Table III. Fluorination of Alcohols with SeF$_4$–Pyridine

| Alcohol	Alkyl fluoride	Bp, °C	% yield
Methyl[a]	Methyl	−78.5[b]	40
Ethyl[a]	Ethyl	−37.1[b]	58
Propyl	Propyl	−2.5[b]	50
Isopropyl	Isopropyl	−9.4[b]	60
Butyl	Butyl	32.5[c]	60
sec-Butyl	sec-Butyl	25.3[c]	65
Isobutyl	tert-Butyl	12.1[d]	65
2-Methyl-2-propyl	tert-Butyl		80
Pentyl	Pentyl	64.2[c]	60
Cyclopropyl	Cyclobutyl	34.0[e]	60
Cyclopropyl, phenylmethyl	Cyclopropyl, phenylmethyl	Dec[f]	56
	4-Phenylbuten-3-yl	Dec[f]	24
2-Cyclohexenyl	2-Cyclohexenyl	Dec[f]	90
1-Phenylcyclobutyl	1-Phenylcyclobutyl	Dec[f]	85
Benzyl	Benzyl	145[g]	100
α-Phenylethyl	α-Phenylethyl	46 (15 mm)[h]	100
β-Phenylethyl	β-Phenylethyl	55 (12 mm)[i]	100
α-Hydroxy-α-phenylacetophenone	α-Fluoro-α-phenylacetophenone	43[j] (mp)	100

[a] Reaction carried out without pyridine. [b] D. V. Grosse, R. C. Wachher, and C. B. Lin, *J. Phys. Chem.*, **44**, 275 (1942). [c] N. B. Chapman and J. C. Levy, *J. Chem. Soc.*, 1673 (1952). [d] V. Desreux, *Bull. Sci. Vog. Acad. Roy. Belg.*, **20**, 457 (1934). [e] M. Hanack and H. Eggensperger, *Chem. Ber.*, **96**, 1341 (1963). [f] These compounds decomposed at room temperature. [g] F. Cramer, K. Pawelzic, and F. W. Lichtentheler, *Chem. Ber.*, **91**, 1555 (1958). [h] K. Wiechert, C. Grueenert, and H. J. Preibisch, *Z. Chem.*, **8**, 64 (1968). [i] C. H. DuPuy and C. A. Bishop, *J. Amer. Chem. Soc.*, **82**, 2535 (1960). [j] R. F. Merritt and J. K. Ruff, *J. Org. Chem.*, **30**, 328 (1965).

analyzed by glc, as well by nmr (^{1}H and ^{19}F) and ir spectroscopy.

The needed selenium tetrafluoride for the reported fluorination reactions was found suitably prepared by converting selenium metal directly in better than 98% yield into SeF$_4$ by reaction with ClF$_3$ using SeF$_4$ itself as solvent for the reaction.

$$3Se + 4ClF_3 \longrightarrow 3SeF_4 + 2Cl_2$$
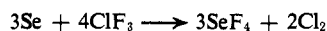
The reaction can be carried out in regular glass apparatus in dry nitrogen atmosphere by adjusting the rate of introduction of ClF$_3$ in relation to the addition of fresh selenium into the system such that exit gases consist only of chlorine. About 20 ml of SeF$_4$ (originally obtained by fluorination of selenium metal) was placed into the glass reaction vessel and about 2 g of selenium metal pellets was added. The mixture was stirred using a magnetic stirrer and ClF$_3$ was introduced below the surface of SeF$_4$ with such a rate that all the ClF$_3$ was absorbed and only chlorine gas was escaping the reaction vessel. The reaction mixture turned dark if ClF$_3$ was introduced too slowly, but as conversion proceeded it became almost colorless. At this time more selenium metal could be added and the introduction of ClF$_3$ continued. The reaction is fastest if the temperature of the reaction mixture is kept around 90°. Control of the temperature is maintained by the rate of introduction of ClF$_3$. Before distilling SeF$_4$ after completion of the reaction we made sure that there was only a small amount of ClF$_3$ dissolved in it,

$$3Se + 4ClF_3 \longrightarrow 3SeF_4 + 2Cl_2$$
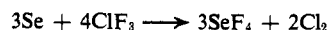
since otherwise distillation could be dangerous. In a typical 8 hour run about 400 g of selenium metal could be reacted. Yield of pure SeF$_4$ obtained (bp 106°) was 98% based on selenium metal used.

Caution! All operation with ClF$_3$ must be carried out with great care as it is extremely reactive and will react vigorously with any organic material and moisture. All selenium compounds must be considered toxic and should be handled with according care. SeF$_4$ and SeOF$_2$ due to their low vapor pressure can be

handled safely, particularly in solution, but are as all active fluorides, hydrolyzed with ease giving HF. All operation should be carried out in a well-vented hood.

We are also studying the utility of SeF$_4$ in other fluorination reactions and will report our results.

