[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Synthesis of Fluorine-Containing Organosilanes

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Fluorine-containing organosilanes have been prepared by the interaction of vinylsilanes with fluoroolefins. Cyclic adducts of the type $CX_2—CF_2—CH_2—CH—(CH_2)_n—SiR_3$ (where X equals fluorine and/or chlorine, n equals 0 to 3, and R equals ethoxy, methyl, and/or chlorine) are obtained when trifluoroiodoethylene was used with the vinylsilanes.

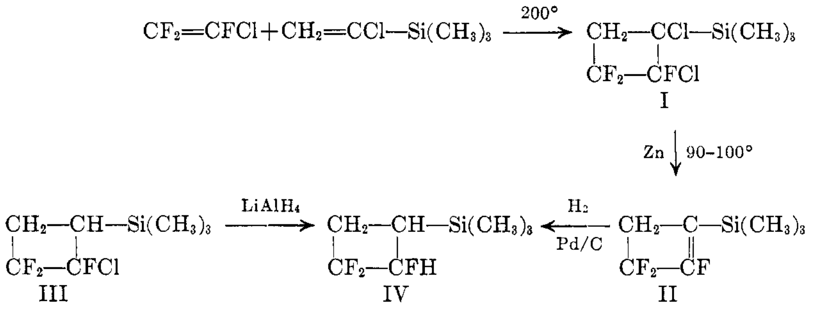
The thermal and chemical stability of the silicon polymers and tetraalkylsilanes[1,2] and the well known inherent stability of the polyfluorocarbons have led to attempts to incorporate the attributes of both systems into fluoroalkyl silicon compounds of high stability.

A number of new fluorine-containing cyclobutylsilanes have been prepared from fluoroolefins and alkenysilanes under conditions which generally favor cyclic codimer reactions rather than linear telomerization. All reactions were carried out in Pyrex combustion tubes at about 200° with hydroquinone and/or Terpene-B as free-radical inhibitors. The rationale for this study was based on the reasoning that the β-fluorine atoms of the cyclobutyl moiety in compounds of the type $CX_2—CF_2—CH_2—CH—SiR_3$ (where X is fluorine and/or chlorine) would be close enough to the silicon atoms to improve or enhance the thermal stability of the silicon-carbon bond. From steric considerations and the well known stability of fluorine-containing cyclobutanes toward alkaline hydrolysis, it was assumed that the fluorine-containing cyclobutyl group would be hydrolytically stable.

Thus, tetrafluoroethylene was codimerized with vinyltrimethylsilane in 82% yields to give $CF_2—CF_2—CH_2—CH—Si(CH_3)_3$. This fluorine-containing cyclobutylsilane was unaffected by dilute hydrochloric acid. Similarly, a 20% solution of potassium hydroxide at 70° for ten hours had no effect on the compound. On the other hand, α-fluorine-containing silanes while thermally stable undergo immediate hydrolysis in cold dilute alkali.[3]

The free radical additions of fluoroalkyl halides to vinylsilanes were also studied. Perfluorovinyl iodide added photochemically to vinyltrimethylsilane to give $CF_2{=}CF—CH_2—CHI—SiCl_3$ and $CF_2{=}CF—CH_2—CHI—Si(CH_3)_3$ in 56% and 16% yields, respectively. These yields are in line with the observation of Tarrant[4] that difluorodibromomethane added more readily to vinyltrichlorosilane than to vinyltrimethylsilane.

The structure of III was established chemically by the reduction of the chlorine atom by lithium aluminum hydride followed by the unequivocal synthesis of IV according to the following scheme:



The dechlorination of I with zinc in butyl cellusolve at 90–100° to the trimethylsilylcyclobutane (II) definitely proved the vicinal character of the chlorine atoms. The *cis-trans* relationship of the chlorine atoms in I is unknown.

The hydrogenation of II to IV with palladium-on-charcoal as a catalyst proceeded quantitatively at room temperature. The chlorine atom in III was reduced in 64% yield by lithium aluminum hydride to give IV. The infrared spectra of IV obtained by both methods were found to be identical.

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(1) H. Rosenberg, J. D. Groves, and E. J. Bartholomew, WADC Technical Report 54-613 Part I (1955).

(2) H. Rosenberg, C. Tamborski, and J. D. Groves, WADC Technical Report 54-613 Part III, (1957).

(3) R. N. Haszeldine, and E. J. Marklow, *J. Chem. Soc.*, 962 (1956).

