

valence complexes,<sup>3,4</sup> accompanied by precipitate formation, which develops when copper(II) and 4-hydroxybenzoxazole are mixed and allowed to stand for several hours.<sup>5</sup> If some oxidation of the phenolic ligand occurs under these conditions, it is certainly not extensive as indicated below. However, in the presence of a copper(I) chelating agent, such oxidation is strongly promoted. This can be demonstrated by extracting an aqueous solution of the chloroform insoluble copper(II) complex of 4-hydroxybenzoxazole with a chloroform solution of 2,9-dimethyl-1,10-phenanthroline (neocuproine), a specific chelating agent for this ion.<sup>6</sup> When this extraction is carried out, practically all of the copper originally present in the aqueous layer is converted into the yellow complex of copper(I) and neocuproine. It can be shown by the method of Nilsson<sup>7</sup> using bis-cyclohexanone-dioxaldihydrazone that the copper was present very predominantly as copper(II) before this extraction.

Convincing evidence for the participation of 4-hydroxybenzoxazole in this oxidation-reduction reaction can be obtained by extracting aqueous solutions containing various ratios of 4-hydroxybenzoxazole:copper(II), with chloroform solutions of neocuproine. The percentage of the total copper obtained in the extract as the copper(I) chelate increases in a linear manner with increasing molar ratio of 4-hydroxybenzoxazole:copper(II) and reaches a maximum of about 90% when this ratio is unity. It is therefore clear that equimolar proportions of 4-hydroxybenzoxazole and copper(II) are involved in the oxidation-reduction reaction.

To our knowledge this is the first example of the oxidation of a phenol by a metal ion, "catalyzed" by a specific chelating agent for the reduced form of the metal ion. Because of the importance of phenol oxidation in biogenesis<sup>8</sup> and the widespread occurrence of copper(II) in phenol oxidases,<sup>9</sup> this type of oxidation-reduction reaction might have important biological implications.

TABLE I

CHELATE FORMATION CONSTANTS FOR COPPER(II)-4-HYDROXYBENZOXAZOLE IN 50% DIOXANE-WATER AT 25°

	Ligand: Metal Ratio		
	8:1	6:1	4:1
Log $K_1$	7.05	7.05	7.16
Log $K_2$	6.49	6.44	6.62
Log $K_1$ (Lane, <i>et al.</i> ) <sup>2</sup>	6.40	...	6.56
Log $K_2$ (Lane, <i>et al.</i> ) <sup>2</sup>	5.85	...	6.18

The neocuproine could promote this phenol oxidation (1) by chelating copper(I) and thereby

(3) I. M. Klotz, G. H. Czerlinski and H. A. Fiess, *J. Am. Chem. Soc.*, **80**, 2920 (1958).

(4) H. M. McConnell and N. Davidson, *ibid.*, **72**, 3168 (1950).

(5) Due to the high dilution, these changes, although they apparently occur, are difficult to perceive during the potentiometric titration.

(6) G. F. Smith and W. H. McCurdy, Jr., *Anal. Chem.*, **24**, 371 (1952).

(7) G. Nilsson, *Acta Chem. Scand.*, **4**, 205 (1950).

(8) D. H. R. Barton and T. Cohen, "Festschrift Arthur Stoll," Birkhauser AG., Basle, 1957, p. 117.

(9) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelates," Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1952, pp. 387-392.

displacing an equilibrium involving weak complexes of copper(I) and copper(II), or (2) by removing copper ions, as copper(I), from the 4-hydroxybenzoxazole-copper(II) complex leaving behind the oxidized form of the phenolic ligand. The electron transfer in the latter process would presumably occur *via* a homolytic cleavage of the metal-oxygen bond similar to that thought to occur in the copper ion catalyzed oxidations of ascorbic acid and pyrocatechol.<sup>9</sup> Taube<sup>10</sup> has cited examples of the catalysis of oxidation-reduction reactions by ligands which stabilize preferentially the oxidized or reduced form of the metal ion.

It is unlikely that a true equilibrium is being displaced because the oxidized form of the 4-hydroxybenzoxazole, presumably a phenol free radical, would be expected to have a very short half-life and to couple readily with another such radical.<sup>8</sup> For this reason we favor the latter reaction path although it is evident that the detailed mechanism remains to be elucidated.

(10) H. Taube, *J. Am. Chem. Soc.*, **77**, 4481 (1955).

