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.

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[10] On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel.

DEPARTMENT OF CHEMISTRY JEROME A. BERSON
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA DAVID WILLNER[10]

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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]

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[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 CARL COLLINS
AND PHYSICS W. W. ROBERTSON
UNIVERSITY OF TEXAS E. E. FERGUSON
AUSTIN 12, TEXAS F. A. MATSEN

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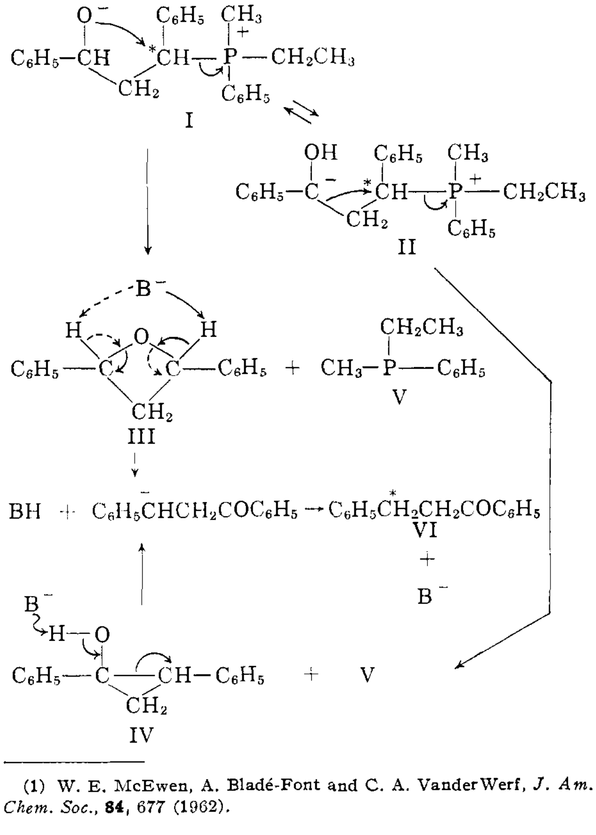
MECHANISM OF THE FORMATION OF BENZYLACETOPHENONE AND METHYLETHYLPHENYLPHOSPHINE FROM METHYLETHYLPHENYLBENZYLIDENEPHOSPHORANE AND STYRENE OXIDE

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,



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