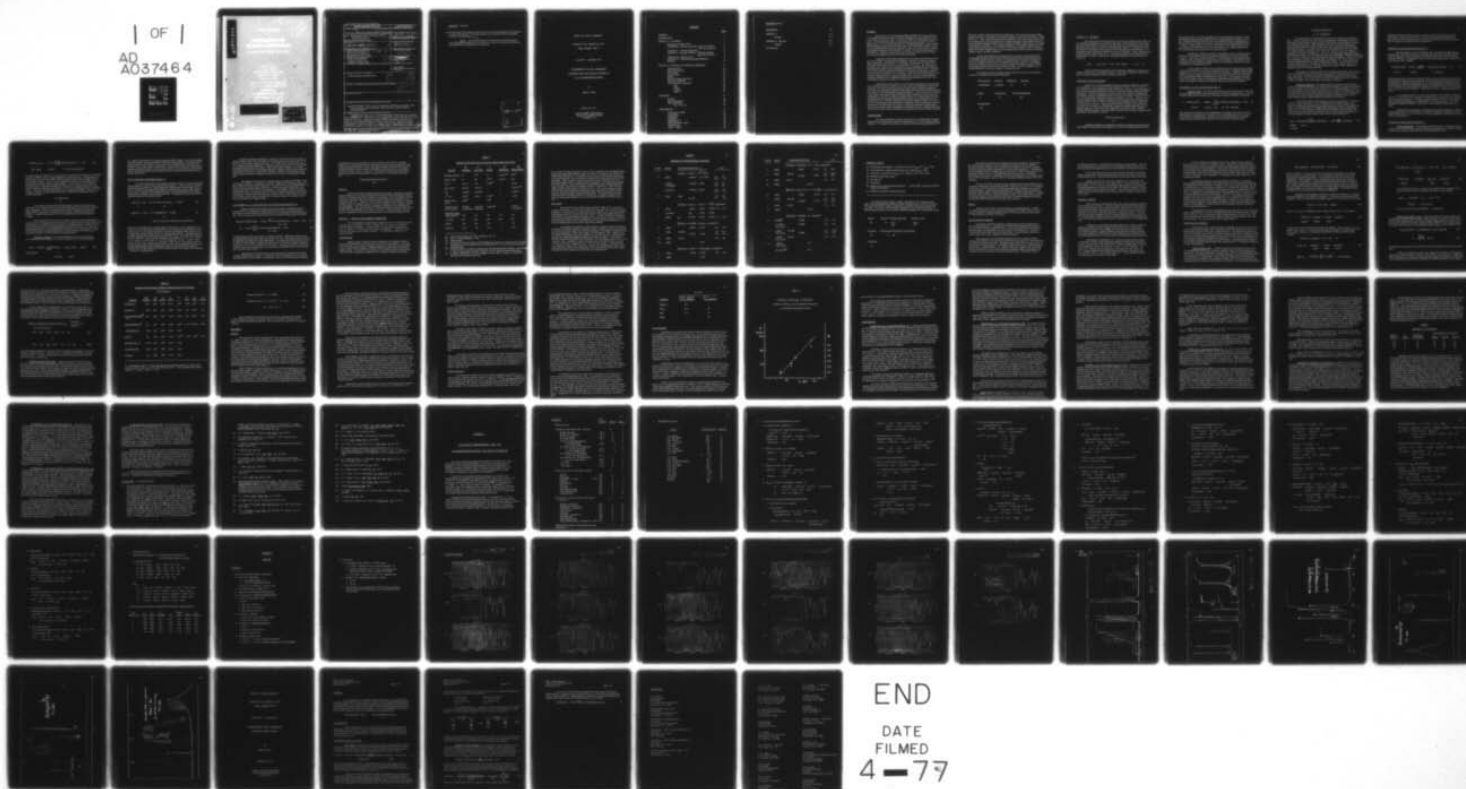AD-A037 464   UNION CARBIDE CORP TARRYTOWN N Y CHEMICALS AND PLAST--ETC F/G 19/1
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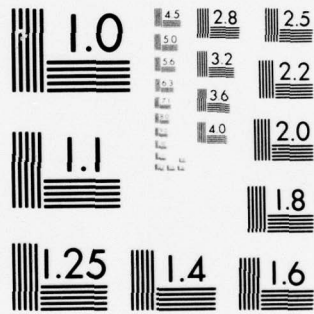   FEB 77 R S NEALE, T C WILLIAMS   N00014-75-C-0791

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MICROCOPY RESOLUTION TEST CHART

DEPARTMENT OF THE NAVY

Office of Naval Research
Arlington, Virginia

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Part I. Silane esters of 2,2,2-fluorodinitroethanol (ROH) have been prepared from chlorosilanes in ~90% yields. The non-compressive shock sensitivity of the high density (1.95 g/cc), crystalline orthoester $(\overline{RO})_4$Si was clearly lower than that of RDX, but the calculated detonation velocities proved similar. Substantially higher boiling points at similar densities (~1.6 g/cc) relative to the reference compound FEFO were realized in the liquid esters $(\overline{RO})_3$SiCH$_3$ and $(\overline{RO})_2$(CH$_3$)SiOSi(CH$_3$)$(\overline{OR})_2$

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ABSTRACT - continued

The sensitivity of the thermally stable product esters toward hydrolysis by atmospheric moisture varied greatly. The energy contents Q of a number of silicon-containing structures were calculated.

Part II. The successful Mannich condensation of fluorodinitroethanol with aminomethyltrimethylsilane is described as a model for the potential high energy functionalization of aminoalkylsilicone polymers.

OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-75-C-0791

FINAL REPORT PART I

April 1975 - September 1976

FLUORODINITRO SILICON COMPOUNDS.

ORGANOSILICON AND SILICATE ESTERS OF

2,2,2-FLUORODINITROETHANOL

by

Robert S. Neale

February 28, 1977

UNION CARBIDE CORPORATION
Chemicals and Plastics Division
Tarrytown, N.Y.

CONTENTS

CONTENTS (cont'd.)

SUMMARY

Silane esters of 2, 2, 2-fluorodinitroethanol (FDNE) have been prepared in ~ 90 % yields by the direct reaction of the alcohol (ROH) with chlorosilanes at 25-70° in the absence of a solvent. One to 1.5 moles of FDNE were employed for each Si-Cl group. The compounds obtained in good purities and useful amounts were III-V, $(RO)_x SiMe_{4-x}$, x = 2-4, and the disiloxane VII, $(RO)_2MeSiOSiMe(OR)_2$, whose ordinary physical properties and multinuclear nmr spectra are summarized in Tables I and II. Less successful syntheses and some alternative routes are also described, especially the attempted hydrolysis of the orthoester V, $(RO)_4Si$, to the linear polysiloxane VI, $+OSi(OR)_2+_x$. Analysis of mixtures of closely related structures such as V and VI was greatly facilitated by the use of ^{29}Si-nmr spectroscopy.

Comparison of the physical properties of the silane esters with those of the reference explosive compound FEFO $(ROCH_2OR)$ revealed a considerably extended upper liquid range in the trisester IV, $(RO)_3SiMe$, and disiloxane VII without loss of substantial lower range values at similar densities (~1.6 g/cc). The sensitivity of the silane esters was low to non-compressive shock, resembling that of the explosive Tetryl rather than RDX; direct comparision with FEFO has not been made. The stability of the esters towards ambient, atmospheric moisture varied greatly according to structure from very good (III, VII) to poor (V), and in the case of the trisester IV was observed to depend upon the % relative humidity; thus, IV was reasonably stable to significant liberation of free FDNE and formation of polysiloxanes only at RH < 40 %. The densities varied from 1.4 (III) to 1.95 g/cc (V).

Calculations were carried out, in lieu of actual experimental measurements, of the estimation of heats of formation, energy contents, and detonation pressures and velocities in the esters prepared as well as in some related, presently hypothetical structures; the compounds encompassed high energy groups bound to Si by both hydrolyzable (oxygen) and non-hydrolyzable groups (methylene). The results (Table III) suggest a good, linear relationship between the density and the detonation velocity in the four compounds III-V and VII, as might be anticipated from their closely related structures. Although the energy contents Q remained about constant, an incremental increase in the quantity $\emptyset$ of ~0.5 unit was found for each OR group added to Si after two; the trisester IV corresponded closely with FEFO in theoretical maximum detonation properties. Comparison of Q and $\emptyset$-values for $SiCH_2R$ vs SiOR type compounds revealed larger $\emptyset$-values in the former but a coincidence of the ultimate $\emptyset$-values, implying little difference in the two types of silanes in detonation energy characteristics at similar densities.
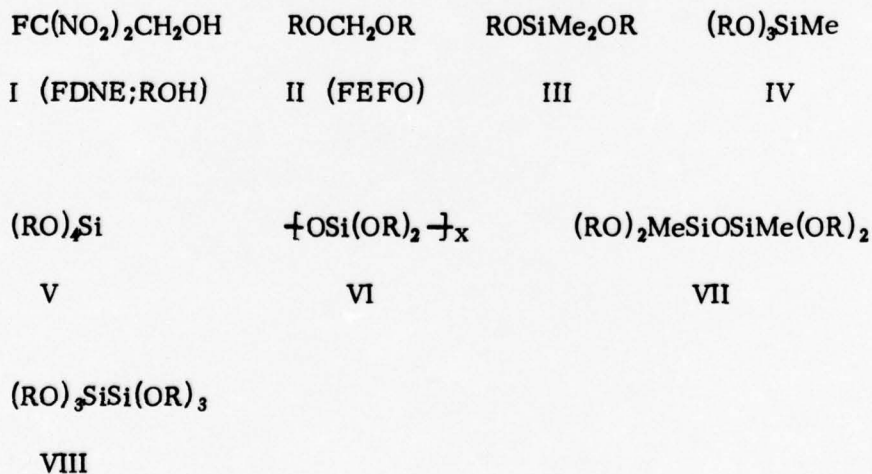
INTRODUCTION

We report herewith the results of that phase of our studies under the subject contract and its extension which deals with silicon esters of 2, 2, 2-fluorodinitroethanol (FDNE, I). The object of the work was to determine whether target compounds III-VIII

and others could be prepared and with what efficiencies, and to ascertain certain of their physical properties, especially the useful liquid ranges as compared to the formal of FDNE (FEFO, II). Thus, it had been proposed that substitution of the central CH_2 group in FEFO by the $SiMe_2$ group to give III might afford the desired increase in liquid range, and that related compounds bearing differing numbers of methyl and FDNE residues per Si atom might similarly prove of interest. The anticipated application of the target compounds as plasticizing liquids potentially superior to FEFO in high energy compositions and in related potential uses further suggested that the characterization data include estimates of hydrolytic stability, density and shock sensitivity.

As the result of informal discussions with the contract manager during 1976, certain additional information on thermochemical properties has been provided and the work emphasis shifted toward the study of "non-hydrolyzable" high energy compounds of silicon, as outlined in the Proposal for Extension of the subject contract. Accordingly, the results obtained to date on the target ester compounds are gathered together in this formal report, which covers the first 6 quarters of work. Our work continues to be reported informally to the project manager on a quarterly basis.

The target esters and related structures referred to above are the following, in which "R" designates the moiety $FC(NO_2)_2CH_2-$.

$FC(NO_2)_2CH_2OH$ $ROCH_2OR$ $ROSiMe_2OR$ $(RO)_3SiMe$

I (FDNE;ROH)   II (FEFO)   III   IV

$(RO)_4Si$ $+OSi(OR)_2+_x$ $(RO)_2MeSiOSiMe(OR)_2$

V   VI   VII

$(RO)_3SiSi(OR)_3$

VIII

RESULTS A. SYNTHESIS

The preparation and characterization of each target compound (except VIII) was accomplished as described in the following subsections. Some comments on the purification of purchased FDNE are included, since the purity of the starting alcohol was a dominant factor in the general success of the esterification reaction 1. This general reaction was uniformly successful in the preparation of the monosilanes and the disiloxane, requiring only minor operational variations for each new compound. Usually, stoichiometric amounts of alcohol could be used $(n = x)$. The physical properties of the compounds are drawn together in Table I, along with the calculated detonation values from the Results, Section B.

$$x \ ROH \ + \ Me_{4-x}SiCl_x \longrightarrow Me_{4-x}Si(OR)_x \ + \ x \ HCl \quad (1)$$

As part of the characterization of each compound, complete nmr spectra were obtained. The results are presented in Table II rather than compound-by-compound in order to facilitate comparisons and accessibility of the data.

Purification of Fluorodinitroethanol

Shortly into our initially planned laboratory synthesis of FDNE via 2, 2-dinitro-1, 3-propanediol,[1] we were able to purchase a quantity of FDNE from Fluorochem, Inc., and our work was subsequently carried out with this material. Information supplied by Fluorochem stated this material to derive from Aerojet's synthesis based on dinitropropanediol. Our initial esterification reaction results, nmr analysis, and distillation revealed the presence of substantial amounts of water in the alcohol (~20 mol-%; 2-3 wt-%) and of high boiling, apparently polymeric materials (~ 5 wt-%). Water is a particular problem because it leads to condensation of chlorosilanes through formation of siloxane bonds Si-O-Si, in competition with the desired esterification, and to hydrolysis of the silane ester products. Drying methylene chloride solutions of the alcohol over molecular sieves (Linde 4A) and subsequent distillation provided FDNE free of all impurities except one. This proved to be compound IX, the mixed formal of FDNE, methanol and formaldehyde, which was slightly concentrated in the higher boiling fractions and present to the extent of 2-6 wt-% .

$$FC(NO_2)_2CH_2OCH_2OCH_3$$
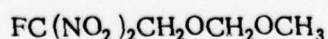
IX

Although the mixed formal impurity IX could not be entirely removed from distilled FDNE, its concentration was reduced to 2-4 mol-% by distilling the sieve-dried
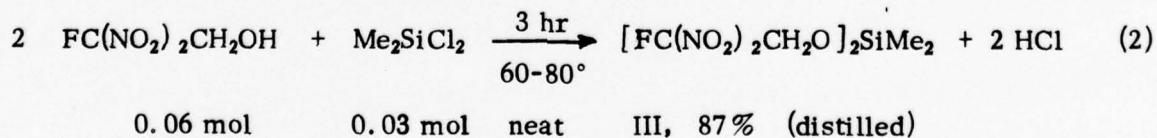
crude alcohol from ~0.4 wt-% conc H_2SO_4 at a bp not exceeding 45°C; similar results obtained upon distilling undried FDNE from acid, except that water collected as a fore-run. Repeated experience showed 70-85 wt-% of distilled FDNE was obtainable from 50-100 g samples of the dried crude while restricting the average concentration of IX to ~ 3 wt-%. Further efforts to remove IX completely were not made because it failed to participate in the esterification reaction and could be more readily stripped from the crude products than removed from the starting alcohol.

Unambiguous, although not rigorous, identification of IX was possible without isolation of a pure sample from its bp,[2] careful examination of the H-nmr spectrum[2] (Table II), and ^{13}C-nmr spectrum (Table II), whose absorption at 96.9 ppm downfield vs TMS was characteristic of the dioxymethylene carbon OCH_2O.[3] Determination of the concentration of IX in FDNE was readily carried out by integration of the H-nmr peaks, as detailed in the Experimental Section.

A small sample of FDNE was also obtained from Fluorochem which was stated to derive from Rockedyne's process involving fluoronitroform. Distillation yielded FDNE containing only 1-?% of IX, and little if any water was present. However, bulk samples recently received directly from Rockedyne have been found to contain 5-10 wt-% water and to yield distilled FDNE containing 2-4% of the formal. This material thus appears to have had an origin similar to that originally obtained and described above; it is being used for the studies involving non-hydrolyzable high energy silanes now underway.

Dimethyl(bis-2,2,2-fluorodinitroethoxy)silane, III

Preferred route. The silane bisester III was best prepared directly from FDNE and dimethyldichlorosilane in approximately the stoichiometric amounts (eq 2). Although distilled FDNE and pure Me_2SiCl_2 were used under anhydrous conditions, an impurity

$$2 \quad FC(NO_2)_2CH_2OH \ + \ Me_2SiCl_2 \ \xrightarrow[\substack{60-80°}]{3\ hr} \ [FC(NO_2)_2CH_2O]_2SiMe_2 \ + \ 2\ HCl \qquad (2)$$

$$0.06\ mol \qquad\qquad 0.03\ mol \quad neat \qquad III, \ 87\% \ \ (distilled)$$

that could not be removed even upon redistillation was obtained to the extent of 2 mol-% and identified as the disiloxane X. Distillation of III proceeded readily on a 10 g scale with no sign of instability of the compound, which proved amenable to gas chromatographic analysis and preparative separation of X at 200-250° in a glass column.

$$RO\,Si(Me)_2\,OSi(Me)_2\,OR$$
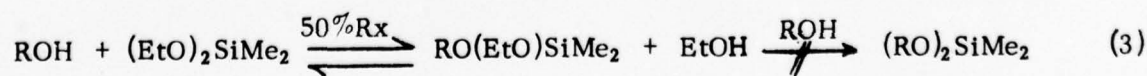
$$X, \quad R \equiv CH_2CF(NO_2)_2$$
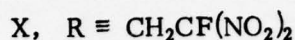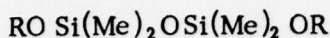
Characterization of III followed from the method of synthesis and analytical data. H-Nmr was particularly useful in that the progression toward higher field of the absorption of methyl groups of types Cl_2SiMe_2, $Cl(RO)SiMe_2$, and $(RO)_2SiMe_2$ facilitated one's following the progress of the esterification reaction; formation of disiloxane X during the latter stages of reaction was apparent from the still higher field absorption of its methyl protons. The shifts, relative areas, and coupling constants of the protons in III and the observed resonances of the methyl ^{13}C, ^{29}Si and ^{19}F were all completely consistent with structure III (Table II). There was a marked progression toward lower field (relative to TMS) of the ^{29}Si resonance in the series $(RO)_2SiMe_2$, $(RO)_3SiMe$, $(RO)_4Si$, but the ^{19}F and ^{13}C resonances in all three compounds remained constant. The proton decoupled $^{13}CH_2$ appeared as a strong, sharp doublet (due to coupling to ^{19}F), which affords a particularly distinct identification of the $FC(NO_2)_2CH_2O-$ residue. The elemental analysis of III was satisfactory in H, F and N but slightly incorrect for C and Si, whether or not allowing for the presence of X. Physical properties are given in Table I and further discussed in Part B of the Results Section.

The sample of X obtained in 95% purity by preparative glpc was characterized by H-nmr, which disclosed a ratio of CH_3 to RO groups of 2:1 rather than the 1:1 ratio in III, and ^{13}C-nmr, in which the distinctive absorption of carbons of the formal type OCH_2O was absent. The ir spectrum of X was nearly identical to that of III, except that stronger absorption in the SiOSi region was evident at ~1050 cm^{-1}.

Alternative syntheses. Two probing experiments quickly established that reaction 2 was adversely affected by the presence of stoichiometric amounts of dry pyridine as an HCl acceptor, since reactions in chloroform at 5° or dimethoxyethane at 20° produced several-fold increases in the disiloxane X at the expense of III. This result reflects the normal behavior of chlorosilanes during alcoholysis, which is known[4] to result in the formation of di- and trisiloxanes along with the desired monosilane esters; however, bases normally reduce siloxane formation by acting as HCl acceptors.

