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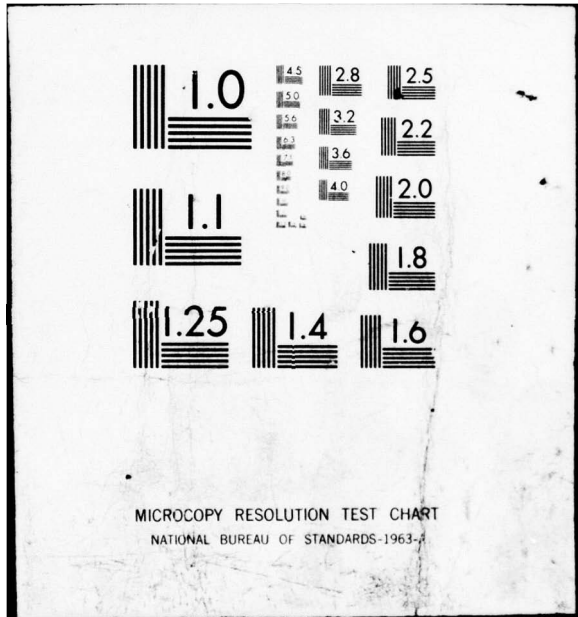
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A Report on Work Sponsored by

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NR093-052/11-29-76 (473)

January 1978

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6 HIGH ENERGY HALOGEN CHEMISTRY.

by

10 Kurt ~~B~~/Baun, P.T./Berkowitz and A.A./Lerdal

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Further work was carried out on the preparation of bis(3-fluoro-3,3-dinitropropyl)polysiloxanes. Bis(3-fluoro-3,3-dinitropropyl)diphenylsilane was dephenylated with bromine in acetic acid to give bis(3-fluoro-3,3-dinitropropyl)silanediol and the disiloxane. Amines catalyzed condensation to cyclic polysiloxanes (3-4 units). Attempts to prepare high molecular weight linear polymers from the cyclic materials with acidic or basic catalysts were unsuccessful. Alkali converted the cyclic polysiloxanes to the monomeric silanediol, which was converted by chlorotrimethylsilane to the bis(trimethylsiloxy)		

20. ABSTRACT (cont'd.)

derivative. The silanediol reacted with dichlorodimethylsilane or with bis-(dimethylamino)dimethylsilane to give mainly low molecular weight polymers. A bis(ureido)dimethylsilane gave a product with a molecular weight of 4440.

Bis(3-hydroxybutyl)diphenylsilane was prepared by the reaction of diphenylsilane with acrolein dimethyl acetal followed by the addition of methyl-lithium to the resulting dialdehyde. Reaction with phosphorous tribromide gave bis(3-bromobutyl)diphenylsilane, which was converted by sodium nitrite displacement and oxidative nitration to bis(3,3-dinitrobutyl)diphenylsilane. Dephenylation with bromine and hydrolysis gave cyclic bis(3,3-dinitrobutyl)-polysiloxanes.

A practical synthetic method for 2-fluoro-2-nitro-1,3-propanediol was found to be the reaction of alkyl fluoronitromalonates with formaldehyde and base. The monotosylate, ditosylate, monotriflate and ditriflate of this diol were prepared. The monotosylate reacted with base to give 2,6-difluoro-7-hydroxy-2,6-dinitro-4-oxa-1-heptyl tosylate. The reaction of the monotriflate with base gave 3-fluoro-3-nitrooxetane. The monotosylate, the ditriflate and the ditosylate reacted with sodium azide to give the corresponding alkyl azides which reacted with propiolic acid to give the corresponding triazoles. The monotosylate and lithium bromide gave 3-bromo-2-fluoro-2-nitro-1-propanol. 3-Fluoro-3-nitrooxetane underwent addition of triflic acid and of hydrochloric acid. The oxetane was polymerized with phosphorous pentafluoride to give a polymer stable to 290° (DTA). The reaction of 2,2-dinitro-1,3-propanediol with triflic anhydride gave the corresponding monotriflate and ditriflate.

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I. INTRODUCTION

Research under Contract N00014-71-C-0176 has been conducted during the period 1 December 1970 to 31 December 1977. This is the Final Report under the above contract, and the work will be continued under Contract N00014-78-C-0147. The work performed through 30 November 1976 has been detailed in the following Annual Summary Reports:

- Fluorochem Report ONR-1-1, January 1972, AD No. 736249
- Fluorochem Report ONR-1-2, January 1973, AD No. 754778
- Fluorodhem Report ONR-1-3, January 1974, AD No. 773942
- Fluorochem Report ONR-1-4, January 1975, AD No. A006468
- Fluorochem Report ONR-1-5, January 1976, AD No. A019807
- Fluorochem Report ONR-1-6, January 1977, AD No. A035349

The objective of this program is to develop new synthetic methods for classes of compounds with potential utility in high energy propellants and explosives. Under this program dichlorine heptoxide was developed as a practical perchlorylating reagent, and its reactions with alcohols, amines, ethers, ketones and olefins were studied. The chemistry of alkyl triflates was studied, and their utility for the etherification of nitroalcohols was demonstrated. The first alkyl perbromate was synthesized. Synthetic methods for nitro and fluorodinitro substituted silicon compounds were developed. The first oxetane with a nitro group on the ring was synthesized and polymerized.

The following journal publications resulted from this contract:

C.D. Beard, K. Baum and V. Grakauskas, "Synthesis of Some Novel Tri-fluoromethanesulfonates and Their Reactions with Alcohols", J. Org. Chem., 38, 3673 (1973).

V. Grakauskas "Fluorammonium Trifluoromethanesulfonate", J. Inorg. Nucl. Chem., 35, 3035 (1973).

K. Baum and C.D. Beard, "Reactions of Dichlorine Heptoxide with Alcohols", J. Am. Chem. Soc., 96, 3233 (1974).

C.D. Beard and K. Baum, "Reactions of Dichlorine Heptoxide with Amines", J. Am. Chem. Soc., 96, 3237 (1974).

C.D. Beard and K. Baum, "Reactions of Silver Perchlorate and of Silver Triflate with Alkyl Iodides. Solvent Inhibition of Isomerization", J. Org. Chem., 39, 3875 (1974).

K. Baum and C.D. Beard, "Reactions of Dichlorine Heptoxide and of Acyl Perchlorates with Ethers", J. Org. Chem., 40, 81 (1975).

K. Baum, C.D. Beard and V. Grakauskas "Preparation of an Alkyl Perbromate", J. Am. Chem. Soc., 97, 267 (1975).

K. Baum and C.D. Beard, "Reactions of Dichlorine Heptoxide and of Hypohalites with Alkyl Iodides", J. Org. Chem., 40, 2536 (1975).

K. Baum, "Reactions of Dichlorine Heptoxide with Olefins", J. Org. Chem., 41, 1663 (1976).

The following manuscripts have been submitted for publication:

K. Baum, D.A. Lerdal and J.S. Horn, "Synthesis of Organosilanes and Polysiloxanes with Nitro and Fluoro Substituents".

D.A. Lerdal and K. Baum, "Synthesis of Bis(3,3-dinitrobutyl)cyclopolysiloxane".

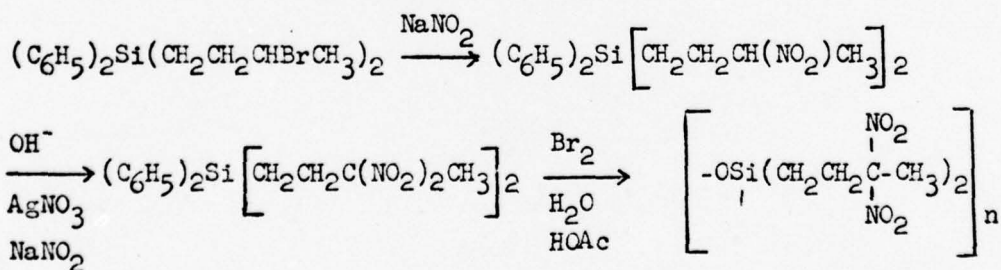
This report covers technical details of the work performed during the period 1 December 1976 to 31 December 1977. During this period, work continued in the area of nitrosilicon chemistry. Work was initiated in the area of synthesis and polymerization of nitrooxetanes.

II. DISCUSSION

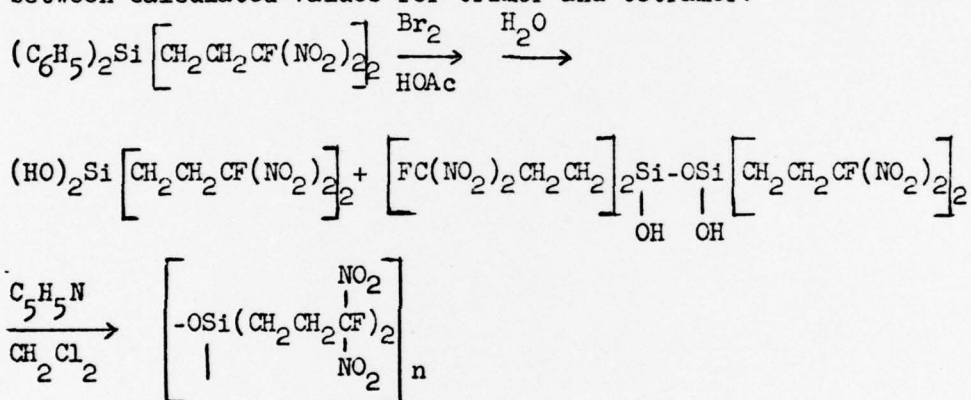
A. Nitrosilicone Chemistry

In the two preceding reports, methods were developed for the introduction of fluorodinitroalkyl groups into simple silanes,¹ and these methods were applied to the preparation of polysiloxanes with the use of phenyl groups to protect reactive silicon sites.² This work, with some subsequent refinements in yields and procedures, comprises Appendix A of this report, a journal manuscript. The route adapted to the preparation of polysiloxanes involves the preparation of haloalkyl diphenylsilanes, displacement of halogen to give the nitro compound, oxidative nitration and fluorination to give the fluorodinitro compound, and replacement of the phenyl group by hydrolyzable halides on silicon.

Work was undertaken to develop an analogous route to polysiloxanes containing internal gem-dinitro groups. This work is detailed in Appendix B. The reaction of bis(3-bromobutyl)diphenylsilane with sodium nitrite gave bis(3-nitrobutyl)diphenylsilane, which underwent oxidative nitration to give bis(3,3-dinitrobutyl)diphenylsilane. Bromination and hydrolysis gave the desired polysiloxane. The product was a stable high-melting solid with an average molecular weight of 1210; the material melted with decomposition at 240-250°C.

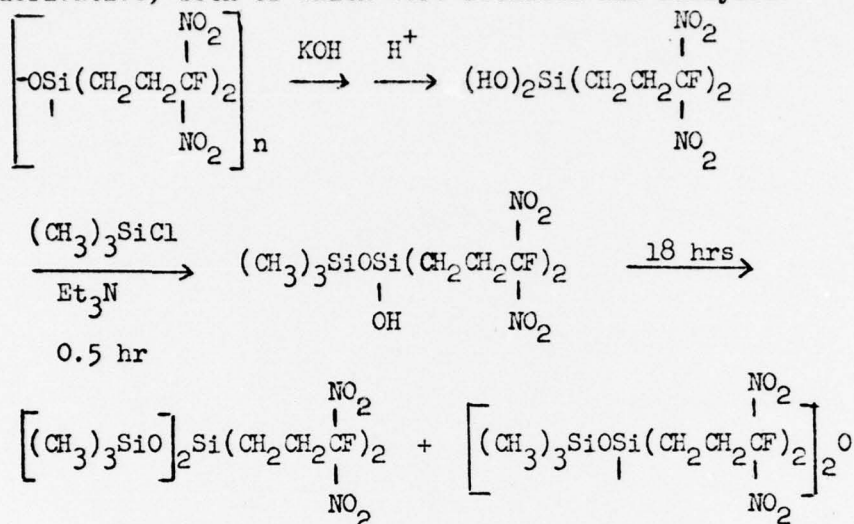


Further work was carried out with the objective of preparing high molecular weight polysiloxanes. The dephenylation of bis(3-fluoro-3,3-dinitropropyl)-diphenylsilane was simplified by using acetic acid as the solvent for bromination. Quenching the reaction with water gave a mixture of bis(3-fluoro-3,3-dinitropropyl)silanediol and the corresponding disiloxane. These compounds were soluble in methylene chloride. The addition of a trace of pyridine or triethylamine to this mixture resulted in silanol condensation to give insoluble cyclic polysiloxanes with an average molecular weight intermediate between calculated values for trimer and tetramer.



