The sublimed, extremely air-sensitive crystals of **2** were found to be suitable for structure determination by X-ray crystallography.[16]

The molecular structure of **2** (Figures 1 and 2) confirms isolation of the monomeric [3]-manganocenophane as its 3,5-dichloropyridine adduct. Important distances and angles are given in the caption to Figure 1. The Mn–C distances in high-spin **2** are comparable to those in high-spin manganocene [2.380 (6) Å] and in 1,1′-dimethylmanganocene [2.433 (8) Å].[1] The two Mn–Cp interactions are the same, as indicated by the Mn–centroid distances. The bridge lies nearly on the pseudotwofold axis (the CP11–CB11–CP21–CB21 plane makes an angle of 6.5° with the Cp(centroid 1)–Mn–Cp(centroid 2) plane, and the nitrogen is placed neatly between pairs of Cp carbons, with nonbonded N- - -C distances near the sum of the van der Waals radii.

Structurally related to **2** are dichloro[1,3-(η^5-cyclopentadienyl)propane]M(IV), M = titanium (**3**), zirconium (**4**), hafnium (**5**).[17] In each of these molecules the $(CH_2)_3$ bridge is rotated ca. 36° away from the pseudotwofold axis, in contrast to **2**. In **3–5** the bridge location 36° away from the pseudotwofold axis accommodates the chlorine ligands—again between pairs of nonbonded carbons. We believe that, at the distances and angles involving the three-carbon link in **2–5**, the location of the link at ca. 0° or 36° to the twofold axis is primarily controlled by the ligand–cyclopentadienyl carbon nonbonded repulsions. On the basis of our examination of Dreiding models, it appears that placement of a $(CH_2)_3$ bridge 72° from the pseudotwofold axis is not likely, because this bridge is too small to span the required distance.

The range of the CCC angles in the bridge in **2** is similar to the 113.9(5)°–117.8(6)° range reported[17] for **3–5**. Even with the large bridge CCC angles in **2**, carbons CB11 and CB21 are displaced 0.11 (1) and 0.10 (1) Å, respectively, from the best Cp planes, to the side opposite manganese.[18] We suggest that unusually high negative charge density on CP11 and CP21 (other CP carbons as well) contributes to additional geminal carbon interactions to open CP11–CB11–CB2 and CP21–CB21–CB2 and that the preferred relief of this strain are bends at CP11–CB11 and CP21–CB21 rather than an increase of θ with increases of four N- - -C nonbonded repulsions.

The bonding in **2** may be described by the bent metallocene model.[2] In the equatorial plane half-filled frontier acceptor orbitals of $1a_1$, b_2, and $2a_1$ symmetry are available to interact with the nitrogen lone pair. The bond to nitrogen is best described as $(2a_1)^2(2a_1{}^*)^1$. The "half-bond" character of this molecular orbital is reflected in the unusually long Mn–N1 interaction [2.310 (6) Å].

In preliminary work, we have found that manganocene binds *two* molecules of 3,5-dichloropyridine under isolation conditions identical with those described for **2**. We are currently investigating $(-CH_2-)_3$ bridge geometric restraints as a possible significant contributor to the dramatic difference in Lewis acidity of **2** compared to $MnCp_2$. We are also working toward isolation of base-free "short-bridge" "electron-imbalanced" metallocenophanes.

Acknowledgment. This work was supported by the University of California Committee on Research, by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by a Grant-in-Aid to J.T.W. from the Society of Sigma Xi. The SQUID Susceptometer system was purchased through a grant to the University of Southern California (NSF CHE 8211349). We thank Professor Christopher Reed and Dr. Peter Boyd for assistance with the SQUID device.

Registry No. 2, 87174-48-9; $Li_2[C_5H_4(CH_2)_3C_5H_4]$, 87174-47-8; $MnBr_2$, 13446-03-2; bis(η^5-2,4-cyclopentadien-1-yl)bis(*N*-3,5-dichloropyridine)manganese, 87174-49-0.

