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Photolysis of p-Phenylenebis(chlorodiazirine), Studied by Matrix Isolation Spectroscopy. Generation, Detection and Characterization of p-Phenylenebis(chloromethylene)

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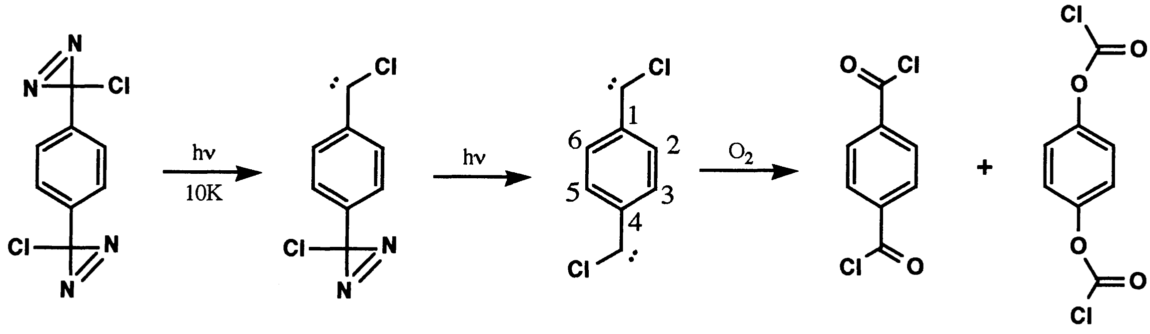
Photolysis of the title bis-diazirine matrix-isolated in Ar at 10 K monitored by IR and UV/vis spectroscopy indicated that the diazirine underwent stepwise elimination of N_2 to produce 3-(4-chlorocarbenophenyl)-3-chlorodiazirine which then eliminated the second N_2 to generate para-phenylene-bis(chloromethylene). The structure of the bis-carbene was discussed based on the spectroscopic data as well as the semiempirical theoretical calculations.

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.1) However, since the dicarbene having the π-moiety of 1,3-benzoquinodimethane framework was established to have a quintet ground state,2) most studies in this field have been devoted to triplet carbene coupled in meta fashion and hence less is known about *direct* interaction of the carbenic center linked in para phenylene system.3,4) During the course of our studies5) on the generation of new reactive intermediates as a result of intramolecular interaction of divalent centers with functional groups, we became interested in revealing the mode of intramolecular interaction between two divalent centers through a π-system. Thus, we investigated intermediates generated by irradiation of p-phenylenebis(chlorodiazirine) (**1**) using matrix isolation spectroscopy.6,7)

Photolysis (λ>350 nm) of **1**8) matrix-isolated in Ar at 10 K resulted in a disappearance of the absorption bands ascribable to the starting material and concurrent appearance of new absorption bands in the IR. Careful analysis of the bands by plotting as a function of irradiation time suggested that the absorption bands were composed of a major, a first growing species (A)9) with a small amount of a second, slowly developing one (B).9) Subsequent irradiation (λ>350 nm) of the matrix containing A and B caused a decrease in the bands ascribable to A and a simultaneous increase in the absorptions due to B. The matrix also took on a distinct yellow hue. In the UV-vis spectra, the formation of weak but structured bands with apparent maximum at 440 nm was observed. Prolonged irradiation of the matrix mainly containing B did not result in any appreciable change in the major absorption. The simplest interpretation of these spectral changes is that the bis-diazirine undergoes stepwise elimination of N_2 to produce (4-chlorocarbenophenyl)diazirine (**2**) as an initial product which then eliminates the second N_2 upon further excitation to afford the 4-

