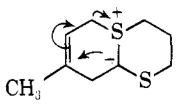
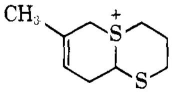
advantages for work on larger scale or for dienes which are not very soluble in methylene chloride.

Treatment of the isoprene adduct **3a** (R_1 = H; R_2 = CH_3) in stirred suspension in tetrahydrofuran under argon with 1 equiv of *n*-butyllithium in pentane at −78° for 20 min and at −78 to 25° over 25 min afforded after evaporative distillation at 80–82° (0.65 mm) the cyclopropyl derivative **4a** (R_1 = H; R_2 = CH_3)[5] as a colorless oil in 96% yield. The pmr spectrum of this product was especially important in structural assignment, since it clearly indicated the presence of methyl at quaternary carbon, cyclopropylmethylene, and C_3-$CCH{=}CH_2$ and trimethylene thioketal units. The conversion of **3a** (R_1 = H; R_2 = CH_3) to **4a** (R_1 = H; R_2 = CH_3) is readily understood in mechanistic terms as proceeding from the ylide **7**. The formation of the rearrangement product **4a** (R_1 = H; R_2 = CH_3) also argues emphatically against structure **8** for the isoprene adduct.[8] In a similar way the adducts **3** from 2,3-dimethylbutadiene and butadiene have been converted, respectively, to **4b** (R_1 = R_2 = CH_3),[5] colorless oil, distilled at 110–115° (bath (0.75 mm), 93% yield), and **4c** (R_1 = R_2 = H),[5] colorless oil, distilled at 72–74° (bath (0.65 mm), 87% yield). The rearrangement **3** → **4** thus represents a novel and highly effective way of using the Diels–Alder reaction for the synthesis of vinylcyclopropane derivatives.



7



8

As expected, the vinylcyclopropane derivatives **4** upon heating to 200° undergo rearrangement to cyclopentenes of structure **5**.[9] The reaction proceeds very cleanly in benzene solution[10] (200°) to afford, starting with the corresponding cyclopropane **4**, the cyclopentenone thioketals (as colorless liquids) **5a** (R_1 = H; R_2 = CH_3)[5] (4 hr heating, 97% yield, bp 85–90° (0.5 mm)), **5b** (R_1 = R_2 = CH_3)[5] (5 hr heating, 95% yield, bp 125–130° (0.7 mm)), and **5c** (R_1 = R_2 = H)[5] (16 hr heating, 97% yield, bp 90–95° (0.6 mm)).

The 3-cyclopentenone thioketals **5** upon gentle hydrolysis could be smoothly converted to the corresponding ketones **6**. For example, treatment of the thioketal **5a** (R_1 = H; R_2 = CH_3), in acetone–water (*ca.* 8:1) with excess mercuric chloride–calcium carbonate for 16 hr at 25° with stirring, afforded 3-methyl-3-cyclopentenone (**6**) (R_1 = CH_3; R_2 = H), in 94% yield by vapor phase chromatographic (vpc) analysis which also revealed the absence of detectable amounts of the isomer 3-methyl-2-cyclopentenone. Filtration of solids, removal of acetone at reduced pressue, extraction with ether, and distillation yielded pure 3-methyl-3-cyclopentenone[5] (infrared max at 5.69 μ in CCl_4 due to carbonyl) uncontaminated by the conjugated isomer (vpc analysis).

The sequence 1,3-diene (**2**) to Δ^3-cyclopentenone (**6**) which is described above extends the Diels–Alder reaction to five-membered carbocycles in a way which is novel and potentially of considerable utility.[11] The process has also been applied successfully to the cyclic substrate 1,3-cyclohexadiene. We hope to report at a later time on the scope of this process and on other methods for the synthesis of Δ^3-cyclopentenones.[12] We are also studying the reactions of **1** with a variety of other substrates including monoolefins.

