A SIMPLE AUTOMATIC PROCEDURE FOR CATALYTIC HYDROGENATIONS IN GLASS APPARATUS AT ATMOSPHERIC PRESSURE

Sir:

We wish to report a simple procedure which makes possible the automatic hydrogenation of large quantities of unsaturated derivatives in glass apparatus at atmospheric pressure.

It was reported previously that olefinic and acetylenic derivatives may be hydrogenated conveniently in glass apparatus by utilizing the new active platinum metal catalysts[1] and hydrogen generated *in situ* from the hydrolysis of sodium borohydride. The procedure called for the manual addition of a standard solution of sodium borohydride in ethanol to the hydrogenation flask at such a rate as to keep the pressure at approximately atmospheric. The procedure proved to be highly satisfactory for relatively rapid reactions, but was somewhat tedious for slow reactions or for reactions involving the hydrogenation of relatively large quantities of material.

This difficulty was overcome by the development of a simple, pressure-activated device for controlling the rate of addition of the borohydride solution (Fig. 1). In this device, a syringe barrel, or a buret fitted to a hypodermic needle, is inserted through a rubber serum cap into a mercury well to a depth adequate to support the column of borohydride solution. As hydrogen is utilized in the hydrogenation flask, the pressure drops 10 to 20 mm. below atmospheric, drawing a small quantity of the borohydride solution through the mercury seal where it rises to the top of the mercury and runs into the flask through the small vent holes located just above the mercury interface. The acidic solution in the flask hydrolyzes the borohydride and the resulting increase in pressure seals the valve. The addition proceeds smoothly to the completion of the hydrogenation, with the amount of the borohydride solution corresponding quantitatively to the amount of unsaturated compound contained in the flask.

The following procedure involving the hydrogenation of diethyl maleate is representative. In a 500-ml. Erlenmeyer flask was placed 5 g. of Darco K-B carbon, 100 ml. of anhydrous ethanol and 5.0 ml. of 0.20 *M* chloroplatinic acid solution. The system was assembled (Fig. 1) and the solution stirred vigorously by a magnetic stirrer as 20 ml. of 1.0 *M* solution of sodium borohydride in ethanol was injected to reduce the catalyst. This was followed in approximately one minute by 25 ml. of concentrated hydrochloric acid to decompose the borohydride and provide a hydrogen atmosphere. The reaction was initiated by injecting 81 cc., 86.0 g., of diethyl maleate. The reaction was complete in 60 to 70 minutes. The reaction solution was filtered to remove catalyst, treated with 5% sodium bicarbonate, and extracted with methylene chloride. Distillation of the extract yielded 77.6 g., 90% yield, of diethyl succinate, b.p. 103–104.5° at 15 mm., n^{20}D 1.4201.

In some cases the presence of a strong acid, such as hydrochloric acid, may be undesirable. In such cases, acetic acid may be utilized. Moreover, by maintaining essentially anhydrous conditions in the hydrogenation flask, one can minimize solubility problems, encountered with higher hydrocarbons, terpenes, and steroids. This procedure is illustrated by the hydrogenation of β-pinene.

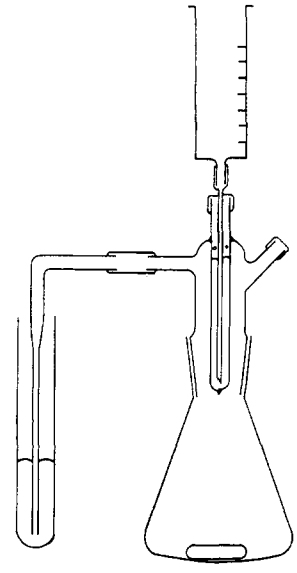

Fig. 1.—Hydrogenation apparatus with automatic valve.

