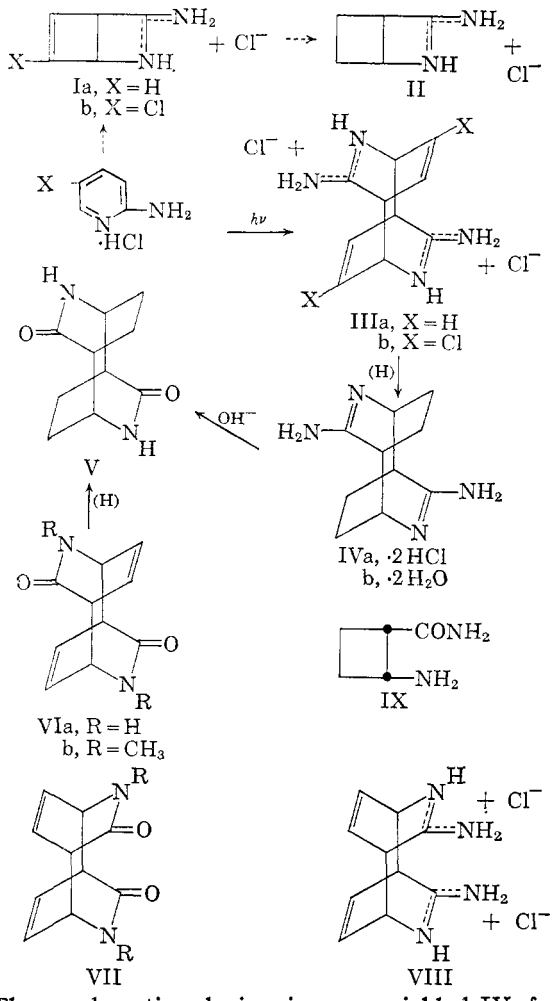

Thus, exhaustive drying *in vacuo* yielded IV, from which IVb could be reconstituted with water. Furthermore, IVa could be formed from either IV or IVb with hydrochloric acid, and it seems highly improbable that a compound of structure IX would undergo cyclization under these mild conditions to the strained (2.2.0) system II. It is interesting to note that IV is hydrolysed only slowly even by hot alkali; by contrast, 2-iminopiperidine is rapidly hydrolysed to 2-piperidone with water.[4]

A detailed study of the crystal structure of these compounds by means of X-ray crystallography is in progress in these laboratories. The anomalous chemical and physical properties of these dimeric materials will be discussed in a forthcoming paper.

(4) T. B. Grave, *J. Am. Chem. Soc.*, **46**, 1460 (1924).

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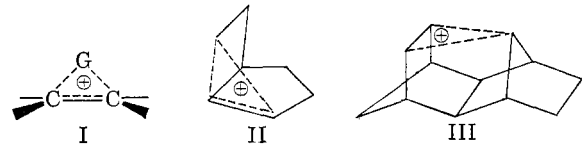
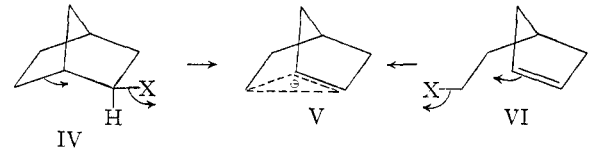
THE π-ROUTE TO A BICYCLOÖCTYL NON-CLASSICAL CATION[1]

Sir:

Many cationic reaction intermediates possess the three-center bonding indicated by formula I. In some ways the most intriguing of these are those species in which the bridging group, G, is methylene. In such cases, species I involves a delocalized two-electron system. Pertinent examples are the norbornyl cation[2] V, species[3] II which is related to the 7-norbornyl and *trans*-2-bicyclo[3.2.0]-heptyl systems, and the octahydrodimethanonaphthyl cation[4] III. In principle, as well as in practice, such cations may be produced by anchimerically assisted ionization of substrates in which the neighboring group contributes either σ- or π-electrons. For the norbornyl cation V, the σ-route may be illustrated by acetolysis of *exo*-norbornyl bromobenzenesulfonate (IV-OBs), which is accelerated relative to the *endo*-epimer by a factor of *ca.* 10^3 and which leads exclusively to racemic



exo-norbornyl acetate[2] (*dl*-IV-OAc). Very recently, Lawton[5a] and Bartlett and Bank[5b] have provided examples of the π-route to the same cation. These investigators reported solvolyses of Δ^3-cyclopentenylethyl arenesulfonates (VI) accelerated relative to the saturated analogs by factors ranging from 6 to more than 10^2, which gave rise essentially exclusively to *exo*-norbornyl solvolysis products.



