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HIGH ENERGY HALOGEN CHEMISTRY

Kurt Baum, et al

Fluorochem, Incorporated

Prepared for:

Office of Naval Research

January 1976

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HIGH ENERGY HALOGEN CHEMISTRY

by

K. Baum, J. S. Horn and D. A. Lerdal

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Nitration	Dichlorine heptoxide	
Fluorination	Perchlorates	
Fluorine	Nuclear magnetic resonance spectra	
	Infrared spectra	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>Fluorodinitroalkyl groups on silicon were constructed by nitrite displacement of halogen, oxidative nitration and fluorination. 3,3-Dinitrobutyl and fluorodinitroethoxymethyl derivatives of silicon were also synthesized. Phenyl was used as a silicon blocking group in the synthesis of (3-fluoro-3,3-dinitropropyl)methyl polysiloxane. Reactions of olefins with dichlorine heptoxide are described.</p>		



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I. INTRODUCTION

The objective of this research program is to synthesize new functional groupings with potential utility in high energy propellants and explosives. During the past year the major emphasis of this research has been on the development of synthetic methods for nitroalkyl and fluoronitroalkyl derivatives of silicon, compounds with potentially superior low temperature flexibility as well as high thermal stability. Work was completed on a study of reactions of olefins with dichlorine heptoxide and a manuscript for journal publication was prepared. This manuscript comprises Appendix A of this report.

The following articles have been published during this report period:

"Reactions of Silver Perchlorate and of Silver Triflate with Alkyl Iodides. Solvent Inhibition of Isomerization," C. D. Beard and K. Baum, J. Org. Chem., 39, 3675 (1974).

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

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

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

The following manuscript is in press:

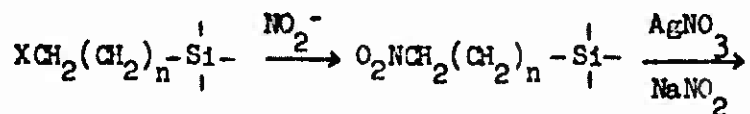
"Reactions of Dichlorine Heptoxide with Olefins," K. Baum

II. DISCUSSION

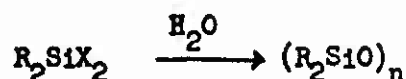
An area of nitro chemistry that has not received attention is the synthesis of compounds with nitroalkyl groups bound to silicon. The exceptional high temperature stability and low temperature flexibility of silicones is well known, and there is a need for energetic materials with similar properties.

The carbon-silicon bond is most commonly formed¹ by the reaction of Grignard reagents or similar reactive organometallics with silicon halides, or by the high temperature reaction of alkyl halides with elemental silicon. The Grignard method cannot be used for preparing nitroalkyl silicon bonds because nitro groups react rapidly with Grignard reagents.² The direct synthesis method³ using alkyl halides and silicon requires reaction temperatures of 250° to 600°, so this method also is incompatible with nitro substituents. Another method that has been used to form silicon-carbon bonds is the free radical catalyzed addition of Si-H bonds to olefins.⁴ This method is potentially applicable, although nitro compounds have been known to interfere with free radical reactions by functioning as chain transfer agents.

The potentially most versatile route to polynitro and fluoronitro silicones is the stepwise introduction of functional groups by displacement, oxidative nitration and fluorination reactions:

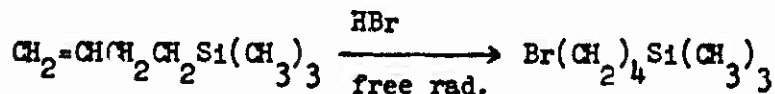


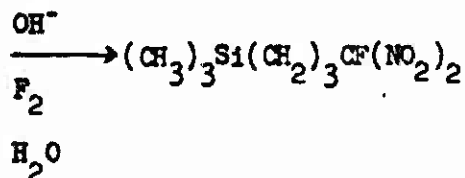
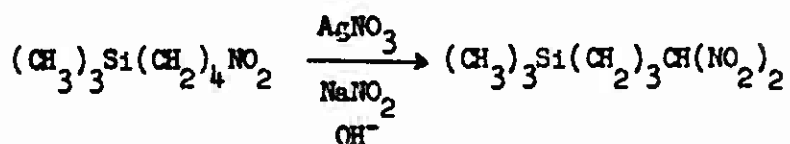
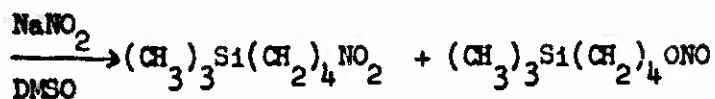
Silicones are prepared by the hydrolysis of dialkylsilyl halides, esters or other labile derivatives.



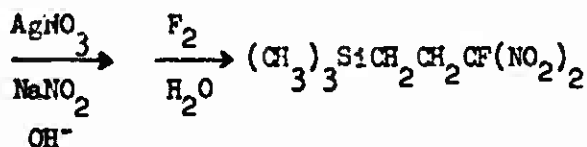
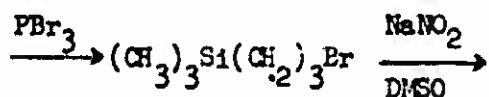
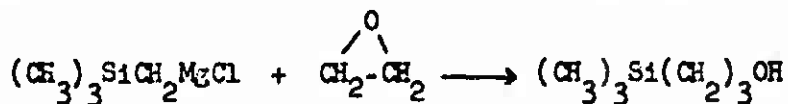
Since these groups cannot survive the hydrolytic conditions required for the above reactions, a more stable blocking group must be found that can be removed at the end of the synthesis sequence. The alternative route of preparing a haloalkyl polysiloxane followed by stepwise introduction of nitro groups is impractical because impurities and byproducts introduced in these steps could not be removed.

Trimethylsilyl Compounds. Exploratory work was carried out using trimethylsilyl derivatives to determine the effect of silicon on the reaction steps involved in the construction of fluorodinitroalkyl groups. Thus, 3-butenyltrimethylsilane, prepared from trimethylchlorosilane and the Grignard reagent of 4-bromo-1-butene, underwent free radical catalyzed addition of hydrogen bromide to give 4-bromobutyltrimethylsilane.⁵ Kornblum has reported that the reaction of alkyl bromides with sodium nitrite in dimethylsulfoxide gives nitroalkanes with alkyl nitrites as byproducts.⁶ This reaction proceeded smoothly with 4-bromobutyltrimethylsilane to give 4-nitrobutyltrimethylsilane. The oxidative nitration reaction⁷ of this compound gave 4,4-dinitrobutyltrimethylsilane, which, under standard aqueous fluorination conditions,⁸ gave 4-fluoro-4,4-dinitrobutyltrimethylsilane. Thus, at least with three intervening methylene groups, the silyl group does not exert any special influence on the reaction sequence.



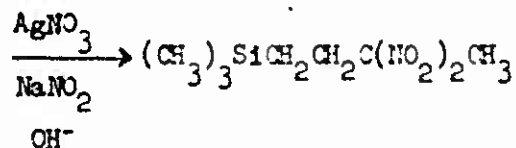
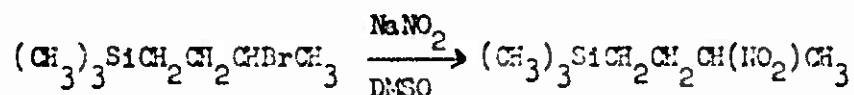


The effect of the chain length of the alkyl group on the reaction sequence was studied. The reaction of chloromethyltrimethylsilane with magnesium and ethylene oxide gave 3-hydroxypropyltrimethylsilane, which, with phosphorous tribromide, gave 3-bromopropyltrimethylsilane.⁹ This compound underwent the sodium nitrite displacement smoothly, followed by the oxidative nitration and aqueous fluorination to give 3-fluoro-3,3-dinitropropyltrimethylsilane.