A second alternative to the preparation of III was also explored. Transesterification of lower silane esters, such as $(MeO)_2SiMe_2$, with FDNE should yield III. Since the commercial methoxysilane compound was grossly impure and not readily upgraded, trial equilibrations were conducted with $(EtO)_2SiMe_2$ instead. Equilibration of neat, 2:1 or 4:1 molar mixtures of FDNE and the ethoxysilane occurred within a few minutes at 35° in nmr tubes in the presence of HCl or H_2SO_4 catalysts but failed to involve any significant reaction of the second of the two ethoxy groups (eq 3).
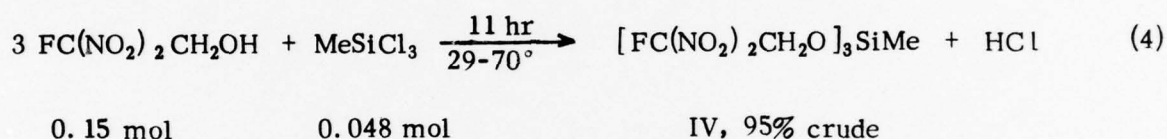
$$ROH + (EtO)_2SiMe_2 \underset{\longleftarrow}{\overset{50\%Rx}{\longrightarrow}} RO(EtO)SiMe_2 + EtOH \overset{ROH}{\not\longrightarrow} (RO)_2SiMe_2 \quad (3)$$

(FDNE)   1 mole

2-4 moles

Continuous removal of ethanol is clearly called for to drive the equilibrium forward.
Unfortunately, ethanol is known[5] to form an azeotrope with the starting ethoxysilane,
and our study of the transesterification procedure was consequently not further pursued
until work began on the preparation of the orthoester V.

Methyl(tris-2,2,2-fluorodinitroethoxy)silane, IV

The stoichiometric reaction of distilled, 96% pure FDNE with 96% $MeSiCl_3$,
containing 4% of the dichlorosilane impurity Me_2SiCl_2, proceeded as illustrated in eq 4.
A Dry Ice condenser was now employed to prevent entrainment loss of the chlorosilane
by the liberated HCl. A single phase reaction mixture was attained only at or above 40°C.
The 22.8 g of crude IV obtained

$$3 \ FC(NO_2)_2CH_2OH \ + \ MeSiCl_3 \ \xrightarrow[29-70°]{11 \ hr} \ [FC(NO_2)_2CH_2O]_3SiMe \ + \ HCl \qquad (4)$$

0.15 mol   0.048 mol   IV, 95% crude

following high vacuum removal of remaining volatiles, such as the formal impurity in the
starting alcohol, appeared spectroscopically pure except for the small amount of bisester
III expected from the dichlorosilane impurity. Safety considerations dictated that only a
small sample be subjected to distillation because of the anticipated very high boiling point,
but the procedure was accomplished without incident to yield 80 wt % of the 4 g pot charge as
pure, colorless trisester IV (Table I). The forerun, 8 wt-%, contained the bisester im-
purity.

A second preparation of IV, carried out using 100% pure $MeSiCl_3$, yielded 35 g
(100 wt-%) of crude IV, free of volatiles, following 10.5 hr reaction at 40-75° and high
vacuum distillative stripping. No bisester was now present, but ~5 wt-% of an only par-
tially esterified silane believed to be $(RO)_2ClSiMe$ was present, along with ~5% of the
disiloxane $(RO)_2MeSiOSiMe(RO)_2$ (compound VII, also synthesized preparatively; see
below).

Characterization of trisester IV followed from the method and yield of synthesis
and nmr data (Table II). Although the C, H elemental analyses were satisfactory, the F, N
and Si values were all ~1% low; however, we do not consider this to detract from the cer-
tainty of the structure IV.

Tetrakis(2,2,2-fluorodinitroethoxy)silane, V

Preferred synthesis. The preparation of the orthoester V according to the gen-
eral reaction 1 required a 50% excess if FDNE (largely recoverable) to ensure complete
reaction of the silicon tetrachloride under convenient conditions (eq 5).

$$FC(NO_2)_2CH_2OH \quad + \quad SiCl_4 \xrightarrow[11.5\ hr]{40-70°} [FC(NO_2)_2CH_2O]_4Si \quad + \quad HCl \qquad (5)$$
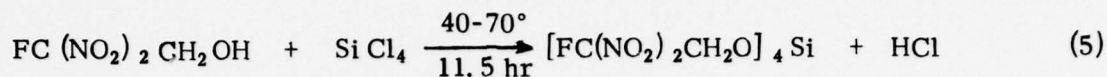
50% excess   0.20 mol   V, 90% (recrystallized)

The chlorosilane was added at 40° in four portions at hourly intervals because of its limited
solubility in FDNE; a Dry Ice reflux condenser was again necessary. Following high vac-
uum removal of excess alcohol (81% of the theoretical amount) along with 50% of the or-
iginal formal impurity, ~15 g of a solid remained which was twice recrystallized from
hot chloroform to afford the final product (Table I). A sharp mp never was observed,
doubtless because of the extreme hydrolytic sensitivity of V toward ambient and surface
moisture and the accumulation of disiloxane XI, which recrystallization failed to completely
remove. Similarly, the elemental analyses were not entirely acceptable (~1% low F and
N values), and nmr spectra showed the presence of FDNE and the disiloxane XI due to
transient hydrolysis.

$$(RO)_3SiOSi(OR)_3$$
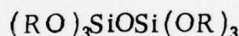
XI

The characterization and purity determinations carried out using the usual
multinuclear nmr analyses therefore gave results dependent upon the particular samples
under examination. The purity results reported are therefore minimum values and,
judging from the experience of handling several samples, probably not typical of the
product as originally obtained after the first recrystallization and before subsequent
handling.

Nmr spectra (Table II) were now recorded in deutero-acetone (although an in-
herently "wetter" solvent than chloroform) because V is insoluble in the latter until heated. The
concentration of free FDNE (in the nmr sample) was estimated from the H-nmr spectrum,
and the relative amounts of V and disiloxane XI from the ^{29}Si spectrum. The latter was
particularly appropriate in differentiating different types of Si as a function of the number
of OR and other types of groups attached; this is well illustrated in the analysis of the
hydrolysis products of V as described in the following section.

Alternative synthesis. The transesterification reaction 6 was examined
more vigorously for the preparation of V than it had been for III, but failed to afford

$$ROH \quad + \quad (MeO)_4Si \xrightarrow[H_2SO_4]{\Delta} (RO)_4Si \quad + \quad (RO)_3SiOMe \quad + \quad MeOH \qquad (6)$$
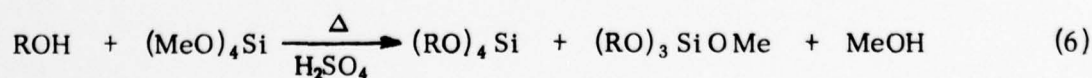
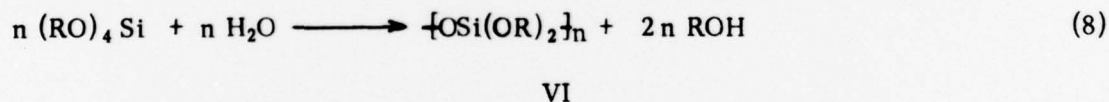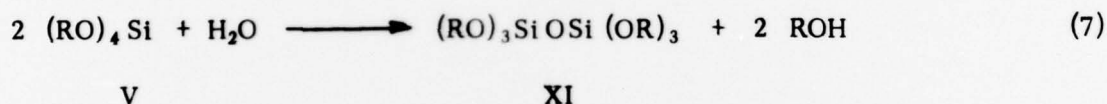(FDNE;excess)   V

2.5 moles   1 mole

the complete replacement of the methoxy groups by FDNE residues. Even when operating under the optimum, balanced conditions of heat and vacuum capable of removing liberated methanol but not excess FDNE, a viscous product was obtained whose composition comprised the molar product mixture shown above. Because this procedure was operationally ponderous and clearly yielded a inferior product relative to the chlorosilane esterification method, transesterification was not further pursued as a method for the synthesis of monomeric silane esters.

Bis(2, 2, 2-fluorodinitroethoxy)polysiloxane, VI

The obvious approach to the preparation of linear polymers VI was the hydrolysis, either stepwise or at once, of two groups of the orthoester V. Removal of just 1 fluorodinitroethoxy group followed by silanol condensation should produce the disiloxane XI (eq 7), whereas removal of two groups should produce the desired linear and/or cyclic oligomers (eq 8). Loss of a third or fourth group would result in highly undesirable cross-linking and gellation to insoluble and unworkable materials. Our studies have shown that selective step wise removal of fluorodinitroethoxy

$$2 \ (RO)_4 Si \ + \ H_2O \longrightarrow (RO)_3 Si O Si (OR)_3 \ + \ 2 \ ROH \qquad (7)$$

$$V \qquad\qquad XI$$

$$n \ (RO)_4 Si \ + \ n \ H_2O \longrightarrow \{OSi(OR)_2\}_n \ + \ 2n \ ROH \qquad (8)$$

$$VI$$

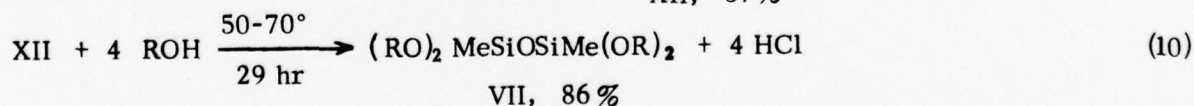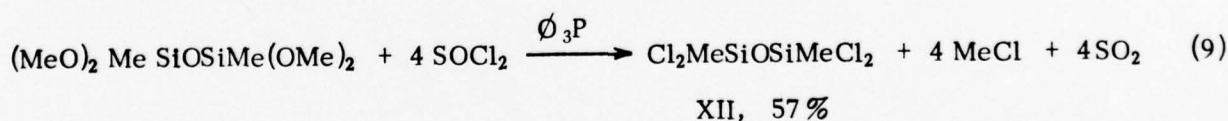[linear VI must also contain end groups $OSi(OR)_3$]

groups is not a feasible route to stable products of the type VI. Thus, hydrolysis of V in acetone or acetone-methylene chloride solvent at room temperature according to the stoichiometry of eq 7 and followed by removal of solvent and liberated FDNE produced a mixture containing an unacceptably high 25 % of unconverted orthoester. During the removal of FDNE, the proportion of end group structures $(RO)_3 Si O Si$ increased at the expense of internal $-OSi(OR)_2-$ units but it decreased again on the addition of water to a solution of the product to approximate the overall stoichiometry of eq 8. Further observation revealed that reaction 8 proceeded to $\sim 90\%$ loss of 1 RO group per mole of V but that removal of the solvent dramatically altered the product composition from one containing predominantly the desired difunctional units VI to one with greatly enhanced amounts of all the other species; removal of liberated FDNE left a mixture still containing ~ 20 mol-% of starting ester V.

In another experiment, hydrolysis of 1 mole of V with 0.5 mole of water (eq 7) in acetone caused reaction of the theoretical 1/4 of Si-OR groups overall but of only 70% of the ester V itself, before removal of solvent. Use of 100% excess of water (2n moles in eq 8) rapidly produced insoluble gels. Generally, hydrolytic conversion of V was favored by increasing its dilution in the solvent. These results point strongly to a reversible equilibrium situation wherein the starting orthoester, despite its facile, partial hydrolytic decomposition in humid air, retains upon hydrolysis in solution a marked concentration and no single type of linear polysiloxane product can be made to overwhelmingly predominate.

The equilibrium mixtures were analyzed using a combination of 220 MH$_z$ H-nmr and ^{29}Si-nmr techniques. In particular, the latter resonances were found to occur at distinctly different chemical shifts in the series n=4,3,and 2 in the structures $(RO)_n{}^{29}Si(OSi)_{1-4}$ which showed increasingly higher field shifts vs TMS as the extent of hydrolysis of RO groups progressed (see Results B, nmr spectra). Unfortunately, the poor resolution and number of scans required even in the FT-^{29}Si-nmr analysis of all but the most concentrated product mixtures precluded distinction among the types of $(OSi(OR)_2)_x$ structures; the 220 H-nmr results clearly revealed a host of structural types in all products except those still diluted in the original solvent.

## 1,3-Dimethyl-1,1,3,3-tetrakis (β, β, β-fluorodinitroethoxy)disiloxane, VII

Although compound VII should be the first hydrolysis-condensation product of the trisester IV, our experience with the nonspecific hydrolysis of V dictated that the disiloxane be prepared instead by esterification of the corresponding tetrachlorodisiloxane XII. The two-step procedure shown in eqs 9 and 10 yielded the crude product VII without

$$(MeO)_2 Me\,SiOSiMe(OMe)_2 \ + \ 4\,SOCl_2 \ \xrightarrow{\phi_3P} \ Cl_2MeSiOSiMeCl_2 \ + \ 4\,MeCl \ + \ 4\,SO_2 \quad (9)$$

XII, 57%

$$XII \ + \ 4\ ROH \ \xrightarrow[29\,hr]{50\text{-}70°} \ (RO)_2\,MeSiOSiMe(OR)_2 \ + \ 4\,HCl \quad (10)$$

VII, 86%

incident following a high vacuum strip of remaining volatiles. Additional purification was not attempted because of the 93-95% spectral purity of VII as first obtained and a projected bp dangerously exceeding 250° under high vacuum. The long reaction time included an 18 hr period at 50° which failed to complete the replacement of SiCl groups, although subsequent heating for 4 hrs at 70° was sufficient for the purpose. Generally, therefore, all the esterifications reported herein according to eq 1 proceeded only sluggishly until reaction temperatures of 60-70° were reached.

Identification of VII followed from its method and yield of synthesis and totally consistent spectral characteristics. In particular, there was coincidence of its infrared spectrum with that of one sample of IV hydrolyzed in the air under non-gellation conditions,

presumably to the same disiloxane VII, and the position of the ^{29}Si-nmr resonance (Table II) was convincingly located in relation to the several similar silane ester compounds prepared in this work. In fact, the regular change in chemical shift of the ^{29}Si resonances with the nature and type of substituents has proved to be an exceptionally diagnostic tool (see Results Section B). On the basis of the ^{29}Si and H-nmr spectra, we have deduced that the single impurity observed in VII is probably the trisiloxane XIII.

$$(RO)_2MeSiOSiMe(OR)OSiMe(OR)_2$$
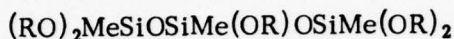
XIII

Disilanes

Little work has been completed on this subject to date. One attempt to esterify hexachlorodisilane to give target compound VIII was carried out with 50% excess FDNE. However, the product proved to be a mixture of orthoester V with a second type of Si-OR compound, and greater than the theoretical amount of FDNE was consumed at reaction temperatures up to 73°. Cleavage of the Si-Si bond obviously had proceeded to a substantial degree under the conditions used, as has been reported[6] to occur in similar reactions with this disilane. The minor product was tentatively identified as the disiloxane XI, $(RO)_3SiOSi(OR)_3$, from its characteristic ^{29}Si-nmr spectrum; the presence of the desired disilane VIII, $(RO)_3SiSi(OR)_3$, was similarly ruled out. A 42% yield of the orthoester, based on completion of the assumed cleavage reaction was isolated following work-up.

RESULTS B. PHYSICAL AND CHEMICAL PROPERTIES

The observed physical and chemical properties of the five products described in Section A are tabulated in Table I, along with the results of calculations of thermochemical properties. As noted earlier, the nmr spectral properties are given in Table II. Infrared spectra are given in Appendix B. Detailed thermochemical information is presented in Appendix A with highlights discussed in a subsection below.

Yield and purity

Except as noted, yields are given for distilled or recrystallized products, and purity determinations were based upon H-nmr and ^{29}Si-nmr analyses. In the case of the orthoester V, the extreme sensitivity to hydrolysis referred to in a preceeding section requires further comment. Although deliberate reaction with stoichiometric amounts of water in a solvent was instantaneous, it was noted that only a certain amount of the orthoester reacted before equilibrium with hydrolysis products was attained.

TABLE I

Physical and Thermochemical Properties of High Energy Silane Esters

Property	III $(RO)_2SiMe_2$	IV $(RO)_3SiMe$	V $(RO)_4Si$	VI $[Si(OR)_2O]_x$	VII $[(RO)_2MeSi]_2O$
Synthesis yield, %	87	73 [a]	90	mixture [b]	(86) [c]
Purity, wt-%	97	100	≥ 82 [d]	mixture	≥ 93
mp °C	19-19.5	~ 25	74-86 [d]	--	~15-20
bp °C (mm)	96 (0.1)	170 (0.3)	--	--	~250(0.1) [e]
$n_D^{°C}$	1.4308^{22}	$1.4412^{22.5}$	--	--	1.4406^{25}
$d^{°C}$ g/cc	1.395^{24}	1.660^{23}	1.938^{25}	--	1.580^{24}
Shock sens H_5 kg-cm	~300 [f]	--	76 [g]	--	--
Hydrolysis rate in air at % RH	nil/46% v. slow/52%	slow/35% rapid/60%	rapid/18%	--	nil/35% v. slow/52%
Calcd max values					
$-\Delta H_f$ kcal/mol	288	391	500	354	719
- Q cal/g	1310	1330	1330	1220	1170
P kbars	153	238	348	--	195
D km/sec	6.38	7.51	8.67	--	6.90

(a) Yield of crude product was 91%, > 96% pure, mp ~ 0°.

(b) From 1:1 reaction $(RO)_4Si + H_2O$.

(c) Crude product.

(d) Hydrolysis occurred even upon careful handling; nmr analysis of a typical sample revealed the presence of 6 wt-% FDNE and 12 wt-% disiloxane XI, at least at the time of analysis.

(e) Estimated value.

(f) ASTM procedure no. D2540 for liquids, except with unsealed sample container; value reduced to only 2.5 kg-cm under the usual compressive shock conditions (sealed sample cup).

(g) M. Kamlet, AWRE test for solids, sandpaper surface; value ~ 300 kg-cm in ASTM test apparatus with unsealed sample cup.

In air of even low relative humidity ($< 35\%$ at $23°C$), hydrolysis also proceeded rapidly in the initial stages and extensively enough in a matter of minutes that the liberation of FDNE became pronounced. The presence of any free alcohol clearly depressed the mp of the pure compound, which we have never observed to be sharp despite normal drying precautions. Minor amounts of hydrolysis should not affect elemental analysis to an appreciable extent, however, unless hydrolysis is extensive and samples are subjected to vacuum "drying," which would remove free FDNE but not the corresponding polysiloxane residues. Since nicely crystalline samples of V appeared to "melt" even upon contact with the surface moisture of metals or glass, it is not surprising that sample transfers and normal handling in spectroscopic work might lead to the observed relatively low purity levels due to such contact hydrolysis. Recrystallization of exposed samples was not particularly effective for purification, as judged by changes in mp, since the polysiloxane impurities were at least partially retained in the fresh precipitates.

Nmr spectra

The multinuclear nmr spectral data presented in Table II were obtained on a variety of instruments. Chemical shifts downfield of the reference are taken as positive throughout. Proton spectra were recorded on a Hitachi R24A or, for superior resolution and integration accuracy, Varian A60, spectrometer. When interpretation became difficult because of the overlapping of patterns, spectra recorded at 220 MHz at Rockefeller University proved highly valuable; unfortunately, even the superior resolution of this instrument is hard put to sort out the complex variety of methylene absorptions due to mixtures of FDNE residues in very closely related environments.

For example, the hydrolysis of the orthoester V produced a host of structural variations in the number and nature of different groups attached to each Si atom; although the variety was clearly evident in the 220-H nmr spectra, overlapping of the patterns still precluded assignment, at least in the absence of ^{19}F-decoupling. Thus, splitting of the $F-C-CH_2-O-Si$ methylene group into a doublet was invariably observed, and the doubled envelope of multiple CH_2 absorptions when present often overlapped. Consequently, ^{29}Si-nmr data proved invaluable, since operation of our Bruker spectrometer with Fourier transform under conditions of gated proton decoupling provided results as shown in Table II and further illustrated below, wherein each change in substitution pattern around Si produced a ^{29}Si resonance in a separate and characteristic region. Only minor differences could not be differentiated, such as the $(RO)_3Si-$ silicon in the simple disiloxane XI vs that present as an end group in the polysiloxane VI.

