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Effects of Electron-Withdrawing Groups on Carbonyl *O*-Oxides. Trifluoroacetophenone *O*-Oxide and Hexafluoroacetone *O*-Oxide

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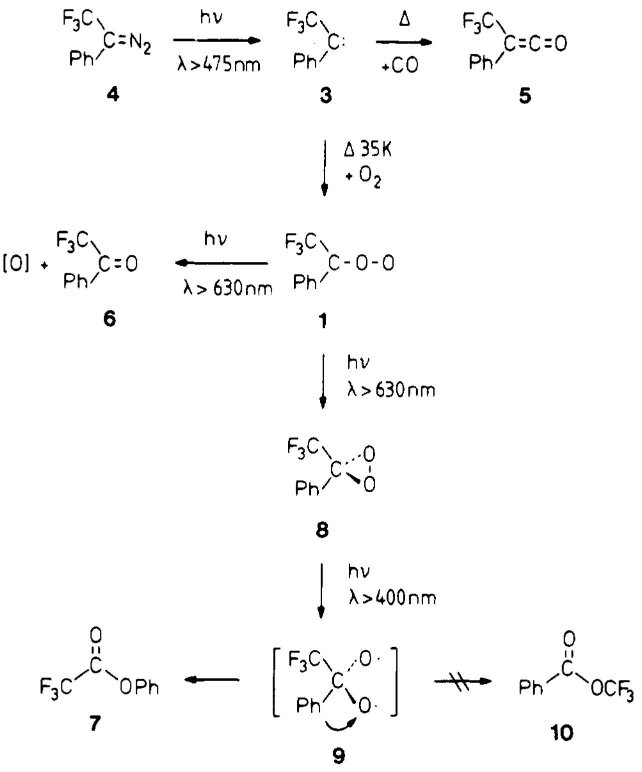
The oxidation of 1-phenyl-2,2,2-trifluoroethylidene and bis(trifluoromethyl)methylene by molecular oxygen was investigated in argon matrices. Both carbenes give carbonyl *O*-oxides in a thermal reaction with O_2. On long-wavelength irradiation ($\lambda > 590$ nm), the carbonyl *O*-oxides split off oxygen atoms to give trifluoroacetophenone and hexafluoroacetone, respectively. Trifluoroacetophenone *O*-oxide also rearranges to phenyl(trifluoromethyl)dioxirane which, on irradiation ($\lambda > 400$ nm), produces phenyl trifluoroacetate. During annealing of O_2-doped matrices containing the carbenes, chemiluminescence was observed. The chemiluminescence spectra closely match the phosphorescence spectra of the corresponding ketones. Fluorescence was not detected, however, proving that the ketones are formed in their triplet excited states.

A number of spectroscopic investigations of carbonyl *O*-oxides in inert gas matrices have been reported in recent years.[1-3] All of these compounds contain either a cyclopentadiene system[1] or an aromatic substituent.[2,3] The carbonyl *O*-oxides show some similar spectroscopic and photochemical properties. They all exhibit in the IR a strong band close to 900 cm^{-1}, assigned to an O–O stretching mode, and in the UV a strong transition at 400–420 nm. On long-wavelength irradiation ($\lambda > 500$ nm), they rearrange to dioxiranes or split off oxygen atoms to give carbonyl compounds.[1-3]

On the basis of semiempirical MINDO/3 calculations, it has been claimed that zwitterionic structures are most important in the ground states of carbonyl *O*-oxides and that the electronic structure is not much changed by substituents.[4] This is in contrast to ab initio calculations, which predict a diradicaloid ground state,[5] and to trapping experiments in solution, which show a large effect of substitution on reactivity.[6] Carbonyl *O*-oxides with electron-donating groups show a higher nucleophilicity than those with electron-withdrawing groups. Although in these trapping experiments some evidence was given that indeed carbonyl *O*-oxides were the active oxygen-transfer reagents,[6] other intermediates, like dioxiranes or oxygen atoms,[7] formed as products of secondary photolysis might play a significant role. Thus it is desirable to observe directly the properties of carbonyl *O*-oxides as a function of substituents.

To elucidate the effect of strong electron-withdrawing groups on carbonyl *O*-oxides, trifluoroacetophenone *O*-oxide (**1**) and hexafluoroacetone *O*-oxide (**2**) were generated in argon matrices at cryogenic temperatures. The spectroscopic properties and the photochemistry of **1** and **2** are compared to the properties of other carbonyl *O*-oxides, especially to those of benzophenone *O*-oxide.

Scheme I



Results

Oxidation of 1-Phenyl-2,2,2-trifluoroethylidene (3). Irradiation ($\lambda > 475$ nm) of 1-phenyl-2,2,2-trifluorodiazoethane (**4**), matrix-isolated in Ar at 10 K, slowly gave carbene **3**, characterized by IR bands at 1408 (m), 1209 (s), 1203 (m), 1163 (s), 1109 (s), 743 (m), and 666 (m) cm^{-1}.[8,9] In the UV–vis spectrum, carbene **3** showed maxima at 415, 420, 429, 435, and 444 nm.

Irradiation ($\lambda > 475$ nm) [Note: the symbol > indicates the use of cut-off filters with 50% transmittance at the wavelength specified.] of diazo compound **4** in Ar matrices

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(1) (a) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213–1215. (b) Dunkin, I. R.; Shields, C. J. *J. Chem. Soc., Chem. Commun.* **1986**, 154–156. (c) Bell, G. A.; Dunkin, I. R.; Shields, C. J. *Spectrochim. Acta* **1985**, *41A*, 1221–1227.

