[Contribution from the Department of Chemistry, Purdue University]

The Addition of Trichlorosilane and Methyldichlorosilane to Tetrachloroethylene

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Trichlorosilane and methyldichlorosilane were added to tetrachloroethylene to yield tetrachloroethyltrichlorosilane and trichlorovinyltrichlorosilane. Trichlorovinyltrichlorosilane and trichlorovinyltrimethylsilane undergo addition reactions with trichlorosilane, methyldichlorosilane, chlorine and *p*-toluenethiol. Pentachloroethyltrichlorosilane with ethylmagnesium bromide gave trichlorovinyltriethylsilane.

Discussion

Addition of trichlorosilane to trichloroethylene and the dichloroethylenes to yield olefinic products has been described by Wagner[3] and Agre.[4a–c] While this work was in progress, a patent[5] was issued which describes the addition of chlorosilanes to tetrachloroethylene to produce unsaturated silanes containing the trichlorovinyl group.

This paper reports a study of the addition of trichlorosilane and methyldichlorosilane to tetrachloroethylene and an investigation of the chemical properties of the addition products. High temperatures (600°) at atmospheric pressure, a free radical initiator (*t*-butyl peroxide) at moderate temperatures (125–140°), and ultraviolet irradiation were studied as conditions for the addition. High temperatures gave only trichlorovinyltrichlorosilane (Table I) in agreement with the work of earlier investigators,[3–5] while *t*-butyl peroxide at lower temperatures gave some 1,1,2,2-tetrachloroethyltrichlorosilane. *t*-Butyl peroxide, the best of the catalysts tried (it is a liquid that is miscible with the reactants and generates free radicals at a measurable rate at moderately high temperatures (125°)[6]), gave only low conversions (Table I). Methyldichlorosilane with *t*-butyl peroxide gave the unsaturated addition compound, trichlorovinylmethyldichlorosilane, and a double addition product, 1,2-bis-(methyldichlorosilyl)-1,2-dichloroethene.

Trichlorovinyltrichlorosilane and Grignard reagents gave the corresponding trialkyltrichlorovinylsilane, with no β-elimination involving the chlorine atoms being observed; this is in accordance with the findings of Agre.[4a,7] Addition of chlorine to trichlorovinyltrichlorosilane gave pentachloroethyltrichlorosilane; this compound on treatment with ethylmagnesium bromide lost chlorine to give trichlorovinyltriethylsilane.

Trichlorosilane added in better conversions to trichlorovinyltrichlorosilane (20.9%) and trichlorovinyltrimethylsilane (44.2%) than to tetrachloroethylene (12.6%). This was expected because of the electron-releasing effect of the silicon atom and the resulting easier attack by the silyl radical.[8] The isolated products were again olefins, except in one case where a small amount of 1,2-bis-(trichlorosilyl)-1,1,2-trichloroethane was isolated.

Table I

Silanes from Tetrachloroethylene

Method	Conversion, %		
	With $SiHCl_3$		With CH_3SiHCl_2[a]
	CCl_2-CCl-$SiCl_3$	CCl_2HCCl_2-$SiCl_3$	CCl_2-CClSi-$(CH_3)Cl_2$
Hot tube (600°) (A)	14	0	..
Ultraviolet irradiation (B)	7.1	1.1	..
t-Butyl peroxide, Carius tubes, 125–130° (C)	12.6	4.7	8.1
t-Butyl peroxide, nickel autoclave, 120–145° (D)	11.5	2.4	18.8

[a] No saturated addition product could be isolated in pure state, but the double addition product, 1,2-bis-(methyldichlorosilyl)-1,2-dichloroethene, was isolated.

Chlorovinylsilanes are known to be readily attacked by alkali to cleave the carbon–silicon bond,[9] and this was found to be true for the trichlorovinyl compounds. Trichlorovinyltrichlorosilane gave trichloroethylene and some dichloroacetylene with strong aqueous potassium hydroxide. Trichlorovinyltrimethylsilane was more stable toward alkali but was also cleaved after several hours at reflux. 1,2-Bis-(trichlorosilyl)-1,2-dichloroethene was readily attacked and gave a violent explosion, probably caused by chloroacetylene. No dichloroethylene was obtained from this reaction.

