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Accounts

Versatile Reactions Undergone by Carbenes and Nitrenes in Noble Gas Matrices at Cryogenic Temperatures

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A series of phenyldiazomethanes and phenyl azides bearing proximate substituents matrix-isolated in Ar at cryogenic temperatures have been photolyzed. Products are characterized mainly by IR spectroscopy in combination with ab initio theoretical calculations. In most cases, several intermediates are produced as a result of interaction between the divalent centers and the proximate functional group; they are photo-interconvertible under these conditions.

Phenylcarbenes and phenylnitrenes having hydrogen donors such as CH_3, OH, and NH_2 groups at the *ortho* position have been shown to abstract hydrogen to form *o*-quinonoid compounds. Both the carbene and nitrene undergo oxygen transfer from the nitro group at the *ortho* position to form the corresponding nitroso compounds. While phenylcarbene interacts with *o*-CO_2Me group to generate the corresponding carbonyl ylide, phenylnitrene undergoes 1,4-MeO shift in its excited states to produce 5-carbonyl-6-methoxyimino-1,3-cyclohexadiene. Interesting differences in the reactivity between carbenes and nitrenes are noted; these are discussed in terms of the electronic configuration, singlet-triplet energy gap and tunneling.

1,3-Bis(diazo) ketones incorporated in five- and seven-membered rings are prepared and photolyzed under matrix conditions. While the seven-membered ring bis(diazo)ketone affords phenanthryne by way of 9,10-cyclopropa-phenanthren-3′-one, the five-membered analogue generates 1,2-cyclopropabenzocyclobutadien-3′-one, which does not undergo photodecarbonylation to form benzocyclobutenyne.

Finally, a series of bis(divalent) species conjugatively connected through aromatic rings are generated and characterized. In both *p*- and *o*-phenylene systems, there is a significant interaction between the benzene nucleus and the divalent substituents. The species are best regarded as *p*- and *o*-quinonoidal biradical structures, respectively, having a singlet ground state with a low-lying excited triplet state.

The last two decades have witnessed tremendous advances in techniques to observe highly elusive species with only fleeting existence at room temperature. Time-resolved laser experiments have permitted the spectroscopic detection of ephemeral species with lifetimes as short as picoseconds.[1)] Generation of extremely reactive molecules under low-temperature matrix isolation conditions has provided considerable information on these otherwise elusive molecules.[2)] Moreover, rapid advance in computational chemistry has made it possible to predict the structures and properties of reactive intermediates fairly precisely.[3)] Thus, understanding of the properties of these highly elusive species has been deepened tremendously. This is especially important, since one of the central objectives of the study of chemistry is sufficient knowledge to permit the forecast of the chemical and physical properties of a substance directly from its structure and since it is the properties of these reactive intermediates which often control the outcome of chemical reaction.

On the other hand, the recent advances have made it easy to study subsequent reactions of these highly transient species under carefully controlled conditions, not to mention under "normal" conditions. For instance, reactive intermediates can be easily excited by using two-laser, two-color techniques, which allow one to study photochemistry of these highly transient species in solution.[4)] Under matrix isolation conditions, such studies can be easily executed since the intermediates have lifetimes of minutes to hours under these conditions. However, since this techniques have been originally developed to detect otherwise unstable species, not much effort has been made to employ this technique for studying further reactions of these highly energetic species. Actually, many reactive species trapped in matrices can be easily excited electronically upon further irradiation to a higher energy state which follows subsequent pathways, if available. Unlike the reaction in solution phase, where excited intermediates immediately decay to form thermodynamically stable compounds, even thermodynamically unstable species which may be produced from the excited state of the initially formed intermediates can survive under these conditions and also undergo subsequent photoexcitation. Therefore, a priori it is possible to obtain a photoequilibrium mixture of several transient species under these conditions. And this is often the case.

1. Apparatus and Techniques

The matrix isolation technique has been the subject of a number of reviews and books.[1)] Thus, we will briefly describe the experimental methods employed to generate and study inert gas matrices. More detailed techniques can be found in specialized articles[1a)] and books.[1d,1e)]

The solid sample is mounted on a holder whose temperature can be lowered and controlled. The holder may be cooled to 4 K by means of a liquid-helium cryostat, or more conveniently to about 10 K by means of a commercially-available, closed-cycle helium refrigerator. Temperatures are routinely controlled by small resistive heaters attached to the refrigerator cold tip near the window holder. For critical applications the temperature sensor is sometime attached to the window itself. The entire cold part must be isolated to exclude air and moisture. For this purpose, a vacuum is applied in the entire assembly which forms the cryostat.

For optical observation, the sample holder and the cryostat have windows or observation ports. The spectroscopic windows depend on the desired spectroscopic technique. Cesium iodide or bromide have proved best for IR studies. These windows are both transparent in the IR and UV for spectroscopy or photolysis and are flexible enough to prevent cracking due to thermal shock. Sapphire is the support of choice for UV-vis experiments, based on its high thermal conductivity. Copper, sapphire, and single-crystal quartz have been used for ESR. The central window is enclosed in a very-high-vacuum shroud. In addition, outer vacuum shroud designs have been also used. The vacuum shroud has an outlet portion connected to a diffusion pump and one or more inlet portions for deposition of the sample on the cold window. Usually some provision is made to allow the central window to be rotated to face either the external windows or the inlet portions.

Matrices can be generated several different ways depending on the volatility and thermal stability of precursor molecules. Matrix samples of volatile compounds are best made by first preparing a gas mixture of the compound and the matrix gas. Host : guest matrix ratios are typically 10^2—10^3 in order to obtain the highest likelihood for good isolation. The gas mixture is then slowly deposited on the cold window. When a compound is too involatile to be handled in this way, it may be deposited simultaneously with the host gas. This technique does not permit one to obtain a reliable estimate of the matrix ratio and can lead to greater amounts of aggregates being deposited. Quite large molecules, however, even porphyrins, have been matrix-isolated in this way.

The temperature at which a matrix is deposited has a pronounced effect on the scattering produced by the solid film. For instance, xenon forms a reasonably transparent matrix when deposited at 66 K, whereas a highly scattering film results when it is deposited below 50 K. The window is then usually cooled to the lowest attainable temperature before irradiation.

Irradiation of matrix-isolated samples often requires more precise control of wavelength than does corresponding solution irradiation, since many reactive intermediates are photolabile themselves and are often interconvertible upon irradiation under these conditions. *For this reason, the wavelength of light used for irradiation will be described specifically throughout this account.*

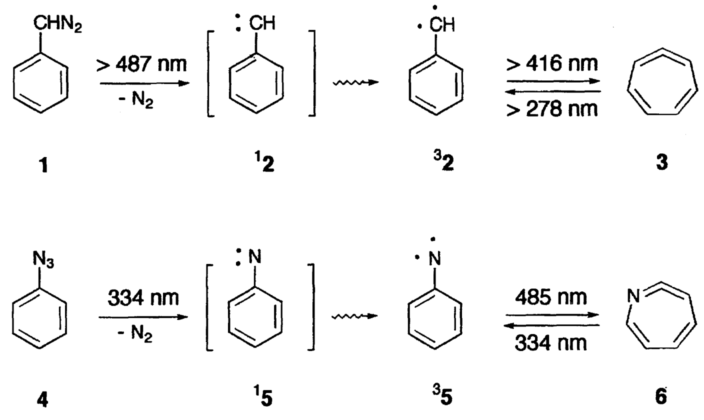
The most difficult aspect of the method is perhaps the assignment of spectra to intermediate structures. IR spectroscopy has been used most heavily to characterize matrix isolated species. Fortunately, a matrix IR spectrum is generally a series of sharp bands showing no rotational structure due to the rigidity of the matrix and the minimization of intermolecular interactions. This enables us to discriminate individual species in mixtures with great ease. In addition, vibrational assignments and normal-coordinate analysis are easier than with gas-phase spectra. The electronic spectra of products may be conveniently correlated with other spectra.

Direct analysis of the spectra and consideration of origins of the intermediates lead to at least hypothetical structures. Ideally, the intermediate can be generated from more than one precursor. Identity of the spectra obtained from several different routes has provided considerable support to structural assignments. In some cases the intermediate may be derived to known products either photochemically or thermally. Isotopic labeling has proven to be essential for assignment of normal modes. Much painstaking and time-consuming work is usually necessary to establish the identity of an intermediate simply based on matrix spectra. Ab initio calculations of vibrational frequencies, however, have been shown to be extremely useful, and have started to be used routinely.

2. Detection and Reaction of Simple Phenylcarbene and Phenylnitrene

Chemistry of divalent carbon species[5,6)] constitutes a central topic in the study of reactive intermediates under matrix conditions, since they can be easily and cleanly generated by photolysis of the corresponding azo precursors even at very low temperature in rigid matrices. Moreover, they are neutral and divalent, and hence they are forced to find some routes to normal tetravalent compounds with only their own resources, without taking external bonding or electrons, under these highly unimolecular conditions. Since they are highly energetic species, those products can be also energetic molecules with highly strained bonds.

For example, irradiation of phenyldiazomethane (**1**) matrix-isolated in Ar at 10 K results in generation of phenylcarbene (^{3}**2**) in its triplet ground states. The triplet carbene (^{3}**2**), though highly elusive at room temperature, exists *infinitely*, as long as matrix conditions are retained, and is easily photoexcited upon further irradiation to produce 1,2,4,6-cycloheptatetraene (**3**) eventually. Surprisingly, photoexcitation of the tetraene **3** reproduces triplet phenylcarbene (^{3}**2**) under these conditions (Scheme 1). The facile photochemi-



Scheme 1.

cal conversion of the triplet carbene to the (singlet) tetraene suggests that there may be a readily accessible excited state of the carbene **2** with a proclivity toward rearrangement.[7]

Essentially the same reaction is observed with monovalent nitrogen species. In the photolysis of phenyl azide (**4**) within matrices, triplet phenylnitrene (^{3}**5**)–didehydroazepine (**6**) photoequilibrium is confirmed (Scheme 1).[8] Furthermore, further irradiation of triplet phenylnitrene (**5**) with short wavelength light ($\lambda > 216$ nm) results in the formation of triplet 2-pyridylmethylene (^{3}**7**). Irradiation of 2-(diazomethyl)pyridine (**8**) under these conditions gives initially triplet 2-pyridylmethylene (**7**) and then triplet phenylnitrene (^{3}**5**). The two triplets are shown to interconvert via the didehydroazepine (**6**) (Scheme 2).[9]

The thermolysis of phenyl azide and various precursors to the three isomeric pyridylmethylenes has shown that the C_6H_5N energy surface is quite slippery, and that the thermal chemistry of these species is rich with carbene/carbene and carbene/nitrene rearrangements.[10] Therefore, it is interesting to note that the low temperature photochemical transformations at 10 K sometimes closely parallel thermal transformations of these systems at temperatures in the vicinity of 1000 K. The only significant difference between the two conditions is that, in the thermolysis in gas phase, the molecules on the energy surface are terminated to form thermodynamically stable products, while under matrix conditions molecules on the high energy surface are surviving and hence can be directly observed.

It is possible to divert the rearrangement from a slippery energy surface to some other energy surface, which may be similarly slippery, if one introduces a functional group, potentially reactive toward diradical centers, on the proximate position, which is expected to open a new route to a series of reactive species.[10,11]

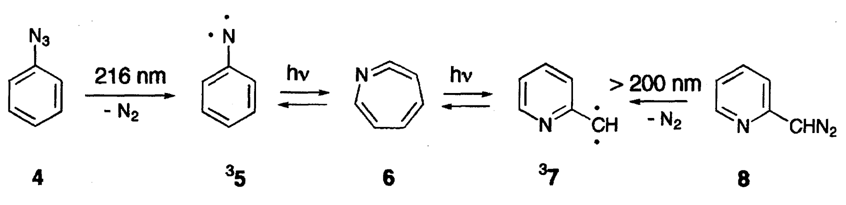
Intramolecular rearrangements are typical reactions for the singlet states of carbenes[5] and nitrenes.[6] Therefore, if the singlet states are formed, they will easily undergo unimolecular reactions under matrix conditions. In solution, the formally spin-forbidden rearrangement of triplet states to singlet products is generally slower than other reactions such as dimerization or H abstraction from the solvent employed. In inert gas matrices at low temperature, however, triplet states are forced to find a route to undergo rearrangement, since intermolecular reaction is largely prohibited due to limited diffusibility.

The present account describes our efforts along this line, where we generated a series of phenylcarbenes and -nitrenes bearing functional groups at the proximate positions in inert gas matrices at low temperatures, characterized the products formed as a result of intramolecular interaction between the diradical center and the proximate functional group, and investigated the reaction mechanism. The study has not only provided a new route to a series of reactive species, as expected, but has also given insight into the new nature of these divalent species, which was otherwise almost impossible to learn about.

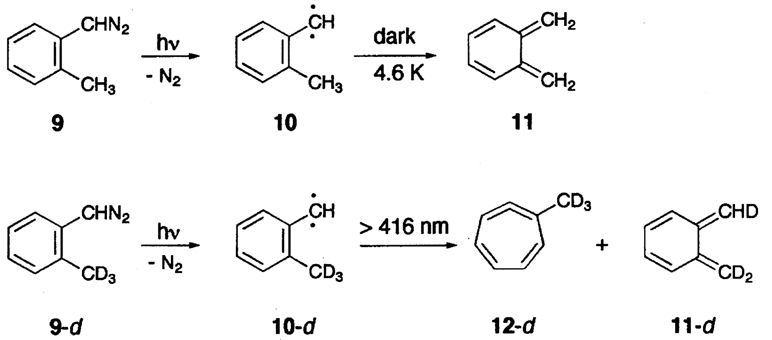
3. Interaction with Active Hydrogens

In solution, 1,2-hydrogen shifts are typical reactions for the singlet states of carbenes and nitrenes, while they are less common for the triplet states. Hydrogen atom migrations (abstractions) from donors are, on the other hand, typical reactions for the triplet states of carbenes, while the singlet states usually undergo insertion into a C–H bond in a concerted manner. Therefore 1,2 H shifts can be regarded as insertion of the singlet carbene into β-C–H bonds.