(2) (a) Sander, W. *Angew. Chem.* **1986**, *98*, 255–256; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 255–257. (b) Sander, W. *Spectrochim. Acta* **1987**, *43A*, 637–646.

(3) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517–1520.

(4) Sawaki, Y.; Kato, H.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3832–3837.

(5) (a) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 7180–7188. (b) Yamaguchi, K.; Ohta, K.; Yabushita, S.; Fueno, T. *J. Chem. Phys.* **1978**, *68*, 4323–4325. (c) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199–7205.

(6) Adam, W.; Dürr, H.; Haas, W.; Lohray, B. *Angew. Chem.* **1986**, *98*, 85–87; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*.

(7) Sander, W. *Angew. Chem.* **1985**, *97*, 964–965; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 988–989.

(8) If the matrix was doped with 1.5% CO, all bands assigned to **3** disappeared on annealing at 40 K. New bands at 2150 (s), 1504 (m), 1323 (s), 1145 (s), and 953 (m) grew in and were assigned to phenyl(trifluoromethyl)ketene (**5**).

(9) The formation of ketenes by the thermal reaction of matrix-isolated free carbenes with CO is a highly specific reaction. For an example, see: Baird, M. S.; Dunkin, I. R.; Hacker, N.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 5190–5195.

0022-3263/88/1953-0121$01.50/0

Table I. IR Spectroscopic Data of Carbonyl *O*-Oxides 1 and 2 Matrix-Isolated in Ar at 10 K (Wavenumbers in cm^{-1})

$[^{16}O_2]$-1	*a*	$[^{16}O_2]$-2	*a*
1354 (m)	−1	1396 (m)	−5[b]
1312 (w)	−1	1373 (m)	−5
1274 (m)	−5	1237 (m)	−12
1194 (m)	−2	1210 (m)	−4
1154 (s)	1	1180 (w)	
1009 (s)	−10, −20[c]	1049 (m)	−18
943 (s)	−35	997 (s)	−35
771 (m)	0	734 (m)	−5
746 (w)			
670 (m)	−12		
655 (w)			

[a] Isotopic shifts after ^{18}O labeling. [b] Due to a very strong peak of 12 at 1389 cm^{-1}, the error in determining the exact peak frequency is large. [c] The band at 1009 cm^{-1} is split to two bands at 999 and 989 cm^{-1}.

doped with 0.5–4% O_2 gave free carbene 3 and the oxidation products trifluoroacetophenone (6) and phenyl trifluoroacetate (7) (Scheme I). These products were identified by comparison with authentic matrix-isolated compounds. The ratio of carbene to oxidation products depended much on the O_2 content of the matrix. At 0.5% O_2, only a small fraction of 3 was oxidized, whereas at 4% O_2 the oxidation of 3 was almost complete and small amounts of ozone were formed in addition. The ratio of the carbonyl peaks of 6 (1729 cm^{-1}) and 7 (1809 cm^{-1}) was always >4:1 and was nearly independent of the O_2 concentration.

After warming the matrix containing 3 and excess O_2 from 10 K to its softening point at 42 K (free warm-up, rate approximately 1 K/min) and recooling to 10 K, all IR bands assigned to 3 disappeared, and new bands assigned to trifluoroacetophenone *O*-oxide were formed (Table I). If $^{18}O_2$ was used in the experiment, the band at 943 cm^{-1} showed a large isotopic shift of 35 cm^{-1} to smaller wavelength. The large isotopic shift, as well as the intensity and the frequency of the band at 943 cm^{-1}, are characteristic for O–O stretching vibrations of carbonyl *O*-oxides.[1-3] In the UV–vis spectra, the disappearance of the carbene spectrum and the formation of an intense, broad band with a maximum at 378 nm was observed. Simultaneously, the matrix turned yellow. The yellow color and a UV maximum near 400 nm are indicative for the formation of carbonyl *O*-oxides.[1-3]

Long-wavelength irradiation ($\lambda > 630$ nm, 10 K) of a matrix containing 1 gave complete conversion of 1 within 20 min, while irradiation with $\lambda > 665$ nm did not give any change in the spectra. Diazo precursor 4 was not reactive on irradiation at this wavelength, and, with $\lambda > 475$ nm, a 10-h irradiation was required to get 80% conversion. This differing photosensitivity allowed complete separation of the photochemistry of 1 and 4 (Figure 1).

The photoproducts of 1 were ketone 6 and 3-phenyl-3-(trifluoromethyl)dioxirane (8). Ester 7 was not formed under these conditions (Scheme I). Dioxiranes do not exhibit strong, characteristic IR bands;[10] the only bands definitely assigned to 8 were found at 1213 (s, C–F stretching vibration), 944 (s), 684 (m), and 643 (m) cm^{-1}. The first two strong bands are very close to corresponding bands in ketone 6 and did not show isotopic shifts >1 cm^{-1} if the experiments were repeated in $^{18}O_2$-doped Ar matrices. Dioxirane 8 was identified by observing its photochemistry (Scheme I). Irradiation of a matrix containing 8 ($\lambda > 400$ nm, 30 min, 10 K) produced ester 7 (Figure 2), but other carbonyl compounds such as the isomeric trifluoromethyl benzoate (10) or ketone 6 were not formed.

