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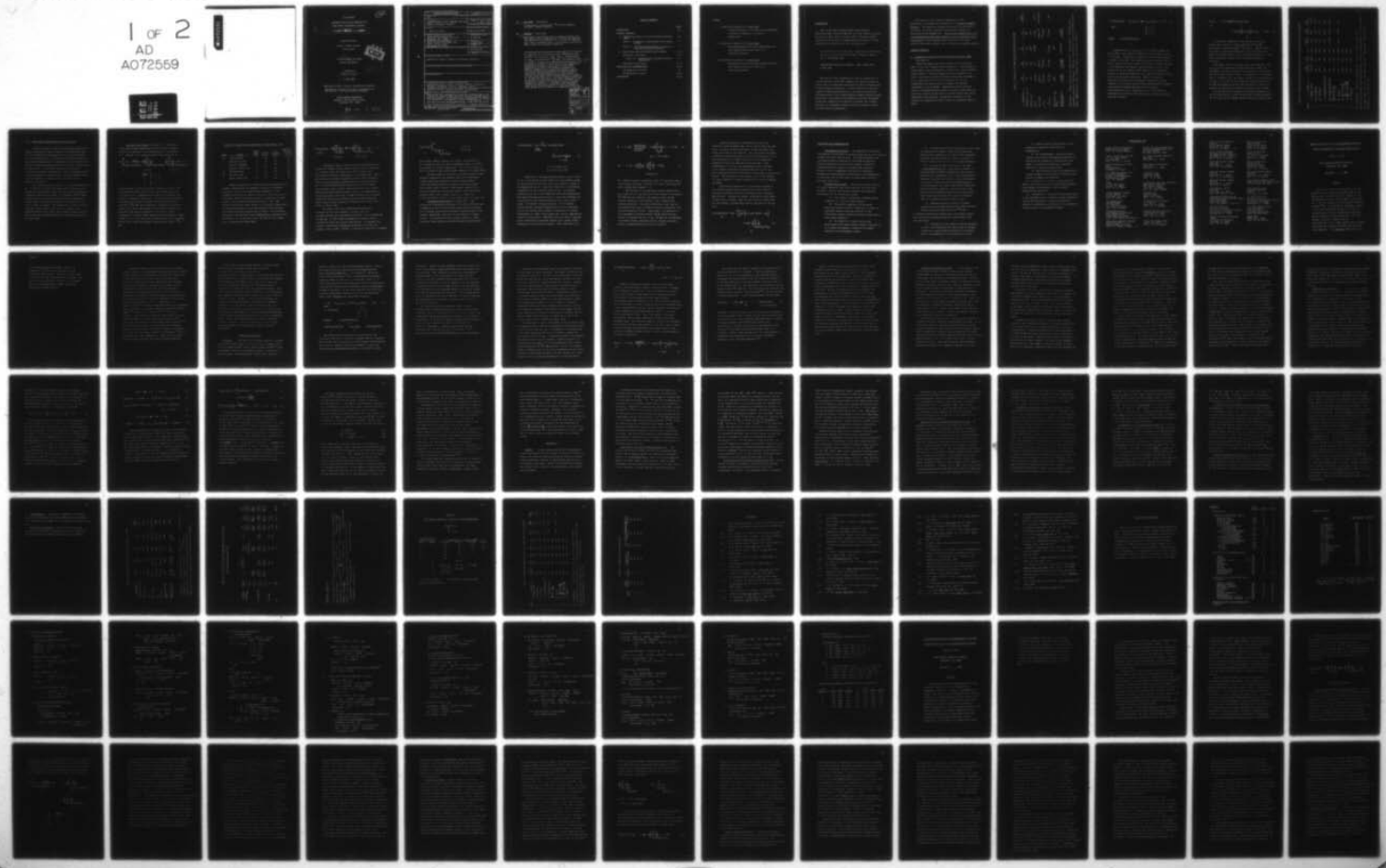

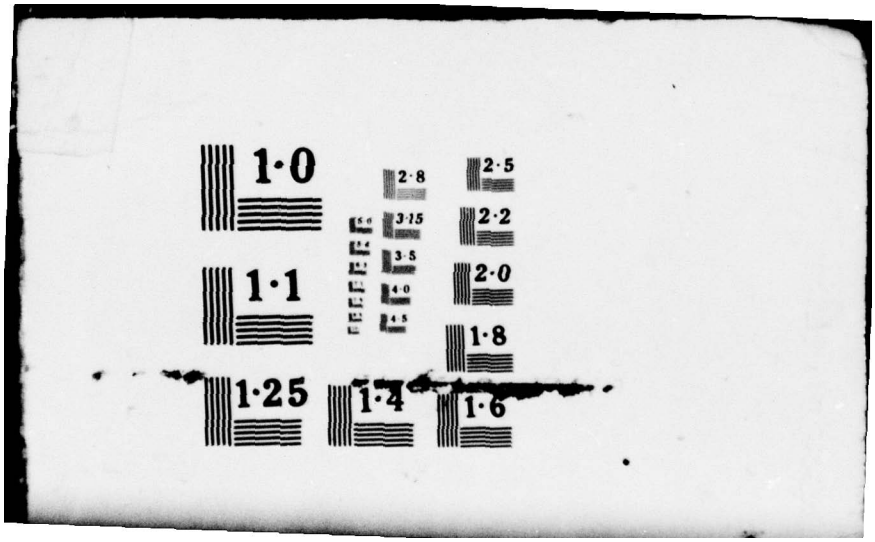
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FINAL REPORT

(4) FLUORODINITRO SILICON COMPOUNDS AND HIGH ENERGY ELASTOMERIC POLYMERS.

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UNION CARBIDE CORPORATION
Chemicals and Plastics Division
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

High energy (HE) organosilane esters were prepared from 2,2,2-fluorodinitroethanol (ROH) and chlorosilanes in 85-90% yields. Physical property, shock sensitivity, and multinuclear NMR data are reported for the monomeric silanes $(RO)_xSiMe_{(4-x)}$ (x = 2-4) and the disiloxane $Me(RO)_2SiOSi(OR)_2Me$, along with calculated heat contents and detonation properties. A general hydrolytic

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sensitivity was observed which increased regularly with the number of RO— groups per Si. Overall, the physical and thermochemical properties of the trisester $(RO)_3SiMe$ most closely resembled those of the reference plasticizer FEFO, except for a desirably higher bp.

Aminoalkyl(methyl)polysiloxane homopolymers were prepared by hydrolysis of the dialkoxysilanes $(R^1O)_2MeSi-Z-NH_2$, with R^1 = Et or Me and Z = CH_2, $(CH_2)_3$, $(CH_2)_3NHCH_2CH_2$, or $(CH_2)_4$, and analyzed by ^{29}Si NMR. The products could be varied to contain up to ~85% linear siloxy units, with the balance as mainly 4 and 5 unit cyclics. The former contained an average of 3-116 spinal siloxy units, depending on structure and method of preparation. Mannich condensations of fluorodinitroethanol with selected monomeric and polymeric aminoalkyl compounds efficiently afforded HE derivatives, whose thermal stabilities declined dramatically in the presence of strongly basic amines and differed markedly at secondary vs tertiary HE amino sites. Average molecular weights up to ~11,000 were realized in the linear components of the HE aminobutyl system, and initial tests of their chain extension to products of elastomeric quality produced flexible but waxy gels. Structures with aminomethyl substituents proved susceptible to partial cleavage of these groups and the formation of undesirable crosslinks.

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ADDENDA

I. Manuscript prepared for J. Org. Chem.

"Organosilane Esters of 2,2,2-Fluorodinitroethanol as Potential Components of Energetic Compositions"

II. Manuscript prepared for J. Org. Chem.

"Aminoalkyl(methyl)polysiloxane Homopolymers and Their Mannich Derivatives from 2,2,2-Fluorodinitroethanol"

III. Manuscript prepared for J. Org. Chem.

"Aminomethyl(methyl)polysiloxane Homopolymers and Their Mannich Derivatives from 2,2,2-Fluorodinitroethanol"

INTRODUCTION

This is the Final Technical Report under Contract N00014-75-C-0791, Project NR 093-054, for work carried out during the period 1 April 1975 to 30 April 1979. Previously issued reports were as follows; no journal publications prior to those comprising the present report have been submitted.

"Fluorodinitrosilicon Compounds. Organosilicon and Silicate Esters of 2,2,2-Fluorodinitroethanol", Technical Report No. 1, 28 February 1977.

"High Energy Elastomeric Polymers", Annual Report 78-1, 24 May 1978.

One object of this program was to test the feasibility of synthesizing high energy (HE) organosilicon esters as potential plasticizers for propellants and explosives and to determine some of their energetic properties. A later object was to test the concept of preparing HE materials in one step by multiple HE functionalization of pre-formed acceptor polymers with pre-formed HE moieties; polysiloxanes with hydrolysis resistant HE pendent groups were targeted as the objects of synthesis for ultimate conversion to elastomeric products useful as energetic binders for solid fuels and explosives.

The results of this study are summarized in three manuscripts to be submitted for publication in Journal of Organic Chemistry. The papers are attached and comprise the main body of the report, following a Technical Overview and statement of Conclusions and Recommendations. The structure numbers used in the various manuscripts have been retained in each corresponding Overview section to avoid confusion when referring to the texts; equations and tables, however, have received new, sequential numbers.

TECHNICAL OVERVIEW

I. Organosilane Esters of 2,2,2-Fluorodinitroethanol (FDNE)

(See Paper I)

Certain HE organosilane ester analogs of the plasticizer FEFO, 3, have been prepared for determination of their densities, liquid ranges, shock and hydrolytic sensitivities, and calculated energy contents. The esters 2a-c and 4 were obtained by the direct, solventless reaction of methylchlorosilanes with FDNE (1, eq 1), which required 1 to 1.5 mol 1 and 40-70° reaction temperatures over several hours to complete the stepwise replacement of Si—Cl groups. Transesterification reactions between 1 and methoxysilanes failed to proceed as efficiently as reaction 1, and use in the latter of an HCl acceptor base led to undesirable side reactions. The physical properties of the products are summarized in Table I with some comparative data of FEFO.

Table I. Properties of High Energy Silane Esters vs FEFO

Property	2a	2b	2c	4	3 FEFO[a]
Synthesis yield, %	87	73[b]	90	86[c]	-
Purity, wt-%	97	100	≥82[d]	≥93	-
Mp °C	19-19.5	∿25	74-86[d]	∿15-20	11-13
Bp °C (mm)	96(0.1)	170(0.3)	-	∿250(0.1)[e]	120-124(0.3)
$n^{°C}_{D}$	$^{22}1.4308$	$^{22}1.4412$	-	$^{25}1.4406$	-
d °C g/cc	$^{24}1.395$	$^{23}1.660$	$^{25}1.938$	$^{24}1.580$	1.607
Shock sens, H_{50} kg-cm	∿300[f]	-	76[g]	-	-
Hydrolysis rate in air/% RH	nil/46% v slow/52%	slow/35% rapid/60%	v rapid/18%	nil/35% v slow/52%	-

[a]See Paper I. [b]Crude yield 91%, purity 96%, mp ∿0°C. [c]Crude product. [d]Variable due to hydrolytic sensitivity. [e]Estimated. [f]Open cup; value 2.5 kg-cm in closed cup ASTM procedure D2540. [g]AWRE test for solids, sandpaper surface; open cup value ∿300 kg-cm.

$$x\ FC(NO_2)_2CH_2OH + Me_{4-x}SiCl_x \longrightarrow Me_{4-x}Si(OR)_x + x\ HCl \quad (1)$$

ROH, 1

2a, x = 2

2b, x = 3

2c, x = 4

$ROCH_2OR$ $(RO)_2MeSiOSiMe(OR)_2$

3 4

Although the mp's of 2a,b and 4 were slightly higher than that of FEFO, small amounts of impurities lowered them to the 0 to -5°C range. Substantial increases in bp were shown by 2b and 4 vs FEFO, as desired. The orthoester 2c proved unusual in its highly crystalline nature and mp vs the other HE esters, and also in its remarkably high density, which exceeded 1.9 g/cc. The sensitivity of the products toward hydrolysis by atmospheric moisture at 18-60% RH comprised a wide range from very low in 2a and 4 to exceptionally high in 2c. However, deliberate hydrolysis of 2c with the stoichiometry required for simple formation of disiloxane 7 gave an equilibrium mixture of products containing 30% unreacted 2c along with 7 and higher, polysiloxanes 10 (eq 2). Hydrolysis with 1.0 H_2O produced unworkable gels instead of the theoretical structures 10 of very long chain lengths.

$$(RO)_4Si \;+\; 0.5\ H_2O \rightleftharpoons (RO)_3SiOSi(OR)_3$$

2c 7

$$+\; (RO)_3SiO\left[Si(OR)_2O\right]_xSi(OR)_3 \;+\; 2\ ROH \qquad (2)$$

10

Of particular importance in the analysis of the pure products and, especially, product mixtures was the NMR observation of natural abundance ^{29}Si nuclei. Chemical shifts were found in proton-decoupled spectra as a function of the number of attached alkoxy, siloxy, and methyl groups per Si atom with a consistency suitable for firm characterization of structures.

Drop weight testing of 2a and 2c gave noncompressive (open cup) H_{50} values significantly higher than that of RDX, but compressive, closed cup testing of 2a revealed a 4-fold greater sensitivity than n-propyl nitrate. Calculations of the compound heats of formation, ΔH_f, and energy contents, Q, were carried out for 2a-c, 4, and some related potential structures (Table II). The derived detonation pressure (DP) and velocity (DV) for 2c suggested a high explosive capability similar to that of RDX.

Considering both the physical and energetic properties of the HE silane esters, a close overall match to FEFO was found in the less volatile but somewhat moisture sensitive trisester 2b.

Table II. Calculated Thermochemical Properties of High Energy Silicon Compounds[a]

Entry	Compd	$-\Delta H_f$ kcal/mol	-Q cal/g	ϕ	Density g/cc	DP kbars	DV km/sec
1	3, $ROCH_2OR$ (FEFO)	177.5[b]	1390[b]	6.457	1.607	260	7.92[b]
2	2a, $(RO)_2SiMe_2$	288	1310	5.036	1.395	152.7	6.38
3	2b, $(RO)_3SiMe$	390.5	1325	5.550	1.66	238.3	7.51
4	4, $(RO)_2MeSiOSiMe(OR)_2$[c,d]	642	1048	5.280	1.58	205.4	7.09
5	12, $(RO)_2MeSiSiMe(OR)_2$[c]	551	1163	5.425	(1.60)[e]	(216.4)	(7.25)
6	$\left[SiMe(OR)O\right]_x$	246.4	1158	4.063	-	-	
7	2c, $(RO)_4Si$	500	1330	5.952[f]	1.938	348.3[f]	8.6
8	10, $\left[Si(OR)_2O\right]_x$	353.8	1221	5.098	-	-	-
9	13, $\left[Si(CH_2R)_2O\right]_x$	239.8	1355	4.922	-	-	-
10	14, $(RCH_2)_4Si$	272	1480	5.811	-	-	-

[a]R = $CH_2CF(NO_2)_2$. [b]Reference values are ΔH_f - 17.55; Q - 1390; DV 7.50 (obsd).

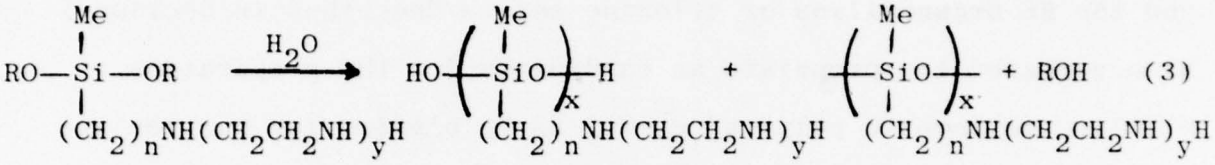
[c]Calcd for dec to SiF_4 + SiO rather than SiO_2. [d]Values for SiO_2 product are (left to right) 642, 1278, .0252, 33.7, 5.23, 1.58, 203.4, and 7.05. [e]Estimated. [f]Also calcd by M. Kamlet: ϕ = 6.025, DP = 352.

II. High Energy Aminoalkyl(methyl)polysiloxanes

Previous efforts by others to prepare and polymerize HE monomers had generally led to relatively low MW products from vinyl or condensation polymerizations of polynitro substrates, and the HE organosilane or siloxane esters described in Section I also appeared inappropriate as candidates for the preparation of stable, elastomeric polymers useful as HE binders for particulate HE compositions. We therefore explored a new approach to potentially elastomeric HE materials in which preformed polymers or chain extendable oligomers bearing functional pendant groups might be energized in a single step by reaction with an appropriate HE moiety.

The systems reported in detail in the appended manuscript nos. II and III contained polysiloxane spinal structures with pendant aminoalkyl groups, which were then energized by Mannich condensation reactions with FDNE. The synthesis and ^{29}Si NMR characterization of acceptor polymers containing aminobutyl or -propyl groups and their HE derivatives are described in the first of these two papers. The maximum ratio of HE to methylene groups per spinal (methyl)siloxy unit was studied in the aminomethylpolysiloxane system, whose preparation and reactions proved less than straightforward and are reported separately in the third paper.

Aminoalkyl Side Chains (see Paper II). Aminoalkyl-(methyl)polysiloxane homopolymers 5 were prepared as Mannich acceptors by hydrolysis of the dialkoxysilanes 4 according to eq 3. Although cyclic structures were always generated, the



(3)

4 linear 5 cyclic 5

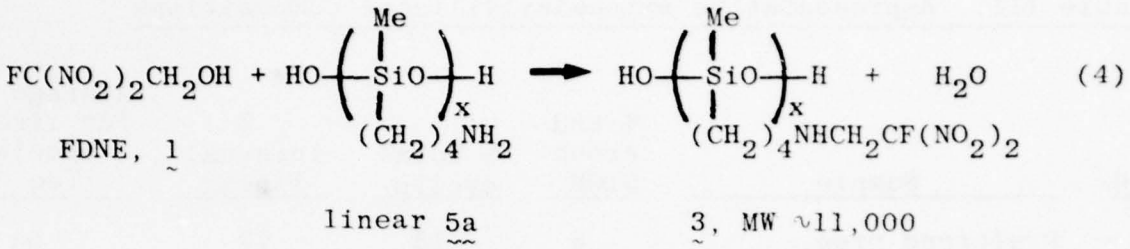
Compd	R	n	y
a	Et	4	0
b	Et	3	0
c	Me	3	1

product mixtures 5 could be varied to contain up to 55% of the desired HO-end blocked linear species with average chains of 6-116 siloxy units, depending on the side chain structures and methods of preparation (Table III). Differentiation and analysis of backbone polysiloxane structures and concentrations were achieved by ^{29}Si NMR, which comprised a substantial and critical element of the work, and average overall molecular weights $\bar{M}_n$ = 1200-2400 could then be calculated; unfortunately, direct measurement of the $\bar{M}_n$ by vapor osmometry proved unreliable. Chain lengths (x in 5, eq 3) were also calculated (Table III), using $\bar{M}_n$ and the total linear and end group concentrations found by ^{29}Si NMR.

Table III. Representative Aminoalkylsilicone Compositions

Compd	Sample	% End group SiOH	% Total cyclic	% Internal linear	Average x for linear species (eq 3)
5a	Preferred prep.	3	18	77	54
	High cyclics prep.	2	79	20	10
	Cyclics + KOH/H_2O	11	13	77	15
	Cyclics + polym. cat.	1	41	58	116
5b	Preferred prep.	6	14	80	29
5c	Preferred prep.	7	14	79	25
	Short linears prep.	26	15	59	6

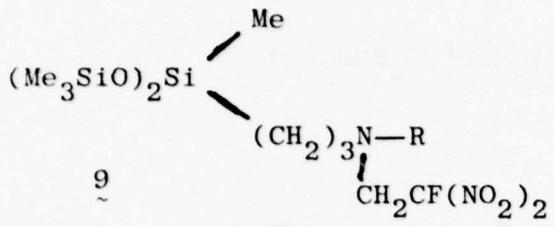
Mannich condensations of FDNE with selected monomeric and polymeric aminoalkylsilicon compounds efficiently afforded HE derivatives, such as the linear polymer component 3 in the aminobutyl system (eq 4); however, both cyclic and linear species were always formed in polymeric products in proportion to those present in the substrate hydrolysate mixtures. Thus, NMR analysis revealed only small changes in the skeletal compositions of the Mannich polymers vs their aminoalkylsilicone precursors and yielded end group concentrations as before. The calculated basicities of HE aminoalkyl groups $RNHCH_2CF(NO_2)_2$ approached that of pryidine, i.e. $\sim$5 pk_a units lower than that of the strongly basic, starting amino groups RNH_2.



(4)

Preliminary study of chain extension polymerization of 3 through its terminal silanol groups revealed a facile conversion to a flexible, waxy, but brittle gel upon treatment with stoichiometric amounts of $MeSi(OAc)_3$ at room temperature. Both 3 and its gellation product decomposed slowly at 80°C, whereas 3 treated with aminosilane extending agents decomposed readily at 40°. An ethylenediaminopropyl hydrolysate 5c, rich in short linear species, gave a product upon reaction with only 1 mol of FDNE which proved markedly unstable, even at room temperature; a contrasting product from 2 mol of FDNE contained close to one HE residue per amino group and showed greatly improved stability under similar storage conditions, decomposing only slowly over a period of several days.

The thermal stability of some model HE aminoalkyl siloxanes was therefore examined. An upper limit for extended stability was found between 100-120°C in the secondary HE siloxane 9b. At 120°, massive decomposition ensued with the liberation of water and a nearly odorless gas. In contrast, the tertiary, N-methylated compound 9d decomposed very slowly and steadily, even at 120°C. Further, a pronounced sensitivity to strongly



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b, R = H

d, R = Me

basic amines, whether protonic or tertiary, was observed in the secondary HE amine 9b, which decomposed readily at ∿100°C in the presence of ≥10 mol-% added amine. The tertiary analog 9d again contrasted to 9b, proving rather unsensitive to added amines.

Incomplete Mannich reactions of acceptor polymers 5 were therefore indicated as the probable source of the decreased thermal stabilities observed in the HE polymer products, reflecting destabilization by residual, basic amino groups. These results imply a need for ∿100% Mannich conversion of acceptor polymer amino groups and, further, that tertiary HE polymers rather than secondary should be considered for maximizing thermal stability in any further pursuit of this work.

Aminomethyl Side Chains (see Paper III). The preparation of monomer 2a according to eq 5 was inefficient and accompanied by both the dialkylation shown and by an apparent Si—C cleavage reaction which ultimately generated some of the N-methyl compound 2b, especially in the presence of ethanol solvent. An alternative route to 2a was studied in a model system but found lacking in several necessary characteristics.

$$(EtO)_2MeSiCH_2Cl + NH_3 \xrightarrow[\text{large excess}]{60^{\circ}} (EtO)_2MeSiCH_2NHR + \underset{\sim}{2}$$

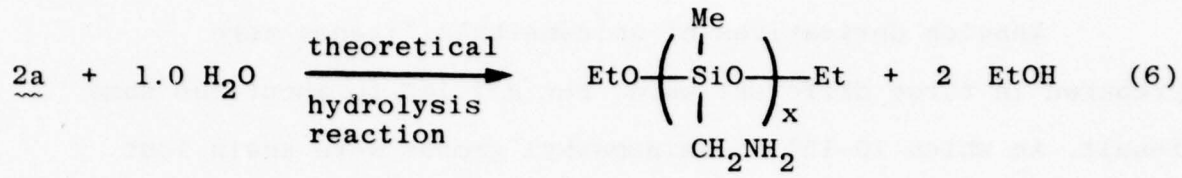
$$\left[(EtO)_2MeSiCH_2\right]_2NH \qquad (5)$$

$$\underset{\sim}{4}\ (14\%)$$

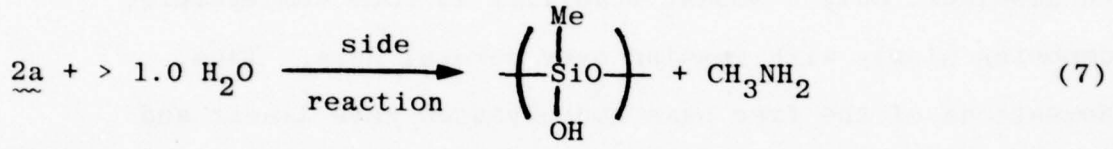
$\underset{\sim}{a}$, R = H (35% yield)

$\underset{\sim}{b}$, R = Me (up to 6%)

Hydrolyses of pure $\underset{\sim\sim}{2a}$ proceeded rapidly, even at 0-25°C, but use of any excess of water beyond the stoichiometric amount for the theoretical reaction 6 also led to partial cleavage of $Si—CH_2NH_2$ bonds (eq 7). Gels then formed due to crosslinking condensation of the resulting silanol sites. In contrast, preparations of the 3- and 4-methylene side chain hydrolysates had required heating with an excess of water and proceeded free of dealkylation side reactions and with total loss of ester groups. The product from $\underset{\sim\sim}{2a}$ and exactly 1.0 mol H_2O was obtained without observable dealkylation but still contained >10% of the original EtO— groups as terminators of a modest preponderance of linear siloxy species $\underset{\sim\sim}{6a}$; cyclics comprised the balance of siloxy units. Hydrolyses with less than 1.0 H_2O gave partial hydrolysates containing residual EtO— groups closely agreeing with the theoretical amounts. When hydrolyzed in aq



6a (x very large)



random units

HCl, however, 2a gave a hydrolysate • HCl (7) containing ∿85% of linear species analogous to 6a but with silanol end groups and short average chain lengths x = 3.

