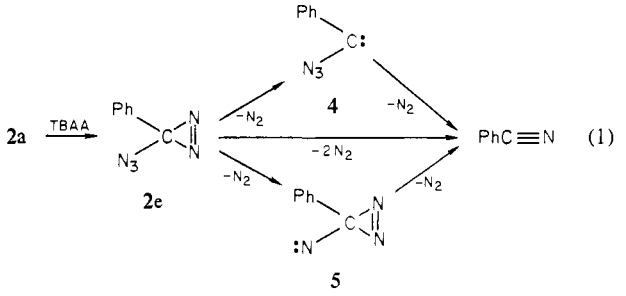
directly demonstrated and synthetically utilized in the following way. TBAC, CH_3CN, and an alkene (4, 10, and 20 mmol, respectively) were stirred with 1 mmol of **2a** (−15 °C, dark, 15 h), whereupon TLC revealed the absence of **2a**. Additional alkene was added and the solution was irradiated ($\lambda > 300$ 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.

(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.

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

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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Received June 17, 1983

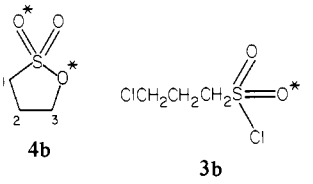
We wish to report a valuable extension of the NMR method of locating oxygen labels and to illustrate its application by demonstrating both the presence and absence of a carbon → sulfur oxygen migration in the chlorination of mercapto alcohols. Our procedure, in addition to utilizing the characteristic 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.

(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) "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).

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

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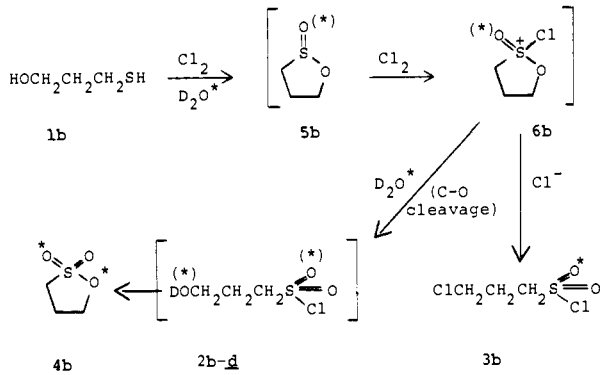
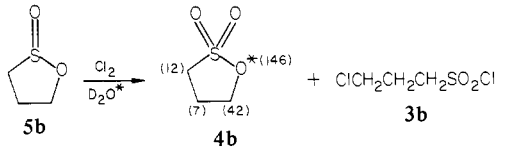
Scheme I



Similarly a 9-ppb shift in the C-1 signal in **3b** compared with the 18-ppb shift found for fully O-labeled[5] **3b** shows **3b** in the reaction product to have one heavy oxygen. The ^{17}O NMR spectrum[3] of natural abundance **4b** has signals at 175 and 146 ppm, assignable from their 2:1 ratio to the sulfonyl and endocyclic oxygens, respectively, while **3b** gives a single peak at 237 ppm; the product mixture had peaks at 146, 175, and 237 ppm in the ratio 2:2:1 thereby confirming the above labeling pattern and product composition. Scheme I gives a reaction pathway consistent with these observations.[6]

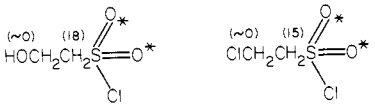
In accord with this picture, chlorination (in D_2O^*) of the sultine **5b** proceeded as follows:



the ^{18}O isotope effects in the ^{13}C NMR spectrum and the single ^{17}O signal (in parentheses, in ppb and ppm, respectively) establish the exclusively endocyclic labeling of **4b**, and the lack of both ^{18}O isotope shifts in the ^{13}C NMR spectrum and enhanced ^{17}O absorption at 237 ppm shows the absence of O label in the **3b**.

In excellent agreement with the notion that **6b** (Scheme I) is the precursor of both **3b** and **4b**, we found that starting with either the mercaptan **1b** or the sultine **5b** addition of NaCl increased the yield of **3b**. A plot of the ratio of **3b** to **4b** in the products vs. $[Cl^-]$ gave a straight line over the full range of chloride ion concentrations used (0.1–4 M); the reaction of **5b** gave essentially the same line[8] as that of **1b**.

In complete contrast to the reaction of **1b**, chlorination of 2-mercapto-1-ethanol (**1a**) proceeds without intramolecular oxygen migration, the products being **2a** (>95%) and a little **3a**, with the



labeling patterns shown deduced from the ^{18}O isotope shifts (in parentheses). We conclude that 2-hydroxyethanesulfonyl chloride (**2a**) is formed by a simple hydrolytic chlorination sequence without participation of the hydroxyl group (presumably because of strain in the four-membered ring counterpart of **5b**), and that the 2-chloroethanesulfonyl chloride arises by way of an *intermolecular* interaction of the reacting sulfur center and the alcohol function, e.g., via an acyclic sulfinic ester. This in turn suggests that the high-yield formation of **3a** by chlorination of **1a** plus a roughly equimolar amount of water,[9] which by its stoichiometry requires transfer of an oxygen from carbon to sulfur, also proceeds by an intermolecular process.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

Registry No. 1b, 19721-22-3; **5b**, 24308-28-9; ^{18}O, 14797-71-8; ^{17}O, 13968-48-4.