(4) P. Tarrant and G. W. Dykes, 128th Meeting American Chemical Society, Minneapolis, Minn., September 1955.

On the basis of the known structures of III and I, it is reasonable to assume that all fluoroolefins of the type, $CF_2 = CX_2$ (where X is fluorine and/or chlorine) codimerize with vinylsilanes to give products of similar structure (*e.g.*, $\underline{CX_2-CF_2-CH_2-CH}-SiR_3$).

This mode of addition seems quite reasonable and the reaction is diagnostic of the conjugative nature of a vinyl group joined to silicon,[5,6] but apparently of small importance in the cyclization reactions described here, as all the alkenylsilanes gave essentially the same kind of products.

The structure of the resultant cyclobutanes was consistent with other proved structures of various codimers of 1,1-difluoro-2,2-dihaloethylene and a conjugated, terminally unsaturated system. However, the activating influence of the silicon atom was more pronounced, the closer it was to the terminal double bond. This is shown by the respective yields in the following series: $\underline{CF_2-CF_2-CH_2-CH}-Si(CH_3)_3$, 82%; $\underline{CF_2-CF_2-CH_2-CH}-CH_2-Si(CH_3)_3$, 73.4%; $\underline{CF_2-CF_2-CH_2-CH}-(CH_2)_3-Si(CH_3)$, 40%.

The influence of the trimethylsilyl group and the trichlorosilyl group on the double bond of the vinyl group was demonstrated to be in the same direction. Thus, when the trichlorosilylcyclobutane obtained from the codimerization of chlorotrifluoroethylene and vinyltrichlorosilane was treated with methyl magnesium bromide, a trimethylsilylcyclobutane was obtained which was identical to the one prepared from the codimerization of chlorotrifluoroethylene and vinyltrimethylsilane. This was also demonstrated in the codimerization reaction of chlorotrifluoroethylene and α-chlorovinyltrichlorosilane and α-chlorovinyltrimethylsilane.

The relative conjugative ability of the trimethylsilyl and the trichlorosilyl groups is less defined; however, it is theorized that the trichlorosilyl group might be more effective in increasing the reactivity of the double bond in the vinyl groups, as the chlorine atoms on the silicon atom would better stabilize the contributing form, $Cl_3Si=CH-\overset{+}{C}HR$ because of their electronegativity. This effect may be slight, however. Under the reaction conditions employed it was not surprising to observe no definite trends in the yields of products, when vinyltrichlorosilane or vinyltrimethylsilane was codimerized with 1,1-difluoro-2,3-dihaloethylenes.

EXPERIMENTAL

Preparation of vinyltrimethylsilane. Vinyltrimethylsilane was prepared in 40–45% yields by the method of Sommer,[7] from the reaction of vinyltrichlorosilane with methylmagnesium bromide.

Preparation of tetrafluoroethylene. Tetrafluoroethylene was prepared by the method of LaZerte[8] by the pyrolysis of sodium perfluorobutyrate. The yield in this reaction was not determined, as only a small amount of tetrafluoroethylene was prepared each time from a large quantity of sodium perfluorobutyrate.

Preparation of 2-chloro-2,3,3-trifluorocyclobutyl trichlorosilane (I). Exactly 16.2 g. (0.10 mole) of vinyltrichlorosilane and 0.1 g. of hydroquinone were placed in a heavy-walled Pyrex combustion tube (19 mm. × 25 mm. × 700 mm.). After the contents of the tube had been frozen in liquid nitrogen, about 23.4 g. (0.20 mole) of chlorotrifluoroethylene was distilled into the tube. Vacuum was applied, the tube sealed, and placed in a steel-jacketed heating assembly and heated at 210° for 14 hr. After cooling in a Dry Ice–isopropyl alcohol mixture, the tube was opened. Vacuum distillation (through a 4-cm. glass helices–packed column) yielded 4.1 g. of vinyltrichlorosilane and 10.7 g. (51.0%) of I, b.p. 59–60° at 15 mm., n_4^{25} 1.4202, d_D^{25} 1.553, MR_D: calcd. 45.86; obsd. 46.15.

Anal. Calcd. for $C_4H_3Cl_4F_3Si$: C, 17.28; H, 1.08; Cl (hydrolyzable) 38.27; F, 20.50. Found: C, 17.36; H, 1.20; Cl, 38.16; F, 20.75.

