

major product. Our work is continuing in order to define the scope of this reaction, and to assess the implications for the mechanisms of other radiation-induced reactions in organic media.

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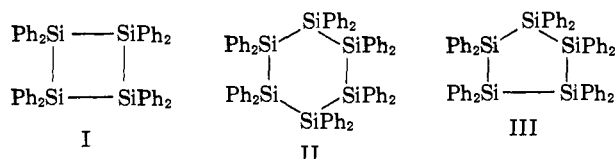
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DECAPHENYLCYCLOPENTASILANE

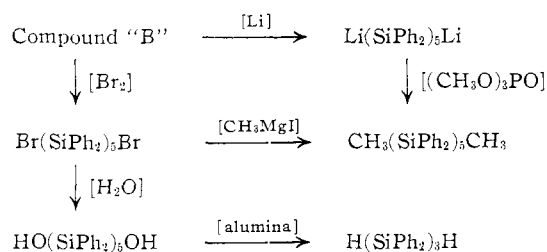
Sir:

The reaction of dichlorodiphenylsilane with sodium^{1,2} or lithium^{2b,3} produces several perphenylated cyclosilanes. One of them, designated Compound "B" by Kipping,^{1a} was first proposed to be octaphenylcyclo-tetrasilane (I)^{1a,b}; and, more recently, to be dodeca-phenylcyclohexasilane (II).³ Both of these proposals were based on molecular weight determinations; the



former on values determined cryoscopically in benzene and camphor^{1a,b} and the latter on values determined cryoscopically in perylene.³ It now has been shown that both proposals were in error and that Compound "B" is decaphenylcyclopentasilane (III). Derivatives of this compound, which had previously been designated as hexasilanes,^{3,4} are in fact 1,5-disubstituted-decaphenylpentasilanes.

Chemical proof for the structure of decaphenylcyclopentasilane has been obtained by two different means starting with decaphenylcyclopentasilane. In a recent publication,⁵ it has been shown that the α,ω -dihydroxy derivative of Compound "B" (decaphenylcyclopentasilane), when chromatographed on basic alumina, provides 1,1,2,2,3,3-hexaphenyltrisilane. This reaction indicates that the dihydroxy compound was a pentasilane and that Compound "B" is the cyclopentasilane.



The lithium cleavage products of Compound "B" were examined to throw more light on the structure of the cyclic polysilane. It was found that when the cyclosilane was allowed to react with lithium in tetrahydrofuran for 2 hr., the cleavage was essentially com-

(1) (a) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830 (1921); (b) F. S. Kipping, *ibid.*, **123**, 2590 (1923); (c) **125**, 2291 (1924); (d) 2719 (1927).

(2) (a) H. Gilman, D. J. Peterson, A. W. Jarvie and H. J. S. Winkler, *J. Am. Chem. Soc.*, **82**, 2076 (1960); (b) A. W. P. Jarvie, H. J. S. Winkler, D. J. Peterson and H. Gilman, *ibid.*, **83**, 1921 (1961).

(3) (a) H. Gilman, D. J. Peterson, A. W. Jarvie and H. J. S. Winkler, *Tetrahedron Letters*, **23**, 5 (1960); (b) H. J. S. Winkler, A. W. P. Jarvie, D. J. Peterson and H. Gilman, *J. Am. Chem. Soc.*, **83**, 4089 (1961).

(4) (a) A. W. P. Jarvie and H. Gilman, *Chem. Ind.* (London), 1271 (1960); (b) A. W. P. Jarvie, H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **27**, 614 (1962); (c) H. J. S. Winkler and H. Gilman, *ibid.*, **27**, 254 (1962).

(5) G. R. Chainani, S. Cooper and H. Gilman, *ibid.*, in press.

plete. Formation of derivatives, using trimethyl or tri-*n*-butyl phosphate⁶ or chlorotrimethylsilane, led to derivatives of the corresponding 1,5-disubstituted compounds, in yields approaching 83%. The constitutions of these compounds were established by elemental analysis and by proton magnetic resonance spectra determinations to obtain aliphatic to aromatic hydrogen atom ratios. 1,5-Dimethyldecaphenylpentasilane was also obtained in high yield from the reaction of methylmagnesium iodide with 1,5-dibromodecaphenylpentasilane.

Molecular weight determinations have been obtained for decaphenylcyclopentasilane (molecular weight 911) by three different methods which gave consistent results. Ebullioscopic determinations in toluene⁷ using octaphenylcyclo-tetrasilane as a standard gave a value of 921 ± 7 (four determinations). An X-ray diffraction study and density determination of decaphenylcyclopentasilane, crystallized from benzene-ethanol, provided a value of 983, in good agreement with a value of 989 calculated for decaphenylcyclopentasilane plus one molecule of benzene, which was subsequently shown to be present. The molecular weight was also determined in benzene using a "vapor phase osmometer"⁸ at several concentrations. Extrapolation to zero concentration gave a value of 912, in excellent agreement with the theoretical value of 911 for decaphenylcyclopentasilane.

Experimental details for the reactions and data presented here and for other polysilanes derived from decaphenylcyclopentasilane will be forthcoming.

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(6) H. Gilman and B. J. Gaj, *ibid.*, **26**, 247 (1961).

(7) C. A. Glover and R. R. Stanley, *Anal. Chem.*, **33**, 447 (1961).

(8) Mechrolab, Inc., Mountain View, Calif.

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THE REDUCTIONS OF *cis*- AND *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ AND $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ BY Fe^{++}

Sir:

We have measured spectrophotometrically the rates of reduction of *cis*- and *trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$ and $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ by Fe^{++} in aqueous perchlorate solutions (no other anions present) at 25°. The results, summarized in Table I, show that the reduction of the *cis* complex is acid-independent for (H^+) varying from 0.072 to 0.219 *M*, whereas that of the *trans* complex is, under the same conditions, strongly acid-dependent. The rate laws (time in minutes) are given by the equations $11.1(\text{Fe}^{++})$ (*cis*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$) and $[4.4 + 82(\text{H}^+)](\text{Fe}^{++})$ (*trans*- $\text{Co}(\text{NH}_3)_4(\text{N}_3)_2^+$). The reduction of $\text{Co}(\text{NH}_3)_5\text{N}_3^{++}$ is acid-independent and obeys the rate law $0.52(\text{Fe}^{++})(\text{Co}(\text{NH}_3)_5\text{N}_3^{++})$.

Because of the substitution-lability of $\text{Fe}(\text{III})$, it cannot be ascertained whether these reactions proceed *via* a bridged or outer-sphere activated complex.¹ However, assuming that bridged activated complexes are operative, reasonable explanations can be advanced for the present observations.

(1) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).