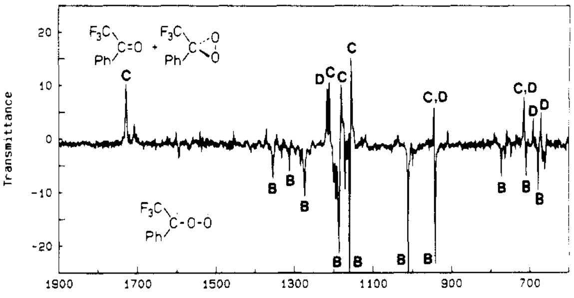

Figure 1. Difference IR spectrum of the photochemistry of 1 in a 1% O_2-doped Ar matrix at 10 K: bottom, bands disappearing; top, bands appearing on irradiation ($\lambda > 630$ nm) of 1. B: bands assigned to 1. C: bands assigned to 6. D: bands assigned to 8.

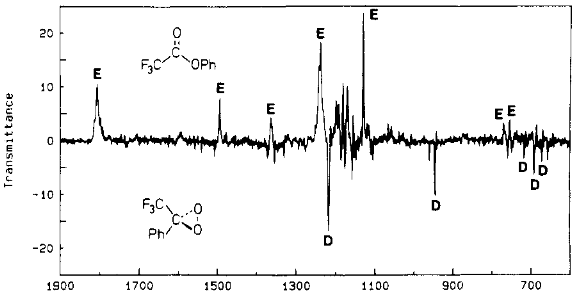

Figure 2. Difference IR spectrum of the photochemistry of 8 in a 1% O_2-doped Ar matrix at 10 K: bottom, bands disappearing; top, bands appearing on irradiation ($\lambda > 400$ nm) of 8. D: bands assigned to 8. E: bands assigned to 7.

Oxidation of Bis(trifluoromethyl)carbene (11). The matrix-isolation and characterization of carbene 11 and some aspects of its photooxidation have already been described in the literature.[11,12] The formation of carbonyl *O*-oxide 2 was not reported, and therefore only the experiments leading to 2 and its subsequent photochemistry are described.

Irradiation ($\lambda > 305$ nm) of 12, matrix-isolated in Ar doped with O_2 (0.5–4%), gave large amounts of the oxidation products described by Hess.[12] The main products were CO_2, hexafluoroacetone (15), trifluoromethyl trifluoroacetate (16), and small amounts of difluorocarbonyl (especially at higher O_2 concentrations). The formation of CO_2 and difluorocarbonyl shows that the required short-wavelength irradiation leads to secondary photooxidation and cleavage of C–F bonds. The amount of free carbene 11 was much smaller than the amount of carbene 3 formed (under the same conditions: Ar/O_2 ratio, *T*) in the experiments described above. The larger yield of oxidation products formed on $\lambda > 305$ nm irradiation compared to $\lambda > 475$ nm irradiation results from the higher mobility of O_2 in solid Ar on the shorter wavelength irradiation. This is explained by local heating of the matrix at the site were the light is absorbed.

When a matrix containing 11 and 1% O_2 was warmed from 10 K to 42 K (free warm-up, rate approximately 1 K/min) and recooled to 10 K, all IR bands assigned to 11 (1344 (s), 1200 (m), 1151 (s), 968 (m) cm^{-1}) disappeared and new bands of carbonyl *O*-oxide 2 grew in (Table I). If the warm-up of the matrix was stopped at 30 K, only small amounts of 2 were produced after 1.5 h. At 35 K the

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(10) Gauss, J.; Cremer, D. *Chem. Phys. Lett.* **1987**, *133*, 420–424.

(11) Mal'tsev, A. K.; Zuev, P. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 957–958.

(12) Hess, T. C. Ph.D. Thesis, University of California, Los Angeles, 1978.

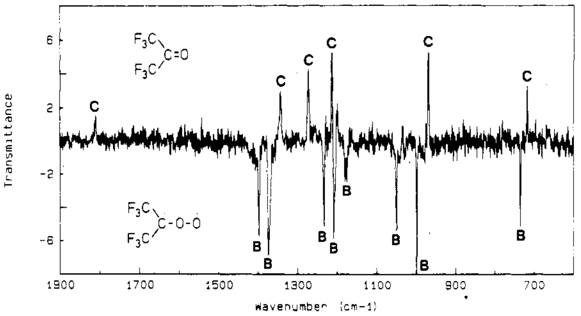

Figure 3. Difference IR spectrum of the photochemistry of **2** in a 0.6% O_2-doped Ar matrix at 10 K: bottom, bands disappearing; top, bands appearing on irradiation (λ > 590 nm) of **2**. B: bands assigned to **2**. C: bands assigned to **15**.

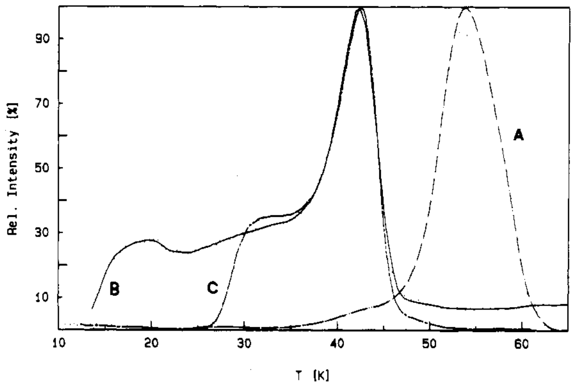

Figure 4. Glow curves obtained from Ar matrices by warming (free warm-up, rate approximately 1 K/min) from 10 to 65 K. A: matrix containing **3**, generated by irradiation (λ > 475 nm) of **4**, and no O_2. B: same conditions as in A, but 1.4% O_2-doped matrix. C: same conditions as in B, but 75 min warming to 25 K prior to recording the glow curve.