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Perfluoromethylenecyclopropane and 1-Trifluoromethyl-2,3,3-trifluorocyclopropene

Sir:

We report the synthesis of a new reactive fluoroolefin, perfluoromethylenecyclopropane (**1**). Reaction of 2,3-dichlorotetrafluoropropene[1] (1 mol) with hexafluoropropylene oxide[2] (1.8 mol) at 185° for 10 hr affords 1-(chlorodifluoromethyl)-1-chloro-2,2,3,3-tetrafluorocyclopropane (75% conversion, 94% yield), bp 58°,[3] which was dechlorinated with Zn in dioxane at 80–100° to afford a 20:1 mixture (70–75% yield) of **1** (bp 5–6°; ir 1818 cm^{-1} (C=CF$_2$); nmr (CCl$_4$) ϕ^* 57.3 (p, 2, $J = 6.6$ Hz), 135.2 (t, 4, $J = 6.6$ Hz)) and 1-trifluoromethyl-2,3,3-trifluorocyclopropene (**2**) (bp *ca.* 7°; ir 1889

(1) (a) J. E. Bissey, H. Goldwhite, and D. G. Roswell, *J. Org. Chem.*, **32**, 1542 (1967); (b) W. T. Miller, Jr., and A. H. Fainberg, *J. Amer. Chem. Soc.*, **79**, 4164 (1957).

(2) For examples of hexafluoropropylene oxide pyrolysis in the synthesis of fluorinated cyclopropanes, see P. B. Sargeant, *J. Org. Chem.*, **35**, 678 (1970).

(3) All compounds gave satisfactory combustion and/or mass spectral analyses. The products were unambiguously characterized by ^{1}H and ^{19}F nmr and ir in all cases.

cm^{-1} (C=C); nmr (CCl$_4$) ϕ^* 60.3 (d of t, 3, J = 7, 3 Hz), 100.0 (d of q, 2, J = 36, 3 Hz), 116.7 (t of q, 1, J = 36, 7 Hz)).[4] Unlike its hydrocarbon analog, pure **1** does not thermally polymerize or rearrange (150°). The ir double bond stretching frequency of **1** is the highest known for a terminal fluoroolefin (C=CF$_2$).[5] *Perfluoromethylenecyclopropane is lethal and must be handled with great care.*[6]

Perfluoromethylenecyclopropane is enormously reactive toward nucleophiles; most alcohols, amines, and water add exothermally to **1** at 0° (Scheme I). In the

Scheme I
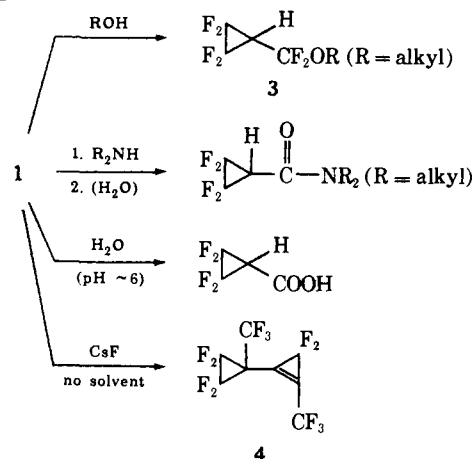
presence of catalytic cesium fluoride and in the absence of solvent, **1** rapidly dimerizes to **4** at 0°. With cesium fluoride (catalytic) in diglyme, **1** reacts violently to give unidentified high oligomers. Cesium fluoride also slowly catalyzes the dimerization of **2** to **4** at room temperature.

Comparison of this reactivity with an acyclic analog, perfluoroisobutylene (PFIB), is instructive. In contrast to **1**, PFIB does not react with water under neutral or acidic conditions;[7] fluoride ion catalyzed PFIB dimerization requires solvent;[8] and PFIB will not react with β,β,β-trifluoroethanol[9] whereas **1** does so at 100° without added base.

Zinc bromide catalyzes the quantitative isomerization of **1** to **2** in diglyme at 100°. The chemistry of **2** is similar to that of perfluorocyclopropene[10,11] and 1,2-

(4) The success of the dechlorination reaction is dependent upon a variety of factors including the choice of solvent, metal, and reaction conditions. To obtain optimum yield and maximize the 1:2 ratio, the reaction must be run in dioxane and the dichloro precursor must be added as rapidly as possible and product swept from the system once the dehalogenation begins. Dropwise addition once the dehalogenation commences reduces the yield to 30–45% and the rearranged isomer **2** increases to ca. 25%. Dehalogenation in ethanol gives only 60% **3** (R = Et), bp 69°, and 20% 1-(chlorodifluoromethyl)-2,2,3,3-tetrafluorocyclopropane, bp 37–39°. Zn dehalogenation in glyme gives a 9% yield of **2** only; Mg in ether fails to react; and Mg or Zn in THF gives tar.

