imally, the Me_3Si group is gauche to the migrating bond, an orientation that allows for only minimal hyperconjugative stabilization of the developing vacancy at the β-C by the γ-C–Si bond.[5]

The results for the cis isomer are quite different; the rate constants are larger than those for the analogous equatorial brosylate, *trans*-4-*tert*-butylcyclohexyl brosylate, particularly in 97T (452x), and the β-*d* isotope effects are much smaller. In the ethanolic solvents, no β-d_4 isotope effect is observed, and the effect in 97T is slightly inverse. The α-*d* isotope effects are also smaller than expected. These results indicate that the reaction involves participation. The consistant formation of small yields of bicyclo[3.1.0]hexane suggest silicon-promoted carbon participation.[16]

The orientation of the two substituents in the transition state is approximately diequatorial rather than diaxial; in this conformation, all four β-C–H bonds have dihedral angles of 60° with the developing p-orbital vacancy, which allows for very little C–H hyperconjugative stabilization and gives small or inverse β-*d* isotope effects. In the alternate, higher energy, 1,3-diaxial conformation[17] two of the β-C-H bonds would be antiperiplanar to the leaving group, favoring hyperconjugation, rearrangement,[6] and large β-d_4 effects, contrary to the observations. Thus the silicon stabilizes the transition state, and presumably the carbonium ion intermediate, through a "W" conformation[18] implicating the "percaudal"[19] interaction which involves overlap of the reacting orbital on the α-carbon with the back lobe of the carbon–silicon bonding orbital. Although earlier workers have speculated on this mode of carbonium ion stabilization, evidence confirming it was not obtained.[20]

Experiments designed to characterize this interaction further are currently in progress.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grants CHE 79-10015 (project support), CHE 81-11957 (GC/MS), and CHE 81-05004 (NMR). The authors thank Western Washington University for the grant of a sabbatical leave to G.S.K. and Raymond S. Gross for his assistance in developing one of the preparative methods used in this study. We thank Dr. Lester Taylor for the GC/MS analysis and Teresa Wright-Kester for the ^{13}C spectra.

Registry No. 1, 99810-99-8; **2**, 99811-00-4; cyclohexene, 110-83-8; *cis*-3-TMS-cyclohexanol, 7452-98-4; bicyclo[3.1.0]hexane, 285-58-5.

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(16) Silicon-promoted carbon participation is chosen to indicate bridging by the γ-carbon through the back lobe of the carbon–silicon bonding orbital.

(17) Kitching, W.; Olszowy, H. A.; Drew, G. M.; Adcock, W. *J. Org. Chem.* **1982**, *47*, 5153.

(18) Nickon, A.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1967**, *89*, 3914.

(19) Davis, D. D.; Black, R. H. *J. Organomet. Chem.* **1974**, *82*, C-30.

(20) Davis[19,21] showed that the W conformation is strongly preferred in cyclopropane formation by 1,3-deoxystannylation. However, they found no evidence that these reactions involved stabilized ion intermediates. Kuivila also concluded that 1,3-deoxystannylation reactions are concerted.[22]

(21) Davis, D. D.; Johnson, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7576.

(22) McWilliam, D. C.; Balasubramanian, T. R.; Kuivila, H. G. *J. Am. Chem. Soc.* **1978**, *100*, 6407.

(23) Shiner, V. J., Jr.; Jewett, J. G. *J. Am. Chem. Soc.* **1965**, *87*, 1382.

Phenoxychlorocarbene. Spectroscopy and Photochemical Interconversion of Geometric Isomers

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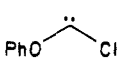
Received September 30, 1985

We wish to describe the first direct observation of phenoxychlorocarbene (**1**) and report evidence for the photochemical interconversion of its two geometric isomers.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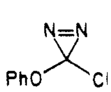
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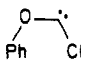
$PhOCHCl_2$
3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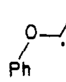
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Irradiation ($\lambda > 360$ nm) of 3-chloro-3-phenoxydiazirine (**2**)[1,2] matrix isolated in argon or N_2 at 10 K (**2**:Ar or N_2 = ca. 1:800) led to disappearance of the IR absorptions of **2** and to growth of new bands shown in figure 1. UV spectra of the same sample in N_2 indicated the loss of **2** and growth of a broad absorption centered at 320 nm. Continued irradiation at these wavelengths destroyed the primary photoproduct bands in both the IR and UV spectra, and produced the photochemically stable products benzoyl chloride, chlorobenzene, and CO (by IR).