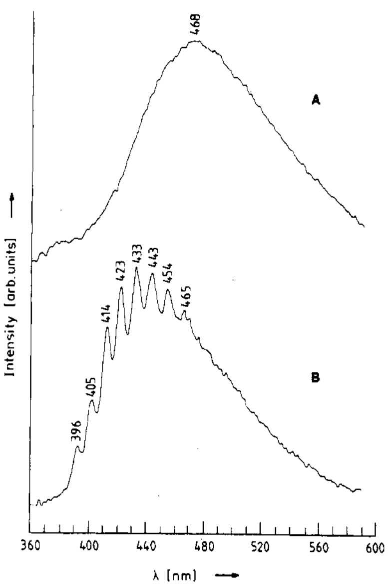

Figure 5. A: chemiluminescence spectrum obtained by first irradiating (λ > 305 nm) a 1.3% O_2-doped Ar matrix and then warming the matrix to 40 K. B: luminescence spectrum (313 nm excitation) of ketone **15**, matrix-isolated in Ar at 10 K. The part of the spectrum exhibiting vibrational fine structure (spacing 550 ± 20 cm^{-1}) is assigned to the fluorescence, the structureless tailing on the long-wavelength side to the phosphorescence of **15**.

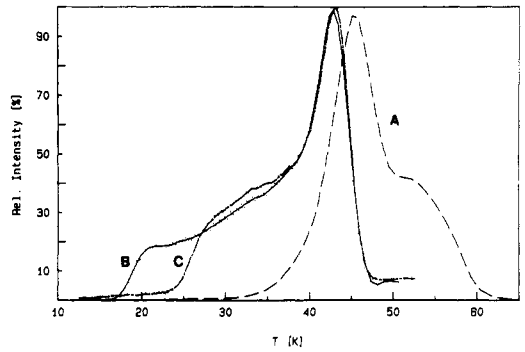

Figure 6. Glow curves obtained from Ar matrices by warming (free warm-up, rate approximately 1 K/min) from 10 to 65 K. A: matrix containing **11**, generated by irradiation (λ > 305 nm) of **12**, and no O_2. B: same conditions as in A, but 1.7% O_2-doped matrix. C: same conditions as in B, but 50 min warming to 23 K prior to recording the glow curve.

reaction was complete within 1 h. If the experiments were repeated by using $^{18}O_2$, the band at 997 cm^{-1} showed a pronounced isotopic shift of 35 cm^{-1} (Table I), characteristic of the O–O stretching mode of carbonyl *O*-oxides.

Carbonyl *O*-oxide **2** proved to be very photolabile: long-wavelength irradiation (λ > 590 nm, 10 K) gave ketone **15** as the only product observable in the IR spectrum (Figure 3). Short-wavelength irradiation (λ > 295 nm) of the matrix obtained did not produce any further changes and especially did not increase the amount of ester **16**.[14]

Chemiluminescence from the Oxidation of Carbenes 3 and 11. During warming a matrix containing **3** and 0.5–4% O_2 from 10–60 K, a bright, blue chemiluminescence was observed. The spectra obtained at 40–55 K were identical with the phosphorescence spectrum of ketone **6**, matrix-isolated in Ar at 10–30 K. The glow curve (temperature dependence of the chemiluminescence) of a matrix containing **3** and no O_2 exhibited a maximum at 54 K (Figure 4A). At this temperature the matrix rapidly evaporated, and the carbene **3** reacted with an air layer on top of the matrix (contamination from small leaks in the vacuum system). If the Ar matrix was doped with 1.5% O_2, the maximum of the glow curve was shifted to 42 K (Figure 4B). At this temperature, O_2 diffuses rapidly in solid Ar.[17] At higher temperatures (T > 50 K), when the matrix rapidly evaporates and the surface contamination is able to react with the matrix material, all free carbene **3** has already reacted and no chemiluminescence is observed.

The glow curves of O_2-containing matrices show the chemiluminescence starting above 15 K (free warm-up, rate 1–1.5 K/min). If the temperature rise was stopped at 25 K, the luminescence decayed within several minutes (non-first-order kinetics). If the temperature was kept at 25 K for 5 min prior to recooling the matrix to 10 K and recording a glow curve, the chemiluminescence started at 26 K. The shape of the glow curve at higher temperatures was not changed by this treatment. The only change in the IR spectrum after 5 min at 25 K was a trace of **1** formed from **3**. Warming the matrix for 75 min to 25 K

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(13) Several examples for thermal isomerizations of this type have appeared in the literature. For a review, see: Barnes, A. J. In *Matrix Isolation Spectroscopy*; Barnes, A. J., Orville-Thomas, W. J., Müller, A., Gaufres, R., Eds.; D. Reidel: Dordrecht, 1981.