2-Bicyclo[2.2.2]- and [3.2.1]octyl systems (IX, X and XII), without the angle strain of their norbornyl analog, are even more instructive for carbonium ion theory. Thus, some time ago, Walborsky[6] had concluded that the bicyclo[2.2.2]-octyl cation was classical. However, it is impossible to account for the behavior of the bicyclo-octyl systems in solvolysis on the basis of classical cationic intermediates. Thus, Le Ny[7] and Goering and Sloan[8] have reported that acetolysis of Δ^4-cycloheptenylmethyl bromobenzenesulfonate[7] (VII) or *cis*-bicyclo[3.2.1]octyl toluenesulfonate[8] (IX-OTs) leads essentially exclusively to *cis*-2-bicyclo[3.2.1]octyl acetate (IX-OAc), none of the epimeric XV-OAc or the rearranged bicyclo-[2.2.2]octyl acetate XIII-OAc being observed. Evidently, acetolysis of the Δ^4-cycloheptenyl-methyl and *cis*-bicyclo[3.2.1]octyl esters VII and

(1) (a) Research supported by the National Science Foundation; (b) results reported by S. Winstein at Symposium on "Dynamic Stereochemistry" at XVIIIth International Congress of Pure and Applied Chemistry, Montreal, Canada, August 6–12, 1961.

(2) (a) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **71**, 2953 (1949); **74**, 1147, 1154 (1952); (b) S. Winstein, *et al.*, *ibid.*, **74**, 1127 (1952).

(3) S. Winstein, F. Gadient, E. T. Stafford and P. E. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).

(4) S. Winstein and R. L. Hansen, *Tetrahedron Letters*, no. 25, 1 (1960).

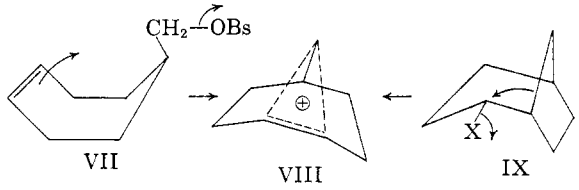
(5) (a) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961); (b) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

(6) H. M. Walborsky, *Experientia*, **9**, 209 (1953).

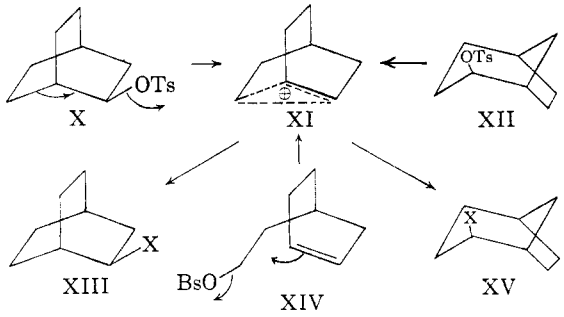
(7) G. Le Ny, *Compt. rend.*, **251**, 1526 (1960).

(8) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1397, 1992 (1961).

IX-OTs provides π- and σ-routes, respectively, to the non-classical cation VIII, which then gives rise to the *cis*-bicyclo[3.2.1]octyl acetate IX-OAc. In solvolysis of the related bicyclo[2.2.2]octyl and *trans*-(*axial*)-bicyclo[3.2.1]octyl toluenesulfonates X and XII, Walborsky[9] and Goering[8] have shown recently that both substrates give rise to the same mixture of [2.2.2]- and *axial*-[3.2.1]-products XIII and XV, none of the epimeric *cis*-[3.2.1]-



product being observed. Also, the [2.2.2]acetate XIII-OAc from optically active [2.2.2]toluenesulfonate X is formed with complete retention of configuration. Anchimerically assisted ionization of X and XII apparently represents the σ-route to the non-classical cation XI which leads only to bicyclo[2.2.2]- and *axial*-bicyclo[3.2.1]octyl products.