That the initial photoproduct absorptions are due to carbene **1** is supported by trapping. Irradiation of diazirine **2** in a N_2 matrix containing HCl (N_2:HCl:**2** = 4500:1:2) gave the above photoproduct IR bands. Warming the matrix to 33 K converted this product to dichloromethyl phenyl ether (**3**)[4] by IR.

The correspondence of the time evolution of the UV spectrum with that of the IR bands of **1** provides strong evidence for the assignment of the 320-nm UV band to **1**. Moreover, the rate of disappearance of the IR absorptions of **1** was found to be greatest when irradiation was in the region of 330–290 nm. Comparison of the UV absorbances of **1** and starting **2** (ϵ ca. 50 cm^{-1} M^{-1})[1] indicates an approximate extinction coefficient of 100 cm^{-1} M^{-1} for the carbene at 320 nm. The UV spectrum of **1** is also quite similar to that observed for methoxychlorocarbene.[3b]

No evidence for the intermediacy of a diazo compound was observed in the IR spectrum, nor were IR absorptions attributable to COCl,[5] benzoyl,[6,7] or phenyl[8] radicals observed. In a similar fashion to methoxychlorocarbene,[3] **1** exhibits strong IR absorptions at frequencies close to 1300 cm^{-1}. This absorption was assigned to a COC antisymmetric stretch in the methoxycarbene; support came from isotopic labeling.[3] The anomalously high frequency was attributed to partial C–O double-bond character, as predicted theoretically. The situation is somewhat more complicated here since the O–aryl stretching modes may also come in this region, and coupling with ring vibrations can cause splitting in the substituent deformations.[9] A reasonable model for carbene **1**, phenyl chloroformate, shows two intense C–O stretches[10] in the region 1100–1200 cm^{-1}. Corresponding vibrations of higher energy in **1** are consistent with C–O stretching modes with significant double-bond character.

Calculations on hydroxymethylene predict the existence of two geometric isomers.[11] Interestingly, irradiations of **1** at different wavelengths, with careful monitoring, indicated two distinct sets of IR absorptions for carbene **1** which exhibited different wavelength dependencies. Irradiation at 366 nm more rapidly destroyed those bands associated with the 1251-cm^{-1} band (species A, Figure 1). Conversely, absorptions associated with the bands at 1285 and 1275 cm^{-1} (species B) were more labile at 304 nm. Moreover, irradiation at 366 nm not only converted A into benzoyl chloride,

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(1) Moss, R. A.; Perez, L. A.; Wlostowska, J.; Guo, W.; Krogh-Jespersen, K. *J. Org. Chem.* **1982**, *47*, 4177.

(2) The matrix-isolation and irradiation details were essentially identical with those described in the methoxychlorocarbene work.[3]

(3) (a) Sheridan, R. S.; Kesselmayer, M. A. *J. Am. Chem. Soc.* **1984**, *106*, 436. (b) Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.*, in press.

(4) The identity of the trapping product was confirmed by independent synthesis according to: Holsboer, D. H.; Scheeren, J. W.; Van der Veek, A. P. M. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 556.

(5) IR: Jacox, M. E.; Milligan, D. E. *J. Chem. Phys.* **1965**, *43*, 866.

(6) The benzoyl radical is reported to absorb in the visible by: Ito, O.; Sakaguchi, T.; Matsuda, M. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1188.

(7) The benzoyl radical should absorb near the reported IR absorption of acetyl at ca. 1800 cm^{-1}: (a) Shirk, J. S.; Pimentel, G. C. *J. Am. Chem. Soc.* **1968**, *90*, 3349. (b) Bennett, J. E.; Graham, S. C.; Mile, B. *Spectrochim. Acta, Part A* **1973**, *29A*, 375.

