Synthesis of Organosilanes and Polysiloxanes with Nitro and Fluoro Substituents[1]

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Nitrite ion displacement of (3-bromopropyl)trimethylsilane, (4-bromobutyl)trimethylsilane, and (3-bromobutyl)trimethylsilane gave the corresponding nitro compounds, which on oxidative nitration gave the *gem*-dinitro compounds. Fluorination of salts of (3,3-dinitropropyl)trimethylsilane and (4,4-dinitrobutyl)trimethylsilane with elemental fluorine or perchloryl fluoride gave (3-fluoro-3,3-dinitropropyl)trimethylsilane and (4-fluoro-4,4-dinitrobutyl)trimethylsilane. Trimethylsilylmethyl triflate and 2-fluoro-2,2-dinitroethanol gave trimethylsilylmethyl 2-fluoro-2,2-dinitroethyl ether. Nitrite displacement, oxidative nitration, and fluorination converted (3-bromopropyl)methyldiphenylsilane to (3-fluoro-3,3-dinitropropyl)methyldiphenylsilane, and dephenylation with bromine gave (3-fluoro-3,3-dinitropropyl)methyldibromosilane, which was hydrolyzed to give polysiloxanes. The latter reacted with hydrofluoric acid to give (3-fluoro-3,3-dinitropropyl)methyldifluorosilane, which with sodium methoxide and aqueous acid gave the corresponding difluorodisiloxane. Bis(3-bromopropyl)diphenylsilane was converted to bis(3-fluoro-3,3-dinitropropyl)diphenylsilane. Stepwise dephenylation with bromine and hydrolysis gave the cyclic trisiloxane.

Although the chemistry of organosilicon compounds has been studied extensively,[2] few examples of this class of compounds with nitro substituents are known. The hydrosilylations of 3-nitropropene, 4,4,4-trinitrobutene, and 4,4-dinitrobutene with trichlorosilane and methyldichlorosilane have been reported,[3,4] and patent literature describes N_2O_3 addition to allylsilanes[5] and silver nitrite displacement of (3-iodopropyl)triethoxysilane.[6] The most commonly used methods of forming carbon–silicon bonds, the reaction of Grignard reagents and similar organometallics with silicon halides and the reaction of elemental silicon with alkyl halides at high temperatures, are not compatible with nitro substituents.

The present study involved the synthesis of *gem*-dinitro- and fluorodinitrosilanes and polysiloxanes by the stepwise introduction of nitro and fluorine moities. Polysiloxanes are usually obtained by the hydrolysis of silicon–halogen bonds, and these bonds are not stable to displacement, nitration, and fluorination reaction conditions. A hydrolytically stable silicon blocking group is therefore needed.

Convenient starting materials for the synthesis of simple nitrosilanes are (3-bromopropyl)trimethylsilane,[7] (4-bromobutyl)trimethylsilane,[8] and (3-bromobutyl)trimethylsilane.[8] Kornblum[9] has reported that the reaction of alkyl bromides with sodium nitrite in dimethyl sulfoxide gives nitroalkanes, with alkyl nitrites as byproducts. These trimethylsilyl compounds underwent this displacement reaction normally.

$$(CH_3)_3Si(CH_2)_nBr \xrightarrow[Me_2SO]{NaNO_2} (CH_3)_3Si(CH_2)_nNO_2 + (CH_3)_3Si(CH_2)_nONO$$

$$n = 3, 4$$

$$(CH_3)_3SiCH_2CH_2CHBrCH_3 \rightarrow (CH_3)_3SiCH_2CH_2CH(NO_2)CH_3 + (CH_3)_3SiCH_2CH_2CH(ONO)CH_3$$

The oxidative nitration reaction[10] was applied to (3-nitropropyl)trimethylsilane, (4-nitrobutyl)trimethylsilane, and (3-nitrobutyl)trimethylsilane to prepare (3,3-dinitropropyl)-trimethylsilane, (4,4-dinitrobutyl)trimethylsilane, and (3,3-dinitrobutyl)trimethylsilane, respectively. Yields were 57–72%.

$$(CH_3)_3Si(CH_2)_nCH_2NO_2 \xrightarrow[NaNO_2,\ OH^-]{AgNO_3} (CH_3)_3Si(CH_2)_nCH(NO_2)_2$$

$$n = 2, 3$$

$$(CH_3)_3SiCH_2CH_2CH(NO_2)CH_3 \rightarrow (CH_3)_3SiCH_2CH_2C(NO_2)_2CH_3$$

The direct fluorination of terminal *gem*-dinitro compounds in aqueous alkaline solution was reported previously to give fluorodinitro compounds.[11] This reaction with (3,3-dinitropropyl)trimethylsilane, using the theoretical amount of base, gave (3-fluoro-3,3-dinitropropyl)trimethylsilane in 31% yield. In the fluorination of (4,4-dinitrobutyl)trimethylsilane, after fluorine uptake ceased, additional base and fluorine were added; a 61% yield of (4-fluoro-4,4-dinitrobutyl)trimethylsilane was obtained. A difficulty in these reactions was that dilute solutions were used because of low solubility of the nitronate salts in water, and acid was formed by competing fluorination of water. Another fluorination reagent that has been used with dinitro compounds, perchloryl fluoride,[12] allows the use of a broader range of solvents. This reagent was used to fluorinate the potassium salt of (3,3-dinitropropyl)-trimethylsilane in equal parts of water, methanol, and dimethylformamide. The fluorodinitro compound was obtained in 85% yield.

$$(CH_3)_3Si(CH_2)_nCH(NO_2)_2 \rightarrow (CH_3)_3Si(CH_2)_nCF(NO_2)_2$$

$$n = 2, 3$$

A fluorodinitroalkylsilane with an ether linkage was obtained by the alkylation of 2-fluoro-2,2-dinitroethanol. Alkyl triflates are sufficiently reactive to alkylate this alcohol in methylene chloride in the presence of a mild heterogeneous base such as potassium carbonate.[13] Under these conditions, trimethylsilylmethyl triflate and 2-fluoro-2,2-dinitroethanol gave trimethylsilylmethyl 2-fluoro-2,2-dinitroethyl ether. This triflate was prepared by the reaction of trifluoromethanesulfonic anhydride with (hydroxymethyl)trimethylsilane, obtained by the published procedure.[14]

$$(CH_3)_3SiCH_2OH + (CF_3SO_2)_2O \rightarrow (CH_3)_3SiCH_2OSO_2CF_3$$

$$(CH_3)_3SiCH_2OSO_2CF_3 + FC(NO_2)_2CH_2OH \xrightarrow[K_2CO_3]{CH_2Cl_2} (CH_3)_3SiCH_2OCH_2CF(NO_2)_2$$

Polysiloxanes are generally prepared by the hydrolysis of dialkyldihalosilanes, and if fluorodinitro-substituted polysiloxanes are to be synthesized by the above methods the silicon–halogen bonds must be generated after the nitro and fluorine groups are introduced. Silicon halides, as well as silicon acetates, silicon methoxides, and similar derivatives,

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would not survive the hydrolytic reaction conditions.[2] However, carbon–silicon bonds can be cleaved by bromine, and the cleavage of phenyl–silicon bonds in this way is particularly facile.[15] Therefore, the approach was taken to build up fluorodinitro groups starting with dialkyldiphenylsilanes containing reactive sites on the alkyl chains.

One such starting material is (3-bromopropyl)methyldiphenylsilane. This compound was obtained initially by the bromination of the hydroboration product of allylmethyldiphenylsilane, prepared, in turn, from allylmagnesium bromide and methyldiphenylchlorosilane.

$$CH_2{=}CHCH_2MgBr + (C_6H_5)_2SiCH_3Cl \rightarrow CH_2{=}CHCH_2Si(C_6H_5)_2CH_3 \xrightarrow[BF_3]{NaBH_4} \xrightarrow[NaOCH_3]{Br_2} CH_3(C_6H_5)_2SiCH_2CH_2CH_2Br$$

A more convenient route to this bromide was based on the hydrosilylation of allyl acetate with methyldiphenylsilane with chloroplatinic acid[16] as catalyst to give a 49% yield of (3-hydroxypropyl)methyldiphenylsilane after hydrolysis. A molar excess of allyl acetate was required. The use of allyloxytrimethylsilane instead of the acetate gave a 71% yield of the alcohol with only a 10% excess of olefin. The use of tris(triphenylphosphine)rhodium chloride[17] as the catalyst instead of chloroplatinic acid increased the yield to 98%. This alcohol was converted to the toluenesulfonate in 62% yield with toluenesulfonyl chloride and pyridine in methylene chloride. The toluenesulfonate was converted to the bromide with lithium or sodium bromide in dimethyl sulfoxide. The yield of this displacement was essentially quantitative on the basis of NMR analysis, and for preparative purposes it was not necessary to isolate the bromide; the subsequent step was carried out with the same solvent.