Supplementary Material Available: Tables of positional and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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[15] The yield of red/orange oil based on $MnBr_2$ was 29% and is believed to be a mixture of monomer and oligomers. The yield of **2** based on the red/orange oil was 11% or an overall yield based on $MnBr_2$ of 3%.

[16] The structure was solved on the basis of a model including disorder in the location of CB2 (29% of CB2's are found "reflected" through the CP11–CB11–CP21–CB21 plane). Reported results involving CB2 are based on the major (71%) CB2 site. A full account of the crystallography is given: Weed, J. T. Ph.D. Thesis, University of California, Riverside, CA, 1983.

[17] (a) Ti(IV): Epstein, E. F.; Bernal, I. *Inorg. Chim. Acta* **1973**, *7*, 211–218. (b) Zr(IV): Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *J. Organomet. Chem.* **1974**, *80*, 79–90. (c) Hf(IV): Saldarriaga-Molina, C. H.; Clearfield, A.; Bernal, I. *Inorg. Chem.* **1974**, *13*, 2880–2885.

[18] Stoeckli-Evans, H.; Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1980**, *194*, 91–101 (definition of β, which is 4.0° in **2**).

Trimethylenemethane Cation Radical: Photosensitized (Electron-Transfer) Generation and Reactivity[1]

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Received May 2, 1983

Because of the unique structural and mechanistic features of a trimethylenemethane species,[2] both the photochemical[3a,b] and thermal[2] reactions of methylenecyclopropanes have been extensively explored. The ordinary photolysis of methylenecyclopropanes, however, seems not to generate any trimethylenemethane species since the photolysis of methylenecyclopropanes differs markedly from their thermolysis.[3] We report here the photosensitized (electron-transfer) generation of a novel trimethylenemethane species, a cation radical, and its reactivity, which provides both the degenerate methylenecyclopropane rearrangement and the very efficient molecular oxygen trapping.

While 2,2-diphenyl-1-methylenecyclopropane **1a**[3c,d] efficiently quenches luminescence of anthraquinone,[4] no chemical change was observed upon irradiation of **1a** with anthraquinone as an electron-acceptor sensitizer in acetonitrile at 15 °C with >350-nm light under Ar. Irradiation of the dideuterio analogue d_2-**1a** under the same conditions, however, provided the degeneracy in d_2-**1a** that is similar to that observed in the thermolysis of d_2-**1a**.[3d] Thus, d_2-**1a** gradually diminished during irradiation with an increase in the ratio of d_2-**1a**′/d_2-**1a** and a ca. 1:1 mixture of d_2-**1a** and d_2-**1a**′ was isolated in a quantitative yield after a 2-h irradiation.[5] The chloranil sensitization also involved the degenerate rearrangement, but neither phenanthraquinone nor benzophenone sensitized. These evidences together with the calculated free-energy change (ΔG)[6] required for the possibility of an electron

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[1] Organic Photochemistry. 64. No. 63, see: Kumagai, T.; Kawamura, Y.; Mukai, T. *Tetrahedron Lett.* **1983**.

[2] Berson, J. A. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, p 311 and references cited therein.

[3] (a) Kende, A. S.; Goldschmidt, Z.; Smith, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 7606. (b) Gros, W. A.; Luo, T.; Gilbert, J. C. *Ibid.* **1976**, *98*, 2019. (c) Gilbert, J. C.; Kurzawa, F. *J. Org. Chem.* **1979**, *44*, 2123. (d) Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 2168.

[4] Quenching experiments were carried out in aerated acetonitrile at 20 °C. The Stern–Volmer slopes ($k_q\tau$) for **1a**, **1b**, **1c**, and **1d** are 1.58×10^3, 9.08×10^2, 1.55×10^4, and 2.60×10^4 M^{-1}, respectively. The quenching rate constants (k_q) for **1a**, **1b**, **1c**, and **1d** are calculated to be 5.6×10^8, 3.2×10^8, 5.5×10^9, and 9.3×10^9 $M^{-1}\,s^{-1}$, respectively, on the basis of the triplet lifetime of anthraquinone, 2.8×10^{-6} s in the above conditions, which was estimated by using a diffusion-controlled quencher, 1,2,4,5-tetramethoxybenzene ($E_{1/2}{}^{ox} = +0.75$ V vs. SCE, $\Delta G = -25.1$ kcal/mol, $k_q\tau = 4.25 \times 10^4$ M^{-1}), by the reported method.[6a]

