

of these multiplets are chemical shifts and may be labeled in values of τ (see Fig. 1).

Other multiplets may be factored in a similar manner once they are recognized.

When the multiplet is partially obscured or cannot be analyzed, the positions of the lines must be reported in terms of the observed data, in cps., at a given spectrometer frequency, relative to some standard (if not TMS the conversion factor should be specified). Both methods were acclaimed at the Second Conference on Experimental Aspects of NMR Spectroscopy, Pittsburgh, Pennsylvania, February 24-25, 1961. The problem is under study by the ASTM Committee E-13.

The tetraethylmethane sample was kindly supplied by Dr. K. W. Greenlee of A.P.I. Project 45 and the difluoroprogesterone by Dr. E. V. Jensen of the University of Chicago. The author gratefully acknowledges the suggestions and criticisms of Drs. F. L. Anet, D. J. Cram, H. S. Gutowsky, W. S. Johnson, B. R. McGarvey, R. E. Richards, J. D. Roberts, W. G. Schneider, B. L. Shapiro and J. N. Shoolery.

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GEORGE SLOMP

RECEIVED AUGUST 14, 1961

AN OPTICALLY INACTIVE INTERMEDIATE IN THE MULTIPLE REARRANGEMENT OF EXO-2-AMINOMETHYLNORBORNANE

Sir:

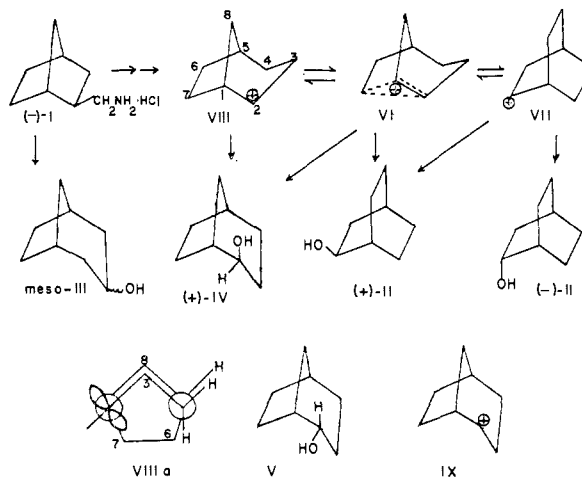
The behavior of *exo*-2-aminomethylnorbornane I on deamination provides an instructive comparison with that of the *endo*-isomer reported elsewhere.¹ In qualitative accord with a previous report,² we find that nitrous acid in acetic acid converts racemic I to a mixture of *ca.* 35-40% of the acetate of bicyclo[2.2.2]octanol-2, II; *ca.* 17-20% of the acetate of bicyclo[3.2.1]octanol-3, III; and *ca.* 35-40% of the acetate of a product previously identified² only as a bicyclo[3.2.1]octanol-2 but now shown to be the *exo*-(*axial*)-isomer IV by comparison of its properties with those known³ to distinguish it from the *endo*-(*equatorial*)-isomer V. From deamination of optically active (-)-I hydrochloride, 40.7% optically pure,⁴ lithium aluminum hydride cleavage of the mixture of acetates and repeated preparative vapor chromatography, there are obtained: optically active II, $[\alpha]_D +8.97^\circ$ (CHCl₃); optically active IV, $[\alpha]_D +5.25^\circ$ (ethanol); and optically inactive III, a *meso* compound (possibly a mixture of epimers). The latter substance presumably represents a mode of ring expansion alternative to that employed in the formation of II and IV.

Although we have no evidence yet on the degree of retention of optical purity in IV, II is partially racemized. The rotation of optically pure II is established by a modification of the isotope dilu-

tion method,⁵⁻⁷ in which x g. of ¹⁴C-labelled racemic II acid phthalate of specific radioactivity C_0 is added to B g. of partially resolved⁸ acid phthalate of rotation α_0 , the mixture again is resolved *via* the brucine salt until material having a new rotation α and radioactivity C is obtained, and the weight E of excess enantiomer in the starting sample is calculated from the equation

$$E^2 = \frac{B[(x+B)^2 - (C_0/C)x(x+B)]}{B - (C_0/C)x(\alpha/\alpha_0)}$$

On this basis, optically pure bicyclo[2.2.2]-2-octyl acid phthalate has $[\alpha]_D 30.5 \pm 3.7^\circ$ (CHCl₃), and optically pure II has $[\alpha]_D 40.0 \pm 4.8^\circ$ (CHCl₃). The stereochemical result in the deamination of I to II is therefore 49-63% retention of optical purity and 37-51% racemization.



