intensity ratio, respectively, were 6.16 and 6.11 (q, $J = 6$ Hz, C-1 H) and 3.48 and 3.56 ppm (br s, CH_3O).

(*R*)- and (*S*)-Mandelic acid [(*R*)- and (*S*)-5] had mp 131–133 and 132–133 °C, respectively [lit.[17] mp 133 and 133 °C; $[\alpha]^{18}_D$ −153.5° (*c* 1.47, absolute C_2H_5OH) and $[\alpha]^{19}_D$ +151.5° (*c* 1.45, absolute C_2H_5OH) for (*R*)- and (*S*)-**5**, respectively].

Methyl (*R*)- and (*S*)-mandelate [(*R*)- and (*S*)-6] had mp 56–57 and 56–58 °C, respectively [lit.[17] mp 58 and 58 °C; $[\alpha]^{20}_D$ −177° (*c* 1.3, $CHCl_3$) and +175° (*c* 1.3, $CHCl_3$) for (*R*)- and (*S*)-**6**, respectively].

(±)-1-Phenylethanol-*1-d* [(±)-7] was obtained by reduction of acetophone in ether with lithium aluminum deuteride. Isolation and distillation gave (±)-**7** (91%) as a colorless oil: bp 100–102 °C (20 mmHg).

(±)-Mandelic-*α-d* acid [(±)-8] was prepared by reduction of benzoylformic acid with sodium borodeuteride by the same procedure as described for the reduction of *p*-chloroacetophone with sodium borohydride. The acid (±)-**8** was obtained (84%) as a white solid: mp 114–117 °C.

(±)-1-Phenylethanol-*O-d* [(±)-9]. (±)-1-Phenylethanol [(±)-**2**] (5.0 g, 8.2 mmol) was added to deuterium oxide (7.0 g, 0.35 mol), and the heterogeneous mixture was shaken for 18 h. The alcohol was extracted into ether (2 × 25 mL), and the ether solution was dried ($MgSO_4$). Evaporation of the ether and distillation of the residue gave (±)-**9** as a colorless oil: bp 98–102 °C (20 mmHg); ^{1}H NMR δ 1.48 (d, 3, $J = 8$ Hz, CH_3), 4.88 (q, 1, $J = 8$ Hz, $CHCH_3$), 7.40 (m, 5, aromatic H).

Methyl (*R*)-mandelate-*O-d* [(*R*)-10] was prepared from methyl (*R*)-mandelate by deuterium exchange in deuterium oxide–methanol-*O-d*. Lyophilization of the mixture gave (*R*)-**10** as a white solid: mp 54–56 °C.

Benzaldehyde-*1-d* (11). To a stirred solution of benzil (13.9 g, 66.1 mmol) in *p*-dioxane (30 mL) was added deuterium oxide (14.4 g, 0.719 mol) and then potassium cyanide (4.68 g, 71.9 mmol) in five portions over 0.5 h. The mixture was stirred for another 0.5 h and then diluted with water (120 mL). The mixture was extracted with ether (3 × 50 mL) and the ether solution washed with saturated sodium bicarbonate (2 × 50 mL) and saturated sodium chloride (2 × 50 mL). After evaporation of the dried ($MgSO_4$) ether solution, distillation gave pure **11** (4.32 g, 61%) as an oil: bp 76–78 °C (22 mmHg) [lit.[18] bp 84–86 °C (30 mmHg)].

(±)-1-(*p*-Chlorophenyl)ethyl Acid Phthalate. A mixture of (±)-1-(*p*-chlorophenyl)ethanol [(±)-**3**] (85.1 g, 0.543 mol), phthalic anhydride (80.5 g, 0.544 mol), and pyridine (86.0 g, 1.09 mol) was stirred overnight at room temperature and then 2 h at 100 °C. The cooled mixture was poured over crushed ice (100 g) and concentrated hydrochloric acid (90 mL), and the mixture was extracted with chloroform (3 × 100 mL). The chloroform solution was evaporated. The residue was neutralized with an excess of saturated sodium carbonate, and the mixture was extracted with ether (2 × 30 mL). The aqueous solution was made acidic (pH 2) by the addition of dilute hydrochloric acid, and the mixture was extracted with ether (3 × 100 mL). The ether solution was dried ($MgSO_4$) and evaporated. Recrystallization of the residue from acetic acid–water (85:15) gave the acid phthalate ester (111 g, 67%): mp 107–108 °C.

Anal. Calcd for $C_{16}H_{13}ClO_4$: C, 63.06; H, 4.30. Found: C, 62.89; H, 4.26.

(±)-1-(*p*-(Trifluoromethyl)phenyl)ethyl acid phthalate was prepared (87%) from (±)-1-(*p*-(trifluoromethyl)phenyl)ethanol [(±)-**4**] by reaction with phthalic anhydride as outlined above for reaction of (±)-**3** with phthalic anhydride, was recrystallized from acetic acid–water (4:1) and had mp 113–114 °C.

Anal. Calcd for $C_{17}H_{13}F_3O_4$: C, 60.36; H, 3.87. Found: C, 60.33; H, 3.86.

***p*-Nitrobenzoate Derivatives.** *p*-Nitrobenzoyl chloride (1.00 g, 5.39 mmol), freshly recrystallized from petroleum ether (bp 35–38 °C), was slowly added with cooling to a stirred solution of the alcohol (4.9 mmol) in pyridine (2.50 g). Stirring was continued for an additional 24 h at room temperature, and the solution was diluted with ether (50 mL). The ether solution was extracted with 2 N hydrochloric acid (3 × 10 mL), saturated sodium bicarbonate (10 mL), and finally saturated sodium chloride (3 × 10 mL). The ether solution was dried ($MgSO_4$) and evaporated. The residue of crude benzoate ester was 85–98% of the theoretical and, when a solid at room temperature, was recrystallized from ethanol. Physical properties are given in Table II.

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Methoxychlorocarbene. Matrix Spectroscopy and Photochemistry

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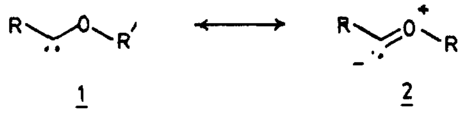
Abstract: Irradiation of 3-chloro-3-methoxydiazirine matrix isolated in argon or nitrogen at 10 K gives methoxychlorocarbene. The carbene was observed by IR and UV spectroscopy. Deuterium and ^{18}O labeling indicated significant C–O double bond character in the carbene, which was exhibited in an intense IR absorption at ca. 1300 cm^{-1}. The time evolution and wavelength dependence of the IR bands indicate two geometric isomers for the carbene, with distinct IR absorptions. The *cis*-carbene shows a significantly lower energy C–Cl stretch than the trans, consistent with an anomeric interaction. Irradiation of the carbene gives acetyl chloride, ketene, and HCl in argon matrices. In nitrogen, small amounts of CO and methylchloride are also observed. Several mechanisms are proposed to explain the photochemical results.

Despite extensive investigations into the structure, reactivity, and spectroscopy of carbenes,[1,2] there is a paucity of experimental information on oxycarbenes (e.g., **1**). Haloalkoxycarbenes were first postulated by Hine in 1953 as intermediates in the reactions of dichlorocarbene with alkoxides.[3] Since that time, oxycarbenes have been suggested as intermediates in thermolyses of norbornadienone ketals[4,5] and ester tosylhydrazone salts.[6,7] These



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novel species have also been invoked in photolyses of various carbonyl containing molecules including formaldehyde,[8] pyruvic acids,[9] cyclobutanones,[10] certain bicyclic ketones,[10] and acylsilanes.[11] Moss[12] and Stevens[13] and their co-workers contemporaneously reported the solution chemistry of methoxychlorocarbene generated from the corresponding diazirine. Most recently, the Moss[14] group has reported the trapping of several additional oxycarbenes produced on thermolyses of diazirines in solution. Oxycarbenes or carbenoids have also been generated by α-elimination reactions[15] and by rearrangements of carbonyl ylides.[16] In contrast to free oxycarbenes, the stable metal complexes of various oxycarbenes have been extensively investigated.[17]