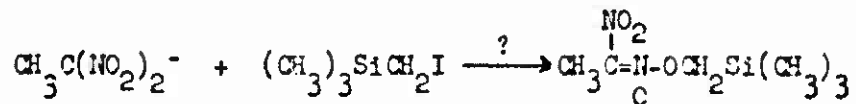


In one experiment in which hydrogen bromide was added to 3-butenyltrimethylsilane, insufficient catalyst was used and the product consisted of a mixture of the 3- and 4-bromobutyltrimethylsilanes. The mixture was treated with sodium nitrite and the resulting mixture of nitro compounds was subjected

to the oxidative nitration. The mixture of gem-dinitro compounds is separated easily because the terminal gem-dinitro compound is soluble in base; 3,3-dinitrobutyltrimethylsilane was isolated and characterized. Thus the synthesis of 3,3-dinitrobutylsilanes is shown to be feasible:



An attempt to extend this reaction to the next lower homolog was unsuccessful. Thus, 2-bromopropyltrimethylsilane was prepared from allyltrimethylsilane and hydrogen bromide. The sodium nitrite displacement could not be accomplished, however, because the compound eliminated HBr immediately in dimethyl sulfoxide to give the α, β -unsaturated silane. An attempted reaction of 1,1-dinitroethane with iodomethyltrimethylsilane in pyridine was also unsuccessful. The starting materials were consumed, but the product decomposed at room temperature. Evidently reaction took place at the oxygen rather than carbon of the ambident nitro salt. An unstable product was also formed from trimethylchlorosilane and the sodium salt of dinitroethane.

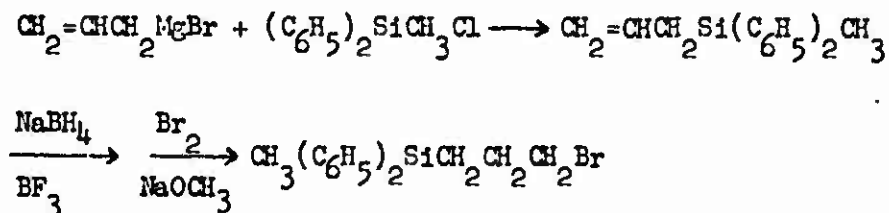


Another energetic model compound that was prepared is trimethylsilylmethyl 2-fluoro-2,2-dinitroethyl ether, $(\text{CH}_3)_3\text{SiCH}_2\text{OCH}_2\text{CF}(\text{NO}_2)_2$. Attempts to prepare the compound from fluorodinitroethanol and chloromethyltrimethylsilane or iodomethyltrimethylsilane were unsuccessful. It was obtained in 45% yield

nitro-substituted silicones requires a blocking group on silicon that is not affected by the reaction conditions encountered in nitrite displacements, oxidative nitrations and fluorinations. Yet, this group should be removable under mild conditions after the synthetic sequence. Groups such as alkoxy, acetoxy or halogen on silicon do not survive hydrolytic conditions. A search of the literature showed that carbon-silicon bonds can be cleaved by halogens and that the cleavage of phenyl-silicon bonds by bromine is particularly facile.¹²

The phenyl group thus appeared to meet the requirements of a silicon blocking group. Since the exploratory work using trimethylsilyl models showed that the fluorodinitropropyl groups on silicon can be constructed readily, the reactions were adapted to the methyldiphenylsilyl analog.

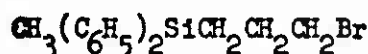
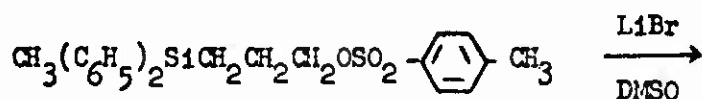
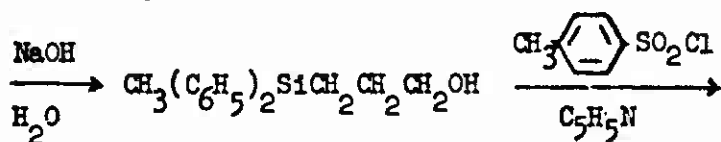
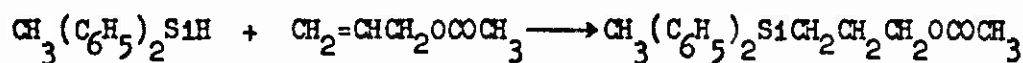
The starting material for the nitro introduction sequence, (3-bromopropyl)methyldiphenylsilane, was obtained by two different procedures. Allylmethyldiphenylsilane was prepared by the reaction of allyl magnesium bromide with chloromethyldiphenylsilane in ether. The product was hydroborated by reacting it with sodium borohydride and boron trifluoride in tetrahydrofuran, and the resulting borane was cleaved with bromine to give the bromopropyl silane.



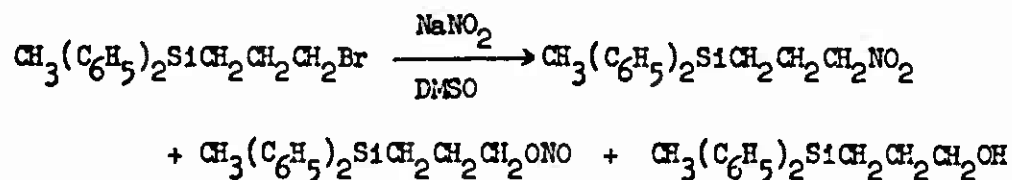
Another procedure, which appears to be more readily adaptable to scale-up, involves the addition of methyldiphenylsilane to allyl acetate, catalyzed by chloroplatinic acid, to give (3-acetoxypropyl)methyldiphenylsilane. The ester

was hydrolyzed with base to give (3-hydroxypropyl)methyldiphenylsilane.

p-Toluenesulfonyl chloride and pyridine in methylene chloride converted this alcohol to the p-toluenesulfonate, which, with lithium bromide in dimethyl sulfoxide, gave the desired bromide.



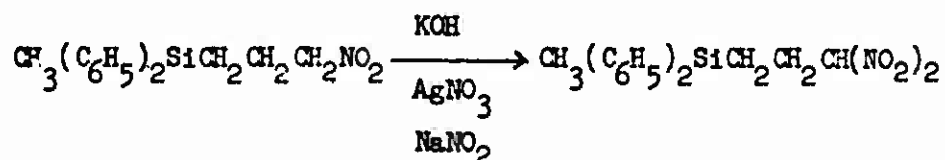
The reaction of (3-bromopropyl)methyldiphenylsilane with sodium nitrite in dimethyl sulfoxide was followed by NMR. A maximum yield was observed after a 40 min reaction period, with a slow loss of product in prolonged reactions. The corresponding nitrite and alcohol were also formed and the nitrite was slowly hydrolyzed to the alcohol under the reaction conditions. In a preparative experiment using a 40 min reaction time, a 50% isolated yield of (3-nitropropyl)methyldiphenylsilane was obtained.



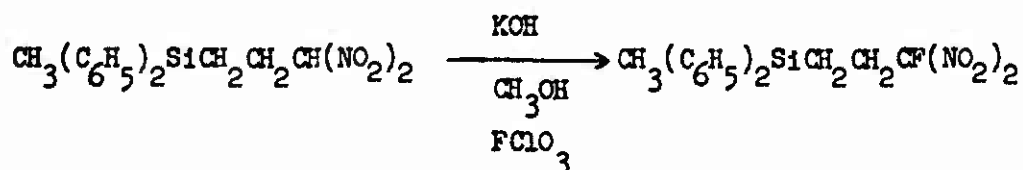
Leaving groups other than bromide were found to be less satisfactory. Thus, the chloride reacted at an impractically slow rate, whereas the toluenesulfonate

or methanesulfonate gave a higher proportion of nitrite in the product mixture.

The oxidative nitration of (3-nitropropyl)methyldiphenylsilane posed no special problems if relatively concentrated potassium hydroxide was used initially to form the salt of the starting material. A 70% yield of (3,3-dinitropropyl)methyldiphenylsilane was obtained as well as 8% recovered starting material.

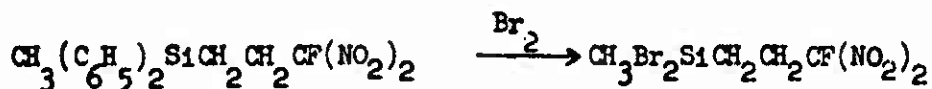


The aqueous fluorination of salts of this dinitro compound did not prove to be satisfactory because of acid-forming side reactions. Fluorination of the sodium salt until the solution was neutral resulted in a 75% recovery of starting material. Repeated addition of sodium hydroxide or potassium hydroxide followed by fluorination resulted in a low yield of impure fluorodinitro product. The potassium salt was fluorinated readily, however, when perchloryl fluoride was used as the fluorinating agent using the reaction conditions developed by Kamlet and Adolph.¹³ The perchloryl fluoride was absorbed completely until the reaction was complete, and a 79% yield of (3-fluoro-3,3-dinitropropyl)methyldiphenylsilane was isolated.

