

Ethyl and *n*-Butyl Tetrahydropyranyl-3,4- d_2 Ether (XVIa and XVIb).—2-Ethoxy- and 2-butoxy- Δ^3 -dihydropyran (XVa and XVb) were prepared by the method of Woods and Sanders¹³ and each was deuterated by homogenous catalysis¹⁴ using $[(C_6H_5)_3P]_2RhCl$ (25 mg) in acetone (10 ml) at room temperature for 18 hr, the solvent and the labeled tetrahydropyranyl ethers (XVIa and XVIb) being separated by vpc.

***n*-Butyl tetrahydropyranyl-4- d_1 ether (XVIIb)** was prepared from *n*-butyl tetrahydropyranyl-3,4- d_2 ether (XVIb) by stirring overnight with *n*-butyl alcohol containing a trace of concentrated hydrochloric acid. The solvent alcohol was fractionally distilled and XVIIb isolated by preparative vpc.

- (13) G. F. Woods and H. Sanders, *J. Amer. Chem. Soc.*, **68**, 2483 (1946).
 (14) W. Voelter and C. Djerassi, *Chem. Ber.*, **101**, 58 (1968).

Ethyl and *n*-Butyl Tetrahydropyranyl-3,3- d_2 Ether (XXa and XXb).—2-Hydroxytetrahydropyran (XVIII, 0.5 g) was heated under reflux for 1.5 hr with deuterium oxide (15 ml) containing deuteriohydrochloric acid (8.8 *N*, 5 drops) and then continuously extracted with ether. Isolation by preparative vpc yielded 2-hydroxytetrahydropyran-3,3- d_2 (XIX, 0.27 g). Condensation of XIX (50 mg) with an excess of ethanol-*O-d* and deuterium oxide containing 3 drops of deuteriohydrochloric acid yielded ethyl tetrahydropyranyl-3,3- d_2 ether (XXa). Similar treatment of *n*-butyl alcohol-*O-d* with 2-hydroxytetrahydropyran-3,3- d_2 (XIX) afforded *n*-butyl tetrahydropyranyl-3,3- d_2 ether (XXb).

Registry No.—I, 4819-83-4; II, 1927-68-0; III, 16315-51-8; IV, 16315-52-9; X, 16315-55-2; XVIa, 16315-56-3; XXa, 16315-57-4.

Mass Spectrometry in Structural and Stereochemical Problems. CLV.¹ Electron Impact Induced Fragmentations and Rearrangements of Some Trimethylsilyl Ethers of Aliphatic Glycols and Related Compounds²

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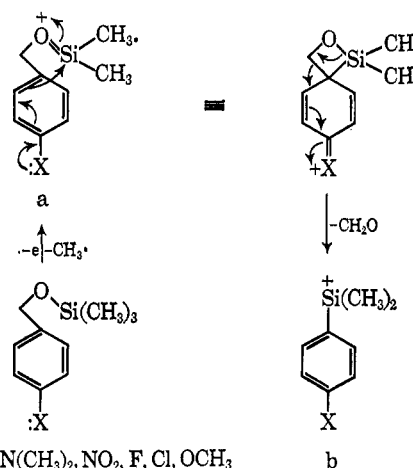
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In view of the importance of trimethylsilyl ethers in gas chromatography, the basic fragmentation modes incurred upon electron bombardment of polymethylene glycol bistrimethylsilyl ethers (III, $n = 2-8$) were elucidated; in all cases ($n = 2-8$), there is encountered a characteristic rearrangement ion (*g*) of mass 147 involving expulsion of the central portion of the molecule. Electron bombardment of the corresponding methoxy- (XI, $n = 2,4,5$), ethoxy- (XIV), and phenoxy- (XVIII, $n = 2-7$) polymethylene trimethylsilyl ethers also produced intense rearrangement peaks analogous to *g*; and in all instances there was encountered a remarkable insensitivity toward ring size (five to eleven membered) in the cyclic transition state. Deuterium and oxygen-18 labeling was employed to elucidate the fragmentation patterns exhibited by XI, XIV, and XVIII. The trimethylsilyloxy function of 2-phenoxyethyl trimethylsilyl ether (XVIII, $n = 2$) was replaced with the triethylsilyloxy and trimethylgermyl groups in order to assess their effect upon the mass spectral behavior of XVIII ($n = 2$). Likewise, the effect of substitution of nitrogen and sulfur atoms for both the phenoxy and trimethylsilyloxy oxygen atoms was examined. Finally, deuterium labeling was employed to elucidate the electron impact induced fragmentation modes of 2-(cyclohexyloxy)ethyl trimethylsilyl ether (XXIX).

In recent years, trimethylsilyl ethers have been extensively employed to facilitate gas chromatographic separation of nonvolatile materials. The development⁴ and widespread usage of mass spectrometers capable of making direct measurements of gas chromatographic effluents has made mass spectral investigations of trimethylsilyl ethers particularly relevant and several studies concerning the mass spectra of trimethylsilyl derivatives of a variety of natural products have recently appeared.⁵ Interest in our laboratory initially focussed on the characteristic fragmentations encountered in sterol trimethylsilyl ethers.⁶ During this work, it became evident that a thorough study of the electron impact promoted fragmentation of various trimethylsilyl ether types must be undertaken in order to permit more precise structural deductions. In a

subsequent study⁷ the fragmentation modes of certain alcohol derivatives were accurately elucidated utilizing deuterium-labeled pentanol trimethylsilyl ethers. Also discussed in that report were several electron impact induced skeletal rearrangements of which the sequential loss of a methyl radical and of formaldehyde in benzyl ether derivatives ($I \rightarrow a \rightarrow b$) is typical (Scheme I).

SCHEME I



(1) For paper CLIV, see S. J. Isser, A. M. Duffield, and C. Djerassi, *J. Org. Chem.*, **33**, 2266 (1968).

(2) Financial assistance (Grant No. AM 04257) from the National Institutes of Health is gratefully acknowledged.

(3) (a) National Science Foundation Predoctoral Fellow (1966-1967); National Institutes of Health Predoctoral Fellow (1967-1968). (b) National Institutes of Health International Postdoctoral Fellow (1965-1966) on leave from University College, Dublin.

(4) For review, see S. Ställberg-Stenhagen and E. Stenhagen in "Topics in Organic Mass Spectrometry," A. L. Burlingame, Ed., Interscience Publishers, Inc., New York, N. Y., 1968, Chapter 5.

(5) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, pp 471-477.

(6) J. Diekman and C. Djerassi, *J. Org. Chem.*, **32**, 1005 (1967).

(7) J. Diekman, J. B. Thomson, and C. Djerassi, *ibid.*, **32**, 3904 (1967).

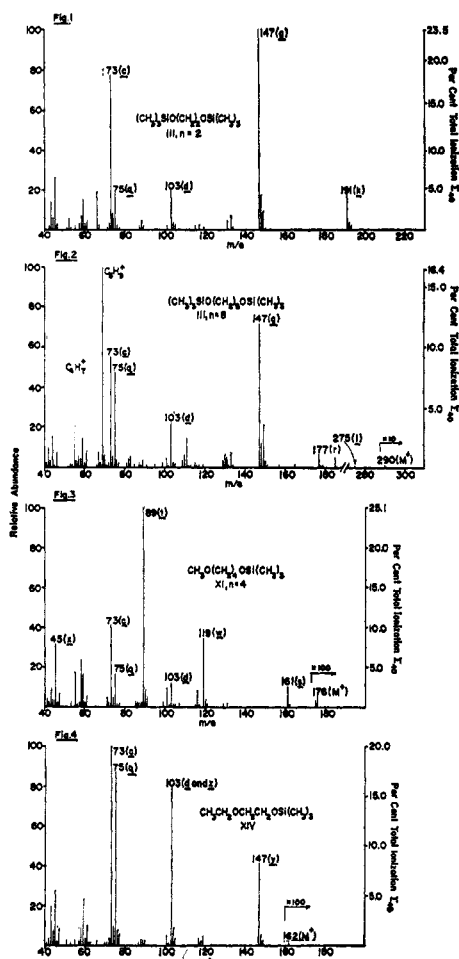


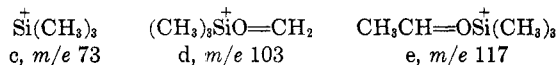
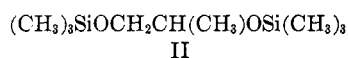
Figure 1.—Mass spectrum (CEC-103C) of ethylene glycol bis-trimethylsilyl ether (III, $n = 2$).

Figure 2.—Mass spectrum (CEC-103C) of 1,8-octanediol bis-trimethylsilyl ether (III, $n = 8$).

Figure 3.—Mass spectrum (CEC-103C) of 4-methoxybutyl trimethylsilyl ether (XI, $n = 4$).

Figure 4.—Mass spectrum (CEC-103C) of 2-ethoxyethyl trimethylsilyl ether (XIV).

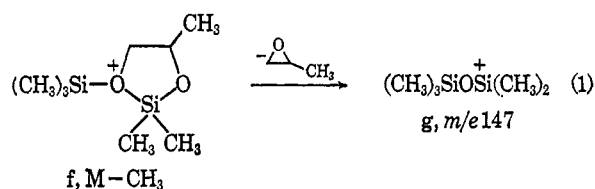
Further interest in the behavior of trimethylsilyl ethers upon electron bombardment was stimulated by the mass spectrum of 1,2-propanediol bis-trimethylsilyl ether (II) tabulated, without specific comment, by Sharkey, *et al.*⁸ The most intense peak in this spectrum occurs at m/e 73 (c) and the α -cleavage fragments d and e are also of appreciable abundance. By contrast with the normal alkyl trimethylsilyl ethers,^{7,8} the $M - CH_3$ peak is very weak (3.5% relative abundance).



The most interesting feature of the spectrum, however, is an abundant species (88% relative abundance) of mass 147 which must have the elemental composition $C_6H_{15}OSi_2$ and for which g seemed to us to be the most plausible representation. In view of the results presented below, we propose that the mass 147 ion (g) is formed by collapse of the cyclic oxonium ion form (f)

(8) A. G. Sharkey, R. A. Friedel, and S. H. Langer, *Anal. Chem.*, **29**, 770 (1957).

of an $M - CH_3$ precursor with elimination of the elements of propylene oxide (eq 1).



In light of the current interest in electron impact induced skeletal rearrangements⁹ and in the reported^{8,10,11} mass spectra of trimethylsilyl derivatives of polyhydroxy compounds, it was decided to examine the mass spectra of the bis-trimethylsilyl, phenyl trimethylsilyl, and methyl trimethylsilyl ethers of a series of polymethylene glycols together with a number of compounds of related structure. Such a study is not only pertinent for practical reasons, but is especially justified on mechanistic grounds because of interesting skeletal rearrangements.

Discussion

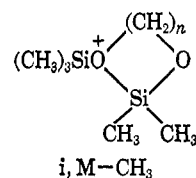
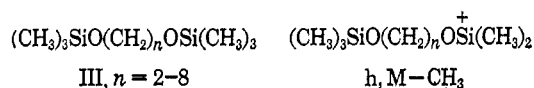
The mass spectra (Figures 1 and 2) of the trimethylsilyl ethers (III) of all polymethylene glycols from C_2 to C_8 show (Table I) an intense peak at m/e 147 having

TABLE I
ABUNDANCE OF THE REARRANGEMENT PEAK g (m/e 147)
IN THE MASS SPECTRA (70 eV) OF THE
POLYMETHYLENE GLYCOL BISTRIMETHYLSILYL ETHERS
 $(CH_3)_3SiO(CH_2)_nOSi(CH_3)_3$

n	CEC-103C ^a		A.E.I. MS-9 ^a	
	% Σ_{40}	% of base peak	% Σ_{40}	% of base peak
2	27.9	100	31.1	100
3	15.3	100	30.5	100
4	23.4	100	33.0	100
5	10.1	72	21.7	100
6	14.9	100	13.1	84
7	12.6	71	15.3	67
8	11.8	72	12.2	53

^a Discussion of this rearrangement peak (g) in the text of this paper is based upon data obtained from spectra recorded on the CEC-103C mass spectrometer; the A.E.I. MS-9 data are included for comparison.

the elemental composition $C_5H_{15}OSi_2$.¹² It is difficult to envisage any reasonable structure for this species other than g. In every case an abundant meta-

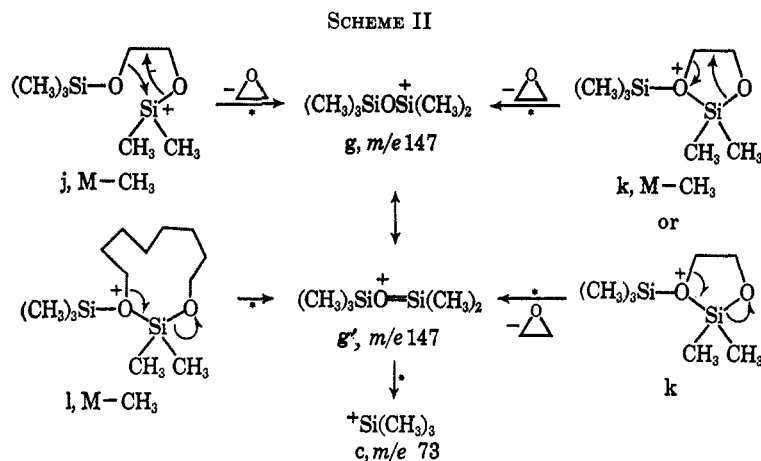


(9) For a complete review, see P. Brown and C. Djerassi, *Angew. Chem. Intern. Ed. Engl.*, **6**, 477 (1967).