The analyses of the hydrolysate product mixtures were not as precise as in the previous systems because of an atypical ^{29}Si NMR spectral complexity and chemical shifts outside rational prediction in the absence of well characterized reference materials. The partial hydrolyses of 2a, however, established which types of products developed successively from increasing amounts of water. Surprisingly, the hydrolysis of the independently prepared N-methyl monomer 2b proved more subject to cleavage than that of 2a, although the corresponding N,N-dimethyl monomer hydrolyzed without cleavage (and gave a greatly increased proportion of cyclic products).

Mannich derivatives of aminomethylsilicones were prepared in three different ways, but all led to about the same result, in which 10-15% of aminomethyl groups were again lost during some stage of the reactions. The condensation reactions of FDNE were nevertheless facile, but gave HE derivatives all of which displayed only a modest stability at room temperature, decomposing slowly with gassing over several days. Thus, condensations of the free base hydrolysates gave linear and cyclic products containing the desired HE units 12, but the EtO— end groups of 6a were replaced by $FC(NO_2)_2CH_2O$— groups in the process. Neutralization of the polymer salt 7 in the presence of 1 gave a product of similar composition but with ill-defined end groups.

The preferred generation of 12 proceeded according to eq 8, wherein monomer 2a was treated with 1 and allowed to hydrolyze concurrently with the stoichiometrically liberated Mannich water. Although the product contained the usual amount of dealkylation residues, these may have resulted largely from the 10% of highly cleavage-prone impurity 2b present in the 2a used.

$$(EtO)_2MeSiCH_2NH_2 \;(2a) + ROH \;(1) \xrightarrow[20^o]{CH_2Cl_2} \left[(EtO)_2MeSiCH_2NHR + H_2O\right] \longrightarrow \left(\begin{array}{c} Me \\ | \\ SiO \\ | \\ CH_2NHCH_2CF(NO_2)_2 \end{array}\right)_x \quad (8)$$

12

CONCLUSIONS AND RECOMMENDATIONS

HE Organosilicon Esters. The preparation of HE esters from FDNE and chlorosilanes or chlorosiloxanes was not only generally feasible but facile and efficient. The observed physical and calculated energetic properties of the products suggested potential application as plasticizer analogs of FEFO or as reduced sensitivity analogs of secondary high explosives. However, a mild to exaggerated sensitivity to hydrolytic decomposition proved generally characteristic and inappropriate to follow-up study in these areas or others where solvolytic reactions could occur.

HE Aminoalkylsilicones. Time did not permit attention to certain experiments that would logically follow the work described. Several encouraging conclusions were supported, nevertheless, by the results now in hand.

(1) The concept of energizing preformed polymer frameworks in 1 step was found feasible.

(2) The specific approach of effecting HE functionalization by Mannich condensation of FDNE with aminoalkyl pendant groups was efficient in the polysiloxane systems studied and should be applicable to other spinal frameworks.

(3) The separation of amino centers from polysiloxane units should probably exceed 1 CH_2 group so as to bypass the apparent, atypically low thermal stability of the aminomethyl system.

(4) Siloxanes with other HE polyaminoalkyl side groups also displayed low thermal stabilities but have been insufficiently examined in the light of new information concerning relevant stability factors, as follows, to properly assess their potential for elastomer formation.

(5) Protonic HE amino structures of the type $-(CH_2)_nNHCH_2CF(NO_2)_2$ were found generally subject to rapid and massive thermal decomposition above certain characteristic temperatures and to facile decomposition induced by strongly basic amines at lower temperatures. In contrast, tertiary analogs $RN(Z)CH_2CF(NO_2)_2$ with Z = Me decomposed only slowly under similar conditions. Tertiary HE amines generally, and particularly those with electron withdrawing groups Z such as NO_2 or CF_3, might therefore prove both more stable and energetic than the secondary materials studied to date.

(6) Reasonably precise analyses of backbone compositions in the hydrolysate polysiloxanes and their HE derivatives were made possible by ^{29}Si NMR.

It therefore appears that further work in the present subject area could prove rewarding and should include study of the following topics.

(1) Preparation of new samples of HE polysiloxanes of the 3- and 4-methylene unit types using the optimum conditions to ensure complete conversion of the amino groups, and examination of the products as follows.

- Thermal analysis (TGA and DTA) for the boundaries of stability and profiles of decomposition.
- Gas chromatography - mass spectroscopic analysis of the volatile decomposition species for identification, mechanistic interpretation, and guide to the action of potentially countering additives or structure modifications.
- Chain extension to gels and examination of tensile strength vs both polymer structure and the gellation reagents and conditions.

(2) Preparation of tertiary, N—NO_2 and N—Me monomer and polymer analogs of secondary HE aminoalkyl-polysiloxanes for assessment of their physical properties and stabilities.

(3) Preparation of copolymeric HE materials based on HO- ended HE silicone oligomers and other terminally reactive HE prepolymers for possibly synergistic benefits of preparation and properties, with emphasis on curing-in-place in compounded HE packages.

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Chicago, Il. 60616
Attn: Dr. A. Tuffis 1

Cordova Chemical Company/
Aerojet General
Sacramento, Ca. 95813
Attn: Dr. Homer 1

Los Alamos Scient.
Laboratory/WX-2
P.O. Box 1663
Los Alamos, NM 87544
Attn: Dr. R. Rogers

Rocketdyne Division
North American Corporation
6633 Canoga Avenue
Canoga Park, Ca. 91304
Attn: Drs. Frankel and Criste 1

TRW Defense and Space Systems
Building 01/2020
Redondo Beach, Ca. 90278
Attn: Dr. Eugene A. Burns 1

Defense Contract Administration
Services Management Area, N.Y.
60 Hudson Street
New York, New York 10003 1

U.S. Naval Research Laboratory
Code 2629
Washington D.C. 20375 6

Naval Research Laboratory
Code 6100
Washington D.C. 20375 1

Fluorochem, Inc.
Irwindale Avenue
Azusa, Ca. 91702
Attn: Dr. K. Baum 1

Lockheed Pal Alto Res. Laboratory
Dept. 52-38, Bldg. 204
3251 Hanover Street
Palo Alto, Ca. 94304
Attn. Mr. Frank Borgardt 1

Hercules, Inc.
Bacchus Works
Magna, Utah 84044
Attn: Dr. J. Farber 1

Teledyne/McCormack Selph
P. O. Box 6
Hollister, Ca. 95023
Attn: Dr. D. Thatcher 1

Stanford Research Institute
333 Ravenswood Avenue
Menlo Park, Ca. 94205 1
Attn: Mr. M. E. Hill

United Technology Center
Coyote, Ca. 95103
Attn: Dr. Stan Abshier 1

Office of Naval Research
Code 473
800 No. Quincy Street
Arlington, Va. 22217
Attn: Dr. R. Miller 10

Office of Naval Research
San Francisco Area Office
760 Market Street - Room 447
San Francisco, Ca. 94102
Attn: Dr. P. A. Miller 1

Naval Air Systems Command
Code 330D
Washington D.C. 20360
Attn: Mr. R. Heitkotter 1

Naval Air Systems Command
Code 440
Washington D.C. 20360
Attn: Dr. H. Rosenwasser 1

Naval Sea Systems Command
SEA-0331
Washington D.C. 20362
Attn: Mr. J. Murrin

Naval Weapons Center
Code 608
China Lake, Ca. 93555
Attn: Dr. Ronald L. Derr 1

John Hopkins University APL
Chemical Propulsion Inform'n Agency
John Hopkins Road
Laurel, Md. 20810
Attn: Mr. Thomas W. Christian 1

Air Force Office of
Scientific Research
Directorate of Chemical Sciences
Bolling Air Force Base
Washington D.C. 20332 1

Lawrence Livermore Laboratory
L-402
University of California
Livermore, Ca. 94550
Attn: Mr. M. Finger 1

Office of Naval Res.
Branch Office
1030 E. Green Street
Pasadena, Ca. 91106
Attn: Dr. R. Marcus 1

Office of Naval Res.
Branch Office
536 South Clark Street
Chicago, Il. 60605 1
Attn: Dr. J. Smith 1

Office of Naval Res.
Branch Office
495 Summer Street
Boston, Ma. 02210
Attn: Dr. L. Peebles 1

Naval Sea Systems Command
SEA-0332
Washington D.C. 20362
Attn: Dr. A. Amster 1

Naval Surface Weapons Center
Research and Technology Dept.-WR
Silver Springs, Md. 20910 1

Naval Weapons Center
Research Department
Code 60
China Lake, Ca. 93555 1

Air Force Office of
Scientific Research
Directorate of Aerospace Sciences
Bolling Air Force Base
Washington D.C. 20332 1

U.S. Army Research Office
Chemistry Division
P. O. Box 12211
Research Triangle Park
North Carolina 27709 1

AFRPL (MKP)
Edwards, Ca. 93523
Attn: Mr. R. Geisler 1

Organosilane Esters of 2,2,2-Fluorodinitroethanol as Potential Components of Energetic Compositions[1]

Robert S. Neale

Union Carbide Chemicals & Plastics

Tarrytown, N.Y. 10591

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Abstract

High energy organosilane esters have been prepared from 2,2,2-fluorodinitroethanol (ROH, 1) and chlorosilanes in 85-90% yields for comparison with the analogous reference compound FEFO, the bisformal of 1. Physical properties and multinuclear NMR data, including ^{29}Si, are reported for $(RO)_xSiMe_{4-x}$ (2a-c, x = 2-4) and $Me(RO)_2SiOSi(OR)_2Me$ (4), along with calculated heat contents and detonation properties. The non-compressive shock sensitivity of the high density (1.95 g/cc) orthoester 2c was lower than that of the common explosive RDX, although the calculated detonation pressures and velocities were comparable. The compressive shock sensitivity

Abstract

of the bisester 2a was very great, however, in contrast to its very low non-compressive shock and thermal sensitivities. Hydrolytic sensitivities varied from low (2a) to exceptionally high (2c). The physical and thermochemical properties of trisester 2b closely resembled those of FEFO, except for a significantly higher bp in 2b.

Considerable interest has long existed in novel organic substances which offer advantageous use as plasticizers, binders, or burn modifiers in solid explosive or propellant compositions. In particular, mobile but non-volatile high energy (HE) plasticizer compounds have been sought which show increased thermal and shock stability without loss in energy content. Increased unit energy contents have also been pursued in combination with reduced shock sensitivities for the safer manufacture and handling of superior explosives and propellants. Of special recent interest have been compounds containing the 2,2,2-fluorodinitroethyl residue, $-CH_2CF(NO_2)_2$, as an energetic moiety;[2,3] numerous studies which define the background organic chemistry of the parent compound, fluorodinitroethanol (FDNE),[4-8] and many of its derivatives[3,4,9-13] are now available. Other work has centered on high energy elastomeric binder materials for certain applications to replace the polyolefin, polyurethane, or polysiloxane rubbers normally[14,15] used. The object has been to help overcome the substantial depletion of net available energy which ordinarily accompanies the presence of non-energetic binders in HE packages,[16] just as plasticizer and other components are sought with the highest energy contents consistent with other necessary properties.

We felt that certain siloxane analogs of energetic hydrocarbon monomers and polymers might prove beneficial as plasticizers or binders in explosive or propellant mixtures. In particular, we anticipated from the well known[17] behavior of silicone monomers and polymers that siloxane-based substances with FDNE residues might possess improved liquid or flexibility character over a broadened range of temperature in comparison with their hydrocarbon analogs. This could help protect against stress fracturing of cast propellants while adding to the net available energy from a given volume of explosive or fuel. Further, it was of interest whether the energetics of detonation would be enhanced by the combustive formation of silicon species, such as solid SiO_2 (ΔH_f -217 kcal/mol vs gaseous CO_2, ΔH_f -94 kcal/mol)[18]. We report below the preparation and properties of some fluorodinitroethoxysilane esters as potential HE plasticizers and, in the two accompanying papers, studies involving HE polymeric systems as potential elastomeric binders. Since our work began, a very different synthetic approach to HE polysiloxane synthesis has been reported.[19]

Results and Discussion

Synthesis. The object of the present work was to prepare silane ester analogs 2a-c of the HE plasticizer compound 3, bis-2,2,2-fluorodinitroethyl formal, commonly known as FEFO,[2,14] and to determine certain of the comparative physical properties of these compounds, including density, liquid range, shock and

hydrolytic sensitivity, and calculated energy content. Data on the related series of silanes with difluoromononitroethoxy groups, $\left[F_2C(NO_2)CH_2O\right]_xSiMe_{4-x}$, is available.[20] The direct, solventless esterification of the corresponding chloro(methyl)-silanes by FDNE according to eq 1 yielded 2a-c (Table I), in effect substituting the central CH_2 group in 3 by the $SiMe_2$ group in 2a and then replacing the Si-Me groups in 2a by $FC(NO_2)_2CH_2O$— residues in 2b and 2c. In all these reactions, distilled 1 was used which unavoidably contained ∿ 2% of the non-interfering methyl formal $ROCH_2OCH_3$ (see Experimental Section).

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

FDNE, 1

R ≡ $CH_2CF(NO_2)_2$

2

a, x = 2

b, 3

c, 4

$ROCH_2OR$ (3)

$(RO)_2MeSiOSiMe(OR)_2$ (4)

$(RO)Me_2SiOSiMe_2(OR)$ (5)

$(EtO)_2SiMe_2$ (6)

$(RO)_3SiOSi(OR)_3$ (7)

The dimethylsilane ester 2a was obtained readily and efficiently from the stoichiometric reactants when the liberated HCl was swept from the reactor by a slow nitrogen stream directed past a Dry Ice condenser, which was necessary to retain the slowly reacting dimethyldichlorosilane at the 70-80° reaction

temperature. Despite strictly anhydrous conditions, 2 mol-% of a co-distilling impurity identified by NMR as the disiloxane 5 was also generated. When conducted in ethanol-free chloroform or dimethoxyethane at ~5° in the presence of pyridine as HCl acceptor, reaction 1 produced 100% pyridine·HCl, but 5-10 fold increases in the yields of 5 at the expense of 2a also resulted. A transesterification of the simple bisester 6 by equilibration with 100% excess 1 at 35° proceeded rapidly but failed to replace more than one ethoxy group per molecule.[21] Distilled 2a proved stable to preparative VPC even at 200-250° in a glass column and was characterized by its method of synthesis and multinuclear NMR spectra (Table II).

The trisester 2b was also prepared without incident. Esterification of $MeSiCl_3$ proceeded only upon solution of the originally immiscible reactants at 40°, and a small amount of 2a accompanied crude 2b when Me_2SiCl_2 was present in the starting chlorosilane. Distillation of 2b was accomplished with removal of 2a and without decomposition, despite the very high bp (Table I). Pure $MeSiCl_3$, however, unexplainedly gave 2b containing ~5% of the silicon units as a mixture of the partially esterified compound $ClMeSi(OR)_2$ with the disiloxane 4.

Orthoester 2c required 50% excess 1 for complete conversion of $SiCl_4$ under the usual conditions. The highly insoluble silane was added portionwise to 1 at 40° to avoid entrainment losses and hasten the reaction rate, which nevertheless remained very slow even after a 65-70° pot temperature had been attained. Crude 2c was heated under vacuum to remove excess 1 and other volatile impurities, and the resulting solidified product was twice crystallized from alcohol-free $CHCl_3$. Unfortunately, because of its extreme hydrolytic sensitivity (see below), 2c could not be obtained free of small amounts of 1 and the disiloxane 7 (Table I), but NMR analysis (Table II) left no doubt of structure. Transesterification was again attempted as an excess of alcohol 1 was heated with $Si(OMe)_4$ in the presence of conc H_2SO_4 catalyst under conditions for selective distillation of methanol, but the reaction again proved resistant to completion as ∿30% of the ultimate product still contained one MeO— group.

The disiloxane 4, also a side product in the synthesis of 2b, was prepared directly from the corresponding tetrachlorodisiloxane 9 (eq 2) in the usual way (eq 1), including a 4 h heating period at 70° after reaction at 50° for 18 h failed to complete the replacement of Si—Cl groups. Transesterification of the methoxydisiloxane 8 with 1 was not attempted. Characterization of 4 followed from coincidence of its IR spectrum with that of monohydrolyzed 2b and from ^{29}Si NMR analysis. In fact, the regular change in chemical shift in the latter resonances with the nature and type of substituents attached to Si has proved to be a very powerful tool for structure determination, as detailed below.

$$(MeO)_2MeSiOSiMe(OMe)_2 \quad (8) \quad + \quad 4\ SOCl_2 \xrightarrow[57\%]{\phi_3P} Cl_2MeSiOSiMeCl_2 \quad (9)$$

$$+ \quad 4\ MeCl \quad + \quad 4\ SO_2 \qquad (2)$$

Attempts to prepare two further types of silane esters related to those described in Table I proved abortive. Although 2b had hydrolyzed in moist air to the disiloxane 4 by selective loss of just one RO— group, hydrolysis of orthoester 2c with stoichiometry for the formation of disiloxane 7 gave an equilibrium mixture of products (eq 3). The theoretical amount of free 1 was present, but 30% of unreacted 2c was also observed along with the polysiloxanes 7 and 10. Solvent stripping increased the product complexity, and vacuum removal of FDNE left a mixture still containing 20% of 2c. Use of 100% excess of the water required for linear polymer formation (1:1 molar ratio) gave unworkable gels. The hydrolytic behavior of 2c in eq 3 resembled that of ethyl silicate, whose products, even from 1 mole of water, routinely include unreacted monomer and require dilute, acidic solution in hydrogen bonding solvents to prevent cross-linking to the point of gellation.

$$(RO)_4Si \quad (2c) \quad + \quad 0.5\ H_2O \underset{25^\circ}{\overset{\text{acetone}}{\rightleftharpoons}} 7 \quad + \quad (RO)_3SiO\left[Si(OR)_2O\right]_xSi(OR)_3 \quad (10)$$

$$+ \quad 2\ ROH \qquad (3)$$

One attempt was also made to generate the disilane ester 11 (the desoxy analog of 7). However, a reaction conducted by analogy to eq 1 for the preparation of 2c, using 50% excess 1, exothermically consumed greater than the theoretical amount of 1 at 70° and produced 2c as the major product, along with some of the disiloxane 7 (eq 4). The presence of 11 was ruled out by the product mixture ^{29}Si NMR data. The yield of 2c was calculated for complete Si—Si cleavage, a reaction known[22] in similar reactions of hexachlorodisilane. If the cleaving reagent was HCl rather

$$Cl_3SiSiCl_3 + 9\ ROH \xrightarrow[1]{} \underset{42\%}{2c} + 7 + \underset{11,\ \text{not detected}}{(RO)_3SiSi(OR)_3} \qquad (4)$$

than ROH, one might profitably use an acceptor base in reaction 4, but the adverse effect of amines in the esterifications noted above and the facile base-catalyzed disproportionation of Si_2Cl_6 to $SiCl_4$ and higher polysilanes[23] argue against this modification. A further complication to the preparation and stability of disilanes containing HE residues from 1 is a potential, internal redox cleavage of Si—Si by NO_2 groups, as suggested by the deoxygenation of aryl nitro compounds by disilanes at well elevated temperatures.[24]

Overall, the HE silane esters described in Table I were obtained in ∿90% yield (before purification, generally unnecessary) by the simple, direct reaction 1, which required temperatures near 70° for completion. Definite indications of stepwise, partial esterification at lower temperatures and controlled stoichiometries were found but not pursued, and removal of HCl by entrainment was clearly superior to trapping with an amine base. The same procedure has also been applied to the preparation of related fluoroalkoxysilane esters,[20,25] and discouragingly low yields (12-66%) of several other halo and nitro substituted alkoxysilanes in the presence of pyridine[26] also reflect our own experience. The only general side reaction was formation of 1-5% of disiloxanes from hydrolysis rather than alcoholysis of Si—Cl groups. The necessary water was not present initially, and the disiloxanes formed only in the later stages of reaction. Presumably, the alcohol 1 reacted with liberated, soluble HCl to produce small amounts of water as the main reactions proceeded, but did so far less competitively vs esterification than ordinarily[27] expected from alcoholyses with less acidic alcohols, where amine HCl-acceptors sometimes proved useful.

Properties and Characterization. The bp and mp of the silane bisester 2a were similar to those of the reference compound FEFO (3) instead of showing the desired increase in liquid range, and the density was undesirably lower. As will become evident below, high density values are necessary for high detonation pressures and velocities, which are important to high specific impulse values in propellants or high brisance in explosives. As expected, both the bp and density increased in the other compounds of Table I as the average number of RO— groups per Si increased, up to the maximum 4 in 2c. Except for crystalline 2c, the mp range was similar in 2a, 2b, and 4, and small amounts of impurities desirably reduced the onset of solidification to $\sim 0^{\circ}$. Overall, the silane trisester 2b was a close analog of 3 in respect to most of the physical constants while possessing a usefully increased bp.

The hydrolytic reactivities of neat 2a-c and 4 exposed to atomspheric moisture comprised a surprisingly wide range. At one extreme were samples of bisester 2a and disiloxane 4, which remained unchanged for days unless the relative humidity (RH) at $20\text{-}25^{\circ}$ exceeded 50%, whereupon very slow hydrolysis occurred. Trisester 2b, however, rapidly hydrolyzed at high % RH to liberate FDNE and generate a gel, but reacted only slowly at 35% RH, ultimately giving 4. Most reactive was 2c, which instantly hydrolyzed on contact with atmospheric moisture or, in dry

nitrogen, moisture adsorbed on glass or brass surfaces which had not previously been baked out. Thus, despite its remarkably high density, the high mp, crystallinity and extreme sensitivity to moisture of 2c made it an unattractive plasticizer candidate. In different applications, and possibly with protective surface coating, however, 2c could prove interesting as an explosive substance in its own right.

Preliminary sensitivity testing was conducted on each new compound prior to and following any purification. A thermal test consisted of dropping small samples onto a porcelain surface maintained at 315°. All of the compounds boiled off with white fumes and left little residue, except for 2c, which produced yellow fumes, left a residue, but showed no sign of detonation. No response was observed upon placing small samples of any of the HE esters on a steel plate and repeatedly striking them with a hammer.

Although not directly related to their ultimate energy contents, a more quantitative measure of the shock sensitivities of the silane esters was of considerable interest, since one continuing goal of properties modification in HE plasticizers is to reduce thermal and shock sensitivities without reducing the levels of stored energy. The data shown in Table I as values of H_{50} refer to the (mass x height) of a falling piston needed to detonate half of a large number of replicate samples by direct impact or by producing a compressive shock wave upon striking the

flexible cover of a sealed sample container. In the latter, closed cup procedure, 2a proved exceedingly sensitive at 4 times the n-propyl nitrate reference H_{50} value. When struck directly by the falling piston in an open cup, however, 2a proved 100-fold less sensitive. The orthoester 2c, in specially baked-out sample cups, was similarly resistant to detonation by direct impact. Further testing[28] of 2c in a procedure designed for solids[15] gave a value (Table I) similar to that for the explosive Tetryl and about twice that of the more sensitive RDX. Overall, the fluorodinitroethoxysilane esters showed substantial thermal and impact stability, although sensitivity to adiabatic, compressive shock could be hazardously high. It is therefore wise not to apply any sudden pressure when handling these compounds, for example, in syringing the somewhat viscous, neat fluids.

Characterizations and purity determinations in the compounds described above followed largely from NMR analyses (Table II), especially the combination of ^{1}H NMR with the greatly simplifying and predictable FT—^{29}Si NMR spectra. The ^{1}H NMR methylene chemical shifts of the $X_3C—CH_2—O$ residues moved regularly to lower field vs the starting alcohol 1 as the number of RO— groups increased per Si atom. Integration (and VPC analysis in the case of 2a) of appropriately unoccluded impurity peaks provided the purity determinations. Although the ^{13}C NMR doublet absorptions of both the methylene (strong and sharp) and X_3C groups (broad

and weak) generally did not differ markedly between compounds, the ^{29}Si spectra confirmed both the major product structures and the identity of silicone-containing impurities implied by the ^{1}H NMR data and method of synthesis.

Thus, from literature data[29] and our own experience it was evident that absorptions of methylsilicon compounds of structures $Me_xSi(OZ)_{4-x}$ appeared in four distinct regions of the ^{29}Si spectral range, depending on the value of x from 1 to 4, and that within each region there lay characteristic subregions defined by the numbers of alkoxy (Z = C) vs siloxy (Z = Si) groups present. The chemical shifts in the HE esters nicely overlaid the major reference regions, except for the bisester 2a value, as shown in Table III. However, the shift response to the number of attached $—OCH_2CF(NO_2)_2$ groups was somewhat greater than to simple alkoxy groups. Thus, the downfield offset of the 2a absorption vs reference values approximated the upfield offset in the methyl-free compounds 2c, 7, and 10, with coincidence occurring in the monomethyl compounds 2b and 4. The presence of the polymer 10 in the 2c hydrolysate was inferred from the ^{29}Si NMR data on the basis of the regular shift-substituent relationships already observed in the other, pure compounds. Disiloxane 7 was identified by ^{29}Si NMR in the absence of 10 following the partial hydrolysis of 2c in humid air, as the co-product 1 was readily quantified by ^{1}H NMR. Further detailing of the equilibrium

mixture from reaction 3, impossible to achieve even from 220-MHz ^{1}H NMR data, should have been possible by integration of the sharp, resolved ^{29}Si NMR peaks, but significant changes in the hydrolysate composition, beyond those of reasonable NOE effects,[30] resulted upon addition of the necessary spin relaxation agent $Cr(acac)_3$.