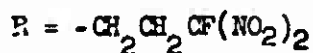
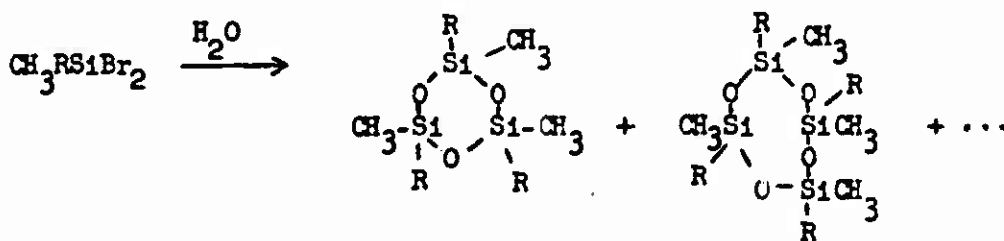


Dephenylation of (3-fluoro-3,3-dinitropropyl)methyldiphenylsilane was accomplished by heating it at 100° with excess bromine. This reaction gave a 78% yield of (3-fluoro-3,3-dinitropropyl)methyldibromosilane, which was characterized by proton and fluorine NMR, although it was too hygroscopic for elemental

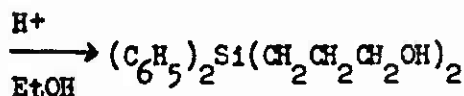
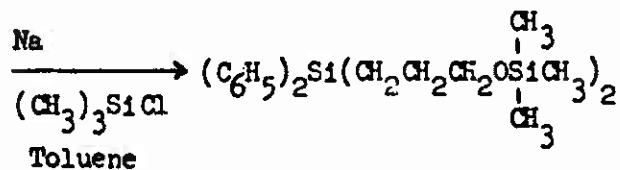
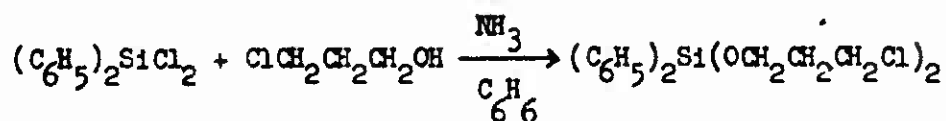
analysis.



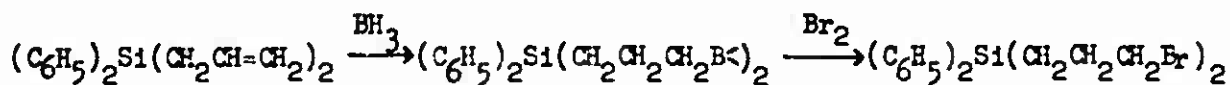
Hydrolysis of this dibromosilane with ice gave an oil that was shown by cryoscopic molecular weight determination (834) and by elemental analysis to consist of a mixture of cyclic polysiloxanes.



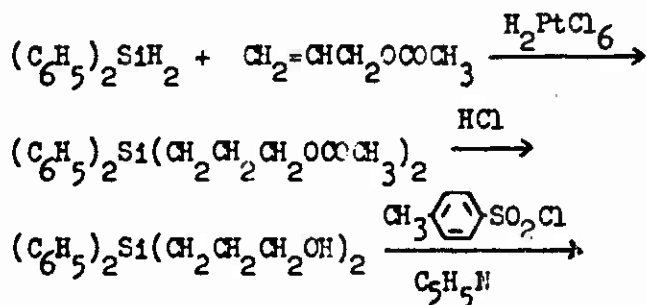
Work was also undertaken to prepare a more energetic polysiloxane, with a second fluorodinitropropyl group in place of the methyl group. The starting material for this work was prepared initially using a rearrangement of haloalkoxy silyl ethers to hydroxyalkyl silanes reported by Speier.¹⁴ Bis-(3-chloropropoxy)diphenylsilane was prepared by the reaction of diphenyldichlorosilane and 3-chloropropanol with ammonia in benzene. This product reacted with sodium and chlorotrimethylsilane in refluxing toluene to give bis-(3-trimethylsiloxypropyl)diphenylsilane. Hydrolysis with acid gave bis-(3-hydroxypropyl)diphenylsilane. This reaction is difficult to carry out on a large scale because rates of addition and the stirring rate must be controlled critically.

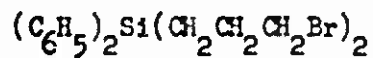
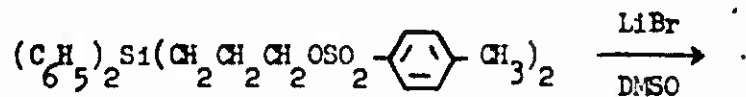


Another route to a difunctional starting material involved hydroboration. Borane in tetrahydrofuran was added to diallyldiphenylsilane, and the resulting borane was brominated to give bis-(3-bromopropyl)diphenylsilane in 24% overall yield.

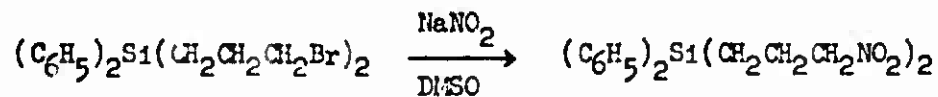


A more practical route for scale-up involved hydrosilylation. Thus, allyl acetate and diphenylsilane gave, with chloroplatinic acid catalysis, bis-(3-acetoxypentyl)diphenylsilane. Alkaline hydrolysis gave the diol, which, with p-toluenesulfonyl chloride and pyridine, was converted to the ditoluenesulfonate. Lithium bromide in dimethyl sulfoxide then gave the dibromide.





Displacement of bromide by nitrite was carried out in dimethylsulfoxide. In this case the ambident nature of the displacement, giving nitro and nitrite, presented a separation problem, but pure dinitro compound was isolated by a combination of column chromatography and recrystallization. A study of the oxidative nitration of this compound is in progress.



III. EXPERIMENTAL

4-Bromobutyltrimethylsilane. This compound was prepared by procedure of Perklev⁵ involving the preparation of the Grignard reagent from 4-bromo-1-butene, its reaction with trimethylchlorosilane to give 3-butenyltrimethylsilane, and free radical catalyzed HBr addition. The latter addition gave 90% primary bromide. One reaction using inadequate initiator gave mainly secondary bromide.

3-Bromopropyltrimethylsilane. This compound was prepared by the procedure of Sommer⁹, the reaction of chloromethyltrimethylsilane with magnesium and ethylene oxide to give 3-hydroxypropyltrimethylsilane followed by reaction with phosphorous tribromide.

4-Nitrobutyltrimethylsilane. To a solution of 1.9 g (0.028 mol) of sodium nitrite in 30 ml of dimethyl sulfoxide was added 2.92 g (0.014 mol) of 4-bromobutyltrimethylsilane. After 3 hrs, 30 ml of water was added and the mixture was extracted with three 15 ml portions of carbon tetrachloride. The carbon tetrachloride solution was washed with 10 ml of water and dried over magnesium sulfate. The NMR spectrum showed 30% nitrite ester (CH_2ONO δ 4.57), and 70% nitro compound. Distillation gave 1.1 g (45%) of 4-nitrobutyltrimethylsilane, bp 54-6° (0.9 mm). An analytical sample was isolated by GLC: NMR (CCl_4) δ 4.27 (t, J= 7 Hz, 2 H, CH_2NO_2), 2.02 (q, J= 7 Hz, 2 H, $\text{CH}_2\text{CH}_2\text{NO}_2$), 1.4 (m, 2 H, $\text{CH}_2\text{CH}_2\text{Si}$), 0.50 (m, 2 H, CH_2Si) and 0.0 (s, 9 H, $(\text{CH}_3)_3\text{Si}$); IR (CCl_4) 2960, 1545, 1435, 1385 and 1255 cm^{-1} .

Anal. Calcd for $\text{C}_7\text{H}_{17}\text{NO}_2\text{Si}$: C, 47.96; H, 9.77; N, 7.99. Found: C, 47.95; H, 9.70; N, 8.11.