A more satisfactory route to the silanediol was found to be the reaction of the polysiloxane with potassium hydroxide in aqueous methanol. The material dissolved, and neutralization with aqueous sodium dihydrogen phosphate gave essentially a quantitative yield of the silanediol. This compound was identified spectrally and by its reaction products with chlorotrimethylsilane and triethylamine. The only product detected from this reaction in ether after 0.5 hr at ambient temperature was trimethylsiloxybis(3-fluoro-

3,3-dinitropropyl)silanol. However, after a 16 hr reaction period, this silanol was converted to a mixture of its disiloxane and its trimethylsilyl derivative, both of which were isolated and analyzed.



Attempts were made to transform the cyclic bis(2-fluoro-2,2-dinitropropyl)-polysiloxanes into linear high molecular weight polymers with acidic or basic catalysts. The results are shown in Table 1. No significant increases in molecular weight were observed. Difficulties were encountered previously² in polymerizing methyl(3-fluoro-3,3-dinitropropyl)siloxane oligomers and the presence of a second bulky and electron-withdrawing fluorodinitropropyl group does not facilitate polymerization.

The bis(3-fluoro-3,3-dinitropropyl) oligomer did not give the corresponding difluorosilane when it was treated with HF under the same conditions that were successfully applied to the methyl(2-fluoro-2,2-dinitropropyl)polysiloxanes.

Table 1. Attempted Polymerization of Cyclic Oligomers

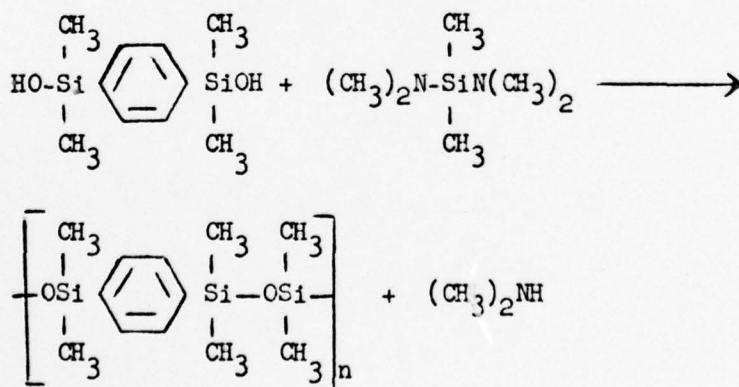
Run	Starting Material MW	Solvent	Temperature	Catalyst	Time	MW
1	1040	-	215°	-	10 min	1030
2	1040	-	230°	-	2 min	800
3	1040	Toluene	110°	CsOH	2 hr	1530*
4	1040	DMF	130°	Et ₃ N	15 min	1010
5	1040	DMF	25°	BAH**	72 hr	915
6	1040	DMF	150°	BAH	15 min	762
7	1040	DMF	80°	CsOH	2 hr	900
8	835	-	200°	CsOH	-	charred
9	1250	EtOH	25°	KOH	10 min	910
10	1250	EtOH	25 to 200°	KOH	10 min at 200°	670
11	1250	-	200°	H ₂ SO ₄	30 min	1224*
12	1250	EtOAc	77°	Pyridine	30 min	1070
13	1250	HOAc	118°	-	1 hr	1110
14	1250	C ₆ H ₅ NO ₂	90°	BAH	1 hr	800

* Substantial decomposition occurred

** Benzyltrimethylammonium hydroxide

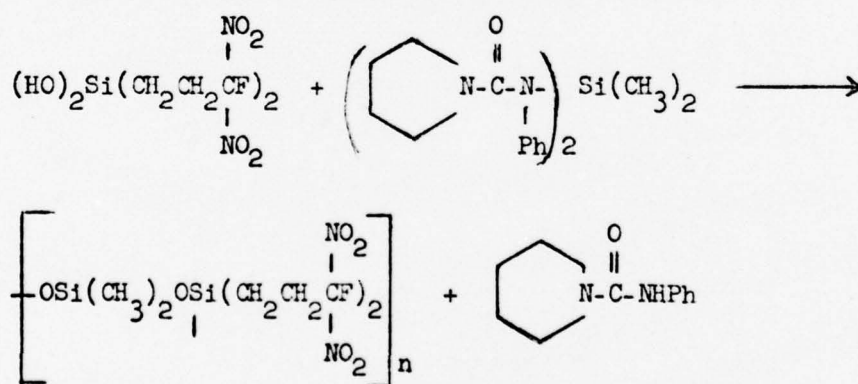
An approach that is used frequently to prepare silicones from monomers with bulky substituents is to copolymerize them with unhindered monomers.³ The flexibility thus introduced counteracts the tendency toward ring formation. Because the ease with which bis(3-fluoro-3,3-dinitropropyl)silanediol reacted with chlorotrimethylsilane, difunctional comonomers were examined. The reaction of dichlorodimethylsilane with this diol was studied under a variety of conditions. Products with molecular weights of 1000 to 1250 were generally obtained using the solvents, methylene chloride, toluene, or dimethyl formamide, without base to remove liberated HCl, or with triethylamine or pyridine. Higher molecular weight products were obtained with ether and triethylamine. In this solvent, higher molecular weight products become insoluble, and gummy resins with a molecular weight of 3500 were isolated in 20% yield. The use of methyltrichlorosilane instead of dichlorodimethylsilane under these conditions gave a brittle polymer with a molecular weight of 3160. Diethoxydimethylsilane did not react with the silanediol.

Bis(dimethylamino)dimethylsilane is a recently reported reagent⁴ for producing high molecular weight polymers from aromatic silanols. It has the advantage of producing volatile dimethylamine as the only byproduct:



Molecular weights, however, of products of this reagent and bis(2-fluoro-2,2-dinitropropyl)silanediol were similar to those obtained using dichlorodimethylsilane and triethylamine. The basic reaction conditions resulting from the liberated amine resulted in darkening and apparent decomposition of the product. Fractional precipitation of the product obtained in refluxing toluene consisted of 50% with a molecular weight of 980 and 50% with a molecular weight of 1720.

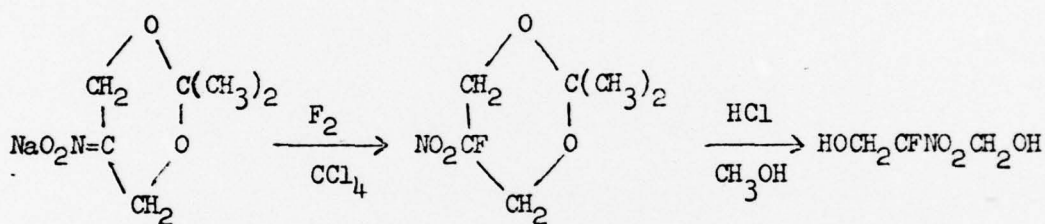
Another dimethylsilyl monomer has recently been reported that liberates only neutral fragments. Bis(ureido)dimethylsilanes have been used to prepare polymers from monomers with silanol groups attached to phthalocyanine⁵ and to carborane backbones.⁶ We obtained the reagent by the reported method⁵ and reacted it with bis(3-fluoro-3,3-dinitropropyl)silanediol in a mixture of chlorobenzene and ether. Fractional precipitation of the product gave a 43% yield of material with a molecular weight of 4440. The product was an almost colorless tacky resin. The decomposition that was evident with the dimethylaminosilane was thus avoided.



B. Chemistry of 2-Fluoro-2-nitropropanediol

Fluorine is known to inhibit anion formation on dinitromethane derivatives,⁷ and this "fluorine effect" has enabled the synthesis of useful alkylation products of 2-fluoro-2,2-dinitroethanol under alkaline conditions. Other 2,2-dinitroalcohols are deformed in the presence of base to give nitronate salts. Even less tendency toward deformation would be expected for 2-fluoro-2-nitropropanediol. The chemistry of this potentially low cost difunctional nitro compound has been little investigated.

This diol was first prepared by the fluorination of the salt of 2,2-dimethyl-5-nitro-1,3-dioxane suspended in carbon tetrachloride.⁸

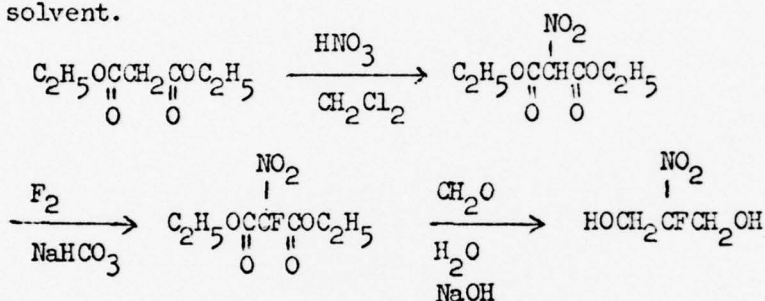


Subsequently, the synthesis of this diol was reported by the direct fluorination of the sodium salt of 2-nitro-1,3-propanediol in aqueous or methanolic solution.⁹ A slow rate of fluorination was used, however, and an exceptionally dilute (1:50) fluorine-nitrogen mixture was used.

In our hands, the direct aqueous fluorination of salts of 2-nitro-1,3-propanediol did not prove to be a convenient preparative method. Attempts to increase the rate of fluorine input, or its concentration to more practical levels resulted in immediate localized firing at the sparger.

Consequently, a more readily fluorinated nitronate salt was utilized, with the objective of converting the product to the desired diol. Diethyl

fluoronitromalonate was obtained conveniently by the previously reported¹⁰ fluorination of diethyl nitromalonate, obtained, in turn, by the nitration of diethyl malonate. The reaction of diethyl fluoronitromalonate with aqueous formaldehyde containing sodium hydroxide resulted in simultaneous ester hydrolysis, decarboxylation of the resulting acid, and formylation. The desired 2-fluoro-2-nitro-1,3-propanediol was isolated in 46% yield. The same yield was obtained with paraformaldehyde and potassium hydroxide, with methanol as the solvent.

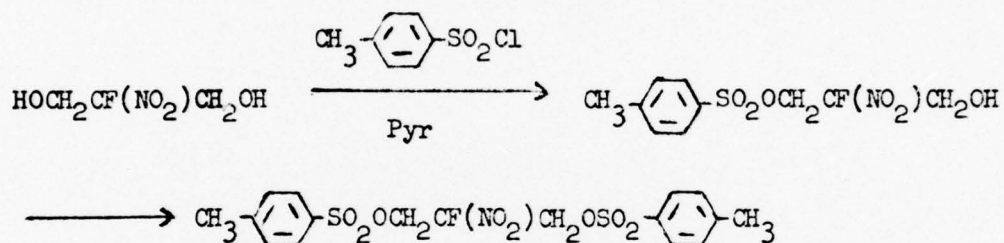


Dimethyl fluoronitromalonate was also used to prepare 2-fluoro-2-nitro-1,3-propanediol, and similar yields were obtained with aqueous formaldehyde and potassium hydroxide. With methanol, paraformaldehyde and sodium hydroxide, however, yields varied from 0 to 93%. Thus, although an unknown impurity may be responsible for yield fluctuations and more work is required, high yields are attainable.

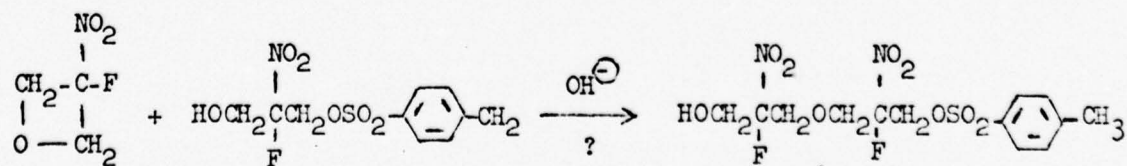
A potentially useful reaction of 2-fluoro-2-nitro-1,3-propanediol is its cyclization to the corresponding oxetane. Nitrooxetanes are virtually unknown. Thus, a trace byproduct of the reaction of tris(hydroxymethyl)nitromethane with PCl_5 was reported to be 3-chloromethyl-3-nitrooxetane with little evidence.¹¹ The Ter Meer reaction of 3,3-bis(chloromethyl)oxetane gave 3,3-bis(nitromethyl)oxetane in 3% yield.¹²

Simple oxetanes are generally obtained by cyclizing monotosylates of 1,3-diols with base.¹³ Whereas other 2-nitro-1,3-diols would present difficulties because of deformylation under these conditions, this problem would not be expected with 2-fluoro-2-nitro-1,3-propanediol.

