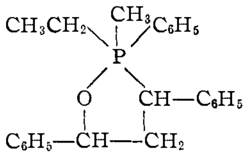
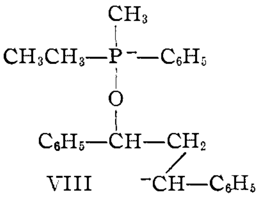
the two most reasonable possibilities are those in which 2,4-diphenyloxetane (III) and 1,2-diphenylcyclopropanol (IV), respectively, are formed as intermediates.[2]

In order to distinguish between these possible mechanisms, use was made of a carbon-14 label in the position marked by an asterisk in I or II.[3] On degradation of the benzylacetophenone (VI), none of the carbon-14 was found in the carbonyl group; all of it was found in the α-carbon of the benzyl group (as shown by the asterisk in VI). Thus, the mechanism proceeding by way of 1,2-diphenylcyclopropanol (IV) is the one that is operative.[4] It is not surprising that the displacement of methylethylphenylphosphine (V) is made by the anionic carbon atom of II rather than by the negative oxygen atom of I. Although the concentration of I undoubtedly is much greater than that of II in an equilibrium mixture of the two species, the nucleophilicity of the carbanion center of II is much greater than that of the alkoxide oxygen of I.

Benzylacetophenone was degraded as follows: (1) a Schmidt reaction was used to convert VI to hydrocinnamanilide.[5] (2) Hydrolysis of the anilide gave hydrocinnamic acid.[6] (3) A portion of the hydrocinnamic acid was subjected to the Schmidt reaction and the carbon dioxide assayed. (4) A second portion of the hydrocinnamic acid was oxidized with alkaline potassium permanganate solution to give benzoic acid. (5) The carbon dioxide evolved from the benzoic acid in a Schmidt reaction was collected and assayed.

It is of interest to speculate on the reasons why I (or II) gives predominantly the phosphine V and the ketone VI, with only relatively small amounts of *trans*-1,2-diphenylcyclopropane and methylethylphenylphosphine oxide being formed.[1] The latter type of reaction was the one observed by Denney and Boskin[7] in the condensation of triphenylcarbethoxymethylenephosphorane with styrene oxide or 1,2-epoxyoctane at an elevated temperature. Consideration of the two probable intermediates[8] for the conversion of I to the phosphine oxide and cyclopropane derivative indicates why this route is not the major one in the system under consideration. Owing to the inductive electron-releasing effect of the methyl and ethyl groups bonded to the phosphorus atom of I, there would be less tendency for the intermediate VII to be formed than would be the analogous case if three electron-withdrawing phenyl groups were bonded to phosphorus. Also, VII, once formed, would have much less tendency to dissociate to the next intermediate, VIII, than would be the case if a carbethoxyl group rather than a phenyl group were bonded to the negatively charged carbon atom. Thus, the reaction in which I gives rise to V and VI is favored over the relatively difficult reaction path leading to methylethylphenylphosphine oxide and *trans*-1,2-diphenylcyclopropane.[9]


VII


VIII

Acknowledgment.—The authors wish to thank Dr. D. R. Christman for the radioanalyses and Miss C. Redvanly for help with the Schmidt reactions.

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[2] The base, B$^-$, is most likely the alkoxide ion, C_6H_5-CH_2CO^- C_6H_5, formed by the action of phenyllithium on styrene oxide (see ref. 1).

[3] Methylethylphenylbenzyl-7-C^{14}-phosphonium iodide was prepared by reaction of methylethylphenylphosphine (W. J. Bailey, S. A. Buckler and F. Marktscheffel, *J. Org. Chem.*, **25**, 1996 (1960)) with benzyl-7-C^{14} iodide. The labeled phosphonium iodide was then treated with phenyllithium and subsequently with styrene oxide in the manner described in reference 1. All of the compounds described in this paper were assayed, and the assays checked within ±4% of the theoretical values.