carbeno phenylcarbene (**3**). Previous observations in this field seems to support this interpretation. Thus, photolysis of 3-phenyl-3-chlorodiazirine matrix-isolated in Ar at 10 K is shown to generate phenylchlorocarbene having major IR absorptions at 1590, 1225, 1170, 848, and 735 cm^{-1} and UV absorption at a λmax of 300 nm.10) Rather strong bands at 1600, 1227 and 1174 cm^{-1} consistent wirh a strongly electron withdrawing group in conjugation with the benzene ring observed for A was indicative of the presence of carbenophenyl group. UV spectra for A showing the apparent maximum at 381, 369, 362, and 298 nm are not coincident with that of phenylchlorocarbene, but, instead, are considered to be characteristic of diazirine function,11) indicating one diazirine group is intact. Subsequent excitation of phenylchlorocarbene is shown to undergo ring-expansion to produce 1-chlorocyclohepta-1,2,4,6-tetraene showing IR bands at 1817 and 1816 cm^{-1} owing to cumulenic double bond along with the complete disappearance of the bands owing to the benzene ring.10b) Irradiation of A, on the other hand, showed no sign of formation of bands ascribable to the cumulenic double bond, to the limit of our IR sensitivity. On the contrary, the presence of strong absorption at 1575 cm^{-1} in B might indicate that ring reorganization did not take place during the phototransformation.



1 **2** **3** **4** **5**

In order to obtain more information for the assignment of B, the following trapping experiments using O_2 were carried out. Irradiation of **1** in Ar matrices doped with 20% O_2 resulted in the formation of two oxidation products plus ozone with no sign of the formation of A and B. A minor oxidation product was assigned as terephthaloyl chloride (**4**) by comparison with the authentic matrix-isolated compound while a main product was tentatively assigned as hydroquinone bis(chloroformate) (**5**). Irradiation of **1** in Ar matrices doped with 3% O_2 at 10 K, on the other hand, gave the absorptions due to B almost exclusively. Warming the matrix containing B and excess O_2 from 10 to 35 K caused a decrease in the band arising from B and a simultaneous increase in the absorptions due to **4** and **5**. These observations can be reasonably understood as indicating that the bis-carbene (**3**) is trapped by O_2 to generate **4** and **5**, since these transformations are now well-documented.12)

Accepting that the final product is the bis-carbene (**3**), it is very important to examine the nature of the interaction between two carbenic centers linked by the para-phenylene moiety. A priori, it is possible to draw **3** either as the bis-carbene structure or as a diradical structure. Phenylchlorocarbene shows rather broad absorption at around 300 nm as have been observed for most simple arylcarbenes,13) while **3** shows the highly structured absorption bands at much longer wavelength, indicating the presence of some sort of interaction between the two carbenic centers. The strongest IR absorption at 1565 cm^{-1} in **1** is not incompatible with the double-bond stretch observed for para-quinodimethanes.[14] In order to gain more insight into the structure of **3**, semiempirical calculations empolying the PM3-ROHF CI (4×4) method[15] were carried out. The results summarized in Table suggested that singlet σ, σ-biradical is the most stable state among those having the possible electronic configuration for the bis-carbene (**3**). Reflecting this stable electronic configuration, optimized geometries for **3** suggest appreciable shortening of the bond between carbenic carbon and C_1 or C_4 (1.347 Å) as well as C_2-C_3 (1.360 Å) and concurrent lengthening of the C_1-C_2 or C_5-C_6 bond (1.434 Å).

Table 1. MNDO-Caluculated State Energy for Several Electronic States of **3**

State	Electronic Configuration	State Energy (eV)
^1B_u	... $(3a_n)^2(10b_u)^1(10a_g)^1$	-9.196696
^3B_u	... $(3a_n)^2(10b_u)^1(10a_g)^1$	-9.127888
^5A_g	... $(3a_n)^1(10b_u)^1(10a_g)^1(4b_g)^1$	-8.260085
^3A_g	... $(3a_n)^1(10b_u)^1(10a_g)^1(4b_g)^1$	-7.812398
^3A_n	... $(3a_n)^1(10b_u)^1(10a_b)^1$	-7.582316
^3B_g	... $(3a_n)^1(10b_u)^1(10a_g)^2$	-7.568524
^3A_g	... $(3a_n)^1(10b_u)^1(10a_g)^1(4b_g)^1$	-7.521779
^1A_g	... $(3a_n)^1(10b_u)^1(10a_g)^1(4b_g)^1$	-7.021805
^1A_n	... $(3a_n)^1(10b_u)^2(10a_g)^1$	-6.911399
^1B_g	... $(3a_n)^1(10b_u)^1(10a_g)^2$	-6.894361
^3A_n	... $(3a_n)^2(10b_u)^1(4b_g)^1$	-6.751761