2-Chloro-2,3,3-trifluorocyclobutyltrimethylsilane (II). *Method 1.* About 14.0 g. (0.141 mole) of vinyltrimethylsilane, 32.3 g. (0.28 mole) of chlorotrifluoroethylene, and 0.1 g. of hydroquinone were sealed in a heavy-walled Pyrex combustion tube and heated for 20 hr. at 210°. The tube was cooled and opened. Vacuum distillation of the product yielded 16.5 g. (54.5%) of II, b.p. 75° at 35 mm., n_D^{25} 1.4062, d_4^{25} 1.132, MR_D: calcd. 46.97, obsd. 47.02.

Anal. Calcd. for $C_7H_{12}F_3ClSi$: C, 38.79; H, 5.58; Cl, 16.36. Found: C, 38.81; H, 5.77, Cl, 16.15.

Method 2. To approximately 0.13 mole of methylmagnesium bromide in 80 ml. of anhydrous ether was added dropwise with stirring a solution of 10.0 g. (0.036 mole) of I in 15 ml. of anhydrous ether. A reflux temperature of 30° was maintained throughout the addition which was then refluxed for an additional 3 hr. The contents of the flask were poured into ice water and neutralized with 10% sulfuric acid. The layers were separated and the aqueous layer extracted three times with small portions of ether. The extracts were combined and dried over Drierite. Following removal of the solvent, vacuum distillation gave 4.95 g. (63.5%) of II, b.p. 85° at 50 mm., n_D^{25} 1.4062. The infrared spectrogram of this material was identical with that of the compound prepared by Method I.

1,2-Dichloroethyltrichlorosilane. The chlorination of vinyltrichlorosilane in silicon tetrachloride carried out according to the method of Wagner,[9] gave a 94% yield of 1,2-dichloroethyltrichlorosilane, b.p. 82–84° at 26 mm., (lit.,[9] b.p. 180–182° at 760 mm.)

α-Chlorovinyltrichlorosilane. Exactly 262.5 g. (1.13 moles) of 1,2-dichloroethyltrichlorosilane and 182.0 g. (1.41 moles) of quinoline were placed in a 500-ml. one-neck flask fitted with a reflux condenser. The temperature was slowly increased to 120°, at which stage a vigorous exothermic reaction took place. Heating was discontinued immediately and the temperature rose rapidly to 150°. After 40 min., the temperature dropped to 60°, and an amber semisolid mass was obtained. The condenser was fitted for downward distillation and the material boiling in the range of 40–125° was collected. Redistillation through a Todd Precise Fractionation Assembly gave 129.2 g. (58.6%) of an α-chlorovinyl-

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(8) J. D. LaZerte, L. J. Hals, R. S. Reid, and G. H. Smith, *J. Am. Chem. Soc.*, **76**, 4525 (1953).

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trichlorosilane, b.p. 117–119° at 626 mm., n_D^{25} 1.4615 (lit.,[10] b.p. 124° at 724 mm., n_D^{20} 1.4638. The above general procedure[7,10,11] was first used by Hurd[12] in the preparation of vinyltrichlorosilane from 2-chloroethyltrichlorosilane.

α-Chlorovinyltrimethylsilane. To approximately 0.43 mole of methylmagnesium bromide in 150 ml. of anhydrous ether was added dropwise with stirring, a solution of 23.0 g. (0.118 mole) of α-chlorovinyltrichlorosilane in 25 ml. of anhydrous ether. A reflux temperature of 30° was maintained throughout the addition which was completed in 45 min. The reaction mixture was then refluxed for an additional 2 hr. The contents of the flask were poured into ice water and neutralized with 10% sulfuric acid. The layers were separated and the aqueous layer extracted three times with small portions of ether. The extracts were combined and dried over Drierite. After removal of the solvent, vacuum distillation gave 9.9 g. (62.3%) of α-chlorovinyltrimethylsilane, b.p. 97° at 624 mm., n_D^{25} 1.4280, (lit.,[7] b.p. 104° at 730 mm., n_D^{20} 1.4299).

1,2-Dichloro-2,3,3-trifluorocyclobutyltrichlorosilane (III). Exactly 29.5 g. (0.15 mole) of α-chlorovinyltrichlorosilane, 34.95 g. (0.30 mole) of chlorotrifluoroethylene, and 0.1 g. of hydroquinone were sealed in a heavy-walled Pyrex combustion tube and heated at 220° for 33 hr. The tube was cooled and opened. Vacuum distillation of the amber liquid gave 38.3 g. (81.7%) of III, b.p. 45–46° at 2 mm., n_D^{25} 1.4493, d_4^{25} 1.644 MR$_D$ calcd.: 50.70, obsd.: 50.97.