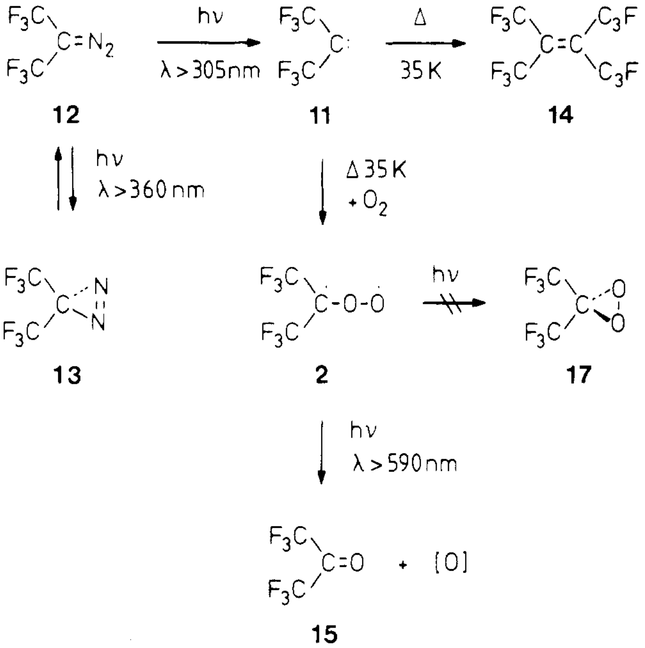
(14) The formation of bis(trifluoromethyl)dioxirane (**17**) cannot be rigorously excluded by these data. Several IR bands of **15** (Ar, 10 K: strong bands at 1345, 1275, 1245, 1212, 981 cm^{-1}) are close to bands reported for **17** (neat, room temperature: 1353, 1276, 1235, 1212, 976 cm^{-1}): Talbott, R. I.; Thompson, P. G. U.S. Pat. 3632606, 1972.

(15) Turro, N. J.; Butcher, J. A., Jr.; Hefferon, G. J. *Photochem. Photobiol.* **1981**, *34*, 517–520.

(16) Wasserman, E.; Barash, L.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 4974–4975.

(17) Pimentel, G. C. In *Formation and Trapping of Free Radicals*; Bass, A. M., Broida, H. P., Eds.; Academic: New York, 1960.

Scheme II



prior to recording the glow curve (Figure 4C) only shifted the beginning of the chemiluminescence to 28 K. After 75 min at 25 K, 20–30% of **3** was reacted to give **1** (observed IR spectroscopically). The formation of **1** is slow at 25 K, whereas the reaction leading to chemiluminescence is fast (cessation of the emission after 5 min). Thus, the formation of **1** is not directly related to the chemiluminescence.

Warming a matrix containing carbene **11** and excess (0.5–3%) O_2 also produced a blue chemiluminescence (Figure 5A). The chemiluminescence spectrum exhibited a broad maximum near 470 nm and was very similar to the phosphorescence of hexafluoroacetone (**15**).[18] The glow curve obtained during warming **11**, matrix-isolated in Ar (no O_2), from 10–60 K (free warm-up, rate 1–1.5 K/min, Figure 6A), shows a maximum at 46 K and a shoulder at 52 K. The maximum is significantly shifted to lower temperatures compared to the glow curve obtained from **3** under the same conditions (Figure 4A) and obtained from other carbenes.[2,7] An explanation for this shift is the rapid diffusion of carbene **11** at $T > 40$ K, visualized by the formation of tetrakis(trifluoromethyl)ethylene (**14**) (Scheme II). At $T > 50$ K, only small amounts of **11** are left, and the chemiluminescence intensity is reduced. Carbene **3** and other carbenes containing larger groups do not diffuse rapidly under the same conditions, and no dimers are formed. In O_2-doped Ar matrices (0.5–3% O_2), the glow curves (Figure 6) were very similar to the glow curves obtained with carbene **3** (Figure 4) under the same conditions.

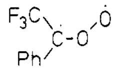
Discussion

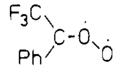
The oxidation products observed in the reactions of carbenes **3** and **11** with O_2 under the conditions of matrix-isolation are typical for the reactions of triplet carbenes.[1-3] The initial step is the addition of O_2 to give carbonyl *O*-oxides **1** and **2**, respectively. These compounds are very labile toward irradiation and rearrange to dioxiranes (only definitely observed for **1**) or split-off oxygen atoms to produce ketones **6** or **15**.

IR Spectra of Carbonyl *O*-Oxides 1 and 2. Compounds **1** and **2** have strong characteristic bands in the IR at 943 and 997 cm^{-1}, respectively, which show isotopic shifts of 35 cm^{-1} if **1** and **2** are doubly ^{18}O-labeled. These large shifts (3.7% and 3.5%) are only possible if O–O stretching modes (doubly labeled) contribute much to these vibrations. The corresponding band in benzophenone *O*-oxide (**18**) was observed at 897 cm^{-1} (35 cm^{-1} or 3.9% isotopic shift),[2a] in *o*-chlorobenzaldehyde *O*-oxide at 901 cm^{-1} (30 cm^{-1} or 3.3% isotopic shift),[2b] and in benzoyl chloride *O*-oxide at 890 cm^{-1} (50 cm^{-1} or 5.6% isotopic shift).[3]

If benzophenone *O*-oxide (**18**) is used as a reference, substitution of one Ph by Cl or two Ph by H and *o*-chlorophenyl does not have much effect on the frequency of the O–O stretching vibration. Substitution of Ph by CF_3, however, gives rise to a 50-cm^{-1} shift per CF_3 group. The isotopic shift in **1**, **2**, and **18** (3.5–3.9%) is not much changed by the CF_3 substitution, and thus the contribution of O–O stretching modes to these vibrations has the same magnitude in all three compounds. Substitution of Ph by the strong electron-withdrawing CF_3 group increases the O–O bond strength in carbonyl *O*-oxides.

For carbonyl *O*-oxide **1**, syn and anti isomers **1a** and **1b** can be formulated. The observation of only one O–O stretching vibration in the IR spectra might be explained either by the fact that only one isomer is formed or that both isomers show the same O–O stretching vibration.