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[8] The rearrangement **3** → **4** by way of **7** is a bicyclic analog of the familiar allylsulfonium ylide rearrangement; see, for example, E. Hunt and B. Lythgoe, *J. Chem. Soc., Chem. Commun.*, 757 (1972). The formulation of the isoprene adduct as **8** would also violate expectations based on the Markovnikov mode of addition of electrophilic carbon of **1** to isoprene.

[9] See C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968, Chapter IX.

[10] We have not investigated thermolysis in the gas phase, but we have no reason to believe that this would not be an equally smooth process.

[11] The synthesis of cyclopentanones from 1,3-dienes by cyclohydroboration [H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **94**, 3567 (1972)] followed by carbonylation [H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969)] deserves mention in connection with the method described here.

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E. J. Corey,* S. W. Walinsky
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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Pentafluorosulfur Hydroperoxide

Sir:

The fluorinated hydroperoxide, CF_3OOH, has been used in the synthesis of new fluorinated peroxides and is prepared by the hydrolysis of $F_3COOC(O)F$.[1–5] The appropriate equation is

$$CF_3OOC(O)F + H_2O \longrightarrow CF_3OOH + CO_2 + HF$$

This communication describes the preparation of F_5SOOH by an analogous reaction

$$F_5SOOC(O)F + H_2O \longrightarrow F_5SOOH + CO_2 + HF$$

and suggests the use of F_5SOOH as a convenient source of the F_5SOO group in synthesis.

The hydrolysis of $F_5SOOC(O)F$ with a stoichiometric amount of H_2O at 0° gives a nearly quantitative yield of F_5SOOH. An excess of water at 0° gives a hydrate of F_5SOOH which makes purification of the product very difficult. An excess of water at 22° leads to the formation of SO_2F_2, O_2, HF, and CO_2.

Pentafluorosulfur hydroperoxide is a stable colorless liquid up to 30° [bp 0° (150 mm)]; it freezes to a colorless solid at −55.6°. The vapor at less than 50 mm of pressure is monomeric (obsd mol wt, 160.1; calcd for monomer, 160.6). When the compound is heated to 85° in a Monel reactor, rapid decomposition as indicated by the following equation occurs

$$0.20F_5SOOH \longrightarrow 0.20OSF_4 + 0.10O_2 + 0.20HF^6$$

The decomposition is analogous to that of F_3COOH which forms COF_2, O_2, and HF on heating.

The infrared shows major absorptions (cm^{-1}) at 3560 (m, OH), 1385 (s, δ OOH), 920 and 880 (vs, SF_5O), 725

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[1] R. L. Talbott, *J. Org. Chem.*, **33**, 2095 (1967).

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[6] The experimental value of HF was 0.18. It was estimated by difference.

(w, SF_5O), and 610 (s, δ SF_5O). The OH stretch and OOH bending are very close to those observed for CF_3OOH.[1,2] The three strong absorptions below 1000 cm^{-1} are typical for SF_5O derivatives.[7-10] The Raman spectrum of F_5SOOH shows a very intense scattering at 735 cm^{-1} which, by analogy to fluorocarbon peroxides, can tentatively be assigned to the O–O stretch.[11]

The ^{19}F nmr of F_5SOOH at 94.1 MHz shows 21 lines which are nearly identical in intensity with the calculated spectrum for an A_4B system with $J/\delta = 0.25$.[12] The ^1H nmr shows a single, somewhat broadened, line at $\delta = -10.03$. No H–F coupling is observed and the broad ^1H nmr signal is due to intermolecular exchange of H on oxygen. A detailed analysis of the ^{19}F nmr spectrum is in progress.

