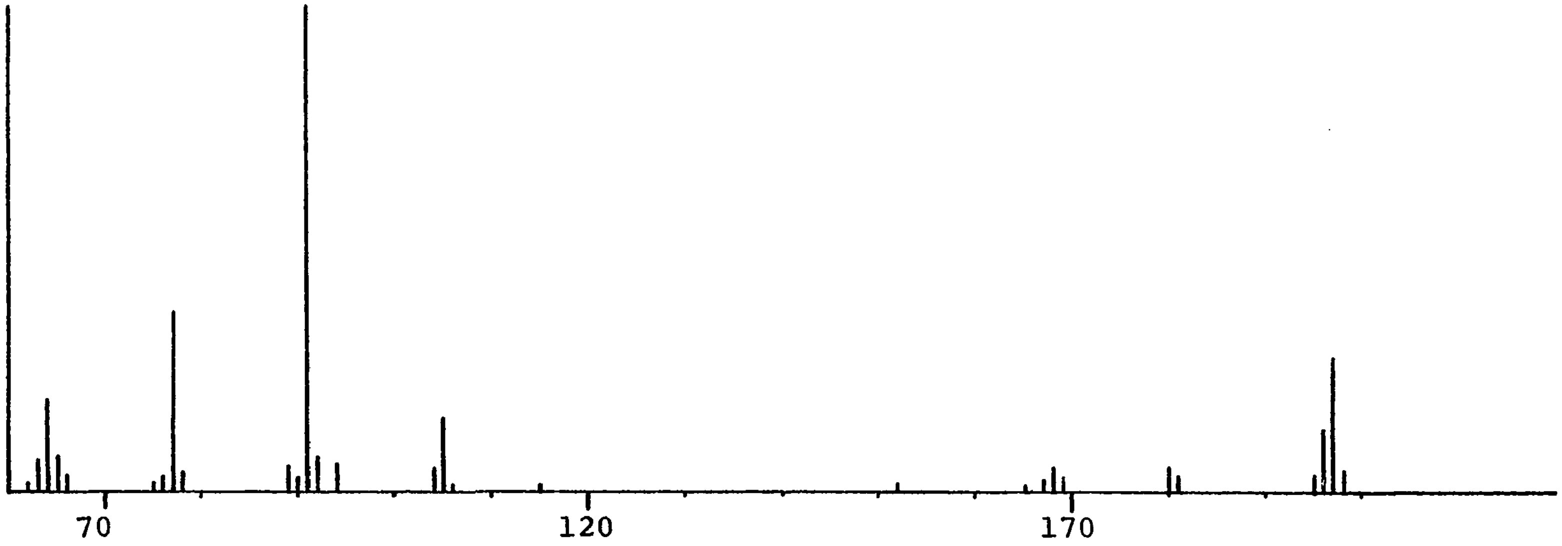
Compound	$M^{+\cdot}$	$M^{+\cdot}$-H	$M^{+\cdot}$-O	$M^{+\cdot}$-OH	$M^{+\cdot}$-CO	$M^{+\cdot}$-CHO	XC_6H_4CO	104	94	91
<u>50</u>	100	8.13	16.3	80.0	0.68	2.70	71.7[c]	11.3[d]	12.3[d]	----
<u>51</u>	13.4	2.74	1.80	3.02	----	1.00	100[c]	4.82[d]	2.16[d]	----
<u>52</u>	98.5	52.0	15.1	26.0	30.2	39.4	31.5[d]	23.3	4.10	100
<u>53</u>	100	32.3	23.9	59.4	11.5	17.8	18.8[d]	15.2[d]	7.30[d]	----
<u>54</u>	100	40.0	36.6	45.0	33.0	34.5	58.7[d]	5.00	1.5	5.00
<u>55</u>	48.3	8.52	1.28	2.56	4.76	6.80	7.45[d]	2.56	5.53	100
<u>56</u>	100	10.9	19.5	1.30	3.02	7.38	10.0[d]	6.52	6.52	19.6

[c] These ions are doublets.

[d] Analogous ions.

Figure 33. Mass spectrum α,N-diphenylnitrone 42 (top)

Figure 34. Mass spectrum α-C^{13}-α,N-diphenylnitrone 57 (bottom)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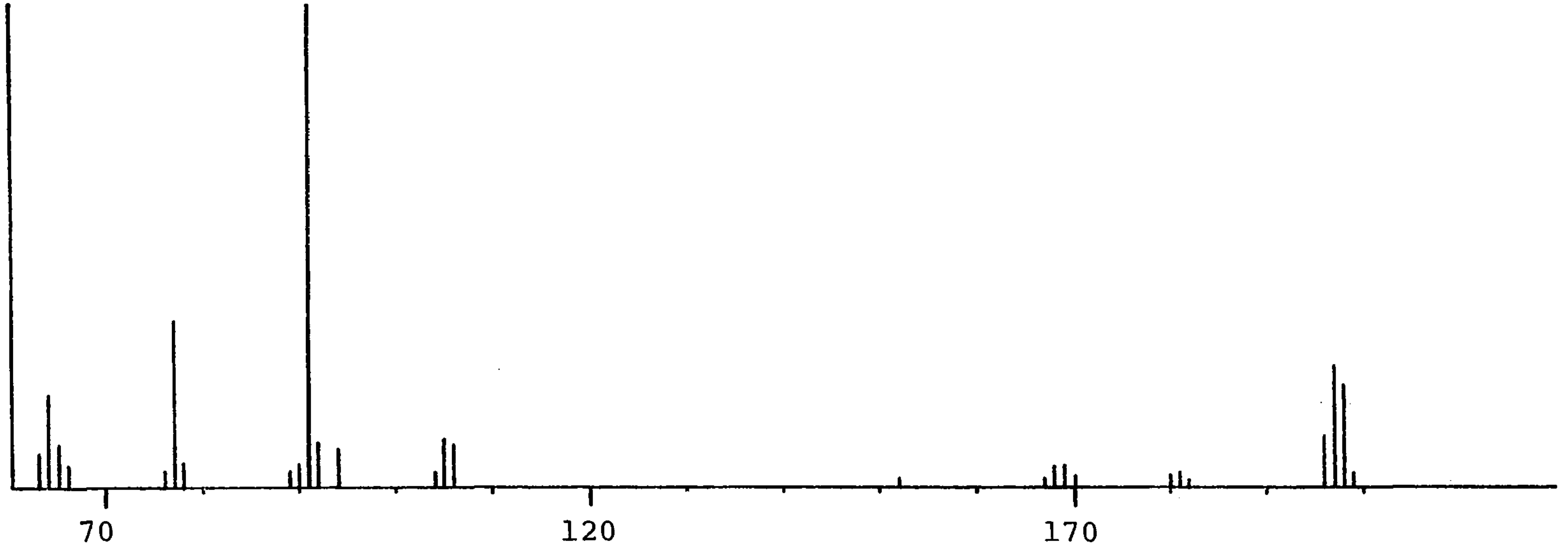
170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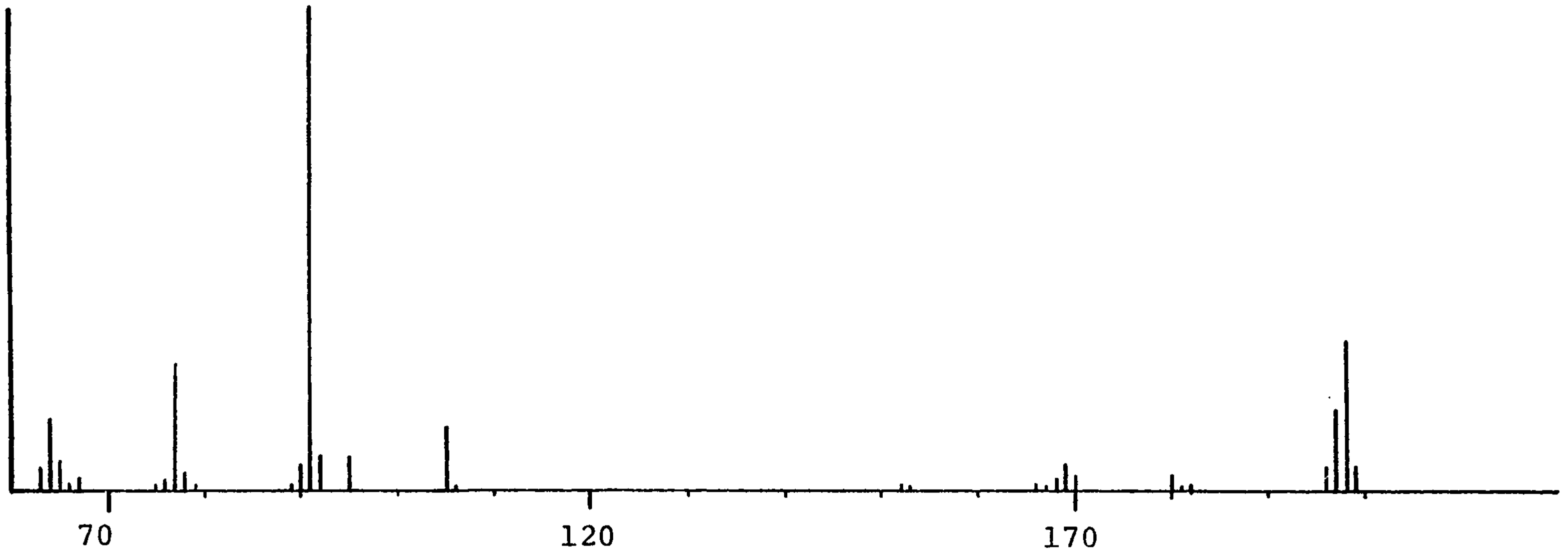
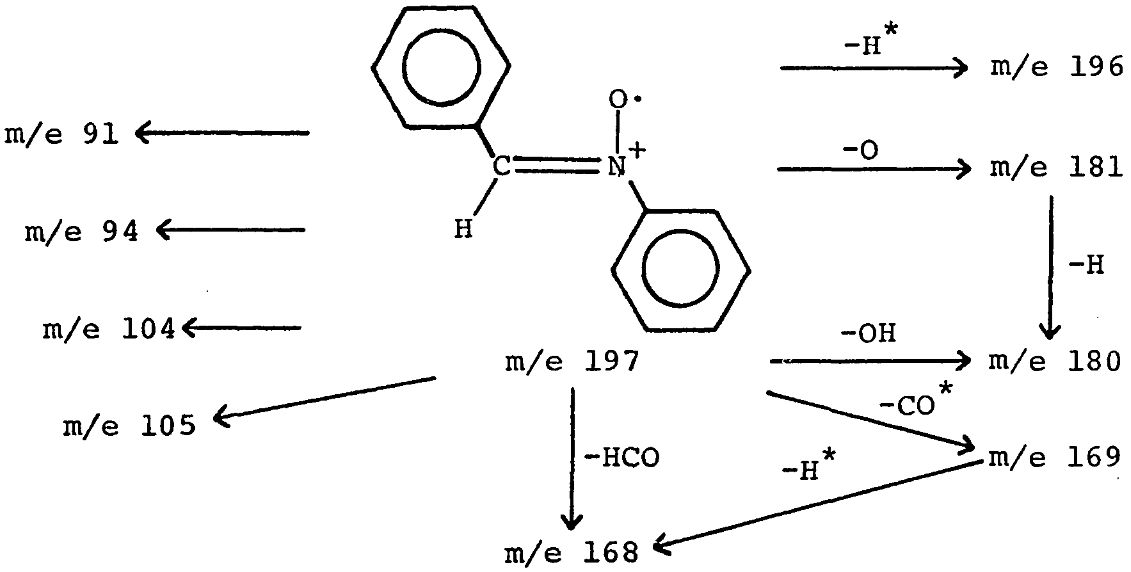
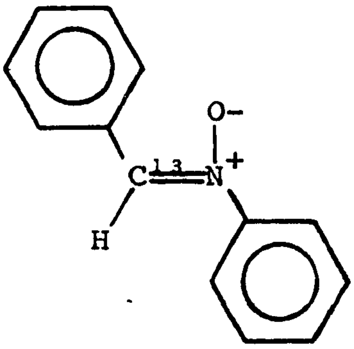


Figure 35. Mass spectrum α-D-α,N-diphenylnitrone <u>58</u>



Scheme 59

94, and 91, must result from rearrangement in the molecular ion. Labeled compounds 57 and 58 were prepared to help clarify the mechanism of formation of these and other ions.



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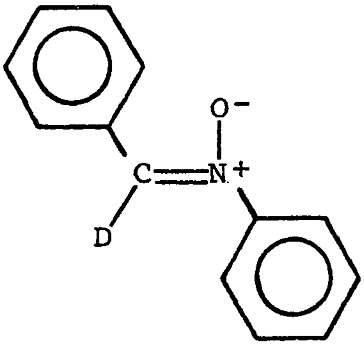

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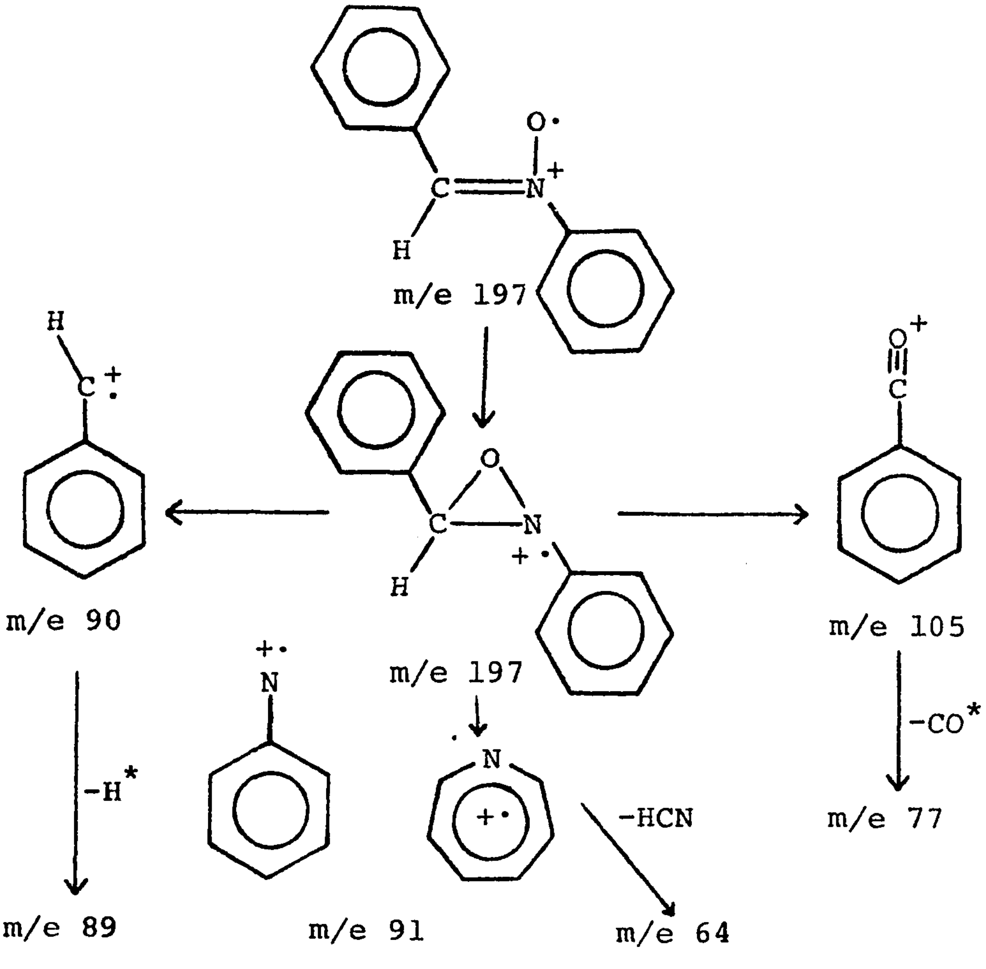
A most interesting feature of the mass spectra of nitrones is their previously noted (92) rearrangement to oxaziridines upon electron impact. The photochemical isomerization of nitrones to oxaziridines is well documented (98, 99) and since parallels in photochemical and mass spectral reactions exist (2), this result was not totally unexpected. Our independent study reinforces the idea that nitrones isomerize to oxaziridines, and demonstrates the importance of an oxaziridine in the formation of m/e 105, 91, and 90 ions in the spectrum of 42 (Scheme 59). The identification by high resolution mass spectroscopy (HRMS) of m/e 91 and m/e 105 as $C_6H_5N^{+\cdot}$ and $C_7H_5O^+$, respectively, and the shift of m/e 105 to m/e 106 for

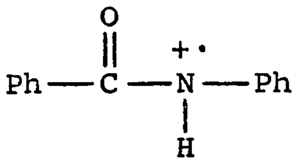


Scheme 60

57, firmly establishes the rearrangement of nitrones to oxaziridines. The oxaziridine intermediate (Scheme 60) can fragment with hydrogen migration to give the benzoyl cation (m/e 105), by loss of benzaldehyde to give m/e 91, or by loss of nitrosobenzene to give m/e 90.

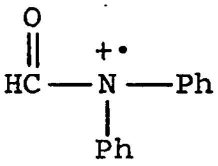
Analogs of the benzoyl cation are observed in the spectra of nitrones 42-56, but are much reduced in intensity for nitrones having a strong electron withdrawing substituent in the para position of the α-phenyl ring due to destabilization of the product ion (Table 5). The m/e 91 ion is generally the base peak for N-phenyl nitrones, suggesting ring expansion to an azatropylium ion which fragments by metastable loss of HCN. Contrary to the results of Larsen et al. (96) our high resolution mass spectrum of 42 shows no evidence for a significant $C_7H_7^+$ species at m/e 91. The ion at m/e 90 in the spectrum of 42 shifts to m/e 91 for 57 and 58 implicating an oxaziridine in its formation. The m/e 90 ion decomposes by the metastable loss of a hydrogen atom in analogy to similar ions generated from oxiranes (100).