1a


1b

Although the O–O stretching vibration is easily localized in the IR spectra of carbonyl *O*-oxides, it is difficult to assign IR bands to C–O stretching vibrations. In **1** a band at 1274 cm^{-1} (5 cm^{-1} or 0.4% isotopic shift) and in **2** a band at 1237 cm^{-1} (12 cm^{-1} or 0.9% isotopic shift) are close to the region where C–O stretching vibrations are expected from theoretical calculations.[10] In **18** the corresponding band was found at 1377 cm^{-1} (8 cm^{-1} or 0.6% isotopic shift). The small isotopic shifts in these bands, compared to C–O stretching vibrations in carbonyl compounds (typically) 30 cm^{-1} or 1.8%),[22] show that these vibrations are highly coupled to other vibrations of the skeleton. If the assignment given above is correct, substitution of Ph by CF_3 shifts the C–O stretching vibration to lower frequencies; the C–O bond strength is decreased.

UV Spectra and Photochemistry of Carbonyl *O*-Oxides 1 and 2. Carbonyl *O*-Oxides exhibit strong transitions in the UV–vis spectra between 395 and 460 nm.[1-3] Substitution of one Ph in **18** by CF_3 in **1** shifts this band from 422 nm[2a] to 378 nm, whereas substitution of Ph by Cl (λ_{max} = 400 nm)[3] or one Ph by H and one Ph by *o*-chlorophenyl (λ_{max} = 406 nm)[2b] has a comparatively smaller effect. Because of the low yields of **2** obtained, it was not possible to observe the corresponding transition for this compound.

To get some insight into the electronic structure of these transitions, CNDO/S[19] calculations on MINDO/3-UHF[20] optimized geometries of a large number of carbonyl *O*-oxides were performed. A general feature of all calculated

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[18] In the gas phase, the luminescence of **15** consists of fluorescence (λ_{max} 415 nm) and phosphorescence (λ_{max} 470 nm). Both parts of the luminescence spectrum are broad and structureless: Gandini, A.; Kutschke, K. O. *Proc. R. Soc. London, Ser. A* **1968**, *306*, 511–528.

[19] Baumann, H. F., ETH Zürich, 1975.

[20] Bischof, P. *J. Am. Chem. Soc.* **1976**, *98*, 6844–6849.

[21] Details of these calculations will be published in a subsequent paper.

[22] Pinchas, S.; Laulicht, I. In *Infrared Spectra of Labeled Compounds*; Academic: New York 1971; p 238.

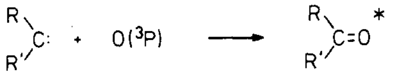
spectra is a strong $\pi \rightarrow \pi^*$ transition between 400 and 500 nm (for **18** λ_{max} = 455 nm, ϵ = 6.8.10^3) and a weak $n \rightarrow \pi^*$ transition between 600 and 800 nm (for **18** λ_{max} = 648 nm, ϵ = 40). The $\pi \rightarrow \pi^*$ transition is the strong one generally easily observed in the visible part of the spectrum. No direct evidence for the $n \rightarrow \pi^*$ transition has been reported, so far. Indirect evidence for the $n \rightarrow \pi^*$ transitions comes from the observation of the photochemistry of **1** if irradiated with $\lambda > 630$ nm, and **2** if irradiated with $\lambda > 590$ nm.

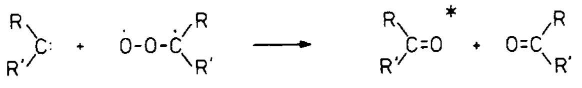
The photoproducts obtained from **1** are ketone **6** and dioxirane **8**; the only photoproduct observed from **2** is ketone **15**. Whether dioxirane **17** is not formed, or only not observable under the experimental conditions used, cannot be decided. If the irradiation ($\lambda > 305$ nm) of **17** does produce ester **16**, then **17** must have been formed in trace amounts; if not, it is very hard to prove the formation of **17** in the presence of large amounts of compounds exhibiting similar IR spectra.[14]

The reaction leading to the formation of **16** in high yields after the initial short-wavelength irradiation ($\lambda > 305$ nm) of O_2-doped matrices does not necessarily involve the oxidation of free carbene **11**. An alternative mechanism is the direct oxidation of photoexcited **12** (or **13**) in a matrix cage. A similar mechanism was discussed for the oxidation of other diazo compounds.[2b]

Chemiluminescence. Observations of chemiluminescence produced in reactions of **3** and **11** in O_2 saturated Freon glasses[15,16] or in O_2-doped Ar matrices[12] have appeared in the literature. In both cases it was shown that the luminescence was similar to the phosphorescence of the corresponding ketone. A consistent mechanistic interpretation of this phenomenon has not been given.

In previous publications,[2,7] I proposed two mechanisms for the reaction step leading to chemiluminescence in carbene oxidations: the combination of a free carbene and an oxygen atom ($O(^3P)$) in its ground state (reaction 1) and oxygen transfer from a carbonyl *O*-oxide to a free carbene (reaction 2).


