ring expansion in I leading directly to non-classical cation VI is stereoelectronically unfavorable. The C.1–C.7 bond in classical cation VIII (*cf.* VIIIa) is, however, properly disposed for conversion to VI. It is not clear whether the source of IV is VIII or VI or both, but in any case, VIII, if present, is not in rapid equilibrium with its conformational isomer IX (a classical bicyclo[3.2.1]-2-octyl cation with a chair cyclohexane), since a product expected[1] from the latter is V, which constitutes at most 1–2% of the reaction product from I.

Of the very few mechanisms compatible with the data on the I → II + IV rearrangement, the one shown is the most closely analogous to that discussed[1] in connection with the rearrangement of *endo*-2-aminomethylnorbornane. We recognize that VIII must either be highly stereospecific in its reaction with solvent to give IV and virtually no V, or else must be a source of only a relatively small fraction of the total IV formed; VIII is assigned a place in the scheme merely to complete the analogy. Note that if the VI → VII step is reversible, some of the mirror image of VI also must be formed; until the degree of retention of optical activity in IV is known, it is not possible to decide whether this occurs. In the formal sense, the only other difference between this scheme and that presented[1] for the isomeric series is that in the present case the two classical cations are not enantiomeric.

Although the mechanisms of this and the companion rearrangement[1] are not yet uniquely fixed in detail, it is already certain that the evidence in both cases requires the postulation of at least two kinds of cationic intermediate.

Acknowledgment.—We are indebted to the National Science Foundation (Grant No. G-11386) for support of part of this work.

---

(10) On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA

JEROME A. BERSON
DAVID WILLNER[10]

RECEIVED DECEMBER 4, 1961

REACTIONS OF THE METASTABLE HELIUM TRIPLETS[1]

Sir:

The helium species He(2^3S) and $He_2(^3\Sigma_u^+)$ are energy-rich, the former lying 19.8 e.v. and the latter approximately 17.2 e.v. above the ground energy. Both species are metastable with natural lifetimes longer than milliseconds so that they can be brought in contact with other gases.

We have directed helium from a microwave discharge containing approximately 10^9 to 10^{10} metastables per ml. through a 3 mm. orifice into a glass vessel containing ~ 10 mm. pressure of reactant gas. For each of the four gases investigated Ne, N^2, O_2, CH_4 a brilliant flame appeared at the orifice of the jet. For neon the flame is red. Its spectrum shows that the color comes principally to neon transitions from excited states lying below 19.8 e.v. For N_2 the color is blue, principally from the main system ($^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$) of N_2^+. For oxygen the color is green, arising from the first negative system ($^4\Sigma_g^- \rightarrow {}^4\Pi_u$) of O_2^+ or blue-white principally from the first and second negative ($^2\Pi_u \rightarrow {}^2\Pi_g$) systems of O_2^+ in combination, depending on the pressure and flow rate. For methane the color is violet, principally from the $^2\Delta \rightarrow {}^2\pi$ and $^2\Sigma^{-a} \rightarrow {}^2\Pi$ transitions of CH.

Related reaction cross sections are being reported elsewhere.[2]

---

(1) This research was supported by the Propulsion Sciences Division, Air Force Office of Scientific Research.

(2) E. E. Benton, E. C. Ferguson, F. A. Matsen and W. W. Robertson, submitted to *Phys. Rev.*; see also *Bull. Am. Phys. Soc.* (Abstracts of 1962 Southwestern APS meeting).

DEPARTMENTS OF CHEMISTRY
AND PHYSICS
UNIVERSITY OF TEXAS
AUSTIN 12, TEXAS

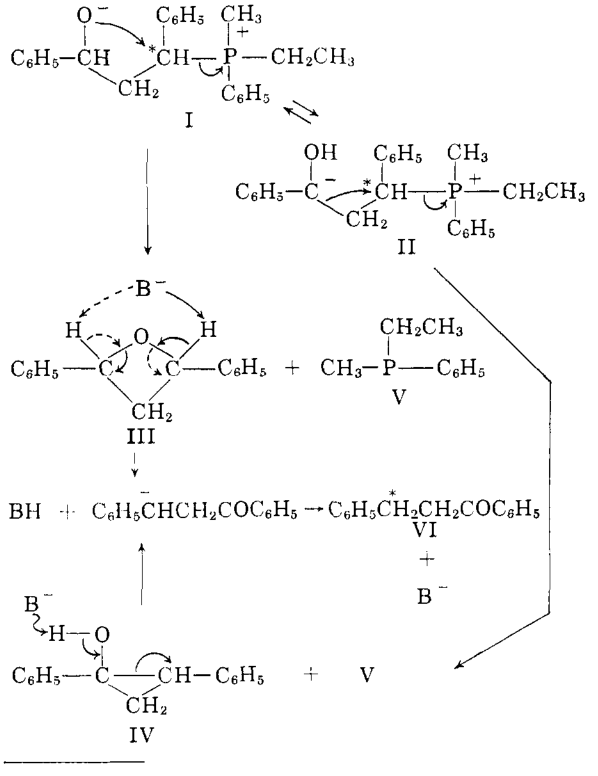
CARL COLLINS
W. W. ROBERTSON
E. E. FERGUSON
F. A. MATSEN

RECEIVED JANUARY 19, 1962

MECHANISM OF THE FORMATION OF BENZYLACETOPHENONE AND METHYLETHYLPHENYLPHOSPHINE FROM METHYLETHYLPHENYLBENZYLIDENEPHOSPHORANE AND STYRENE OXIDE

Sir:

In the accompanying communication[1] it is reported that the lithium iodide adduct of methylethylphenyl-(1,3-diphenyl-3-hydroxypropyl)-phosphonium betaine (I) precipitates when styrene oxide is added to an ether solution of methylethylphenylbenzylidenephosphorane. When I is heated to a temperature of 190–200° in decalin suspension, a number of products are formed, but the major ones are methylethylphenylphosphine (V) and benzylacetophenone (VI). Of various conceivable mechanisms for the formation of these products,



---

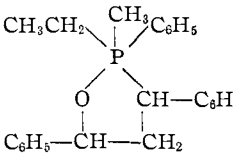
(1) W. E. McEwen, A. Bladé-Font and C. A. VanderWerf, *J. Am. Chem. Soc.*, **84**, 677 (1962).

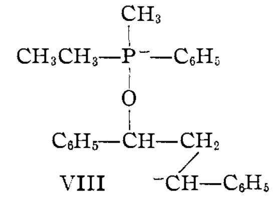
the two most reasonable possibilities are those in which 2,4-diphenyloxetane (III) and 1,2-diphenylcyclopropanol (IV), respectively, are formed as intermediates.[2]

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.

DEPARTMENT OF CHEMISTRY WILLIAM E. MCEWEN
ASSOCIATED UNIVERSITIES, INC.
BROOKHAVEN NATIONAL LABORATORY
UPTON, L. I., N. Y. ALFRED P. WOLF

RECEIVED DECEMBER 21, 1961

---

[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.

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.

---

[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.