3-Nitropropyltrimethylsilane. The reaction of 5.9 g (0.0315 mol) of 3-bromopropyltrimethylsilane with 3.24 g (0.047 mol) of sodium nitrite in 40 ml of dimethyl

sulfoxide by the above procedure gave a 28:56:16 ratio of nitrite to nitro to starting material and/or alcohol. Distillation gave 3.54 g (64%) of 90% pure 3-nitropropyltrimethylsilane, bp 55-8° (2 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, CH₂Si) and 0.0 (s, 9 H, (CH₃)₃Si): IR (CCl₄) 2970, 1545, 1430, 1380 and 1250 cm⁻¹. The NMR signals assigned to the nitrite were 5.0 (s, 9 H, CH₃Si), 0.5 (m, 2 H, CH₂Si), 1.6 (m, 2 H, CH₂CH₂CH₂) and 4.50 (t, J= 7, 2 H, CH₂ONO).

Anal. Calcd for C₆H₁₅NO₂Si: C, 44.69; H, 9.38; N, 8.68. Found: C, 44.74; H, 9.38; N, 8.67.

4,4-Dinitrobutyltrimethylsilane. A mixture of 0.6 g (0.015 mol) of sodium hydroxide, 2.62 g (0.015 mol) of 4-nitrobutyltrimethylsilane and 6 ml of water was stirred at 80° 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 hrs 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-dinitrobutyltrimethylsilane, a colorless oil, bp 71-4° (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= 7 Hz, 2 H, CH₂CH), 1.47 (m, 2 H, CH₂CH₂Si), 0.57 (m, 2 H, CH₂Si) and 0.0 (s, 9 H, (CH₃)₃Si); IR (CCl₄) 2970, 1570, 1330 and 1250 cm⁻¹.

Anal. Calcd for C₇H₁₆N₂SiO₄: C, 38.17; H, 7.32; N, 12.72. Found: C, 38.38; H, 7.32; N, 12.66.

3,3-Dinitropropyltrimethylsilane. The above procedure using 4.0 g (0.025 mol) of 3-nitropropyltrimethylsilane gave 2.1 g (40%) of 3,3-dinitropropyltrimethylsilane, a colorless oil, bp 70-72° (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) and 0.08 (s, 9 H, (CH₃)₃Si); IR (CCl₄) 2970, 1570, 1335 and 1260 cm⁻¹.

Anal. Calcd for C₆H₁₄N₂O₄Si: C, 34.94; H, 6.84; N, 13.58. Found, C, 35.28; H, 6.90; N, 13.47.

4-Fluoro-4,4-dinitrobutyltrimethylsilane. Fluorine diluted with nitrogen (1:5) was bubbled into an ice cooled stirred solution prepared from 1.45 g (0.0066 mol) of 4,4-dinitrobutyltrimethylsilane, 0.5 g of potassium hydroxide and 250 ml of water. When the yellow color of the solution was bleached, an additional 0.4 g of potassium hydroxide was added and the fluorination was continued until the color was bleached again. The product was extracted with three 20 ml portions of ether and dried over magnesium sulfate. Removal of the solvent gave 1.05 g (61%) of 90% pure 4-fluoro-4,4-dinitrobutyltrimethylsilane. An analytical sample was obtained by GLC: proton NMR (CCl₄) δ 2.67 (d of t, J_{HF} = 19 Hz, J_{HH} = 7 Hz, 2 H, CH₂CF), 1.44 (m, 2 H, CH₂CH₂Si), 0.53 (m, 2 H, CH₂Si) and 0.0 (s, 9 H, (CH₃)₃Si); fluorine NMR (CCl₄) δ 102.8 (broad t, (NO₂)₂CF); IR (CCl₄) 2970, 1590, 1350 and 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.

3-Fluoro-3,3-dinitropropyltrimethylsilane. By the above procedure, 1.6 g (0.0078 mol) of 3,3-dinitropropyltrimethylsilane gave 0.9 g of 60% pure 3-fluoro-3,3-dinitropropyltrimethylsilane (31% yield). An analytical sample was obtained by GLC: proton NMR (CCl₄) δ 2.57 (m, 2 H, CH₂CF), 0.50 (m, 2 H, CH₂Si) and 0.08

(s, 9 H, $(\text{CH}_3)_3\text{Si}$); fluorine NMR δ 106.0 (broad t); IR (CCl_4) 2970, 1590, 1320, 1260 and 1190 cm^{-1} .

Anal. Calcd for $\text{C}_6\text{H}_{13}\text{N}_2\text{O}_4\text{SiF}$: C, 32.13; H, 5.84; N, 12.49. Found: C, 32.34; H, 5.62; N, 12.43.

3,3-Dinitrobutyltrimethylsilane. A 3:2 mixture of 3-bromobutyltrimethylsilane and 4-bromobutyltrimethylsilane was treated with sodium nitrite to give the isomeric mononitro compounds. Oxidative nitration by the above procedure gave a mixture of 3,3-dinitrobutyltrimethylsilane and 4,4-dinitrobutyltrimethylsilane. The latter was removed from a carbon tetrachloride solution of the mixture by extraction with sodium hydroxide. An analytical sample of 3,3-dinitrobutyltrimethylsilane was isolated by GLC: NMR (CCl_4) δ 2.34 (m, 2 H, $(\text{NO}_2)_2\text{CCH}_2$), 2.02 (s, 3 H, $(\text{NO}_2)_2\text{CCH}_3$), 0.40 (m, 2 H, CH_2Si) and 0.05 (s, 9 H, $(\text{CH}_3)_3\text{Si}$); IR (CCl_4) 2970, 1565, 1330, 1260 and 1195 cm^{-1} .

Anal. Calcd for $\text{C}_7\text{H}_{16}\text{N}_2\text{O}_4\text{Si}$: C, 38.16; H, 7.32; N, 12.72. Found: C, 37.98; H, 7.19; N, 11.71.

Hydroxymethyltrimethylsilane. This compound was obtained by a published method¹¹ using the reaction of chloromethyltrimethylsilane with magnesium, followed by hydrolysis:

Trimethylsilylmethyl Trifluoromethanesulfonate. A solution of 4.5 g (0.0435 mol) of hydroxymethyltrimethylsilane 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° (9 mm). An analytical

sample was isolated by GLC: proton NMR (CCl_4) δ 4.07 (s, 2 H, CH_2Si), 0.08 (s, 9 H, $(\text{CH}_3)_3\text{Si}$); fluorine NMR δ 74.3 (s); IR (film) 1410, 1210, 1150, 960 and 870 cm^{-1} .

Anal. Calcd for $\text{C}_5\text{H}_{11}\text{O}_3\text{F}_3\text{Si}_3$: C, 25.40; H, 4.69. Found: C, 25.23; H, 4.65.

A minor side product which codistilled in the forerun was isolated by GLC and identified as bistrimethylsilylmethyl ether, $(\text{CH}_3)_3\text{SiCH}_2\text{OCH}_2\text{Si}(\text{CH}_3)_3$: NMR (CCl_4) δ 3.13 (s, 4 H, CH_2O) and 0.06 (s, 18 H, CH_3Si); IR (film) 2970, 2920, 2860, 2820, 1420, 1260, 1090 and 860 cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_{22}\text{Si}_2\text{O}$: C, 50.46; H, 11.64. Found: C, 50.52; H, 11.64.

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 trifluoromethanesulfonate and 2.3 g of 2-fluoro-2,2-dinitroethanol in 5 ml of methylene chloride, and the mixture was stirred for 16 hrs. 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° (0.75 mm). An analytical sample was prepared by GLC: proton NMR (CCl_4) δ 4.35 (d, 2 H, $J=18\text{ Hz}$, CH_2CF), 3.23 (s, 2 H, CH_2Si) and 0.02 (s, 9 H, $(\text{CH}_3)_3\text{Si}$); fluorine NMR (CCl_4) δ 110.25 (broad t); IR (film) 2975, 2925, 1600, 1320, 1250, 1125, 870 and 860 cm^{-1} .

Anal. Calcd for $\text{C}_6\text{H}_{13}\text{N}_2\text{O}_5\text{SiF}$: 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 hrs, 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 hr period. The solution was refluxed for 1 hr 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 one l portions of ether. The combined ether solutions were dried over magnesium sulfate and distilled to give 1397 g (73%) of allylmethyldiphenylsilane, bp 93° (0.1 mm): NMR (neat) δ 0.0 (s, 3 H, CH_3Si), 1.5 (d, $J = 7$ Hz, 2 H, $\text{C}=\text{C}-\text{CH}_2\text{Si}$), 1.5 (m, 2 H, $\text{CH}_2=\text{C}$), 5.3 (m, 1 H, $\text{C}=\text{CHCH}_2\text{Si}$), 6.6-6.9 (m, 10 H, C_6H_5); IR (film) 1640, 1440, 1270, 1170 and 1130 cm^{-1} .

Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_2\text{Si}$: 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 hr 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 reaction mixture was heated at reflux for 2.5 hrs and then 10 ml of methanol was added. Then, 27.3 ml (0.50 mol) of bromine and sodium methoxide solution (from 11.4 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 reaction mixture. The reaction temperature was kept at 25-30° by means of an ice bath. The reaction mixture was poured into a mixture of 250 ml of 50% potassium carbonate and 250 ml of cyclohexane. The

mixture was agitated 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 with 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° (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) and 7.2 (m, 10 H, C₆H₅).

Anal. Calcd for C₁₆H₁₉Br: C, 60.19; H, 5.96. Found: C, 60.36; H, 6.01.

(3-Hydroxypropyl)methyldiphenylsilane. Methyldiphenylsilane (100 g, 0.49 mol) was added at 90° over a period of 4 hrs, with stirring, to a mixture of 100 g (1.0 mol) of allyl acetate and 0.10 ml of a 0.1 M chloroplatinic acid solution in isopropanol. When half of the methyldiphenylsilane was added an additional 0.10 ml of the chloroplatinic acid solution was added. Excess allyl acetate was distilled 15 min after the addition was completed. The residue was dissolved in 150 ml of methanol and a solution of 20 g of sodium hydroxide in 40 ml of water was added dropwise. After the mixture was stirred for 2 hrs, 200 ml of water was added, and the mixture was neutralized with hydrochloric acid. The product was extracted with methylene chloride, dried over magnesium sulfate and distilled to give 65 g (50%) of (3-hydroxypropyl)methyldiphenylsilane, bp 130-140° (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, CH₂-O) and 7.0 (s, 10 H, C₆H₅).

(3-Propyl)methyldiphenylsilane p-Toluenesulfonate. p-Toluenesulfonyl chloride (3.5 g, 0.0184 mol) was added to a solution of 29 g (0.118 mol) of (3-hydroxypropyl)methyldiphenylsilane and 14.6 g (0.184 mol) of pyridine in 60 ml of

methylene chloride at 0°. The mixture was kept at 0-5° for 18 hrs and 40 ml of ice water was added. The water layer was extracted with 40 ml of methylene chloride, and the combined organic layers were washed with 2-30 ml portions of water. Solvent was removed and the product was crystallized from ether to give 46 g (95%) (3-propyl)methyldiphenyl p-toluenesulfonate, mp 68-69°: NMR (CDCl₃)

δ 7.3 (d of d, 4 H, C₆H₄-Si), 7.2 (broad s, 10 H, C₆H₅), 3.85 (t, J= 6.5, 2 H, CH₂O-), 2.40 (s, 3 H, CH₃-C₆H₄), 1.6 (m, 2 H, CH₂CH₂Si), 1.0 (m, 2 H, CH₂Si) and 0.50 (s, 3 H, CH₃Si).

Anal. Calcd for C₂₃H₂₆O₃SiS: C, 67.28; H, 6.38. Found: C, 67.44; H, 6.48.

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

(3-Nitropropyl)methyldiphenylsilane. 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° 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 with 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 hr 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 vaporated to give 45.4 g (50%) of (3-nitropropyl)methyldiphenylsilane. An analytical sample was obtained by molecular distillation: bp 152° (0.22 mm); NMR (CDCl_3) δ 0.3 (s, 3 H, CH_3Si), 1.2 (m, 2 H, CH_2Si), 2.1 (m, 2 H, $\text{CH}_2\text{CH}_2\text{Si}$), 4.2 (t, $J = 7$ Hz, 2 H, CH_2NO_2) and 7.3 (m, 10 H, C_6H_5); IR (film) 1550, 1435, 1395, 1260, 1190, 1165 and 1125 cm^{-1} .

Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2\text{Si}$: 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 hr. 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° 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 with saturated sodium chloride solution and dried over magnesium sulfate. The ether was removed and the NMR spectrum of the residue showed a 70% yield of (3,3-dinitropropyl)methyldiphenylsilane and starting material (8%). NMR (CDCl_3) δ 0.7 (s, 3 H, CH_3Si), 1.3 (m, 2 H, CH_2Si), 2.6 (m, 2 H, $\text{CH}_2\text{CH}_2\text{Si}$), 6.0 (t, $J = 7$ Hz, 1 H, CH) and 7.4 (m, 10 H, C_6H_5).

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

1440, 1370, 1330, 1270, 1200 and 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)methyldibromosilane. A mixture of 12.5 ml (0.230 mol) of bromine and 20.0 g (0.0574 mol) of (3-fluoro-3,3-dinitropropyl)methyldiphenylsilane was heated at 100° for 2 hrs under nitrogen. The product was evacuated at 25 mm at room temperature for 90 min. Distillation gave phenyl bromide, bp 60° (0.15 mm), a 0.5 g intermediate fraction, and 15.8 g (77.8%) of (3-fluoro-3,3-dinitropropyl)methyldibromosilane, a colorless liquid, bp 68° (0.14 mm): proton NMR (CDCl_3) δ 1.1 (s, 3 H, CH_3Si), 1.4 (m, 2 H, CH_2Si), and 2.9 (m, 2 H, $\text{CH}_2\text{CH}_2\text{Si}$): fluorine NMR (CDCl_3) ϕ 103.5 (t, 17 Hz). The material was too hygroscopic for commercial microanalysis.

(3-Fluoro-3,3-dinitropropyl)methylsiloxane. A solution of 14.2 g (0.0401 mol) of (3-fluoro-3,3-dinitropropyl)methyldibromosilane in 50 ml of ether was poured onto 75 g of crushed ice and the mixture was stirred for 30 min. The ether layer was washed with two 50 ml portions of water and with 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 hrs at 90° (0.07 mm) to give 7.7 g (91.4%) of an oily product: cryoscopic molecular weight (dioxane) 834; n_D^{20} 1.462; proton NMR (CDCl_3) δ 0.2 (s, 3 H, CH_3Si), 0.7 (m, 2 H, CH_2Si), 2.7 (m, 2 H, $\text{CH}_2\text{CH}_2\text{Si}$); fluorine NMR (CDCl_3) ϕ 104.1 (t, J = 17 Hz); IR (film) 3600, 3450, 2900, 2650, 1600, 1440, 1380, 1330, 1280, 1210, 1190 and 1080 cm^{-1} .

Anal. Calcd for $\text{C}_4\text{H}_7\text{N}_2\text{FO}_5\text{Si}$: C, 22.86; H, 3.33; N, 13.33. Found: C, 22.98; H, 3.55; N, 13.41.

Bis-(3-chloropropoxy)diphenylsilane. Anhydrous ammonia was passed through

a stirred solution of 81.6 g of 93% pure diphenyldichlorosilane (0.30 mol) and 56.7 g (0.60 mol) of 3-chloropropanol in 600 ml of dry benzene at 5° 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 176-9° (0.21 mm): NMR (CDCl₃) δ 1.95 (quintet, J = 6 Hz, 4 H, CH₂CH₂CH₂), 3.55 (t, J = 6 Hz, 4 H, CH₂OSi), 3.8 (t, J = 6 Hz, 4 H, ClCH₂) and 7-7.7 (m, 10 H, C₆H₅).

Anal. Calcd for C₁₈H₂₂O₂Cl₂Si: C, 58.54; H, 5.96. Found: C, 58.19; H, 5.90.

Bis-(3-trimethylsiloxypropyl)diphenylsilane. A round bottom flask charged with 25 ml of toluene and 2.71 g (0.118 mol) of sodium was fitted with a stirrer, a thermometer, a reflux condenser and a dropping funnel containing 12.95 g (0.119 mol) of chlorotrimethylsilane. The toluene was heated to reflux and sufficient chlorotrimethylsilane was added to lower the boiling point to 101°. Bis-(3-chloropropoxy)diphenylsilane (10 g, 0.027 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 refluxed for an additional 30 min period, cooled, filtered and distilled to give 3.3 g (28%) of bis-(3-trimethylsiloxypropyl)diphenylsilane, bp 156° (0.07 mm): NMR (CDCl₃) δ 0.0 (s, CH₃Si), 1.0 (m, 4 H, CH₂Si), 1.5 (m, 4 H, CH₂CH₂CH₂), 3.3 (t, J = 6 Hz, 4 H, CH₂OSi) and 7.0 (m, 10 H, C₆H₅).

