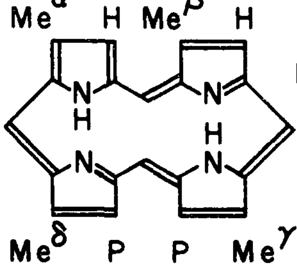
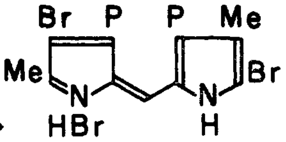
CYTODEUTEROPORPHYRIN[1]

Sir:

Warburg degraded cytohemin, the prosthetic group of the *sauerstoffübertragende Ferment* and of cytochrome-*a*, to cytodeuteroporphyrin, I, a dicarboxylic acid. Although the yields of methylmaleinimide and hematinic acid obtained on oxidizing I suggested a deuteroporphyrin isomeric with II, its tribromo-derivative revealed three free positions, not two.[2] This and the low carbon in the hematinic acid could be rationalized by assuming that the latter contained its des-methyl derivative. I, if derived from protoporphyrin IX, might then be II, H for Me$^{\gamma}$ or Me$^{\delta}$.



II



III

P = CH_2CH_2COOH

2 - Methyl - 5 - carboxy - pyrrole - 4 - propionic acid (from its ester[3]), m.p. 132° dec. (Found: C 54.68; H, 5.81; N, 6.99), decarboxylated to 2-methyl-pyrrole-4-propionic acid, m.p. 80° (Found: C, 62.50; H, 7.13). This with 2-formyl-4-methyl-5-carboxypyrrole-3-propionic acid[4] gave 4,5′-dimethyl - 5 - carboxypyrromethene - 3,3′ - dipropionic acid hydrobromide, m.p. 160° dec. (Found: C, 48.87; H, 4.94; N, 6.35; Br, 17.98), brominated to III which contained perbromide. In methylsuccinic acid at 200°, III and 3,5,4′-trimethyl-4,3′,5′-tribromopyrromethene hydrobromide[5] gave as expected an alkyl porphyrin removed by chloroform extraction, a tetra-propionic acid and 1,3,5-trimethyl-porphin-6,7-dipropionic acid, II, H for Me$^{\delta}$, isolated as a discrete symmetrical band ($K = 1.6$) by countercurrent distribution between 0.28% HCl and ether. Its methyl ester, m.p. consistently 198–202° (Found: C, 71.31; H, 6.16; N, 10.44), formed a copper complex, m.p. 236–240°, and a tribromo-derivative, m.p. *ca.* 285° dec. (Found: Br, 32.11). X-Ray powder photographs showed that this ester separated as variable mixtures of two polymorphic forms from cold methanol but consistently as a single third form from hot.

Warburg's I ester, < 1 mg., melted at 194–198° (lit. 188°, bromo-derivative 298°), undepressed with the ester of II, H for Me$^{\delta}$. Its X-ray powder photograph represented one of the two first mentioned synthetic forms but after it crystallized from hot methanol its photograph was identical with that of the third.

We fused cytohemin concentrates from beef or horse heart with resorcinol and cleanly separated I from some II by countercurrent distribution. Its identity with II, H for Me$^{\delta}$, was shown by the m.p (198–202°) mixed m.p. and infrared mull spectrum of the ester, the m.p. (237–239°) and mixed m.p. of its copper complex, and by X-ray photographs of these, of the free acid, and of the bromo-ester (m.p. *ca.* 280–300 dec.).

We also synthesized II, H for Me$^{\alpha}$, and H for Me$^{\gamma}$. Like II, H for Me$^{\beta}$,[2] neither resembled I.

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[1] Issued as N.R.C. Document.

[2] O. Warburg, H. S. Gewitz and V. Völker, *Z. Naturforschung*, **10b**, 541 (1955). We have continued this work at the suggestion of Professor Warburg, who kindly provided a specimen of cytodeuteroporphyrin methyl ester from horse heart.

[3] S. F. MacDonald and R. J. Stedman, *Can. J. Chem.*, **33**, 458 (1955).

[4] A related sequence is described by H. Fischer, W. Siedel, and L. T. d'Ennequin, *Ann.*, **500**, 156 (1933).

[5] H. Fischer and H. Scheyer, *Ann.*, **434**, 248 (1923).

[6] N.R.C. Postdoctoral Fellow.