The loss of CO and CHO (HRMS) from the molecular ion of 42 gives ions at m/e 169 and m/e 168. Rearrangement of the oxaziridine intermediate to 59 or 60 would account for the observed losses of CO and CHO. Complete label retention in the metastable loss of CO from 57 indicates, however, that 59 and 60, and therefore any oxaziridine is unimportant in their



$\mathrm{Ph}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{+\cdot}{\mathrm{N}}}-\mathrm{Ph}$

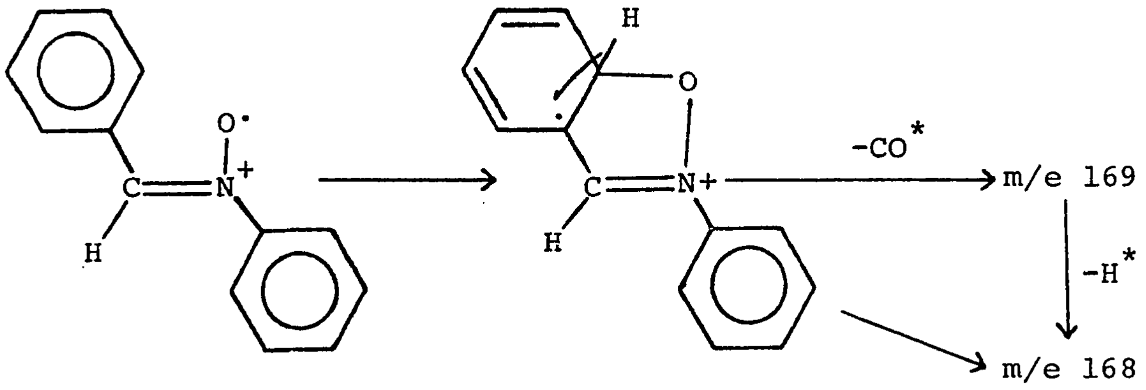
59



$\mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{Ph}}{\overset{+\cdot}{\mathrm{N}}}-\mathrm{Ph}$

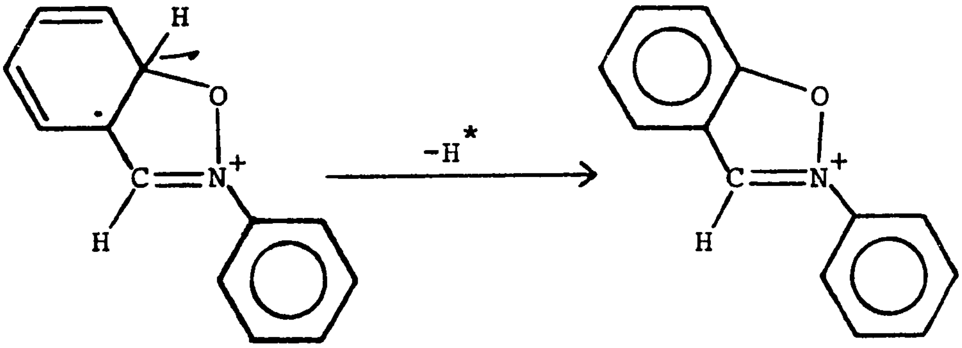
60

formation. In analogy to the observed loss of CO from azoxy compounds (90, 91), the source of carbon in this fragmentation must be the ortho-carbons of the α-phenyl ring as depicted in Scheme 61. The $M^{+\cdot}$-CHO ion can occur either by the subsequent metastable loss of hydrogen or according to Larsen et al. (96) by the sequence $M^{+\cdot}$-H-CO. The sequence $M^{+\cdot}$-CO-F for 49 and the absence of an $M^{+\cdot}$-CO ion for 48 (Table 5) agrees with the proposed mechanism.



Scheme 61

Labeled compound 58 provides pertinent information on the m/e 196, 180, 104, and 94 ions. The intense $M^{\ddagger}$-1 ion (m/e 196) shifts to m/e 197 in the spectrum of 58 (Figure 35) suggesting that the metastable loss of hydrogen occurs by an intramolecular substitution reaction on the α-phenyl ring, probably with randomization of hydrogen, as depicted in Scheme 62. This mechanism is consistent with the metastable loss of $CH_3\cdot$ from

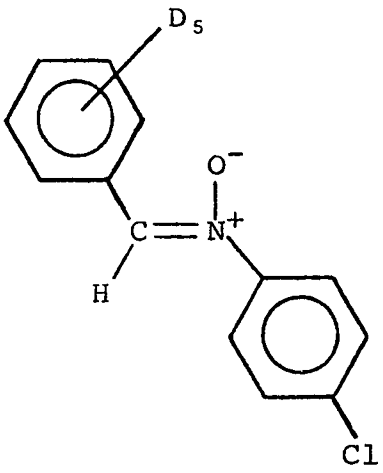


m/e 197 m/e 196

Scheme 62

48 and the metastable loss of F• from 49. The presence of an $M^{\ddagger}$-2 ion in the mass spectrum of 61 lead Larsen et al. (96) to a similar conclusion. Electron withdrawing para substituents on the α-phenyl ring reduce the intensity of this ion, while electron donating substituents have little effect (Table 5).

Hydroxyl loss from 42 must occur by the consecutive loss of oxygen and the α-hydrogen as illustrated in Scheme 63, since m/e 180 does not shift to m/e 181 for 58. This mechanism



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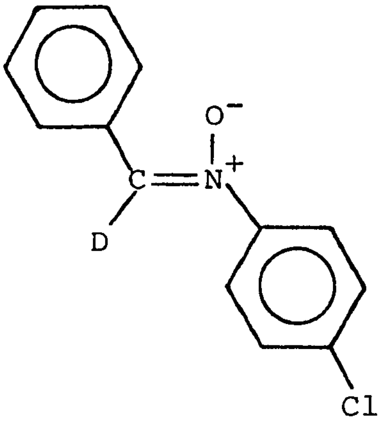
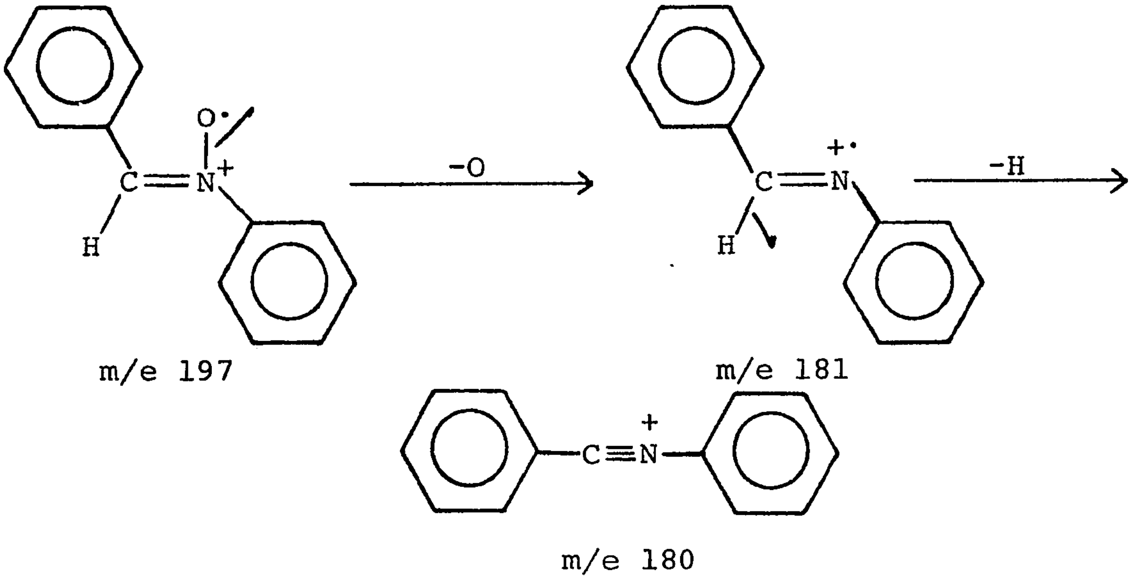


62

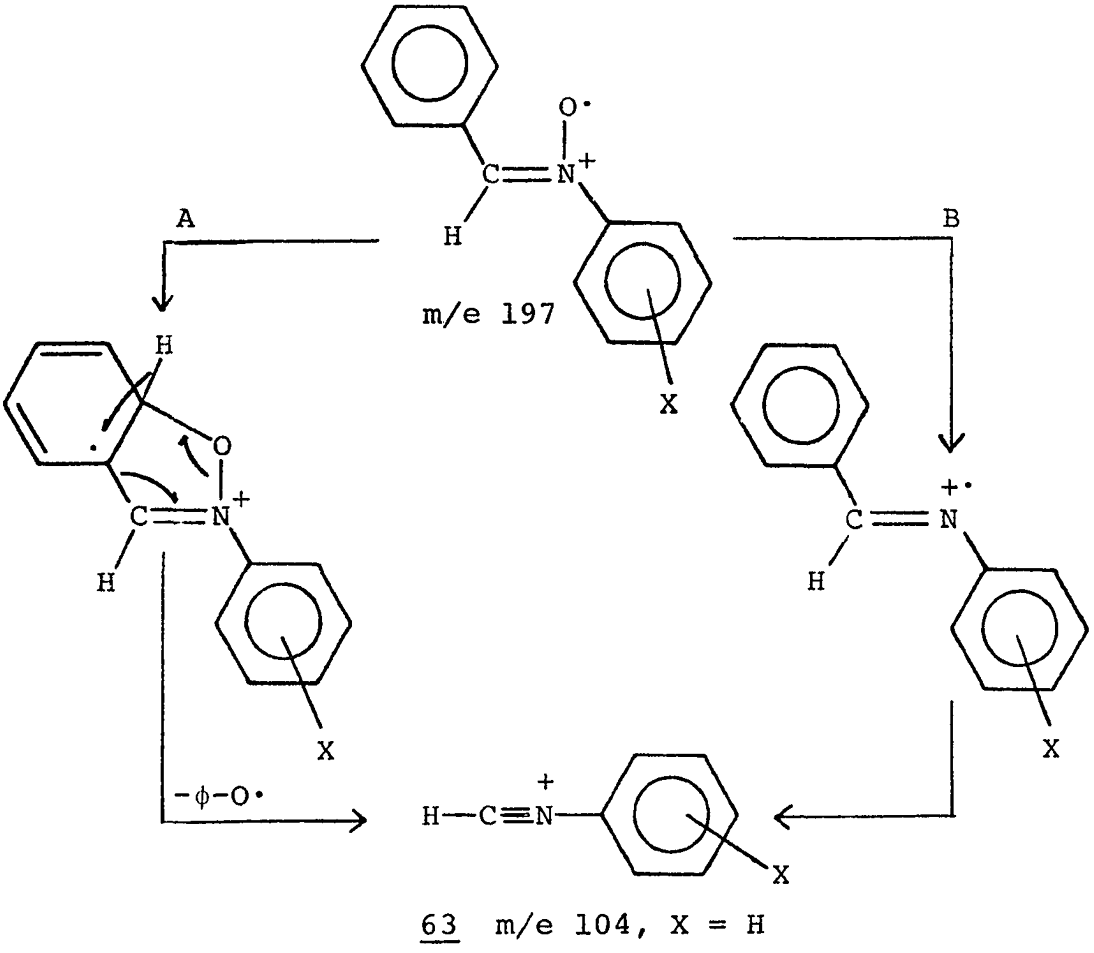
accounts for slightly more than 85% of the observed OH loss with the remainder probably occurring by hydrogen loss from the α-phenyl ring as must occur for the observed loss of OH in triarylnitrones (see next section). Larsen *et al.* (96)



Scheme 63

investigated the mass spectrum of 62, and concluded that OH loss occurs exclusively by loss of oxygen and the α-hydrogen.

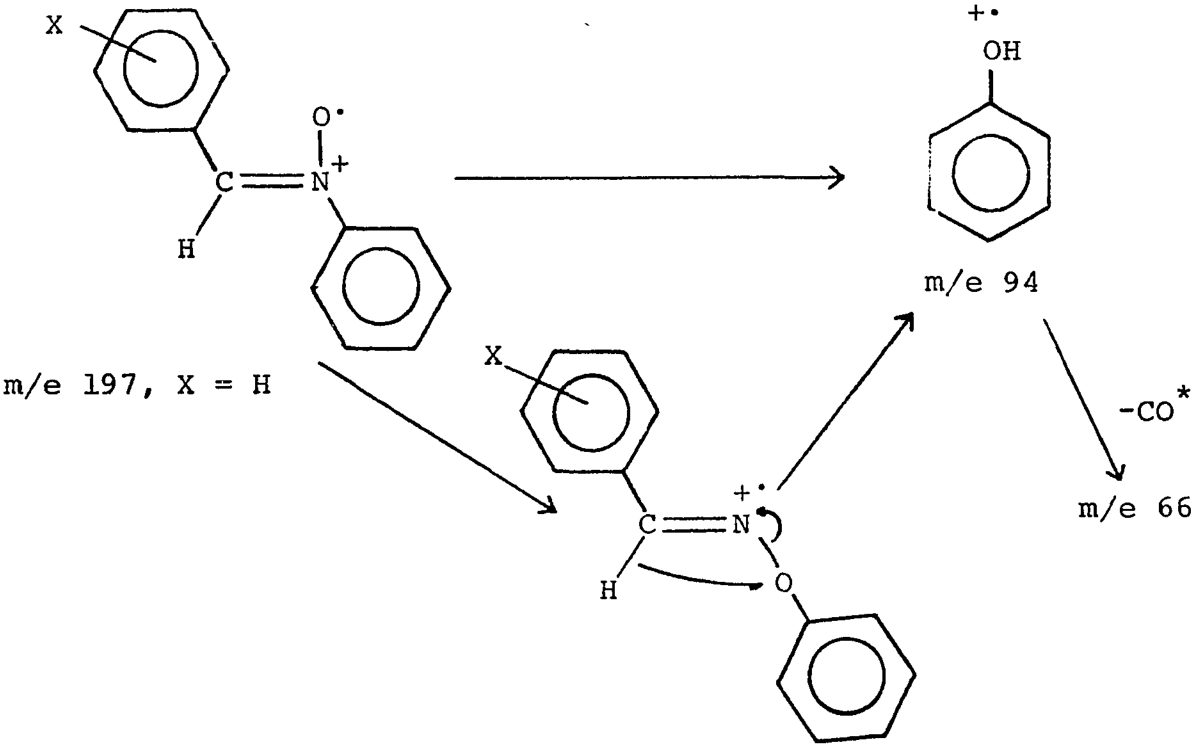
The identification of m/e 104 as $C_7H_6N^+$ by HRMS and the shift of m/e 104 to m/e 105 for 57 and 58 suggests structure 63 (Scheme 64) for this ion. Consistent with this proposal is the observation of an m/e 104 ion for 49 and the shift of m/e 104 to m/e 118 for 50 and 51. Two mechanisms A and B (Scheme 64) involving the direct loss of a phenoxy radical, or the consecutive loss of oxygen and a phenyl radical, respectively,



Scheme 64

could account for this ion. The m/e 104 ion further fragments by the metastable loss of HCN.

The m/e 94 ion ($C_6H_6O^{+\cdot}$ by HRMS) corresponds to a phenolic ion formed in a process reminiscent of a nitro-nitrite rearrangement as indicated in Scheme 65. Consistent with this mechanism is the shift of m/e 94 to m/e 95 for 58, the shift to m/e 108 for 51, and the absence of a shift for nitrones bearing a substituent on the α-phenyl ring. The m/e 94 ion fragments further by the metastable loss of carbon monoxide.