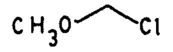
Oxygen substitution as in **1** introduces a significant perturbation on the electronics and chemistry of carbenes. The overlap between the oxygen lone pair and the carbene empty p orbital dominates the electronics in these systems, favoring singlet ground states substantially over triplets.[18] High-level ab initio calculations predict significant C–O double bond character as suggested by resonance structure **2**.[19-21] This interaction is predicted to lead to shortened C–O bond lengths and significant barriers to cis–trans isomerization. For example, calculations predict a C–O bond length of 1.320 Å (cf., 1.474 Å in methanol), and a barrier of 27.5 kcal/mol for trans to cis rotation in the simplest member of this family, hydroxymethylene.[19]

In trapping experiments on alkoxycarbenes, it has been found that the oxygen substitution increases the nucleophilicity of these intermediates.[4,12-14] This undoubtedly reflects contributions of resonance-stabilized structures such as **2**. Moss and co-workers[12,14] have scrutinized the reactions of methoxychlorocarbene and phenoxychlorocarbene with various olefins. Dramatically, the carbenes show nucleophilic selectivity in their additions to electron-poor olefins and electrophilic selectivity in additions to electron-rich olefins. This behavior, termed ambiphilic character by Moss,[12] contrasts the majority of simple carbenes which exhibit electrophilic properties. These results have been nicely rationalized on the basis of frontier molecular orbital interactions.[12,14]

The unimolecular rearrangements interrelating oxycarbenes and carbonyl groups have raised considerable speculation. The intermediacy of hydroxymethylene in formaldehyde photochemistry is still open to conjecture, although products consistent with the generation of this species in matrix photolyses have been reported.[8] Theoretical considerations suggest that the photochemical cyclobutanone to oxycarbene rearrangement occurs in a stepwise fashion via α-cleavage followed by recombination at oxygen.[22] On the basis of stereospecific ring expansions, however, Quinkert and co-workers have argued for concerted 1,2-shifts.[23] Similarly, the rearrangement process of oxycarbenes to ketones is poorly understood. Again, in principle, concerted and stepwise 1,2-shifts are possible. The observation of free-radical-derived products in ester tosylhydrazone salt pyrolyses, however, suggests that oxycarbenes thermally undergo C–O homolytic fragmentation.[6,7]

In contrast to the spectroscopic characterization of a large number of triplet carbenes,[1] only several singlet ground-state carbenes have been directly observed. ESR spectroscopy, which has been instrumental in understanding the structures of triplet carbenes, is powerless on singlets. We are aware of only one report of the observation of an oxycarbene. Quinkert and co-workers[24] observed UV spectra of thermally labile species generated on low-temperature photolyses of cyclobutanones. These species, which exhibited maxima at ca. 360 nm, were assigned the corresponding oxycarbene structures.

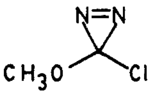
We have begun a program to investigate the spectra, structures, and photochemistry of matrix-isolated oxycarbenes. We have recently reported preliminary results on our initial entry into these systems, methoxychlorocarbene (**3**).[25] These experiments afforded the first IR spectrum of an alkoxycarbene and supported the suggestion of partial C–O double-bond character. We now wish to describe these experiments in detail and to report new results which strengthen our earlier conclusions.



3

Results and Discussion

Generation and Characterization of Methoxychlorocarbene (3). The starting material, 3-chloro-3-methoxydiazirine (**4**), was synthesized according to the procedure of Smith and Stevens.[14] Due to the reported explosive nature of **4**, the material was trapped as a solution in diethyl phthalate and reevaporated into our gas-handling manifold as needed. Similarly, d_3- (**5**) and ^{18}O-labeled (**6**) diazirines were generated from the corresponding isouronium salts.



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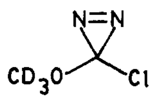

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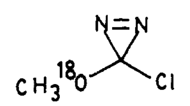

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Deposition of **4** in an argon or N_2 matrix at 23 K (ca. 500 to 1000:1 argon or N_2 to **4**) gave the IR spectrum shown in Figure 1a, and a UV spectrum showing characteristic structured diazirine $n\pi^*$ absorption at 330, 345, and 362 nm (Figure 2a).[26] Broadband irradiation ($\lambda > 340$ nm) of the sample cooled to 10 K

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(26) The observed IR spectra show slightly different band positions depending on whether nitrogen or argon matrices were used. Nitrogen gave better optical quality, although small amounts of carbene dimer were observed at higher matrix ratios (e.g., <700:1).

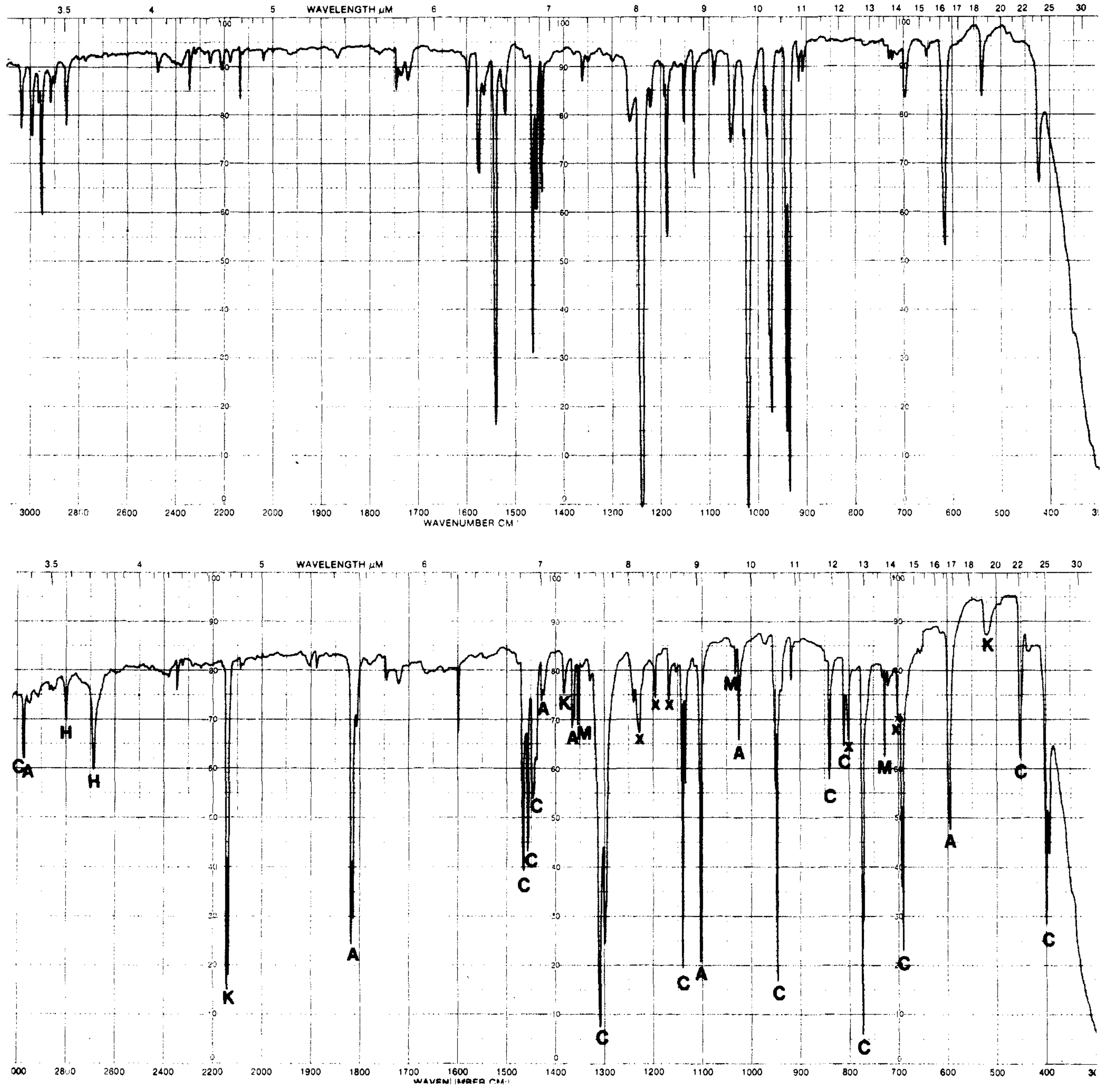

Figure 1. (a, top) IR spectrum of 3-chloro-3-methoxydiazirine (**4**) matrix-isolated in N_2 at 10 K (700:1 N_2 to **4**). (b, bottom) Same sample after 40 h at 370 nm. Bands labeled C are due to **3**, A = acetyl chloride, K = ketene, H = HCl, M = methyl chloride, X = dimer **8**.

resulted in a rapid decrease in starting material bands and concurrent appearance of new bands in the IR. The initial products are photolabile and reach a maximum at about 15 min of irradiation. These products gradually disappear on further irradiation to form acetyl chloride, ketene, and HCl, determined by comparison with independently prepared matrix-isolated samples. A more selective irradiation, with a monochromator and high-pressure mercury source (370 nm), gives a greater steady-state concentration of initial photoproducts (Figure 1b). In the UV spectrum taken at this stage, starting material absorption has disappeared, and a new broad absorption with a maximum at 318 nm has grown in (Figure 2b). Similar UV spectra are observed in 3-methylpentane, although the photoproduct exhibits a λ_{max} of 313 nm.