DIVISION OF PURE CHEMISTRY
NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

G. S. MARKS[6]
D. K. DOUGALL[6]
E. BULLOCK[6]
S. F. MCDONALD

RECEIVED JULY 25, 1958

SYNTHESIS OF THE WURTZITE FORM OF SILICON CARBIDE

Sir:

We have found that the product of the thermal decomposition at 1500 ± 50° of 0.006 mole fraction CH_3SiCl_3 in H_2, at a flow rate of 1200 ml./min., contains crystals of the long-missing wurtzite form of silicon carbide. The crystals were deposited on the graphite wall of the furnace tube, as clusters of transparent blue, green, or colorless prismatic needles. The crystals are often stepped, and often have globular masses of cubic silicon carbide at one or both ends, or at the discontinuities in the stepped crystals. The longest crystals are 2–3 mm. in length and up to 0.2 mm. in diameter. Prism, pyramid, and basal faces are observed on some of the larger crystals. The needles show high birefringence typical of α silicon carbide, and parallel extinction indicating the c axis to be along the needle axis.

X-Ray rotation, Laue, Weissenberg zero and upper-level photographs have been taken with a number of the crystals, using Cu and Mo radiation. The crystals have been rotated about both the a and c axis, and all results are consistent with the wurtzite or (in the nomenclature of Ramsdell[1]) the 2H structure.[1] The unit cell dimensions, as measured from a Weissenberg photograph with a crystal rotating about the a axis, are $a = 3.076$, $c = 5.048$ Å. The space group is $P6_3mc$. The interplanar spacings, measured from a powder photograph of the material, may all be indexed on the basis of the above cell; however, intensity measurements have not as yet been made. The measured lines account for 23 of the 26 possible reflections for the 2H structure which are accessible with Cu radiation.

The apparent reason for the failure to find 2H silicon carbide until now is probably that nearly all investigators have limited themselves to study of crystals grown in the commercial silicon carbide furnaces, where, presumably, conditions are not favorable for growth of the 2H form. One fact now apparent is that α-SiC can be grown at relatively low temperatures where only β-SiC was pre-

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[1] L. S. Ramsdell, *Am. Mineral.*, **32**, 64 (1947).

viously thought to be formed. Complete details of the synthesis, and the crystallographic measurements, will be reported later.

RESEARCH AND DEVELOPMENT DIVISION
THE CARBORUNDUM COMPANY KENNETH M. MERZ
NIAGARA FALLS, NEW YORK ROBERT F. ADAMSKY

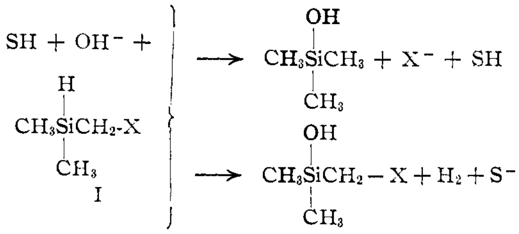
RECEIVED NOVEMBER 10, 1958

BASE-CATALYZED REARRANGEMENT OF HYDRIDE ION FROM SILICON TO CARBON WITH DISPLACEMENT OF HALIDE ION AT THE MIGRATION TERMINUS

Sir:

The concept of a pentacovalent silicon intermediate, Si(5), in the base-catalyzed solvolyses of triorganosilanes,[1] whose geometry approximates a trigonal bipyramid in which the entering group (hydroxide) and the group ultimately displaced (hydrogen) may form an angle near 90° with the central silicon,[2] leads to the view that the original four bonds to silicon must undergo considerable excitation and loosening in the conversion of Si(4) to Si(5) since this change would also involve the conversions: Si(4), sp^3 bonding, neutral $\rightarrow$ Si(5), sp^3d bonding, unit formal negative charge.[3] On the basis of these considerations it was of considerable interest to determine whether the hydrogen functions in chloromethyldimethylsilane (I, X = Cl) and in iodomethyldimethylsilane (I, X = I) become sufficiently activated in the Si(5) complex formed with hydroxide ion to act as intramolecular reducing groups for the carbon-halogen bonds, which must, themselves, undergo considerable activation in the change from Si(4) to Si(5)

We wish to report the synthesis of these silanes, their novel and rapid rearrangement upon treatment with KOH in 95% ethanol, and the proof that these rearrangements are intramolecular



$$\left.\begin{array}{c} SH + OH^- + \\ \overset{\displaystyle H}{\underset{\displaystyle CH_3}{CH_3\overset{|}{\underset{|}{Si}}CH_2\text{-}X}} \\ I \end{array}\right\} \begin{array}{ll} \longrightarrow \overset{\displaystyle OH}{\underset{\displaystyle CH_3}{CH_3\overset{|}{\underset{|}{Si}}CH_3}} + X^- + SH & (1) \\ \longrightarrow \overset{\displaystyle OH}{\underset{\displaystyle CH_3}{CH_3\overset{|}{\underset{|}{Si}}CH_2}} - X + H_2 + S^- & (2) \end{array}$$

Reduction of chloromethyldimethylchlorosilane with lithium aluminum hydride in ether solution gave chloromethyldimethylsilane (I, X = Cl) in 59% yield having b.p. 81.5° (732 mm.). Found: Si, 25.6; Cl, 32.14. Treatment of I with sodium iodide in dry acetone gave iodomethyldimethylsilane (I, X = I) in 35% yield having b.p. 128° (731 mm.), $n^{20}D$ 1.5043, and d^{20} 1.542. Found: Si, 14.1; *MR*D, 38.5.