[5] The structures of d_2-**1a** and d_2-**1a**′ were determined by comparisons of ^1H NMR chemical shifts with those reported.[3d]

[6] (a) Calculated by using half-wave reduction potentials ($E_{1/2}{}^{red}$)[6b] and triplet energies (E_T)[6c] of the sensitizers and oxidation potentials[8] of **1**: Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) $E_{1/2}{}^{red}$(chloranil) = +0.01 V vs. SCE, $E_{1/2}{}^{red}$(anthraquinone) = −0.94 V vs. SCE, and $E_{1/2}{}^{red}$(phenanthraquinone) = −0.66 V vs. SCE: Peover, M. E. *J. Chem. Soc.* **1962**, 4540. $E_{1/2}{}^{red}$(benzophenone) = −1.72 V vs. SCE: Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1973. (c) E_T(chloranil) = 62 kcal/mol: Kasha, M. *Chem. Rev.* **1947**, *41*, 401. E_T(anthraquinone) = 62.7 kcal/mol and E_T(benzophenone) = 69.2 kcal/mol: Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973. E_T(phenanthraquinone) = 50 kcal/mol: Farid, S.; Scholz, K.-H. *J. Chem. Soc., Chem. Commun.* **1969**, 572.

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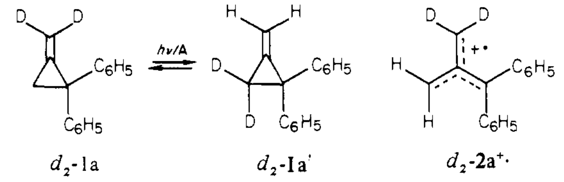
Table I. Calculated ΔG Values for Electron-Transfer Process between **1** and Sensitizer Triplets and Isolated Yields (%) of Dioxolanes 3 and 4

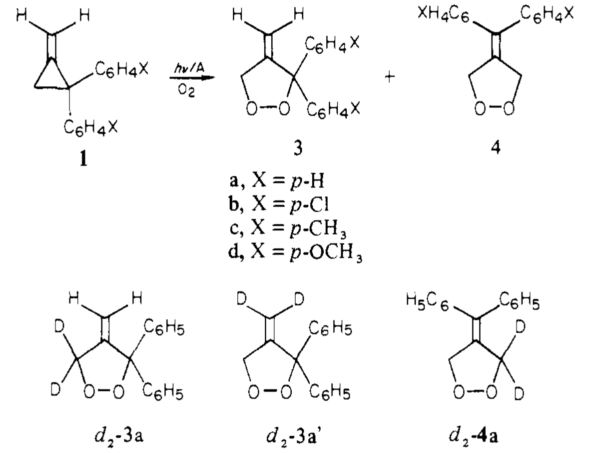
	1b				1a				1c				1d			
	ΔG,[a]	yield			ΔG,[a]	yield			ΔG,[a]	yield			ΔG,[a]	yield		
sensitizer	kcal/mol	3b	4b	con[b]	kcal/mol	3a	4a	con[b]	kcal/mol	3c	4c	con[b]	kcal/mol	3d	4d	con[b]
chloranil	−20.3	51	19	81	−21.4	53	14	79	−25.6	62	10	85	−32.5	56	*c*	66
anthraquinone	+0.9	20	9	44	−0.2	25	8	40	−4.4	43	13	69	−11.3	58	4	73
phenanthraquinone	+7.2	no reaction			+6.0	*c*	*c*	8	+1.9	17	*c*	32	−5.0	40	3	64
benzophenone	+12.4	no reaction			+11.3	no reaction			+7.1	no reaction			+0.2	40	*c*	53

[a] See ref 6. [b] Con: conversion of **1** after 30-min irradiation. [c] Less than 2% yields.

