carbon (eq 2). Since the claimed retention is based on

$$\underset{[\alpha]^{25}\mathrm{D}\ -6.0^\circ}{CH_3{*}CHBrCOOC_2H_5} + IrClCO(PMePh_2)_2 \xrightarrow[\text{CH}_2\text{Cl}_2\ \text{room temp}]{\text{4 days}} \text{oxidative addition complex} \xrightarrow{Br_2} \underset{[\alpha]^{25}\mathrm{D}\ -4^\circ}{CH_3{*}CHBrCOOC_2H_5} \quad (2)$$

the assumption that the bromine cleavage occurs with retention of configuration, and since bromine cleavages with inversion have been reported, it has been suggested that this claim be held in abeyance until more definitive results are obtained.[7,8]

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(7) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971); F. R. Jensen and D. D. Davis, *ibid.*, **93**, 4048 (1971); F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **93**, 5283 (1971).

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Macrocyclic Transition States in Mass Spectrometry. Long-Chain α,ω-Bis(trimethylsilyl) Ethers

Sir:

Transition-state ring size is often a critical factor in mass spectrometry, and most commonly involves rings of six members,[1] although numerous examples[2] of both larger and smaller rings are available. However, it has been previously shown that interactions between remotely situated functional groups in conformationally mobile[3] long-chain molecules can lead to fragmentation reactions which proceed through large-ring transition states having no apparent ring size requirements.[4]

In order to test for an upper limit to transition-state ring size in reactions of this type, mass spectra of the trimethylsilyl ethers **1–4**[5] were examined. We wish to

$$Me_3SiO(CH_2)_nOSiMe_3$$
$$\mathbf{1}, n = 10 \quad \mathbf{3}, n = 34$$
$$\mathbf{2}, n = 22 \quad \mathbf{4}, n = 46$$

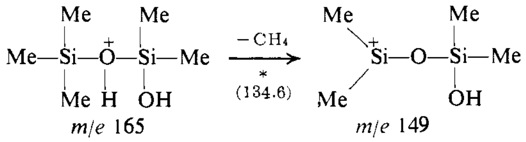
report evidence for intramolecular reactions between the terminal functions, which not only involve transition-state macrocycles of up to 49 members, but become increasingly favorable with increasing chain length and constitute the major fragmentation path in the spectra of **2–4**.

Table I. Abundance (% Σ_{40})[a] of Selected Ions from the Mass Spectra of **1–4**

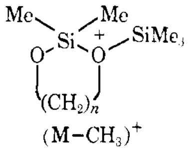
m/e	**1**	**2**	**3**	**4**
165	0.26	2.9	5.4	7.2
149	4.6	15	16	17
147	10.5	5.2	2.8	1.9

[a] Sum of all isotopic species.

Our choice of **1–4** was dictated by knowledge that in short-chain bis(trimethylsilyl) ethers the silyl groups readily interact to form the prominent rearranged species *m/e* 147 ($Me_3SiO^+SiMe_2$).[11,12] Of much lesser importance in the short-chain homologs is *m/e* 165, which retains two hydrogens but no carbons from the polymethylene chain, and further decomposes by elimination of methane.[11] The present results (Table I) unexpectedly show the increasing prominence of *m/e* 165



and 149 with increasing chain length, while *m/e* 147 becomes less important. We view the formation of *m/e* 165 as arising from a cyclized M − CH_3 ion, earlier proposed as the precursor of *m/e* 147 from short-chain (n = 2–8) silyl ethers.[12] To shed more light on the origin of the two alkyl chain hydrogens which are retained in *m/e* 165, analogs of **2** were examined which



$(M-CH_3)^+$

$n = 10, 22, 34, 46$

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(1) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 155–162.

(2) (a) W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, **86**, 2375 (1964); S. Meyerson and L. C. Leitch, *ibid.*, **86**, 2555 (1964); (b) M. Katoh and C. Djerassi, *Chem. Commun.*, 1385 (1969); (c) A. N. H. Yeo and D. H. Williams, *Org. Mass Spectrom.*, **2**, 231 (1969).

(3) For a recent review and discussion of various effects of winding or coiling of the alkyl chain upon fragmentation, see S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, **93**, 2244 (1971).

(4) For examples and leading references, see (a) J. A. McCloskey and M. J. McClelland, *ibid.*, **87**, 5090 (1965); (b) R. Brandt and C. Djerassi, *Helv. Chim. Acta*, **51**, 1750 (1968); (c) G. Eglinton, D. H. Hunneman, and A. McCormick, *Org. Mass Spectrom.*, **1**, 593 (1968); (d) G. H. Draffan, R. N. Stillwell, and J. A. McCloskey, *ibid.*, **1**, 669 (1968); (e) J. Diekman, J. B. Thompson, and C. Djerassi, *J. Org. Chem.*, **34**, 3147 (1969); (f) R. E. Wolff and A. Caspar, *Tetrahedron Lett.*, 1807 (1970); (g) E. White, V, and J. A. McCloskey, *J. Org. Chem.*, **35**, 4241 (1970).