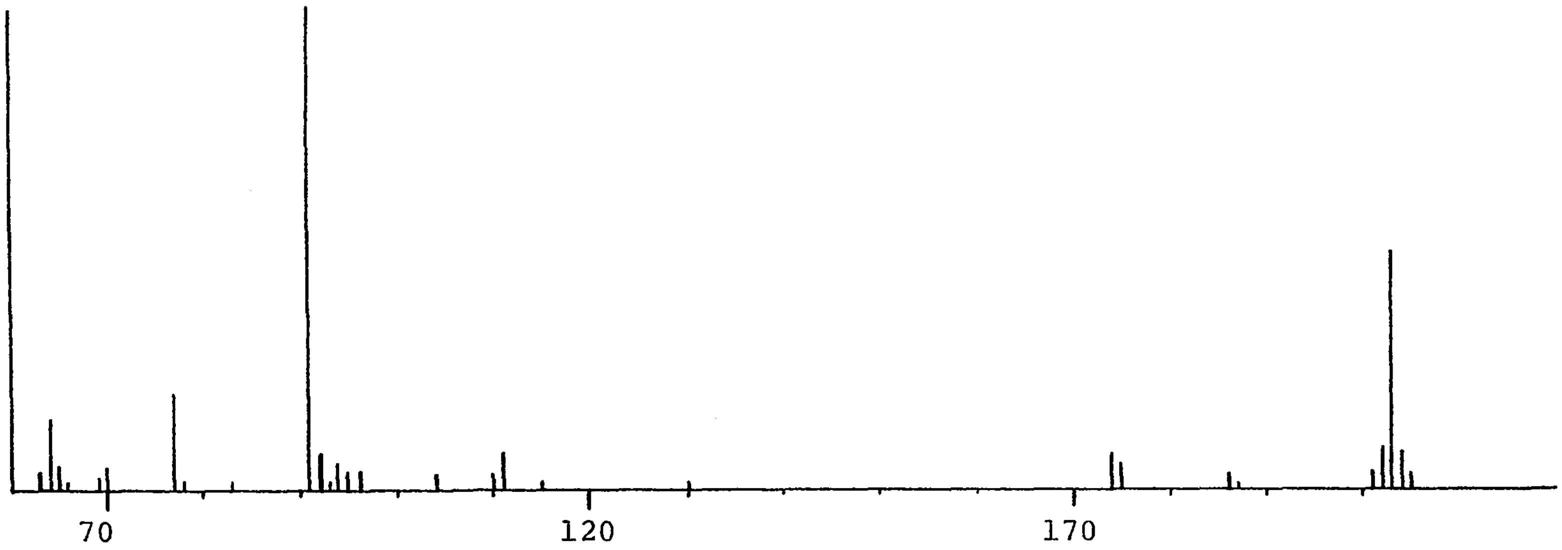


Scheme 65

As mentioned previously the mass spectra of other nitrones are very similar to that of 42. This fact is emphasized by the

Figure 36. Mass spectrum N-phenyl-α-(2-thienyl)-nitrone <u>55</u> (top)

Figure 37. Mass spectrum α-(1-naphthyl)-N-phenylnitrone <u>52</u> (bottom)


70
120
170

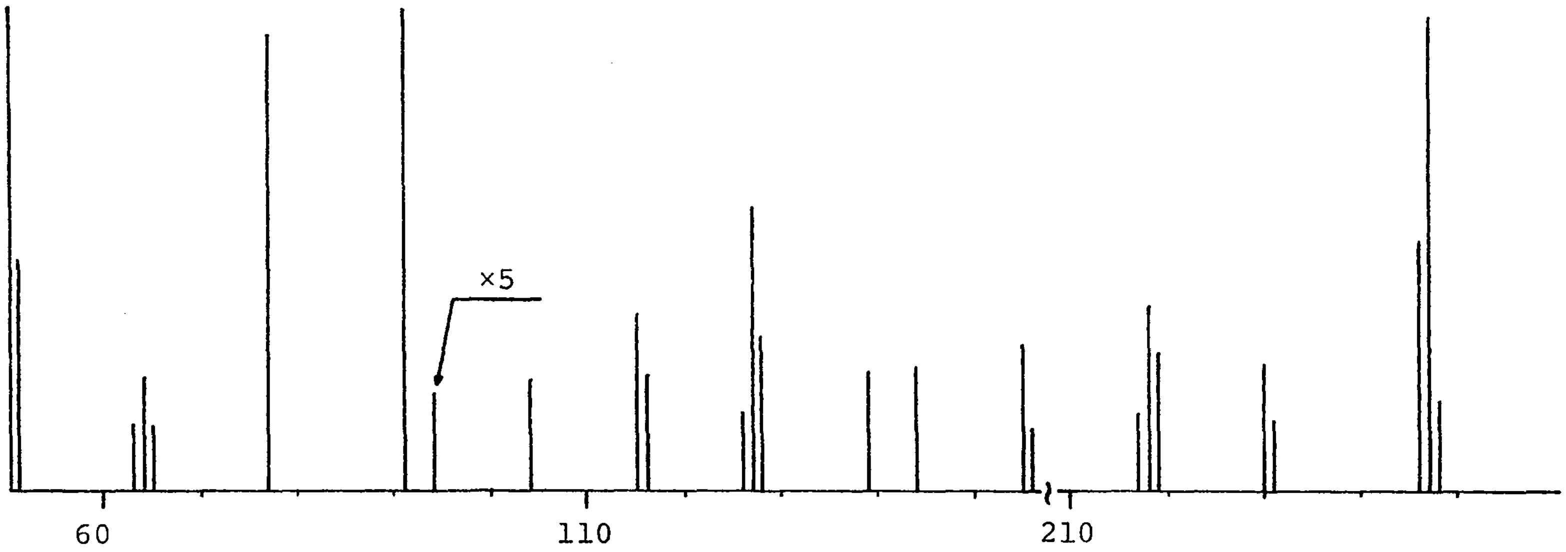
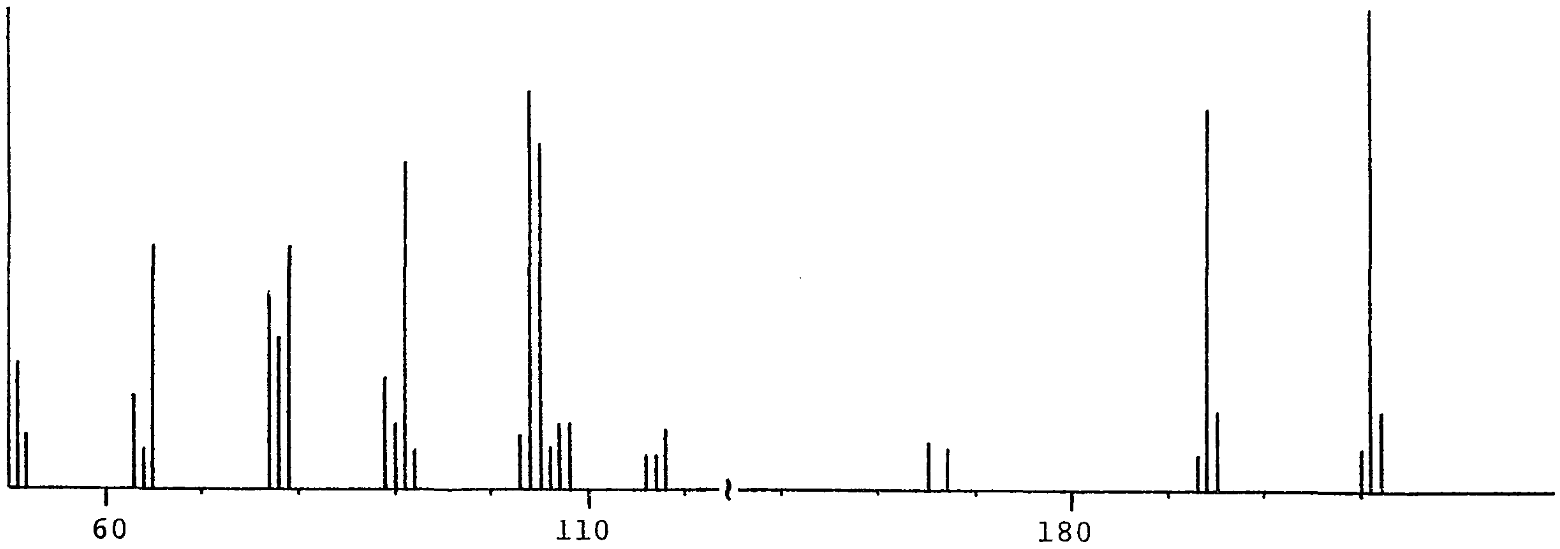
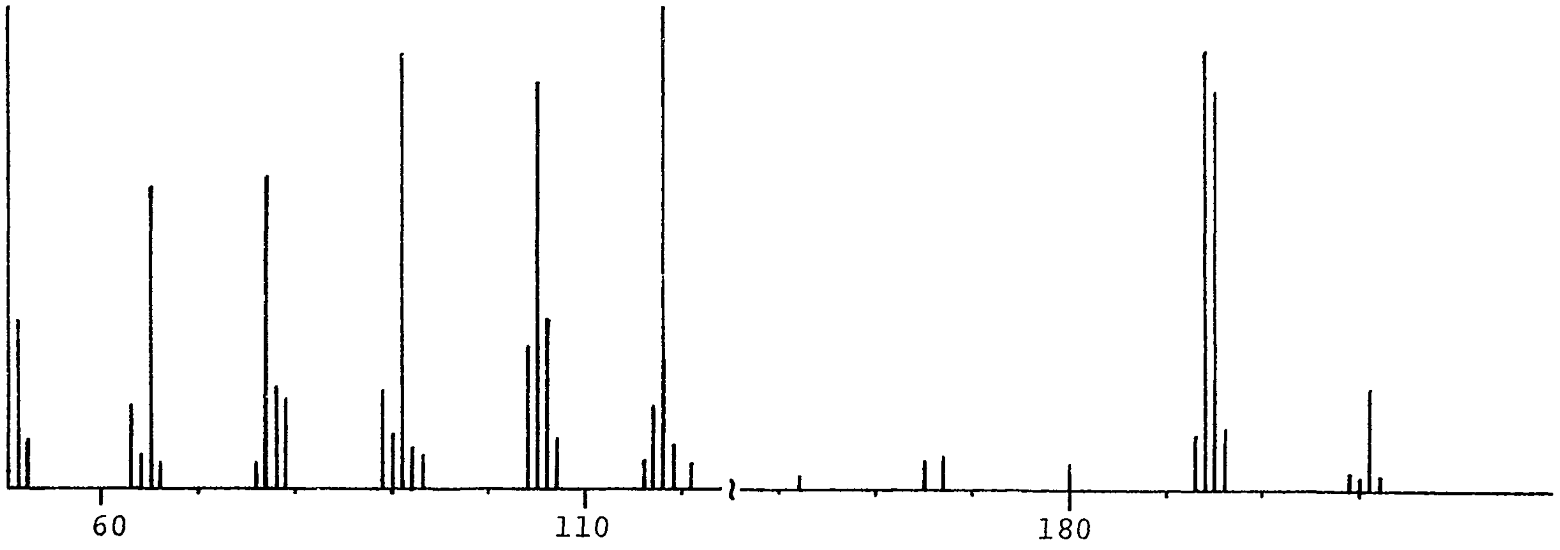

×5
60
110
210

Figure 38. Mass spectrum N-(o-methylphenyl)-α-phenylnitrone 50 (top)

Figure 39. Mass spectrum, heated inlet, N-(o-methylphenyl)-α-phenylnitrone 50 (bottom)


60
110
180

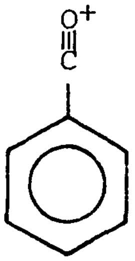

60
110
180

spectrum of N-phenyl-α-(2-thienyl)-nitrone <u>55</u> (Figure 36) in which all of the fragmentations described for <u>42</u> are observed in spite of an α-heteroaromatic ring. The spectra are altered, nevertheless, by changing certain structural features.

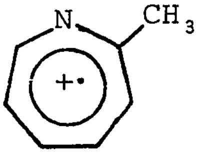
Compounds with a large aromatic ring, such as naphthyl or anthryl, on the α-carbon show interesting differences. For example, α-(1-naphthyl)-N-phenylnitrone <u>52</u> (Figure 37) exhibits increased losses of H, OH, CO, and CHO from the molecular ion as well as a decrease in the intensity of the m/e 94 ion (Table 5). These effects are undoubtably due to an interaction between the oxygen of the nitrone group and the <u>peri</u> position of the naphthalene ring. Such an interaction might also account for the probable naphthol ion at m/e 144. Another interesting feature of the spectrum is the formation of a relatively intense aldehyde ion at m/e 156 (15%). Similar changes are observed for α-(9-anthryl)-N-phenylnitrone <u>54</u>. The aldehyde ion (m/e 206) in this case, fragments by the metastable loss of CO just like 9-anthraldehyde.

Alterations in the mass spectra can occur from <u>ortho</u> effects, too. This effect is observed in the intense metastable loss of OH from α-mesityl-N-phenylnitrone <u>48</u> (Table 5). Further manifestations of this effect in <u>48</u> are the absence of an $M^{+\cdot}$-CO ion and the low intensity of the mesitoyl cation and m/e 91. The low intensity of the latter ions is probably due to steric hindrance in forming the oxaziridine intermediate.

Similar ortho effects are observed for substituents on the N-phenyl ring. The spectrum of N-(o-methylphenyl)-α-phenylnitrone 50 (Figure 38), for example, shows a large metastable loss of OH, and essentially no loss of CO from the molecular ion. The m/e 105 ion in the spectrum of 50 corresponds to 64 and 65 as shown by the subsequent metastable losses of CO and H. The m/e 91 ion is the tropylium ion. A combination of the ortho effect and the large α-aromatic ring effect is observed for 53.



64

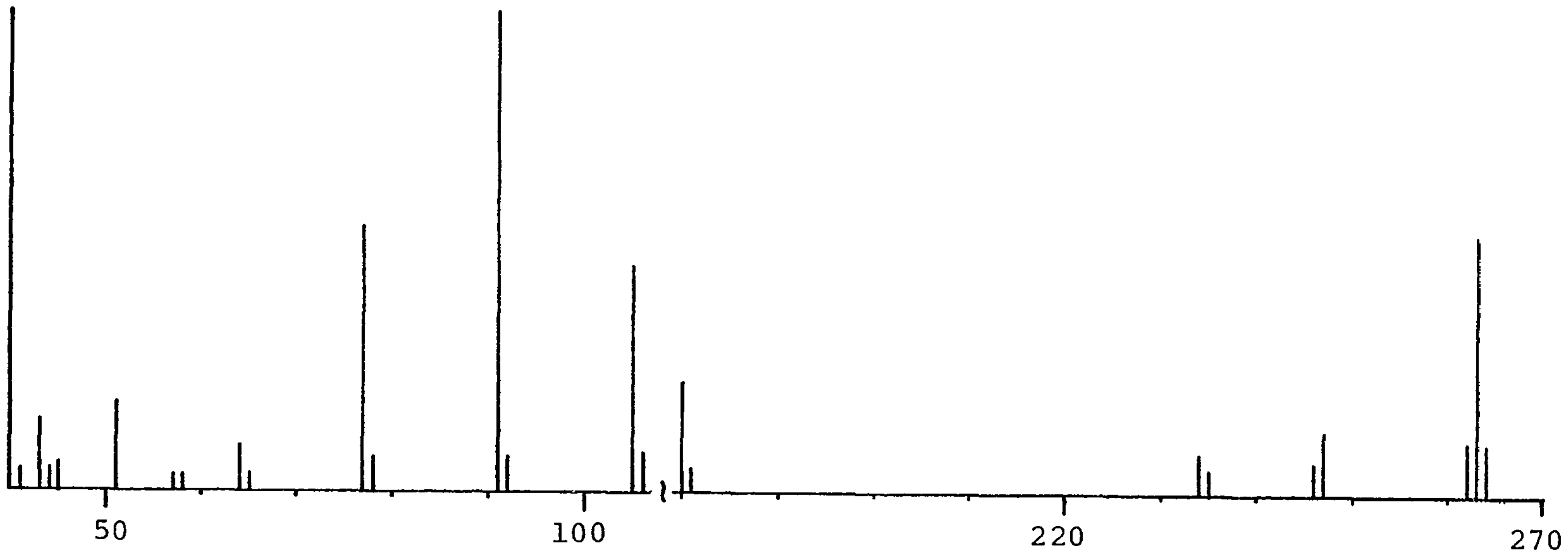


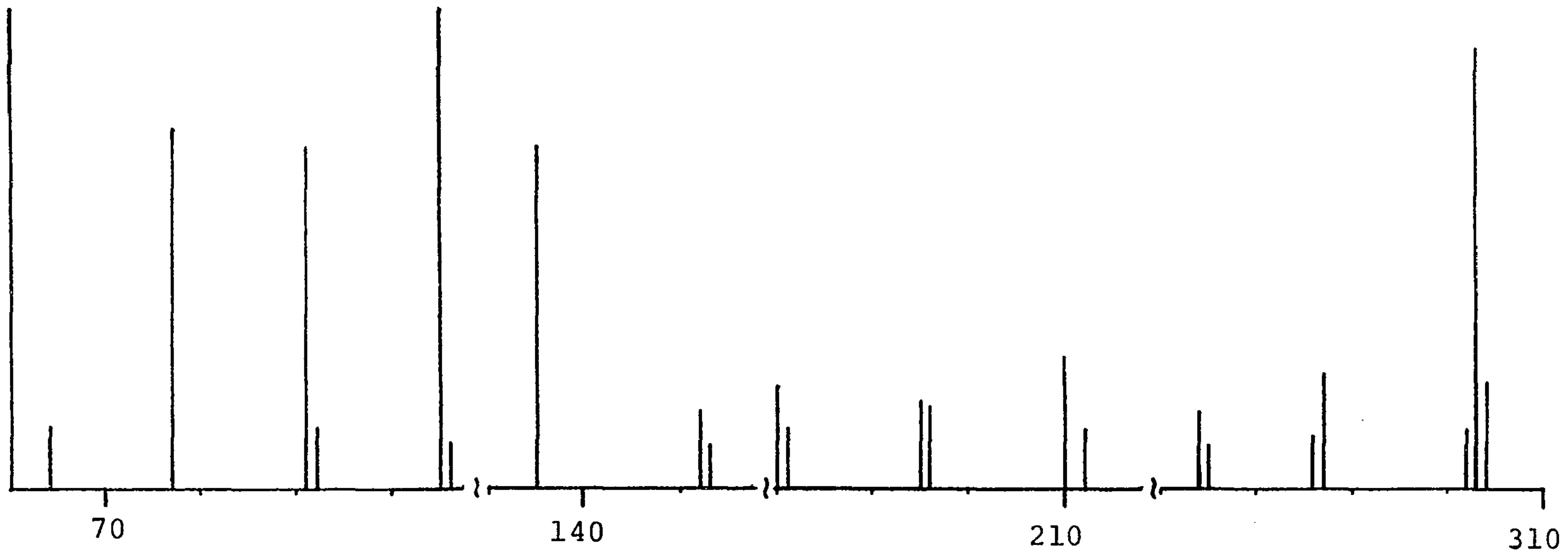
65

Thermal effects can also alter the mass spectra of nitrones. A comparison of the direct inlet and heated inlet spectra for 50 (Figure 38 and 39) reveals quite different intensities for the ions at m/e 211, 195, 118, 104, and 91. Similar effects were observed for α,N-diphenylnitrone 42 and other nitrones. In general, the same ions are observed, but with quite different relative intensities for the heated inlet system. Contrary to the results of Larsen et al. (96), the loss of oxygen from the molecular ion increases considerably

Figure 40. Mass spectrum α,N-triphenylnitrone _66_ (top)

Figure 41. Mass spectrum α-(_p_-methoxyphenyl)-α,N-diphenylnitrone _67_ (bottom)

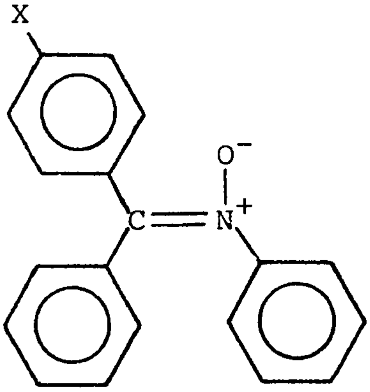

50
100
220
270


70
140
210
310

using a heated inlet system.

