experiment were identical with the spectra obtained from authentic compounds.

Attempted Addition of Carbon Tetrachloride to Trichlorovinyltrimethylsilane.—Trichlorovinyltrimethylsilane (23.3 g., 0.12 mole) and carbon tetrachloride (70.5 g., 0.46 mole) were placed into a quartz flask and irradiated with light from a mercury vapor lamp for 2 weeks. An atmosphere of purified nitrogen was maintained throughout the experiment. Practically all the starting materials were recovered from the greenish reaction mixture.

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WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Addition of Trichlorosilane and Methyldichlorosilane to Fluorine- and Chlorine-containing Olefins

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Trichlorosilane and methyldichlorosilane were added using ultraviolet irradiation and peroxides to 1,1,2-trichloro-3,3,3-trifluoropropene to give trifluorodichloropropenyltrichlorosilane and trifluorodichloropropenylmethyldichlorosilane, respectively. Trichlorosilane and methyldichlorosilane were added to 3,3,3-trifluoropropene and to 2,3,3,4,4,4-hexafluorobutene, and trichlorosilane was added to chlorotrifluoroethylene to give chlorotrifluoroethyltrichlorosilane. The products were converted to their trimethyl and triethyl derivatives. Trifluorotetrachloropropyltrichlorosilane gave trifluorodichloropropenyltriethylsilane with ethylmagnesium bromide.

Discussion

Trichlorosilane has been added with[3a–e] or without[3f,g] catalysts to olefins. Since this work was initiated, two reports have appeared on the addition of trichlorosilane to fluorine-containing olefins[4,5]; these involve the addition of trichlorosilane to 1,1-difluoroethylene with a platinum-on-charcoal catalyst and to tetrafluoroethylene photochemically.

The addition of methyldichlorosilane to olefins has been less extensively investigated.[3c–f,6a–c] Additions of trichlorosilane and methyldichlorosilane to olefins containing chlorine atoms at the carbon atoms forming the double bond have been shown to form olefinic products[7a–f] by subsequent dehydrohalogenation of the original saturated adduct.

This paper reports the addition of trichlorosilane and methyldichlorosilane to the fluorine-containing olefins, perfluoropropene, 2,3,3,4,4,4-hexafluorobutene and 3,3,3-trifluoropropene, and to the olefins containing both fluorine and chlorine, namely, 1,1,2-trichloro-3,3,3-trifluoropropene and chlorotrifluoroethylene. Ultraviolet irradiation and *t*-butyl peroxide were both used as initiators and the latter proved to be more dependable because it is a liquid miscible with the reactants and generates free radicals at a measurable rate at elevated (125°) temperatures.[8]

The reactivity of the olefins studied increased as the influence of fluorine on the character of the double bond decreased. Thus, 3,3,3-trifluoropropene gave better conversions than 2,3,3,4,4,4-hexafluorobutene, while perfluoropropene gave only traces of an addition compound (Table I). The inertness of perfluoropropene in these reactions was somewhat surprising since it has been reported to add trifluoromethyl iodide[9] and since it adds bromine under the influence of ultraviolet irradiation to give an 83% yield of 1,2-dibromo-1,1,2,-3,3,3-hexafluoropropane.

The proposed mechanism for the addition reaction[10] postulates the formation of a silyl free radical, the addition of this free radical to the olefin, and the removal of a hydrogen from the silane by the resulting radical to generate another silyl radical. This mechanism explains the lesser reactivity of methyldichlorosilane because the silyl free radical may be considered as electrophilic, and if the methyldichlorosilyl radical obtained from methyldichlorosilane is the reactive species in the addition of methyldichlorosilane to olefins, it should be less electrophilic than the trichlorosilyl radical due to the electron-supplying influence of the methyl group.

Although the addition of trichlorosilane and methyldichlorosilane to 1-olefins has been shown to yield the 1-isomer exclusively,[10] the addition compound of trichlorosilane to 3,3,3-trifluoropropene could be either $CF_3CH_2CH_2SiCl_3$ (I) or CF_3-

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[1] Polymer Research Laboratories, Dow Chemical Co.

[2] A portion of a thesis submitted by G. W. R. Puerckhauer to Purdue University in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June, 1956.