(5) **1–4** were prepared by heating the corresponding diol (200 μg) with bis(trimethylsilyl)trifluoroacetamide (20 μl) (PCR Inc., Gainesville, Fla.) and 1% trimethylchlorosilane at 100° for 1 hr. 1,10-Decanediol was obtained commercially; the remaining diols were prepared by reduction of the corresponding C_{22}, C_{34}, and C_{46} diacids with borane in tetrahydrofuran.[6] The diacids were obtained by the method of Hünig,[7] starting with the morpholine enamines of cyclohexanone (C_{22}) and cyclododecanone[8] (C_{34}, C_{46}), by Wolff–Kishner reduction of the intermediate diketo dicarboxylic acids. All intermediate and final products were checked by gas chromatography and mass spectrometry[9] and exhibited satisfactory mass spectra.[10] Gas chromatography of **3** and **4** indicated the presence of later eluting components which did not interfere with their mass spectra. Eluting peaks of **1–4** (total ion current) were shown to be homogeneous by repeated scanning of mass spectra during elution.

(6) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 199.

(7) S. Hünig, E. Lücke, and W. Brenninger, *Org. Syn.*, **43**, 34 (1963); S. Hünig and E. Lücke, *Chem. Ber.*, **92**, 652 (1959); S. Hünig and H.-J. Buysch, *ibid.*, 100, 4017 (1967); C. Wakselman, *Bull. Soc. Chim. Fr.*, 3763 (1967).

(8) S. Hünig, H.-J. Buysch, H. Hoch, and W. Ferdle, *ibid.*, 100, 3996 (1967); C. Wakselman, *C. R. Acad. Sci., Ser. B*, **261**, 759 (1965).

(9) Mass spectra were recorded on an LKB 9000 instrument (70 eV, ion source 250°), utilizing the gas chromatographic inlet (3 ft, 1% SE-30 conditioned for high temperatures: **1**, 125°; **2**, 215°; **3**, 273°; **4**, 312°). Spectra were recorded on the apex of the eluting peak, free of contamination by minor, later eluting components.

(10) Full mass spectra of **1–4** have been submitted to the Archives of Mass Spectral Data, Wiley-Interscience, New York, N. Y.

(11) J. A. McCloskey, R. N. Stillwell, and A. M. Lawson, *Anal. Chem.*, 40, 233 (1968).

(12) J. Diekman, J. B. Thompson, and C. Djerassi, *J. Org. Chem.*, 33, 2271 (1968).

Table II. Origin of Deuterium in *m/e* 165 and *m/e* 149 from **2a–d**

m/e		Per cent[a]			
		α	β	γ	δ
165	d_1[b]	16.1	25.8	27.7	27.4
	d_2	1.0	3.7	2.7	3.3
149	d_1	10.2	17.2	19.1	17.2
	Calcd[c]	9.1	16.6	16.6	17.0

[a] Corrected for presence of protium resulting from incomplete labeling. [b] Maximum possible total for all positions is 200%, or 100% per deuterium atom. [c] Calculated for *m/e* 149 and equal to one-half the deuterium content of *m/e* 165: % d_2 + 0.5% d_1.

were systematically labeled[13] on the first four carbons from both ends (α,α-d_4, **2a**; β,β-d_4, **2b**; γ,γ-d_4, **2c**; δ,δ-d_4, **2d**). The results, shown in Table II, reveal that approximately 59% of the hydrogen involved in the formation of *m/e* 165 originates from the first four positions. This double hydrogen transfer is not site specific, but shows great preference for those positions which are sterically accessable to oxygen atoms in the cyclic M − CH_3 precursor. The absence of site specificity is also reflected in *m/e* 149 which, as shown by comparison of the last two lines of Table II, retains statistically half of the label regardless of its positional origin.[15]

At progressively shorter chain lengths, the cyclic M − CH_3 complex can be expected to become conformationally less flexible. As a consequence, interactions between ether oxygens and the first several methylene groups become more restricted, ultimately resulting in the decreased abundance of *m/e* 165 and 149 which is observed at short chain lengths.[12] For very large values of *n*, the reaction occurring between the termini of a long chain bears a distinct similarity to an ion–molecule reaction,[16] as recently demonstrated in a study of the chemical ionization mass spectra of α,ω-diols.[17] In fact, the ring-closure reaction of M − CH_3 ion in the present case has analogy in the intermolecular formation of adducts between various siliconium ions and heteroatom-containing molecules, reported by Harvey and his collaborators.[18] Clearly, the occurrence of major fragments from reactions between the termini of very long chains represents further strong evidence for the ability of these molecules to extensively wind and coil in the vapor phase, doubtless due to such factors as dipole interactions and internal solvation.[3] Equally important, recognition of such processes is crucial in the application of mass spectrometry for the determination of molecular structure.