(8) IR: Pacansky, J.; Brown, D. W. *J. Phys. Chem.* **1983**, *87*, 1553.

(9) Bellamy, L. "The Infrared Spectra of Complex Molecules", 3rd ed.; Chapman and Hall: London, **1975**.

(10) Bacaloglu, V. R.; Bacaloglu, I.; Csunderlik, C.; Ostrogovich, G. *J. Prakt. Chem.* **1971**, *313*, 331.

(11) Goddard, J. D.; Schaefer, H. F., III *J. Chem. Phys.* **1979**, *70*, 5117.

0002-7863/86/1508-0844$01.50/0

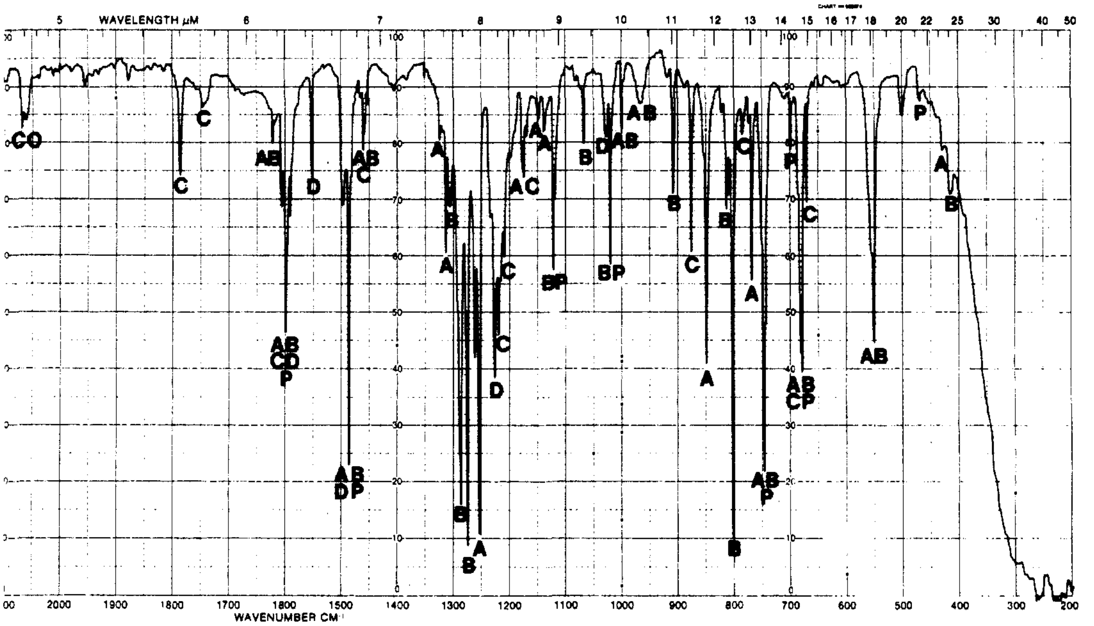

Figure 1. IR spectrum of 3-chloro-3-phenoxydiazirine (**2**) matrix isolated in N_2 at 10 K (800:1 N_2/**2**) after a 6-h irradiation at 366 nm. Bands labeled A and B are assigned to carbenes **5** and **4**, C is benzoyl chloride, D is **2**, and P is chlorobenzene.