Mass Spectra of Triarylnitrones

The mass spectra of several triarylnitrones 66-73 were investigated to determine the effect of replacing the α-hydrogen with an aromatic ring and to extend our understanding of the fragmentations of nitrones. The mass spectra of the parent



66 X = H

67 X = CH_3O

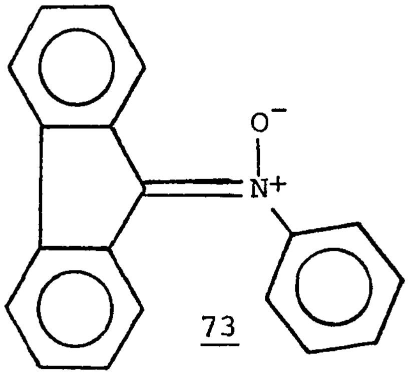
68 X = CH_3

69 X = Cl

70 X = F

71 X = CN

72 X = NO_2



73

compound 66 and a nitrone with a substituent 67 are presented in Figures 40 and 41. The important fragmentations of the other triarylnitrones are outlined in Table 6.

The spectra are very similar to those obtained for diaryl and arylheteroaromatic nitrones. Intense $M^{+\cdot}$ and $M^{+\cdot}-1$ ions are observed in all spectra, and the high intensity of the latter

Table 6. Mass spectra of triarylnitrones with peak heights expressed as percent of base peak

	66	67	68	69[a]	70	71[b]	72[c]	73
$M^{+\cdot}$	54.2	92.0	64.8	80.7	32.4	----	4.80	100
$M^{+\cdot}-H$	11.0	12.5	14.5	11.4	4.21	----	----	75.5
$M^{+\cdot}-O$	13.4	24.2	6.17	13.6	5.27	----	5.20	27.8
$M^{+\cdot}-OH$	6.70	10.7	4.42	6.42	3.68	----	0.98	23.0
$M^{+\cdot}-CO$	5.12	8.93	5.88	12.1	3.42	----	0.68	4.60
$M^{+\cdot}-CHO$	8.42	16.0	10.0	10.0	3.69	----	0.59	6.75
$M^{+\cdot}-O\phi$	23.4	27.7	12.6	18.6	23.6	----	2.85	----
$M^{+\cdot}-o\phi X$	----	21.4	16.8[d]	15.7	5.00	----	4.80	----
XC_6H_5CO	----	71.5	26.4	35.0	10.0	----	0.19	----
C_6H_5CO	47.5	100	47.9	45.7	8.15	----	3.93	----
91	100	71.5	100[a]	100	100	----	100	75.5

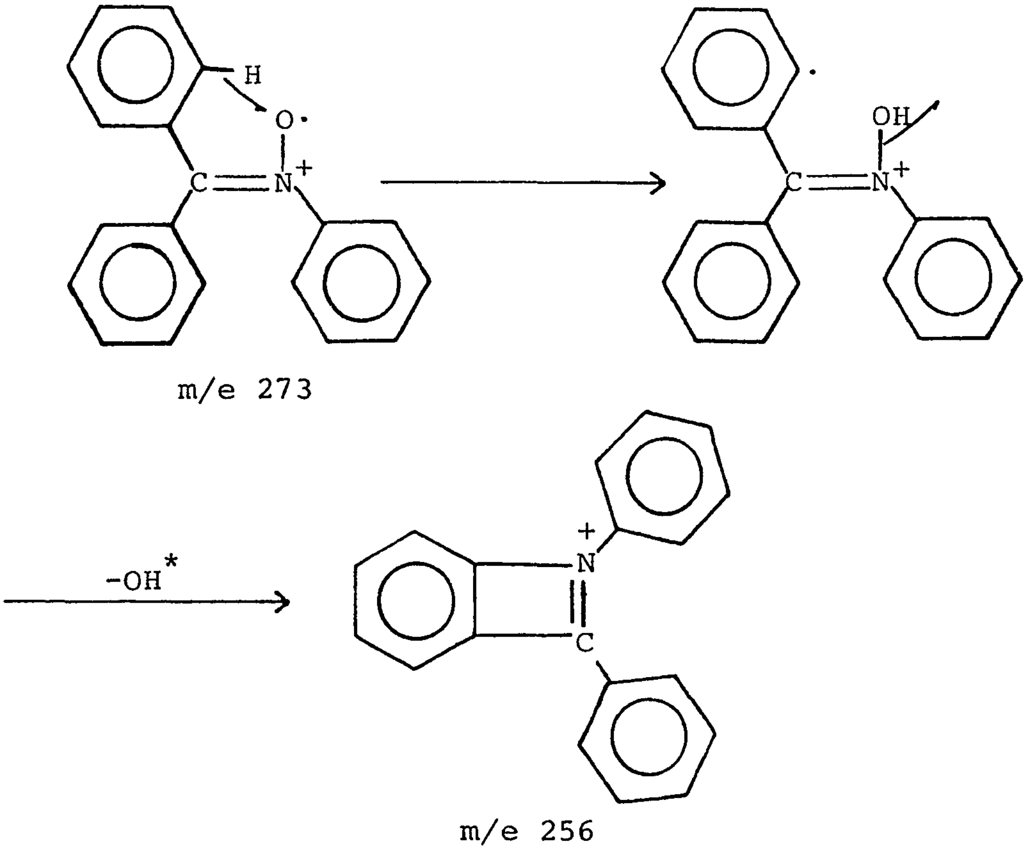
[a] Peaks for major isotope only.

[b] Spectrum obtained only at low electron energies.

[c] The extreme high intensity of m/e 91 make the other ions of low abundance.

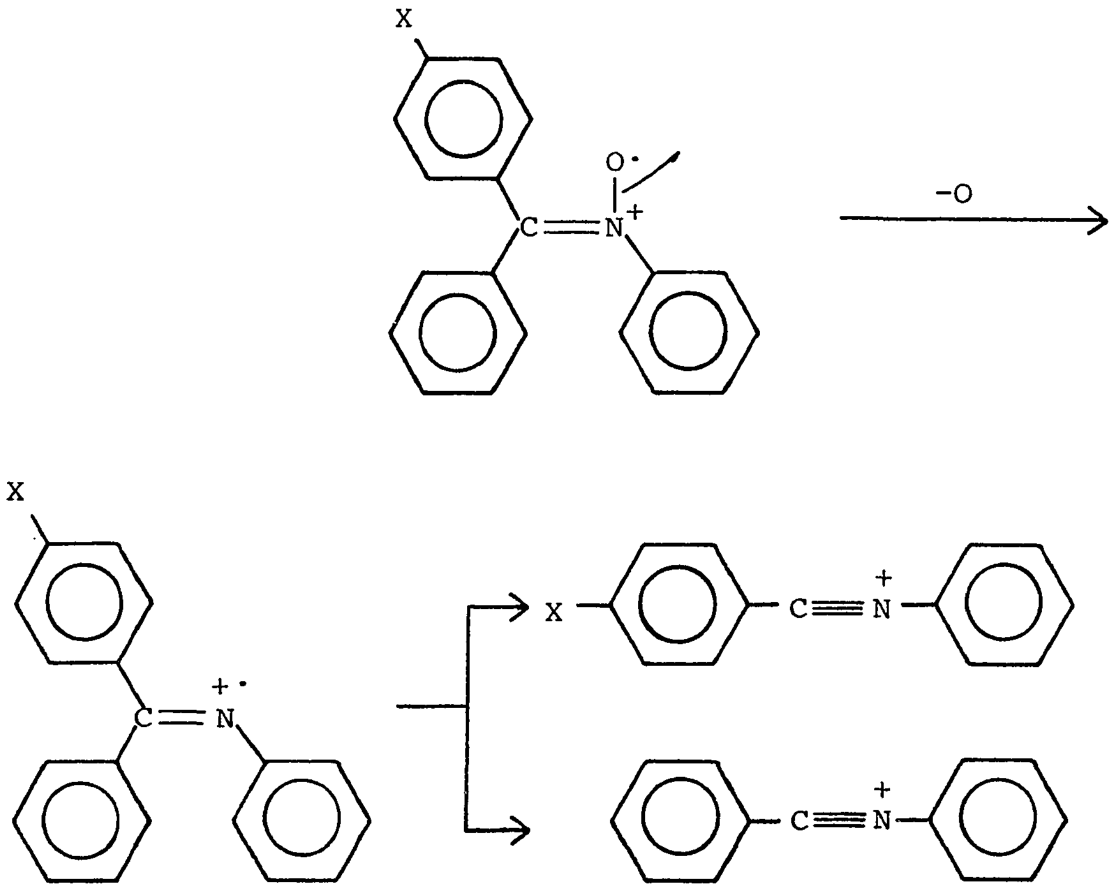
[d] Doublet.

ion for 73, where the α-aromatic rings are held stericly rigid, suggests a mechanism analogous to that proposed for diarylnitrones in its formation. Losses of O and OH occur, but the relative intensity of these ions are reversed from that observed for diarylnitrones. A metastable at m/e 240.1 suggests that OH loss from 66 occurs by a hydrogen abstraction mechanism as depicted in Scheme 66. The absence of an α-hydrogen precludes the mechanism proposed for diarylnitrones. In analogy to nitrostyrenes the abstraction reaction is probably a specific process.



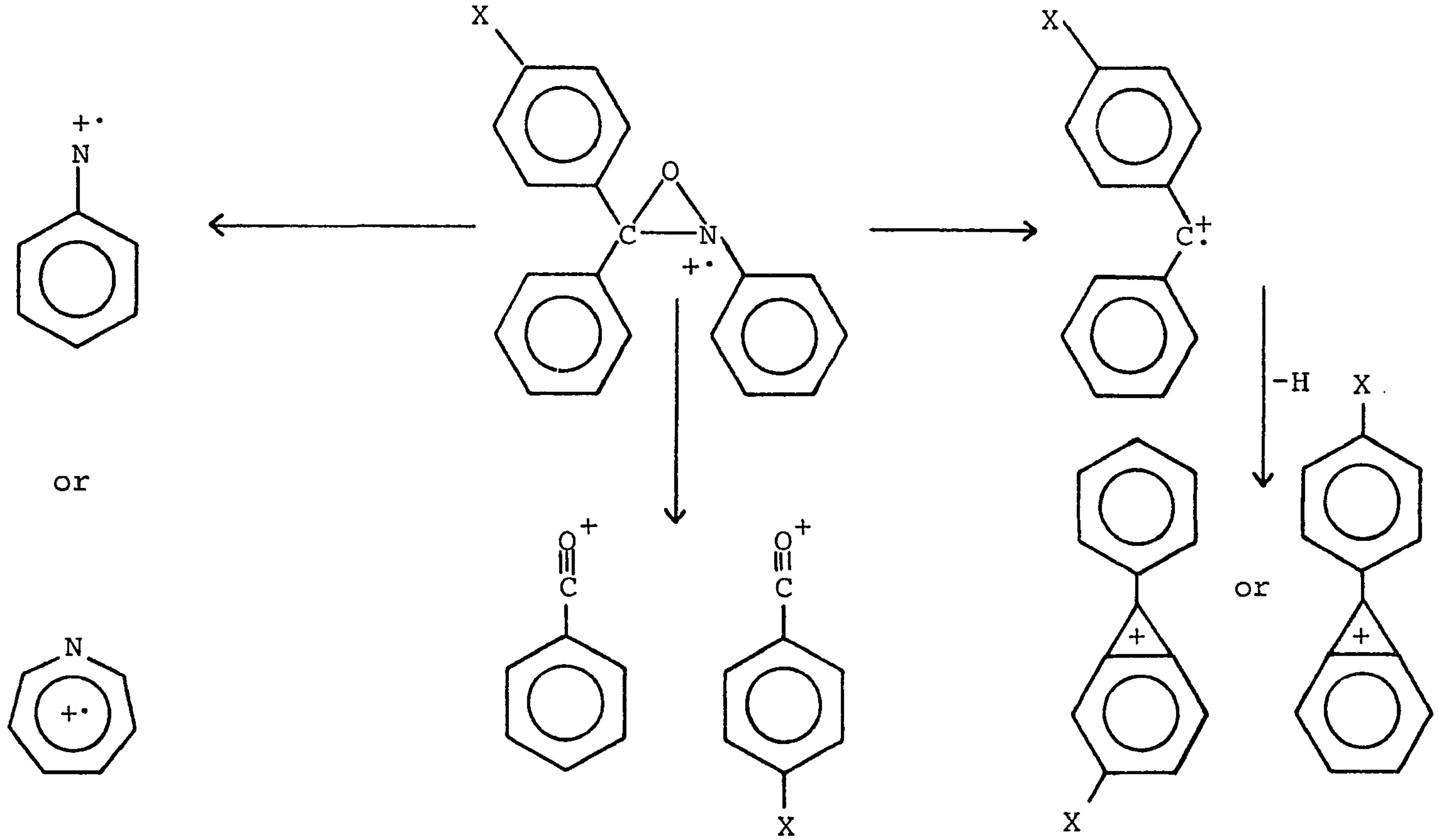
Scheme 66

The $M^{+\cdot}$-CO and $M^{+\cdot}$-CHO ions observed for triarylnitrones must be formed in a process analogous to that described for diarylnitrones in Scheme 61. The loss of oxygen followed by one of the α-aromatic rings generates ions of the type illustrated in Scheme 67 in analogy to the m/e 104 and $M^{+\cdot}$-OH ions observed for diarylnitrones. The absence of an α-hydrogen prevents the formation of an m/e 94 ion.



Scheme 67

The rearrangement of triarylnitrones to oxaziridines under mass spectrometric conditions again plays an important role in fragmentation. The oxaziridine can decompose in several ways (Scheme 68): by loss of nitrosobenzene to give



Scheme 68

diaryl analogs of the m/e 90 ion observed for 42, by migration of one of the α-aryl groups to give a benzoyl or substituted benzoyl cation, and by loss of a diarylketone to give the previously mentioned m/e 91 ion. In analogy to m/e 90 the diaryl analog can decompose by the metastable loss of hydrogen. The m/e 91 ion again often corresponds to the base peak in the spectra of triarylnitrones (Table 6).

The observation of aryl migration to a cation radical on nitrogen in the oxaziridine to give benzoyl and substituted benzoyl cations suggested the possibility of determining mass spectral migratory aptitudes for substituted aryl rings relative to phenyl. The migratory ability of an aryl ring will be the inverse of the intensity of its benzoyl cation. The study was done at 20 eV to minimize the subsequent decomposition reactions of the benzoyl cations, and the results presented in Table 7 indicate the following migratory aptitudes: $\underline{p}\text{-NO}_2 > \underline{p}\text{-CH}_3\text{O} > \underline{p}\text{-CN} > \underline{p}\text{-CH}_3 > \underline{p}\text{-Cl} > \underline{p}\text{-H} > \underline{p}\text{-F}$.

The migratory aptitudes for p-CN and $\underline{p}\text{-NO}_2$ are certainly not in their expected order. The phenyl group must migrate better than p-CN or $\underline{p}\text{-NO}_2$ substituted aryl groups. Apparently destabilization of the benzoyl cation by resonance interaction with the p-CN and $\underline{p}\text{-NO}_2$ substituents causes these ions to be of extraordinarily low abundance compared to the unsubstituted benzoyl cation giving the observed results. Essentially, product ion stability has displaced migratory aptitude as the

Table 7.[a] Migratory aptitudes for triarylnitrones 67-72 at 20 eV

X	ϕ-C=O	X-ϕ-C=O	ϕ-C=O/X-ϕ-C=O
OCH_3	23.8	5.60	4.25
CH_3	12.0	5.45	2.20
Cl	5.75	5.50	1.04
H	----	----	1.00
F	2.63	5.26	0.50
CN	3.80	1.27	3.00
NO_2	2.36	0.47	5.00

[a] Peak intensities for benzoyl cations are expressed as a percent of the sum of all ions between m/e 40 and $M^{+\cdot}$.

determining factor in benzoyl cation intensities. In agreement with this proposal is the low intensity of the p-CN and p-NO_2 substituted benzoyl cations observed for 43 and 46, respectively (Table 5). Hammett substituent effect studies to be discussed later also support this conclusion. The actual migratory aptitudes should be: p-CH_3O>p-CH_3>p-Cl>p-H>p-F>> p-CN and p-NO_2. These results are slightly different from the migratory aptitudes obtained by Brown and Djerassi (101) for migration to a cation radical center on oxygen in a study on carbonates: p-CH_3O>p-H>p-CH_3>>p-F, p-CN and p-NO_2. The subject of group migration is of current interest, and has been recently reviewed (102) in regard to bond forming reactions.