There are fundamental differences in the reactivity of phenylcarbene and phenylnitrene with respect to C–H bonds.



Scheme 2.



Scheme 3.

Singlet phenylcarbene inserts into C–H bonds, while singlet phenylnitrene does not, possibly because ring expansion to form didehydroazepine is so fast. Furthermore, triplet phenylcarbene readily abstracts hydrogen atoms from donors, while triplet nitrene does not.[12]

Interaction of the divalent species with the donors containing heteroatom X–H bonds is somewhat different from that with ones containing only C–H bonds. Singlet phenylcarbene, for instance, interacts preferentially with the lone-pair electrons on the heteroatom to generate ylides which undergo subsequent reaction, while the triplet abstracts hydrogen atoms from mainly C–H bonds rather than X–H bonds in the donors. Reactions of phenylnitrenes with such donors are essentially the same as those observed in hydrocarbon solvents.

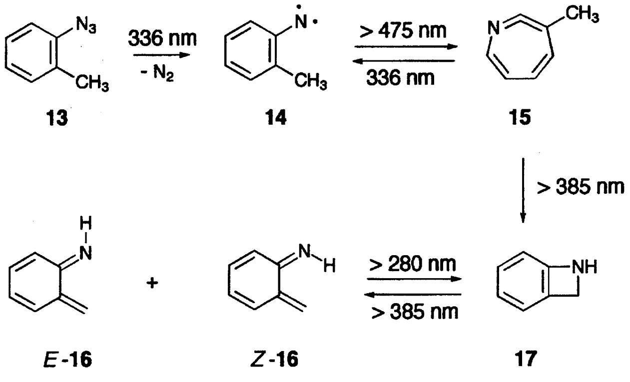
The reactions undergone by phenylcarbenes and -nitrenes bearing active hydrogens at the *ortho* positions within inert matrices are quite different from those expected from the results in solution phase and are mostly 1,4-H migrations to form *o*-quinoid compounds; equilibrium with the ring-expanded isomer, generally observed with unsubstituted systems, is not observed.

3.1 H Migration from Methyl Group. The chemistry of 2-tolylcarbene within matrices has been thoroughly studied by McMahon and Chapman.[13] Irradiation ($\lambda > 470$ nm, Ar, 15 K) of 2-tolyldiazomethane (**9**) gave *o*-quinodimethane (**11**) as a major product along with small amounts of triplet 2-tolylmethylene (**10**). Triplet 2-tolylmethylene (**10**) was thermally unstable even at 15 K and decayed to **11** (Scheme 3). Irradiation ($\lambda > 470$ nm, Ar, 15 K) of 2-(trideuteriomethyl)phenyldiazomethane (**9**-*d*), on the other hand, produced triplet 2-(trideuteriomethyl)phenylmethylene (**10**-*d*), which was found to be fairly stable; no decay to trideuterio-*o*-xylylene (**11**-*d*) was observed even at 59 K. Irradiation ($\lambda > 420$ nm) of **10**-*d* generated 1-(trideuteriomethyl)-1,2,4,6-cycloheptatetraene (**12**-*d*) as the major product along with **11**-*d* as a minor product (Scheme 3).

The thermal rearrangement of carbene was followed by IR and UV-vis spectroscopy at temperatures as low as 4.6 K. From the small temperature dependence of the rate and the large kinetic isotope effect observed on deuteration of the methyl group, a tunneling mechanism was proposed.

The chemistry of 2-tolylnitrene (**14**) observed by Sander and co-workers presents a striking contrast to that of 2-tolylmethylene (**10**).[14] Irradiation ($\lambda = 336$ nm, Ar, 10 K) of 2-tolyl azide (**13**) gave triplet 2-tolylnitrene (**14**) almost exclusively, which was found to be completely stable; under the conditions of matrix isolation, a thermal hydrogen shift is observed neither in argon (annealing at 40 K) nor in xenon (annealing at 80 K). Irradiation ($\lambda > 475$ nm) of the triplet **14** produced 3-methyl-1-aza-1,2,4,6-cycloheptateraene (**15**) almost exclusively. Again no products expected as a result of 1,4-H migration such as 5-imino-6-methylene-1,3-cyclohexadiene (**16**) or benzazetine (**17**) were detected. Irradiation ($\lambda > 475$ nm) of **15** resulted in the rearrangement back to **14**. However, at $\lambda > 385$ nm irradiation, **15** rearranged to benzazetine (**17**), presumably via nitrene **14** and the imine **16** as intermediates (vide infra) (Scheme 4).

3.2 H Migration from Hydroxy Group.[15] Irradiation ($\lambda > 300$ nm, Ar, 10 K) of 2-hydroxyphenyldiazomethane (**18**), generated in situ by photodeprotection of the "masked" diazo compound developed by Eschenmoser,[16] resulted in the formation of a product showing maxima at 1600, 1453, and 790 cm^{-1}, as the characteristic absorptions ascribable to diazo and hydroxy groups disappeared. The product was stable under these conditions, but started to decompose upon irradiation with shorter wavelength light ($\lambda > 254$ nm) to afford a secondary photoproduct. This secondary product was found to reproduce the initial product upon irradiation with light of $\lambda > 350$ nm. The secondary product was assigned as *o*-benzoquinonemethide (**22**) by direct comparison with the spectra of **22** obtained by photodecarbonylation of 2(3*H*)-benzofuranone (**20**).[17] The most likely structure for the initial product which is produced from 2-hydroxyphen-



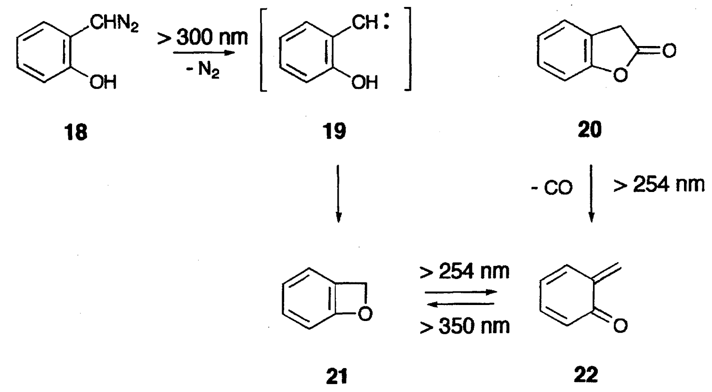
Scheme 4.

ylcarbene (**19**) and is in photoequilibrium with **22** is then benzoxetene (**21**) (Scheme 5). Support is lent to the assignment by theoretical calculations. The vibrational frequencies calculated (HF/6-31G(d)) for these molecules match the experimental data quite well not only for **22** but also for **21**. The optimized structures of both **21** and **22** are planar, and while **22** has an *o*-quinonoid structure, with alternating single and double bond, **21** has a benzenoid structure with the four-membered ring only slightly twisted. IR spectra obtained by photolysis of **18** showed no additional bands which could be assigned to 2-hydroxyphenylcarbene (**19**).[15]

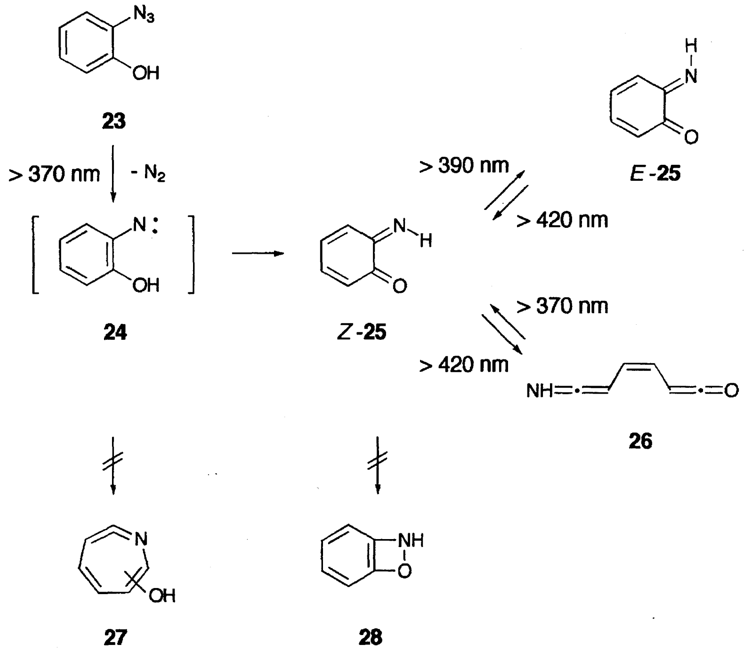
Irradiation ($\lambda > 370$ nm, Ar, 10 K) of 2-hydroxyphenyl azide (**23**) resulted in rapid disappearance of both bands due to azide and hydroxy groups to produce at least three major products, all of which were interconvertible upon irradiation. Two products exhibited a C=O stretching absorption and were assigned as a geometrical mixture of 6-imino-2,4-cyclohexadien-1-ones (**25**), which would be produced as a result of 1,4-H migration in photolytically generated 2-hydroxyphenylnitrene (**24**), while the third product showed a band attributable to the cumulenic double bond and was assigned as 6-imino-1,3,5-hexatrien-1-one (**26**), expected to be formed by ring-opening of **25** (Scheme 6).

Theoretical calculations (HF/6-31G(d)) not only support these assignments but also specify the stereochemical isomers. The calculated frequencies for *Z*- and *E*-**25** suggest that the product showing the C=O stretching higher in frequency is *E* isomer, while the one showing lower stretching is *Z*. The optimized geometries of both isomers of **25** are planar and have an *o*-quinonoid structure. The *Z* isomer was calculated to be more stable than the *E* isomer by 6.6 kcal mol^{-1}, presumably due to the formation of hydrogen bonding between the imino hydrogens due to the carbonyl oxygen atoms. Calculations also predict that, among four rotamers possible for the bisketene monoimines (**26**), *E*, *E*-isomer is the likely structure.

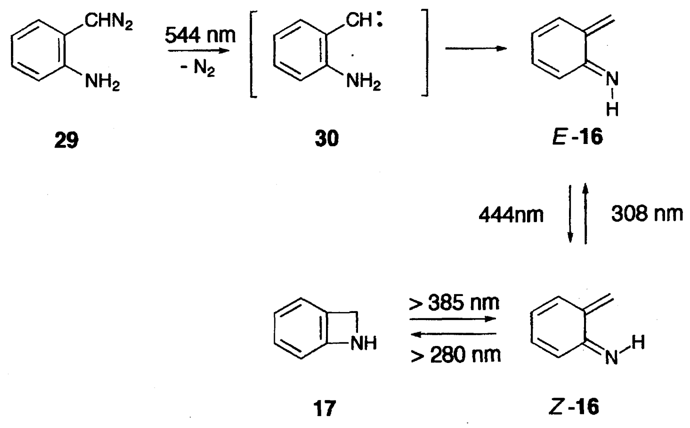
No additional IR bands, which may be attributable not only to 2-hydroxyphenylnitrene (**24**) but also to 1-aza-1,2,4,6-cycloheptatetraene (**27**), ring-expansion product of **24**, or oxazete (**28**), a closed-form of **25**, were observed.[18—20]



Scheme 5.



Scheme 6.



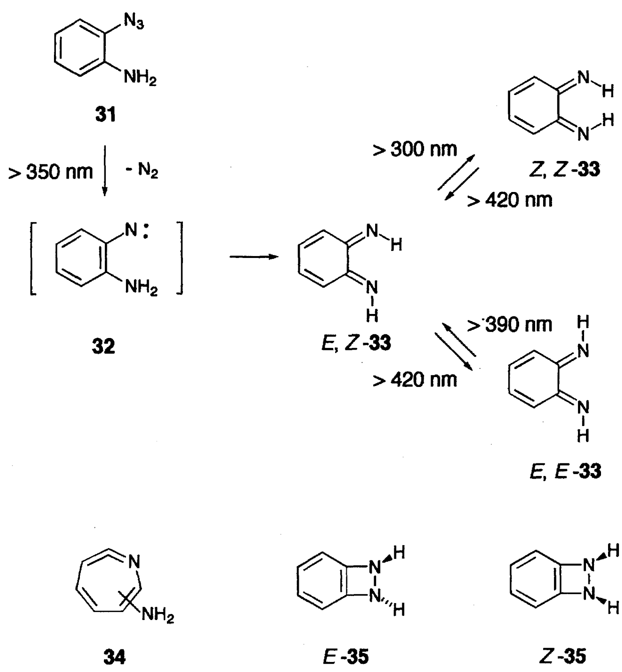
Scheme 7.

3.3 H Migration from Amino Groups. The chemistry of 2-aminophenylcarbene was investigated by Sander and co-workers.[14] Irradiation ($\lambda > 544$ nm, Ar, 10 K) of 2-aminophenyldiazomethane (**29**) gave a single product with intense IR absorptions at 1643, 1537, 1085, and 866 cm^{-1}. Irradiation ($\lambda > 444$ nm, Ar, 10 K) of the product resulted in the decomposition to form a secondary product with intense peaks at 1530, 1075, 897 and 772 cm^{-1}. The secondary product yielded the initial product upon irradiation at 308 nm, but afforded a third product when irradiated with light of $\lambda > 385$ nm. The third product reproduced the second product upon irradiation with light at $\lambda > 280$ nm. Thus, three products are shown to be photointerconvertible under these conditions. These compounds were assigned to *E*- and *Z*-isomers of *o*-benzoquinonemethide imine (**16**), presumably produced as a result of 1,4-H migration in the carbene **30**, and benzazetine (**17**), a closed form of **16** based on ab initio calculation of the IR spectra (MP2-FC/6-31G(d)) and comparison with other related ortho quinonoid systems (Scheme 7). *E*-**16** is calculated to be almost planar, while in the *Z*-isomer, the steric interaction of the inwards pointing hydrogen atoms leads to a twisting of the NH and CH_2 groups by 22°. *E*-**16** was estimated to be slightly more stable than the *Z*-isomer. The optimized structures exhibit the expected alternation of single and double bonds for **16**, while a benzenoid structure with the four-membered ring only slightly twisted is shown for **17**. Again, the carbene **30** was not detected either by IR or by ESR. A sensitive reaction for the identification of matrix-isolated triplet carbenes is the thermal reaction with molecular oxygen to form carbonyl *O*-oxides, which are readily characterized by IR or UV-vis spectroscopy.[21] Annealing of 2% O_2-doped argon matrices containing the products of photolysis of **29** at 30—35 K did not yield a carbonyl oxide, indicating that the stationary concentration of carbene **30** in the matrix must be small.