[3] The following are representative: (a) C. A. Burkhard and R. H. Krieble, THIS JOURNAL, **69**, 2687 (1947); (b) E. W. Pietrusza, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 484 (1948); (c) G. H. Wagner and C. O. Strother, U. S. Patent 2,632,013 (1953); (d) D. B. Hatcher, U. S. Patent 2,555,589 (1951); (e) R. D. Lipscomb, U. S. Patent 2,570,462 (1951); (f) A. J. Barry, L. DePree, J. W. Gilkey and D. E. Hook, THIS JOURNAL, **69**, 2916 (1947); (g) E. P. Plueddemann, U. S. Patent 2,642,447 (1953).

[4] G. H. Wagner, U. S. Patent 2,637,738 (1953).

[5] R. N. Haszeldine and R. J. Marlow, *J. Chem. Soc.*, 962 (1956).

[6] (a) A. J. Barry, D. E. Hook and L. DePree, U. S. Patent 2,626,-268 (1953), British Patent 632,824 (1949); (b) R. H. Krieble, U. S. Patent 2,524,529 (1950); (c) British Patent 661,094 (1951).

[7] (a) C. L. Agre, THIS JOURNAL, **71**, 300 (1949); (b) C. L. Agre and W. Hilling, *ibid.*, **74**, 3895 (1952); (c) C. L. Agre, U. S. Patent 2,682,512 (1954); (d) J. W. Gilkey, U. S. Patent 2,723,986 (1955); (e) E. T. McBee, C. W. Roberts and G. W. R. Puerckhauer, THIS JOURNAL, **79**, 2326 (1957); (f) G. H. Wagner, U. S. Patent 2,637,738 (1953).

[8] J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 1336 (1948). It was shown that *t*-butyl peroxide is superior to acetyl peroxide, benzoyl peroxide or ultraviolet irradiation as an initiator for these additions. Stainless steel retards the addition, hence the reactions were carried out in all-glass apparatus.

[9] R. N. Haszeldine, *J. Chem. Soc.*, 3559 (1953).

[10] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **69**, 188 (1947).

$CH(CH_3)SiCl_3$ (II). In order to distinguish between structures I and II, the product was converted to the trimethoxy derivative; this was found to be identical with 3,3,3-trifluoropropyltrimethoxysilane prepared by a different procedure.[11] By analogy, the addition compound of trichlorosilane to 2,3,3,4,4,4-hexafluorobutene is presumed to be $CF_3CF_2CHFCH_2SiCl_3$ (III).

In comparison to the addition of trichlorosilane to tetrachloroethylene, one would expect the silane to add to 1,1,2-trichloro-3,3,3-trifluoropropene to give an olefinic product[7e]; experimental evidence supported this, and trifluorodichloropropenyltrichlorosilane was isolated. Methyldichlorosilane added less readily and gave also an olefinic product, trifluorodichloropropenylmethyldichlorosilane. The addition product could be either $CF_3CCl{=}CClSiCl_3$ (IV) or $CF_3C(SiCl_3){=}CCl_2$ (V). These compounds were distinguished by alkaline cleavage.[12] Although the physical constants of the resulting olefins are relatively close,[13] the melting point of the olefin obtained by alkaline cleavage of the addition product to 1,1,2-trichloro-3,3,3-trifluoropropene agreed with that for 1,1-dichloro-3,3,3-trifluoropropene and the addition compound is therefore compound V.

The literature and the evidence presented indicate that chlorosilanes will add to chlorinated olefins to give chiefly an unsaturated addition product which arises by the elimination of the elements of hydrogen chloride, while fluorinated olefins such as 2,3,3,4,4,4-hexafluorobutene or 1,1-difluoroethylene gave saturated addition products. It seemed, therefore, of interest to investigate the addition of trichlorosilane to an olefin that contained both fluorine and chlorine at the double bond. Chlorotrifluoroethylene was used and gave a saturated addition product that was somewhat unstable at its boiling point but could be prepared in analytical purity by relatively rapid rectification of a previously distilled sample.

According to the observations made by Sommer and co-workers[14] on the behavior of β-chloroalkylsilanes, 2,3,3,4,4,4-hexafluorobutyltrichlorosilane might be expected to undergo elimination reactions involving the β-fluorine atom with Grignard reagents and bases. However, this β-fluorine is more stable than β-chlorine since even excess of ethylmagnesium bromide with I or III gave the triethyl derivatives with no observed loss of fluorine. Moreover, the products were stable to base under such vigorous conditions as prolonged refluxing with 40% potassium hydroxide. Agre[3] and McBee, *et al.*,[7e] observed that β-chlorovinylsilanes will not undergo reduction or β-elimination with Grignard reagents. Trifluorodichloropropenyltrichlorosilane behaved similarly and the trimethyl and triethyl compounds were prepared by a known procedure[15] with methylmagnesium iodide and ethylmagnesium bromide, respectively.