TABLE II

NMR Data for Fluorodinitroethoxy Compounds

Nucleus	Solvent	Compound and Spectrum, δ				J, H$_z$	
		$FC(NO_2)_2$ — CH_2O — H$\underline{}^{(a)}$, FDNE					
^{1}H	CDCl$_3$	4.70(d,d)	3.31-3.45(t)			H,F H,H	15.7 7.0
	4 CDCl$_3$ + 1 d$_6$-acetone	4.70(d,d)	5.20(t)			H,F H,H	17.5 (b)
	d$_6$-acetone	4.75(d,d)	5.62(t)			H,F H,H	17.6 7.0
^{13}C	CDCl$_3$	121(d)				F,C	290.
		61.1(d)				F,C	20.4
		$FC(NO_2)_2$ — CH_2O — CH_2O — $CH_3\underline{}^{(c)}$, Compound IX					
H	CHCl$_3$	4.67(d)	4.74(s)	3.45(s)		H,F	17.5
	d$_6$-acetone	(d)	4.72(s)	3.36(s)			
C	CDCl$_3$	(e)	64.8(d)	96.9(s)	56.0(s)	F,C	20.4
		$\left[FC(NO_2)_2 — CH_2O\right]_2$ Si(CH$_3$)$_2$, Compound III					
H	CDCl$_3$	4.81(d)	0.27(s)			H,F	17.2
C	CDCl$_3$	120.6(d)				F,C	290.
		61.5(s)	-4.5(s)			F,C	18.1
^{19}F	CDCl$_3$	54.4(t)				H,F	(f)
^{29}Si	CDCl$_3$		7.7(s)				
		$\left[FC(NO_2)_2 — CH_2O — Si(CH_3)_2\right]_2$ O, Compound X					
H	CDCl$_3$	4.74(d)	0.18(s)			H,F	18.0
C	CDCl$_3$		-2.2(s)				

Nucleus	Solvent	Compound and Spectrum,			J, H_z	

$$\left[FC(NO_2)_2 - CH_2O\right]_3 Si - CH_3, \text{ Compound IV}$$

Nucleus	Solvent					
H	$CDCl_3$		4.87(d)	0.39(s)	H,F	16.5
C	$CDCl_3$	121.8(d)			F,C	280.7
			63.15(d)	-7.95(s)	F,C	20.8
F	$CDCl_3$	52.7(t)			H,F	15.7
Si	$CDCl_3$			-39.6(s)		

$$\left[(FC(NO_2)_2 - CH_2O)_2 - Si - (CH_3)\right]_2 O, \text{ Compound VII}$$

Nucleus	Solvent					
H	$CDCl_3$		4.83(d)	0.37(s)	H,F	17.8
C	$CDCl_3$	134.2(d)			F,C	293.
			64.05(d)	-7.23(s)	F,C	29.3
F	$CDCl_3$	53.1(t)			H,F	15.7
Si	$CDCl_3$			-47.1(s)		

$$\left[FC(NO_2)_2 - CH_2O\right]_4 - Si, \text{ Compound V}$$

Nucleus	Solvent					
H	$CHCl_3$ (g)		4.93(d)		H,F	15.0
	3.5 $CDCl_3$ + 1 d_6-acetone		5.08(d)		H,F	15.5
C	3 $CDCl_3$ + 1 d_6-acetone	119.4(d)			F,C	291.5
			62.5(d)		F,C	22.6
F	3 $CDCl_3$ + 1 d_6-acetone	54.4(t)			H,F	15.5
Si	1 $CDCl_3$ + 9 d_6-acetone			-88.7		
	d_6-acetone (h)			-87.9		

Footnotes to Table II

(a) Lit[23] (solvent not specified): δ CH$_2$ 5.80, OH 3.97 (J_{HF} 15.9, J_{HH} 7.0 Hz).

(b) Usual triplet now contains doubled center line; apparent J_{HH} 7.0 Hz.

(c) Lit[2] (CCl$_4$): δ CCH$_2$O 4.58 (J_{HF} 17.5), OCH$_2$O 4.67(s), CH$_3$ 3.36(s).

(d) Masked by FDNE also present.

(e) Not observed.

(f) Unresolved.

(g) Sample from transesterification (MeO)$_4$Si + excess FDNE, impure and therefore soluble in chloroform.

(h) Mixture with siloxane hydrolysis products.

The chemical shifts, δ (ppm vs TMS), observed for ^{29}Si resonances in the silane esters and hydrolysis products described in Results Section A were the following. There was little effect (1-2 ppm) of chloroform vs acetone *solvent where comparisons* were made. The region of RO-functional Si absorption clearly reflects the number of attached methyl groups; as usual, the RO- symbolism designates the FC(NO$_2$)$_2$CH$_2$O- group.

(RO)$_4$Si	(RO)$_3$SiO $+$ Si(OR)$_2$O $\}_x$ Si(OR)$_3$	$+$ Si(OR) O$_{3/2}$ $\}_x$
-88	-94 -98 to 100	-106 to -108

(RO)$_3$SiMe	(RO)$_2$MeSiO $+$ Si(OR)(Me) O $\}_x$ SiMe(OR)$_2$
-40	-47 -56

(RO)$_2$SiMe$_2$

+8

The only shortcomings of the method are the lack of integration capability and the relatively low sensitivity, which precluded the observation of strong, definitive spectra from dilute solutions, such as result when Si comprises only a minor contribution to the molecular weight of the sample (as in the present compounds). Unfortunately, the spin relaxation benefits of added $Cr(acac)_3$ could not be utilized in examination of our hydrolysis mixtures, since the compound catalyzed changes in their compositions. Nevertheless, the analysis of compounds and mixtures lacking the Si-C-H residues useful in H- or ^{13}C-nmr analysis, such as V and VI, was highly simplified through our [29]Si-nmr capability.

[13]C-nmr and ^{19}F-nmr spectra were also recorded on the Bruker instrument with no unusual results apart from the strong doublet [13]CH$_2$ peak due to the ^{19}F-C-^{13}C splitting noted earlier, which characterizes all these compounds under conditions of broad band proton decoupling. It should also be noted that the F-^{13}C doublet carbon absorption was uniformly weak and diffuse, although possessed of the expected 10-fold larger ^{19}F coupling constants relative to the once removed methylene carbon. The fluorine spectra showed the expected coupling to the methylene protons but provided little analytical information; the chemical shifts in Table II are referred to C_6F_6 reference.

Density

Density values for pure vs crude products were indistinguishable. No effort was made to obtain more precise values than resulted from a simple syringe and microbalance technique for liquids and displacement of an inert liquid with the solid product V. The accuracy was at least ± 0.01 g/cc.

Shock and thermal sensitivity

Preliminary sensitivity testing was conducted on each new compound prior to and following purification. A thermal test was performed by dropping small samples onto a porcelain surface maintained at 315°C. None of the compounds described herein displayed signs of decomposition, with the exception of the orthoester V. Instead of the usual boil-off into white fumes with little residue, V produced yellow fumes and a small residue, but no sign of detonation could be observed.

Shock sensitivity was qualitatively assayed by the firm striking of samples resting unrestrained on a steel plate with both the flat and the edge of a 1-lb claw hammer. No response was noted in any case. Quantitative drop weight tests were also carried out with bisester III and orthoester V at the Union Carbide Laboratories in South Charleston, West Virginia. ASTM Procedure No. D2540 for liquids was applied to III, wherein the sample was sealed in a small volume and shock provided by sudden compression of the air above as the coverplate was struck by the falling weight. Compound III showed a

remarkable sensitivity $\geq$ 4 times that of the reference, n-propyl nitrate. However, when the impacting rod was allowed to strike the sample directly in the absence of the cover plate (non-compressive shock), a 100-fold lower sensitivity was observed.

Tests of the orthoester were carried out in specially dried, oven-baked sample cups to prevent contact hydrolysis; under the non-compressive shock conditions described above, a low level of sensitivity similar to that of III was observed.

Samples of both III and V were also submitted to Dr. M. Kamlet at the Naval Surface Weapons Center in Silver Spring, Md., for sensitivity testing. (Subsequent samples, i.e. of IV and VII, have not been shipped because of new problems in shipping regulations.) Compound V was tested, now using a procedure for solids which constitutes normal practice in the field. [7] The value given in Table I was reported to the writer by telephone and is dealt with further in the Discussion Section of this report.

Hydrolytic sensitivity

Some mention has already been made of the variable hydrolytic sensitivity of the silane esters in moist air. One must always anticipate that Si-OR bonds can be heterolytically broken upon reaction with water, but the rates of such reactions depend upon the number of oxy-linked groups, the electronic and steric nature of R, catalysis, and the water solubility of the esters, among other factors. [8] We have examined the relative stability of III-VII towards moisture normally present in the air as an indication of whether problems in routine handling need be anticipated, but we have not studied the hydrolysis in solution, except for that of V in the preparation of VI.

Hydrolysis was observed by exposing samples of the silanes on different surfaces to ambient air and recording their infrared spectra at various times. When hydrolysis occurred, key changes in the ir were the early development of OH and SiOSi absorption. Obvious gellation could result after extensive reaction, and specific bands due to FDNE became clearly evident unless the hydrolysis had proceeded relatively slowly, in which event the liberated alcohol largely evaporated.

Examination of compounds III, IV, V and VII revealed that the tendency for hydrolytic sensitivity toward ambient atmospheric moisture was much more a function of the structure of the silane and the % relative humidity then of the nature of the supporting surface and presence of acidic or basic catalysts. The bisester III showed no sign of change after 17 hr exposure in 46% RH air at 23°; another, similarly treated sample showed only traces of hydrolysis after 22 hr at 47-55% RH. It is not certain whether the % RH remained at precisely the indicated levels for the entire test periods.

In stark contrast to the stability of III was the "melting" of the orthoester V after only 10 min at 18% RH on a dry glass surface. Apparently, the FDNE formed in the first minutes of exposure acted both as solvent and melting point depressant toward V and accelerated the transformation to a liquid, whose free FDNE content was observed to be very high. Even contact hydrolysis was rapid, as observed when micro samples loaded into brass cups in a dry box preparatory to use in drop weight testing were found to "melt" while still in the dry atmosphere; oven baking of the sample cups prior to use obviated the problem.

An intermediate behavior was observed with the trisester IV, $(RO)_3SiMe$, whose substitution pattern obviously falls midway between that of the dimethyl compound III, $(RO)_2SiMe_2$, and the orthoester V, $(RO)_4Si$. Thus, IV was relatively stable, like III, at low RH but, like V, quite sensitive at higher RH. At 35-40% RH, hydrolysis had proceeded only slowly after 4 hr on glass, and a gel-free sample was obtained after 24 hr whose ir spectrum was superimposable upon that of the disiloxane VII, except for traces of residual FDNE that had not yet evaporated. At 50-60% RH, however, hydrolysis was extensive after only 20 min and led to gellation after 1 hr. Some differences in gross hydrolysis rate of a lower order of magnitude were also noted with IV as a function of sample purity and the nature and acidity of the support. Samples of lesser purity and those tested on acidified or copper supports showed somewhat reduced hydrolytic decomposition. Representative ir spectra of III-IV before and after exposure to humid air are reproduced in Appendix B.

The disiloxane VII prepared independently of the hydrolysis of IV (eq 10) proved stable in 35-42% RH air for 40 hr, and suffered only minor decomposition after a further 18 hr at 52% RH. There is therefore a rather pronounced effect of structure and % RH (water concentration) on the hydrolytic stability of these high energy silane esters in the air which may or may not be mirrored in their solution behavior.

Thermochemical calculations

At the request of the contract manager, calculations were carried out of certain thermochemical data relating to the energy content of the high energy silane esters prepared in this work and of some other, related structures. The quantities requested were the heat of formation, the theoretical maximum chemical energy of the detonation reaction and the theoretical maximum detonation pressure and velocity; the latter calculations were carried out according to the guidelines provided in ref. 7. The results and full details of the calculations employed have been reported informally. We present below an outline of the procedures used and summary table of the results (Table III); the detailed calculations are given in Appendix A.

Heat of formation, ΔH_f. The initial quantity to be determined in each case is the compound heat of formation. Although a special technique involving rotating bomb calorimetry[9] (to ensure completeness of combustion), exists for the experimental determination of ΔH_f in complex Si and F- containing compounds, the necessary facilities were not available to us. Consequently, values of ΔH_f were calculated as the difference between the heats of formation of the component radicals and the dissociation energies D of the bonds broken to produce the radicals (eq 11), following the usual assumption of ideal gas

$$\Delta H_f \text{ (compound)} = \sum \Delta H_f \text{ (radicals)} - \sum \text{D-values} \tag{11}$$

behavior at 298°K.[10] The necessary values for the heats of formation of the radicals were either taken from the literature or, when unknown, calculated in various ways. The key value, ΔH_f (FC(NO$_2$)$_2$CH$_2$O ·), was calculated from the reported[7] value of ΔH_f(FEFO). When individual, stepwise bond dissociation energies were not known or readily subject to calculation, an average dissociation energy $\bar{D}$ could be calculated over a group of initially identical bonds, as for Si—O in structures (RO)$_4$Si, or the total (D$_T$) of the various D-values could be found from model compound data without individual differentiation, such as for the 4 bonds to Si in (RO)$_2$SiMe$_2$. The operational values $\bar{D}$ and D$_T$ are not to be afforded any real physical significance.

Although all the calculations performed are detailed in Appendix A, we abstract below the calculation of ΔH_f (RO)$_4$Si, compound V, to illustrate the general procedures employed. Thus, for the gas phase dissociation reaction 12, the ΔH_f of the ester is found

$$(RO)_4Si \longrightarrow 4 \, RO \cdot + Si \text{ (gas)} \tag{12}$$
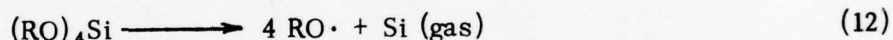
$$V$$

from eq 13, whose rearrangement of terms yields the form of eq 11. The unknown

$$4 \, \bar{D} \text{ (Si-OR)} = 4 \, \Delta H_f(RO) + \Delta H_f(Si) - \Delta H_f(RO)_4Si \tag{13}$$

$$\text{unknown} \qquad \text{unknown} \qquad \text{known}$$

quantities are the Si-OR dissociation energies and ΔH_f(RO), whereas $\Delta H_f Si_{(g)} = \Delta H_{\text{sublimation}}$ (Si) is known. To approximate the requisite quantities, we assume that $\bar{D}$ for Si-OR in (RO)$_4$Si is closely approximated by that in (EtO)$_4$ and then calculate ΔH_f(RO).

$$\bar{D} \text{ (Si-O) in (EtO)}_4 Si \longrightarrow 4 \, EtO + Si$$
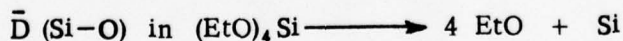
$$4 \, \bar{D} \text{ (Si -O)} = 4 \, \Delta H_f(EtO) + \Delta H_f(Si) - \Delta H_f(EtO)_4 Si \tag{14}$$

$$\text{known} \qquad \text{known} \qquad \text{known}$$

$$\bar{D} \text{(Si -O)} = \frac{4 \, (-6.7) + 106 - (-322)}{4} = 100.3 \text{ kcal/mol}$$

then, $\Delta H_f (RO \cdot)$ in $RO\text{-}CH_2\text{-}OR \longrightarrow 2\ RO + CH_2$ is found by

FEFO

$$2\ \bar{D}\ (RO\text{-}CH_2) = 2\ \Delta H_f(RO) + \Delta H_f\ (CH_2) - \Delta H_f\ (FEFO) \qquad (15)$$

unknown   known   known

The unknown $\bar{D}\ (RO\text{-}CH_2)$ is assumed equal to $\bar{D}\,(EtO\text{-}CH_2)$ in diethyl formal, and all the terms necessary to calculate $\Delta H_f(RO)$ are then available.

$$2\ (82.6) = 2\ \Delta H_f(RO) + 90 - (-177.5),\ \text{and}$$

$$\Delta H_f(RO) = -51.2\ \text{kcal/mol}$$

Eq 13 can then be solved for $\Delta H_f(RO)_4 Si = -500$ kcal/mol.

Energy content, ΔH_{det} and Q . The heat of reaction for the decomposition of a compound to a group of specified, small, stable molecules in a preferred order of formation from the available atoms is the heat of detonation, ΔH_{det} (kcal/mol), and provides a measure of the theoretical maximum chemical energy available in such a process (eq 16). The energy content per gram, Q, is obtained by dividing ΔH_{det} by the molecular weight.

$$\Delta H_{det}\ (\text{compound}) = \sum \Delta H_f(\text{products}) - \Delta H_f\ (\text{compound}) \qquad (16)$$

$$Q = \frac{\Delta H_{det}}{\text{Mol. Wt.}} \quad (\text{kcal/g}) \qquad (17)$$

The quantity Q is then used in the calculation of detonation pressure and velocity as shown below.

Clearly, the solution of eq 16 for each compound can be made to vary depending upon what the nature and relative amounts of the products are assumed to be. Consistency with standard practice is assured by writing the following gaseous products in the order given with the maximum molar yield of each allowed by the elemental composition: SiF_4, $SiO_2(s)$,

HF, H_2O, CO_2, CO, N_2. Any excess of carbon is assumed to appear as solid carbon. Literature values are taken for the heats of formation of each product, wherein elements obtained in their standards states, such as N_2, have $\Delta H_f = 0$. Although the argument can be made that low energy $SiO_{(g)}$ and not the highly stable $SiO_{2\,(s)}$ should be the silicon-containing product at the high temperatures of actual detonations or controlled burns,[11] calculation either way does not necessarily result in an appreciable difference in the final detonation velocity. This is illustrated by the following data for the disiloxane VII.

For the compound VII, decomposition may be written in two ways (18a, b), if one assumes SiF_4 to be the most favored product. However, at the anticipated several thousand degrees temperature of a detonation reaction, one might well find much of the divalent species SiF_2, which exists in preference to $Si + SiF_4$, for example, at $> 1300°$ and low pressures,[12] unless the high pressure of detonation should favor the tetravalent Si fluoride over the divalent species or even oxide over fluoride products.

$$\left[FC(NO_2)_2CH_2O\right]_2 MeSiOSiMe\left[OCH_2CF(NO_2)_2\right]_2 \xrightarrow[\text{detonation}]{\text{theoretical}}$$

VII, $C_{10}H_{14}F_4N_8O_{21}Si_2$

$$SiF_4 + SiO_2 + 7H_2O + 6CO_2 + 4C + 4N_2 \qquad (18a)$$

or

$$SiF_4 + SiO + 7H_2O + 6CO_2 + CO + 3C + 4N_2 \qquad (18b)$$
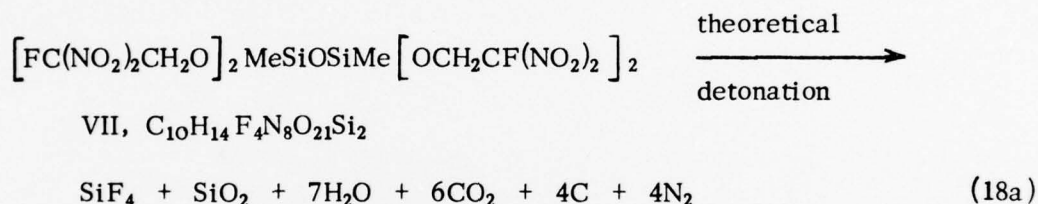
From eq 16 and the appropriate ΔH_f for VII and for products (see Appendix), the energy content of VII based on 18a is -1.28 kcal/g vs -1.05 based on 18b, clearly a marked difference of 20 %. However, calculations of detonation pressure and velocity as next described reduces this difference.

Detonation pressure and velocity. Empirical equations 19 and 20 have been derived[7] whereby the theoretical detonation pressures and velocities may be calculated from density (ϱ) and energy content (Q) data. An intermediate quantity $\emptyset$ (eq 21) takes into account the energy content of the compound, the number of moles of gaseous detonation products per gram (N), and the average molecular weight of the gaseous products (M). Since detonation route 18b in the above disiloxane example yields more moles of gas than route 18a, the difference in energy contents is overcome and both routes lead to the same calculated detonation pressure and velocity (Table III).

