

# Organofluorosilicates in Organic Synthesis. XVI.<sup>1)</sup> Synthesis of Organopentafluorosilicates *via* the Diels-Alder, Ene, and Friedel-Crafts Reaction. Their Transformations to Organic Halides and Alcohols

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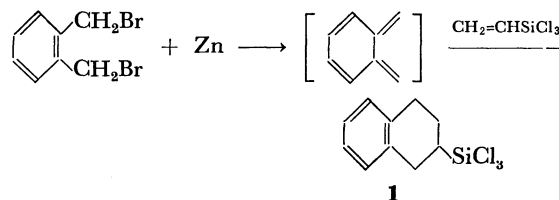
Described herein are several representative examples of cleavage reactions of otherwise hardly accessible organopentafluorosilicates which are obtainable *via* the Diels-Alder reaction, ene reaction, and the Friedel-Crafts reaction of vinyl-, ethynyl-, or allyl-trichlorosilanes. The Diels-Alder reaction between vinyltrichlorosilane and *o*-xylylene generated *in situ* by debromination of  $\alpha,\alpha'$ -dibromo-*o*-xylene afforded (1,2,3,4-tetrahydro-2-naphthyl)-trichlorosilane which was converted to the corresponding silicate. The silicate reacted with NBS and MCPBA to give the respective bromide and alcohol. The Diels-Alder reaction between ethynyltrichlorosilane and methyl coumalate gave a mixture of meta and para isomers of methyl (trichlorosilyl)benzoate in the ratio of 55/45, the silicate of which reacted with NBS to give two positional isomers of methyl bromobenzoate. The electronic effect of the methoxycarbonyl group on the Si–C bond cleavage was small. The silicate derived from 4-octenyl-trichlorosilane which was obtained by the ene reaction between vinyltrichlorosilane and 1-hexene afforded, upon treatment with NBS, 4-octenyl bromide in the ratio of *E/Z*=83/17. The sterically crowded neophylsilicate obtainable *via* the Friedel-Crafts reaction of 2-methyl-1-propenyltrichlorosilane with benzene underwent the cleavage reaction with NBS in methanol. Neophyl bromide was formed with  $\text{CuBr}_2$  in a low yield, no product being formed arising from rearrangement of the neophyl radical.

The Diels-Alder reaction,<sup>2)</sup> ene reaction,<sup>3)</sup> and the Friedel-Crafts reaction<sup>4)</sup> of the compounds containing silyl groups provide the useful methods for preparation of organosilanes. Since the trichlorosilyl group has strong electron-withdrawing ability, vinyltrichlorosilane and ethynyltrichlorosilane are efficient dienophiles and enophiles which readily react with various dienes and olefins to give the corresponding adducts containing the trichlorosilyl group.<sup>2a–d)</sup> The Friedel-Crafts reaction of allylic trichlorosilanes with aromatic compounds has been known to give rise to the introduction of the aromatic ring onto the carbon  $\beta$  to the silicon atom. Such organotrichlorosilanes that are usually difficult to prepare by hydrosilylation of olefins or acetylenes are expected to be useful precursors of organopentafluorosilicates. Thus we have developed a new methodology involving the synthesis of organosilicates *via* the Diels-Alder reaction, ene reaction, and the Friedel-Crafts reaction followed by their characteristic reactions with electrophiles. One of the unique applications of such methodology has already been demonstrated in the previous paper,<sup>5)</sup> where the Diels-Alder reaction between vinyltrichlorosilane and cyclopentadiene followed by hydrogenation and silicate formation gave 2-norbornylpentafluorosilicate which reacted with NBS or  $\text{Br}_2$  to afford 2-norbornyl bromide. This paper describes several new aspects on the reactivity of organopentafluorosilicates which are otherwise hardly accessible.

## Results and Discussion

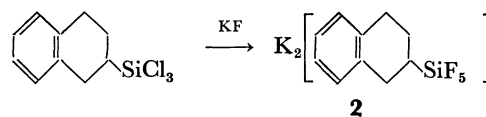
**Preparation and Reaction of 1,2,3,4-(Tetrahydro-2-naphthyl)pentafluorosilicates.** Since *o*-xylylene (5,6-dimethylene-1,3-cyclohexadiene) is known to be a highly reactive diene which readily reacts with various dienophiles to give the 1,2,3,4-tetrahydronaphthalene derivatives,<sup>6)</sup> we examined the Diels-Alder reaction between vinyltrichlorosilane and *o*-xylylene generated *in*

*situ* by debromination of  $\alpha,\alpha'$ -dibromo-*o*-xylene. A solution of  $\alpha,\alpha'$ -dibromo-*o*-xylene in acetonitrile was slowly added to a mixture of zinc powder and vinyltrichlorosilane in acetonitrile at 50 °C. After work-up (1,2,3,4-tetrahydro-2-naphthyl)trichlorosilane (**1**), the Diels-Alder adduct, was isolated by distillation in 55% yield.



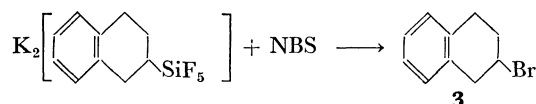
Acetonitrile was the most suitable among the solvents examined. The reaction in DMF, which had usually been used for debromination of  $\alpha,\alpha'$ -dibromo-*o*-xylene, THF, or ethyl acetate did not give the Diels-Alder adduct at all, but gave a mixture of unidentified products. Without solvent  $\alpha,\alpha'$ -dibromo-*o*-xylene was recovered unchanged. The reaction was also examined at three different temperatures (20 °C, 50 °C, and acetonitrile reflux), and the reaction at 50 °C gave the most satisfactory result.