A common difficulty in comparing results of different spectroscopic measurements on matrix-isolated reactive intermediates is the possibility that the separate spectra arise from different species. This problem is particularly acute in comparisons of IR and UV spectra of intermediates. The greater sensitivity and broader range of extinction coefficients in UV can serve to highlight minor side products. Our approach to this problem was twofold. First, the time evolution of the UV and IR spectra were shown to be the same. In this case, the IR peaks of photoproduct shown in Figure 1b and the broad UV absorption in Figure 2b rise and fall together on irradiation. Second, a more stringent criterion for identity rests on a correlation of the UV spectrum with the wavelength dependence of photodestruction of the intermediate's IR bands. This test was also passed in these experiments. Irradiations were performed with a Xe arc lamp, which has approximately linear output over the 290–360-nm region,[27] through a monochromator. The rate of photochemical conversion of the species whose spectra are shown in Figure 1b reasonably matched the UV spectrum in Figure 2b over this wavelength region. These results provide convincing evidence that the IR and UV spectra describe the same species.

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[27] The linear output through the monochromator was confirmed with a power meter.

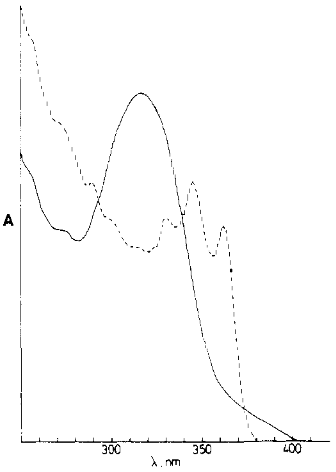
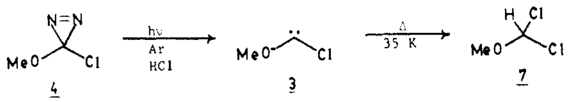


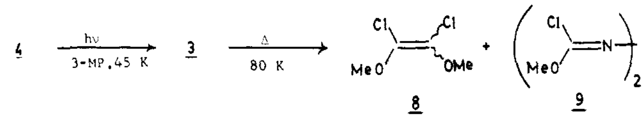
Figure 2. (a) (- - -) UV spectrum of diazirine **4** matrix-isolated in N_2 at 10 K (400:1 N_2 to **4**). (b) (—) Same sample after 9-h irradiation at 370 nm. Note that the absolute intensities in the two spectra are only approximately the same due to difficulties in centering the matrix in the spectrometer.

The method of generation and subsequent photochemistry suggest that the initial photoproduct is methoxychlorocarbene (**3**). This conclusion was supported by trapping experiments. Diazirine **4** was deposited in an argon matrix containing HCl (Ar/HCl = 1200:1; the diazirine was directly deposited through another inlet).



Irradiation gave mainly carbene **3** and a small amount of dichloromethyl methyl ether (**7**). The identity of **7** was ascertained by comparison with IR spectra of authentic material deposited in Ar/HCl matrices. Warming the matrix caused the bands of **3** to disappear with concomitant growth of the bands of **7**.

Carbene **3** could also be characterized by dimerization and by reaction with **4**. Irradiation (λ > 340 nm) of a 3-methylpentane matrix of **4** (3-MP/**4** = 40:1) gave a broadened IR spectrum of **3** (Figure 3a). Although the matrix absorptions obscured some of the carbene IR bands, several could be discerned, along with a few new absorptions. On warming the matrix, the carbene was stable until 80 K, at which temperature the carbene peaks slowly disappeared and peaks due to dimer **8** and azine **9** grew in. The identities of the diffusion products were determined by comparison with authentic samples isolated from larger scale low-temperature irradiations of **4**. These products have been reported previously,[13] although their stereochemistry has not been determined. Compound **8** clearly arises from bimolecular reaction of carbene **3**.



The azine **9** has been postulated to come from attack of carbene **3** on starting diazirine **4**.[13] When most of the starting diazirine was destroyed with monochromatic light (vide supra) before warming, only dimer **8** was observed (Figure 3b). We see no intermediates by IR in these conversions. It is interesting to note, however, that on warming a transient, red color formed in the glass which disappeared when the medium became fluid. The corresponding UV–vis spectrum exhibited a broad absorption centered at 510 nm. It is tempting to speculate that this color arises from an intermediate ylide formed from attack of **3** on **4** (or on acetyl chloride), although we have no direct evidence in support of this contention.

We carefully ascertained, to the limits of our IR sensitivity, the absence of chlorooxirane. Chlorooxirane was also found to be stable to our photolysis conditions. Comparison with the IR spectra of methyl chloride, independently isolated in appropriate matrices, showed that this product was not present in the argon photolyses but was formed to a minor extent in N_2. A small amount of α-chloroacetaldehyde, generated in the thermal gas-phase decomposition of **4**, was occasionally observed in the IR spectra of initially deposited material. This minor impurity neither increased nor decreased throughout the irradiations described. Finally, no evidence for an intermediate diazo compound in the irradiation of **4** was observed in the region 1900–2100 cm^{-1}. Although such a compound might be unstable to the irradiation conditions, careful photolyses with monochromatic light also showed no evidence for diazo intermediacy. Possible free-radical products CH_3,[28] ClCO,[29] and CH_3CO[30] have been characterized in inert matrices. We observe no evidence for significant amounts of these intermediates during our irradiations, although a small band grows and disappears in the region of 1900 cm^{-1} which may be due to ClCO.[29]

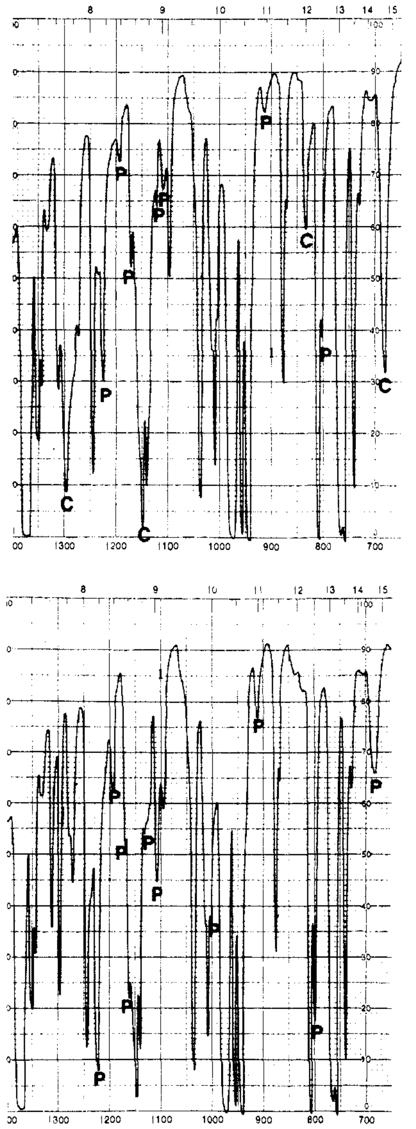


Figure 3. (a, top) IR spectrum of 3-methylpentane matrix of diazirine **4** (40:1 3-MP to **4**) at 45 K after 12-h irradiation at 370 nm. C = carbene **3**, P = dimer **8**. (b, bottom) IR spectrum of same sample after warming to 80 K for 3 h.