Treatment of chloromethyldimethylsilane (I, X = Cl) with 0.0539 *M* KOH in 95% ethanol gave an extremely rapid evolution of hydrogen (reaction was complete in less than 15 seconds) which corresponded to 31% of the theoretical (31% solvolysis, reaction 2) and a precipitate of KCl, 67% yield (in good accord with the expected 69% rearrangement, reaction 1). The expected disiloxanes, condensation products of the silanols from (1) and (2), also were obtained in good yields. A similar experiment with iodomethyldimethylsilane (I, X = I) gave 11% solvolysis (2) and 89% rearrangement (1).

Base-catalyzed solvolysis of phenyldimethylsilane in the presence of bis-(chloromethyl)-tetramethyldisiloxane gave 100% hydrogen and no reduction of the C–Cl bonds in the latter. Furthermore, treatment of I (X = Cl) with 0.04 *M* KOH in 70% dioxane–30% D_2O gave 77% rearrangement product which contained no C–D bonds as shown by an infrared spectrum.

The relatively small change in the ratio (1)/(2) with change from $-CH_2Cl$ to $-CH_2I$, compared to the large change in solvolysis rates with change from RCl to RI (iodides are generally more reactive by a factor of $\sim 10^2$),[4] suggests a common Si(5) intermediate for (1) and (2) in which the $-CH_2X$ group and the hydrogen function form an angle near 90° with the silicon atom (a geometry exceedingly favorable for back attack by the activated hydrogen function on the $-CH_2X$ group). These interesting rearrangements are receiving further study.

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[1] $R_3SiH + OH^- + SH \rightarrow R_3SiOH + H_2 + S^-$, where SH represents solvent (95% ethanol) and $-d[\text{silane}]/dt = k_2[\text{silane}][OH^-]$.

[2] L. H. Sommer and O. F. Bennett, THIS JOURNAL, **79**, 1008 (1957); L. H. Sommer, O. F. Bennett, P. G. Campbell and D. R. Weyenberg, *ibid.*, **79**, 3295 (1957).

[3] The sp^3d hybrid orbital, although present in PF_5 and PCl_5 in the vapor state, is uncommon and certainly of much higher energy than sp^3. Formation of an Si(6) intermediate containing two hydroxide groups is untenable on kinetic grounds, and such an intermediate containing one hydroxide and one solvent molecule is unlikely on steric grounds and contrary to other evidence which cannot be detailed here.

[4] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 602 (1956).

COLLEGE OF CHEMISTRY AND PHYSICS L. H. SOMMER
THE PENNSYLVANIA STATE UNIVERSITY W. P. BARIE, JR.
UNIVERSITY PARK, PA. D. R. WEYENBERG

RECEIVED NOVEMBER 19, 1958

REACTIVITY AT BRIDGEHEAD SILICON. II. 1-SILABICYCLO[2.2.2]OCTANE

Sir:

The special geometry associated with bridgehead atoms in medium-sized bicyclic systems has led to an important use of these compounds in the determination of the stereochemical requirements of S_N1 and S_N2 displacements on carbon.[1,2]

In previous work,[3] reactivity at the bridgehead silicon atom of 1-silabicyclo[2.2.1]heptane (I) was found to be greatly enhanced relative to $(C_2H_5)_3SiH$. The objective of synthesizing a bridgehead silicon compound that would be almost free of strain (in order to obviate unusual reactivity at

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[1] Bridgehead chlorides containing the bicyclo[2.2.1]heptane system are inert toward nucleophilic reagents (back attack is not possible) and have greatly reduced reactivity toward halophilic reagents: P. D. Bartlett and L. H. Knox, THIS JOURNAL, **61**, 3184 (1939); P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950); W. von E. Doering and E. F. Schoenewalt, *ibid.*, **73**, 2333 (1951).

[2] The bridgehead bromide, 1-bromobicyclo[2.2.2]octane shows greatly *enhanced reactivity* compared to the more strained 1-bromobicyclo[2.2.1]heptane in solvolysis reactions with or without added Ag^+ as a catalyst. However, even the former is less reactive than *t*-butyl bromide by a factor of five powers of ten. W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher and W. P. Whelan, Jr., THIS JOURNAL, **75**, 1008 (1953).

[3] L. H. Sommer and O. F. Bennett, *Ibid.*, **79**, 1008 (1957); L. H. Sommer, O. F. Bennett, P. G. Campbell and D. R. Weyenberg, *ibid.*, **79**, 3295 (1957).