addition product could be isolated from the reaction mixture.

Triphenylgermyllithium with Benzaldehyde.—A solution of triphenylgermyllithium was prepared by stirring 10.0 g. (0.0165 mole) of hexaphenyldigermane with excess lithium wire in 60 ml. of dry tetrahydrofuran overnight. After removal of the excess lithium a solution of 3.5 g. (0.033 mole) of freshly distilled benzaldehyde in 20 ml. of dry tetrahydrofuran was added during 0.5 minute. Heat was evolved and Color Test I was negative at the end of the addition. After a further 5 min. stirring the reaction mixture was poured into dilute acetic acid. On workup as usual this gave, after recrystallization from petroleum ether (b.p. 60–70°), 9.0 g. (66%) of triphenylgermylphenylcarbinol, m.p. 103–105°. Recrystallization raised the melting point to 105–107°. A mixed melting point with the material obtained by reduction of benzoyltriphenylgermane with lithium aluminum hydride in 63% yield, m.p. 106–107°, was not depressed. The infrared spectra were identical.

Triphenylgermyllithium with Benzophenone.—To the triphenylgermyllithium prepared from 15.0 g. (0.025 mole) of hexaphenyldigermane in 30 ml. of dry tetrahydrofuran was added a solution of 9.0 g. (0.05 mole) of benzophenone in 50 ml. of tetrahydrofuran over 1 min. Heat was evolved and the reaction mixture changed from dark brown to dark green. Color Test I was negative and after 5 min. additional stirring the reaction mixture was drowned in dilute hydrochloric acid. Workup of the reaction gave, on crystallization from hexane, 18.2 g. (75%) of triphenylgermyldiphenylcarbinol, m.p. 145–155°. Recrystallization from hexane–benzene raised the melting point to 153–157°. Also obtained from the mother liquor was 0.65 g. (4%) of hexaphenyldigermoxane, m.p. 180–183°.

The triphenylgermyldiphenylcarbinol was identified by mixed melting point with an authentic sample obtained by the same route as was triphenylsilyldiphenylcarbinol.[1] Benzhydryltriphenylgermane, m.p. 156–159°, was obtained in 43% yield from benzhydryllithium and triphenylbromogermane. This was brominated with N-bromosuccinimide in 83% yield to give bromobenzhydryltriphenylgermane, m.p. 182–187°. Hydrolysis of this compound with silver acetate in acetone–benzene–water gave triphenylgermyldiphenylcarbinol in 76% yield, m.p. 153–156°. The infrared spectrum was consistent with the proposed structure, and was almost identical with that of triphenylsilyldiphenylcarbinol.

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Dichlorofluoromethanesulfenyl Chloride

BY WILLIAM A. SHEPPARD AND JOHN F. HARRIS, JR.

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The compound resulting from reaction of mercuric difluoride with trichloromethanesulfenyl chloride has been shown to be dichlorofluoromethanesulfenyl chloride and not trichloromethanesulfenyl fluoride. The sulfenyl chloride structure has been demonstrated by characteristic sulfenyl chloride reactions, such as conversion to disulfides and addition to olefins, in conjunction with the n.m.r. F^{19} chemical shift.

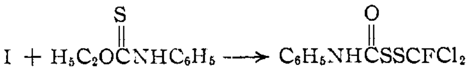
Trifluoromethanesulfenyl chloride was recently reported by Tullock[1] to be the main product resulting from fluorination of trichloromethanesulfenyl chloride with sodium fluoride in hot tetramethylenesulfone or acetonitrile. Difluorochloromethanesulfenyl chloride was also obtained as a low yield by-product but no products resulting from replacement of the chlorine on sulfur with fluorine were found.

$$\mathrm{CCl_3SCl + NaF \longrightarrow CF_3SCl + CF_2ClSCl + CF_3SSCF_3}$$

More recently, however, Kober[2] reported that the fluorination of trichloromethanesulfenyl chloride with mercuric difluoride in methylene chloride led to the formation of compound I, with the empirical formula $\mathrm{CCl_3FS}$, to which was assigned the sulfenyl fluoride structure, $\mathrm{CCl_3SF}$ (Ia). In view of the work of Tullock[1] and previous reports of unsuccessful attempts to convert sulfenyl chlorides to sulfenyl fluorides with fluorinating agents,[3–6] (including mercuric difluoride) we undertook an examination of compound I to see whether it was indeed the sulfenyl fluoride Ia or the expected isomeric sulfenyl chloride, $\mathrm{CFCl_2SCl}$ (Ib).