Thermochemical Calculations. It is clearly of interest in compounds designed for the release of energy by controlled combustion or detonation to estimate potential performance when actual measurement is impractical. To do this, we first calculated the heats of formation, ΔH_f, of the HE silane esters described above and then used the results in calculation of the chemical energy contents. Finally, from empirical formulas[15,31] which presume compound combustion to specified small molecule products and utilize observed density values, we arrived at the ultimately desired estimates of maximum theoretical detonation velocity and pressure given in Table IV. The initial quantity to be determined in each case was therefore the compound ΔH_f. Although the special technique of rotating bomb calorimetry[32] exists for the complete combustion of complex Si and F containing compounds in the experimental determination of ΔH_f values, the necessary facilities and time were unavailable. Consequently, we obtained ΔH_f values 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 5).[33] The necessary radical fragment values were taken from the literature or deduced in various ways. The calculation of ΔH_f for 2c, below, illustrates the general procedures and assumptions used; details of other calculations of ΔH_f and the derived data are available in a Supplemental Appendix.

$$\Delta H_f \text{ (compound)} = \sum \Delta H_f \text{ (radicals)} - \sum \text{D—values} \qquad (5)$$

We considered first the gas phase dissociation reaction 6 to calculate ΔH_f(2c) from eq 7. To solve eq 7, estimation was required of the dissociation energy of the four Si—OR bonds and the value of ΔH_f(RO·), since only ΔH_f(Si gas) = ΔH_{sub} (Si solid) was known.[18] Assuming D_{total}(Si—OR) over all four bonds in the HE compound 2c was well approximated by the value for the model compound $(EtO)_4Si$, we first solved eq 8 using literature data.[18,33,34] Next, the value of ΔH_f(RO·) was derived from eq 10 using the known[15] ΔH_f of FEFO (3), although the unknown quantity D_{total}(RO—CH_2—OR) had first to be determined, assuming it equal to the value for the analogous diethyl formal (calculated from bond additivity data[34]). We then computed ΔH_f(RO·) = -51.2 kcal/mol, and the desired ΔH_f(2c) followed from eq 7, appearing in Table IV along with other ΔH_f values similarly derived.

$$(RO)_4Si \rightarrow 4\ RO\cdot + Si\ gas \quad (6)$$

$$\Delta H_f(RO)_4Si = 4\ \Delta H_f(RO\cdot) + \Delta H_f(Si\ gas) - D_{total}(Si{-}OR) \quad (7)$$

$$D_{total}(Si{-}OEt) = 4\ \Delta H_f(EtO\cdot) + \Delta H_f(Si) - \Delta H_f(EtO)_4Si =$$

$$401.2\ kcal/mol \quad (8)$$

$$RO{-}CH_2{-}OR \rightarrow 2\ RO\cdot + CH_2 \quad (9)$$

$$2\ \Delta H_f(RO\cdot) = \Delta H_f(CH_2) - D_{total}(RO{-}CH_2{-}OR) - \Delta H_f(FEFO) \quad (10)$$

With compound heats of formation in hand, energy contents, Q (Table IV), followed readily from eq 12, which required the heats of detonation from eq 11. The formation of products from the available atoms in the preferred order SiF_4, SiO_2(solid), HF, H_2O, CO_2, CO, N_2, and C (solid) was adopted for eq 11, with ΔH_f values taken from the literature;[35] elements obtained in their standard states, of course, had $\Delta H_f = 0$, e.g. N_2(gas) and C(solid). Calculation of Q for our example 2c followed from such values according to eq 13; very little difference resulted when SiO_2 was assumed instead of SiF_4 as the silicon product.

$$\Delta H_{det}(\text{compound}) = \sum \Delta H_f(\text{products}) - \Delta H_f(\text{compound}) \quad (11)$$

$$Q\ (\text{kcal/g}) = \frac{\Delta H_{det}}{\text{mol wt}} \quad (12)$$

$$\left[FC(NO_2)_2CH_2O\right]_4Si \xrightarrow{\text{det}} SiF_4 + 4\ H_2O + 8\ CO_2 + 4\ N_2 \quad (13)$$

Two uncertainties in calculations of Q should be mentioned. At the anticipated several thousand degrees temperature of a detonation reaction,[36] one might find much of the divalent species SiF_2, since its presence is favored relative to Si + SiF_4 at >1300° and low pressures.[37] However, the high pressure of detonation would greatly influence the situation and could also affect the preference for SiF_4 vs SiO_2 products. Similarly, it is uncertain that stable, solid SiO_2 would exist in preference to gaseous SiO during a detonation, since the equilibria $2\ SiO_2 \rightleftharpoons 2\ SiO + O_2$ at 1800°[38] and $SiO_2 + Si \rightleftharpoons 2\ SiO$ at >1200° and low pressure[37] lie well to the right. Although the calculated energy contents Q were affected by assuming SiO vs SiO_2 products, the difference was generally overcome in making the final calculations of detonation pressure and velocity, as illustrated next, due to differences in the moles of gaseous products produced.

The final computations were carried out with the empirical[15,31] formulas 15 and 16 to find the detonation pressures and velocities, DP and DV, of Table IV when the necessary densities, ρ, were known. The preliminary quantities ϕ were calculated in eq 14 from the Q-values, the mols of gaseous detonation products per g of sample (N), and the average molecular weight of the gaseous products (M). For example, N for eq 13 was 17 ÷ MW(2c) = 0.0266 mol/g, and M was [Σ MW of n moles of each gaseous product] ÷ Σ n = 37.65 g/mol. Overall, the accuracy of calculations reported in Table IV seems sufficient to

$$\phi = NM^{\frac{1}{2}} Q^{\frac{1}{2}} \tag{14}$$

$$DP = 15.58\ \rho^2 \phi \tag{15}$$

$$DV = 1.01\ \phi^{\frac{1}{2}}(1 + 1.3\ \rho) \tag{16}$$

permit comparison of the data with that of other known or potential HE compounds, despite the multiple approximations made, since the value of DP of 2c agreed very well with that calculated elsewhere (see Table IV). Thus, general practice in the field may well involve procedures similar to those employed here. Table IV also contains values calculated for structures not actually synthesized in this work in order to study some effects of structural modifications. In the absence of density data, one cannot compute DP or DV (eqs 15, 16), but we estimated ρ for the disilane analog 12 (entry 5) of the disiloxane 4 to assess the

impact of removing the siloxane oxygen. Thus, the similar densities of other disilane, disiloxane pairs[39] $(RO)_3SiSi(OR)_3$ vs $(RO)_3SiOSi(OR)_3$ with R = Me or Et were presumed to hold in 4 vs 12 to give the estimated values shown in parenthesis in Table IV.

Consideration of only the four esters 2a-2c and 4 revealed a constant energy content in 2a-2c but increasing values of DV of roughly 1 km/sec per substitution of Si-Me by Si—OR, as expected from the increasing ρ and ϕ values. Replacement of one methyl group of 2a by a siloxane group as in 4 also generated an increase in DV, despite a large drop in energy content Q, but only about half that of substitution by an RO— group. Replacement of both methyl groups, as in 10, largely restored the energy content and gave a ϕ-value equal to 2a; this promises a higher DP and DV in 10 than 2a if the density of 10 should exceed that of 2a. A highly linear dependence of DV on density in the series 2a, 4, 2b, and 2c was revealed in the graphical relationship $DV = 0.49 + 4.22\rho$. As was true of its physical properties, the ultimate detonation parameters of 2b came closest to FEFO, whereas 2c showed calculated energetics similar to the explosive RDX (DV = 8.5-8.8 km/sec[15,31]).

The carbon bonded HE siloxanes shown in Table IV, entries 9 and 10, illustrate the effect on the energetics of substituting hydrolytically stable CH_2 links for hydrolyzable oxy links between Si and the HE residues $—CH_2CF(NO_2)_2$. Polymer 13 was

also of interest as the object of a recent synthetic study.[19] Calculation showed an energy content in 13 once again in the range shown by 2a-c, i.e. larger than in 10, but a DV precursor value ϕ about the same as that of 10. This suggests that a density difference in 13 vs 10 would be necessary to generate an increase in detonation values. Similarly, the tetraalkyl compound 14 showed increased Q but similar ϕ values relative to the tetraalkoxysilane 2c. Overall, similar detonation properties might therefore be expected in a given HE silane ester vs its alkylmethylene analog. Calculation for the hydrocarbon HE polymer $\left[C(CH_2R)_2CH_2\right]_x$, wherein the spinal siloxy unit Si—O of 13 was replaced by the C—CH_2 repeating units, gave Q = 1250 and ϕ = 5.367, values also similar to those in the siloxane systems.

Experimental

CAUTION! Certain compositions based on fluorodinitroethanol have proved violently unstable in the past,[5,6] and it is prudent that reactions and distillations be carried out behind adequate shielding. However, no uncontrolled reactions were encountered in this work. Caution is also advised in avoiding skin contact with 1 or any of its silane esters, since severe burns can result.

Fluorodinitroethanol was obtained from Fluorochem, Inc., or Rocketdyne Division, Rockwell International, and purified as described below. ^{1}H NMR spectra were recorded on a Hitachi R24A or Varian A60 spectrometer. ^{13}C, ^{19}F, and ^{29}Si FT—NMR data were obtained on-site on a Brucker HFX 90 modified for multinuclear capability. Operated in a gated proton decoupling mode to reduce the NOE,[30] the ^{29}Si spectra required 1000-2000 scans because of the relatively low Si atom concentrations deriving from the high compound MW's and the usual problems of low ^{29}Si NMR sensitivity ($\sim$ 1% vs proton—NMR) and low isotopic abundance of ^{29}Si (4.7%). The values of H_{50} were obtained at Union Carbide's South Charleston laboratories, except as noted. Bp's in ^{o}C were recorded at pressures measured on the pot side of distillation cold traps. VPC spectra were obtained on methylphenylsilicone gum supported on Chromosorb W in SS columns or, preparatively, on dimethylsilicone gum/glass columns. Elemental analyses were by Galbraith Laboratories, Inc.

Purification of 2,2,2-Fluorodinitroethanol (1). The alcohol was received in CH_2Cl_2 solution also containing water, polymer, and an unknown impurity 15, identified as the methyl formal of 1, $CH_3OCH_2OCH_2CF(NO_2)_2$. When 0.5 wt % conc H_2SO_4 was added to stripped, crude 1, distillation at 70-80^{o} oil bath temperature afforded 2-10% water and then 75 wt % vs the crude of constant boiling 1, typically 98% pure along with 2% of 15;

bp 37.5-39° (0.4 mm), n_D^{23} 1.4323, d^{22} 1.575 g/cc. When the acid was omitted, water was removed in a forerun as before but the purity of 1 decreased from 98 to 95% as distillation progressed in the jacketed 60 cm x 0.6 cm glass column with tantalum wire spiral. There was no advantage in pre-drying the solution of 1 with molecular sieves before stripping. The 2-5% of impurity 15, was identified in concentrated samples from its bp [lit.[6] 58-61° (1.5 mm)], ^{1}H NMR, and ^{13}C NMR spectra (Table II), especially the characteristic O—$^{13}CH_2$—O absorption [lit.[40] $CH_3OCH_2OCH_3$ δ 94.2]. The variety of literature values[5,7,13,41] for purified 1 suggest that rarely had it been obtained free of impurities. Analysis for the concentration of 15 followed from integration of the isolated ^{1}H NMR CH_3O— peak in $CDCl_3$ solvent, and required addition of CF_3COOD to collapse the overlying HO triplet absorption of 1 at δ 3.30 and move it 0.7 ppm downfield. No reaction[42] appeared to accompany the exothermic solution of 1 in d_6-acetone, which doubtless generated H-bonded complexes in the manner of F_3CCH_2OH;[43] acetone was necessary for the solution of pure 2c and useful with 1 to shift the still coupled HO triplet downfield of even the X_3CCH_2 methylene peaks to δ 5.60.

Dimethyl(bis-2,2,2-fluorodinitroethoxy)silane (2a). In the absence of a Dry Ice condenser, the esterification reaction proceded stepwise and incompletely due to loss of the chlorosilane, as follows. To an oven-dried 100 ml 4-necked RB

flask fitted with thermometer, septum, condenser, and nitrogen inlet was added 5.86 mL (o.06 mol) of 96% pure 1; lines were rigged to permit nitrogen to be passed through or bypass the pot. To the mechanically stirred alcohol was then added 3.6 mL (0.03 mol) of pure Me_2SiCl_2 using a glass syringe and fresh SS needle. The solution obtained was heated to 78° over 1.5 h with magnetic stirring and bypass nitrogen and was then cooled. NMR analysis revealed the presence of both 2a and the half ester $(RO)ClSiMe_2$ (δ SiMe 0.53 ppm), but none of the dichlorosilane (δ 0.81 ppm); 25% of 1 remained unreacted. Further heating at 70-83° for 2.5 h with nitrogen flushing to remove HCl completely converted the half ester to 2a with consumption of half the residual 1.

Another reaction under a Dry Ice condenser with continuous, slow nitrogen flushing facilitated a nearly quantitative conversion of stoichiometric reactants as HCl was evolved between 40-70° over 5 h. The majority of this crude product was then distilled through a 100 x 12 mm micro Vigreaux column from a pot with air capillary bleed to yield 8.4 g of 2a, bp 103-105° (0.2 mm), n_D^{23} 1.4302-1.4304, using a temperature monitored glass wood-packed mantle as heat source. Redistillation removed the disiloxane 5 to give pure 2a (Tables I and II). 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.

Disiloxane 5 was isolated for spectral identification (Table II; prep VPC at 200-250°) from its 1:4 mixture with 2a resulting from stoichiometric addition of KOH-dried pyridine to a mixture of 1 and Me_2SiCl_2 in $CHCl_3$ at 0-5° over 30 min, followed by stirring at 25° for 3 h. Compound 5, n_D^{23} 1.4218, showed increased IR absorption vs 2a in the SiOSi region at ~ 1050 cm^{-1}; an ever higher boiling component was also isolated whose 1050 cm^{-1} absorption was stronger still and indicative of a logical trisiloxane structure.

Methyl(tris-2,2,2-fluorodinitroethoxy)silane (2b). An apparently stepwise esterification ensued when 5.70 mL (0.048 mol) of $MeSiCl_3$ (containing 4% Me_2SiCl_2) was added to 14.7 mL of 96% 1 (0.145 mol) at 25° and the stirred mixture heated under the Dry Ice condenser with slow nitrogen flushing. Relative gassing rates were observed at the silicone oil exit bubbler by temporarily isolating the reactor from the nitrogen flow. Solution occurred at 33° and was followed in 5 min by moderate gas evolution at 42°. When the temperature had risen to 55° after 3 h, the gassing rate roughly doubled but then ceased after a further 3 h at 55-67°. The nitrogen flush was then slowly increased during 4 h at 64-73° and the cooled orange product stripped at 65-85° (0.1 mm) to remove volatile impurities and any unreacted 1. Crude 2b, 21.9 g, n_D^{23} 1.4416, proved stable to the preliminary thermal and shock tests, and a 4 g sample was therefore distilled at a heat bath temperature 195-210° to give

pure 2b (Tables I and II). Most samples of 2b, and all which contained small amounts of 4, remained fluid at 0° indefinitely, although some did crystallize and were melted in bulk to produce the mp recorded. Anal. Calcd for $C_7H_9F_3N_6O_{15}Si$: C, 16.74; H, 1.81. Found: C, 17.04; H, 1.98.

Tetrakis(2,2,2-fluorodinitroethoxy)silane (2c). In the dried reactor was heated 18.5 g (0.12 mol) of 1, accompanied by 1.8 g of 15, an unusually high formal impurity level. With slow nitrogen flushing past the Dry Ice condenser, electronic grade $SiCl_4$ (2.3 mL, 0.02 mol) was added at 40° in 4 parts at 1 h intervals to maintain homogeneity. The solution temperature was then increased to 65° over 3 h as occasional refluxing persisted. After overnight interruption, heating was continued 1.5 h at 65-70°, and nitrogen flushing was then slowly increased during the final 3 h. No condensate was found in the nitrogen line Dry Ice trap. The homogeneous, yellow product oil partially crystallized upon transfer at 25° to a 50 mL pot using a warmed, smooth bore glass syringe and clean, large bore SS needle. The 19.7 g of mixture was stirred magnetically during pot-to-pot distillation of excess 1 and impurity 15 in a 60-85° heat bath at 0.25 mm, but splattering of the residue was nevertheless pronounced. The 14.7 g of semi-solid product was then heated to solution at 58° under nitrogen with 28 mL alcohol-free $CHCl_3$. Massive crystallization produced 2c as dense, white platelets, collected by filtration under nitrogen using a 5 mL cold solvent rinse,

mp 56-79° (12.2 g, 95% yield). One recrystallization from 2 mL $CHCl_3$ per g gave the final sample (Table I) with 94% recovery; further crystallizations failed to improve the mp. The recovery of excess 1 by distillation (4.1 g) and from filtrates (1.1 g) was 90%. 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. Although two elements were low, there seemed no doubt from spectral evidence (Tables II and III) of the composition of 2c, which always contained small amounts of 1 and 7 from surface contact hydrolysis.

1,2-Dimethyl-1,1,2,2-tetrachlorodisiloxane (9). To 357 g (3.0 mol, 25% excess) of $SOCl_2$ in a dry 1-L 4-necked flask with mechanical stirrer, condenser, thermometer, and addition funnel was added under dry nitrogen 3.2 g (0.012 mol) of triphenylphosphine in 0.5 g portions at 4°. The resulting solution was warmed to 52°, and 135 g (0.60 mol) of 1,2-dimethyl-1,1,2,2-tetramethoxydisiloxane 8 [Silar Laboratories; NMR δ ^{29}Si, -48.4; ^{13}C, -6.85 (Me), 50.1 (OMe), -4.7 (impurity)] was added over ~ 2 h as the temperature of the yellow, foaming solution rose to 71°. The solution was cooled overnight and reheated 7 h at 65-75° to complete the reaction (VPC). A small, lower phase was removed, the upper layer stripped, and the 132 g of residue distilled to afford 83 g (57%) of >98% pure 9, bp 142-144°,

d^{24} 1.295 g/cc, NMR δ ^{1}H, 0.85; ^{13}C, 5.9; ^{29}Si, -15.1 [lit.[39] bp 141°, d^{20} 1.3021]. A slightly higher boiling impurity may have been a trisiloxane, as suggested by its very similar ^{1}H and ^{13}C NMR peaks at 0.78 and 7.7 ppm.

1,3-Dimethyl-1,1,3,3-tetrakis(2,2,2-fluorodinitroethoxy)-disiloxane (4). To 12.2 g (0.05 mol) of 9 was added one-third the stoichiometric amount of 1. Solution was effected by heating the mixture under magnetic stirring and a slow sweep of nitrogen to 60° over 30 min, and the remaining 1 was added over 3 h. An acidic gas was slowly and continuously evolved during 4 h at 60-68°, and ^{1}H NMR analysis then revealed only 35% esterification of Si—Cl groups. Further heating for 18 h at 50° under a water condenser produced 90% conversion, but completion of the reaction required a final 4 h at 70°. Some 9 must have been lost, since ∿15% of unreacted 1 remained and only 30.8 g (86%) of the expected 4 was obtained following high vacuum stripping. About 7% of an impurity was calculated by ^{1}H NMR integration and identified as a tri- or higher siloxane from a -55.9 ppm ^{29}Si NMR peak (Table III).

Reaction of Hexachlorodisilane with 1. The two-phase mixture produced upon addition of 0.15 mol (50% excess) 1 to 0.017 mol of 95% pure disilane, bp 148°, d^{23} 1.55, was well stirred and soon produced rapid gas evolution at 25° with spontaneous cooling to 18°, and a viscous, colorless solution then resulted after 1.25 h

at 23° with cessation of gassing. Precipitation 10 min later gave a slurry, which was heated to 60° under a slow nitrogen sweep. Solution occurred, as an exothermic reaction ensued over 30 min and was controlled at 70-73° while a lemon-yellow color formed in the pot and then transferred to the bubbler. The straw-colored residue was further heated at 65-70° for 6 h until gas evolution had ceased. ^{29}Si and ^{1}H NMR analyses revealed the presence of 2c and 7 and ruled out the desired 11, since no absorption in the -10 to -20 ppm region was found; we had anticipated a downfield (less negative) shift of ∿40 ppm in 11 vs 7, based on the shift shown by $Cl_3SiSiCl_3$ at -6.2 vs that of $Cl_3SiOSiCl_3$ at -45.6 ppm. Crystallization of 2c proceeded at 5°, and recrystallization from $CHCl_3$ gave 8.8 g, mp 62-72°.

Hydrolyses of 2c. The complex mixtures resulting from hydrolyses of 2c to 1, 7, and 10 in acetone were incompletely resolved by ^{1}H NMR, even at 220 MH_3 (Rockefeller Institute). The results of varying the water and solvent concentrations on the directly resulting product mixtures are shown in Table V. A scaled-up product from 1 to 8.7 g of starting 2c under the conditions of entry 3 was then analyzed by ^{1}H and ^{29}Si NMR in three stages of workup: reaction solution, solvent stripped (20° at 1 mm), and 1-stripped (65° at 0.5 mm). Removal of solvent greatly decreased the amounts of the desired linear or cyclic hydrolysate species of type $(RO)_2Si(OSi\equiv)_2$ to ∿20% of the total and generated ∿25% of cross-linked sites of the type $(RO)Si(OSi\equiv)_3$. However, further changes upon removal of 1 were relatively small.

Acknowledgments. The author is indebted to Mr. Roland Bishop for obtaining the multinuclear NMR spectra and to Messrs. J. A. Fisher and G. E. Snyder for the in-house drop weight testing data.

Supplemental Information. The reference values and calculations involved in the preparation of Table IV and some related data have been provided as Supplemental Information.

Table I. Properties of High Energy Silane Esters vs FEFO

Property	2a	2b	2c	4	3 FEFO[a]
Synthesis yield, %	87	73[b]	90	86[c]	—
Purity, wt-%	97	100	≥82[d]	≥93	—
Mp °C	19-19.5	∿25	74-86[d]	∿15-20	11-13
Bp °C (mm)	96(0.1)	170(0.3)	—	∿250(0.1)[e]	120-124(0.3)
$n_D^{°C}$	^{22}1.4308	^{22}1.4412	—	^{25}1.4406	—
d °C g/cc	^{24}1.395	^{23}1.660	^{25}1.938	^{24}1.580	1.607
Shock sens, H_{50} kg-cm	∿300[f]	—	76[g]	—	—
Hydrolysis rate in air/% RH	nil/46% v slow/ 52%	slow/35% rapid/60%	v rapid/ 18%	nil/35% v slow/ 52%	—

[a] Refs 5,15. [b] Crude yield 91%, purity 96%, mp ∿0°C. [c] Crude product.

[d] Variable due to hydrolytic sensitivity. [e] Estimated.

[f] Open cup; value 2.5 kg-cm in closed cup ASTM procedure D2540.

[g] AWRE test for solids, sandpaper surface;[15] open cup value ∿300 kg-cm

Table II. $^{1}H, ^{13}C, ^{19}F$, and ^{29}Si-NMR Chemical Shifts[a] (ppm) and Coupling Constants[b] (Hz)

Group	Nucleus	1	15 $ROCH_2OCH_3$[c]	2a	5	2b	4	2c[d]
$-CF(NO_2)_2$	F			-108.6		-110.4	-108.2	-108.7
	($J_{H,F}$)			(unresolved)		(15.7)	(15.7)	(15.5)
	C	121.0		120.6		121.8	134.2	119.4
	($J_{C,F}$)	(290)		(290)		(281)	(293)	(292)
$O-CH_2-CX_3$	H	4.70[e]	4.67	4.81	4.74	4.87	4.83[f]	5.08
	($J_{H,F}$)	(15.7)	(17.5)	(17.2)	(18.0)	(16.5)	(17.8)	(15.5)
	C	61.1	64.8	61.5		63.2	64.1	62.5
	($J_{C,F}$)	(20.4)	(20.4)	(18.1)		(20.8)	(29.3)	(22.6)
$Si-CH_3$	H		3.45	0.27	0.18	0.39	0.37	
	C		56.0	-4.5	-2.2	-7.95	-7.23	
Si	Si[g]			7.7		-39.6	-47.1	-88.7[h]

Footnotes - Table II

[a] $CDCl_3$ solvent, TMS reference (except ^{19}F, referred to $CFCl_3$); negative δ-values denote upfield of reference. [b] Doublets, except ^{19}F triplets. [c] Resonances of OCH_2O methylene were δ ^1H, 4.74; ^{13}C, 96.9 [lit.[6] ^1H (CCl_4) δ 4.58 (J 17.5, OCH_2CX_3); 4.67 (OCH_2O); 3.36 (CH_3)]. [d] Solvent was 3:1 $CDCl_3$-d_6-acetone. [e] Secondary splitting by OH (d, J 7.0, in absence of acids). Value in d_6-acetone was δ 4.75 (J 17.6).