A Hammett plot of the data in Table 7 according to the method of McLafferty and Bursey (103) gave the results shown in Figure 42. This system is particularly well suited to such a study since many of the objections to treatment of mass spectral data in this manner (48) are obviated by carrying out the comparisons within the same molecule. Figure 42 exhibits one straight line with a positive ρ value of 0.66 for the $\underline{p}$-CH_3O, $\underline{p}$-CH_3, and $\underline{p}$-Cl substituents and another straight line with a negative ρ value of 1.10 for the $\underline{p}$-F, $\underline{p}$-CN and $\underline{p}$-NO_2 substituents. The results suggest that the aryl groups bearing $\underline{p}$-CH_3O, $\underline{p}$-CH_3, and $\underline{p}$-Cl substituents migrate better than phenyl and feel a decrease in the charge on nitrogen as the positive charge transfers to the α-carbon in the transition state leading to fragmentation of the oxzairidine, hence the positive ρ value. For $\underline{p}$-F, $\underline{p}$-CN, and $\underline{p}$-NO_2 aryl groups, the phenyl ring migrates better, and the substituted aryl groups left behind feel the increase of charge on the α-carbon in the transition state, thus giving a negative ρ value. These results suggest that the transition state for fragmentation of the oxaziridine by this pathway resembles products as expected (104).

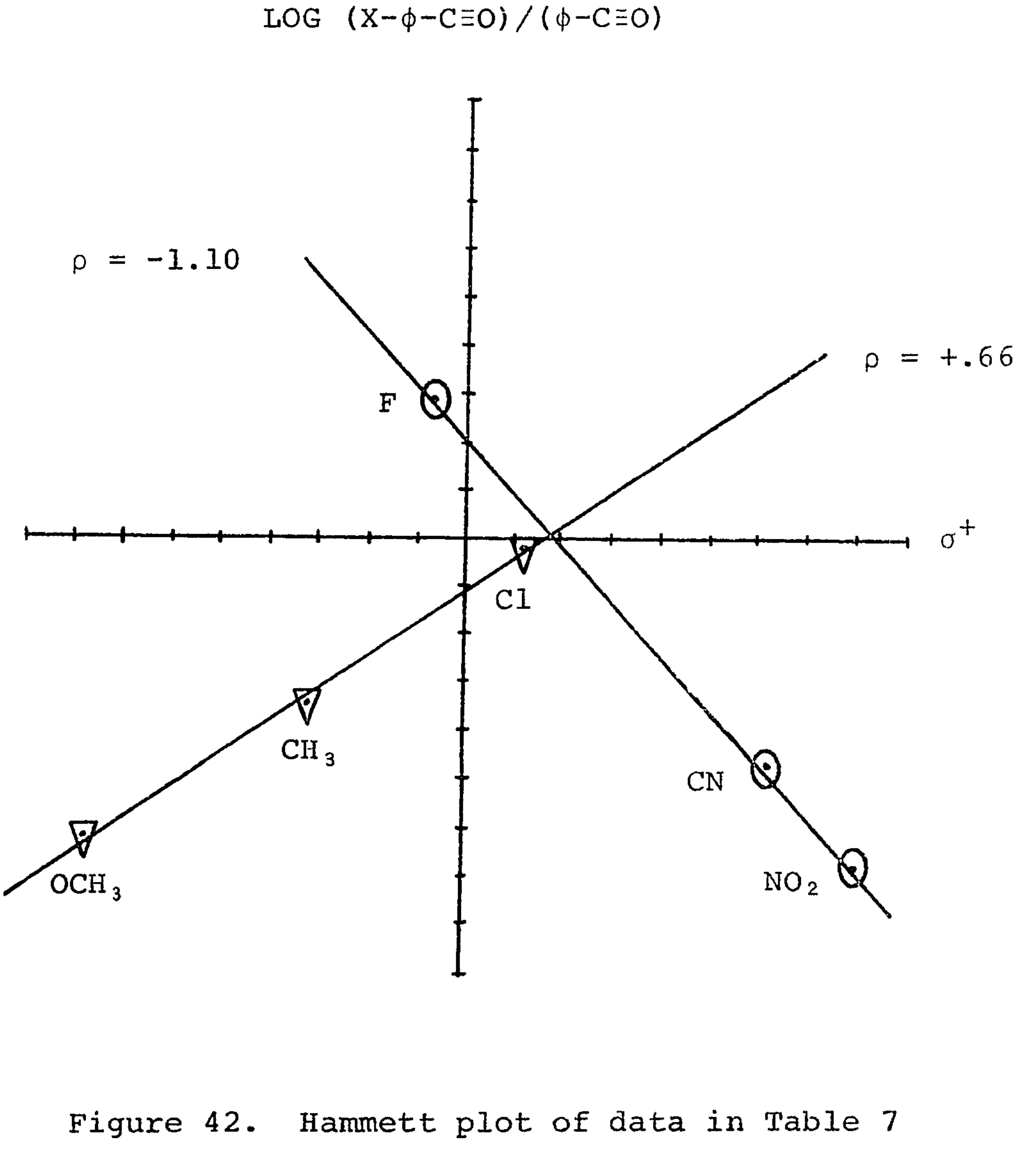
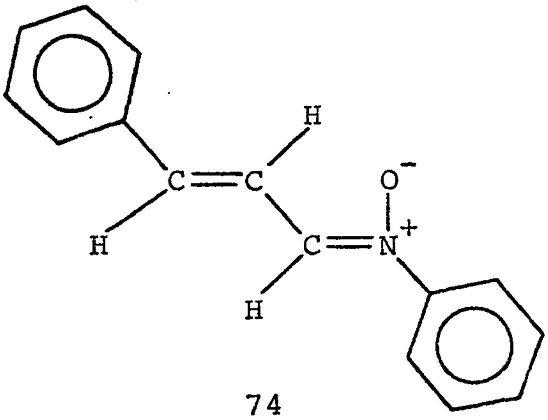


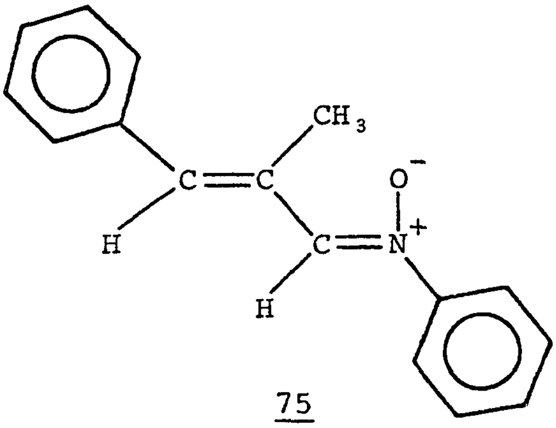
Figure 42. Hammett plot of data in Table 7

Mass Spectra of Conjugated Nitrones

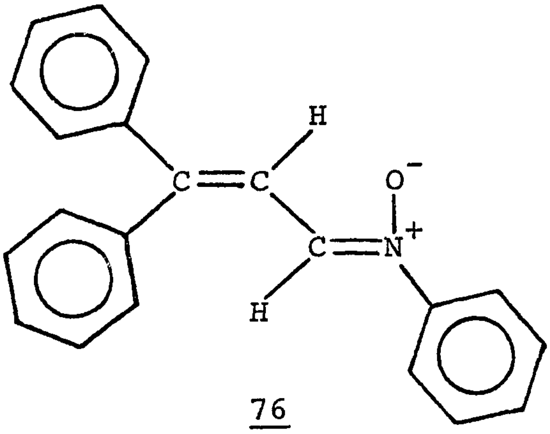
The mass spectra of several conjugated nitrones 74-78 were investigated to determine the effect of extended conjugation on



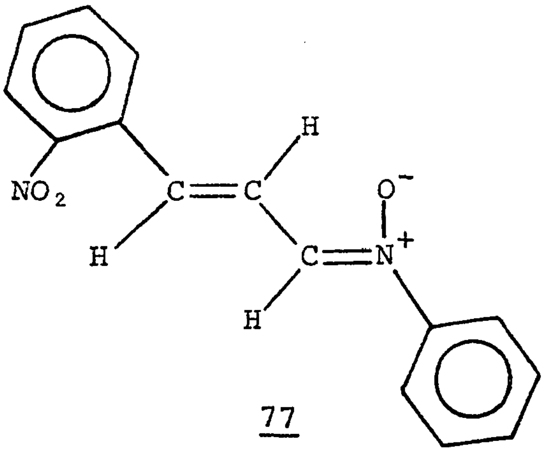
74



75



76



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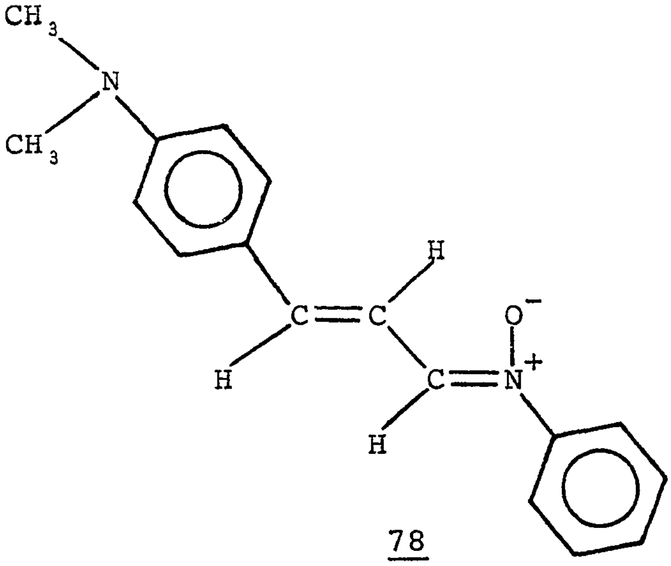


78

Table 8. Mass spectra of conjugated nitrones with peaks expressed as percent of base peak

	Compound				
	74	75[a]	76	77[a]	78
$M^{+\cdot}$	100	94.9	23.1	7.5	100
$M^{+\cdot}-H$	13.1	13.2	----	----	6.72
$M^{+\cdot}-O$	10.2	5.27	6.9	2.69	5.77
$M^{+\cdot}-OH$	31.6	18.4	20.1	4.84	30.8
$M^{+\cdot}-CHO$	11.6	5.27	1.97	1.61	11.5
$M^{+\cdot}-\phi$	63.7	63.0	20.1	2.69	21.2
RCO[b]	8.7	13.2	3.94	0.53	44.3
$M^{+\cdot}-C_6H_5NO$	40.6	31.5	28.6	2.69	7.68
$M^{+\cdot}-C_6H_6NO$	88.2	71.2	100	2.15	38.4
$X-\phi-C{\equiv}O$	50.7	55.3	69.0	1.61	7.7
94	4.35	0.00	0.98	3.77[c]	0.57
91	88.2	26.3	12.3	17.2	13.5

[a] Base peak m/e 77.

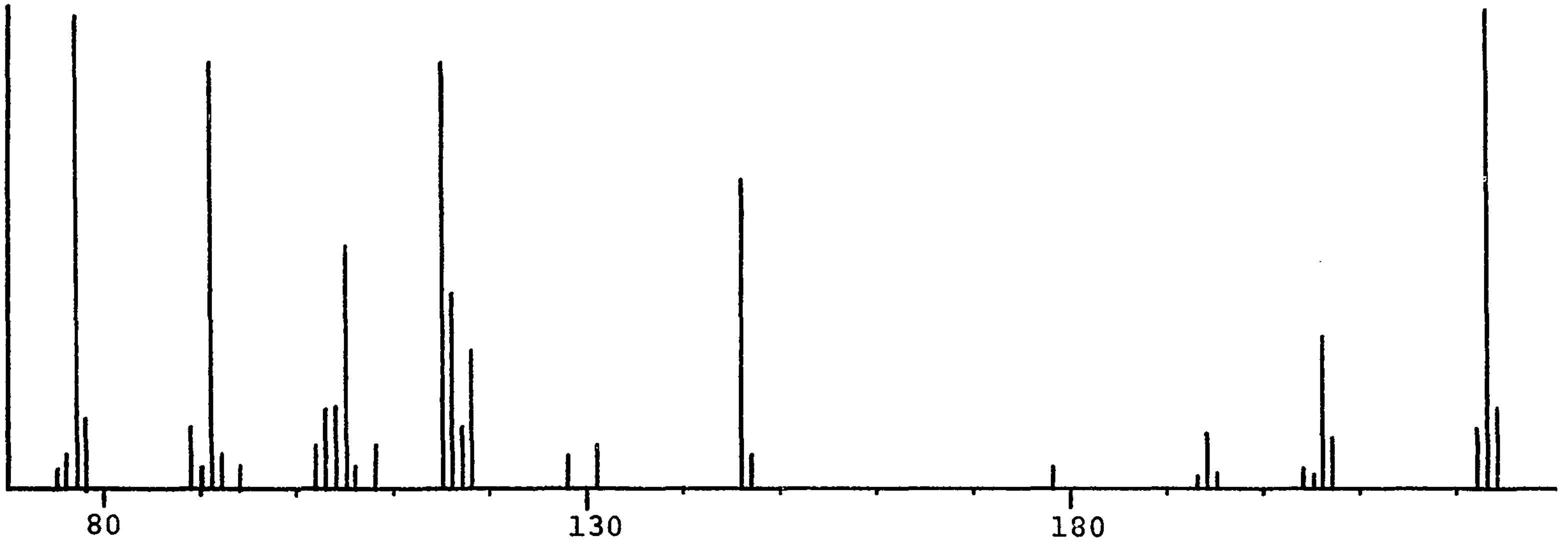
[b] R = styryl or substituted styryl.

[c] Largely isotope contribution from m/e 93.

the mass spectra of nitrones, and to determine whether parallels in fragmentation exist between conjugated nitrones and those nitrones already discussed. The main fragmentations of the parent compound, N-phenyl-α-styrylnitrone 74 (Figure 43),

Figure 43. Mass spectrum N-phenyl-α-styrylnitrone 74 (top)

Figure 44. Mass spectrum α-(α-deuteriostyryl)-N-phenylnitrone 79 (bottom)