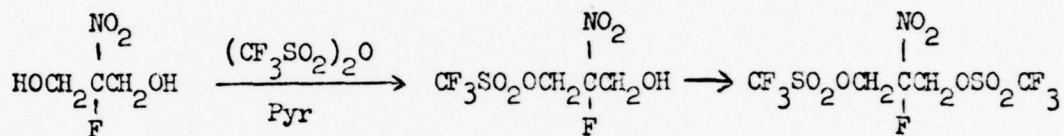
The tosylation of 2-fluoro-2-nitro-1,3-propanediol proceeded normally. When p-toluenesulfonyl chloride was treated with a molar excess of the diol and pyridine, to minimize ditosylate formation, in refluxing chloroform, a 78% yield of monotosylate and a 10% yield of ditosylate were obtained. The excess diol was recovered by extraction. When an excess of p-toluenesulfonyl chloride was used in pyridine a 67% yield of the ditosylate was isolated.



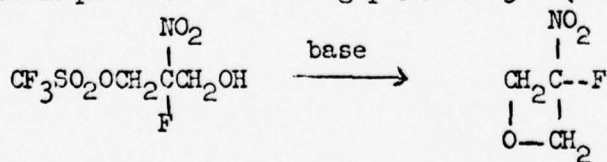
The cyclization of the monotosylate to the oxetane was attempted with potassium hydroxide in aqueous dioxane. The reaction was complete in 5 min at room temperature and gave an almost quantitative yield of a product identified as 2,6-difluoro-7-hydroxy-2,6-dinitro-4-oxa-1-heptyl tosylate. The same product was obtained using potassium carbonate as the base. A possible mechanism for this reaction involves the desired cyclization to the oxetane. If the oxetane is exceptionally labile to nucleophilic ring opening it could react at a rate faster than the cyclization with the remaining monotosylate.



A more reactive leaving group, triflate, was examined with the expectation of increasing the rate of the cyclization. The addition of 2-fluoro-3-hydroxy-2-nitropropyl triflate to the oxetane should take place at a rate similar to that of the tosylate, so the oxetane might survive. This monotriflate was obtained in 52% yield from 2-fluoro-2-nitropropanediol with theoretical amounts of triflic anhydride and pyridine, but the yield was increased to 67% by a 3-stage reaction with diol in excess. The corresponding ditriflate was obtained in 75% yield using the appropriate stoichiometry.

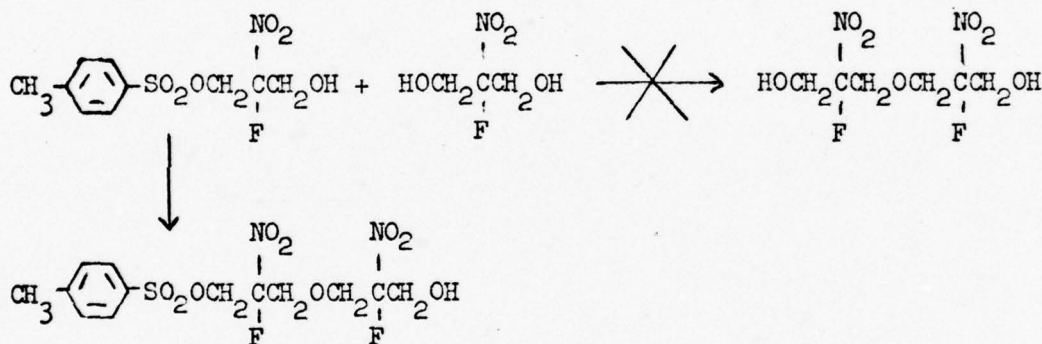


Indeed, 3-fluoro-3-nitrooxetane was obtained from the monotriflate with a variety of basic reagents. Thus, potassium hydroxide in water or aqueous dioxane gave the oxetane in about 50% yield with a reaction time of less than 15 min. Triethylamine in chloroform gave similar yields, but 20 hrs was required. The use of DBU (1,5-diazabicyclo-[5.4.0]undec-5-ene) as the base in methylene chloride gave a 62% yield of the oxetane in a 15 min reaction period. Pyridine, however, failed to give the oxetane but, instead underwent N-alkylation by the triflate, on the basis of NMR evidence. The oxetane is a colorless liquid with a boiling point of 31° (1.5 mm).



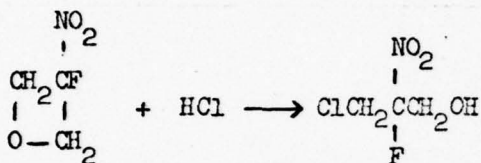
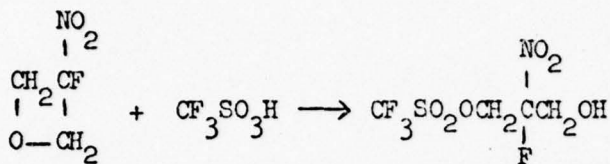
The availability of the oxetane offered the opportunity to prove or disprove the proposed mechanism for the dimerization of the above monotosylate. Thus, equimolar amounts of the monotosylate and the oxetane were treated with potassium hydroxide in aqueous dioxane. The tosylate was converted rapidly to its dimer while the oxetane was unchanged. Thus, the oxetane was not an intermediate in the dimerization.

A comparison of the reactivity of the monotosylate with related compounds was made. The dimerization of the monotosylate with KOH in aqueous dioxane was not affected by the addition of 2-fluoro-2-nitropropanediol, although the reactivities of the hydroxyl groups of the two compounds would be expected to be similar.



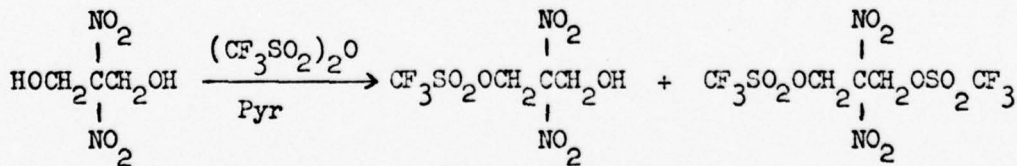
Other displacement reactions of the tosylate and triflates of 2-fluoro-2-nitropropanediol were examined briefly. Both the monotosylate and ditosylate reacted with sodium azide in dimethyl sulfoxide at 65° to give the corresponding azido derivatives. These were identified as the corresponding triazoles obtained by the cycloaddition of propiolic acid. The direction of this addition was not established.

chloride with triflic acid gave 2-fluoro-3-hydroxy-2-nitropropyl trifluoromethanesulfonate. The oxetane also reacted with concentrated hydrochloric acid to give 3-chloro-2-fluoro-2-nitro-1-propanol.



The polymerization of 3-fluoro-3-nitrooxetane was accomplished in methylene chloride solution with the use of phosphorous pentafluoride as catalyst. The product is a crystalline polymer soluble in dimethyl formamide and in dimethyl sulfoxide. Its molecular weight is 2500, determined by vapor osmometry in dimethyl formamide. The polymer is a diol on the basis of NMR hydroxyl area. DTA showed a melting point (endotherm) of 234° and onset of decomposition at 290°C. The density of the material is 1.5885.

Work was initiated with the objective of preparing the analogous dinitro compounds. The reaction of 2,2-dinitro-1,3-propanediol with triflic anhydride gave the corresponding mono- and ditriflate:



III. EXPERIMENTAL

Bis(2-fluoro-2,2-dinitropropyl)silanediol. A mixture of 0.50 g (1.45 mmol) of bis(2-fluoro 2,2-dinitropropyl)polysiloxanes, 2.9 ml of 1M potassium hydroxide and 5 ml of methanol was stirred for 10 min. The resulting solution was added to a mixture of 15 ml of ether, 5 ml of 1M sodium dihydrogen phosphate, and 25 ml of water. The aqueous phase was extracted with three 15 ml portions of ether, and the combined ether solutions were washed with 15 ml of water and with 12 ml of saturated sodium chloride solution. The solvent was removed and the residue was dried under vacuum for 30 min to give 0.51 g (97%) of bis(2-fluoro-2,2-dinitropropyl)silanediol: NMR (CDCl_3) δ 3.6 (s, 2 H, OH), 2.9 (m, 4 H, CH_2CF), and 0.8 (m, 4 H, CH_2Si).

Reaction of bis(2-fluoro-2,2-dinitropropyl)silanediol with chlorotrimethylsilane. The above diol (0.51 g, 1.40 mmol) in 5 ml of ether was added with stirring to a solution of 0.96 g (8.85 mmol) of chlorotrimethylsilane and 0.87 g (8.6 mmol) of triethylamine in 30 ml of ether. After 30 min 20 ml of water was added. The ether layer was dried and stripped of solvent. The residue was found on the basis of NMR to contain only trimethylsiloxybis(3-fluoro-3,3-dinitropropyl)silanol: NMR (CDCl_3) δ 2.8 (m, 4 H, CH_2CF) 2.75 (br.s, 1 H, OH), 0.83 (m, 4 H, CH_2Si) 0.30 (s, 9 H, CH_3). This silanol was dissolved in 10 ml of ether and was added to 0.3 g (2.9 mmol) chlorotrimethylsilane and 0.29 g (2.9 mmol) of triethylamine in 20 ml of ether. The mixture was stirred for 16 hrs and was then washed with water. After the ether was stripped, the residue was extracted with Skelly F, in which it was partially soluble.

Column chromatography (silica gel, $\text{CCl}_4 + 5\% \text{CH}_2\text{Cl}_2$) of the material soluble in Skelly F yielded 0.26 g (35%) of bis(trimethylsiloxy)bis-(3-fluoro-3,3-dinitropropyl)silane, a colorless oil: NMR (CCl_4) δ 2.80 (m, 4 H, CH_2CF), 0.80 (m, 4 H, CH_2Si) and 0.30 (s, 18 H, $(\text{CH}_3)_3\text{Si}$); IR (film) 2970, 1590, 1320,

1260, 1070, 850, 805 and 760 cm^{-1} .

Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{N}_4\text{O}_{10}\text{Si}_3\text{F}_2$: C, 28.34; H, 5.15; N, 11.02. Found: C, 30.12; H, 5.27; N, 10.88.

Chromatography (silica gel, CH_2Cl_2) of the material insoluble in Skelly F yielded 0.34 g (55%) of trimethylsiloxy bis(3-fluoro-3,3-dinitropropyl)disiloxane, mp 132-3 $^{\circ}$: NMR (CDCl_3) δ 2.80 (m, 8 H, CH_2CF), 0.80 (m, 8H, CH_2Si) and 0.30 (s, 18 H, $(\text{CH}_3)_3\text{Si}$); IR (KBr) 2970, 1590, 1320, 1260, 1220, 1070, 850, 810 and 760 cm^{-1} .

Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{N}_8\text{O}_{19}\text{Si}_4\text{F}_4$: C, 25.28; H, 4.00; N, 13.16. Found: C, 25.58; H, 4.02; N, 13.24.

Bis(3-fluoro-3,3-dinitropropyl)polysiloxane. Bromine, 3.2 g, (20 mmol) was added to 2.5 g (5.16 mmol) of bis-(3-fluoro-3,3-dinitropropyl)diphenylsilane in 20 ml of acetic acid. After the solution was refluxed for 45 min, an additional 0.5 g of bromine and 10 ml of water were added. The mixture was heated to 100 $^{\circ}$ for 10 min and was allowed to stand at ambient temperature overnight. The mixture was added to 100 ml of water and was extracted with methylene chloride. One drop of triethylamine was added. Filtration gave 1.52 g (85%) of bis-(3-fluoro-3,3-dinitropropyl)polysiloxane (MW = 1250).

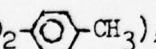
Reaction of Bis(N-pyrrolidino-N'-phenylureido)dimethylsilane with Bis-(2-fluoro-2,2-dinitropropyl)silane diol. A flame dried 50 ml flask fitted with a magnetic stirrer and septum adaptor was charged with a solution of 7.8 mmol of bis(N-pyrrolidino-N'-phenylureido)dimethylsilane in 10 ml of chlorobenzene, and the solution was cooled to 0 $^{\circ}$. A solution of 2.80 g (7.7 mmol) of bis(2-fluoro-2,2-dinitropropyl)silane diol in 10 ml of ether was added dropwise by syringe with stirring at 0 $^{\circ}$. The mixture was stirred at ambient temperature for 1 hr. Solvent was removed under vacuum, and 30 ml of chloroform was ad-

ded. The chloroform layer was decanted from insoluble material. The chloroform was removed and the residue was washed with ether and chloroform was added. The resulting insoluble material was combined with the original chloroform-insoluble material. The material was dissolved in methylene chloride and precipitated with chloroform to give, after vacuum drying, 1.38 g (43%) of polymer with a molecular weight of 4,440. The material was a tacky pale yellow resin with a ratio of dimethylsilyl to fluorodinitropropylsilyl units of 0.90 (NMR).