[f] Discrepancy vs ^{19}F-spectrum unexplained. [g] *Without spin relaxation agent.*

[h] Solvent was 1:9 $CDCl_3$-d_6-acetone.

Table III.

^{29}Si Chemical Shifts as a Function of Oxy Substituents

$$Me_aSi(OSi\equiv)_b$$
$$|$$
$$(OC\equiv)_{4-a-b}$$

Compound Defined by (a + b)		Approximate -δ (ppm) vs TMS[a]			
Ref.	Exptl	a = 0	a = 1	a = 2	a = 3
4		105	65	22	- 6
3		99	58	12	-17
2		92	49	3	
1		86	41		
0		79			
	3		55.9[b]		
	2	98-100 (10)	47.1 (4)	-7.7 (2a)	
	1	94 (7)	39.6 (2b)		
	0	88.7 (2c)			

[a] In CCl_4 or $CDCl_3$. [b] Trisiloxane, unisolated minor product in synthesis of 4.

Table IV. Calculated Thermochemical Properties of High Energy Silicon Compounds[a]

Entry	Compound	$-\Delta H_f$ kcal/mol	-Q cal/g	N mol/g	M g/mol	ϕ	ρ g/cc	DP kbars	DV km/sec
1	3, $ROCH_2OR$ (FEFO)	177.5[b]	1390[b]	.0312	30.81	6.457	1.607	260	7.92[b]
2	2a, $(RO)_2SiMe_2$	288	1310	.0275	25.60	5.036	1.395	152.7	6.38
3	2b, $(RO)_3SiMe$	390.5	1325	.0279	29.86	5.550	1.66	238.3	7.51
4	4, $(RO)_2MeSiOSiMe(OR)_2$[c,d]	642	1048	.0280	33.90	5.280	1.58	205.4	7.09
5	12, $(RO)_2MeSiSiMe(OR)_2$[c]	551	1163	.0272	34.20	5.425	(1.60)[e]	(216.4)	(7.25)
6	$-[SiMe(OR)O]_x-$	246.4	1158	.0236	25.60	4.063			
7	2c, $(RO)_4Si$	500	1330	.0266	37.65	5.952[f]	1.938	348.3[f]	8.67
8	10, $-[Si(OR)_2O]_x-$	353.8	1221	.0257	32.22	5.098			
9	13, $-[Si(CH_2R)_2O]_x-$	239.8	1355	.0260	26.44	4.922			
10	14, $(RCH_2)_4Si$	272	1480	.0269	31.53	5.811			

[a] R ≡ $CH_2CF(NO_2)_2$. [b] Values cited in ref 15 are ΔH_f - 177.5; Q - 1390; DV 7.50 (obsd).

[c] Calcd for dec to SiF_4 + SiO rather than SiO_2. [d] Values for SiO_2 product are (left to right) 642, 1278, .0252, 33.7, 5.23, 1.58, 203.4, and 7.05. [e] Estimated, see text.

[f] Also calcd by M. Kamlet[44] ϕ = 6.025, DP = 352.

Table V. Composition of 2c Hydrolysates

Entry	Molar H_2O/2c	mL Acetone	%-Hydrolysis of RO— groups	Si group in hydrolysate, % 2c	$(RO)_3Si$—	$(RO)_2Si$=
1	0.5	2	27	30	34	36
2	0.5	1	25	24	33	43
3	1.0	2	47	10	20	70
4	1.0	1	40	14	22	64

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Supplemental Information

Details of calculations summarized on Contents page A2 are given, following procedures similar to those illustrated in the paper. Single bond X-Y dissociation energies are denoted as usual by D(X-Y), but arbitrary terminology has also been introduced where D_T denotes the total of the dissociation energies of n identical bonds to Si, whose average value is identified as $\bar{D}$. Unless specified otherwise, R denotes the HE group $—CH_2CF(NO_2)_2$. All thermochemical calculations are made for gas phase reactions at 298^{O} K, with negative values showing exothermicity. Reference numbers refer to those of the paper.

CONTENTS

	Value kcal/mol	Section	Page A-
Reference values		I	3
Calculation of preliminary data, kcal/mol		II	4
$\bar{D}$ (EtO-CH_2-OEt)	82.6	A	4
$\bar{D}$ (EtO-Si) in $(EtO)_4Si$	100.3	B	4
$\bar{D}$ (Et-Si) in Et_4Si	74.7	C	4
D_T in $(EtO)_2SiMe_2$	359.6	D	4
D (Si-O) in $Me_3SiOSiMe_2OSiMe_3$		E	4
2 of 4 bonds broken	35.8	1	4
4 of 4 bonds broken	112.8	2	5
D_T (monomer unit) in $-[Si(OEt)_2O]_x-$		F	5
1 of 2 Si-O bonds broken	227.2	1	5
2 of 2 Si-O bonds broken	417.0	2	5
D_T (monomer unit) in $-[Si\ Et_2O]_x-$			
1 of 2 Si-O bonds broken	176.0	G	5
D_T (monomer unit) in $-[MeSi(OEt)O]_x-$			
1 of 2 Si-O bonds broken	205.0	H	6
ΔH_f (RO·)	- 51.2	I	6
ΔH_f (R·)	- 15.1	J	6
ΔH_f (RCH_2·)	- 19.8	K	7
Calculation of ΔH_f of compounds, kcal/mol		III	7
$(RO)_4Si$	-500	A	7
$(RO)_2SiMe_2$	-288	B	7
$-[Si(OR)_2O]_x-$ (4 ways)	-353 to -363	C	7
$-[SiR_2O]_x-$	-230	D	8
$-[Si(CH_2R)_2O]_x-$	-240	E	9
$(RCH_2)_4Si$	-272	F	9
$(RO)_3SiMe$	-391	G	9
$(RO)_2MeSiOSiMe(OR)_2$	-642	H	9
$(RO)_2MeSiSiMe(OR)_2$	-551	I	10
$-[MeSi(OR)O]_x-$	-246	J	10
Calculation of ΔH_{det} (kcal/mol) and Q (cal/g) of compounds		IV	10
$(RO)_4Si$, compound 2c	-854	A	10
$(RO)_2SiMe_2$, compound 2a	-478	B	10
$-[Si(OR)_2O]_x-$, compound 10	-427	C	10
$-[Si(CH_2R)_2O]_x-$	-469	D	11
$(RCH_2)_4Si$	-937	E	11
$(RO)_3SiMe$, compound 2b	-665	F	11
$-[MeSi(OR)O]_x-$	-246	G	11
$(RO)_2MeSiSiMe(OR)_2$, compound 12	-812	H	11
$(RO)_2MeSiOSiMe(OR)_2$, compound 4	-914 to -613	I	12
Detonation parameters vs decomposition mode of compound VII		V	12

I. REFERENCE VALUES

Entry		Value (kcal/mol)	Reference
ΔH_f (FEFO) $\underset{\sim}{(3)}$		-177.5	15
ΔH_f $(EtO)_2SiMe_2$		-199.	34
ΔH_f $(EtO)_4Si$		-322.	34
$\Delta H_f = \Delta H_{sub}$ (Si)		106.	18
ΔH_f (CH_2)		90.	33
ΔH_f (CH_3)		34.	33
ΔH_f (CH_2CH_3)		25.7	33
ΔH_f $(CH_2CH_2CH_3)$		21.	33
ΔH_f (SiO)		- 24.2	18
	or	- 21.4	38
ΔH_f (EtO)		- 6.7	33
ΔH_f (Et_4Si)		- 90.	34
ΔH_f $(Me_3SiOSiMe_2OSiMe_3)$		-350.	34
ΔH_f (O atom)		59.6	33
ΔH_f (SiO_2 solid)		-217.5	18
ΔH_f (SiF_4)		-370.	35
ΔH_f (HF)		- 64.8	18
ΔH_f (H_2O)		- 57.8	18
ΔH_f (CO_2)		- 94.05	18
D (Si-CH_3)		76.	a
D (Si-Si)		75 $\pm$ 8	b
D (Si-O)		106.	c
	or	115.1	32

a S. J. Band, I. M. T. Davidson, C. A. Lambert, and I. L. Stephenson, Chem. Comm., 723 (1967). b P. Potzinger, A. Ritter, and J. Krause, Z. Naturforsch. 30a, 347 (1975). c Ref 17, page 90.

II. CALCULATION OF PRELIMINARY VALUES

A. $\bar{D}$ (RO-CH_2-OR), model R = Et

Calculated ΔH_f $(EtO)_2CH_2$ from bond additivity values[34] = -88.5

$$2\,\bar{D}(EtO\text{-}CH_2) = 2\Delta H_f(EtO) + \Delta H_f(CH_2) - \Delta H_f(EtO)_2CH_2$$

$$2\,\bar{D}(EtO\text{-}CH_2) = 2(-6.7) + 90 - (-88.5)$$

$$\bar{D}(EtO\text{-}CH_2) = 82.6$$

B. $\bar{D}$(RO-Si), model R = Et, in $(RO)_4Si$

$$4\,\bar{D}(EtO\text{-}Si) = 4\Delta H_f(EtO) + \Delta H_f(Si) - \Delta H_f(EtO)_4Si$$

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

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

C. $\bar{D}$(R-Si); model R = Et, in R_4Si

$$4\,\bar{D}(Et\text{-}Si) = 4\Delta H_f(Et) + \Delta H_f(Si) - \Delta H_f(Et)_4Si$$

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

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

D. D_{total} (Si - bonds) in $(RO)_2SiMe_2$, model R = Et

$$D_T = 2\Delta H_f(EtO) + 2\Delta H_f(Me) + \Delta H_f(Si) - \Delta H_f(EtO)_2SiMe_2$$

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

$$D_T = 359.6, \text{ all 4 bonds to Si}$$

E. $\bar{D}$ (Si-O) in model trisiloxane $Me_3SiOSiMe_2OSiMe_3$

1) Dissociation to SiO as a product

For the reaction

$Me_3SiOSiMe_2OSiMe_3 \longrightarrow 8\,CH_3 + 2SiO + Si$, and

assuming $\bar{D}$ (Si-Me) = D(Si-Me)

$$2\,\bar{D}(Si\text{-}O) + 8\,\bar{D}(Si\text{-}CH_3) = 8\Delta H_f(CH_3) + 2\Delta H_f(SiO) + \Delta H_f(Si) - \Delta H_f(\text{trisiloxane})$$

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

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

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

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. 34 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[34] ΔH_f (monomer) = -148.8

$$D_T = 2(25.7) + (-24.2) - (-148.8)$$

$$= 176.$$

H. D_T in model polymer unit $\frac{}{}$MeSi(OEt) O$\frac{}{}$,

decomposition to SiO

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

Calc.[34] 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. $\Delta H_f(RO\cdot)$

$$\underset{\text{FEFO}}{RO\text{-}CH_2\text{-}OR} \longrightarrow 2(RO) + CH_2$$

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

(use II-A) (known)

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

J. $\Delta H_f(R\cdot)$

$$ROCH_2OR \longrightarrow RO + CH_2 + O + R$$

$$2\bar{D}(RO\text{-}CH_2) + D(O\text{-}R) = \Delta H_f(OR) + \Delta H_f(CH_2) + \Delta H_f(O) + \Delta H_f(R) - \Delta H_f(FEFO)$$

to calculate D(O-R) use

$$RO\cdot \longrightarrow R\cdot + O \text{ with model R = Me}$$

$$D(O\text{-}CH_3) = \Delta H_f(CH_3) + \Delta H_f(O) - \Delta H_f(OCH_3)$$
$$= 34 + 59.6 - 2 = 95.6$$

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

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[34] of 1 C - C and 2(C-H) bonds.

III. CALCULATION OF ΔH_f FOR COMPOUNDS (kcal/mol)

A. $(RO)_4Si$ ($\longrightarrow 4\,RO + Si(g)$)

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

assume $\bar{D}(Si\text{-}OR) = \bar{D}(Si\text{-}OEt)$ (see II-B)

$$4\,(100.3) = 4(-51.2) + 106 - \Delta H_f (RO)_4Si$$
$$\Delta H_f (RO)_4Si = -500.$$

B. $(RO)_2SiMe_2$ ($\longrightarrow 2\,RO + 2\,Me + Si(g)$)

$$D_T (Si\text{ - bonds}) = 2\Delta H_f (RO) + 2\Delta H_f (Me) + \Delta H_f (Si) - \Delta H_f (RO)_2\,SiMe_2$$

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. $\{Si(OR)_2O\}$ 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 $\{Si(OEt)_2O\}$ in II-F-1.

$$\{Si(OR)_2O\} \longrightarrow 2\,(OR) + SiO$$
$$D_T = 2\Delta H_f (OR) + \Delta H_f (SiO) - \Delta H_f (\text{monomer unit})$$
$$227.2 = 2\,(-51.2) + (-24.2) - \Delta H_f (\text{monomer})$$
$$\Delta H_f (\text{monomer}) = -353.8$$

2) Use D_T calcd for $\frac{}{}Si(OEt)_2O\frac{}{}$ in II-F-2.

$\frac{}{}Si(OR)_2O\frac{}{} \longrightarrow 2(OR) + Si + O$

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

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

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

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)

$\frac{}{}Si(OR)_2O\frac{}{} \longrightarrow 2(OR) + SiO$

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

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

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

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

$\frac{}{}Si(OR)_2O\frac{}{} \longrightarrow 2RO + Si + O$

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

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

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

D. $\frac{}{}Si(R)_2O\frac{}{}$ $(\longrightarrow 2R + SiO)$

$D_T(\text{Si} \equiv \text{bonds}) = 2\Delta H_f(R) + \Delta H_f(SiO) - \Delta H_f(\text{monomer})$

(from II-G) (from II-J)

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

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

E. $\{Si(CH_2R)_2O\}$ ($\longrightarrow 2\,CH_2R + SiO$)

D_T (Si ≡ bonds) = $2\Delta H_f(CH_2R) + \Delta H_f(SiO) - \Delta H_f$ (monomer)

(use II-G) (from II-K)

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

ΔH_f (monomer) = -239.8

F. $(RCH_2)_4Si$ ($\longrightarrow 4\,RCH_2 + Si$)

$4\bar{D}$ (Si-R) = $4\Delta H_f(CH_2R) + \Delta H_f(Si) - \Delta H_f(RCH_2)_4Si$

(from II-C) (from II-K)

$4(74.7) = 4(-19.8) + 106 - \Delta H_f(RCH_2)_4Si$

$\Delta H_f(RCH_2)_4Si = -272$

G. $(RO)_3SiMe$ ($\longrightarrow 3\,RO + Si + Me$)

$3\bar{D}$ (Si-OR) + D(Si-Me) = $3\Delta H_f(RO) + \Delta H_f(Si) + \Delta H_f(Me) - \Delta H_f(RO)_3SiMe$

(from II-B)

$3(100.3) + 76 = 3(-51.2) + 106 + 34 - \Delta H_f(RO)_3SiMe$

$\Delta H_f(RO)_3SiMe = -390.5$

H. $(RO)_2MeSiOSiMe(OR)_2$ ($\longrightarrow 4\,RO + 2\,Me + SiO_{(g)} + Si_{(g)}$)

$4D(Si-OR) + 2D(Si-Me) + D(Si-OSi) = 4\Delta H_f(RO) + 2\Delta H_f(Me) + \Delta H_f(SiO) + \Delta H_f(Si) - \Delta H_f$(compd)

ΔH_f (compd) = $\sum \Delta H_f$ (products) - $\sum$ D-values

$= [4(-51) + 2(34) + (-24) + 106] - [4(100) + 2(76) + 35.8]$

$= -641.8$

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

I. $(RO)_2MeSiSiMe(OR)_2$ $(\longrightarrow 4(RO) + 2Me + 2Si_{(g)})$

$4\bar{D}(Si\text{-}OR) + 2D(Si\text{-}Me) + D(Si\text{-}Si) = 4\Delta H_f(RO) + 2\Delta H_f(Me) + 2\Delta H_f(Si) - \Delta H_f(compd)$

$\Delta H_f(compd) = \sum \Delta H_f(products) - \sum D\text{-values}$

$= [4(-51) + 2(34) + 2(106)] - [4(100) + 2(76) + 75]$

$= -551$

J. Monomer unit in $\{MeSi(OR)O\}$ $(\longrightarrow RO + SiO + Me)$

$D_T(RO\text{-}Si + Si\text{-}O + Si\text{-}Me) = \Delta H_f(RO) + \Delta H_f(SiO) + \Delta H_f(Me) - \Delta H_f(compd)$

$\Delta H_f(compd) = \sum \Delta H_f(products) - D_T$

$= [(-51) + (-24) + 34] - 205$ (see II-H)

$= -246$

IV. CALCULATION ΔH_{det} FOR COMPOUNDS

A. $(RO)_4Si$ $\Delta H_{det} = \sum \Delta H_f(products) - \Delta H_f(compound)$

$[FC(NO_2)_2CH_2O]_4Si \longrightarrow SiF_4 + 4H_2O + 8CO_2 + 4N_2$

MW 640.3, $C_8H_8F_4N_8O_{20}Si$

$\Delta H_{det} = [-370 + 4(-57.8) + 8(-94.05)] - [-500]$

$= -853.6$ kcal/mol or -1330 cal/g

[Values are -884.7 kcal/mole or -1320 cal/g for SiO_2 as product instead of SiF_4]

B. $(RO)_2SiMe_2$

$[FC(NO_2)_2CH_2O]_2Si(CH_3)_2 \longrightarrow SiO_2 + 2HF + 4H_2O + 2CO_2 + 4C_{(s)} + 2N_2$

MW 364.3, $C_6H_{10}F_2N_4O_{10}Si$ (solid)

$\Delta H_{det} = [-217.5 + 2(-64.8) + 4(-57.8) + 2(-94.05)] - [-288]$

$= -478.4$ kcal/mol or -1313 cal/g

C. $\{Si(OR)_2O\}$

$\{(FC(NO_2)_2CH_2O)_2SiO\} \longrightarrow SiO_2 + 2HF + H_2O + 4CO_2 + 2N_2$

MW 350, $C_4H_4F_2N_4O_{11}Si$

$\Delta H_{det} = [-217.5 + 2(-64.8) + (-57.8) + 4(-94.05) - [-353.8]$

$= -427.3$ kcal/mol or -1221 cal/g

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, $C_6H_8F_2N_4O_9Si$

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

$= -468.8$ 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, $C_{12}H_{16}F_4N_8O_{16}Si$

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

$= -936.6$ 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, $C_7H_9F_3N_6O_{15}Si$

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

$= -665.1$ kcal/mol 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

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

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

H. $(RO)_2\ MeSiSiMe(OR)_2$

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

$C_{10}H_{14}F_4N_8O_{20}Si_2$, 698

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

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

I. $(RO)_2MeSiOSiMe(OR)_2$

$(MeSi[OCH_2CF(NO_2)_2]_2)_2O \longrightarrow$ 5 different sets of products (a-e)

$C_{10}H_{14}F_4N_8O_{21}Si_2$, 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 4

Mode (Section IV-I)	-Q Cal/g	N Mol/g	M Av g/mol	Ø	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

Aminoalkyl(methyl)polysiloxane Homopolymers and Their Mannich Derivatives From 2,2,2-Fluorodinitroethanol[1]

Robert S. Neale

Union Carbide Chemicals & Plastics

Tarrytown, N.Y. 10591

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Abstract

Aminoalkyl(methyl)polysiloxane homopolymers were prepared by hydrolysis of the dialkoxysilanes $(RO)_2MeSi—Z—NH_2$ with Z = $(CH_2)_3$, $(CH_2)_3NHCH_2CH_2$, or $(CH_2)_4$. The products could be compositionally varied to contain up to ~85% HO-end blocked linear species with average chains composed of 6-116 spinal siloxy units, depending on structure and method of preparation. Mannich condensations of 2,2,2-fluorodinitroethanol with selected monomeric and polymeric aminoalkylsilicon compounds quantitatively afforded high energy (HE) derivatives, whose thermal stabilities declined dramatically in the presence of strongly basic amines

and differed markedly in secondary vs tertiary HE aminoalkyl structures. Molecular weights averaging ~11,000 for the linear components were realized in the HE aminobutyl system, and preliminary probing of their chain extension to potential HE elastomers produced flexible, waxy gels at room temperature. The cyclic, end group, and internal linear siloxane units were generally well differentiated and quantified by ^{29}Si NMR.

In the preceding paper[2] it was shown that monomeric esters prepared from 2,2,2-fluorodinitroethanol (FDNE, 1) and chlorosilanes could be highly energetic, but their undesirable sensitivity to hydrolytic decomposition made them unattractive for general use as plasticizers in HE compositions. We now report a feasibility study of HE silicone polymers as potential elastomeric binders for solid propellants, in which HE groups have been linked to spinal siloxy units through non-hydrolyzable silicon-carbon bonds.

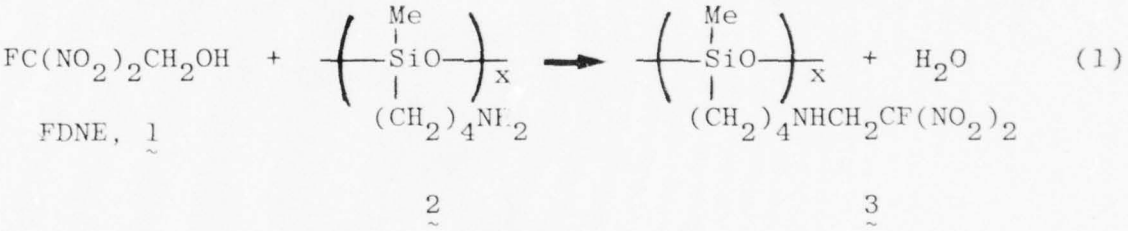
Although various binder substances can facilitate the casting, handling and storage of solid propellant fuels and explosives, they should also possess a rubbery quality over a range of use conditions to absorb mechanical shock and provide adequate resistance to hazardous fractures of the charge. Ordinary organic or silicone binder rubbers serve the purpose, but they do not contain the built-in oxidizing power necessary for auto-combustion and thereby detract from the net energy outputs of HE compositions by consuming rather than generating energy. Elastomeric HE binder polymers have therefore been sought which incorporate the required oxidizing groups.

Several types of such energy-enriched polymers have been described, but rarely have high molecular weights or elastomeric quality been achieved. The usual synthesis approach has been to prepare HE monomers for free radical, epoxy, or condensation

polymerization to products with either spinal hydrocarbon chains, bearing HE acrylic[3-6] or ether[7] residues, or spinal polyether,[8] polyester,[9] or polyurethane[10] units with pendant polynitroalkyl groups. This approach also failed to provide high MW polysiloxanes by hydrolytic condensation of HE silane dibromides.[11] The general failure to achieve high MW's was not surprising in view of the bulky and electronically unfavorable nature of polynitro groups, which are very efficient radical chain terminators.[5] A further drawback to the method has been the multi-step monomer preparations usually required, which were often not highly efficient overall or conducive to attractive scale-up.

We have therefore studied an alternative approach to potentially elastomeric HE polymers. The procedure calls first for the preparation of soluble, linear backbone structures of moderate MW which bear pendant groups capable of condensing with HE reagents. In a second step, the acceptors are efficiently energized in 1 step to form soluble HE derivatives. The products are finally chain extended through appropriate end group treatment with linking reagents to generate high MW polymers during the final compounding of HE compositions. Described below is a demonstration of the spinal energization approach in the preparation of HE polysiloxanes via Mannich condensation of alcohol $\underset{\sim}{1}$, a convenient source of the HE moiety $-CH_2CF(NO_2)_2$, with acceptor aminoalkylpolysiloxane units $\underset{\sim}{2}$ as illustrated in

eq 1. Mannich reactions of 1 have previously proved facile with simple amines[12] and yielded products[13] of incompletely known but acceptable[14] stabilities for the purpose of initial investigation. The synthesis and ^{29}Si NMR characterization of acceptor polymers containing aminobutyl or -propyl groups and some HE derivatives are described. In a companion paper[15] are presented similar studies involving aminomethyl side chain polysiloxanes.



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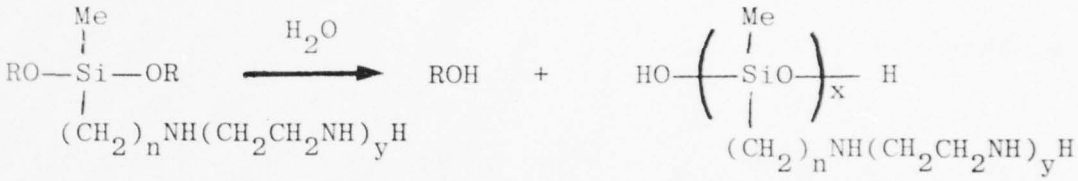
Results and Discussion

Aminoalkyl(methyl)silicone Acceptor Polymers. The first problem was to prepare well-defined, linear aminoalkylsilicones with end groups unreactive in the Mannich reaction with 1 but amenable to later chain extension to higher MW materials. The hydrolysis of silane bisester monomers 4 was selected as a general route to the target series of polymers 5 bearing silanol end groups, for which an extensive inventory of direct or indirect (by intermediate derivatization) chain extending techniques exists. The systems 5 were of interest with 1 to 4 side chain methylene groups and with both mono and polyamino

functionality, since we anticipated that the fewer the number o CH_2 groups per ultimate HE amino group, the greater would be th energy content available for autocombustion. The systems 5a-c are described below, with the analogous monomethylene system treated separately[15] because of its highly atypical behavior.