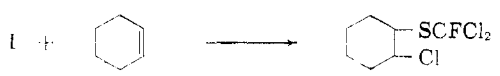
A sample of compound I was prepared by the reaction of trichloromethanesulfenyl chloride with mercuric difluoride.[2] This compound was found to have a single sharp n.m.r. fluorine resonance with the F^{19} chemical shift corresponding to that normally observed for a $\mathrm{CCl_2F}$ group and not that reported for sulfur fluoride derivatives.[7] The following reactions, characteristic of sulfenyl chlorides, were carried out with this compound.

$$\mathrm{I + KI \longrightarrow FCl_2CSSCCl_2F} \qquad (1)$$



$$\mathrm{I + H_5C_2O\overset{\overset{S}{\|}}{C}NHC_6H_5 \longrightarrow C_6H_5NH\overset{\overset{O}{\|}}{C}SSCFCl_2}$$

(2)[8]



(3)

In each case, the products were shown by analysis to have the correct fluorine content for the proposed structures, and were further shown to have a F^{19} chemical shift similar to the starting compound I and corresponding to a $\mathrm{CFCl_2}$ group. If compound I were the sulfenyl fluoride Ia, the fluorine would either have been lost during reaction (reactions 1 and 2) or else the F^{19} chemical shift would have changed significantly (reaction 3). It is thus concluded that the compound reported by Kober to be trichloromethanesulfenyl fluoride (Ia) is actually dichlorofluoromethanesulfenyl chloride (Ib).

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Experimental[9]

Dichlorofluoromethanesulfenyl Chloride.—The reaction of 90 g. (0.485 mole) of trichloromethanesulfenyl chloride with 100 g. (0.42 mole) of mercuric difluoride was carried out as described by Kober.[2] The product was distilled through a 45-cm. spinning band column to give 32.1 g. (39% yield based on CCl_3SCl) of dichlorofluoromethanesulfenyl chloride, b.p. 97–98°, $n^{25}{}_D$ 1.4767.[25]

Anal. Calcd for CCl_3FS: F, 11.2; S, 18.9. Found: F, 11.0; S, 19.1.

The infrared spectrum was extremely simple and contained absorption at 5.6 μ (medium weak), 9.5 μ, (strong) 10.8 μ (medium), and about 12 μ (very strong, broad).[11] The n.m.r. fluorine spectrum consisted of a single sharp resonance; the F^{19} chemical shift is listed in Table I.

Bis-(dichlorofluoromethyl) Disulfide.—A solution of 12.6 g. (0.075 mole) of dichlorofluoromethanesulfenyl chloride in 45 ml. of ether was shaken with a solution of 24.9 g. (0.075 mole) of potassium iodide in 45 ml. of water. A vigorous exothermic reaction was noted, and the dark color of iodine appeared immediately. The ether layer was separated, washed with saturated sodium bisulfite solution until all of the I_2 color was removed, and then washed with water and dried over anhydrous magnesium sulfate. The ether was distilled and the residual oil fractionated through a spinning band column. There was thus obtained 3.58 g. (36% yield) of bis-(dichlorofluoromethyl) disulfide, b.p. 103° (36 mm.), $n^{25}{}_D$ 1.5155.

Anal. Calcd. for $C_2Cl_4F_2S_2$: C, 9.0; Cl, 52.9; F, 14.2; S, 23.9. Found: C, 9.1; Cl, 52.6; F, 14.4; S, 24.5.

The infrared spectrum was similar to that of the starting material Ib and contained strong absorption at 9.4, 10.95, and 12 μ (broad). The n.m.r. F^{19} chemical shift (single resonance) is given in Table I.

Reaction of I with Ethyl N-Phenylthionocarbamate.—A solution of 1.0 g. (0.0059 mole) of I in 5 ml. of benzene was added all at once to a solution of 1.07 g. (0.0059 mole) of ethyl N-phenylthiocarbamate in 15 ml. of benzene. The mixture was stoppered at once and allowed to stand for 1 hour. The mixture was then filtered to remove a small amount of suspended solid, and the filtrate was allowed to evaporate to dryness. There was thus obtained 1.55 g. (92%) of crude dichlorofluoromethyl N-phenylcarbamoyl disulfide melting at 88–93°. After several recrystallizations from cyclohexane, the product was obtained as small white needles, m.p. 95–96°.