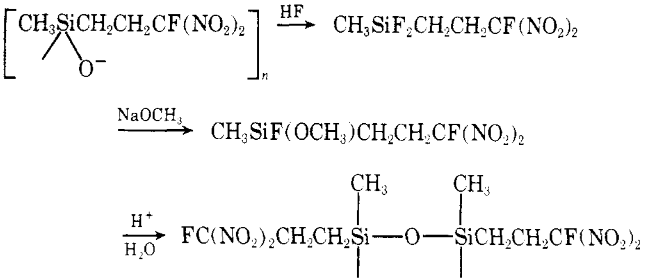
$$CH_3(C_6H_5)_2SiH + CH_2{=}CHCH_2OSi(CH_3)_3 \rightarrow CH_3(C_6H_5)_2SiCH_2CH_2CH_2OSi(CH_3)_3 \xrightarrow[H_2O]{H^+} CH_3(C_6H_5)_2SiCH_2CH_2CH_2OH \xrightarrow[Pyr,\ CH_2Cl_2]{TsCl} CH_3(C_6H_5)_2SiCH_2CH_2CH_2OSO_2C_6H_4CH_3\text{-}p \xrightarrow[Me_2SO]{NaBr} CH_3(C_6H_5)_2SiCH_2CH_2CH_2Br$$

The displacement of the bromide[18] with sodium nitrite in dimethyl sulfoxide gave the nitro compound, as well as the corresponding nitrite and alcohol. The nitro compound was separated from the other products by extracting the mixture with potassium hydroxide, and the isolated yield was 50%. Oxidative nitration of (3-nitropropyl)methyldiphenylsilane gave (3,3-dinitropropyl)methyldiphenylsilane in 70% yield, an undistillable oil characterized by NMR. Salts of this *gem*-dinitro compound had low solubility in water, and attempted fluorinations in this medium with elemental fluorine were unsuccessful. Fluorination with perchloryl fluoride in methanol, however, gave a 79% yield of (3-fluoro-3,3-dinitropropyl)methyldiphenylsilane. Heating this fluorinated compound with bromine then gave (3-fluoro-3,3-dinitropropyl)methyldibromosilane in 78% yield. The dibromide was too labile hydrolytically for elemental analysis but was identified spectrally and by its hydrolysis product.

$$CH_3(C_6H_5)_2SiCH_2CH_2CH_2Br \xrightarrow[Me_2SO]{NaNO_2} CH_3(C_6H_5)_2SiCH_2CH_2CH_2NO_2 \xrightarrow[NaNO_2,\ OH^-]{AgNO_3} CH_3(C_6H_5)_2SiCH_2CH_2CH(NO_2)_2 \xrightarrow[CH_3OH]{FClO_3} CH_3(C_6H_5)_2SiCH_2CH_2CF(NO_2)_2 \xrightarrow{Br_2} CH_3Br_2SiCH_2CH_2CF(NO_2)_2$$

The hydrolysis of this dibromide gave cyclic polysiloxanes, with the number of units depending on the hydrolysis conditions. Thus, treating the dibromide in ether solution with ice gave the tetramer on the basis of vapor osmometric molecular weight. The same molecular weight was obtained when a sample of the neat dibromide was hydrolyzed by atmospheric moisture. On the other hand, when a methylene chloride solution was hydrolyzed, a molecular weight corresponding to the trimer was obtained.

The polysiloxane reacted with hydrofluoric acid in aqueous ethanol to give an 80% yield of (3-fluoro-3,3-dinitropropyl)methyldifluorosilane. The dibromide also gave the difluoride, probably via an in situ hydrolysis. The difluoride reacted with sodium methoxide to give a compound assigned on the basis of NMR spectra to be (3-fluoro-3,3-dinitropropyl)methylmethoxyfluorosilane. A pure sample of this compound was not isolated. Advantage was taken of the relative stability of fluorine–silicon bonds toward acids.[19] Treating the crude methoxyfluoride with aqueous acid gave 1,3-bis(3-fluoro-3,3-dinitropropyl)-1,3-dimethyl-1,3-difluorodisiloxane, isolated readily by distillation.



$$\left[CH_3SiCH_2CH_2CF(NO_2)_2\ \ O^-\right]_n \xrightarrow{HF} CH_3SiF_2CH_2CH_2CF(NO_2)_2 \xrightarrow{NaOCH_3} CH_3SiF(OCH_3)CH_2CH_2CF(NO_2)_2 \xrightarrow[H_2O]{H^+} FC(NO_2)_2CH_2CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle F}{Si}}{-}O{-}\overset{\displaystyle CH_3}{\underset{\displaystyle F}{Si}}CH_2CH_2CF(NO_2)_2$$

The synthesis of bis(3-fluoro-3,3-dinitropropyl)polysiloxanes was also undertaken with the use of phenyl as a blocking group. The starting material for this work was prepared initially using a rearrangement of haloalkoxysilyl ethers to hydroxyalkylsilanes as reported by Speier.[20] Bis(3-chloropropoxy)diphenylsilane was prepared by the reaction of dichlorodiphenylsilane and 3-chloropropanol with ammonia in benzene. This product reacted with sodium and chlorotrimethylsilane in refluxing toluene to give bis(3-trimethylsilyloxypropyl)diphenylsilane. Hydrolysis with acid gave bis(3-hydroxypropyl)diphenylsilane.

$$(C_6H_5)_2SiCl_2 + ClCH_2CH_2CH_2OH \xrightarrow[C_6H_6]{NH_3} (C_6H_5)_2Si(OCH_2CH_2CH_2Cl)_2 \xrightarrow[(CH_3)_3SiCl]{Na,\ Toluene} (C_6H_5)_2Si[CH_2CH_2CH_2OSi(CH_3)_3]_2 \xrightarrow[EtOH]{H^+} (C_6H_5)_2Si(CH_2CH_2CH_2OH)_2$$

Another route to a difunctional starting material involved hydroboration. Borane in tetrahydrofuran was added to diallyldiphenylsilane, and the resulting borane was brominated to give bis(3-bromopropyl)diphenylsilane in 24% overall yield.

$$(C_6H_5)_2Si(CH_2CH{=}CH_2)_2 \xrightarrow{BH_3} (C_6H_5)_2Si(CH_2CH_2CH_2B)_2 \xrightarrow{Br_2} (C_6H_5)_2Si(CH_2CH_2CH_2Br)_2$$

A reaction scheme analogous to that used to prepare the

(2-fluoro-2,2-dinitropropyl)methylsilane derivatives provided a more practical route to the preparation of bis(2-fluoro-2,2-dinitropropyl)silicon compounds. Thus, the hydrosilylation of allyloxytrimethylsilane with diphenylsilane catalyzed by tris(triphenylphosphine)rhodium chloride gave, after hydrolysis, a 68% yield of bis(3-hydroxypropyl)diphenylsilane. Lower yields resulted from the use of allyl acetate as the olefin or chloroplatinic acid as the catalyst. The alcohol was converted to the *p*-toluenesulfonate which, in turn, was treated with sodium bromide in dimethyl sulfoxide to give the dibromide in 84% overall yield. The dimethyl sulfoxide solution could be used in the nitrite reaction without workup. The dibromide was also prepared from the alcohol with phosphorus tribromide in 67% recrystallized yield.

$$(C_6H_5)_2SiH_2 + CH_2{=}CHCH_2OSi(CH_3)_3 \rightarrow (C_6H_5)_2Si[CH_2CH_2CH_2OSi(CH_3)_3]_2$$

$$\xrightarrow[H^+]{H_2O} (C_6H_5)_2Si(CH_2CH_2CH_2OH)_2$$

$$\xrightarrow[\substack{1.\ TsCl,\ Pyr,\ CH_2Cl_2 \\ 2.\ NaBr,\ Me_2SO}]{PBr_3\ or} (C_6H_5)_2Si(CH_2CH_2CH_2Br)_2$$

The reaction of bis(3-bromopropyl)diphenylsilane in dimethyl sulfoxide with sodium nitrite gave bis(3-nitropropyl)diphenylsilane in 34% yield. Oxidative nitration of this compound gave bis(3,3-dinitropropyl)diphenylsilane in 38% yield. Fluorination of the potassium salt of this compound was carried out in a mixture of water, methanol, and dimethylformamide with perchloryl fluoride as the fluorinating agent. An 85% yield of bis(3-fluoro-3,3-dinitropropyl)diphenylsilane was obtained.

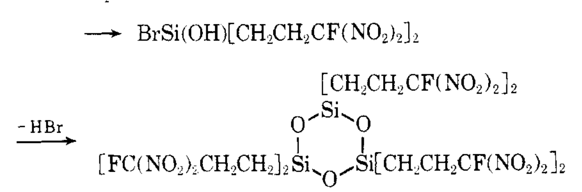
$$(C_6H_5)_2Si(CH_2CH_2CH_2Br)_2$$

$$\xrightarrow[Me_2SO]{NaNO_2} (C_6H_5)_2Si(CH_2CH_2CH_2NO_2)_2$$

$$\xrightarrow[NaNO_2,\ OH^-]{AgNO_3} (C_6H_5)_2Si[CH_2CH_2CH(NO_2)_2]_2$$

$$\xrightarrow{FClO_3} (C_6H_5)_2Si[CH_2CH_2CF(NO_2)_2]_2$$

This diphenylsilane could not be dephenylated completely with bromine under the conditions that were used with (3-fluoro-3,3-dinitropropyl)methyldiphenylsilane; the reaction ceased when approximately half of the phenyl groups were cleaved. However, when water was added after this initial reaction was completed, bromine consumption resumed. A white solid, mp 207–209 °C, was isolated in 67% yield and was identified by molecular weight and analysis as the cyclic trisiloxane. Apparently, the second fluorodinitropropyl group inhibits the dephenylation to the extent that only one phenyl group is removed. The accelerating effect of water on the dephenylation is rationalized on the basis of the hydrolysis of the initially formed phenylbromosilane. The resulting silanol or its dimer is dephenylated more readily than the bromosilane.



$$(C_6H_5)_2Si[CH_2CH_2CF(NO_2)_2]_2 \xrightarrow{Br_2} C_6H_5SiBr[CH_2CH_2CF(NO_2)_2]_2$$

$$\xrightarrow[Br_2]{H_2O} C_6H_5Si(OH)[CH_2CH_2(NO_2)_2]_2$$

$$\longrightarrow BrSi(OH)[CH_2CH_2CF(NO_2)_2]_2$$

$$\xrightarrow{-HBr}$$

Experimental Section

NMR and IR spectra were recorded with a Varian T-60 spectrometer and a Perkin-Elmer 700 spectrometer, respectively. Molecular weights were determined with a Mechrolab 301A vapor osmometer. A Varian 920 gas chromatograph with a 12 ft × 3/8 in aluminum column packed with 12% QF-1 on 60–80 mesh Chromosorb W was used for GLC separations. Previously described safety precautions for fluorodinitro compounds[11,12] were observed.