Scheme I



Scheme II



transfer between **1a** and each triplet sensitizer (Table I) suggest that the degenerate rearrangement proceeds via the cation radical d_2-**2a**$^{+\cdot}$ generated by an electron-transfer process, but not by an ordinary energy-transfer process (Scheme I).

For the further confirmation of the generation of the cation radical, the capability of trapping molecular oxygen[7] was tested for **1a**, d_2-**1a**, and the para-substituted isomers **1b**, **1c**, and **1d** whose oxidation potentials[8] linearly correlate with the Hammett constant σ_p^+. When a solution of **1a** with anthraquinone or chloranil in oxygen-saturated acetonitrile was irradiated, dioxolanes **3a** (mp 72 °C)[9] and **4a** (mp 130 °C)[9] were isolated, but oxygenation was suppressed under both phenanthraquinone and benzophenone sensitizations. As expected, d_2-**1a** afforded a 1:1 mixture of d_2-**3a** and d_2-**3a**′ together with d_2-**4a**.[10] It should be noted that the electron-acceptor sensitizers effective to the degenerate rearrangement are effective to the oxygenation reaction too. Thus, the intermediacy of the cation radical is likely suggested again for the oxygenation reaction (Scheme II).

Scheme III

$$^{3}\mathrm{A}^{*} + d_2\text{-}\mathbf{1a} \rightarrow \mathrm{A}^{-\cdot} + d_2\text{-}\mathbf{1a}^{+\cdot}$$

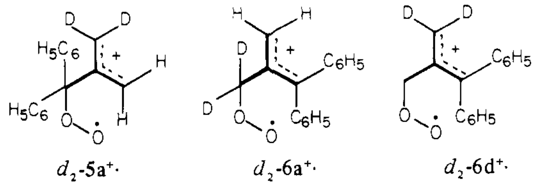
$$d_2\text{-}\mathbf{1a} \leftarrow d_2\text{-}\mathbf{1a}^{+\cdot} \rightleftarrows d_2\text{-}\mathbf{2a}^{+\cdot} \rightleftarrows d_2\text{-}\mathbf{1a}'^{+\cdot} \rightarrow d_2\text{-}\mathbf{1a}'$$

$$d_2\text{-}\mathbf{2a}^{+\cdot} + \mathrm{O}_2 \rightarrow d_2\text{-}\mathbf{5a}^{+\cdot} + d_2\text{-}\mathbf{6a}^{+\cdot} + d_2\text{-}\mathbf{6a}'^{+\cdot}$$

$$d_2\text{-}\mathbf{5a}^{+\cdot} \rightarrow d_2\text{-}\mathbf{3a} + d_2\text{-}\mathbf{3a}'$$

$$d_2\text{-}\mathbf{6a}^{+\cdot} \rightarrow d_2\text{-}\mathbf{3a} + d_2\text{-}\mathbf{4a}$$

$$d_2\text{-}\mathbf{6a}'^{+\cdot} \rightarrow d_2\text{-}\mathbf{3a}' + d_2\text{-}\mathbf{4a}$$



If this mechanism is correct, phenanthraquinone and benzophenone should sensitize the oxygenation reactions of the more electron-donating isomers such as **1c** and **1d**, which more efficiently quench luminescence of anthraquinone than **1a**[4] because an electron-transfer process can be still expected in these combinations as shown in the table. In fact, **1c** was oxygenated under the phenanthraquinone sensitization as well as anthraquinone and chloranil, and **1d** was oxygenated even under the benzophenone sensitization. The less electron-donating **1b** was expectedly oxygenated only under chloranil and anthraquinone sensitizations. In terms of the capability of trapping molecular oxygen, a trimethylenemethane cation radical appeared to capture molecular oxygen more efficiently than cyclic trimethylenemethane triplet biradicals,[11] which were reported to consume molecular oxygen under the moderately pressurized conditions. The isolated yields of dioxolanes[12] were listed in Table I.