Irradiation ($\lambda > 350$ nm, Ar, 10 K) of 2-aminophenyl azide (**31**) produced al least three major products. Disappearance of the amino bands and rather significant changes in the aromatic deformation region suggest that aminophenylnitrene (**32**) is not involved but 5,6-diimino-1,3-cyclohexadiene (**33**), expected to be formed as a result of 1,4-H migration in the nitrene, is the most likely structure (Scheme 8). Ab initio calculations (HF/6-31G(d)) showed that all possible isomers of the diimines **33** have a true energy minimum and that *E*, *Z*-**33** was planar and the most stable isomer, whereas *E*, *E*-**33** was also planar but the most unstable one, lying 7—8 kcal mol^{-1} higher in energy than *E*, *Z*-**33**. It is probable that the planar *E*, *Z* isomer is stabilized by hydrogen bonding, whereas the destabilization of the *E*, *E*-isomer is caused by the repulsive interactions of the lone pairs at the nitrogen atoms. All of the isomers were shown to be photointerconvertible. Thus, irradiation of the initial photomixtures with light of $\lambda > 300$ nm tended to increase the band due to the formation of Z, Z-**33**. Irradiation of this mixture with light of $\lambda > 390$ nm gave *E*, *E*-**33**, while longer wavelength irradiation ($\lambda > 420$ nm) resulted in an increase in the band due to *E*, *Z*-**33**.

No other products such as nitrene and its seven-membered isomer (**34**) and/or benzodiazetine (**35**), a ring-closed isomer of the diimine **33**, were detected during the photolysis.[18—20)]

3.4 Mechanistic Insights into H Migration. The



Scheme 8.

present observations provide some insight into the mechanisms of intramolecular H migration to a diradical center.

There is a fundamental difference in the reactivities of triplet 2-tolylcarbene and -nitrene. A similar difference has been observed by Platz and co-workers for triplet 1-naphtylcarbene and -nitrene;[22] irradiation of 1-(diazomethyl)-8-methylnaphthalene in organic glasses at 4 K directly gave 1,8-naphthoquinodimethane without showing any sign of formation of the carbene, while the corresponding nitrene is completely stable in organic glasses at temperature up to 77 K. Both the hydrogen shift in the excited diazo compound and hydrogen tunneling in the carbene were proposed as reasonable mechanism for the formation of the quinodimethane. Due to the short distance, the hydrogen has to move, a tunneling process seems to be reasonable.

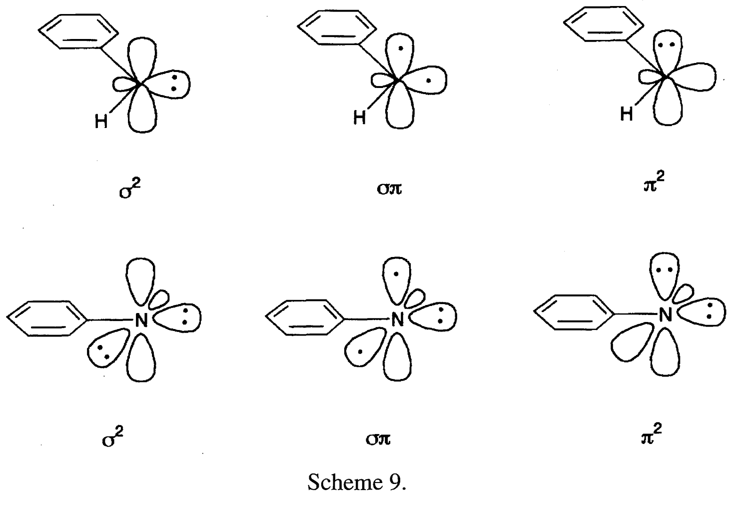
On the other hand, there is essentially no difference in the reactivities of phenylcarbenes and -nitrenes bearing hydroxy or amino groups at the *ortho* position in terms of 1,4-H shift. Thus, in all of the cases, the stationary concentration of divalent species in the matrix considered to be not high enough to be detected by IR and/or by ESR. Obviously more experiments are required to deduce whether the divalent species are thermally labile at 10 K and rapidly rearrange to *o*-quinonoid compounds, or the quinonoid compounds are formed via excited states of precursor compounds and the divalent species are not involved at all. But, for the sake of simplicity, we wish to discuss those differences, supposing that the H migration is taking place to the diradical center.

The reaction in the singlet state is usually believed to proceed in a concerted fashion. This causes steric constraints, especially in the transition state of intramolecular reactions. Thus, in the case of a carbene, the σ^2 configuration is expected to be the lowest singlet configuration while the $\sigma\pi$ configuration is the most probable one of the triplet state (Scheme 9). In the case of phenylcarbene, the most stable planar conformer must be the one with the vacant π orbital perpendicular to the plane of the benzene ring, where interaction of the vacant π orbital with the aromatic π bond is achieved (Scheme 9). Since this type of π-bonding is much less significant in the perpendicular conformer, the rotational barrier of the singlet ring is significant. In the case of triplet phenylcarbene, both in the planar and perpendicular conformers, interactions occur between the ring π electrons and the half-filled orbital. Therefore, the rotational barrier is low. The calculated (HF/3-21G) rotational barriers for the singlet and triplet are 11.2 and 5.7 kcal mol^{-1}, respectively.[23]

It was shown that, while most intermolecular C–H insertion reactions of phenylcarbene proceed by a concerted singlet mechanism, intramolecular C–H insertion reactions follow a triplet abstraction-recombination mechanism, especially when the TS requires a small-membered ring. For example, in the intramolecular C–H insertion of 2-alkoxyphenylcarbene affording 2,3-dihydrobenzofurans, the concerted insertion of the singlet involving both the π and σ orbital which interact with σ-C–H bonds requires the rotation. This results in loss of benzylic stabilization and deformation of bond angles. In contrast, the transfer of σ-H to the half-filled, in-plane σ orbital of the triplet carbene can proceed via a favorable six-membered transition state, in which the benzylic resonance is not disturbed.[24] If one applies similar TS structure considerations to the 1,4 H migration, the abstraction from the triplet state is energetically more favorable than the concerted migration in the singlet carbene.

The same explanation cannot be applied to the reaction of phenylnitrene unless one takes into account the change in electronic configuration. If one considers singlet phenylnitrene as a planar and approximately *sp*-hybridized species with the nitrogen lone pair in a $\sigma\pi$ orbital and two nearly degenerate π-orbitals, σ and π, $\sigma\pi$ is thought to be the lowest singlet configuration of the phenylnitrene, since the two π orbitals are nearly degenerate (Scheme 9).[12]

This difference in the electronic configuration can explain the difference in reactivity between phenylcarbene and phenylnitrene (both in the singlet state). Thus, while singlet phenylcarbene undergoes a concerted insertion reaction with a C–H bond,[5] analogous reactions of singlet phenylnitrenes are rare.[6] Assuming that concerted insertion reactions of singlet carbene involve the coordination of the empty π orbital with a pair of electrons in a σ bond, this type of coordination is not possible for the singlet nitrene.



Scheme 9.

Triplet phenylnitrene abstracts hydrogen atoms from alkanes rather slowly relative to triplet arylcarbenes.[6] Since triplet nitrene should have the same orbital occupancy ($\sigma\pi$) as triplet carbene, this effect probably has a thermodynamic origin. The H abstraction reaction of triplet methylene from methane to give two methyl radicals is exothermic ($\Delta H = -5.6$ kcal mol^{-1}),[25] but the corresponding reaction of triplet nitrene with methane to form methyl and amino radicals is actually endothermic ($\Delta H = +7.7$ kcal mol^{-1}).[26] This analysis can be extrapolated to triplet phenylcarbene and -nitrene.

Another important factor which influences the reactivity difference between phenylcarbene and phenylnitrene is the singlet-triplet energy gap (ΔG_{ST}) and intersystem crossing (ISC) rate. Kinetic studies and chemical trapping studies of phenylcarbene suggest that ΔG_{ST} is small, probably less than 2 kcal mol^{-1}.[27] However, spectroscopy and theory agree that ΔG_{ST} of phenylnitrene is large, approximately 17—18 kcal mol^{-1}.[28,29]

Spin orbit coupling should also be taken into account for intersystem crossing efficiency. Theory predicts that intersystem crossing in σ^2 configuration of singlet carbene is allowed because two orthogonal zwitterionic orbitals are coupled, while it is forbidden in the open-shell, lowest energy $\sigma\pi$ configuration of singlet nitrene. Thus, triplet carbene can often react from an easily accessible, highly reactive singlet, since ΔG_{ST} is small and intersystem crossing rates are high. This is not true for phenylnitrene; triplet nitrene will not reform the more reactive singlet states because ΔG_{ST} is much too large.

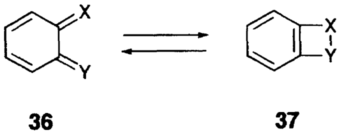
A decrease in ΔG_{ST} should also favor the reaction pathway proceeding from the triplet states. Thus, if the hydrogen migration takes place on the triplet surface, the process must involve surface crossing, i.e., there is a time of spin inversion and of chemical events. Thus, triplet to singlet intersystem crossing occurs prior to H migration to the singlet surface, or surface crossings occur after the triplet has began to abstract a hydrogen atom.[30] In either case, a decrease in ΔG_{ST} and increase in ICS rates results in an increase in hydrogen transfer efficiency.

Thus, if one assumes that the H migration proceeds mainly on a classical energy surface, the reactivity differences observed with 2-tolyl system (**10** and **14**) agree well with those expected for typical triplet phenylcarbenes and -nitrenes. In this respect, the reactions observed with 2-hydroxy- (**24**) and 2-aminophenylnitrenes (**32**) are rather unusual in that they undergo H migration very efficiently and resemble those of phenylcarbene. Taking into account the strong π-donating ability of hydroxy and amino groups, electronic effects must play an important role in this case. It is well known in carbene chemistry that electron-donating groups stabilize the electrophilic singlet more than they do the radical-like triplet.[31] Presumably, π-donating groups stabilize singlet nitrene as well by stabilizing the σ^2 configuration, thus making ΔG_{ST} smaller. It was proposed that ring expansion of singlet phenylnitrene to form azacyclopheptatetraene occurs in the π^2 configuration which is usually not so high in energy compared to the σ^2 and $\sigma\pi$ configuration.[12] Thus, the stabilization of the σ^2 configuration relative to the π^2 configuration should result in an increase in the ring expansion barrier. This could explain the complete absence of ring-expansion product in the reaction involving **24** and **32**. Thus, π-donating substituents may make the arylnitrene look more like phenylcarbene.[32]

If tunneling is of importance, as has been confirmed in the H migration reaction of 2-tolylcarbene,[13] one should consider the width and the height of the barrier of the reaction.[33,34] Since the distance of the hydrogen atom closest to the reactive center corresponds to the tunneling distance, comparing the distance is intriguing. Semiempirical calculations (PM3) indicate that the distance of the migrating hydrogen atoms of 2-methyl, 2-amino, and 2-hydroxy groups to the triplet carbenic center is 2.51 (**10**), 2.47 (**30**), and 2.39 Å (**19**), respectively, while that with the corresponding nitrene series is 2.90 (**14**), 2.57 (**32**), and 2.47 Å (**24**), respectively. Thus, the largest distance is estimated for 2-tolylnitrene **14** among the six diradical species employed and this could result in significant decreases in H migration rate, particularly if tunneling is involved.

3.5 *O*-Benzoquinone–Benzocyclobutene Valence Isomerization. The results also show that phenylcarbenes and -nitrenes bearing active hydrogens at the *ortho* position can serve as very promising and clean precursors for a series of *ortho* quinonoid compounds, which are known to be intermediates of relevance in a variety of areas. Thus, they are widely used in organic synthesis, in particular for carrying out "reverse electron demand" Diels–Alder reaction with electron rich alkenes. They are also known to be powerful electrophiles and are believed to have widespread occurrence as intermediates in biochemical transformations. Most of the methods reported to date for generating these species involve high-temperature thermolysis and/or use of highly derivatized or structurally complex precursors.[35] In this respect, the present method has an advantage in that these species are easily generated from rather simple molecules very efficiently even at very low temperature in matrix conditions, which enable one to observe and study these otherwise highly elusive species with great ease.

On the other hand, relative stabilities of *o*-quinonoid forms (**36**) with respect to their closed forms, benzo-condensed heterocyclic ring systems (**37**), are of special interest (Scheme 10).[36—39] For instance, benzocyclobutene (**37**, $X = Y = CH_2$) and benzothiete (**37**, $X = CH_2$, $Y = S$)[37] are both isolated and exist under ambient conditions, while their open form isomers (**36**) are often generated by their thermal ring opening reaction, thus suggesting that the closed forms are thermodynamically more stable isomers. On the other



36 **37**

Scheme 10.

hand, while *o*-benzoquinone (**36**, X = Y = O) is detected at low temperature, its closed form (**37**, X = Y = O) has never been observed.