The presence of a strong ca. 1300-cm^{-1} band in the IR spectrum of **3** is at first sight puzzling. A reasonable model for this compound, chloromethyl methyl ether, has only CH_2-scissoring vi-

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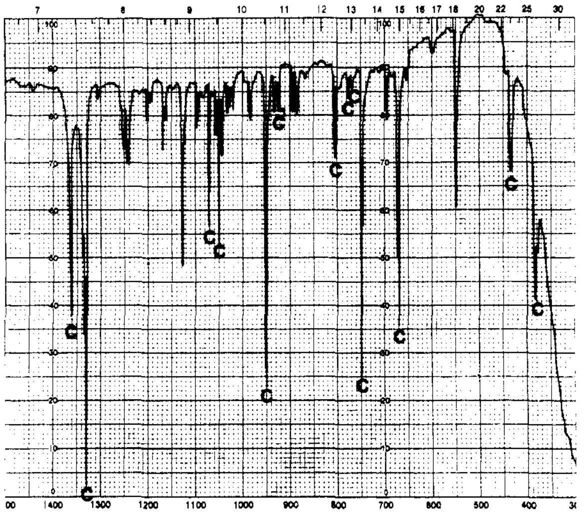


Figure 4. IR spectrum of diazirine-d_3 **5** matrix-isolated in N_2 at 10 K (1000:1 N_2 to **5**) after 10-h irradiation at 370 nm. C = carbene-d_3 **10**. Absorptions at 1128, 1028, 1033, 951, and 549 cm^{-1} are due to acetyl-d_3 chloride. Smaller absorptions are residual starting material and ketene-d_2.

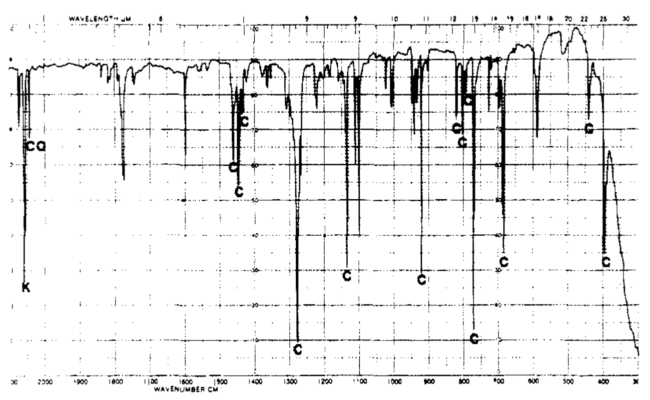


Figure 5. IR spectrum of [^{18}O]diazirine **6** matrix-isolated in N_2 at 10 K (1000:1 N_2 to **6**) after 8-h irradiating at 370 nm. C = [^{18}O]carbene **11**, K = [^{18}O]ketene, and CO = carbon [^{18}O]monoxide. Bands at 1775, 1421, 1361, 1100, 941, and 587 cm^{-1} are due to [^{18}O]acetyl chloride and those at 2115, 2110, 1378, and 576 cm^{-1} are due to [^{18}O]ketene.

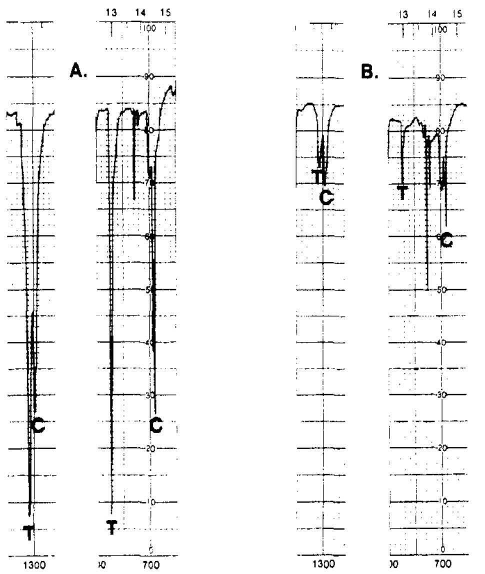
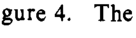


Figure 6. Partial IR spectrum of C–O and CCl stretching regions for carbene **3** matrix-isolated in N_2 at 10 K. T = *trans*-carbene **13** and C = *cis*-carbene **12**. The narrow peaks at 720 and 725 cm^{-1} are methyl chloride. (A) After 33-h irradiation at 370 nm. (B) After 5.5-h additional irradiation at 340 nm.

brations in this region.[31] Similarly, methyl chloroformate has no major absorptions at these frequencies but has an intense C–O–C antisymmetric stretch at ca. 1200 cm^{-1}.[32] To probe the nature of this unusual absorption, isotopic labeling experiments were performed. Irradiation of the diazirine-d_3 **5** matrix-isolated at 10 K gave the corresponding carbene **10**, whose IR spectrum is shown in Figure 4. The 1300-cm^{-1} band is found to shift to ca. 1325 cm^{-1}. These results indicate that this absorption is not due to an unusual C–H deformation, since deuterium substitution shifts CH_3-bending vibrations ca. 300 cm^{-1} to lower frequency.[31,32] The intensity of the absorption suggests that it might be assignable to a C–O stretch. This is supported by ^{18}O labeling. Irradiation of argon-matrix-isolated diazirine **6** gave the IR spectrum of the [^{18}O]carbene **11** shown in Figure 5.



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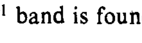
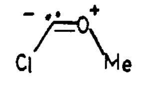


11

Only two absorptions show significant perturbations. The 1300-cm^{-1} absorptions shift down to ca. 1272 cm^{-1}, and the 950-cm^{-1} band shifts to 926 cm^{-1}. The magnitudes of these shifts identify these absorptions as C–O stretches. Although these bands undoubtedly correspond to antisymmetric and symmetric C–O–C combinations, the shifts agree well with Hooke's law calculations of 31- and 23-cm^{-1} decreases for substitution of ^{18}O in simple C–O stretches at these frequencies.[33]

The high 1300-cm^{-1} C–O vibration indicates considerable C–O double-bond character (vide infra). Two geometric isomers, **12** and **13**, are thus possible. Careful scrutiny of the IR spectra of the photolyses of **4** in N_2 and Ar matrices reveals evidence for two sets of carbene bands that show somewhat different behavior as a function of time and irradiation wavelength. As shown in Figure 6A, initial irradiation of the diazirine **4** at 370 nm creates a greater intensity of the absorptions at 1310 and 774 cm^{-1} than corresponding bands at 1300 and 690 cm^{-1}. Continued irradiation at 370 nm, or more rapidly at 340 nm, causes all the peaks to decrease in intensity, but those at 1310 and 774 cm^{-1} are destroyed more rapidly than their counterparts. Eventually, inversion of the intensities of the absorptions is observed (Figure 6B). Alternatively, irradiation of the carbene mixture at 290 nm causes more rapid destruction of the bands at 1300 and 690 cm^{-1}.[34]



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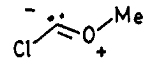
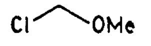


13

Vibrational Analysis and Structure of Methoxychlorocarbene (3). Logical models for the vibrational spectra of methoxychlorocarbene (**3**) are chloromethyl methyl ether (**14**) and methyl chloroformate (**15**). The vibrational spectra of both compounds have been analyzed in detail.[31,32] The vibrations of ether **14** most pertinent for comparison are 1120, 925, and 650 cm^{-1} for the COC antisymmetric, COC symmetric, and CCl stretches, respectively.[31]



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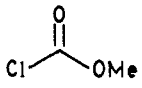

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Similarly of note are the corresponding vibrations at 1203, 947,

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(31) (a) Jones, R. G.; Orville-Thomas, W. J. *J. Chem. Soc.* **1964**, 692. (b) Imaishi, H. *J. Sci. Hiroshima Univ., Ser. A* **1975**, *39*, 337.

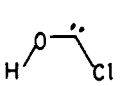
(32) (a) Katon, J. E.; Griffin, M. G. *J. Chem. Phys.* **1973**, *59*, 5868. (b) Durig, J. R.; Griffin, M. G. *J. Mol. Spectrosc.* **1977**, *64*, 252.

(33) Pinchas, S.; Laulicht, I. "Infrared Spectra of Labelled Compounds"; Academic Press: New York, 1971.