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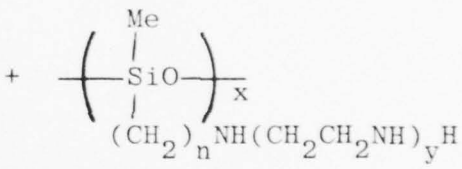
linear 5



cyclic 5

R	Compound	n	y
Et	a	4	0
Et	b	3	0
Me	c	3	1

Most straightforward was the aminobutyl system. Monomer 4a was hydrolyzed under conditions which produced either highly cyclic or highly linear products 5a, but always a mixture of both. Although purely linear hydrolysates were ideally desired for chain extension, small amounts (10-20%) of non-volatile 4-5 unit cyclics in the later HE derivatives were considered acceptable and possibly useful in providing a plasticizing effect in the final HE compositions. The ubiquitous presence of cyclics was not unusual, since polyorganosiloxanes generated by hydrolysis of monomers or by catalytic ring opening processes are expected to contain varying amounts of small cyclics at equilibrium.[16] Experience has also shown cyclics to be favored upon dilution of spinal Si—O units (in a solvent or in the polymer itself) and by bulky[17] side chains. When volatile, cyclics can be stripped from residual polymers,[18] but this was impractical with the present high boiling materials. Although strongly basic catalysts, such as $\equiv SiO^-$ or RO^- species, are required for rapid SiOSi scission and equilibration, organic amines catalyze rapid ester hydrolysis and silanol condensation to siloxanes. The hydrolyses of monomers 4 therefore required no added catalyst and proceeded with a minimum of siloxane backbone rearrangement.

Various operations on monomer 4a or its initial hydrolysate mixtures 5a produced an array of products with significant compositional differences (Table I), whose characterization by ^{29}Si NMR analysis are discussed separately below. As a convenient shorthand, we employ the symbolism HOD_xH to refer to hydroxy-terminated, linear polysiloxanes of chain length x in which each of the units D is a difunctional siloxy species —(Me)Si(R)O— and R is any type of aminoalkyl group. (Normally in polysiloxane chemistry, D specifically denotes dimethylsiloxy units —$SiMe_2O$—, and modified D-units receive modified and complicating notation.) Cyclics are therefore represented here by D_x, or by "cyclic(x)". Thus, hydrolysis of 4a with 4 mol of water at 60° and vacuum work-up at 60-100° (the preferred procedure, see Experimental Section) produced 5a containing ∿20 wt-% of siloxy units as $D_{4,5}$ species and ∿80% of linears with average composition $HOD_{54}H$. A contrasting product containing 79% $D_{4,5}$ resulted, however, upon hydrolysis at 60-100° in the presence of Me_4NOH catalyst and azeotropic dehydration with boiling toluene. This high cyclics product proved convertible with water and KOH at 90° and vacuum stripping to a mixture containing 86-88% linears with either relatively short average chains $HOD_{15}H$, or longer chains $HOD_{43}H$, depending on the stripping temperature. Less efficient conversion of cyclics to linear species was achieved at 150° with catalytic aqueous NaOH,

whereas an anhydrous tetramethylammonium silanolate catalyst induced very rapid ring opening polymerization to produce a gel at 100°. This slowly liquefied upon stripping at 150° to a highly viscous product, which nevertheless contained 41% cyclic units mixed with long chain species averaging $HOD_{116}H$. No monoalkylsilicon species were observed in any of these materials, which confirmed the absence of aminobutyl group cleavage under the range of conditions studied. The measured number average molecular weights M_n fell in the range 1700-2400 for highly linear mixtures with 40-50 unit chains, which were roughly consistent with those calculated from the ^{29}Si NMR compositional analyses (Table VII). No evidence for residual EtO end groups was found in 5a, but direct wet analysis for silanol concentration as a check on the NMR data could not be made in the presence of excess primary amino groups. Taken together, the results showed that a range of aminobutyl acceptor polymer compositions 5a could be prepared for subsequent Mannich derivatization with FDNE.

Two types of aminopropylpolysiloxanes were prepared, 5b with simple aminopropyl groups analogous to 5a, and 5c with ethylenediaminopropyl residues for increased concentration of HE groups per Si atom. The preferred hydrolysis procedure afforded 5b with 86% linear components averaging $HOD_{29}H$, similar to the corresponding 4-methylene product 5a. Monomer 4b, however, and hence hydrolysate 5b, contained 8% of the β-isomer bearing the

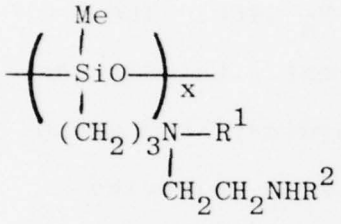
aminoethyl side group $—CH(CH_3)CH_2NH_2$, which had accompanied the synthesis of 4b from allylamine and $(EtO)_2MeSiH$. The preferred hydrolysis of 4c yielded 5c with composition similar to that of 4b (Table I), whereas hydrolysis at 25° with 35° vacuum stripping produced the much shorter average species $HOD_{6.5}H$ and a single cyclic component D_4.

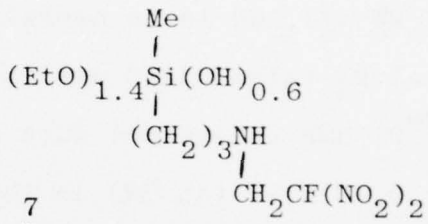
High Energy Polymers. Work was limited to certain preliminary, evaluative experiments pending identification of the structural features necessary for promoting a maximum of thermal and chemical stability (see section below). Both highly cyclic and linear aminobutyl hydrolysates 5a were treated in CH_2Cl_2 with exactly stoichiometric amounts of 1 to give viscous, yellow oils containing polymer units 3 (eq 1). The Mannich reaction occurred with no spectrally definable residues of either FDNE or unconverted amino groups, and changes in the compositional mix of polysiloxane backbone structures originally present in the highly linear 5a were small, although not negligible. Thus, two unidentified components of 3 absorbed near the cyclic(5) ^{29}Si NMR region (Table VI), as the total cyclics including these species rose from 18 to 31%. This result and the largely analogous energization of the aminomethylsilicones[15] implied that efficient Mannich generation of HE products similar to 3 was feasible in which the backbone structures would substantially resemble those

of the precursor acceptor polymers. The entire variety of linear components HOD_xH in 5a described in Table I therefore stood available for energization to provide examples of 3 with x averaging about 10-116 and linear M_n values 2670-31,000. The actual HE product 3 was prepared from 75% linear 5a containing average units $HOD_{41}H$ (Table I, entry 2) and thus contained linear HE species of MW ∿11,100 in an overall mixture of M_n 4480. The experimental M_n value ∿5850 was in rough agreement. Calculation from the ^{29}Si NMR analytical data suggested a hydroxyl end group content of 0.12 wt-% (as OH) in this material, upon which the stoichiometries of chain extending reactions were based.

HE derivatives were also prepared from an ethylenediaminopropyl hydrolysate 5c containing 85% of short average chains $HOD_{6.5}H$ (Table I, entry 11), using sufficient FDNE for Mannich condensation at one vs both amino groups. The neat product 6a from 1 mol of 1 proved relatively unstable at 25°, turning deeply red and less soluble in CH_2Cl_2 while slowly gassing, and its characterization was therefore not attempted. A highly viscous, lemon yellow oil 6b was obtained from 2 mol of 1, however, whose spectral analyses revealed all the HE residues to be nitrogen-bound; any small amounts of residual, free amino groups could not be distinguished. Although sample-unrelated problems precluded reliable integration of the ^{29}Si NMR spectrum, significant growth in the concentration of small cyclic species

relative to 5c was apparent, and slow gassing upon probing the neat sample did occur after several days standing at 23°. Further study of other 5c materials was then deferred until the thermal stability differences could be better resolved with model compounds (see below).





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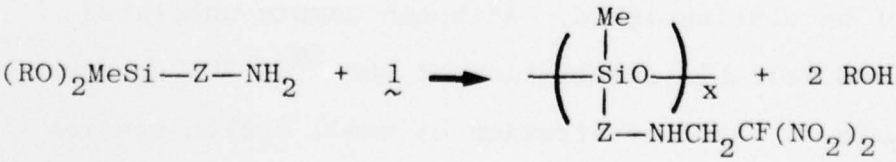
6a, $R^1 = H$, $R^2 = CH_2CF(NO_2)_2$

b, $R^1 = R^2 = CH_2CF(NO_2)_2$

Three different monomers with 3 or 4 side chain methylene groups were then subjected to Mannich reaction with 1 to determine whether the liberated water (eq 1) could be utilized in concommittant hydrolyses of the ester groups (eq 2) to afford HE products directly (eq 3) in the absence of drying agents.



(3)

Reaction of the ethylenediamino ester 4c with 2 mol of FDNE produced a product containing unreacted 1, very few residual MeO— groups, and ^{1}H NMR group areas consistant with the efficient formation of siloxy units of structure 6b. However, the material darkened, thickened, and slowly gassed during further high vacuum treatment and became slowly suffused with microbubbles spreading from points of contact with a glass probe. Analysis of the spinal framework by ^{29}Si NMR was therefore omitted in consideration for the longevity of the instrument. An efficient Mannich reaction of the diethoxysilane 4b and 1 gave the HE aminopropyl product 7 with hydrolysis of only 30% of the ester groups and no evidence for significant silanol condensation to polysiloxane species, in contrast to the behavior of 4c. A monoalkylsilane ester 8, 3-aminopropyltrimethoxysilane, quantitatively yielded Mannich-energized amino groups along with an average loss of methoxy groups close to the theoretical 2 of 3. More detailed analysis, however, revealed a mixture of products in the highly fluid oil representing all four hydrolysis levels with loss of 0 to 3 methoxy groups per Si. Further condensation of this product to a gelled HE silicone resin would be expected upon extended hydrolysis.

Analysis and Characterization. Synthesized monomeric compounds were readily characterized from their straightforward methods of preparation and routine spectral data. The hydrolysate acceptor polymers and their Mannich derivatives from 1 were first analyzed by ^{1}H NMR, which established that

hydrolyses generally occurred with full retention of the monomer alkyl group structures and without observable retention of alkoxy residues, although HO— groups could not be observed directly in the presence of NH species. The high efficiency of Mannich derivatization followed unmistakably from the chemical shift values. All the HE NCH_2CX_3 methylene doublets at δ 3.7-4.0 (Table II) appeared well upfield of the OCH_2CX_3 group position[2] (δ 4.7-5.0) while yielding integral proton counts relative to other side chain or Si—Me groups. Residual 1 and its impurity formal[2] could therefore be readily quantified, although distinction of 1 from $SiOCH_2CX_3$ species required measurement of any HO— concentration by difference from the expected NH levels. Coincidence of the NCH_2CX_3 absorption region with that characterizing several reference compounds (Table II) was taken as confirmation of the assignment. The ^{19}F, ^1H coupling constants of 19-20 Hz were slightly higher than in the oxy units (15-18 Hz)[2] and provided additional differentiation.

Although invaluable for defining the side chain chemistry, ^1H NMR was an impractical tool for distinguishing between and quantifying the different siloxane structural units in the polymeric materials. The preceeding analyses were therefore complemented with detailed, proton-decoupled ^{29}Si NMR studies[19] to provide a rewarding basis for the overall structural results

discussed above. Some points of reference for the polymeric materials were the ^{29}Si resonances of the monomers shown in Table III, where the chemical shift effects of MeO— vs EtO— substitution and of the value of n in $Si(CH_2)_nN<$ are evident. Two problems generally required resolution before comparative analyses of polymer mixtures could be carried out. The first was to rationally correlate the observed resonances with structural units in each of the systems, and the second was to accurately integrate the spectra. Molecular weight values could then be calculated, cleavage reactions quantified, and compositional estimates of the final HE products drawn.

Peak assignments were made first in the aminobutyl polymers 5a. Resonances in certain known species were compared with those of dimethylpolysiloxanes, which established that the shifts in both systems were similar and differed only by an upfield offsetting value in 5a of 0.80 ± 0.15 ppm relative to TMS. Thus, data[20] for the dimethyl system and variously end-blocked analogs when adjusted by the offset value compared well with values determined for distilled 3- and 4-membered aminobutylcyclosiloxanes 5a (Table IV). The cyclic(3) species was then found to react completely and selectively vs cyclic(4) with 1.5 mol H_2O per mol of trimer to generate ring-opened products, whose absorptions coincided with the values predicted from the dimethyl data and permitted assignment as the expected linear species. The free standing cyclic(5) peak was assigned by similar comparisons from

other samples of 5a, all of which gave consistant resonance values for each different siloxane species. The composite chemical shifts are recorded in Table V, along with the dimethyl and other aminoalkyl polymer data. Although the end group in 5a failed to absorb at the location predicted in Table IV, its formation from the hydrolyzed cyclic trimer and resonance position near the 17-18 ppm region characteristic of R_3SiOX monomers (R = Me, Et, C_6H_5; X = Et, H) made assignment of the linear end group L-1 very reasonable. Not included in our assignments or compositional analyses were any cyclic(6) species, predicted from the dimethyl data to nearly superimpose on the high field linear-2 peak near 22.9 ppm. In fact, slightly larger integrated values were always found for the L-2 peak vs the end group values (Table VI), implying the presence of the expected small amounts of cyclic(6) compounds on the order of 20% of cyclic(5) species.

The assignments in the two aminopropyl systems 5b and 5c (Table V) reflect the strong resemblance of their overall resonance patterns to those of highly linear 5a, especially the clear standing cyclic(4) and predominant internal linear peaks. Further, constant shift values were found between 5b and 5c, despite their very different aminoalkyl side groups, implying the absence of highly specific side chain conformational effects on the chemical shifts. The offset of group shifts vs the dimethyl system (0.5 ± 0.2 ppm upfield) was now smaller than in 5a. This was consistent with the smaller shifts (∿0.25 ppm) vs $(EtO)_2SiMe_2$ in monomers 4b and 4c (corrected for the ester group effect, Table III) than in 4a (0.4 ppm).

The ^{29}Si NMR spectra of Mannich derivatives appeared strikingly similar to those of their acceptor polymer precursors (Table V). Minor differences included the presence of small, often multiple new peaks and the downfield appearance of silanol end groups in 3 and 6b (near the position predicted from the dimethyl reference system). The change in end group position from 16 to 12 ppm upon Mannich derivatization of 5a and 5c may represent a concentration or H-bonding effect, since $CDCl_3$ dilution of 6b restored the higher value, whereas a highly cyclic sample of acceptor polymer 5a showed the lower value at approximately the same dilution.

Integration of the spectra was necessary for the determination of relative group concentrations. This required the addition of $Cr(acac)_3$ as a spin relaxation agent to overcome adverse nuclear Overhauser effects and permit the measurement of reliable integrals.[21] Although the sample compositions appeared stable during the typically 1000-2000 scans employed, instantaneous changes by added Cr prior to the collection of data after 50-75 scans cannot be ruled out. However, such changes were clearly encountered only in the spectra of the exceptionally reactive aminobutyl cyclic trimer (Table IV). Differences between spectra recorded ± $Cr(acac)_3$ were generally small as judged from the relative shapes and heights of peaks, except for an enhancement of polymer end group absorptions by added Cr. In

Table VI are collected the compositional data obtained by integration for selected aminobutyl and -propyl polymers. Spectra recorded after neat ageing of the acceptor polymers at room temperature for 3 mo showed only the ethylenediamino system had suffered small changes with time, favoring an increase in cyclics.

Once the compositional analyses were in hand (Table I), we could estimate the average chain lengths of the linear components of the acceptor polymer mixtures by simply calculating the number of linear siloxy units for every two end groups, necessarily assuming that the measurement of end group concentrations was accurate and that the linear species did not include higher cyclics. Unfortunately, the accuracy of end group measurements at the usual 1-5% levels encountered was probably ±0.5% absolute, which introduced an error in the cited range of ± 50 to 10%. Overall, a relatively constant 80-85% of linear units appeared to be the maximum possible in the aminobutyl and aminopropyl homopolymers, although the range in average chain length was quite large (Table I).

Some overall M_n molecular weight values were also calculated from the ^{29}Si NMR compositional data and compared with values measured directly by vapor pressure osmometry (Table VII). Both techniques suffered from weaknesses, and the resulting data were therefore not highly precise. The NMR method was subject to the problem just described in accurately determining end group

concentrations and hence in calculating the relative number of moles of different structures in a given weight of sample. VPO proved operationally unreliable, yielding highly variable $\bar{M}_n$ values which sometimes compared poorly with the more consistently obtained NMR results (see Experimental Section).

The HE polymer densities showed the expected increase with decreasing methylene group dilution, as the value ∿1.3 in the aminobutyl system rose to ∿1.4 g/cc in the ethylenediaminopropyl products 6b. Since the HE product from $(MeO)_3Si(CH_2)_3NH_2$ (8) and (1), which contained more CH_2 but no Si—Me groups, also had a density ∿1.4 g/cc (with the probability of increase on further hydrolytic condensation), it is unlikely that the higher densities realized in the HE silane esters[2] can be attained in long chain HE silicone polymers unless both Si-alkyl substituents contain HE groups, as attempted in the earlier[11] work.

Properties of HE Derivatives. Although the neat aminobutyl HE product 3 proved completely stable over several months at room temperature, it was found to suffer slow gassing and produce a spongy foam upon several h heating at 80°. During polymer chain extension tests (see below), 3 produced similar foams at lower temperatures in the presence of basic reagents. Further, the HE trisiloxane 9b, prepared as a model substrate for N-nitration, also suffered substantial thermolysis, decomposing exothermically upon attempted distillations at >100° pot

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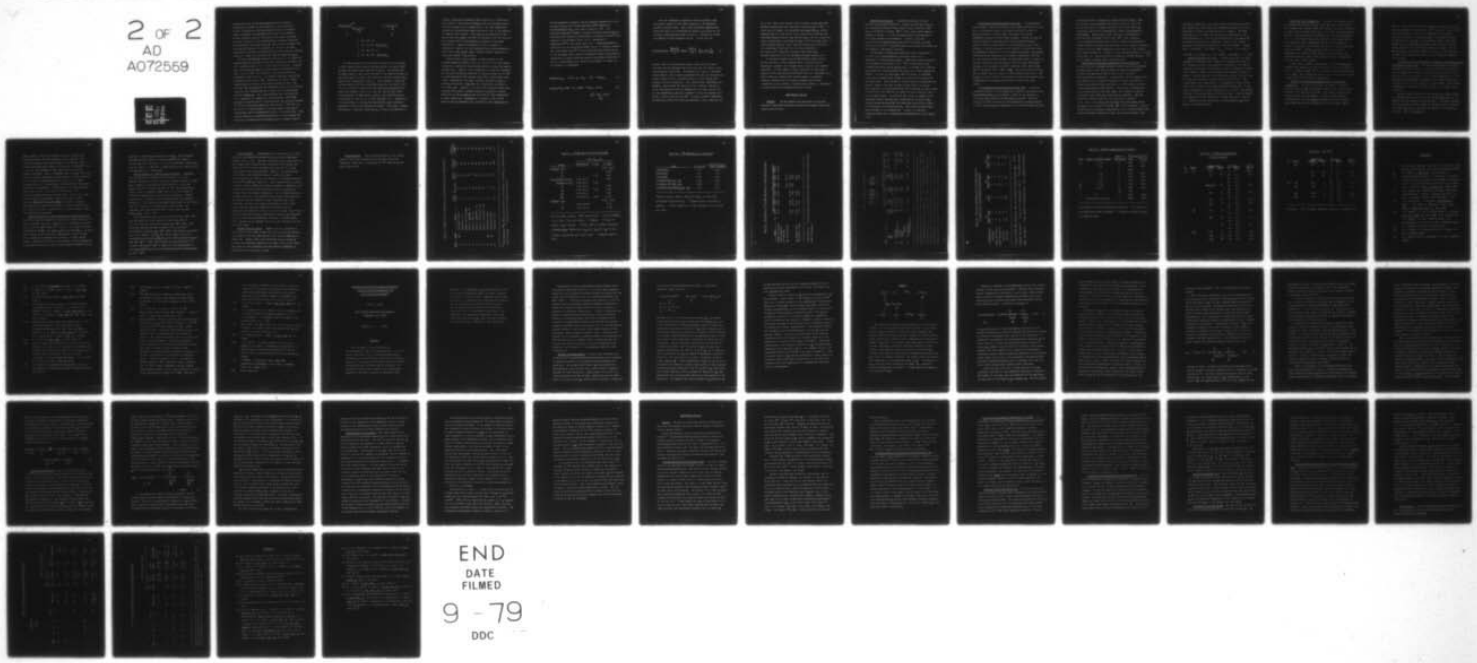

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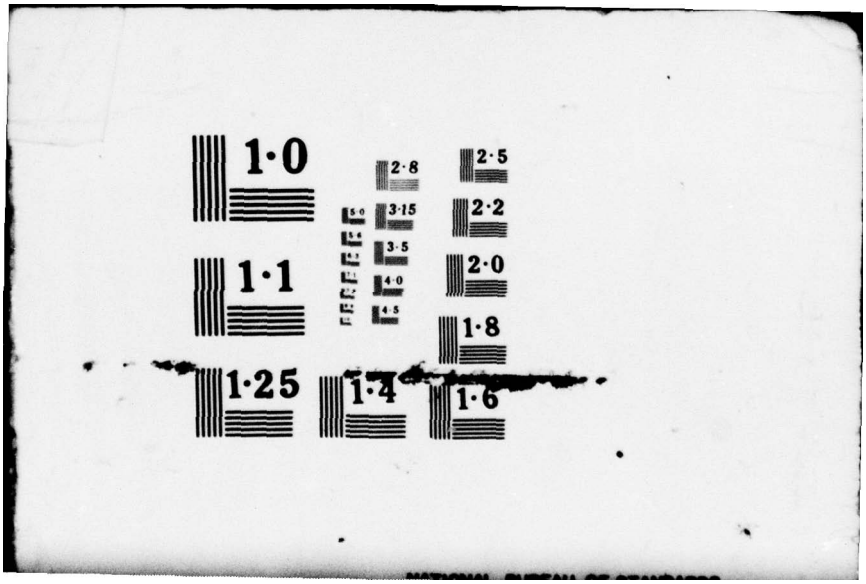
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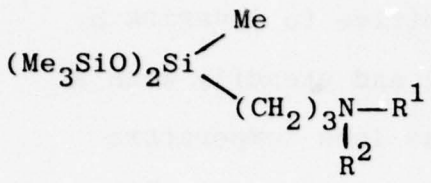
temperatures, and the HE ethylenediaminopropyl products decomposed on storage at room temperature, as noted above. Clearly, the promise of HE aminoalkylsilicones as potential binder elastomers was dependent upon whether these adverse thermal responses could be effectively and simply countered. Since 6a, with one of its ethylenediamino nitrogens unreacted, had proved much less stable than 6b, wherein both nitrogens had been Mannich alkylated, we examined the influence of amine substitution and other structural factors on the relative thermal stabilities among the four model HE compounds 9b,d and 10b,d.

We first prepared 9b from both an excess of 1, to ensure as complete Mannich conversion of the amino groups as possible, and with a 25% deficiency of 1, to leave unreacted groups. Although neat, well-stripped samples of both products decomposed in air after $\leq$ 16 h at 120°, the completely alkylated 9b remained unchanged at 100° over 7 h. In contrast, partially reacted 9b decomposed within 2 h at 100°, liberating a volatile liquid composed mainly of water, while suffering 28% wt loss. The 1610 cm^{-1} NO_2 IR absorption was completely absent in the residue, along with the ^1H NMR peaks due to both types of N-methylene protons $CCH_2NCH_2CX_3$. New, broad IR peaks near 1740 and 1660 cm^{-1}, suggestive of carbonyl or imine residues, and ^1H NMR resonances characteristic of =C—H protons was observed instead. The fully alkylated 9b sample was then heated at 100° with 25 25 mol-% of a simple primary or tertiary amine, resulting in surprisingly facile decomposition within 1 h in both tests. This clearly indicated a pronounced sensitivity in the secondary HE amine 9b to decomposition by strongly basic, aliphatic amines.



