deuterium oxide produced allogibberic acid containing 4.67% excess deuterium, as expected from a precursor with an 8,9 double bond (*cf.* gibberellenic acid[6] 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 form the *seco* keto esters derived from the oxidation of ring D of methyl allogibberate and of the acetate of methyl α-dihydrogibberellate ($([\alpha])^{CH_3OH}_{314} + 1070$ in both cases). Gibberellic acid is therefore Ia,[7,8] subject only to rigorous confirmation of the C_8 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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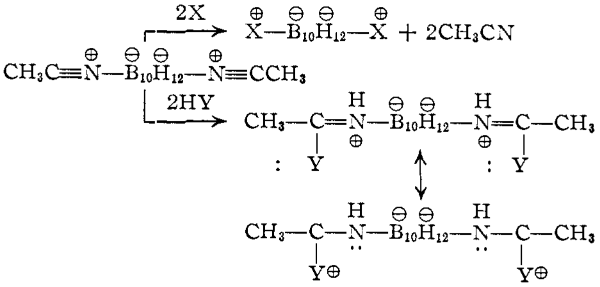
RECEIVED SEPTEMBER 8, 1959

THE REACTIONS OF BIS-ACETONITRILE DECABORANE WITH AMINES

Sir:

The structure of bis-acetonitrile decaborane recently reported by Lipscomb and Reddy[1] 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 $B_{10}H_{12}\cdot 2CH_3CN\cdot 2R_2NH$ (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 adducts indicated above (Y = –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 $B_{10}H_{12}[N(C_2H_5)_3]_2$ both of which melted at 233–235° dec. One derivative apparently was covalent, benzene soluble and could be converted to bis-triphenylphosphine decaborane[2] 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 $B_{10}H_{10}^{-2}$ ion.

[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).

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RECEIVED JULY 30, 1959

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 reported[3] to form adducts with two or four moles of alkali metal formulated as Ar_3POM_2 and Ar_2POM_3 + 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

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

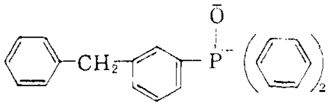
[2] K. Issleib and H. O. Frolich, *Z. Naturforsch.*, **14b**, 349 (1959).

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

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

alkali metals utimately contain the same radical anion, different phosphorus-containing anions are formed. A solution of two moles of sodium per mole of triphenylphosphine oxide in 1,2-dimethoxyethane reacts with benzyl chloride forming benzyldiphenylphosphine oxide in 77% yield. The predominant portion of the cleaved phenyl group forms benzene. Methyldiphenyl- and ethyldiphenylphosphine oxides and tetramethylenebis-(diphenylphosphine oxide) were prepared similarly in 65, 62 and 66% yields by reaction with methyl iodide, ethyl bromide and tetramethylene bromide, respectively.

When, however, solutions of two moles of lithium or potassium per mole of triphenylphosphine oxide were treated with benzyl chloride, the only product isolated was a compound $C_{25}H_{21}PO$, m.p. 237–238°, formed in 20% yield. *Anal.* Calcd. for $C_{25}H_{21}PO$: C, 81.52; H, 5.71; P, 8.42; mol. wt., 368. Found: C, 80.81, 80.30; H, 6.17, 6.04; P, 8.01; mol. wt., 385. This compound has infrared absorption bands at 1185, 790 and 720 cm.$^{-1}$, indicating it to be a *m*-substituted tertiary phosphine oxide consistent with its formulation as diphenyl (α-phenyl-*m*-tolyl) phosphine oxide, I.



I

Reaction of benzyldiphenylphosphine oxide with sodium resulted in the formation of phosphine oxide "ylid,"[5] since reaction with ethyl bromide formed (α-ethylbenyl)-diphenylphosphine oxide, m.p. 185–186° in 35% yield. *Anal.* Calcd. for $C_{21}H_{21}PO$: C, 78.73; H, 6.61; P, 9.67; mol. wt., 320. Found: C, 78.59; H, 6.90; P, 9.78; mol. wt., 330.

Ethyldiphenylphosphine oxide, however, after reaction with sodium and then benzyl chloride, formed benzylethylphenylphosphine oxide in 39% yield.

