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 oxygen¹³ 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.

Exchange Reactions of Halodiazirines. Synthesis of Fluorodiazirines

D. Phillip Cox, Robert A. Moss,* and Jacek Terpinski

Department of Chemistry, Rutgers University New Brunswick, New Jersey 08903 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 bromoor 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 aryland (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*-Bu₄N⁺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 $\sim 10\%$ 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-



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 $3 \times$ 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, ¹³C, and ¹⁹F NMR spectroscopy.⁸ Additionally, photolyses of 2c ($\lambda > 300$ nm) in Me₂C=CMe₂, Me₂C=CHMe, and Me₂C=CH₂ 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-3H₂O in CH₃CN 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 spectroscopically¹¹ and by thermolysis with excess, degassed Me₂C=CMe₂ (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-Bu₄N⁺CN⁻ $(TBAC)^{13}$ in 3 mL of dry CH₃CN (0 °C, 5 h) gave the thermally unstable cyanophenyldiazirine 2d. This exchange could be in-

(9) Lawrynowicz, W.; Cox, D. P., unpublished work in this laboratory. (10) Moss, R. A.; Przybyla, J. R. Tetrahedron 1969, 25, 647.

⁽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.

⁽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.;

 ⁽²⁾ Graham, W. H. J. Am. Chem. 306, 1965, 97, 4550. Moss, K. A.,
Włostowska, J.; Guo, W.; Fedorynski, M.; Springer, J. P.; Hirshfield, J. M.
J. Org. Chem. 1981, 46, 5049.
(3) Mitsch, R. A.; Neuvar, E. W.; Koshar, R. J.; Dybvig, D. H. J. Heterocycl. Chem. 1965, 2, 371. Mitsch, R. A. Ibid. 1966, 3, 245. Mitsch, R.
A. J. Org. Chem. 1968, 33, 1847. Zollinger, J. L.; Wright, C. D.; McBrady,
J. U. Elwing, P. M. Elwing, F. A. Watching, C. A. Mitsch, P. A. Mossawa, and A. Markawa, an J. J.; Dybvig, D. H.; Fleming, F. A.; Kurhajec, G. A.; Mitsch, R. A.; Neuvar, E. W. *Ibid.* **1973**, *38*, 1065. Meyers, M. D.; Frank, S. *Inorg. Chem.* **1965**, 5, 1455.

^{(4) (}a) Krogh-Jespersen, K. Tetrahedron Lett. 1980, 21, 4553. Krogh-Jespersen, K.; Young, C. M.; Moss, R. A.; Włostowski, M. Ibid. 1982, 23. 2339.

⁽⁵⁾ Włostowska, J.; Moss, R. A.; Guo, W.; Chang, M. J. Chem. Commun. 1982, 432.

¹⁹⁸², 432. (6) Cf.: Pless, J. J. Org. Chem. **1974**, 39, 2644. See also: Sharma, R. K.; Fry, J. L. J. Org. Chem. **1983**, 48, 2112. (7) Moss, R. A.; Perez, L. A.; Guo, W.; Włostowska, J.; Krogh-Jespersen, K. J. Org. Chem. **1982**, 47, 4177. (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 , CCl₄) 7.5–7.2 (m, 3 H, aryl), 7.2–6.9 (m, 2 H, aryl); ¹⁹F NMR (CFCl₃, CDCl₃) –154 ppm; ¹³C NMR (δ (Me₄Si), CDCl₃) diazirine C at 70.7 (d, J¹³_{CF} = 264 Hz). For **2b** and **2a**, diazirine carbon ¹³C resonances appear at δ 47.1 and 38.0. respectively.

^{38.0,} respectively.

⁽¹¹⁾ IR (neat, cm⁻¹) 1545 (s, N=N), 1270, 1195 (br, s, CF and CO); UV $(\lambda_{max}, nm, isooctane)$ 356 (ϵ 200), 350 κ , 339 (ϵ 183), 325 κ ; ¹H NMR (δ , CCl₄) ~7.20 (m, aryl); ¹⁹F NMR (CFCl₃, CDCl₃) -116 ppm; ¹³C NMR (δ (Me₄Si), CDCl₃) diazrine C at 86.7 (d, J^{13}_{CF} = 271 Hz). ¹³C diazrine C resonances appear at δ 68.9 and 55.8 for 3a and bromophenoxydiazirine, respectively

^{(12) &}lt;sup>1</sup>H NMR (δ , CCl₄) 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. (13) Kobler, H.; Munz, R.; Gasser, G. A.; Simchen, G. *Liebigs Ann. Chem.*

^{1978, 1937.}

directly demonstrated and synthetically utilized in the following way. TBAC, CH₃CN, 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, Me₂C=CMe₂ and Me₂C=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 Me₂C=CMe₂ or Me₂C=CH₂ gave only an oily red polymer; neither cyanophenoxydiazirine nor cyanophenoxycyclopropanes were detectable.

Stirring diazirine **2a** with a 6-fold excess of anhydrous *n*-Bu₄N⁺N₃⁻ (TBAA)¹⁶ in CH₃CN at 25 °C gave N₂ evolution (manometric $k_{obsd} \sim 1.1 \times 10^{-4} \text{ s}^{-1}$, $t_{1/2} \sim 110$ 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 2N₂ or sequentially via either the azidocarbene **4** or the nitrenodiazirine **5** (eq 1). Neither **4** nor **5** could be



trapped with $Me_2C=CMe_2$. If such intermediates intervene, they must be short-lived. A possibly related process converts 2-azi-do-2,3-dimethylazirine to N_2 and 2 molecules of acetonitrile.¹⁷ Attempted exchanges between TBAA and **3a** or bromophen-oxydiazirine 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 ¹⁹F NMR indicated the product to be diazirine 3b in \geq 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 ¹⁹F and ¹³C NMR spectra, respectively. We thank the National Science Foundation for financial support.