[4] It is of interest that Robinson has suggested the same type of rearrangement of a cyclopropanol derivative as one step in the biogenesis of artemisia ketone: R. Robinson, "The Structural Relations of Natural Products," Clarendon Press, Oxford, 1955, p. 14. The base-catalyzed isomerization of cyclopropanol derivatives to open-chain carbonyl compounds has been reported by a number of workers: R. Breslow and C. Yuan, *J. Am. Chem. Soc.*, **80**, 5991 (1958); L. Skattebol and J. D. Roberts, *ibid.*, **80**, 4085 (1958); G. W. Stahl and D. L. Cottle, *ibid.*, **65**, 1782 (1943).

[5] D. Bigiavi and M. Marri, *Gazz. chim. ital.*, **54**, 99 (1924).

[6] E. Erlenmeyer, *Ann.*, **137**, 327 (1866).

[7] D. B. Denney and M. J. Boskin, *J. Am. Chem. Soc.*, **81**, 6330 (1959).

[8] D. B. Denney, Paper No. 69, Division of Organic Chemistry, 139th National Meeting of the American Chemical Society, St. Louis, Mo., 1961.

[9] It is of significance that the reaction of triphenylbenzylidenephosphorane with styrene oxide affords triphenylphosphine oxide (80% yield) triphenylphosphine (8%), benzylacetophenone (0.3%), 1,3-diphenylpropan-1-ol (1.5%), a mixture of *cis*-1,3-diphenylpropene, the *trans* isomer and *trans*-1,2-diphenylcyclopropane (50% yield, molar ratio 30:65:5), and an unidentified ketoalcohol. Evidently an intermediate analogous to VII is formed readily, as expected on the basis of the argument cited above, but an intermediate analogous to VIII is not produced easily, this also being anticipated on the basis of the above argument. The major reaction path is, therefore, a thermal decomposition of the intermediate analogous to VII to give triphenylphosphine oxide and the two isomeric 1,3-diphenylpropenes. The latter compounds do not arise by pyrolysis of *trans*-1,2-diphenylcyclopropane since it is recovered unchanged when subjected to the conditions of the reaction: A. Bladé-Font, Ph.D. Thesis, Kansas University, 1960.

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RECEIVED DECEMBER 21, 1961

REACTION OF OPTICALLY ACTIVE METHYLETHYLPHENYLBENZYLIDENEPHOSPHORANE WITH STYRENE OXIDE

Sir:

Denney and Boskin[1] have reported that ethyl *trans*-2-phenylcyclopropanecarboxylate (II) is produced in 21% yield, together with triphenylphosphine oxide, in the reaction of triphenylcarbethoxymethylene-phosphorane (I) with styrene oxide at 190–200°. In like manner, ethyl *trans*-2-*n*-hexylcyclopropanecarboxylate is obtained in 51% yield on reaction of I with 1,2-epoxyoctane at 210–220°.[2] Denney has suggested[2] that the mechanism of the reaction, as illustrated with styrene oxide, is I → II.

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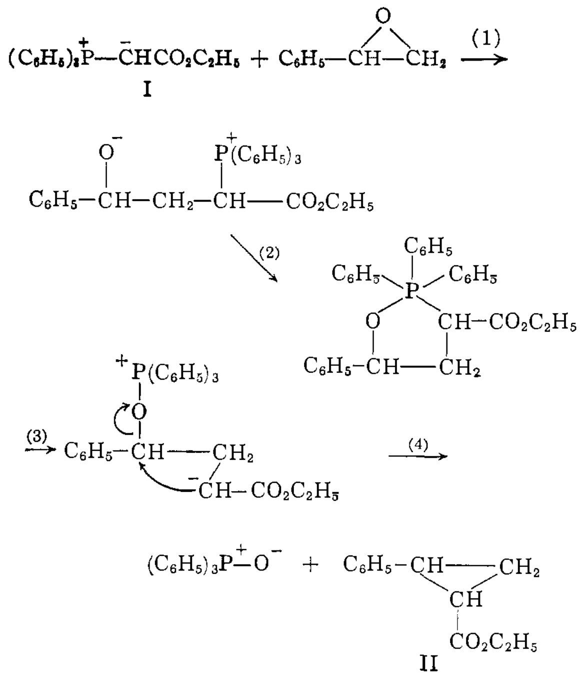
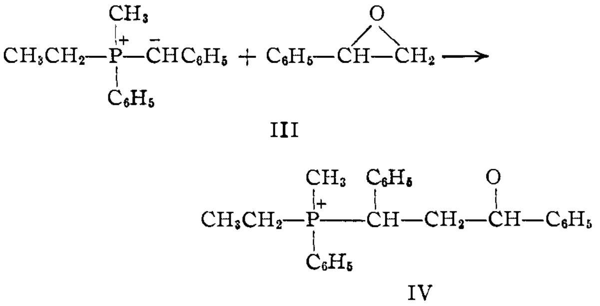
[1] D. B. Denney and M. J. Boskin, *J. Am. Chem. Soc.*, **81**, 6330 (1959).

