

mechanism involving the intermediacy of triplet 1,2-dimethylcyclopropane in the triplet methylene reaction.

Further work now in progress on this system and more detailed interpretation will be presented at a later date.

**Acknowledgments.** The author thanks the Research Corporation and the National Science Foundation for funds which made this work possible.

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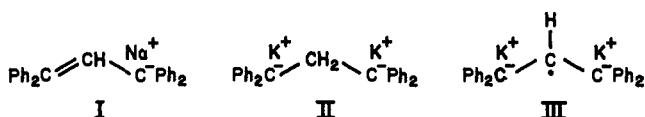
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### The Tetraphenylallyl Dianion Radical

Sir:

Sodium-potassium alloy reduction of the allylic anion I yields the dianion II. This unexpected reaction has been shown to proceed through the dianion radical III.<sup>1</sup>

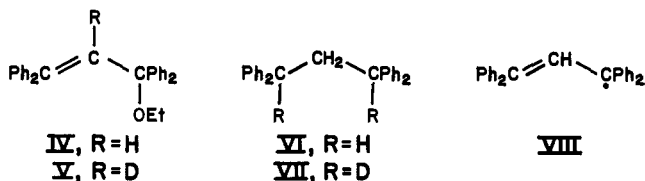


Reaction of the allylic anion I or the ethyl ether IV<sup>2</sup> with sodium-potassium alloy in ether or dimethoxyethane yielded after 8 hr. 1,1,3,3-tetraphenylpropane (VI)<sup>3</sup> (78%). Quenching with D<sub>2</sub>O resulted in the



Figure 1. First derivative e.s.r. spectrum of the dianion radical III in dimethoxyethane.

incorporation of two atoms of deuterium, giving VII, as shown by n.m.r. and mass spectrometry. In contrast, treatment of the allylic ether IV with sodium for 3 days followed by quenching with D<sub>2</sub>O resulted in the production of 1,1,3,3-tetraphenylpropene-d<sub>3</sub> (80%); none of the propane VII could be detected in the total crude reaction product.<sup>4</sup>



When a dimethoxyethane solution of the anion I or

(1) Related investigations have been reported by P. Brassem, R. E. Jesse, and G. J. Hoijtink, *Mol. Phys.*, **7**, 587 (1964); P. H. Rieger, I. Bernal, W. H. Rheinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963); P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962); and N. L. Bauld, *J. Am. Chem. Soc.*, **86**, 2305, 3894 (1964).

(2) W. Schlenk and E. Bergmann, *Ann.*, **463**, 228 (1928).

(3) D. Vorlander and C. Siebert, *Ber.*, **39**, 1024 (1906).

the ether IV was shaken with sodium-potassium alloy and the electron spin resonance (e.s.r.) spectrum measured immediately thereafter, a strong doublet ( $a = 7.6 \pm 0.3$  gauss,  $g = 2.0025 \pm 0.0001$ ) was observed. This spectrum is shown in Figure 1. The radical thus produced has an apparent half-life of ca. 30 min. at 25°. It is quite stable at -50°. At room temperature the signal can be regenerated several times simply by vigorously shaking the e.s.r. tube. That the doublet is due to the hydrogen atom on the central carbon atom of the propene chain was shown by preparing the deuterium-substituted ether V. This compound when treated with sodium-potassium alloy showed a singlet in its e.s.r. spectrum. Further, the doublet was not observed when tetraphenylpropane, tetraphenylpropene, or tetraphenylcyclopropane were treated with the alloy under the reaction conditions.<sup>5</sup> Thus, in order that the dianion radical may be observed, it is necessary that each of the carbon atoms of the propene chain be in the sp<sup>2</sup> configuration. As expected, no free radical could be detected by e.s.r. when sodium was allowed to react with the tetraphenylpropenyl ether IV.

For purposes of approximate comparison, Ziegler's radical VIII<sup>7</sup> was prepared. It shows a doublet ( $a = 8.0 \pm 0.3$  gauss,  $g = 2.0025 \pm 0.0001$ ) very similar in appearance to that of the dianion radical III. In particular, as in the case of III, hyperfine splitting from the hydrogens on the benzene rings was not detected.<sup>8</sup> The larger than normal splitting value for the vinyl hydrogen<sup>9</sup> is presumably due to out-of-plane twisting of the molecule.<sup>10</sup>

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(4) Reduction with potassium metal in ether gives, after 1 week, a mixture (80% yield) composed of three parts of tetraphenylpropane one part of tetraphenylpropene.