(17) Reference 4b. See also: Gallagher, T. C.; Storr, R. C. Tetrahedron Lett. 1981, 22, 2905.

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

J. F. King,* S. Skonieczny, K. C. Khemani, and

J. B. Stothers*

Department of Chemistry University of Western Ontario London, Ontario, Canada N6A 5B7 Received June 17, 1983

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 \rightarrow sulfur oxygen migration in the chlorination of mercapto alcohols. Our procedure, in addition to utilizing the characteristic α and β ¹⁸O isotope effects on ¹³C NMR spectra,¹ takes advantage of the fact that ¹⁸O-labeled compounds from commercial sources² normally have a considerable enrichment in ¹⁷O content, which makes it possible to obtain further information about the environment of the oxygen label from the ¹⁷O NMR spectrum of the same sample.³

In previous work⁴ we showed that aqueous chlorination of 2-mercapto-1-ethanol (1a) and 3-mercapto-1-propanol (1b) proceeds as follows:

$$HOCH_{2}CH_{2}SH \xrightarrow{Cl_{2}, H_{2}O} HOCH_{2}CH_{2}SO_{2}Cl + ClCH_{2}CH_{2}SO_{2}Cl \\ 2a \qquad 3a \\ HOCH_{2}CH_{2}CH_{2}SH \xrightarrow{Cl_{2}, H_{2}O} + ClCH_{2}CH_{2}CH_{2}SO_{2}Cl \\ 1b \qquad 4b \qquad 3b \\ HOCH_{2}CH_{2}CH_{2}SH \xrightarrow{Cl_{2}, H_{2}O} + ClCH_{2}CH_{2}CH_{2}SO_{2}Cl \\ ClCH_{2}CH_{2}CH_{2}SH \xrightarrow{ClCH_{2}SH} + ClCH_{2}CH_{2}CH_{2}SO_{2}Cl \\ ClCH_{2}CH_{2}CH_{2}SH \xrightarrow{Cl_{2}, H_{2}O} + ClCH_{2}CH_{2}CH_{2}SO_{2}Cl \\ ClCH_{2}CH_{2}CH_{2}SH \xrightarrow{ClCH_{2}SH} + ClCH_{2}CH_{2}CH_{2}CH_{2}SO_{2}Cl \\ ClCH_{2}CH_{2}CH_{2}SH \xrightarrow{ClCH_{2}SH} + ClCH_{2}CH_{2}CH_{2}SO_{2}Cl \\ ClCH_{2}CH_{2}CH_{2}SH \xrightarrow{ClCH_{2}SH} + ClCH_{2}CH_{2}CH_{2}SO_{2}Cl \\ ClCH_{2}CH_{2}CH_{2}CH_{2}SH \xrightarrow{ClCH_{2}SH} + ClCH_{2}CH_{2}CH_{2}CH_{2}SO_{2}Cl \\ ClCH_{2}CH_{2}CH_{2}CH_{2}SH \xrightarrow{ClCH_{2}SH} + ClCH_{2}CH_{2}CH_{2}CH_{2}SO_{2}Cl \\ ClCH_{2}CH_{2}CH_{2}CH_{2}CH_{2}SO_{2}Cl \\ ClCH_{2}CH_{2$$

We have now carried out these reactions in oxygen-labeled² 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 ¹³C NMR spectrum³ 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 ¹⁸O-induced ¹³C 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 labeled⁵ shows that the endocyclic oxygen and one of the sulfonyl oxygens are labeled in the reaction product.

⁽¹⁴⁾ Ławrynowicz, G.; Cox, D. P., unpublished work in this laboratory. The synthetic procedure for this cyanophenylcarbene generation is currently being optimized.

⁽¹⁵⁾ Petrellis, P. C.; Dietrich, H.; Meyer, E.; Griffin, G. W. J. Am. Chem. Soc. 1967, 89, 1967. Petrellis, P. C.; Griffin, G. W. Chem. Commun. 1967, 691.

⁽¹⁶⁾ Brändström, A.; Lamm, B.; Palmertz, I. Acta Chem. Scand., Ser. B 1974, B28, 699.

⁽¹⁾ Risley, J. M.; VanEtten, R. L. J. Am. Chem. Soc. 1979, 101, 252-253. Darensbourg, D. J. J. Organomet. Chem. 1979, 174, C70-C76. Vederas, J. C. J. Am. Chem. Soc. 1980, 102, 374-376.

^{(2) &}quot;Water-¹⁸O (not normalized) (98 atom % ¹⁸O, 95 atom % D)", and containing 0.5 atom % ¹⁷O, 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 Cl₂ for 15 s through a solution of the substrate (0.1–0.5 mmol) in D₂O* (0.2–1.0 mL) cooled in an ice bath, followed by immediate workup by extraction with CH₂Cl₂ and evaporation of solvent.

⁽³⁾ NMR spectra were recorded at 50.3 (¹³C) and 27.1 MHz (¹⁷O) with a Varian XL-200. The ¹⁸O 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 ¹⁷O spectra obtained by using a spin-echo sequence gave shieldings to ± 1 ppm. Integrations have estimated precisions of $\pm 10\%$ (¹⁷O) and $\pm 5\%$ (¹³C and ¹H).

⁽⁴⁾ King, J. F.; Hillhouse, J. H. J. Chem. Soc., Chem. Commun. 1981, 295-296; Can. J. Chem. 1983, 61, 1583-1593.