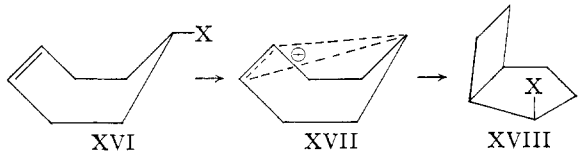


For the π-route to cation XI, one can visualize starting with the Δ^3-cyclohexenylethyl system XIV, instead of VII employed by Le Ny,[7] and we now have investigated the solvolysis of bromobenzenesulfonate[10] XIV, m.p. 25–26°. The corresponding alcohol, n^{25}D 1.4809, was obtained from hydroboration-oxidation of 4-vinycyclohexene using excess diene; m.p. of 3,5-dinitrobenzoate,[10] 63–64°. With 0.01 *M* XIV in a 0.02 *M* acetic acid solution of sodium acetate, good first order kinetics of acetolysis were observed, the rate constant at 75.1° being 7.4×10^{-6} sec.$^{-1}$. This value is four times the one obtained with the saturated analog[10] of XIV, m.p. 37–38°. From the acetolysis of XIV at 100° and treatment of the product with lithium aluminum hydride, there was obtained an alcohol mixture which vapor phase chromatographic analysis showed was 20% cyclohexenylethanol and 80% of a 54:46 mixture of [2.2.2]-alcohol XIII-OH and *axial*-[3.2.1]-alcohol XV-OH, respectively. By preparative vapor phase chromatography, the three fractions were separated and identified further by m.p., m.p. of derivatives, and infrared spectrum:[8,9] (i) *axial*-alcohol XV-OH, m.p. 197–198°, m.p. of bromobenzenesulfonate, 62–63°, m.p. of *p*-nitrobenzoate, 94–95°, (ii) [2.2.2]-alcohol XIII-OH, m.p. 208–210°, m.p. of bromobenzenesulfonate, 79–80°, (iii) cyclohexenylethanol, m.p. of 3,5-dinitrobenzoate, 63–64°. Acetolysis of the mixed bromobenzenesulfonate, m.p. 44–55°, from the combined fractions (i) and (ii) led to a 53:47 mixture of alcohols XIII-OH and XV-OH.

In 0.02 *M* sodium formate in formic acid at 75.1°, the cyclohexenylethyl bromobenzenesulfonate XIV solvolyzes with a rate constant of 4.0×10^{-4} sec.$^{-1}$, faster than the saturated analog by roughly one power of ten. The isolated alcohol product from this formolysis is again the 54:46 mixture of [2.2.2]-alcohol XIII-OH and *axial*-alcohol XV-OH, the cyclohexenylethanol content now being almost negligible.

The present work shows that the unsaturated ester XIV tends to solvolyze predominantly by way of anchimerically assisted ionization to the non-classical cation XI. Thus, there is now unique and compelling evidence for this cation from the π-route of formation, as well as the σ, the distinction between the two carbonium ions VIII and XI being maintained whether the ions are produced by π- or σ-routes.

The pair of unsaturated systems, VII and XIV, which have been demonstrated to lead to isomeric non-classical ions and thus contrasting over-all structural and stereochemical results, represents only one example in a broader theme. The usual stereoelectronic considerations allow one to conceive other such pairs of unsaturated derivatives which would be related to isomeric bridged ions if these are formed in preference to classical ones. For example, a conceivable pair of systems includes Δ^2-cyclopentenylethyl, related to ion II, and Δ^4-cycloheptenyl, XVI, which is related to ion XVII and thus *cis*-2-bicyclo[3.2.0]heptyl derivatives XVIII.



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(9) H. M. Walborsky, M. E. Baum and A. A. Youssef, *J. Am. Chem. Soc.*, **83**, 988 (1961).

(10) Correct carbon and hydrogen analyses were obtained for all new compounds.

THE PHOTOCHEMICAL REARRANGEMENT OF 4,4-DIPHENYLCYCLOHEXADIENONE. PAPER I ON A GENERAL THEORY OF PHOTOCHEMICAL REACTIONS[1]

Sir:

Organic photochemistry has not shared the mechanistic sophistication of ground state organic chemistry. A number of years ago we initiated a program to search for general principles governing organic photochemistry.

The photolysis of cyclohexa-2,5-dien-1-ones seemed of special interest not only because of the intriguingly profound molecular rearrangements occurring[2] but also because of an inherent enigma. While the skeletal rearrangements were suggestive

(1) Supported by the National Science Foundation.

(2) *Cf.* D. H. R. Barton, J. McGhie and M. Rosenberger, *J. Chem. Soc.*, 1215 (1961), for references.