In the present study, both isomers are observed in some cases where photoequilibrium is usually attained, while only one isomer, usually an open form, is formed in other cases. Therefore, it is quite interesting to estimate thermodynamic properties of the valence isomers more quantitatively. Thus, we calculated the relative stabilities of the quinonoid and closed forms as well as the transition state (TS) energies of the interconversion with the same level of the theory (MP2/6-31G(d)//HF/6-31G(d)). The results summarized in Table 1 indicates that the predicted relative energies are in good agreement with the experimental observations. Thus, benzocyclobutene and benzothiete are calculated to be more stable than the corresponding quinonoid forms by some 20 kcal mol^{-1} and kinetically also fairly stable with respect to ring-opening. The quinonoid forms are, on the other hand, predicted to be kinetically less stable with respect to ring-closure. This is exactly what is observed with benzocyclobutene and benzothiete.

It is very interesting to learn that, in the case of benzoxetene (**21**) and benzoazetine (**17**), both of which are shown to be in photoequilibrium with the quinonoid forms, theory predicts that there is only a slight difference in the thermodynamic stabilities between the open and closed forms. Moreover, theory also predicts that both **21** and **17** are kinetically fairly stable with respect to the ring opening. Benzoxetene was believed to be unstable because it easily underwent ring-opening to generate *o*-benzoquinonemethide **22**, which then polymerized.[40] This might be true in gas phase at higher temperatures where the experiments were usually carried out. The magnitude of the TS energy predicts that the closed forms can exist even under ambient conditions if it has no other reaction channel than ring-opening. Actually, 2-acetylbenzoxetenes are shown to be stable in solution at low temperature.[41] More, recently, even benzoxetene itself is confirmed to be stable even at room temperature.[42]

In case of *o*-benzoquinone mono- (**25**) and di-imines (**33**), where only open forms are detected, the corresponding closed forms (**28** and **35**, respectively) are calculated to be thermodynamically fairly unstable. The difference in the photochemical reactivities cannot be explained simply by the energy difference of the ground-state molecules. For instance, although the energy differences between the quinone (e.g., **25**) and the ring-opened bisketene isomers (e.g., **26**) are small, the photochemical ring-opening reaction is observed only with the quinone **25**, not with quinone diimine **33**. Obviously, the nature of electronically excited states must play an important role. Although TS energy for the ring closure is estimated to be fairly large, that for the reverse reaction is also calculated to be sizable. Therefore, the closed form is predicted to be kinetically stable at least with respect to the ring opening.

Table 1. Relative Energies (in kcal mol^{-1}) for Each Stationary Points of *o*-Quinone (**36**)–Benzocyclobutene (**37**) Valence Tautomerization Calculated at the MP2/6-31G(d)//HF/6-31G(d) Level of Theory

X	Y	**36**	TS	**37**
CH_2	CH_2	0	16.1	−22.9
CH_2	S	0	22.3	−19.7
CH_2	NH	0 (**16**)	31.0	−5.8 (**17**)
CH_2	O	0 (**22**)	40.3	5.1 (**21**)
NH	NH	0 (**33**)	50.0	25.3 (**35**)
NH	O	0 (**25**)	60.3	43.0 (**28**)

4. Interaction with Oxygen

Oxygen compounds play an important role in the chemistry of carbenes.

The reaction between triplet ground state carbenes and triplet O_2 to give stable singlet products is spin-allowed and is expected to be very rapid. The reaction has been well-studied by both laser flash photolysis[43] and matrix isolation spectroscopy.[21] LFP studies showed that the reaction of simple triplet carbenes with O_2 proceeds nearly at diffusion limit rate in solution to form the corresponding carbonyl oxides.[43] The reaction takes place even at a temperature as low as 20 K when triplet carbenes are generated in O_2-doped matrices to form the carbonyl oxides. The reaction of nitroxides, e.g., 2, 2,6,6-tetramethylpiperidine N-oxide, also proceeds smoothly with triplet carbene to form the corresponding ketone in essentially quantitative yield.[44]

While the reaction of the singlet state with these paramagnetic species is rather slow,[44] oxygen transfer reactions from diamagnetic oxides, e.g., amine oxides and sulfoxides, are known for the singlet.[45] Singlet carbenes react with oxygen-containing heteroatom compounds such as alcohols, ethers, and ketones, mostly by initial electrophilic attack on the lone pair electrons of the oxygen atom to generate ylides.[5] Subsequent reactions of these ylides are highly dependent upon their structure. Oxonium ylides, for instance, undergo the Stevens rearrangement[46] while carbonyl ylides undergo cyclization to form oxiranes, 1,4-H shift to give enol ethers and intermolecular 1,3-dipolar addition.[47] Oxygen migration from amine oxides might also proceed through the corresponding ylides.

Reactions of phenylnitrene are again quite different from those of carbenes, probably for the reasons described above. Thus, the reaction of the triplet states with triplet O_2 is not so efficient as that of the triplet carbenes. Triplet phenylnitrene itself does not react appreciably when generated in O_2-doped matrices at low temperatures.[48] Singlet phenylnitrene undergoes ring expansion so rapidly that it is not trapped by the oxygen containing compounds.

Not only phenylcarbene but also -nitrene, however, is found to react equally efficiently with oxygen of NO_2 and CO_2Me groups at the *ortho* position under matrix conditions although the reaction modes are somewhat different from each other, probably reflecting the significant difference in the inherent reactivity.

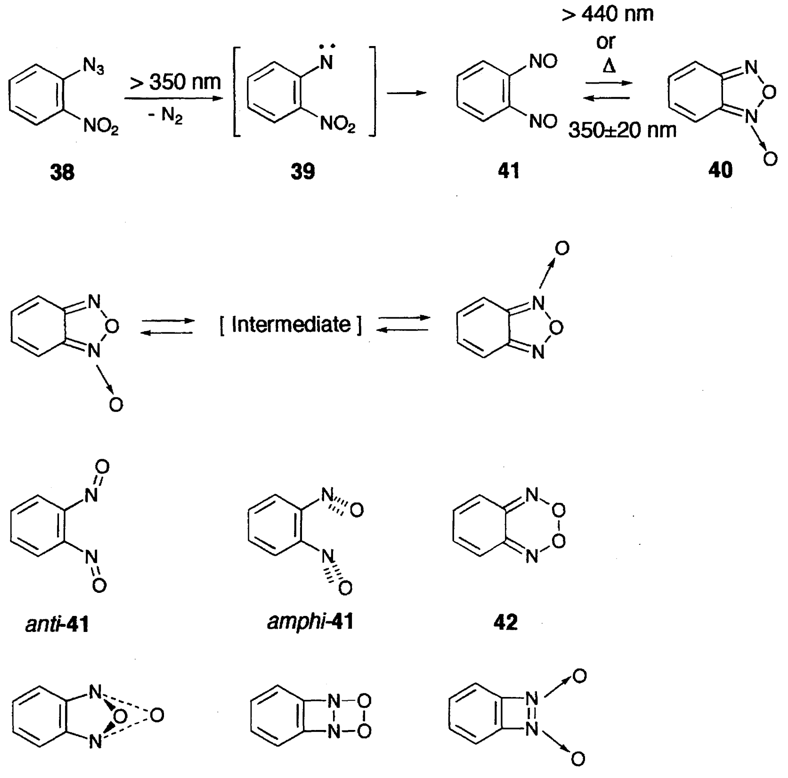
4.1 Oxygen Migration from Nitro Group. 2-Nitrophenylnitrene. Benzofuroxan- *o*- dinitrosobenzene

Tautomerization.[49—51] Photolysis ($\lambda > 350$ nm, Ar, 12 K) of 2-nitrophenyl azide (**38**) resulted in a disappearance of the IR bands assigned to the nitro stretching vibrations as well as the intense azide stretching peaks to produce a product showing IR bands at 1622, 1513, and 1102 cm^{-1}. In the UV-vis spectra, the disappearance of the azide spectrum and the formation of a very intense absorption with a maximum at 278 nm and absorptions with vibrational structures in the region 320—380 nm were observed. Upon irradiation with long-wavelength light ($\lambda > 440$ nm), the intensities of the initial product bands decreased significantly to give a secondary product exhibiting IR bands at 1622, 1597, and 1545 cm^{-1} and UV-vis absorption with maxima at 358 and 372 nm, which reproduced the initial product with short-wavelength light ($\lambda > 350$ nm). Thus, the two photoproducts were shown to be photoconvertible. The thermal reversal was also observed when an Ar matrix containing the initial product was warmed slowly to 35—40 K. The species formed on irradiation with long-wavelength light was easily identified as benzofuroxan (**40**) by direct comparison with the matrix-isolated IR spectrum of an authentic sample.

Although benzofuroxan (**40**) was first synthesized over 100 years ago, considerable disagreement over its structure plagued researchers for many years. It was only in the 1960s that the currently accepted view arose that benzofuroxan rapidly interconverts between two tautomeric forms through a symmetric intermediates (Scheme 11). *anti-* and *amphi*-Dinitrosobenzene (**41**) and the peroxide (**42**), bridged (**43**), three-ring (**44**), and cyclobutadiene-like structures (**45**) have been suggested as possible intermediates for this tautomerization.[52,53] Therefore, the initially formed species which is photoconvertible with benzofuroxan is considered to be one of these proposed intermediates. The structure which explains the spectroscopic data best is dinitrosobenzene (**41**) since monomeric aromatic *C*-nitroso compounds have a characteristic strong N=O stretching frequency at 1490—1520 cm^{-1} and bands at 1100 and 800±50 cm^{-1} associated with C–N vibration.[54] Alternative structures such as **42**—**45** do not fit the spectroscopic data (Scheme 11). The stability of **41** in Ar matrices may be due to formation of the *anti* conformer and its inability to undergo internal rotation about one of the C–N bonds back to the reactive *amphi* conformer. Photon absorption by *anti*-form or simply warming to a temperature above 40 K would supply the necessary energy to effect this conformational change.[49—51]

Further support for the identity of **41** came from an ab initio quantum mechanical study. DZP second-order perturbation theory (MP2) energies for **40**, *anti-* and *amphi*-**41** suggest that *anti-* and *amphi*-**41** lie 12.0 and 12.9 kcal mol^{-1} above **40**, respectively, while all other possible intermediates (**42**—**45**) lie considerably higher in energy. The vibrational frequencies were calculated for those compounds and were compared with the experimental vibrational frequencies observed with **41**, which indicated that the calculated frequencies for *anti*-**41** provide the best match to the experimental data.[55]

The long-waited elusive intermediate in the tautomerization of **40** is thus generated, detected and fully characterized,



Scheme 11.

which terminated the argument about this structurally and chemically controversial molecule.

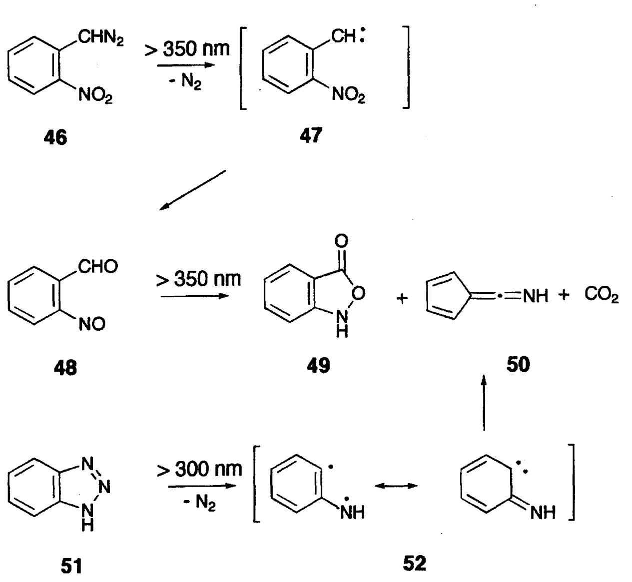
2-Nitrophenylcarbene. Carbene-to-Nitrene Rearrangement.[56] The chemistry undergone by phenylcarbene with the *o*-nitro group is somewhat different from that of phenylnitrene. Photolysis ($\lambda > 350$ nm, Ar, 10 K) of the precursor diazomethane (**46**) gave 2-nitrosobenzaldehyde (**48**) almost exclusively, without showing any sign of formation of other possible intermediates such as nitrophenylcarbene (**47**) and/or anthranil oxide. Irradiation of **46** in 2% O_2-doped argon matrices at 10 K, followed by annealing the matrix also afforded nitrosobenzaldehyde. However, when the irradiation was carried in Ar doped with 20% O_2, 2-nitrobenzaldehyde was formed with O_3 at the expense of **48**. It is well-known that carbenes with triplet ground state generated in an oxygen-doped matrix generally react with the doped O_2 upon annealing the matrix to give the corresponding carbonyl oxides which, at high O_2 concentration, react with O_2 to produce the ketones and O_3. Typical conditions are 0.5—2% O_2 in argon at 30—35 K. The observations suggest, therefore that the stationary concentration of 2-nitrophenylcarbene (**47**) in the matrix must be small.

2-Nitrosobenzaldehyde (**48**), which is also not very stable compound but can be easily generated by heating *trans*-2, 2′-di(formyl)azobenzene *N*,*N*′-dioxide,[57] decomposed upon continued irradiation ($\lambda > 350$ nm) to produce two major products along with CO_2. The product exhibiting a strong carbonyl band at 1800 cm^{-1} was assigned to 2,1-benzisoxazol-3(1*H*)-one (**49**), while the other, showing a cumulenic double bond at 2040 cm^{-1}, was assigned to iminomethylenecyclopentadiene (**50**) (Scheme 12). The latter compound was generated in situ by photolysis of 1,2,3-benzotriazole (**51**) in Ar at 10 K.[58] By analogy with photolysis of **51**, **50** could be formed by photodecarboxylation of **49** by way of 2-imino-3,5-cyclohexadienylidene intermediate (**52**). However, **49** was photostable upon extended irradiation with the light $\lambda > 350$ nm and underwent photodecarboxylation only when irradiated with the short wavelength light ($\lambda > 300$ nm) to produce **50** and CO_2. These observations suggest that **49** was not precursor for **50** at least in the photochemical transformation of **48** with the $\lambda > 350$ nm light.

