source of the δ-carbon atom of the δ-aminolevulinic acid.[2] It can be seen from Table II that the same C^{14} distribution pattern was found in protoporphyrin synthesized from δ-aminolevulinic acid-5-C^{14} and from glycine-2-C^{14}; 50% of the C^{14} activity resides in the pyrrole rings and 50% in the methene bridges.

TABLE II

DISTRIBUTION OF C^{14} ACTIVITY IN PROTOPORPHYRIN SYNTHESIZED FROM δ-AMINOLEVULINIC ACID-5-C^{14} AND FROM GLYCINE-2-C^{14}

Fragments of porphyrin	Molar activity (%) in fragments of porphyrin synthesized from δ-Aminolevulinic acid-5-C^{14}, %	Molar activity (%) in fragments of porphyrin synthesized from Glycine-2-C^{14} (ref. 6), %
Protoporphyrin	100	100
Pyrrole rings A + B (methylethylmaleimide)[a]	24.5	24.6
Pyrrole rings C + D (Hematinic acid)[a]	25.2	25.3
Pyrrole rings A + B + C + D	49.7	49.9
Methene bridge carbon atoms	50.3	50.1

[a] Obtained from protoporphyrin as previously described.[6,7]

Our finding that δ-aminolevulinic acid is an intermediate in porphyrin synthesis has been confirmed in two recent communications.[8,9]

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(8) A. Neuberger and J. J. Scott, *Nature*, **172**, 1093 (1953).

(9) E. I. B. Dresel and J. E. Falk, *ibid.*, **172**, 1185 (1953).

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FIRST STEP IN THE HYDROLYSIS OF PENTABORANE

Sir:

Normally, the identification of intermediate products resulting from the hydrolysis of boron hydrides is difficult to obtain because of the ease with which they hydrolyze; however, by immobilizing the water molecules we were able to obtain evidence for the occurrence of such intermediates in the case of diborane.[1,2] Now, by means of the mass spectrometer and with the technique of using "bound water" in silica gel[1] we have succeeded in identifying the first step in hydrolysis pentaborane.

Purified pentaborane gas was passed through a shallow bed of silica gel containing only bound water, and then led directly into a Consolidated Engineering model 21-103 mass spectrometer. Mass spectra of the gaseous products were taken immediately and after intervals of 20, 40 and 60 minutes exposure time of pentaborane to the silica gel. By stripping the mass spectrum for pure pentaborane from these spectra, we obtained a residual pattern whose peak heights as a function of mass numbers (m/e) is illustrated in Fig. 1.

The height of the residual peaks based upon a relative peak height of 100 at $m/e = 59$ (highest peak height in pentaborane spectrum) was largest in the spectrum obtained after the 20 minutes exposure time, and decreased with time. The residual pattern in the spectrum taken immediately after the pentaborane was exposed to the silica gel was very small. The amount of hydrogen generated in the hydrolytic reaction increased with time. Mass spectra taken immediately and at short intervals after mixing pentaborane and water vapor showed no residual pattern except for hydrogen.

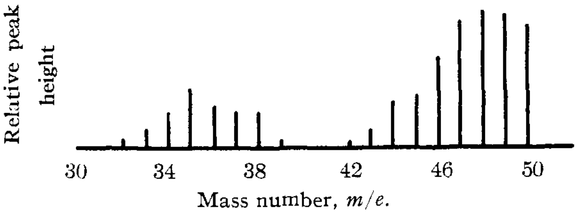

Fig. 1.—Residual mass spectrum resulting from hydrolysis of pentaborane.

The residual pattern given above is very similar to the mass spectrum of tetraborane[3] for which the principal monoisotopic species is B_4H_6. We believe the first step in the hydrolysis of pentaborane to be the removal of a borine by the "bound water" with subsequent generation of hydrogen.[1] From a comparison of the models for pentaborane[4] and tetraborane[5] the removal of any one of the four basal borons of pentaborane would leave the tetraborane skeleton.

That the "bound water" in silica removes a borine from pentaborane can also be demonstrated by boron and hydrogen balances of what is retained on the silica and what is recovered in the volatile portion of the products. By adding water to the silica after all volatile material has been pumped off the solid, one can measure the amount of active hydrogen gasometrically and the amount of boron by titration with mannitol and standard base. Silica must be filtered from the solution before titration of the boron. In one experiment pentaborane from a carbon tetrachloride slush ($-23°$) was passed through a bed of silica at room temperature into a liquid nitrogen trap. The noncondensable gas (hydrogen) was compressed into a gasometer by means of a toepler pump. The amount of hydrogen gas generated during the pentaborane hydrolysis was approximately the same as that found after the addition of water to the silica. The ratio of active hydrogen to boron in the silica was found to be slightly greater than unity. Thus the over-all ratio of hydrogen (hydride) to boron accounted was *ca.* 2.5 instead of the expected value of 3.0 for borine. This difference can be attributed to errors of measurement because of the small amounts of material involved. The material caught in the liquid nitrogen trap was found to be a mixture of pentaborane and an unstable product which decomposed at room temperature over a period of hours to give hydrogen and a fibrous-looking solid boron hydride.

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(1) I. Shapiro and H. G. Weiss, *J. Phys. Chem.*, **57**, 219 (1953).

(2) H. G. Weiss and I. Shapiro, THIS JOURNAL, **75**, 1221 (1953).

(3) To be published.

(4) K. Hedberg, M. E. Jones and V. Schomaker, *Proc. Natl. Acad. Sci.*, **38**, 679 (1952).

(5) M. E. Jones, K. Hedberg, and V. Schomaker, THIS JOURNAL, **75**, 4116 (1953); C. E. Nordman and W. N. Lipscomb, *ibid.*, **75**, 4116 (1953).

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