(3-Nitropropyl)trimethylsilane. A solution of 10 g (0.145 mol) of sodium nitrite and 11.3 g (0.055 mol) of (3-bromopropyl)trimethylsilane[8] in 120 mL of dimethyl sulfoxide was stirred for 3 h at ambient temperature. Water (500 mL) was added, and the product was extracted with three 50-mL portions of carbon tetrachloride. The NMR spectrum showed (3-nitropropyl)trimethylsilane (69% yield), (3-nitritopropyl)trimethylsilane (25%), and starting material and the alcohol (5% combined). Distillation gave 2.2 g (9.5%) of (3-nitritopropyl)trimethylsilane, bp 48–50 °C (16 mm), and 5.9 g (60%) of 95% pure (3-nitropropyl)trimethylsilane, bp 62–64 °C (1 mm). An analytical sample was isolated by GLC: NMR (CCl_4) δ 4.20 (t, *J* = 7 Hz, 2 H, CH_2NO_2), 1.87 (m, 2 H, CH_2CH_2Si), 0.50 (m, 2 H, CH_2Si), 0.0 (s, 9 H, $(CH_3)_3Si$); IR (CCl_4) 2970, 1545, 1430, 1380, 1250 cm^{-1}. Anal. Calcd for $C_6H_{15}NO_2Si$: C, 44.69; H, 9.38; N, 8.68. Found: C, 44.74; H, 9.38; N, 8.67.

The nitrosation[21] of (3-hydroxypropyl)trimethylsilane provided an independent synthesis of (3-nitrotopropyl)trimethylsilane: NMR (CCl_4) δ 4.50 (t, 2 H, CH_2ONO), 1.7 (m, 2 H, CH_2CH_2Si), 0.5 (m, 2 H, CH_2Si), 0.0 (s, 9 H $(CH_3)_3Si$); IR (film) 1645, 1605, 1260, 850, 800 cm^{-1}.

(4-Nitrobutyl)trimethylsilane. A solution of 1.9 g (0.028 mol) of sodium nitrite and 2.92 g (0.014 mol) of (4-bromobutyl)trimethylsilane[8] in 30 mL of dimethyl sulfoxide was stirred for 3 h at ambient temperature. Water (30 mL) was added, and the product was extracted with three 15-mL portions of carbon tetrachloride. The carbon tetrachloride solution was washed with 10 mL of water and was dried over magnesium sulfate. Distillation gave 1.1 g (45%) of (4-nitrobutyl)trimethylsilane, bp 54–56 °C (0.9 mm). An anlytical sample was isolated by GLC: NMR (CCl_4) δ 4.27 (t, *J* = 7 Hz, 2 H, CH_2NO_2), 2.02 (q, *J* = 7 Hz, 2 H, $CH_2CH_2NO_2$), 1.4 (m, 2 H, CH_2CH_2Si), 0.50 (m, 2 H, CH_2Si), 0.0 (s, 9 H, $(CH_3)_3Si$); IR (CCl_4) 2960, 1545, 1435, 1385, 1255 cm^{-1}. Anal. Calcd for $C_7H_{17}NO_2Si$: C, 47.96; H, 9.77; N, 7.99. Found: C, 47.95; H, 9.70; N, 8.11.

(3-Nitrobutyl)trimethylsilane. A solution of 4.3 g (0.020 mol) of (3-bromobutyl)trimethylsilane and 4.1 g (0.06 mol) of sodium nitrite in 50 mL of dimethyl sulfoxide was stirred at ambient temperature for 3 h. The solution was diluted with 200 mL of water, and the product was extracted with three 25-mL portions of carbon tetrachloride. The NMR spectrum of the solution indicated a 55% yield of (3-nitrobutyl)trimethylsilane, a 25% yield of (3-nitritobutyl)trimethylsilane, and 12% unreacted bromide. Distillation gave 1.0 g of a mixture of nitrite and bromide, bp 56–62 °C (10 mm), and 2.0 g of 80% pure (3-nitrobutyl)trimethylsilane (45% yield), bp 58–60 °C (1 mm). Redistillation gave 95% pure product (NMR), and an analytical sample was isolated by GLC: NMR (CCl_4) δ 4.30 (sextet, 1 H, $CHNO_2$), 1.75 (m, 2 H, CH_2CH_2Si), 1.42 (d, 3 H, CH_3CHNO_2), 0.4 (t, 2 H, CH_2Si), 0.0 (s, 9 H, $(CH_3)_3Si$); IR (film) 2970, 1545, 1260, 865, 845 cm^{-1}. Anal. Calcd for $C_7H_{17}NO_2Si$: C, 47.96; H, 9.77; N, 7.99. Found: C, 48.09; H, 9.66; N, 7.68.

The nitrite was identified by hydrolysis with acetic acid in methanol to give the alcohol, which was isolated by preparative GLC: NMR (CCl_4) δ 3.48 (sextet, 1 H, CHOH), 2.9 (broad s, 1 H, OH), 1.3 (m, 2H, CH_2Si), 1.05 (d, 3 H, CH_3CHOH), 0.40 (m, 2 H, CH_2Si), 0.0 (s, 9 H $(CH_3)_3Si$); IR 3350 (OH), 2950, 1250, 860, 850, 840 cm^{-1}.

The alcohol was reconverted by a standard procedure[21] to the nitrite with identical spectra: NMR (CCl_4) δ 5.30 (sextet, 1 H, CHONO), 1.7 (m, 2 H, CH_2CH_2Si), 1.40 (d, *J* = 7 Hz, 3 H, CH_3CH), 0.55 (m, 2 H, CH_2Si), 0.0 (s, 9 H, $(CH_3)_3Si$); IR (film) 2970, 1640, 1600, 1260, 880, 850, 800 cm^{-1}. The 1640-, 1600-, and 800-cm^{-1} peaks are assigned[22] to ONO.

(3,3-Dinitropropyl)trimethylsilane. A solution of 5.6 g (0.035 mol) of (3-nitropropyl)trimethylsilane, 2.58 g (0.039 mol) of potassium hydroxide, and 2.7 g (0.039 mol) of sodium nitrite in 25 mL of water and 25 mL of methanol was added quickly to a well-stirred mixture of 13.3 g (0.078 mol) of silver nitrate in 25 mL of water and 50 mL of ether. The mixture was stirred for 2 h at room temperature, and 25 mL of saturated sodium chloride was added. The silver deposits were filtered off, and the ether layer was separated, dried, and distilled to give 5.7 g (71%) of 90% pure (3,3-dinitropropyl)trimethylsilane, bp 70–72 °C (0.2 mm). An analytical sample was obtained by GLC: NMR (CCl_4) δ 5.88 (t, *J* = 7 Hz, 1 H, $CH(NO_2)_2$), 2.38 (m, 2 H, CH_2CH_2Si), 0.55 (m, 2 H, $\mathrm{CH_2Si}$), 0.08 (s, 9 H, $\mathrm{(CH_3)_3Si}$); IR ($\mathrm{CCl_4}$) 2970, 1570, 1335, and 1260 cm^{-1}. Anal. Calcd for $\mathrm{C_6H_{14}N_2O_4Si}$: C, 34.94; H, 6.84; N, 13.58. Found: C, 35.28; H, 6.90; N, 13.47.

(4,4-Dinitrobutyl)trimethylsilane. A mixture of 0.6 g (0.015 mol) of sodium hydroxide, 2.62 g (0.015 mol) of (4-nitrobutyl)trimethylsilane, and 6 mL of water was stirred at 80 °C until a solution was formed. The solution was cooled to room temperature, and 1.1 g (0.015 mol) of sodium nitrite was added. The resulting solution was added quickly to a well-stirred, ice-cooled mixture of 5.1 g (0.030 mol) of silver nitrate, 12 mL of water, 12 mL of ether, and 2 drops of 1 N sodium hydroxide. The mixture was stirred at room temperature for 2 h and filtered, and the precipitate was washed with ether. The ether layer of the filtrate, combined with the washings, was dried over magnesium sulfate and distilled to give 1.9 g (57%) of (4,4-dinitrobutyl)trimethylsilane, a colorless oil, bp 71–74 °C (2 mm). An analytical sample was isolated by GLC: NMR ($\mathrm{CCl_4}$) δ 5.97 (t, J = 7 Hz, 1 H, $\mathrm{CH(NO_2)_2}$), 2.43 (q, 2 H, $\mathrm{CH_2CH}$), 1.47 (m, 2 H, $\mathrm{CH_2CHSi}$), 0.57 (m, 2 H, $\mathrm{CH_2Si}$), 0.0 (s, 9 H, $\mathrm{(CH_3)_3Si}$); IR ($\mathrm{CCl_4}$) 2970, 1570, 1330, 1250 cm^{-1}. Anal. Calcd for $\mathrm{C_7H_{16}N_2SiO_4}$: C, 38.17; H, 7.32; N, 12.72. Found: C, 38.38; H, 7.32; N, 12.66.