(5) All of the tetraphenylpropane derivatives discussed above gave the e.s.r. spectrum of the biphenyl anion radical<sup>6</sup> on prolonged contact with the sodium-potassium alloy.

(6) A. Carrington and J. Santos Veiga, *Mol. Phys.*, **5**, 21 (1962).

(7) K. Ziegler, *Ann.*, **434**, 34 (1932). In the present work this radical was prepared by oxidation of the anion I using tetramethylethylene dibromide. The resulting radical is stable in the solid state under nitrogen. The e.s.r. signal of this radical has decreased in intensity by roughly half after standing for 4 months at room temperature while sealed in an e.s.r. tube in dimethoxyethane solution.

(8) Cf. J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **23**, 2441 (1955); and A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 157, 164. The latter makes reference to the work of D. C. Reitz, *J. Chem. Phys.*, **34**, 701 (1961), who has succeeded in resolving the spectrum of pentaphenylcyclopentadienyl which was previously reported as a single line: J. E. Wertz, C. F. Koelsch, and J. L. Vivo, *ibid.*, **23**, 2194 (1955).

(9) Cf. R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963), and references cited therein.

(10) The author is indebted to Dr. A. L. Kwiram for this suggestion and for his assistance in the measurement of the  $g$  values. The  $g$  values were measured by means of a proton gaussmeter and a transfer oscillator in conjunction with a Hewlett-Packard counter.

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### The Structure of Ophiobolin, a C<sub>25</sub> Terpenoid Having a Novel Skeleton

Sir:

A metabolic product, ophiobolin, of the plant pathogenic fungus *Ophiobolus miyabeanus*<sup>1</sup> was first isolated

from the cultured broth by Ishibashi and Nakamura in 1958.<sup>2,3</sup> Subsequently, *Helminthosporium turcicum* and other *Helminthosporium* species fungi, also known as pathogens of plant diseases, were found to produce ophiobolin and structurally related compounds.<sup>4</sup> The physiological activities of these compounds have been reported.<sup>5</sup>

Ophiobolin [ $C_{25}H_{36}O_4$ <sup>6</sup>; mol. wt. 400 (mass spectroscopy), m.p. 182°,  $[\alpha]^{29D} +270^\circ$ ] has the following spectral properties:  $\lambda_{max}^{EtOH}$  238 m $\mu$  ( $\epsilon$  13,800),  $\nu_{max}^{CHCl_3}$  3500, 1743, 1674, and 1633  $cm^{-1}$ , indicating that this compound contains a hydroxyl, an  $\alpha,\beta$ -unsaturated carbonyl group, and a ketone function in a five-membered ring. The nature of the oxygen atoms and some carbon atoms is revealed by the n.m.r. spectrum,<sup>7</sup> which shows signals at 0.82 (singlet, 3 H), 1.08 (doublet,  $J = 6.5$ , 3 H), 1.34 (singlet, 3 H), and 1.70 (singlet, 6 H), due to five methyl groups, at 7.13 (triplet,  $J = 8$ , 1 H) and 9.26 (singlet, 1 H), due to an  $\alpha$ -substituted  $\alpha,\beta$ -unsaturated aldehyde system, and at 5.15 (doublet,  $J = 8$ , 1 H) and 4.43 (quartet,  $J = 8$ , 1 H) due to an olefinic proton and a methine proton  $\alpha$  to an ether linkage, respectively; the ethereal methine and olefinic protons are vicinal. Additional signals at 2.46 and 2.77 (AB type quartet,  $J = 20$ , 2 H) and at 3.20<sup>8</sup> (doublet,  $J = 11$ , 1 H) can be assigned to methylene and methine protons, respectively, with each group adjacent to a carbonyl function.