Although some of the product II apparently is formed *via* the optically active non-classical cation VI (previously postulated^{8,9b} in the solvolysis of II, OBs instead of OH, and in the solvolysis of 3-cyclohexenylethyl *p*-bromobenzenesulfonate^{9a}), VI cannot be the sole intermediate, since II then would be formed with complete retention of optical purity. The possibility is not excluded that transannular hydride shift in VI (from C.4 to C.2) may account for part of the racemization, but a simple explanation is provided by the inactive classical cation VII. Although partial racemization in the formation of II is established definitely by the above data, the experimental error in this result and in that reported⁸ for the acetolysis of the optically active *p*-bromobenzenesulfonate of II ($82 \pm 15\%$ retention) is almost large enough to allow the possibility that the two results are the same. It remains to be seen whether this is indeed the case.

The multiple rearrangement of I may be stepwise, like that of the *endo*-isomer,¹ since an initial

(1) J. A. Berson and P. Reynolds-Warnhoff, *J. Am. Chem. Soc.*, **84**, 682 (1962).

(2) K. Alder and R. Reubke, *Chem. Ber.*, **91**, 1525 (1958).

(3) A. A. Youssef, M. E. Baum and H. M. Walborsky, *J. Am. Chem. Soc.*, **81**, 4709 (1959).

(4) J. A. Berson, J. S. Walla, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff and D. Willner, *ibid.*, **83**, 3986 (1961).

(5) S. Graff, D. Rittenberg and G. L. Foster, *J. Biol. Chem.*, **133**, 745 (1940).

(6) J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4083 (1959); J. A. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959).

(7) H. L. Goering and J. T. Doi, *ibid.*, **82**, 5850 (1960).

(8) By the method of H. M. Walborsky, M. E. Baum and A. A. Youssef, *ibid.*, **83**, 988 (1961).

(9) (a) S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961); (b) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1397 (1961).

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 expected¹ 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 discussed¹ 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 presented¹ 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 rearrangement¹ 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.

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RECEIVED DECEMBER 4, 1961

REACTIONS OF THE METASTABLE HELIUM TRIPLETS¹

Sir:

The helium species He(²S) and He(³Σ_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 10⁹ to 10¹⁰ 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, N₂, O₂, CH₄ 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 N₂ the color is blue, principally from the main system (²Σ_u⁺ → ²Σ_g⁺) of N₂⁺. For oxygen

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

the color is green, arising from the first negative system (⁴Σ_g⁻ → ⁴Π_u) of O₂⁺ or blue-white principally from the first and second negative (²Π_u → ²Π_g) systems of O₂⁺ in combination, depending on the pressure and flow rate. For methane the color is violet, principally from the ²Δ → ²π and ²Σ^{-a} → ²Π transitions of CH.

Related reaction cross sections are being reported elsewhere.²

(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).

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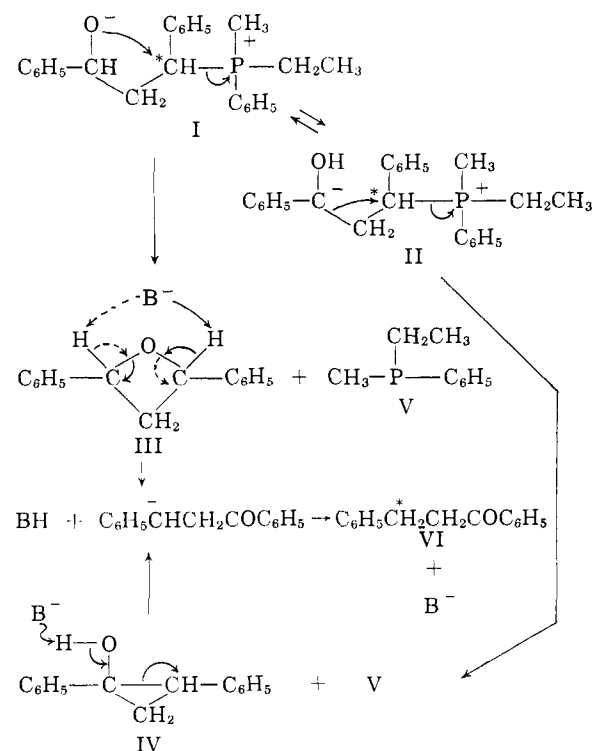
CARL COLLINS
W. W. ROBERTSON
E. E. FERGUSON
F. A. MATSEN

RECEIVED JANUARY 19, 1962

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

Sir:

In the accompanying communication¹ 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).