(10) W. Richter, M. Vecchi, W. Vetter, and W. Walther, *Helv. Chim. Acta*, **50**, 364 (1967).

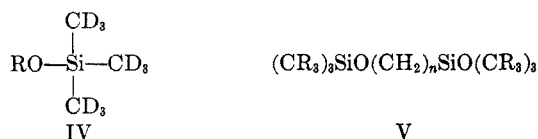
(11) G. Peterson, O. Samuelson, K. Anjou, and E. Sydow, *Acta Chem. Scand.*, **21**, 1251 (1967).

(12) The composition of all fragments discussed in this report were confirmed, when necessary, by high-resolution mass measurements.



stable ion¹³ is observed for the formation of *g* from an $M - \text{CH}_3$ progenitor, and it seems likely that the silicon-oxygen bond is already formed in the precursor. Intuitively, it appears more probable that the remarkably small decrease in the abundance of the m/e 147 species with increasing chain length (Table I) is better explained in terms of the collapse of a cyclic oxonium ion (i) rather than a $1, (n + 2)$ shift of the trimethylsilyloxy group in the open-chain form (h) of the $M - \text{CH}_3$ precursor. Thus, in the case of III ($n = 2$), a 1,4 shift in *j* seems as likely as the formation and collapse of *k*, but for III ($n = 8$) a direct 1,10 shift is improbable. This, of course, still leaves unanswered the problem of the surprising ease of formation (albeit, with equal ease of fragmentation-rearrangement) of a cyclic $M - \text{CH}_3$ ion such as *l* (Scheme II).

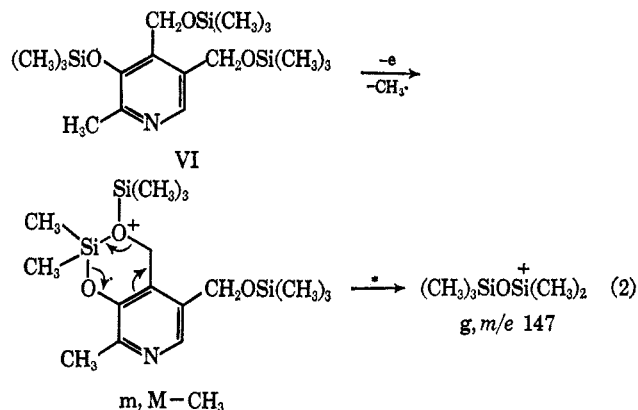
McCloskey, *et al.*,¹⁴ have recently developed a unique method of labeling the methyl groups of trimethylsilyl ethers with deuterium atoms (IV). This process greatly facilitates the obtaining of structural information on fragment ions especially in cases where high-resolution mass measurements do not provide adequate data (e.g., the mechanistic fate of methyl hydrogens in trimethylsilyl derivatives). The utility of this label-



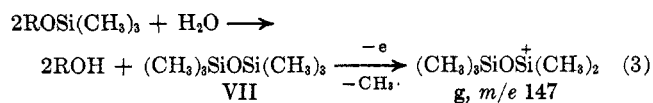
ing technique is illustrated by the mass spectra of 1,10-decanediol bistrimethylsilyl ether (V, $n = 10$, $R = \text{H}$), 1,22-docosane bistrimethylsilyl ether (V, $n = 22$, $R = \text{H}$), and their corresponding labeled analogs ($R = \text{D}$). These compounds also exhibit abundant m/e 147 peaks; and on the basis of the appropriate mass shift (m/e 147 \rightarrow m/e 162) in the labeled species, McCloskey, *et al.*,¹⁴ likewise postulate structure *g* for the ion of mass 147. It is interesting to note that they find no metastable ion for the formation of the mass 147 species from an $M - \text{CH}_3$ progenitor.

Richter, *et al.*,¹⁰ encountered an intense m/e 147 peak in the mass spectrum of the trimethylsilyl deriva-

tive of pyridoxine (VI), and they also postulate, with metastable evidence, its genesis from a cyclic oxonium ion $M - \text{CH}_3$ precursor ($m \rightarrow g$) (eq 2).



A very common impurity⁷ often contaminating trimethylsilyl ethers, which have been exposed to atmospheric moisture, is hexamethyldisiloxane (VII) (eq 3). Unfortunately, the base peak in the mass spec-

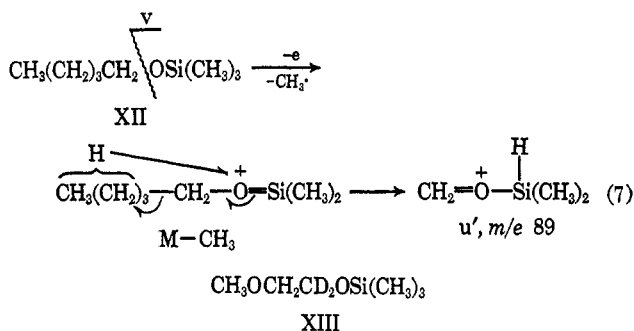


trum¹⁵ of hexamethyldisiloxane (VII) occurs at m/e 147. In order to ensure that every precaution was taken to prevent the formation of this impurity, it was decided to record the mass spectrum of an equimolar mixture of the bistrimethylsilyl (III, $n = 2$) and bistriethylsilyl (VIII) ethers of ethylene glycol which were synthesized and stored in the same manner as were the polymethylene glycol bistrimethylsilyl ethers (III). If any impurity were formed, one would expect contamination by three compounds (VII, IX, and the mixed product X). Therefore, the mass spectrum of the equimolar mixture would be expected to exhibit, aside from the expected m/e 147 and m/e 261 (n) peaks which are found, respectively, in the mass spectra of bistrimethylsilyl (III, $n = 2$) and bistriethylsilyl (VIII) ether of ethylene glycol alone, peaks at m/e 175 (o , $M - \text{C}_2\text{H}_5$) and m/e 189 (p , $M - \text{CH}_3$) due to fragmentation of the presumed impurity (X) (eq 4). In fact, no peaks were encountered at m/e 175 or m/e 189, whereupon we feel confident that the m/e 147 peak observed in bistri-

(13) The observation of a metastable ion for a given process is indicated in the fragmentation schemes by an asterisk beside the arrow.

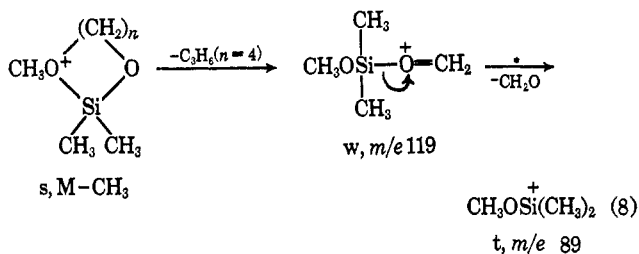
(14) J. A. McCloskey, R. N. Stillwell, and A. M. Lawson, *Anal. Chem.*, **40**, 233 (1968). We wish to express our appreciation to Professor McCloskey for a copy of his manuscript prior to publication.

(15) V. H. Dibeler, F. L. Mohler, and R. M. Reese, *J. Chem. Phys.*, **21**, 180 (1953).



As in the case of the bistrimethylsilyl ethers (III), the formation of the rearrangement ion *t* is not greatly affected (see Table II) by ring size (in *s* or an equivalent transition state). In the mechanism shown above (*s* → *t*) it is assumed that the oxygen atom attached to the methyl group is retained, by analogy with the phenoxy series (see below), where evidence from isotope labeling is available.

In addition one may note that the molecular ions are very weak, *M* - CH₃ is moderately abundant ($\Sigma_{40} = 7.8$) when *n* = 2 and weak ($\Sigma_{40} = 2.5$ and 0.8, respectively) when *n* = 4 or 5. In all three compounds, the trimethylsilyl cation (*c*, $\Sigma_{40} = 10-18$) and the α -cleavage fragment (*x*, $\Sigma_{40} = 8-10$) are prominent with the alternative α -cleavage ion (*d*, $\Sigma_{40} = 3-5$) being less abundant (see, for instance, Figure 3). When *n* = 4 and 5 a species of mass 119 ($\Sigma_{40} = 8-9$) appears for which structure *w* is proposed. In a manner analogous to the fragmentation pattern (*i* → *r* → *g*) observed in the case of polymethylene glycol bistrimethylsilyl ethers (III, *n* = 3-8), it is felt that *w* is generated from an *M* - CH₃ precursor (*s*); and observation of a metastable peak at *m/e* 66.7 (calcd $89^2/119 = 66.6$) supports the postulated elimination of formaldehyde from this species (*w*) to yield *t* (*m/e* 89) (eq 8).



The two most intense peaks in the spectrum (Figure 4) of 2-ethoxyethyl trimethylsilyl ether (XIV) are at *m/e* 73 (*c*, $\Sigma_{40} = 20.0$) and *m/e* 75 (*q*, $\Sigma_{40} = 17.0$); the *M* - CH₃ (*m/e* 147) peak is moderately abundant ($\Sigma_{40} = 8.2$). The sole remaining prominent peak occurs at *m/e* 103 ($\Sigma_{40} = 15.8$), 95% of which is due to a species of the composition C₄H₁₁OSi. This fragment could conceivably arise by three different fragmentation modes.

Simple α cleavage would produce species *d*, whereas loss of a silylmethyl group (XIV → *y*) followed by skeletal rearrangement and elimination of ethylene oxide from *y* would yield the fragment ion *z*. A third alternative would be fission of the ethoxyl methyl group to produce the *M* - CH₃ species *aa* which also could rearrange and eliminate ethylene oxide to yield *d'* (Scheme III). Although the two ions (*d* and *d'*) are of identical structure, they derive their methylene groups from a different portion of the parent molecule.

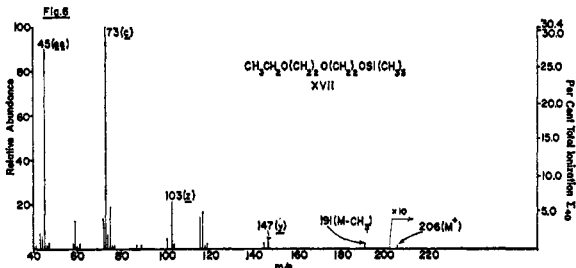
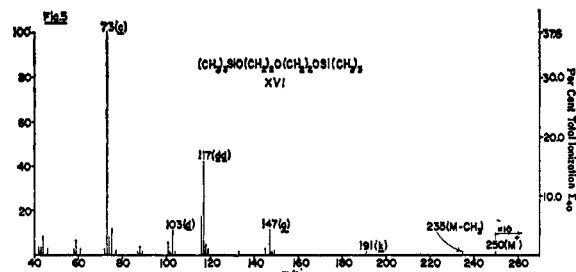
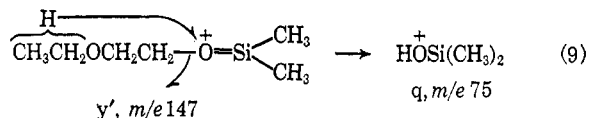


Figure 5.—Mass spectrum (Atlas CH-4) of diethylene glycol bistrimethylsilyl ether (XVI).

Figure 6.—Mass spectrum (Atlas CH-4) of carbitol trimethylsilyl ether (XVII).