Bis-(3-hydroxypropyl)diphenylsilane from Bis-(3-trimethylsiloxypropyl)-diphenylsilane. A solution of 3.3 g (7.44 mol) of bis-(3-trimethylsiloxypropyl)-diphenylsilane in 5 ml of 95% ethanol was acidified with one drop of concentrated hydrochloric acid and water was added to make the solution turbid (1 ml). After 30 min, the product was distilled to give 1.5 g (67%) of bis-(3-hydroxypropyl)-

diphenylsilane, bp 178-180 (0.07 mm), mp 83-84°: 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) and 6.9 (m, 10 H, C_6H_5); IR (film) 3300, 3050, 2900, 1430, 1190 and 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-hydroxypropyl)diphenylsilane from Bis-(3-chloropropoxy)diphenylsilane.

A round bottom flask charged with 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 trimethylchlorosilane. The toluene was heated to reflux and sufficient chlorotrimethylsilane was added to lower the boiling point to 101°. Bis-(3-chloropropoxy)diphenylsilane (80.6 g, 0.2185 mol) was mixed with the remaining trimethylchlorosilane and the mixture was added dropwise into the flask with vigorous stirring over a 30 min period. The solution was filtered and 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 hr, 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 180-220 (0.17 mm).



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°. The solution was stirred for 30 min at 0° and for 30 min at 20°. 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° by means of a water bath. Cyclohexane (100 ml) was added and the solution was extracted with 100 ml of 50% potassium carbonate. The aqueous layer was extracted with three 50 ml portions of cyclohexane. The combined organic layers were washed with two 100 ml portions of water and with 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° (0.06 mm): NMR (CDCl₃) δ 1.2 (m, 4 H, CH₂Si), 1.8 (m, 4 H, CH₂CH₂Si), 3.25 (t, J = 6 Hz, 4 H, BrCH₂) and 7.15 (m, 10 H, C₆H₅).

Anal. Calcd for C₁₈H₂₂Br₂Si: C, 50.70; H, 5.16. Found: C, 51.88; H, 5.35.

Bis-(3-hydroxypropyl)diphenylsilane by Hydrosilylation. To 25 g (0.25 mol) of refluxing allyl acetate was added 0.10 ml of 0.1 N H₂PtCl₆ in 2-propanol. Then 12 g (0.065 mol) of diphenylsilane was added dropwise over a period of 3 hrs. The solution was refluxed for 1 hr and the excess allyl acetate was distilled. The crude bis-(3-acetoxypropyl)diphenylsilane was dissolved in 30 ml of methanol and a solution of 5.2 g (0.13 mol) of sodium hydroxide in 10 ml of water was added. The mixture was stirred 2 hrs at room temperature and was then neutralized with hydrochloric acid. Water (100 ml) was added and the product was extracted with methylene chloride and stripped of solvent. The residue was chromatographed on a silica gel column eluting with methylene chloride and with 30% methanol in methylene chloride. Recrystallization from ether-petroleum ether gave 8 g (41%) bis-(3-hydroxypropyl)diphenylsilane, mp 83-4°.

Bis-(3-propyl)diphenylsilane Di-p-toluenesulfonate. 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°. After 20 hrs 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-propyl)diphenylsilane di-*p*-toluenesulfonate: NMR (CDCl₃) δ 7.4 (d of d, 8 H, , 7.2 (m, 10 H, C₆H₅), 3.97 (t, 4 H, CH₂O), 2.47 (s, 6 H, , 1.7 (m, 4 H, CH₂CH₂Si) and 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 the *p*-toluenesulfonate. A solution of 19.8 g (0.0325 mol) of bis-(3-propyl)diphenyl di-*p*-toluenesulfonate and 10 g (0.115 mol) of lithium bromide in 60 ml of dimethyl sulfoxide was stirred for 4 hrs. 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.

Similar results were obtained using sodium bromide instead of lithium bromide.

Bis-(3-nitropropyl)diphenylsilane. A solution of 5 g (0.0725 mol) of sodium nitrite and 11g (0.0258 mol) of bis-(3-bromopropyl)diphenylsilane in 50 ml of dimethyl sulfoxide was stirred for 1.5 hrs and then was diluted with 150 ml of water. The product was extracted with three 30 ml of portions of carbon tetrachloride. The carbon tetrachloride solution was washed with water, dried and solvent was removed. The residue was chromatographed on silica gel using an equal mixture of methylene chloride and carbon tetrachloride for elution.

Recrystallization from ether-petroleum ether gave 1.0 g (11%) of bis-(3-nitropropyl)diphenylsilane, white crystals, mp 84.5-85.5°: NMR (CDCl₃) δ 7.3 (s, 10 H, C₆H₅), 4.3 (t, 4 H, CH₂NO₂), 2.0 (m, 4 H, CH₂CH₂Si) and 1.1 (m, 4 H, CH₂Si); IR(CCl₄) 1540, 1430, 1380, 1120 and 710 cm⁻¹.

Anal. Calcd for C₁₈H₂₂O₄N₂Si: C, 60.31; H, 6.19; N, 7.81. Found: C, 60.15; H, 6.04; N, 7.62.

IV. REFERENCES

1. For reviews see: V. Bazant, V. Chvalovsky and J. Rathousky, "Organosilicon Compounds," Academic Press, New York, N.Y., 1965; W. Noll, "Chemistry and Technology of Silicones," Academic Press, New York, N.Y., 1968.
2. A. K. Hoffman, *et al.*, J. Am. Chem. Soc., **86**, 646 (1964); A. Hass and E. F. Riley, Chem. Rev., **32**, 373 (1943); A. Dronov, *et al.*, Ann., **585**, 220 (1954).
3. E. G. Rochow, U. S. Patent 2,380,995 (1941); A. L. Klebansky and V. S. Fikhtengolts, J. Gen. Chem. U.S.S.R., **27**, 2693 (1957); M. Vavuska, Chem. Listy, **51**, 319 (1957).
4. J. L. Speier and J. A. Webster, J. Org. Chem., **21**, 1044 (1956); E. W. Pietrusza, L. H. Sommer and F. C. Whitmore, J. Am. Chem. Soc., **70**, 484 (1948); V. A. Ponomarenko, V. G. Cherkaev, A. D. Petrov and N. A. Zadorozhnyi, Bull. Acad. Sci. USSR, Sect. Chem., 238 (1958).
5. T. Perklev, Svensk Kemisk Tidskrift, **65**, 216 (1953); Chem. Abstr., **49**, 1541 (1955).
6. N. Kornblum, R. K. Blackwood and D. D. Mooberry, J. Am. Chem. Soc., **78**, 1501 (1956).
7. R. B. Kaplan and H. Schechter, J. Am. Chem. Soc., **83**, 3535 (1961).
8. V. Grakauskas and K. Baum, J. Org. Chem., **33**, 7080 (1968).
9. L. H. Sommer, R. E. Van Strien and W. C. Whitmore, J. Am. Chem. Soc., **71**, 3056 (1949).
10. C. D. Beard, K. Baum and V. Grakauskas, J. Org. Chem., **38**, 3673 (1973).
11. H. Chih-tang and W. Pao-jen, Acta Chimica Sinica, **23**, 291 (1957);

Chem. Abstr. 52, 19911 (1958).

12. R. A. Benkeser and P. E. Brumfield, J. Am. Chem. Soc., 73, 4770 (1951); A. Ladenburg, Chem. Ber., 40, 2274 (1907); F. S. Kipping and N. W. Cusa, J. Chem. Soc., 1088 (1935).
13. M. J. Kamlet and H. G. Adolph, J. Org. Chem., 33, 3073 (1968).
14. J. L. Speier, J. Am. Chem. Soc., 74, 1003 (1952).