80
130
180

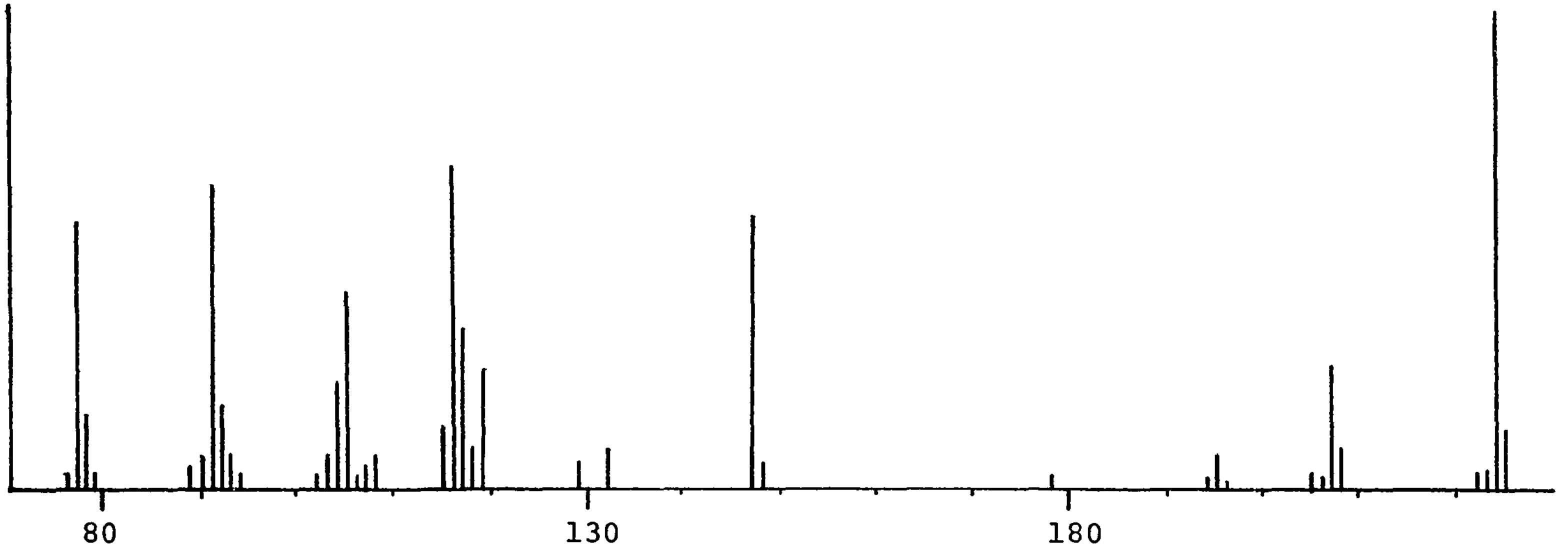
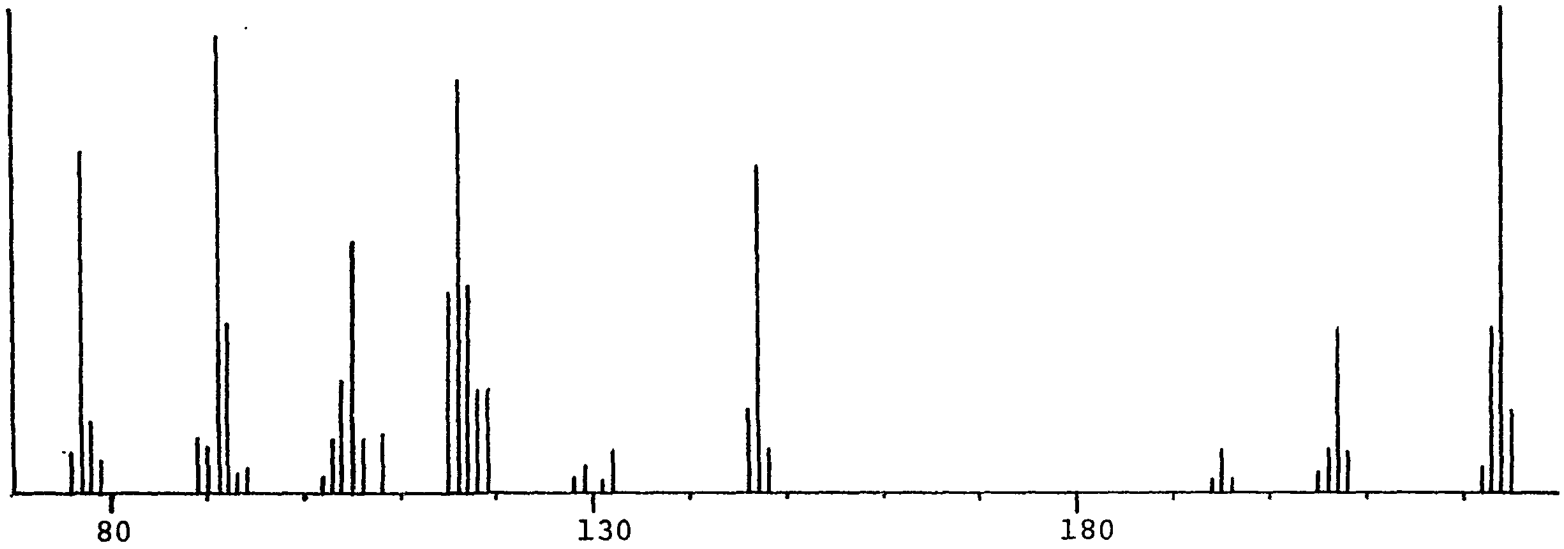
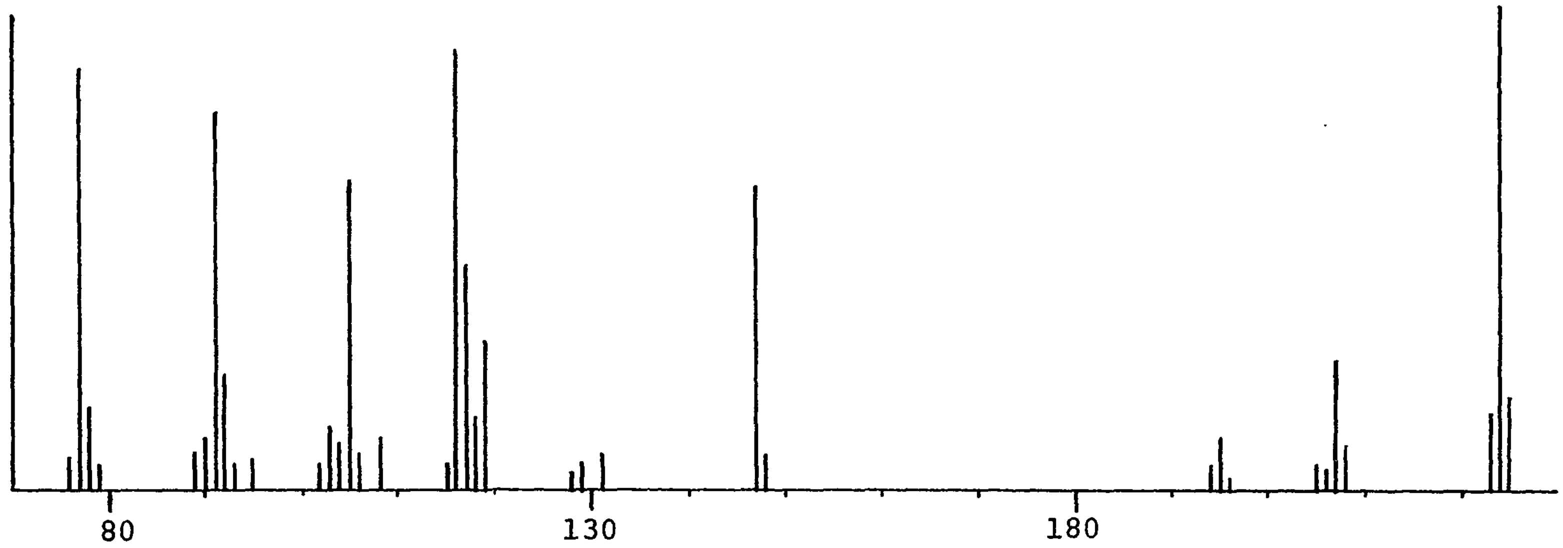

80
130
180

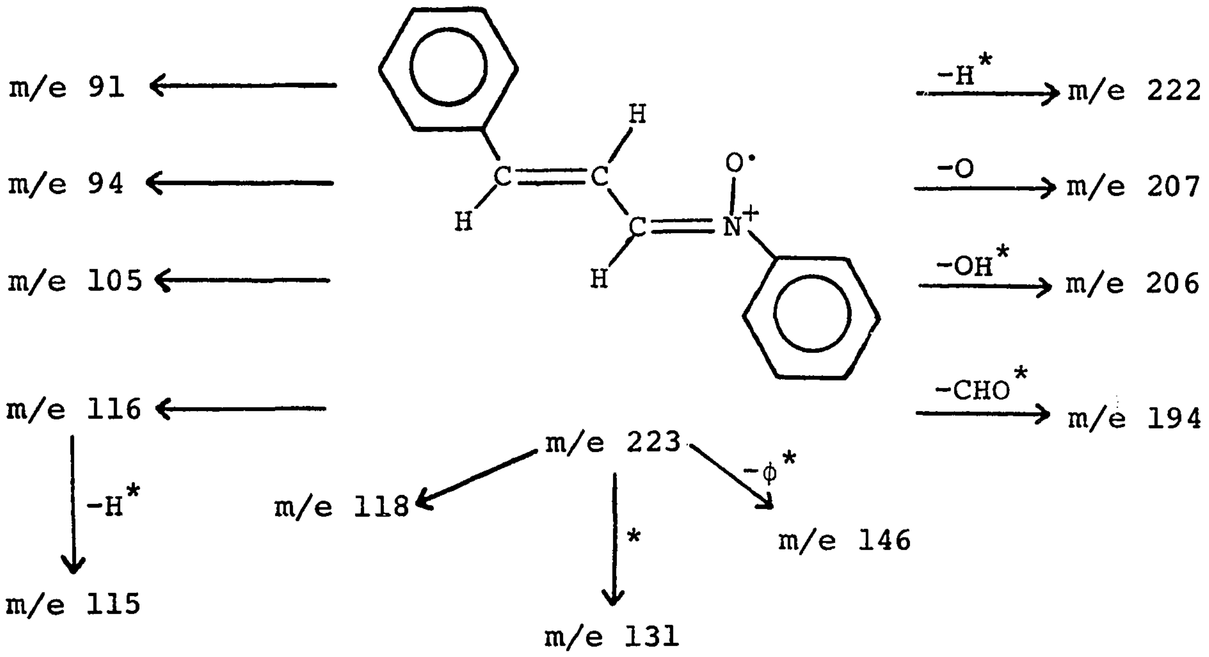
Figure 45. Mass spectrum α-(β-deuteriostyryl)-N-phenylnitrone <u>80</u> (top)

Figure 46. Mass spectrum α-deuterio-N-phenyl-α-styrylnitrone <u>81</u> (bottom)


80
130
180


80
130
180

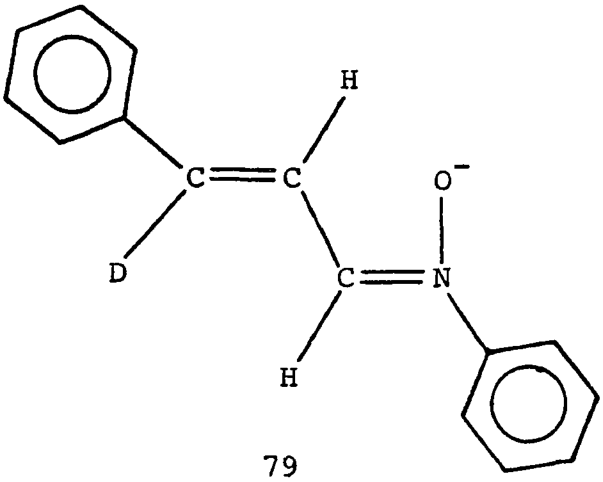
are outlined in Scheme 69, and were found to be general for the other conjugated nitrones studied (Table 8). To better



Scheme 69

understand the mechanisms leading to the observed fragmentations for 74 and the other conjugated nitrones, the labeled compounds 79-81 were prepared and their spectra recorded (Figures 44-46).

The m/e 91 ion and the cinnamoyl cation (m/e 131) observed in the spectrum of 74 indicate that conjugated nitrones also rearrange to oxaziridines under mass spectrometric conditions. The loss of nitrosobenzene from the oxaziridine results in the formation of an ion at m/e 116 which fragments by the subsequent metastable loss of hydrogen, probably forming the



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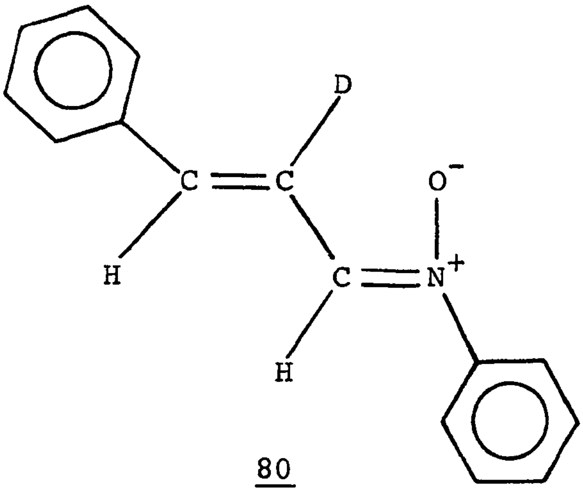
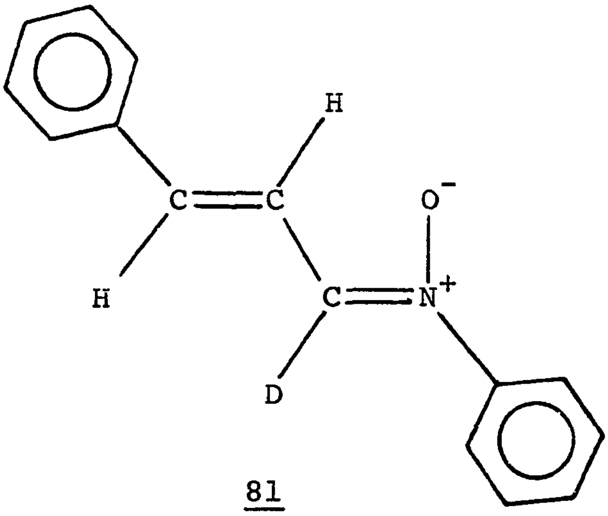


80



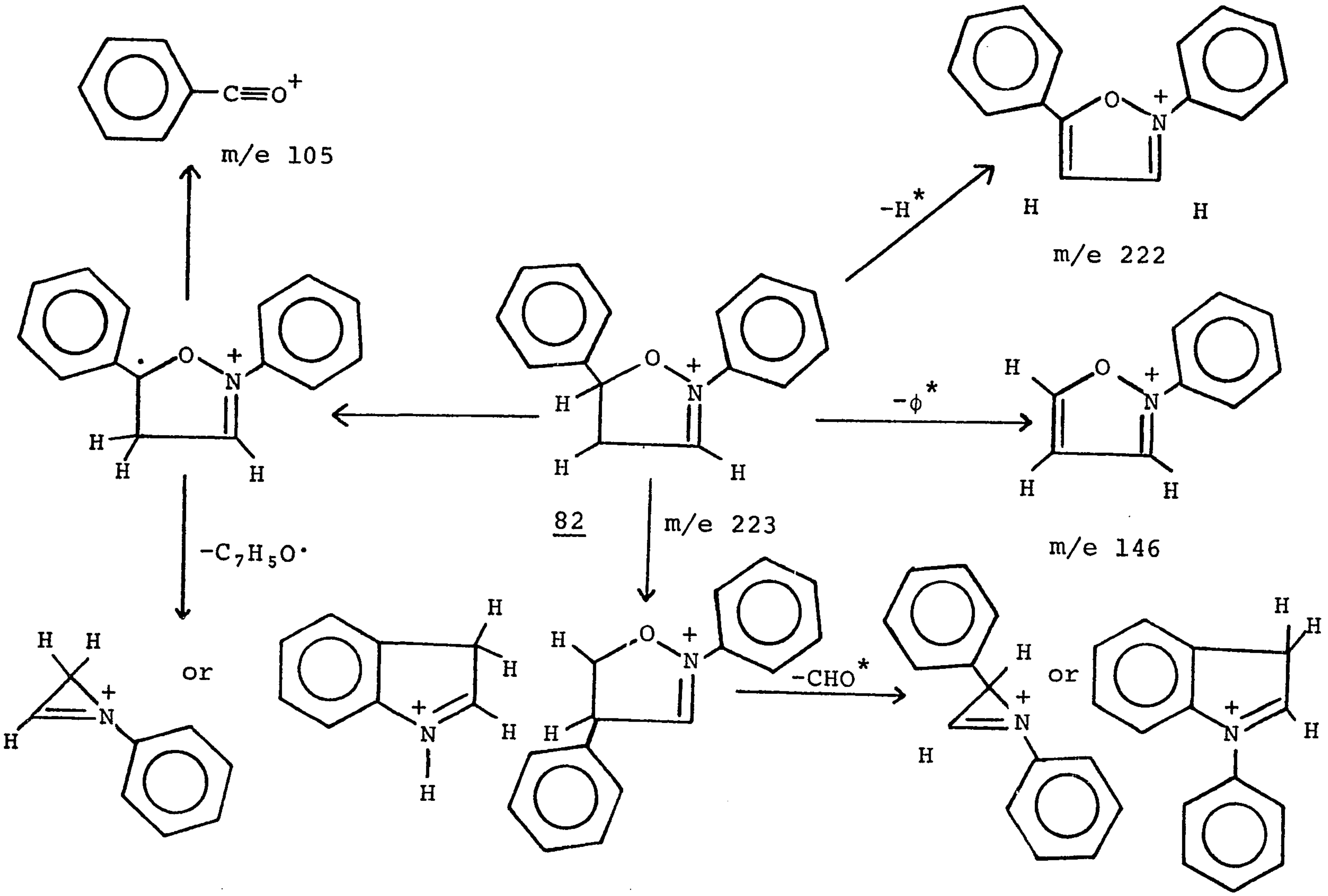
81

indenyl cation at m/e 115.

Contrary to simple nitrones, labeling results from 81 show that the oxaziridine from 74 can fragment by the loss of CHO to account for 16% of the M$^{+\cdot}$-CHO ion. Labeled compound 79 indicates that 8% of the CHO loss originates from the carbon atom α to the styryl ring, while compound 80 rules out the β-carbon atom as a participant in the fragmentation. The labeling results strongly suggest that the metastable loss of CHO from 74 occurs in a multi-site process with the remaining 76% loss of CHO involving one or both of the phenyl rings. The slight but real loss of CO from 74, which grows at lower electron energies, agrees with the participation of a phenyl ring in behavior reminiscent of diarylnitrones. A mechanism involving hydrogen randomization seems unlikely in view of the observed CDO losses from 79 and 81 and the absence of an $M^{+\cdot}$-CDO ion for 80. It is interesting to note that 75 loses both CHO and CH_3CO from the molecular ion.

The metastable loss of hydrogen from 74 occurs by intramolecular attack on the carbon atom α to the styryl ring to give a stable diphenylisoxazole ion as depicted in Scheme 70. This mechanism is supported by the metastable loss of deuterium from 79, the shift of m/e 222 to m/e 223 for 80 and 81, and the absence of an $M^{+\cdot}$-1 ion for 76. The five membered ring intermediate 82 (Scheme 70) proposed for loss of hydrogen also accounts for many of the other fragmentations observed for conjugated nitrones.

Phenyl migration in 82 with the subsequent loss of CHO can readily account for the previously discussed contribution of the α-carbon atom to the $M^{+\cdot}$-CHO ion observed for 74. The metastable loss of a phenyl ring from 74 to generate the intense ion at m/e 146 must occur from 82 to give a stable phenylisoxazole ion as indicated in Scheme 70 since losses of 122 and 120 mass units occur for 77 and 78, respectively.



Scheme 70

Labeling results from 79-81 suggest that the m/e 118 ion is formed in part by hydrogen migration in 82 with loss of a benzoyl radical. Hydrogen migration with cleavage to give a benzoyl cation (Scheme 70) must also be an important process as evidenced by the intense m/e 105 ion observed in the spectra of 74, 75, and 76. The identity of the m/e 105 ion and its proposed mode of formation are supported by the absence of a shift for m/e 105 in the spectra of 79-81, the shift of m/e 105 to m/e 150 and m/e 148 for 77 and 78, respectively, and the subsequent metastable loss of carbon monoxide from m/e 105. The high intensity of the m/e 105 ion for 76 with two phenyl rings on the α-carbon atom is again consistent with the proposed mechanicm for formation of m/e 105.

Several fragmentations not involving an oxaziridine or 82 occur and are of some interest. The loss of oxygen from the molecular ion of 74 generates the ion at m/e 207, but the subsequent loss of the γ-hydrogen atom does not occur to give the $M^{+\cdot}$-OH ion since 81 exhibits only loss of OH from the molecular ion. The absence of an $M^{+\cdot}$-OD ion for 79 and 80 suggests that the metastable loss of OH from 74 occurs by hydrogen abstraction from one of the phenyl rings. The loss of a styryl radical following loss of oxygen accounts in part for the m/e 104 ion as evidenced by a partial shift of m/e 104 to m/e 105 for 81.