A firm distinction among the three pathways was reached by synthesis of the *d*₅-ethoxy analog XV. In the mass spectrum of this compound, one would expect fragment *d* to remain at mass 103, whereas *z* would shift to *m/e* 108 and *d'* to *m/e* 105. In actual fact, the spectrum of XV revealed that 42% of the *m/e* 103 peak results from α cleavage (*d*) and 58% from the rearrangement ion (*z*); as might be expected, species *d'* does not contribute to the *m/e* 103 peak. This spectrum also indicated that, in the formation of the dimethylsilanol ion (*q*, *m/e* 75), 71% of the hydrogen transfer occurs from the ethoxy group (*y'* → *q*) (eq 9).



With the intention of obtaining some information on the relative ease of rearrangement through a five- and eight-membered-ring form of an *M* - CH₃ precursor, the mass spectra of diethylene glycol bistrimethylsilyl ether (XVI, see Figure 5) and carbitol trimethylsilyl ether (XVII, see Figure 6) were examined, since these compounds may yield either a five- or eight-membered-ring oxonium ion (*bb* or *cc*, respectively) by ejection of a methyl radical. The latter (*cc*) could then decompose directly to the rearrangement ion (*g* or *z*), while the former (*bb*) could yield *g* or *z* in a two-step process by way of *k* (*M* - CH₃ from III, *n* = 2) or *y* (*M* - CH₃ from XIV). Unfortunately the rearrangement peaks in the spectra of both XVI and XVII (see Figures 5 and 6, respectively) are quite weak, *viz.* 0.4 and 0.9% Σ_{40} for the first rearrangement ion (*k* and *y*, respectively) and 4.1 and 6.4% Σ_{40} for the second rearrangement ion (*g* and *z*, respectively). In neither case is a metastable ion observed¹⁷ for the direct formation of *g* or *z* from *M* - CH₃ (*cc*) but strong metastable ions are present for the two-step

(17) Metastable ions were recorded using an Atlas CH-4 mass spectrometer in conjunction with the logarithmic transfer recorder described by R. T. Aplin, H. Budzikiewicz, H. S. Horn, and J. Lederberg, *Anal. Chem.*, **37**, 776 (1965).

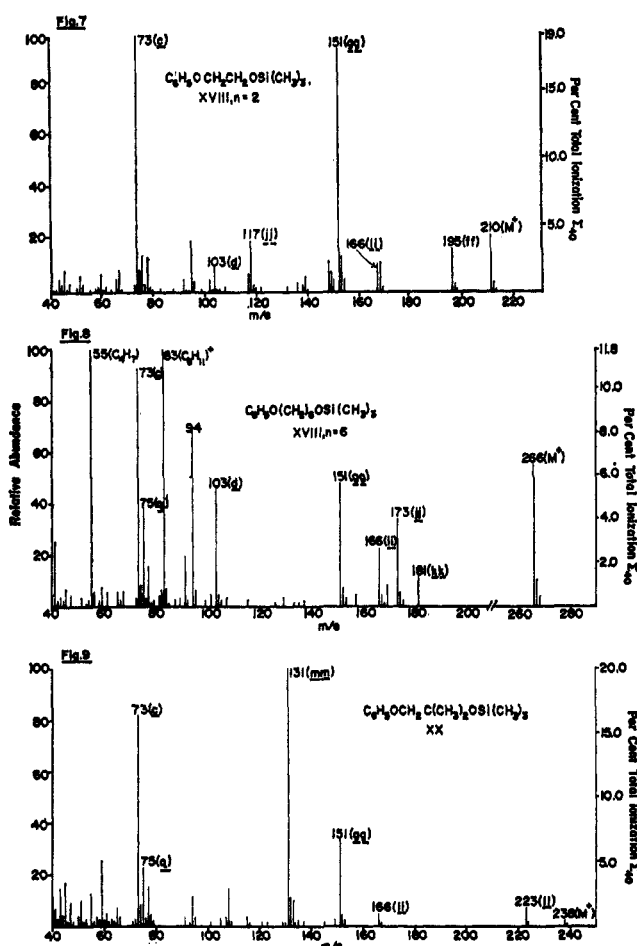
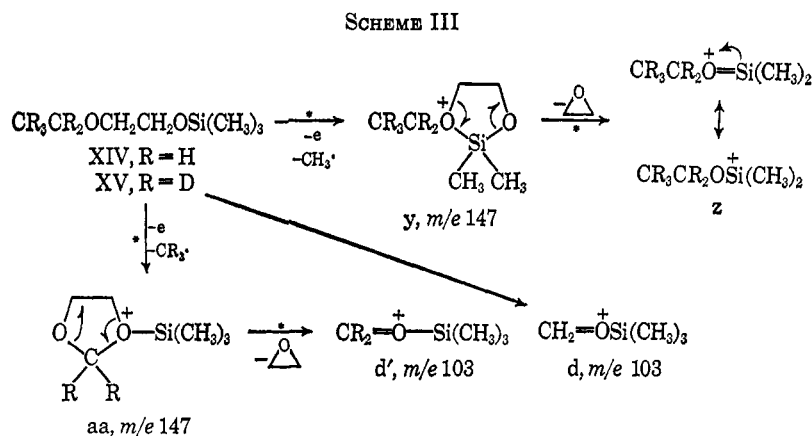


Figure 7.—Mass spectrum (AEI-MS-9) of 2-phenoxyethyl trimethylsilyl ether (XVIII, $n = 2$).

Figure 8.—Mass spectrum (AEI-MS-9) of 6-phenoxyhexyl trimethylsilyl ether (XVIII, $n = 6$).

Figure 9.—Mass spectrum (CEC-103C) of 2-phenoxy-1,1-dimethylethyl trimethylsilyl ether (XX).

rearrangement (*via* *bb*) (Scheme IV). When the ionization potential is reduced, the ion yield of the first rearrangement ion increases to a much greater extent (from 0.4% at 70 eV to 2.0% at 15 eV for *k* and from 0.9% at 70 eV to 3.0% at 15 eV for *y*) than does the yield of the second rearrangement fragment (from 4.1% at 70 eV to 7.9% at 15 eV for *g* and from 6.4% at 70 eV to 7.0% at 15 eV for *z*). One may conclude, therefore, that in accord with expectation, a five-membered ring is favored over an eight-membered counterpart.

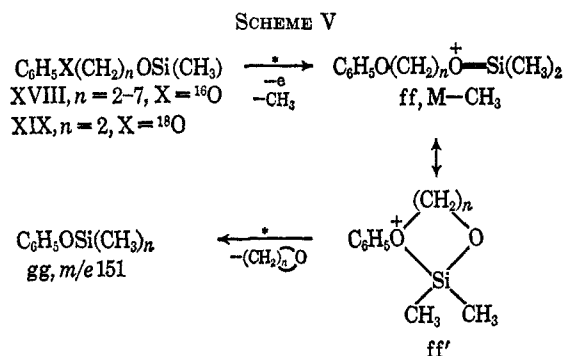
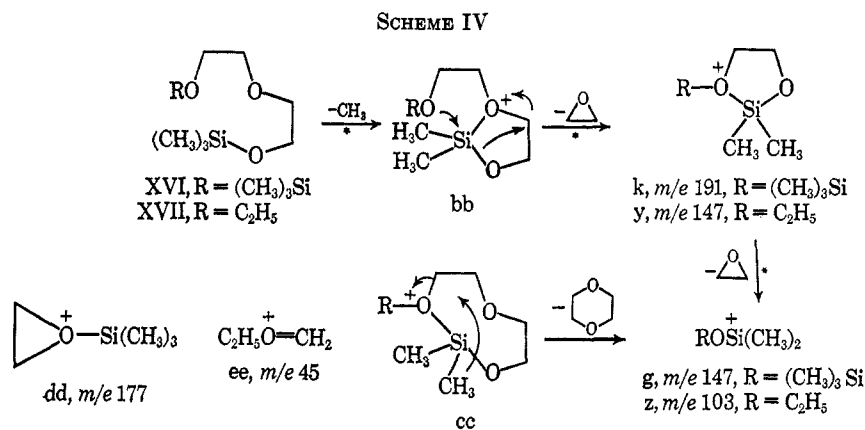
The base peak in the 70-eV spectra of both XVI and XVII (see Figures 5 and 6, respectively) is due to the trimethylsilyl cation (m/e 73, $\Sigma_{40} = 37.6$ and 30.4, respectively). Only one other peak exceeds 25% relative intensity in each spectrum; m/e 117 (plausibly represented as *dd*, $\Sigma_{40} = 15.8$) for XVI (Figure 5) and m/e 45 (the α -cleavage ion *ee*, $\Sigma_{40} = 27.4$) for XVII (Figure 6).

Despite the precautions taken in ensuring that the rearrangement ion *g* (m/e 147) in the mass spectra of the polymethylene glycol bistrimethylsilyl ethers (III, $n = 2-8$) was not due to impurity, it was decided to synthesize a series of compounds in which an analogous fragmentation scheme would produce a rearrangement ion which could not have a mass of 147. To this end, the spectra of the phenoxy polymethylene trimethylsilyl ethers (XVIII, $n = 2-7$) were recorded (see, for example, Figures 7 and 8). A rearrangement pattern analogous to that incurred in the polymethylene glycol bistrimethylsilyl ethers (III) involves cleavage of a methyl radical from the molecular ion to yield the $M - \text{CH}_3$ species (*ff*, $n = 2-7$) which can be depicted as a cyclic oxonium ion (*ff'*, $n = 2-7$) (Scheme V). Loss of the neutral polymethylene oxide ($n = 2-7$) then gives the rearranged fragment *gg* (m/e 151, $\text{C}_8\text{H}_{11}\text{OSi}$), which is an important peak in the 70-eV spectra (see Table III) of all phenoxy polymethylene trimethylsilyl

TABLE III
ABUNDANCE OF THE REARRANGEMENT PEAKS (*gg*) (m/e 151)
AND *ii* (m/e 166) IN THE MASS SPECTRA
OF THE PHENOXY POLYMETHYLENE TRIMETHYLSILYL ETHERS
 $\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ (XVIII)

n	m/e 151		m/e 166		m/e 151		m/e 166	
	70 eV	12 eV	70 eV	12 eV	70 eV	12 eV	70 eV	12 eV
	% Σ_{40}	% of base peak	% Σ_{40}	% of base peak	% Σ_{40}	% of base peak	% Σ_{40}	% of base peak
2	18.1	95	2.1	11
3	17.6	98	3.8	13	2.3	13	6.7	23
4	11.0	51	1.2	2	4.5	21	16.2	28
5	6.7	48	0.5	2	2.4	17	8.1	21
6	5.7	48	0.5	2	2.6	22	7.0	28
7	4.8	24	0.5	2	2.2	11	5.4	18

ethers (XVIII, $n = 2-7$). Like the rearrangement peak (m/e 147) in the mass spectra of III (see Table I), the m/e 151 peak decreases markedly with increasing chain length at 70 eV. As was mentioned previously, this tendency may reflect the difficulty in formation of a cyclic $M - \text{CH}_3$ species (*ff'*) as chain length increases;



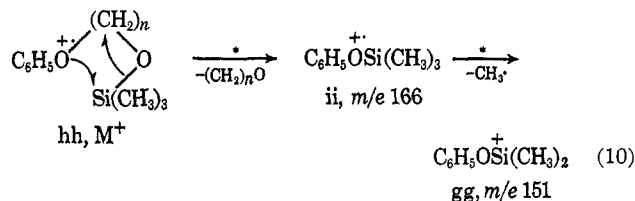
or if one assumes this process involves a 1, (n + 2) shift, the trend is to be expected.

One important labeling experiment was performed on the β-phenoxyethyl trimethylsilyl ether (XVIII, n = 2), namely, incorporation of ¹⁸O into the phenoxy oxygen atom to confirm the fact that the silyl oxygen was eliminated in the rearrangement process (XVIII → gg). As expected the m/e 151 peak was shifted quantitatively to m/e 153 in the spectrum of XIX.

The molecular ion increases and the M - CH₃ ion decreases in abundance as the polymethylene chain is lengthened. It was felt that the daughter-parent relationship between the m/e 151 ion (gg) and the M - CH₃ species (ff) would be indicated by observation of a decrease in per cent total ionization of m/e 151 and a corresponding increase of M - CH₃ when the spectra are recorded at 12-eV ionizing energy (see Table III). In actual fact, at 12 eV the rearrangement species still decrease (Σ₄₀ = 3.8 when n = 2 and 0.5 when n = 7) in abundance with increasing chain length but the expected large increase in the abundance of the M - CH₃ precursor was not observed. This anomaly suggested the possibility of other more favorable fragmentation modes for generation of the rearrangement peak and subsequent analysis of the metastable ions provided the clue to alternative formulations.