The phenyl cleavage of triphenylphosphine and triphenylphosphine oxide by sodium is consistent with the initial formation of a radical anion either adsorbed at the metal surface or in low concentration in solution which collapses to phenyl radical and phosphide or phosphinite anion. Phenyl radical may then dimerize or form phenide ion by oxidizing a second mole of sodium. This scheme is supported by the formation of phenyllithium during the cleavage of triphenylamine[1] and by the ease with which free radicals are reduced by alkali metals.[6]

The reaction of lithium or potassium with triphenylphosphine oxide, however, may involve ring metalation prior to reaction with halide as evidenced by the formation of I. Further experiments to clarify the behavior of these and related organophosphorus compounds are in progress.

(5) L. Horner, H. Hoffman and H. G. Wippel, *Ber.*, **91**, 61 (1958).

(6) H. E. Bent and N. B. Keevil, THIS JOURNAL, **58**, 1228 (1936).

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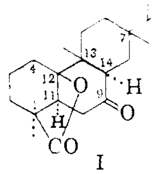
RECEIVED AUGUST 24, 1959

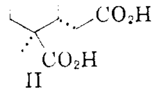
THE ABSOLUTE CONFIGURATION OF ROSENONOLACTONE AND RELATED DITERPENOIDS

Sir:

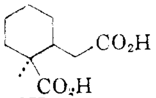
Evidence previously adduced[1,2] indicates that rosenonolactone, a diterpenoid metabolite of *Trichothecium roseum* Link, has the structure and *relative* stereochemical configuration (I), in which no configurational assignment was allocated to the substituents at C-7. We now wish to present evidence which conclusively establishes the *absolute* configuration of several diterpenoids of the rosenonolactone group, such stereochemical information being of crucial importance in defining the nature of the biogenetic precursor(s)[3] of these mold metabolites.



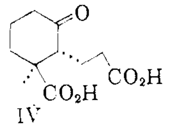
I



II



III



IV

A comparison of the optical rotatory dispersion curves[4] of (−)-*trans*-2-methyl-2-carboxy-6-ketocyclohexylacetic acid (II),[5] derived (after epimerization of the initially formed *cis*-acid) from ring A of rosenonolactone,[2,6] and of (−)-*trans*-2-methyl-2-carboxy-6-ketocyclohexylpropionic acid, the absolute configuration of which has been unequivocally established as (IV),[7] shows that both compounds exhibit a negative Cotton effect and that the rotatory dispersion curves are almost superimposable. The conformations of (II) and (IV) will be identical and hence the C_{10} acid derived from ring A has the absolute configuration (II).

Independent verification of this assignment was made by Clemmensen reduction of II, which provided (−)-*cis*-2-methyl-2-carboxycyclohexylacetic acid (III) of known absolute configuration.[8]

(1) B. Green, A. Harris, W. B. Whalley and H. Smith, *Chemistry and Industry*, 1369 (1958).

(2) A. Harris, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 1799 (1958); B. Green and W. B. Whalley, *ibid.*, in press.

(3) See "Ciba Foundation Symposium on the Biosynthesis of Terpenes and Sterols," Churchill, London, 1959, pp. 239–242 (by D. Arigoni), and pp. 258–260 (by A. J. Birch and H. Smith).

(4) For introduction to this approach see C. Djerassi, *Bull. Soc. Chim. France*, 741 (1957); C. Djerassi "Optical Rotatory Dispersion. Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., Chapter 10.

(5) The structure of the acid II has now been confirmed by synthesis of its racemate: alkylation of Hagemann's ester with ethyl chloroacetate, then alkaline cleavage furnished 2-methyl-6-ketocyclohex-1-ene acetic acid: addition of cyanide and alkaline saponification provided *d,l*-II.

(6) A. Robertson, W. R. Smithies and E. Tittensor, *J. Chem. Soc.*, 879 (1949).

(7) H. Inhoffen, S. Schütz, P. Rossberg, O. Berges, K.-H. Nordsiek, H. Plenio and E. Höroldt, *Ber.*, **91**, 2626 (1958).

(8) F. Gautschi, O. Jeger, V. Prelog and R. B. Woodward, *Helv. Chim. Acta*, **38**, 296 (1955).