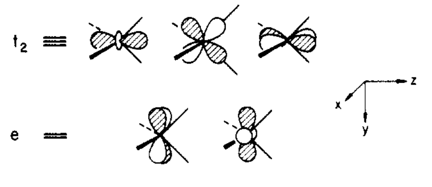
Table II. Extended Hückel Parameters

orbital		H_{ii}, eV	exponents[a]	
			ζ_1	ζ_2
H	1s	−13.4	1.3	
C	2s	−21.4	1.62k	
	2p	−11.4	1.625	
O	2s	−32.3	2.275	
	2p	−14.8	2.275	
Co	4s	−9.21	2.0	
	4p	−5.29	2.0	
	3d	−13.18	5.55 (0.5679)	2.10 (0.6059)

[a] Two Slater exponents are listed for 3d functions. Each is followed in parentheses by the coefficients in the double-ζ expansion.

Can we rationalize this band structure in terms of the familiar two below three splitting of tetrahedral molecular complexes reproduced in **32**? Since there are two metal atoms per unit cell,



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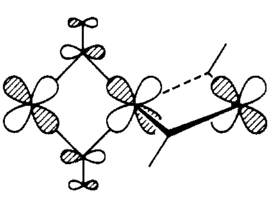
we should find two bands of each type in Figure 5. The e set clearly transforms into the clustered bands 21, 24, 25, and 26. They lie below the Fermi energy for d^8 and are quite narrow as the interaction is of δ type. Because the intermetallic distance is large, we expect to locate the six t_2 set bands directly above these four, but only the z^2 bands 27 and 28 appear where predicted. The intracell antibonding xz and yz combinations form the degenerate bands 22 and 23. They are pushed down by a σ-bonding interaction with the carbonyl π^*, as shown in **33**, for example, at the zone center for yz. The intracell bonding counterparts become the degenerate pair 30 and 31. Their interaction with the carbonyl π^* is π bonding, but the effect is over shadowed by their σ antibonding character with the carbonyl lone pairs, as sketched in **34** for yz at the zone center. The bands are pushed high up in energy and undergo an avoided crossing with the degenerate set 33 and 34 which carry the d character at the zone edge. The net result is a four below one splitting which although



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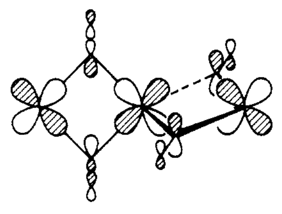

34

unusual for tetrahedral coordination is certainly comfortable for the d^8 system.

It seems reasonable that somewhere one or more of these polymeric structures has already been created but has been lost in the tar of a reaction vessel. Their existence would not be without precedence. Take, for instance, the alkoxy polymers[26] or Haines' polymeric $[Rh_2(\mu_2\text{-}Cl)_2(\mu_2\text{-}PH_2)_2(CO)_2]_n$[27] which assumes the geometry of **c** with pendant CO groups. Given the variety and abundance of structures utilizing the carbonyl ligand in molecular organometallic chemistry, we think it is not unlikely that in due time the carbonyl unit will prove to be just as versatile and productive in the field of solid-state chemistry. We await the synthetic and structural work that will move us from speculations to real chemistry.

Acknowledgment. We are grateful to the National Science Foundation for its support of this work through Research Grant CHE 8406119. Thanks are extended to Jane Jorgensen and Elisabeth Fields for careful rendering of the drawings.

Appendix

The calculations were of the extended Hückel type with weighted H_{ij}'s[29] with parameters (see Table II) taken from previous work.[30] Distances used throughout are Co–Co = 2.36 Å, Co–C = 1.82 Å, C–O = 1.20 Å, Co–Cp centroid = 1.724 Å. The geometry of molecular and extended "puckered" structures was defined by setting C–C = 2.36 Å for carbonyls straddling the metal–metal bond.

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Reaction of Phenylchlorocarbene in Oxygen-Doped Matrices

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Contribution from the S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and the Department of Chemistry, University of Prince Edward Island, Charlottetown, Prince Edward Island, Canada C1A AP3. *Received July 11, 1985*

Abstract: Irradiation of phenylchlorodiazirine at 10 K matrix isolated in argon gives phenylchlorocarbene. The carbene was characterized by IR, UV, and trapping with HCl. Warming an argon matrix containing O_2 and the carbene to 35 K caused reaction to give the corresponding carbonyl oxide. The yellow-green (λ_{max} 400 nm) carbonyl oxide was characterized by IR, UV, and $^{18}O_2$ labeling. Photolysis of the carbonyl oxide with visible light gave the corresponding dioxirane, benzoyl chloride, and ozone. The dioxirane, which showed only absorption tailing into the visible, was characterized by IR, $^{18}O_2$ labeling, and subsequent photochemistry. Irradiation of the dioxirane ($\lambda > 420$ nm) gave mainly phenyl chloroformate and a small amount of chlorobenzene and CO_2. Possible mechanisms for the novel spin-forbidden O_2 addition are discussed.