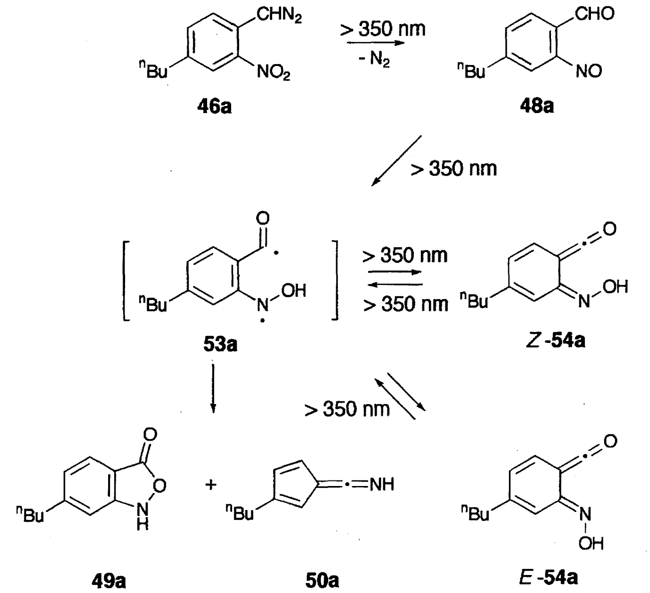
Photochemical processes in noble gas matrices sometimes result in the generation of reactive intermediates in vibrationally excited states which undergo subsequent reactions faster than they cool off to the thermally relaxed states and therefore an intermediate supposed to be involved often becomes elusive even under these conditions.[59] One of the effective ways to decrease the rate of reaction in a vibrationally hot species is to introduce an alkyl chain in the reactive species, thereby increasing the number of vibrational modes.

Thus, in order to gain some insight into the intermediates which may be invisible presumably due to subsequent reactions in vibrationally excited states, the precursory diazomethane bearing butyl group was used. Irradiation ($\lambda > 350$ nm) of **46a** resulted in the formation of the corresponding nitrosobenzaldehyde **48a**. Continued irradiation afforded hydroxyimino ketene derivatives (**54a**), whose formation can be reasonably interpreted in terms of the intramolecular hydrogen abstraction by the excited nitroso group, by analogy with a similar photochemical transformation of 2-nitrobenzaldehyde leading to *o*-nitrosobenzoic acid (Scheme 13).[60] It has been demonstrated that 4-nitrosobenzonitrile undergoes H abstraction upon irradiation in 2-propanol solution to give the hydroxyl aminyl radical (ArN–OH) which is shown to lead to the hydroxylamine (ArNHOH).[61] Thus, it is conceivable to propose that 2-nitorosobenzaldehyde also undergoes H abstraction from the proximate formyl group even within low-temperature matrices. The assignment was unambigously supported by the generation of **54** from an independent source, i.e., *N*-hydroxyisatine (**55**) (Scheme 14).

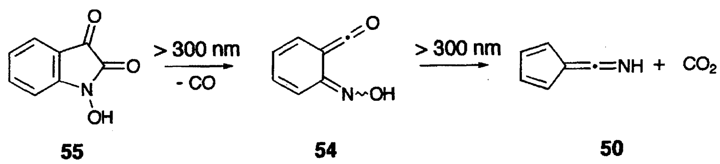
In the photolysis of **48a**, two isomers were formed; the one showing sharp absorption at 2094 cm^{-1} was produced



Scheme 12.



Scheme 13.



Scheme 14.

initially and gradually decomposed to give isoxazolone and imine along with the other isomer (2094 cm^{-1}), which did not appreciably lead to **49a** and **50a**, at least in time ranges where the initially formed isomer underwent decomposition. The observation is reasonably explained as indicating that **54a** either undergoes ring closure to form **49a** or is isomerized to the geometrical isomer.[62] Probably the first formed isomer must be the *Z* isomer (*Z*-**54a**) since in this isomer, oxime hydroxy and ketene groups are suitably situated for the cyclization, while the slowly formed isomer should be the *E*.

Z-**54a** also produced **50a** along with **49a** and *E*-**54a** upon irradiation with the longer wavelength light ($\lambda > 350$ nm), which did not induce decomposition of **49a** to **50a**. Simultaneous formation of these three products in the irradiation of *E*-**54a** indicates that the reactions proceed through a common intermediate. By analogy with the photochemical reaction of nitrobenzene containing a C–H bond at the ortho position,[60] 1,4-OH shift in the 1,4-biradical (**53**), generated by the intramolecular H abstraction of the excited nitroso group, to form 2-carboxyphenylnitrene (**55**) is proposed. The possibility was actually supported by the facts that photolysis ($\lambda > 350$ nm, Ar, 10 K) of 2-carboxyphenyl azide, a precursor for **55**, afforded **50** and CO_2 as major product along with **49**. 3-Carboxy-1-aza-1,2,4,6-cycloheptatetraene (**56**), presumably formed as a result of ring expansion of **55**, was also detected. Careful examination of the spectral changes during irradiation of **48** reveals the appearance of the bands ascribable to the tetraene (**56**). These observations suggest that the nitrene (**55**) is a precursor for **50** in the photolysis of **48** with the longer wavelength light ($\lambda > 350$ nm). Presumably, the nitrene generated as a result of 1,4-OH shift in the nascent 1,4-biradical **53** abstracts H from carboxylic group at the ortho position to generate a 1,4-biradical (**57**), in competition with ring expansion forming **56**, which then either undergoes intramolecular coupling leading to **49** or loses CO_2 to produce the imine (**50**) by way of **52** (Scheme 15).

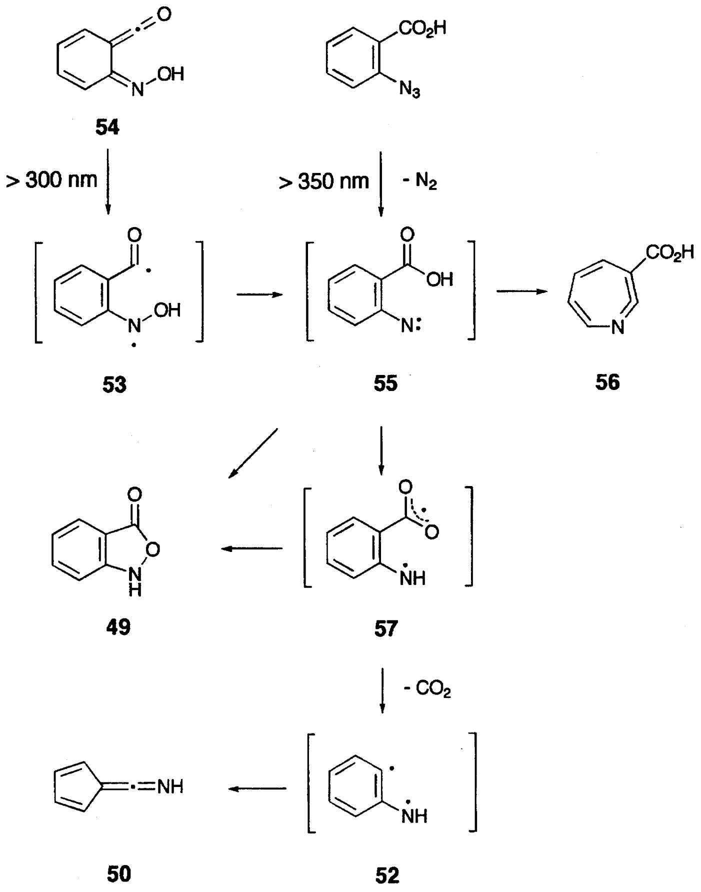
The overall reaction indicates that 2-nitrophenylcarbene (**47**) undergoes, in formal sense, carbene (**47**)-to-nitrene (**55**) rearrangement by a net intramolecular redox reaction. Thus, the first oxygen is transferred directly from the nitro group to the carbenic center. The next oxygen transfer proceeds stepwise, that is, by initial H transfer from the original carbenic center to the reducing center, thus activating both donor and acceptor centers, followed by accepting the second oxygen in the reduced form. Carbene-nitrene rearrangement has been shown in the thermolysis of phenyl azide and various precursors to the three isomeric pyridylmethylenes. The low-temperature photochemical conversion on the C_6H_5N energy surface in argon matrices studied by matrix isolation spectroscopy has confirmed that the C_6H_5N energy surface is quite slippery, and the chemistry of these species is rich with carbene-carbene and carbene-nitrene rearrangement. Obviously, the present rearrangement is completely different in terms of the mechanism from those thus far reported.

4.2 Interaction with Ester Groups. 2-(Methoxycarbonyl)phenylnitrene.[63] Photolysis ($\lambda > 350$ nm, Ar, 10 K) of phenyl azide (**58**) bearing a CO_2Me group at the ortho position gave at least five major products; they are two products showing C=O stretching absorption bands due to intact methoxycarbonyl groups (1757 and 1734 cm^{-1}), one exhibiting a considerably shifted C=O stretching absorption (1856 cm^{-1}) and two having strong, sharp bands due to cumulenic double bonds (2118 and 2088 cm^{-1}). Interestingly, all of those five products were found to be interconvertible upon irradiation.

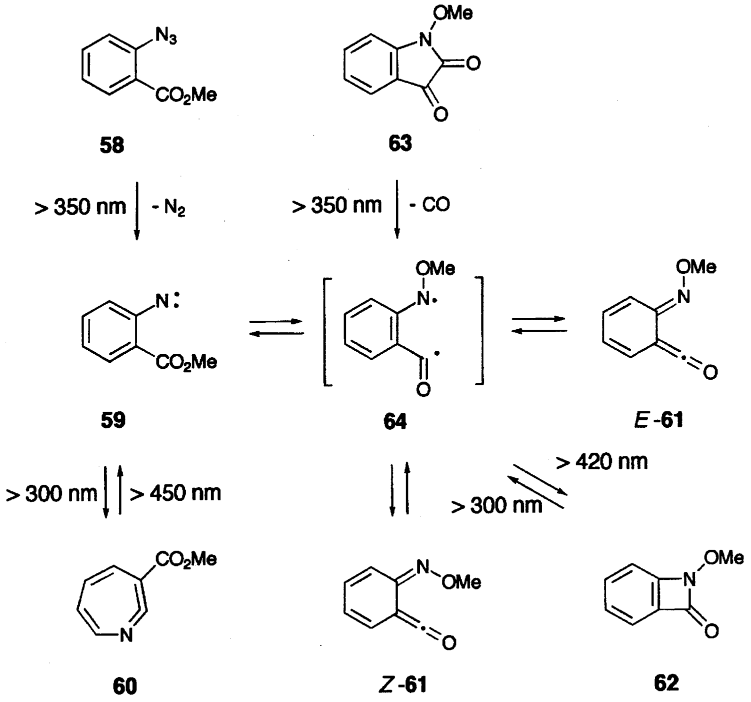
One of the products having an intact CO_2Me group also exhibited a rather intense band at 1887 cm^{-1} due to a strained heterocumulenic bond and therefore assigned to 3-(methoxycarbonyl)-1-aza-1,2,4,6-cycloheptatetraene (**60**). The other product bearing an intact CO_2Me group which was in photoequilibrium with **60** is most likely 2-(methoxycarbonyl)phenylnitrene (**59**) in the triplet state. On the other hand, the products showing sharp bands due to ketene functional groups were assigned to the geometrical mixture of 5-carbonyl-6-methoxyimino-1,3-cyclohexadiene (**61**). The one showing the shifted carbonyl absorption was then assigned as *N*-methoxyazetinone (**62**) which can be produced as a result of photocyclization of the diene (**61**) (Scheme 16).

It was found that *N*-methoxyisatin (**63**) underwent decarbonylation upon irradiation ($\lambda > 350$ nm, Ar, 10 K) to result in the formation of essentially the same product mixtures as those obtained in the photolysis of **58** (Scheme 16). These observations not only verified unequivocally the assignments of the product structures, but also provide some insights into the reaction mechanism for the photointerconversion. Thus, since photodecarbonylation of **63** should lead to the generation of 1,4-biradical species (**64**), which either undergoes the electron redistribution to give the ketenes (**61**) or cyclizes to form the azetinone (**62**), this species (**64**) must also intervene as a common intermediate in the interconversion between **59**, **61**, and **62**. The simplest explanation for this reaction is a 1,4-N→C shift of the MeO group in the excited state of the ketenes. An alternative backward pathway for the photointerconversion of the nitrene (**59**) to the ketene (**61**) is then a 1,4-C→N MeO shift in the excited-state nitrene (**59**).

The results should be compared with that observed in the reaction involving 2-carboxyphenylnitrene **55** (Scheme 15) which can be also generated from the corresponding ketene **54** as a result of 1,4-N→C OH shift upon photoexcitation



Scheme 15.



Scheme 16.

but can not regenerate **54**, since the nitrenic center is trapped irreversibly by a reactive OH group at the *o*-position.

The present observation is also to be compared with the photointerconversion including phenylnitrene and isomeric pyridylmethylenes within matrices. For example, irradiation ($\lambda > 200$ nm, Ar, 12 K) of a 4-(diazomethyl)pyridine gives triplet 4-pyridylmethylene, which, upon further irradiation, isomerizes to give 3-pyridylmethylene, 2-pyridylmethylene, and phenylnitrene via the isomeric azacycloheptatetraene, the isomeric compositions being dependent upon the wavelength of light irradiated.[8] The present results suggest that such phenylnitrene–pyridylmethylenes photointerconversion usually occuring on the very slippery energy surface with many different energy points is not only attained but also is channeled into a new and equally slippery energy surface once a methoxycarbonyl group is introduced at the *ortho* position of the phenylnitrene. This new surface also has different entry points where even the isatin (**63**) is found to be a precursor for the phenylnitrene involved in this new photointerconversion.