Chlorine was added in good yields to trifluorodichloropropenyltrichlorosilane to give trifluorotetrachloropropyltrichlorosilane which underwent reduction with ethylmagnesium bromide to give back trifluorodichloropropenyltriethylsilane. This reduction seems to be a general reaction for silanes of this structure as pentachloroethyltrichlorosilane underwent a similar reaction.[7e]

The results of the addition reactions are summarized in Table I and the new compounds in Tables II and III.

Table I

Silane Addition Products

	Addition, %			
	Trichlorosilane		Methyldichlorosilane	
	Ultraviolet	$(t\text{-}BuO)_2$	Ultraviolet	$(t\text{-}BuO)_2$
Perfluoropropene	1	1	..	..
2,3,3,4,4,4-Hexafluorobutene	29.3	52.1	8.6[b]	45.8
3,3,3-Trifluoropropene	72	75.3	3.6[c]	69.5
1,1,2-Trichloro-3,3,3-trifluoropropene[a]	9.3	33.5	..	21.2
Chlorotrifluoroethylene	19.1	37.7	..	..

[a] This addition was also brought about by passing a mixture of 1,1,2-trichloro-3,3,3-trifluoropropene (1 mole) and trichlorosilane (1.2 mole) through a horizontal tube (20 mm. interior diameter) that was heated over a 20-cm. zone to 580–620°. Although extensive carbonization took place, 3.9% of trifluorodichloropropenyltrichlorosilane could be obtained; this reaction did not take place below 510°. [b] 8.5 days irradiation. [c] 90 hr. irradiation, impure product.

Experimental

Materials.—3,3,3-Trifluoropropene[16] and 2,3,3,4,4,4-hexafluorobutene[17] were prepared by published methods. Trichlorosilane and methyldichlorosilane (pure grade) were purchased from Anderson Laboratories and used without further purification. 1,1,2-Trichloro-3,3,3-trifluoropropene was obtained from Columbia Organic Chemicals Co., Inc., and chlorotrifluoroethylene from General Chemicals Division, Allied Chemical and Dye Corp.

Addition of Trichlorosilane and Methyldichlorosilane to Olefins.—The following experiments exemplify the different methods used to add trichlorosilane and methyldichlorosilane to 3,3,3-trifluoropropene, 2,3,3,4,4,4-hexafluorobutene, 1,1,2-trichloro-3,3,3-trifluoropropene and chlorotrifluoroethylene.

Ultraviolet Initiation.—A Carius tube was charged with 9.2 g. (0.096 mole) of 3,3,3-trifluoropropene and 39 g. (0.29 mole) of trichlorosilane and exposed to irradiation from an AH-1 bulb (Gartner Scientific Co.) for 90 hr. Olefin (0.9 g.) and trichlorosilane (21.3 g.) were recovered from the tube and 16 g. (72% based on olefin) of 3,3,3-trifluoropropyltrichlorosilane, b.p. 112.9–114.8°, was obtained by rectification.

***t*-Butyl Peroxide Initiation.**—3,3,3-Trifluoropropene (12.8 g., 0.13 mole), *t*-butyl peroxide (1.5 g., 0.01 mole) and trichlorosilane (52.1 g., 0.39 mole) were distributed over three Carius tubes that were sealed under a purified nitrogen atmosphere (Fieser train) and heated in a tube furnace for 60 hr. at 125–130°. The reaction mixture gave 30.3 g. (0.22 mole) of trichlorosilane and 22.3 g. (75.3%) of 3,3,3-trifluoropropyltrichlorosilane, b.p. 112.8–113.7°.

Although attempts to run these reactions in a stainless steel autoclave gave poor conversions, a nickel-clad autoclave was a satisfactory reaction vessel. A glass liner, filled with 219.6 g. (1.1 moles) of 1,1,2-trichloro-3,3,3-trifluoropropene, 12.83 g. (0.088 mole) of *t*-butyl peroxide and 448 g. (3.3 moles) of trichlorosilane was placed in a nickel-clad autoclave

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[11] E. T. McBee, C. W. Roberts, G. F. Judd and T. S. Chao, This Journal, **77**, 1292 (1955).