(3,3-Dinitrobutyl)trimethylsilane. A mixture of 5.95 g (0.34 mol) of (3-nitrobutyl)trimethylsilane, 3 g of potassium hydroxide, 30 mL of water, and 30 mL of methanol was heated with stirring at 65 °C until a homogeneous solution was formed. Sodium nitrite (3.0 g, 0.043 mol) was added, and the solution, at room temperature, was added rapidly with stirring to a mixture of 100 mL of ether and 15 g (0.088 mol) of silver nitrate in 50 mL of water. The mixture was stirred 1.5 h, and 50 mL of saturated aqueous sodium chloride was added. The silver deposits were filtered off, and the ether layer was separated, dried, and distilled to give 5.38 g (72%) of (3,3-dinitrobutyl)trimethylsilane: bp 77–79 °C (0.1 mm); NMR ($\mathrm{CCl_4}$) δ 2.34 (m, 2 H, $\mathrm{(NO_2)_2CCH_2}$), 2.02 (s, 3 H, $\mathrm{(NO_2)_2CCH_3}$), 0.40 (m, 2 H, $\mathrm{CH_2Si}$), 0.05 (s, 9 H, $\mathrm{(CH_3)_3Si}$); IR ($\mathrm{CCl_4}$) 2970, 1565, 1330, 1260, 1195 cm^{-1}. Anal. Calcd for $\mathrm{C_7H_{16}N_2O_4Si}$: C, 38.16; H, 7.32; N, 12.72. Found: C, 37.98; H, 7.19; N, 11.71.

(3-Fluoro-3,3-dinitropropyl)trimethylsilane. A solution of 1.6 g (0.0078 mol) of (3,3-dinitropropyl)trimethylsilane and 0.44 g (0.0078 mol) of potassium hydroxide in 250 mL of water was fluorinated[11] at 0 °C until the solution became colorless. The product was extracted with three 20-mL portions of ether, dried, and distilled to give 0.9 g (31% yield) of 60% pure (3-fluoro-3,3-dinitropropyl)trimethylsilane, by 66–71 °C (0.5 mm). An analytical sample was obtained by GLC: proton NMR ($\mathrm{CCl_4}$) δ 2.57 (m, 2 H, $\mathrm{CH_2CF}$), 0.50 (m, 2 H, $\mathrm{CH_2Si}$), 0.08 (s, 9 H, $\mathrm{(CH_3)_3Si}$); fluorine NMR ϕ 106.0 (broad t); IR ($\mathrm{CCl_4}$) 2970, 1590, 1320, 1260, 1190 cm^{-1}. Anal. Calcd for $\mathrm{C_6H_{13}N_2O_4SiF}$: C, 32.13; H, 5.84; N, 12.49. Found: C, 32.34; H, 5.62; N, 12.43.

A solution of 5.13 g (0.025 mol) of (3,3-dinitropropyl)trimethylsilane and 2.0 g (0.03 mol) of potassium hydroxide in a mixture of 30 mL of water, 30 mL of methanol, and 30 mL of dimethylformamide was fluorinated with perchloryl fluoride[12] at ambient temperature until the gas was no longer absorbed by the solution. The solution was diluted with water, and the product was extracted with carbon tetrachloride and distilled to give 4.8 g (85%) of (3-fluoro-3,3-dinitropropyl)trimethylsilane, bp 68–71 °C (0.5 mm).

(4-Fluoro-4,4-dinitrobutyl)trimethylsilane. A solution of 1.45 g (0.0066 mol) of (4,4-dinitrobutyl)trimethylsilane and 0.5 g (0.0076 mol) of potassium hydroxide in 250 mL of water was fluorinated at 0 °C until the solution became colorless. An additional 0.4 g (0.006 mol) of potassium hydroxide was added, and fluorination was continued until the solution again became colorless. The product was extracted with three 20-mL portions of ether, dried over magnesium sulfate, and distilled to give 1.05 g (61%) of 90% pure (4-fluoro-4,4-dinitrobutyl)trimethylsilane. An analytical sample was obtained by GLC: proton NMR ($\mathrm{CCl_4}$) δ 2.67 (d of 5, J_{HF} = 19, J_{HH} = 7 Hz, 2 H, $\mathrm{CH_2CF}$), 1.44 (m, 2 H, $\mathrm{CH_2CH_2Si}$), 0.53 (m, 2 H, $\mathrm{CH_2Si}$), 0.0 (s, 9 H, $\mathrm{(CH_3)_3Si}$); fluorine NMR ($\mathrm{CCl_4}$) ϕ 102.8 (broad t, $\mathrm{(NO_2)_2CF}$); IR ($\mathrm{CCl_4}$) 2970, 1590, 1350, 1255 cm^{-1}. Anal. Calcd for $\mathrm{C_7H_{15}N_2O_4SiF}$: C, 35.28; H, 6.34; N, 11.76. Found: C, 35.24; H, 6.30; N, 11.64.

Trimethylsilylmethyl Trifluoromethanesulfonate. A solution of 4.5 g (0.0435 mol) of (hydroxymethyl)trimethylsilane[14] and 3.43 g (0.0435 mol) of pyridine in 30 mL of methylene chloride was added with stirring over a 45-min period to a solution of 12.2 g (0.043 mol) of trifluoromethanesulfonic anhydride in 30 mL of methylene chloride. After 15 min the solution was poured over ice. The methylene chloride solution was dried over sodium sulfate and distilled to give 7.0 g (68%) of trimethylsilylmethyl triflate, bp 49–51 °C (9 mm). An analytical sample was isolated by GLC: proton NMR ($\mathrm{CCl_4}$) δ 4.07 (s, 2 H, $\mathrm{CH_2Si}$), 0.08 (s, 9 H, $\mathrm{(CH_3)_3Si}$); fluorine NMR ϕ 74.3 (s); IR (film) 1410, 1210, 1150, 960, 870 cm^{-1}. Anal. Calcd for $\mathrm{C_5H_{11}O_3F_3SiS}$: C, 25.40; H, 4.69. Found: C, 25.23; H, 4.66.

Trimethylsilylmethyl 2-Fluoro-2,2-dinitroethyl Ether. Potassium carbonate (6 g) was added to a solution of 3.5 g (0.0148 mol) of trimethylsilylmethyl trifluoromethane sulfonate and 2.3 g of 2-fluoro-2,2-dinitroethanol in 5 mL of methylene chloride, and the mixture was stirred for 16 h. This suspension was added with stirring to a mixture of 30 mL of ice water and 30 mL of carbon tetrachloride. The carbon tetrachloride layer was washed with 10 mL of water, dried over magnesium sulfate, and distilled to give 1.56 g (45%) of trimethylsilylmethyl 2-fluoro-2,2-dinitroethyl ether, bp 52 °C (0.75 mm). An analytical sample was prepared by GLC: proton NMR ($\mathrm{CCl_4}$) δ 4.35 (d, 2 H, J = 18 Hz, $\mathrm{CH_2CF}$), 3.23 (s, 2 H, $\mathrm{CH_2Si}$), 0.02 (s, 9 H, $\mathrm{(CH_3)_3Si}$); fluoride NMR ($\mathrm{CCl_4}$) ϕ 110.25 (broad t); IR (film) 2975, 2925, 1600, 1320, 1250, 1125, 870, 860 cm^{-1}. Anal. Calcd for $\mathrm{C_6H_{13}N_2O_5SiF}$: C, 29.99; H, 5.45; N, 11.66. Found: C, 30.22; H, 5.33; N, 11.75.

Allylmethyldiphenylsilane. A solution of 1452 g (12 mol) of allyl bromide in 2.5 L of absolute ether was added dropwise with stirring, over a period of 3.5 h, to a suspension of 389 g (16 mol) of magnesium turnings in 2.5 L of absolute ether. An efficient reflux condenser was used, equipped with a drying tube. Excess magnesium was removed by filtration, and 1862 g (8 mol) of chloromethyldiphenylsilane was added dropwise over a 1 h period. The solution was refluxed for 1 h and was allowed to stand overnight at room temperature. A solution of 642 g (12 mol) of ammonium chloride in 2 L of water and then 3 L of water were added slowly, using a reflux condenser to control the exotherm. The aqueous layer was separated and extracted with three 1-L portions of ether. The combined ether solutions were dried over magnesium sulfate and distilled to give 1397 g (73%) of allylmethyldiphenylsilane: bp 93 °C (0.1 mm); NMR (neat) δ 0.0 (s, 3 H, $\mathrm{CH_3Si}$), 1.5 (d, J = 7 Hz, 2 H, $\mathrm{C{=}C{-}CH_2Si}$), 4.3 (m, 2 H, $\mathrm{CH_2{=}C}$), 5.3 (m, 1 H, $\mathrm{C{=}CHCH_2Si}$), 6.6–6.9 (m, 10 H, $\mathrm{C_6H_5}$); IR (film) 1640, 1440, 1270, 1170, 1130 cm^{-1}. Anal. Calcd for $\mathrm{C_{18}H_{24}O_2Si}$: C, 80.67; H, 7.56. Found: C, 80.45; H, 7.56.