(1,2,3,4-Tetrahydro-2-naphthyl)trichlorosilane could be readily converted into the corresponding silicate **2** in 97% yield on treatment with KF in ethanol. Treatment of the adduct with aqueous KF resulted in lower yield.

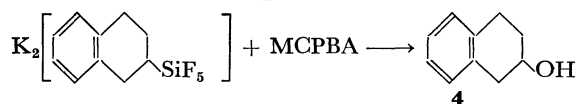


The silicate **2** thus obtained was found to react with NBS in dioxane to give the corresponding bromide **3** in 52% yield. The product was contaminated with a small amount of naphthalene which was considered to be formed by bromination of the benzylic

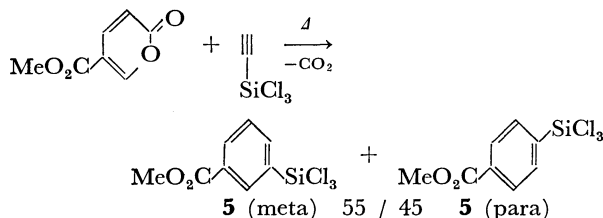
carbon of the initial product followed by the dehydrobromination. The formation of naphthalene, however, could not be retarded even in the presence of a radical inhibitor such as 2,4,6-tri-*t*-butylphenol.



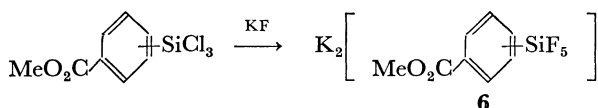
Silicate **2** also reacted exothermically with MCPBA<sup>7)</sup> in DMF to give 1,2,3,4-tetrahydro-2-naphthol **4** in 65% yield. The result shows that vinyltrichlorosilane provides a vinyl alcohol equivalent in the Diels-Alder reaction. 1,2,3,4-Tetrahydro-2-naphthol is known to be an effective insect repellent with the requisite properties of low irritancy and low toxicity, and several procedures for its preparation have been reported involving hydrogenation of 2-naphthol.<sup>8)</sup> The present procedure provides a new alternative route to this highly valuable insect repellent.



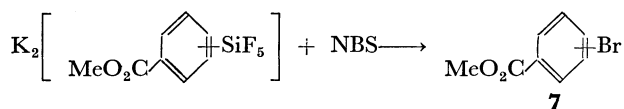
**Preparation and Reaction of (Methoxycarbonylphenyl)pentafluorosilicate.** The Diels-Alder reaction between methyl coumalate and ethynyltrichlorosilane<sup>2e)</sup> followed by spontaneous decarboxylation afforded methyl (trichlorosilyl)benzoate **5** in 90% yield. GLC analysis of the methylated (MeMgBr in ether) product showed that both meta and para isomers were formed in the ratio of 55/45, showing a poor regioselectivity.



The mixture of meta- and para-trichlorosilyl derivatives was converted into the corresponding silicate **6** by treatment with KF in water in the usual manner (54% yield).



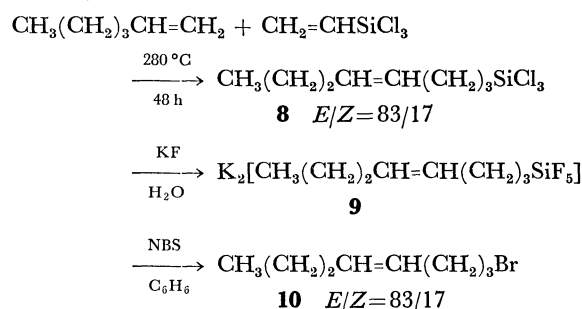
The silicate thus obtained was allowed to react with one equiv of NBS in methanol to give a mixture of meta and para isomers of methyl bromobenzoate **7** in the ratio of 58/42 (54% yield). The use of a half equiv of NBS did not change the product ratio significantly, implying that both the meta- and para-silicate have similar reactivities toward NBS.



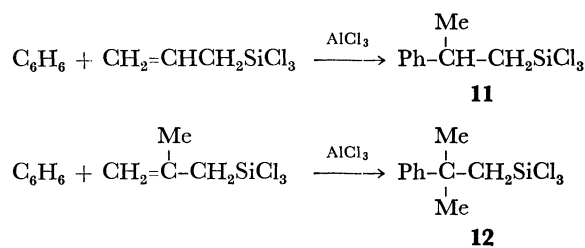
It should be mentioned here that the unusually low ionization potentials assignable to the  $\pi$ - and Si-C  $\sigma$ -bonding electrons, suggested by the MO calculation,<sup>5)</sup> may screen the rather small substituent effects

and level up the reactivities of the meta and para isomers.

**Preparation and Reaction of 4-Octenylpentafluorosilicate.** 4-Octenylpentafluorosilicate was prepared *via* the ene reaction between vinyltrichlorosilane and 1-hexene.<sup>3)</sup> Heating a mixture of vinyltrichlorosilane and 1-hexene at 280 °C for 48 h gave 4-octenyltrichlorosilane (**8**) in 52% yield. The adduct, a mixture of the *E* and *Z* isomers (*E/Z*=83/17), was converted into the silicate on treatment with aqueous KF in the usual manner. 4-Octenylpentafluorosilicate (**9**) thus obtained was relatively unstable and decomposed after standing at room temperature for 1 month. IR analysis of the decomposed matters showed characteristic bands of the hexafluorosilicate. The 4-octenylsilicate reacted with NBS exothermically to give a mixture of (*E*)- and (*Z*)-4-octenyl bromide (**10**) in 36% yield in the ratio of *E/Z*=83/17.