2-Fluoro-2-nitro-1,3-propanediol. A. A suspension of 89.2 g (0.40 mole) of diethyl fluoronitromalonate in 80 ml (1.0 mole) of 37% aqueous formaldehyde was cooled in an ice-bath to 2°C. A solution of 66.0 g (1.60 mole) of sodium hydroxide in 400 ml of water was then added dropwise with vigorous stirring over 100 minutes, below 10°C. After the reaction mixture was stirred overnight in an ice-bath, it was filtered and the filtrate was extracted with ethyl acetate (3 x 1000 ml). The ethyl acetate solution was dried over sodium sulfate and distilled (0.17 mm/170° bath) to give 25.5 g (45.9%) of 2-fluoro-2-nitro-1,3-propanediol: mp 86-87°C; ¹H NMR (acetone-D₆) 3.90 (d, J=6 Hz, 2 H, -CH₂-), 4.20 (t, J= 6 Hz, 2 H, -CH₂-), 4.80 (t, J= 6 Hz, 2 H, -OH); ¹⁹F NMR (acetone-D₆) δ 145.6 (quintet, J= 16 Hz). IR(CH₂Cl₂) 3620 (-OH), 1575, 1335 (-NO₂), 1040 cm⁻¹ (C-F).

B. To a suspension of 24.5 g (0.11 mol) diethyl fluoronitromalonate and 8.8 g (0.275 mol) of paraformaldehyde in 110 ml of methanol, at -9°C, was added 7.28 (0.11 mol) of potassium hydroxide in 55 ml of methanol dropwise over 27 minutes. After 45 minutes, the reaction temperature was raised to 0°. No precipitate remained after 1 hr. The reaction mixture was diluted with 330 ml of water and

the pH was adjusted to 5 with concentrated hydrochloric acid. The reaction mixture was saturated with sodium chloride and extracted with ethyl acetate (3 x 275 ml). The ethyl acetate solution was dried and stripped. Toluene was twice added and removed in vacuo to leave 12.3 g of semisolid residue. Vacuum distillation gave 6.99 g (45.7%) of 2-fluoro-2-nitro-1,3-propanediol.

2-Fluoro-3-hydroxy-2-nitro-1-propyl p-Toluenesulfonate. To a refluxing solution of 2.78 g (0.020 mol) of 2-fluoro-2-nitro-1,3-propanediol and 1.6 ml (0.020 mol) of pyridine in 28 ml of chloroform was added dropwise over 2-1/2 hours a solution of 1.91 g (0.010 mol) of p-toluenesulfonyl chloride in 28 ml of chloroform. Refluxing was continued for 3 hours and then the reaction mixture was stirred at room temperature for 15 hours. As TLC indicated that some p-toluenesulfonyl chloride remained, the reaction mixture was refluxed an additional 2 hours. The chloroform solution was washed with 10 ml of water, with two 10 ml portions of 1.0 M HCl, and then with 10 ml of water, and was dried over sodium sulfate. Removal of the chloroform gave 2.6 g of a white solid, which was recrystallized from 26 ml of methylene chloride and 30 ml of Skelly F to give 1.6 g of 2-fluoro-3-hydroxy-2-nitro-1-propyl p-toluenesulfonate. A second recrystallization gave an analytical sample: mp 88-89°; $^1\text{H NMR}$ (CDCl_3) δ 2.40 (s, 3 H, CH_3), 2.90 (broad s, 1 H, -OH), 4.00 (d, $J = 16$ Hz, 2 H, $-\text{CH}_2\text{-OH}$), 4.52 (d, $J = 16$ Hz, 2 H, $-\text{CH}_2\text{-OTs}$); 7.40 (m, 5 H, Ph) $^{19}\text{F NMR}$ (CDCl_3) δ 138.8 (quintet, $J = 16$ Hz). IR (CH_2Cl_2) 3620 (-OH), 1585 (NO_2), 1380, 1195, 1180 ($-\text{OSO}_2\text{-}$  -CH_3), 1020 cm^{-1} (C-F).

Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{FNSO}_6$: C, 40.96; H, 4.12; N, 4.78. Found: C, 40.77; H, 4.11; N, 4.57.

The mother liquor from the above crystallization was chromatographed


(silica gel, CH_2Cl_2 -EtOAc) to give an additional 0.68 g of monotosylate, for a combined yield of 2.28 g (77.8%), and 0.44 g (10.0%) of the corresponding ditosylate.

The water extract and the first acid extract were combined and extracted with ethyl acetate (3 x 20 ml). The solution was dried over sodium sulfate, and ethyl acetate was removed to give 1.3 g of 2-fluoro-2-nitro-1,3-propanediol.

2-Fluoro-2-nitro-1,3-propylene Di-p-toluenesulfonate. To a solution of 1.12 g (8.0 mmol) of 2-fluoro-2-nitro-1,3-propanediol in 20 ml of pyridine was added dropwise over 15 minutes with stirring 6.10 g (32.0 mmol) of p-toluenesulfonyl chloride in 20 ml pyridine. After 17 hours, the reaction mixture was poured into 240 ml of ice water. The resulting solid precipitate was filtered and washed with water and with Skelly F. The combined filtrate and water wash was extracted with methylene chloride (2 x 50 ml), and the methylene chloride extract was then washed with cold 50% aqueous hydrochloric acid (2 x 50 ml) and with 50 ml of water. The methylene chloride was dried and in vacuo to give 0.3 g of a syrup. The above solid and the syrup were combined and recrystallized from 40 ml of ethanol to give 2.05 g of ditosylate. The mother liquor was stripped and the residue was crystallized from 8 ml ethanol to give an additional 0.35 g for a combined yield of 2.40 g (67.1%) of 2-fluoro-2-nitro-1,3-propylene Di-p-toluenesulfonate. An analytical sample was recrystallized from ethanol: mp 90-91°; $^1\text{H NMR}$ (CDCl_3) δ 2.43 (s, 6 H, CH_3), 4.47 (d, $J=16$ Hz, 4 H, $-\text{CH}_2-$), 7.43 (m, 10 H, Ph); $^{19}\text{F NMR}$ (CDCl_3) ϕ 136.8 (quintet $J=16$ Hz).

Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{FNS}_2\text{O}_3$: C, 45.63; H, 4.06; N, 3.13. Found: C, 45.64; H, 4.17; N, 3.17.

2,6-Difluoro-7-hydroxy-2,6-dinitro-4-oxa-1-heptyl p-Toluenesulfonate. To

a solution of 0.147 g (0.50 mmol) 2-fluoro-3-hydroxy-2-nitro-1-propyl tosylate in 0.75 ml of dioxane and 0.20 ml of H₂O was added 0.55 ml of a 1.0 M KOH solution. After the mixture was stirred at room temperature for 1 hour, 3.5 ml of water was added and the product was extracted with ethyl acetate (2 x 5 ml), and dried over sodium sulfate. Removal of ethyl acetate in vacuo gave 0.101 g (97.6% crude yield) of a product which contained only trace impurities. Purification was effected by an analytical sample prepared by TLC (4:1CH₂Cl₂-EtOAc), followed by crystallization from methylene chloride-Skelly F: mp 89-90°; ¹H-NMR (CDCl₃) δ 2.43 (s, 3 H, CH₃), 4.03 (d, J= 16 Hz, 7 H, 3 x CH₂-OH), 4.43 (d, J= 16 Hz, 2 H, CH₂-OTs) 7.40 (m, 5 H, Ph); ¹⁹F-NMR (acetone) φ 140.6 (broad s, 1 F), 142.2 (broad s, 1 F). IR(CH₂Cl₂) 3625 (-OH), 1580 (-NO₂), 1380, 1195, 1180 (-O-SO₂--CH₃), 1030 cm⁻¹ (C-F).

Anal. Calcd for C₁₃H₁₆F₂N₂SO₉: C, 37.68; H, 3.89; N, 6.76. Found: C, 38.79; H, 4.18; N, 6.90.

3-Azido-2-fluoro-2-nitro-1-propanol. A solution of 0.293 g (1.0 mmol) of sodium azide in 3 ml of dimethyl sulfoxide was heated in a 55-60°C bath for 66 hrs. The reaction mixture was cooled, diluted with 18 ml of water, and extracted with methylene chloride (3 x 10 ml). The methylene chloride solution was washed with water (2 x 10 ml) and dried over sodium sulfate. Removal of the methylene chloride left 0.110 g of a yellow oil, which was found by NMR to contain some monotosylate and some DMSO, as well as 3-azido-2-fluoro-2-nitro-1-propanol: ¹H-NMR (CDCl₃) δ 3.90 (d, J= 16 Hz, 2 H, -CH₂OH), 4.00 (d, J= 16 Hz, 2 H, -CH₂-N₃) (the two doublets overlap and appeared as a pseudoquartet); ¹⁹F-NMR (CDCl₃) φ 137.0 (quintet, J= 16 Hz). IR (CDCl₃) 2150 (-N₃), 1565, 1360 cm⁻¹ (-NO₂).

The crude azide (0.110 g) and .050 g (0.7 mmol) propiolic acid were dissolved in 0.6 ml chloroform. After standing at room temperature for 54 hours, the resulting solid was filtered and washed with chloroform to give 0.054 g of 1-(2-fluoro-3-hydroxy-2-nitro-propyl)-4-(or 5-)-carboxy-1,2,3-triazole. After several days an additional 0.023 g deposited from the chloroform solution for a combined yield of 0.077 g. Recrystallization of a portion from acetonitrile-carbon tetrachloride gave an analytical sample: mp 175-177°; $^1\text{H NMR}$ (acetone- D_6) δ 4.23 (m, $J=16$ Hz, CH_2OH) 5.53 (m, $J=16$ Hz, $\text{CH}_2\text{-N-}$), 7.27 (broad s, 1 H, CO_2H), 8.33 (s, 1 H, triazole), $^{19}\text{F NMR}$ (acetone- D_6) ϕ 139.2 (quintet, $J=16$ Hz).

Anal. Calcd for $\text{C}_6\text{H}_7\text{FN}_4\text{O}_5$: C, 30.78; H, 3.01; N, 23.93. Found: C, 31.30; H, 2.91; N, 24.75.

3-Bromo-2-fluoro-2-nitro-1-propanol. A solution of 0.293 g (1.0 mmol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl tosylate and 0.261 g (3.0 mmol) of lithium bromide (dried overnight at 140°C) in 3.0 ml of dimethyl sulfoxide was stirred in a 65°C bath for 5 days. No starting material was detected by $^{19}\text{F NMR}$ after 2 days. The reaction mixture was cooled, diluted with 27 ml of water and extracted with methylene chloride (3 x 15 ml). The methylene chloride solution was washed with water (5 x 25 ml) and dried over sodium sulfate. Removal of methylene chloride in vacuo gave 0.048 g (23.7%) of essentially pure 3-bromo-2-fluoro-2-nitro-1-propanol as a brown syrup: $^1\text{H NMR}$ (CDCl_3) δ 2.63 (broad s, 1 H, -OH), 4.03 (m, 4 H, - CH_2 -); $^{19}\text{F NMR}$ (DMSO) ϕ 134.2 (quintet, $J=16$ Hz).

1,3-Diazido-2-fluoro-2-nitropropane. A. A solution of 0.447 g (1.0 mmol) of 2-fluoro-2-nitro-1,3-propylene ditosylate and 0.200 g (3.0 mmol) of sodium azide in 5 ml of dimethyl sulfoxide was heated in a 65° bath for 20 hours. The reaction mixture was cooled, diluted with 45 ml of water and then was extracted

with methylene chloride (3 x 20 ml). The methylene chloride solution was washed with water (5 x 30 ml) and then was dried over sodium sulfate. Removal of methylene chloride in vacuo gave 0.184 g (97.4% yield) of 1,3-diazido-2-fluoro-2-nitropropane (no impurities in $^1\text{H NMR}$) as a yellow oil: $^1\text{H NMR}$ (CDCl_3) δ 3.87 (d, $J=16$ Hz); $^{19}\text{F NMR}$ (CDCl_3) δ 133.8 (quintet, $J=16$ Hz). IR (CDCl_3) 2150 ($-\text{N}_3$), 1580, 1320 ($-\text{NO}_2$) cm^{-1} .