This communication describes the complete structure and stereochemistry of ophiobolin, including the absolute configuration as determined by X-ray crystallographic analysis of its bromomethoxy derivative.<sup>9</sup> Treatment of ophiobolin (I) with 1 mole of bromine in methanol in the presence of sodium acetate afforded a monobromo derivative II, m.p. 155–157° ( $C_{26}H_{39}O_5Br$ ). The n.m.r. spectrum of II shows a new signal due to a methoxyl group at 3.23 (singlet, 3 H) and a signal due to a methine proton attached to the same carbon atom as an electronegative group at 4.03 (singlet, 1 H). The olefinic proton signal at 5.15 in I disappears, the signal at 1.70 due to two methyls of an isopropylidene group shifts to 1.35, and a methine proton signal on an ether linkage occurs as a triplet at 4.03. Since the other assignable signals are essentially unchanged from that of I, this compound must differ structurally from the parent compound only in possessing a bromine atom and a methoxyl group in the side chain.<sup>10</sup>

The bromomethoxy derivative II, crystallized from ether, was found to be an orthorhombic system with space group  $P2_12_12_1$ , with the unit cell dimensions  $a = 13.19$ ,  $b = 22.27$ , and  $c = 8.46$  Å. The density was determined to be 1.40  $g./cm.^3$  by flotation in an

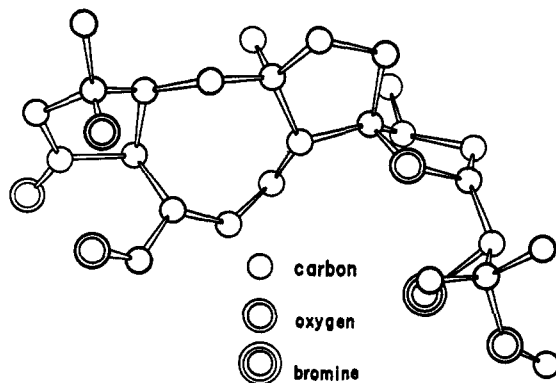
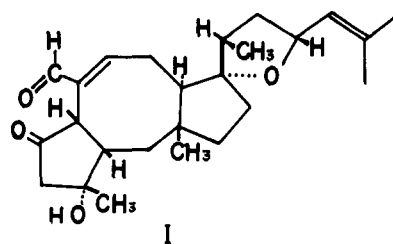
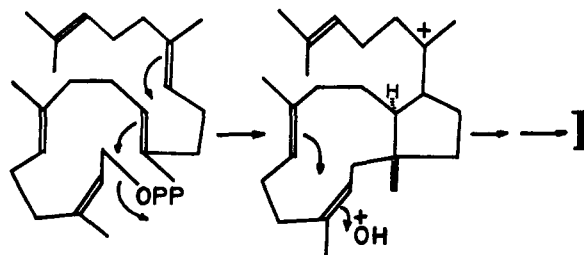


Figure 1. Molecular structure of ophiobolin methoxy bromide (II).

aqueous solution of potassium iodide, which corresponds to the calculated value 1.37  $g./cm.^3$  with four molecules in a cell. Three-dimensional intensity data about the  $c$  and  $a$  axes were collected by the multiple-film equi-inclination Weissenberg method with  $Cu K\alpha$  radiation. A total of 1499 reflections were estimated visually. The structure was solved by the heavy atom method with several Fourier and difference Fourier syntheses. The parameters were then refined by three cycles of diagonal least squares to an  $R$  value of 0.143. Finally, a full-matrix least-squares refinement was carried out. The final  $R$  value was 0.114. The absolute configuration was determined by the anomalous dispersion method.<sup>11</sup> The perspective drawing of the molecule indicating the absolute configuration is shown in Figure 1. This result reveals that the structure of ophiobolin including the absolute configuration is as expressed by I.



From biogenetic considerations, it is apparent that ophiobolin (I) is terpenoid in nature and is probably constructed from five isoprene units linearly linked head to tail; this is the first example of such a  $C_{25}$  terpenoid. The cyclization scheme for this biogenesis from a hypothetical precursor, geranylgeranyl pyrophosphate (or a biochemical equivalent), may be formulated as shown.



In addition to ophiobolin (I), three other congeners were isolated from the cultured broth of *Helminthos-*

(11) Of the 22 pairs of reflections for which the intensity difference in  $I(hkl)$  and  $I(\bar{h}\bar{k}l)$  is expected to be measurable, 21 pairs showed significant difference.