Trichlorovinyltrimethylsilane was treated with *p*-toluenethiol and sodium ethoxide in ethanol to prepare the same product obtained from *p*-toluenethiol and trichloroethylene. In view of the structure of the addition compound obtained from trichloroethylene and sodium ethoxide,[10] the product is thought to be *p*-tolylmercapto-1,2-dichloroethene.[11]

During chlorination of trichlorovinyltrimethylsilane most of the methyl hydrogens were sub-

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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 for the degree of Doctor of Philosophy, June, 1956.

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

[4] (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).

[5] J. W. Gilkey, U. S. Patent 2,723,986 (1955).

[6] J. H. Raley, F. F. Rust and W. E. Vaughan, This Journal, **70**, 1336 (1948).

[7] However, elimination of chlorine from the trichlorovinyl group was expected, since R. Binaghi, *Gazz. chim. ital.*, **57**, 669 (1927), obtained acetylene from hexachloroethane and ethylmagnesium bromide through a 1,2-dichloroethylene intermediate.

[8] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, This Journal, **69**, 188 (1947). The influence of the methyl groups enhances this electron-releasing effect; hence, the higher yields with trichlorovinyltrimethylsilane.

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

[10] O. C. Stephens, *J. Chem. Soc. Ind.*, **43**, 313T (1924).

[11] Treatment of trichlorovinyltrimethylsilane with sodium ethoxide in ethanol gave a similar result, trimethylethoxysilane, 1,2-dichlorovinyl ethyl ether and ethyl chloroacetate being the products. The first two products arose directly from trichlorovinyltrimethylsilane, while ethyl chloroacetate arose from 1,2-dichlorovinyl ethyl ether in the basic medium; *cf.* A. Geuther and F. Brockhoff, *J. prakt. Chem.*, [2] **7**, 101 (1873).

stituted before addition to the double bond occurred. Two products, $CCl_3CCl_2Si(CCl_3)_3$ (I) and $CCl_3CCl_2Si(CCl_3)_2CHCl_2$ (II), were obtained. Compound II was distinguished from the isomeric compounds, $C_2HCl_4Si(CCl_3)_3$ (III), which could arise by addition of hydrogen chloride, formed during the reaction to the trichlorovinyl group, by treatment with alkali. If structure II were correct, tetrachloroethylene would be obtained by this cleavage, whereas structure III would give trichloroethylene or dichloroacetylene. Tetrachloroethylene was isolated confirming structure II.

Experimental

Materials.—Tetrachloroethylene (a gift from E. I. du Pont de Nemours and Co.) was dried over phosphorus pentoxide and rectified. Trichlorosilane and methyldichlorosilane (Pure Grade unless otherwise indicated) were obtained from Anderson Laboratories and used without further purification.

Addition of Trichlorosilane to Tetrachloroethylene. Hot Tube (Method A).—A mixture of 950 g. (5.72 moles) of tetrachloroethylene and 1163 g. (8.6 moles) of technical trichlorosilane was dropped into a Vycor tube of 20 mm. i.d., loosely packed with Raschig rings and heated over a 20-cm. zone in a tube furnace. The temperature, maintained at 570–595°, was measured by a thermocouple inserted between the Vycor tube and heating element. A steady stream of purified nitrogen (Fieser train) was passed through the apparatus during the experiment (presence of oxygen caused explosions). The exit gases were liquefied in an air-cooled and a Dry Ice trap connected in series. The trap contents gave on distillation: unreacted starting materials (91.5 g., 0.68 mole of trichlorosilane and 642 g., 3.9 moles of tetrachloroethylene); 898 g. of by-product silicon tetrachloride and chlorinated disilanes, b.p. 47–111°; 94.5 g. of a carbon-containing by-product, b.p. 170–173°; a forerun; and 139.3 g. (9.2% based on starting olefin) of trichlorovinyltrichlorosilane, b.p. 193° (748 mm.) (reported[5] b.p. 93° (30 mm.)). A silane to olefin ratio of 2:1 gave an improved conversion (*ca.* 14% at 600°).

Below 385° conversion of trichlorosilane to tetrachlorosilane occurred without the formation of trichlorovinyltrichlorosilane and extensive decomposition took place above 670°.