The azide (0.184 g) and 0.159 g (2.27 mmol) of propiolic acid were dissolved in 1.0 ml of chloroform. After standing at room temperature for 54 hours, the resulting solid was filtered and washed with chloroform to give 0.234 g of 1,3-bis [1-(4-(or 5-)-carboxy-1,2,3-triazolo)]-2-fluoro-2-nitropropane. An analytical sample was crystallized from acetonitrile-carbon tetrachloride: mp 163-170 $^\circ$; $^1\text{H NMR}$ (acetone- D_6) δ 5.77 (m, 4 H, $-\text{CH}_2-$), 7.73 (s, 2 H, CO_2H), 8.57 (s, 2 H, triazole); $^{19}\text{F NMR}$ (acetone- D_6) δ 134.0 (quintet, $J=16$ Hz).

Anal. Calcd for $\text{C}_9\text{H}_8\text{FN}_7\text{O}_6$: C, 32.84; H, 2.45; N, 29.78. Found: C, 31.84; H, 2.65; N, 29.21.

B. A solution of 0.407 g (1.0 mmol) of 2-fluoro-2-nitro-1,3-propylene ditriflate and 0.225 g (3.3 mmol) of sodium azide in 5.5 ml of dimethyl sulfide was stirred at room temperature for 22 hrs, diluted with 50 ml of water, and then extracted with methylene chloride (3 x 17 ml). The methylene chloride solution was washed with water (5 x 25 ml) and dried over sodium sulfate. Removal of the methylene chloride in vacuo gave 0.195 g (100%) of a brown liquid, which was shown by $^1\text{H NMR}$ to contain only 1,3-diazido-2-fluoro-2-nitropropane and trace impurities.

2-Fluoro-3-hydroxy-2-nitro-1-propyl Triflate. To a solution of 17.4 g (0.124 mol) of 2-fluoro-2-nitro-1,3-propanediol and 6.0 ml (0.074 mol) of pyri-

dine in 210 ml of ether, was added 10.9 ml (0.065 mol) of triflic anhydride in 210 ml of ether dropwise over 25 minutes. The reaction temperature was kept below 26°C. After 16 hrs of stirring, the resulting precipitate was filtered and washed with ether (2 x 40 ml). Removal in vacuo of the ether gave 26.2 g of a white solid, which was partitioned between 300 ml of methylene chloride and 60 ml of water. The methylene chloride layer was separated, washed with 30 ml water, dried over sodium sulfate, and applied to a 125 g silica gel column (methylene chloride). Elution with 500 ml of methylene chloride gave 2.216 g (8.9%) of ditriflate, and further elution with 500 ml of 9:1 methylene chloride-ethyl acetate gave 13.26 g (78.9%) of the monotriflate. An analytical sample was recrystallized from methylene chloride - Skelly F at -10° to give a colorless hygroscopic solid: mp 29-30°; ¹H NMR (CDCl₃) δ 2.65 (broad s, 1 H, -OH), 4.10 (d, J= 14 Hz, 2 H, CH₂OH), 5.07 (m, J= 14 Hz, 2 H, CH₂O-SO₂CF₃); ¹⁹F NMR (CDCl₃) δ 72.0 (s, 3 F, CF₃), 139.4 (quintet, J= 14 Hz, 1 F, O₂N-C-F); IR (CH₂Cl₂) 3625 (-OH), 1580, 1350 (-NO₂), 1420, 1220, 1140, 900 (-OSO₂CF₃), 1000 cm⁻¹ (C-F).

Anal. Calcd for C₄H₅F₄NSO₆: C, 17.22; H, 1.86; N, 5.17. Found: C, 17.82; H, 1.75; N, 5.31.

The combined water washes were extracted with ethyl acetate (3 x 100 ml). The product was dried by twice adding toluene and removing in vacuo, leaving 8.70 g of recovered 2-fluoro-2-nitro-1,3-propanediol.

2-Fluoro-2-nitro-1,3-propylene Ditriflate. To a solution of 5.8 g (0.02 mol) of triflic anhydride in 10 ml of chloroform was added, dropwise over 20 minutes, a solution of 1.39 g (0.010 mol) of 2-fluoro-2-nitro-1,3-propanediol and 1.8 ml (0.022 mol) of pyridine in 10 ml of chloroform. Water bath cooling

was used. After 3 hrs, the chloroform solution was washed with ice-water (2 x 10 ml), dried over sodium sulfate, and stripped in vacuo to give 3.2 g of a solid residue. The residue was applied to a 64 g silica gel column (methylene chloride), and eluted with methylene chloride. The first 300 ml contained 2.80 g (75.5%) of 2-fluoro-2-nitro-1,3-propylene ditriflate. An analytical sample was recrystallized from methylene chloride-Skelly F: mp 57-58° C; $^1\text{H NMR}$ (CDCl_3) δ 4.93 (d, J = 14 Hz); $^{19}\text{F NMR}$ (CDCl_3) ϕ 71.8 (s, 6 F, CF_3), 136.7 (quintet, J = 14 Hz, 2 F, $\text{O}_2\text{N-C-F}$). IR (CH_2Cl_2) 1595, 1320 ($-\text{NO}_2$), 1420, 1220, 1140, 900 (OSO_2CF_3), 10005 cm^{-1} (C-F).

Anal. Calcd for $\text{C}_5\text{H}_4\text{F}_7\text{NS}_2\text{O}_8$: C, 14.90; H, 1.00; N, 3.47. Found: C, 15.30; H, 0.91; N, 3.61.

3-Fluoro-3-nitrooxetane. A. To a solution of 0.271 g (1.00 mol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate in 26 ml of water was added 1.00 ml of 1.0 M KOH. After 1 hr, the reaction mixture was extracted with methylene chloride (2 x 10 ml). The solution was dried over sodium sulfate, and the methylene chloride was distilled off to leave an orange liquid residue. Preparative GLC (8 ft x 0.375 in. column of 12% QF-1 on Chromosorb W, 100°C) gave 0.017 g (14.0%) of 3-fluoro-3-nitrooxetane: $^1\text{H NMR}$ (CDCl_3) δ 4.97 (sextet); $^{19}\text{F NMR}$ (CDCl_3) ϕ 127.7 (quintet, J = 14 Hz); IR (CH_2CH_2) 1575, 1345 ($-\text{NO}_2$), 1000 (C-F) cm^{-1} ; $n_D^{24.5} = 1.4281$.

Anal. Calcd for $\text{C}_3\text{H}_4\text{FNO}_3$: C, 29.76; H, 3.33; N, 11.58. Found: C, 30.13; H, 3.35; N, 12.07.

B. To a solution of 5.42 g (0.020 mol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate in 36 ml of methylene chloride was added a solution of 3.1 ml (0.0207 mol) of 1,5-diazabicyclo(5.4.0) undec-5-ene (DBU) in 18 ml

methylene chloride dropwise over 12 min (below 24°). The reaction mixture was stirred for 75 minutes. Chromatography on a 30 g silica gel column and elution with methylene chloride gave 2 g of crude oxetane. Vacuum distillation gave 1.486 g (61.4%) of 3-fluoro-2-nitrooxetane: bp 31° (1.5 mm). The use of the silica gel column for removal of the DBU triflic acid salt was employed as the salt was not extracted from methylene chloride by water.

Reaction of 2-Fluoro-3-hydroxy-2-nitro-1-propyl Triflate with Pyridine. To a solution of 0.068 g (0.25 mmol) of 2-fluoro-3-hydroxy-2-nitro-1-propyl triflate in 0.70 ml of CDCl₃ was added 40 μl (0.50 mmol) of pyridine. After 24 hrs ¹⁹F NMR indicated the almost complete replacement of the quintet at 139.6 ppm and doublet at 73.2 ppm of the monotriflate. After 4 days the disappearance of the monotriflate was complete: ¹H NMR (CDCl₃) δ 4.05 (broad d, 2 H, CH₂-OH-); 4.78 (broad s) and 5.42 (broad d) (3 H, CH₂-N- and -OH); ¹⁹F NMR (CDCl₃) δ 77.4 (s), 136.4 (quintet, J= 16 Hz).

3-Chloro-2-fluoro-2-nitro-1-propanol. To 0.062 g (0.5 mmol) of 3-fluoro-3-nitrooxetane was added 0.5 ml of concentrated hydrochloric acid. After 6 min ¹⁹F NMR indicated no oxetane remained. After 140 min, the reaction mixture was diluted with 4.5 ml of water, neutralized with potassium, hydroxide, and extracted with methylene chloride (3 x 5 ml). After the solution was dried over sodium sulfate, the methylene chloride was removed in vacuo to give 0.037 g (48.8%) of essentially pure 3-chloro-2-fluoro-2-nitro-1-propanol as a brown liquid: ¹H NMR (CDCl₃) δ 2.47 (broad s, 1 H, -OH); 4.12 (m, 4 H, CH₂); ¹⁹F NMR (CDCl₃) δ 136.8 (quintet, J= 16 Hz).

Reaction of 2,2-Dinitro-1,3-propanediol with Triflic Anhydride. To a solution of 1.66 g (0.010 mol) of 2,2-dinitro-1,3-propanediol and 0.81 ml

(0.010 mol) of pyridine in 15 ml of ether, was added 1.70 ml (0.010 mole) of triflic anhydride in 15 ml of ether dropwise over 9 minutes at 12-18°. The reaction mixture was stirred at room temperature for 2 hrs. The resulting precipitate was then filtered and washed with ether. Removal of the ether in vacuo gave 3.0 g of a yellow liquid, which was taken up in 20 ml of methylene chloride. The solution was dried over sodium sulfate and stripped of solvent. Chromatography (60 g silica gel), on elution with 100 ml of CH₂Cl₂ and 50 ml of 95:5 CH₂Cl₂-EtOAc gave 0.607 g (14.0%) of 2,2-dinitro-1,3-propylene ditriflate: mp 51-52°; ¹HNMR (CDCl₃) δ 5.26 (s); ¹⁹FNMR (CDCl₃) φ 72.0 (s); IR (CH₂Cl₂) 1590, 1305 (-NO₂), 1425, 1220, 1140, 930 (-OSO₂CF₃), 1000 cm⁻¹ (C-F). Elution with 9:1 CH₂Cl₂-EtOAc gave 1.395 g (46.8%) of 2,2-dinitro-3-hydroxy-1-propyl triflate: mp 42-43°C; ¹HNMR (CDCl₃) δ 2.76 (broad s, 1 H, -OH); 4.52 (s, 2 H, CH₂-O-H); 5.21 (s, 2 H, -CH₂-O-SO₂CF₃); ¹⁹FNMR (CDCl₃) φ 72.4 (s); IR (CH₂Cl₂) 3620 (-OH), 1585, 1320, (-NO₂), 1420, 1220, 1140, 840 (-OSO₂CF₃), 995 cm⁻¹ (C-F).

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Synthesis of Organosilanes and Polysiloxanes with Nitro and Fluoro Substituents¹

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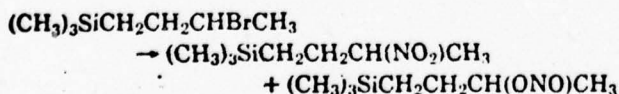
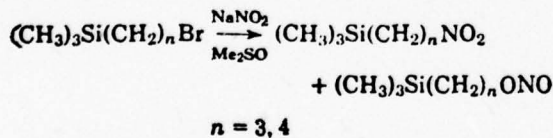
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Nitrite ion displacement of (3-bromopropyl)trimethylsilane, (4-bromobutyl)trimethylsilane, and (3-bromobutyl)trimethylsilane gave the corresponding nitro compounds, which on oxidative nitration gave the *gem*-dinitro compounds. Fluorination of salts 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.

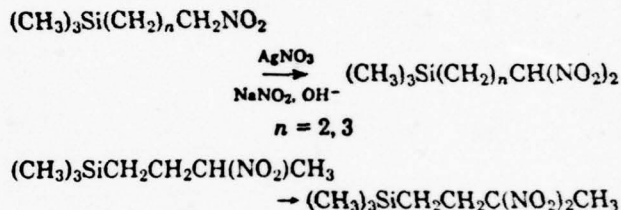
Although the chemistry of organosilicon compounds has been studied extensively,² few examples of this class of compounds with nitro substituents are known. The hydrosilylations of 3-nitropropene, 4,4,4-trinitrobutene, and 4,4-dinitrobutene with trichlorosilane and methyldichlorosilane have been reported,^{3,4} and patent literature describes N_2O_3 addition to allylsilanes⁵ 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 moieties. 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.