(3-Bromopropyl)methyldiphenylsilane from Allylmethyldiphenylsilane. A solution (150 mL) of 29.6 g (208.3 mol) of boron trifluoride etherate in dry tetrahydrofuran was added over a 1 h period, with stirring, to 350 mL of a tetrahydrofuran solution of 119 g (0.50 mol) of allylmethyldiphenylsilane and 5.94 g (0.156 mol) of sodium borohydride. The mixture was heated at reflux for 2.5 h, and then 10 mL of methanol was added. Then, 27.3 mL (0.50 mol) of bromine and sodium methoxide solution (from 14.4 g, 0.625 mol of sodium and 300 mL of methanol) were added simultaneously at such a rate as to maintain a yellow color in the mixture. The temperature was kept at 25–30 °C by means of an ice bath. The mixture was agitated with 250 mL of 50% potassium carbonate and 250 mL of cyclohexane until the strong yellow color faded. The layers were separated, and the aqueous layer was extracted with three 100 mL portions of cyclohexane. The combined organic layers were washed with three 300-mL portions of water and 150 mL of saturated sodium chloride, dried over potassium carbonate, and distilled to give 79 g (49.5%) of (3-bromopropyl)methyldiphenylsilane: bp 176–210 °C (0.3 mm); NMR ($\mathrm{CDCl_3}$) δ 0.5 (s, 3 H, $\mathrm{CH_3Si}$), 1.1 (m, 2 H, $\mathrm{CH_2Si}$), 1.8 (m, 2 H, $\mathrm{CH_2CH_2Si}$), 3.2 (t, J = 7 Hz, 2 H, $\mathrm{BrCH_2}$), 7.2 (m, 10 H, $\mathrm{C_6H_5}$). Anal. Calcd for $\mathrm{C_{16}H_{19}BrSi}$: C, 60.19; H, 5.96. Found: C, 60.36; H, 6.01.

(3-Hydroxypropyl)methyldiphenylsilane. Allyloxytrimethylsilane[23] (1162 g, 8.94 mol) was added dropwise to a mixture of 1539 g (7.77 mol) of methyldiphenylsilane and 80 mg of tris(triphenylphosphine)rhodium chloride at 130 °C over a 3 h period. The solution was added dropwise with stirring, over a 1.5 h period, to a solution of 3 L of methanol and 800 mL of 1 N hydrochloric acid. The mixture was stirred overnight, and an equal volume of water was added. The aqueous solution was extracted with 3 L of methylene chloride. The combined methylene chloride solution was washed with water and saturated salt solution and was dried with sodium sulfate. The solvent was removed by distillation to give 1950 g (98%) of (3-hydroxypropyl)methyldiphenylsilane: bp 130–140 °C (0.03 to 0.07 mm); NMR ($\mathrm{CDCl_3}$) δ 0.48 (s, 3 H, $\mathrm{CH_3}$), 0.95 (m, 2 H, $\mathrm{CH_2Si}$), 1.4 (m, 2 H, $\mathrm{CCH_2C}$), 2.0 (s, 1 H, OH), 3.12 (t, J = 6 Hz, 2 H, $\mathrm{CH_2O}$), 7.0 (s, 10 H, $\mathrm{C_6H_5}$). Anal. Calcd for $\mathrm{C_{16}H_{20}SiO}$: C, 74.95; H, 7.86. Found: C, 74.80; H, 8.07.

(3-*p*-Toluenesulfonatopropyl)methyldiphenylsilane. Toluenesulfonyl chloride (1597 g, 8.38 mol) and then 766 mL (9.53 mol) of pyridine were added to a solution of 1950 g (7.62 mol) of crude (3-hydroxypropyl)methyldiphenylsilane in 1950 mL of methylene chloride at 4 °C. The mixture was stirred overnight and was poured into water. The methylene chloride layer was separated, and the aqueous layer was extracted once with methylene chloride. The combined methylene chloride solution was washed with water, with 1 N hydrochloric acid, and with saturated salt solution and was then dried with sodium sulfate. Most of the solvent was removed by distillation. The product was crystallized from 1200 mL of ethyl ether and 1200 mL of Skelly F to give 1925 g (62%) of (3-*p*-toluenesulfonatopropyl)methyldiphenylsilane: mp 68–69 °C; NMR ($CDCl_3$) δ 7.3 (d of d, 4 H, CC_6H_4Si-*p*), 7.2 (broad s, 10 H, C_6H_5), 3.85 (t, J = 6.5, 2 H, CH_2O), 2.40 (s, 3 H, $CH_3C_6H_5$), 1.6 (m, 2 H, CH_2CH_2Si), 1.0 (m, 2 H, CH_2Si), 0.50 (s, 3 H, CH_3Si). Anal. Calcd for $C_{23}H_{26}O_3SiS$: C, 67.28; H, 6.38. Found: C, 67.44; H, 6.48.

(3-Bromopropyl)methyldiphenylsilane from Toluenesulfonate. A solution of 3.5 g (0.04 mol) of lithium bromide and 5.98 g (0.0146 mol) of (3-propyl)methyldiphenylsilane *p*-toluenesulfonate in 25 mL of dimethyl sulfoxide was stirred at ambient temperature for 3 h. Water (10 mL) was added, and the product was extracted with three 10-mL portions of carbon tetrachloride. The combined organic layers were washed with 10 mL of water, dried, and stripped of solvent. The residue consisted of 4.2 g (90%) of 90% pure (3-bromopropyl)methyldiphenylsilane.

(3-Nitropropyl)methyldiphenylsilane. The addition of 99.6 g (1.26 mol) of sodium nitrite to a solution of 101 g (0.317 mol) of (3-bromopropyl)methyldiphenylsilane in 500 mL of dimethyl sulfoxide resulted in a temperature rise to 30 °C over a 40 min period. The mixture was added to 2.5 L of water, and the product was extracted with four 300-mL portions of carbon tetrachloride. The carbon tetrachloride solution was washed with three 600-mL portions of water and 300 mL of saturated sodium chloride, and the solvent was removed. The NMR spectrum of the residue showed a 52% yield of the nitro compound (δ 4.2), a 20% yield of the nitrite (δ 4.4), and a 15% yield of the alcohol and/or bromide (δ 3.3).

The mixture was stirred for 1 h with 80 mL of 5 N potassium hydroxide, and 320 mL of water was added. The mixture was extracted with two 100-mL portions of ether. The aqueous solution was acidified to pH 6 with acetic acid, and the product was extracted with four 100-mL portions of methylene chloride. The methylene chloride solution was dried over magnesium sulfate and evaporated to give 45.4 g (50%) of (3-nitropropyl)methyldiphenylsilane. An analytical sample was obtained by molecular distillation: bp 152 °C (0.22 mm); NMR ($CDCl_3$) δ 0.3 (s, 2 H, CH_3Si), 1.2 (m, 2 H, CH_2Si), 2.1 (m, 2 H, CH_2CH_2Si), 4.2 (t, J = 7 Hz, 2 H, CH_2NO_2), 7.3 (m, 10 H, C_6H_5); IR (film) 1550, 1435, 1395, 1260, 1190, 1165, 1125 cm^{-1}. Anal. Calcd for $C_{16}H_{19}NO_2Si$: C, 67.37; H, 6.67; N, 4.91. Found: C, 67.57; H, 6.62; N, 4.64.

(3,3-Dinitropropyl)methyldiphenylsilane. A mixture of 68.4 g (0.24 mol) of (3-nitropropyl)methyldiphenylsilane and 53 mL of 5 N potassium hydroxide was stirred for 1 h. The resulting solution was diluted with 212 mL of water, and 22.9 g (0.29 mol) of sodium nitrite in 200 mL of water was added. The solution was cooled with an ice bath, and a cold solution of 90 g (0.53 mol) of silver nitrate in 400 mL of water and 800 mL of cold ether were added rapidly with efficient stirring. The mixture was stirred for 30 min at 0 °C and for 90 min at room temperature. Saturated sodium chloride solution (100 mL) was then added, and after 15 min the mixture was filtered and the precipitate was washed with water and ether. The combined filtrate and washings were acidified to pH 6 with acetic acid, and the layers were separated. The aqueous layer was extracted with ether, and the combined ether solutions were washed with water and saturated sodium chloride solution and dried over magnesium sulfate. The ether was removed, and NMR analysis of the residue, 64 g, showed a 70% yield of (3,3-dinitropropyl)methyldiphenylsilane and 8% starting material: NMR ($CDCl_3$) δ 0.7 (s, 3 H, CH_3Si), 1.3 (m, 2 H, CH_2Si), 2.6 (m, 2 H, CH_2CH_2Si), 6.0 (t, J = 7 Hz, 1 H, CH), 7.4 (m, 10 H, C_6H_5).