Combining these experimental results, it should be clear that a trimethylenemethane cation radical serves as a key intermediate both for the degenerate rearrangement and oxygenation reaction of **1**. A plausible electron-transfer mechanism can be rationalized as follows: the initial reductive quenching of the excited triplet sensitizer ^{3}A* by d_2-**1a** generates d_2-**1a**$^{+\cdot}$ and the sensitizer anion radical A$^{-\cdot}$, the former of which in turn collapses to d_2-**2a**$^{+\cdot}$, and

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(7) Schaap, A. P.; Lopez, L.; Anderson, S. D.; Gagnon, S. D. *Tetrahedron Lett.* **1982**, 5493. Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663. Futamura, S.; Kusunose, S.; Ohta, H.; Kamiya, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 1223. Mizuno, K.; Kamiya, N.; Otsuji, Y. *Chem. Lett.* **1983**, 477.

(8) The half-wave oxidation potentials of **1a** (+1.83 V vs. SCE), **1b** (+1.88 V vs. SCE), **1c** (+1.65 V vs. SCE), and **1d** (+1.35 V vs. SCE) were measured by cyclic voltammetry at a platinum electrode in acetonitrile with 0.1 M tetraethylammonium perchlorate as a supporting electrolyte.

(9) **3a**: mp 72 °C; *m/e* 238 (M$^+$, 30%), 206 (M$^+$ − 36, 100%); ^{1}H NMR (CCl_4) δ 4.74 (2 H, dd, J = 2.2, 2.2 Hz), 4.86 (1 H, td, J = 2.2, 0.8 Hz), 5.22 (1 H, td, J = 2.2, 0.8 Hz), 7.13–7.34 (10 H, m). **4a**: mp 130 °C; *m/e* 238 (M$^+$, 39%), 206 (M$^+$ − 32, 100%); ^{1}H NMR (CCl_4) δ 4.61 (4 H, s), 7.02–7.33 (10 H, m).

(10) At the 22.5% conversion of a mixture of d_2-**1a** and d_2-**1a**′, the ratio of d_2-**1a** and d_2-**1a**′ was 97:3, while the yields of a mixture of d_2-**3a** and d_2-**3a**′ and the isomeric dioxolane d_2-**4a** were 14 and 6%, respectively.

(11) Wilson, R. M.; Geiser, F. *J. Am. Chem. Soc.* **1978**, *100*, 2225.

(12) ^{1}H NMR spectra of dioxolanes (in CCl_4): **3b** δ 4.73 (2 H, dd, J = 2.0, 2.0 Hz), 4.84 (1 H, td, J = 2.0, 0.8 Hz), 5.26 (1 H, td, J = 2.0, 0.8 Hz), 7.09–7.50 (8 H, m); **4b** δ 4.68 (4 H, s), 7.08–7.50 (8 H, m); **3c** δ 2.30 (6 H, s), 4.67 (2 H, dd, J = 2.0, 2.0 Hz), 4.80 (1 H, t, J = 2.0 Hz), 5.16 (1 H, t, J = 2.0 Hz), 6.97–7.21 (8 H, m); **4c** δ 2.30 (6 H, s), 4.57 (4 H, s), 6.88–7.08 (8 H, m); **3d** δ 3.69 (6 H, s), 4.67 (2 H, dd, J = 2.1, 2.1 Hz), 4.79 (1 H, td, J = 2.1, 0.5 Hz), 5.14 (1 H, td, J = 2.1, 0.5 Hz), 6.70 (4 H, m), 7.16 (4 H, m); **4d** δ 3.67 (6 H, s), 4.56 (4 H, s), 6.62–7.10 (8 H, m).

then the recombination to d_2-**1a**$^{+}\cdot$. and d_2-**1a**$'^{+}\cdot$ followed by the back electron transfer probably from $A^{-}\cdot$ furnishes the degenerate rearrangement. The fact that **1** did not isomerize to the thermodynamically more stable isomers, 1-(diphenylmethylene)cyclopropane, may suggest that d_2-**2a**$^{+}\cdot$ may be a bisected species in which the pivot carbon does not enter the allylic system because of steric restrictions. Molecular oxygen[13] then captures d_2-**2a**$^{+}\cdot$ faster than recombination,[10] giving d_2-**5a**$^{+}\cdot$, d_2-**6a**$^{+}\cdot$, and d_2-**6a**$'^{+}\cdot$, and the cyclization followed by the back electron transfer gives dioxolanes (Scheme III).