**Reactions of Organopentafluorosilicates Synthesized via the Friedel-Crafts Reaction of Allylic Trichlorosilanes.** In this study, we carried out the Friedel-Crafts reaction of allyl-, 2-methylpropenyl-, and crotyl-trichlorosilane. Of particular interest is that the method provides the most convenient route to otherwise hardly accessible (2-methyl-2-phenylpropyl)trichlorosilane (**12**) (hereafter abbreviated to neophyltrichlorosilane).



We have found that crotyltrichlorosilane gave a mixture of two positional isomers, (2- and 3-phenylbutyl)trichlorosilane, **13** and **14**. The initial product **13** isomerized thermally to the 3-phenyl isomer **14** in the presence of aluminum chloride, eventually the equilibrium mixture, **13/14**=9/91, being formed. Only **14** was isolated in a pure state by fractional distillation. The results show that the  $\text{Cl}_3\text{Si}$ - group, unlike the  $\text{Me}_3\text{Si}$ - group,<sup>9)</sup> exhibits no stabilizing effect on the  $\beta$ -carbocation, and the  $\gamma$ -secondary carbocation is thermally more stable.

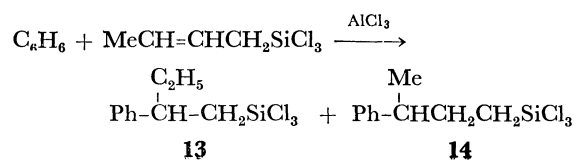
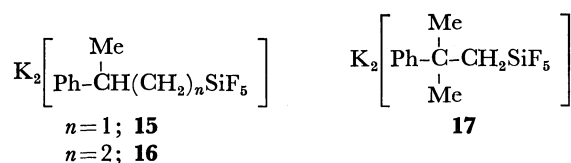


TABLE 1. REACTIONS OF PHENYL-SUBSTITUTED SILICATES WITH NBS OR CuBr<sub>2</sub>

Silicate	Reagent	Conditions	Product	Yield/% <sup>a)</sup>
$K_2 \left[ \begin{array}{c} \text{Me} \\   \\ \text{Ph}-\text{CHCH}_2\text{SiF}_5 \end{array} \right]$	NBS	Et <sub>2</sub> O, r.t., 4 h	Me	84
		MeOH, r.t., 2 h	$\text{Ph}-\text{CHCH}_2\text{Br}$	48
	CuBr <sub>2</sub>	Et <sub>2</sub> O, r.t., 6 h		53
$K_2 \left[ \begin{array}{c} \text{Me} \\   \\ \text{Ph}-\text{CH}(\text{CH}_2)_2\text{SiF}_5 \end{array} \right]$	NBS	MeOH, r.t., 5 h	Me	71
	CuBr <sub>2</sub>	Et <sub>2</sub> O, r.t., 6 h	$\text{Ph}-\text{CH}(\text{CH}_2)_2\text{Br}$	55
$K_2 \left[ \begin{array}{c} \text{Me} \\   \\ \text{Ph}-\text{C}-\text{CH}_2\text{SiF}_5 \\   \\ \text{Me} \end{array} \right]$	NBS	Et <sub>2</sub> O, r.t., 4 h	Me	trace <sup>b)</sup>
		MeOH, r.t., 5 h	$\text{Ph}-\text{C}-\text{CH}_2\text{Br}$	53
		MeOH, r.t., 20 h	Me	62
	CuBr <sub>2</sub>	Et <sub>2</sub> O, reflux, 4 h		16 <sup>c)</sup>

a) Determined by GLC. b) PhCMe<sub>2</sub>CH<sub>2</sub>SiF<sub>3</sub> was formed in 76% yield. c) PhCMe<sub>2</sub>CH<sub>2</sub>SiF<sub>3</sub> was formed in 71% yield.

The silicates, even the sterically crowded neophyl derivative **17**, could be readily prepared in the usual manner (KF in water).



The transformation of these silicates to the corresponding bromides has been examined with NBS or CuBr<sub>2</sub>.<sup>10)</sup> The results are summarized in Table 1. The reactivity of these silicates may reflect primarily the steric effect on the cleavage reactions. These three silicates were converted to the bromides in satisfactory yields. It seems interesting to note that the most crowded neophylsilicate **17** was cleaved in MeOH, but in ether dissociation of the silicate to the corresponding trifluorosilane occurred exclusively. With CuBr<sub>2</sub> silicates **15** and **16** gave the corresponding bromides in fair yields, while silicate **17** took the dissociation process predominantly, together with the formation of neophyl bromide in a low yield. As reported previously,<sup>10)</sup> the CuX<sub>2</sub>-cleavage of alkylsilicates may proceed through an alkyl radical intermediate, but the neophylsilicate gave no rearranged product, showing that the halogen-transfer proceeds much faster than the neophyl radical rearrangement, the rate of which has been estimated to be 10<sup>5</sup> s<sup>-1</sup> at 100 °C.<sup>11)</sup> This observation is consistent with the previous result on the 5-hexenylsilicate which gave no cyclization

product upon treatment with CuBr<sub>2</sub>; the rate of the cyclization of 5-hexenyl radical being reported to be 10<sup>5</sup> s<sup>-1</sup> at 25 °C.<sup>12)</sup>