Ultraviolet Initiation (Method B).—A dry 300-ml. quartz flask, connected through a condenser and a Dry Ice trap to a 20-cm. mercury seal,[12] was filled with 83 g. (0.5 mole) of tetrachloroethylene and 203 g. (1.5 moles) of trichlorosilane, swept with nitrogen, and exposed for 90 hr. to the irradiation from a mercury vapor lamp. The flask contents turned red-brown during this period. Trichlorosilane (168 g., 1.2 moles) and tetrachloroethylene (73 g., 0.44 mole) and a small intermediate cut consisting of silicon tetrachloride were obtained by distillation. The residue was rectified to give 9.4 g. (7.1%) of trichlorovinyltrichlorosilane, b.p. 66.5–69.5° (6.5 mm.), and 1.6 g. (1.1%) of 1,1,2,2-tetrachloroethyltrichlorosilane, b.p. 97–98° (2.5 mm.).

TABLE II

ABSORPTION BANDS OF UNSATURATED SILANES BETWEEN 6 AND 7 μ

Compound	Absorption between 6 and 7 μ[a,b]
Trichlorovinyltrichlorosilane	6.52(s)
Trichlorovinyltrimethylsilane	6.49(s)
Trichlorovinyltriethylsilane	6.50(s), 6.86(m)
1,2-Bis-(trichlorosilyl)-1,2-dichloroethene	6.12(w), 6.72–6.75(s)
1,2-Bis-(methyldichlorosilyl)-1,2-dichloroethene	6.20(vw), 6.64(s)

[a] A Perkin-Elmer no. 21 double beam infrared spectrometer was used. [b] s = strong, m = medium strong, w = weak, vw = very weak.

***t*-Butyl Peroxide Initiated (Method C).**—Tetrachloroethylene (44 g., 0.27 mole), *t*-butyl peroxide (3.2 g., 0.022 mole) and trichlorosilane (108 g., 0.8 mole) were distributed in equal proportions over 4 Carius tubes, which were sealed under an atmosphere of purified nitrogen (Fieser train) and heated for 60 hr. at 125–130° in a furnace. The contents of the tubes were combined and 92 g. (0.68 mole) of trichlorosilane and 36 g. (0.22 mole) of tetrachloroethylene recovered. The residue was rectified to give 8.9 g. (12.6%) of trichlorovinyltrichlorosilane, b.p. 74° (10 mm.), and 3.8 g. (4.7%) of 1,1,2,2-tetrachloroethyltrichlorosilane, b.p. 97.5–99° (3 mm.).

Method D.—The preceding experiment was repeated in a glass-lined, nickel-clad autoclave. The same proportions of reactants at 125–140° for 60 hr. gave 11.5% of trichlorovinyltrichlorosilane and 2.4% of 1,1,2,2-tetrachloroethyltrichlorosilane.

Trichlorosilane was added to trichlorovinyltrichlorosilane and trichlorovinyltrimethylsilane, methyldichlorosilane to tetrachloroethylene and trichlorovinyltrimethylsilane using method C. Method D gave better results than method C in the addition of methyldichlorosilane to tetrachloroethylene (see Table I).

1,2-Bis-(trichlorosilyl)-1,2-dichloroethane with Alkali.—A concentrated solution of potassium hydroxide (130 g. in 250 ml. of water) was placed in a 500-ml., three-necked flask, and to it was added 28 g. (0.07 mole) of 1,2-bis-(trichlorosilyl)-1,2-dichloroethene. The flask was connected through an ice-cooled trap to the atmosphere. The initially formed white precipitate dissolved on warming. Cooling the flask brought about a violent explosion in the trap and the connecting line. This explosion could have been caused by chloroacetylene formed in this reaction.

Trichlorovinyltrichlorosilane with Alkali.—To a concentrated solution of potassium hydroxide (90 g. in 200 ml. of water) in a 300-ml., three-necked flask was added 22 g. (0.083 mole) of trichlorovinyltrichlorosilane. A white precipitate formed which dissolved on heating and a small layer formed on the bottom of the flask. Several small explosions took place in the flask. After cooling, the small organic layer was separated, dried over Drierite and distilled to give 4 g. (36.7%) of trichloroethylene, b.p. 86.5–86.7° (747 mm.), n^{20}_D 1.4773–1.4775. Huntress lists[13] b.p. 86–88°, n^{20}_D 1.4775–1.47782.

