then the recombination to d_2-**1a**$^{+}$· and d_2-**1a**$'^{+}$· followed by the back electron transfer probably from A^{-}· 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**$^{+}$· 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**$^{+}$· faster than recombination,[10] giving d_2-**5a**$^{+}$·, d_2-**6a**$^{+}$·, and d_2-**6a**$'^{+}$·, 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**$^{+}$·, 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.

(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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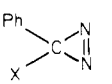
Bromo- and chloro-substituted aryl-, alkyl-, and alkoxycarbenes are available from the corresponding diazirines,[1] which are prepared by hypohalite oxidations of appropriate amidines.[2] Fluorodiazirines, however, cannot be synthesized in this way, so that these important precursors of *free* fluorocarbenes 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

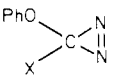
1

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.

When heated to 50 °C at 0.01 mmHg for 20 h, commercially available *n*-Bu$_4$N^{+}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 (^{1}H 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 chloro-



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



3a, X = Cl
b, X = F

phenoxydiazirine (**3a**)[7] are converted to the corresponding, novel fluorodiazirines **2c** and **3b** in 65% and 55% isolated yields.

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 ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.[8] Additionally, photolyses of **2c** ($\lambda > 300$ nm) in Me$_2$C=CMe$_2$, Me$_2$C=CHMe, and Me$_2$C=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·3H$_2$O in CH$_3$CN 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$_2$C=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$_4$N^{+}CN^{-} (TBAC)[13] in 3 mL of dry CH$_3$CN (0 °C, 5 h) gave the thermally unstable cyanophenyldiazirine **2d**. This exchange could be in-

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(6) Cf.: Pless, J. *J. Org. Chem.* **1974**, *39*, 2644. See also: Sharma, R. K.; Fry, J. L. *J. Org. Chem.* **1983**, *48*, 2112.
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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; ^{1}H 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$_4$Si), 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.
(9) Ławrynowicz, W.; Cox, D. P., unpublished work in this laboratory.
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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; ^{1}H NMR (δ, CCl$_4$) ~7.20 (m, aryl); ^{19}F NMR (CFCl$_3$, CDCl$_3$) −116 ppm; ^{13}C NMR (δ(Me$_4$Si), 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) ^{1}H 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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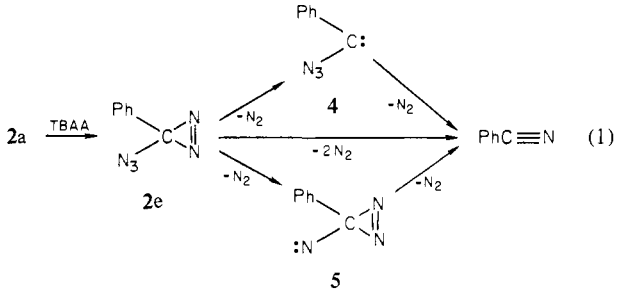
directly demonstrated and synthetically utilized in the following way. TBAC, CH_3CN, and an alkene (4, 10, and 20 mmol, respectively) were stirred with 1 mmol of **2a** (−15 °C, dark, 15 h), whereupon TLC revealed the absence of **2a**. Additional alkene was added and the solution was irradiated ($\lambda > 300$ nm, −15 °C, 4 h). Thus, $Me_2C{=}CMe_2$ and $Me_2C{=}CHMe$ were converted in 37% and 25% isolated yields (based on **2a**) to the cyanophenylcyclopropane derivatives expected from the trapping of cyanophenylcarbene.[14] The cyclopropanes were identical (NMR) with authentic samples prepared by an alternative synthesis.[15] TBAC exchange also converted **2b** to **2d** but attempted exchanges with diazirine **3a** in the presence of $Me_2C{=}CMe_2$ or $Me_2C{=}CH_2$ gave only an oily red polymer; neither cyanophenoxydiazirine nor cyanophenoxycyclopropanes were detectable.

Stirring diazirine **2a** with a 6-fold excess of anhydrous *n*-$Bu_4N^+N_3^-$ (TBAA)[16] in CH_3CN at 25 °C gave N_2 evolution (manometric $k_{obsd} \sim 1.1 \times 10^{-4}$ s^{-1}, $t_{1/2} \sim 110$ min) and a 90% yield of benzonitrile, identified by spectroscopic comparisons to an authentic sample. A similar reaction with chlorodiazirine **2b** was very much slower (still incomplete after 7 days) and gave only 40% of PhCN as well as 16% of recovered **2b**. We attribute the formation of benzonitrile to the decomposition of an unstable, intermediate azidophenyldiazirine (**2e**), which might occur concertedly with loss of $2N_2$ or sequentially via either the azidocarbene **4** or the nitrenodiazirine **5** (eq 1). Neither **4** nor **5** could be



(1)

trapped with $Me_2C{=}CMe_2$. If such intermediates intervene, they must be short-lived. A possibly related process converts 2-azido-2,3-dimethylazirine to N_2 and 2 molecules of acetonitrile.[17] Attempted exchanges between TBAA and **3a** or bromophenoxydiazirine did not proceed at 0 or 25 °C.