Anal. Calcd. for $C_4H_2F_3Cl_5Si$: C, 15.38; Cl, 56.70. Found: C, 15.38; Cl, 56.52.

1,2-Dichloro-2,3,3-trifluorocyclobutyltrimethylsilane (IV). *Method 1.* About 8.0 g. (0.0595 mole) of α-chlorovinyltrimethylsilane, 14.0 g. (0.12 mole) of chlorotrifluoroethylene, and 0.1 g. of hydroquinone were sealed in an air-free heavy-walled Pyrex combustion tube and heated for 28 hr. at 210°. The tube was cooled and opened. Vacuum distillation of the product yielded 7.6 g. (51.0%) of IV, b.p. 82° at 25 mm., n_D^{25} 1.4315, d_4^{25} 1.243, MR$_D$ calcd.: 51.81, obsd.: 52.29.

Anal. Calcd. for $C_7H_{11}Cl_2F_3Si$: C, 33.47; H, 4.42; Cl, 28.23. Found: C, 33.87; H, 4.49; Cl, 28.11.

Method 2. To approximately 0.87 mole of methylmagnesium bromide in 500 ml. of anhydrous ether was added dropwise a solution of 75.2 g. (0.24 mole) of III in 100 ml. of anhydrous ether. A gentle reflux was maintained throughout the addition which was completed in 70 min. The reaction mixture was refluxed for an additional 9 hr. The excess Grignard reagent was decomposed by slowly pouring the contents of the flask into ice water, then neutralized with 10% sulfuric acid. The layers were separated and the aqueous layer was extracted four times with small portions of ether. The extracts were combined and dried over Drierite. After solvent removal, vacuum distillation yielded 50.4 g. (83.7%) of IV, b.p. 82–83° at 25 mm., n_D^{25} 1.4312. The infrared spectrogram of this product was identical with that of the compound prepared by Method 1.

2,3,3-Trifluoro-1-cyclobutenyltrimethylsilane (V). Approximately 3.3 g. (0.051 mole) of hydrochloric acid–activated zinc dust (activated prior to use by the addition of 1 ml. of concd. hydrochloric acid to 3.5 g. of the zinc dust in 5–10 ml. of solvent), 10.0 g. (0.04 mole) of IV, and 30 ml. of butyl cellosolve were placed in a 100-ml. three-neck flask fitted with a stirrer and reflux condenser. The temperature was slowly increased to 75°, and after 1 hr. the solution was only slightly turbid. The temperature was then gradually increased to 95° and maintained there for 4 hr. At the end of this time the stirred solution was light gray, indicative of some zinc chloride formation. The temperature was then raised to 105° and maintained for 1 hr.; the reaction mixture had turned white and contained only a small amount of unchanged zinc. The flask was cooled to 40° and a vacuum of 10 mm. was applied directly to the flask. Heating and stirring were resumed and at 60–75° about 5 ml. of a colorless liquid collected in a trap maintained at −70°. After washing with water, the condensate was taken up in 15 ml. of ether and dried over Drierite. Vacuum distillation yielded 3.2 g. (44.5%) of V, b.p. 40–41° at 29 mm., n_D^{25} 1.3878, d_4^{25} 1.010, MR$_D$ calcd.: 41.66, obsd.: 42.08.

Anal. Calcd. for $C_7H_{11}F_3Si$: C, 46.64; H, 6.14; F, 31.62. Found: C, 46.89; H, 5.92; F, 31.30.

The preparation of V from IV proved the vicinal character of the chlorine atoms in IV. This reaction had been carried out a number of times with other solvents such as acetone and ethyl alcohol. The yields of V with these solvents were in the low range of 6.8–13.9%. These solvents were probably too low-boiling to effect the dechlorination.

2,3,3-Trifluorocyclobutyltrimethylsilane (VI). *Method 1.*[13, 14] Exactly 10.0 g. (0.046 mole) of II in 15 ml. of anhydrous ethers was added slowly with heating to a suspension of 3.06 g. (0.0805 mole) of lithium aluminum hydride in 20 ml. of ether under reflux conditions. The addition was completed in 2 hr. and the mixture was then refluxed for an additional 2 hr. After cooling to 0°, about 50 ml. of 10% sulfuric acid was slowly added to decompose the excess lithium aluminum hydride. The ether layer was combined with two ether extracts and dried over Drierite. Vacuum distillation gave four fractions boiling in the range of 60–72° at 44 mm. Each of these fractions gave two peaks when further fractionated by gas chromatography at 140° (Aerograph Master A-100; Silicone Oil Column). The first fraction was identified at VI, and the second as II, n_D^{25} 1.4062. About 3.4 g. of unchanged II and about 3.75 g. (64.4%) of VI were recovered, b.p. (est.) 62–65° at 44 mm., n_D^{25} 1.3927, d_4^{25} 1.028, MR$_D$ calcd.: 42.13; obsd.: 42.27.