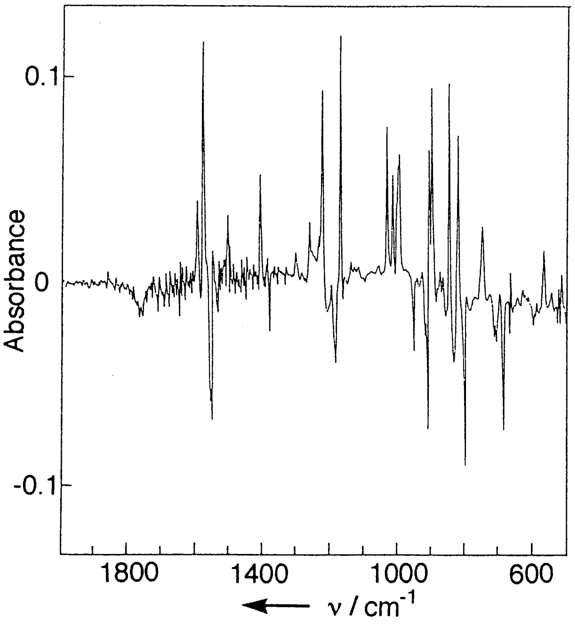


Fig. 1. IR Difference spectrum of an Ar matrix at 10K. Positive peaks are assigned to **2**. Negative peaks are obtained after 2h irradiation of **2** and assigned to **3**.

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6) During the course of this work, we happened to know that Zuev and Sheridan also investigated the photolysis of **1** using matrix isolation techniques, which is in good agreement with ours; P. Zuev and R. S. Sheridan, *J. Am. Chem. Soc.*, in press.

7) Photolysis of 1,4-diazidobenzene in Ar at 20 K was also studied and is appearing: T. Ohana, A. Ouchi, H. Moriyama, and Y. Yabe, *J. Photochem. Photobiol. A: Chem.*, in press.

8) This diazirine [**1**: IR (Ar, 10 K) 1600 (s), 1581 (s), 1569 (w), 1521 (w), 1509 (s), 1413 (s), 1266 (m), 1201 (w), 1143 (w), 1036 (s), 1007 (m), 1004 (m), 921 (m), 912 (s), 903 (vs), 879 (w), 823 (s), 699 (w), 568 (m) cm^{-1}; UV/vis (Ar, 10 K) 391, 383, 379, 358, 351, 282, 260 nm.] was prepared by following essentially the same procedure reported for 3-chloro-3-phenyldiazirine starting from terephthalonitrile by way of terephthalamidine dihydrochloride; W. H. Graham, *J. Am. Chem. Soc.*, **87**, 4396 (1965); A. Padwa, M. J. Pulwer and T. J. Blacklock, *Org. Synth.*, **60**, 53 (1981). Caution*: The bis-diazirine (**1**) was found to be extremely shock- sensitive.*

9) A=**2**: IR (Ar, 10 K) 1600 (vs), 1566 (m), 1509 (m), 1413 (m), 1387 (w), 1238 (w), 1227 (vs), 1174 (vs), 1019 (m), 1000 (m), 917 (s), 903 (s), 850 (vs), 837 (w), 823 (m), 748 (m), 568 (m) cm^{-1}; UV/vis (Ar, 10 K) 381, 369, 362, 342, 298 nm.
B=**3**: IR (Ar, 10 K) 1582 (s), 1386 (w), 1190 (m), 1019 (m), 958 (m), 939 (w), 918 (s), 896 (w), 805 (m), 709 (w), 689 (m), 600 (w) cm^{-1}; UV/vis (Ar, 10 K) 440 nm.

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