(34) The cis–trans assignments for the other bands of **3** are less clear-cut due to overlaps and smaller intensities. We see no evidence for photochemical cis–trans isomerization.

and 821 cm^{-1} in ester **15**.[32] The ester is perhaps a better model because of the similarity of the electron-deficient carbonyl center to the singlet carbenic carbon. Moreover, ether **14** is known to have a gauche geometry.[31] The ester **15** is thought to exist in planar form with the methyl syn to the carbonyl[32] and thus might present a better model at least for the *trans*-carbene **13**.

Structural conclusions based on C–O vibrational frequencies of esters and ethers are somewhat tenuous. Strong coupling to other vibrations clouds the relation of C–O stretching frequencies to electronics and geometry.[35] Nevertheless, it must be noted that the COC antisymmetric stretch of **3** is significantly higher than that found in the similar molecules **14** and **15** or in other ethers and esters.[35] Schaefer and co-workers[19] have calculated, with ab initio methods, the expected IR frequencies for *cis*- and *trans*-hydroxymethylene. The C–O stretches are predicted to occur at 1269 and 1271 cm^{-1} (corrected),[36] respectively. The anomalously high frequencies correspond to shorter than usual C–O bond lengths attributed to partial C–O double-bond character. Ab initio calculations performed by Clark (6-31 G)[21] on hydroxychlorocarbene indicate that significant double-bond character should similarly be revealed in the C–O stretching frequencies of **16** and **17**.



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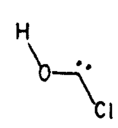
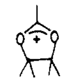


17

It is interesting to contrast carbene **3** with CCl_2, which has been well-characterized by IR in inert gas matrices. Andrews[38] has suggested that CCl_2 shows no C–Cl double-bond character. This conclusion was based on the similarity of the C–Cl stretching force constants of the carbene and those of CCl_4. A logical model for the C–O stretch in an oxycarbene is a carbonyl oxonium salt.[39,40] Unfortunately, the IR spectra of such species have not been investigated in detail. The oxonium species **18**[41] and **19**,[42] however, both have IR absorptions in the 1500-cm^{-1} region which have been tentatively ascribed to partial C–O double bonds.[43]



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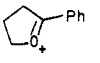

19

The time evolution and wavelength dependencies of the bands attributed to **3** suggest two different geometric isomers with dissimilar IR absorptions. Two strong absorptions corresponding to the two isomers of **3** are observed in the 650–800-cm^{-1} region. Comparison with the IR spectra of **14** and **15** suggests that these bands are due to C–Cl stretches. In ester **15**, the C–Cl absorption shifts 59 cm^{-1} to lower frequency on perdeuteration.[32] This result indicates significant coupling between the CH deformations and the C–Cl stretch. A similar shift is seen in the two carbene isomers. Deuteration gives C–Cl stretches shifting from 780 to 755 and from 700 to 680 cm^{-1} for the two isomers of **3**. A small difference in C–O stretches at 1310 and 1300 cm^{-1} (Figure 6) for the *trans*- and *cis*-carbenes is also seen, consistent with calculations on the isomers of hydroxymethylene.[19] One possible explanation for the large difference in C–Cl frequencies is anomeric oxygen lone-pair donation into the C–Cl σ^* orbital in the cis compound, lowering the C–Cl stretching frequency. Such effects are well-established in less exotic molecules.[44] This reasoning would suggest that the higher C–Cl frequency corresponds to the trans isomer, **13**. Ab initio calculations by Clark[21] on **16** and **17** also support this contention.

Ultraviolet Spectrum of 3. To our knowledge, only one previous report of an oxycarbene UV spectrum exists. Quinkert and co-workers[24] found that irradiation of several cyclobutanones in glasses at 77 K gave thermally labile intermediates that exhibited maxima in the region of 360 nm. The absorptions were suggested to arise from oxycarbenes such as **20**. Moreover, the wavelength of absorption was likened to $n\pi^*$ transitions in the isoelectronic cis azo compounds. The absorption spectra of only a handful of singlet carbenes have been reported. Singlet methylene itself shows a complicated visible spectrum with a $^1A_1$–$^1B_1$ transition spread between 550 and 950 nm.[45] Halogen substitution moves these absorptions to increasingly higher energies. For example, HCF absorbs in the region 430–600 nm,[46] and HCCl absorbs from 550 to 820 nm.[47] Similarly, CCl_2 (480–560 nm),[48] CF_2 (220–270 nm),[49] and CFCl (360–390 nm)[50] have been observed by UV. Schaefer and Goddard predict a vertical transition for S_0 to S_1 *trans*-hydroxymethylene at 392 nm.[19,51]

20

Interestingly, carbene **3** lies between CF_2 and CFCl in its energy of absorption. This may reflect the intermediate donor characteristics of O vs. F and Cl. Increased overlap between the heteroatom lone pair and the empty carbenic p orbital is expected to raise the energy of the π^* orbital in this system and thus increase the $n\pi^*$ energy.[18] The broad UV absorption of **3** does not permit us to resolve components of cis and trans isomers. The wavelength dependence of disappearance of the IR spectra of the two geometric isomers, however, suggests that the trans isomer **13** absorbs at longer wavelengths than the cis isomer **12**. Specifically, irradiation with monochromatic light at 370 nm causes more rapid decrease of the trans than the cis isomer, seen by comparison of the 774- and 690-cm^{-1} IR absorptions. Conversely, irradiation at 290 nm destroys the *cis*-carbene more rapidly than the trans. A very approximate extinction coefficient for the carbene mixture can be determined. Comparison of the intensity of the starting diazirine $n\pi^*$ absorption (ϵ = 50 mol L^{-1} cm^{-1}) with the final carbene UV intensity, and assuming ca. 75% conversion to carbenes, gives an estimated ϵ = 65 mol L^{-1} cm^{-1} for the carbene. This estimation is crude, but it may be of interest to those investigators wishing to seek these species in solution.

Photochemistry of 3. On irradiation, **3** gives three products in argon matrices: acetyl chloride, ketene, and HCl. In nitrogen, a trace of methyl chloride and CO is also observed. The broad, low-energy HCl IR absorption indicates that the HCl is hydrogen-bonded to the ketene formed. Similar effects have been observed in inert matrices containing HCl and H-bond acceptors.[52] The ketene absorption is split into two peaks in both argon and nitrogen. Although carbon monoxide also overlaps these fre-

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

(36) These numbers have been lowered 15% from the ab initio calculations to correct for the usual overestimation these methods produce for vibrational frequencies.[37]

(37) Hess, B. A., Jr.; Schaad, L. J.; Polavarapu, P. L. *J. Am. Chem. Soc.* **1984**, *106*, 4348.

(38) Andrews, L. *J. Chem. Phys.* **1968**, *48*, 972, 979.

(39) Pittman, C. U., Jr.; McManus, S. P.; Larsen, J. W. *Chem. Rev.* **1972**, *72*, 357.

(40) Keating, J. T.; Skell, P. S. In "Carbonium Ions", Olah, G. A., Schleyer, R. v. R., Ed.; Wiley-Interscience: New York, 1973; Vol. II, p 573.

(41) King, J. F.; Allbutt, A. D. *Can. J. Chem.* **1969**, *47*, 1445.

(42) Ward, H. R.; Sherman, P. D., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 3612.

(43) Unfortunately, the presence of two geometric isomers renders a more informative normal coordinate analysis extremely difficult. We are currently attempting to model the carbene IR spectra with MNDO calculations.

(44) McKean, D. C. *Chem. Soc. Rev.* **1978**, *7*, 399 and references therein.

(45) Herzberg, G.; Johns, J. W. C. *Proc. R. Soc. London, Ser. A.* **1966**, *265*, 107.

(46) Merer, A. J.; Travis, D. N. *Can. J. Phys.* **1966**, *44*, 525.

(47) Merer, A. J.; Travis, D. N. *Can. J. Phys.* **1966**, *44*, 1541.

(48) Jacox, M. E.; Milligan, D. E. *Chem. Phys.* **1976**, *16*, 195.

(49) Smith, C. E.; Jacox, M. E.; Milligan, D. E. *J. Mol. Spectrosc.* **1976**, *60*, 381.