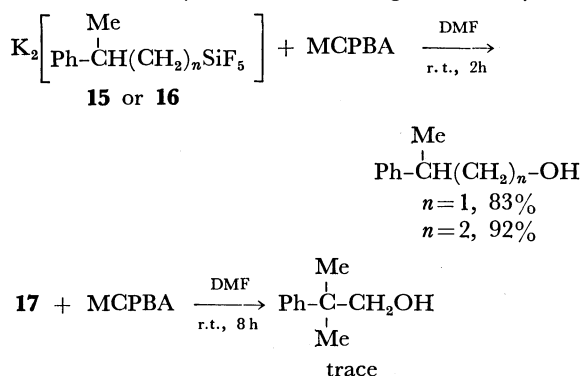
The MCPBA-cleavage reaction was also examined. Silicates **15** and **16** reacted smoothly with MCPBA to give the corresponding alcohols in high yields. In contrast, neophylsilicate **17** was reluctant to react under the similar conditions, indicative of the importance of the steric effect also in the MCPBA cleavage.

## Experimental

**General.** Infrared spectra were recorded on a Hitachi EPI-G3 grating infrared spectrometer. <sup>1</sup>H NMR spectra were determined with a JEOL JNM-MH-100 (100 MHz) spectrometer in carbon tetrachloride. Chemical shifts (δ) are recorded in ppm downfield from Me<sub>4</sub>Si. Mass spectra were measured on a JEOL JMS-D300 mass spectrometer connected with a JEOL LGC-20K gas chromatograph, equipped with a 1 m glass column packed with OV-17 (1%) on Chromosorb B, and a JMA-2000 data processing system. Ionization voltage was 24 eV for all compounds. GLC analyses and preparative purification were performed on a Shimadzu GC-4B gas chromatograph, equipped with a 3 m column packed with 30% Silicone DC550 on Chromosorb B or Celite 545. GC peak integrals were recorded using a Shimadzu Chromatopac C-E1B integrator.

**Materials.** Vinyltrichlorosilane provided by Shin-etsu Chemical Co., Ltd. was purified by distillation. Ethynyltrichlorosilane<sup>2c)</sup> allyl-, 2-methylpropenyl- and 2-butenyltrichlorosilanes<sup>13)</sup> and methyl coumalate<sup>14)</sup> were prepared according to the reported method. All solvents were dried in the usual manner and distilled before use. Other chemicals were used as obtained commercially.

**1,2,3,4-Tetrahydro-2-naphthyltrichlorosilane (I).** Vinyltrichlorosilane (161.5 g; 1.00 mol), zinc powder (90% purity, 21.8 g; 0.30 mol) and dry acetonitrile (100 ml) were placed in a three-necked flask equipped with a reflux condenser, a mechanical stirrer, and a dropping funnel. α,α'-Dibromo-o-xylene (26.4 g; 0.10 mol) in acetonitrile (260 ml) was added dropwise at 50 °C with stirring over a period of 19 h. After the addition was completed the reaction mixture was stirred further at 50 °C for 4 h. The solvent and excess vinyltrichlorosilane were evaporated. Pentane was added to the residue and the insoluble matters were removed by filtration. The solvent was evaporated and the residue was distilled under reduced pressure (118–127 °C/5 mmHg) to



give 20.07 g of the crude product, which was purified by fractional distillation to give 14.31 g (54% yield) of pure **1**: bp 122–127 °C/5 mmHg; mp 23.5–25.0 °C;  $^1\text{H}$  NMR 1.55–1.9 (m, 2H), 2.05–2.35 (m, 1H), 2.7–3.05 (m, 4H), 7.00 (br s, 4H); MS  $m/e$  (%) 268 ( $\text{M}^+ + 4$ , 4), 266 ( $\text{M}^+ + 2$ , 14), 264 ( $\text{M}^+$ , 14), 131 ( $\text{M}^+ - \text{SiCl}_3$ , 100); Found: Cl, 40.48%. Calcd for  $\text{C}_{10}\text{H}_{11}\text{Cl}_3\text{Si}$ : Cl, 40.04%.

**1,2,3,4-Tetrahydro-2-naphthylpentafluorosilicate (2).** 1,2,3,4-Tetrahydro-2-naphthyltrichlorosilane (6.94 g; 26.1 mmol) was added dropwise to a mixture of KF (37.92 g; 653 mmol) and ethanol (76 ml) at 0 °C. After the addition the mixture was stirred at room temperature overnight. The mixture was poured into 150 ml of cold water in order to dissolve an excess of KF and the resulting KCl. White powder was separated by filtration, and washed with water, ethanol, and ether. Drying under vacuum gave 8.41 g (97% yield) of potassium 1,2,3,4-tetrahydro-2-naphthylpentafluorosilicate: IR (KBr) 3060(w), 3010(w), 2900 (m), 2830(m), 1445(m), 1255(m), 1050(m), 769(s), 738(s), 650(vs), 523(s)  $\text{cm}^{-1}$ . The product was not analytically pure, but used in the subsequent reaction without further purification.