In the 250-ml. flask was placed 5 g. of Darco K-B carbon, 100 ml. of anhydrous ethanol and 5.0 ml. of a 0.20 *M* solution of chloroplatinic acid in ethanol. After addition of 20 ml. of 1.0 *M* sodium borohydride in ethanol to reduce the catalyst, 10.0 ml. of acetic acid was added. The hydrogenation was initiated by the addition of 78.5 ml., 68 g., of (−)-β-pinene. There was isolated 60.0 g., 87%, pinane, b.p. 164–165.5° at 740 mm., n^{20}D 1.4618, $[\alpha]^{25}$D −21.3°.

In some cases it might be desirable to generate hydrogen in one flask as the hydrogen is being absorbed in the hydrogenation flask. For large scale hydrogenations this has the advantage of reducing the amounts of solvent which must be handled. The following procedure is representative. Hydrogen was generated by adding a 2.5 *M* solution of sodium borohydride in water to aqueous acetic acid in a generator fitted with the valve previously described. In the stirred hydrogenation flask, a 500-ml. Erlenmeyer, was placed 5 g. of carbon, 100 ml. of ethanol, 5.0 ml. of 0.20 *M* chloroplatinic acid in ethanol, and 20 ml. of 1.0 *M* sodium borohydride in ethanol. Ethyl oleate, 179 ml. (155 g.), was added, and the flask connected to the generator. The system was flushed with hydrogen from the generator, acetic acid (10.0 ml.) injected into the hydrogenation flask, and the hydrogenation allowed to proceed. The reaction was complete in two hours. The solution was filtered, and added slowly to ice-water to recover ethyl stearate, m.p. 32–33°, in 91% yield.

The procedure was applied successfully to the hydrogenation of 500 g. of ethyl oleate, using a 1-l. flask with a larger quantity of catalyst.

The controlled generation of hydrogen should be very helpful even in cases where it is desired to

(1) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 1493, 1494, 1495, 2827 (1962).

follow literature procedures for hydrogenations. For example, the hydrogenation of cholesterol is a capricious reaction. However, Hershberg, *et al.*, reported that the erratic tendencies of this reaction could be overcome by performing the hydrogenation with platinic oxide in ethyl acetate in the presence of a small quantity of perchloric acid.[2] The reaction was carried out (on a scale 1/150 that described) utilizing the automatic hydrogen generator. The reaction required approximately one hour for completion. By doubling the amount of platinic oxide, the hydrogenation was complete in 20 min.

These new procedures should greatly facilitate laboratory-scale hydrogenations. The technique is also proving valuable for chemical analysis and for following the rates of hydrogenation.

We wish to acknowledge the generous assistance of Engelhard Industries, Inc., in supplying the chloroplatinic acid utilized in this study.

(2) E. B. Hershberg, E. Oliveto, M. Rubin, H. Staeudle and L. Kuhlen, *J. Am. Chem. Soc.*, **73**, 1144 (1951).

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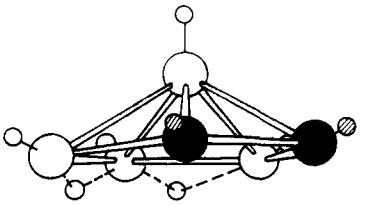
THE SYNTHESIS OF $B_4C_nH_{2n+4}$ COMPOUNDS FROM PENTABORANE-9 AND ALKYNES CATALYZED BY 2,6-DIMETHYLPYRIDINE

Sir:

Compounds having the general formula $B_4C_nH_{2n+4}$ (I) have been prepared from reactions between pentaborane-9 and several alkynes (propyne, 2-butyne, and 1-pentyne) in the presence of 2,6-dimethylpyridine. The stoichiometry of the reaction is believed to be

$$B_5H_9 + R{-}C{\equiv}C{-}R' + \text{2,6-dimethylpyridine} \longrightarrow B_4H_6C_2RR' + \text{2,6-dimethylpyridine}{\cdot}BH_3$$

