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 adduct[2] (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 points[3] 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]

$$B_2H_4(PF_3)_2 + H_2 \longrightarrow 2BH_3PF_3$$

	H_2 consumed		PF_3 recovered		BH_3[b] recovered	
$B_2H_4(PF_3)_2$	Obsd	Calcd	Obsd	Calcd	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_6	$B_2H_6 + PF_3$ recovered		B_4H_{10}	
$B_2H_4(PF_3)_2$	added	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_5H_9; no H_2. [d] 0.008 mmole each of B_5H_9 and B_5H_{11}; trace of H_2.

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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(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.

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 analysis[4] 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 reduction[5] to dicyclopentyl. The degree of unsaturation was found by mass spectral analysis of each photoproduct and of dicyclopentyl-d_4 obtained by deuteriodiimide[6] 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]

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(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 × 0.25 in., at 74°.

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

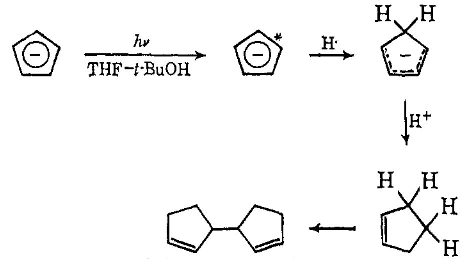
(6) Deuteriodiimide was prepared *in situ* from CH_3OD, CD_3COOD, and disodium azodicarboxylate (*cf.* ref 5).

(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

[vinyl, τ 4.36 (4); methine allylic, 7.3 (2); allylic, 7.7 (4); methylene, 8.0–8.8 (4)], are consistent with the postulated structures. Identities were confirmed by comparison with authentic *meso*- and *dl*-3-(3′-cyclopentenyl)cyclopentenes, prepared by Grignard coupling of 3-chlorocyclopentene.

That of all possible dimeric photoproducts only these dicyclopentenyls are observed, and in equal amounts, suggests that the final step in product formation is coupling of cyclopentenyl radicals,[9] perhaps produced *via* hydrogen abstraction by photoexcited cyclopentadienide to give an anion radical which is then protonated (eq 1).



(1)

Since the photochemical event occurring with cyclopentadiene in neutral or less basic solution differs entirely from that observed under the present, more strongly basic, conditions, cyclopentadienide *per se* must be involved in conversion to the dicyclopentenyls. Also, since yields of Ia,b are not enhanced when a 50:50 mixture of cyclopentadiene and cyclopentadienide is photolyzed, neither ground- nor excited-state cyclopentadiene is implicated in the reaction. Furthermore, the photoproducts are not produced when *t*-butyl alcohol is absent from the THF–sodium cyclopentadienide photolysis solution.

In an experiment designed to locate the source of the abstracted hydrogen atom, all exchangeable protons in the reaction system were replaced by deuterium. Perdeuteriocyclopentadienide was prepared from perdeuteriocyclopentadiene and photolyzed in the presence of 20% *t*-butyl alcohol-O-*d*. The 3,3′-dicyclopentenyls obtained in this experiment were shown by mass spectral analysis to be perdeuterated. Consequently, photoexcited cyclopentadienide is not hydrogen abstracting from solvent in the customary fashion (*i.e.*, from the methyl groups of *t*-butyl alcohol or the α-methylenes of tetrahydrofuran). Abstraction of the hydrogen atom bonded to oxygen would not be expected on the basis of bond strengths; however, there is available from photoexcitation sufficient energy for this reaction, and this hydroxylic hydrogen may well be in an optimal position for abstraction. Close association in the ground state between exchangeable protons and cyclopentadienide may be favored because of hydrogen bonding or solvation of sodium ions, which in turn are associated with cyclopentadienide. The resulting chemistry is, then, expected to be a unique consequence of carbanion photoexcitation in protic solvent.

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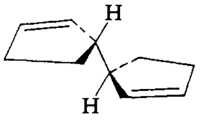
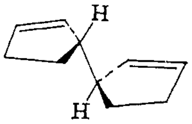
influence on each other than do those of the *meso* isomer. Thus Ib, exhibiting greater olefinic fine splitting, is assigned the *dl* configuration.



Ia



Ib

(9) Equal amounts of the hydrocarbons Ia,b have been obtained by the benzophenone-sensitized photolysis of neat cyclopentene, presumed to generate cyclopentenyl radicals (K. S. Sidhu, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, **44**, 531 (1966). The configurational assignments suggested by these authors are opposite to those proposed herein.[8]

(10) National Science Foundation Fellow, 1964–1966, and Weiss Fellow, 1966–1967.

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New Synthesis of Cyclobutadieneiron Tricarbonyl

Sir:

Metal complexes of substituted cyclobutadienes have been prepared either through cycloaddition of acetylenes catalyzed by metal carbonyls or metal complexes,[1] by demetalation of heterocyclopentadienes,[2] by ligand transfer reaction,[3] or by the reduction of 3,4-dihalocyclobutenes with suitably chosen metal carbonyls.[4] Of these, only the latter method has been successfully applied to the synthesis of a complex of the parent hydrocarbon itself, namely cyclobutadieneiron tricarbonyl.[4b] We now report the preparation of this substance in essentially one step from α-pyrone.

Photolysis of α-pyrone (**1**) in ether solution has been reported to give the photoproduct **2** in quantitative yield.[5] When iron pentacarbonyl is added to these solutions and irradiation is continued for a brief period, both cyclobutadieneiron tricarbonyl (**3**) [infrared (C≡O) 4.87, 5.05 μ; nmr τ 6.00 (CCl_4); ultraviolet $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 215, 360 mμ (ϵ 19,000, 84); mass spectroscopy *m/e* 192, 164, 136, 108] and α-pyroneiron tricarbonyl (**4**) are formed in 10–15% combined yield.[6] The relative yields of these two substances appear to vary somewhat with temperature. At −15° **3** is the principal component in the reaction mixture but at room temperature both products are formed in approximately equal amounts.[7]

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(1) W. Hübel, E. H. Braye, A. Clauss, E. Weiss, D. A. Brown, G. S. D. King, and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959); W. Hübel and R. Merenyi, *J. Organometal. Chem.* (Amsterdam), **2**, 213 (1964); A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961); P. M. Maitlis, D. F. Pollock, M. L. Games, and W. J. Pryde, *Can. J. Chem.*, **43**, 470 (1965). These and the citations in ref 2–4 are illustrative only. A more complete listing of references is to be found in the review of P. M. Maitlis, *Advan. Organometal. Chem.*, **1**, 95 (1966).

(2) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961).

(3) P. M. Maitlis and A. Efraty, *J. Organometal. Chem.* (Amsterdam), **4**, 172, 175 (1965); P. M. Maitlis and M. L. Games, *J. Am. Chem. Soc.*, **85**, 1887 (1963).

(4) (a) R. Criegee and G. Schroeder, *Ann.*, **623**, 1 (1959); (b) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

(5) E. J. Corey and J. Streith, *ibid.*, **86**, 950 (1964). No more than 1% α-pyrone remains at the end of the reaction.

(6) The low yield of **3** and **4** has been shown to be due principally to photolytic decomposition of both of these substances under the conditions of their formation. The decomposition of **3** by ultraviolet light has been reported recently by W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strauszand, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

(7) The ratio of products was estimated by determination of the nmr spectrum of the mixture after the crude reaction product had been chromatographed on alumina. Alternatively the α-pyrone complex **4** may be separated from **3** either by crystallization of **4** from pentane solution or by fractional sublimation of **3** at room temperature and 0.1 mm.