Further experiments are continuing on the photosensitized (electron-transfer) sigmatropic rearrangements and will be reported soon.

Registry No. 1a, 25152-47-0; **1b**, 87190-08-7; **1c**, 87190-09-8; **1d**, 87190-10-1; **2a**$^{+}\cdot$, 87190-11-2; **3a**, 87190-12-3; **3b**, 87190-14-5; **3c**, 87190-15-6; **3d**, 87190-18-9; **4a**, 87190-13-4; **4b**, 87190-16-7; **4c**, 87190-17-8; **4d**, 87190-19-0; chloranil, 118-75-2; anthraquinone, 84-65-1; phenanthraquinone, 84-11-7; benzophenone, 119-61-9; 9,10-dicyanoanthracene, 1217-45-4.

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(13) The generation of superoxide anion radical seems to be unfeasible because chloranil, anthraquinone, and phenanthraquinone sensitize oxigenations in spite of endothermic electron transfers from these sensitizer anion radicals to oxygen. The possibility of the generation, however, can not be completely ruled out because a singlet sensitizer such as 9,10-dicyanoanthracene also sensitizes both the degenerate rearrangement and oxygenation of d_2-**1a**. Details will be reported separately.

Exchange Reactions of Halodiazirines. Synthesis of Fluorodiazirines

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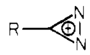
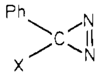
Received June 27, 1983

Bromo- and chloro-substituted aryl-, alkyl-, and alkoxycarbenes are available from the corresponding diazirines,[1] which are prepared by hypohalite oxidations of appropriate amidines.[2] Fluorodiazirines, however, cannot be synthesized in this way, so that these important precursors of *free* fluorocarbenes have hitherto been generated by hazardous direct fluorination procedures.[3] A simple and potentially general synthesis of monofluorodiazirines could be based upon F/Br or F/Cl exchange reactions of bromo- or chlorodiazirines. Graham's early suggestion that such exchanges might solvolytically proceed via diazirinium ions (e.g., **1**) was not supported by calculations indicating **1** (R = H) to have a *negative* delocalization energy and to be thermodynamically unstable relative to its linear (triplet) $HNCN^+$ isomer.[4a] Nevertheless, more recent calculations suggest that ion pairs involving cations **1** might be obtainable in polar solvents.[4b] Indeed, we found that bromophenyldiazirine could be converted to the unstable methoxyphenyldiazirine by treatment with methoxide ion in dimethylacetamide/HMPA.[5] This caused us to reexamine the scope of diazirine exchange chemistry, and we now disclose a significant expansion, which permits the preparation of new aryl- and (aryloxy)diazirines (and derived carbenes), including the first two examples of fluorodiazirines prepared without recourse to fluorination with elemental fluorine.

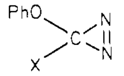


1

When heated to 50 °C at 0.01 mmHg for 20 h, commercially available n-$Bu_4N^+F^-$ (TBAF) trihydrate (mp, 60–62 °C, Aldrich Chemical Co.) melts with loss of most of its water of hydration. The resultant TBAF contains ~0.1 equiv of water (^1H NMR), has suffered ~10% decomposition to tributylamine and 1-butene, and *remains a liquid at 25 °C.*[6] Upon simply stirring with this TBAF preparation, neat bromophenyldiazirine (**2a**)[2] or chlorophenoxydiazirine (**3a**)[7] are converted to the corresponding, novel fluorodiazirines **2c** and **3b** in 65% and 55% isolated yields.



