TABLE I

Expt.[a]	Reaction time, min.	Mole % acetyl chloride consumed	Mole % material recovered	Acetylferrocene, g.	Diacetylferrocene, g.	k_2/k_1 (apparent)
1[b]	150	72.6	72	0.090	0.480	10.9
2[c]	12	62.5	86	0.546	0.131	0.45
3[d]	150	84.0	85	1.034	None	0
4[e]	150	22.8	87	0.120	0.095	6.8
5[f]	150	92.1	91	0.660	0.280	0.40

[a] All reactions were carried out at 0°, in methylene chloride, employing one gram of ferrocene and a mole ratio of $AlCl_3$:AcCl:ferrocene of 2:1:1. [b] Average of three runs. [c] Average of two runs. [d] Reaction run under conditions of tenfold dilution. [e] Solution saturated with hydrogen chloride prior to addition of reactants; average of two runs. [f] Magnesium amalgam added prior to addition of reactants.

reduction in the mole per cent. of acyl halide consumed (compare expts. 4 and 1), while the apparent rate constant ratio is abnormally large considering the extent of reaction (compare expts. 4 and 2). Conversely, initial addition of amalgamated magnesium leads to consumption of the hydrogen chloride generated, with a consequent reduction in the apparent value of k_2/k_1 (expt. 5). The expected effect of dilution on the equilibrium concentration of the complex salt and consequently on the course and extent of reaction is well illustrated in experiment 3.

The complex salt has been isolated as a pale green solid (dec. *ca.* 125°), by precipitation with ligroin, from methylene chloride solutions. [*Anal.* Calcd. for $(C_{10}H_{10}Fe{\cdot}HAlCl_4)_n$: ferrocene, 52.5; Al, 7.6. Found: ferrocene, 54.0; Al, 8.1; neut. equiv., 89. Found: 86.] Decomposition of the substance with water regenerates ferrocene, accompanied by small amounts of the ferricinium cation, to which impurity the salt owes its green color.

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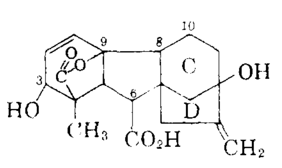
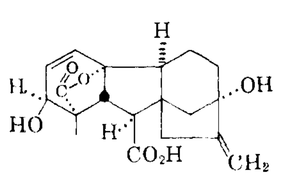
THE STEREOCHEMISTRY OF GIBBERELLIC ACID

Sir:

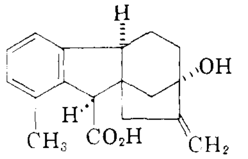
The revised structure I has been demonstrated recently for gibberellic acid by Cross, *et al.*[1] We wish to report work which extends our previous results[2] on the stereochemistry of allogibberic acid (II) to that of gibberellic acid itself.