The observation in all spectra of a metastable peak at m/e 137.3 (calcd 151²/166 = 137.4) suggested the possible genesis of the mass 151 rearrangement ion by fission of a methyl radical from a species of mass 166 (ii, C₆H₁₄OSi); although relatively weak at 70 eV (see Table III), this peak appears in the spectra of all phenoxypolymethylene trimethylsilyl ethers (XVIII). This odd-electron species (ii) results from rearrangement of the molecular ion (hh) with elimination of the central portion of the molecule—a transition (hh → ii) which

is also supported by the appropriate metastable peaks. It appears (see Table III) that at 70 eV this 1, (n + 2) shift reaches a peak when a 1,6 relationship is encountered, and surprisingly does not decrease significantly with increasing chain length (n = 5, 6, 7 are about equal). One must note, however, that at 70 eV the mass 166 species fragments further to form gg (m/e 151) and that the data with regard to amount of 1, (n + 2) shifts would be much more significant when obtained at 12 eV where further decomposition of ii would be minimized (eq 10). Indeed, at this ionizing



energy, there is a definite decrease (see Table III) in the intensity of the m/e 166 peak with increasing chain length after reaching its maximum when n = 4.

Another important fragmentation to be discussed in the case of the phenoxypolymethylene trimethylsilyl ethers (XVIII, n = 2-7) involves a series of peaks (jj) for which there is no analogy in the polymethylene glycol bistrimethylsilyl (III) and the methoxypolymethylene trimethylsilyl (XI) ether series. Fission of a phenoxy radical from the molecular ion (hh) generates a fragment ion which can be formulated as a cyclic oxonium ion (jj), but quantitative statements about preferred ring size should only be based on low (12 eV) voltage spectra (see Table IV), as there is in every case (n =

TABLE IV
ABUNDANCE OF PEAK jj IN THE MASS SPECTRA
OF THE PHENOXYPOLYMETHYLENE TRIMETHYLSILYL ETHERS
C₆H₅O(CH₂)_nOSi(CH₃)₃ (XVIII)

n	70 eV			12 eV		
	m/e	% Σ ₄₀	% of base peak	% Σ ₄₀	% of base peak	
2	117	3.8	20	
3	131	5.0	28	12.5	43	
4	145	21.5	100	57.8	100	
5	159	10.6	76	38.6	100	
6	173	4.0	34	14.8	59	
7	187	0.6	3	2.4	8	

2-7), a large metastable peak corresponding to further decomposition of jj to yield the trimethylsilyl cation c (m/e 73) (eq 11). As is illustrated by the 12-eV spectra

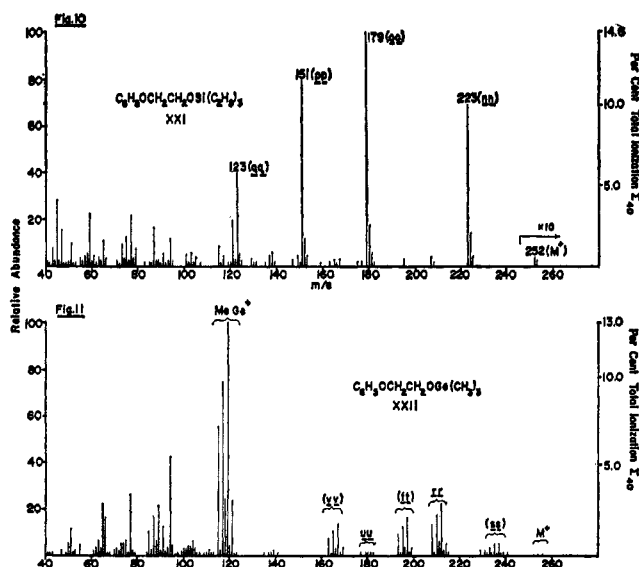
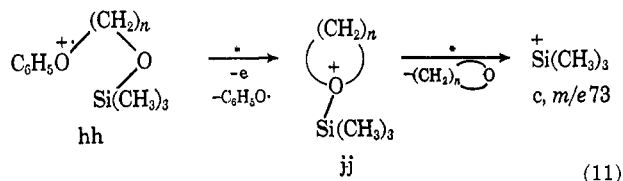


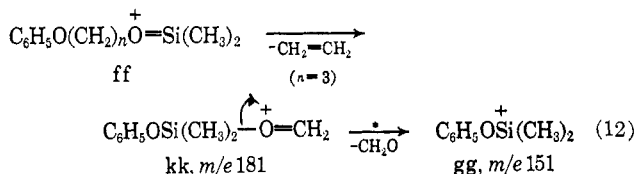
Figure 10.—Mass spectrum (CEC-103C) of 2-phenoxyethyl triethylsilyl ether (XXI).

Figure 11.—Mass spectrum (CEC-103C) of 2-phenoxyethyl trimethylgermanium oxide (XXII).

(Table IV), ring size appears to be particularly important in this fragmentation. In the case where *jj* exists as a five- and six-membered ring (*jj*, $n = 4$, and *jj*, $n = 5$, respectively) it produces the base peak; however, in the less favorable eight-membered structure ($n = 7$, m/e 181) the peak is insignificant (8% relative intensity).



Rearrangement of the $\text{M} - \text{CH}_3$ fragment (*ff*) to yield *kk* (m/e 181) and subsequent loss of formaldehyde to yield m/e 151 (*gg*) (eq 12) in a manner analogous to the fragmentation sequence ($i \rightarrow r \rightarrow g$) in the spectra of III ($n = 3-8$) occurs to a minor extent in XVIII when $n = 3-7$; this peak decreases with increasing chain length ($\Sigma_{40} = 3.8$ when $n = 3$ and 1.2 when $n = 7$). In all cases, except when $n = 7$, a metastable peak is observed at m/e 126.0 (calcd $151^2/181 = 126.0$).

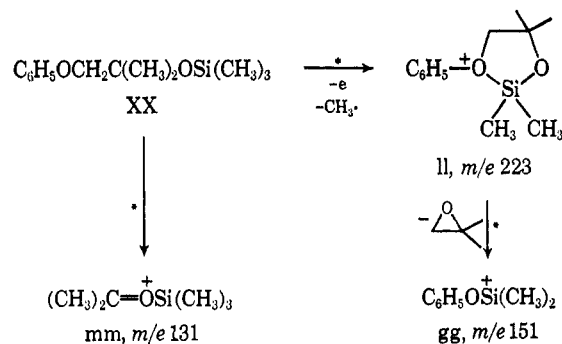


Another fragment found in the spectra of XVIII is the intense peak at m/e 73 (*c*, 10–20% Σ_{40}); metastable peaks indicate that *jj* and the α -cleavage ion *d* (m/e 103, $\Sigma_{40} = 4.0 \pm 1.5$) are progenitors of this ion. This supports the conclusions made in a previous paper⁷ disclaiming the postulated⁸ formation of *c* (m/e 73) by direct fission of the molecular ion. Also, at 70 eV, intense hydrocarbon peaks appear at m/e 55 (C_4H_7) when $n = 4, 6$, and 7; at m/e 69 (C_5H_9) when $n = 5$; and at m/e 83 (C_6H_{11}) when $n = 6$. Finally, as the methylene chain length increases, there is encountered

an intense peak at m/e 94 ($\Sigma_{40} = 8-9$ when $n > 4$). High-resolution mass measurements indicate an elemental composition of $\text{C}_6\text{H}_8\text{O}$ thus suggesting that m/e 94 is generated by a hydrogen transfer process to yield a phenol-like odd-electron species.

As in the case of the benzyl trimethylsilyl ethers,⁷ the presence of a branched chain causes a pronounced decrease in the amount of rearrangement species formed following electron bombardment, although the effect is not so great as in the benzyl series. In the mass spectrum (Figure 9) of 1,1-dimethyl-2-phenoxyethyl trimethylsilyl ether (XX), the $\text{M} - \text{CH}_3$ peak (*ll*, m/e 223) is weak ($\Sigma_{40} = 1.4$), the trimethylsilyl cation (*c*, m/e 73) is abundant ($\Sigma_{40} = 1.4$), and the rearrangement ion (*gg*, m/e 151) carries 6.8% of the total ion current. The base peak, m/e 131 ($\Sigma_{40} = 16.4$), is due to the α -cleavage ion (*mm*), which is greatly favored because of the high degree of branching at the fission site (Scheme IV).

SCHEME VI

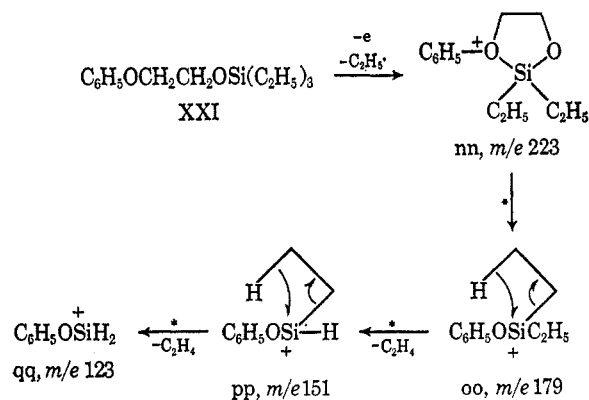


It was decided to record the spectrum of 2-phenoxyethyl triethylsilyl ether (XXI) in order to ascertain whether replacing the silylmethyl groups with the slightly bulkier silylethyl groups would inhibit the amount of skeletal rearrangement. The base peak (m/e 179) in this mass spectrum (Figure 10) is indeed associated with the rearrangement ion *oo* (m/e 179, $\Sigma_{40} = 14.6$) resulting from loss of ethylene oxide from the $\text{M} - \text{C}_2\text{H}_5$ precursor *nn* (m/e 223, $\Sigma_{40} = 10.0$). The two other prominent peaks (m/e 151 and m/e 123) in this spectrum (Figure 10) are generated by the hydrogen rearrangement processes which have been found⁷ to be characteristic of all triethylsilyl ethers. Expulsion of two successive ethylene molecules from the rearrangement ion (*oo*) yields *pp* (m/e 151, $\Sigma_{40} = 11.5$) and *qq* (m/e 123, $\Sigma_{40} = 5.8$). In this particular instance, the triethylsilyl moiety certainly has no retarding effect upon the rearrangement process, as the ion *oo* (m/e 179) and two of its daughter ions (*pp* and *qq*) contribute 41.9% of the total ion current (Scheme VII).

It was also decided to ascertain what effect replacing the silicon atom with germanium would have upon the rearrangement process. The rearrangement persisted in the case of the trimethylgermanium oxide (XXII), whose spectrum (Figure 11) shows a series of rearrangement ions followed by successive losses of methyl radicals. No metastable ion was observed and it is not known whether *tt* ($\Sigma_{40} = 5.0$, total isotopic species¹⁸) is formed by an initial loss of ethylene oxide, through *rr*

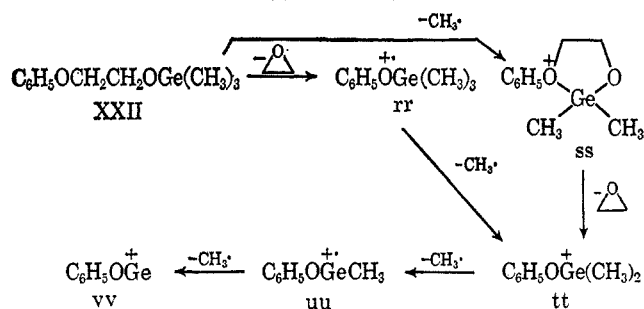
(18) The stable isotopes of germanium are Ge^{70} (20.5%), Ge^{72} (27.4%), Ge^{73} (7.7%), Ge^{74} (36.6%) and Ge^{76} (7.8%).

SCHEME VII



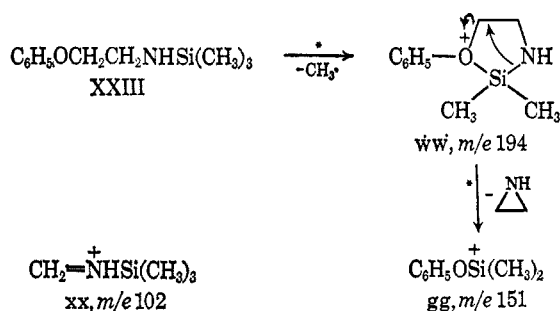
($\Sigma_{40} = 8.0$, total isotopic species), from the molecular ion, or through a cyclic $\text{M} - \text{CH}_3$ intermediate ss ($\Sigma_{40} < 0.1$, total isotopic species). Including the ions uu ($\Sigma_{40} = 0.5$, total isotopic species) and vv ($\Sigma_{40} = 4.0$, total isotopic species) (Scheme VIII), the total rearrangement yield is 17.5% of the total ion current. The molecular ion is extremely weak and the trimethylgermanium cation $[(\text{CH}_3)_3\text{Ge}^+]$ accounts for the base peak ($\Sigma_{40} = 36.0$, total isotopic species).