2a, X = Br
b, X = Cl
c, X = F
d, X = CN
e, X = N_3



3**a**, X = Cl
b, X = F

The preparation of **2c** from 1.25 mmol of **2a** with a 4-fold excess of TBAF required 4 h at 25 °C. The crystalline product mass was quenched with water and extracted 3× with pentane. HPLC-pure **2c** was obtained from the dried and stripped extract by Kugelrohr distillation at 45–50 °C (14 mmHg). Fluorophenyldiazirine was characterized by IR, UV, and ^1H, ^{13}C, and ^{19}F NMR spectroscopy.[8] Additionally, photolyses of **2c** ($\lambda > 300$ nm) in $Me_2C{=}CMe_2$, $Me_2C{=}CHMe$, and $Me_2C{=}CH_2$ gave 50–70% of the anticipated fluorophenylcarbene adducts,[9] identical with authentic samples from an alternative synthesis.[10] Fluorodiazirine **2c** could be similarly prepared from TBAF and chlorophenyldiazirine **2b** (74%), but the exchange was slower (16 h, 25 °C). Conversions of **2a** or **2b** to **2c** could also be done directly with $TBAF{\cdot}3H_2O$ in CH_3CN solution, but the reactions were very slow.

Fluorophenoxydiazirine **3b** was prepared from **3a** by stirring with 2-fold excess liquid TBAF at 0–5 °C for 16 h. Workup (see above) gave 55% of pure **3b** (bp 50 °C (14 mmHg). The new diazirine was identified spectroscopically[11] and by thermolysis with excess, degassed $Me_2C{=}CMe_2$ (150 °C, 3 h, sealed tube), which gave 35% of 1-fluoro-1-phenoxy-2,2,3,3-tetramethylcyclopropane,[12] the expected addition product of fluorophenoxycarbene.

Stirring 1 mmol of **2a** with 3 mmol of dry n-$Bu_4N^+CN^-$ (TBAC)[13] in 3 mL of dry CH_3CN (0 °C, 5 h) gave the thermally unstable cyanophenyldiazirine **2d**. This exchange could be in-

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(1) Review: Liu, M. T. H. *Chem. Soc. Rev.* **1982**, *11*, 127.

(2) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396. Moss, R. A.; Włostowska, J.; Guo, W.; Fedorynski, M.; Springer, J. P.; Hirshfield, J. M. *J. Org. Chem.* **1981**, *46*, 5049.

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(8) IR (neat, cm^{-1}) 1565, 1555 (s, N═N), 1165, 1155 (s, CF); UV (λ_{max}, nm, isooctane) 386 (ϵ 285), 382 sh, 366 (ϵ 296), 348 sh; ^1H NMR (δ, CCl_4) 7.5–7.2 (m, 3 H, aryl), 7.2–6.9 (m, 2 H, aryl); ^{19}F NMR ($CFCl_3$, $CDCl_3$) −154 ppm; ^{13}C NMR (δ(Me_4Si), $CDCl_3$) diazirine C at 70.7 (d, $J_{^{13}CF}$ = 264 Hz). For **2b** and **2a**, diazirine carbon ^{13}C resonances appear at δ 47.1 and 38.0, respectively.

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(11) IR (neat, cm^{-1}) 1545 (s, N═N), 1270, 1195 (br, s, CF and CO); UV (λ_{max}, nm, isooctane) 356 (ϵ 200), 350 sh, 339 (ϵ 183), 325 sh; ^1H NMR (δ, CCl_4) ~7.20 (m, aryl); ^{19}F NMR ($CFCl_3$, $CDCl_3$) −116 ppm; ^{13}C NMR (δ(Me_4Si), $CDCl_3$) diazirine C at 86.7 (d, $J_{^{13}CF}$ = 271 Hz). ^{13}C diazirine C resonances appear at δ 68.9 and 55.8 for **3a** and bromophenoxydiazirine, respectively.

(12) ^1H NMR (δ, CCl_4) 1.0 (d, $^4J_{HF}$ = 2.5 Hz, 6 H, 2 Me), 1.2 (d, $^4J_{HF}$ = 1.2 Hz, 6 H, 2 Me), 6.8–7.4 (m, 5 H, aryl). Anal. C, H.

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