**2-Bromo-1,2,3,4-tetrahydronaphthalene (3).** A mixture of 1,2,3,4-tetrahydronaphthylpentafluorosilicate (997 mg; 3.0 mmol), 2,4,6-tri-*t*-butylphenol (8.6 mg), NBS (587 mg; 3.3 mmol), and dry dioxane (10 ml) was stirred at 50 °C for 16 h. Pentane was added and insoluble matters were removed by filtration. After evaporation of the solvent the residue was dissolved in pentane. The solution was washed with water and dried over  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent bulb-to-bulb distillation (200 °C/3 mmHg) of the residue gave 326 mg (52% yield) of 2-bromo-1,2,3,4-tetrahydronaphthalene which was contaminated with ca. 10% of naphthalene: IR (liquid film) 3070, 3020, 2945, 1580, 1495, 1450, 745  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.95–2.5 (m, 2H), 2.6–3.05 (m, 2H), 3.05–3.5 (m, 2H), 4.2–4.55 (m, 1H), 6.8–7.2 (m, 4H); MS  $m/e$  (%) 212 ( $\text{M}^+ + 2$ , 27), 210 ( $\text{M}^+$ , 32), 131 ( $\text{M}^+ - \text{Br}$ , 100); High MS 210.0055 (Calcd for  $\text{C}_{10}\text{H}_{11}^{79}\text{Br}$ , 210.0041), 212.0029 (Calcd for  $\text{C}_{10}\text{H}_{11}^{81}\text{Br}$ , 212.0021).

**1,2,3,4-Tetrahydro-2-naphthol (4).** A mixture of (1,2,3,4-tetrahydro-2-naphthyl)pentafluorosilicate (1.662 g; 5.0 mmol), *m*-chloroperbenzoic acid (90% pure, 1.150 g; 6.0 mmol as active oxygen), dry DMF (10 ml) was stirred at 50 °C for 14 h. Ether was added and the mixture was washed with water and aq  $\text{NaHCO}_3$ , and dried over  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent bulb-to-bulb distillation (150 °C/3 mmHg) of the residue gave 482 mg (65% yield) of 1,2,3,4-tetrahydro-2-naphthol: An analytical sample was purified by preparative GLC.  $n_D^{20}$  1.5607 (lit.<sup>8</sup>)  $n_D^{25}$  1.5630; IR (liquid film) 3700–3100 (br. OH), 3060, 3020, 2920, 1580, 1490, 1450, 1040, 740  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 1.5–2.1 (m, 2H), 1.98 (br s, 1H), 2.5–3.15 (m, 4H), 3.85–4.15 (m, 1H), 6.92 (br s, 4H); MS  $m/e$  (%) 148 ( $\text{M}^+$ , 13), 130 ( $\text{M}^+ - \text{H}_2\text{O}$ , 100).

**Methyl (Trichlorosilyl)benzoate (5).** A mixture of methyl coumalate (3.10 g; 20.1 mmol), ethynyltrichlorosilane (5.85 g; 37 mmol), and hydroquinone (50 mg) was heated at  $175 \pm 5$  °C (bath temperature) until the methyl coumalate was completely consumed (ca. 50 h). The extent of the reaction could be monitored by GLC analysis or  $^1\text{H}$  NMR. After the reaction was completed the mixture was distilled under reduced pressure to give 4.9 g (90% yield) of methyl (trichlorosilyl)benzoate: bp 154–155 °C/21 mmHg; Found: Cl, 39.04%. Calcd for  $\text{C}_8\text{H}_7\text{Cl}_3\text{O}_2\text{Si}$ : Cl, 39.46%.

The product appeared as a single peak on GLC (Silicone DC550 or SE 30), but  $^1\text{H}$  NMR showed that the product consisted of meta and para isomers. Since the ratio could

not be determined by the  $^1\text{H}$  NMR spectrum, an aliquot (293 mg, 1.08 mmol) of the product was methylated ( $\text{MeMgBr}$  in ether, 15 mmol, reflux, 2 h). Usual work-up and distillation gave a distillate (151 mg) boiling over the range of 190–220 °C/15 mmHg (bath temperature). GLC analysis of the distillate showed the formation of two major products (A and B) in the ratio of 55:45, together with two minor ones. Products were isolated by preparative GLC (Silicone DC550, 200 °C). Product A, having the shorter retention time, was characterized as 2-(3-trimethylsilylphenyl)-2-propanol: mp 70.5–71.0 °C (lit.<sup>15</sup>) 62–63 °C; IR (KBr) 755, 710  $\text{cm}^{-1}$  (1,3-disubstituted benzene);  $^1\text{H}$  NMR 0.27 (s, 9H), 1.52 (s, 6H), 2.13 (br s, 1H), 7.1–7.6 (m, 4H). The other major product B was identified as the para isomer, 2-(4-trimethylsilylphenyl)-2-propanol: a liquid contaminated with some decomposition products (lit.<sup>15</sup>) mp 52–52.5 °C; IR (liquid film) 820  $\text{cm}^{-1}$  (1,4-disubstituted benzene);  $^1\text{H}$  NMR 0.25 (s, 9H), 1.15 (s, 6H), 7.37 (s, 4H). The two minor products were collected as a mixture and characterized as the dehydrated olefinic compounds of the above two products:  $^1\text{H}$  NMR 0.25 and 0.27 (total 9H), 2.15 (br s, 3H), 5.0–5.1 (m, 1H), 5.25–5.35 (m, 1H), 7.25–7.55 (m, 4H). High MS  $m/e$  190.1184 (Calcd for  $\text{C}_{12}\text{H}_{18}\text{Si}$ , 190.1179).