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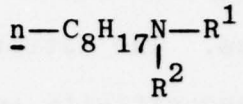

10

a, $R^1 = R^2 = H$

b, $R^1 = H$, $R^2 = CH_2CF(NO_2)_2$

c, $R^1 = Me$, $R^2 = H$

d, $R^1 = Me$, $R^2 = CH_2CF(NO_2)_2$

We then probed for the influence on stability of secondary vs fully substituted, tertiary HE amino groups, using the model siloxane and hydrocarbon compounds 9 and 10. The primary and secondary amines a and c were converted to the Mannich products b and d and heated at 100 or 120° with up to 25 mol-% added amines (Table VIII, Experimental Section). The secondary siloxane 9b proved stable at 100° but decomposed massively with 33% wt loss in 1 h at 110-120°, whereas the N-Me analog 9d decomposed very slowly and steadily over 3 h at both 100 (5%) and 120° (18%). In the presence of added amines, however, 9b suffered several fold greater wt loss in 1 h at 100° than 9d in 3 h. Thermolysis of the secondary vs tertiary HE aminoalkylsiloxanes therefore appeared to involve two different processes. The former, perhaps autocatalytic, generated large amounts of water and exhibited a

distinct temperature threshold highly sensitive to lowering by basic amines. The latter proceeded slowly and steadily with a relative insensitivity to added amines, was less temperature responsive, and generated significant water only in the presence of added protonic amines. This behavior was mirrored in the hydrocarbon pair 10b,d, although the decompositions now occurred more rapidly than in the analogous siloxanes at equivalent temperatures. Despite differences in rate or manner of thermolysis, however, all the decompositions produced moderate to total loss of NO_2 groups, again forming products suggestive of imine and carbonyl functionality.

These results point strongly to amino protons in the secondary Mannich products from 1 as a point of critical thermal sensitivity, capable of facilitating relatively rapid and massive decomposition. However, since thermolysis in both the secondary and tertiary systems was observed to varying extents at 100-120°, it seems improbable that analogs would prove significantly more stable, although the less basic and more energetic $N—NO_2$ or $N—COCF_3$ derivatives of 9b might be of particular interest in their own right. Overall, it is clear that tertiary rather than secondary HE polymeric products should be prepared to ensure moderation of any decompositions initiated by high temperatures or basic impurities. Decomposition related to that in the models 9 and 10 presumably also occurred at room temperature in

the HE aminomethyl polymers, and was perhaps responsible for the etching of glass vials containing distilled[12] samples of $CH_2=CHCH_2NHCH_2CF(NO_2)_2$ after dark storage at 5-23°. The observed thermolyses suggest a process involving reverse Mannich reactions after attack of strong bases at relatively acidic[24] N-H centers of the secondary amines (eq 4), analogous to fragmentation[25] of the alkoxy anion of 1. Dehydrohalogenation could occur in the tertiary HE amines (eq 5) to liberate fluoride ion, which might assist[26] in the further Nef-like decomposition of the secondary nitro centers to generate carbonyl functionality. Elimination of amines from the present β-nitroamine structures to leave α,β-unsaturated nitro species was blocked, of course, by the absence of β-hydrogens.

$$RNHCH_2CF(NO_2)_2 \xrightarrow{B} RN = CH_2 + BH^+ \ ^-CF(NO_2)_2 \qquad (4)$$

$$R_2NCH_2CF(NO_2)_2 \longrightarrow HF + R_2NCH = C(NO_2)_2 \longleftrightarrow \qquad (5)$$

$$R_2\overset{+}{N} = CHC(NO_2) = N(O)\overset{-}{O}$$

Once the thermolytic properties had been defined, some preliminary results on the chain extension of HE aminobutyl polymers 3 became clear. Thus, chain extending reagents were mixed with neat 3 in stoichiometric amounts calculated for the end group concentrations given in Table I, allowing for either end capping or chain extension (eq 6). It was left for

$$XMe_2SiOD_xSiMe_2X \xleftarrow[(a)]{2Me_2SiX_2} HOD_xH \xrightarrow[(b)]{Me_2SiX_2} \left[Me_2SiOD_x\right]_y \qquad (6)$$

further study to differentiate between these desired silanol reactions and any analogous ones involving the N-H centers, which would generate cross-links. We examined four types of candidate linking agents, most of which possessed more than the two reactive groups X shown in eq 6, but whose third or fourth groups were assumed relatively unreactive. Two alkoxysilanes, $MeSi(OMe)_3$ and $Si(OMe)_4$, used without the usual Sn or Ti catalysts, failed at either concentration level to substantially thicken 3 after 4 da at room temperature, and only a moderate effect was observed with methyl silicate after 16 h at 55°. In sharp contrast, $MeSi(OAc)_3$ thickened 3a within 8 h at 23° and produced a clear, waxy gel in 3

da at the 1 mole level (eq 6b), while 2 moles (eq 6a) gave only moderate thickening after 4 da (and a foam-free gel at 55°). A third type of reagent, the bisaminosilane $Me_2Si(NMe_2)_2$, had no apparent effect at the 2 mole level, except for an initial and subsiding gassing reaction upon mixing, gave a gel in 4 da at the lower concentration, and produced foams at 55° at either level. A fourth reagent species, which combined alkoxysilane reactivity with aminoalkyl functionality in 8, also generated a gel foam at 55°, doubtless reflecting the strong base destabilizing effect on the secondary HE amino centers of 3.

It therefore appears that HE aminoalkylsilicones can be gelled in place or chain extended short of gellation with appropriate reagents, but strongly basic reactants are counter-indicated. All the samples formed foamed gels at the 2 mole additive level upon heating from 60-85° over 6 h, including the 3 control and the acetoxysilane treated sample, but greater stability should accrue to systems prepared with careful elimination of any residual, strongly basic groups or, especially, tertiary rather than secondary HE amino centers.

Experimental Section

CAUTION! The HE compositions described in this work should be considered potentially explosive and highly toxic upon contact with the skin.

Materials and Spectra. Fluorodinitroethanol (1) was purified as previously[2] detailed. Silanes 4a (98% pure) and 4c were available from prior work; redistillation gave 4c in 96% purity, bp 69-72° (0.05 mm), $n_D^{23.5}$ 1.4475, whose major impurity appeared to be 4b. 1,1,1,3,5,5,5-Heptamethyltrisiloxane was a 98.5% pure production intermediate. N-methyl- (15) and N-allyl-2,2,2-fluorodinitroethylamine were prepared in 87-89% yields as directed.[12] Allylmethylamine was obtained from Fluka via the Tridom Co. and used as received.

VPC analyses of amines were achieved without tailing on a ss 15-ft x ¼-in methylphenylsilicone gum column with a Chromosorb T (fluorocarbon) support. NMR spectra were obtained on the instruments previously[2] cited. ^{29}Si FT NMR spectra were recorded with gated proton decoupling at 17.88 MHz over a 5000 Hz sweep width by collecting 8192 real points at a probe temperature ∿304°K. A 15 μsec R_f pulse gave ∿68° flip angle, as 500-2000 cycles were recorded using 1.6384 sec acquisition time and 2.40 sec pulse delay. Only the 600 or 1200 Hz region of absorption was printed, usually with zero filling to 8192 points full scale. Little benefit in resolution derived from recording the usual number of points over only 2400 Hz (at double the usual spectrum time of ∿2 h for 2000 scans). In selected test cases, no change in the integrated values resulted upon increasing the recovery times (proton decoupling gated OH) following data acquisition in $CDCl_3$ in the presence of 0.05 M $Cr(acac)_3$. Side bands of major peaks were included in the integrations. In D_2O, an effective relaxation agent was a triethylenetetraminehexacetic acid complex of Gd.

3-Aminopropyl(diethoxy)methylsilane (4b). Diethoxymethylsilane (Silar), 127.8 g (0.95 mol), was treated with 59.9 g (1.05 mol) of allylamine (Aldrich) and then 0.05 mol-% (vs SiH) of H_2PtCl_6 catalyst (0.08 M in DME; ∿725 ppm as Pt) and was immediately heated to reflux under nitrogen. Failure to heat the mixture resulted in gassing and a silane disproportionation reaction, which occurred slowly to give $MeSi(OEt)_3$ (11) in the presence of either the amine or the catalyst (or both) but could be quenched by addition of 1 wt-% powdered anh K_2CO_3. The product from heating the reactants to an internal temperature 118° over 6 h was twice distilled through a helix-packed column to remove 11 and give fractions containing 4b in ∿60% yield with decreasing amounts of the β-isomer; bp 52-54° (0.55 mm), n_D^{22} 1.4232-1.4255 [lit.[27] bp 85-88° (8 mm), n_D^{25} 1.4260]. Use of 0.01 mol-% catalyst gave a similar result, except at a much reduced rate (15 h). The presence of the β-isomer (see Discussion Section) was deduced from ^1H NMR analysis and quantified by VPC as ∿10% of the total product.

3-(3-Aminopropyl)heptamethyltrisiloxane (9a). A reaction conducted similarly to the preparation of 4b was carried out with $Me_3SiOSiH(Me)OSiMe_3$ and allylamine, except in the presence of 1 wt-% anh K_2CO_3 and only 85 ppm H_2PtCl_6 catalyst. Half the catalyst was used initially as the temperature increased from 65 to 110°, and the balance added after 8 h, along with make-up amine

calculated by VPC to balance the remaining hydrosiloxane. When the solution color darkened from yellow to black at 135°, the mixture was cooled, filtered, and distilled to give 75% of 9a containing 8-15% of the corresponding β-adduct $(Me_3SiO)_2Si(Me)$-$CH(Me)CH_2NH_2$. Redistillation gave fractions containing 83 to 99.5% pure 9a, bp 66-67° (1.0-1.5 mm), n_D^{23} 1.4139 (constant). Totally undifferentiated by VPC, the two isomers were analyzed by 90 MHz ^1H NMR by ascribing the deficiency of the C—CH_2—C absorption of 9a vs the total NCH_2 absorption in the mixture to the β-isomer, whose methyl doublet at δ 0.945 (J 7.5 Hz) and ABX pattern of the CH_2N group (Table II, footnote d) were confirmed by 220 MHz analysis. The purest sample of 9a was later converted to 9b.

Heptamethyl-3-(N-methyl-3-aminopropyl)trisiloxane (9c). To 29.8 mL (0.11 mol) heptamethyl(3H)trisiloxane and 0.25 g powdered anh K_2CO_3 held at 90° under nitrogen was added 30 ppm $H_2Pt^+Cl_6$ catalyst and immediately 15% of the 11.0 mL (0.115 mol) allylmethylamine co-reactant. An exothermic reaction ensued, died upon addition of two similar increments of amine, and did not resume upon further 30 ppm catalyzation at 100° despite the brief, violent gassing which then resulted. The balance of amine and a final 30 ppm catalyst were then added, and a moderate exotherm developed to hold 105° over 15 min before subsiding. Heat was applied to maintain 100° for 1.5 h and 115° for another 1.5 h. The cooled mixture was decanted from light brown solids and distilled, bp 44-51° (0.35 mm), n_D^{24} 1.4125 (constant), to give an 83% yield of a mixture of 9c with 75 to 5 % of the β-isomer from first distillation fraction to last; the fraction richest in 9c

was used to prepare 9d. The isomer ratios calculated from VPC at 160° agreed with those based upon ^{1}H NMR peak heights of the two N-Me peaks (β-isomer 0.03 ppm upfield of γ-isomer). The CH_2N methylene in the β-isomer again produced an ABX pattern, and a C—Me absorption at δ 0.95 was observed when the overlapping NH was displaced downfield by added D_2O. Overall, the β-isomer comprised a surprisingly high 44% of the total product. ^{1}H NMR (9c) δ 0.00 (SiMe), 0.08 ($SiMe_3$; $J_{^{13}C,H}$ 117 Hz), 0.47 ($SiCH_2$,m), 1.02 (NH), 1.52 (CCH_2C, m), 2.44 (N—Me), 2.59 (NCH_2, t, J 7.2 Hz).

Preferred Hydrolysis of 4a-c. Products 5a-c high in linear components of moderate chain lengths were prepared according to the following procedure and analyzed as discussed. To a 500 mL 4-necked pot equipped with mechanical stirrer, condenser, nitrogen cover, addition funnel, and thermometer was charged 0.5 mol of monomer. Two mol H_2O were then added with stirring at 20-25° over 5 min and the resulting solution heated at 60° for 3 h. The cooled product was transferred to a stripping pot using a 25 mL water rinse, rotated at 30° under 20-30 mm pressure for 1 h and then at atmospheric nitrogen pressure for 1 h at 60°, and pressure filtered if necessary using a 10 mL water rinse. Final stripping was carried out at 60° (20 mm) for 1 h and then 100° (1 mm) for 1 h. Transfers of the water white, viscous products 5a-c were made in a nitrogen dry box.

Other Hydrolysis Products 5a. A highly cyclic sample of 5a was prepared by heating 2 mol 4a, 8 mol H_2O, and 1.44 g (0.008 mol) $Me_4NOH \cdot 5\ H_2O$ catalyst under total reflux for 90 min (head 72°, pot 96°), slowly removing distillate to bp >80°, and then holding 90-95° in the pot during an increasing rate of nitrogen sparging over 1 h. The mixture was cooled, 300 mL toluene added, and the whole reheated under a Dean-Stark trap at a pot temperature 95-105°, continuing for 2 h after an initial low boiling material had been removed. Toluene was then taken off as the pot temperature was raised to 165° and held 3 h to decompose the ammonium silanolate species (end of amine odor at the head) and give the final, yellow product.

A short chain, highly linear material containing $HOD_{17}H$ was prepared from highly cyclic 5a by heating 59 g with 8 mL H_2O and 1 mL of 1 M KOH at 80-90° for 5 h, cooling, neutralizing with 2 mL of 1 N H_2SO_4, and stripping the faintly hazy solution with a 20 mL toluene rinse at 50° and 30 → 2 mm pressure.

4-[N-2,2,2-Fluorodinitroethyl] aminobutyl(methyl)polysiloxane (3). To 13.2 g (0.10 eq) of 5a (Table I, entry 2) stirred in 100 mL CH_2Cl_2 was added slowly 10.0 mL of 1 (0.10 mol, 97% pure, d^{23} 1.56 g/cc) at 22-26°. The mixture turned cloudy before the addition was complete. After stirring had been continued 22 h, 30 g anh Na_2SO_4 was added to absorb the upper, water phase and was then filtered off (1.22 g wt gain, 68% of

theory). The yellow filtrate was stripped, eventually at 30-35° and 1 mm pressure, to give 27.7 g 3, d^{23} 1.31 g/cc. The wt excess over the theoretical (27.15 g) corresponded to the Mannich water not recovered in the drying agent, but spectral analysis nevertheless left no doubt of the complete alkylation of amino groups, as all $—CH_2CF(NO_2)_2$ residues except those of the 3% formal impurity[2] in 1 were clearly bound to nitrogen. The ^1H NMR spectrum in d_6-acetone showed two types of Si—Me species at δ 0.083, 0.125 (peak height ratio 4:5) but otherwise resembled that in $CDCl_3$.

N,N'-bis-2,2,2-Fluorodinitroethyl-3-[N-2-aminoethyl] aminopropyl-(methyl)polysiloxane (6b). The ethylenediaminopropyl precursor silicone 5c (Table I, entry 11), 8.0 g (0.05 eq of siloxy units), in 50 mL CH_2Cl_2 was treated at 15° with 10.0 mL of 97% 1 (0.10 mol) over 3 min and allowed to stir at room temperature for 18 h, whereupon 25 g anh Na_2SO_4 was added to the 2-phase mixture and filtered off after 1 h to remove 1.5 g water (83%). The filtrate afforded 21.9 g (101%) of 5c, d^{23} 1.40 g/cc, as a heavy, lemon yellow oil.

Another reaction directed to the preparation of 6b utilized the liberated Mannich water to effect *in situ* hydrolysis of the product from the dimethoxy monomer 4c and 1. Following overnight reaction as above, however, pools of insoluble liquid, presumed to be the usual water, floated on the surface of the reaction solution. When 15 g Na_2SO_4 was

added, however, only 0.1 g increase in wt was found in the recovered sulfate, and the insoluble liquid remained. The filtrate and washes were then stripped, but bubbling in the residue continued under vacuum at 15 and then 1 mm (30-35°) over 3 h as the color darkened to deep amber and the viscosity markedly increased. Upon 4 h standing under nitrogen, the 13.4 g (103%) of residue continued to slowly generate a nearly odorless gas, but later stripping produced no clear wt loss. When contacted with a ss or glass probe, the residue soon developed a profusion of microbubbles. ^{1}H NMR analysis in $CDCl_3$ revealed ~10% of the alcohol 1, two types of SiMe groups, but overall good group areas for structure 6b. It was later found that the starting 4c probably contained an amount of the bissilane $\left[(MeO)_2MeSi(CH_2)_3NHCH_2\right]_2$ sufficient to produce observable cross linking on hydrolysis; although rationalizing the viscosity build-up, unreacted basic centers probably caused the decomposition described.

Mannich Reaction of 1 with Aminopropyltrimethoxysilane (8). The crude silane was prepared by boiling the ethoxy ester with 10 moles of methanol per mole, stripping, and repeating the process twice to give 8, n_D^{23} 1.4220, d^{23} 1.40 g/cc, of average structure calculated by ^{1}H NMR to be $(MeO)_{2.5}(EtO)_{0.1}Si(CH_2)_3NH_{1.6}$, in which about 2 parts of an Si—N cyclic compound per 3 parts of non-cyclic structures accounted for the dearth of alkoxy and NH groups. Reaction of 0.03 mol of this product with stoichiometric 1 as above gave 8.3 g of a fluid, yellow Mannich product with the

theoretical 1 MeO group remaining on average. The integrated ^{29}Si NMR spectrum, however, clearly showed[28] four types of silicon species in the ratio 11:11:16:12 containing 1 alkyl group each but from 3 to 0 MeO, HO, or RNH groups per Si along with the corresponding 0 to 3 ≡SiO groups.

Mannich Adducts for Thermal Stability Tests. Compounds 9b,d and 10b,d were prepared from 25% excess 1 to ensure complete conversion of amino groups by treating 0.02 mol of amine 9a,c or 10a,c in 15 mL CH_2Cl_2 in the presence of 4.0 g anh Na_2SO_4 at 0-6°, stirring at 20-25° for 18 h, and stripping out excess 1 and its impurity formal over 1 h in a pot heated at 50-70° and equipped with capillary bleed agitation. Product structures were inferred from the spectral data and method of preparation. Both 10b and d had doubled NO_2 bands in the IR near 1600 cm^{-1}, whereas the siloxanes gave single peaks. All compounds except 9d contained 3-5% of ester type residues $FC(NO_2)_2CH_2O$— near δ 4.64.

From redistilled 10a, 99.5%, bp 53.5° (5.5 mm), n_D^{23} 1.4271, were obtained 75% of the theoretical water and 100% of N-(2,2,2-fluorodinitroethyl)octylamine 10b, n_D^{24} 1.4406; from 99.7% 10c, 69% H_2O and 98% of N-methyl-N-(2,2,2-fluorodinitroethyl)octylamine 10d, n_D^{24} 1.4388; from 95% 9a (containing 5% of the β-isomer), 75% H_2O and 104% of 3-[1,1,1,3,5,5,5-heptamethyl-3-trisilanoxanyl]propyl-N-(2,2,2-fluorodinitroethyl)-amine 9b, $n_D^{22.5}$ 1.4270; and from 95% 9c (containing 5% of the β-isomer) 67% H_2O and 100% of 3-[1,1,1,3,5,5,5-heptamethyl-3-trisilanoxanyl]propyl-N-(2,2,2-fluorodinitroethyl)-N-methylamine 9d, n_D^{24} 1.4240.

Vapor Osmometry. Measurements were carried out on a Knauer Osmometer and Temperature Measuring System (Utopia Instrument Company, Joliet, Ill). The more consistent sets of data resulted when samples were dissolved and maintained in 50° toluene and measured at 70° over 7-8 concentrations from 0.3 to 1.8 g/dL using sample-conditioned syringes. However, the resulting $\bar{M}_n$ values (Table VII) sometimes failed to agree with those calculated from the moles of each species in a mixture determined from the ^{29}Si NMR data (Table VI). Since warming basic siloxanes in dilute solution might have effected changes in composition and solubility, we believe the calculated values of $\bar{M}_n$ were more accurate than those directly measured. All the samples partially (10-30%) oiled out of the cooled 1.5-2% toluene stock solutions and proved even less soluble at lower concentrations. The recovered, insoluble oils proved considerably richer in HO— groups than the fractions remaining in solution, but no significant differences in total cyclics were found. Only erratic data were obtained from 5a in DME solvent, and the $\bar{M}_n$ determined for 5c in water differed markedly from that in toluene (Table VII), perhaps from an improper use of an ionic reference for the non-ionic sample.

Thermal Stability Tests. Samples (∿0.2 g) contained in small vials or test tubes fitted with slotted corks were heated in a sand bath for the times and with the results summarized in Table VIII. Weight losses were determined after cooling and removing any condensate adhered to the upper walls of the tubes. The onset of visual decomposition was marked by darkening or gassing with the evolution of water.

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Table I. Compositions of Aminobutyl- and Aminopropylsilicone Homopolymers[a]

Entry	Compd	Sample	% End Group	% Cyclic(4)	% Total Cyclic	% Internal Linear	Calcd x for Average HOD_xH
1	5a	Preferred Polymer	3	11	18	77	54
2		Precursor to 3	4	11	16	79	41
3		Highly cyclic polymer	2	47	79	20	10
4		Entry 3, H_2O/KOH; vac	11	8	13	77	15
5		Entry 4, 150° vac	4	10	14	82	43
6		Entry 3, NaOH/150°; vac	3	20	32	66	46
7		Entry 3, N^+cat/150°; vac	1	26	41	58	116
8		Entry 3, N^+cat/100°; vac	4	16	29	68	34
9	5b	Preferred polymer	6	9	14	80	29
10	5c	Preferred polymer	7	11	14	79	25
11		Precursor to 6b	26	15	15	59[b]	6.5

[a] From integrated ^{29}Si NMR spectra obtained in the presence of $Cr(acac)_3$; nearest percent of total Si atoms. [b] Including 21% of L-2 groups (see Table V).

Table II. ^1H NMR Data for N—C—H Protons[a]

Compd	δ ppm ($J_{H,F}$ H_z) $CH_2CF(NO_2)_2$[b]	N—CH_3	N—CH_2[c]
Monomers, 4a-c			2.64 - 2.67
9a			2.61[d]
9c		2.44	2.59
$Me_3SiCH_2NHCH_2CF(NO_2)_2$	3.89 (19.2)		2.22
$CH_3NHCH_2CF(NO_2)_2$	3.88 (19.0)	2.52	
9b	4.00 (19.0)		2.80
9d	3.74 (20.0)	2.39	2.56
10b	3.87 (19.5)		2.70
10d	3.70 (20.2)	2.38	2.54
Polymers, 5a-c			2.62 - 2.66
3	3.88 (19.0)[e]		2.70
6b	3.84 (19.2)		2.70[f]

[a] 60 or 90 MH_z in $CDCl_3$. Other group shifts δ 1.40-1.55 (CCH_2C), 1.0-1.5 (NH), 0.45-0.65 ($SiCH_2$). [b] Doublet. [c] Center of triplet, where relevant. [d] Value 2.69 in β-isomer containing $\equiv SiCH(Me)CH_2NH_2$; ABX pattern (J_{AB} 12.5, J_{AX} 6.0, J_{BX} 7.6 H_z). [e] Value in d_6-acetone was δ 4.02 (19.5). [f] Dominant peak of group.

Table III. ^{29}Si NMR Spectra of Monomers[a]

Compd	-δ (no Cr)[b]	Downfield shift, ppm, Cr-added
$(Me_2N)_2SiMe_2$	1.71	0.59
$(MeO)_2SiMe_2$	1.71	1.05
$(EtO)_2SiMe_2$	5.39	0.89
$(EtO)_2MeSi(CH_2)_4NH_2$ (4a)	5.79	0.67
$(EtO)_2MeSi(CH_2)_3NH_2$ (4b)	5.67[c]	0.51
$(MeO)_2MeSi(CH_2)_3NHCH_2CH_2NH_2$ (4c)	1.94	0.33

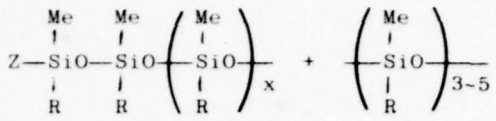
[a] Shifts in ppm vs TMS in ∿25% (vol) $CDCl_3$, or ∿50% $CDCl_3$ containing 0.05 M $Cr(acac)_3$. [b] Upfield shifts from TMS are negative. [c] Minor signal at δ -6.28, presumably from β-isomer (see text).

Table IV. Assignment of ^{29}Si NMR Resonances in Aminobutylsilicones

Sample	Cr	-δ ppm (area-%) for linear and cyclic species[a]					
		L-1	L-2	L-3	C(3)	C(4)	C(5)
Dimethylsilicones, offset upfield by 0.80 ppm	-	12.13	22.99	22.79	9.62	20.01	22.43
5a, cyclic(3,4)[b]	-				9.45	20.15	
	+	16.51	23.20	22.78	9.46	20.17	
		(4)	(trace)	(26)	(32)	(38)	
5a, product from cyclic(3,4) + H_2O	+	16.41	23.11	22.73		20.07	
		(14)	(11)	(37)		(38)	

[a] See Table V. [b] Linear products observed with added Cr appeared to derive mainly from C(3) species.