SCHEME VIII



Substitution of a nitrogen atom for the oxygen atom in the case of the benzyl trimethylsilyl ethers⁷ caused only a small decrease in the amount of rearrangement species. Replacement of the trimethylsilyloxy group of 2-phenoxyethyl trimethylsilyl ether (XVIII, $n = 2$) (Scheme IX) by a trimethylsilylamino group results

SCHEME IX



in a more pronounced decrease (Table V) in the amount of rearrangement ion (gg), but the latter still remains a prominent feature ($\Sigma_{40} = 6.4$) in the spectrum of XXIII. Two other peaks exceed the latter in intensity, namely, the trimethylsilyl cation c (m/e 73, $\Sigma_{40} = 15.2$) and the α -cleavage ion xx (m/e 102, $\Sigma_{40} = 29.3$). The molecular ($\Sigma_{40} = 0.3$) and $\text{M} - \text{CH}_3$ (ww , $\Sigma_{40} = 0.9$) ions are both weak.

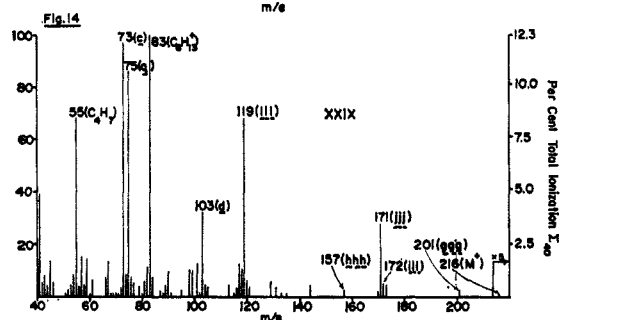
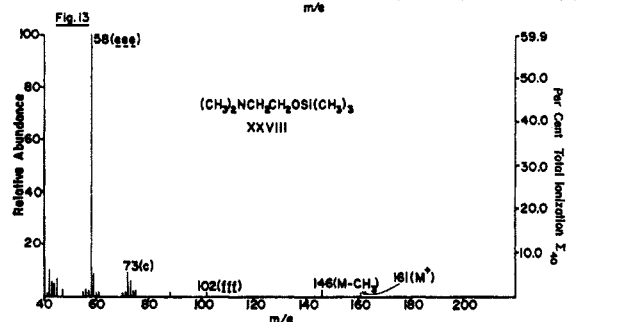
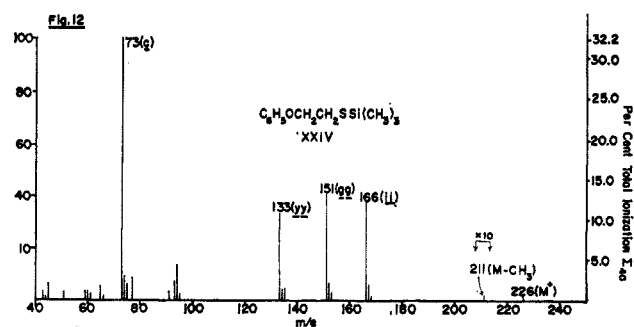


Figure 12.—Mass spectrum (AEI-MS-9) of 2-phenoxyethyl trimethylsilyl sulfide (XXIV).

Figure 13.—Mass spectrum (CEC-103C) of 2-N,N-dimethylaminoethyl trimethylsilyl ether (XXVIII).

Figure 14.—Mass spectrum (AEI-MS-9) of 2-(cyclohexyloxy)ethyl trimethylsilyl ether [XXIX, $\text{C}_6\text{H}_{11}\text{OCH}_2\text{CH}_2\text{OSi}(\text{CH}_3)_3$].

TABLE V

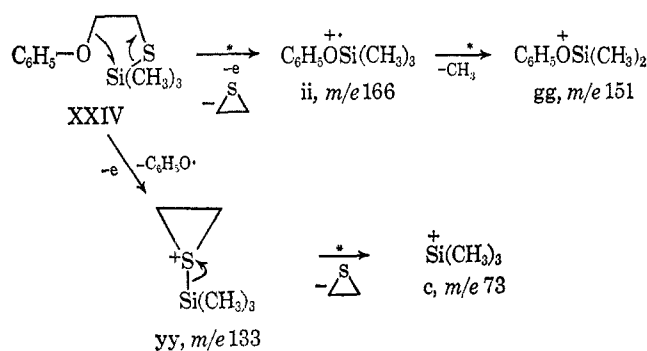
ABUNDANCE OF REARRANGEMENT ION IN THE MASS SPECTRA (70 eV) OF $\text{C}_6\text{H}_5\text{XCH}_2\text{CH}_2\text{YSi}(\text{CH}_3)_3$

Compound	X	Y	m/e	% Σ_{40}	% of base peak
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OSi}(\text{CH}_3)_3$ (XVIII, $n = 2$)	O	O	151	18.1	95
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{NHSi}(\text{CH}_3)_3$ (XXIII)	O	N	151	6.4	22
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{SSi}(\text{CH}_3)_3$ (XXIV)	O	S	151	13.2	41
$\text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_2\text{OSi}(\text{CH}_3)_3$ (XXV)	N	O	150	1.6	3
$\text{C}_6\text{H}_5\text{SCH}_2\text{CH}_2\text{OSi}(\text{CH}_3)_3$ (XXVI)	S	O	167	1.6	7
$\text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_2\text{NHSi}(\text{CH}_3)_3$ (XXVII)	N	N	150	0	0

Unlike the benzyl trimethylsilyl sulfides⁷ which exhibit very weak rearrangement peaks upon electron bombardment 2-phenoxyethyl trimethylsilyl sulfide (XXIV) shows (see Figure 12 and Table V) a very prominent rearrangement peak gg (m/e 151, $\Sigma_{40} = 13.2$).¹⁹ There is no metastable evidence for loss of ethylene sulfide from an $\text{M} - \text{CH}_3$ (m/e 211, $\Sigma_{40} = 0.05$) precursor; however, a large metastable peak is found at m/e 137.4 (calcd $151^2/166 = 137.4$) corresponding to expulsion of a methyl radical from the m/e 166 fragment (ii, $\Sigma_{40} = 12.2$) (Scheme X). As in the

(19) The parent thiol exhibited a slight thermal instability; therefore, its trimethylsilyl derivatives (XXIV) was adsorbed on activated charcoal and introduced using the direct probe inlet into the TO-4 ion source (heated only by the filament current to ca. 70°) of the Atlas CH-4 mass spectrometer. The recorded spectrum was practically identical with Figure 12 indicating that all peaks resulted from electron bombardment and not thermally induced reactions.

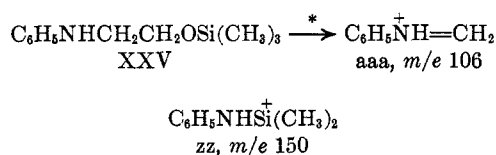
SCHEME X



case of the phenoxy polymethylene trimethylsilyl ethers (XVIII), there appears to be a significant amount of rearrangement of the molecular ion with expulsion of ethylene sulfide to yield m/e 166 (ii) which subsequently decomposes to m/e 151 (gg). Thus, as in the case of the benzyl trimethylsilyl sulfides⁷ there does not appear to be a large amount of rearrangement through an $M - \text{CH}_3$ intermediate to give the m/e 151 ion (gg). The fact that the rearrangement peak originates almost entirely by rearrangement of the molecular ion is very obvious when the spectrum is recorded at 12 eV. Here, one finds neither an m/e 151 nor an $M - \text{CH}_3$ peak, whereas m/e 166 becomes the most intense one ($\Sigma_{40} = 41.2$).

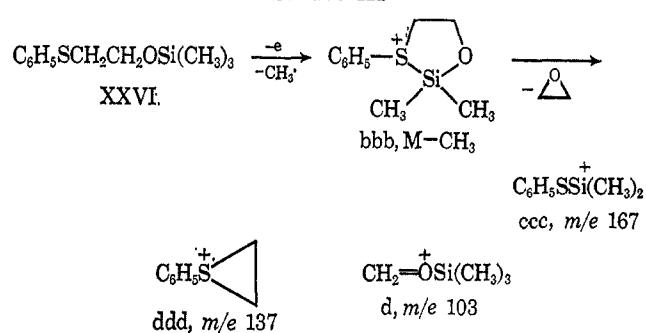
The base peak in the spectrum (Figure 12) of 2-phenoxyethyl trimethylsilyl sulfide (XXIV) is due to the trimethylsilyl cation c (m/e 73, $\Sigma_{40} = 32.2$). Both low voltage measurements and a metastable peak show that c arises by loss of ethylene sulfide from an m/e 133 precursor (yy, $\Sigma_{40} = 10.6$), the latter being the only other important peak remaining in the spectrum. High-resolution measurements show this fragment of mass 133 to have an elemental composition of $\text{C}_5\text{H}_{13}\text{SSi}$, thus suggesting a fragmentation sequence (XXIV \rightarrow yy \rightarrow c) analogous to that found in the case of the phenoxy polymethylene trimethylsilyl ethers (XVIII \rightarrow jj \rightarrow c).

In order to assess further the effect of replacing oxygen with nitrogen and sulfur, the spectra of 2-phenylamino- (XXV) and 2-thiophenoxyethyl trimethylsilyl ether (XXVI) were recorded. Interestingly, unlike 2-phenoxyethyl trimethylsilyl amine (XXIII), a very small amount of rearrangement ion zz (m/e 150, $\Sigma_{40} = 1.6$) is found (see Table V) in the spectrum of XXV, which is completely dominated by the α -cleavage ion (aaa, m/e 106, $\Sigma_{40} = 51.4$). The molecular ion ($\Sigma_{40} = 6.5$), the $M - \text{CH}_3$ peak ($\Sigma_{40} = 3.2$), and the trimethylsilyl cation ($\Sigma_{40} = 4.9$) are all quite weak in this spectrum.



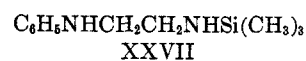
Substitution of sulfur (XXVI) for oxygen also causes a dramatic decrease in the amount of rearrangement species (see Table V); this result parallels more closely the behavior of the benzyl trimethylsilyl sulfides (Scheme XI).⁷ The rearrangement ion ccc (m/e 167) contributes only 1.6% of the ion current. The

SCHEME XI



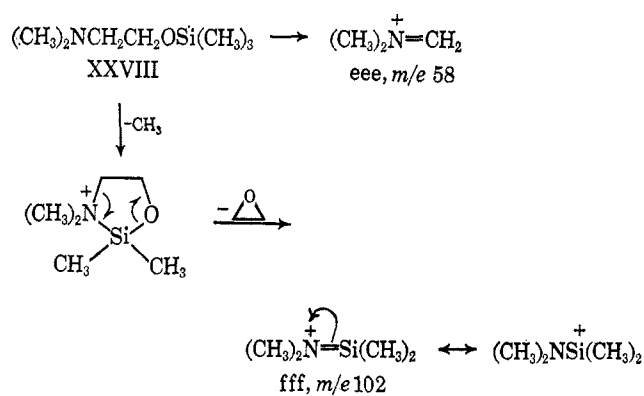
base peak in the spectrum is at m/e 73 (c , $\Sigma_{40} = 22.8$) and the remaining prominent species are the molecular ion ($\Sigma_{40} = 9.1$), $M - \text{CH}_3$ (bbb, $\Sigma_{40} = 11.4$), ddd (m/e 137, $\Sigma_{40} = 7.5$), and the α -cleavage fragment d ($\Sigma_{40} = 9.3$).

As might be expected (see Table V), the spectrum of N' -phenyl- N -(trimethylsilyl)ethylenediamine (XXVII) contains no rearrangement peak (zz , m/e 150). As in the case of XXV, the α -cleavage fragment aaa (m/e 106, $\Sigma_{40} = 23.3$) provides the base peak; the other α -cleavage ion (xx , m/e 102) is the second most intense peak ($\Sigma_{40} = 17.5$). Other abundant ions include the trimethylsilyl cation (c , $\Sigma_{40} = 11.2$) and the phenyl cation (m/e 77, $\Sigma_{40} = 6.5$).