Trichlorovinyltrimethoxysilane.—From 31.2 g. (0.12 mole) of trichlorovinyltrichlorosilane and a mixture of 13.6 g. (0.43 mole) of methanol and 28.8 g. (0.36 mole) of pyridine there was obtained, using the previously described procedure,[14] 20.5 g. (68%) of trichlorovinyltrimethoxysilane, b.p. 94.5–95° (12 mm.), n^{20}_D 1.4646, d^{20}_4 1.345.

This compound did not hydrolyze appreciably with water or dilute acid but was attacked by alkali.

Anal. Calcd. for $C_5H_9Cl_3O_3Si$: C, 23.86; H, 3.58; Cl, 42.34; M_R, 51.24. Found: C, 24.12; H, 3.86; Cl, 42.08; M_R, 51.65.

Grignard Reactions: Preparation of Alkyl Derivatives.—From 14.4 g. (0.054 mole) of trichlorovinyltrichlorosilane and 5.29 g. (0.22 g. atom) of magnesium turnings in 150 ml. of anhydrous ether and 30.9 g. (0.22 mole) of methyl iodide in 50 ml. of anhydrous ether there was obtained[14] 9.3 g. (84.5%) of trichlorovinyltrimethylsilane, b.p. 82° (31 mm.), n^{20}_D 1.4890, d^{20}_4 1.189.

Anal. Calcd. for $C_5H_9Cl_3Si$: C, 29.48; H, 4.42; Cl, 52.32; M_R, 48.96. Found: C, 29.51; H, 4.50; Cl, 52.46; M_R, 49.94.

Trichlorovinyltrimethylsilane was prepared in a similar way from trichlorovinyltrimethoxysilane and from trichlorovinylmethyldichlorosilane in 60.6 and 50.9% yields, respectively.

Trichlorovinyltriethylsilane, b.p. 113° (11 mm., n^{20}_D 1.4986, d^{20}_4 1.141, was obtained from trichlorovinyltrichlorosilane in 73.7% yield using the same procedure[14] with 7 moles of ethylmagnesium bromide used per mole of silane to make certain any reduction of the β-chlorine substituent would be evidenced; no reduction was observed.

Anal. Calcd. for $C_8H_{15}Cl_3Si$: C, 39.12; H, 6.11; Cl, 43.38; M_R, 62.85. Found: C, 39.30; H, 6.36; Cl, 43.74; M_R, 63.13.

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[12] E. W. Pietrusza, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **70**, 484 (1948).

[13] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[14] E. T. McBee, C. W. Roberts and G. W. R. Puerckhauer, THIS JOURNAL, **79**, 2329 (1957).

TABLE III

SILANE ADDITION COMPOUNDS

Compound	B.p.[a] °C.	Mm.	Percentage composition[c] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
$CCl_2{=}CClSiCl_3$	193	748	9.06	8.99	..	..	80.38	80.38
$CHCl_2CCl_2SiCl_3$	97–98	2.5	7.96	7.78	0.33	0.49	82.09	81.92
$CCl_2{=}CClSi(CH_3)Cl_2$	105.8–106.6	42	14.73	14.69	1.23	1.47	72.57	72.80
$Cl_2(CH_3)SiCCl{=}CClSi(CH_3)Cl_2$[b]	79.5–80.5	0.8	14.86	14.97	1.86	2.01	65.94	65.89
$Cl_3SiCCl{=}CClSiCl_3$	87.5–88.3	1.5	6.59	6.60	..	..	78.02	77.81
$Cl_3SiCHClCCl_2SiCl_3$	134.5–138.5	1.6	5.99	6.06	0.25	0.24	79.87	79.62
$Cl_3SiCCl{=}CClSi(CH_3)_3$	87	3	19.81	19.70	2.98	3.00	58.59	58.69
$Cl_2(CH_3)SiCCl{=}CClSi(CH_3)_3$	94.4–95	6	25.62	25.46	4.27	4.25	50.18	50.31

[a] All boiling points are corrected. [b] This compound was isolated from accumulated distillation residues of the addition of methyldichlorosilane to tetrachloroethylene. [c] All analyses by Dr. Yeh, Purdue University.