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RECEIVED MAY 1, 1961

### 1,3,5,7-TETRACHLORO-1,3,5,7-TETRASILA-ADAMANTANE

Sir:

We have recently characterized a chlorosilane of unusual properties which tends to confirm the mechanism of chlorosilane hydrolysis postulated by Sommer, *et al.*<sup>1</sup> The material is believed to be a bridgehead compound of adamantane structure containing four potentially reactive sites as shown in Fig. 1. The substance was produced in a high pressure reaction of  $\text{SiCl}_4$  and  $(\text{CH}_3)_3\text{SiCl}$  in the presence of  $\text{AlCl}_3$ . During the course of the reaction the reactor became overheated and probably reached 500° or higher. Formation of other cyclic materials under similar conditions has been reported.<sup>2,3</sup> The 1,3,5,7-tetrachloro-1,3,5,7-tetrasiladamantane was isolated as impure tabular crystals showing bipyramids, with the top face well developed. The crystals appeared during the distillation of the residue between cuts of the cyclics  $[(\text{CH}_3)_2\text{SiCH}_2]_3$  and  $[(\text{CH}_3)_2\text{SiCH}_2]_4$ . The yield was about 0.1%. The crystals were sublimed and recrystallized from toluene. The presence of one or more persistent impurities was noted, however, and tend to minimize the value of the analytical data in proving the structure.

*Anal.* Calcd. for  $\text{Si}_4\text{C}_6\text{H}_{12}\text{Cl}_4$ : C, 21; H, 3.5; Si, 33; Cl, 42; mol. wt., 338.4. Found: C, 24.1; H, 4.6; Si, 27.7; Cl, 43.6; mol. wt., 348.

(1) L. H. Sommer, C. L. Frye, M. C. Musolf, G. A. Parker, P. G. Rodewald, K. W. Michael, Y. Okaya and R. Pepinsky, *J. Am. Chem. Soc.*, **83**, 2210 (1961).

(2) G. Fritz, *Z. Naturforsch.*, **12b**, 123 (1957).

(3) G. Fritz, D. Habel, K. Kummer and G. Teichmann, *Z. anorg. u. allgem. Chem.*, **302**, 60 (1959).

The infrared spectrum, as in the case of adamantane and hexamethylenetetramine<sup>4</sup> is relatively simple, and is given in Table I. It is significant

TABLE I

Wave length, microns	Interpretation
3.42 (VW)	C-H stretch
7.38 (M)	CH <sub>2</sub> scissors
9.70 (S)	CH <sub>2</sub> wag
12.58 (M)	SiC stretch
14.0 (W)	CH <sub>2</sub> rock
19.0 (S)	SiCl stretch

that only bands characteristic of SiCH<sub>2</sub>Si are present in the 2–12 micron region, and that no SiCH<sub>3</sub> or SiCH<sub>2</sub>Cl bands are observed.<sup>5</sup> A band of variable intensity at 12.23 microns is ascribed to impurity. X-Ray studies show a molecular weight of 335. A nuclear magnetic resonance spectrum on a benzene solution of the material shows a single strong line at  $\delta = -0.265$  parts per million referred to (CH<sub>3</sub>)<sub>4</sub>Si, plus three small impurity lines.

The most striking property of this molecule is the resistance to hydrolysis of its SiCl bond. On numerous occasions crystals have been dissolved in diethyl ether (in which they are sparingly soluble) or dioxane, water added, and the bulk of the material recovered unchanged upon evaporation of the solvent. Such behavior seems inconsistent with the well-known rapid hydrolysis of the SiCl bond. Sommer,<sup>1</sup> however, recently has proved that the hydrolysis of chlorosilanes is highly stereospecific and proceeds with inversion of configuration. Thus, a backside attack must be involved in hydrolysis. Molecular models of 1,3,5,7-tetrachloro-1,3,5,7-tetrasiladamantane show that it fits together rigidly without appreciable strain, and with no opportunity for other than a frontal attack on the SiCl linkages.<sup>6</sup>

Attempts to methylate the compound with CH<sub>3</sub>MgCl were unsuccessful, and only partial reaction, if any, was observed.

(4) R. Mecke and H. Spiesecke, *Spectrochim. Acta*, **7**, 387 (1956).

(5) A. L. Smith, *ibid.*, **16**, 87 (1960).