Carbonyl oxides and the isomeric dioxiranes have generated considerable interest as intermediates in ozonolyses,[1] and in oxidations of diazo compounds,[2] carbenes,[3] and carbonyl compounds.[4] Recently, several groups have reported direct observations of

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(1) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1.

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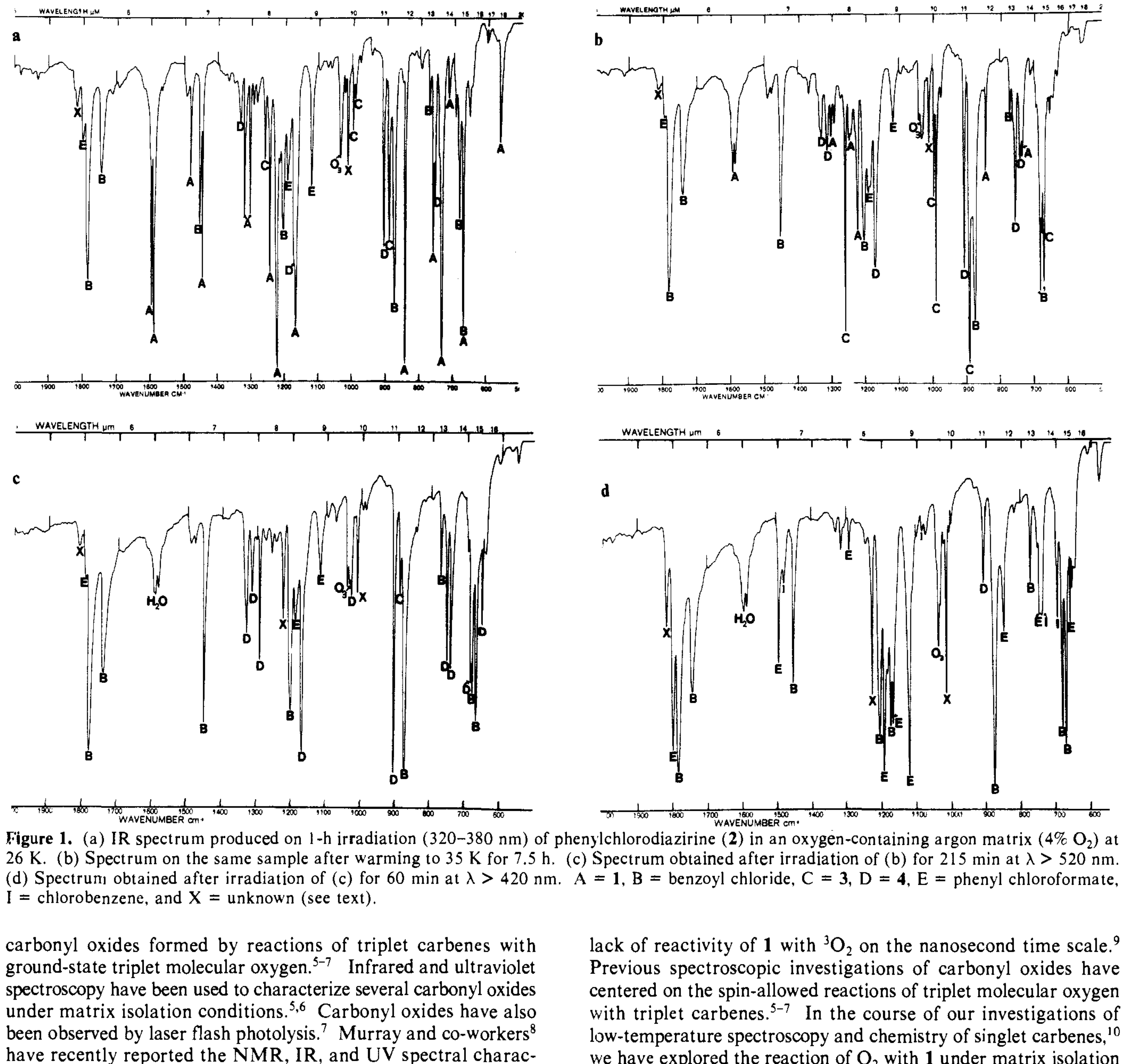