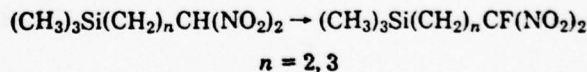
Convenient starting materials for the synthesis of simple nitrosilanes are (3-bromopropyl)trimethylsilane,⁷ (4-bromobutyl)trimethylsilane,⁸ and (3-bromobutyl)trimethylsilane.⁸ Kornblum⁹ has reported that the reaction of alkyl bromides with sodium nitrite in dimethyl sulfoxide gives nitroalkanes, with alkyl nitrites as byproducts. These trimethylsilyl compounds underwent this displacement reaction normally.



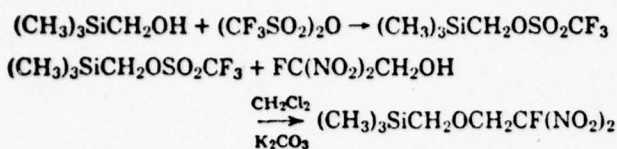
The oxidative nitration reaction¹⁰ was applied to (3-nitropropyl)trimethylsilane, (4-nitrobutyl)trimethylsilane, and (3-nitrobutyl)trimethylsilane to prepare (3,3-dinitropropyl)trimethylsilane, (4,4-dinitrobutyl)trimethylsilane, and (3,3-dinitrobutyl)trimethylsilane, respectively. Yields were 57-72%.



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.

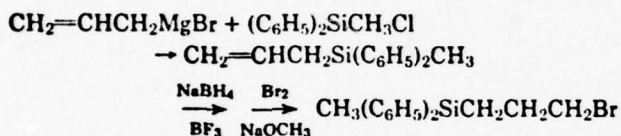


A fluorodinitroalkylsilane with an ether linkage was obtained by the alkylation of 2-fluoro-2,2-dinitroethanol. Alkyl triflates are sufficiently reactive to alkylate this alcohol in methylene chloride in the presence of a mild heterogeneous base such as potassium carbonate.¹³ Under these conditions, 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

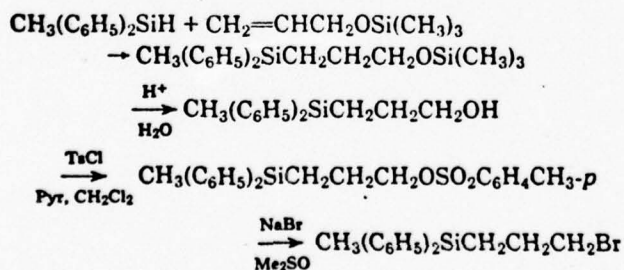


Polysiloxanes are generally prepared by the hydrolysis of dialkyldihalosilanes, and if fluorodinitro-substituted polysiloxanes are to be synthesized by the above methods the silicon-halogen bonds must be generated after the nitro and fluorine groups are introduced. Silicon halides, as well as silicon acetates, silicon methoxides, and similar derivatives, 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)methyl-diphenylsilane. This compound was obtained initially by the bromination of the hydroboration product of allylmethyl-diphenylsilane, prepared, in turn, from allylmagnesium bromide and methylchlorodiphenylsilane.

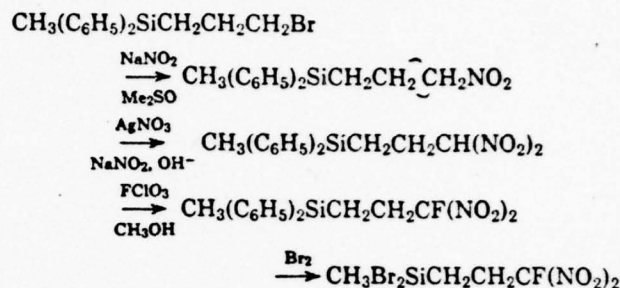


A more convenient route to this bromide was based on the hydrosilylation of allyl acetate with methyl-diphenylsilane with chloroplatinic acid¹⁶ as catalyst to give a 49% yield of (3-hydroxypropyl)methyl-diphenylsilane after hydrolysis. A molar excess of allyl acetate was required. The use of allyloxytrimethylsilane instead of the acetate gave a 71% yield of the alcohol with only a 10% excess of olefin. The use of tris-(triphenylphosphine)rhodium chloride¹⁷ 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.



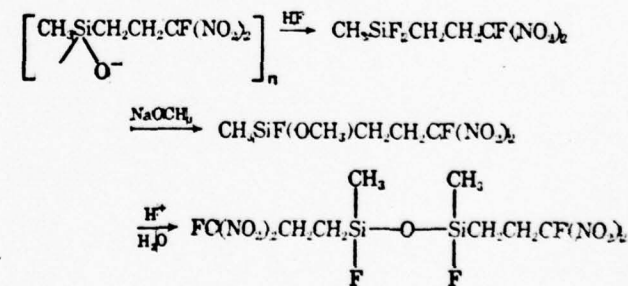
The displacement of the bromide¹⁸ with sodium nitrite in dimethyl sulfoxide gave the nitro compound, as well as the corresponding nitrite and alcohol. The nitro compound was separated from the other products by extracting the mixture with potassium hydroxide, and the isolated yield was 50%. Oxidative nitration of (3-nitropropyl)methyl-diphenylsilane gave (3,3-dinitropropyl)methyl-diphenylsilane 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)methyl-diphenylsilane. Heating this fluorinated compound with bromine then gave (3-fluoro-3,3-dinitropropyl)methyl-dibromosilane in 78% yield. The dibromide was too labile hydrolytically for elemental analysis but was identified spectrally and by its hydrolysis product.



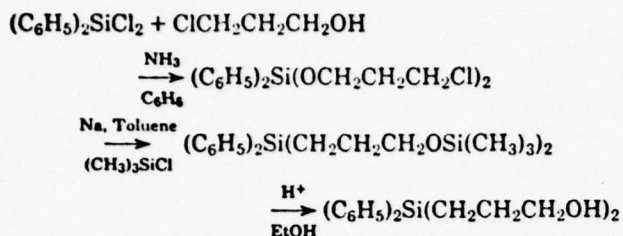
The hydrolysis of this dibromide gave cyclic polysiloxanes, with the number of units depending on the hydrolysis conditions. Thus, treating the dibromide in ether solution with ice gave the tetramer on the basis of vapor osmometric molecular weight. The same molecular weight was obtained when a sample 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)methyl-difluorosilane. 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)methyl-methoxyfluorosilane. 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.

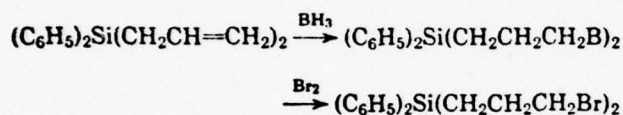


The synthesis of bis(3-fluoro-3,3-dinitropropyl)polysiloxanes was also undertaken with the use of phenyl as a blocking group. The starting material for this work was prepared initially using a rearrangement of haloalkoxysilyl ethers to hydroxyalkylsilanes as reported by Speier.²⁰ Bis(3-chloropropoxy)diphenylsilane was prepared by the reaction of dichlo-

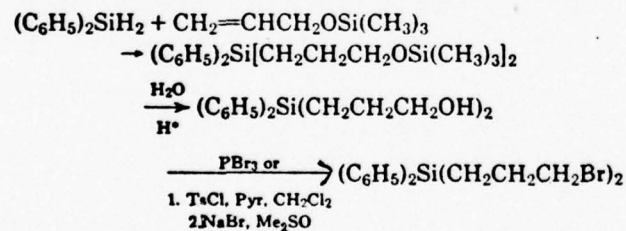
rodiphenylsilane and 3-chloropropanol with ammonia in benzene. This product reacted with sodium and chlorotrimethylsilane in refluxing toluene to give bis(3-trimethylsilyloxypropyl)diphenylsilane. Hydrolysis with acid gave bis(3-hydroxypropyl)diphenylsilane.



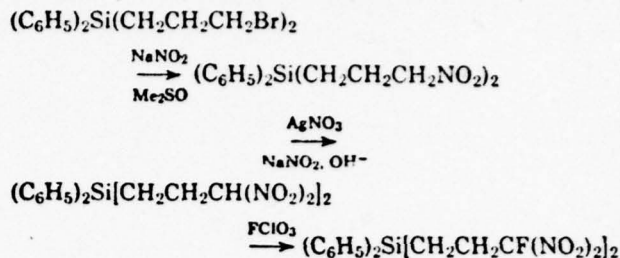
Another route to a difunctional starting material involved hydroboration. Borane in tetrahydrofuran was added to diallyldiphenylsilane, and the resulting borane was brominated to give bis(3-bromopropyl)diphenylsilane in 24% overall yield.



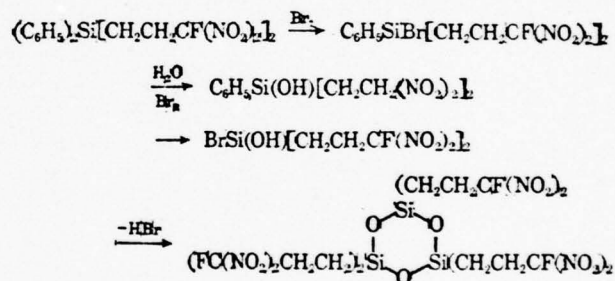
A reaction scheme analogous to that used to prepare the (2-fluoro-2,2-dinitropropyl)methylsilane derivatives provided a more practical route to the preparation of bis(2-fluoro-2,2-dinitropropyl)silicon compounds. Thus, the hydrosilylation of allyloxytrimethylsilane with diphenylsilane catalyzed by tris(triphenylphosphine)rhodium 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.



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.



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.



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 \times $\frac{3}{8}$ 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)trimethylsilane⁹ 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 (CCl₄) δ 4.20 (t, *J* = 7 Hz, 2 H, CH₂NO₂), 1.87 (m, 2 H, CH₂CH₂Si), 0.50 (m, 2 H, CH₃Si), 0.0 (s, 9 H, (CH₃)₃Si); IR (CCl₄) 2970, 1545, 1430, 1380, 1250 cm⁻¹. Anal. Calcd for C₆H₁₅NO₂Si: C, 44.69; H, 9.38; N, 8.68. Found: C, 44.74; H, 9.38; N, 8.67.

The nitrosation²¹ of (3-hydroxypropyl)trimethylsilane provided an independent synthesis of (3-nitropropyl)trimethylsilane: NMR (CCl₄) δ 4.50 (t, 2 H, CH₂ONO), 1.7 (m, 2 H, CH₂CH₂Si), 0.5 (m, 2 H, CH₂Si), 0.0 (s, 9 H (CH₃)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)trimethylsilane⁸ 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 analytical sample was isolated by GLC: NMR (CCl₄) δ 4.27 (t, J = 7 Hz, 2 H, CH₂NO₂), 2.02 (q, J = 7 Hz, 2 H, CH₂CH₂NO₂), 1.4 (m, 2 H, CH₂CH₂Si), 0.50 (m, 2 H, CH₂Si), 0.0 (s, 9 H, (CH₃)₃Si); IR (CCl₄) 2960, 1545, 1435, 1385, 1255 cm⁻¹. Anal. Calcd for C₇H₁₇NO₂Si: 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-nitrobutyl)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 (CCl₄) δ 4.30 (sextet, 1 H, CHNO₂), 1.75 (m, 2 H, CH₂CH₂Si), 1.42 (d, 3 H, CH₃CHNO₂), 0.4 (t, 2 H, CH₂Si)₂ 0.0 (s, 9 H, (CH₃)₃Si); IR (film) 2970, 1545, 1260, 865, 845 cm⁻¹. Anal. Calcd for C₇H₁₇NO₂Si: 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 (CCl₄) δ 3.48 (sextet, 1 H, CHOH), 2.9 (broad s, 1 H, OH), 1.3 (m, 2 H, CH₂Si), 1.05 (d, 3 H, CH₃CHOH), 0.40 (m, 2 H, CH₂Si), 0.0 (s, 9 H (CH₃)₃Si); IR 3350 (OH), 2950, 1250, 860, 850, 840 cm⁻¹.

