Preparative Electrochemical Oxidation of Cyclic Peralkylsllanes

James Y. Becker* and Elias Shakkour

Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84120, Israel Robert West*

Department of Chemistry, University of Wisconsin, Madison, WI 53706, USA

<u>Summary</u>. The electrochemical oxidation of cyclic peralkylsilanes undergo ring opening followed by further Si-Si bond cleavage and reaction with BF4⁻ to form α, ω -difluorosilanes, F-(SiR₂)_n-F, as major products.

Cyclic peralkylsilanes exhibit unique behavior which distinguishes these compounds from saturated catenates of carbon.¹ In some ways the properties of the cyclosilanes resembles those of poly-unsaturated or aromatic hydrocarbons: they show strong long wavelength ultraviolet absorption bands, form charge-transfer complexes with π -acceptors,² and undergo reduction to electron-delocalized anion-radicals.³ Some of the cyclosilanes can also be oxidized to cation-radicals, which have been observed and studied by ESR spectroscopy.⁴ In these species also, the ESR spectra indicate that the unpaired electron is fully delocalized over the ring. A few organic compounds of silicon have previously been investigated by cyclic voltammetry.⁵ A recent study of alkyl derivatives of group 14 elements has shown that these compounds undergo irreversible oxidation, with oxidation potentials which are linearly related to first ionization energies.⁶ A series of linear permethylsilanes, Me(SiMe₂)_nMe where n = 2 to 6, was studied by Boberski and Allred, who found that the oxidation potentials decrease with increasing chain length, and are correlated with UV spectra and with Sandorfly C calculations.⁷

Recently, two groups⁸ determined the oxidation potentials for a series of cyclosilanes by cyclic voltammetry. In general, these compounds display at least two anodic waves separated by 0.2-0.4V. The first oxidation potential is from 1.1 to 1.4V and the second one is from 1.4 to 1.9V (vs SCE). The first oxidation potentials (Ep^1) for the cyclosilanes depend both upon ring size and on the nature of substituents on silicon. The oxidation potentials increase going from three- to four- to higher membered rings, with the lowest potential of all found for the highly strained compound, [(t-Bu)₂Si]₃. In the dimethyl and diethyl series there is little difference between potentials for five-, six- and seven-membered rings, but in the two rotane series, the five-membered rings undergo oxidation at lower potentials than the six-rings. Permethylcyclosilanes (Me₂Si)_n with n > 9 show significantly lower oxidation potentials than for n = 5 to 9.

In general, the oxidation potentials are well correlated with electronic absorption energies which similarly increase with increasing ring size from n = 3 to 6, and then decrease above n = 9. Ionization potentials have been determined only for a few cyclosilanes, but those which are known are consistent with the E_{P}^{1} values obtained. For example, Si4 rings show lower ionization potentials^{9,10} than Si5 and Si6.¹¹ As the ring size decreases below six silicon atoms, the constraints on the Si-Si-Si bond angles evidently increase the energy of the highest occupied Si-Si s orbitals, as proposed earlier.^{10,12}

The present communication reports for the first time on the results obtained from preparative electrolysis of two cyclosilane derivatives: dodecamethylcyclohexasilane ([Me₂Si]₆, 1) and deca-n-propylcyclopentasilane ([n-Pr₂Si]₅, 2). In a typical experiment, 248 mg (0.435 mmol) of 2 were added to the anode compartment of an 'H'-type cell containing a 35 ml solution of CH₂Cl₂-CH₃CN (4:1 v/v) - 0.1M Et₄NBF₄. The electrolysis was conducted at controlled potential of 1.25V (vs Ag/AgCl), on Pt foil. Pulsing to 0.5V every 10sec for 1sec was necessary to maintain an initial current of 15-20mA. The starting material disappears (by t.l.c.) after cosuming 108 Coulombs (2.5 F/mol) and the current decreases to ~1.5 mA. Workup involves stripping of the solvent, adding water and extracting three times with dichloromethane or diethyl ether, followed by drying the organic phase over MgSO₄ and filtration. After solvent evaporation the mass yield is \sim 75%. The product distribution after GLC and GC/MS analysis is described in the Table. In the case of 1, the electrolysis was also stopped when all starting material was consumed. However, at that stage, the electricity consumption was 4 F/mol and the current was still relatively high (~6 mA). With the same workup, the mass yield is only ~50%, probably because all products containing Si₁-Si₃ units evaporate with solvents. Therefore, in order to avoid an error in yield estimation the results included in Table for 1 stem from direct analysis (GC/MS) of the product mixture after electrolysis and before workup.

<u>(R2Si)n</u>				<u>F- (R2Si)n -F (%)</u> b					
	F/mol	n =1	2	3	4	5	6	Other products	
1	4.0	5.5	27	12	49.5	1.5	0.5	F- (Me2Si)2-OH	
								F- (Me2Si)3-OH	
								F- (Mc ₂ Si)5-OH	
								F- (Me2Si)5-H	
2	2.5	1	54	30	10	-		F- (n-Pr2Si)3-OH	
								F- (n-Pr2Si)3-H	
								H-(n-Pr2Si)3-OH	
								F- (n-Pr2Si)5-OH	

^a Controlled potential electrolysis, in an 'H'-type divided cell, on Pt anode; Conc. 12-14-mM in CH₂Cl₂-CH3CN(4:1) - 0.1M Et4NBF4.

^b An average of two experiments. The % and characterization is based mainly on GLC and GC/MS (EI or CI whenever necessary); DB-1 packed column, 30m long, 60-250°C/8°C/min. 1H-, 13C- and 29Si-NMR are available for the major product obtained in each entry.