Figure 1. (a) IR spectrum produced on 1-h irradiation (320–380 nm) of phenylchlorodiazirine (**2**) in an oxygen-containing argon matrix (4% O_2) at 26 K. (b) Spectrum on the same sample after warming to 35 K for 7.5 h. (c) Spectrum obtained after irradiation of (b) for 215 min at $\lambda > 520$ nm. (d) Spectrum obtained after irradiation of (c) for 60 min at $\lambda > 420$ nm. A = **1**, B = benzoyl chloride, C = **3**, D = **4**, E = phenyl chloroformate, I = chlorobenzene, and X = unknown (see text).

carbonyl oxides formed by reactions of triplet carbenes with ground-state triplet molecular oxygen.[5-7] Infrared and ultraviolet spectroscopy have been used to characterize several carbonyl oxides under matrix isolation conditions.[5,6] Carbonyl oxides have also been observed by laser flash photolysis.[7] Murray and co-workers[8] have recently reported the NMR, IR, and UV spectral characterization of several alkyl dioxiranes, generated at room temperature by the direct oxidation of ketones.

Phenylchlorocarbene (**1**) has been the subject of several laser time-resolved spectroscopic investigations as a prototypic singlet carbene.[9] One signature for this ground-state multiplicity is the lack of reactivity of **1** with $^3O_2$ on the nanosecond time scale.[9] Previous spectroscopic investigations of carbonyl oxides have centered on the spin-allowed reactions of triplet molecular oxygen with triplet carbenes.[5-7] In the course of our investigations of low-temperature spectroscopy and chemistry of singlet carbenes,[10] we have explored the reaction of O_2 with **1** under matrix isolation conditions. We now wish to report the thermal reaction of **1** with $^3O_2$ at 35 K and spectroscopic evidence for the sequential formation of a carbonyl oxide and a dioxirane.

Irradiation (Corning 7-37 bandpass filter, 320–380 nm) of phenylchlorodiazirine (**2**) matrix isolated in argon at 10 K gave carbene **1**. The carbene has major IR absorptions at 1590, 1225, 1170, 848, and 735 cm^{-1}. Intense bands at 1590 and 1225 cm^{-1} are consistent with a strongly electron withdrawing group in conjugation with the aromatic ring.[11] The UV spectrum of the same sample shows a λ_{max} of 300 nm, consistent with the spectra reported by other workers for **1**.[9] The carbene structure was confirmed by thermal trapping. The carbene could be photochemically generated in an argon matrix containing HCl (Ar:HCl:**2**, 940:3:1). Warming to 38 K for several hours caused disappearance of the carbene IR bands and the concomitant growth of absorptions due to benzal chloride.[12]

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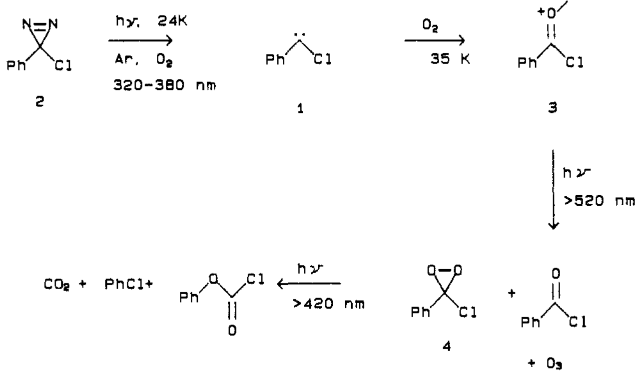
Scheme I



Interestingly, a small IR peak at 2050 cm^{-1} is also observed in the irradiations of **2**. This band could be destroyed selectively by irradiation with visible light ($\lambda > 380$ nm). These results suggest that this band may be due to phenylchlorodiazomethane.[13] The stability of this molecule to the initial irradiation conditions indicates that it is not an intermediate in the formation of **1**. No other bands are observed for this minor species, and it is stable to the thermal trapping reactions below.