[12] G. H. Wagner and A. N. Pines, *ibid.*, **71**, 3567 (1949).

[13] A. L. Henne, *et al.*, *ibid.*, **63**, 3478 (1941); **64**, 1157 (1942).

[14] L. H. Sommer, G. M. Goldberg, E. Dorfman and F. C. Whitmore, *ibid.*, **68**, 1083 (1946).

[15] F. C. Whitmore, L. H. Sommer, P. A. DiGiorgio, W. A. Strong, R. E. Van Strien, D. L. Bailey, H. K. Hall, E. W. Pietrusza and G. T. Kerr, *ibid.*, **68**, 476 (1946).

[16] E. T. McBee, C. G. Hsu, O. R. Pierce and C. W. Roberts, *ibid.*, **77**, 915 (1955).

[17] E. T. McBee, D. H. Campbell and C. W. Roberts, *ibid.*, **77**, 3149 (1955).

TABLE II

TRICHLOROSILANE AND METHYLDICHLOROSILANE ADDUCTS

Compound	B.p.[a] °C.	Mm.	Composition,[b] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found	Fluorine Calcd.	Fluorine Found
$CF_3CH_2CH_2SiCl_3$	112.8–113.7	751	15.55	15.74	1.73	2.01	46.04	46.04	24.62	21.71
$CF_3CH_2CH_2Si(CH_3)Cl_2$	121–122	737	22.75	22.80	3.31	3.46	33.65	33.50	27.00	25.44
$CF_3CF_2HCFCH_2SiCl_3$	127–127.8	758	16.02	15.80	1.00	1.14	35.56	35.50	38.06	37.02
$CF_3CF_2HCFCH_2Si(CH_3)Cl_2$	128–129.1	746	21.50	21.28	2.15	2.34	25.45	25.48	40.86	40.72
$CF_3C(SiCl_3){=}CCl_2$	77.5–78.5	35	12.06	12.22	..	..	59.46	59.31	19.10	19.43
$CF_3C(SiCH_3){=}CCl_2$	76–76.5	32	17.27	17.38	1.08	1.38	51.08	50.82	...	...
$CF_3CCl(SiCl_3)CHCl_2$	78–78.5	3.8	10.75	10.76	0.30	0.46	63.58	63.89	17.01	13.61
$C_2HClF_3SiCl_3$	117	746	9.52	9.34	0.40	0.64	56.35	56.40	22.61	22.81

[a] All boiling points are corrected. [b] Carbon, hydrogen and chlorine analyses obtained from Dr. C. S· Yeh, Purdue University. Fluorine analyses obtained from Clark Microanalytical Laboratories, Urbana, Ill.

TABLE III

TETRAALKYL SILANES

Compound	Yield, %	B.p.[c] °C.	Mm.	$n^{20}D$	d^{20}_4	Composition,[d] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Fluorine Calcd.	Fluorine Found	Mr[e] Calcd.	Mr Found
$CF_3CH_2CH_2Si(CH_3)_3$	58[a]	94.3–95.1	750	1.3576	0.896	42.35	42.35	7.65	7.60	33.53	33.69	40.89	41.63
$CF_3CH_2CH_2Si(C_2H_5)_3$	76.1	166.1–167.8	753	1.3962	0.961	50.94	50.91	8.94	8.63	26.87	26.78	53.53	53.07
$C_2F_5CHFCH_2Si(CH_3)_3$	36.3[b]	109.8–111.5	747	1.3441	1.133	35.29	35.04	5.04	5.03	47.90	47.21	44.35	44.51
$C_2F_5CHFCH_2Si(CH_3)(C_2H_5)_2$	64	154–155	747	1.3687	1.115	40.60	40.86	6.01	6.23	42.86	41.37	53.61	53.79
$C_2F_5CHFCH_2Si(C_2H_5)_3$	66.3	173.1	753	1.3800	1.110	42.86	43.12	6.43	6.47	40.71	39.95	58.24	58.45
$CF_3C(Si(CH_3)_3){=}CCl_2$	40.4	157	756	1.4322	1.243	30.38	30.17	3.80	3.78	24.05[f]	24.28	49.94	49.48
$CF_3C(Si(C_2H_5)_3){=}CCl_2$	72.7	119	28	1.4532[i]	1.193	38.71	38.84	5.38	5.38	20.47[g]	20.42	63.83	63.25
$C_2HClF_3Si(CH_3)_4$	42.9	43–44	43[h]	1.3887–90[i]	1.134	31.50	31.82	5.25	5.18	29.39	29.50	39.84	39.73