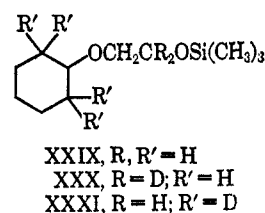


Finally, it may be noted that even in the spectrum (Figure 13) of the dimethylamino compound XXVIII, in which the α -cleavage ion (eee , m/e 58) carries 60% of the total ion current, the rearrangement ion (fff) is still observable (m/e 102, $\Sigma_{40} = 0.6$) (Scheme XII).

SCHEME XII

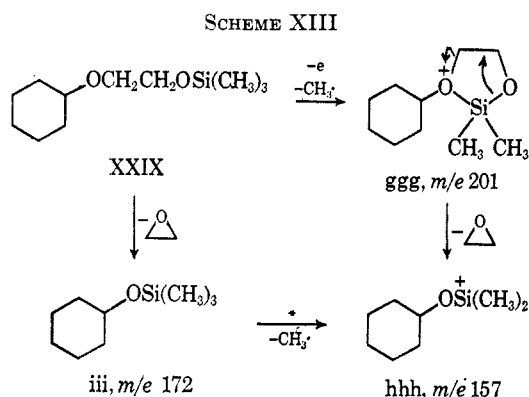


The last few spectra to be discussed result from an attempt to bridge the gap in structure between 2-ethoxyethyl (XIV) and 2-phenoxyethyl (XVIII, $n = 2$) trimethylsilyl ether. Consequently, the mass spectrum of 2-(cyclohexyloxy)ethyl trimethylsilyl ether (XXIX) was recovered. It is interesting to note that, although this spectrum (Figure 14) exhibits many peaks

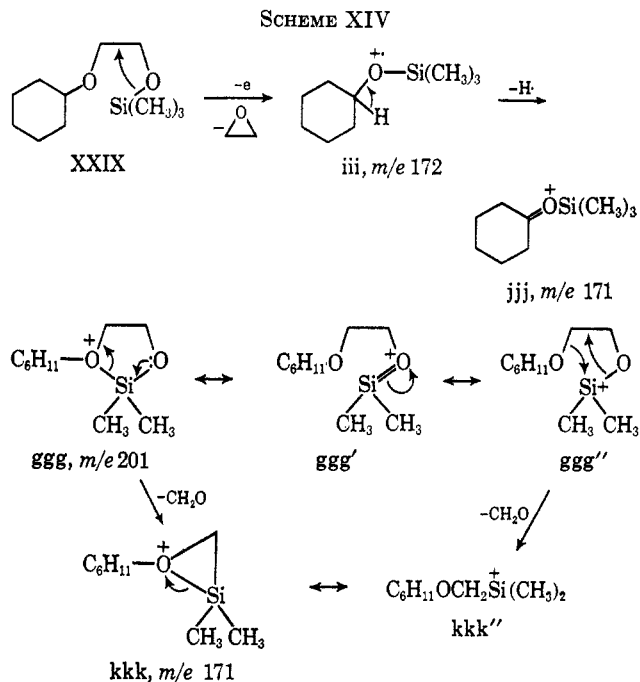


derived by pathways analogous to those found in the previous cases, a few of the most abundant peaks were found to be unique.

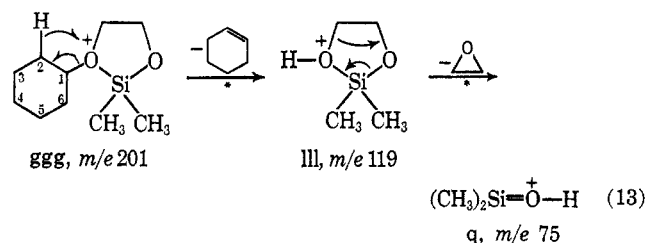
Typical of many trimethylsilyl ethers, the molecular ion (m/e 216) is weak ($\Sigma_{40} = 0.1$), the $M - CH_3$ peak ggg (m/e 201) is surprisingly weak ($\Sigma_{40} = 0.2$), the trimethylsilyl cation c (m/e 73) is very strong ($\Sigma_{40} = 11.9$), and the α -cleavage ion d (m/e 103, $\Sigma_{40} = 3.9$) is relatively abundant. Hydrocarbon peaks are also very intense with the cyclohexyl ion (m/e 83) accounting for the base peak ($\Sigma_{40} = 12.3$) and m/e 55 (C_4H_7) contributing 8.4% of the total ion current. It was rather surprising to find that loss of propylene oxide from the rearranged $M - CH_3$ species ggg (m/e 201) in the usual manner to yield a rearrangement ion hhh (m/e 157, $\Sigma_{40} = 0.2$) hardly occurs. In fact, the minute metastable peak at m/e 143.3 (calcd $157^2/172 = 143.3$) suggests that what little hhh is forming probably has the m/e 172 species (iii , $\Sigma_{40} = 0.6$) as its progenitor (Scheme XIII).



The appearance of a moderately abundant peak at m/e 171 ($\Sigma_{40} = 3.3$), which becomes one of the primary peaks ($\Sigma_{40} = 11.6$) when the spectrum is recorded at 12 eV, suggested a fragmentation mode which had not been encountered previously. High-resolution mass measurements showed this moiety to have the elemental composition $C_9H_{19}OSi$, and it was felt that one possible mode of genesis for this fragment might involve a two-step process ($XXIX \rightarrow iii \rightarrow jjj$). No metastable peaks could be located, however, either for the initial loss of the elements of ethylene oxide from the molecular ion or for subsequent expulsion of a hydrogen atom from the species of mass 172; furthermore, the m/e 171 peak increases in intensity when the spectrum is recorded at low voltage, making the loss of a hydrogen atom from the m/e 172 species an unlikely occurrence. An alternative formulation for the genesis of the mass 171 ion involves loss of formaldehyde from an $M - CH_3$ precursor (ggg , m/e 201). For descriptive purposes this process can be visualized as occurring either from the open-chain species ggg'' to yield kkk'' or from the alternate resonance form ggg to yield kkk (Scheme XIV). Again, there is no metastable evidence for this transition. Two labeling experiments were performed which support the occurrence of either of these fragmentation schemes. As expected, the spectrum of the α -labeled analog XXX reveals no shift of m/e 171, whereas the spectrum of the cyclohexyl-labeled analog XXXI indicates a shift in mass to m/e 175.



The final fragmentation to be discussed involves the intense ($\Sigma_{40} = 8.4$) m/e 119 peak which completely dominates ($\Sigma_{40} = 22.3$) the 12-eV spectrum. High-resolution mass measurements indicate an elemental composition of $C_4H_{11}O_2Si$ for this species and the labeling experiments (see Table VI) indicate the possible formation of a cyclic species as well as occurrence of a hydrogen transfer process. A small metastable peak at m/e 70.5 (calcd $119^2/201 = 70.4$) suggested that the m/e 119 ion is generated by loss of cyclohexene from the $M - CH_3$ ion ($ggg \rightarrow ll$, eq 13). This process obeys the



labeling results (Table VI) in that the ethylene chain is retained (see XXX) and the cyclohexyl group is lost (see XXXI). Although the hydrogen transfer process is indicated as occurring from the C-2 position of the cyclohexyl moiety, only 53% originates from the C-2 and C-6 positions and the remainder must come from the unlabeled portion of the cyclohexyl ring.

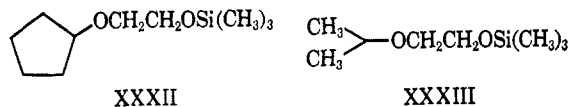
TABLE VI
SHIFTS OF THE m/e 171, m/e 119, AND m/e 75 PEAKS
IN THE MASS SPECTRA OF THE DEUTERIUM-LABELED
2-(CYCLOHEXYLOXY)ETHYL TRIMETHYLSILYL ETHERS
(XXX AND XXXI)

Compound	Isotopic composition, %	m/e 171 ^a	m/e 119 ^a	m/e 75 ^a
XXX	100 d_2	171	121	75
XXXI	92.3 d_4 , 7.7 d_3	175	119 (42%) 120 (53%)	75 (59%) 76 (41%)

^a Corrected for natural isotope abundance and calculated deuterium isotope composition.

The fact that the mass 119 ion becomes the most abundant one ($\Sigma_{40} = 22.3$) at 12 eV suggested the possibility of its further fragmentation at 70 eV. Indeed a metastable ion at m/e 47.2 (calcd $75^2/119 = 47.3$) indicates that III decomposes to the dimethylsilanol ion (q) (eq 13) of mass 75 ($\Sigma_{44} = 10.6$). This process is also supported by deuterium-labeling evidence (see Table VI).

The mass spectra of the cyclopentyloxy (XXXII) and isopropyl (XXXIII) analogs were also recorded. Com-



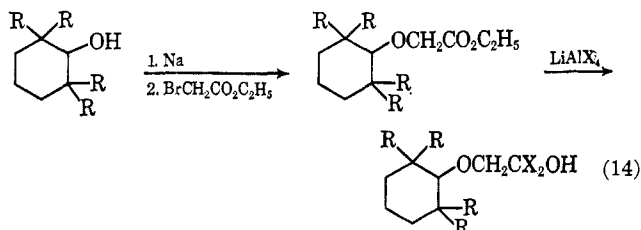
pound XXXII exhibited a spectrum exactly analogous to that of XXIX, and, although there are slight intensity variations, XXXIII behaves in a sufficiently similar fashion so as to not warrant any further discussion.

Synthesis of Labeled Compounds

The discussion of the synthesis of labeled compounds needs to include only a description of the preparation of the parent alcohols, as in practically all cases the common silylating agent, hexamethyldisilazane,^{6,7,20} was utilized to convert the alcohols, amines, and mercaptans into their trimethylsilyl ether derivatives. Occasionally (XXIV and XXVII) it was necessary to employ the stronger silylating agent bis-N,O-(trimethylsilyl)acetamide.²¹

Synthesis of 1,1-*d*₂-2-methoxyethanol was accomplished by reducing 2-methoxyacetic acid with lithium aluminum deuteride to yield the product in high isotopic purity. Preparation of 2-*d*₅-ethoxyethanol involved conversion of perdeuterioethanol into *d*₅-ethyl bromide in a sealed-tube reaction utilizing hydrobromic acid and concentrated sulfuric acid. Subsequent reaction of the bromide with an equivalent amount of sodium metal and a threefold excess of ethylene glycol yielded the desired labeled analog.

It was necessary to synthesize two deuterium labeled analogs (XXX and XXXI) in the 2-(cyclohexyloxy)-ethyl trimethylsilyl ether series. The first compound, 1,1-*d*₂-2-(cyclohexyloxy)ethanol was prepared (eq 14)



by reaction of the sodium salt of cyclohexanol with 2-bromoethyl acetate to yield 2-(cyclohexyloxy)ethyl acetate; subsequent reduction with lithium aluminum deuteride ($X = D$) yielded the desired compound ($R = H$, $X = D$). Utilizing this same scheme but replacing lithium aluminum deuteride ($X = D$) with lithium aluminum hydride ($X = H$) and cyclohexanol ($R = H$) with 2,2,6,6-*d*₄-cyclohexanol ($R = D$) yielded the

second analog 2',2',6',6'-*d*₄-2-(cyclohexyloxy)ethanol (eq 12, $R = D$, $X = H$).

The final labeled compound to be discussed is the oxygen-18 analog of 2-phenoxyethanol (XXXIV). Reaction of the sodium salt of ¹⁸O-enriched phenol with chlorohydrin yielded the desired product.