[2] D. B. Denney, Paper No. 69, Division of Organic Chemistry, 139th National Meeting of the American Chemical Society, St. Louis, Mo., 1961.



Having optically active methylethylphenylbenzylphosphonium iodide available,[3] we decided to investigate the stereochemistry, with respect to the phosphorus atom, of this type of reaction. In the first experiments, however, racemic material was used in order to determine suitable conditions and to find out what products would be formed. The quaternary phosphonium salt was insoluble in anhydrous ether, but, by the gradual addition of an ether solution of phenyllithium to the mixture, the salt was converted to the soluble methylethylphenyl benzylidenephosphorane (III). About 0.02 mole of phenyllithium was required to bring 0.0149 mole of the salt into solution. On addition of 0.025 mole of styrene oxide to the solution, with subsequent stirring of the reaction mixture for 30 minutes at room temperature, a solid precipitated. That this precipitate was the lithium iodide adduct of methylethylphenyl - (1,3-diphenyl-3-hydroxypropyl)-phosphonium betaine (IV) could be demonstrated by its behavior toward hot potassium hydroxide solution; the compound was cleaved to give 1,3-diphenylpropan-1-ol,[4] methylethylphenylphosphine oxide[5,6] and lithium iodide.

When the adduct IV plus other material obtained on evaporation of the original ether solution was suspended in decalin and heated at a temperature of 190–200° for three hours, a complex mixture of products resulted, and several compounds were isolated: methylethylphenyl-phosphine[7] (35–60% yield in various experiments), benzylacetophenone[8] (12–31%), methylethylphenylphosphine oxide[5,6] (4–14%), 1,3-diphenylpropan-1-ol[4] (6–12%), a mixture of *cis*-1,3-diphenylpropene,[9] *trans*-1,3-diphenylpropene[9] and *trans*-1,2-diphenylcyclopropane[10] (9–14 % yield of the mixture, which, on the basis of vapor phase chromatographic analysis, consisted of a 14:80:6 molar ratio of the hydrocarbons in the order cited above).



When the same sequence of operations was carried out with (+)-methylethylphenylbenzylphosphonium iodide in place of the racemic salt, the methylethylphenylphosphine oxide, produced in 12% yield, was dextrorotatory, $[\alpha]^{25}_{D}$ + 12.5° (*c* 4.735 in methanol), whereas the methylethylphenylphosphine (49%) was racemic. With levorotatory phosphonium salt as starting material, the methylethylphenylphosphine oxide (13%) was levorotatory, $[\alpha]^{25}_{D}$ −11.3° (*c* 2.115 in methanol), and the methylethylphenylphosphine again was racemic. Thus, on the basis of these results and data previously reported,[6,11] it can be concluded that the phosphorus atom of optically active methylethylphenylbenzylphosphonium iodide undergoes about 50% net inversion in that part of the over-all reaction which leads to the phosphine oxide.