A competing reaction involving the decomposition of pentaborane to give two moles of 2,6-dimethylpyridine-borane and $(BH)_x$ polymer[1] prevents the quantitative formation of I. In the absence of 2,6-dimethylpyridine alkynes do not react noticeably with pentaborane at ambient temperature. 2,6-Dimethylpyridine also has been shown to catalyze a rearrangement in pentaborane[2] and in pentaborane derivatives.[3,4]

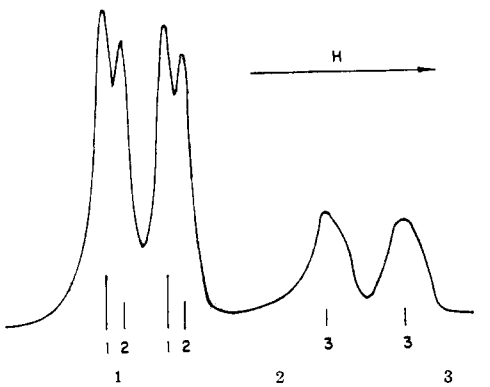


I[6]

○, Boron; ○, Hydrogen; ●, Carbon; ◍, R and R′

	R	R′
(a)	—H	—CH_3 (from propyne)
(b)	—CH_3	—CH_3 (from 2-butyne)
(c)	—H	—$CH_2CH_2CH_3$ (from 1-pentyne)

Fig. 1.—The basic structure of $B_4C_nH_{2n+4}$ compounds.[6]



Compound	δ[a]	J, c./s.	δ	J	δ	J
Ia	2.1	152	5.1	151	49.9	175
Ib	3.7	151	7.2	156	47.7	186
Ic	1.7	156	4.8	156	49.7	175

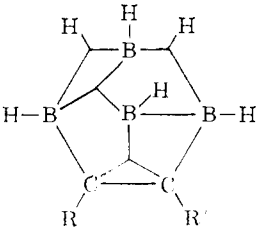
[a] Relative to $BF_3{\cdot}Et_2O$; T. Onak, H. Landesman, R. E. Williams and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

Fig. 2.—The B^{11} n.m.r. spectra and δ and J values of the $B_4C_nH_{2n+4}$ compounds.

The procedure adopted to prepare I was to shake vigorously a 1:1:5 mole ratio mixture of pentaborane, alkyne, and 2,6-dimethylpyridine for two to ten hours at ambient temperature. I was isolated after the addition of excess boron trifluoride ethyl etherate to the reaction mixture and the subsequent separation of the volatiles by vapor phase chromatography. The general formula $B_4C_nH_{2n+4}$ for I was determined on the basis of elemental and mass spectroscopic analysis as well as B^{11} and H^1 n.m.r. evidence.

Anal. Calcd. for $B_4C_5H_{14}$, Ic: C, 51.16; H, 12.02. Found: C, 51.01; H, 12.40.

The B^{11} and H^1 n.m.r. spectra indicate that the structure is similar to B_6H_{10}[5] and that two of the base borons are identical. The structure depicted in Fig. 1 for I is compatible with the data.[6] The



I′

(1) A similar decomposition of pentaborane with trimethylamine has been observed by A. B. Burg, *J. Am. Chem. Soc.*, **79**, 2129 (1957).

(2) B^{11} nuclear magnetic resonance studies show the deuterium in 1-deuteriopentaborane equilibrates between the apical and basal (and perhaps bridge) positions within one hour in the presence of 2,6-dimethylpyridine.

(3) T. P. Onak, *J. Am. Chem. Soc.*, **83**, 2584 (1961).

(4) R. N. Grimes and W. N. Lipscomb, *Proc. Nat. Acad. Sci.*, **48**, 496 (1962).

(5) R. E. Williams, S. G. Gibbons and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 6164 (1959); *J. Chem. Phys.*, **30**, 333 (1959).

(6) I′ is a projection formula of I in which bonding electrons are accounted in terms of two and three center bonds. The two and three center bonds between the apical and basal atoms are depicted in only one of many canonical forms.