The alcohol was reconverted by a standard procedure²¹ to the nitrite with identical spectra: NMR (CCl₄) δ 5.30 (sextet, 1 H, CHONO), 1.7 (m, 2 H, CH₂CH₂Si), 1.40 (d, J = 7 Hz, 3 H, CH₃CH), 0.55 (m, 2 H, CH₂Si), 0.0 (s, 9 H, (CH₃)₃Si); IR (film) 2970, 1640, 1600, 1260, 880, 850, 800 cm⁻¹. The 1640-, 1600-, and 800-cm⁻¹ peaks are assigned²² 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 (CCl₄) δ 5.88 (t, J = 7 Hz, 1 H, CH(NO₂)₂), 2.38 (m, 2 H, CH₂CH₂Si), 0.55 (m, 2 H, CH₂Si), 0.08 (s, 9 H, (CH₃)₃Si); IR (CCl₄) 2970, 1570, 1335, and 1260 cm⁻¹. Anal. Calcd for C₆H₁₁N₂O₄Si: 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-dinitro-

butyl)trimethylsilane, a colorless oil, bp 71–74 °C (2 mm). An analytical sample was isolated by GLC: NMR (CCl₄) δ 5.97 (t, J = 7 Hz, 1 H, CH(NO₂)₂), 2.43 (q, J = Hz, 2 H, CH₂CH), 1.47 (m, 2 H, CH₂CHSi), 0.57 (m, 2 H, CH₂Si), 0.0 (s, 9 H, (CH₃)₃Si); IR (CCl₄) 2970, 1570, 1330, 1250 cm⁻¹. Anal. Calcd for C₇H₁₆N₂O₄Si: 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 (CCl₄) δ 2.34 (m, 2 H, (NO₂)₂CCH₂), 2.02 (s, 3 H, (NO₂)₂CCH₃), 0.40 (m, 2 H, CH₂Si), 0.05 (s, 9 H, (CH₃)₃Si); IR (CCl₄) 2970, 1565, 1330, 1260, 1195 cm⁻¹. Anal. Calcd for C₇H₁₆N₂O₄Si: 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 fluorinated¹¹ 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, bp 67–71 °C (0.5 mm). An analytical sample was obtained by GLC: proton NMR (CCl₄) δ 2.57 (m, 2 H, CH₂CF), 0.50 (m, 2 H, CH₂Si), 0.08 (s, 9 H, (CH₃)₃Si); fluorine NMR δ 106.0 (broad t); IR (CCl₄) 2970, 1590, 1320, 1260, 1190 cm⁻¹. Anal. Calcd for C₆H₁₃N₂O₄SiF: 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 fluoride¹² 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 (CCl₄) δ 2.67 (d of s, J_{HF} = 19, J_{HH} = 7 Hz, 2 H, CH₂CF), 1.44 (m, 2 H, CH₂CH₂Si), 0.53 (m, 2 H, CH₂Si), 0.0 (s, 9 H, (CH₃)₃Si); fluorine NMR (CCl₄) δ 102.8 (broad t, (NO₂)₂CF); IR (CCl₄) 2970, 1590, 1350, 1255 cm⁻¹. Anal. Calcd for C₇H₁₅N₂O₄SiF: 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)trimethylsilane¹⁴ 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 (CCl₄) δ 4.07 (s, 2 H, CH₂Si), 0.08 (s, 9 H, (CH₃)₃Si); fluorine NMR δ 74.3 (s); IR (film) 1410, 1210, 1150, 960, 870 cm⁻¹. Anal. Calcd for C₆H₁₁O₃F₃Si: 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 (CCl₄) δ 4.35 (d, 2 H, *J* = 18 Hz, CH₂CF), 3.23 (s, 2 H, CH₂Si), 0.02 (s, 9 H, (CH₃)₃Si); fluoride NMR (CCl₄) δ 110.25 (broad t); IR (film) 2975, 2925, 1600, 1320, 1250, 1125, 870, 860 cm⁻¹. Anal. Calcd for C₆H₁₃N₂O₂SiF: 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, CH₃Si), 1.5 (d, *J* = 7 Hz, 2 H, C=C-CH₂Si), 4.3 (m, 2 H, CH₂=C), 5.3 (m, 1 H, C=CHCH₂Si), 6.6-6.9 (m, 10 H, C₆H₅); IR (film) 1640, 1440, 1270, 1170, 1130 cm⁻¹. Anal. Calcd for C₁₅H₂₄O₂Si: 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 (CDCl₃) δ 0.5 (s, 3 H, CH₃Si), 1.1 (m, 2 H, CH₂Si), 1.8 (m, 2 H, CH₂CH₂Si), 3.2 (t, *J* = 7 Hz, 2 H, BrCH₂), 7.2 (m, 10 H, C₆H₅). Anal. Calcd for C₁₆H₁₉BrSi: C, 60.19; H, 5.96. Found: C, 60.36; H, 6.01.

(3-Hydroxypropyl)methyldiphenylsilane. Allyloxytrimethylsilane²³ (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 (CDCl₃) δ 0.48 (s, 3 H, CH₃), 0.95 (m, 2 H, CH₂Si), 1.4 (m, 2 H, CCH₂C), 2.0 (s, 1 H, OH), 3.12 (t, *J* = 6 Hz, 2 H, CH₂O), 7.0 (s, 10 H, C₆H₅). Anal. Calcd for C₁₆H₂₀O₂Si: C, 74.95; H, 7.86. Found: C, 74.80; H, 8.07.

(3-*p*-Toluenesulfonatopropyl)methyldiphenylsilane. Toluene sulfonfyl 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 (CDCl₃) δ 7.3 (d of d, 4 H, C₆H₄Si-*p*), 7.2 (broad s, 10 H, C₆H₅), 3.85 (t, *J* = 6.5, 2 H, CH₂O), 2.40 (s, 3 H, CH₃), 1.6 (m, 2 H, CH₂CH₂Si), 1.0 (m, 2 H, CH₂Si), 0.50 (s, 3 H, CH₃Si). Anal. Calcd for C₂₃H₂₆O₃Si: C, 67.28; H, 6.38. Found: C, 67.44; H, 6.48.

(3-Bromopropyl)methyldiphenylsilane from Toluene sulfonate. A solution of 3.5 g (0.04 mol) of lithium bromide and 5.95 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%) 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 (CDCl₃) δ 0.3 (s, 2 H, CH₃Si), 1.2 (m, 2 H, CH₂Si), 2.1 (m, 2 H, CH₂CH₂Si), 4.2 (t, *J* = 7 Hz, 2 H, CH₂NO₂), 7.3 (m, 10 H, C₆H₅); IR (film) 1550, 1435, 1395, 1260, 1190, 1165, 1125 cm⁻¹. Anal. Calcd for C₁₆H₁₉NO₂Si: 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 (CDCl₃) δ 0.7 (s, 3 H, CH₃Si), 1.3 (m, 2 H, CH₂Si), 2.6 (m, 2 H, CH₂CH₂Si), 6.0 (t, *J* = 7 Hz, 1 H, CH), 7.4 (m, 10 H, C₆H₅).

(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)methylphenylsilane: 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 $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_4\text{FSi}$: C, 55.17; H, 4.88; N, 8.04. Found: C, 55.02; H, 5.12; N, 8.09.

(3-Fluoro-3,3-dinitropropyl)methyl-dibromosilane. A mixture of 12.5 mL (0.230 mol) of bromine and 20.0 g (0.0574 mol) of (3-fluoro-3,3-dinitropropyl)methylphenylsilane 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), 1.05-g intermediate fraction, and 15.8 g (78%) of (3-fluoro-3,3-dinitropropyl)methyl-dibromosilane, 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)methyl-dibromosilane 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_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 $\text{C}_8\text{H}_7\text{N}_2\text{FO}_2\text{Si}$: 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)methyl-difluorosilane. (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)methyl-difluorosilane: 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, $\text{CH}_2\text{CF}(\text{NO}_2)_2$); fluorine NMR (CDCl_3) ϕ 104.5 (t, $J = 16$ Hz, 1 F, $\text{F}(\text{NO}_2)_2\text{C}$), 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 $\text{C}_8\text{H}_7\text{F}_3\text{N}_2\text{O}_4\text{Si}$: 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)methyl-dibromosilane 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)methyl-difluorosilane.

Reaction of (3-fluoro-3,3-dinitropropyl)methyl-difluorosilane 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)methyl-difluorosilane 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, $\text{CH}_2\text{C}(\text{NO}_2)_2\text{F}$), 3.5 (s, 3 H, CH_3OSi); fluorine NMR (CDCl_3) ϕ 104.7 (t, $J = 16$ Hz, 1 F, $\text{CF}(\text{NO}_2)_2\text{F}$), 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 155 °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 05.5 (t, $J = 20$ Hz, 2 F, $\text{FC}(\text{NO}_2)_2$), 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 $\text{C}_{26}\text{H}_{24}\text{F}_8\text{N}_4\text{O}_{12}\text{Si}_2$: 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 dichloro diphenyl silane (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, $\text{CH}_2\text{CH}_2\text{CH}_2$), 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 $\text{C}_{18}\text{H}_{22}\text{O}_2\text{Cl}_2\text{Si}$: 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, $\text{CH}_2\text{CH}_2\text{Si}$), 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 $\text{C}_{18}\text{H}_{24}\text{O}_2\text{Si}$: 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 5% 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 allyloxytrimethylsilane, 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 PBr₃. Bis(3-hydroxypropyl)diphenylsilane (1490 g, 4.96 mol) was added to a solution of 1043 g (3.86 mol) of phosphorous 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 (CDCl₃) δ 1.2 (m, 4 H, CH₂Si), 1.8 (m, 4 H, CH₂CH₂Si), 3.25 (t, *J* = 6 Hz, 4 H, BrCH₂), 7.15 (m, 10 H, C₆H₅). Anal. Calcd for C₁₈H₂₂Br₂Si: 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 (CDCl₃) δ 7.4 (d of d, 8 H, -C₆H₄-*p*), 7.2 (m, 10 H, C₆H₅), 3.97 (t, 4 H, CH₂O), 2.47 (s, 6 H, -C₆H₄CH₃-*p*), 1.7 (m, 4 H, CH₂CH₂Si), 1.0 (m, 4 H, CH₂Si). Anal. Calcd for C₃₂H₃₆O₆S₂Si: 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 (CDCl₃) δ 7.3 (s, 10 H, C₆H₅), 4.3 (t, 4 H, CH₂NO₂), 2.0 (m, 4 H, CH₂CH₂Si), 1.1 (m, 4 H, CH₂Si); IR (CCl₄) 1540, 1430, 1380, 1120, 710 cm⁻¹. Anal. Calcd for C₁₈H₂₀O₄N₂Si: 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 ethylene chloride and Skelly F, giving 34.5 g (38% yield) of bis(3,3-dinitropropyl)diphenylsilane: mp 96–97 °C; NMR (CDCl₃) δ 7.40 (3, 10 H, C₆H₅), 6.01 (t, *J* = 7 Hz, 2 H, CH(NO₂)₂), 2.4 (m, 4 H, CH₂CH₂Si), 1.2 (m, 4 H, CH₂Si); IR (CHCl₃) 1570, 1330, 1120 cm⁻¹. Anal. Calcd for C₁₈H₂₀N₄O₈Si: 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 water, 200 mL methanol, and 200 mL of dimethyl formamide 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 (CDCl₃) δ 7.35 (s, 10 H, C₆H₅), 2.63 (m, 4 H, CH₂CH₂Si), 1.17 (m, 4 H, CH₂Si); fluorine NMR (CDCl₃) δ 105.7 (*J*_{HF} = 18 Hz); IR (KBr) 1590, 1430, 1320, 1260, 1200, 1100, 700 cm⁻¹. Anal. Calcd for C₁₈H₁₆O₈N₄F₂Si: 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, CH₂CF), 1.20 (m, 4 H, CH₂Si); fluorine NMR (acetone-*d*₆) δ 106.0; IR (KBr) 1590, 1320, 1270, 1210, 1090 cm⁻¹. Anal. Calcd for C₆H₈N₄O₉F₆Si₃: 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)trimeth-

ylsilane, 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; chloromethyl diphenylsilane, 144-79-6; allylmethyl diphenylsilane, 17922-43-9; (3-bromopropyl)methyl diphenylsilane, 64035-66-1; allyloxytrimethylsilane, 18146-00-4; (3-hydroxypropyl)methyl diphenylsilane, 64035-67-2; toluenesulfonyl chloride, 98-59-9; (3-*p*-toluenesulfonatopropyl)methyl diphenylsilane, 64035-68-3; (3-nitropropyl)methyl diphenylsilane, 64035-69-4; (3,3-dinitropropyl)methyl diphenylsilane, 64035-70-7; (3-fluoro-3,3-dinitropropyl)methyl diphenylsilane, 64035-71-8; (3-fluoro-3,3-dinitropropyl)methyl dibromosilane, 64035-72-9; (3-fluoro-3,3-dinitropropyl)methyl difluorosilane, 64035-73-0; (3-fluoro-3,3-dinitropropyl)methyl methoxyfluorosilane, 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; (CF₃SO₂)₂O, 358-23-6.