Anal. Calcd. for $C_7H_{13}F_3Si$: C, 46.12; H, 7.19; F, 31.27. Found: C, 45.83; H, 5.07; F, 31.42.

Method 2. Exactly 2.75 g. (0.0153 mole) of V in an excess of ethyl alcohol was hydrogenated in a quantitative hydrogenating assembly utilizing 10% palladium-on-carbon as the catalyst. The absorption of 0.015 mole of hydrogen was complete in 15 min. The catalyst was filtered under suction through a fritted glass funnel. The filtrate was then shaken with water in a separatory funnel; the organic layer was separated and taken up in 10 ml. of ether and dried over Drierite. Following removal of the solvent, a pure sample of VI was obtained by gas chromatography. The infrared spectrogram of the material was identical with the compound prepared by Method 1.

The preparation of VI by the reduction of II definitely proved the structure of the latter.

2,2-Dichloro-3,3-difluorocyclobutyltrimethylsilane (VII). Exactly 37.2 g. (0.28 mole) of 1,1-difluoro-2,2-dichloroethylene, 14.0 g. (0.14 mole) of vinyltrimethylsilane, and 0.1 g. of hydroquinone were sealed in a heavy-walled Pyrex combustion tube and heated for 24 hr. at 220°. The tube was cooled and opened. Vacuum distillation of the product gave 23.0 g. (70.8%) of VII, b.p. 78° at 7 mm., n_D^{25} 1.4390, d_4^{25} 1.181, MR$_D$ calcd.: 51.78; obsd.: 51.88.

Anal. Calcd. for $C_7H_{12}F_2Cl_2Si$: C, 36.06; H, 5.19; Cl, 30.42. Found: C, 36.03; H, 5.39; Cl, 30.25.

2,2-Dichloro-3,3-difluorocyclobutyltriethoxysilane (VIII). Approximately 26.6 g. (0.20 mole) of 1,1-difluoro-2,2-dichloroethylene, 19.0 g. (0.10 mole) of vinyltriethoxysilane and 0.1 g. of hydroquinone were sealed in a heavy-walled Pyrex combustion tube and heated at 200° for 26 hr. The tube was cooled and opened. Vacuum distillation of the material yielded 18.6 g. (57.5%) of VIII, b.p. 107–108° at 6 mm., n_D^{25} 1.4201, d_4^{25} 1.197, MR$_D$ calcd.: 67.95, obsd.: 68.33.

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(13) R. N. Haszeldine, and J. E. Osborne, *J. Chem. Soc.*, 61 (1956).

(14) M. W. Buxton and J. C. Tatlow, *J. Chem. Soc.*, 1177 (1954).

Anal. Calcd. for $C_{10}H_{18}F_2Cl_2O_3Si$: C, 37.15; H, 5.61; Cl, 21.94. Found: C, 36.93; H, 5.62; Cl, 21.74.

Allyltrimethylsilane. To approximately 0.36 mole of allylmagnesium chloride[15] in 100 ml. of anhydrous ether was added with stirring a solution of 32.6 g. (0.30 mole) of trimethylchlorosilane in 100 ml. of ether. A gentle reflux was maintained throughout the addition which was completed in 50 min. The solution was refluxed for an additional 4 hr. The reaction mixture was then poured into ice water and neutralized with 10% sulfuric acid. The ether layer was combined with three extracts and dried over Drierite. Following removal of the solvent, distillation of the light yellow oil through a Metroware Vigreux Fractionation Assembly gave 20.2 g. (59%) of allyltrimethylsilane, b.p. 77–79° at 628 mm., n_D^{25} 1.4042 (lit.,[16] b.p. 84.9° at 737 mm., n_D^{20} 1.4074).