Attempted Preparation of 1,2-Bis-(trimethylsilyl)-1,2-dichloroethene.—From 31 g. (0.096 mole) of 1,2-bis-(methyldichlorosilyl)-1,2-dichloroethene in 50 ml. of anhydrous ether and 14 g. (0.58 g. atom) of magnesium turnings in 500 ml. of anhydrous ether and 81.8 g. (0.58 mole) of methyl iodide in 100 ml. of anhydrous ether, no isolable pure product was obtained. An attempt to prepare this compound from 1-(trichlorosilyl)-2-(trimethylsilyl)-1,2-dichloroethene using the same technique also gave no isolable product.

Pentachloroethyltrichlorosilane.—A Carius tube was charged with 9.3 g. (0.13 mole) of dry chlorine and 24 g. (0.09 mole) of trichlorovinyltrichlorosilane and irradiated with light from an AH-1 bulb (Gartner Scientific Co.) for 3 days. After removal of the excess chlorine under reduced pressure, the white solid residue was distilled to give 28.6 g. (94.1%) of pentachloroethyltrichlorosilane, b.p. 98.7° (6 mm.).

Anal. Calcd. for C_2Cl_8Si: C, 7.14; Cl, 84.52. Found: C, 6.98; Cl, 84.32.

Trichlorovinyltriethylsilane from Pentachloroethyltrichlorosilane.—A solution of 28.4 g. (0.085 mole) of pentachloroethyltrichlorosilane in 50 ml. of anhydrous ether was added dropwise at 0° to a solution prepared from 18.5 g. (0.76 g.-atom) of magnesium turnings in 500 ml. of anhydrous ether and 82.9 g. (0.76 mole) of ethyl bromide in 100 ml. of anhydrous ether. The resulting mixture was stirred for 4 hr. at room temperature, 9 hr. at reflux temperature, the ether distilled and the residue heated on a steam-bath for 5 hr. After the ether was returned to the flask, the mixture was decomposed with ice and dilute hydrochloric acid, the aqueous layer extracted with ether and the combined ether layers dried over Drierite. Rectification gave 13.2 g. (63.6%) of trichlorovinyltriethylsilane, b.p. 87.3–88° (3 mm.), n^{20}_D 1.4986, d^{20}_4 1.140.

The infrared spectrum of this compound was identical with that of the trichlorovinyltriethylsilane prepared from trichlorovinyltrichlorosilane.

Chlorination of Trichlorovinyltrimethylsilane.—A Carius tube was charged with 5.8 g. (0.08 mole) of chlorine and 2 g. (0.01 mole) of trichlorovinyltrimethylsilane and irradiated for 4 days with light from an AH-1 bulb. From the opened tube there was isolated 4.5 g. of a white solid, m.p. 132–139.5°; this was recrystallized several times from petroleum ether to give the product, m.p. 134.2–135.1°.

Anal. Calcd. for $C_5Cl_{14}Si$: C, 10.26; Cl, 84.94. Found: C, 10.40; Cl, 84.99.

In a subsequent experiment, 4.06 g. (0.02 mole) of trichlorovinyltrimethylsilane and 21 g. (0.3 mole) of chlorine irradiated for 9 days with light from an AH-1 bulb gave 11.7 g. of a white solid, m.p. 130–132°, after one recrystallization from petroleum ether (b.p. 35–37°). On repeated recrystallization from petroleum ether (b.p. 65–67°), the solid had a m.p. 128.3–128.6°. A mixed melting point with the compound obtained in the preceding experiment gave m.p. 129–131.8°.

Anal. Calcd. for $C_5HCl_{14}Si$: C, 10.91; H, 0.18; Cl, 83.82. Found: C, 10.84; H, 0.25; Cl, 83.90, 84.10.

This compound (5.7 g.) was refluxed with a 40% aqueous potassium hydroxide solution. The mixture was steam distilled and the aqueous layer extracted with ether. After drying and removal of the solvent, 0.7 g. of tetrachloroethylene,[13] b.p. 119–120.8°, n^{20}_D 1.5004, was obtained.