References and Notes

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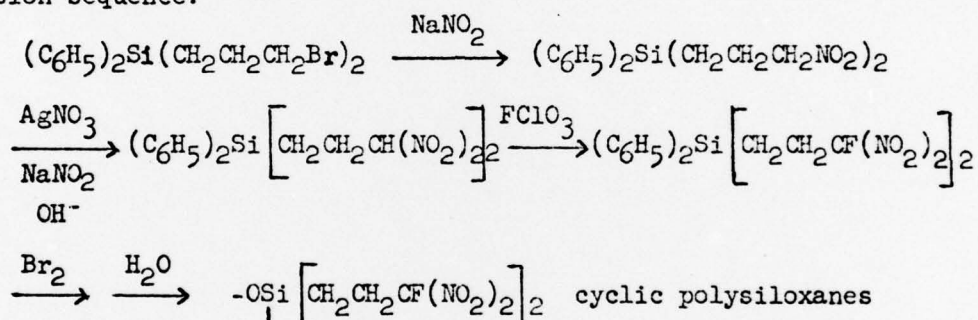
Appendix B

Synthesis of Bis-(3,3-dinitrobutyl)cyclopolysiloxanes¹

Duane A. Lerdal and Kurt Baum*

Contribution from Fluorochem, Inc.
Azusa, California 91702

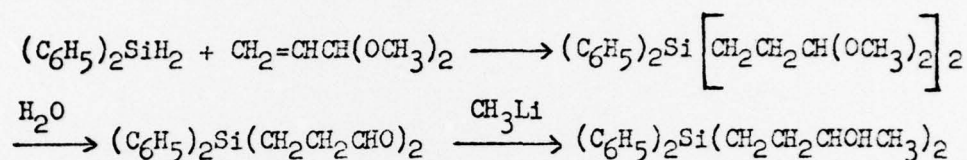
We have reported² the synthesis of (3-fluoro-3,3-dinitropropyl)methylpolysiloxanes and of bis(3-fluoro-3,3-dinitropropyl)polysiloxanes by the stepwise introduction of nitro groups and fluorines with displacement reactions, oxidative nitrations and fluorinations. Phenyl groups were used as silicon blocking groups, and were removed by bromination at the end of the reaction sequence.



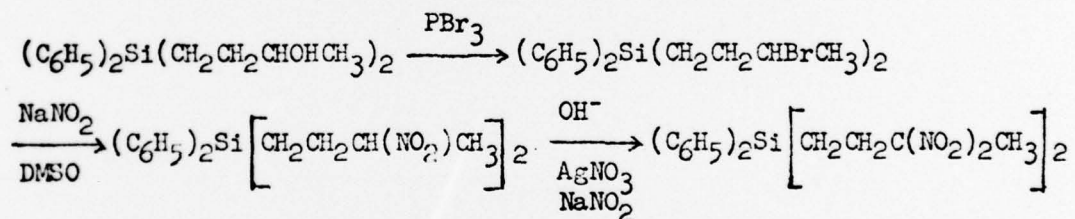
The synthesis of an analogous series of compounds with internal gem-dinitro groups was undertaken in the present work. The starting material was obtained by a sequence of reactions beginning with the hydrosilylation of acrolein dimethyl acetal with diphenylsilane. The hydrosilylation of acrolein, as well as α,β -unsaturated ketones and esters, with triethylsilane has been reported to take place by 1,4-addition, yielding enol silyl ethers.^{3,4} However, acrolein acetal and triethylsilane in the presence of chloroplatinic acid gave, after hydrolysis, 3-(triethylsilyl)propionaldehyde.³

For the addition of diphenylsilane to allyl compounds,² tris(triphenylphos-

phine)rhodium chloride⁵ was found to be a more effective catalyst than chloroplatinic acid. Under these conditions, the adduct of acrolein dimethyl acetal and diphenylsilane was obtained, and aqueous hydrolysis converted it to bis(3-oxopropyl)diphenylsilane. This aldehyde underwent such rapid self-condensation that it could not be analyzed. However, it reacted with methyllithium in ether to give bis(3-hydroxybutyl)diphenylsilane, a crystalline solid.



The reaction of this alcohol with phosphorous tribromide in ether gave the corresponding dibromide. Bis(3-bromobutyl)diphenylsilane underwent displacement with sodium nitrite in dimethyl sulfoxide to yield bis(3-nitrobutyl)diphenylsilane. Oxidative nitration⁶ of the salt of this nitro compound with sodium nitrite and silver nitrate, in a mixed solvent consisting of water, methanol and ether, gave bis(3,3-dinitrobutyl)diphenylsilane.



Dephenylation with bromine was similar to that of the analogous fluorodinitropropyl compound.² Only one phenyl group was removed readily in an inert solvent, but hydrolysis of the resulting bromosilane to the silanol facilitated removal of the second phenyl. A convenient one pot procedure utilized glacial acetic acid as the solvent for the initial bromination, with

water added to complete the bromination and hydrolysis. A cyclic polysiloxane with a molecular weight between trimer and tetramer was obtained, which melted at 240-250° (dec.).

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.

Bis(3-hydroxybutyl)diphenylsilane. A solution of 18.4 g (0.1 mol) of diphenylsilane, 22 g (0.215 mol) of acrolein dimethyl acetal and 0.01 g of tris(triphenylphosphine)rhodium chloride in 25 ml of benzene was refluxed for 4 hours. An additional 0.01 g of catalyst was added and the solution was refluxed for 2 hours. The solvent was stripped under vacuum and the residue was added to a mixture of 100 ml of water, 20 ml of ethanol, 0.5 ml of concentrated hydrochloric acid and 0.2 g of potassium iodide. Ethanol and methanol were distilled off slowly until the head temperature reached 80°. The mixture was cooled and the product was extracted with three 50 ml portions of ether, dried and stripped of solvent. The aldehyde, which polymerized on standing, was dissolved immediately in 50 ml of ether and the solution was added dropwise to 150 ml of 1.5 M methyllithium in ether. The mixture was refluxed for 15 min, cooled and acidified with 10% hydrochloric acid. The ether layer was separated, washed with 50 ml of water, dried and stripped. Bis(3-hydroxybutyl)diphenylsilane (27%, mp 91-2°) was isolated by crystallization from carbon tetrachloride and Skelly F. IR (KBr) 3300, 2900-3000, 1430, 1120 and 705 cm^{-1} : NMR (CDCl_3) δ 7.40 (broad s, 10 H, C_6H_5) 3.72 (sex-

tet, 2 H, $\underline{\text{CHOH}}$), 2.17 (s, 2 H, OH) and 1.0-1.8 (m, 14 H, $\underline{\text{CH}_3\text{CHOHCH}_2\text{CH}_2}$):

Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{O}_2\text{Si}$: C, 73.12; H, 8.59. Found: C, 73.19; H, 8.73.

Bis(3-bromobutyl)diphenylsilane. A solution of 9.0 g (0.0275 mol) of bis(3-hydroxybutyl)diphenylsilane and 8.6 g (0.032 mol) of phosphorous tribromide in 30 ml of ether was stirred at ambient temperature for 90 hrs. The solution was added to 100 ml of ice-water and the product was extracted with three 30 ml portions of carbon tetrachloride. The combined organic layers were washed with water, dried and stripped of solvent. The product was purified by column chromatography (silica gel and carbon tetrachloride) followed by crystallization from Skelly F, to give 6.5 g (48%) bis(3-bromopropyl)diphenylsilane, mp $61-2^\circ$: IR (film) 2900-3000, 1425, 1225, 1190, 1120, 740 and 710, nmr (CDCl_3) δ 7.5 (broad s, 10 H, C_6H_5), 4.2 (sextet, 2 H, CHBr), 2.0 (m, 4 H, $\underline{\text{CH}_2\text{CH}_2\text{Si}}$) 1.85 (d, $J=7\text{Hz}$, 6 H, CH_3) and 1.4 (m, 4 H, CH_2Si).

Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{SiBr}_2$: C, 52.87; H, 5.77. Found: C, 52.88; H, 5.77.

Bis(3-nitrobutyl)diphenylsilane. A solution of 6.0 g (13.0 mmol) of bis(3-bromobutyl)diphenylsilane and 12.0 g (174 mmol) of sodium nitrite in 30 ml of dimethyl sulfoxide was stirred for 3 hrs at 25°C . The solution was added to 250 ml of water and was extracted with three 25 ml portions of carbon tetrachloride. The combined organic layers were washed with water, dried and stripped of solvent. Column chromatography and crystallization from carbon tetrachloride and Skelly F, yielded 1.5 g (29%) of bis(3-nitrobutyl)diphenylsilane, mp $84-5^\circ$: IR (KBr) 2900, 1530, 1430, 1320, 1180, 1110 and 700 cm^{-1} ; nmr (CDCl_3) δ 7.3 (broad s, 10 H C_6H_5), 4.5 (sextet, 2 H, CHNO_2), 1.4

(m, 4 H, $\text{CH}_2\text{CH}_2\text{Si}$), 1.5 (d, $J=7\text{Hz}$, 6 H, CH_3) and 1.1 (m, 4 H, CH_2Si).

Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_4\text{Si}$: C, 62.15; H, 6.78; N, 7.25. Found: C, 61.93; H, 6.58; N, 7.39.

Bis(3,3-dinitrobutyl)diphenylsilane. Bis(3-nitrobutyl)diphenylsilane (1.2 g, 3.1 mmol) was dissolved, with stirring at 70° , in a mixture of 5 ml of methanol, 13 ml of water and 6.2 mmol of potassium hydroxide. The solution was cooled to room temperature and 2.2 g (6.2 mmol) of sodium nitrite was added. The resulting solution was added quickly to a vigorously stirred mixture of 2.2 g (13 mmol) of silver nitrate, 15 ml of water and 20 ml of ether. After 5 min an additional 25 ml of ether was added and the mixture was stirred for 2 hrs. Saturated sodium chloride (10 ml) was added and the mixture was filtered. The precipitate was washed with ether, and the combined ether layers were dried and solvent was evaporated. Column chromatography (silica gel, methylene chloride) and crystallization (carbon tetrachloride, Skelly F) gave 0.90 g (61%) of bis(3,3-dinitrobutyl)diphenylsilane, mp $70-1^\circ$: IR (film) 3,000, 2900, 1550, 1420, 1380, 1320, 1190, 1110, 1020, 845, 785 and 700 cm^{-1} ; nmr (CDCl_3) 7.37 (broad s, 10 H, C_6H_5), 2.4 (m, 4 H, $\text{CH}_2\text{-CH}_2\text{Si}$), 2.07 (s, 6 H, CH_3) and 1.1 (m, 4 H, CH_2Si).

Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_8\text{Si}$: C, 50.41; H, 5.09; N, 11.76. Found: C, 50.71; H, 5.15; N, 11.96.

Bis(3,3-dinitrobutyl)cyclopolysiloxanes. A solution of 3.0 g (6.3 mmol) of bis(3,3-dinitrobutyl)diphenylsilane and 1 ml (18 mmol) of bromine in 20 ml of glacial acetic acid was refluxed for 30 min. Water (100 ml) was added and the mixture was refluxed for 10 min. The solution was cooled to room temperature and 20 ml of methylene chloride was added. A fine white precipitate

was filtered and the methylene chloride layer dried, and one drop of triethylamine was added. After 24 hrs, additional precipitate was isolated by filtration to give a total of 1.5 g (70%) of a mixture of cyclic bis(3,3-dinitrobutyl)polysiloxanes, mp (dec) 240-250°: IR (KBr) 2900, 1545, 1320, 1200, 1090 and 1010 cm^{-1} ; nmr (D_3CCOCD_3) δ 2.7 (m, 4 H, $\text{CH}_2\text{CH}_2\text{Si}$), 2.20 (s, 6 H, CH_3) and 1.0 (m, 4 H, CH_2Si); molecular weight (vapor phase osmometer, 2-butanone), 1210 \pm 5% (trimer = 1014, tetramer = 1352).

Anal. Calcd for $\text{C}_8\text{H}_{14}\text{N}_4\text{O}_9\text{Si}$: C, 28.40; H, 4.17; N, 16.56. Found: C, 28.06; H, 4.03; N, 16.21.

References and Notes

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