α-(2,2,3,3-Tetrafluorocyclobutyl)methyltrimethylsilane (IX). Exactly 8.5 g. (0.075 mole) of allyltrimethylsilane, 10 g. (0.10 mole) of tetrafluoroethylene, 0.1 g. of hydroquinone, and 0.25 ml. of Terpene B were sealed in a heavy-walled Pyrex combustion tube and heated for 8 hr. at 150°, 10 hr. at 175°, and 20 hr. at 210°. The tube was cooled and opened. Vacuum distillation of the product yielded 1.5 g. of allyltrimethylsilane and 8.3 g. (63.4%) of IX, b.p. 62–63° at 25 mm., n_D^{25} 1.3828, d_4^{25} 1.058, MR$_D$ calcd.: 46.99, obsd.: 47.21.

Anal. Calcd. for $C_8H_{14}F_4Si$: C, 44.84; H, 6.58; F, 35.47. Found: C, 44.64, H. 6.56; F, 35.20.

4-Pentene-1-ol. This alcohol was prepared from tetrahydrofurfuryl alcohol in 55% over-all yield by the method of Snyder and Brooks.[17]

5-Bromopentene-1. A solution of 74.0 g. (0.86 mole) of 4-pentene-1-ol and 24.0 g. (0.30 mole) of dry pyridine was placed in a 200-ml. three necked, round bottom flask fitted with a stirrer, a low temperature thermometer, and a dropping funnel with a pressure equalizing side-arm. The solution was cooled to −40° and 95.0 g. (0.35 mole) of phosphorus tribromide was added at such a rate that the temperature remained at −30° to −40°. The solution was stirred at −40° for an additional hour, then warmed to room temperature. The flask was heated to 60°, a vacuum of 1 mm. applied directly to the flask, and the crude bromide collected in a trap maintained at −70°. The crude product was washed with a cold 10% sodium bicarbonate solution, diluted with ether, and dried over Drierite. Distillation through a Todd Precise Fractionation Assembly gave 68.0 g. (53.2%) of 5-bromopentene-1, b.p. 118–120° at 625 mm., n_D^{25} 1.4600, (lit.,[15] b.p. 127° at 770 mm.).

4-Pentenyltrimethylsilane (X). A solution of 14.9 g. (0.10 mole) of 5-bromopentene-1 in 30 ml. of anhydrous ether was added with stirring at room temperature to 1.6 g. (0.23 g.-atom) of finely cut lithium metal in 100 ml. of ether. After initiation of the reaction the flask was cooled to 0 to −5°. The addition was completed in 1 hr. and the mixture stirred for an additional 30 min. at 5°.

To this solution of freshly prepared lithium reagent, a solution of 8.9 g. (0.90 mole) of trimethylchlorosilane in 20 ml. of ether was added under gentle reflux conditions. The addition was completed in 45 min. and thereafter the mixture was refluxed for an additional 8 hr. The reaction mixture was poured into ice water, neutralized with 10% hydrochloric acid, and extracted three times with small portions of ether. The extracts were combined and dried over Drierite. Following removal of the solvent, distillation gave 10.3 g. (80.5%) of X, b.p. 132° at 628 mm. n_D^{25} 1.4172, d_4^{25} 0.747, MR$_D$ calcd.: 48.33, obsd.: 48.04.

Anal. Calcd. for $C_8H_{18}Si$: C, 67.52; H, 12.75. Found: C, 67.82; H, 12.55.

α-(2,2,3,3-Tetrafluorocyclobutyl)n-propyltrimethylsilane (XI). Exactly 8.8 g. (0.062 mole) of X, 10.0 g. (0.10 mole) of tetrafluoroethylene, and 0.1 g. of hydroquinone were sealed in a heavy-walled Pyrex combustion tube and heated at 24 hr. at 218°. The tube was cooled and opened. Vacuum distillation gave 2.5 g. of unchanged X and 4.24 g. (40.0%) of XI, b.p. 41–42° at 5 mm., n_D^{25} 1.3936, d_4^{25} 1.038, MR$_D$ calcd.: 56.05, obsd.: 55.88.

Anal. Calcd. for $C_{10}H_{18}F_4Si$: C, 49.60; F, 31.36. Found: C, 49.86; F, 31.73.

1-Iodo-3,4,4-trifluoro-3-butenyltrimethylsilane (XII). Exactly 20.8 g. (0.10 mole) of perfluorovinyliodide and 10.0 g. (0.10 mole) of vinyltrimethylsilane were placed in an evacuated 2-l. Pyrex irradiation vessel. The vessel and reactants were irradiated with a 100-watt ultraviolet lamp for 18 days. The dark purple liquid was shaken with mercury to remove the free iodine and then filtered. Vacuum distillation of the light pink liquid gave a 5.0 g. (16.3%) of XII, b.p. 93–94° at 30 mm., n_D^{25} 1.4625. Vapor phase chromatography showed this fraction to be pure. An analytical sample collected from the chromatograph had the following physical properties: n_D^{25} 1.4630, d_4^{25} 1.4936, MR$_D$ calcd.: 56.85, obsd.: 56.65.