Attempts to introduce only one chlorine atom into one of the methyl groups of trichlorovinyltrimethylsilane by the above technique and the use of an excess of the silane were unsuccessful, leading to polychlorinated or unreacted materials.

Trichlorovinyltrimethylsilane and *p*-Toluenethiol.—In a 300-ml., three-necked flask (stirrer, addition funnel, Friedrich condenser protected with a calcium chloride tube) was placed 75 ml. of absolute ethanol and 2.53 g. (0.11 mole) of sodium. To this solution was added 12.4 g. (0.1 mole) of *p*-toluenethiol in 60 ml. of absolute ethanol followed by 20.3 g. (0.1 mole) of trichlorovinyltrimethylsilane. The mixture was refluxed for 46 hr. The resulting solid (5 g.) was filtered and proved to be sodium chloride. The filtrate was evaporated to give a yellow liquid, which was separated into two fractions by simple distillation: b.p. 114–127° (3 mm.), 15.2 g., and b.p. 165–270° (3 mm.), 2.7 g.

Part of the lower boiling fraction was rectified to give *p*-tolylmercaptodichloroethene, b.p. 127–127.5° (3 mm.), n^{19}_D 1.5966–1.5970, d^{20}_4 1.270.

Anal. Calcd. for $C_9H_8Cl_2S$: C, 49.32; H, 3.66; Cl, 32.42; S, 14.61; M_R, 58.72. Found: C, 49.62; H, 3.65; Cl, 32.15; S, 14.86; M_R, 58.86.

Another part of the lower boiling fraction was oxidized to the sulfone: 2.8 g. (0.013 mole) of *p*-tolylmercaptodichloroethene was refluxed for 2.5 hr. with 95 ml. of glacial acetic acid and 10 ml. of 30% hydrogen peroxide and then allowed to stand overnight. The solution was evaporated and a dark gray mass was left, which gave after recrystallization from ethanol 1.2 g. of a brown solid. Several recrystallizations from ethanol gave a white crystalline product, m.p. 76–77°; reported[15] for the oxidized addition product of *p*-toluenethiol to trichloroethylene, m.p. 74–77°. A mixed melting point of our compound with the one prepared by McManimie gave no depression.

Trichlorovinyltrimethylsilane and Sodium Ethoxide.—Absolute ethanol (400 ml.) and 7.59 g. (0.33 g.-atom) of sodium was placed into a 1000-ml., three-necked flask (stirrer, Friedrich condenser, addition funnel through which dry nitrogen was admitted). To this solution was added 61 g. (0.3 mole) of trichlorovinyltrimethylsilane. The resulting mixture was refluxed for 46 hr. A white precipitate was formed during this period. The solution was filtered and 19 g. (0.32 mole) of sodium chloride remained. The filtrate was rectified to give 37.4 g. of trimethylethoxysilane–ethanol azeotrope, b.p. 66° (744 mm.), n^{20}_D 1.3729; an ethanol fraction, b.p. 77.5–78° (744 mm.); and 11.1 g. (30.5%) of ethyl chloroacetate,[13] b.p. 63° (34 mm.), 141.7° (747 mm.), n^{20}_D 1.4217, d^{20}_4 1.150.

The trimethylethoxysilane–ethanol azeotrope was poured into water and the silane layer washed with water, dried over Drierite and rectified to give 15.5 g. (43.7%) of trimethylethoxysilane,[16] b.p. 75° (742 mm.), n^{20}_D 1.3747, d^{20}_4 0.762.

The first third of the ethanol fraction yielded on dilution with water a heavy layer, which was washed with water, dried over Drierite and rectified to give 10 g. (23.6%) of 1,2-dichlorovinyl ethyl ether,[13] b.p. 42.2° (31 mm.), 126–127.6° (746 mm.), n^{21}_D 1.4519, d^{20}_4 1.197.

The infrared spectra of the compounds obtained in this

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(15) R. J. McManimie, Ph.D. Thesis, Purdue University, 1953, p. 43

(16) R. O. Sauer, This Journal, **66**, 1707 (1944).

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).