2-(Methoxycarbonyl)phenylcarbene.[64] The chemistry undergone by 2-(methoxycarbonyl)phenylcarbene (**66**) is rather simple, in contrast to that of the corresponding phenylnitrene (**59**). Thus, irradiation ($\lambda > 350$ nm, Ar, 10 K) of the precursor diazomethane (**65**) afforded only two photoproducts, which were again photointerconvertible. Thus, the initially formed product gradually transformed, upon continued irradiation ($\lambda > 350$ nm), to the secondary product which reproduced the initial photoproduct on irradiation with shorter wavelength light ($\lambda > 254$ nm). Since both products exhibit no bands ascribable to the C=O stretching band, they should be not carbene (**66**) itself, but the products formed as a result of the interaction with the adjacent C=O group. The most likely initial product is then the carbonyl ylide (**67**). Since the reversible photoisomerization of carbonyl ylides to the corresponding oxiranes was well-documented,[65] the secondary product can be assigned to 1,2-expoxy-1-methoxybenzocyclobutene (**68**) (Scheme 17). The IR spectra showing the presence of the intact *ortho*-fused benzene skeleton, the methoxy-substituted carbonyl ylide moiety and the epoxy framework appear to support these structures.

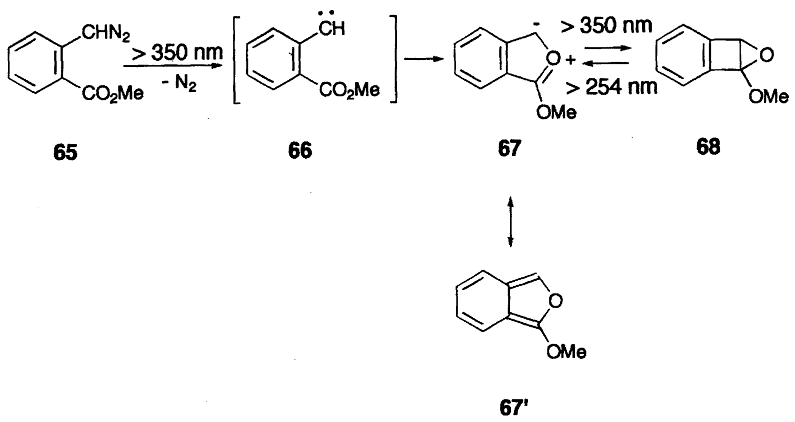
When the Ar matrix was doped with 5—20% O_2, no IR peaks assignable to **67** and **68** were formed. The major photoproduct in O_2-containing matrix was identified as 2-(methoxycarbonyl)benzaldehyde, indicating that **67** is formed via the carbene (**66**). However, the formation of the ylides was not quenched at all in matrices containing low O_2 concentration.

4.3 Mechanistic Insights into Oxygen Migration. Photolysis of 2-nitrophenyldiazomethane (**46**) and azide (**38**) both results in the formation of oxygen migration product. Since both phenylcarbene and -nitrene are not observed, we are not sure whether the nitroso compounds are formed either from the diradical species or directly via excited state of the precursors. However, again for the sake of simplicity, we assume that the divalent species are responsible for the migration.

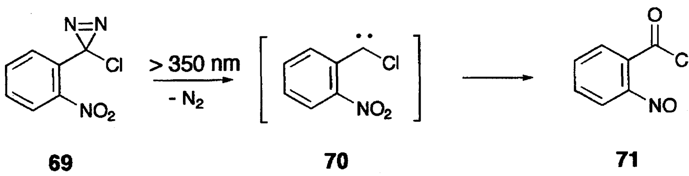
Carbenes do abstract oxygen atoms from suitable donors such as N-oxides, nitroxides, carbon dioxide, PF_3O, or epoxide.[45] It has been shown that α-nitro carbene is very labile and rearranges to nitrosoformaldehyde with nearly zero activation energy.[66,67] Thus, the results with 2-nitrophenylcarbene serve as another example of oxygen atom abstraction by carbenes. We are not sure which multiplicities are responsible for the migration, simply based on the presently available data. As the previous oxygen migration reactions take place most likely in the singlet state, it may be that nascent singlet carbene is trapped by the adjacent oxygen atom of the 2-nitro group.

Since all the carbenes thus far employed in this study are considered to have potentially triplet ground states, we attempted to generate chloro(2-nitrophenyl)carbene (**70**), a potential singlet ground-state carbene. Irradiation ($\lambda > 350$ nm, Ar, 10 K) of 3-chloro-3-(2-nitrophenyl)diazirine (**69**) again resulted in the formation of 2-nitrosobenzoyl chloride (**71**), no other transient absorption ascribable to either carbene (**70**) or other intermediates being detected (Scheme 18).[56] These observations support the idea that the singlet carbenes are responsible for oxygen migration.

On the other hand, a similar oxygen migration reaction to nitrenic center is not known at least in solution at ambient temperature. In thermolysis of *o*-substituted phenyl azide at



Scheme 17.



Scheme 18.

much higher temperatures, benzocyclic products as a result of formal attack of "nitrene" on the oxygen of the *o*-substituents are often formed. Formation of benzofuroxans by thermolysis of 2-nitrophenyl azides is such an example. In many of those reactions, nitrenes are presumed as intermediates although other intermediates, e.g., precursor azides are not rigorously excluded.

Those facts, coupled with observations that anthranil oxide, an intermediate expected for oxygen migration in 2-nitrophenylcarbene (**47**) in the photolysis of **46**, is not observed may suggest that *o*-dinitrosobenzene (**41**) is formed only by way of benzofuroxan (**40**), not directly from 2-nitrophenylnitrene (**39**).

4.4 Mechanistic Insights into Interaction with Carbonyl Group. Photolysis of phenyldiazomethane and phenyl azide bearing methoxycarbonyl group at the *ortho* position provides a completely different result, which can also be consistent with the difference in reactivities between these two diradical species.

The reactions of singlet carbene with carbonyl compounds to form carbonyl ylides are well-documented. Intervention of carbenes, not excited diazo precursors, has been demonstrated by laser flash photolysis studies.[68] Therefore, it is likely that singlet carbene is responsible for the formation of the ylide, although the reaction from the triplet involving surface crossing cannot be excluded. An attack of carbene on the alkoxy oxygen atom of esters to generate the oxonium ylide is also a possible option. However, it has been shown that such oxonium ylide is thermodynamically less stable than the carbonyl ylide and are only formed at higher temperatures in gas phase.[11b]

Interactions of nitrenic centers with carbonyl groups are not well-documented. Again, in the thermolysis of phenyl azide bearing *o*-carbonyl groups, benzocyclic products, formally formed as a result of interaction between nitrene and carbonyl oxygen, are produced. No such product is detected in the present photolysis. The observations that triplet phenylnitrene (**59**) in photoequilibrium with the corresponding didehydroazepin (**60**) is formed even in the presence of the *o*-substituent suggest that direct interaction of nitrene center either in the singlet or in triplet is not efficient. This may also imply that benzocyclic products formed in the thermolysis of phenyl azide having *o*-carbonyl substituents are not derived from the corresponding nitrenes.

Triplet nitrenes **59** instead "abstract" a methoxy group in its excited state presumably as a result of 1,4 shift in the 1,4-biradical structures (**64**).

5. Photolysis of Cyclic 1,3-Bis(diazo) Ketones An Approach to Strained Compounds

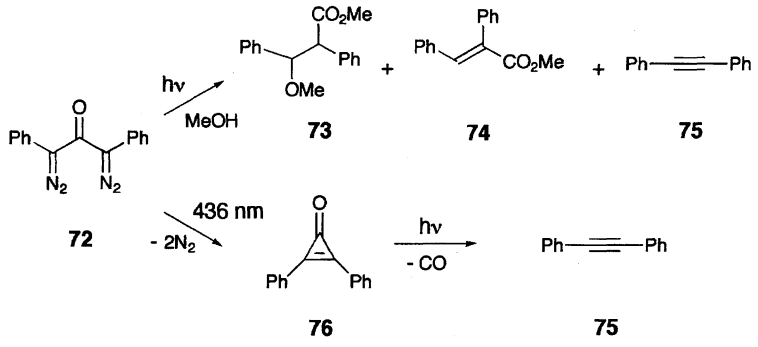
Matrix isolation has shown its greatest powers to study the theoretically interesting molecules. Strained cycloalkynes, molecules with triple bonds deviating significantly from linearity are one of the central topics in this field.[69] Cyclooctyne is the last carbocyclic parent compound that is stable under "normal" conditions. The deviation from linearity in this compound, 21.5°, is reflected in its increased reactivity. Chemists have been challenged to generate and characterize cycloalkynes with more bent triple bonds by using matrix isolation techniques in order to test the limits of chemical bonds. Theoretical predictions concerning these molecules have become very precise and hence facilitate the experimental approaches to those challenging molecules. Thus, cyclohexyne,[70] didehydrobenzene,[71] and even tetradehydrobenzene[72] have been already generated and characterized.

Carbenes and nitrenes have been successfully employed as precursors for such strained molecules, since those highly energetic species can be electronically excited upon further irradiation to much higher energetic states, which then are forced to find some routes to normal tetravalency.

Cyclic α-diazo ketones are especially useful precursors for such study since they are easily prepared and, more importantly, rather stable and also since they generate α-keto carbenes, upon irradiation, which usually undergo ring contraction as a result of Wolff rearrangements.[73] 1,3-Bis(diazo) ketones are much more attractive precursors since they can provide cyclopropenone, a precursor for strained triple bonds, as a result of intramolecular interaction of the carbenic center with carbene and/or diazo functions in the same molecule.

For instance, the irradiation of bis(α-diazobenzyl) ketone (**72**) in methanol produces methyl 3-methoxy-2,3-diphenylpropionates (**73**), presumably as a result of a Wolff rearrangement, together with methyl 2-phenylcinnamate (**74**) and diphenylacetylene (**75**). Photolysis of **72** with longer-wavelength light, on the other hand, gives diphenylcyclopropenone (**76**) which undergoes photodecarbonylation to form the acetylene (**75**) (Scheme 19).[74] A similar reaction is also found in the catalytic decomposition of 2,4-bis(diazo)-1,5-diphenyl-1,3,5-pentanetrione, which ultimately affords dibenzoylacetylene by way of dibenzoylcyclopropenone.[75]

The formation of cyclopropenone does not seem to occur when the bis(diazo) ketone functions are located in a cyclic system, at least in fluid state photolysis at room temperature. Thus, decomposition of 2,6-bis(diazo)cyclohexanone (**77**) in methanol produces isomeric methyl cyclopentene-3-carboxylates.[74] However, when irradiation is carried out in



Scheme 19.

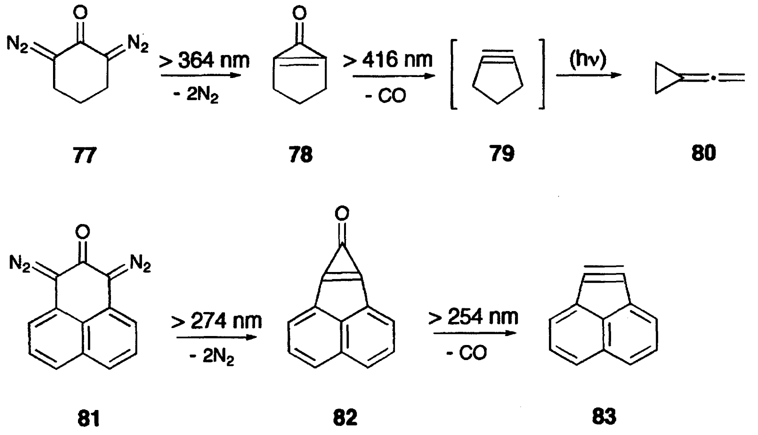
an inert gas matrix at low temperature, the cyclopropenone incorporated into a bicyclic system is not only detected but is also shown to undergo photodecarbonylation to generate highly strained cyclic alkyne. Thus, the irradiation ($\lambda > 274$ nm, Ar, 10 K) of **77** gives expected bicyclo[3.1.0]-hex-1(5)-en-6-one (**78**), which then undergoes decarbonylation upon further irradiation ($\lambda > 254$ nm) to result in the formation of vinylidenecyclopropane (**80**), presumably by way of photolabile cyclopentyne (**79**) (Scheme 20).[76] A similar reaction is observed with 1,3-bis(diazo)-2,3-dihydro-2-phenalenone (**81**), which eventually affords acenaphthylyne (**83**) by decarbonylation of initially formed 1,2-cyclopropaacenaphtlylen-3′-one (**82**) upon irradiation within an argon matrix (Scheme 20).[76]

As an extension of such study, we have prepared two new bis(diazo) ketones incorporated in five- and seven-membered rings and photolyzed under matrix conditions.