Appendix A

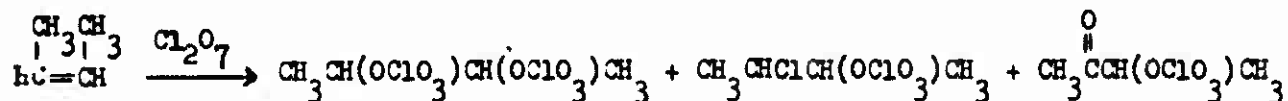
Reactions of Dichlorine Heptoxide with Olefins¹

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The reaction of dichlorine heptoxide in carbon tetrachloride with olefins was studied. Propene gave isopropyl perchlorate and 1-chloro-2-propyl perchlorate. Cis- and trans-2-butene gave 3-keto-2-butyl perchlorate, 2,3-butane dperchlorate and 3-chloro-2-butyl perchlorate; the latter was formed stereospecifically by trans addition. 2,3-Dimethyl-2-butene gave 2,2-diperchloratopropane and 2,2-dimethyl-3,3-diperchloratobutane which were also synthesized from the reactions of acetone and pinacolone with dichlorine heptoxide. The addition of water to dichlorine heptoxide in carbon tetrachloride provided a convenient anhydrous perchloric acid reagent, that with 1,1-difluoroethylene allyl chloride, propene and ethylene gave, respectively, 1,1-difluoroethyl perchlorate, 1-chloro-2-propyl perchlorate, isopropyl perchlorate and ethyl perchlorate.

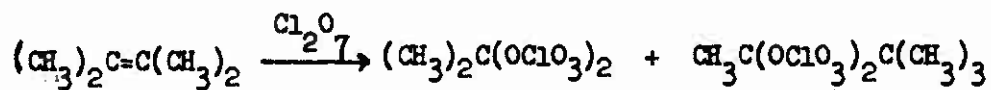
the first reported example of a carbonyl compound with a covalent perchlorate group.



trans-2-butene gave the same product mixture that cis-2-butene did, with the exception of the stereochemistry of the 3-chloro-2-butyl perchlorate. This product from the two olefins was distinguishable by GLC, and in each case only one isomer was observed. Structural assignments were made by synthesizing 3-chloro-2-butyl perchlorate from dichlorine heptoxide and 3-chloro-2-butanol of known configuration. Lucas and Garner⁶ showed that the addition of hydrochloric acid to the 2-butene oxides in stereospecifically a trans addition; cis-2-butene oxide gives threo-3-chloro-2-butanol and trans-2-butene oxide gives erythro-3-chloro-2-butanol. The reaction of dichlorine heptoxide with alcohols should not affect the carbon stereochemistry. It was found that the 3-chloro-2-butyl perchlorate thus prepared from cis-2-butene oxide was identical with that obtained from cis-2-butene and dichlorine heptoxide, and that from trans-2-butene oxide was identical with the trans-2-butene product. Thus, the formation of 3-chloro-2-butyl perchlorate from 2-butene and dichlorine heptoxide is a trans addition.

A completely substituted olefin, 2,3-dimethyl-2-butene, was also examined. A product insoluble in carbon tetrachloride was obtained that was identified as a mixture of 2,2-diperchloratopropane and 2,2-dimethyl-3,3-diperchloratobutane. The former was prepared previously from acetone and perchloric acid⁷, and the latter was characterized by the proximity of the NMR chemical shift of the methyl adjacent to the perchlorates to that of 2,2-diperchloratopropane.

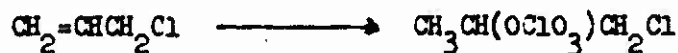
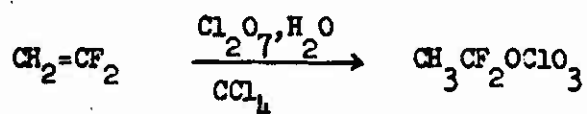
Treating the mixture in methylene chloride with sodium bicarbonate gave acetone and pinacolone.

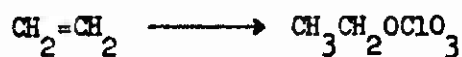
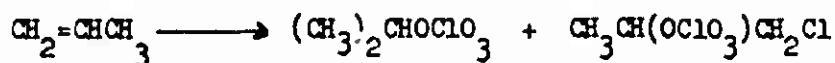


Both 2,2-diperchloratopropane and 2,2-dimethyl-3,3-diperchloratobutane were prepared, in yields of 70% and 52%, respectively, from the ketones and dichlorine heptoxide in carbon tetrachloride. This reaction is more convenient and provides higher yields than the anhydrous perchloric acid method⁷ for preparing gem-diperchlorates.



Electronegatively substituted olefins were unreactive with dichlorine heptoxide in carbon tetrachloride. Thus, 1,1-difluoroethylene and allyl chloride gave only trace amounts of 1,1-difluoroethyl perchlorate and 1-chloro-2-propyl perchlorate, respectively, the perchloric acid adducts, apparently resulting from the spurious introduction of water. The yields of these perchlorates were increased to 76% and 91%, respectively by introducing water into the reaction mixture. Under these conditions, propene gave a 65% yield of isopropyl perchlorate and a 10% yield of 1-chloro-2-propyl perchlorate. Ethylene was also unreactive with dichlorine heptoxide, but with water added, a 63% yield of ethyl perchlorate was obtained. The addition of water to the dichlorine heptoxide solution is an experimentally convenient source of small amounts of anhydrous perchloric acid for additions to olefins under mild conditions.





A gaseous product with the properties of chlorine dioxide was generally observed in the olefin-dichlorine heptoxide reaction mixtures. This compound would be formed when dichlorine heptoxide functions as an oxidizing agent; oxidation products have been observed previously in dichlorine heptoxide reactions^{4,5}. Chlorine dioxide has been reported⁸ to react with olefins to give trans-2-chloro alcohols, as well as epoxides and other oxidation products. This compound provides a possible route to the observed products from 2-butene, although other mechanisms are possible. The products from 2,3-dimethyl-2-butene are also attributable to oxidation reactions. Pinacolone would be obtained by the pinacol rearrangement of the epoxide or glycol, and acetone would be formed by an oxidative cleavage similar to the well-known reactions of periodic acid.

Experimental Section

NMR spectra were recorded with a Varian T-60 spectrometer and ir spectra were recorded with a Perkin-Elmer 700 spectrometer. A Varian 920 chromatograph was used for GLC determinations.

Dichlorine heptoxide was utilized as a 0.3 M reagent in carbon tetrachloride, prepared by the previously described method². Caution: alkyl perchlorates are sensitive explosives if not diluted with solvent, and previously noted precautions should be observed².

Reaction of Propene with Dichlorine Heptoxide. Dichlorine heptoxide in carbon tetrachloride (2 ml, 0.6 mmol) was placed in a 25 ml flask with a

magnetic stirrer and fitted with a stopcock syringe adapter. Air was partially removed by syringe and 3 ml (0.6 mmol) of propene was added. The mixture was stirred 24 hrs. A yellow gas soluble in carbon tetrachloride presumably ClO_2 , was removed by a brief application of vacuum. NMR analysis of the carbon tetrachloride solution showed isopropyl perchlorate (32% yield) and 1-chloro-2-propyl perchlorate (17%). Isopropyl perchlorate was identified by comparison with an authentic sample². An analytical sample 1-chloro-2-propyl perchlorate was isolated by GLC (5 ft x 0.25 in column of 12% QF-1 on Chromosorb W, 60°): NMR (CCl_4) δ 1.62 (d, 3 H, $J=6$ Hz, CH_3), 3.67 (d, 2 H, $J=7$ Hz, CH_2) and 5.17 (m, 1 H, CH); IR (CCl_4) 1005, 1230 and 1265 cm^{-1} .

Anal. Calcd for $\text{C}_3\text{H}_6\text{Cl}_2\text{O}_4$: C, 20.37; H, 3.42. Found: C, 20.08; H, 3.11.

1-Chloro-2-propyl Perchlorate. A 2:1 mixture of 1-chloro-2-propanol and 2-chloro-1-propanol was prepared from propylene oxide and hydrochloric acid by the reported method⁹. A sample of 1-chloro-2-propanol, the major component, was isolated by GLC (8 ft x 0.375 in column of 12% QF-1 on Chromosorb W, 70°). The compound (0.012 ml) was stirred with 1 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride for 16 hrs. The solution was washed with water and dried over sodium sulfate. The product was identical (NMR, IR and GLC) with the product from propene.