[a] From 3,3,3-trifluoropropylmethyldichlorosilane. [b] From 2,3,3,4,4,4-hexafluorobutyltrichlorosilane, 13.4% from 2,3,3,-4,4,4-hexafluorobutylmethyldichlorosilane. [c] All boiling points are corrected. [d] Carbon–hydrogen analyses by Dr. C. S. Yeh, Purdue University; fluorine analyses by Clark Microanalytical Laboratories, Urbana, Ill. [e] Bond refractions calculated by K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940), and E. L. Warrick, THIS JOURNAL, **68**, 2435 (1946), were used. [f] Calcd.: Cl, 29.96. Found: Cl, 30.01. [g] Calcd.: Cl, 25.48. Found: Cl, 25.24. [h] Distilled with decomposition at 117-120° (743 mm.). Calcd.: Cl, 18.63. Found: Cl, 18.20. [i] At 22°.

(750-ml. capacity) and heated at 140–155° (external temperature) for 46 hr. The reaction mixture gave, on rectification, 244.3 g. of chlorosilanes, b.p. 30–80°, 69.4 g. (0.35 mole) of unreacted 1,1,2-trichloro-3,3,3-trifluoropropene and 110 g. (33.5%) of trifluorodichloropropenyltrichlorosilane, b.p. 77.5–78.5° (35 mm.). The residue from this distillation was combined with the residues from other runs and rectified to give the saturated addition product, trifluorotrichloropropyltrichlorosilane.

Structure Proof of Trifluorodichloropropenyltrichlorosilane.—Trifluorodichloropropenyltrichlorosilane (101.6 g., 0.34 mole) was added dropwise to a warm solution of 250 g. of potassium hydroxide in 550 ml. of water. The solution was stirred under a nitrogen atmosphere and the exit gases led into a series of ice and Dry Ice traps. After all of the silane had been added, the reaction mixture was heated and refluxed for 45 min. There was no organic layer in the flask after cooling.

The organic layers from the traps were separated, combined, dried over Drierite and rectified to give 5 g. of 1,1-dichloro-3,3,3-trifluoropropene, b.p. 54.3–55° (uncor.), b.p. 53.5–54.2° (cor.), $n^{21}D$ 1.3682, m.p. −88° to −83° (uncor.); reported[13]: for 1,1-dichloro-3,3,3-trifluoropropene, b.p. 55.1°, 54.5°, $n^{20}D$ 1.3688-1.3690, m.p. −87.2°; for 1,2-dichloro-3,3,3-trifluoropropene, b.p. 53.7°, $n^{20}D$ 1.3670, m.p. −109.2°.

Part of the olefinic product was treated with bromine in carbon tetrachloride to give the dibromide, b.p. 71° (23–24 mm.), $n^{20}D$ 1.4788-1.4791.

Anal. Calcd. for $C_3HBr_2Cl_2F_3$: C, 11.08; H, 0.38; Br, 49.23; Cl, 21.84; F, 17.54. Found: C, 11.36; H, 0.46; Br, 50.81; Cl, 20.07; F, 19.00.

Addition of Trichlorosilane to Perfluoropropene.—Perfluoropropene[18] (48.6 g., 0.32 mole), *t*-butyl peroxide (3.8 g., 0.026 mole) and trichlorosilane (131.7 g., 0.97 mole) were distributed over 4 Carius tubes, which were sealed under an atmosphere of purified nitrogen (Fieser train) and heated in a furnace for 60 hr. at 125–132°. Most of the starting materials were recovered and the residue distilled to give 5.7 g. of fluorine-containing materials, b.p. 95–104°, from which 0.8 g. of a liquid, b.p. 99–99.2°, was isolated. This product contained fluorine and hydrolyzable chlorine atoms and is believed to be the desired addition compound 1,1,-2,3,3,3-hexafluoropropyltrichlorosilane.

Similar results were obtained, the conversion being always below 1%, with ultraviolet irradiation on 10 weeks exposure, with benzoyl peroxide at various temperatures up to 190°, by passing over silica gel at 250–500°, or without catalyst in an autoclave at 250°. No reaction except some halogen interchange took place with aluminum chloride.