TABLE III

Calculated Thermochemical Properties of High Energy Silicon Compounds

$$R \equiv FC(NO_2)_2CH_2 -$$
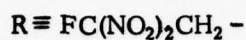
Compound	$-\Delta H_f$ kcal/mol	$-Q$ cal/g	N mols/g	M g/mol	$\emptyset$	ℓ g/cc	P kbars	D km/sec
$(RO)_2SiMe_2$, III	288.	1310	.0275	25.60	5.036	1.395	152.7	6.38
$(RO)_3SiMe$, IV	390.5	1325	.0279	29.86	5.550	1.66	238.3	7.51
$(RO)_2MeSiOSiMe(OR)_2$ [a,b], VII	642	1048	.0280	33.90	5.280	1.58	205.4	7.09
$(RO)_2MeSiSiMe(OR)_2$ [a]	551	1163	.0272	34.20	5.425	(1.60 ?)	(216.4)	(7.25)
$-[SiMe(OR)O]-_x$	246.4	1158	.0236	25.60	4.063			
$(RO)_4Si$, V	500	1330	.0266	37.65	5.952 [c]	1.938	348.3 [c]	8.67
$-[Si(OR)_2O]-_x$, VI	353.8	1221	.0257	32.22	5.098			
$-[Si(CH_2R)_2O]-_x$	239.8	1355	.0260	26.44	4.922			
$(RCH_2)_4Si$	272	1480	.0269	31.53	5.811			

[a] Decomposition to SiO. [b] Values assuming SiO_2 as detonation product are, in order left to right: 642, 1278, .0252, 33.7, 5.23, 1.58, 203.4 and 7.05. [c] Also calculated by M. Kamlet, reported [13] to be $\emptyset$ = 6.025; P = 352.

$$\text{Detonation pressure} \quad P = 15.58\, \varrho^2 \emptyset \tag{19}$$

$$\text{Detonation velocity} \quad D = 1.01\, \emptyset^{1/2}\, (1 + 1.3\varrho) \tag{20}$$

$$\emptyset = NM^{1/2}\, \emptyset^{1/2} \tag{21}$$

Some calculations have also been carried out for compounds whose densities are not known; the $\emptyset$-values are given for these so that estimates of P and D may be made for assumed densities (parentheses). All such results are collected in the summary Table III.

DISCUSSION

Synthesis

The preparation of target compounds III-VII was accomplished with efficiencies of ~90% via reaction 1, the direct esterification of chlorosilanes with FDNE involving elimination of gaseous HCl. The same method was employed in some recently reported[14] Russian work on the preparation of a series of β, β, β- difluoromononitroethoxysilane esters, and elsewhere[15] in the preparation of some perfluoroalkoxysilanes. Alternate methods proved inferior, including use of a base as HCl acceptor in reaction 1 and trans-esterification of alkoxysilanes with FDNE; the potential reaction of other functional silanes such as acetoxy or ureido compounds, with FDNE in a manner analgous to transesterification was not investigated for lack of time and necessity. The use of pyridine as HCl acceptor in ether solvent has been employed in other recent Russian work for the preparation of halo and nitro-substituted alkoxysilanes,[16] but the low yields (12-66%) suggest that side reactions were a significant problem in that work, just as we observed in ours. Grignard displacement of perfluoroalkoxy groups from the orthoesters has also been employed to prepare mixed alkyl-alkoxysilanes.[17]

Minor variations in the general reaction 1 were employed depending on the particular reactant volatility, solubility in FDNE, and reactivity. To avoid entrainment losses of volatile chlorosilanes, general use of a Dry Ice condenser through which the liberated HCl must pass is recommended. Elevated temperatures clearly enhanced chlorosilane solubilities in FDNE (~70°) but had to be balanced against the resulting increase in volatility and loss of the monomeric chlorosilanes. An excess of FDNE also favored more rapid and complete reactions but was found necessary only in the preparation of the orthoester V.

All the reactions, except the attempted esterification of hexachlorodisilane to give VIII (see below), proceeded relatively cleanly to the desired products and produced only one type of by-product, the corresponding siloxane compounds containing one more Si-O-Si group than was present initially, such as X and XI. Although the mechanism of Si-O-Si formation has not been studied here, it is unlikely that it is a consequence of moisture in the well-dried reactants or apparatus which could lead to chlorosilane hydrolysis and subsequent silanol condensation; furthermore, the siloxanes appeared only in the very last stages of reaction. The occurrence of siloxane products during the alcoholysis of chlorosilanes normally cannot be avoided due to some degree of reaction of HCl with the alcohol ROH to give RCl and H_2O, especially with alcohols prone to form species with carbonium ion-like character.[4] This would not be expected of the very acidic alcohol FDNE, however, which should resemble phenol in its resistance to conversion to the chloride. Normally, amines are employed as HCl acceptors and, sometimes, catalysts, to increase the yields of esters, although siloxanes can form even then.[4] In our work, surprisingly, pyridine as an HCl acceptor actually enhanced the siloxane formation rather than reducing it, for reasons we have not attempted to define, and was thus contra-indicated. The extent of siloxane formation was usually only 1-5 wt-% and did not represent a serious complication; distillation, when feasible, offered a convenient means of purification. Only in the case of the orthoester V did siloxane formation become a real problem, mainly during work-up, due to the exceptional hydrolytic sensitivity of V.

Also true of the compounds III-VII generally was the invaluable assistance afforded by multinuclear nmr analyses for the characterization and determination of ester purities. Although these analyses have been described in the preceeding section of this report, the FT-^{29}Si—nmr technique deserves separate mention for emphasis of its critical role in this work. Thus, for the definition of the number of alkoxy and methyl groups attached to each Si atom in the product or impurity compounds, the highly specific changes in the ^{29}Si resonance shift (vs tetramethylsilane reference) attributable to the substitution pattern proved invaluable, especially for analysis of orthoester V and its hydrolysis products.

This technique should prove equally useful for any related work which may yet be carried out involving the preparation of high energy organosilicone polymers, since analysis for end groups and cross-linking would be greatly facilitated. A limitation, however, is a simple molecular weight effect. When a given Si atom is surrounded by substituents with a net high molecular weight, such as in the present polynitroalkoxy structures, and a variety of different Si atoms are present, the effective concentration of each Si is necessarily low vs the total substrate and prevents detailed analysis of any but concentrated solutions of the substrate. Ordinarily, however, it is not a problem to prepare sufficiently concentrated sample solutions, especially of relatively simple compounds; the presence of 0.5-1% wt/vol per type of Si in the sample solution proved sufficient to yield useful results if spin relaxation agents [Cr(acac)$_3$] could be tolerated, although concentrations 5-fold higher were clearly preferable.

When present, methyl groups attached to Si also yielded characteristic chemical shifts in the ^{13}C-nmr spectra as a function of their number, but the differences were

insufficiently large to permit analysis of more closely related structures, such as CH_3-SiOR vs CH_3-Si-OSi, in the absence of reference compounds. The ^{19}F-nmr spectra were not of particular value in this work, since the F-environment was always that of an FDNE residue.

As noted in the Results Section, hydrolysis of V failed to yield the desired polymers VI, $\{OSi(OR)_2\}_x$ either linear (with end groups) or cyclic, except as mixtures with a number of other structures, including the starting orthoester $Si(OR)_4$. This result and the observed changes in equilibrium mixture with changes in concentration and temperature were highly reminiscent of the situation long known to obtain in the hydrolysis of ethyl silicate, $(EtO)_4Si$, wherein reaction with water leaves much unreacted orthoester (14% at ~40% hydrolysis of total ethoxy groups), and solutions must be prepared dilute, acidic, and in H-bonding solvents to prevent cross-linking to the point of gellation. [18] The only significant difference between V and ethyl silicate in hydrolysis was that the latter requires a catalyst to effect rapid reaction.

The failure of the disilane $Cl_3SiSiCl_3$ to undergo simple alcoholysis with FDNE, and to suffer Si—Si cleavage instead, was not surprising. Whether the cleavage is the result of reaction of the starting chloro or product alkoxydisilane has not been determined, nor has the cleaving agent been identified, e.g., HCl vs ROH. In line with the poor performance of HCl acceptors in alcoholysis of chlorosilane monomers and the facile base catalyzed redistribution of Cl_6Si_2 to $SiCl_4$ and higher polysilanes,[19] we have not attempted to esterify this disilane in the presence of amine bases. It appears more fruitful to determine whether some ratio of methyl-to-chloro substituents exists per Si atom which permits substitution but not cleavage of disilanes. If time permits, the compounds $MeCl_2SiSiCl_2Me$, $MeCl_2SiSiClMe_2$, and $Me_2ClSiSiClMe_2$ will be treated with FDNE in order to establish this point.

One potential complication in the preparation and stability of disilanes containing FDNE residues follows from the reported deoxygenation of aryl nitro compounds by disilanes, which has been studied as a function of disilane structure at 240°C and interpreted in terms of nitrene intermediates. [20] Whether similar reduction of aliphatic nitro groups and formation of siloxanes might occur during the attempted alcoholysis of chloromethyldisilanes by FDNE or subsequent heating of the alkoxymethyldisilane products may be defined by any further work in this area.

Physical properties

The object of the synthesis work was to obtain compounds whose physical properties (Table I) could be evaluated, especially against the bisformal "FEFO," compound II, which has bp 120-124° (10 mm), mp 11-13°, ρ 1.607 g/cc.[7] The bisalkoxydimethylsilane III, the dimethylsilicon analog of FEFO, had a moderately lower density than FEFO but a moderately enhanced bp ~175° (10 mm); it was hydrolytically stable at 23° to normal atmospheric moisture. The trisalkoxymonomethylsilane IV, on the other hand, had an even

more extended liquid range relative to FEFO (estimated bp 245° at 10 mm), despite a slightly higher mp. However, the mp of IV was readily depressed to the 0-5° range in the presence of small amounts of impurities, and one can contemplate the deliberate addition of III to lower the mp without significantly altering the favorably high density of IV. The disiloxane VII, with a similar density and mp to that of IV, had an even higher estimated bp (350° at 10 mm) and, like III, was hydrolytically stable in the air during normal handling. Compound IV, however, was reasonably inert to atmospheric moisture only at relative humidities < 40 % at 23°, for the possible reasons discussed below.

The tetraalkoxysilane V broke the pattern of liquidity at or near room temperature, presumably because of its greatly enhanced symmetry, and proved to be a nicely crystalline compound of very high density but extreme hydrolytic sensitivity, even in air of relative humidity < 20% at 23°, which led to handling and analytical problems. A potential hazard in working with V is therefore defined by its hydrolytic liberation of the relatively volatile and toxic FDNE. Because V is so dense, however, its admixture with other compounds such as III, IV or VII in certain applications might offer attractive possibilities when energy content is a critical consideration.

The exposure of IV to ambient air resulted in differing rates of FDNE liberation and siloxane formation depending upon the conditions of the exposure. Although compound purity and surface material and acidity had small effects on the initial, highly qualitative hydrolysis rates, the major effect was that of the airborne water concentration as expressed by the relative humidity at 22-24°. We have observed facile evaporation of FDNE which has been liberated from hydrolytic exposure of V in a well but not excessively ventilated laboratory location (1 m outside a hood drawing 50-100 cu-ft/min), and we tentatively rationalize the hydrolytic dependence of IV on humidity as follows. At high humidities, the absorption of water by FDNE liberated at the interface of IV with the air may occur more rapidly than FDNE can evaporate, with the result that more and more water is drawn into the otherwise hydrophobic sample. This would lead to multiple alkoxy group hydrolysis and irreversible formation of cross-linked, insoluble polysiloxane gels. At low humidities, however, the rate of FDNE evaporation may now compete favorably with that of water absorption, thereby removing the mechanism of water solubilization and accordingly limiting the hydrolysis rate. Ultimately, the disiloxane VII was produced from IV at RH < 40%, presumably reflecting a substantially greater hydrolysis rate of the first alkoxy group compared to the remaining two. Whether similar results would obtain for hydrolysis of III-VII in solution as a function of water concentration and solubility has not been explored.

It is difficult to assess the relative shock sensitivities of the silane esters vs FEFO for lack of overlapping reference data. Low sensitivities to non-compressive shock of III and V have been determined as described in the Results Section, but only the solid compound V has been tested under the standard[7] drop weight testing conditions for which data on other solid, explosive compounds, including FEFO, are available.[7] Data for V, Tetryl and RDX were reported to the writer by telephone from Silver Spring and indicated V to resemble the relatively stable Tetryl rather than the 2-fold more sensitive RDX. However, FEFO, RDX and Tetryl were all assigned similar sensitivities in ref. 7, as illustrated below, with RDX appearing ~ 4-fold less sensitive than reported by Kamlet. Comparison of V vs FEFO is therefore not possible on the basis of the data at hand.

1234567890

1234567890

1234567890

1234567890

$$H_{50} \text{ (cm)}$$

Compound	Kamlet, telephone 2.5 kg, sandpaper	Ref. 7 5 kg, sandpaper
$(RO)_4Si$, V	30.5	--
Tetryl	30.5	28
RDX	15.8	28
FEFO	--	28

Thermochemistry

Calculations are summarized in Table III both for compounds actually prepared and for potential, pure monomers or polymer units. The latter include structures containing high energy groups bound to Si through CH_2 groups as well as through oxygen atoms. The calculation of detonation pressures (P) and velocities (D) requires knowledge of compound densities and hence could be carried out only for the known compounds prepared in this work. Given the $\emptyset$-values, however, one can readily calculate P and D for "best-guess" or other density values, as we have done for the disilane $(RO)_2MeSiSiMe(RO)_2$. Thus, for alkoxydisilanes vs alkoxydisiloxanes, the known minor density differences between the hexamethoxy and hexaethoxy pairs[21] can be presumed to hold for higher alkoxy compounds. One could therefore assume for the disilane a density 1.60 g/cc by analogy to that of the corresponding disiloxane VII and calculate values of P = 216.4 kbars and D = 7.25 km/sec. Of course, when the densities of 2 compounds are similar, eqs 19 and 20 show that comparison of $\emptyset$ or $\emptyset^{1/2}$ values immediately reveal the proportional differences between the compounds in P and D.

Considering only the four compounds III, IV, V and VII of known densities, two points are worthy of note. Clearly, as the number of FDNE residues per Si atom increases, the $\emptyset$-values increase, although the energy contents Q remain about constant. The increment in $\emptyset$ is about 0.5 unit per OR group. Furthermore, if one plots density vs detonation velocity for the four compounds, a good linear relationship results (circles, Fig. 1), i.e., $D = 0.49 + 4.22(\varrho)$. Whether this reflects coincidence or a real degree of internal consistency is open to question. The correlation of ϱ vs $\emptyset$, also shown in Fig. 1 (crosses), is less well defined.

When the two non-hydrolyzable structures containing $SiCH_2R$ groups are compared to the corresponding alkoxysilane compounds V and VI, a high coincidence of $\emptyset$-values results despite significant differences in Q. Thus, unless the densities of the $SiCH_2R$ compounds differ substantially from those of the corresponding SiOR compounds or the basis of our computations proves erroneous, we would anticipate little difference in P and D

FIG. 1

Correlation of Density ρ with Detonation

Velocity D (Circles) and the Quantity ϕ (Crosses)

in   Fluorodinitroethoxysilane Esters
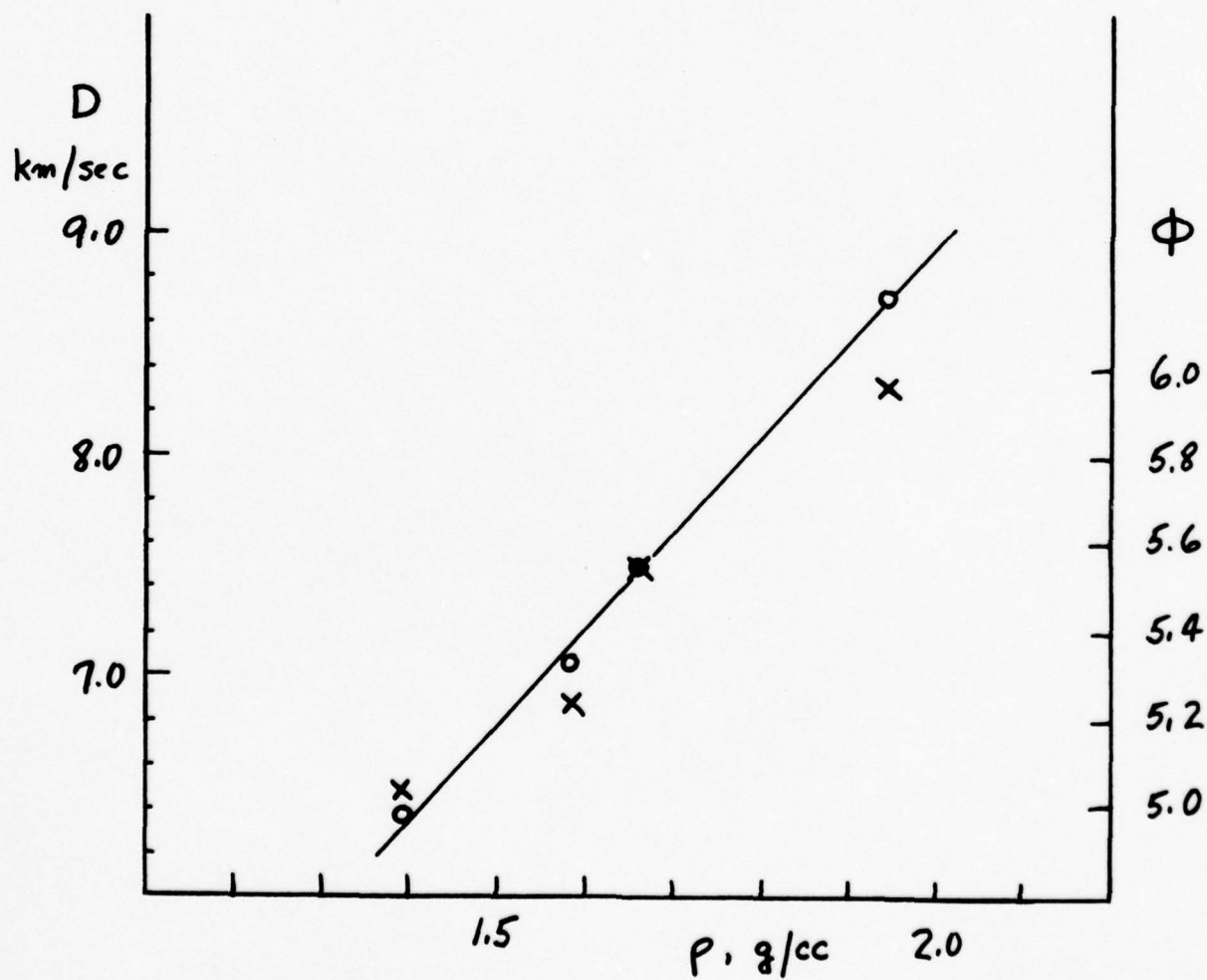
values between the corresponding hydrolyzable vs non-hydrolyzable silanes.

The consideration of physical properties in the preceding subsection suggests the trisester IV or disiloxane VII as preferred candidates to extend the liquid range of FEFO but reduce the shock sensitivity without losing density. Comparison of the energy contents and detonation properties of IV and VII vs FEFO reveals a close match between FEFO and IV, with VII delivering a somewhat lower theoretical D. Thus, FEFO is cited[7] to have Q = − 1390 cal/g and D = 7.50 km/sec; we calculate the same Q but a higher D (7.94). Overall, therefore, ester IV possesses very favorable properties relative to FEFO except for a sensitivity to atmospheric moisture at high relative humidities.

EXPERIMENTAL

Purification of 2,2,2- fluorodinitroethanol (I). A typical, preferred procedure was the following. One hundred thirty ml of a 33 wt-% solution of FDNE in methylene chloride, as received from Fluorochem, Inc., was dried over 15 g of Linde 4A Molecular Sieves for 1.5 hr with occasional swirling and then stripped to 62.5 g of crude I. To this was added with swirling 12 micro drops (0.30 g) of conc H_2SO_4. Distillation of 61.8 g (39 ml) was carried out using a 50 ml pot with a capillary nitrogen bleed and a 60 cm x 0.6 cm i.d. heated column containing a snugly fitted 16 ga tantalum wire spiral for fractionation. Five fractions were collected at 0.40 - 0.45 mm pressure (measured on the pump side of the cold trap), bp 37.5-39.5°; 8.5 g of a dark, viscous residue remained. The silicone oil heating bath temperature was maintained at 72-82° throughout.