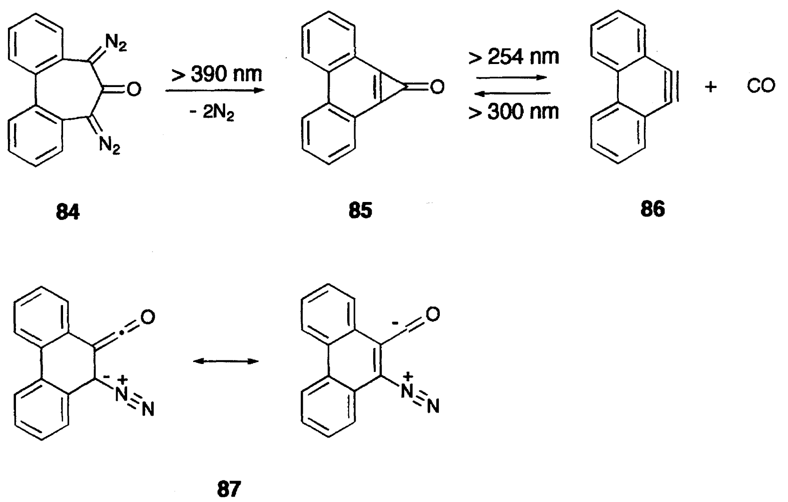
5.1 Photolysis of 2,7-Bis(diazo)-3,4,5,6-dibenzocyclohepta-3,5-dien-1-one. Phenanthryne.[77] Irradiation ($\lambda > 350$ nm, Ar, 10 K) of bis(diazo)cycloheptadienone (**84**) gave 9,10-cyclopropa-phenanthren-3′-one (**85**) as an initial photoproduct (Scheme 21). The assignment is based on its rather strong absorption at 1862 cm^{-1}, characteristic of cyclopropenone C=O stretching absorption,[78] and the C–H deformation of the aromatic group, very similar to that of the starting compound. No other peaks assignable to an intermediate leading to the cyclopropenone, e.g., α-diazo ketene (**87**) were observed during photolysis. Moreover, irradiation of **84** in Ar doped with 2% O_2 also resulted in the formation of **85** almost exclusively. Warming the matrix containing the propenone (**85**) and O_2 to 70 K in the dark did not result in any appreciable change in the spectrum. Only when **84** was irradiated in Ar doped with 23% O_2, complex bands in carbonyl regions, presumably owing to the oxidation of carbenes, appeared. These results clearly suggest that the stationary concentration of carbene in the matrix must be small.

The diazo ketone **84** is expected to undergo the Wolff rearrangement to give diazo ketene (**87**) quite easily, owing to the aromatization energy gained through phenanthro ring formation by this process. In the matrix, **87** will be produced with excess energy and will lose the second N_2 to form the propenone (**85**) before undergoing thermal relaxation. Since elimination of N_2 from diazomethanes is estimated to entail less than 30 kcal mol^{-1},[79] the intermediates, produced from the electronically excited state of **84**, should still have enough excess energy for transfer to the vibrational mode of the second diazo group to eliminate the remaining N_2. The process is also favored by the generation of phenanthro structure in the final product.

Irradiation of the cyclopropenone **85** with shorter wavelength light ($\lambda > 254$ nm) gave rise to the absorption band due to CO (2138 cm^{-1}) along with a slight shift of the C–H deformation absorption of the aromatic ring. The spectral changes are best explained in terms of photodecarbonylation of **85** to generate phenanthryne (**86**) (Scheme 21). The band



Scheme 20.



Scheme 21.

at 1862 cm^{-1}, originally assigned to a cyclopropenone C=O absorption band, remained even when prolonged irradiation was carried out until no appreciable change in spectrum was observed. It is very tempting to assume that the 1862 cm^{-1} band is due to the CC triplet bond stretching vibration, since a weak band at 1846 cm^{-1} observed for benzyne is unambiguously assigned as the CC triple bond stretching vibration based on ab initio theoretical calculations (MP2/6-31G(d)).[71c)]

Further support of this assignment was obtained from the observation that irradiation of the matrix containing CO and **86** with light of $\lambda > 300$ nm resulted in regeneration of the absorption due to the cyclopropenone **85** at the expense of CO and **86**, and that shorter wavelength irradiation again reproduced CO and **86**. This observation is best explained to mean that phenanthryne reacts with CO upon photoexcitation to produce **85**. Benzyne is shown to react with CO upon photoexcitation to give, in this case, cyclopentadienylideneketene, which regenerates benzyne and CO upon shorter wavelength irradiation.[71c)] On the other hand, 3,3,6,6-tetramethylcyclohexyne, generated by thermolysis of the corresponding cyclopropenone also reacts with CO upon photoexcitation to afford, in this case, the starting cyclopropenone.[70b)]

The exact mechanism of this interesting photoreaction is not known. However, if one assumes that the reactions take place in a stepwise fashion by way of a common 1,3-biradical intermediate, the formation of cyclopropenone can be easily understood in terms of coupling of the biradical, while that of the ethenone could result from the Wolff type rearrangement of the ketene carbene form. In other words, the initial step of the reaction is the same, while the following pathway is dependent on the structure. In this way, benzyne and phenanthryne might lead to formally different products in the photoreaction with CO.

5.2 Photolysis of 1,3-Bis(diazo)indan-2-one.[80)] These observations prompted us to apply the analogous pathway for the synthesis of a more strained and challenging cycloalkyne, i.e., cyclobutyne, by using 1,3-bis(diazo) ketone incorporated in a five membered ring.

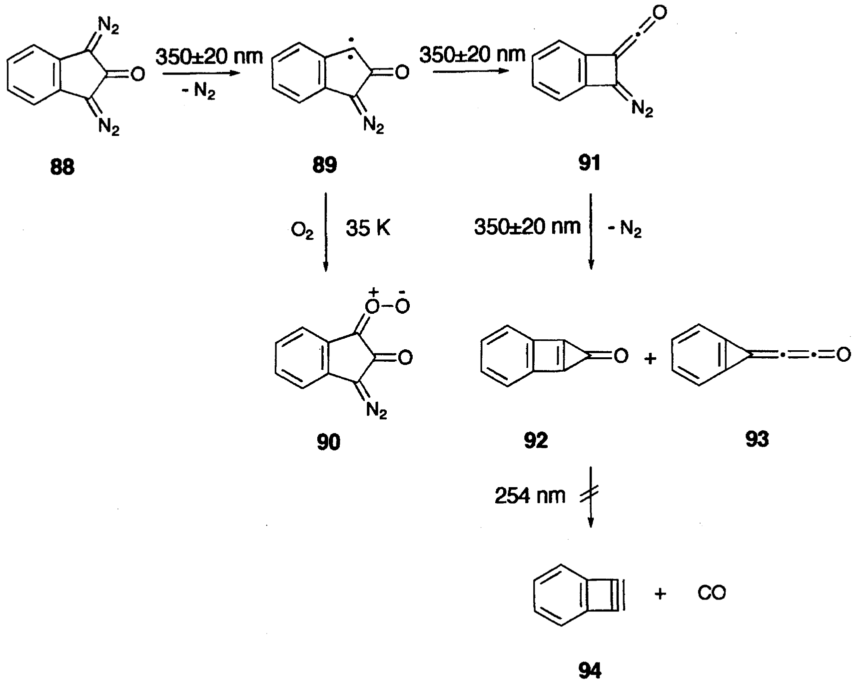
Irradiation (λ =350±20 nm, Ar, 10 K) of the 1,3-bis(diazo)indan-2-one (**88**) gave diazo ketocarbene **89**, which was assigned based on the C=O stretch at 1647 cm^{-1}, somewhat shifted to lower frequencies compared to that of the starting compound, and on ESR signals (D = 0.3631, E = 0.0225 cm^{-1}). The assignment was further supported by trapping experiments using O_2. Thus, when the Ar matrix was doped with 1% O_2, warming the matrix containing **89** to 35 K caused the complete disappearance of **89** and the generation of a new species which was reasonably assigned to the corresponding carbonyl oxide (**90**), produced by the reaction of the triplet **89** keto carbene with O_2 (Scheme 22).

Continued irradiation (λ =350±20 nm) resulted in the decomposition of the α-keto carbene to form the diazo ketene **91**, having an intense IR peak at 2106 cm^{-1} and weak peaks at 1569, 1066, and 542 cm^{-1}. The formation of the diazo ketene **91** is explained by a photochemical Wolff rearrangement of the triplet diazo keto carbene **89**. The stepwise Wolff rearrangement in matrix, which proceed through an α-keto carbene, has been noticed in the irradiation of diazo ketone, which fails to undergo a Wolff rearrangement in solution.[81)]

Further irradiation ($\lambda > 350$ nm) of the diazo ketene **91** gave a mixture of a ketone with a strained carbonyl function and a compound with a cumulenic structure. One showing characteristic IR bands at 1813, 1800, and 1783 cm^{-1} is assigned to the cyclopropenone **92**, while the other with the 2106 cm^{-1} band is assigned to the propadienone **93**, which could be formed by a Wolff-type rearrangement of the ketene carbene generated from **91** (Scheme 22).

The two photoproducts of **91** were completely unreactive even under prolonged short-wavelength irradiation ($\lambda > 200$ nm). Thus, we could not synthesize benzocyclobutenyne (**94**) by an approach starting with **88**. The failure in the photodecarbonylation of **92** might be attributed to the fact that the photostationary state between **92** and **94** with CO largely favors the former.

Cyclobutyne itself has been the subjects of diverse experimental and theoretical studies. Szeimies reported evidence that a bicyclic cyclobutyne derivative rearranged to a cyclopropylidenemethylene.[82)] Adams has synthesized several



Scheme 22.

metal complexes with cyclobutyne as a ligand.[83] However, these are not prepared directly from cyclobutyne. In 1992, Schaefer predicted a barrier of 25 $\mathrm{kcal\,mol^{-1}}$ for isomerization of cyclobutyne to butatriene and suggested that cyclobutyne should be "makeable" based on the calculation with TCSCF methods.[84] However, in 1995, Johnson investigated by MCSCF(4,4)/6-31 G* and MP4/6-31*//MP2/6-31* calculations and predicted that cyclobutyne rearranges to cyclopropylidene carbene with little or no barrier and hence its observation should be difficult or impossible.[85]

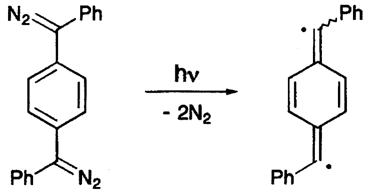
Benzocyclobutenyne (**94**) does not exist either at the HF or at the DFT level of theory.[86a] At the MP2 level of theory a minimum is found, but one of the calculated vibrational frequencies has an unreasonably high value (more than 6000 $\mathrm{cm^{-1}}$), suggesting that this level of theory is also not adequate. On the other hand, **94** is found to be in a minimum when a simple two configuration wavefunction[86b] is used. However, more sophisticated calculations are needed to determine if **94** is indeed a real minimum on the C_8H_4 potential energy surface and whether a reasonable barrier to the ring-opened vinylidene (which seems to be the prefered reaction path of **94**) exists.[86c]

6. Structure of Bis(diradical) Species Conjugatively Connected through Aromatic Rings

Intramolecular interaction of two carbenic centers in organic π-conjugated open-shell systems has been attracting continued and ever-increasing attention in the light of recent growing interests in high-spin molecules as potential organic magnetic materials.[87] However, since the dicarbene having the π-moiety of 1,3-benzoquinodimethane framework was established to have a quintet ground states,[88] most studies in this field have been devoted to triplet carbene coupled in meta fashion. Thus, connecting the divalent subunits in a conjugative manner has been intentionally avoided. It is very interesting, however, to disclose structural and chemical features of these species formed as a result of direct interaction since they are an equally important class of intermediates in many aspects, even though less important in terms of technical application such as organic magnetic materials. Research along this line has proceeded gradually by using matrix isolation techniques that reveal interesting facets of these intermediates.

6.1 Bis(carbenes) in *p*-Phenylene Systems. *p*-Phenylenebis(phenylmethylene) (**96**), where two phenylcarbene units are connected by *p*-phenylene linker, was first generated in the 1960s by photolysis of the precursor bis(diazomethane) **95** and characterized mainly by ESR.[89] Wasserman and co-workers estimated that the two unpaired electrons are separated by a distance of approximately 4 Å and proposed *p*-phenylenebis(methylene) structure **96** with the triplet ground state based on ESR data obtained in 1,4-dibenzoylbenzene glassy matrix.[89a] Later, Itoh[89b] and Sixl and co-workers[89c] carried out ESR measurement using a host single crystal and showed that the triplet state was thermally populated above the singlet ground state by only 202 and 120 $\mathrm{cm^{-1}}$, respectively (Scheme 23).[89d]

Matrix isolation studies were first carried out in 1993 by Sheridan and co-workers[90] and by us[91] for *p*-phenylenebis(chloromethylene) system. Irradiation ($\lambda > 350$ nm, Ar, 10 K) of precursor *p*-phenylenebis(chlorodiazirine) (**97**) resulted in stepwise decomposition of the diazirine to give the monocarbene (**98**), as an initial product, which eventually led to the biscarbene (**99**). Spectroscopic and reactivity evidence indicated that a diradical ($\sigma^2\pi^2$) is favored over a biscarbene ($\sigma^2\sigma^2$) electronic configuration (Scheme 24). For



95 **96**

Scheme 23.

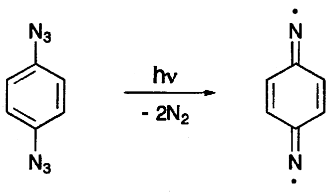
instance, the IR spectrum resembles that of benzoyl chloride, the UV-vis exhibits highly structured bands at visible region and it abstracts H from methane to give **100** even at 47 K, showing dramatically enhanced reactivity over that of chlorophenylcarbene.

More recently, Sheridan and co-workers[92] showed that *p*-phenylene(biscarbene) electronic configurations can be switched from the biradical ($\sigma^2\pi^2$) to biscarbene ($\sigma^2\sigma^2$) structures by a substituent. Irradiation (λ = 385 nm, N_2, 12 K) of *p*-phenylenebis(fluorodiazirine) (**101**) again resulted in a stepwise decomposition of the diazirine to produce primarily monocarbene monodiazirine (**102**), which underwent decomposition upon further irradiation (λ = 374 nm, N_2, 12 K) to produce the biscarbene (**103**). The criteria used to characterize the structure for *p*-phenylene-bis(chloromethylene) (**99**) indicate that **103** is a bis-closed-shell-carbene ($\sigma^2\sigma^2$) rather than a biradical. Thus, the IR spectrum of **103** is characteristic of a *p*-disubstituted aromatic, the UV-vis spectrum is nearly identical to those of monofluorophenylcarbene, and no H abstraction from methane up to 60 K is observed in this case. Moreover, the geometry of biscarbene **103** optimized by RHF/6-31G(d) level of theory indicates no quinoidal distortions in **103** (Scheme 24). These observations can be reasonably explained in terms of a significant difference in π-donating and σ-accepting properties between chlorine and fluorine; the observations imply that the fine balance between electronic configurations in *p*-linked systems can be selectively tipped toward either diradicals or biscarbene via these subtle substituent effects.