**(Methoxycarbonylphenyl)pentafluorosilicate (6).** Methyl trichlorosilylbenzoate (2.52 g; 9.35 mmol) was added dropwise to a solution of KF (13.6 g; 234 mmol) in water (20 ml) at 0 °C with vigorous stirring. After stirring at room temperature for 5 h the mixture was filtered, washed with water, ethanol, and ether, and then dried *in vacuo*. The silicate weighed 1.76 g (54% yield): IR (KBr) 3020(w), 2970(w), 1730(s), 1710(s), 1600(w), 1440(m), 1300(s), 1265 (m), 1195(w), 1167(w), 1130(m), 1095(m), 1020(w), 847(w), 747(m), 720(w), 675(vs), 660(sh), 580(w), 557(w), 492(w), 470(w), 455(w)  $\text{cm}^{-1}$ ; Found: C, 28.26; H, 2.33; F, 27.81%. Calcd for  $\text{C}_8\text{H}_7\text{F}_5\text{K}_2\text{O}_2\text{Si}$ : C, 28.56; H, 2.10; F, 28.24%.

**Methyl Bromobenzoate (7).** **Reaction of  $\text{K}_2[\text{MeO}_2\text{CC}_6\text{H}_4\text{SiF}_5]$  with NBS.** A mixture of the silicate **6** (172 mg; 0.51 mmol), NBS (93 mg; 0.52 mmol), and methanol (5.0 ml) was stirred at room temperature for 24 h. After usual work-up GLC analysis showed a single peak, the retention time of which was the same as that of authentic methyl 4-bromobenzoate. GLC yield was 54%. The product was isolated by column chromatography on silica gel (hexane/benzene 1/1).  $^1\text{H}$  NMR showed that the product was a mixture of meta and para isomers of methyl bromobenzoate:  $^1\text{H}$  NMR 3.86 and 3.87 (total 3H), 7.25 (t,  $J=8$  Hz), 7.35–7.67 (m), 7.78–7.97 (m), 8.05–8.15 (m), (total 4H). High MS  $m/e$  213.9640 (calcd for  $\text{C}_8\text{H}_7\text{O}_2^{79}\text{Br}$ , 213.9630), 215.9599 (Calcd for  $\text{C}_8\text{H}_7\text{O}_2^{81}\text{Br}$ , 215.9609). The very close two signals due to the methyl protons were separated by the addition of  $\text{Eu}(\text{fod})_3$ ,  $\text{fod}=1,1,1,2,2,3,3$ -heptafluoro-7,7-dimethyl-4,6-octanedionato. For example, a solution of the sample (0.0338 M) containing  $\text{Eu}(\text{fod})_3$  (0.0169 M) in  $\text{CCl}_4$  exhibited two methyl signals at  $\delta$  5.15 for the para isomer and at 4.85 for the meta isomer. In this way, the meta/para ratio of the product was determined to be 58/42.

The silicate (328 mg; 0.975 mmol) was allowed to react with a half equiv of NBS (90 mg; 0.506 mmol) in methanol (5.0 ml) at room temperature for 5 h. The insoluble precipitate was filtered and washed with ether. The organic layer and the washings were combined and analyzed by GLC which indicated that the bromide was formed in 40% yield. The  $^1\text{H}$  NMR spectrum of the isolated product showed that the meta/para ratio was 57–60/43–40. The filter cake was further treated with NBS (100 mg) in methanol (5.0 ml) as above to give the bromide in 14% yield, the

meta/para ratio being 50/50.

**4-Octenyltrichlorosilane (8).**<sup>3)</sup> A mixture of 1-hexene (10.10 g; 120 mmol) and vinyltrichlorosilane (10.0 g; 62 mmol) was heated in a sealed tube at 280 °C for 48 h. After the reaction, distillation of the reaction mixture gave 7.85 g (52% yield) of 4-octenyltrichlorosilane: bp 63–64 °C/7 mmHg; <sup>1</sup>H NMR 0.94 (t, *J*=6 Hz, 3H), 1.1–1.85 (m, 6H), 1.85–2.3 (m, 4H), 5.0–5.6 (m, 2H). GLC analysis of the product showed two peaks in a ratio of 17/83, probably due to the *Z* and *E* isomers.

**4-Octenylpentafluorosilicate (9).** To a solution of KF (32.0 g; 550 mmol) in deionized water (48 ml) was added dropwise 4-octenyltrichlorosilane (5.40 g; 22.0 mmol) at 0 °C. After the addition the mixture was stirred overnight at room temperature. White powder thus obtained was separated by filtration, and washed with water, ethanol, and ether. After drying under vacuum 4.64 g (68% yield) of 4-octenylpentafluorosilicate was obtained: IR (KBr) 2950 (m), 2900(m), 1460(w), 1375(w), 970(w), 745(s), 640(vs), 540(m), 445(m) cm<sup>-1</sup>; Found: C, 28.02; H, 4.50; F, 28.23%. Calcd for C<sub>8</sub>H<sub>16</sub>F<sub>5</sub>K<sub>2</sub>Si: C, 30.75; H, 4.84; F, 30.40%.