(6) One of the referees, L. H. Sommer, had these comments: "At first sight, the results appear inconsistent with previous reactivity data for bridgehead silicon. Actually, they afford strong support for the previously advanced concept of Si(5) intermediates in which the entering and leaving groups may be at 90° to each other in the trigonal bipyramidal addition complex (see L. H. Sommer and O. F. Bennett, *J. Am. Chem. Soc.*, **79**, 1008 (1957) and subsequent publications on bridgehead silicon). The order of reactivity with LiAlH<sub>4</sub> for I, 1-chloro-1-silabicyclo[2,2,1]heptane, II, *n*-Bu<sub>3</sub>SiCl, and III, 1-chloro-1-silabicyclo[2,2,2]octane, is: I >> II > III (M. C. Musolf, Ph.D. Thesis, The Pennsylvania State University, 1960), and the tetrasiladamantane system, IV, should have less reactive SiCl than III on the grounds that formation of Si(5) from IV would necessarily involve: (i) serious angular distortion of the tetrahedral O-Si-C bond angles of all four ring-locked silicon atoms, because of the nature of the ring-system in IV—a very unfavorable I-strain factor would obtain since IV is a perfectly symmetrical unstrained structure; (ii) serious steric hindrance, due to the fact that each silicon atom in IV bears three substituents that are highly substituted at the  $\beta$ -position (*i.e.*, Cl(CH<sub>2</sub>)<sub>2</sub>-Si(CH<sub>2</sub>)<sub>2</sub>), a situation that does not obtain for III. It is noteworthy that bridgehead reactivity for Si(5) mechanisms (addition intermediates, sp<sup>3</sup> bonding) and for carbonium ion mechanisms (dissociation or ionization intermediates, sp<sup>2</sup> bonding) turn out to have (a not expected) inverse structure dependence; for the preparative hydrolysis of 1-bromoadamantane see: H. Stetter, M. Schwarz and A. Hirschhorn, *Ber.*, **92**, 1629 (1959)."

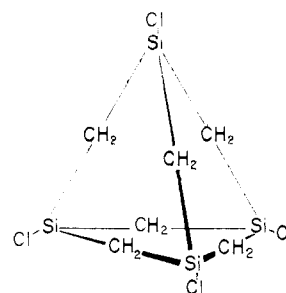


Fig. 1

We are indebted to Dr. E. B. Baker of the Dow Chemical Company for the n.m.r. spectrum.

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RECEIVED JUNE 12, 1961

### SILICONIUM IONS AND CARBONIUM IONS AS REACTION INTERMEDIATES

Sir:

Despite the gradually emerging outlines of a better general understanding of the mechanisms of organosilicon reactions *via* studies of kinetics and stereochemistry, the situation with regard to the status of siliconium ions as reaction intermediates has remained exceedingly obscure (*vide infra*). On the basis of earlier qualitative studies of aliphatic organosilicon compounds, we had attributed certain remarkably rapid reactions of the aliphatic carbon-silicon bond to: "electron-release from silicon to electronically-deficient beta carbon."<sup>1</sup> However, it was not possible to decide—on the basis of the qualitative data then available—whether or not such electron-release was assisted by simultaneous nucleophilic attack on silicon, even with electrophilic reagents such as aluminum chloride or mineral acids.

From the (personal) conviction that *trialkyl* silicon cations, R<sub>3</sub>Si<sup>+</sup>, and *trialkyl* carbon cations, R<sub>3</sub>C<sup>+</sup>, may, in certain circumstances, be of comparable stability relative to their precursors<sup>2</sup>; and that a siliconium ion mechanism would be isolable, provided that due care was exercised in the choice of reactant and reagent structures for the purpose of decreasing the probability of reaction by direct displacement or Si(5) mechanism paths,<sup>2,3</sup> we have been led to undertake quantitative

(1) L. H. Sommer, D. L. Bailey and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2869 (1948); L. H. Sommer, L. J. Tyler and F. C. Whitmore, *ibid.*, **70**, 2872 (1948); L. H. Sommer and N. S. Marans, *ibid.*, **72**, 1935 (1950); L. H. Sommer and R. P. Ploch, *ibid.*, **76**, 1606 (1954).

(2) Use of the term "stability" as applied to cations is, of course, extremely hazardous unless it is recognized—as we have tried to do herein—that relative equilibria and relative rates depend upon differences between reactant states and product states for the former, and between reactant states and transition states for the latter. See the basic Hammett equations for relative rates and relative equilibria: L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 78; F. P. Price and L. P. Hammett, *J. Am. Chem. Soc.*, **63**, 2387 (1941).

(3) For example, if it is known that Me<sub>3</sub>SiCl and Me<sub>3</sub>CCl solvolyse by different mechanisms, but it is also known that the former is far more reactive than the latter in solvolysis (*cf.*, A. D. Allen and G. Modena, *J. Chem. Soc.*, 3671 (1957)), then the data do not compel