6.2 Bis(nitrenes) in *p*-Phenylene Systems. *p*-Phenylenebis(nitrene) (**105**) was also first generated in the 1960s and characterized by ESR.[93] Earlier researchers reported that the bis(nitrene) had a quinonoidal structure with triplet ground state.[93a] Although the lowest energy structure is predicted to be nearly degenerate singlet and triplet states with a small preference for the triplet by 60 cal mol^{-1} at the SDCI/DZ level of theory,[94] more recent ESR study showed that it has singlet ground state with a small S–T gap of 0.7 kcal mol^{-1}.[95] The quinonoidal structure was confirmed by the matrix IR spectra of the dinitrene, which exhibit the strong absorption peaks of 1759 and 1775 cm^{-1} ascribable to C=N stretching (Scheme 25).[93b]

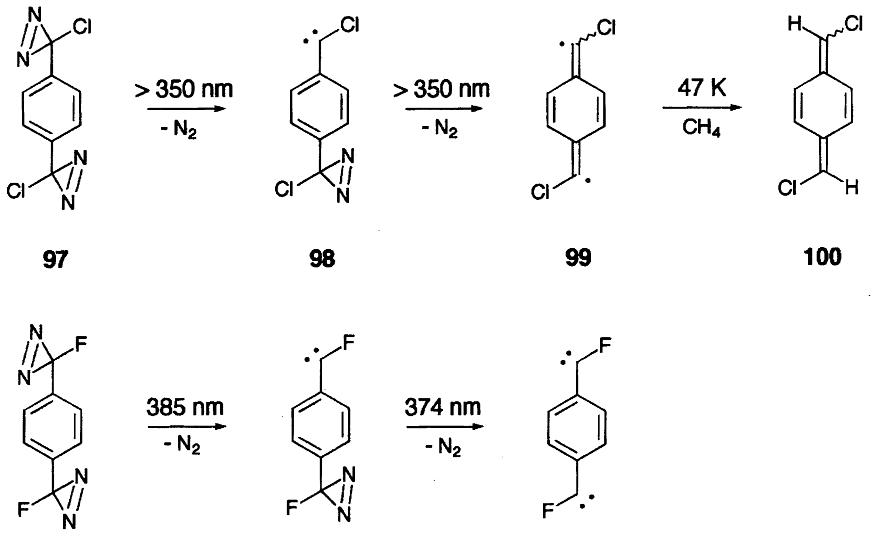
A series of dinitrenes connected by π-conjugating linkers such as biphenyl,[96] stilbene,[97] tolane,[98] azobenzene,[95] 1,4-diphenyl-1,3-butadiene,[99] and 1,8-diphenyl-1,3,5,7-octatriene[99] have been investigated and also shown to have quinonoidal structures, presumably with nearly degenerate singlet and triplet states.

6.3 Bis(diradical) Species in *o*-Phenylene Systems.[100] Almost nothing is known concerning electronic configurations of a diradical center connected in *o*-phenylene linker, although product analysis studies were reported.



104 **105**

Scheme 25.



101 **102** **103**

Scheme 24.

Irradiation ($\lambda > 350$ nm, Ar, 10 K) of 1,2-diazidobenzene (**106**) resulted in a total disappearance of the bands ascribable to the azido groups to give a single product (**A**). ESR spectra (Ar, 12 K) do not display the transitions expected for either a triplet or a quintet species, which suggests that compound **A** possesses a singlet ground state.

The product **A** underwent decomposition either upon irradiation with shorter wavelength light ($\lambda > 254$ nm) to afford *Z, Z*- and *E, E*-1,4-dicyano-1,3-butadiene (**107**) or upon warming the matrix containing **A** from 10 to 25 K to produce, in this case, only *Z, Z*-isomer (Scheme 26).

Decomposition of **106** was investigated previously at much higher temperatures. Thus, Hall and co-workers carried out the thermolysis of **106** in refluxing decalin and found that *Z, Z*-**107** was produced exclusively.[101] Yabe photolyzed **106** in an EPA matrix at 77 K and also obtained *Z, Z*-**107** quantitatively, no intermediates being detected even at this low temperature.[102] On the other hand, Rees et al. attempted to generate 2-benzotriazolylnitrene (**108**) by oxidation of the corresponding amine and again isolated *Z, Z*-**107** in high yield.[103]

From these observations, the product **A** generating **107** is either the nitrene **108** formed as a result of loss of one nitrogen molecule, followed by cyclization, or *o*-phenylenebis(nitrene) **109** generated by simultaneous loss of two nitrogen molecules. Since the vibrational frequencies calculated for the optimized structure of **108** (MP2/6-31G(d)) did not coincide with the IR spectra observed for **A**, the bis(nitrene) **109** is proposed as the most plausible structure for **A**.

In order to obtain more information concerning the structure of **109**, ab initio MO calculations were carried out. The optimized geometries (MCSCF/6-31G(d)//6-31G(d)) show that there is a strong π interaction between a benzene nucleus and substituents in the lowest singlet and triplet states. This means that they exist as 3,5-cyclohexadiene-1,2-diylidenebis(aminyl radical) (**109B**) rather than localized *o*-phenylenebis(nitrene) (**109A**). In the lowest quintet state, on the other hand, the optimized geometries exhibit a weak π conjugation between a benzene nucleus substituents. The triplet and quintet states are calculated to lie above the singlet ground state by ca. 1 and 30 kcal mol^{-1}, respectively.[100]

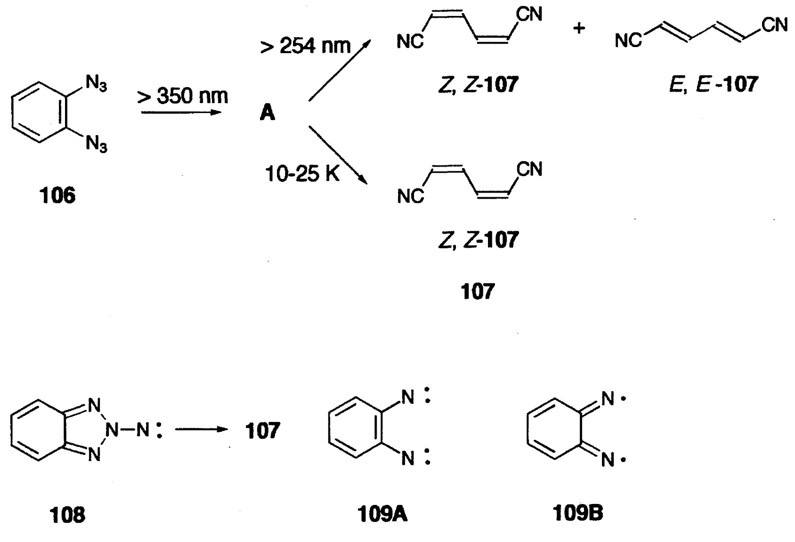
Irradiation ($\lambda > 350$ nm, Ar, 10 K) of 2-azidophenyldiazomethane (**110**) also resulted in a simultaneous disappearance of the bands ascribable to the diazo and azido groups to afford single product **B**. The product **B** also underwent similar decomposition either upon irradiating with shorter wavelength light ($\lambda > 254$ nm) to produce *Z, Z*- and *E, E*-1-cyanohexa-1,3-dien-5-ynes (**111**) or upon thawing the matrix containing **B** from 10 to 35 K to produce only *Z, Z*-isomer.

In analogy with the decomposition of **106**, either 2-carbenophenylnitrene (**114**) or 2-indazolylnitrene (**112**) is proposed as a possible structure for the product. Rees and co-workers generated the nitrene **112** by oxidation of the corresponding amine and found that **112** undergoes ring-expansion to form 1,2,3-benzotriazine (**113**) in solution at room temperature and that the cyano acetylene **111** is formed only when **113** is generated at much higher temperatures in gas phase (e.g., 450 °C/0.01 Torr, 1 Torr = 133.322 Pa).[104] Since no bands ascribable to the nitrene **112** were detected in the product mixture spectra in the photolysis of **110**, 2-carbenophenylnitrene **114** is proposed as the most likely structure for **B** (Scheme 27).

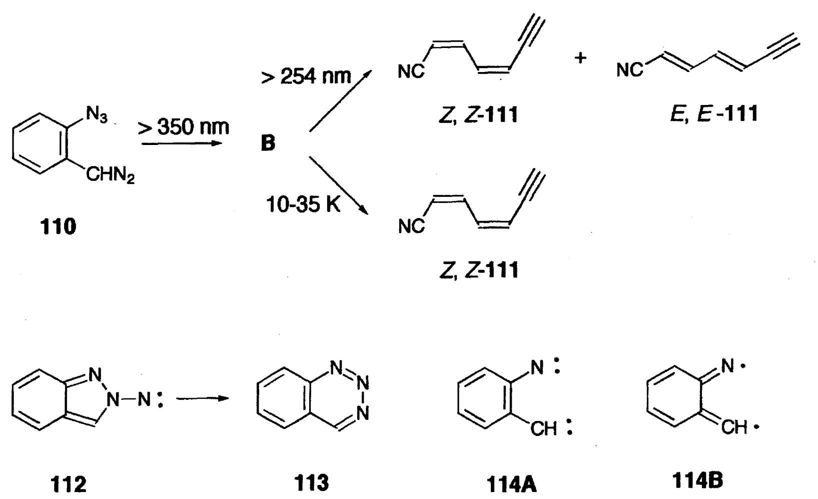
As with the *o*-phenylenebis(nitrene) **109**, the optimized geometries of singlet and triplet are quite similar and indicative of a strong interaction between the benzene nucleus and the substituents i.e., **114B**. Again the singlet appears to be slightly preferred, whereas the quintet state lies much higher in energy.[100]

Concluding Remarks

This account demonstrates the powerful role of matrix isolation techniques to understand the role of reactive intermediates in organic reactions. For instance, obvious differences in reactivities between carbenes and nitrenes are often noted even under these conditions and are shown to be reflecting the inherent reactivity observed under normal conditions. The



Scheme 26.



Scheme 27.

long-waited elusive intermediates in the tautomerization of benzofuroxan are generated and fully characterized.

This account also clearly illustrates that the reactions undergone by carbenes and nitrenes in noble gas matrices at cryogenic temperatures are distinctively and fruitfully different from those in solution at ambient temperatures. This is not simple "slow-motion pictures" of fast reactions of "the real world", but rather a new world of chemistry where highly elusive species with only fleeting existence at room temperature are playing "leading" roles in reaction. The ability of matrix-isolation techniques to halt a reaction in midstride enables us to start a new reaction from this point.

For example, triplet ground state molecules are often shown to be in photoequilibrium with singlet molecules under matrix condition, which is usually exceptional in solution reaction. The reaction of highly strained cyclic triple bond with CO to form the cyclopropenone under irradiation will not be attained under ambient conditions. 1,4-Migration in the excited state of *o*-quinonoid compounds and photochemical Wolff rearrangement of triplet α-keto carbene are also rare in solution. Moreover, photochromism including more than two isomers is rather routinely observed within a matrix.

The methods also enable chemists to challenge the structural limit of chemical bonds involved in organic molecules. Only attempts to generate cycloalkynes are reported here. A more challenging and exotic molecule such as *trans*-cyclohexene, Mobius benzene,[105] and even hexa(dehydro)benzene (C_6)[106] is being challenged. The bulk of the work described here has centered on the generation of reactive species by photochemical methods. Flash vacuum pyrolysis (FVP) can be also used to combine with matrix isolation spectroscopy. A new technique in gas-phase pyrolysis having considerable advantages over standard FVP appears, where contact time in flash pyrolysis is decreased up to 10 μs, and the sample is subjected to a temperature gradient of over 1600 K within 50 μs.[107]

Two points should be noted finally. Recent advances in computer technology both in hardware and software have dramatically increased the reliability and accuracy of computational chemistry. This is especially helpful in the matrix isolation study where IR is the most heavily utilized techniques. The most difficult aspect of the work is the assignment of spectra to intermediate structures. The most reliable method thus far has been to generate proposed intermediate from several different precursors. This pains-taking and time-consuming work has prevented chemists from utilizing the techniques with ease. Ab initio calculations with high level of theory of IR frequencies are now able to be carried out with great ease even by the matrix isolationists themselves, which make structural and vibrational assignments very easily. Once the most difficult part of the research is facilitated, the research in this field will flourish.

Another intriguing point to note is introduction of molecular containers; the inner phase of molecular container compounds is particularly suitable for stabilizing reactive species.[108] Thus, in the inner cavity of a hemicarcerand, cyclobutadiene is shown be stable even at room temperature,[109] and even benzyne becomes significantly long-lived ($t_{1/2}=205$ s) in solution at -75 °C.[110] Thus, the container is expected to be an interfield to connect the events in matrices at cryogenetic temperature and those in solution at ambient temperature. If such inert reaction fields are more easily available to organic chemists, the reactions observed within noble gas matrices will become much more familiar.

The author is grateful to his colleagues named in the references and those currently in his group for their time-consuming and time-taking efforts, without which this work would not have been realized.

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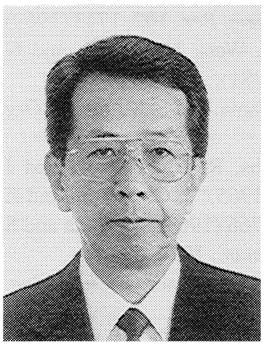

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