Perfluoroisobutylene did not yield any isolable products when treated with trichlorosilane and *t*-butyl peroxide at 125–130°.

3,3,3-Trifluoropropyltrimethoxysilane.—3,3,3-Trifluoropropyltrichlorosilane (42 g., 0.18 mole) in 160 ml. of dry petroleum ether (b.p. 60–70°) was placed into a 500-ml., three-necked flask (stirrer, Friedrich condenser, addition funnel), and methanol (19.9 g., 0.62 mole) and pyridine (42.9 g., 0.54 mole) were added dropwise at 0°. After standing overnight the pyridine hydrochloride was removed by filtration and the filtrate rectified to give 24.9 g. (63%) of 3,3,3-trifluoropropyltrimethoxysilane, b.p. 141–142° (740 mm.), $n^{21}D$ 1.3546, $d^{20}D$ 1.137.[11]

Attempted conversion of this compound to 3,3,3-trifluoropropyltriethylsilane with ethylmagnesium bromide gave only impure material, the infrared spectrum of which indicated silicon–oxygen bonds.

Alkyl Derivatives.—The following experiment exemplifies the preparation of the alkyl derivatives: a Grignard solution was prepared in a 500-ml. three-necked flask from 9.06 g. (0.37 g.-atom) of magnesium turnings in 250 ml. of anhydrous ether and 40.7 g. (0.37 mole) of ethyl bromide in 50 ml. of anhydrous ether. After this solution was stirred for 2 hr., 27.9 g. (0.093 mole) of 2,3,3,4,4,4-hexafluorobutyltrichlorosilane in 25 ml. of anhydrous ether was added dropwise at 0°. The mixture was stirred for 4 hr. at room temperature and for 12 hr. at reflux temperature. The ether was distilled and the residue heated on a steam-bath for 4 hr. The distilled ether was returned to the flask and the solids broken up and suspended by stirring. The mixture was decomposed with ice and dilute hydrochloric acid. The separated water layer was extracted with ether and the combined ether layers were dried over Drierite. Rectifi-

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[18] L. H. Hals, T. S. Reid and G. H. Smith, THIS JOURNAL, **73**, 4054 (1951).

cation gave 17.3 g. (66.3%) of 2,3,3,4,4,4-hexafluorobutyltriethylsilane, b.p. 173.1°.

The methyl Grignard reactions were run with a 33% excess of Grignard reagent over the theoretically required amount, while a larger excess was used in ethyl Grignard reactions in order to ensure finding any reaction of the β-halogen substituent.

All the tetraalkyl compounds derived from trifluoropropyltrichlorosilane and hexafluorobutyltrichlorosilane were found to be stable toward concentrated hydrochloric acid and 40% aqueous potassium hydroxide at reflux for 14 hr.

Trifluorotetrachloropropyltrichlorosilane.—A Carius tube was charged with 12.1 g. (0.17 mole) of dry chlorine and 27.8 g. (0.093 mole) of trifluorodichloropropenyltrichlorosilane, sealed under a purified nitrogen atmosphere, and irradiated with light from an AH-1 bulb (Gartner Scientific Co.) for 3 days. After removal of the excess chlorine *in vacuo* the white solid residue was distilled to give 31.7 g. (94.9%) of trifluorotetrachloropropyltrichlorosilane, b.p. 118–120° (8.5 mm.). This compound hydrolyzed only slowly in dilute acid.

Anal. Calcd. for $C_3Cl_7F_3Si$: C, 9.74; Cl, 67.28; F, 15.42. Found: C, 10.02; Cl, 67.01; F, 14.79.

Trifluorodichloropropenyltriethylsilane from Trifluorotetrachloropropyltrichlorosilane.—A solution of 30.5 g. (0.075 mole) of trifluorotetrachloropropyltrichlorosilane in 50 ml. of anhydrous ether was added at 0° to a Grignard solution prepared from 12.81 g. (0.54 g.-atom) of magnesium turnings in 300 ml. of anhydrous ether and 57.7 g. (0.54 mole) of ethyl bromide in 100 ml. of anhydrous ether. The resulting suspension was stirred at reflux temperature for 12 hr., the ether distilled, the residue heated on a steam-bath for 5 hr., the ether added again, the mixture decomposed with ice and hydrochloric acid, the aqueous layer extracted with ether and the combined ether layers dried over Drierite. Rectification gave 11.8 g. (56.2%) of trifluorodichloropropenyltriethylsilane, b.p. 112.5–113.5° (23 mm.), $n^{20}D$ 1.4534–1.4535, d^{20}_4 1.189.

