COMMUNICATIONS TO THE EDITOR

DISPLACEMENT REACTIONS ON THE $B_{10}H_{12}$ UNIT

Sir:

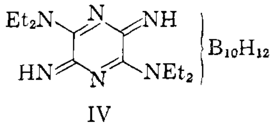
We wish to report two transformations of the compound $B_{10}H_{12}\cdot 2CH_3CN$[1] (I) which indicate that the $B_{10}H_{12}$ unit is transferred from one ligand to another.

Treatment of decaborane with diethylcyanamide in diethyl ether at room temperature produces hydrogen and the air stable and crystalline compound $B_{10}H_{12}\cdot 2(C_2H_5)_2NCN$ (II) which melts at 145° dec. (calcd.: B, 34.17; H, 10.19; C, 37.94; N, 17.70. Found: B, 31.32; H, 10.31; C, 37.89; N, 16.65). Approximately one mole of hydrogen is evolved per mole of product formed. The infrared spectrum of II contains strong C≡N stretching at 2300 cm.$^{-1}$ (C≡N in diethylcyanamide at 2210 cm.$^{-1}$). This indicates that the $B_{10}H_{12}$ unit is attached by the amino nitrogens of the two diethylcyanamide molecules in II. Treatment of I with diethylcyanamide in refluxing benzene produces II in high yield with the displacement of acetonitrile (recovered from run in *p*-xylene).

Decaborane and triphenylphosphine react in diethyl ether at the reflux temperature to produce a crystalline compound $B_{10}H_{12}\cdot 2(C_6H_5)_3P$ (III) (calcd.: B, 16.78; H, 6.56; C, 67.05; P, 9.61. Found: B, 15.78; H, 6.91; C, 64.13; P, 9.56) which is stable without melting to above 300°. Again, approximately one mole of hydrogen is evolved per mole of compound produced. Both II and III are recrystallized easily from polar solvents such as methylene chloride. Treatment of I or II with triphenylphosphine in hot acetonitrile and benzene, respectively, produces pure III. Attempts to convert III to II with excess diethylcyanamide were unsuccessful as were attempts to convert II to I by treatment with acetonitrile. The chart summarizes these transformations.

$$\begin{tikzcd}
B_{10}H_{12}\cdot 2CH_3CN \arrow[dd, "(C_2H_5)_2NCN"'] \arrow[rrd, "(C_6H_5)_3P"] & & \\
& B_{10}H_{14} \arrow[lu, "-H_2"', "CH_3CN"] \arrow[ld, "-H_2", "(C_2H_5)_2NCN"'] \arrow[r, "(C_6H_5)_3P", "-H_2"'] & B_{10}H_{12}\cdot 2(C_6H_5)_3P \\
B_{10}H_{12}\cdot 2(C_2H_5)_2NCN \arrow[rru, "(C_6H_5)_3P"'] & &
\end{tikzcd}$$

Liquid hydrogen cyanide and II react slowly at room temperature to produce the brilliant red, crystalline compound $B_{10}H_{12}\cdot 2(C_2H_5)_2NCN\cdot 2HCN$ (IV). (Calculated: B, 29.22; H, 9.18; C, 38.89; N, 22.69. Found: B, 29.39; H, 9.49; C, 38.51; N, 22.54.) The compound IV is extremely stable toward water and mild oxidizing agents such as acetone. Its infrared spectrum exhibits N–H (3300 cm.$^{-1}$) and N=C (1630 cm.$^{-1}$) stretching. As in I, II and III, B–H stretching is observed at 2500 cm.$^{-1}$. In the ultraviolet λ_{max} 450 mμ, ϵ 9.5 × 10^3. The partial structure of IV is tentatively formulated as



IV

The relatively great sizes of triphenylphosphine and the postulated ligand of IV place considerable steric limitations upon the possible bonding sites of the $B_{10}H_{12}$ unit. It appears clear, however, that the $B_{10}H_{12}$ unit functions as a discrete electron deficient species.

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[1] R. Schaeffer, THIS JOURNAL, **79**, 1006 (1957).

PHOTO-γ-TROPOLONE METHYL ETHER

Sir:

Irradiation[1] of an aqueous solution of γ-tropolone methyl ether[2] (IA) gave photo-γ-tropolone methyl ether (II) in good yield. This represents the first instance of photoisomerization in a simple, monocyclic troponoid compound.[3]

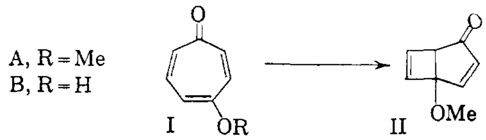

Photo-γ-tropolone methyl ether (b.p. 34° at 0.1 mm.), obtained by fractional distillation of the methylene chloride extract of the filtered aqueous solution from the irradiation, showed an infrared maximum at 5.85 μ (but no intense maximum in the 6.2 μ region) and $\lambda_{max}^{95\%\ EtOH}$ 243 mμ (14,900) and 328 mμ (1780). Hydrogenation of II over platinum gave a dihydro derivative, III, ($\lambda_{max}^{CHCl_3}$ 5.85 μ and $\lambda_{max}^{95\%\ EtOH}$ 215 mμ (3,200)) and a tetrahydro derivative, IV, ($\lambda_{max}^{CHCl_3}$ 5.75 μ; no high intensity absorption in the ultraviolet). The photoisomer II did not show chemical or physical properties characteristic of enol ethers. Dilute acid did not alter II; however, refluxing II in dilute hydrochloric acid for 6–7 hours gave a high yield of γ-tropolone (IB) identified by its characteristic ultraviolet spectra in alcohol and 0.1 *N* sodium hydroxide.[4,5] Similar acid treatment of dihydrophoto-γ-tropolone methyl ether (III) gave 2-cyclohepten-1,4-dione (V). For comparison, 2-cyclohep-

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[1] Sunlight and mercury arc sources gave the same product.

[2] J. Meinwald and O. L. Chapman, THIS JOURNAL, **80**, 633 (1958).

[3] The naturally occurring alkaloid colchicine has previously been found to yield three photoproducts (R. Grewe and W. Wolf, *Ber.*, **84**, 621 (1951), and F. Šantavý, *Biol. Listy*, **31**, 246 (1950)). The structures of two of the photoproducts are known (E. J. Forbes, *J. Chem. Soc.*, 3864 (1955) and P. D. Gardner, R. L. Brandon and G. R. Haynes, THIS JOURNAL, **79**, 6334 (1957)).

[4] L. Nozoe, T. Mukai, Y. Ikegami and T. Toda, *Chem. and Ind.*, 66 (1955).

[5] R. B. Johns, R. S. Coffey and A. W. Johnson, *ibid.*, 658 (1955).