The ion at m/e 94 in the spectrum of 74 shifts to m/e 95 for 81 suggesting that this ion has a phenolic structure, and is formed in a process analogous to that described for the m/e 94 ion in the spectra of diarylnitrones (Scheme 65). The m/e 94 ion is of negligible importance (Table 8) for the other conjugated nitrones investigated.

The mass spectra of other conjugated nitrones are analogous to 74 (Table 8), but additional interesting fragmentations occur for 76 and 77. The loss of CO from the molecular ion of conjugated nitrones is usually of low abundance, but this ion is equal in intensity to the $M^{+\cdot}$-CHO ion for 76. The presence of a nitro group in 77 causes many other fragmentations to occur and implies that charge localization can occur on either the nitro or nitrone functional groups.

Mass Spectra of N-Alkylnitrones

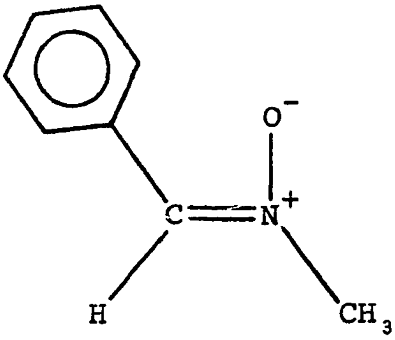
The N-alkylnitrones 82-86 were prepared and their mass spectra investigated to determine the effect of replacing the N-phenyl ring with an alkyl group. The main effect of the N-alkyl group appears to be stabilization of the oxaziridine intermediate since ions corresponding to the benzoyl cation and $RN^{+\cdot}$ are of low abundance (Table 9). This result might have been expected since $RN^{+\cdot}$ cannot undergo ring expansion to a stable azatropylium ion, and N-alkyl oxaziridines are known to be more stable than diaryl oxaziridines at least in solution chemistry (98, 99). The loss of an alkyl nitroso species still

Table 9. Mass spectra of N-alkylnitrones with peak intensities expressed as a percent of base peak

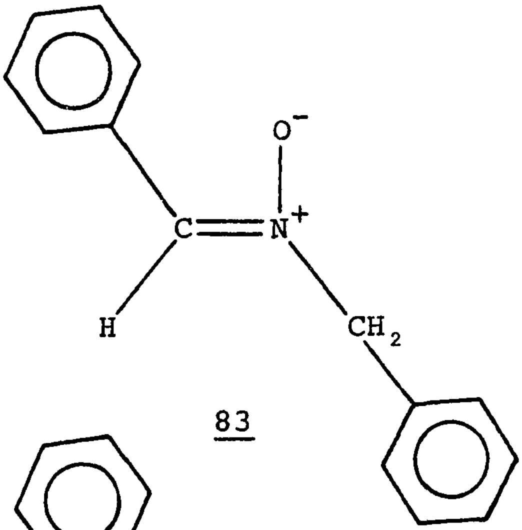
Compound	$M^{+\cdot}$	$M^{+\cdot}$-H	$M^{+\cdot}$-O	$M^{+\cdot}$-OH	$M^{+\cdot}$-CO	$M^{+\cdot}$-CHO	ϕ-C=O^{+}	R-N$^{+\cdot}$
<u>82</u>[a]	100	94.8	4.00	8.46	1.70	6.78	8.46	----
<u>83</u>	22.5	0.83	1.24	0.93	----	----	5.67[b]	5.67[b]
<u>85</u>	68.3	2.27	5.43	38.0	----	----	5.43	----

[a] Corrected for doublets from HRMS data.

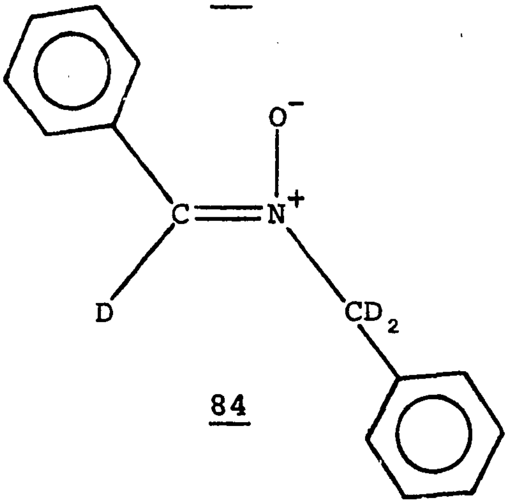
[b] Possible doublet.



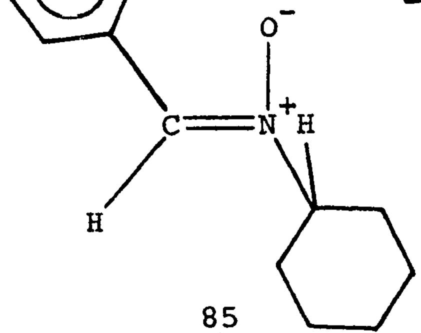
<u>82</u>



<u>83</u>



<u>84</u>

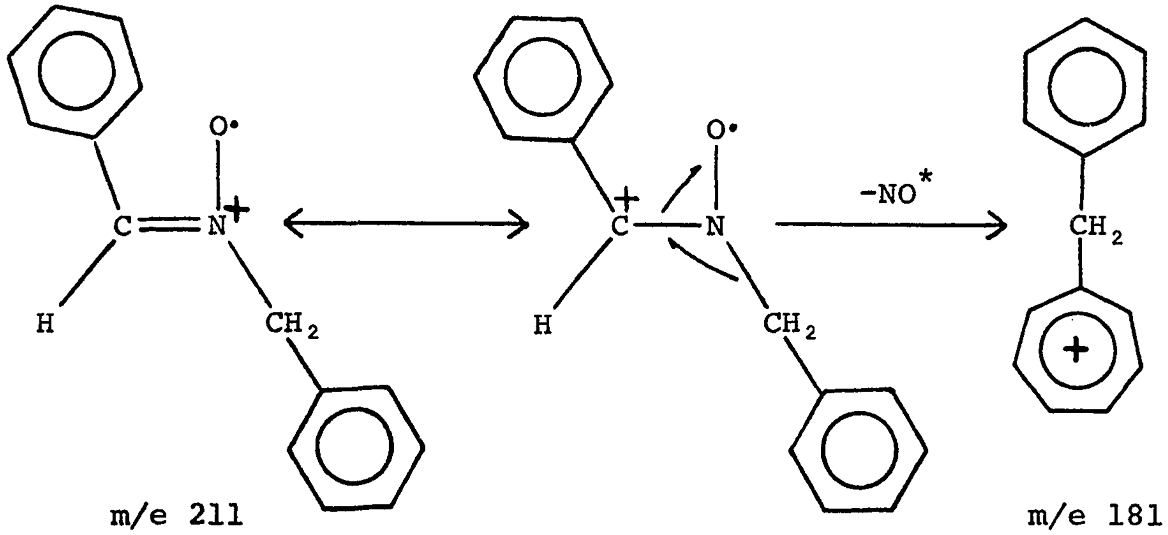


<u>85</u>

occurs to give the m/e 90 ion.

N-alkyl substitution also causes a pronounced reduction in the intensity of $M^{+\cdot}$-CO and $M^{+\cdot}$-CHO ions. These ions are essentially nonexistent for 83 and 85, and are of moderate intensity for 82. HRMS indicates that the interesting loss of CH_2N from 82 contributes 90% to the $M^{+\cdot}$-28 ion. With the exception of the above fragmentations and m/e 94, the other fragmentations of N-alkylnitrones are analogous to diarylnitrones.

The metastable loss of thirty mass units from 83 occurs to give a moderately intense ion at m/e 181 (10% of the base peak m/e 91). The shift of this ion to m/e 184 for 84 suggests that this fragmentation corresponds to the loss of NO perhaps as depicted in Scheme 71. The loss of OH from 83 must not occur by the consecutive losses of oxygen and the α-hydrogen since 84 loses primarily OH. This fragmentation probably

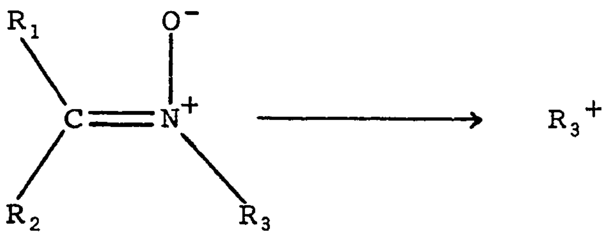


Scheme 71

involves hydrogen abstraction from the ortho positions of the benzyl phenyl ring in a six membered cyclic transition state.

Summary

Although a variety of skeletal rearrangement reactions occur in the spectra of nitrones, they do have certain common features which are useful in structural analysis. First, all the nitrones investigated gave clearly discernable molecular ions. Second, the loss of oxygen from the molecular ion occurred in all instances, and is useful in establishing the nitrone functional group in a molecule. Third, in the course of this investigation, it became apparent that the group bonded to nitrogen cleaves preferentially to give an intense aryl or alkyl cation as indicated in Scheme 72, thus establishing the identity of the group bonded to nitrogen. Finally, the other rearrangement ions discussed above can be used to definitely establish the identification of a molecule as a nitrone.



Scheme 72

EXPERIMENTAL

Instruments and Methods

All mass spectra were obtained on an Atlas MAT model CH 4 single focusing mass spectrometer operating at 70 electron volts, 3,000 volts accelerating potential, and a total ionizing current in the range 15-20 μA. Most samples were also run at lower electron energies. The Hammett plot data is the result of reproducible duplicate runs, and it was further demonstrated that changing the ratio of cis-trans isomers did not effect the relative intensities of the benzoyl cations.

Infrared spectra (ir) were recorded on a Perkin-Elmer Model 21 spectrometer. All nuclear magnetic resonance (nmr) spectra were taken on a Varian Associates Model A-60 spectrometer at 60 MHz. Chemical shift values are reported in parts per million (ppm), δ units, relative to tetramethylsilane as internal standard.

Melting points were obtained on a Fisher-Johns melting point apparatus. All melting points and boiling points are uncorrected and reported in degrees centigrade. All pressures are expressed in millimeters of mercury. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan or Chemalytics Inc., Tempe, Arizona.

Unless otherwise specified the aldehydes, ketones, and hydroxylamines used in the preparations described below were obtained from commercial sources.

Preparations

α,N-Disubstituted nitrones

Equal mmole quantities of the appropriate aldehyde and hydroxylamine were mixed in ethanol and allowed to set for 24 hours in the dark at room temperature according to the procedure of Wheeler and Gore (105) to give the following nitrones after recrystallization from ethanol:

α,N-diphenylnitrone (42): mp 112-113° (lit. (105) mp 114°).

α-(p-cyanophenyl)-N-phenylnitrone (43): mp 154-155°; ir ($CHCl_3$) 4.5 μ (C≡N).

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.67; H, 4.50. Found: C, 75.87; H, 4.53.

α-(p-methoxyphenyl)-N-phenylnitrone (44): mp 118° (lit. (105) mp 116°).

α-(p-hydroxyphenyl)-N-phenylnitrone (45): mp 215° (lit. (105) mp 212°).

α-(p-nitrophenyl)-N-phenylnitrone (46): mp 190° (lit. (105) mp 189°).

α-(o-hydroxyphenyl)-N-phenylnitrone (47): mp 119° (lit. (105) mp 119°).

α-mesityl-N-phenylnitrone (48): mp 171-172° (lit. (106) mp 170°).

α-pentaflourophenyl-N-phenylnitrone (49): mp 135-136°.

Anal. Calcd for $C_{13}H_6F_5NO$: C, 54.36; H, 2.09. Found:

C, 54.44; H, 2.20.

N-(<u>o</u>-methylphenyl)-α-phenylnitrone (<u>50</u>): mp 120-121°; nmr ($CDCl_3$) δ 2.5 (s, 3, CH_3), 7.2-7.6 (m, 8), and 8.4 (m, 2, α-<u>o</u>-H).

<u>Anal</u>. Calcd for $C_{14}H_{13}NO$: C, 79.62; H, 6.16. Found: C, 79.57; H, 6.08.

N-(<u>p</u>-methylphenyl)-α-phenylnitrone (<u>51</u>): mp 124° (lit. (105) mp 123°).

α-(1-naphthyl)-N-phenylnitrone (<u>52</u>): mp 140-141°; nmr ($CDCl_3$) δ 7.4-8.1 (m, 11), 8.7 (s, 1, α-H), and 9.8 (d, 1, peri H).

<u>Anal</u>. Calcd for $C_{17}H_{13}NO$: C, 82.59; H, 5.26. Found: C, 82.42; H, 5.30.

N-(<u>o</u>-methylphenyl)-α-(1-naphthyl)-nitrone (<u>53</u>): mp 166.5-168.5°; nmr ($CDCl_3$) δ 2.5 (s, 3, CH_3), 7.2-8.1 (m, 10), 8.3 (s, 1, α-H), and 9.85 (d, 1, peri H).

<u>Anal</u>. Calcd for $C_{18}H_{15}NO$: C, 83.14; H, 5.75. Found: C, 83.27; H, 5.90.

α-(9-anthryl)-N-phenylnitrone (<u>54</u>): mp 236-238°; nmr ($CDCl_3$) δ 7.3-7.6 (m, 7), 7.8-8.2 (m, 6), 8.5 (s, 1), and 8.8 (s, 1).

<u>Anal</u>. Calcd for $C_{21}H_{15}NO$: C, 84.83; H, 5.05. Found: C, 84.69; H, 5.19.

N-phenyl-α-(2-thienyl)-nitrone (<u>55</u>): mp 91-92°.

<u>Anal</u>. Calcd for $C_{11}H_9NOS$: C, 65.02; H, 4.43; N, 6.95.

Found: C, 65.15; H, 4.47; N, 6.94.

α-ferrocenyl-N-phenylnitrone (<u>56</u>): mp 137-138°; nmr ($CDCl_3$) δ 4.3 (s, 5), 4.6 (s, 2), 5.1-5.3 (m, 2), 7.2-7.6 (m, 3), and 7.7-8.0 (m, 2).

<u>Anal</u>. Calcd for $C_{17}H_{15}FeNO$: C, 66.80; H, 5.23. Found: C, 66.74; H, 5.05.

α-C^{13}-α,N-diphenylnitrone (<u>57</u>): mp 112-113°. Low voltage mass spectrometry indicated the following label incorporation: 47% C^{12} and 53% C^{13}.

α-deuterio-α,N-diphenylnitrone (<u>58</u>): mp 112°. Low voltage mass spectrometry indicated the following label incorporation: 3.2% d_0, 95.2% d_1, and 1.6% d_2.

N-phenyl-α-styrylnitrone (<u>74</u>): mp 154-155° (lit. (107) mp 150-151°).

α-(β-methylstyryl)-N-phenylnitrone (<u>75</u>): mp 74-75°; ir ($CHCl_3$) 6.25 μ (C=C); nmr ($CDCl_3$) δ 2.3 (d, 3, CH_3), and 7.1-7.8 (m, 12).

<u>Anal</u>. Calcd for $C_{16}H_{15}NO$: C, 81.10; H, 6.37. Found: C, 81.18; H, 6.46.

α-(α-phenylstyryl)-N-phenylnitrone (<u>76</u>): mp 142-143°; nmr ($CDCl_3$) δ 7.1-7.8 (m).

<u>Anal</u>. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72. Found: C, 84.21; H, 5.65.

α-(<u>o</u>-nitrostyryl)-N-phenylnitrone (<u>77</u>): mp 105-105.5°; ir ($CHCl_3$) 6.25 μ (C=C), 6.55 μ (NO_2), and 7.42 μ (NO_2); nmr

($CDCl_3$) δ 7.2-8.0 (m).

Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 76.25; H, 5.12. Found: C, 76.20; H, 5.15.

α-(p-dimethylaminophenyl)-N-phenylnitrone (78): mp 206-208° dec; ir ($CHCl_3$) 6.25 μ (C=C); nmr ($CDCl_3$) δ 3.0 (s, 6, CH_3), and 6.7-7.8 (m, 12).

Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.67; H, 6.81. Found: C, 76.58; H, 6.71

α-(α-deuteriostyryl)-N-phenylnitrone (79): mp 155-156°. Low voltage mass spectrometry indicated the following label incorporation: 3.32% d_0 and 96.68% d_1.

α-(β-deuteriostyryl)-N-phenylnitrone (80): mp 154-155°. Low voltage mass spectrometry indicated the following label incorporation: 22.2% d_0 and 77.8% d_1.

α-deuterio-N-phenyl-α-styrylnitrone (81): mp 154-155°. Low voltage mass spectrometry indicated the following label incorporation: 2.44% d_0, 96.2% d_1, 1.11% d_2, and 0.25% d_3.

p-Cyanotoluene

This compound was prepared from p-toluidine according to the procedure of Clarke and Reed (108): ir (CCl_4) 4.5 μ (C≡N).

p-Cyanobenzaldehyde

The procedure of Lieberman and Connor (109) was used to prepare p-cyanobenzaldehyde by oxidiation of p-cyanotoluene: mp 94° (lit. (81) mp 92-93°); ir (CCl_4) 4.5 μ (C≡N) and 5.85

μ (C=O).

α-C^{13}-Benzaldehyde

This compound was prepared as previously described on page 125 of this thesis.

α-Deuteriobenzaldehyde

The desired compound (1.78 g) was prepared by the procedure of Wiberg (67).

α-Deuteriocinnamaldehyde

The desired compound was prepared as previously described on page 134 of this thesis.

β-Deuteriocinnamaldehyde

This compound was prepared as previously described on page 135 of this thesis.