Anal. Calcd. for $C_8H_6Cl_2FNOS_2$: Cl, 24.8; F, 6.6. Found: Cl, 24.0; F, 6.7.

The infrared spectrum was in agreement with the proposed structure. The n.m.r. F^{19} chemical shift (single resonance) is given in Table I.

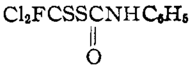
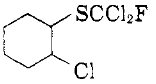
Reaction of I with Cyclohexene.—A mixture of 10 g. (0.059 mole) of I, 20 ml. of cyclohexene and 50 ml. of ethylene chloride was stirred for 1 hour. Upon distillation of the reaction mixture, there was obtained 6.8 g. (46%) of dichlorofluoromethyl 2-chlorocyclohexyl sulfide, b.p. 59° (0.2 mm.)–63°(0.25 mm.), $n^{25}{}_D$ 1.5157.

Anal. Calcd. for $C_7H_{10}Cl_3FS$: Cl, 42.3; F, 7.5. Found: Cl, 41.6; F, 7.7.

The n.m.r. F^{19} chemical shift (single resonance) is given in Table I. The structure of the product was further confirmed by the infrared spectrum.

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA[a]

Compounds	Frequency displacement,[b] c.p.s. at 40 mc.
Cl_2FCSCl	−2025
$Cl_2FCSSCCl_2F$	−2248
 $Cl_2FCSS\underset{\displaystyle O}{\overset{}{\underset{\Vert}{C}}}NHC_6H_5$	−2110
	−2500

[a] Spectra were obtained by means of a high-resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, Palo Alto, Calif., operating at approximately 9,988 gauss for fluorine. [b] Spectra were calculated in terms of displacement in cycles per second (c.p.s.) from the fluorine resonance of trifluoroacetic acid. Negative frequency displacements indicate resonances occurring at lower field relative to the reference.

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(9) Melting points are uncorrected.

(10) In ref. 2, the yield of product b.p. 96–101° was reported to be 42.2 g. (51.5%).

(11) The absorption at 5.6 μ is unexpected for this type of molecule. A sample (1.5 ml.) of the compound was gas chromatographed (6 ft., 3/4 in. copper tube column, packed with 20% telomer oil of tetrafluoroethylene-propylene on "Chromosorb" and heated at 50°; helium carrier gas, flow rate 600 ml./min.; retention time 25.5 min.) and no significant amount of impurity was detected. Two fractions of the chromatographed product were shown to have infrared spectra identical to that of the original sample. It would appear that the absorption at 5.6 μ is not due to an impurity.

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The Chemistry of Sulfur Tetrafluoride. VII. Synthesis of Organic Fluorides by Halogen Exchange with Sulfur Tetrafluoride

BY C. W. TULLOCK, R. A. CARBONI, R. J. HARDER, W. C. SMITH AND D. D. COFFMAN

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Sulfur tetrafluoride has been found to undergo halogen exchange with chloro- and bromomethanes, chloroalkanes and -alkenes, aryl chlorides, cyanuric chloride and chloropyrimidines. Usually only partial substitution of fluorine for chlorine or bromine resulted. At the elevated temperatures used, chloroalkenes and hexachlorobenzene were converted to chlorofluoroalkanes and chlorofluorocyclohexenes, respectively.

Replacement of chlorine or bromine atoms bonded to carbon by fluorine has been accomplished with such agents as hydrogen fluoride, potassium fluoride, antimony trifluoride, antimony pentafluoride or chlorofluoride, and also by means of the less frequently used silver monofluoride, manganese trifluoride, cobalt trifluoride and chromium trifluoride.[1] Similar replacements have now been carried out by the use of sulfur tetrafluoride, which is a unique agent[2,3] for the replacement of carbonyl oxygen by fluorine and which is readily available from sulfur dichloride and sodium fluoride.[4]

Fluorohalomethanes from Carbon Tetrachloride or Carbon Tetrabromide.—Chlorofluoromethanes

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