

deuterium oxide produced allogibberic acid containing 4.67% excess deuterium, as expected from a precursor with an 8,9 double bond (*cf.* gibberellenic acid⁶ which has the $\Delta^{1,8}$ system). Strong, but not rigorous, evidence for the (α) stereochemistry in gibberellic acid as in allogibberic acid is given by the close correspondence in shape and intensity of the rotatory dispersion curve from the *seco* keto esters derived from the oxidation of ring D of methyl allogibberate and of the acetate of methyl α -dihydrogibberellate ($[\alpha]_{314}^{\text{CH}_3\text{OH}} + 1070$ in both cases). Gibberellic acid is therefore Ia,^{7,8} subject only to rigorous confirmation of the C₈ stereochemistry.

(6) K. Gerzon, H. Bird, Jr., and D. Woolf, Jr., *Experientia*, **13**, 487 (1957).

(7) The same conclusion has been reached by Cross, *et al.*, and it was agreed that each group submit its results simultaneously for publication.

(8) We wish to thank Dr. L. H. Sarett and Merck, Sharp, and Dohme for the generous gift of the Gibberellic acid used in these studies.

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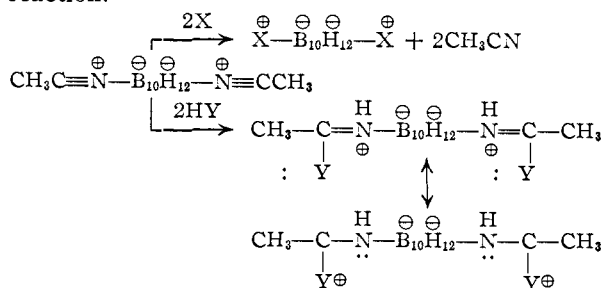
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THE REACTIONS OF BIS-ACETONITRILE DECABORANE WITH AMINES

Sir:

The structure of bis-acetonitrile decaborane recently reported by Lipscomb and Reddy¹ would *a priori* suggest two types of reaction: displacement of the acetonitrile ligand by another ligand (X) and the addition of an HY molecule (where Y carries an unshared pair of electrons) to the acetonitrilium portion of the molecule. The former reaction has been previously reported.² We now wish to report evidence for the second type of reaction.



Treatment of bis-acetonitrile decaborane with benzene solutions of ethylamine, diethylamine, *n*-propylamine and di-*n*-propylamine at the reflux temperature produced high melting derivatives whose infrared spectra were characterized by N-H and C=N stretching bands. Proton exchange of these compounds with deuterium oxide resulted in deuteration of the N-H groups. The positions of the C=N bands in the infrared were unchanged by this treatment. No B-H exchange was observed. Analyses of these compounds were in agreement with the general formulation $\text{B}_{10}\text{H}_{12}\cdot 2\text{CH}_3\text{CN}\cdot 2\text{R}_2\text{NH}$ (where R is alkyl or hydrogen). All products of this type failed to react with triphenylphosphine.²

The analyses and infrared spectra of these materials are best rationalized in terms of the

(1) W. N. Lipscomb and J. van der Mass Reddy, *THIS JOURNAL*, **81**, 754 (1959).

(2) M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **80**, 6685 (1958).

adducts indicated above ($\text{Y} = \text{—NRH}$ or —NR_2). The stability of these compounds toward ethanol and triphenylphosphine further suggests the presence of a strongly basic ligand such as an amidine.

In contrast to these results the reaction of triethylamine with bis-acetonitrile decaborane in the presence of boiling benzene produced two isomeric materials of composition $\text{B}_{10}\text{H}_{12}[\text{N}(\text{C}_2\text{H}_5)_3]_2$ both of which melted at $233\text{--}235^\circ$ dec. One derivative apparently was covalent, benzene soluble and could be converted to bis-triphenylphosphine decaborane² by treatment with triphenylphosphine in hot benzene. The other isomer was a benzene insoluble salt which displayed N-H stretching in the infrared and from which a triphenylphosphine derivative could not be formed. Treatment of the benzene soluble isomer with additional triethylamine in hot benzene produced the benzene insoluble isomer in 60% yield. Similar treatment of decaborane with triethylamine also produced the ionic compound in high yield. Equilibration of both compounds with deuterium oxide in such solvents as acetonitrile, dioxane and tetrahydrofuran gave both NH and BH exchange in the case of the ionic compound but no exchange was observed with the covalent compound. The amine molecules apparently both are present in the ionic species as diethylammonium ions since a bis-tetramethylammonium compound can be prepared from it by simple treatment with tetramethylammonium chloride in aqueous ethanol. These preliminary results suggest the presence of a $\text{B}_{10}\text{H}_{10}^{-2}$ ion.

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REACTION OF AROMATIC PHOSPHINE OXIDES WITH ALKALI METALS

Sir:

In contrast to the conversion of triphenylphosphine to diphenylphosphide anion by alkali metals,^{1,2} triaryl phosphine oxides have been reported³ to form adducts with two or four moles of alkali metal formulated as Ar_3POM_2 and $\text{Ar}_3\text{POM}_3 + \text{ArM}$, respectively. Since unlike electronic configurations about phosphine and phosphine oxide phosphorus might be responsible for these differences, it was of interest to examine further the behavior of phosphine oxides with alkali metals.

We wish to report that solutions of triphenylphosphine oxide in 1,2-dimethoxyethane react with lithium or sodium to form biphenyl radical anion identified by its e.p.r. spectrum.⁴ If potassium is used, a different paramagnetic species is formed initially whose spectrum consists of eleven lines split by 1.75 gauss. With excess potassium this species slowly disappears and is replaced by biphenyl radical anion.

Although solutions obtained from different

(1) D. Wittenberg and H. Gilman, *J. Org. Chem.*, **23**, 1063 (1958).

(2) K. Issleib and H. O. Frolich, *Z. Naturforsch.*, **14b**, 349 (1959).

(3) F. R. Hein, H. Plust and H. Pohlenmann, *Z. anorg. allgem. Chem.*, **272**, 25 (1953).

(4) E. de Boer, *J. Chem. Phys.*, **25**, 190 (1956).