

Diborane(4)-Bis(trifluorophosphine) Adduct

Sir:

Previously diborane(4) has been known only as the stable essentially unreactive bis(triphenylphosphine) adduct.¹ We have prepared an analogous less stable but synthetically more useful adduct by treating the triborane(7)-dimethyl ether adduct² (1.22 mmoles) with trifluorophosphine (21.0 mmoles) at -15° for 6 hr in a vessel (7-ml volume) designed to withstand 35-atm pressure. The product was separated by fractionation from a U tube cooled to -45° through U tubes cooled to -95 , -120 , and -145° into one cooled to -196° . Gas chromatography using a mineral oil-on-Firebrick column at -10° separated residual dimethyl ether from condensate collected at -95° . This gave pure product with about 50% attrition through decomposition on the column. Prior to any use the product was repurified by fractional condensation to obtain material which deposited as needle-shaped crystals at -120° . Melting points³ on individually purified samples were -114.5 , -114.2 , and -114.3° .

Vapor density determinations gave molecular weight values of 192 and 188; calculated for $B_2H_4(PF_3)_2$: 202. This corresponds to 10 and 15% decomposition during 3-4-min warming to room temperature.

Infrared frequencies were determined on a Perkin-Elmer Model 21 spectrometer with NaCl optics for the range 3000-800 cm^{-1} and on a Beckman IR-10 grating spectrometer using AgCl cell windows for the range 800-300 cm^{-1} . The absorbances observed in units of cm^{-1} were: 2403 (s) and 2353 (s) for BH_2 stretching; 1120 (m) for BH_2 wagging; and a PQR branching system centered at 940 (*vs*) for PF_3 stretching and 612 (s) for B-P stretching.

Two essentially quantitative reactions at room temperature provided analytical data. The one with hydrogen cleaved the boron-boron bond with the results shown in Table I. Tetraborane was obtained from the reaction with diborane as shown in Table II.

Table I^a

$B_2H_4(PF_3)_2 + H_2 \longrightarrow 2BH_3PF_3$						
$B_2H_4(PF_3)_2$	H_2		PF_3		BH_3^b	
	consumed	Obsd Calcd	recovered	Obsd Calcd	recovered	Obsd Calcd
0.34	0.32	0.34	0.66	0.68	0.63	0.68
0.40	0.41	0.40	0.76	0.79	0.79	0.80

^a Quantities in millimoles. ^b Recovered as trimethylamine borane.

Table II^a

$B_2H_4(PF_3)_2 + B_2H_6 \longrightarrow B_4H_{10} + 2PF_3$						
$B_2H_4(PF_3)_2$	B_2H_6 added	$B_2H_6 + PF_3$		B_4H_{10}		
		recovered	Obsd Calcd	Obsd	Calcd	
0.22	0.76	0.43 ^b	0.44 ^b	0.18 ^c	0.22	
0.18	3.81	3.85	3.99	0.21 ^d	0.18	

^a Quantities in millimoles. ^b PF_3 only. ^c 0.017 mmole of B_2H_6 ; no H_2 . ^d 0.008 mmole each of B_3H_9 and B_5H_{11} ; trace of H_2 .

(1) B. M. Graybill and J. K. Ruff, *J. Am. Chem. Soc.*, **84**, 1062 (1962).

(2) Details of this preparation will be given in another paper.

(3) A. E. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N.Y., 1933, p 183.

Decomposition of the adduct gives a large yield of hexaborane(12). Other experiments are in progress to apply the ready reactivity of this substance to preparation of new boron hydride derivatives.

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Photolysis of Sodium Cyclopentadienide

Sir:

In this communication we describe our studies on the ultraviolet irradiation of sodium cyclopentadienide, apparently the first inquiry into the chemical behavior of a *bona fide* photoexcited carbanion.¹

A 0.3 M solution of sodium cyclopentadienide in 20% *t*-butyl alcohol-80% tetrahydrofuran was irradiated for 2 hr,² during which time samples were analyzed by vpc. Bicyclo[2.1.0]pent-2-ene,³ a normal cyclopentadiene photolysis product, was not formed under these conditions; however, when excess cyclopentadiene was present, bicyclo[2.1.0]pent-2-ene was produced. Vpc analysis⁴ of nonpolar material revealed equal amounts of two dimeric, colorless photoproducts, representing approximately 5% of consumed starting material. In addition, smaller amounts of unidentified colored hydrocarbons as well as considerable polymeric material were recovered.

Evidence presented below reveals that the dimeric photoproducts are the *meso*- and *dl*-3-(3'-cyclopentenyl)cyclopentenes (I). The carbon skeletons were established by catalytic hydrogenation and diimide reduction⁵ to dicyclopentyl. The degree of unsaturation was found by mass spectral analysis of each photoproduct and of dicyclopentyl-*d*₄ obtained by deuteriodiimide⁶ reduction. Controlled diimide reduction of the mixture of photoproducts resulted in a single partial reduction product, 3-cyclopentylcyclopentene (II). The photoproducts exhibited only end absorption in the ultraviolet, indicating that the double bonds are not conjugated. These data, as well as the nmr spectra^{7,8}

(1) The related case of phenyllithium photolysis was reported by E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Am. Chem. Soc.*, **87**, 4964 (1965).

(2) The reaction medium was prepared by treatment of cyclopentadiene with sodium in tetrahydrofuran followed by addition of *t*-butyl alcohol. All solutions were dry, oxygen free, and maintained under nitrogen. Irradiations were carried out using a 450-w Hanovia high-pressure mercury arc lamp.

(3) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **88**, 846 (1966).

(4) Succinate polyester of diethylene glycol column, 2 m \times 0.25 in., at 74° .

(5) E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *J. Am. Chem. Soc.*, **83**, 3725 (1961).

(6) Deuteriodiimide was prepared *in situ* from CH_3OD , CD_3COOD , and disodium azodicarboxylate (*cf.* ref 5).

(7) Nmr spectra were measured in carbon tetrachloride solution at 38° , using a Varian A-60 spectrometer.

(8) Nuclear magnetic resonance spectra of the photoproducts are identical except for fine splitting in the olefinic region. Significantly, the olefinic splitting of one isomer (Ia) resembles that of the partial reduction product II. In terms of the most favorable conformations (Ia,b) the environment of the olefinic hydrogens of *meso*-3-(3'-dicyclopentenyl)cyclopentene, in which the double bonds lie on opposite sides of the molecule, resembles the environment of the olefinic hydrogens in II. On the basis of this argument, compound Ia is the *meso* isomer. In the most stable conformation of the *dl* isomer, the double bonds reside on the same side of the molecule (Ib), and it is reasonable that because of their proximity the double bonds of the *dl* isomer would exert greater