(1)


(2)

Under conditions of matrix-isolation, reaction 2 is only important for small carbenes that are able to diffuse rapidly in solid Ar, or at temperatures where the matrix rapidly evaporates. Evidence for the formation of $O(^3P)$ came from the temperature dependence of the chemiluminescence.[2,7] The chemiluminescence starts at temperatures ($T > 15$ K) where only atoms but not larger particles like O_2 diffuse rapidly.[23] In one case, $O(^3P)$ was detected chemically.[7]

The glow curves (luminescence intensity as a function of temperature during warming the matrix from 10 to 60 K, warm-up rate 1–1.5 K/min) from the oxidations of **3** and **11** are very similar to the glow curves obtained in other carbene oxidations[2,7] (Figures 4 and 6) show several common features. (1) The chemiluminescence starts around 15 K. At this temperature the diffusion of O_2 in solid Ar is extremely slow. (2) A plateau or slow increase of the intensity is observed between 20 and 30 K. If the warm-up process of the matrix is stopped at a temperature in this region, the chemiluminescence decays within <5 min. The diffusion of O_2 is slow at this temperature, and complete reaction of the carbenes takes several hours. This shows that the reaction of free carbenes and O_2 is not the reaction producing chemiluminescence. Glow curves taken after the annealing show a "memory effect": the luminescence now starts at a temperature slightly higher than the temperature the matrix was kept at. (3) The luminescence maximum is reached near 42 K, depending on the O_2 concentration. At this temperature the diffusion of O_2 in solid Ar is fast (complete reaction within minutes). All free carbene reacts with O_2, and no further luminescence is observed at temperatures where the Ar rapidly evaporates and the reaction with the surface contamination is possible ($T > 50$ K).

The source of $O(^3P)$, required for the chemiluminescence according to reaction 1, is the photochemical decomposition of **1** or **2** (Schemes I and II), witnessed by the production of ketones **6** or **15**. Possible scavengers of $O(^3P)$ are O_2 or N_2, but N_2O is not formed, and O_3 is formed only at very high O_2 concentrations (>5%). Although $O(^3P)$ diffuses rapidly in solid Ar at $T > 8$ K,[23] it was shown by van de Bult et al. that it can be kept at 10 K for periods longer than 24 h and that luminescence, associated with atom recombination, lasts until the substrate reaches 60 K.[24] Fournier et al. observed the formation of molecular complexes between atoms and the matrix host prior to diffusion.[25] Therefore, it cannot be decided if the high temperature (>40 K) part of the glow curve is produced by unreacted $O(^3P)$, released from Ar complexes, or if more $O(^3P)$ is produced by the reaction of carbenes **3** or **11** and O_2 (Schemes I and II). At $T > 40$ K the diffusion of O_2 is fast enough but there is no evidence from the IR spectra (see paragraph at the end of paper about supplementary material) that the thermal reaction of carbenes and O_2 produces ketones and $O(^3P)$.

The chemiluminescence spectra for the reactions of carbenes **3** and **11** are identical with the phosphorescence spectra of ketones **6** and **15**, respectively. Aryl ketones have an effective intersystem crossing (ISC), and thus observation of only phosphorescence does not necessarily mean that the ketones are initially formed in their triplet states. From the fact that no fluorescence of **15** (with a less effective ISC) is observed, it can be concluded that **15** is formed initially in a triplet excited state.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer PE580 spectrometer interfaced to a Hewlett Packard 86 microcomputer. UV–vis spectra were obtained on a Varian Cary 17 D spectrometer connected to a Hewlett Packard 9835 microcomputer via a Hewlett Packard 3421 A data acquisition unit. Fluorescence and phosphorescence spectra were taken on a home-built instrument; light source, Osram XBO 150 W xenon high pressure arc lamp or HBO 200 W/2 mercury high pressure arc lamp in an Oriel lamp housing, Spex Minimate monochromator and various band pass filters for stray light rejection; detector, Optical multichannel analyzer consisting of an PARC OMA II system and Jobin Yvonne HR 320 polychromator with a 150 lines/mm grating (slit width 50–500 μm). The OMA was able to record a 250-nm range of the spectrum between 200 and 800 nm (0.5 nm/channel).

Matrix-Isolation Spectroscopy. Matrix experiments were performed by standard techniques[26] using an Air Products CSW-202 Displex closed cycle helium cryostat. CsI cold windows and KBr outer windows were used in the IR experiments; a saphire

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[23] For a review of reactions of matrix-isolated atoms, see: Perutz, R. N. *Chem. Rev.* **1985**, *85*, 77–96.

[24] Van de Bult, C. E.; Allamandola, L. J.; Baas, F.; van Ijzendoorn, L.; Greenberg, J. M. *J. Mol. Struct.* **1980**, *61*, 235–238.

[25] Fournier, J.; Lalo, C.; Deson, J.; Vermeil, C. *J. Chem. Phys.* **1977**, *66*, 2656–2659.

cold window and quartz outer windows were used in the UV–vis experiments. A nickel-plated, polished copper block was used to deposit matrices for obtaining luminescence spectra. The temperature of the matrix was controlled by an Air Products APD-E controller (gold vs Chromel thermocouple) or by an Lake Shore DRC 81C controller (silicon diode sensor) interfaced to a HP86 microcomputer.

Argon (Messer Griesheim, 99.9995%), oxygen (Messer Griesheim, 99.998%), $[^{18}O_2]$oxygen (Ventron, 99.8% isotopic purity), and very volatile organic compounds (**12**, **15**) were mixed in a gas handling system by standard manometric techniques. The ratio argon/oxygen/compound in typical experiments was 1000/10/1. Less volatile compounds were directly sublimed on the cold window and simultaneously a large excess of argon/oxygen was deposited. The degree of matrix-isolation was monitored by observing the line width of the IR bands as a function of the argon/compound ratio. Matrices were generally deposited at 28–30 K (ca. 15 mmol/h) to obtain optically clear matrices. Deposition at lower temperatures gave more highly scattering matrices but otherwise the same results.