Irradiation of **2** in an argon matrix containing O_2 (Ar:O_2:**2** = 800:35:1) gives the carbene **1** plus a number of other bands in the IR (Figure 1a). Warming the matrix to 35 K for ca. 6 h causes a slow decrease in the bands of **1** and a simultaneous increase of the absorptions at 1260, 990, 890, and 675 cm^{-1} (Figure 1b). This new intermediate (C) is remarkably photolabile, decreasing even with the visible irradiation from the IR glower. Insertion of a silicon filter ($\lambda > 1100$ nm) between the IR source and the sample, however, allowed IR spectra to be obtained without destruction of C. The matrix also takes on a distinct yellow-green hue during the warming, although the electronic spectrum of the matrix only shows a broad band with maximum at 400 nm tailing to longer wavelengths.[14]

Photolysis of C with visible light (Corning 3-68, $\lambda > 520$ nm) causes the complete disappearance of this intermediate, formation of additional benzoyl chloride and ozone, and increase of an intermediate with strong IR bands at 1330, 1291, 1170, 905, 751, 741, and 685 cm^{-1} (D, Figure 1c). Simultaneously, the color in the matrix is bleached; the visible absorption of C disappears. The action spectrum of photolysis of C roughly matches the visible absorption observed. The sample containing C was irradiated at 5-nm intervals over 325 to 535 nm with the Xe lamp, which is approximately linear through this region, through a monochromator. The rate of conversion of C to D followed the observed electronic spectrum, confirming that the IR and UV–vis spectra correspond to the same species.

No new UV–vis maximum corresponding to D is observed in the region between 400 nm and wavelengths where the other photoproducts begin to absorb strongly (ca. 300 nm). In concentrated matrices an absorbance tail out beyond 400 nm could be seen, however.[14] Subsequent irradiation (Corning 3-73, $\lambda > 420$ nm) rapidly converts D mainly into phenyl chloroformate, with small amounts of phenyl chloride and CO_2 also formed (Figure 1d). The absorption tail is also destroyed in the UV spectrum.

A reasonable mechanistic scenario comprising the above observations is shown in Scheme I. The observation of moderate amounts of all intermediates after initial irradiation is undoubtedly due to adventitious photolysis despite the band-pass filter.[15]

Several workers have reported UV observations of intermediates formed on reaction of triplet carbenes with O_2.[5,7] The intermediates, suggested to be carbonyl oxides, all have broad absorptions with maxima in the range of 410–460 nm. GVB calculations by Goddard and co-workers[16] also suggest that carbonyl oxides should be electronically similar to ozone and might thus show visible absorption. Hence, we suggest that intermediate C has the carbonyl oxide structure **3**. The carbonyl oxide formed from diphenylcarbene exhibits a λ_{max} at 410 nm. A somewhat shorter wavelength absorption for **3**, observed at 400 nm, is consistent with less conjugation.

Isotopic labeling also supports the structure assignment for **3**. The three strong bands in the IR at 1260, 990, and 890 cm^{-1} for this intermediate shift to 1251, 1245 (split), 982, and 840 cm^{-1} with use of $^{18}O_2$ (98% double labeled). The shift in the 890-cm^{-1} absorption is similar to the 48-cm^{-1} decrease in stretching frequency observed in going from $^{16}O_3$ to ^{16}O–^{18}O–^{18}O.[17] Moreover, the strong intensity of this absorption is more consistent with the carbonyl oxide structure **3** than a ring-breathing mode for **4**. The observation of isotopic shifts in the other bands of **3** also lessens the possibility that this species is a loosely bound complex between carbene **1** and O_2.

We suggest that D has the dioxirane structure **4**. The photochemical conversion of this intermediate to phenyl chloroformate clearly indicates that both oxygen atoms are still present in **4**. Although most of the IR bands of **4** shift less than 10 cm^{-1} on use of $^{18}O_2$, one weak band shifts from 1030 to 982 cm^{-1} and a moderate band shifts from 741 to 715 cm^{-1}. These absorptions may correspond to ring-breathing modes. Dimethyldioxirane[8] exhibits several weak absorptions in the region 1080 to 1030 cm^{-1} and a strong absorption at 784 cm^{-1} which may be due to similar deformations.

There have been several reports of UV spectral data for dioxiranes.[8,18] Dimethyl- and methylethyldioxirane exhibit UV absorptions at 335 and 333 nm, respectively, with moderate extinction coefficients (ca. 200), and tailing into the visible.[8] Bis(trifluoromethyl)dioxirane, on the other hand, has been reported to have a λ_{max} at 306 nm.[18] It is thus reasonable that the electron-withdrawing phenyl and chloro substituents shift the maximum of **4** to a wavelength where it would not be observed in our experiments.[14] The observation of tailing absorption into the visible and the photochemical conversion at wavelengths as long as 420 nm is consistent with this assignment, however.