Anal. Calcd. for $C_7H_{12}F_3ISi$: C, 27.28; H, 3.93; F, 18.49. Found: C, 27.42; H, 4.20; F, 18.79.

1-Iodo-3,4,4-trifluoro-3-butenyltrichlorosilane (XIII). Exactly 10.4 g. (0.05 mole) of perfluorovinyliodide and 8.06 g. (0.05 mole) of vinyltrichlorosilane were placed in an evacuated 2-l. Pyrex irradiation vessel. The vessel and its reactants were subjected to a 100-watt ultraviolet source for 12 days. The very dark purple liquid was shaken with mercury to remove the free iodine and then quickly filtered. Vacuum distillation gave 10.4 g. (56.2%) of XIII, b.p. 79–80° at 22 mm., n_D^{25} 1.4882, d_4^{25} 1.933, MR$_D$ calcd.: 55.54, obsd.: 55.07.

Anal. Calcd. for $C_4H_3Cl_3ISi$: C, 13.00, H, 0.82; F, 15.43. Found: C, 13.29; H, 1.06; F, 15.72.

2,2,3,3-Tetrafluorocyclobutyltrimethylsilane (XIV). Approximately 20.0 g. (0.20 mole) of tetrafluoroethylene, 20.4 g. (0.20 mole) of vinyltrimethylsilane, and 0.2 g. of hydroquinone were sealed in a heavywalled Pyrex combustion tube and heated for 36 hr. at 210°. The tube was cooled, opened, and the nonvolatile liquid filtered. Vacuum distillation yielded 7.0 g. of vinyltrimethylsilane and 22.3 g. (82.0%) of XIV, b.p. 65–66° at 60 mm., n_D^{25} 1.3741, MR$_D$ calcd.: 42.16, obsd.: 42.23.

Anal. Calcd. for $C_7H_{12}F_4Si$: C, 41.98; H, 6.04. Found: C, 41.98; H, 5.80.

Hydrolysis studies. A. Five grams of XIV and 50 ml. of dilute hydrochloric acid were placed in a 100-ml. flask and heated with stirring at 80° for 75 hr. The starting material was recovered unchanged.

B. Similarly, a 10-g. sample of XIV and 50 ml. of 20% solution of potassium hydroxide was heated with stirring at 70° for 10 hr. The starting material was recovered unchanged.

2,2,3,3-Tetrafluorocyclobutyldichloromethylsilane (XV). About 20.0 g. (0.20 mole) of tetrafluoroethylene, 28.2 g. (0.20 mole) of vinylmethyldichlorosilane, and 0.2 g. of hydroquinone were sealed in a heavy-walled Pyrex combustion tube and heated for 36 hr. at 210°. The tube was cooled and opened. Vacuum distillation gave 10.5 g. of vinylmethyldichlorosilane and 21.5 g. (71.2%) of XV, b.p. 65° at 39 mm., n_D^{25} 1.3943, d_4^{26} 1.382, MR$_D$ calcd.: 42.42, obsd.: 42.10.

Anal. Calcd. for $C_5H_6F_4Cl_2Si$: C, 24.70; H, 2.47. Found: C, 25.00; H, 2.67.

Infrared spectra. A number of workers[18–21] have observed

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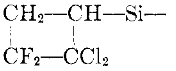
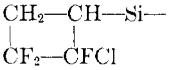
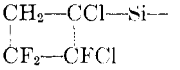
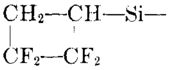
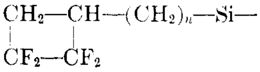
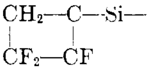
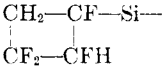
that cyclobutane and monosubstituted cyclobutanes absorb in the 10.85–11.10 μ region. These bands have tentatively been assigned to CH_2 rocking frequencies. If this assignment to the CH_2 modes of vibration is correct, absorption in this region would not be expected in fully substituted materials. Reid and Sack[22] confirmed this by the observation that fully substituted cyclobutanes absorb in the 11.25–11.65 μ region and not in the 10.85–11.10 μ range. Marrison[23] further pointed out that octafluorocyclobutane does not absorb in the 10.85–11.10 μ region.