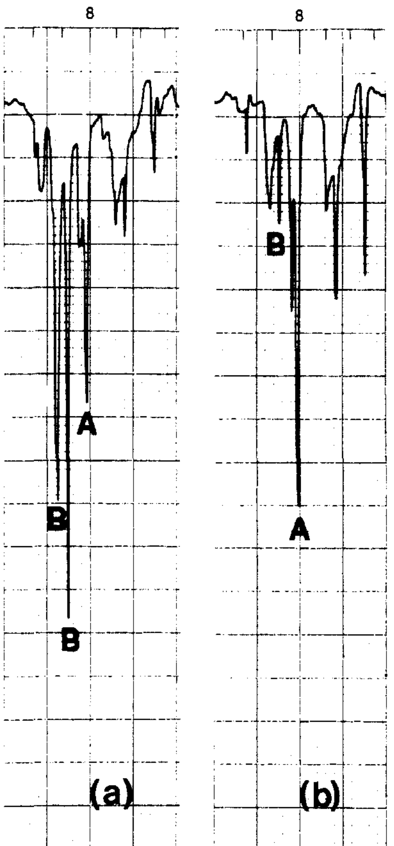

Figure 2. (a) IR spectrum of similar matrix of **2**, over the region 1350–1150 cm^{-1}, after an 18-h irradiation at 366 nm (3-nm band-pass). (b) Same sample after irradiation at 304 nm (6-nm band-pass) for 1.5 h.

chlorobenzene, and CO but also caused an increase in the bands of B. Similarly, irradiation at 304 nm converted a portion of B into A, along with generating the other photoproducts (Figure 2). The UV spectrum of **1** could not, unfortunately, be resolved into two components. The broad absorption of **1** shifted slightly to longer wavelengths on irradiation at 304 nm, however, and to shorter wavelengths with 366-nm photolysis.

The photochemical interconversion and the similarity of the IR spectra confirm that these two species are the cis and trans isomers **4** and **5**. We have reported that the trans isomer of methoxychlorocarbene is more labile at longer wavelengths than is the cis.[3b] By analogy, we thus tentatively assign the trans structure **5** to isomer A. *cis*-Methoxychlorocarbene exhibits a considerably lower energy C–Cl stretch than does the trans isomer.[3b] We have attributed this effect to anomeric lone-pair donation from oxygen into the C–Cl bond in the cis isomer. Isomer **4** (B) shows an intense band at 800 cm^{-1} which is likely the C–Cl stretch. The analogous absorption for trans isomer **5** (A) is thus apparently at 850 cm^{-1}.

Irradiation of **1** leads to both rearrangement to benzoyl chloride and loss of CO to produce chlorobenzene. Short-wavelength decarbonylation of matrix-isolated benzoyl chloride is extremely inefficient. Hence, adiabatic rearrangement of **1** to excited acid chloride,[3] followed by fragmentation, is not a likely route to chlorobenzene. Other possibilities are phenyl–O or C–Cl cleavage of **1** to radical pairs, followed by decarbonylation and recombination, or rearrangement to benzoyl chloride. Fragmentation/recombinations in this fashion could also provide geometric isomerization pathways. No difference in ratios of the three photoproducts can be observed on irradiation of **4** or **5**, which is consistent with these possibilities. The photochemistry of methoxychlorocarbene can be rationalized on the basis of similar cleavages.[3] We are currently exploring the mechanisms for photochemical isomerization and fragmentation of these novel carbenes.[12-14]

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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(12) Geometric isomers have been previously observed in triplet carbenes by ESR spectroscopy,[13] and the photochemical interconversion of these species reported in one case.[13d]

(13) (a) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129. (b) Hutton, R. S.; Manion, M. L.; Roth, H. D. Wasserman, E. *J. Am. Chem. Soc.* **1974**, *96*, 4680. (c) Hutton, R. S.; Roth, H. D. *J. Am. Chem. Soc.* **1978**, *100*, 4324. (d) Murai, H.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1980**, *102*, 1421. (e) Murai, H.; Torres, M.; Strausz, O. P. *Chem. Phys. Lett.* **1980**, *70*, 358. (f) Hutton, R. S.; Roth, H. D.; Manion Shilling, M. L.; Suggs, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 5147.

(14) Irradiation of **2** in 3-methylpentane glasses at 10 K makes **1** only inefficiently, in contrast to the methoxychloro case.[3] Mainly CO (and presumably chlorobenzene) is produced, and no benzoyl chloride is observed. The relation of this novel matrix effect to the photochemical processes of **1**, radical pair involvement in particular, is under investigation.