Experimental Section²²

Trimethylsilyl Ethers and Amines.^{7,8,20}—A mixture of 1.0 mmol of the appropriate alcohol or amine and 0.5 mmol of hexamethyldisilazane²³ (1.0 mmol in the case of bistrimethylsilyl ethers) was heated under reflux with 1 drop of trimethylchlorosilane²³ until evolution of ammonia ceased (1–4 hr for primary and secondary alcohols, 3–5 hr for primary diols, and 12–20 hr for tertiary alcohols and for the amines). The trimethylsilyl derivatives were isolated from the reaction mixture by preparative gas-liquid partition chromatography; Table VII indicates

TABLE VII
RETENTION TIMES OF TRIMETHYLSILYL DERIVATIVES

Compound	Column temperature, °C	Retention time, min.
(CH ₃) ₃ SiOCH ₂ CH ₂ OSi(CH ₃) ₃ (III, <i>n</i> = 2)	125	1.3
(CH ₃) ₃ SiO(CH ₂) ₃ OSi(CH ₃) ₃ (III, <i>n</i> = 3)	125	1.8
(CH ₃) ₃ SiO(CH ₂) ₄ OSi(CH ₃) ₃ (III, <i>n</i> = 4)	145	1.9
(CH ₃) ₃ SiO(CH ₂) ₅ OSi(CH ₃) ₃ (III, <i>n</i> = 5)	145	3.0
(CH ₃) ₃ SiO(CH ₂) ₆ OSi(CH ₃) ₃ (III, <i>n</i> = 6)	160	1.8
(CH ₃) ₃ SiO(CH ₂) ₇ OSi(CH ₃) ₃ (III, <i>n</i> = 7)	155	2.7
(CH ₃) ₃ SiO(CH ₂) ₈ OSi(CH ₃) ₃ (III, <i>n</i> = 8)	155	4.2
(C ₂ H ₅) ₃ SiO(CH ₂) ₂ OSi(C ₂ H ₅) ₃ (VIII)	140	11.1
CH ₃ OCH ₂ CH ₂ OSi(CH ₃) ₃ (XI, <i>n</i> = 2)	100	1.0
CH ₃ O(CH ₂) ₄ OSi(CH ₃) ₃ (XI, <i>n</i> = 4)	110	2.5
CH ₃ O(CH ₂) ₅ OSi(CH ₃) ₃ (XI, <i>n</i> = 5)	110	3.6
C ₂ H ₅ OCH ₂ CH ₂ OSi(CH ₃) ₃ (XIV)	100	1.5
(CH ₃) ₃ SiOCH ₂ CH ₂ OCH ₂ CH ₂ OSi(CH ₃) ₃ (XVI)	155	1.4
C ₂ H ₅ OCH ₂ CH ₂ OCH ₂ CH ₂ OSi(CH ₃) ₃ (XVII)	135	2.0
C ₆ H ₅ O(CH ₂) ₂ OSi(CH ₃) ₃ (XVIII, <i>n</i> = 2)	176	11.6
C ₆ H ₅ O(CH ₂) ₃ OSi(CH ₃) ₃ (XVIII, <i>n</i> = 3)	200	3.7
C ₆ H ₅ O(CH ₂) ₄ OSi(CH ₃) ₃ (XVIII, <i>n</i> = 4)	190	2.4
C ₆ H ₅ O(CH ₂) ₅ OSi(CH ₃) ₃ (XVIII, <i>n</i> = 5) ^a	160	4.8
C ₆ H ₅ O(CH ₂) ₆ OSi(CH ₃) ₃ (XVIII, <i>n</i> = 6) ^a	165	4.9
C ₆ H ₅ O(CH ₂) ₇ OSi(CH ₃) ₃ (XVIII, <i>n</i> = 7) ^a	173	5.3
C ₆ H ₅ OCH ₂ C(CH ₃) ₂ OSi(CH ₃) ₃ (XX)	140	3.5
C ₆ H ₅ OCH ₂ CH ₂ OSi(C ₂ H ₅) ₃ (XXI)	180	3.7
C ₆ H ₅ OCH ₂ CH ₂ OSi(CH ₃) ₃ (XXII)	155	1.8
C ₆ H ₅ OCH ₂ CH ₂ NHSi(CH ₃) ₃ (XXIII)	145	3.7
C ₆ H ₅ OCH ₂ CH ₂ SSi(CH ₃) ₃ (XXIV)	190	5.1
C ₆ H ₅ NHCH ₂ CH ₂ OSi(CH ₃) ₃ (XXV)	180	3.0
C ₆ H ₅ SCH ₂ CH ₂ OSi(CH ₃) ₃ (XXVI)	212	1.6
C ₆ H ₅ NHCH ₂ CH ₂ NHSi(CH ₃) ₃ (XXVII)	165	5.1
(CH ₃) ₂ NCH ₂ CH ₂ OSi(CH ₃) ₃ (XXVIII)	95	1.5
C ₆ H ₁₁ OCH ₂ CH ₂ OSi(CH ₃) ₃ (XXIX)	110	14.0
C ₆ H ₁₁ OCH ₂ CH ₂ OSi(CH ₃) ₃ (XXXII)	85	12.0
C ₆ H ₇ OCH ₂ CH ₂ OSi(CH ₃) ₃ (XXXIII)	50	7.1

^a Separation was done on 1% SE-30 on Chromosorb W with a He flow rate of 100 cc/min.

(22) Melting points (uncorrected) were determined on the Kofler block and infrared absorption spectra were measured with a Perkin-Elmer Model 137 Infracord spectrophotometer. The 70-eV mass spectra recorded on the CEC Model 21-103C instrument were obtained by Mr. N. S. Garcia using a 200° heated, all-glass inlet system. In addition, the spectra of some of the compounds were measured by Dr. A. M. Duffield on an Atlas CH-4 mass spectrometer with an ion-source temperature of 190°. High-resolution measurements and also low-resolution spectra of many of the compounds were carried out by Mr. R. G. Ross using an A.E.I. MS-9 instrument equipped with a 200° heated inlet system. All of the trimethylsilyl derivatives were prepared on a small scale and purified by gas chromatography on a 6 ft × 0.75 in. stainless-steel column packed with 10% GE SF-96 on Chromosorb W with a He flow rate of 150 cc/min.

(23) Hexamethyldisilazane, trimethylchlorosilane, triethylchlorosilane, and bis(trimethylsilyl)acetamide were purchased from Pierce Chemical Co., Rockford, Ill.

(20) S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

(21) J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Amer. Chem. Soc.*, **88**, 3390 (1966).

the retention time and column temperature for each derivative. In most cases the yields of the colorless liquids were essentially quantitative. The accurate molecular weight of each compound was determined by mass spectrometry in order to assure identity of the product.

2-Phenoxyethyl Trimethylsilyl Sulfide (XXIV).—A mixture of 3 ml of acetonitrile, 308 mg of 2-phenoxyethyl mercaptan, and 450 mg of bis(trimethylsilyl)acetamide²³ was heated under reflux for 20 hr and the trimethylsilyl derivative was isolated by preparative gas-liquid partition chromatography (see Table VII). The infrared spectrum indicated typical trimethylsilyl absorptions: λ_{\max} 8.0, 11.8, and 13.3 μ (Me_3Si).

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{OSSi}$: mol wt, 226. Found: mol wt (mass spectrometry), 226.

N'-Phenyl-N-(trimethylsilyl)ethylenediamine (XXVII).—Utilizing 272 mg of N-phenylethylenediamine (Aldrich Chemical Co.) a procedure identical with that employed in the case of 2-phenoxyethyl trimethylsilyl sulfide (XXIV) yielded the desired trimethylsilyl derivative (XXVII).

Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{N}_2\text{Si}$: mol wt, 208. Found: mol wt (mass spectrometry), 208.

Ethylene Glycol Bistriethylsilyl Ether (VIII).—To 124 mg of ethylene glycol in 10 ml of dry benzene was added 100 mg of sodium metal. The mixture was heated gently under reflux for 24 hr, cooled, and a solution of 610 mg of triethylchlorosilane²³ in 5 ml of dry benzene was added. The mixture was again gently heated under reflux for 24 hr, cooled, and filtered, and the benzene was removed by means of a rotary evaporator. Isolation by means of gas-liquid partition chromatography (see Table VII) gave VIII in 73% yield. The infrared spectrum exhibited characteristic absorptions at λ_{\max} 8.1, 11.8, 13.4, and 9.2 μ (SiO).

Anal. Calcd for $\text{C}_{14}\text{H}_{34}\text{O}_2\text{Si}_2$: mol wt, 290. Found: mol wt (mass spectrometry), 290.

2-Phenoxyethyl Triethylsilyl Ether (XXI).—Employing 273 mg of 2-phenoxyethanol, 50 mg of sodium metal, and 300 mg of triethylchlorosilane, a procedure identical with that utilized in the synthesis of VIII yielded 2-phenoxyethyl triethylsilyl ether (XXI).

Anal. Calcd for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Si}$: mol wt, 252. Found: mol wt (mass spectrometry), 252.

2-Phenoxyethyltrimethylgermanium Oxide (XXII).—A mixture of 138 mg of 2-phenoxyethanol and 25 mg of sodium metal in 5 ml of anhydrous benzene was stirred under reflux for 24 hr and cooled. Slowly, 200 mg of trimethylgermanium bromide (prepared by the method of Satgé²⁴) in 5 ml of dry benzene was added and the mixture was heated under reflux for an additional 20 hr. After cooling, filtering, and removing the benzene on a rotary evaporator, the product was isolated by preparative gas-liquid partition chromatography (see Table VII) in approximately 50% yield.

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}_2\text{Ge}$: mol wt, 256.²⁵ Found: mol wt (mass spectrometry), 256.

1,1- d_2 -2-Methoxyethanol.—To a well-stirred suspension of 400 mg of lithium aluminum deuteride in 20 ml of anhydrous ether at 0° was added dropwise 450 mg of 2-methoxyacetic acid (Eastman Organic Chemicals, Rochester, N. Y.) in 15 ml of anhydrous ether. After complete addition the mixture was heated under reflux for 3 hr and the excess lithium aluminum deuteride decomposed by the dropwise addition (at 10°) of a saturated sodium sulfate solution. The mixture was filtered, dried over anhydrous magnesium sulfate, and again filtered, and the ether was stripped on a rotary evaporator yielding 350 mg of 1,1- d_2 -2-methoxyethanol whose mass spectrum showed the isotopic composition to be 98% d_2 and 2% d_1 .

d_5 -2-Ethoxyethanol.—A mixture of 1 ml of perdeuterioethanol (d_6),²⁶ 3 ml of 48% hydrobromic acid, and 1 ml of concentrated sulfuric acid was placed in a sealed tube and heated on a steam bath for 20 hr. The tube was cooled in an ice bath and opened; the mixture was washed twice with water. Pure d_5 -ethyl bromide (1.5 g) was distilled at reduced (aspirator) pressure from the water through Indicating Drierite into a vessel cooled to -40° using a short-path distillation apparatus.

In a dry nitrogen atmosphere was placed 2.43 g of ethylene glycol and 305 mg of finely divided sodium metal; the mixture

was stirred and gently heated. After the reaction of the sodium and ethylene glycol was completed, the labeled ethyl bromide was slowly added, and, following the initial vigorous reaction, the mixture was heated under reflux for 2 hr, cooled, filtered, and distilled at 90° (200 mm) yielding 940 mg of d_5 -2-ethoxyethanol whose mass spectrum revealed the following isotopic composition: 98% d_5 and 2% d_0 .

3-Phenoxypropan-1-ol.—Reduction of 1 g of 3-phenoxypropionic acid with 1 g of lithium aluminum hydride utilizing the same procedure used in the reduction of 2-methoxyacetic acid yielded 750 mg of a colorless liquid after purification by preparative gas-liquid partition chromatography (10% GE SF-96 on Chromosorb W with a He flow rate of 100 cc/min at 200°). The infrared spectrum showed absorptions characteristic of 3-phenoxypropan-1-ol at λ_{\max} 3.0, 8.0, 9.4, 13.2, and 14.4 μ .

*Anal.*²⁷ Calcd for $\text{C}_{10}\text{H}_{20}\text{O}_2\text{Si}$: mol wt, 224. Found: mol wt (mass spectrometry), 224.

4-Phenoxybutan-1-ol.—Reduction of 5.4 g of 4-phenoxybutyric acid with 1.7 g of lithium aluminum hydride was accomplished by the procedures discussed previously except that the mixture was heated under reflux for 12 instead of 2 hr. The product (4.6 g) exhibited infrared absorptions at λ_{\max} 3.05, 8.05, 9.5, 13.2, and 14.4 μ (lit.²⁸ 3.15, 8.1, 9.6, 13.2, and 14.4 μ).

*Anal.*²⁷ Calcd for $\text{C}_{13}\text{H}_{22}\text{O}_2\text{Si}$: mol wt, 238. Found: mol wt (mass spectrometry), 238.