(5) Terminal fluoroolefins display C=C stretching frequencies at ca. 1700–1790 cm^{-1}. For example, PFIB absorbs at 1751 cm^{-1}. See J. K. Brown and K. J. Morgan, *Advan. Fluorine Chem.*, **4**, 263 (1965).

(6) Preliminary inhalation toxicity studies on **1** indicate toxicity approaching that of PFIB. For a discussion of PFIB toxicity, see J. W. Clayton, Jr., *Fluorine Chem. Rev.*, **1**, 231 (1967).

(7) PFIB hydrolyzes rapidly in aqueous THF at 25°, see D. C. England and C. G. Krespan, *J. Amer. Chem. Soc.*, **88**, 5582 (1966). However, the hydrolysis fails in water alone or in aqueous glyme at 25° (D. C. England, private communication).
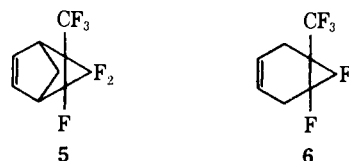
(8) (a) D. L. Muller, U. S. Patent 3,389,187 (1968); (b) see J. A. Young, *Fluorine Chem. Rev.*, **1**, 377, 394 (1967).

(9) R. J. Koshar, T. C. Simms, and F. W. Hoffman, *J. Amer. Chem. Soc.*, **79**, 1741 (1957).

(10) P. B. Sargeant and C. G. Krespan, *J. Amer. Chem. Soc.*, **91**, 415 (1969).

(11) P. B. Sargeant, *J. Amer. Chem. Soc.*, **91**, 3061 (1969).

bis(trifluoromethyl)-3,3-difluorocyclopropene.[11] Cyclopentadiene reacts with **2** at 0° to give **5**, and butadiene gives **6** at 100°.[12]

5   6

Perfluoromethylenecyclopropane homopolymerizes at 25° in the presence of perfluoropropionyl peroxide initiator to an insoluble white solid [mp 272° (DTA), 5% weight loss 244° (TGA); 50% weight loss, 340°] which displays its maximum ir absorption band at 1719 cm^{-1}. Structure **7** is assigned to the homopolymer.

7
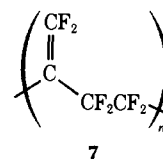
The double bond (C=CF$_2$) stretching frequency of perfluoroallene homopolymer which contains repeating perfluoroallyl units appears at 1720 cm^{-1}.[13] Olefin **2** does not homopolymerize.

A proposed polymerization mechanism is shown in Scheme II. Hydrocarbon cyclopropylcarbinyl radicals

Scheme II
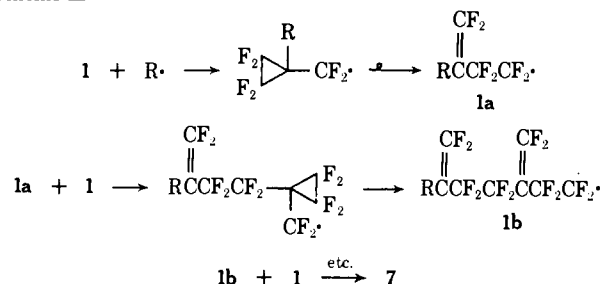
are well known to rearrange,[14] although no examples are known for fluorocarbon radicals.[15]

Perfluoromethylenecyclopropane readily copolymerizes with a variety of vinyl comonomers including tetrafluoroethylene, chlorotrifluoroethylene, vinyl fluoride, vinylidene fluoride, acrylonitrile, and styrene. All copolymers contain pendant C=CF$_2$ unsaturated sites and can be cross-linked with bis nucleophiles in the absence of dehydrofluorinating agents. Incorporating small amounts of monomer **1** therefore allows for cross-linking while maintaining the basic integrity of the vinyl polymer backbone.

(12) The cycloadditions of **1** are discussed in the following communication, B. E. Smart, *J. Amer. Chem. Soc.*, **96**, 929 (1974).

(13) (a) R. E. Banks, R. N. Hazeldine, and D. R. Taylor, *J. Chem. Soc.*, 978 (1965); (b) T. L. Jacobs and R. S. Bauer, *J. Amer. Chem. Soc.*, **78**, 4815 (1956); (c) J. D. McCullough, R. S. Bauer, and T. L. Jacobs, *Chem. Ind. (London)*, **3**, 706 (1957).

(14) J. K. Kochi, Ed., "Free Radicals," Wiley, New York, N. Y., 1973, pp 96–97, 399–406.

(15) A po sible alternative mechanism involves initial radical attack at CF$_2$ to generate a cyclopropyl radical followed by ring opening to a propagating allyl radical. However, this is less attractive since cyclopropyl and perfluorocyclopropyl radicals do not generally rearrange: P. Krusic, P. Meakin, and B. E. Smart, unpublished results. See also ref 14, pp 398–399.

Bruce E. Smart