Following a forerun, the last four fractions, all containing about 3.6 mol-% of the formal IX, were combined to afford purified I as used, net 47.2 g, n_D^{23} 1.4323, d^{22} 1.575 g/cc. In the absence of H_2SO_4, an increasing index of refraction attended increasing fraction numbers, typically n_D^{22} 1.4328 ⟶ 1.4318, as nmr analysis revealed an increasing content of IX of typically 2 ⟶ 5%. The effect of temperature upon the refractive index of I was normal, as illustrated by two samples both containing ∼ 2 mol-% of IX, $n_D^{21.5}$ 1.4336 and n_D^{26} 1.4316. When insufficient or no pre-drying of the crude FDNE occurred, water was obtained in the cold trap before substantial distillation of the alcohol began, whether or not H_2SO_4 was used. A pure sample of IX was neither isolated nor synthesized; only its bp 58-61° (1.5 mm) and H-nmr spectrum (Table II) have been reported.[2]

The physical constants of the distilled FDNE were in reasonable agreement with those reported for the compound: d^{20} 1.5851 g/cc;[22] n_D^{20} 1.4338[22] or n_D^{25} 1.4430;[23] bp 55° (0.5 mm);[24] 38-39° (0.1 mm);[23] or 62-66° (1-2 mm);[22] mp 7°[22] or 12°.[24] The ir spectrum of I is reproduced in Appendix B and agreed with the reported spectra.[22-24]

The H-nmr spectra of FDNE samples facilitated the analysis for the contained impurity IX, which proved impractical for us by glpc due to decomposition of I. Although the $X_3CCH_2OCH_2$- portion of the spectrum of IX superimposes on the methylene resonances of I, integration of the upfield OCH_3 singlet of IX and allowance for the 4/3 greater area

due to the remaining 4 protons permitted separation of the spectra of mixtures of I + IX by area and yielded mol-% purity estimates. In order to isolate the OCH_3 peak, it was necessary to collapse the FDNE-OH triplet and shift its resonance slightly downfield from the OCH_3 peak which it overlaps in $CDCl_3$ solvent; this was accomplished by the addition of traces of CF_3COOD. Alternatively, the coupled OH resonance could be isolated well downfield of even the $X_3C\,CH_2$ group (a doublet of a doublet due to ^{19}F primary splitting and lesser coupling to the OH) by using d_6-acetone solvent instead of $CDCl_3$. Spectra illustrating these solvent effects and the spectrum of IX are given in Appendix B. The presence of water in FDNE samples was indicated when the CH_2: OH area ratio fell below the usually exact 2:1 value.

Although solution of FDNE in acetone resulted in a significant exotherm, no indication of the formation of new products, such as the ketal, was noted even after several days. The exotherm was thus assumed to reflect the formation of H-bonded complexes of FDNE with acetone, analagous to the similar behavior of F_3CCH_2OH.[25]

<u>Dimethyl(bis-2,2,2-fluorodinitroethoxy)silane (III)</u>. The synthesis of III required the direct, stoichiometric reaction of FDNE with Me_2SiCl_2 (eq 2). To a 100 ml 4-necked flask oven-dried at 140° and fitted with thermometer, septum, stopcock, and water-cooled reflux condenser was added 5.86 ml (0.06 mol) of distilled, 96% pure FDNE. The stopcock and condenser exit were fitted with a nitrogen line set up to permit passage through or by-passing the pot; the nitrogen exited through a silicone oil bubbler. To the magnetically stirred alcohol was then added via syringe 3.6 ml (0.03 mol) of pure Me_2SiCl_2. The resulting solution was heated to 78° over 1.5 hr with a very slow stream of nitrogen in the by-pass mode, whereupon the mixture was cooled and left to stand overnight. Nmr analysis of an aliquot sample revealed the presence of both the desired bisester III, $(RO)_2SiMe_2$, and the half-reacted silane $ROSiMe_2Cl$, the latter from its absorption at δ 0.53 ppm, intermediate between that of III and the starting silane at 0.81 ppm in $CHCl_3$. About 25% of the alcohol remained unreacted.

The solution was reheated at 70-83° for 2.5 hr under a very slow flushing stream of nitrogen to remove residual HCl. This resulted in complete conversion of the monoester and of half of the remaining alcohol. On the assumption that some volatilization loss of the starting Me_2SiCl_2 had occurred, an amount equal to 10% of the original charge of the silane was added and the solution heated 1 hr at 74-81° without nitrogen flushing and a final 1 hr at 81° with flushing. However, a small amount of FDNE still remained. A majority of the crude product (8.9 g) was then distilled through a 10 cm x 12 mm i.d. micro Vigreaux column from a 15-ml pot with capillary air bleed to afford 0.45 g of a forerun, bp ~ 30° (0.15 mm), and 8.4 g of III, bp 103-105° (0.2 mm), n_D^{23} 1.4302-1.4304. The pressure in this and all other micro scale distillations cited was measured between the pot and the cold trap. The presence of an impurity was indicated by an H-nmr Si-Me peak at highfield not due to III and subsequently found to characterize the disiloxane X.

This product and a similar sample of III were redistilled under the same conditions to afford the purest sample (Table I), although X was still observed in the later fractions. The mp shown in Table I was determined on the bulk material. The nmr spectral data for III are given in Table II, and the ir spectrum is included in Appendix B along with that of X.

Anal. Calcd for $C_6H_{10}F_2N_4O_{10}Si$: C, 19.78; H, 2.77; F, 10.43; N, 15.38; Si, 7.71. Found: C, 20.45; H, 2.72; F, 10.29; N, 15.32; Si, 6.43. The calcd values for a mixture of III with 3 mol-% of disiloxane X are very little different from those for the pure compound. Galbraith laboratories performed all the elemental analyses reported herein

in duplicate, the average of which are given, and state that Si was determined by fusing the sample with Na_2O_2 in a Parr Bomb, washing the resulting sodium silicates and fluoride with water, neutralizing, and subjecting the solution to colorimetric or atomic absorption analysis.

A pure sample of disiloxane X was isolated by preparative glpc using a reaction product III (see below) particularly rich in X and other impurities, once it became apparent that the impurities were most likely a mixture of polysiloxanes, $ROMe_2Si[OSiMe_2]n$ $OSiMe_2OR$, wherein compounds with n = 0 (compound X), 1 and 2 were indicated by glpc and ir examination of distillation fractions and residues. Thus, peaks were eluted at 200° from a stainless steel column containing methylphenylsilicone gum SE52 on ChromosorbW packing in the regular progression with time typical of polysiloxane homolog mixtures. In samples with increased amounts of high boilers relative to the main component $(RO)_2SiMe_2$, the ir intensity in the 1050 cm^{-1} SiOSi region was proportionately larger. The preparative-scale separation of III and X was achieved on a methylsilicone glass column at 200-250°, which also afforded a few microliters of the next to elute peak, presumably the (tri)siloxane above (n = 1, compound XIV). Reinjection of the separated fractions using the stainless steel column proved X to be ~95% pure and stable to the separation conditions, but indicated some decomposition of the bisester III occurred unless the glass column and injector were used. The nmr spectrum of disiloxane X, n_D^{23} 1.4218, is summarized in Table II; the ir spectrum of XIV is given in Appendix B.

An alternative procedure for the preparation of III involved the dropwise addition of 0.052 mol of KOH-dried pyridine to a mixture of 0.052 mol FDNE and 0.026 mol of Me_2SiCl_2 in 15 ml of pure $CHCl_3$ at 0°- 5° over 30 min and stirring the resulting colorless solution for 3 hr as it warmed to 25°. The chloroform had been freed of stabilizer ethanol by passing it through an Al_2O_3 column. Work-up by concentration and precipitation of pyridine·HCl (100%) by ether dilution and reconcentration yielded a crude product containing a roughly 4:1 mixture of bisester III with disiloxane X. A product even richer in impurities was produced from a similar reaction in dimethoxyethane solvent at 0° (mixture FDNE + pyridine in DME added to chlorosilane in DME); distillation of this afforded the samples from which X and XIV were later separated.

Methyl(tris-2,2,2-fluorodinitroethoxy)silane (IV). Compound IV was prepared similarly to III except that a Dry Ice reflux condenser was now employed to prevent entrainment loss of the volatile chlorosilane in the liberated HCl gas. To 14.7 ml of 96% FDNE (0.145 mol) was added 5.70 ml (0.048 mol) of $MeSiCl_3$ (containing 4% of Me_2SiCl_2, for which no allowance was made) at 25° and the resulting 2-phase mixture stirred while heat was applied. The system was temporarily closed through the bubbler in order to premit observation of the rate of gas evolution with time and temperature. After 20 min, the mixture became homogeneous at 33° and began a moderate rate of gas evolution five minutes later at 42°. Heating was continued to 55° over an additional 3 hr, whereupon the rate of gas evolution roughly doubled. A final 3 hr heating at 55-67° led to cessation of significant gassing, and the now orange solution was cooled under nitrogen. A 4-hr period of flushing the stirred solution at 64-73° with an increasingly more rapid stream

of nitrogen followed, and the crude product was then stripped in a micro pot-to-pot still at 65-85° heat bath temperature to yield 1.7 g of distillate, bp 37-38° (0.1 mm), and 21.9 g (91% of theoretical, unadjusted for transfer losses) of crude IV as the residue, n_D^{23} 1.4416.

It was determined that crude IV appeared stable to high temperature, boiling off from a 315° porcelain surface without decomposition, and to shock, showing little sign of reaction to being struck repeatedly on a steel plate by a hammer. A 4.0 ml (6.41 g) sample was then subjected to micro pot-to-pot distillation; a bp ~ 155° (0.1 mm) was first estimated from a bp vs mol wt plot of the known compounds I, $FC(NO_2)_2 CH_2OSiMe_3$, [26] III, and the complete 4-silane series $[F_2C(NO_2)CH_2O]_n SiMe_{4-n}$.[14] There was obtained 80 wt-% of the pot charge as pure IV (Table I) at a heat bath temperature 195-210°; the forerun contained the bisester impurity III. The nmr data are given in Table II, and the ir spectrum in Appendix B.

Anal. Calcd for $C_7H_9F_3N_6O_{15}$ Si: C, 16.74; H, 1.81; F, 11.35; N, 16.73; Si, 5.59. Found: C, 17.04; H, 1.98; F, 9.99; N, 15.89; Si, 4.88.

An alternative to distillative purification was suggested when the undistilled balance of crude IV partially crystallized after 2-wk standing at 0-5°. Cold decantation removed impure IV and left IV in as pure a state as provided by distillation. Unfortunately, the initial crystallization required was both slow and unpredictable among various pure and crude samples of IV. For example, crude IV as prepared from pure MeSiCl₃ (see Results Section A) remained totally fluid at 0° over 2 mo.

Tetrakis (2,2,2-fluorodinitroethoxy)silane (V). A 50% excess relative to the chlorosilane of distilled FDNE (0.12 mol, 18.5 g, accompanied by 1.8 g of the impurity formal IX) was warmed to 40° with good stirring under nitrogen in the dried apparatus previously described for IV. Electronic grade SiCl₄ (0.08 mol, 2.3 ml) was slowly added beneath the surface in 4 equal portions at 1 hr intervals to maintain homogeneity, although this was probably not necessary to a successful reaction. The system was maintained open to a very slow nitrogen stream at the condenser exit except when observation of the gas evolution rate was desired.

One hour after the final addition of chlorosilane, the internal temperature was increased to 65° over 3 hr as occasional refluxing continued. The esterification proceeded steadily but rather slowly, apparently limited by the relatively low reaction temperature required by the volatility of SiCl₄ and its insolubility in the alcohol. Following an overnight interruption at 23°, the solution was further heated at 65-70° for 1.5 hr and then for 3 hr under a slowly increased rate of nitrogen flushing. The homogeneous, yellow oil which resulted upon cooling remained liquid at 25° but began crystallizing upon transfer of most of it (19.7 g) to a 50 ml single-necked pot for distillation of the excess FDNE and other volatiles. The dry, glass syringe employed for the transfer had a 15-gauge stainless steel needle and Teflon ring-sealed plunger. No condensate was found in the nitrogen line cold trap.

The now solidified reaction mixture was warmed under the well-insulated micro Vigreaux column at 7 mm pressure, and the resulting melt was then stirred magnetically at 0.25 mm for distillation of FDNE at an external pot temperature of 60-85°. Spattering of the semi-solid residue in the pot was pronounced as 4.8 g of distillate was obtained, bp ~ 30°, which contained 4.1 g of FDNE and 0.7 g of IX. The 14.7 g of residue was heated to solution at 58° (external) under dry nitrogen with 26 ml of alcohol-free chloroform along with the 2 ml of chloroform solution plus solids obtained on rinsing the original reaction pot, and massive crystallization followed upon cooling. The crystals were collected with the minimum exposure to air, short of working in a dry-box, by dumping the entire, chilled mixture with one motion into a dry, 60-ml Buchner funnel rigged to operate under nitrogen. The funnel was immediately recapped and the filtrate rapidly forced through the coarse frit into a nitrogen-protected receiver by nitrogen pressure. A rinse of the crystallization pot with 5 ml of cold solvent was similarly filtered, and the precipitate of dense, white platelets was blown dry with nitrogen to give 12.2 g (95 % vs $SiCl_4$) of V, mp 56-79°. Transfers and samplings were carried out in a dry box under N_2.

The crystallization filtrate was evaporated to 3.2 g of residue, estimated by nmr to contain 1.4 g of FDNE, ~ 1 g of V and 0.16 g of IX. The total recovery of excess FDNE was thus 5.5 g (90 %), and of formal IX 0.86 g (48 %).

Recrystallization of V from 2 ml $CHCl_3$ per gram afforded 94 wt % recovery of solids (89% yield). Further recrystallizations failed to improve the mp, despite one's carrying out of all operations involving air contact with V, except filtration as above, in a dry box. The ir spectrum of V was recorded in CH_2Cl_2 solution (Appendix B), and nmr spectra in pure, dry d_6-acetone because of solubility considerations (Table II).

Anal. Calcd for $C_8H_8F_4N_8O_{20}Si$; C, 15.00; H, 1.26; F, 11.87; N, 17.50; Si, 4.39. Found: C, 14.60; H, 1.54; F, 11.06; N, 16.44; Si, 4.21. Minor hydrolysis of V to FDNE and siloxanes should not affect the elemental analyses except for H as long as no losses occur.

Hydrolysis of orthoester V to polysiloxanes VI. Illustrative of the preparative and analytical results are the following experimental results based on the stoichiometries of reactions 7 and 8. In small scale experiments, 0.5 or 1 mole of water (in 1 ml of acetone) per mole of orthoester V was added to 1 g of V in 1 ml of acetone at 23°. The resulting solutions, along with those containing half the solvent concentration, were analyzed by H-nmr (220 MHz); greater relative amounts of water produced gels before spectra could be recorded the next day. The 4-peak CH_2 pattern due to free ROH (FDNE) lay well up-field of the complex CH_2 pattern due to ester residues ≡SiOR, and the alcohol-OH triplet lay conveniently down-field; no reaction between FDNE and the ketone solvent had been observed in previous studies, although the heat of solution was substantial. Within the CH_2- products absorption envelope, the pattern was doubled by proton coupling to ^{19}F, and chemical shifts in $(RO)_x Si(OSi)_{4-x}$ structures progressed marginally up-field as x decreased from 4 to 2. The chemical shift differences were slightly more pronounced in the more dilute solutions.

Best estimates were made of the overlapping peak areas of the partial structures with x = 2, 3 and 4 using 100 Hz sweep width expanded spectra of the ester region. The relative amounts of free alcohol and total ester compounds were calculated, and the percentages of x = 2 vs 3 vs 4 partial structures determined vs the total ester contents, (Table IV). These solutions proved too dilute for confirmatory [29]Si-nmr analysis even after 30,000 scans and could only be analyzed in the presence of Cr (acac)[3]. Unfortunately, the spin relaxation catalyst also affected the equilbria, so that the peaks representing the various types of Si atoms (see p 15) showed a marked change in the relative amounts of tetra vs dialkoxy-Si in favor of the former. These hydrolysis solutions therefore showed about the theoretical amount of Si-OR hydrolytic cleavage overall at both stoichiometries, but the selectivity for formation of the theoretical products (eqs 7 and 8) was poor, even before any subsequent work-up.

TABLE IV

Hydrolysis of 1.0 g of $(RO)_4$ Si

Relative Mols H_2O	ml Acetone	% Hydrolysis of RO-Groups	% Group type in ester mixture		
			$(RO)_4$ Si	$(RO)_3$ Si-	$(RO)_2$ Si=
0.5	2	27	30	34	36
0.5	1	25	24	33	43
1.0	2	47	10	20	70
1.0	1	40	14	22	64

Hydrolysis on a larger scale using 8.7 g of V with equimolar water in 20 ml of acetone was then carried out with analyses performed at the three stages of work-up: 1) reaction solution, 2) solvent only removed (1 mm vacuum at 20°), and 3) liberated alcohol also removed (65°, 0.5 mm). Analysis revealed ~ 55% hydrolysis of RO-Si groups at work-up stages 1 and 2, with allowance (as above) for disiloxane impurity already present in the starting orthoester. However, the low level of remaining V and high concentration of the desired difunctional materials VI present at stage 1 gave way on solvent removal to substantial reduction of VI in favor of starting material V and disiloxane XI. Only relatively minor changes occurred at the final stage 3. The 220 MHz H-nmr spectra were now too complex for further, meaningful analysis of the amounts of the different types of silicon. Although small changes in the [29]Si-nmr spectra of the stages 2 vs 3 product mixtures were noted, they were not nearly as marked as the change from stage 1 and showed similar compositions including (from peak heights) : 19% of $(RO)_4$ Si, 12% of a compound tentatively believed to be $(RO)_3$ SiOH, 22% of $(RO)_3$ $\underline{Si}$ O Si type structures, 21% of $(RO)_2$ Si $(OSi)_2$ type, and 26% of RO $\underline{Si}$ $(OSi)_3$ type (cross-linking). The [29]Si-nmr spectrum of the stage 3 product is included in Appendix B.

1, 2-Dimethyl-1, 1, 2, 2- tetrachlorodisiloxane (XII). The precursor to di-siloxane VII was prepared by chlorination of the available tetramethoxydisiloxane ana-log according to eq 9. To 357 g (3.0 mol, 25% excess) of $SOCl_2$ in an oven-dried 1-l 4-necked flask with mechanical stirrer, condenser, thermometer, and addition funnel, all maintained under a dry nitrogen cover, was added 3.2 g (0.012 mol) of triphenyl-phosphine in 0.5 g portions at 4°. The resulting solution was then warmed to 52°, and 135 g (0.60 mol) of 1, 2-dimethyl-1, 1, 2, 2-tetramethoxydisiloxane (Silar Laboratories) was added over ~2 hr as the temperature of the yellow, foaming solution rose to 71°. Overnight stirring at 25° was followed by 7 hr further heating at 65-75° to complete the reaction, whose progress was followed by glpc. A small lower phase was separated from the cooled reaction mixture, and the upper layer was stripped to 132 g of crude product. Distillation afforded 83.1 g (57%) of >98% pure XII, bp 142-144°, d^{24}1.295 g/cc. A small impurity was revealed from its slightly longer glpc retention time, slightly (0.067 ppm) higher field H-nmr and lower field ^{13}C-nmr (δ 7.7) Si-Me peak, and slight concentration in higher boiling distillation fractions vs the main component XII. On the basis of these indications and the presence of a corresponding impurity in the starting methoxy compound, the unknown was presumed to be the trisiloxane $MeCl_2SiOSiClMeOSiCl_2Me$. Nmr (δ), compound XII: H, 0.85; ^{13}C, 5.9; ^{29}Si, -15.0 ppm. The starting methoxy compound had δ: ^{29}Si, -48.4; ^{13}C, -6.85 (Me), 50.1 (OMe); impurity, ^{13}C, -4.7 ppm.