(5) The fully labeled samples were obtained from the chloromercaptan $Cl(CH_2)_nSH$ under conditions in which the only source of oxygen was D_2O^* (>95 atom % ^{18}O).

(6) Scheme I does not specify the origin of the sultine **5b**; the following gives the labeling shown and finds analogy for each step in the valuable pioneering studies of Douglass and co-workers.[7]

1b → $HO(CH_2)_3SCl$ → $HO(CH_2)_3SCl_3$ → $HO(CH_2)_3SOCl$ → **5b**

(7) (a) Douglass, I. B.; Farah, B. S.; Thomas, E. G. *J. Org. Chem.* **1961**, *26*, 1996–1999. (b) Douglass, I. B. *Ibid.* **1965**, *30*, 633–635.

(8) From **5b** the product ratio **3b**:**4b** = 1.01$[Cl^-]$ + 0.12; **3b**/**4b** from **1b** is given by 1.02$[Cl^-]$ + 0.06 with $r > 0.997$ in both cases.

(9) Gilbert, E. E. *Synthesis* **1969**, 3–10.

Perannulanes. A New Class of Fused Polycyclic Compounds

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Received July 5, 1983

Betweenanenes, by virtue of the crisscross arrangement of the two bridging chains, show highly attenuated olefinic reactivity.[1] The effect is most pronounced with the lower homologues (**I**, $a = 10$, $b = 8$; $a = b = 10$) (Scheme I). These olefins survive even prolonged exposure to electrophiles such as peroxycarboxylic acids and dihalocarbenes.[2] As expected, double-bond reactivity is gradually restored with an increase in bridging chain length (e.g., **I**, $a = 22$, $b = 10$; $a = 26$, $b = 10$).[2]

For some time now we have been interested in preparing betweenanenes with functionalized bridges capable of transannular [2 + 1] cycloaddition to the encapsulated double bond. In the simplest case (Figure 1), a betweenanene carbene **II** could be expected to afford the addition products **III** or **IV**, depending upon the preferred geometry of the addition and the values of b and c. Likewise, the bicyclic carbene **V** of Z geometry could afford the isomeric products **VI** or **VII**. Extending the concept to transannular [2 + 2] and [2 + 2 + 2] cycloadditions of appropriate tricyclic dienes and tetracyclic trienes leads to the analogous polycyclic structures **VIII** and **IX** (Figure 2). We propose the name "perannulanes"[3] for the homologous series of polycyclics of which **III**–**IX** are members. Perannulanes are perceived as fully annulated cycloalkanes in which rings of varying size are fused to each side of a central ring. The prefix "tri, tetra, penta," etc. denotes the number of central ring sides and the bracketed numbers "a, b, c," etc. indicate the length of each bridging chain.

As a result of recent improvements in *trans*-cycloalkene synthetic methodology[4] we have been able to devise an efficient route to betweenanenes with features favorable to the transannular carbene addition depicted in eq 1 (figure 1). The sequence (Scheme II) employs S_N2' addition of a propargylmagnesium bromide–CuI complex to prepare the *trans*-cyclododecenylcarbinol **2** from the cyclododecylidene oxirane **1**.[4,5] As in previous cases, this addition was both stereoselective and regioselective. Addition of the same organocopper reagent to the phosphate derivative **3** afforded the bis(acetylene) **4**.[4] Hydroboration of this triisopropylsilyl-substituted acetylene with dicyclohexylborane followed

(1) Marshall, J. A.; Lewellyn, M. *J. Am. Chem. Soc.* **1977**, *99*, 3508–3510.

(2) Marshall, J. A. *Acc. Chem. Res.* **1980**, *13*, 213–218. Nakazaki, M.; Yamamoto, K.; Yanagi, J. *J. Am. Chem. Soc.* **1979**, *101*, 147–151. Nakazaki, M., Yamamoto, K. *J. Synth. Org. Chem., Jpn.* **1981**, *39*, 624–632.

(3) "Per"—containing the largest possible or a relatively large portion of a (specific) element. "Annular"—relating to rings.

(4) Marshall, J. A.; Flynn, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 3360–3362.

(5) Use of the ((trimethylsilyl)propargyl)magnesium bromide–CuI complex in this reaction led to appreciable allene product resulting from γ-substitution on the propargyl moiety. Cf.: Corey, E. J.; Ricker, C. *Tetrahedron Lett.* **1982**, *23*, 719–722.

0002-7863/83/1505-6515$01.50/0