The infrared spectrum of this compound was identical with the one of trifluorodichloropropenyltriethylsilane prepared from trifluorodichloropropenyltrichlorosilane.

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WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Cleavage of Ethers by Hydrogen Bromide

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The relative reactivities of several alkyl groups have been determined in the internal competitive reaction RR'O + HBr = (RBr, R'Br) + (R'OH + ROH). With initial mole fraction hydrogen bromide of about 0.65, relative reactivities at 26° are: methyl 11.1, ethyl 1.00, propyl 1.00, butyl 0.93, *i*-butyl 0.053, *i*-propyl 0.87, 3-pentyl 4.2 and cyclopentyl 3.8. The first five groups are cleaved apparently by an SN2 reaction, the last three by a reaction to which there is considerable SN1 contribution. The relative reactivities of secondary alkyl groups in ethers decrease with decreasing mole fraction of hydrogen bromide. In the competitive reaction of butyl ether and propyl alcohol with hydrogen bromide, the ether reacts about 7.5 times faster at an initial mole fraction of hydrogen bromide of 0.63; about 1.4 times faster at an initial mole fraction of 0.32. At the higher initial mole fraction, butyl ether reacts about 12 times faster than isopropyl alcohol.

Despite the importance of the alkyl–oxygen bond in organic chemistry, relatively little mechanistic attention has been given to its cleavage in simple ethers and alcohols. Although both ethers and alcohols involve similar factors, the investigation of ethers offers advantages which will appear in the discussion.

The alkyl–oxygen bond cannot be cleaved by displacement reactions in alkyl ethers and alcohols as such but only in complexes in which considerable positive charge is transferred to the oxygen atom, *e.g.*, in such species as R_2OH^+ and $R_2O:BCl_3$.[1] In the present work, hydrogen bromide is employed as the cleaving agent. Cleavage by hydrogen bromide of primary alkyl–oxygen and of tertiary alkyl–oxygen bonds seems to occur by typical SN2 and SN1 reactions, respectively.[1] The nature of the cleavage of secondary alkyl–oxygen bonds is in doubt.

The stoichiometry of the reaction is

$$R'RO + HBr = (R'Br, RBr) + (ROH, R'OH) \quad (1)$$

Determination of the ratio R'Br/RBr in the product gives the relative rates of cleavage of the two alkyl–oxygen bonds in the unsymmetrical ether, R'RO. The relative rates of displacement of two groups attached to the same center is an unusually favorable case of competitive reactions.[2] The present paper reports the results of the cleavage of a number of unsymmetric ethers and of the relative rates of cleavage of butyl ether *vs.* propyl and isopropyl alcohols in conventional competitive reactions.

Experimental Procedure

Materials.—The following ethers were prepared by the Williamson synthesis: methyl butyl, b.p. 69.2°; ethyl butyl, 91.9°; propyl butyl, 116.2°; isobutyl butyl, 138.8°; cyclopentyl butyl, 168°; isopropyl propyl, 80°; isobutyl propyl, 107°; 1-ethylpropyl propyl, 128.5°; and diisobutyl, 120-121°. Since unreacted alcohol usually would form an azeotrope with the ether, gross quantities of alcohol were removed by formation of borate esters[3] followed by distillation. Certain ethers were next chromatographed on silica gel with elution by methanol. The ethers were then fractionated from sodium in a 50-plate Stedman column. Butyl ether (Eastman Kodak Co., White Label) was given the last treatment. The infrared absorption spectra of these and the other compounds employed in this research are presented in the doctoral thesis of Milton E. Fuller, Northwestern University, 1956.

The following alkyl halides were either commercial materials subjected to purification or compounds prepared from the corresponding alcohols by standard methods: butyl bromide and isobutyl bromide, Eastman Kodak Co., White

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[1] R. L. Burwell, Jr., *Chem. Revs.*, **54**, 615 (1954).

[2] Such cleavage of ethers resembles the cleavage of unsymmetric dialkylmercury, RR'Hg + HCl = (RH, R'H) + (RHgCl, R'HgCl); M. S. Kharasch and A. L. Flenner, THIS JOURNAL, **54**, 674 (1932).

[3] C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, p. 163.