The mechanism(s) of the diazirine exchange reactions reported here are under active investigation. Preliminary evidence is consistent with the intermediacy of substituent-stabilized diazirinium ions **1**, R = Ph or PhO. Thus, after equimolar 10-fold excesses of diazirines **2b** and **3a** had been allowed to compete for 1 equiv of anhydrous TBAF at 0–5 °C, HPLC and ^{19}F NMR indicated the product to be diazirine **3b** in ≥95% purity. The preferential formation of the phenoxy-substituted fluorodiazirine is in keeping with a kinetically controlled exchange proceeding through a cationic intermediate such as **1**, R = PhO. Presumably, the diazirinium ion is intimately paired with a halide counterion.[4b]

The reactions described here greatly enlarge the scope and potential of diazirine chemistry. We are continuing our mechanistic and synthetic studies of these and related diazirines and of their derivative carbenes.

Acknowledgment. We are grateful to Dr. D. Z. Denney and to R. Beveridge for ^{19}F and ^{13}C NMR spectra, respectively. We thank the National Science Foundation for financial support.

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Combined ^{17}O NMR Spectra and ^{18}O Isotope Effects in ^{13}C NMR Spectra for Oxygen Labeling Studies. Carbon → Sulfur Oxygen Migration in the Aqueous Chlorination of Mercapto Alcohols

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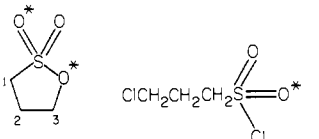
We wish to report a valuable extension of the NMR method of locating oxygen labels and to illustrate its application by demonstrating both the presence and absence of a carbon → sulfur oxygen migration in the chlorination of mercapto alcohols. Our procedure, in addition to utilizing the characteristic α and β ^{18}O isotope effects on ^{13}C NMR spectra,[1] takes advantage of the fact that ^{18}O-labeled compounds from commercial sources[2] normally have a considerable enrichment in ^{17}O content, which makes it possible to obtain further information about the environment of the oxygen label from the ^{17}O NMR spectrum of the same sample.[3]

In previous work[4] we showed that aqueous chlorination of 2-mercapto-1-ethanol (**1a**) and 3-mercapto-1-propanol (**1b**) proceeds as follows:

$$\underset{\textbf{1a}}{HOCH_2CH_2SH} \xrightarrow{Cl_2,\ H_2O} \underset{\textbf{2a}}{HOCH_2CH_2SO_2Cl} + \underset{\textbf{3a}}{ClCH_2CH_2SO_2Cl}$$

$$\underset{\textbf{1b}}{HOCH_2CH_2CH_2SH} \xrightarrow{Cl_2,\ H_2O} \underset{\textbf{4b}}{\text{cyclic sulfonyl chloride}} + \underset{\textbf{3b}}{ClCH_2CH_2CH_2SO_2Cl}$$

We have now carried out these reactions in oxygen-labeled[2] D_2O. 3-Mercapto-1-propanol (**1b**) gave a 2:1 mixture of **4b** and **3b** with the indicated positions of the heavy oxygen atoms being assigned as shown below. The ^{13}C NMR spectrum[3] of the reaction mixture



showed two sets of three singlets appropriate for **4b** and **3b**. With the addition of natural abundance **4b** a third set of three singlets was apparent very slightly downfield from those for labeled **4b**; the ^{18}O-induced ^{13}C shifts for the latter are 21, 6, and 43 ppb for C-1, C-2, and C-3, respectively. Comparison of these with the corresponding values of 31, 7, and 46 ppb found for **4b** with all three oxygens labeled[5] shows that the endocyclic oxygen and one of the sulfonyl oxygens are labeled in the reaction product.

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(2) "Water-^{18}O (not normalized) (98 atom % ^{18}O, 95 atom % D)", and containing 0.5 atom % ^{17}O, i.e., about 12 times natural abundance, supplied by MSD Isotopes Division of Merck Frosst Canada Inc., Montreal, Canada. Reactions were typically carried out by bubbling Cl_2 for 15 s through a solution of the substrate (0.1–0.5 mmol) in D_2O* (0.2–1.0 mL) cooled in an ice bath, followed by immediate workup by extraction with CH_2Cl_2 and evaporation of solvent.

(3) NMR spectra were recorded at 50.3 (^{13}C) and 27.1 MHz (^{17}O) with a Varian XL-200. The ^{18}O shifts were measured with an estimated precision of ±0.1 Hz (±2 ppb; 1 ppb = 0.001 ppm) with sweep widths of 1.5–2 K with 32 K transforms. The ^{17}O spectra obtained by using a spin–echo sequence gave shieldings to ±1 ppm. Integrations have estimated precisions of ±10% (^{17}O) and ±5% (^{13}C and ^{1}H).

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