1, 3-Dimethyl-1, 1, 3, 3- tetrakis (β, β, β,- fluorodinitroethoxy)disiloxane (VII). To 12.2 g (0.05 mol) of XII in the reactor described above for IV was added 30% of the stoichiometric amount (0.20 mol, after allowance for the formal IX of FDNE with good stirring under a very slow sweep of nitrogen. The inhomogeneous mixture was heated to 60° over 30 min, when solution occurred, and dropwise addition of the alcohol was resumed to completion over 3 hr. Acidic gas was liberated slowly but continuously until the mixture was cooled after a further 4 hr at 60-68°. Nmr analysis revealed only 35% esterification of the Si-Cl groups at that point, however, and heating was re-sumed for 18 hr at 50°, now without Dry Ice condenser coolant, to afford 90% reaction. A final 4 hr at 70° produced a mixture wherein none of the Si-Cl groups, but 19% of the FDNE, remained. Compound VII was obtained in ~95% purity following a high vacuum pot-to-pot strip at 25-60° internal pot temperature (Table I). The yield of the yellow oil, which solidified only after 1 wk at 5° and then had a bulk mp ~15-20°, was 30.8 g after correction for aliquot sample removal.

Nmr spectra are summarized in Table II; the ir spectrum of VII is reproduced in Appendix B along with the illustrative ^{13}C and ^{19}F spectra. H-Nmr spectra of methyl protons in partially esterified XII were conveniently analyzed by the well-separated res-onances due to starting material and product moieties $SiMeCl_2$ and $SiMe(OR)_2$ and the intermediate SiMeCl(OR) structure (δ ~0.65 ppm; 3 types depending on the other half of the molecule). The impurity XIII in VII (see Results Section A) was revealed most clearly in the ^{29}Si-nmr spectrum by a peak at -55.9 ppm, whose location required 1 methyl group attached to the Si; the relative peak heights suggested a maximum 7 wt-% of XIII, and the H-nmr results concurred.

Hexachlorodisilane reaction with FDNE.   The disilane was distilled before use, bp 148°, d^{23} 1.55.   A sample (95% pure, 0.017 mol) was added to 0.15 mol of FDNE (97% pure, 50% excess) at 25° in the reactor described previously.   Stirring the two-phase mixture led to rapid gas evolution, consequent cooling to 18°, and finally a viscous, colorless solution at 23° after 1.25 hr with cessation of gassing.   Precipitation began 10 min later.   The resulting slurry was heated to 60°, whereupon solution occurred and a mildly exothermic reaction then took place over 30 min and was controlled at 70-73°.   A lemon yellow color appeared, which was slowly transferred to the bubbler under slow nitrogen sweeping of the reaction pot.   Following the exotherm, heating at 65-70° was continued for 6 hr, when the slow gas evolution from the now pale straw-colored solution had ceased.

Nmr and ir analyses of the product mixture revealed that reaction of greater than the theoretical amount of FDNE had occurred, no Si-H was present, and four compounds comprised the mixture apart from FDNE.   From the ^{29}Si-nmr resonance positions (δ -89.4 and -95.4 ppm) and peak heights and the 220 H-nmr areas it was obvious that the two major compounds were orthoester V and disiloxane XI in ~2:1 molar ratio.   The desired disilane VIII was ruled out except as one of the two very minor products by the absence of ^{29}Si absorption in the expected region near -16 ppm; we assumed the same effect upon chemical shift of the siloxane oxygen in VII vs VIII as observed in $Cl_3SiSiCl_3$, -6.2 ppm, vs $Cl_3SiOSiCl_3$, -45.6 ppm).

Separation of the oil from precipitated solids in the product mixture after 15 hr at 5° and recrystallization of the residue from chloroform afforded 8.8 g of V, mp 62-72°, a yield of 42% assuming total cleavage of the disilane.

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$FC(NO_2)_3$ (Grakauskas and Baum, loc. cit; M. J. Kamlet and H. G. Adolph, J. Org. Chem., 33, 3073 (1968)) and formylation of the fluoronitroform with H_2O_2-formaldehyde (Kamlet and Adolph, loc. cit.).

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APPENDIX A

CALCULATED THERMOCHEMICAL DATA FOR

FLUORODINITROALKOXYSILICON AND RELATED COMPOUNDS

The sources of data and computations employed in arriving at the results summarized in Table III (Results Section) are given in the following pages of Appendix A. When necessary bond dissociation or heat of formation data was lacking, estimates were obtained either by analogy to similar bonds in similar compounds for which data were available, or by calculations based on group incremental contributions to compound heats of formation.[27]

Once the heats of detonation had been calculated, eqs 19 and 20 of the Results Section were applied to the determination of the values of $\emptyset$, P and D given in Table III. The quantity N is the number of moles of <u>gas</u> produced in the decomposition reaction assumed for the compound, divided by the compound molecular weight, i.e., moles of gas per gram of compound. The quantity M is the total grams of gaseous products per mole of compound, divided by the total number of moles of gases, i.e., average mol wt per mol of gas. The dependence of P and D on the decomposition mode assumed is illustrated in Section V for the disiloxane VII in greater detail than was presented in the Results Section.

A bond dissociation energy for the bond X - Y is denoted $D(X - Y)$. The symbol $\overline{D}$ denotes the average bond dissociation over more than one identical bond when all three have been broken; D_T denotes the total bond dissociation energy of three or four bonds to Si without individual differentiation. In each case, "R" denotes the group $-CH_2CF(NO_2)_2$ unless specified otherwise. All thermochemical calculations are made for gas phase reactions at 298°K ; negative values denote exothermicity.

<u>CONTENTS</u>

I. REFERENCE VALUES

Entry		Value (kcal/mol)	Reference
ΔH_f (FEFO)		-177.5	7
ΔH_f (EtO)$_2$SiMe$_2$		-199.	27
ΔH_f (EtO)$_4$Si		-322.	27
$\Delta H_f = \Delta H_{sub}$ (Si)		106.	28
ΔH_f (CH$_2$)		90.	10
ΔH_f (CH$_3$)		34.	10
ΔH_f (CH$_2$CH$_3$)		25.7	10
ΔH_f (CH$_2$CH$_2$CH$_3$)		21.	10
ΔH_f (SiO)		- 24.2	28
	or	- 21.4	11
ΔH_f (EtO)		- 6.7	10
ΔH_f (Et$_4$Si)		- 90.	27
ΔH_f (Me$_3$SiOSiMe$_2$OSiMe$_3$)		-350.	27
ΔH_f (O atom)		59.6	10
ΔH_f (SiO$_2$ solid)		-217.5	28
ΔH_f (SiF$_4$)		-370.	13
ΔH_f (HF)		- 64.8	28
ΔH_f (H$_2$O)		- 57.8	28
ΔH_f (CO$_2$)		- 94.05	28
D (Si-CH$_3$)		76.	29
$\underline{D}$ (Si-Si)		75 $\pm$ 8	31
$\overline{D}$ (Si-O)		106.	30
		115.1	9

II.   CALCULATION OF PRELIMINARY VALUES

A. $\bar{D}$ (RO-CH$_2$-OR), model R = Et

Calculated ΔH_f (EtO)$_2$CH$_2$ from bond additivity
values [27] = -88.5

$2\,\bar{D}(\text{EtO-CH}_2)$ = $2\Delta H_f$ (EtO) + ΔH_f (CH$_2$) - ΔH_f (EtO)$_2$CH$_2$

$2\,\bar{D}(\text{EtO-CH}_2)$ = $2(-6.7)$ + 90 - (-88.5)

$\bar{D}(\text{EtO-CH}_2)$ = 82.6

B. $\bar{D}$(RO-Si), model R = Et, in (RO)$_4$Si

$4\,\bar{D}(\text{EtO-Si})$ = $4\Delta H_f$ (EtO) + ΔH_f (Si) - ΔH_f (EtO)$_4$Si

= $4(-6.7)$ + 106 - (-322)

$\bar{D}(\text{EtO-Si})$ = 100.3

C. $\bar{D}$(R-Si); model R = Et, in R$_4$Si

$4\,\bar{D}(\text{Et-Si})$ = $4\,\Delta H_f$ (Et) + ΔH_f (Si) - ΔH_f (Et)$_4$Si

= $4(25.7)$ + 106 - (-90)

$\bar{D}(\text{Et-Si})$ = 74.7

D. D_{total} (Si - bonds) in (RO)$_2$SiMe$_2$, model R = Et

D_T = $2\Delta H_f$ (EtO) + $2\Delta H_f$ (Me) + ΔH_f (Si) - ΔH_f (EtO)$_2$SiMe$_2$

= $2(-6.7)$ + $2(34)$ + 106 - (-199)

D_T = 359.6, all 4 bonds to Si

E. $\bar{D}$ (Si-O) in model trisiloxane Me$_3$SiOSiMe$_2$OSiMe$_3$

1)   Dissociation to SiO as a product

For the reaction
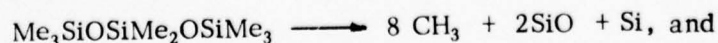
Me$_3$SiOSiMe$_2$OSiMe$_3$ $\longrightarrow$ 8 CH$_3$ + 2SiO + Si, and
assuming $\bar{D}$ (Si-Me) = D(Si-Me)

$2\,\bar{D}(\text{Si-O})$ + $8\,\bar{D}(\text{Si-CH}_3)$ = $8\Delta H_f$ (CH$_3$) + $2\Delta H_f$(SiO) + ΔH_f (Si)
$- \Delta H_f$ (trisiloxane)

$$2\,\bar{D}\,(Si\text{-}O) \ + \ 8\,(76) \ = \ 8\,(34) \ + \ 2\,(-24.2) \ + \ 106 \ - \ (-350)$$

$$\bar{D}\,(Si\text{-}O) \ = \ 35.8, \text{ a very low value due to}$$

$$D(Si\text{-}O) \text{ of the monoxide } = \ 189.8 \text{ (calc'd)}$$

2) Dissociation to Si + O products

$$Me_3SiOSiMe_2OSiMe_3 \longrightarrow 8\,CH_3 \ + \ 3Si \ + \ 2\,O$$
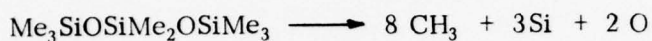
$$4\,\bar{D}\,(Si\text{-}O) \ + \ 8\,\bar{D}\,(Si\text{-}Me) \ = \ 8\,\Delta H_f\,(Me) \ + \ 3\Delta H_f\,(Si) \ + \ 2\Delta H_f\,(O)$$
$$- \ \Delta H_f \text{ (trisiloxane)}$$

$$4\,\bar{D}\,(Si\text{-}O) \ + \ 8\,(76) \ = \ 8\,(34) \ + \ 3\,(106) \ + \ 2\,(59.6) \ - \ (-350)$$

$$\bar{D}\,(Si\text{-}O) \ = \ 112.8$$

F. D_T in model polymer unit $\{Si(OEt)_2O\}$

1) Decomp. to SiO product (1 of 2 Si-O bonds broken)

$$D_T\,(2\,Si\text{-}OEt \ + \ Si\text{-}O) \ = \ 2\Delta H_f\,(EtO) \ + \ \Delta H_f\,(SiO) \ - \ \Delta H_f \text{ (monomer)}$$

Calculate from ref. 27 ΔH_f (monomer unit) $= -264.8$

$$D_T \ = \ 2\,(-6.7) \ + \ (-24.2) \ - \ (-270.3)$$
$$= \ 227.2$$

2) Decomposition to Si + O (all 4 bonds to Si broken)

$$D_T\,(Si\,\equiv) \ = \ 2\Delta H_f\,(EtO) \ + \ \Delta H_f\,(Si) \ + \ \Delta H_f\,(O) \ - \ \Delta H_f \text{ (monomer)}$$
$$= \ 2\,(-6.7) \ + \ 106 \ + \ 59.6 \ - \ (-270.3)$$
$$= \ 417.0$$

G. D_T (Si $\equiv$ bonds) in model polymer unit $\{Si(Et)_2O\}$,
   dissociation to SiO

$$D_T\,(2\,Si\text{-}Et \ + \ Si\text{-}O) \ = \ 2\Delta H_f\,(Et) \ + \ \Delta H_f\,(SiO) \ - \ \Delta H_f \text{ (monomer)}$$

Calculate[27] ΔH_f (monomer) $= -148.8$

$$D_T \ = \ 2\,(25.7) \ + \ (-24.2) \ - \ (-148.8)$$
$$= \ 176.$$

H. D_T in model polymer unit -[MeSi(OEt) O]-,

decomposition to SiO

$$D_T \text{(Si-Me + Si-OEt + Si-O)} = \Delta H_f \text{(EtO)} + \Delta H_f \text{(SiO)}$$
$$+ \Delta H_f \text{(Me)} - \Delta H_f \text{(compound)}$$

Calc.[27] ΔH_f (compd):

8	C-H	-30.64
1	C-C	2.73
1	C-O	-12.0
1	C-Si	-6.0
3	Si-O	-156.0
		-201.9

$$D_T = -6.7 - 24.2 + 34 - (-201.9)$$
$$= 205$$

I. $\Delta H_f \text{(RO} \cdot \text{)}$

$$\text{RO-CH}_2\text{-OR} \longrightarrow 2\text{(RO)} + \text{CH}_2$$
FEFO
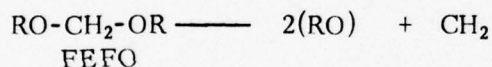
$$2\overline{D} \text{(RO-CH}_2\text{)} = 2\Delta H_f \text{(RO)} + \Delta H_f \text{(CH}_2\text{)} - \Delta H_f \text{(FEFO)}$$
(use II-A)   (known)

$$2(82.6) = 2\Delta H_f \text{(RO)} + 90 - (-177.5)$$
$$\Delta H_f \text{(RO)} = -51.2$$

J. $\Delta H_f \text{(R} \cdot \text{)}$
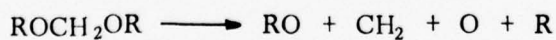
$$\text{ROCH}_2\text{OR} \longrightarrow \text{RO} + \text{CH}_2 + \text{O} + \text{R}$$
$$2\overline{D} \text{(RO-CH}_2\text{)} + D\text{(O-R)} = \Delta H_f \text{(OR)} + \Delta H_f \text{(CH}_2\text{)} + \Delta H_f \text{(O)}$$
$$+ \Delta H_f \text{(R)} - \Delta H_f \text{(FEFO)}$$

to calculate D(O-R) use
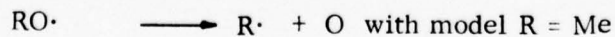
$$\text{RO} \cdot \longrightarrow \text{R} \cdot + \text{O with model R = Me}$$
$$D\text{(O-CH}_3\text{)} = \Delta H_f \text{(CH}_3\text{)} + \Delta H_f \text{(O)} - \Delta H_f \text{(OCH}_3\text{)}$$
$$= 34 + 59.6 - 2 = 95.6$$

$$2(82.6) + 95.6 = -51.2 + 90 + 59.6 + \Delta H_f \text{(R)} - (-177.5)$$
$$\Delta H_f \text{(R)} = -15.1$$

K. $\Delta H_f (RCH_2 \cdot)$

for reaction $R\,CH_2 \cdot \longrightarrow R \cdot + CH_2$
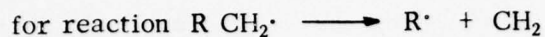
$$D(R\text{-}CH_2) = \Delta H_f (R) + \Delta H_f (CH_2) - \Delta H_f (RCH_2)$$

Calculate $D(R\text{-}CH_2)$, with model $R = Et$

$$D(Et\text{-}CH_2) = \Delta H_f (Et) + \Delta H_f (CH_2) - \Delta H_f (propyl)$$
$$= 25.7 + 90 - 21 = 94.7$$

$$94.7 = -15.1 + 90 - \Delta H_f (RCH_2)$$

$$\Delta H_f (RCH_2) = -19.8$$

Compare value -20.0 obtained from $\Delta H_f (R)$ plus contribution [27] of 1 C - C and 2(C-H) bonds.

III.   CALCULATION OF ΔH_f FOR COMPOUNDS

A. $(RO)_4 Si \ (\longrightarrow 4\,RO + Si\,(g))$

$$4\,\overline{D}(Si\text{-}OR) = 4\,\Delta H_f (RO) + \Delta H_f (Si) - \Delta H_f (RO)_4 Si$$
assume $\overline{D}(Si\text{-}OR) = \overline{D}(Si\text{-}OEt)$ (see II-B)

$$4(100.3) = 4(-51.2) + 106 - \Delta H_f (RO)_4 Si$$

$$\Delta H_f (RO)_4 Si = -500.$$

B. $(RO)_2 SiMe_2 \ (\longrightarrow 2\,RO + 2\,Me + Si\,(g))$

$$D_T (Si \text{-} bonds) = 2\Delta H_f (RO) + 2\Delta H_f (Me) + \Delta H_f (Si) - \Delta H_f (RO)_2 SiMe_2$$
assume D_T same as calcd for $R = Et$ (see II-D)

$$359.6 = 2(-51.2) + 2(34) + 106 - \Delta H_f (RO)_2 SiMe_2$$

$$\Delta H_f (RO)_2 SiMe_2 = -288$$

C. $\{Si(OR)_2 O\}$ unit

Compare 4 values resulting from use of separate vs totaled D-values, and decomposition to SiO vs Si + O.

1)   Use total D-values calcd for $\{Si(OEt)_2 O\}$ in II-F-1.

$$\{Si(OR)_2 O\} \longrightarrow 2\,(OR) + SiO$$
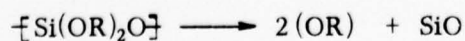
$$D_T = 2\Delta H_f (OR) + \Delta H_f (SiO) - \Delta H_f (monomer\ unit)$$

$$227.2 = 2(-51.2) + (-24.2) - \Delta H_f (monomer)$$

$$\Delta H_f (monomer) = -353.8$$

2) Use D_T calcd for $\text{-[Si(OEt)}_2\text{O]-}$ in II-F-2.

$$\text{-[Si(OR)}_2\text{O]-} \longrightarrow 2(OR) + Si + O$$
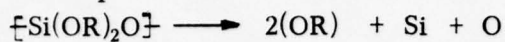
$$D_T = 2\,\Delta H_f\,(OR) + \Delta H_f\,(Si) + \Delta H_f\,(O) - \Delta H_f\,(\text{monomer})$$

$$417.0 = 2(-51.2) + 106 + 59.6 - \Delta H_f\,(\text{monomer})$$

$$\Delta H_f\,(\text{monomer}) = -353.3$$

3) Use separate Si-O bond energies.