**1-Bromo-4-octene (10).** 4-Octenylpentafluorosilicate (937 mg; 3.0 mmol) was allowed to react with NBS (587 mg; 3.3 mmol) in dry benzene (5.0 ml) at room temperature for 3 h. GLC analysis of the reaction mixture showed that two products were formed in a ratio of 17/83. The GCMS spectra of them showed the same parent peaks (*m/e*=192 and 190), indicating that they were isomers of bromooctene. The major product was isolated by preparative GLC: *n*<sub>D</sub><sup>20</sup> 1.4687; IR (liquid film) 970 cm<sup>-1</sup> (*trans*-CH=CH-); <sup>1</sup>H NMR 0.90 (t, *J*=6 Hz, 3H), 1.15–1.6 (m, 2H), 1.7–2.35 (m, 6H), 3.36 (t, *J*=6 Hz, 2H), 5.1–5.6 (m, 2H). Irradiation at the methylene protons adjacent to the double bond gave AB quartet (*J*=16 Hz): MS *m/e* (%) 192 (M<sup>+</sup>+2, 18), 190 (M<sup>+</sup>, 19), 150 (22), 148 (24), 111 (M<sup>+</sup>-Br, 8), 69 (100); High MS *m/e* 190.0381 (calcd for C<sub>8</sub>H<sub>15</sub><sup>79</sup>Br, 190.0353), 192.0350 (calcd for C<sub>8</sub>H<sub>15</sub><sup>81</sup>Br, 192.0333). On the basis of these spectral data the major product was identified as (*E*)-1-bromo-4-octene. The minor product could not be isolated; it was probably the (*Z*)-1-bromo-4-octene.

**Friedel-Crafts Reaction between Allylic Trichlorosilanes and Benzene.**

A typical procedure is given for the reaction of 2-methylpropenyltrichlorosilane. To a mixture of 27 g (0.142 mol) of 2-methylpropenyltrichlorosilane and benzene (118 g; 1.5 mol) was added 3.3 g (25 mmol) of freshly sublimed aluminum chloride at 0 °C with stirring. After stirring at 0 °C for 15 min the mixture was stirred at room temperature. A slightly exothermic reaction occurred and was completed in about 3 h. Dried sodium chloride (11.5 g) was added and the mixture was stirred at room temperature for 0.5 h and then under refluxing for another 0.5 h. The resulting black mixture was filtered quickly under suction through a filter aid (Hyfrosuper cell). The filtrate was distilled, after evaporation of benzene, to give (2-methyl-2-phenylpropyl)trichlorosilane (neophyltrichlorosilane) (**12**) as a colorless liquid boiling at mainly 99–100 °C/7 mmHg in 72% yield (29.1 g); <sup>1</sup>H NMR 1.57 (s, 6H), 2.00 (s, 2H), 7.15–7.45 (m, 5H). (Found: Cl, 39.37%).

(2-Phenylpropyl)trichlorosilane (**11**) was prepared in a similar manner: bp 98–106 °C/3 mmHg; <sup>1</sup>H NMR 1.40 (d, *J*=7 Hz, 3H), 1.70–1.85 (m, 2H), 3.17 (sextet, *J*=7 Hz, 1H), 7.0–7.3 (m, 5H). (Found: Cl, 41.54%).

**Friedel-Crafts Reaction of Crotyltrichlorosilane with Benzene.** To a mixture of crotyltrichlorosilane (28.4 g; 0.15 mol) and dry benzene (133 ml; 1.5 mol) was added aluminum chloride (2.2 g). An exothermic reaction started and benzene began to reflux. The reaction was controlled by inter-

mittent cooling with a water bath. After the exothermic reaction ceased, the mixture was heated to reflux for 1 h. Sodium chloride-treatment, filtration, and distillation gave 34.9 g (87% yield) of a colorless liquid boiling over the range of 99–102 °C/4 mmHg. The fraction consisted of two isomers. Fractional distillation through a column packed with glass helices gave 11.8 g (29% yield) of (3-phenylbutyl)trichlorosilane (**14**) as the major product: bp 98–102 °C/2 mmHg; <sup>1</sup>H NMR 1.05–1.45 (m) and 1.30 (d, *J*=7 Hz) (total 5H), 1.7–2.0 (m, 2H), 2.70 (sextet, *J*=7 Hz, 1H), 7.0–7.4 (m, 5H). (Found: Cl, 39.84%). The minor product could not be isolated pure but characterized by <sup>1</sup>H NMR to be (2-phenylbutyl)trichlorosilane (**13**): <sup>1</sup>H NMR 0.78 (t, *J*=7 Hz, 3H), *ca.* 1.6–2.0 (m, 4H), *ca.* 2.6–3.0 (m, 1H), *ca.* 7.0–7.45 (m, 5H).

The isomer distribution was dependent upon the reaction conditions. The reaction was followed by GLC which showed the following ratios of **13/14**: 63/37 (0 °C, 10 min), 54/46 (0 °C, 20 min), 56/44 (0 °C, 1 h), 38/62 (r.t., 24 h), 13/87 (reflux, 1 h), 9/91 (reflux, 2 h).

**Preparation of Silicates.** Preparation of silicates was performed in a similar manner to that described in the previous paper<sup>6)</sup> (RSiCl<sub>3</sub>/KF=1/25, in water, 0 °C—r.t., overnight). Yield, infrared absorption bands, and analytical data are given below.