Table V. ^{29}Si NMR Spectra of Polymer Units[a]



L-1 L-2 L≥3 C(3) to C(5)

Compd	R	Z	-δ ppm, no $Cr(acac)_3$[b] (0.3 to 0.6) L-1	(0.2 to -0.1) L-2	(0.2 to -0.2) L≥3	(0 to -0.1) C(3)	C(4)	C(5)
	Me[c]	Me_3SiO	21.59	22.19	21.99	8.82	19.21	21.63
	Me	HO	11.33	21.57	21.98			
	Me	EtO	13.52	21.96	22.09			
	Me	Me_2N	10.6 ± 0.4	22.8 ± 0.1	22.2 ± 0.1			
5a	$(CH_2)_4NH_2$	HO	16.5 ± 0.3[d]	23.17	22.70	9.45	20.15	22.40
3	$(CH_2)_4NHCH_2CF(NO_2)_2$	HO	11.91	23.05[e]	22.73		20.11	22.41
5b	$(CH_2)_3NH_2$	HO	16.35 ± 0.2	22.91	22.36		19.76	22.09
5c	$(CH_2)_3NH$ $CH_2CH_2NH_2$	HO	16.6 ± 0.3	22.91	22.30		19.74	22.05
6b	$(CH_2)_3N(CH_2CF(NO_2)_2)$ $CH_2CH_2NHCH_2CF(NO_2)_2$	HO	12.02[f]	22.64[g]	22.30[g]	9.24	19.92	22.12

[a] See Table III, footnote a. Linear (L) and cyclic (C) polymer units denoted by chain position or ring size. Single values usually reflect composite of multiple samples with a maximum ±0.1 ppm variation. [b] Range of shifts due to added $Cr(acac)_3$ are shown at column headings, with (-) upfield. [c] Dimethylsilicone values from ref 20, with 0.3 ppm downfield solvent correction (from d_6-acetone to $CDCl_3$). [d] Except 12,49 in highly cyclic 5a. [e] Not observed in highly linear 3, where new peaks appeared near C(5) at 21.54 and 21.95 ppm. [f] Value 16.55 upon further $CDCl_3$ dilution or addition of <5% d_6-acetone. Minor peak at 11.77 in $CDCl_3$ (12.22 on dilution; not observed in the presence of d_6-acetone). [g] Observed only upon addition of <5% d_6-acetone.

Table VI. Relative Concentrations of Siloxane Units in Polymers with 3- and 4-Methylene Side Chains[a]

Siloxane unit	5a		3	5b		5c	
	Fresh	Aged	Fresh	Fresh	Aged	Fresh	Aged
End group	3	2	3	6	6	7	8
Linear position 2	4	3	[b]	8	5	9	8
Linear position >2	73	76	67	72	74	70	61
Cyclic(4)	11	12	9	9	7	11	14
Cyclic(5)	7[c]	7	13[d]	5	8[e]	3	9[e]

[a] Area-% by ^{29}Si NMR integration; data for preferred acceptor polymers 5a-c. [b] Not observed, see Table V. [c] Also 2% of a second peak (δ -22.1). [d] Also 8% of two new peaks, see Table V. [e] Two similarly sized peaks near δ -22.2, separated by 0.06 ppm.

Table VII. Number Average Molecular Weights

Compd	Sample of Table (entry)	Number of VPO Points[a]	Value M_n by method	
			VPO	^{29}Si NMR
5a	I (1)	8	2540	2321
	(2)	4	1834	2236
		8	1689	
	(5)	4	2131	2000
	(7)	4	1715	1268
	(3)	4	607	650
5b	I (9)	8	1417	1870
5c	I (10)	8	3925	2340
		8[b]	816	
3	VI	4	5847	4437[c]
	From highly cyclic 5a	4	2668	1325[c]

[a] In toluene at 70° with polystyrene reference. [b] In water with Na polystyrenesulfonate reference. [c] Based on precursor polymer plus added HE group.

Table VIII. Thermal Decompositions of Model HE Amines

°C	Sample	Added amine		Wt loss		Visual
		Compd	Mol-%	%	Hours	dec, h
100	9b	none	0	0	7.	None
		9a	25	16	1.5	0.8
				33	2.0	
				38	3.2	
		$RNHCOCF_3$[a]	25	12	2.0	2.0
				29	3.2	
		10a	25	20	1.5	0.3
				39	4.2	
		9a	10	5	2.5	0.8
		10a	10	14	2.0	0.5
				37	4.2	
	9d	none	0	5	3.1	3.1
				13	4.2	
		10a	25	9	3.1	3.1
				18	4.2	
			10	9	3.1	3.1
				16	4.2	
	10b	none	0	b	2.5	1.0
		9a	10	25	1.5	0.3
		10a	25	33	2.0	0.5

Table VIII. Continued

°C	Sample	Added amine Compd	Added amine Mol-%	Wt Loss %	Wt Loss Hours	Visual dec, h
	10d	none	0	0	2.	1.5
				8	5.	
		10a	25	9	2.5	0.8
		10c	25	0	2.	1.5
				13	5.	
120	9b	none	0	33	1.2	1.0
	9d	none	0	9	2.0	1.5
				18	3.5	
	10b	none	0	33	0.9	<0.9
	10d	none	0	7	1.2	1.2
				12	1.5	

[a] From 9a. [b] Not recorded; extensive visual dec, confirmed by IR.

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(14) Product purifications involving temperatures to $\sim 100^{\circ}$ were often employed. Only the primary, parent fluorodinitroethylamine has been found hazardously unstable: H. G. Adolph, J. Org. Chem. 37, 747 (1972); H. G. Adolph and M. J. Kamlet, ibid. 34, 45 (1969).

(15) R. S. Neale, J. Org. Chem., in press (paper 3).

(16) Kinetic control can sometimes be utilized to favor high polymers, since the rate of catalyzed ring opening often exceeds that of small ring formation from linear species in many types of silicones, with the "revision resistance" of quite variable magnitude: Y. K. Kim and M. O. Riley, U.S. Pat. 3,975,362 (1976).

(17) The absence of polymerization beyond small cyclics in the hydrolysis of HE silane bromides[11] probably reflects this effect.

(18) For example, see B. A. Ashby, U.S. Pat. 4,096,160 (1978).

(19) ^{29}Si NMR spectra are normally recorded with proton-decoupling to simplify and sharpen the weak signals produced by the low natural abundance (4.7%) of ^{29}Si nuclei.

(20) G. C. Levy and J. D. Cargioli, Ch 17 in "NMR Spectroscopy of Nuclei Other Than Protons", T. Axenrod and G. A. Webb, Eds, Interscience, 1974.

(21) The paramagnetic $Cr(acac)_3$ provides an electron-nuclear mechanism for rapid and uniform relaxation of the ^{29}Si nuclear spins[20,22] which swamps out other, slower relaxation modes, especially dipole-dipole nuclear spin magnetic moment interactions with spin-saturated protons. The nonuniform competition of the latter with other relaxation pathways (the nuclear Overhauser effect) depends on the differing Si-substituent groups and leads to variable signal strengths, whose integrations therefore provide unrealistic measures of relative concentrations of different Si-containing species. The NOE is negative, due to the negative magnetic moment of ^{29}Si, and hence tends to decrease, null, or invert signals compared to proton coupled (nonsaturated) spectra, rather than producing the typical signal amplifications common in ^{13}C NMR. The NOE is

also cumulative, depending on the duration of proton irradiation,[23] but can be mitigated by the technique of gated proton decoupling, which cuts off the proton radiation in the recovery segment of the repetitious pulse-acquisition-recovery cycle used in FT-NMR.[32]

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(24) We calculate the pK_A of 10b to be 4.5-6 in dilute aqueous solution, i.e. about 5 units more acidic than 10a and similar to that we calculate for 1.

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(26) J. H. Clark, J. M. Miller, and K.-H. So, J. C. S. Perkin I, 941 (1978). Although not identified as the expected N_2O, we did observe formation of a nearly odorless gas in closed containers of slowly decomposing samples.

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Aminomethyl(methyl)polysiloxane Homopolymers and Their Mannich Derivatives from 2,2,2-Fluorodinitroethanol[1]

Robert S. Neale

Union Carbide Chemicals and Plastics,

Tarrytown, N.Y. 10591

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Abstract

The preparation of aminomethylsilanes $(EtO)_2MeSiCH_2NR^1R^2$ (2) from $(EtO)_2MeSiCH_2Cl$ and excess amines, hydrolyses of 2 to aminomethyl(methyl)polysiloxanes 6, and facile Mannich conversions of both 2 and 6 with 2,2,2-fluorodinitroethanol (1) to the fluorodinitroethylamino derivatives 12 are described. An alternative route to the primary amino monomer 2 was explored in the model amidation of Me_3SiCH_2Cl with

$KNHCOCF_3$. The hydrolyses of 2 proceeded readily with stoichiometric amounts of water, but those involving the primary or secondary amino compounds proved highly sensitive to a deaminative Si-C cleavage side reaction, and the hydrolysates 6 contained more cyclics and shorter average linear chains than had homologous materials[2] with 3- or 4-methylene side chains. Dealkylation also accompanied generation of the high energy Mannich products 12, which uniformly possessed only limited thermal stability at room temperature.

Predominantly linear polysiloxanes bearing pendant amino functionality separated from Si by 3 or 4 side chain methylene groups have been prepared as Mannich reaction precursors for high energy (HE) derivatization with 2,2,2-fluorodinitroethanol (1, FDNE = ROH).[2] The Mannich products were desired, in turn, as hydrolytically and thermally stable HE polymers convertable to higher MW, elastomeric forms suitable for use as binders in explosive or propellant compositions. In order to maximimze the weight of energy generating residues per spinal siloxy unit, however, we were particularly interested in preparing HE derivatives of aminomethylsilicones, which offered the shortest possible aminoalkyl link of HE groups to Si. We now describe the results obtained in this system, which proved atypical of the homologous, higher methylene systems. Thus, in both the preparation of the aminomethyl acceptor polymers and preparation of FDNE derivatives, Si-C cleavage proved a significant and ubiquitous side reaction resulting in loss of aminomethyl side chains and the formation of a corresponding number of cross-linking sites.

Monomers and Hydrolysates. Following the previously successful route,[2] aminomethyl(methyl)polysiloxanes 6 were targeted as hydrolysis products of aminomethyl(diethoxy)methylsilane monomers 2. The primary amino monomer 2a was prepared from $(EtO)_2MeSiCH_2Cl$ upon reaction with a large excess of ammonia,[3] although not very efficiently. Workup after 24 h at 60° in a rocking autoclave gave 88% of NH_4Cl, essentially free of other salts, and 90 wt-% crude 2a, which clearly contained at least two

major types of aminomethylsilane products. Distillation separated a small amount of

$(EtO)_2MeSiCH_2NR^1R^2$ (2) $(EtO)_3SiMe$ (3) $[(EtO)_2MeSiCH_2]_2NH$ (4)

2a, $R^1 = R^2 = H$

2b, $R^1 = H$, $R^2 = Me$

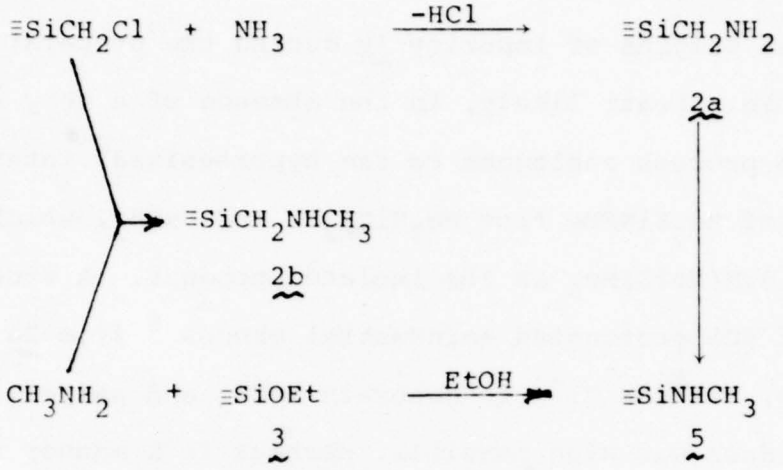
2c, $R^1 = R^2 = Me$

byproduct 3 from the final 35% yield of pure 2a, and further distillation of the 45% pot residue gave the bisamine 4 in 14% yield, identified by ^1H NMR and analogy to prior[3,4] experience. Inexplicably, successive fractions of 2a, which differed only in their minor contents of 3 according to careful ^1H and ^{13}C NMR and VPC analyses, reproducibly gelled at progressively shorter times upon reaction with excess water, although 3 was found not to be responsible. Another reaction conducted near the 100-120°/6 h reference conditions (lit.[3] 50% yield of 2a) gave even more complex high boilers, the same 35% yield of 2a, and an impurity which co-distilled with 2a and showed ^1H NMR peaks in the N-C-H region at δ 2.42 and 2.04 in ~3:2 ratio, indicative of the N-methyl compound 2b. A third preparation of 2a was carried out in the presence of ethanol to assist solubilization of the reactants and favor monoamine formation,[5] but the yields of 2a (39%) and 4 (22%) hardly improved, while the amount of impurity in 2a rose substantially to ~6% and proved immune from fractionation or VPC separation. The impurity was later confirmed as 2b from the VPC

and NMR spectral data of the pure compound prepared from the chloride and excess methylamine in 51% yield. No evidence for N-Et compounds was found.

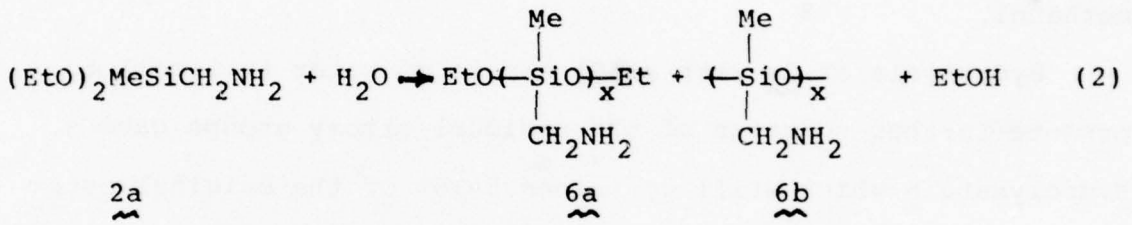
Several origins of impurity 2b during the preparation of 2a were possible. Least likely, in the absence of a very strong base, was a process analogous to the hypothesized[3] intermediate generation of $Me_3SiNHMe$ from Me_3SiCH_2Cl and $NaNH_2$, which then yielded $Me_3SiN(Me)SiMe_3$ as the isolated product. A sacrificial cleavage of HCl-protonated aminomethyl groups [6] from 2a by a nucleophile, such as Cl^-, to generate $MeNH_2$ and unspecified silane residues was also possible, perhaps in a manner related to the hydride cleavage of certain quaternary aminomethylsilanes in the generation of ylide intermediates.[7] The subsequent alkylation of $MeNH_2$ by the chloromethylsilane to give 2b could not proceed, however, unless the strongly basic amine remained unprotonated, but this appeared an unlikely situation in the presence of an excess of the relative acid NH_4Cl. Additional observations of the hydrolytic behavior of 2a, discussed below, suggested a third pathway to 2b via rearrangement of 2a to the (methylamino)silane 5, followed by solvolysis (Scheme I). Both the latter routes to 2b could be enhanced by a polar solvent or reactants, which would help solubilize HCl or its salts and stabilize any ionic components of a rearrangement transition state or intermediate.

Scheme I



The hydrolysis of 2a was highly sensitive to the conditions imposed. It was first found that reactions with 5 mol of water per mol of 2a in methanol at 0-25° and vacuum stripping gave products with varying but inevitable cleavage of the aminomethyl group, resulting in liquids or gels, depending on the particular samples of 2a used. On standing, these hydrolysates continued to liberate methylamine and suffer increasing degrees of cross-linking. Such behavior stands in contrast to the previously reported[3] generation of water-soluble thermoplastic polymers from 2a in water or alcoholic solution. An unusual solid was isolated from hydrolyses of one particular sample of 2a. It dissolved in $CDCl_3$ only upon prior melting of the sample and, sometimes, slowly recrystallized, mp 86-89.5°. ^1H NMR implied the approximate structure[8] HOD_3H.

Hydrolyses conducted in dimethoxyethane solvent with linited amounts of water were more successful. Assuming amine-catalyzed silanol condensation to be facile, 1 mol of water should ideally effect reaction 2, wherein hydrolysate 6 contains only linear species 6a with infinitely long chains (and negligible EtO-end group concentrations). In practice, treatment of



(2)

2a 6a 6b

pure 2a with exactly 1.0 H_2O reproducibly generated an oily product containing only traces of impurity structures and showing no evidence of aminoalkyl group loss by ^1H NMR integration. A substantial concentration of cyclopolysiloxane components 6b (at least 4 species, not yet identified) was present along with linears 6a, however, as were 10-15% of unreacted Si-OEt groups. Normally, one would expect a less completely stoichiometric hydrolysis reaction than was presently observed, since homologous ethoxy esters such as the 3- and 4-methylene aminoalkylsilanes previously studied[2] generally lose, on average, less than 1 of their 2 ester groups under similarly mild conditions.

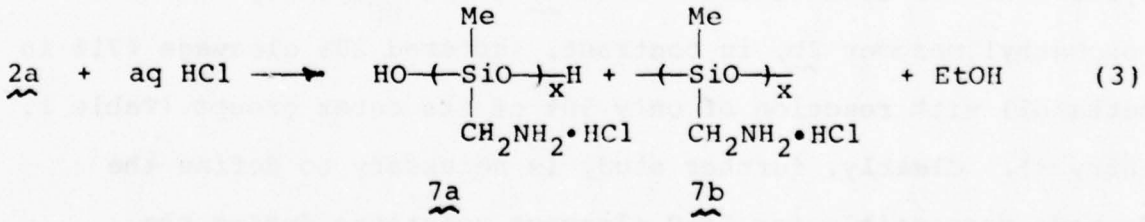
Stable neat for 6 da at 0°, a $CDCl_3$ solution of 6 upon standing in the dark at room temperature generated a ringing ^1H NMR singlet at ∿2.4 ppm, near the absorption of the nonringing N-methyl peak of the impurity 2b in monomer 2a. The new impurity

peak continued to grow in the absence of added nucleophiles and was found to correlate with an increasing concentration of Si-C cleavage residues observed by ^{29}Si NMR. This implicated the rearrangement of aminomethyl to methylamino species shown in Scheme I. In water, of course, any Si-N bonds would hydrolyze to give SiOH units, and condensation to crosslinked Si-O-Si products would soon follow and produce the gels ultimately observed in aq methanol.

Hydrolysis of 2a with a 10% excess of water (1.1 mol) to promote further reaction of the residual ethoxy groups gave a hydrolysate 6 which still contained 5-10% of the original ester groups. However, low concentrations of monoalkylsilicon cleavage products were now observed by ^{29}Si NMR and increased markedly during several h standing in $CDCl_3$ at 23°; only the absorption due to linear structures correspondingly decreased. Aminomethyl groups therefore appeared to be labilized in the presence of any excess of the theoretical water of eq 2, whatever the mechanism of the cleavage process. Hydrolyses of 2a with a deficiency of water, however, gave products whose ^{1}H NMR spectra indicated the theoretical disiloxane $EtOD_2Et$ from 0.5 H_2O, or tetrasiloxane $EtOD_4Et$ from 0.75 H_2O, both without aminomethyl group cleavage. The compositions of some representative ethoxy end-capped hydrolysates 6 are given in Table I, entries 1-3, along with data for other aminomethyl system products described below. Overall, it was clear that cleavage-free, highly linear aminomethylsilicone oligomers of substantial chain lengths were not readily accessible from 2a for use as precursors to HE derivatives of the

linearity or MW achieved[2] in the 3- and 4-methylene side chain systems.

Three alternative approaches to 6 or the corresponding HE derivatives were then considered: deactivation of the amino group during hydrolysis of 2a to hinder cleavage; Mannich reaction of 2a with 1 and concurrent, stoichiometric hydrolysis of the very reactive ester groups by the product water (see following section); and amino functionalization of preformed chloromethylpolysiloxanes. Full protonation was examined first as an amino deactivation technique, despite the possibility of acid catalyzed rearrangement noted above. Surprisingly, addition of 2a to the theoretical amount of aq 3 N HCl required for salt formation, followed by stripping at 35°, gave a tacky, waxy solid 7 containing no unreacted Si-OEt groups and showing no sign of Si-C cleavage under NMR analysis (eq 3). The theoretical ratios of group integrals for protonated 6 were found for 7 in D_2O,



although at least 7 different Si-Me peaks were observed which rapidly changed in relative importance over 2 h standing in the NMR solution at 23°. The major siloxy entity was of the end group silanol type, the linear species (7a) averaged $HOD_{3.3}H$, and cyclics (7b) now comprised only 15% of the total components (see

Experimental Section). Although neutralization of 7 with aq NaOH liberated methylamine and produced a gel in one experiment, better control of conditions might well have produced a product with greatly reduced cleavage.

In another approach to deactivative amino group protection and as a potential method of purifying 2a, we prepared its trifluoroacetamide 8, $(EtO)_2MeSiCH_2NHCOCF_3$, whose distillation completely removed the N-methyl impurity 2b. The hydrolysis of the relatively acidic amide was examined only briefly. Although Si-C cleavage was apparently avoided, the extent of retention of amide functionality remained unclear.

The behavior of N-substituted analogs of 2a bearing alkyl instead of electron-withdrawing groups was then probed by hydrolyzing the mono- and dimethyl compounds 2b and 2c with 1.1 H_2O in DME. The dimethyl monomer 2c reacted without observable Si-C cleavage but lost 98% of its original Si-OEt groups to yield the analog hydrolysate of 6, which contained twice the apparent cyclics as had been obtained from 2a (Table I, entry 9). The monomethyl monomer 2b, in contrast, suffered 20% cleavage (71% in methanol) with reaction of only 90% of its ester groups (Table I, entry 8). Clearly, further study is necessary to define the factors responsible for Si-C cleavage reactions during the hydrolysis of aminomethylsilane esters.

Study of the amination of chloromethylpolysiloxanes was begun using Me_3SiCH_2Cl as a model. A method was needed that would completely exclude dialkylation side reactions and thereby prevent cross-linking in polymeric substrates, such as an analog

of the cumbersome Gabriel technique (see Experimental Section). A fascinating variety of techniques suitable for primary amine synthesis in monomeric compounds has been recorded.[9] None, however, seemed free of all the operational characteristics unacceptable in poly(chloromethyl) systems. Thus, it seemed necessary to avoid highly polar reagents requiring aqueous solvents, generation of insoluble intermediates, use of hazardous reagents on a large scale, difficult or incompatible deprotection procedures, and any requirement for bromide rather than chloride starting materials. We therefore elected to evaluate the alkylation of potassium trifluoroacetamide (9), encouraged by the ready methylation of N-alkyl derivatives by MeI,[10] the facile hydrolysis of the alkylated amides under mildly basic conditions,[10,11] and generally high solubility of both the salt and amide products in ethereal solvents.

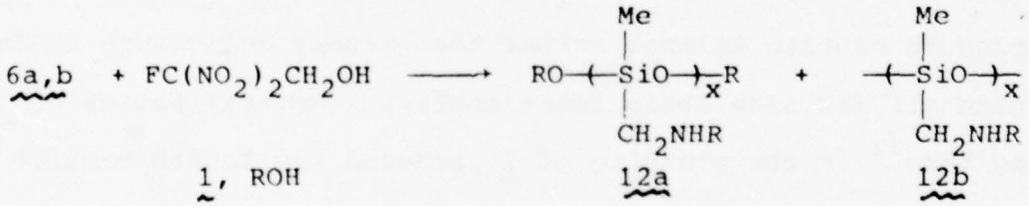
After unsuccessful efforts to prepare 9 in highly pure form and explorations of various reaction conditions, the encouraging but still unsatisfactory results of eq 4 were obtained at 1:1 reagent stoichiometry to give the amide 10. Despite maintenance of anhydrous conditions, 20-25% of 9 invariably suffered deamination during the reaction to give a K salt strongly suggestive of solvated $KOCOCF_3$, just as the initial preparation of 9 could not be carried out cleanly. Use of excess 9 or DMSO solvent failed to compensate for the resulting incomplete conversion of the chloride, and an experiment in DME with added NaI for the catalytic, *in situ* conversion of the chloride to the more reactive iodide[12] failed to prove encouraging. A more serious

problem was the formation of the bisalkylation product 11 as an indicator of probable cross-linking in polychloro substrates, which were therefore not studied. Compound 11 was obtained along with H_2NCOCF_3, presumably via reaction of 9 with 10 and alkylation of the resulting salt; the yields of 11 and trifluoroacetamide were calculated on this basis. In a single trial, $(EtO)MeSiCH_2Cl$ failed to yield a product analogous to 10 upon reaction according to eq 4.

$$\underset{77\%\ \text{conv.}}{Me_3SiCH_2Cl} + \underset{9}{KNHCOCF_3} \xrightarrow[84^\circ]{DME} \underset{10,\ 66\%}{Me_3SiCH_2NHCOCF_3} + \underset{78\%}{KCl} + \underset{11\%}{H_2NCOCF_3} + \underset{11,\ 12\%}{[Me_3SiCH_2]_2NCOCF_3} + \underset{23\%}{[KOCOCF_3]} \quad (4)$$

High Energy Derivatives. Mannich reactions of 1 with various aminomethylsilicon compounds proceeded as readily as had those[2] involving aminopropyl or aminobutyl structures, but were accompanied by dealkylation side reactions of the type found during the preparation and hydrolysis of monomer 2a. Four different HE aminomethyl polymer preparations were carried out, but all produced surprisingly similar results (Table I, entries 4-7). Upon treatment with 1.05 mol of 1 in CH_2Cl_2, a cleavage-free hydrolysate from 2a and 1.0 H_2O afforded a fluid product containing HE units of both linear (12a) and cyclic (12b) types (eq 5). The starting 10% of EtO- end groups was lost, however, and a new product 13, the Mannich derivative from 1 and the cleavage

product CH_3NH_2, was now found, as ^{29}Si NMR confirmed ∿16% of Si-C cleavage residues among the siloxy units. A Mannich reaction of the hydrolysate from 2a and 0.75 H_2O, which contained about one-third of the total siloxy units as EtO- ended species, was then carried out with a calculated excess of 1 sufficient to satisfy any tendency for replacement of EtO- groups by $FC(NO_2)_2CH_2O$- residues. Nearly 90% of such end group replacement was observed in the resulting product mixture, and some 10-15% of cleavage products were again produced. After standing 1-4 da at 20-25°, both HE products slowly developed micro gas bubbles where disturbed by a probe (as had the HE derivatives from the ethylanediaminopropyl system)[2] and showed clear signs of decomposition (IR) after heating at 60° for 3 h. Not characterized in the detail possible in other systems,[2] these HE aminomethyl materials contained ∿50% cyclic siloxy units 12b, along with linear species 12a of relatively short 2-10 unit chains.