The mass spectrum of SF_5OOH at a variety of ionization potentials and source temperatures gives F_3SO^+ (*m/e* 105) as the most intense ion followed by FSO^+ (67), F_2SO^+ (86), F_3S^+ (89), and F_2S^+ (70). In addition, an intense ion at *m/e* 32 is observed corresponding to O_2^+, providing support for the decomposition of the compound to form O_2 and the presence of an O–O grouping. No parent ion above background could be observed and heavier ions such as F_5SOO^+ and F_5SO^+ were also absent. The observed mass fragmentation is very similar to certain other SF_5OX derivatives, especially where X is Cl or NF_2.[8,9] However, it is also similar to that of SOF_4[10] and the possibility that the spectrum is due entirely to the decomposition products of F_5SOOH cannot be ruled out.

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Darryl D. DesMarteau
Department of Chemistry, Kansas State University
Manhattan, Kansas 66506

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Determination of Carbonium Ion Stabilities by Ion Cyclotron Resonance Spectroscopy

Sir:

Substituent effects on carbonium ion stabilities have been used extensively to explain patterns of chemical reactivity.[1] Using trapped ion cyclotron resonance techniques[2-7] it should in principle be possible to determine relative carbonium ion stabilities from studies of hydride transfer equilibria (eq 1) in the gas phase. Con-

$$R_1^+ + R_2H \rightleftharpoons R_2^+ + R_1H \qquad (1)$$

sistent with previous results,[8] we have found the forward and reverse rate constants for reaction 1 to be slow for interesting pairs of carbonium ions (*e.g.*, *tert*-butyl and isopentyl) with equilibrium being established only after several hundred collisions.[9] *We wish to report an alternate and more successful approach for the determination of carbonium ion stabilities involving study of the halide transfer equilibria generalized in eq 2.* Cho-

$$R_1^+ + R_2X \rightleftharpoons [R_1\overset{+}{X}R_2]^* \rightleftharpoons R_2^+ + R_1X \qquad (2)$$

sen to exemplify these studies is a consideration of the relative stabilities of the fluoromethyl cation ($CH_nF_{3-n}^+$, $n = 0$–3). The effects of fluorine substituents on carbonium ion stabilities are of particular interest since they exhibit ambiguous behavior.[10,11] While dative π bonding from fluorine p–π orbitals to the empty carbon p orbital is a stabilizing effect, the large electronegativity of fluorine relative to hydrogen serves to destabilize positive charge on carbon.

Both the occurrence of halide transfer processes and the intermediacy of halonium ions in the reactions of carbonium ions with alkyl halides have been documented in continuing studies in our laboratory.[12,13] For example, the major fragment ions derived from methylene fluoride are CH_2F^+ and CHF_2^+. Reaction 3

$$CHF_2^+ + CH_2F_2 \longrightarrow CH_2F^+ + CHF_3 \qquad (3)$$

accounts for the disappearance of CHF_2^+ at higher pressures or long reaction times, the product CH_2F^+ being unreactive with CH_2F_2.[13] Similarly, in the case of fluoroform, the fragment ion CF_3^+ reacts to generate CHF_2^+, which is unreactive with CHF_3.[13] Hence, in a mixture of CH_2F_2 with CHF_3, reaction 3 can proceed reversibly. This conjecture is confirmed by the data shown in Figure 1. In Figure 1a the relative abundances of CH_2F^+ and CHF_2^+ are observed not to vary significantly with time beyond 100 msec.[3] From the relative ion abundances and known neutral concentrations, an equilibrium constant $K = 0.65$ is derived for reaction 3. To check that equilibrium is established, a *time delay ion ejection technique* is used. In the trapped ion timing sequence an irradiating radiofrequency field is switched on at 100 msec (Figure 1b) and used to continuously remove CH_2F^+ in a time short compared to the time between collisions. Thus reaction 3 can proceed only to the right, causing the subsequent decay of CHF_2^+. From an analysis of the resulting kinetic data, the forward ($k_f = 1.4 \times 10^{-10}$ cm^3 $molecule^{-1}$ sec^{-1}) and reverse ($k_r = 2.2 \times 10^{-10}$ cm^3 $molecule^{-1}$ sec^{-1}) rate

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