5-Phenoxybutan-1-ol.—A mixture of 3 g of 4-phenoxybutan-1-ol (see above), 3 ml of concentrated sulfuric acid, and 9 ml of 48% hydrobromic acid was heated under reflux for 24 hr. After cooling and washing twice with water, the mixture was extracted three times with ether and the ethereal extracts were dried over anhydrous magnesium sulfate. The solution was filtered, the ether removed on a rotary evaporator, and 2.8 g of 4-phenoxybutyl bromide collected by distillation at 133–135° and 10 mm (lit.²⁹ 151–155° and 16 mm). Utilizing the procedure and apparatus described in previous work,⁷ 2.0 g of 4-phenoxybutyl bromide was converted into its Grignard reagent with 404 mg of magnesium. Subsequent carbonation with anhydrous carbon dioxide⁷ yielded a solid material whose infrared spectrum was characteristic of 5-phenoxyvaleric acid: $\lambda_{\max}^{\text{Nujol}}$ 3.3 (broad), 5.8, 8.0, 9.6, 13.3, and 14.4 μ . Reduction of 5-phenoxyvaleric acid with 475 mg of lithium aluminum hydride according to previously described procedures yielded 5-phenoxybutan-1-ol as indicated by its infrared spectrum: λ_{\max} 3.0, 8.0, 9.6, 13.3, and 14.4 μ .

*Anal.*²⁷ Calcd for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Si}$: mol wt, 252. Found: mol wt (mass spectrometry), 252.

6-Phenoxyhexan-1-ol.—Using procedures described above 624 mg of 6-phenoxyhexanoic acid (K & K Laboratories, Hollywood, Calif.) was reduced with 114 mg of lithium aluminum hydride to yield 6-phenoxyhexan-1-ol whose infrared spectrum exhibited absorptions at λ_{\max} 3.0, 8.05, 9.7, 13.2, and 14.4 μ .

*Anal.*²⁷ Calcd for $\text{C}_{15}\text{H}_{26}\text{O}_2\text{Si}$: mol wt, 266. Found: mol wt (mass spectrometry), 266.

7-Phenoxyheptan-1-ol.—Applying a synthetic sequence identical with that used in the synthesis of 5-phenoxybutan-1-ol, 1.7 g of 6-phenoxyhexan-1-ol was converted into 1.8 g of 6-phenoxyhexyl bromide. Formation of the corresponding Grignard reagent and subsequent carbonation yielded a solid material which melted at 53–55° without recrystallization (lit.³⁰ mp 55°). The infrared spectrum verified the identity of the compound as 7-phenoxyheptanoic acid: $\lambda_{\max}^{\text{Nujol}}$ 3.3 (broad), 5.8, 8.0, 9.6, 13.3, and 14.4 μ . Reduction of this acid with lithium aluminum hydride yielded 7-phenoxyheptan-1-ol which melted at 32–35° (lit.³¹ mp 34°) and exhibited infrared absorptions at λ_{\max} 3.0, 8.05, 9.6, 13.2, and 14.5 μ .

*Anal.*²⁷ Calcd for $\text{C}_{16}\text{H}_{28}\text{O}_2\text{Si}$: mol wt, 280. Found: mol wt (mass spectrometry), 280.

2- ^{18}O -Phenoxyethanol.—To a solution of 46 mg of sodium metal in 1 ml of absolute ethanol was added slowly 186 mg of ^{18}O -phenol³² (10% enriched) followed by the addition of 160 mg of

(27) Mass spectral analysis was performed on the trimethylsilyl ether rather than on the parent compound.

(28) E. L. Eliel, B. E. Nowak, R. A. Daignault, and V. G. Badding, *J. Org. Chem.*, **30**, 2441 (1965).

(29) R. F. Brown and G. H. Schmid, *ibid.*, **27**, 1289 (1962).

(30) E. Dobrowolska and Z. Eckstein, *Przem. Chem.*, **42**, 556 (1963).

(31) E. R. Littmann and C. S. Marvel, *J. Amer. Chem. Soc.*, **52**, 287 (1930).

(32) Oxygen-18 enriched phenol was purchased from Yeda Research and Development Co., Rehovoth, Israel.

(24) J. Satgé, *Ann. Chim.*, **6**, 519 (1961).

(25) The calculated molecular weight assumes the mass of the germanium atom to be 74, the mass of its most abundant isotope (see ref 18).

(26) Perdeuterioethanol was purchased from Stohler Isotope Chemicals, Azusa, Calif.

chlorohydrin in 0.5 ml of absolute ethanol. The mixture was heated under reflux for 18 hr and, after removal of the ethanol by distillation on a steam bath, the residue was diluted with water and extracted with three 10-ml portions of ether; the combined ethereal extracts were washed three times with 5 ml of 10% aqueous potassium hydroxide. After washing with water, drying over anhydrous magnesium sulfate, and evaporating the solvent, the pale yellow oil was purified by preparative gas-liquid partition chromatography (10% GE SF-96 on Chromosorb W with a He flow rate of 100 cc/min at 210°) to yield 40 mg of ¹⁸O-phenoxyethanol identical in all respects with the unlabeled compound.

2-Phenoxy-1,1-dimethylethanol.—To a stirred solution of methylmagnesium iodide, prepared from 960 mg of magnesium and 5.68 g of methyl iodide, in 50 ml of anhydrous ether was added, over a period of 1 hr, 1.66 g of the methyl ester of 2-phenoxyacetic acid. The mixture was heated under reflux for 7 hr, cooled, and treated with aqueous ammonium chloride followed by the addition of dilute sulfuric acid until the solution became clear. The ethereal layer was separated, washed with water and aqueous sodium bicarbonate, and dried over anhydrous magnesium sulfate. After filtration and removal of the ether on a rotary evaporator, preparative gas-liquid partition chromatography yielded 2-phenoxy-1,1-dimethylethanol as indicated by its infrared spectrum: λ_{\max} 2.95, 8.0, 9.5, 13.2, and 14.4 μ .

*Anal.*²⁷ Calcd for C₁₃H₂₂O₂Si: mol wt, 238. Found: mol wt (mass spectrometry), 238.

2-Phenoxyethylamine.—Utilizing previously discussed procedures, 1 g of 2-phenoxyacetamide was reduced with 1 g of lithium aluminum hydride to yield 2-phenoxyethylamine as indicated by infrared absorptions at λ_{\max} 2.95, 3.1, 8.05, 13.2, and 14.4 μ .

*Anal.*²⁷ Calcd for C₁₁H₁₉NOSi: mol wt, 209. Found: mol wt (mass spectrometry), 209.

2-Phenoxyethyl Mercaptan.—Utilizing previously discussed procedures, 2-phenoxyethanol was converted into 2-phenoxyethyl bromide which was subsequently converted into a pale yellow solid upon reaction with potassium ethyl xanthate according to Djerassi, *et al.*³³ After three recrystallizations from hexane, a colorless solid was obtained, mp 50–52°, and was shown to be homogeneous by analytical thin layer chromatography performed on silica gel G. The infrared spectrum indicated characteristic absorptions at $\lambda_{\max}^{\text{Nujol}}$ 8.0, 8.3, 9.4, 13.2, and 14.4 μ .

Anal. Calcd for C₁₁H₁₄OS₂: C, 54.55; H, 5.82; S, 26.44; mol wt, 242. Found: C, 54.32; H, 5.77; S, 26.76; mol wt (mass spectrometry), 242.

Reduction of 2-phenoxyethylethyl xanthate was accomplished according to the procedure of Djerassi, *et al.*,³³ with the following variations. The initial addition to lithium aluminum hydride was performed at 0° instead of room temperature, and the resulting mixture was not refluxed for 4 hr,³³ but instead stirred at room temperature for 24 hr. After decomposition of the excess lithium aluminum hydride, the product was isolated by threefold extraction with ether, drying over anhydrous magnesium sulfate, filtration, and removing the ether on a rotary evaporator. Distillation yielded 2-phenoxyethyl mercaptan, bp 105–108° and 7 mm (lit.³⁴ bp 108–109° and 8 mm) which decomposed at high temperature to yield a mixture of phenol and three unidentified compounds. Infrared absorptions were observed at λ_{\max} 3.9 (weak), 8.0, 13.3, and 14.4 μ .

Anal. Calcd for C₈H₁₀OS: mol wt, 154. Found: mol wt (mass spectrometry), 154.

(33) C. Djerassi, M. Gorman, F. X. Markley, and E. B. Oldenburg, *J. Amer. Chem. Soc.*, **77**, 568 (1955).

(34) E. N. Prilezhakva, N. P. Petukhava, and M. F. Shostakovski, *Dokl. Akad. Nauk SSR*, **154**, 160 (1964).

2-Thiophenoxyethanol.—According to previously described procedures, 2-thiophenoxyacetic acid was reduced with lithium aluminum hydride to yield 2-thiophenoxyethanol: λ_{\max} 3.0, 9.5, 13.5, and 14.5 μ .

*Anal.*²⁷ Calcd for C₁₁H₁₆OSSi: mol wt, 226. Found: mol wt (mass spectrometry), 226.

2-(Cyclohexyloxy)ethanol.—In a moisture-free atmosphere 240 mg of sodium metal was added to 1.1 g of cyclohexanol in 8 ml of dry ether, and the mixture stirred for 12 hr at room temperature. To the resulting yellow suspension was added 1.2 g of ethyl bromoacetate in 12 ml of dry ether and the solution again stirred for 12 hr. After filtration, the ethereal solution was immediately reduced with 520 mg of lithium aluminum hydride in the normal manner to produce 2-(cyclohexyloxy)ethanol after purification by preparative gas-liquid partition chromatography (15% Carbowax on Chromosorb W with a He flow rate of 80 cc/min at 195°). The infrared spectrum indicated characteristic absorptions at λ_{\max} 2.95, 8.95, and 9.4 μ .

*Anal.*²⁷ Calcd for C₁₁H₂₄O₂Si: mol wt, 216. Found: mol wt (mass spectrometry), 216.

1,1-*d*₂-2-(Cyclohexyloxy)ethanol.—Utilizing the identical procedure employed in the synthesis of 2-(cyclohexyloxy)ethanol, except that lithium aluminum hydride was replaced by lithium aluminum deuteride, 1,1-*d*₂-(cyclohexyloxy)ethanol was prepared. Its mass spectrum indicated an isotopic composition of 100% *d*₂.

2',2',6',6'-*d*₄-(Cyclohexyloxy)ethanol.—Conditions identical with those employed in the synthesis of 2-(cyclohexyloxy)ethanol were utilized to synthesize this labeled analog except cyclohexanol was replaced by 2,2,6,6-*d*₄-cyclohexanol, synthesized by the method of Seibl and Gümman,³⁵ The mass spectrum of 2',2',6',6'-*d*₄-2-(cyclohexyloxy)ethanol indicated an isotopic composition of 92% *d*₄ and 8% *d*₃.

2-(Cyclopentyloxy)ethanol and 2-Isopropylethanol.—These analogs were prepared according to the procedure used in the synthesis of 2-(cyclohexyloxy)ethanol except that cyclohexanol was replaced by cyclopentanol and isopropyl alcohol, respectively.

Registry No.—III (*n* = 2), 7381-30-8; III (*n* = 8), 16654-42-5; VIII, 13175-68-3; XI (*n* = 4), 16654-44-7; XIV, 16654-45-8; XVI, 16654-74-3; XVII, 16654-46-9; XVIII (*n* = 2), 16654-47-0; 3-phenoxypropan-1-ol, 6180-61-6; XVIII (*n* = 3), 16654-49-2; 2-phenoxyethyl ethyl xanthate, 16654-50-5; XVIII (*n* = 4), 16654-51-6; 5-phenoxyptan-1-ol, 16654-52-7; XVIII (*n* = 5), 16654-53-8; 6-phenoxyhexan-1-ol, 16654-54-9; XVIII (*n* = 6), 16654-55-0; 7-phenoxyheptan-1-ol, 16654-56-1; XVIII (*n* = 7), 16654-57-2; 2-phenoxy-1,1-dimethylethanol, 13524-74-8; XX, 16654-59-4; XXI, 16654-60-7; XXII, 16654-61-8; XXIV, 16654-62-9; XXVII, 16654-63-0; XXVIII, 16654-64-1; XXIX, 16654-65-2; XXX, 16654-66-3; XXXI, 16654-67-4; 2-phenoxyethylamine 1758-46-9; 2-phenoxyethylamine trimethylsilyl derivative, 16654-69-6; 2-thiophenoxyethanol, 699-12-7; 2-thiophenoxyethanol trimethylsilyl ether, 16654-71-0; 2-(cyclohexyloxy)ethanol, 1817-88-5; 2-(cyclohexyloxy)ethanol trimethylsilyl ether, 16654-73-2.

(35) J. Seibl and T. Gümman, *Helv. Chim. Acta*, **46**, 2857 (1963).