(3-Fluoro-3,3-dinitropropyl)methyldiphenylsilane. The above crude product containing 53.5 g (0.162 mol) of (3,3-dinitropropyl)methyldiphenylsilane was dissolved in a solution of 0.217 mol of potassium hydroxide in 900 mL of methanol. The solution was placed in a 2-L flask equipped with a glass dip tube for introducing perchloryl fluoride, a thermometer, a magnetic stirrer, and an ice bath. The flask was vented to the fume-hood atmosphere by means of a mineral oil bubbler, and another bubbler as well as an inverted vacuum trap (to prevent suck back) were placed between the dip tube and a perchloryl fluoride cylinder. Perchloryl fluoride was passed into the solution at 10 °C until it was no longer absorbed (2 h). Then, 1000 mL of water was added, and the solution was stirred 1 h at room temperature. An additional 1500 mL of water was added, and the mixture was made basic (pH 12) with potassium hydroxide. The product was extracted with four 400-mL portions of methylene chloride. The methylene chloride solution was washed with three 1000-mL portions of water, dried, and stripped of solvent. The residue, 58.5 g, was chromatographed on a 750 g column of dry silica gel, using carbon tetrachloride (30 L) for elution, to give 44.5 g (79%) of (3-fluoro-3,3-dinitropropyl)methyldiphenylsilane: proton NMR ($CDCl_3$) δ 0.6 (s, 3 H, CH_3Si), 1.1 (m, 2 H, CH_2Si), 2.7 (m, 2 H, NO_2CCH_2), 7.2 (m, 10 H, C_6H_5); fluorine NMR ($CDCl_3$) ϕ 104.4 (t, J = 22 Hz); IR (film) 1590, 1440, 1370, 1330, 1270, 1200, 1120 cm^{-1}. Anal. Calcd for $C_{16}H_{17}N_2O_4FSi$: C, 55.17; H, 4.88; N, 8.04. Found: C, 55.02; H, 5.12; N, 8.09.

(3-Fluoro-3,3-dinitropropyl)methyldibromosilane. A mixture of 12.5 mL (0.230 mol) of bromine and 20.0 g (0.0574 mol) of (3-fluoro-3,3-dinitropropyl)methyldiphenylsilane was heated at 100 °C for 2 h under nitrogen. The product was evacuated at 25 mm at room temperature for 90 min. Distillation gave phenyl bromide, bp 60 °C (0.15 mm), a 0.5-g intermediate fraction, and 15.8 g (78%) of (3-fluoro-3,3-dinitropropyl)methyldibromosilane, a colorless liquid: bp 68 °C (0.14 mm); proton NMR ($CDCl_3$) δ 1.1 (s, 3 H, CH_3Si), 1.4 (m, 2 H, CH_2Si), 2.9 (m, 2 H, CH_2Si); fluorine NMR ($CDCl_3$) ϕ 103.5 (t, J = 17 Hz). The material was too hygroscopic for commercial microanalysis.

(3-Fluoro-3,3-dinitropropyl)methylpolysiloxane. A solution of 14.2 g (0.0401 mol) of (3-fluoro-3,3-dinitropropyl)methyldibromosilane in 50 mL of ether was poured onto 75 g of crushed ice, and the mixture was stirred for 30 min. The ether layer was washed with two 50-mL portions of water and 50 mL of saturated sodium chloride solution. The solution was dried over magnesium sulfate, and the solvent was removed. The residue was dried for 3 h at 90 °C (0.07 mm) to give 7.7 g (91.4%) of an oily product: proton NMR ($CDCl_3$) δ 0.2 (s, 3 H, CH_3Si), 0.7 (m, 2 H, CH_2Si), 2.7 (m, 2 H, CH_2CH_2Si); fluorine NMR ($CDCl_3$) ϕ 104.1 (t, J = 17 Hz); IR (film) 3600, 3450, 2900, 2650, 1600, 1440, 1380, 1330, 1280, 1210, 1190, 1080 cm^{-1}. Anal. Calcd for $C_4H_7N_2FO_5Si$: C, 22.86; H, 3.33; N, 13.33. Found: C, 22.98; H, 3.55; N, 13.41; mol wt, 834.

The use of methylene chloride as the hydrolysis solvent gave a similar product with mol wt 562.

(3-Fluoro-3,3-dinitropropyl)methyldifluorosilane. (3-Fluoro-3,3-dinitropropyl)methylpolysiloxane (13.5 g, 64.3 mmol of monomer) was dissolved in 50 mL of ethanol, 25 mL of 48% hydrogen fluoride, and 15 mL of water. The mixture was agitated for 24 h and then diluted with water. The product was extracted with methylene chloride, and the methylene chloride solution was washed with water and saturated salt solution and dried over sodium sulfate. The solvent was evaporated, and the residue was distilled to give 12 g (80%) of (3-fluoro-3,3-dinitropropyl)methyldifluorosilane: bp 67 °C (3 mm); NMR ($CDCl_3$) δ 0.4 (t, J = 6 Hz, 3 H, CH_3Si), 0.9 (m, 2 H, CH_2Si), 2.9 (m, 2 H, $CH_2CF(NO_2)_2$); fluorine NMR ($CDCl_3$) ϕ 104.5 (t, J = 16 Hz, 1 F, $F(NO_2)_2C$), 132.3 (sextet, J = 6 Hz, 2 F, SiF_2); IR (film) 1600, 1435, 1370, 1325, 1275, 1220, 1190, 1065, 1025, 930, 910, 870, 860, 830, 805 cm^{-1}. Anal. Calcd for $C_4H_7F_3N_2O_4Si$: C, 20.69; H, 3.02; H, 12.07. Found: C, 20.67; H, 2.88; N, 12.52.

A mixture of 33 g (0.0932 mol) of (3-fluoro-3,3-dinitropropyl)methyldibromosilane and 15.7 g (0.373 mol) of sodium fluoride was dissolved in 100 mL of ethanol, 25 mL of 48% hydrogen fluoride, and 15 mL of water with agitation. After 3 days, the mixture was poured into water and extracted twice with methylene chloride. The organic solution was washed with water and saturated salt solution and dried over sodium sulfate. The solvent was evaporated, and the residue was distilled to give 17.8 g (82%) of (3-fluoro-3,3-dinitropropyl)methyldifluorosilane.

Reaction of (3-fluoro-3,3-dinitropropyl)methyldifluorosilane with Sodium Methoxide. A solution of 5.4 g (0.1 mol) of sodium methoxide in 30 mL of dry methanol was added dropwise to 23.2 g (0.1 mol) of (3-fluoro-3,3-dinitropropyl)methyldifluorosilane with ice bath cooling. After 0.5 h, the methanol was evaporated and the residue was distilled at 79–85 °C (3 mm) to give a mixture of starting material (20%), dimer (18%), and product (62%). The yield of (3-fluoro-3,3-dinitropropyl)methylmethoxyfluorosilane was 13.9 g (57%) by quantitative NMR: NMR ($CDCl_3$) δ 0.3 (d, J = 6 Hz, 3 H, CH_3Si), 0.8 (m, 2 H, CH_2Si), 2.8 (m, 2 H, $CH_2C(NO_2)_2F$), 3.5 (s, 3 H, CH_3OSi); fluorine NMR ($CDCl_3$) ϕ 104.7 (T= J = 16 Hz, 1 F, $CF(NO_2)_2F$), 138.1 (sextet, J = 6 Hz, 1 F, FSi); IR (film) 1600, 1440, 1375, 1330, 1275, 1215, 1195, 1100, 1065, 1030, 915, 880, 855, 835, 810 cm^{-1}.

1,3-Bis(3-fluoro-3,3-dinitropropyl)-1,3-dimethyl-1,3-difluorodisiloxane. A solution containing 1.25 g (5.12 mmol) of (3-fluoro-3,3-dinitropropyl)methylmethoxyfluorosilane in 25 mL of methanol, 5 mL of water, and 1 mL of concentrated sulfuric acid was stirred for 20 h. The solution was poured into water, and the product was extracted with methylene chloride, washed with water and saturated salt solution, and dried over sodium sulfate. The solvent was evaporated, and the residue was distilled to give 0.7 g (62%) of 1,3-bis(3-fluoro-3,3-dinitropropyl)-1,3-dimethyl-1,3-difluorodisiloxane: bp 158 °C (0.2 mm); NMR (neat) δ 0.3 (d, J = 6 Hz, 6 H, CH_3Si), 0.9 (m, 4 H, CH_2Si), 2.9 (m, 4 H, CH_2CF); fluorine NMR (neat) ϕ 105.5 (t, J = 20 Hz, 2 F, $FC(NO_2)$), 132.0 (sextet, J = 6 Hz, 2 F, FSi); IR (film) 1590, 1435, 1365, 1320, 1235, 1100, 1025, 970, 910, 875, 855, 820, 800, 780 cm^{-1}. Anal. Calcd for $C_8H_{14}F_4N_4O_9Si_2$: C, 21.72; H, 3.17; N, 12.67. Found: C, 21.88; H, 3.05; N, 13.50.