An attractive interpretation of this stereochemical result is that inversion of the configuration of the phosphorus atom occurs when methylethylphenylphosphine oxide and the conjugate base of 1,3-diphenylpropene are formed from IV by way of one or more of the three possible intermediates or transition states of the type of V in which both the attacking and departing groups occupy basal positions of the trigonal bipyramid; retention of configuration results when the intermediate or transition state has the type of geometry shown in VI, VII or VIII, these being but a few of many possiblities.[12,13]

Inasmuch as the amount of *trans*-1,2-diphenylcyclopropane formed in the reaction was but a very

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(3) K. F. Kumli, W. E. McEwen and C. A. VanderWerf, *J. Am. Chem. Soc.*, **81**, 248 (1959).

(4) P. Pfeiffer, E. Kalckbrenner, W. Kunze and K. Levin, *J. prakt. Chem.*, **119**, 109 (1928).

(5) J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt and W. Samuel, *Ann.*, **449**, 213 (1926).

(6) K. F. Kumli, W. E. McEwen and C. A. VanderWerf, *J. Am. Chem. Soc.*, **81**, 3805 (1959).

(7) A. Michaelis, *Ann.*, **181**, 265 (1876).

(8) C. W. Shoppee, *J. Chem. Soc.*, 2567 (1928).

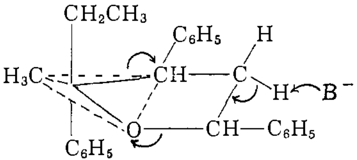
(9) R. Stoermer and C. Thier, *Ber.*, **58**, 2607 (1925).

(10) H. E. Knipmeyer, Ph.D. Thesis, University of Illinois, 1956.

(11) A. Bladé-Font, C. A. VanderWerf, and W. E. McEwen, *J. Am. Chem. Soc.*, **82**, 2396 (1960).

(12) See the discussion of Haake and Westheimer on the stereochemistry of hydrolysis and oxygen exchange in phosphoric acid esters: P. C. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961).

(13) The base, B⁻, is most likely the alkoxide ion, $C_6H_5—\overset{O^-}{CH}—CH_2—C_6H_5$, arising by attack of phenyllithium on styrene oxide. As a matter of fact, small amounts of *trans*-stilbene were isolated when the crude mixture of hydrocarbons, alcohols and ketones was distilled *in vacuo* and the distillate subjected to chromatography on alumina. The *trans*-stilbene undoubtedly arose by dehydration of phenylbenzylcarbinol during the distillation step.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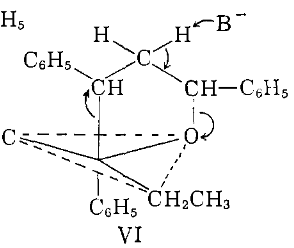
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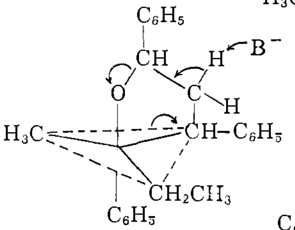
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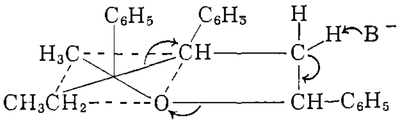
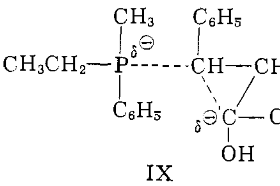

VIII

small fraction of the product mixture, the amount of methylethylphenylphosphine oxide formed in conjunction with the cyclopropane derivative was also small. On the basis of Denney's mechanism,[2] it is conceivable that the phosphorus atom might be inverted, might retain the same configuration or undergo both stereochemical transformations by competitive paths. In fact, one or more of the many possible intermediates exemplified by V, VI, VII or VIII should be involved in step (2) of Denney's mechanism.