Besides formation of **4**, photolysis of **3** gives benzoyl chloride and ozone.[15] These products are reasonably derived via O transfer from **3** to O_2. On irradiation, **4** produces mainly phenyl chloroformate. This rearrangement likely occurs via O–O cleavage followed by a phenyl shift. A small amount of CO_2 and chlorobenzene are also formed, suggesting that some Cl loss competes. An additional product, X, is also generated from **4** (Figure 1d). The structure of this product, which is stable to further irradiation at shorter wavelengths, is unknown. Comparison to authentic matrix isolated samples indicates that it is not benzoic anhydride, benzoyl peroxide, or phenyl benzoate. This minor pathway is under current investigation.

We believe that this is the first observation of both a carbonyl oxide and a dioxirane in a carbene oxidation. These results may

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(12) Irradiation of the carbene (>280 nm) gives slow (16 h) conversion to a new product whose structure is yet unknown. This product was found to be unreactive to oxygen under our conditions. O. L. Chapman and A. Mooring (UCLA) have indicated to us that they have also observed **1** in argon matrices (personal communication).

(13) This diazo compound has not been reported previously. Only several halo diazo compounds have been observed. Regitz, M. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; John Wiley: New York, 1978; Part 2, p 696.

(14) The UV spectra are difficult to obtain due to light scattering by the matrix, particularly after warming. Moreover, the intense carbene absorption partially overlaps the weaker absorption of C. The final photoproduct absorptions and scattering may similarly obscure the UV of D. Although the absorption of D tails out to the visible, no color was observed in the matrix after destruction of C. The matrix was quite thin, however, and we have previously observed that it is often difficult to observe colors from weakly absorbing species under these conditions.

(15) The IR spectrum between 950 and 1100 cm^{-1} is particularly complex, with all species exhibiting bands in this region, making assignments difficult. The band at 1040 cm^{-1} is tentatively assigned to ozone, although other products, e.g., X, may overlap this absorption.

(16) (a) Harding, L. B.; Goddard, W. A., III *J. Am. Chem. Soc.* **1978**, *100*, 7180. (b) Wadt, W. R.; Goddard, W. A., III *J. Am. Chem. Soc.* **1975**, *97*, 3004.

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help to resolve conflicting reports in the addition of cyclopentadienylidene to O_2. Two groups have published substantially different IR spectra for the adduct resulting at low temperature. Although Dunkin and Bell[5a] generated the initial addition product by thermal reaction at 35 K, Chapman and Hess[6] produced their adduct by photolysis of the corresponding diazo compound at 10 K with wavelengths >418 nm. Our results suggest that the carbonyl oxide initially formed would not be observable under the latter irradiation conditions and that the detected product was likely the dioxirane. Dunkin and Bell[5a] report smaller isotopic shifts than we observe, although their UV spectra and ours are quite similar.

One final point of interest is the problem of how a singlet carbene and triplet oxygen react at 35 K, while reaction is slow at room temperature.[9] Room temperature solution investigations indicate that **1** is a ground-state singlet carbene.[9] Although the singlet–triplet energy gap is not known, slow reaction with O_2 at 20 °C would indicate that the triplet is not appreciably populated. Negative activation energies for carbene additions to olefins are well-established.[19] These anomalous kinetics have been attributed to complex formation or to the importance of entropic barriers.[19] A complex formed between **1** and O_2 might facilitate intersystem crossing before addition. Alternatively, the spin-forbidden barrier may manifest itself primarily in a large entropy of activation.[20] If the addition has a negligible enthalpic barrier, lower temperatures would then facilitate reaction. It is interesting to note that apparent spin forbidden reactions of matrix isolated *triplet* carbenes with CO and N_2 have been observed previously.[5,21] Further work to clarify these points is underway.[22]

Experimental Section

General. Details of our matrix isolation equipment and general experimental techniques can be found elsewhere.[10b] Phenylchlorodiazirine was prepared following Graham's procedure.[23] UV-vis spectra of matrix isolated species were recorded on a Perkin-Elmer Hitachi 200 spectrometer. Transmission curves for cutoff filters were recorded on a Cary Model 118 spectrometer. Infrared spectra were recorded on a Beckmann IR 4250 spectrometer. Doubly labeled $^{18}O_2$ was prepared via electrolysis of 98% ^{18}O water obtained from Mound research.