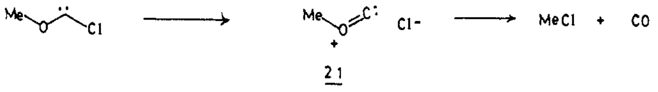
(50) Tiel, J. J.; Wampler, F. B.; Rice, W. W. *Chem. Phys. Lett.* **1979**, *65*, 425.

(51) A handful of aryl halo carbenes thought to be ground-state singlets have also been observed by UV: Cox, D. P.; Gould, I. R.; Hacker, N. D.; Moss, R. A.; Turro, N. J. *Tetrahedron Lett.* **1983**, *24*, 5313.

(52) Barnes, A. J.; Halam, H. E.; Scrimshaw, G. F. *Trans. Faraday Soc.* **1969**, *65*, 3159, 3172.

quencies, the [^{18}O]carbene spectra clearly indicate no more than a trace of CO in argon and only a small amount in N_2. The ^{18}O shifts for ketene and CO are substantially different, such that [^{18}O]ketene absorbs at 2115 and 2110 cm^{-1} [53] and C^{18}O absorbs at 2080 cm^{-1}.[54] These molecules are thus discernible in the labeled spectra. The reason for the splitting of the ketene band is not known but might arise from two different arrangements of ketene, HCl, and N_2 in the matrix sites. The nascent N_2 appears to play some role in this splitting; the ketene formed on direct irradiation of acetyl chloride (vide infra) is not split.

These results contrast the room-temperature solution or gas-phase decomposition of **4**, where the major products are CO and methyl chloride.[13] The thermal products have been attributed to cleavage to the isoacylium cation **21**, followed by Cl$^-$ attack on methyl. The absence of characteristic free-radical products under varied conditions led Stevens and Smith to conclude that homolytic cleavage was not occurring.[13] An ionization process to give a species such as **21** in the gas phase seems impossibly high in energy, however, and the corresponding homolytic cleavage may be more likely. Of particular note is that no rearrangement to acetyl chloride or insertion to chlorooxirane has been observed in thermal reactions of **4**.[13]

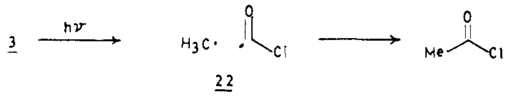


The mechanistic pathways interconverting oxycarbenes and carbonyl compounds are in general poorly understood. Consideration of hydroxymethylene as an intermediate in formaldehyde chemistry has led to a number of quantum mechanical calculations that address these questions.[19,20,55] A concerted in-plane migration of hydrogen in S_0 *trans*-hydroxymethylene to S_0 formaldehyde has a barrier predicted by the most recent high-level ab initio calculations to be 31 kcal/mol.[19] Probably owing to greater difficulty in calculations with open-shell systems, less computational work has been performed on the rearrangements of S_1 and T_1 hydroxymethylene. Large basis set calculations with CI inclusion predict a considerable barrier of 30 kcal/mol for the S_1 hydroxymethylene to S_1 formaldehyde rearrangement.[55a] Less-sophisticated calculations predict a barrier of 45 kcal/mol for the corresponding triplet carbene to triplet formaldehyde conversion.[55b]

The photochemical rearrangements of cyclobutanones to oxycarbenes have provided experimental opportunities to probe questions of concerted vs. stepwise rearrangements. The generation of biradical products concurrent with oxycarbenes in cyclobutanone photochemistry suggests the possible intermediacy of a common biradical. Quinkert and co-workers showed, however, that irradiation of appropriately α-substituted cyclobutanones gives retention of stereochemistry in the oxycarbene products.[23] This was was taken as evidence in support of concerted C-to-O rearrangement, bypassing possible biradical intermediates. It has been noted,[22] however, that bond formation more rapid than bond rotation would still leave open the possibility of an intermediate biradical.

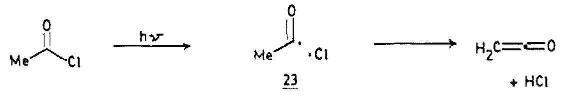
The mechanisms of oxycarbene-to-carbonyl conversions have been less studied. Generation of acyclic alkoxy and dialkoxy carbenes via ester tosylhydrazone salt pyrolyses leads predominantly to alkyl radical products and CO.[6] Similar thermolyses of lactone tosylhydrazone salts have been shown, in convincing work of Agosta and co-workers,[7] to produce carbonyl products together with biradical-derived compounds. The simplest hypothesis to encompass these results is that C–O cleavage occurs in the oxycarbenes to give biradicals or radical pairs. The photochemical rearrangement of oxycarbenes to carbonyls has not been previously experimentally addressed, however.

Several mechanisms can be proposed to explain the matrix photochemistry of carbene **3**, although none are completely satisfactory. In particular, the formation of HCl and ketene must be accounted for. Similar to the proposed thermal chemistry of alkoxycarbenes is the possibility that α-cleavage to give radical pair **22** occurs, followed by recombination within the matrix cage, to give acetyl chloride (eq 1).



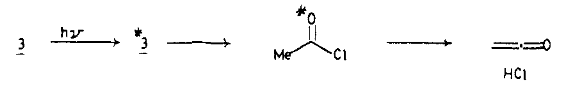
(1)

Although appealing in simplicity, eq 1 does not account for elimination of HCl. As can be seen, however, the product acetyl chloride has the correct CCO connectivity to generate ketene. Acetyl chloride does not absorb light at these wavelengths. Shorter wavelengths (>270 nm), on the other hand, do convert matrix-isolated acetyl chloride to ketene and HCl. This novel reaction has been observed previously in an argon matrix.[56] A reasonable mechanism involves C–Cl cleavage to radical pair **23**, followed by disproportionation to products (eq 2). Radical disproportionations under these conditions are well-known.[57]



(2)

One possibility to explain the formation of ketene from **3** is thus adiabatic rearrangement of S_1 carbene to S_1 acetyl chloride, followed by the characteristic excited acetyl chloride reactions (eq 3). One requirement for this possibility is that rearrangement



(3)

of excited carbene to excited acid chloride must be exothermic. A reasonable estimate for the thermodynamics of this rearrangement can be made on the basis of ab initio calculations of Rondan et al.,[18] who have predicted the energetics of the isodesmic reaction shown in eq 4 ($\Delta H_{\text{rxn}}^{\text{calcd}} = -60.3$ kcal/mol).

$$:CH_2 + CH_3Cl + (CH_3)_2O \rightarrow 2CH_4 + CH_3O\ddot{C}Cl \quad (4)$$

Use of the known ΔH_f of $^1CH_2$,[60] and those of the other molecules in eq 4,[58,59] gives an estimated $\Delta H_f = 15$ kcal/mol for **3**. Since this value is critical to our further arguments, this method was checked on three known halogenated carbenes. Similar use of the appropriate isodesmic reactions calculated in ref 18 predict ΔH_f of 74, –42, and 18 kcal/mol for CCl_2, CF_2, and CFCl, respectively. The reported ΔH_f values for these carbenes are 39, –49, and –2 kcal/mol.[59] It is thus likely that the use of eq 4 underestimates the stability of **3** by ca. 15–35 kcal/mol. Nevertheless, use of the heat of formation[61] of acetyl chloride (–60.1 kcal/mol), the minimum energy of light necessary to rearrange acetyl chloride (280 nm, 102 kcal/mol), and the minimum energy of light which causes photolysis of carbene **3** (380 nm, 75 kcal/mol) indicates that rearrangement of S_1 carbene to S_1 acetyl chloride is 13–33 kcal/mol exothermic.

The preceding analysis indicates that adiabatic transformation of excited carbene **3** to excited acetyl chloride is thermodynamically feasible. Ab initio calculations,[55a] however, predict that similar rearrangement of excited hydroxymethylene to excited formaldehyde would have a barrier of ca. 30 kcal/mol. A barrier to this rearrangement is perhaps not unexpected since the reaction mimics 1,2-shifts in radicals, which are unfavorable on orbital symmetry grounds.[62]

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[53] Although the IR of ^{18}O-labeled ketene has not been reported, the ketene doublet is readily assignable by its intensity in the labeled spectra.

[54] Maki, A. G. *J. Chem. Phys.* **1961**, *35*, 931.