$\bar{D}$ (Si-OR) calcd for orthoester (II-B), and

$\bar{D}$ (Si-OSi) calcd for trisiloxane decomp. to SiO (II-E-1)

$$\text{-[Si(OR)}_2\text{O]-} \longrightarrow 2\,(OR) + SiO$$
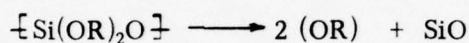
$$2\bar{D}\,(Si\text{-}OR) + D(Si\text{-}O) = 2\Delta H_f\,(RO) + \Delta H_f\,(SiO) - \Delta H_f\,(\text{monomer})$$

$$2(100.3) + (35.8) = 2(-51.2) + (-24.2) - \Delta H_f\,(\text{monomer})$$

$$\Delta H_f\,(\text{monomer}) = -363.$$

4) As in (3) except using fragmentation to $Si + O$ with
with $D(Si\text{-}O)$ from II-E-2

$$\text{-[Si(OR)}_2\,O]-} \longrightarrow 2\,RO + Si + O$$
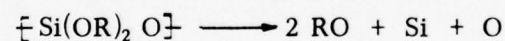
$$2\bar{D}\,(Si\text{-}OR) + 2D(Si\text{-}O) = 2\Delta H_f\,(RO) + \Delta H_f\,(Si) + \Delta H_f\,(O) - \Delta H_f\,(\text{monomer})$$

$$2(100.3) + 2(112.8) = 2(-51.2) + 106 + 59.6 - \Delta H_f\,(\text{monomer})$$

$$\Delta H_f\,(\text{monomer}) = -363.$$

D. $\text{-[Si(R)}_2\text{O]-}\ (\longrightarrow 2\,R + SiO)$

$$D_T\,(Si\equiv \text{bonds}) = 2\Delta H_f\,(R) + \Delta H_f\,(SiO) - \Delta H_f\,(\text{monomer})$$
$$\qquad \text{(from II-G)} \qquad \text{(from II-I)}$$

$$176 = 2\,(-15.1) + (-24.2) - \Delta H_f\,(\text{monomer})$$

$$\Delta H_f\,(\text{monomer}) = -230.4$$

E. $+Si(CH_2R)_2O+$ $(\longrightarrow 2\ CH_2R\ +\ SiO)$
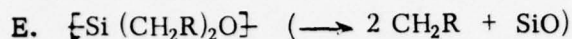
D_T (Si $\equiv$ bonds) = $2\ \Delta H_f\ (CH_2R)\ +\ \Delta H_f\ (SiO)\ -\ \Delta H_f\ (monomer)$
   (use II-G)   (from II-J)

$176 = 2(-19.8)\ +\ (-24.2)\ -\ \Delta H_f\ (monomer)$

$\Delta H_f\ (monomer)\ =\ -239.8$

F. $(RCH_2)_4\ Si$ $(\longrightarrow 4\ RCH_2\ +\ Si)$

$4\ \overline{D}\ (Si-R)\ =\ 4\Delta H_f(CH_2R)\ +\ \Delta H_f\ (Si)\ -\ \Delta H_f\ (RCH_2)_4\ Si$
  (from II-C)   (from II-J)

$4(74.7)\ =\ 4(-19.8)\ +\ 106\ -\ \Delta H_f\ (RCH_2)_4\ Si$

$\Delta H_f\ (RCH_2)_4\ Si\ =\ -272$

G. $(RO)_3\ SiMe$ $(\longrightarrow 3\ RO\ +\ Si\ +\ Me)$
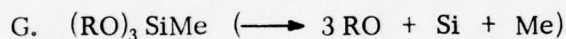
$3\ \overline{D}\ (Si-OR)\ +\ D(Si-Me)\ =\ 3\Delta H_f\ (RO)\ +\ \Delta H_f\ (Si)\ +\ \Delta H_f\ (Me)\ -\ \Delta H_f\ (RO)_3 SiMe$
  (from II-B)

$3(100.3)\ +\ 76\ =\ 3(-51.2)\ +\ 106\ +\ 34\ -\ \Delta H_f\ (RO)_3\ SiMe$

$\Delta H_f\ (RO)_3\ SiMe\ =\ -390.5$

H. $(RO)_2\ MeSiOSiMe\ (OR)_2$ $(\longrightarrow 4\ RO\ +\ 2\ Me\ +\ SiO_{(g)}\ +\ Si_{(g)})$
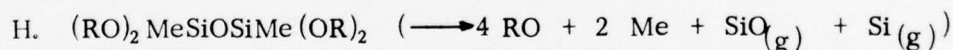
$4D\ (Si-OR)\ +\ 2\ D(Si-Me)\ +\ D(Si-OSi)\ =\ 4\Delta H_f(RO)\ +\ 2\Delta H_f(Me)$
$+\ \Delta H_f(SiO)\ +\ \Delta H_f(Si)\ -\ \Delta H_f(compd)$

$\Delta H_f\ (compd)\ =\ \sum \Delta H_f\ (products)\ -\ \sum D\text{-values}$
$=\ [4\ (-51)\ +\ 2(34)\ +\ (-24)\ +\ 106]\ -\ [4(100)\ +\ 2(76)\ +\ 35.8]$
$=\ -641.8\ kcal/mol$

Note: Value of D(Si-OSi) is that for formation
   SiO as a product; see II-E-1

D.　$+Si(CH_2R)_2O+$

$+(FC(NO_2)_2CH_2CH_2)_2SiO+ \longrightarrow SiO_2 + 2HF + 3H_2O + 2CO_2 + 4C + 2N_2$
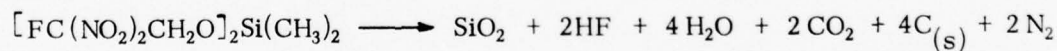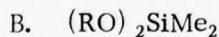
MW 346, $C_6H_8F_2N_4O_9Si$

$\Delta H_{det} = [-217.5 + 2(-64.8) + 3(-57.8) + 2(-94.05)] - [-239.8]$

$\qquad = -468.8$ kcal/mol or -1355 cal/g

E.　$(RCH_2)_4Si$

$(FC(NO_2)_2CH_2CH_2)_4Si \longrightarrow SiF_4 + 8H_2O + 4CO_2 + 8C + 4N_2$
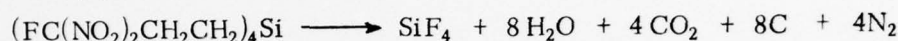
MW 632, $C_{12}H_{16}F_4N_8O_{16}Si$

$\Delta H_{det} = [-370 + 8(-57.8) + 4(-94.05)] - [-272]$

$\qquad = -936.6$ kcal/mol or -1480 cal/g

F.　$(RO)_3SiMe$

$[FC(NO_2)_2CH_2O]_3SiCH_3 \longrightarrow SiO_2 + 3HF + 3H_2O + 5CO_2 + 2C + 3N_2$
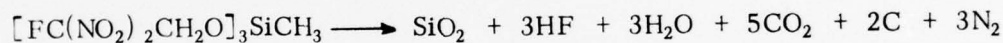
MW 502, $C_7H_9F_3N_6O_{15}Si$

$\Delta H_{det} = [-217.5 + 3(-64.8) + 3(-57.8) + 5(-94.05)] - [-390.5]$

$\qquad = -665.1$ or -1325 cal/g

G.　Monomer unit in $+MeSi(OR)O+$

$+MeSi[OCH_2CF(NO_2)_2]O+ \longrightarrow SiO_2 + HF + 2H_2O + CO_2 + 2C + N_2$
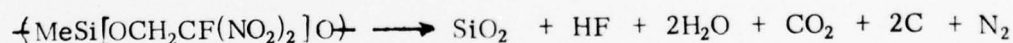
$C_3H_5FN_2O_6Si,$　212

$\Delta H_{det} = [(-217.5) - 64.8 - 2(57.8) - 94.05] - [-246.4]$

$\qquad = -245.6$ kcal/mol or -1158 cal/g

H.　$(RO)_2MeSiSiMe(OR)_2$

$(MeSi[OCH_2CF(NO_2)_2]_2)_2 \longrightarrow SiF_4 + SiO + 7H_2O + 6CO_2 + 4C + 4N_2$

$C_{10}H_{14}F_4N_8O_{20}Si_2,$　698

$\Delta H_{det} = [-370 - 24 - 7(57.8) - 6(94.05)] - [-551]$

$\qquad = -811.9$ kcal/mol or -1163 cal/g

I. $(RO)_2 MeSiOSiMe(OR)_2$

   $(MeSi[OCH_2CF(NO_2)_2]_2)_2 O \longrightarrow$ 5 different sets of products (a-e)
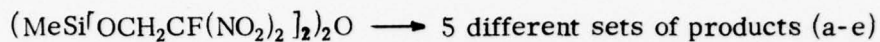
   (see also Results Section, eqs 18a, b)

   $C_{10}H_{14}F_4N_8O_{21}Si_2$, 714

   (a) $SiF_4 + SiO_2(s) + 7H_2O + 6CO_2 + 4C + 4N_2$

   (b) $SiF_4 + SiO(g) + 7H_2O + 6CO_2 + CO + 3C + 4N_2$

   (c) $4HF + 2SiO_2(s) + 5H_2O + 6CO_2 + 4C + 4N_2$

   (d) $4HF + 2SiO(g) + 5H_2O + 7CO_2 + 3C + 4N_2$

   (e) $4HF + 5H_2O + 8CO_2 + 2C + 2Si + 4N_2$
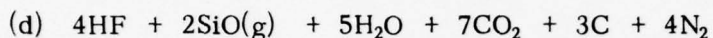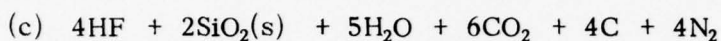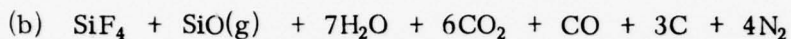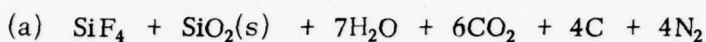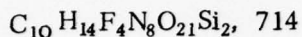
ΔH_{det}

   (a) $= [-370 - 217.5 - 7(57.8) - 6(94.05)] - [-642] = -914.4$ kcal/mol

   (b) $= [-370 - 24 - 7(57.8) - 6(94.05) - 26.4] - [-642] = -747.3$

   (c) $= [-4(64.8) - 2(217.5) - 5(57.8) - 6(94.05)] - [-642] = -905.5$

   (d) $= [-4(64.8) - 2(24.2) - 5(57.8) - 7(94.05)] - [-642] = -613.0$

   (e) $= [-4(64.8) - 5(57.8) - 8(94.05)] - [-642] = -658.6$

V. DETONATION PARAMETERS vs DECOMPOSITION MODE OF DISILOXANE VII

Mode (Section IV-I)	-Q Cal/g	N Mol/g	M Av g/mol	$\emptyset$	Density g/cc	P Kbars	D Km/sec
a	1278	.0252	33.7	5.23	1.58	203.4	7.05
b	1048	.0280	33.9	5.28	1.58	205.4	7.09
c	1268	.0266	28.7	5.07	1.58	197.1	6.95
d	858	.0308	30.8	5.01	1.58	194.8	6.90
e	923	.0294	30.2	4.91	1.58	190.9	6.83

APPENDIX B

SPECTRA

CONTENTS

II. Nmr spectra

    A. Fluorodinitroethanol (FDNE), I; 60 MHz H-nmr.

        1. In $CDCl_3$, containing ~5 mol-% formal $ROCH_2OCH_3$, IX

        2. In $CDCl_3$, containing ~3.5 mol-% IX, with added deutero-trifluoroacetic acid, 5 dps, to collapse OH coupling.

        3. In d_6-acetone, containing 3.5 mol-% IX, expanded scale.

    B. Disiloxane VII, $(RO)_2MeSiOSiMe(OR)_2$, in $CDCl_3$

        1. ^{19}F-nmr

        2. ^{13}C-nmr

    C. Polysiloxanes "VI" from hydrolysis of V; ^{29}Si-nmr in d_6-acetone (broad, underlying absorption due to silicone component of probe construction).

I. INFRARED SPECTRA

A 1a

A 1b

A 2

B

C

D
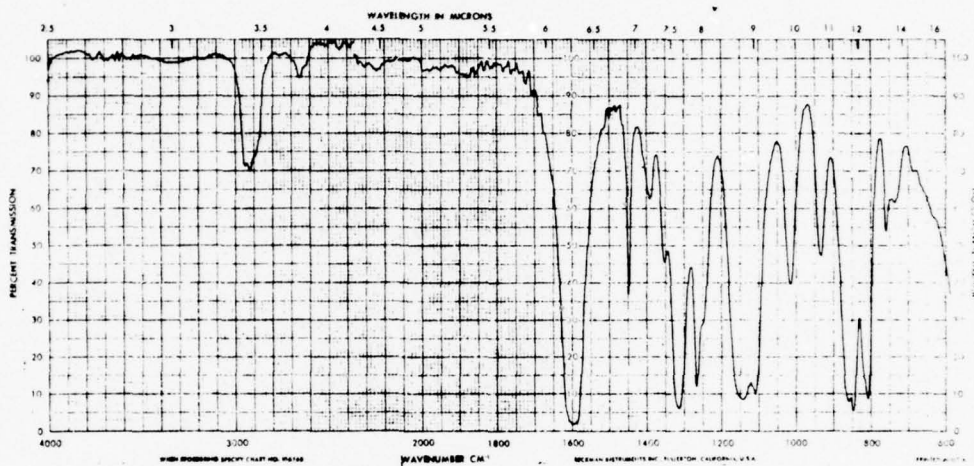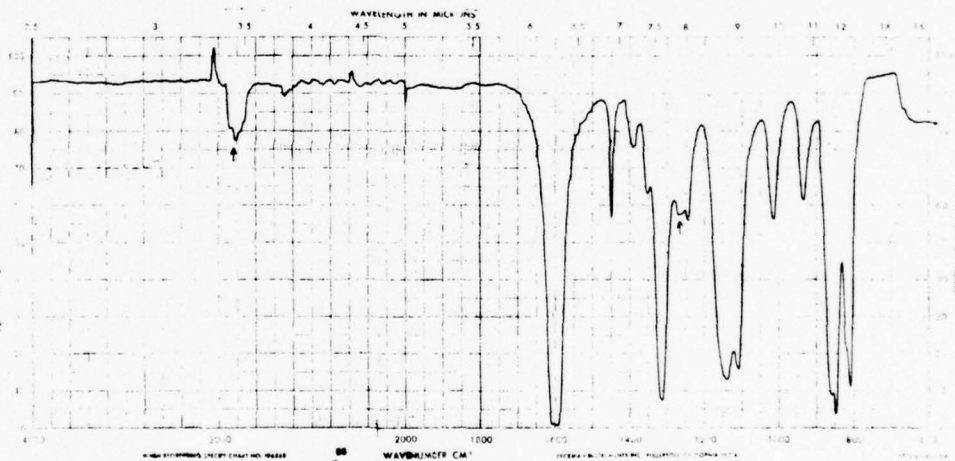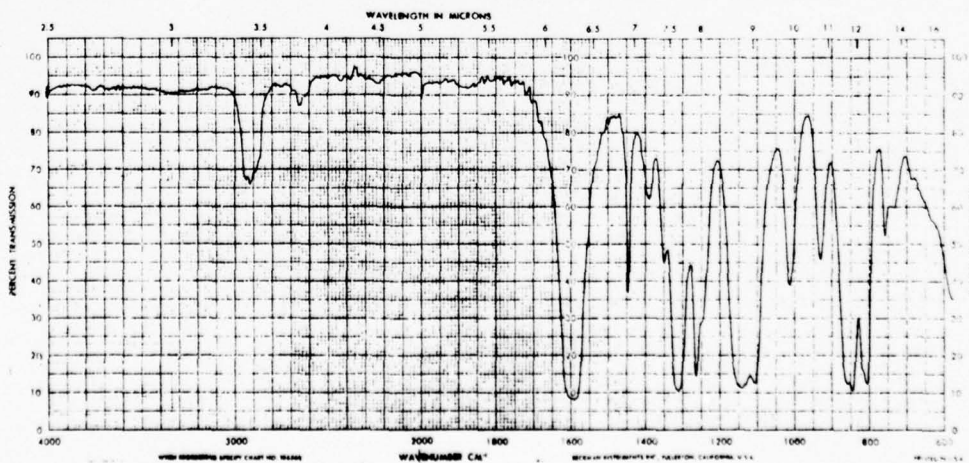
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E 1

E 2

E 3

E 4

F 1

F 2

G 1

G 2

G 3

H 1

H 2

II. NMR SPECTRA

A 2

INT. AMP - 0.4
SWEEP TIME 250

RK 0.05
SWEEP WIDTH - 110
SWEEP TIME 1000
SP AMP - 2.0
OFFSET 466 HZ

INT. AMP 2.0

INT AMP 2.0

RF 0.05
SWEEP WIDTH - 250
SWEEP TIME 1000
AMP 2.0
RF 0.05

96.5 % FC(NO$_2$)$_2$CH$_2$OH
b   a

3.5% FC(NO$_2$)$_2$CH$_2$OCH$_2$OCH$_3$
e   d   c

(d_6-ACETONE)