γ-Deuteriocinnamaldehyde

This compound was prepared as previously described on page 136 of this thesis.

N-Phenylhydroxylamine

Zinc dust reduction of nitrobenzene according to the procedure of Kamm (110) gave N-phenylhydroxylamine: mp 83-84° (lit. (110) mp 83-84°).

N-(o-Methylphenyl)-hydroxylamine

This compound was prepared by zinc dust reduction of *o*-nitrotoluene using the procedure of Kamm (110): mp 40-41° (lit. (105) mp 43°).

N-(p-Methylphenyl)-hydroxylamine

The desired compound was prepared from *p*-nitrotoluene using the procedure of Kamm (110): mp 81° (lit. (111) mp 80°).

General preparation of triarylnitrones

The hydrazones of various *para* substituted benzophenones were prepared using the procedure of Szmant and McGinnis (112) or that of Huttel, Riedl, Martin, and Franke (113). The hydrazones were oxidized to diazo compounds with silver oxide according to the procedure of Schroeder and Katz (114). The filtered ether solution of the diazo compound was treated with enough nitrosobenzene to discharge the red to violet color of the diazo compound according to a modification of the procedure of Johnson (115). After the initial vigorous evolution of nitrogen, the nitrones generally crystallized out of solution. The crystals were filtered and recrystallized from ethanol to give the following triarylnitrones:

α,α,N-triphenylnitrone (66): mp 223-225° (lit. (115) mp 223-225°).

α-(*p*-methoxyphenyl)-α,N-diphenylnitrone (67): mp 128-144° cis and trans isomers; nmr ($CDCl_3$) δ 3.75 (s, CH_3), 3.85 (s,

CH_3), and 6.8-7.4 (m).

Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.20; H, 5.61. Found: C, 79.17; H, 5.71.

α-(p-methylphenyl)-α,N-diphenylnitrone (68): mp 187-196° cis and trans isomers; nmr ($CDCl_3$) δ 2.3 (s, CH_3), 2.4 (s, CH_3), 7.1-7.4 (m), and 7.9-8.1 (d).

Anal. Calcd for $C_{20}H_{17}NO$: C, 83.51; H, 5.93. Found: C, 83.51; H, 5.84.

α-(p-chlorophenyl)-α,N-diphenylnitrone (69): mp 184-186°.

Anal. Calcd for $C_{19}H_{14}ClNO$: C, 74.20; H, 4.55. Found: C, 74.26; H, 4.53.

α-(p-flourophenyl)-α,N-diphenylnitrone (70): mp 226-230° cis and trans isomers.

Anal. Calcd for $C_{19}H_{14}FNO$: C, 78.33; H, 4.84. Found: C, 78.44; H, 4.85.

α-(p-cyanophenyl)-α,N-diphenylnitrone (71): mp 191-194° cis and trans isomers; ir ($CHCl_3$) 4.5 μ (C≡N).

Anal. Calcd for $C_{20}H_{14}N_2O$: C, 80.50; H, 4.73. Found: C, 80.62; H, 4.62.

α-(p-nitrophenyl)-α,N-diphenylnitrone (72): mp 81-88° cis and trans isomers; ir ($CHCl_3$) 6.65 μ (NO_2), and 7.43 μ (NO_2); nmr ($CDCl_3$) δ 7.1-7.5 (m), and 7.8-8.2 (m).

Anal. Calcd for $C_{19}H_{14}N_2O_3$: C, 71.60; H, 4.43. Found: C, 71.68; H, 4.36.

9-Fluorenone hydrazone

The hydrazone of 9-fluorenone was prepared by the procedure of Wieland and Roseau (116): mp 149° (lit. (116) mp 149°).

9-Diazofluorenone

The desired compound was prepared according to the procedure of Nenitzescu and Solomonica (117).

N-Phenyl-9-fluorenoneketoxime (73)

The procedure of Johnson (115) was used to prepare N-phenyl-9-fluorenoneketoxime 73: mp 200° (lit. (115) mp 200°).

N-Methyl-α-phenylnitrone (82)

The procedure of Brady, Dunn, and Goldstein (118) was used to prepare 82: mp 83° (lit. (118) mp 83°).

N-Benzyl-α-phenylnitrone (83)

The desired compound was prepared by the oxidation of N,N dibenzylhydroxylamine with yellow mercuric oxide according to the procedure of Wragg and Stevens (119): mp 80° (lit. (119) mp 82°).

N-(α,α-Dideuteriobenzyl)-α-deuterio-α-phenylnitrone (84)

The reduction of 14.6 g of methylbenzoate with 2.3 g of lithium aluminum deuteride in the convential manner gave 10.74 g of α,α-dideuteriobenzyl alcohol which treated with 47.0 g of Lucas reagent gave 7.05 g α,α-dideuteriobenzyl chloride: bp 30°/0.5 mm. The labeled benzyl chloride was reacted with 2.04 g of hydroxylamine hydrochloride according to the procedure of Wragg and Stevens (119) to give 2.45 g of N,N-di-(α,α-dideuteriobenzyl)-hydroxylamine: mp 121-123°. Oxidiation of the hydroxylamine according to the procedure of Wragg and Stevens (119) gave 1.28 g of 84: mp 82-83°. Low voltage mass spectrometry indicated the following label incorporation: 1.32% d_2 and 98.68% d_3.

N,N-Dibenzylhydroxylamine

This compound was prepared by the procedure of Wragg and Stevens (119): mp 123° (lit. (119) mp 123°).

N-Cyclohexyl-α-phenylnitrone (85)

The desired compound was prepared by the method of Thesing and Sirrenberg (120): mp 84-85° (lit. (120) mp 86°).

Cyclohexylhydroxylamine

The procedure of Schultz (121) was used to prepare cyclohexylhydroxylamine: mp 136-138° (lit. (121) mp 136.5-138°).

Nitrosobenzene

The procedure of Coleman, McCloskey, and Staurt (122) was used in the preparation of nitrosobenzene: mp 67° (lit. (122) mp 64-67°).

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APPENDIX A

Calculations Involving Labeled
β-Methyl-β-nitrostyrene 8

Calculation for $M^{\overset{+}{\cdot}}$-H/D in 11

m/e 162	m/e 163	
3.00	9.50	
	- 7.85	Contribution of D_2 species to m/e 163
3.00	1.65	
	- 0.30	Contribution of C^{13} to m/e 163
3.00	1.35	
- .11		Contribution of D_2 species to m/e 162
2.89	1.35	

Total = 2.89 + 1.35 = 4.24

Loss of H = 1.35/4.24 × 100 = 32%

Loss of D = 2.89/4.24 × 100 = 68%

The following losses of H/D are predicted for randomization of H and D in the phenyl ring:

Loss of H = 2/5 × 100 = 40%

Loss of D = 3/5 × 100 = 60%

Accurate calculations could not be made for the other labeled compounds.

Calculation for $M^{+\cdot}$-OH/OD in 11

m/e 148	m/e 149	
12.50	15.00	
	- 1.28	Contribution of C^{13} to m/e 149
12.50	13.72	

Total = 12.5 ÷ 13.72 = 26.22

Loss of OH = 13.72/26.22 × 100 = 52.4%

Loss of OD = 12.50/26.22 × 100 = 47.6%

Note, no correction was made for $M^{+\cdot}$-OH/OD from the D_2 species. The following losses of OH/OD are predicted for randomization of H and D in the phenyl ring, assuming abstraction from the phenyl ring only:

Loss of OH = 2/5 × 100 = 40%

Loss of OD = 3/5 × 100 = 60%

Calculation for $M^{+\cdot}$-OH/OD in 9

m/e 146	m/e 147	
7.00	13.00	
	- 0.70	Contribution of C^{13} to m/e 147
7.00	12.30	
- 2.97		Contribution of D_0 to m/e 146
4.03	12.30	

Total = 4.03 + 12.30 = 16.33

Loss of OH = 12.30/16.33 × 100 = 75.5%

Loss of OD = 4.03/16.33 × 100 = 24.5%

The following losses of OH/OD are predicted for randomization of H and D in the phenyl ring, assuming abstraction from the phenyl ring only:

Loss of OH = 4/5 × 100 = 80%

Loss of OD = 1/5 × 100 = 20%

The following losses of OH/OD are calculated for a deuterium isotope effect of the magnitude necessary to give the results observed for 11 assuming abstraction from the phenyl ring with randomization:

$3(D)/X_{(H+D)} = 0.476$ See calculation for 11

$X_{(H+D)} = 6.3$

$X_H = 6.3 - 3(D) = 3.3$

$2H_{\text{Effective}} = 3.3$

$H_{\text{Effective}} = 1.65$

Each hydrogen atom is worth 1.65 times a deuterium atom as far as abstraction from the phenyl ring is concerned for 11.

Total effective (H+D) for 9 = 1.65(4) + 1 = 7.60

Loss of OH = 6.60/7.60 × 100 = 86.9%

Loss of OD = 1/7.60 × 100 = 13.1%

No loss of OD was observed for 10, and 12 after correcting for unlabeled species.

Calculation for $M^{\ddagger}$-CHO/CDO in 11

Unlabeled 8:

m/e 133	m/e 134	m/e 135	
10.00	5.50	26.50	
	- 1.00		Contribution of C^{13} to m/e 134

10.00	4.50	26.50	
		- .41	Contribution of C^{13} to m/e 135
10.00	4.50	26.09	

Total = 10.00 + 4.50 + 26.09 = 40.59

The following peak intensities are expressed as a percent of the Σ m/e 133-135.

m/e 133	m/e 134	m/e 135
24.6	11.1	64.3

Labeled <u>11</u>:

m/e 134	m/e 135	m/e 136	
12.50	3.50	26.50	
	- 1.24		Contribution of C^{13} to m/e 135
12.50	2.26	26.50	
		- .21	Contribution of C^{13} to m/e 136
12.50	2.26	26.29	

Total = 12.50 + 2.26 + 26.29 = 41.05

The following peak intensities are expressed as a percent of the Σ m/e 134-136.

m/e 134	m/e 135	m/e 136	
30.50	5.51	63.99	
- 24.60			Correction for $M^{\overset{+}{\cdot}}$-NO to m/e 134
5.90	5.51		

Total = 5.90 + 5.51 = 11.41

Loss of CHO = 5.51/11.41 × 100 = 46.75%

Loss of CDO = 5.90/11.41 × 100 = 53.25%

Similar calculations were not done for 9 and 10.

Calculation for M-HNO_2/DNO_2 and subsequent loss of H/O

	m/e	m/e	m/e	m/e	m/e	m/e	m/e
Compound[1]	115	116	117	118	119	120	121
8	55.6	25.4	15.0	2.76			
12	18.2	55.7	9.56	14.1	2.38		
11	--	3.29	24.7	35.0	19.7	15.5	1.75

Sequence one:

Contribution to m/e 116 = 15.84/25.4 × 100 = 62.5%

Contribution to m/e 115 = 18.2/55.6 × 100 = 33%

Sequence two:

Contribution to m/e 116 = 9.56/25.4 × 100 = 37.5%

Contribution to m/e 115 = 37.4/55.6 × 100 = 67%

25.40 m/e 116 in 8
- 9.56 m/e 117 in 12
15.84 Loss of DNO_2 from 12

55.70 m/e 116 in 12
- 15.84 Loss of DNO_2 from 12
39.60 Loss of H,HNO_2 from 12

19.70 m/e 119 in 11
- 15.84 Loss of DNO_2 from 12
3.86 Loss of HNO_2 other than α-HNO in 11

---

[1] Peak intensities expressed as percent of Σ m/e 115-121 after correcting for C^{13}

9.56	m/e 117 in 12
- 3.86	Loss of HNO_2 other than α-HNO_2 in 11
5.70	Loss of DNO_2 from the ring of 11

Loss of HNO_2 from the phenyl ring of 11 =

3.86/9.56 × 100 = 40.5%

Loss of DNO_2 from the phenyl ring of 11 =

5.70/9.56 × 100 = 59.5%

Calculation for the statistical loss of HNO_2/DNO_2 from the phenyl ring of 11:

Loss of HNO_2 = 2/5 × 100 = 40%

Loss of DNO_2 = 3/5 × 100 = 60%

Calculations for the further loss of H/D:

35.00	m/e 118 in 11
- 18.20	m/e 115 in 12
16.80	Loss of DNO_2 and H,HNO_2 from 11
5.70	Loss of DNO_2 from 11
11.10	Loss of H,HNO_2 from 11 not involving the α-hydrogen atom.
24.7	m/e 117 in 11 corresponding to loss D,HNO_2 and H,DNO_2.
3.29	m/e 116 in 11 corresponding to loss of D,DNO_2.

Total = 3.29 + 24.70 + 11.10 = 39.09

Intensity m/e 118 = 11.10/39.09 × 100 = 28.4%

Intensity m/e 117 = 24.70/39.09 × 100 = 63.0%

Intensity m/e 116 = 3.29/39.09 × 100 = 8.6%

The following calculation is for the statistical loss of H/D after the initial loss of HNO_2/DNO_2 from 11. In this calculation it is assumed that all of the remaining hydrogen and deuterium atoms in the m/e 119 and m/e 118 ions become equivalent before the subsequent loss of H/D. The 2/5 and 3/5 used in the calculation correspond to the original statistical ratios for the formation of the m/e 119 and m/e 118 ions by loss of HNO_2/DNO_2 with randomization of hydrogen and deuterium in the phenyl ring of 11. Since there are a total of eight hydrogen and deuterium atoms in the m/e 119 ion the chance of further losing hydrogen are 5/8 and deuterium 3/8. These fractions times the statistical intensity of m/e 119 gives the calculated contribution to m/e 118 and m/e 117. In a similar manner the contribution of m/e 118 to m/e 117 and m/e 116 can be calculated. The actual calculation is shown below:

m/e 116	m/e 117	m/e 118	m/e 119
		3/5	2/5
	3/8×215	5/8×215	
2/8×315	6/8×315		
6/40	24/40	10/40	
15%	60%	25%	

Calculations Involving Labeled Nitrodienes

Calculation for $M^{+\cdot}$-CHO/CDO in 33

m/e 146	m/e 147	
11.00	46.50	
	− 1.13	Contribution of C^{13} to m/e 147
11.00	45.87	
− 1.40		Contribution of D_0 to m/e 146
9.60	45.87	

Total = 9.60 + 45.87 = 55.47

Loss of CHO = 45.87/55.47 × 100 = 82.5%

Loss of CDO = 9.60/55.47 × 100 = 17.5%

Calculation for $M^{+\cdot}$-CHO/CDO in 34

m/e 146	m/e 147	
11.00	22.00	
	− 1.13	Contribution of C^{13} to m/e 147
11.00	20.87	
− 6.00		Contribution of D_0 to m/e 146
5.00	20.87	

Total = 5.00 + 20.87 = 25.87

Loss of CHO = 20.87/25.87 × 100 = 80.7%

Loss of CDO = 5.0/25.87 × 100 = 19.3%

Calculation for $M^{+\cdot}$-CHO/CDO in 35

No observed loss of CDO after correcting for D_0 species.

APPENDIX B

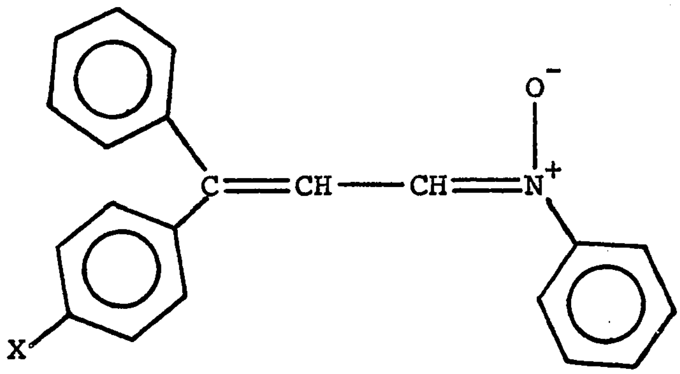
Suggestions for Further Research

In the course of writing this thesis several ideas concerning a logical extension of this research have come to mind. In the historical it was noted that the elimination of nitrous acid occurs from tertiary nitroalkanes to give an olefin (4). Later work by other authors (10) lead to the suggestion that this loss occurred by hydrogen abstraction since γ-hydrogens were available in the compounds studied. Labeling work should be done to establish the validity of this proposal.

Further labeling of the phenyl ring of 1-nitro-4-phenylbutadiene <u>29</u> should be carried out to prove the hydrogen randomization mechanism proposed for loss of CHO from <u>29</u> and to prove that the hydrogen lost in the $M^{+\cdot}-HNO_2$ ions comes from the phenyl ring. Then too, the mass spectra of other simple alkyl nitroolefins should be examined to determine whether the fragmentations observed for 4-methyl-2-nitropent-2-ene are general.

The pyrolysis studies presented in the thesis only concern nitrostyrenes and clearly require more work to establish the scope of the observed reaction. In this regard the pyrolytic behavior of heteroaromatic, conjugated, and alkyl nitroolefins should be studied. The pyrolysis of conjugated nitroolefins is of particular interest since initial nucleophilic attack could occur on the α or γ carbon atoms to give two different sets of products. The scope of the thermal nitro-nitrite process observed for nitrotriphenylethylene 21 should also be examined for other nitroolefins with a phenyl ring on the same carbon atom as the nitro group.

The work on nitrones is complete with the exception of conjugated nitrones. The phenyl rings of N-phenyl-α-styryl-nitrone 74 should be labeled with deuterium to establish the mechanisms for loss of OH and CHO from the molecular ion of 74. Finally the five membered ring intermediate 82, which leads to a benzoyl cation after hydrogen migration for 74, provides an opportunity to determine mass spectral migratory apptitudes to a carbon radical site for substituted aryl rings relative to phenyl in nitrones of the type 86.



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