- (1) This fungus has been reclassified as *Cochliobolus miyabeanus*.
- (2) K. Ishibashi and R. Nakamura, *J. Agr. Chem. Soc. Japan*, **32**, 739 (1958).
- (3) Cochliobolin (M. Orsenigo, *Phytopathol. Z.* **29** 189, (1957)) and ophiobalin (A. Neelameghan, *Hindustan Antibiot.*, **2**, 13 (1959)) are suspected to be identical with ophiobolin.
- (4) K. Ishibashi, *J. Agr. Chem. Soc. Japan*, **35**, 323 (1961); **36**, 226 (1962); *J. Antibiot.*, **A15**, 88 (1962).
- (5) K. Ishibashi, *J. Agr. Chem. Soc. Japan*, **36**, 649 (1962).
- (6) The molecular formula was previously reported as  $C_{24}H_{32}O_4$ .
- (7) Chemical shifts are expressed in  $\delta$  values from tetramethylsilane, and coupling constants in c.p.s.
- (8) This signal overlaps with a hydroxyl proton signal which can be removed by  $D_2O$  treatment.
- (9) The detailed results of the X-ray analysis will be published elsewhere.
- (10) The ultraviolet spectrum of II is identical with that of I, and the infrared spectrum differs only in the fingerprint region.

*porium zizaniae* and *Ophiobolus heterostrophus*, i.e., zizanin A, m.p. 121° (C<sub>25</sub>H<sub>38</sub>O<sub>3</sub>), zizanin B,<sup>4</sup> m.p. 173° (C<sub>25</sub>H<sub>38</sub>O<sub>4</sub>), and a compound, m.p. 136° (C<sub>25</sub>H<sub>34</sub>O<sub>3</sub>). The structural relationship between these congeners and the chemical reactions of ophiobolin will be published elsewhere.

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### Homogeneous Catalytic Hydrogenation of Ethylene and Acetylene with Four-Coordinated Iridium and Rhodium Complexes. Reversible Catalyst-Substrate Adducts<sup>1</sup>

Sir:

Square-planar carbonyl complexes of univalent iridium<sup>2</sup> and rhodium,<sup>3</sup> *trans*-[MX(CO)(Ph<sub>3</sub>P)<sub>2</sub>] (M = Ir, Rh; X = halogen), catalyze reactions of ethylene, propylene, and acetylene with molecular hydrogen in benzene or toluene solutions at subatmospheric pressures of the reacting gases and at relatively mild temperatures (40–60°). Unlike previously reported examples of homogeneous catalytic hydrogenations in solution,<sup>4</sup> these systems *combine* the following important features.

(a) The compositions, properties, and structures<sup>5</sup> of the catalyst complexes are known.<sup>2,3</sup> Their solution chemistry and infrared spectral data ( $\nu_{\text{CO}}$ ) indicate that their *trans* square-planar configurations prevail in solution<sup>6,7</sup>; that is to say, the identities of the *actual* catalysts are known with reasonable certainty.

(b) The iridium complexes react *reversibly* with 1 mole of hydrogen per complex.<sup>1b</sup> Equation 1 illustrates the formation of the hydrogen adducts; the two

(1) (a) Activation of Molecular Hydrogen and Related Molecules by Transition Metal Complexes. II. (b) For part I, see L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).

(2) L. Vaska and J. W. DiLuzio, *ibid.*, **83**, 2784 (1961).

(3) (a) Prepared by the same method<sup>2</sup> as [IrX(CO)(Ph<sub>3</sub>P)<sub>2</sub>]; (b) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

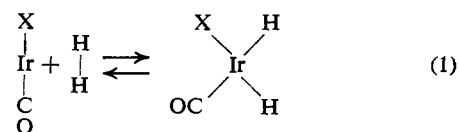
(4) See, for example, these recent reports (and the references cited therein): (a) F. H. Jardine, J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Ind. (London)*, 560 (1965); (b) J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun. (London)*, 131 (1965); (c) M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Am. Chem. Soc.*, **85**, 4014 (1963); (d) R. D. Cramer, E. L. Jenner, R. V. Lindsay, Jr., and U. G. Stolberg, *ibid.*, **85**, 1691 (1963); (e) J. Kwiatek, I. L. Mador, and J. K. Seyler, "Reactions of Coordinated Ligands," *Advances in Chemistry Series*, No. 37, American Chemical Society, Washington, D. C., 1963, p. 201.

(5) The *trans* square-planar structures of the isostructural [MX(CO)-(Ph<sub>3</sub>P)<sub>2</sub>] (ref. 2) have been confirmed by X-ray studies on [RhCl(CO)-(Ph<sub>3</sub>P)<sub>2</sub>]: S. F. Watkins, J. M. Obi, and L. F. Dahl, private communication from L. F. Dahl to L. Vaska, 1965.