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(13) α,α-d_4-1,22-Docosanediol was prepared by $LiAlD_4$ reduction of the corresponding diacid. The remaining d_4-diols were synthesized by chain elongation (reduction to the diol and conversion to the corresponding bromide, then nitrile, and followed by hydrolysis) of the appropriate α,α-d_4-dicarboxylic acids, which were derived[14] by heating the acid (370 mg) with basic D_2O (2 ml, 50 mg of Na) in a stainless steel bomb for 2 weeks at 200°. After trimethylsilylation,[5] mass spectra of **2a–d** were acquired completely free of contamination by minor glc peaks, and showed deuterium incorporation levels of 95–97.5%.

(14) J. G. Atkinson, J. J. Csakvary, G. T. Herbert, and R. S. Stuart, *J. Amer. Chem. Soc.*, **90**, 498 (1968).

(15) These data do not mean that the two hydrogens in *m/e* 165 are equivalent with regard to loss of methane. Likewise, the methyl groups in *m/e* 165 cannot be distinguished, and *m/e* 149 can also have the structure $Me_3SiO^+SiMeOH$.

(16) We thank Dr. F. H. Field for first bringing this similarity to our attention.

(17) I. Dzidic and J. A. McCloskey, *J. Amer. Chem. Soc.*, **93**, 4955 (1971).

(18) D. J. Harvey, M. G. Horning, and P. Vouros, *Chem. Commun.*, 898 (1970); *Anal. Lett.*, 489 (1970).

Phosphepanium Salts. Nucleophilic Substitution at Heterocyclic Phosphorus with Complete Inversion of Configuration

Sir:

Recent work has shown that the stereochemistry of nucleophilic substitution at phosphorus contained in saturated heterocyclic phosphonium salts varies with ring size, although complete inversion of configuration has never before been observed. Thus a comparison of such systems, where benzyl is the leaving group and hydroxide ion the nucleophile, can be summarized as follows: (a) cis and trans isomers of phosphetanium salts **1** and **2** decompose to give *identical mixtures* of the cis and trans isomers of **3** and **4**, respectively;[1] (b) pure cis and trans isomers of the phospholanium salts **5**[2] and **6**[3] undergo alkali cleavage with *complete retention* of configuration at phosphorus to yield the respective oxides **7** and **8**; and (c) each of the pure *cis*- and *trans*-phosphorinanium salts of structure **9** leads to *mixtures* of stereoisomeric oxides (**10**) of *different composition*[4] indicating the absence of a common intermediate between the isomeric salts and the oxides formed.

We now wish to report that a still different stereochemical result is realized upon hydroxide cleavage of the *cis*- and *trans*-1-benzyl-4-methyl-1-phenylphosphepanium bromide salts (**11**).[5] Within limits of experimental error it has been determined that substitution occurs with *complete inversion* of configuration at phosphorus to yield **12**. Apparently, the greater flexibility of the seven-membered ring, as compared to the smaller rings previously studied, permits accommodation of C–P ring bonds in comparatively unstrained equatorial positions in the phosphorane intermediate **14**. The significance of this work lies in the fact that the seven-membered ring represents the smallest ring system in this series which allows complete inversion of configuration at phosphorus. Therefore, there is in evidence a return to the "McEwen mechanism," first observed for the base-induced conversion of the acyclic, optically pure methylethylphenylbenzylphosphonium iodide to optically pure methylethylphenylphosphine oxide of opposite configuration *via* the unstrained intermediate **15**.[6] Also, the results obtained for the cleavage of the di-

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(1) S. E. Cremer, R. J. Chorvat, and B. C. Trivedi, *Chem. Commun.*, 769 (1969).

(2) K. L. Marsi, *ibid.*, 846 (1968); *J. Amer. Chem. Soc.*, **91**, 4724 (1969).

(3) W. Egan, G. Chauviere, K. Mislow, R. T. Clark, and K. L. Marsi, *Chem. Commun.*, 733 (1970).

(4) K. L. Marsi and R. T. Clark, *J. Amer. Chem. Soc.*, **92**, 3791 (1970).

(5) These compounds were prepared by an adaptation of the Märkl cyclization procedure [G. Märkl, *Angew. Chem., Int. Ed. Engl.*, **2**, 620 (1963)]. Further details of the synthesis will be published elsewhere. Stereochemical assignments of the isomers of **11**, **12**, and **13** have not yet been made but are not essential to the discussion of the stereochemistry of the reactions reported herein.