A 3

$[FC(NO_2)_2CH_2O)_2\, \overset{\underset{\displaystyle CH_3}{|}}{Si}\,]_2\, O$

$^{19}F\text{-}NMR$

EXTERNAL C_6F_6

[Z]-decoupled

B 1

$$[FC(NO_2)_2CH_2O]_2 Si \begin{matrix} CH_3 \\ | \\ | \end{matrix} O$$

13C-NMR

B 2

MIXTURE FROM 1:1 REACTION

$(RO)_4 Si + H_2O$

d_6-ACETONE, Cr $ACAC_3$

^{29}Si-NMR

TMS

OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-75-C-0791
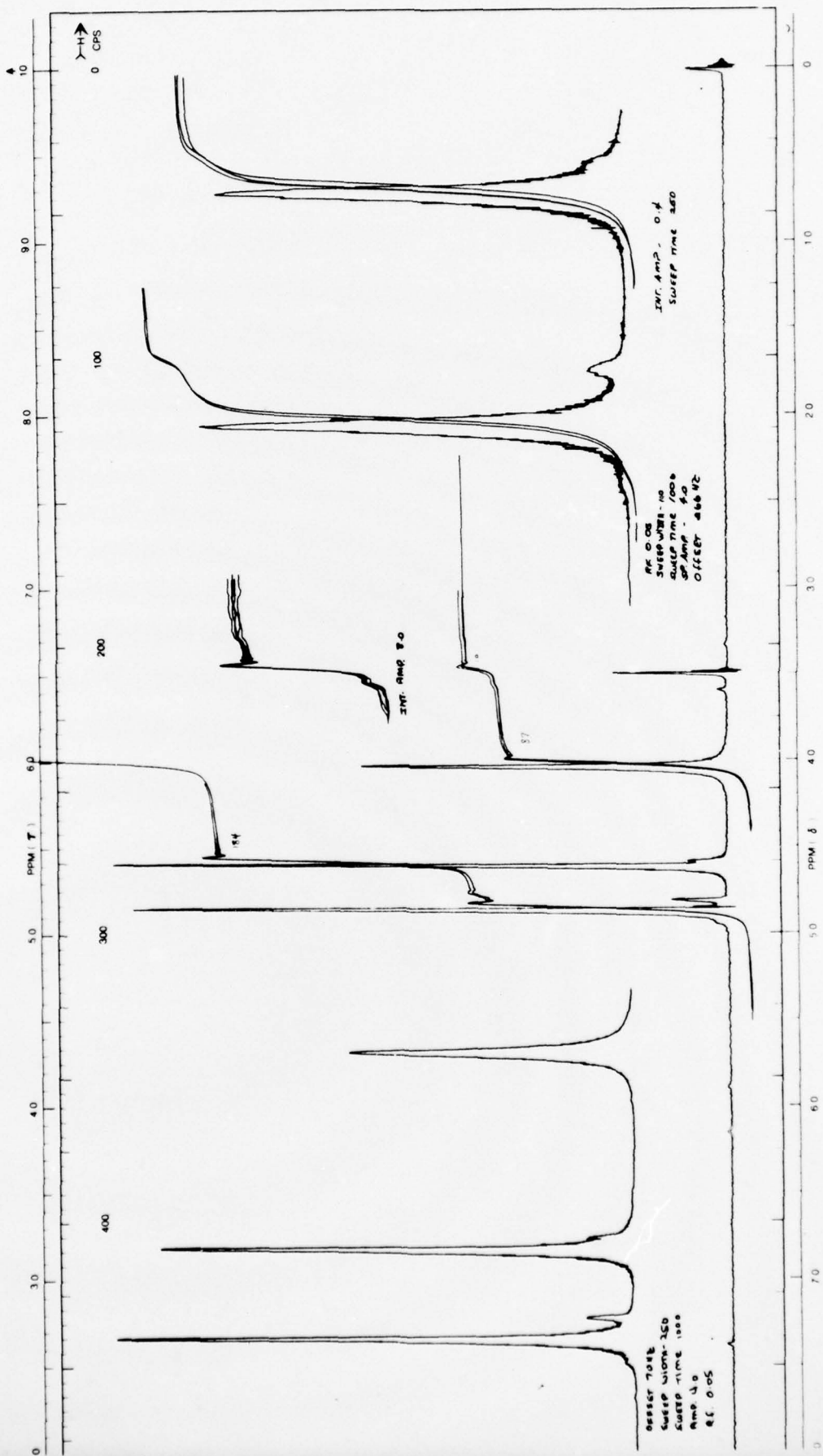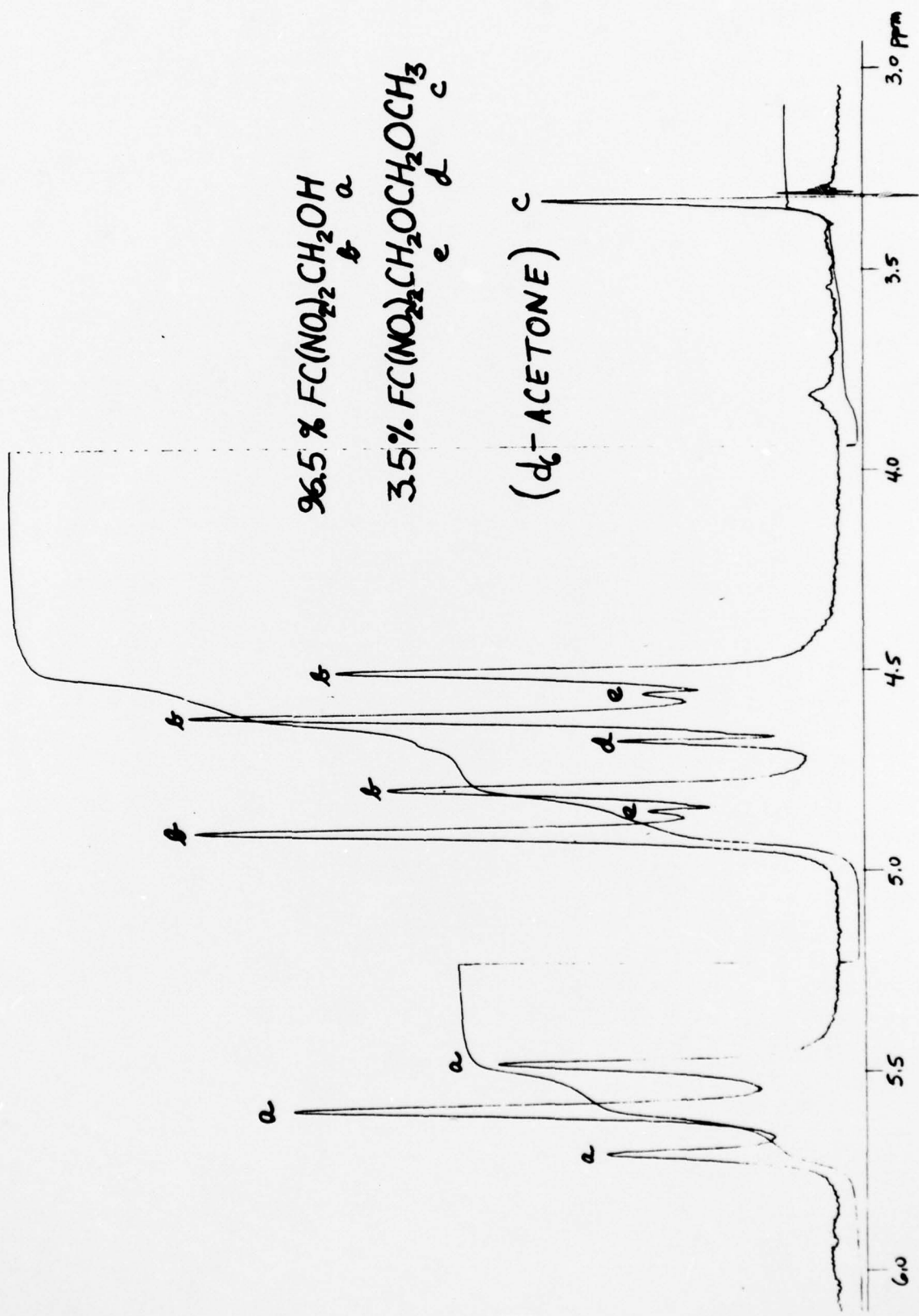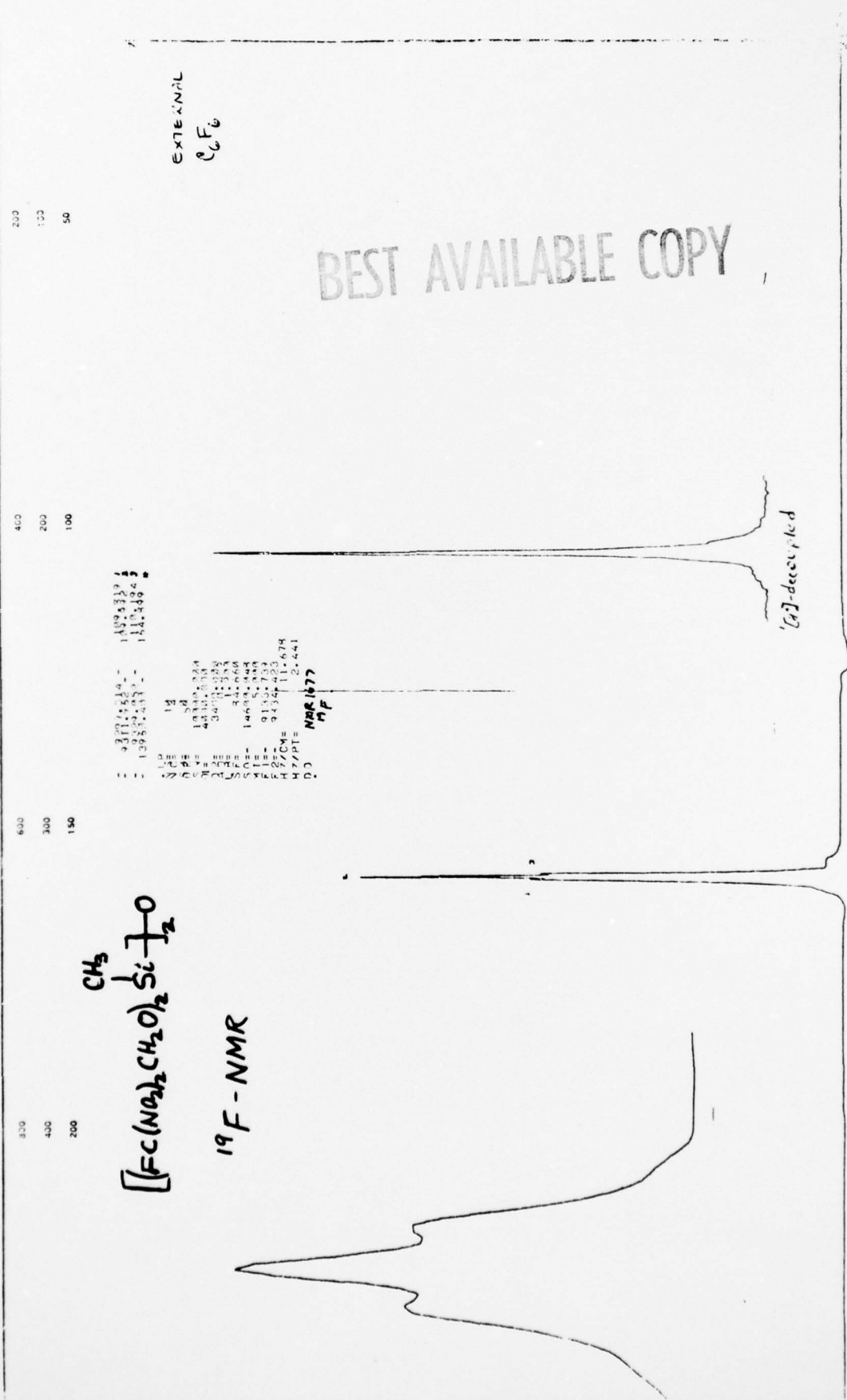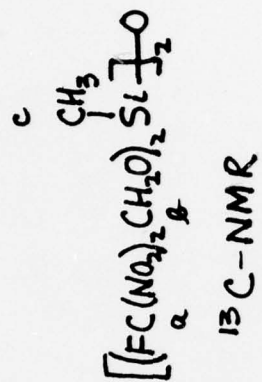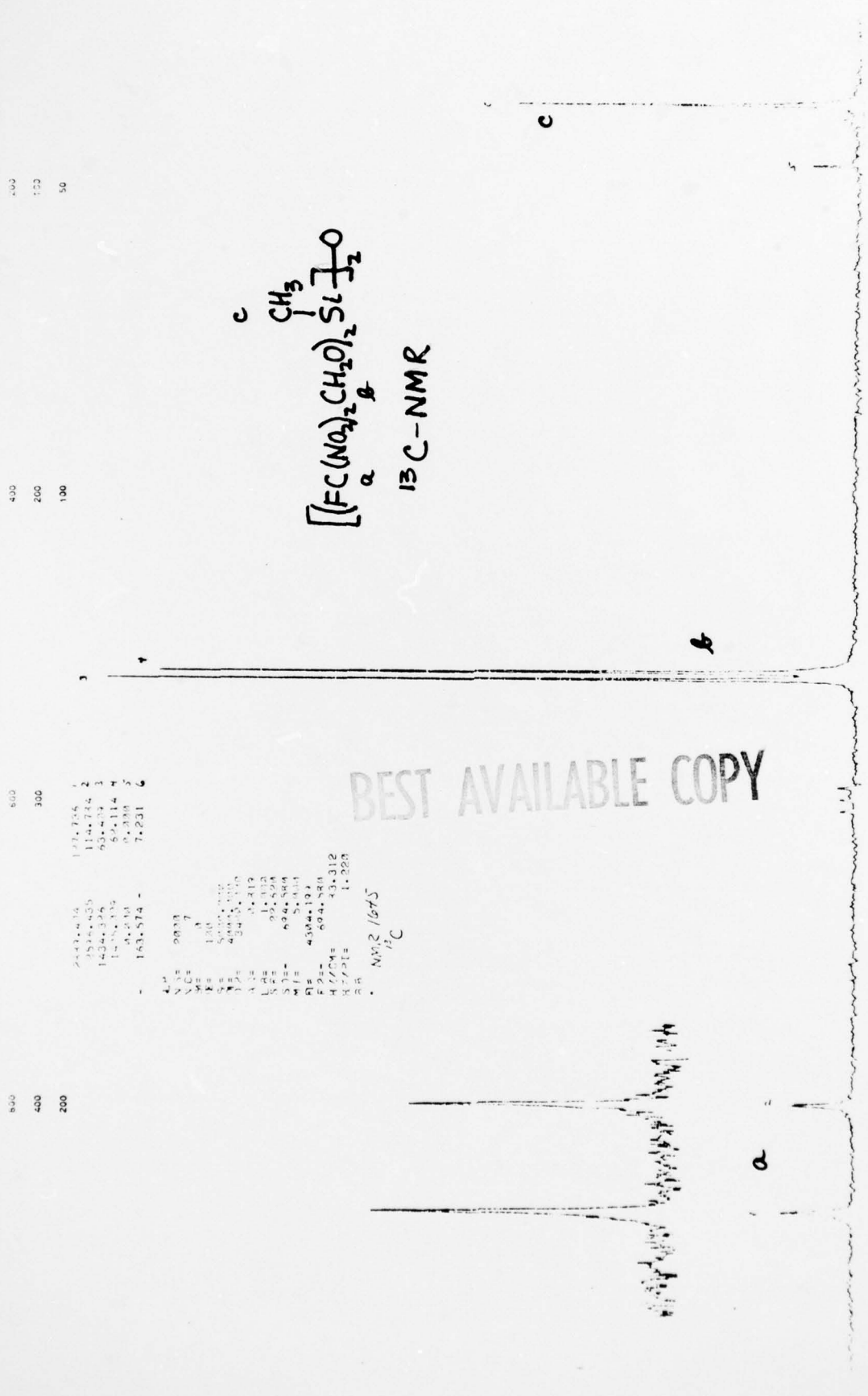
FINAL REPORT PART II

October 1976 - February 1977

FLUORODINITRO SILICON COMPOUNDS.

NONHYDROLYZABLE SILANES

by

Robert S. Neale

February 28, 1977

UNION CARBIDE CORPORATION
Chemicals and Plastics Division
Tarrytown, N. Y.

SUMMARY

A new approach to the synthesis of high energy silanes is described wherein pre-formed high energy residues are linked to silicon in one step through non-hydrolyzable aminoalkyl groups. The concept should be applicable to the preparation of both monomeric and polymeric materials. Results on the synthesis of two model compounds are described, which demonstrate the feasibility of the approach. Thus, the monosubstituted silane I has been prepared in good yield, and work is underway on the synthesis of II.
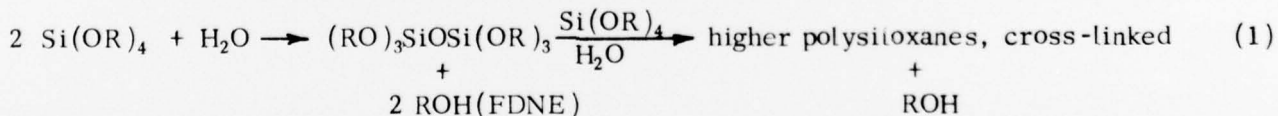
$$Me_3SiCH_2NHCH_2CF(NO_2)_2 \qquad\qquad Me_2Si[CH_2NHCH_2CF(NO_2)_2]_2$$
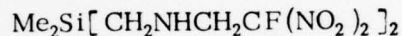
$$\text{I} \qquad\qquad\qquad\qquad\qquad \text{II}$$

INTRODUCTION

Work on high energy (H. E.) silane esters has been de-emphasized during this quarter in favor of efforts in the area of nominally non-hydrolyzable compounds. A formal Technical Report on the synthesis and properties of H. E. silane esters covering the period April, 1975, through September, 1976, has been written and is in the process of preparation and issue.

NON-HYDROLYZABLE SILANES

The concept. The silane esters prepared during the previous quarters had the advantage of direct synthesis from readily available chlorosilanes and a pre-formed H. E. compound, fluorodinitroethanol (FDNE), but in some instances suffered from a tendency toward facile hydrolytic decomposition of the SiOR groups (eq 1) and a resulting

$$2\ Si(OR)_4 + H_2O \longrightarrow (RO)_3SiOSi(OR)_3 \xrightarrow{\ \frac{Si(OR)_4}{H_2O}\ } \text{higher polysiloxanes, cross-linked} \qquad (1)$$
$$+ \qquad\qquad\qquad\qquad\qquad\qquad +$$
$$2\ ROH(FDNE) \qquad\qquad\qquad\qquad\qquad ROH$$

difficulty in handling the materials. We proposed under the extended subject contract to make an initial evaluation of a route to high energy compounds which retained the very important benefit of 1-step introduction of in tact H. E. groups but avoided the formation of the potentially hydrolyzable SiOR groups in silane esters.

Thus, as one of several potential methods, the preparation of compounds was envisioned in which H. E. residues could be introduced via α- to δ- aminoalkyl linkages to silicon rather than through hydrolyzable oxygen linkages. Once proved feasible in the model monomer silanes I and II, related monomers could be prepared, and one could also contemplate similar H. E. functionalization of pre-formed primary or secondary amino functional polymers

or pre-polymers as an improved route to potentially elastomeric compounds (which could contain either siloxane or hydrocarbon backbones).

$$Me_3SiCH_2NHR \qquad\qquad RNHCH_2SiMe_2CH_2NHR$$

I, $R = CH_2CF(NO_2)_2$ II, $R = CH_2CF(NO_2)_2$

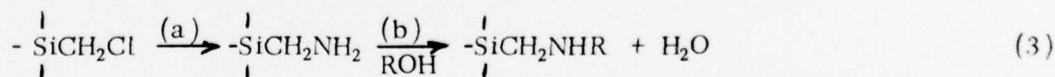III, $R = H$ IV, $R = H$

The general concept is illustrated in eq 2, wherein addition of the H. E. groups can occur through appropriate functionality (shaded circles) by either addition to or substitution of the reactive groups (unshaded circles) in monomers or polymers.


$$(2)$$
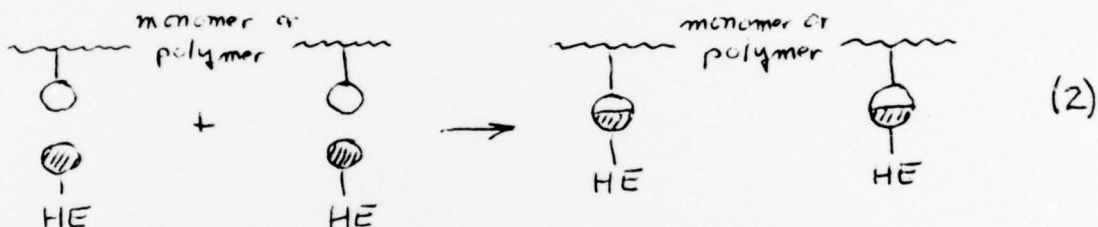
Syntheses which permit the introduction of bulky, H. E. groups all at once in the preparation of monomeric or polymeric compounds are felt to be generally more amenable to success than those which involve a step-wise building-up of the desired H. E. groups.

Synthesis of model compounds. The preparation of model compounds I and II was targeted initially to test the feasibility of employing α-aminoalkyl bridges between silicon and $-CH_2CH(NO_2)_2$ groups and to assess the stability of the resulting products. Synthesis of the starting aminomethylsilanes III and IV, followed by Mannich reactions with FDNE, is under study (eq 3). A route for step (a) was required which would be more appropriate than direct amination for the conversion of chloro to primary or secondary

$$- \overset{|}{\underset{|}{Si}}CH_2Cl \xrightarrow{(a)} -\overset{|}{\underset{|}{Si}}CH_2NH_2 \xrightarrow[ROH]{(b)} -\overset{|}{\underset{|}{Si}}CH_2NHR + H_2O \qquad (3)$$

amino groups in polychloroalkyl compounds, since amination would surely produce linear and cross-linked (from NH_3) polymeric amines unsuitable for reaction step (b). The Gabriel synthesis was selected and afforded aminomethyltrimethylsilane (III) through the normal phthalimide intermediate in good yield (eq 4). The same procedure is now being
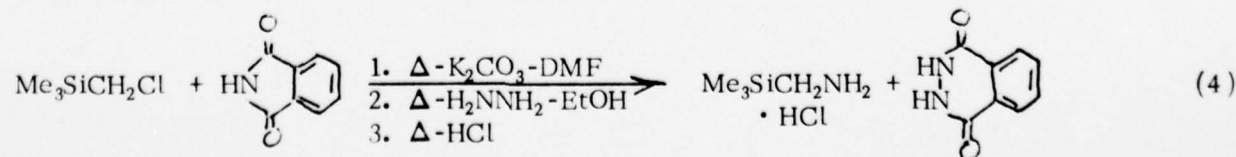
applied to the preparation of the bis compound IV, with favorable early results.

      Reaction of III with FDNE proved highly facile and produced the desired
Mannich product I in good yield and crude purity (eq 5). Certain problems in distillation
of I have recently appeared; although apparently not serious, we have accordingly not yet
obtained highly purified I for controlled determination of its stability.

$$Me_3SiCH_2NH_2 \ + \ FDNE \ \xrightarrow{H_2O} \ Me_3SiCH_2NHCH_2CF(NO_2)_2 \hspace{2cm} (5)$$

$$I$$
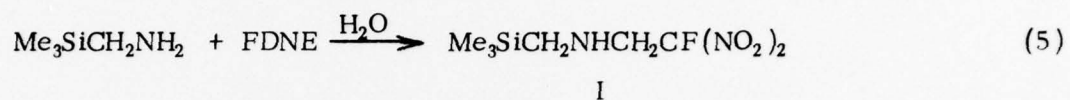
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