In this work, the infrared spectra of fluorine-containing cyclobutylsilanes of the type, $\underbrace{CX_2—CF_2—CH_2—CH}$—$(CH_2)_n$-$SiR_3$ (where R equals chlorine and/or methyl, n equals 0 to 3 and X equals fluorine and/or chlorine) have been studied. On the basis of the above discussion, these compounds would be expected to absorb in the 10.85–11.10 μ region, as one CH_2 group remains unsubstituted. In the twelve spectra studied this was found to be the case, however, in a somewhat wider region. Generally, a narrow range of absorption was observed for a particular cyclobutyl group as illustrated in the Table I.

TABLE I

TENTATIVE BAND ASSIGNMENTS TO THE CYCLOBUTYL GROUP

Structure	Number of Spectra	Assumed Ring Vibrations (μ)
	2	11.15–11.18
	2	10.85–10.92
	2	11.07–11.10
	2	11.27–11.30 (10.78–10.75)
	2	10.85–10.93
	1	10.93
	1	10.93

The spectra of two compounds having the $\underbrace{CF_2—CF_2—CH_2—CH}$— group, each exhibited two absorption bands in the 10.75–11.30 μ region. The proper assignment of the band attributable to the CH_2 rocking mode cannot be made, thus both absorptions are included in Table I. The intensity of the bands in the 10.85–10.93 μ region decreases as the number of insulating CH_2 groups between the $\underbrace{CF_2—CF_2—CH_2—CH}$— group and the silicon atom increases, as the contributory effect of the cyclobutyl group in the molecule is minimized.

The spectra of tetramethylsilane and the linear alkyltrichloro- and alkyltrimethylsilanes prepared in this work do not show unassignable absorption bands in the 10.85–11.25 μ region (*e.g.*, in the spectra of $CH_2{=}CH—(CH_2)_3Si(CH_3)_3$ the band at 11.00–11.05 μ is assigned to CH_2 out of plane bending of the vinyl group).[24] In addition, the spectra of a number of CH_2-containing fluorocyclobutanes have been found to absorb in the 10.94–11.06 μ region. In contrast, perhalocyclobutanes (without a CH_2 group) have no absorption bands in this region.[25]

The assignments made here are necessarily tentative, as they are based on the study of a limited number of compounds of a particular class.

Vibrations attributed to the Si—CH₃ group. There has been some dispute over the proper assignment (whether deformation or rocking) of the absorption bands at 11.75 and 8.0 μ, both arising from the vibrations of the methyl group bonded to silicon.[26–28] Recent evidence[26,28–30] indicates that the band in the 11.75 μ region is due to silicon-methyl unsymmetrical rocking and the band in the 8.0 μ region is attributable to symmetrical deformation vibrations of the methyl group attached to the silicon atoms. Both these bands were observed in the spectra of these fluorocyclobutyltrimethylsilanes. These bands were noticeably absent in the spectra of all monosubstituted trichlorosilanes studied.

Carbon-hydrogen deformation and stretching frequencies. The absorption band at 6.97 μ in the spectra of $\underbrace{CFCl—CF_2—CH_2—CH}$—$SiCl_3$ and the band at 7.07 μ in the spectra of $\underbrace{CFCl—CF_2—CH_2—CCl}$—$SiCl_3$ are attributed to bending modes of the CH_2 group in the cyclobutane ring. The shift to the longer wave length in the spectra of the latter is apparently due to the substitution of a hydrogen atom by a chlorine atom in the position adjacent to the CH_2 group in the ring.[23] The position of this band remains relatively constant (6.95–7.17 μ) throughout the remainder of the series. It is masked to a degree by the asymmetrical deformation of the methyl group on the silicon atom and by the CH_2 deformations in the ethyl group in C_2H_5—O—Si.

An absorption band in the 3.40 μ region is assigned the carbon-hydrogen stretching modes in the cyclobutyl group and in the methyl groups bonded to silicon, primarily the latter. Thus, this band appreciably decreases in the spectra of the fluorocyclobutyltrichlorosilanes with a shift to shorter wave lengths (3.1–3.3 μ).

Vibrations attributed to the Si—O—C and Si—Cl linkages. In the spectra of $\underbrace{CCl_2—CF_2—CH_2—CH}$—$Si(OC_2H_5)_3$, there is a broad double band with peaks at 9.05 and 9.23 μ. One or both of these bands are attributed to the Si—O—C stretching vibration.

An assignment for the silicon-chlorine absorption was not attempted since it apparently occurs in a region beyond 15 μ.

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