+ RNHMe (5)

A new approach was tested to reduce cleavage in the HE products 12 and produce higher concentrations of linear components. The facile, stoichiometric hydrolysis of 2a described above promised an equally facile hydrolysis using the water stoichiometrically generated during a concurrently run Mannich

reaction of 2a. Although the aminopropyl analog of ester 2a had suffered little hydrolysis in such a procedure,[2] 1:1 reaction of 2a with 1 at 0-25° now gave a very fluid product which retained only 11% of the EtO- groups and closely resembled the previous Mannich products prepared from pre-formed hydrolysates. Unfortunately, ∿15% cleavage again accompanied the reaction, and the product slowly foamed after several days storage at 23°. It was therefore simpler to generate 12 directly from the monomer 2a than to proceed through the hydrolysate 6. We should note that the sample of 2a treated with 1 as described had actually contained 10% of 2b as well. This was probably detrimental, since pure 2b had later proved more cleavage-prone than 2a during hydrolysis and was found to yield a HE product upon reaction with 1 which soon gelled, appearing in all respects to have suffered substantial decomposition.

Hydrolysate hydrochloride 7 was the only aminomethylsilicone appearing to contain silanol rather than ethoxy end groups while retaining all its side chain functionality. Neutralization of 7 with aq base[13] in the presence of 1 produced the fourth Mannich product. This contained only traces of 13, although the usual ∿13% cleavage residues were found in the siloxy units, which appeared to contain $FC(NO_2)_2CH_2O$- residues at both the Si cleavage sites and end group positions. The product composition markedly resembled that obtained from the free base hydrolysates 6, however, and a flexible, yellow foam again formed due to slow gassing during 5 da at 20-25°.

All four reactions to produce HE, linear, cleavage-free

polymers thus had succeeded only partially, and the instability of all the neat products at room temperature stood in marked contrast to the substantially higher thermal stability of HE aminoalkylsilicones with longer methylane side chains.[2]

Characterization of Products. Both the preparation and hydrolysis of the aminomethyl monomer 2a were notably beset with dealkylation side reactions. The level of the N-Me impurity 2b which accompanied the preparation of some samples of 2a was readily measured by ^{1}H NMR integration, once its identity had been established. Hydrolysates of pure 2a, some of which contained or acquired the apparent rearrangement species ≡SiNHMe (5) absorbing at δ 2.4, were analyzed for Si-C cleavage using the area insufficiencies of the methylene group peaks. In samples where the characteristic δ 2.4 peak appeared only upon ageing, correction of the integrated N-Me peak value to that of its precursor methylene group CH_2N by x 0.67 gave a total for the latter absorption equal to the theoretical 2.0 protons. Hydrolysates of 2b and 2c were similarly analyzed for total cleavage from the integrated absorptions due to $SiCH_2N$ protons. The formation and hydrolysis of Si-N intermediates during Mannich condensations of aminomethyl substrates accounted for the generation of 13, but its formation from HE side chain species vs free CH_3NH_2 could not be defined. The presence and amount of 13 was tagged by observation and integration of its isolated δ 2.5 peak. The presence of Mannich products 12 was readily deduced from the ^{1}H NMR absorptions at δ 3.93 (J 19.0 Hz) in all the samples, as anticipated from the HE polymers previously[2] reported.

The differentiation and quantification of aminomethylsiloxy units in acceptor and HE polymers by ^{29}Si NMR proved less precise than in the higher homologs. In the absence of polymeric reference compounds of known structure and because of the significantly upfield shifted resonances of 2a-c vs the aminopropyl or -butyl monomers[2], it was not feasible to make assignments in 6 or 12 by analogy to the homologous polymers, and the general occurrence of multiple peaks within each envelope of absorption added further complication. The headings assigned in Table I were therefore derived on the following basis. The first three entries show hydrolysates from 2a produced using 50 to 110% of the theoretical water for linear polymer formation (eq 2). With the concentrations of EtO- end groups established by ^{1}H NMR, the first new species observed in the ^{29}Si NMR spectrum was presumed to be the disiloxane (x = 2, entry 1), which marked the 17 ppm resonance as due to terminal Si atoms. Increasing amounts of hydrolysis water were then expected to give products with a substantial increase in small, linear species (x = 4, entry 2), followed by the formation of cyclics in higher hydrolysates (x = ∞, entry 3), as assigned.

Trifunctional Si units, i.e. those which contained only one C-bonded substituent group, resulted from cleavage of aminomethyl groups and were readily obvious from their high field ^{29}Si shifts[14]. Peaks from the hydrochloride polymer 7 in D_2O appeared at 1.5-2 ppm higher field than those from 6 in $CDCl_3$, but fell into similarly patterned groups (see Experimental Section). The N-methylated hydrolysates reported in Table I (entries 8, 9)

produced equally familiar resonance patterns, but with shifts upfield of those of the primary amino structures (entires 1-3) and similar to those in the HE products (entries 4-7). Despite the satisfying regularity of the ^{29}Si resonance patterns, we could not be certain that all the peaks appearing within a given absorption envelope represented similar structures, i.e. all cyclics or all linears. In one instance, in particular, the HE end group units of 12a clearly appeared to absorb in the cyclic(4) region. This was indicated by comparison of the integrated peaks before and after Mannich condensation (entries 2 vs 4), in conjunction with the prior determination by ^{1}H NMR that the ethoxy end groups in 6 had been converted to the HE ester type in 12.

In a departure from the methodology previously used,[2] we recorded the ^{29}Si NMR data for polymers only in the presence of the spin relaxation agent $Cr(acac)_3$, needed for integration. Since a marked nulling of the signal from monomer 2a was observed in the absence of Cr, and no substantial differences were apparent in the spectra of 6 ± Cr, it was felt that Cr-free data would not prove generally useful. Very rapid compositional changes induced by added Cr remained a hidden possibility, however. The end group and cyclics analyses presented in Table I led to the calculation[2] of $M_{\bar{N}}$ values and chain lengths; the direct measurement of $M_{\bar{N}}$ by VPO was not attempted.

Experimental Section

CAUTION! The materials described should be treated with great care and adequate protection against hazards of explosion or toxic dermal contact.

Fluorodinitroethanol (1) was purified as previously described.[14] Chloromethyl(diethoxy)methylsilane was used as received from Silar Laboratories [99%, ^{1}H NMR δ 2.80 (CH_2Cl)]. Trifluoroacetamide (Aldrich) was twice recrystallized to C, H, F, and N analytical purity from 3 mL $CHCl_3$ (as received) per g; mp 72-75°. Potassium t-butoxide (Aldrich) titrated to 97.9% purity. Spectral analyses were obtained as described previously.[2] Temperatures are given in °C.

[Diethoxy(methyl)silyl]methylamine (2a). To a dry, nitrogen filled 3 L ss autoclave was charged 273.8 g (1.5 mol) of chloromethyl(diethoxy)methylsilane. The vessel was then closed, chilled in Dry Ice, further charged with 760 g (44.7 mol) of ammonia through ss lines and fittings, heated with rocking to 50-80° during 3 h, rocked without heat 16 h, heated again at 60° for 24 h, cooled and vented. Anh ether (1 L) was added through a port and the liquids displaced with nitrogen pressure through a glass dip tube into a dry container. The solids, 70.7 g (88% as NH_4Cl), were similarly transferred with a total 1.5 L ether and then pressure filtered after the combined sample and washes had stood at -10° for 16 h. ^{1}H NMR showed two types of CH_2N peaks in 3:2 ratio in the 219 g of crude liquid obtained upon stripping the ether filtrate, and distillation produced 96 g of impure 2a.

Redistillation removed 3 and gave 2a in 3 fractions, bp 32-34° (1.5 mm), $n_D^{24.5}$ 1.4128, d^{23} 0.918 g/cc, in 35% yield [lit.[3] bp 67.5° (24 mm), n_D^{20} 1.4120-6]. Despite the absence of spectral differences between them (^1H and ^{13}C NMR, IR, VPC), each succeeding fraction more rapidly than the last liberated a volatile amine and gelled upon treatment with 5 mol H_2O in methanol. Only traces of the N-Me impurity 2b, which accompanied the preparation of 2a in the presence of 200 mL abs ethanol, were found. ^1H NMR (2a) δ 0.14 (Si-Me), 1.19 (t, C-Me), 0.89 (NH), 2.17 (CH_2N), 3.74 (CH_2O); ^{29}Si NMR δ -9.80, nearly nulled [normally sized and shifted 0.28 ppm downfield in the presence of 0.05 M $Cr(acac)_3$].

Although the ^1H NMR spectrum of the distillation residue, 96.2 g, very closely resembled that of the bisalkylation product 4 distilled from it, only 32 g (14%) of pure 4 was obtained, bp 61.5° (0.05 mm), $n_D^{24.5}$ 1.4178; ^1H NMR δ 0.14 (Si-Me), 0.80 (NH), 1.24 (C-Me), 2.18 (CH_2N), 3.83 (CH_2O).

Similar reactions were carried out with methyl- and dimethylamine instead of ammonia in a stirred 1 L autoclave at 20-25° for 48 h. From 0.25 mol of the chloride and 6.3 mol methylamine were obtained 14.5 g of hydrochloride salt (86%) and 39.8 g of crude 2b (91%), whose VPC spectrum at 180° showed a principal peak at the retention time of 2a but no 3 or high boiler analogous to 4. Distillation, however, generated 3 and gave only 21.6 g (51%) of >99% pure N-methyl[diethoxy(methyl)-silyl]methylamine (2b), bp 48.5-49° (5 mm), n_D^{23} 1.4095; ^1H NMR δ 0.13 (Si-Me), 0.80 (NH), 1.20 (C-Me), 2.04 (CH_2N), 2.46 (N-Me), 3.82 (CH_2O); ^{29}Si NMR δ -10.38, shifted 0.24 ppm down-

field by $Cr(acac)_3$.

From the chloride and 4.5 mol dimethylamine were obtained 95% of hydrochloride salt and 42.1 g (89% as 2c) of liquid containing both 3 and a high boiler (VPC, 180°). Distillation afforded 39% of >98% pure (and 10% of 96-98% pure) N,N-dimethyl[diethoxy(methyl)silyl]methylamine (2c), bp 49.5° (6 mm), n_D^{23}1.4089, d^{23} 0.876 g/cc, accompanied by 2-4% of 3, which continued to form during the distillation. ^1H NMR δ 0.19 (Si-Me), 1.18 (C-Me), 1.88 (CH_2N), 2.24 (N-Me), 3.79 (CH_2O); ^{29}Si NMR δ -10.79, shifted 0.30 ppm downfield by $Cr(acac)_3$.

N-[Diethoxy(methyl)silylmethyl]trifluoroacetamide (8). A 0.02 mol sample of 2a containing ∿15% of 2b was converted cleanly to 8 upon reaction[15] with 5% molar excess ethyl trifluoroacetate in 10 mL $CHCl_3$ at 5-10°, standing 2 h at 23°, and stripping. This method avoids the difficultly removed trifluoroacetic acid coproduct resulting from use of trifluoroacetic anhydride and the accompanying replacement of ethoxy groups by CF_3CO_2- residues (observed in both 2a and the aminobutyl homolog). Distillation gave 76% of 8, bp 64.5-65° (0.6 mm), whose fractions showed a single, broad VCP peak at 180° but a change from a single to a twinned CH_2N peak in the ^1H NMR spectrum: δ 0.24 (Si-Me), 1.22 (t, C-Me), 2.92 and 2.85 (CH_2N), 3.82 (q, CH_2O), 7.43 (NH, broad and unstructured). A doubled C=O IR peak in 8 (1700, 1720 cm^{-1}) also characterized 10 and two other $RNHCOCF_3$ compounds prepared from aminobutyl or -propylsilanes. No sign of residual 2b or its amide was found in distilled 8.

Trimethylsilylmethylamine Hydrochloride (14•HCl). The intermediate N-(trimethylsilylmethyl)phthalimide was prepared[9a] in 83% yield, bp 115 (0.3 mm), n_D^{26} 1.5397 [lit.[9a] bp 117 (2 mm [sic]), n_D^{20} 1.5427], from trimethylsilylmethyl chloride, phthalimide, and K_2CO_3 in DMF. Reactions using preformed potassium phthalimide in DMSO or DMF were unproductive. The Gabriel procedure was completed[9a] by treating the phthalimide with a 7% deficiency of $H_2NNH_2 \cdot 1.5\ H_2O$ in ethanol followed by aq HCl decomposition of the phthalhydrazide salt, to give 96% phthalhydrazide and 98% crude 14•HCl. The latter was readily freed of water-insoluble impurities but still melted at 224-234° [lit.[9a] mp 242-3°] despite recrystallization from isopropanol or acetonitrile. However, it was important to exclude any impurities such as the suspected $H_2NNH_2 \cdot HCl$ prior to reaction of 14 with 1 in order to prevent the formation of $H_2NNHCH_2CF(NO_2)_2$, a potentially hazardous[16] side product. The free base was therefore generated from 14•HCl and aq KOH under ether, distilled as a 2-4% ethanol azeotrope, bp 94.5° [lit.[9a] bp pure compd 94°], ^1H NMR δ 2.10 (CH_2N), and reconverted to pure 14•HCl, mp 244-6°, in 72% overall yield from the phthalimide.

Potassium trifluoroacetamide (9). To a 300 mL flask with magnetic stirbar, nitrogen cover, thermometer and inlet port was added 31.2 g (0.276 mol) of pure trifluoroacetamide and 60 mL Molecular Sieve-dried DME. The resulting solution was chilled to 0° and then treated at 0-7° via glass syringe (Teflon needle) with a suspension of potassium t-butoxide (31.2 g, 0.30 mol) prepared in 100 mL DME under anhydrous conditions. The exo-

thermic reaction moderated greatly when half the base had been added. The final champagne-colored, slightly cloudy solution was warmed to 17° over 45 min and then stripped, ultimately at 35° (2 mm). The solids were broken up and stirred rapidly with 200 mL anh ether for 1 h, the supernatent liquid decanted, the procedure repeated twice, and the final solids dried to give 40.9 g (98%) 9, mp 151-154° (shrinkage), then 154-165°; dec 165-169°. The same values were observed in an earlier sample prepared from stoichiometric reagents but using predominantly pure t-butanol instead of DME solvent. Precipitation of a sample of the product from a 50% wt/vol solution in DME with ether (5 volumes) gave a residue with mp 131-136°, whether or not dried under vacuum at 56° for 1 h, followed by dec at 136-160°. Evaporation of the original ether washes of 9 left 1.6 g of an oil found to contain the parent trifluoroacetamide. Anal. Calcd for C_2HF_3KNO (9): C, 15.89; H, 0.67; F, 37.71; K, 25.87; N, 9.27. Found: C, 15.52; H, 0.61; F, 34.39; K, 25.09; N, 7.29.

N-[Trimethylsilylmethyl]trifluoroacetamide (10). To a dry 100 mL 4-necked pot equipped with thermometer, nitrogen cover, condenser, septum, and magnetic stirbar was added (in a drybox) 12.1 g of 9 (0.08 mol, if pure) prepared with stoichiometric reagents. To this was added 30 mL dry DME to give a solution, and 11.7 mL (0.084 mol) of Me_3SiCH_2Cl was added all at once via syringe. The resulting solution (slurry from the 9 described above) was heated after 30 min to 85° and maintained there 4.5 h. A fine powder (KCl) began to precipitate at ~60°. VPC analysis using known mixtures and two columns gave the results of eq 4.

Filtration, with DME washings, gave 4.6 g KCl, and stripping afforded 16.7 g of a 2-phase liquid whose working with up to 40 mL CH_2Cl_2 produced a solution and precipitate. The solids, 2.8 g, mp 132-42°, were separated from the final 12.3 g of crude 10, 11, and H_2NCOCF_3 and found to comprise the theoretical amount of $KOCOCF_3 \cdot \frac{1}{4}$ MeOH expected for the observed 22% side reaction of 9. Anal. Calcd for the 0.25 methanolate salt: C, 16.87; H, 063; F, 35.60; K, 24.42. Found: C, 16.67; H, 0.61; F, 35.29; K, 22.60; N, 0.18.

Distillation of crude 10 gave ~99% pure amide, bp 46.5-47° (0.6 mm), n_D^{22} 1.4010, d^{23} 1.07 g/cc, which contained a very small amount of high boiler 11. ^{1}H NMR (10) δ 0.10 ($SiMe_3$), 2.93 (CH_2N), 7.70 (NH, broad); ^{13}C NMR δ -3.22 (CH_3), 30.48 (CH_2), 116.1 (q, $J_{C,F}$ 287 Hz, CF_3), 157.2 (q, $J_{C,F}$ 37 Hz, C=O). Anal. Calcd for $C_6H_{12}F_3NOSi$: C, 36.17; H, 6.07; F, 28.61; N, 7.03; Si, 14.09. Found: C, 36.06; H, 6.07; F, 28.38; N, 7.08; Si, 13.97.

Preferred Hydrolyses of 2. The pure monomer 2a, 0.011 mol in 2 mL DME, was treated slowly with 0.011 mol H_2O in 2 mL DME with good stirring and nitrogen gas agitation at 0-5° and then allowed to warm to 20°. The resulting, clear solution was stripped for 15 min at 28° (17 mm) and then 10 min (1 mm) to produce a still, mobile oil 6, in which no volatile amine odor was evident; ^{1}H NMR δ 2.12-2.15 (CH_2N, various samples). The hydrolysate from 2b and 10% excess H_2O absorbed at δ 2.47 (N-Me) and 2.05 (CH_2N), and that from 2c at δ 2.25 ($N-Me_2$) and 1.85 (CH_2N).

Hydrolysis of 2a with Aq HCl. To 19 mL of well stirred 3 N HCl at 0° was slowly added 9.0 g (0.056 mol) of pure 2a. The

cloudy solution was filtered (medium glass frit), allowed to stand 1 h at 10-23°, stripped at 30-35° for 1 h at aspirator pressure, left overnight at 23°, and finally stripped under high vacuum to give 7.15 g of tacky solid 7, which became free flowing on 5 wk standing without significant change in the ^{1}H NMR spectrum. ^{1}H NMR (D_2O, vs DSS ref) δ 0.32-0.50 (7 peaks, Si-Me), 2.53 (CH_2N), 4.62 (NH_3^+) in appropriate area ratios. Also present was broad absorption totalling ~0.4 H, suggestive of the SiOH end group concentration indicated by ^{29}Si NMR, but appearing in the amide region at ~7.5 ppm. ^{29}Si NMR (D_2O vs DSS) - δ 12.1 (2a·HCl, 5 area-%), 18.8 (end group, 47%), 24.1-25.7 (cyclics, 5 peaks, 15%), 26.4-27.2 (linears, 3 peaks, 33%), and no dealkylation residues.

N-(2,2,2-Fluorodinitroethyl)aminomethyl(methyl)polysiloxane (12). A cleavage free hydrolysate 6 (0.017 eq), freshly prepared from 2a and 1.0 H_2O, was treated in 20 mL CH_2Cl_2 over 4 min at 0-5° with 0.0175 mol of 97% pure 1. An initial yellow color persisted, 5 g anh Na_2SO_4 was added immediately, and the solution was allowed to warm to room temperature over 20 min. After 3 h stirring, the solution was left to stand overnight and then separated from the drying agent, which had absorbed 87% of the theoretical amount of water. The 4.1 g of residue from high vacuum stripping, d^{23} 1.42 g/cc, no longer contained the EtO-groups present in 6 but did possess minor ^{1}H NMR doublet absorption at δ 4.67 (J 16.4 Hz) characteristic[14] of $FC(NO_2)_2CH_2OSi\equiv$ residues. Since the principal HE group absorption, however, was clearly due to Mannich products, the presence of HE endblocked

linear species 12a was implied. The yield of 12 was 94% of theory, assuming replacement of ethoxy by HE groups. Also present was the trapped CH_3NH_2 product 13, whose N-Me peak (δ 2.52) integration related it to cleavage of <5% of aminomethyl side groups. However, ^{29}Si NMR revealed 16% of Si species containing only one carbon bonded group (Table I, entry 5), as the ^1H NMR peak at δ ~2.4 indicative of the rearrangement species 5 (Scheme I) was also observed in 12, along with the expected $SiCH_2N$ peak at δ 2.20.

A highly similar HE product 12 was obtained upon treatment of monomer 2a directly with equimolar alcohol 1 in the absence of a drying agent (Table I, entry 7), or upon neutralization of 7 in the presence of 1 as follows. To a well stirred mixture of 2.5 g (0.02 mol) 7, 2.0 mL (0.02 mol) 1, 5 mL H_2O, and 20 mL CH_2Cl_2 was added dropwise 3.3 mL 6 N NaOH (0.02 eq) at 0-5°. A deep yellow color developed during addition of the last 10% of base and resided in the emulsified aqueous phase until the mixture was allowed to warm to 20°. A mild exotherm was then controlled as the color shifted to the lower phase, which was separated after 1 h, combined with washes of the aqueous phase, dried and stripped to 4.5 g of heavy, yellow oil. Since the Mannich alkylation apparently did not proceed until ~20°, a better procedure would have been to neutralize slowly at 20-25° to reduce the exposure of free aminomethyl groups to the aqueous, cleavage promoting environment.

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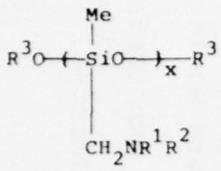
Table I. ^{29}Si NMR Spectra and Compositions of Aminomethysilicones[a]



Entry	R^1	R^2	R^3	Nominal[c] x	Sample origin	- δ ppm[b] (area %, total for type) Ethoxy end group	Cyclic(4) and HE end group	Internal linear[d]	Trifunctional[e]
1[f]	H	H	Et	2	2a + 0.5 H_2O	16.9 (50)	none	24.6 (17)	50.2 (trace)
2[g]				4	2a + 0.75 H_2O	16.8 (35)	22.5, 23.0 (12)	24.6 (50)	none
3				∞	2a + 1.1 H_2O	17.0 (2)	22.4, 22.6, 22.7, 23.0 (29)	24.5 (55)	64.1-65.5 (14)
4	H	HE[h]	HE[h]	4	Entry 2 + 1	16.5 (1)	23.5, 24.1 24.7 (52)	25.9, 26.7 (34)	63.5-65.5 (14)
5				∞	Product (2a + 1.0 H_2O) + 1		24.1, 24.6 (46)	26.0, 26.6 (38)	62.0-66.0 (16)

Table I continued ^{29}Si NMR Spectra and Compositions of Aminomethysilicones[a]

Entry	R^1	R^2	R^3	Nominal[c] x	Sample origin	- δ ppm[b] (area %, total for type) Ethoxy end group	Cyclic(4) and HE end group	Internal linear[d]	Trifunctional[e]
6				3.3[i]	7 + 1		22.7, *24.2* 24.7 (42)	25.4, *26.0*, 26.9 (45)	62.0-67.4 (13)
7				∞	2a + 1	18.5 (2)	*24.2*, 24.7 (34)	26.1, *26.2*, 26.8 (45)	54.0-57.7 (4) 63.6-65.5 (15)
8	H	Me	Et	∞	2b + 1.1 H_2O	17.2 (5)	23.6, 24.1 (20)	25.7, 25.9 (48)	55.0 (5) 63.2-67.8 (22)
9	Me	Me	Et	∞	2c + 1.1 H_2O	16.1 (2)	23.9, 24.1 (53)	25.7, *26.3*, 26.9 (44)	none

[a]In ~50% (vol) $CDCl_3$ with 0.05 M Cr(acac)$_3$. [b]Assignments tentative; highly dominant peaks italicized. [c]Based on theoretical hydrolysis stoichiometry. [d]May contain cyclic(5) species. [e]Broad, diffuse peaks; types $(\equiv SiO)_2Si(Me)$-Z with Z = OSi≡, OH, OR, or NR_2. [f]Also contained 33% unreacted 2a. [g]Also 4% 2a. [h]HE is $CH_2CF(NO_2)_2$. [i]Observed.

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