Scheme



The products described in the Table show that both cyclic peralkylsilanes, 1 and 2, undergo ring opening followed by further oxidative fragmentation and chemical reactions, mainly with BF_4^- anion from the electrolyte. This behaviour does not resemble neither that of alicyclic hydrocarbons¹³ nor that of benzene or alkyl-substituted benzenes¹⁴, in at least two respects: a) the cyclic peralkylsilanes are oxidized at lower (by *ca* 0.5-2 V) anodic potentials, and b) they undergo Si-Si bond cleavage and fragmentation rather than substitution¹³, polymerization, dimerization or side-chain reactions¹⁴. Both differences could stem from the weakness of the Si-Si bond relative to the bond energies of C-C or C-H.

A possible mechanism which describes the formation of all products is outlined in the Scheme. The initially formed unstable cyclic cation-radical (I) is a highly reactive intermediate which may undergo an attack by BF_4^- anion to form the radical (III), or Si-Si bond cleavage to generate a straight-chain cation-radical (II) which could then react with BF_4^- to form the same entity, III. Intermediate III could undergo further oxidation to the cation V, or abstract a hydrogen atom from its surroundings to generate IV. Cation V may react with water (which could be present in trace amount) or BF_4^- to form VI and VII, respectively. For simplicity, the Scheme shows that only products like IV, VI and VII undergo further oxidative cleavage to generate their lower homologues. However, other fragmentation pathways could stem from intermediates, e.g., III or V. Certainly,

the presented mechanistic scheme is an over-simplified one. Interestingly, no homologues higher than Si₆ (from 1) or Si₅ (from 2) due to Si-Si bond recombination were detected. This observation indicates that the further oxidation of the silicon radical intermediates is much faster and therefore preferred over their recombination, under the experimental conditions. The resulting positive silicon species then gain energy by forming products containing Si-F, Si-O or Si-H bonds.¹⁵

Attempts were made to trap intermediate species of type I-III or V. Derivative 1 was electrolyzed in the presence of two-fold excess of cyclohexene at a potential corresponding to the first oxidation of 1. The results after workup indicate that no cyclohexylsilicon derivatives were formed. However, the relative yield of the longest difluoro derivative, F-(Me₂Si)₆-F, becomes predominant.

Undoubtedly, the chosen electrolyte plays an important role in the nature of products obtained. Therefore, electrochemical study in the presence of other electrolytes, solvents and anode materials, as well as at higher potentials, is underway. Furthermore, it would be interesting to establish why the products containing an even number of Si atoms, as shown in the Table, are the prevailing ones.

References

- 1. R. West and E. Carberry, Science, 189, 179 (1975); R. West, Pure Appl. Chem., 54, 104 (1982).
- 2. V.F. Traven and R. West, J. Am. Chem. Soc., 85, 6824 (1973).
- 3. C.L. Wadsworth, R. West, Y. Nagai, H. Watanabe and T. Muraoka, Organmetallics, 4, 1664 (1985) and reference cited therein.
- 4. H. Bock, W. Kaim, M. Kira and R. West, J. Am. Chem. Soc., 101, 7667 (1979).
- 5. E.M. Genies and F. EL Omar, Electrochim. Acta, 28, 541 (1983) and references cited therein.
- 6. R.J. Klingler and J.K. Kochi, J. Am. Chem. Soc., 102, 4790 (1980).
- 7. W.G. Boberski and A.L. Allred, J. Organometal. Chem., 88, 65 (1975).
- H. Watanabe and Y. Nagai in H. Sakurai, ed., Organosilicon and Bioorganosilicon Chemistry, Ellis Horwood Ltd., Chichester, U.K. p. 107-114 (1985); F. Shafiee and R. West, Silicon, Germanium, Tin & Lead Compounds., 9, 1-10 (1986).
- 9. H. Watanabe, T. Okawa, M. Kato and Y. Nagai, J. Chem. Soc. Chem. Commun., 781 (1983).
- 10. T.F. Block, M. Beirnbaum and R. West, J. Organometal. Chem., 131, 199 (1977).
- 11. H. Bock and W. Ensslin, Angew. Chem. Int., Ed. Engl., 10, 1404 (1971).
- H. Gilman and G.R. Schwebke, Advan. Organometal. Chem., 1, 89 (1964); R. West in "Comprehensive Organomettalic Chemistry", E. Abel, ed., Pergamon Press Ltd., Oxford, England, 1982, Ch. 9.4, p. 365-397.
- M. Fleischmsnn and D. Pletcher, Tet. Lett., 255 (1968); J. Bertram, M. Fleischmsnn and D. Pletcher, idem., 349 (1971); T.M. Siegel, L.L. Miller and J.Y. Becker, J. Chem. Soc. Chem. Commun., 341(1974).
- See for example : W.C. Neikam and M.M. Desmond, J. Am. Chem. Soc., 86, 4811 (1964); H. Lund, Acta Chem. Scand., 11, 1323 (1957); J.O. Howell, J.M. Goncalves, C. Amatore, L. Klasinc, R.M. Wightman and J.K. Kochi, J. Am. Chem. Soc., 106, 3968 (1984); L. Eberson and B. Olofsson, Acta Chem. Scand., 23, 2355 (1969); V.D. Parker, J. Elrctroanal. Chem., 21, App. 1 (1969).
- R. Walsh, in "The Chemistry of Organic Silicon Compounds", in the series "The Chemistry of Functional Groups", (S. Patai and Z. Rappoport, Eds.), Wiley and Sons, New York, 1989, Chap. 5, pp. 371-391.

(Received in UK 29 June 1992)