[55] (a) Kemper, M. J. H.; van Dijk, J. M. F.; Bulk, H. M. *J. Am. Chem. Soc.* **1978**, *100*, 7841. (b) Altmann, J. A.; Csizmandia, I. G.; Yates, K.; Yates, P. *J. Chem. Phys.* **1977**, *66*, 298.

[56] Shirk, J. S. Ph.D. Thesis, University of California—Berkeley, 1967.

[57] Pacansky, J.; Dupuis, M. *J. Am. Chem. Soc.* **1982**, *104*, 415.

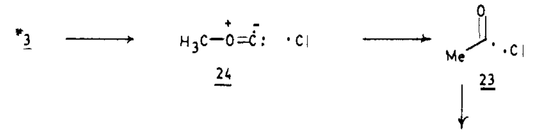
[58] Cox, J. C.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970.

[59] Lias, S. G.; Karpas, Z.; Liebman, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 6089. We thank Prof. Liebman for a preprint of this work.

[60] Lengel, R. K.; Zare, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 7495.

[61] Shaw, R. "The Chemistry of Acid Derivatives"; Wiley: New York, 1979; Part 1; Supplement B, p 65.

An alternate mechanism for rearrangement and ketene formation is shown in eq 5. Interestingly, similar C–Cl heterolytic cleavages have been proposed in the thermal reactions of chloroalkoxycarbenes (vide supra).[13,63] The energy of intermediate



(5)

24 is difficult to estimate. Lias, Karpas, and Liebman[59] have predicted a C–Cl bond strength of 89 ± 7 kcal/mol for FCCl. If the C–Cl bond is comparable in **3**, intermediate **24** would be energetically unreachable in 380-nm (75 kcal/mol) irradiation of **3**. Moreover, it is not clear whether or not **24** would be able to rearrange to **23** under the reaction conditions.

It is interesting to note that small amounts of methyl chloride and CO are observed in the photolysis of **3** in nitrogen matrices but not in argon. Irradiation of acetyl chloride in either matrix does not give this product. Observation of this product may indicate that cleavage of, e.g., **24** to methyl and CO occurs to some extent and that recombination in the nitrogen cage is for some reason less favorable than in the argon surroundings. Alternatively, methyl chloride may arise from some cleavage to radical pair **22**. More certain conclusions cannot be made on the basis of this limited data, and these possibilities are under investigation.

Summary. We have presented the first detailed spectroscopic characterization of an alkoxycarbene, methoxychlorocarbene (**3**). The IR and UV spectra of **3** indicate significant interaction between the carbene carbon and the adjacent oxygen lone pair, as predicted by theory. Interestingly, close scrutiny of the IR spectra indicate two distinct geometric isomers for the carbene. The photochemistry of carbene **3** is yet not completely understood. Although the rearrangement to acetyl chloride is not immediately surprising, the formations of ketene and HCl are emigmatic. Neither mechanism proposed, adiabatic rearrangement or initial C–Cl cleavage, is entirely satisfactory. We hope that further enlightenment will come from similar experiments on other substituted alkoxyhalocarbenes currently in progress.

Experimental Section

General. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a Bruker WP-200 SY instrument and were measured in parts per million (ppm) from TMS unless otherwise noted. Preparative VPC was performed on a GOW MAC Series 550 thermal conductivity instrument using helium as the carrier gas. Anhydrous *p*-toluenesulfonic acid was prepared from the monohydrate by drying under vacuum at 35 °C for 10 h in the presence of phosphorous pentoxide. The sodium hypochlorite used was commercially available bleach, 5.25% by weight available hypochlorite. Methanol-^{18}O was made by the procedure of Sawyer[64] starting from 98% ^{18}O-labeled water (Cambridge Isotope Laboratories).

Matrix Isolation Experiments. Matrices were prepared on a 2.4-cm CsI window affixed to the cold tip of an Air Products CS-202 Displex closed-cycle helium cryostat. Temperatures were measured by using a 0.07% iron doped gold-chromel thermocouple imbedded in the cold tip and controlled by an Air Products digital temperature indicator/controller. Infrared spectra were recorded on a Beckman Series 4250 spectrophotometer, and UV spectra were recorded on a Perkin-Elmer Hitachi 200 spectrometer. Argon and nitrogen gases were purchased from Matheson at a minimum purity of 99.999%. 3-Methylpentane, purchased from Aldrich, was washed with concentrated sulfuric acid, followed by sodium hydroxide and water, and then dried. The solvent was then distilled on a spinning-band column prior to use. Broad-band irradiations were accomplished with a Varian EIMAC 300 W high-pressure Xe arc illuminator with quartz optics, a water filter, and the appropriate Corning cutoff filter. The action spectrum of the carbene was generated with the light from this combination passed through a Corning 7-54 band-pass filter (to remove most visible light) and then through a Bausch & Lomb dual-slit monochromator at 3-nm bandwidth.[27] Other monochromatic irradiations reported in the text were performed with this monochromator in combination with a high-pressure 200-W Hg arc source (Bausch & Lomb SP 200). System vacuum was measured with a Kontes-Martin cold cathode gauge while sample pressures were measured with a MKS Instruments Inc. Baratron. A standard vapor-mixing technique was used for the depositions in which a measured amount of material was evaporated into a 3.5-L gas manifold, followed by a measured amount of the matrix medium. Typical medium-to-sample ratios ranged from 500 to 1000:1 using argon or nitrogen as the medium or 40:1 using 3-methylpentane as the medium. Routinely 100–150 torr of the inert gas mixture were deposited. Deposition rates, measured by a decrease in pressure in the gas manifold, ranged from 0.5 to 1.0 torr/min with argon and nitrogen and from 0.5 to 1.0 torr/h with 3-methylpentane. Argon deposition temperatures ranged from 23 to 26 K, nitrogen was deposited at 26 K, and 3-methylpentane was deposited at 65 K. Following deposition, the matrix was cooled to the lowest temperature attainable with the refrigerator (10–11 K) where irradiation and spectral measurements were performed. IR spectra were taken numerous times at varying concentrations of the starting diazirine and at varying extents of conversion.

Syntheses. 3-Chloro-3-methoxydiazirine (4). The diazirine was synthesized by the procedure of Smith and Stevens.[13] From a 1:700 mixture of **4** in nitrogen, a total of 150 torr was deposited over 2.5 h: IR (nitrogen matrix) 3035 w, 2990 w, 2970 w, 2950 m, 2900 vw, 1575 m, 1564 w, 1542 s, 1520 w, 1464 m, 1457 m, 1445 m, 1239 vs, 1187 m, 1055 w, 1020 vs, 972 s, 941 s, 935 vs, 907 vw, 616 m, 540 w, and 423 w cm^{-1}.

***O*-Methylisouronium *p*-Toluenesulfonate-d_3.**[13] Cyanamide (0.5 g, 12 mmol) was dissolved in 5.5 mL of methanol-d_4 in a 25-mL round-bottom flask. The solution was cooled in ice and stirred while 2.05 g (12 mmol) of anhydrous *p*-toluenesulfonic acid was carefully added. After the addition was complete, a reflux condenser was added and the system was kept under a nitrogen atmosphere at 51 °C for 48 h. The solvent was removed in vacuo until a paste formed, and subsequent trituration with 10 mL of anhydrous diethyl ether and filtration gave 2.30 g (77%) of a white solid: mp 132–34 °C; ^{1}H NMR (Me_2SO-d_6) δ 2.28 (s, 3 H), 7.12 (d, 2 H, J = 8 Hz), 7.48 (d, 2 H, J = 8 Hz), and 8.46 (br s, 3 H).

3-Chloro-3-methoxydiazirine-d_3 (5). The d_3 isouronium salt was converted into the diazirine-d_3 by the same procedure as for the parent diazirine above. A total of 150 torr of a 1:1000 mixture of **5** in nitrogen was deposited over 3.5 h: IR (nitrogen matrix) 2274 w, 2245 w, 2240 w, 2210 w, 2135 w, 2075 w, 1549 m, 1535 m, 1252 vs, 1245 vs, 1224 vw, 1097 s, 1064 m, 1055 w, 1042 vs, 1020 w, 1000 w, 983 m, 932 s, 894 m, 855 s, 696 w, 600 m, and 415 w cm^{-1}.