Bis(3-chloropropoxy)diphenylsilane. Anhydrous ammonia was passed through a stirred solution of 81.6 g of 93% pure dichlorodiphenylsilane (0.30 mol) and 56.7 g (0.60 mol) of 3-chloropropanol in 600 mL of dry benzene at 5 °C until it was no longer absorbed. The solution was filtered and distilled to give 93.5 g (84.5%) of bis(3-chloropropoxy)diphenylsilane: bp 176–179 °C (0.21 mm); NMR ($CDCl_3$) δ 1.95 (quintet, J = 6 Hz, 4 H, $CH_2CH_2CH_2$), 3.55 (t, J = 6 Hz, 4 H, CH_2OSi), 3.8 (t, J = 6 Hz, 4 H, $ClCH_2$), 7–7.7 (m, 10 H, C_6H_5). Anal. Calcd for $C_{18}H_{22}O_2Cl_2Si$: C, 58.54; H, 5.96. Found: C, 58.19; H, 5.90.

Bis(3-hydroxypropyl)diphenylsilane from Bis(3-chloropropoxy)diphenylsilane. A round-bottom flask containing 175 mL of dry toluene and 22.2 g (0.964 mol) of sodium was fitted with a stirrer, a thermometer, a reflux condenser, and a dropping funnel containing 103 g (0.963 mol) of chlorotrimethylsilane. The toluene was refluxed, and sufficient chlorotrimethylsilane was added to lower the boiling point to 101 °C. Bis(3-chloropropoxy)diphenylsilane (80.6 g, 0.2185 mol) was mixed with the remaining chlorotrimethylsilane, and the mixture was added dropwise into the flask with vigorous stirring over a 30 min period. The solution was filtered and, the solvent was removed under reduced pressure. The residue was dissolved in 150 mL of absolute ethanol, and 30 mL of 5% hydrochloric acid was added slowly with cooling. The mixture was stirred for 1 h, and the ethanol and water were then removed under vacuum. The product was washed with 100 mL of saturated potassium carbonate and distilled to give 33.5 g (51%) of bis(3-hydroxypropyl)diphenylsilane: bp 178–185 °C (0.07 mm); mp 83–84 °C, NMR ($CDCl_3$) δ 0.7–1.7 (m, 8 H, CH_2CH_2Si), 2.58 (s, 2 H, OH), 3.2 (t, J = 6 Hz, 4 H, OCH_2), 6.9 (m, 10 H, C_6H_5); IR (film) 3300, 3050, 2900, 1430, 1190, 1120 cm^{-1}. Anal. Calcd for $C_{18}H_{24}O_2Si$: C, 72.00; H, 8.00. Found: C, 71.68; H, 8.26.

Bis(3-bromopropyl)diphenylsilane from Diallyldiphenylsilane. A solution of borane in tetrahydrofuran (35.02 mL, 0.96 M) was added dropwise with stirring under nitrogen to a solution of 13.2 g (0.05 mol) of diallyldiphenylsilane in 100 mL of dry tetrahydrofuran at 0 °C. The solution was stirred for 30 min at 0 °C and for 30 min at 20 °C. Then 1 mL of methanol was added to destroy excess borane. Bromine (5.4 mL, 0.101 mol) and sodium methoxide solution (from 2.53 g, 0.110 mol, of sodium and 30 mL of methanol) were added simultaneously at a rate such that the reaction mixture remained yellow. The reaction temperature was maintained at 23–30 °C by means of a water bath. Cyclohexane (100 mL) was added, and the solution was extracted with 100 mL of 50% potassium carbonate. The aqueous layer was extracted with three 50 mL portions of cyclohexane. The combined organic layers were washed with two 100 mL portions of water and 100 mL of saturated sodium chloride and dried over anhydrous potassium carbonate. Distillation gave 5.1 g (24%) of bis(3-bromopropyl)diphenylsilane, bp 182 °C (0.06 mm), spectrally identical to the compound characterized below. This material was handled as an oil; seed crystals were not available.

Bis(3-hydroxypropyl)diphenylsilane by Hydrosilylation. A mixture of 1500 g (7.33 mol) of 90% diphenylsilane, 0.1 g of tris(triphenylphosphine)rhodium chloride, and 200 g of allyloxytrimethylsilane was heated to 100 °C. Heating was stopped and the temperature rose to 120 °C. Additional allyoxytrimethylsilane, a total of 2800 g (21.6 mol), was added at a rate sufficient to maintain reflux. This solution was added to a solution of 15 mL of concentrated HCl and 600 mL of water in 3 L of methanol. After 24 h, the product was extracted with methylene chloride. Crystallization from methylene chloride and Skelly F yielded 1500 g (68%) of bis(3-hydroxypropyl)diphenylsilane.

Bis(3-bromopropyl)diphenylsilane from PBr_3. Bis(3-hydroxypropyl)diphenylsilane (1490 g, 4.96 mol) was added to a solution of 1043 g (3.86 mol) of phosphorus tribromide in 3 L of ether, which was maintained at room temperature by a water bath. The mixture was stirred for 72 h and then was added to ice. The product was extracted with water, dried, stripped of solvent, and extracted into Skelly F, giving 1683 g of semicrystalline, 90% pure bis(3-bromopropyl)diphenylsilane. Recrystallization from ethanol gave 1400 g (67%) of bis(3-bromopropyl)diphenylsilane: mp 48–49 °C; NMR ($CDCl_3$) δ 1.2 (m, 4 H, CH_2Si), 1.8 (m, 4 H, CH_2CH_2Si), 3.25 (t, J = 6 Hz, 4 H, $BrCH_2$), 7.15 (m, 10 H, C_6H_5). Anal. Calcd for $C_{18}H_{22}Br_2Si$: C, 50.72; H, 5.20. Found: C, 50.74; H, 5.17.

Bis(3-*p*-toluenesulfonatopropyl)diphenylsilane. Pyridine (11.3 g, 0.14 mol) and 25 g (0.13 mol) of *p*-toluenesulfonyl chloride were added to a solution of 15 g (0.050 mol) of bis(3-hydroxypropyl)diphenylsilane in 50 mL of methylene chloride at 0 °C. After a 20 h reaction period at room temperature, the mixture was washed successively with water, 1 N hydrochloric acid, water, and saturated sodium bicarbonate. The solution was dried over magnesium sulfate, and the solvent was removed to give 31.6 g (85% yield) of 85% pure bis(3-*p*-toluenesulfonatopropyl)diphenylsilane, an oil. An analytical sample was isolated by column chromatography on silica gel using methylene chloride as the elution solvent: NMR ($CDCl_3$) δ 7.4 (d of d, 8 H, $-C_6H_4-$ (p)), 7.2 (m, 10 H, C_6H_5), 3.97 (t, 4 H, CH_2O), 2.47 (s, 6 H, $-C_6H_4CH_3$-p), 1.7 (m, 4 H, CH_2CH_2Si), 1.0 (m, 4 H, CH_2Si). Anal. Calcd for $C_{32}H_{36}O_6S_2Si$: C, 63.28; H, 5.96. Found: C, 63.20; H, 6.29.

Bis(3-bromopropyl)diphenylsilane from *p*-Toluenesulfonate. A solution of 19.8 g (0.0325 mol) of bis(3-*p*-toluenesulfonatopropyl)diphenylsilane and 10 g (0.115 mol) of lithium bromide in 60 mL of dimethyl sulfoxide was stirred for 4 h. Water (150 mL) was then added, and the product was extracted with three 40 mL portions of carbon tetrachloride. The carbon tetrachloride solution was washed with 30 mL of water, dried, and stripped of solvent to give 11.3 g (74% yield) of 90% pure (by NMR) bis(3-bromopropyl)diphenylsilane. Identical results were obtained using sodium bromide instead of lithium bromide.

A solution of 1200 g (6.2 mol) of *p*-toluenesulfonyl chloride and 480 g (6.1 mol) of pyridine in 1600 mL of methylene chloride was added, with stirring and ice bath cooling, to 900 g (3.0 mol) of bis(2-hydroxypropyl)diphenylsilane in 1600 mL of methylene chloride. An additional 40 g (0.5 mol) of pyridine was added 1 h after this addition was completed. The mixture was stirred for 2 h at room temperature and was then washed with four 400 mL portions of water, dried over magnesium sulfate, and stripped of solvent. The residue was added to 825 g (8 mol) of sodium bromide and 2000 mL of dimethyl sulfoxide, and the mixture was stirred for 94 h. Water (4000 mL) was added, and the aqueous layer was extracted with two 250-mL portions of carbon tetrachloride. The combined organic layers were washed with 1000 mL of water and dried over sodium sulfate. Skelly F (5 L) was added, and the precipitated material was dried under vacuum to give 1135 g of 95% pure (NMR) bis(3-bromopropyl)diphenylsilane (84% yield).

Bis(3-nitropropyl)diphenylsilane. A solution of 530 g (7.7 mol) of sodium nitrate and 723 g (1.7 mol) of bis(3-bromopropyl)diphenylsilane in 6 L of dimethyl sulfoxide was stirred for 1.5 h and then was diluted with 12 L of water. The product was extracted with three 1000 mL portions of carbon tetrachloride, washed with 1000 mL of water, dried over sodium sulfate, and stripped of solvent. Crystallization and recrystallization from carbon tetrachloride and Skelly F gave 203 g (33%) of bis(3-nitropropyl)diphenylsilane, white crystals: mp 84.5–85.5 °C; NMR ($CDCl_3$) δ 7.3 (s, 10 H, C_6H_5), 4.3 (t, 4 H, CH_2NO_2), 2.0 (m, 4 H, CH_2CH_2Si), 1.1 (m, 4 H, CH_2Si); IR (CCl_4) 1540, 1430, 1380, 1120, 710 cm^{-1}. Anal. Calcd for $C_{18}H_{22}O_4N_2Si$: C, 60.31; H, 6.19; N, 7.81. Found: C, 60.15; H, 6.04; N, 7.62.