Irradiations were carried out by using the same lamps as described for obtaining luminescence spectra or by an Osram HBO 500 W/2 mercury high pressure arc lamp. To avoid unnecessary heat load of the matrix, IR irradiation was absorbed by a 10-cm path length of water and by a Schott KG 1 filter (if only $\lambda > 300$ nm was required). For broad-band irradiation Schott cut-off filters were used (50% transmittance at the wavelengths specified); for narrow-band irradiation interference filters (Schott or Oriel) were used to isolate mercury lines.

Chemiluminescence Spectroscopy. Details of obtaining chemiluminescence spectra with an optical multichannel analyzer (OMA) and simultaneously glow curves (total luminescence as a function of the matrix temperature) are given elsewhere.[2b] The warm-up experiments were performed by either switching off the displex system at 10 K (free warm-up, giving a temperature rise of approximately 1 K/min in a highly reproducible manner) or by digitally controlling the temperature rise (0.5–2 K/min). In the free warm-up experiments the first and second stage of the expander module warm up simultaneously, and the first stage is always warmer than the second stage. This prevents the argon from subliming rapidly from the cold window to the first stage at temperatures where its vapor pressure is appreciable ($T > 35$ K). The matrix evaporated rapidly at $T > 55$ K. If only the second stage (cold window) is warmed by a heater, the argon sublimes rapidly to the cold first stage at $T > 43$ K and thus the usable temperature range is reduced. Otherwise, the results up to 43 K were identical with those in the free warm-up experiments.

Chemiluminescence spectra and glow curves were generally taken from matrices deposited on CsI windows. This allowed us to take IR spectra both prior to and after warming the matrix. Control experiments with matrices deposited on the surface of a nickel-plated copper block (high thermal conductivity to avoid small temperature differences between the center and outer portions of the matrix) did not show a dependence of the shape of the glow curves from the matrix support.

Materials. Sodium trifluoroacetophenone tosylhydrazide was prepared by treating the tosylhydrazone, dissolved in dry CH_2Cl_2, with 1.1 equiv of NaH (50% suspension in mineral oil). After removing the CH_2Cl_2 in vacuo, the residue was washed three times with pentane. The yellow salt was stored at −40 °C in an N_2 atmosphere and was stable at room temperature for several days. 1-Phenyl-2,2,2-trifluorodiazoethane (**4**)[27] was generated by gently heating the salt to 32–35 °C and directly sublimed on the cold window. IR (Ar, 10 K): 3074 (w), 2098 (s), 2090 (vs), 1605 (m), 1506 (s), 1368 (m), 1362 (m), 1353 (s), 1328 (s), 1275 (m), 1175 (s), 1150 (s), 1131 (s), 959 (s), 747 (m), 670 (m) cm^{-1}.

Bis(trifluoromethyl)diazomethane (**12**)[28] and hexafluoroacetone[29] were synthesized according to literature procedures. Phenyl trifluoroacetate was obtained from the reaction of phenol and trifluoroacetic acid anhydride[30] and was distilled prior to use. Trifluoroacetophenone (Aldrich) and trifluoroacetic acid anhydride (Aldrich) were reagent grade substances.

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Registry No. **1**, 111351-10-1; **2**, 111351-11-2; **3**, 81123-05-9; **6**, 434-45-7; **8**, 111351-13-4; **11**, 3142-79-8; **15**, 684-16-2; **18**, 111351-12-3.

Supplementary Material Available: IR, UV, and luminescence spectra of compounds prepared (3 pages). Ordering information is given on any current masthead page.

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(26) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597–7606.

(27) Diderich, G. *Helv. Chim. Acta* **1972**, *55*, 2103–2112.

(28) Sohn, D.; Sundermeyer, W. *Chem. Ber.* **1982**, *115*, 3334–3339.

(29) Anello, L. G.; van der Puy, M. *J. Org. Chem.* **1982**, *47*, 377–378.

(30) Weygand, F.; Röpsch, A. *Chem. Ber.* **1959**, *92*, 2095–2099.

Methyl Substituent Effects on Electrophilic Additions to Some Benzobicyclooctadienes

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Methyl hypoiodite (prepared from iodine plus iodic acid in methanol) has been added to 2-methyl-5,8-dimethoxy-1,4-dihydro-1,4-ethanonaphthalene. Four products were isolated and their structures established by 2-D NMR techniques. The stereochemistry of the epoxidation of the above olefin (and its 5,8-diacetoxy analogue) was studied in ether and in methylene chloride by using a series of substituted peroxybenzoic acids. The mechanistic implications of this work are considered in comparison with earlier work on the unsubstituted double bond analogues.

In recent years, a number of examples of electrophilic additions to benzobicyclooctadienes have been reported.[1-3] Paquette and co-workers[2] studied the stereochemistry of the addition of a number of electrophiles (*m*-chloroperbenzoic acid, oxymercuration, methylene addition, singlet oxygen) to 2-methyl-5,8-dimethoxy-1,4-dihydro-1,4-

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(1) (a) Provolotskaya, N. N.; Limasova, T. I. Berus, E. I.; Exner, O.; Barkhash, V. A. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, *6*, 1615. (b) Vorozlitsov, I. N.; Berus, E. I.; Derendvaev, B. G.; Barkhash, V. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1969**, *39*, 2264.

(2) Paquette, L. A.; Bellamy, F.; Wells, G. J.; Bohm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1981**, *103*, 7122.

(3) (a) Smith, W. B.; Stock, L.; Cornforth, Sir J. *Tetrahedron* **1983**, *39*, 1379. (b) Smith, W. B.; Saint, C.; Johnson, L. *J. Org. Chem.* **1984**, *49*, 3771. (c) Smith, W. B. *Ibid.* **1985**, *50*, 5731.