***O*-Methylisouronium *p*-Toluenesulfonate-^{18}O.** Cyanamide (0.26 g, 6.2 mmol) was dissolved in methanol-^{18}O (1.0 g, 31 mmol) in a 10-mL round-bottom flask. While cooling in ice and stirring, anhydrous *p*-toluenesulfonic acid (1.07 g, 6.2 mmol) was added. A reflux condenser was added, and the system was kept under nitrogen at 51 °C for 48 h. Removal of the solvent in vacuo, trituration with 10 mL of anhydrous diethyl ether, and filtration gave 1.22 g (79%) of the [^{18}O]isouronium salt: mp 134 °C; ^{1}H NMR (Me_2SO-d_6) δ 2.29 (s, 3 H), 3.92 (s, 3 H), 7.13 (d, 2 H, J = 8 Hz), 7.49 (d, 2 H, J = 8 Hz), and 8.49 (br s, 3 H).

3-Chloro-3-methoxydiazirine-^{18}O (6). The ^{18}O-labeled diazirine was synthesized from the labeled isouronium salt by the same procedure as for the parent compound above. A total of 152 torr of a 1:1000 mixture of **6** in nitrogen was deposited over 3.5 h: IR (nitrogen matrix) 3040 w, 3000 w, 2995 w, 2960 w, 2920 vw, 2905 w, 2805 w, 1562 m, 1536 m, 1465 m, 1457 w, 1445 w, 1243 m, 1222 vs, 1204 vw, 1187 w, 1150 vw, 1038 m, 1024 w, 1007 s, 967 m, 940 m, 933 s, 915 vw, 904 w, 607 m, 538 w, and 412 w cm^{-1}.

Chlorooxirane.[65] Ethylene oxide (6.6 g, 150 mmol) was condensed into a 50-mL round-bottom flask cooled to −5 °C. To the flask was added 1.4 g (13 mmol) of *tert*-butylhypochlorite. While keeping the solution cooled to 0 °C, it was irradiated with a 175-W incandescent bulb until the yellow color had dissipated (2 h). After allowing the excess ethylene oxide to boil off, the crude product was subjected to preparative VPC: 10 ft × $^{1}/_{4}$ in. 15% OV-101 on Chrom W AW DMCS 60/80, retention time (RT) = 11 min at 25 °C; ^{1}H NMR ($CDCl_3$ δ 2.80 (dd, 1 H, J = 1.4, 2.7 Hz), 1.88 (dd, 1 H, J = 2.7, 4.7 Hz), and 4.95 (dd, 1 H, J = 1.4, 4.7 Hz); IR (argon matrix from 2000 to 400 cm^{-1}) 1320 s, 1300 m, 1261 m, 1000 m, 905 vs, 794 vs, 736 m, 732 w, 649 s, and 645 m cm^{-1}.

3-Chloro-3-methoxydiazirine in 3-Methylpentane at 77 K. 3-Chloro-3-methoxydiazirine (92 mg, 0.87 mmol) was mixed with 3.32 g (38.5 mmol) of 3-methylpentane in a Pyrex irradiation vessel and degassed with

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three freeze–pump–thaw cycles. Irradiation at 77 K with the Xe arc lamp and Corning O-52 cutoff filter ($\lambda > 340$ nm) for 10 h, followed by thawing of the glass, converted the diazirine completely into products. The product mixture was subjected to preparative VPC: 4 ft × $^{1}/_{4}$ in., 10% Ov-101 on Chrom P 60/80, RT = 3.5 and 12 min, respectively, for 1,2-dichloro-1,2-dimethoxyethane (**8**) and 1,4-dichloro-1,4-dimethoxy-2,3-diazabuta-1,3-diene (**9**) at 85 °C; ^{1}H NMR spectra identical with those reported in ref 14; IR **8** (NaCl, neat) 3015, 2975, 2945, 2890, 2835, 1655, 1450, 1222, 1193, 1157, 1108, 995, 932, 842, and 796 cm^{-1}; IR **9** (CS_2) 3010, 2990, 2960, 2940, 2820, 1625, 1440, 1255, 1212, 1168, 1090, 1010, and 799 cm^{-1}.

Methoxychlorocarbene (3): IR (N_2 matrix, after photolysis of **4** for 33 h with $\lambda = 370$ nm) 2975 w, 1475 m, 1465 m, 1445 m, 1439 m, 1309 vs, 1299 m, 1140 s, 947 s, 840 m, 810 w, 773 vs, 690 m, 451 m, 400 m, and 394 m cm^{-1}.

Methoxychlorocarbene-d_3 (10): IR (N_2 matrix, after photolysis of **5** for 2 h with $\lambda = 370$ nm) 2180 w, 1362 m, 1329 vs, 1305 vw, 1071 m, 1050 m, 950 s, 925 w, 805 m, 794 vw, 777 w, 769 w, 749 s, 669 m, 434 m, 383 m, and 377 w cm^{-1}.

[^{18}O]Methoxychlorocarbene (11): IR (N_2 matrix, after photolysis of **6** for 6 h with $\lambda = 370$ nm) 2975 w, 1462 m, 1446 m, 1435 w, 1277 s, 1267 m, 1135 m, 920 m, 820 m, 803 m, 793 w, 770 s, 683 m, 441 m, 394 m, and 389 w cm^{-1}.

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Structure and Exchange Behavior of Cryptand 111 and Its Inside Protonated Products

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Abstract: The structure of the cryptand 111 (**1**) and its inside protonated species $[111\text{-H}]^+$ **2** and $[\text{H-}111\text{-H}]^{2+}$ **3** have been studied by infrared spectroscopy. X-ray crystal structures of all three compounds are also presented and discussed in correlation with the IR data. The structure of **1** is complicated by the existence of disorder not encountered in **2** and **3**. The encapsulated protons in **2** and **3** are covalently bonded to the nitrogens, whereby the NH in **2** is weaker than in **3**, as evidenced by their distances (91.6 and 84.4 pm in **2** and **3**, respectively). The exchange behavior of **2** and **3** has been investigated with the help of exchange reactions of the tritiated analogues $[111\text{-T}]^+$ and $[\text{T-}111\text{-T}]^{2+}$. The results are discussed with respect to the IR data and the crystal structures. It is concluded that **3** is much more stable than **2**. **3** resists in different aqueous solutions an exchange of the encapsulated protons and therefore is suitable for the fixation of tritium.

1. Introduction

Macrocyclic diamines including cryptands are known to yield, on treatment with acid, inside as well as outside protonation products. This property can be attributed to the inherent ability of the ligands to exist in any one of the three possible exo–endo conformations first discussed by Simons and Park.[1]

In the large flexible compounds, e.g., cryptand 222, the rate of interconversion of the conformers into one another is quite fast, and the endo–endo (in,in) configuration is assumed to be predominant[2] although other conformations may also occur depending on the substitution in the bridge, as evidenced by the pyridine-substituted cryptand 222 with flattened nitrogens.[3] The mechanism of protonation in the flexible ligands is of the direct proton-transfer type and may involve diffusion of the attacking proton into the molecular cavity and/or conformational change from "in" to "out" followed by protonation.[2]

Small- and medium-ring bicyclic diamines on the other hand may be geometrically strained and less flexible. This imposes restrictions on the interconversion either completely or partially. The first case leads to a situation in which the nitrogens are exo–exo, e.g., in 1,4-diazabicyclo[2.2.2]octane (DABCO).[4] The second case provides a mixture of exo–exo, exo–endo, and endo–endo. The protonation reactions are therefore complicated, and in some cases, they do not follow the classical mechanism. A comprehensive evaluation of experimental data in this respect warrants knowledge of the structures of these ligands, and this is scarce.

Alder and Session, having synthesized a large number of medium-ring bicyclic amines, could obtain the crystal structures of only the 1,6-diazabicyclo[4.4.4]tetradecane and its monoprotonated ion.[5-7] Lehn and Dye prepared the cryptand 111 and studied its structure as well as the kinetics and thermodynamics of protonation by means of high-resolution NMR.[8-10]

Figure 1 shows the structural formula of the cryptand 111 and its inside protonation forms. The ligand exists predominantly in the in–in conformation with an interconversion energy of 40.96 kJ/mol. Protonation is slow and yields outside as well as inside protonated ions. Especially the inside protonation species **2** and **3** resist neutralization under severe conditions.

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