Bis(3,3-dinitropropyl)diphenylsilane. Bis(3-nitropropyl)diphenylsilane (73 g, 0.204 mol) was added with stirring to 33 g (0.5 mol) of potassium hydroxide in 50 mL of water and 250 mL of methanol. When solution was complete, 200 mL water and 34.5 g (0.5 mol) of sodium nitrite were added. This solution was quickly added to an ice bath cooled mixture of 170 g of silver nitrate (1 mol) in 300 mL water and 500 mL of ether. After the mixture was stirred at room temperature for 2 h, 200 mL of saturated sodium chloride solution was added. The silver precipitate was filtered, and the solution was made slightly acidic with acetic acid. The ether layer was separated, washed, dried, and stripped. The product was crystallized from methylene chloride and Skelly F, giving 34.5 g (38% yield) of bis(3,3-dinitropropyl)diphenylsilane: mp 96–97 °C; NMR ($CDCl_3$) δ 7.40 (3, 10 H, C_6H_5), 6.01 (t, J = 7 Hz, 2 H, $CH(NO_2)_2$), 2.4 (m, 4 H, CH_2CH_2Si), 1.2 (m, 4 H, CH_2Si); IR ($CHCl_3$) 1570, 1330, 1120 cm^{-1}. Anal. Calcd for $C_{18}H_{20}N_4O_8Si$: C, 48.21; H, 4.50; N, 12.49. Found: C, 48.32; H, 4.59; N, 12.29.

Bis(3-fluoro-3,3-dinitropropyl)diphenylsilane. Perchloryl fluoride was bubbled into a vigorously stirred solution of 40 g of bis(3,3-dinitropropyl)diphenylsilane (0.009 mol) and 13.2 g of potassium hydroxide (0.2 mol) in 150 mL of water, 200 mL of methanol, and 200 mL of dimethylformamide at room temperature. When gas uptake stopped, water was slowly added and the product precipitated out. Filtration yielded 42 g of a light tan solid. Recrystallization gave 36.6 g (85% yield) of white crystalline product: mp 85–86 °C; proton NMR ($CDCl_3$) δ 7.35 (s, 10 H, C_6H_5), 2.63 (m, 4 H, CH_2CH_2Si), 1.17 (m, 4 H, CH_2Si); fluorine NMR ($CDCl_3$) ϕ 105.7 (J_{HF} = 18 Hz); IR (KBr) 1590, 1430, 1320, 1260, 1200, 1100, 700 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_8N_4F_2Si$: C, 44.63; H, 3.75; N, 11.57. Found: C, 44.84; H, 3.85; N, 11.39.

1,1,3,3,5,5-Hexakis(3-fluoro-3,3-dinitropropyl)cyclotrisiloxane. A solution of 10 g (0.021 mol) of bis(3-fluoro-3,3-dinitropropyl)diphenylsilane in 25 mL of methylene chloride and 25 mL of acetic acid was stirred with 10 g (0.0625 mol) of bromine for 3 days. Water

(10 mL) was added, and the reaction mixture was stirred for 24 h. The solution was washed with water, and the solvent was removed. The product was redissolved in methylene chloride, and 2 g of bromine was added. Crystals slowly formed and after 4 days 4.8 g (67% yield) of 1,1,3,3,5,5-hexakis(3-fluoro-3,3-dinitropropyl)cyclotrisiloxane was isolated by filtration. The product was recrystallized from ethyl acetate and Skelly F to give white crystals: mp 207–209 °C; proton NMR (acetone-d_6) δ 3.14 (m, 4 H, CH_2CF), 1.20 (m, 4 H, CH_2Si); fluorine NMR (acetone-d_6) ϕ 106.0; IR (KBr) 1590, 1320, 1270, 1210, 1090 cm^{-1}. Anal. Calcd for $C_6H_8N_4O_9F_2Si$: C, 20.83; H, 2.33; N, 16.19. Found: C, 21.00; H, 2.36; N, 16.17; mol wt (vapor phase osmometer/EtOAc), 1010 ± 5% (trimer = 1038).

Registry No.—Sodium nitrite, 7632-00-0; (3-bromopropyl)trimethylsilane, 10545-34-3; (3-nitropropyl)trimethylsilane, 64035-55-8; (3-hydroxypropyl)trimethylsilane, 2917-47-7; (4-bromobutyl)trimethylsilane, 18379-55-0; (4-nitrobutyl)trimethylsilane, 64035-56-9; (3-bromobutyl)trimethylsilane, 18379-54-9; (3-nitrobutyl)trimethylsilane, 64035-57-0; (3-hydroxybutyl)trimethylsilane, 18387-24-1; (3-nitrotobutyl)trimethylsilane, 64035-58-1; (3,3-dinitropropyl)trimethylsilane, 64035-59-2; (4,4-dinitrobutyl)trimethylsilane, 64035-60-5; (3,3-dinitrobutyl)trimethylsilane, 64035-61-6; (3-fluoro-3,3-dinitropropyl)trimethylsilane, 64035-62-7; (4-fluoro-4,4-dinitrobutyl)trimethylsilane, 64035-63-8; (hydroxymethyl)trimethylsilane, 3219-63-4; trimethylsilylmethyltriflate, 64035-64-9; 2-fluoro-2,2-dinitroethanol, 17003-75-7; trimethylsilylmethyl 2-fluoro-2,2-dinitroethyl ether, 64035-65-0; allyl bromide, 106-95-6; chloromethyldiphenylsilane, 144-79-6; allylmethyldiphenylsilane, 17922-43-9; (3-bromopropyl)methyldiphenylsilane, 64035-66-1; allyloxytrimethylsilane, 18146-00-4; (3-hydroxypropyl)methyldiphenylsilane, 64035-67-2; toluenesulfonyl chloride, 98-59-9; (3-p-toluenesulfonatopropyl)methyldiphenylsilane, 64035-68-3; (3-nitropropyl)methyldiphenylsilane, 64035-69-4; (3,3-dinitropropyl)methyldiphenylsilane, 64035-70-7; (3-fluoro-3,3-dinitropropyl)methyldiphenylsilane, 64035-71-8; (3-fluoro-3,3-dinitropropyl)methyldibromosilane, 64035-72-9; (3-fluoro-3,3-dinitropropyl)methyldifluorosilane, 64035-73-0; (3-fluoro-3,3-dinitropropyl)methylmethoxyfluorosilane, 64035-74-1; 1,3-bis(3-fluoro-3,3-dinitropropyl)-1,3-dimethyl-1,3-difluorodisiloxane, 64035-75-2; dichlorodiphenylsilane, 80-10-4; 3-chloropropanol, 627-30-5; bis(3-chloropropoxy)diphenylsilane, 63802-06-2; bis(3-hydroxypropyl)diphenylsilane, 34564-72-2; diallyldiphenylsilane, 10519-88-7; diphenylsilane, 775-12-2; bis(3-bromopropyl)diphenylsilane, 64035-76-3; bis(3-*p*-toluenesulfonatopropyl)diphenylsilane, 64035-77-4; bis(3-nitropropyl)diphenylsilane, 64035-78-5; bis(3,3-dinitropropyl)diphenylsilane, 64035-79-6; bis(3-fluoro-3,3-dinitropropyl)diphenylsilane, 64035-80-9; 1,1,3,3,5,5-hexakis(3-fluoro-3,3-dinitropropyl)cyclotrisiloxane, 64035-81-0; $(CF_3SO_2)_2O$, 358-23-6.

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$^{13}C-^{13}C$ Spin Coupling Constants within the Bicyclo[2.2.2]octane and Bicyclo[3.2.1]octane Systems

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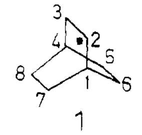
A series of eight derivatives of the bicyclo[2.2.2]octane and the bicyclo[3.2.1]octane system with a ^{13}C label have been synthesized. The $^{13}C-^{13}C$ spin coupling constants have been measured and interpreted in terms of substituent and conformational dependence.

The early work on carbon–carbon spin coupling constants mainly centered on directly bonded carbon atoms. The substituent dependence, the effect of orbital hybridization, and the sign of these coupling constants were investigated by the research groups of Roberts,[1] Grant,[2] and Maciel.[3] Early theoretical work by Pople[4] again focussed on the interpretation of $^1J_{C,C}$. More recently the interest shifted to two- and three-bond coupling constants,[5] both in experimental[6] and in theoretical[7] work. The current interest in $^{13}C-^{13}C$ couplings apparently seems to be threefold: (i) in a series of papers[8] the usefulness of both direct and long-range coupling constants in determining biosynthetic pathways is demonstrated; (ii) the conformational dependence of carbon coupling constants is investigated;[9] and (iii) the mechanism of carbon coupling constant transmission in π systems is open to question.[10]

Very recent theoretical predictions on the angular dependence of $^{13}C-^{13}C$ spin couplings[11] led us to continue our studies of compounds[9] in which the labeled carbon atom is directly part of a rigid bi- or tricyclic system, whereby the carbon–carbon long-range coupling constants are not subject



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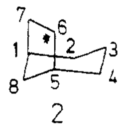

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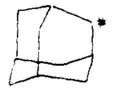

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