(6) D. M. Adams, "Spectroscopy," *The Institute of Petroleum*, London, 1962, p. 265.

(7) L. Vaska, forthcoming publications.

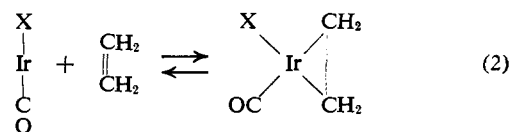
*trans*-Ph<sub>3</sub>P (not shown in the diagram) of [IrX(CO)-(Ph<sub>3</sub>P)<sub>2</sub>] and [H<sub>2</sub>IrX(CO)(Ph<sub>3</sub>P)<sub>2</sub>] are normal to the plane of the paper (see (c) below). Volumetric measure-



ments of hydrogen absorption (in toluene) indicate that the reaction is first order with respect to the Ir complex. At 20° and a constant pressure of 700 mm. of hydrogen, a practically complete conversion to the dihydride is observed (pseudo-first-order  $k = 3.2 \times 10^{-4} \text{ sec.}^{-1}$ , [Ir] =  $2.3 \times 10^{-3} \text{ M}$ ).<sup>8</sup> At higher temperatures and/or lower hydrogen pressures, the reverse reaction becomes appreciable, and the equilibrium (eq. 1) shifts to the left.

(c) The hydrogen adducts, [H<sub>2</sub>IrX(CO)(Ph<sub>3</sub>P)<sub>2</sub>], have been isolated<sup>9</sup> and characterized,<sup>1b</sup> and the molecular configurations of these catalytic intermediates (*cis*-(H)<sub>2</sub>-*trans*-(Ph<sub>3</sub>P)<sub>2</sub>, see eq. 1) have been established by infrared (crystals and solutions) and n.m.r. (solutions) measurements.<sup>7</sup>

(d) The iridium complexes react *reversibly* with ethylene, acetylene, and other unsaturated substrates at ambient conditions<sup>8</sup> (eq. 2). For example, volumetric



measurements of ethylene absorption by [IrI(CO)-(Ph<sub>3</sub>P)<sub>2</sub>] in toluene at 26° and 700 mm. of C<sub>2</sub>H<sub>4</sub> (constant) indicate formation of a colorless adduct, assumed to be [(C<sub>2</sub>H<sub>4</sub>)IrI(CO)(Ph<sub>3</sub>P)<sub>2</sub>] (ca. 70% conversion; the chloro complex is less reactive toward ethylene; with acetylene, rather irreproducible results have been obtained thus far). Although the addition compounds have not been isolated owing to their rapid dissociation in the absence of excess substrate, the structure of the ethylene adducts shown in eq. 2 (the two *trans*-Ph<sub>3</sub>P are normal to the plane of the paper) is assumed by analogy with that of the corresponding oxygen complex, [O<sub>2</sub>IrCl(CO)(Ph<sub>3</sub>P)<sub>2</sub>],<sup>10</sup> and the established orientation of olefins in metal-olefin compounds.<sup>11</sup> A recent report gives evidence for extensive  $\sigma$  bonding in the closely related complex, [(C<sub>2</sub>F<sub>4</sub>)IrCl(CO)(Ph<sub>3</sub>P)<sub>2</sub>].<sup>12</sup>

The catalytic experiments<sup>13</sup> were carried out by adding the reactants (initially:  $p_{\text{H}_2}$  290–620 mm.;  $p_{\text{alkene}}$  or  $p_{\text{alkyne}}$  270–440 mm.) to an air-free solution of the complex ( $1.3$ – $15 \times 10^{-3} \text{ M}$ ), stirring the solution (20–80°, 7–26 hr.), and observing changes of total

(8) With [RhCl(CO)(Ph<sub>3</sub>P)<sub>2</sub>], volumetric measurements have failed to give evidence for hydrogen or ethylene uptake at these conditions.

(9) Pure crystals are colorless; they are best obtained from "concentrated" toluene solutions, [Ir]  $\geq 10^{-2} \text{ M}$ ; oxygen must be rigorously excluded (*cf.* ref. 1b).

(10) (a) L. Vaska, *Science*, **140**, 809 (1963); (b) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965).

(11) See, for example, P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Cryst.*, **13**, 149 (1960).

(12) R. Cramer and G. W. Parshall, *J. Am. Chem. Soc.*, **87**, 1392 (1965).

(13) Ranges of employed conditions in parentheses.