**K<sub>2</sub>[PhCHMeCH<sub>2</sub>SiF<sub>5</sub>] (15):** 54%; IR (KBr) 3020(w), 2950(w), 2875(m), 2810(w), 1602(w), 1520(w), 1490(m), 1450(m), 1360(w), 1277(w), 1255(w), 1225(w), 1192(w), 1100(w), 1072(w), 910(w), 768(s), 740(s), 702(s), 640(br, vs), 540(m), 500(m), 482(m), 450(m) cm<sup>-1</sup>; Found: C, 32.10; H, 3.40%. Calcd for C<sub>9</sub>H<sub>11</sub>F<sub>5</sub>K<sub>2</sub>Si: C, 33.73; H, 3.46%.

**K<sub>2</sub>[PhCHMeCH<sub>2</sub>CH<sub>2</sub>SiF<sub>5</sub>] (16):** 78%; IR (KBr) 3025(w), 2950(sh), 2900(s), 2840(w), 1603(w), 1520(br, w), 1492(m), 1450(m), 1370(w), 1258(w), 1215(w), 1180(w), 1150(w), 1075(w), 1032(w), 900(br, w), 785(w), 750(s), 725(s), 700(s), 645(br, vs), 550(w), 518(m), 490(w), 450(m) cm<sup>-1</sup>; Found: C, 34.82; H, 3.88; F, 29.60%. Calcd for C<sub>10</sub>H<sub>13</sub>F<sub>5</sub>K<sub>2</sub>Si: C, 35.91; H, 3.92; F, 28.40%.

**K<sub>2</sub>[PhCMe<sub>2</sub>CH<sub>2</sub>SiF<sub>5</sub>] (17):** 63%; IR (KBr) 3050(w), 3010(w), 2970(m), 2950(m), 2925(m), 2900(m), 2875(m), 1600(w), 1580(w), 1520(br, m), 1495(m), 1440(w), 1370(m), 1352(m), 1263(m), 1200(w), 1190(w), 1100(br, w), 1075(w), 1032(w), 860(w), 790(m), 770(m), 735(s), 717(s), 702(s), 655(vs), 630(vs), 550(m), 505(m), 445(m) cm<sup>-1</sup>; Found: C, 35.19; H, 3.91; F, 27.30%. Calcd for C<sub>10</sub>H<sub>13</sub>F<sub>5</sub>K<sub>2</sub>Si: C, 35.91; H, 3.92; F, 28.40%.

**Cleavage Reactions with NBS and CuBr<sub>2</sub>.** The cleavage reactions of **15–17** were carried out in a similar manner to that described above and previously. The reaction conditions are listed in Table 1. Products were characterized as follows.

**PhCHMeCH<sub>2</sub>Br:** *n*<sub>D</sub><sup>20</sup> 1.5488; <sup>1</sup>H NMR; 1.41 (d, *J*=7 Hz, 3H), 3.10 (sextet, *J*=7 Hz, 1H), 3.3–3.62 (m, 2H), 7.1–7.45 (m, 5H); MS *m/e* (%) 200 (M<sup>+</sup>+2, 6), 198 (M<sup>+</sup>, 6), 105 (100), 91 (11); High MS *m/e* 198.0041 (calcd for C<sub>9</sub>H<sub>11</sub><sup>79</sup>Br; 198.0043), 200.0027 (calcd for C<sub>9</sub>H<sub>11</sub><sup>81</sup>Br; 200.0025). **PhCHMeCH<sub>2</sub>CH<sub>2</sub>Br:** <sup>1</sup>H NMR 1.30 (d, *J*=7 Hz, 3H), 2.10 (q, *J*=7 Hz, 2H), 2.85–3.45 (m, 3H), 7.05–7.35 (m, 5H); MS *m/e* (%) 214 (M<sup>+</sup>+2, 4), 212 (M<sup>+</sup>, 4), 105 (100); High MS *m/e* 212.0190 (calcd for C<sub>10</sub>H<sub>13</sub><sup>79</sup>Br; 212.0199), 214.0202 (calcd for C<sub>10</sub>H<sub>13</sub><sup>81</sup>Br; 214.0182).

**PhCMe<sub>2</sub>CH<sub>2</sub>Br:** *n*<sub>D</sub><sup>20</sup> 1.5458; <sup>1</sup>H NMR 1.45 (s, 6H), 3.50 (s, 2H), 7.1–7.45 (m, 5H); High MS *m/e* 212.0153 (calcd for C<sub>10</sub>H<sub>13</sub><sup>79</sup>Br; 212.0199), 214.0200 (calcd for C<sub>10</sub>H<sub>13</sub><sup>81</sup>Br; 214.0182).

**The MCPBA Cleavage of 15–17.** These cleavage

reactions were also performed in the same manner as described above and previously. PhCHMeCH<sub>2</sub>OH was identified by IR spectrum (*cf.* The Aldrich Library of IR Spectra, 616A) and <sup>1</sup>H NMR: 1.23 (d, *J*=7 Hz, 3H), 2.70–3.0 (m, 1H), 2.92 (s, 1H), 3.52 (d, *J*=7 Hz, 2H), 7.0–7.3 (m, 5H). PhCHMeCH<sub>2</sub>CH<sub>2</sub>OH: *n*<sub>D</sub><sup>20</sup> 1.5185; IR (neat) 3325, 1045, 760, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR 0.90 (br s, 1H), 1.26 (d, *J*=7 Hz, 3H), 1.77 (q, *J*=7 Hz, 2H), 2.87 (sextet, *J*=7 Hz, 1H), 3.45 (dt, *J*=7 Hz and 3 Hz, 2H), 7.05–7.25 (m, 5H). (Found: C, 80.00; H, 9.67%).

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