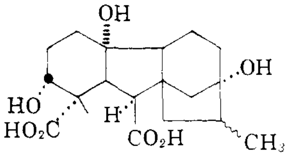
I



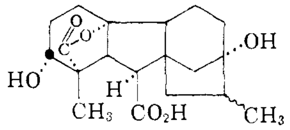
Ia



II



III



IV

1. **The Lactone Ring.**—Its relationship to the β-oriented two carbon bridge of ring D follows from the demonstration that the lactone is α-oriented. Tetrahydrogibberellic acid, m.p. 273–275° (reported[3] m.p. 273–274°), was hydrolyzed at room temperature for eighteen hours with 20% sodium hydroxide solution. This resulted in a diacid (III), the dimethyl ester of which, m.p. 185–187° (found: C, 63.60; H, 8,32), has $[\alpha]^{\mathrm{EtOH}}_{\mathrm{D}}$ − 40.3°. Refluxing the diacid for two hours with ethyl acetate containing a drop of concentrated hydrochloric acid gave a lactonic acid (IV) isomeric with tetrahydrogibberellic acid. IV had m.p. (285) 293–295° and gave a methyl ester, m.p. (185) 196–200°, $\gamma_{\max}^{\mathrm{CHCl_3}}$ 5.7, 5.8 μ (found: C, 66.15; H, 7.72), $[\alpha]^{\mathrm{EtOH}}_{\mathrm{D}}$ + 34.4°. The lactonic acid (IV) *has the same lactone ring system as gibberellic acid:* oxidation of methyl gibberellate with managanese dioxide gave the corresponding ketone, m.p. 186–188.7°, $\lambda_{\max}^{\mathrm{EtOH}}$ 228 mμ (7500) (found: C, 66,72; H, 6.05). Reduction of the unsaturated ketone with platinum oxide in acetic acid gave a substance identical (infrared, mixed melting point) with V-methyl ester. This establishes that V differs from tetrahydrogibberellic acid *only* at the C_3 secondary hydroxyl. The large positive rotation difference between the lactonic ester V and the conformationally related diester III establishes the α-orientation of the lactone ring.[4]

2. **The C_5 Hydrogen.**—This hydrogen must be β-oriented for the following reason: Should the C_5 hydrogen be α, C_6 would be axial to ring A and the C_6 carboxyl group, which is known to be β,[2] would have the less stable of the two possible orientations. Base hydrolysis of the *methyl ester* of tetrahydrogibberellic acid followed by relactonization gave the same 3-epitetrahydrogibberellic acid (IV) obtained from hydrolysis of the acid itself. Since IV has the original orientation of the carboxy group, no epimerization has taken place and C_6 must be equatorially linked to ring A.

3. **The C_3 Hydroxyl.**—Our observation (*vide supra*) that the 3-epi configuration of IV is formed on catalytic hydrogenation of the 3-ketone from gibberellic acid implies α-stereochemistry for the 3-epi series (adsorption from the β-side, *trans* to the lactone). Consequently, gibberellic acid must have a 3-β-hydroxyl. The same conclusion is reached[5] by noting that the base epimerization at C_3 must imply axial → equatorial transformation (presumably *via* dealdolization–realdolization).

4. **The C_8 Hydrogen.**—The α-oriented C_1 hydrogen of allogibberic acid (II) is not the same as the original C_8 hydrogen of gibberellic acid: Transformation of I into II with hydrogen chloride in

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(1) B. E. Cross, J. F. Grove, J. MacMillan, J. S. Moffatt, T. P. C. Mulholland, J. C. Seaton and N. Sheppard, *Proc. Chem. Soc.*, in press.

(2) G. Stork and H. Newman, THIS JOURNAL, **81**, 3168 (1959).

(3) Y. Sumiki, A. Kawarada, H. Kitamura, Y. Seta and N. Takahashi, Abstract No. 460 in F. H. Stodola, "Source Book on Gibberellin 1828–1957," U. S. Dept. of Agriculture, 1958.

(4) W. Klyne, *Chem. and Ind.*, 1198 (1954).

(5) B. E. Cross, J. F. Grove, J. MacMillan, T. P. Mulholland and N. Sheppard, *Proc. Chem. Soc.*, 221 (1958).

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 ($([\alpha])_{314}^{CH_3OH}$ + 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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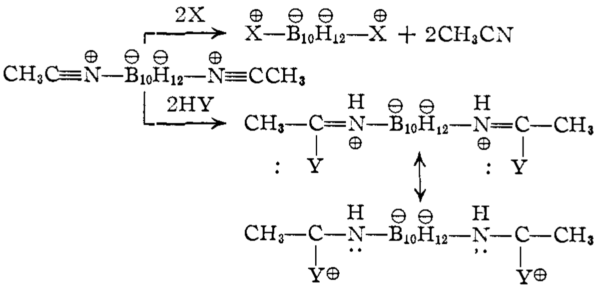
RECEIVED SEPTEMBER 8, 1959

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

[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).