As shown in the accompanying communication,[14] methylethylphenylphosphine and benzylacetophenone arise from IV by way of the transition state IX. The fact that the phosphine is racemic is undoubtedly the result of the thermal racemization of the optically active phosphine (presumably formed with retention of configuration of the phosphorus atom) at the reaction temperature of 190–200°.[15,16]


IX

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RECEIVED DECEMBER 21, 1961

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[14] W. E. McEwen and A. P. Wolf, *J. Am. Chem. Soc.*, **84**, 676 (1962).

[15] L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffman and P. Beck, *Tetrahedron Letters*, 161 (1961).

[16] D. C. Velez, J. W. Johnson, C. A. VanderWerf and W. E. McEwen, unpublished observations.

ACTIVATION OF HYDROGEN BY A TRANSITION METAL COMPLEX AT NORMAL CONDITIONS LEADING TO A STABLE MOLECULAR DIHYDRIDE

Sir:

The discovery of a quadricovalent iridium(I) complex, $[IrCl(CO)(Ph_3P)_2]$,[1] has afforded access to novel chemical reactions which are believed to offer new opportunities for understanding and study of certain vital processes of catalysis.

The compound responsible for this development shows a striking reactivity at normal conditions toward a large number of molecules (*e.g.*, hydrogen, oxygen, sulfur, organic halides, organic acids, hydrides of group VIIA, VIA elements, *etc.*). Yet, it displays properties which are remarkably well suited for a convenient investigation of its chemical behavior: its crystals are durable in air and stable thermally[1]; its relevant reactions represent additions to the quadricovalent species to yield octahedral complexes of Ir(III) (*cf.* equations 1, 5). These reactions are accompanied by characteristic shifts of the stretching frequency of the coördinated carbon monoxide (to higher ν) in the infrared spectrum. Indeed, the (*only one*) CO group in the molecule provides a singular means of detecting reactions, following their course, and inquiring into the nature of the products through the extent of $\Delta\nu_{CO}$.

In this communication we report a reaction with molecular hydrogen, and some related observations which contribute to the understanding of metal–hydrogen interactions in this and other systems.

When hydrogen (one atm., 25°) is bubbled through a solution of $[IrCl(CO)(Ph_3P)_2]$ in benzene, the color of the initially yellow solution (2×10^{-2} *M*) becomes lighter, followed by the appearance of yellow-white crystals (2 hr.). After allowing it to stand under hydrogen (same conditions) for one day a 55% yield of the crystalline product is obtained.[2] Infrared spectrum (Table I), elemental analysis, molecular weight data, non-electrolytic character (in nitrobenzene and acetone), diamagnetism, and reactions of the compound (see below) suggest that it is best formulated as a molecular dihydride of tervalent iridium, $[IrH_2Cl(CO)(Ph_3P)_2]$. (*Anal.* Calcd. for $IrClP_2C_{37}H_{32}O$: Ir, 24.6; Cl, 4.5; P, 7.9; C, 56.8; H, 4.12; O, 2.05; mol. wt., 782. Found: Ir, 24.8; Cl, 4.5; P, 7.9; C, 56.5; H, 4.15; O, 2.04; mol. wt. in benzene, 772.)

$$[Ir^{I}Cl(CO)(Ph_3P)_2] + H_2 \xrightarrow[25°]{} [Ir^{III}H_2Cl(CO)(Ph_3P)_2] \quad (1)$$

Treatment of $[IrCl(CO)(Ph_3P)_2]$ (in benzene) with deuterium[3] gives the corresponding dideuteride, $[IrD_2Cl(CO)(Ph_3P)_2]$, showing an X-ray diffraction pattern identical with that of the dihydride (according to visual examination). Two noteworthy isotope effects are evident from the infrared spectra (Table I): ν_{CO} in the dideuteride lies markedly higher than in the dihydride; the crystals of the dideuteride apparently exhibit only one ν_{IrD} while

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[1] L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).

[2] In $CHCl_3$ the rate of the reaction with H_2 is faster, but the purity of the product has been found to suffer. A partial interaction has been observed also between the *crystals* of $[IrCl(CO)(Ph_3P)_2]$ and hydrogen (1 atm., 25°).

[3] Courtesy of Dr. W. Keith Hall.