Photolyses were carried out with use of a Varian EIMAC 300-W high-pressure Xe arc illuminator with quartz optics and water filter. Monochromatic light was obtained with a Bausch and Lomb monochromator with use of a 1-mm slit opening which provided a bandpass of 6 nm and appropriate cutoff filters to remove 2nd order wavelengths. The following Corning bandpass and cutoff filters were used: 3-68 (5% T at 530 nm, 50% T at 540 nm, 80% T at 560 nm), 3-73 (3% T at 420 nm, 60% T at 430 nm, 80% T at 450 nm), 7-37 (8% T at 320 nm, 35% T at 340 nm, 45% T at 360 nm, 20% T at 380 nm, 1% T at 390 nm).

Phenylchlorocarbene. In a typical experiment, between 60 and 100 torr of a mixture of phenylchlorodiazirine and argon (1:700) were deposited at the rate of 0.5 torr/m, from a 3 L manifold, at 24–25 K. IR bands for phenylchlorodiazirine were present at 1570 (s), 1495 (m), 1445 (m), 1335 (w), 1255 (m), 1030 (s), 1010 (s), 905 (vs), 750 (s), 682 (s), and 660 (s) cm^{-1}. Photolysis at 11 K for 45 min with Corning filter 7-37 (320–380 nm) produced phenylchlorocarbene with IR bands at 1600 (m), 1590 (s), 1480 (w), 1450 (m), 1321 (w), 1308 (m), 1248 (m), 1225 (vs), 1205 (w), 1170 (s), 1000 (w), 848 (vs), 762 (m), 735 (vs), 672 (s), and 565 (w) cm^{-1}.

HCl Trapping of Phenylchlorocarbene. Ninety torr of a mixture of phenylchlorodiazirine, HCl, and argon (1:3:940) were deposited at the rate of 0.75 torr/min at 25K. Photolysis at 25 K for 45 min with Corning filter 7-37 produced phenylchlorocarbene, by IR. Warming at 38 K for 3.75 h caused new bands of weak of medium intensity to grow in at 845, 840, 742, 700, and 575 cm^{-1}, which compare well with an authentic sample of benzal chloride matrix isolated in argon/HCl at 25 K.

Oxygen Trapping of Phenylchlorocarbene. In a typical experiment, 150–200 torr of phenylchlorodiazirine, oxygen, and argon (1:35–50:800) were deposited at the rate of 0.67 torr/min at 26 K. Photolyses and warmings are described in the text. Infrared bands for the observed intermediates are as follows. C: 1368 (w), 1260 (s), 1195 (m), 999 (m), 990 (s), 890 (vs), 750 (m), and 675 (m) cm^{-1}. D: 1330 (m), 1315 (w), 1291 (m), 1170 (s), 1075 (w), 1030 (w), 905 (vs), 751 (m), 741 (m), 685 (m), and 651 (w) cm^{-1}.

$^{18}O_2$ Trapping of Phenylchlorocarbene. Experimental conditions were identical with the unlabeled oxygen run (vide supra). Infrared bands for the observed intermediates are as follows. C: 1362 (w), 1338 (w), 1251 (s), 1245 (s), 1189 (m), 1032 (w), 999 (w), 982 (s), 840 (vs), 839 (s), 760 (m), 680 (m), and 675 (m) cm^{-1}. D: 1325 (m), 1318 (m), 1282 (s), 1162 (vs), 1075 (w), 982 (m), 900 (vs), 750 (m), 715 (m), 682 (s), 650 (m), 645 (w), and 550 (w) cm^{-1}.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We are also grateful to Professor O. L. Chapman for communication of unpublished results.

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(20) See, for example: Rule, M.; Mondo, J. A.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2209.

(21) Chapman, O. L.; Sheridan, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 3690.

(22) One of us has obtained evidence that **1** reacts with O_2 in solution. Liu, M. T. H.; Kohmoto, S.; Jefford, C. W., unpublished results.

(23) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(24) **Note Added in Proof**: Dunkin and Shields (*J. Chem. Soc., Chem. Commun.* **1986**, 154) have very recently observed the photochemical conversion of cyclopentadienone *O*-oxide to the corresponding dioxirane, consistent with our above speculation.