Reaction of cis-2-Butene with Dichlorine Heptoxide. Dichlorine heptoxide (0.6 mmol) and cis-2-butene (0.6 mmol) were reacted for 4 hrs by the procedure used with propene. Analysis by NMR based on methyl signals showed 0.18 mmol (30%) 3-chloro-2-butyl perchlorate and 0.012 mmol (2%) 3-keto-2-butyl perchlorate. A similar reaction with 0.5 g of lithium perchlorate added gave the same yield of 3-chloro-2-butyl perchlorate but 0.12 mmol (20%) of 3-keto-2-butyl

perchlorate.

Sufficient products for identification were obtained by adding 30 mmol of cis-2-butene to a mixture of 100 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride and 10 g of lithium perchlorate at 0°. After 2 hrs of stirring at ambient temperature, the solution was washed with water, dried over sodium sulfate, and passed through a 2 x 32 cm slurry-packed column of silica gel. The product was eluted with carbon tetrachloride and the eluent was monitored by NMR. The 3-chloro-2-butyl perchlorate was contained in the first 100 ml of eluent. The next 50 ml contained no product, and the following 250 ml contained 3-keto-2-butyl perchlorate. The solutions of both compounds were concentrated to 25 ml by vacuum distillation with a Holzmann column, and analytical samples were isolated by GLC. The solution containing the 3-chloro-2-butyl perchlorate was distilled at ambient temperature into a -78° receiver at 20 to 0.1 mm. The residue, dissolved in carbon tetrachloride, was shown by NMR to contain 1.5 mmol (5%) of 2,3-butane diperchlorate⁴. 3-Chloro-2-butyl perchlorate was isolated from the distillate by GLC using a 5 ft x 0.25 in column of 12% QF-1 on Chromosorb W, 100 cc/min helium, 70°, 15 min: NMR (CCl₄) δ 1.55 (d, 3 H, J= 6 Hz, CHClCH₃), 1.58 (d, 3 H, J= 6 Hz, CHClO₄CH₃), 4.25 (m, 1 H, CHCl) and 5.05 (m, 1 H, CHClO₄); IR (CCl₄) 1230 and 1265 cm⁻¹; the mass spectrum showed peaks at m/e 63, 65 (C₂H₄Cl), 91, 93 (C₄H₈Cl), 127, 129 (C₂H₄ClO₄) and 175, 177, 179 (C₃H₅Cl₂O₄).

A sample of 3-keto-2-butyl perchlorate was isolated from its carbon tetrachloride solution by GLC (5 ft x 0.25 in column of 12% QF-1 on Chromosorb W, 100 cc He(min, 90°, 10 min retention time): NMR (CCl₄) δ 1.61 (d, 3 H, J= 7 Hz, CH₃CH), 2.30 (s, 3 H, CH₃CO) and 5.12 (q, 1 H, J= 7 Hz, CHCH₃); IR (CCl₄) 1720 (C=O), 1020, 1240 and 1270 cm⁻¹ (ClO₄).

Anal. Calcd for $C_4H_7ClO_5$: C, 28.17; H, 4.13. Found: C, 28.32; H, 4.10.

Reaction of trans-2-Butene with Dichlorine Heptoxide. The reaction of trans-2-butene with dichlorine heptoxide proceeded in the same manner as that of cis-2-butene, and the product mixtures were indistinguishable with the exception of the stereochemistry of the 3-chloro-2-butyl perchlorate. Its GC retention time was 16 min, compared to 15 min for the product from cis-2-butene described above.

3-Chloro-2-butyl Perchlorates. Preparative GLC of commercial 2-butene oxide, a mixture of cis and trans isomers (0.375 in x 12 ft column of 12% QF-1 on Chromosorb W, 100 cc/min He, 24^o) gave trans-2-butene oxide, retention time 20 min, n_D^{20} 1.3741 (reported n_D^{20} 1.3736) and cis-2-butene oxide, retention time 26 min, n_D^{20} 1.3821 (reported n_D^{20} 1.3826). To 0.015 ml of trans-2-butene oxide and to 0.030 ml of cis-2-butene oxide, each in a GC collection tube, was added 0.15 ml of concentrated hydrochloric acid at 0^o, and the mixtures were kept at ambient temperature for 1 hr. Each product was extracted with 0.1 ml of methylene chloride after 0.15 ml of water was added. The crude chlorohydrins, 0.008 ml from trans-2-butene oxide and 0.02 ml from cis-2-butene oxide, were each added to 1 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride. After 24 hrs, each reaction mixture was washed with 0.5 ml of water and dried over sodium sulfate. NMR showed only 3-chloro-2-butyl perchlorate. Mixed GLC showed that the product from cis-2-butene oxide was identical with that from cis-2-butene and dichlorine heptoxide, and the product from trans-2-butene oxide was identical with that from trans-2-butene and dichlorine heptoxide.

Reaction of 2,3-Dimethyl-2-butene with Dichlorine Heptoxide. 2,3-Dimethyl-2-butene (0.0708 g, 0.84 mmol) was added to 15 ml of 0.3 M dichlorine heptoxide

at -10° . The mixture was kept at -10° for 18 hrs in order to allow the product to separate, although the reaction appeared to be substantially complete in 1 hr. The liquid product, lighter than carbon tetrachloride, was separated. The NMR spectrum (CDCl_3) showed only prominent peaks assigned to 2,2-diperchloratopropane⁷ and to 2,2-dimethyl-3,3-diperchloratobutane. Quantitative NMR using chloroform as a standard and CD_3NO_2 as solvent because of higher product solubility, showed 0.195 mmol (11.6% based on 2 mols per mol olefin) 2,2-diperchloratopropane and 0.195 mmol (23%) 2,2-dimethyl-3,3-diperchloratobutane.

Reaction of Ketones with Dichlorine Heptoxide. Acetone (0.044 ml, 0.60 mmol) was added to 3 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride at -5° . A separate liquid phase formed immediately: NMR (CDCl_3) δ 2.59 (s) identical with that reported for 2,2-diperchloratopropane⁷. The yield, 70%, was determined by quantitative NMR allowing a similar reaction mixture to stand 18 hrs at -20° , removing the carbon tetrachloride by syringe, and dissolving the product in 1 ml of CD_3NO_2 : δ 2.61.

By the same procedure, pinacone gave 2,2-dimethyl-3,3-diperchloratobutane (52%): NMR (CDCl_3) δ 1.28 (s, 9 H), δ 2.48 (s, 3 H); NMR (CD_3NO_2) δ 1.33 (s, 9 H), δ 2.67 (s, 3 H).

Reactions of Olefins with Perchloric Acid. Water (0.0080 g, 0.44 mmol) was stirred with 2 ml of 0.3 M dichlorine heptoxide in carbon tetrachloride for 30 min in a 25 ml flask fitted with a syringe valve. The flask was evacuated partially and 0.6 mmol of 1,1-difluoroethylene was added by syringe. NMR analysis using chlorobenzene as a quantitative reference showed only 1,1-difluoroethyl perchlorate (0.46 mmol, 76%): proton NMR (CCl_4) δ 1.95 (t, J = 14 Hz); fluorine

NMR δ 69.52 (q, J = 14 Hz); IR (CCl_4) 1390 (m), 1280 (vs), 1200 (s), 1150 (s), 1130 (s), 1030 (s), 970 (s) and 920 cm^{-1} (s).

By this procedure, propene gave isopropyl perchlorate (65%) and 1-chloro-2-propyl perchlorate (10%) in 24 hrs.

Allyl chloride gave 1-chloro-2-propyl perchlorate (91%) in 24 hrs by this procedure.

Ethylene gave ethyl perchlorate² (63%) in 24 hrs.

References

- (1) This work was supported by the Office of Naval Research.
- (2) K. Baum and C.D. Beard, J. Am. Chem. Soc., 96, 3233 (1974).
- (3) C.D. Beard and K. Baum, J. Am. Chem. Soc., 96, 3237 (1974).
- (4) K. Baum and C.D. Beard, J. Org. Chem., 40, 81 (1975).
- (5) K. Baum and C.D. Beard, J. Org. Chem., 40, 2536 (1975).
- (6) H. J. Lucas and H.K. Garner, J. Am. Chem. Soc., 70, 990 (1948).
- (7) K. Baum, J. Am. Chem. Soc., 92, 2927 (1970).
- (8) B.O. Lindgren, Acta Chem. Scand., 19, 7 (1965).
- (9) C.A. Stewart and C.A. VanderWerf, J. Am. Chem. Soc., 76, 1259 (1954).
- (10) C.E. Wilson and H.J. Lucas, J. Am. Chem. Soc., 58, 2399 (1936).