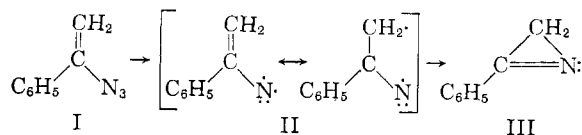


investigation of the decomposition products of vinyl azides was undertaken. Presumably the vapor phase pyrolysis^{1c} of α -azidostyrene (I)



could lead to the formation of styryl azene (II). Of the several conceivable reaction paths open to such an intermediate, it was thought that a likely possibility might be ring closure to give an azacyclopentene. Quite gratifyingly, the pyrolysis of I resulted in a 65% yield of 2-phenylazirine (III).

That III arises by cyclization of II appears quite plausible since any reaction of the double bond of I with the azide moiety would more likely involve the terminal nitrogen atom of the azide leading to a triazole in a manner analogous to tetrazole formation from imino azide derivatives.³ The ready formation of this novel unsaturated ring system is essentially analogous to the formation of cyclopropenes from alkenylcarbenes.⁴

Although azacyclopentenes have been postulated as intermediates in the Neber reaction,⁵ only one such compound, 2-(2,4-dinitrophenyl)-3-methyl-2-azirine, has been isolated and its structure established.⁶ Thus the formation of III from I is not only interesting in itself, but represents the first example of what appears to be a useful method for preparing azacyclopentenes—work is now in progress along these lines.

2-Phenylazirine (III) [calcd. for $\text{C}_8\text{H}_7\text{N}$: C, 82.02; H, 6.02; N, 11.96; mol. wt., 117. Found: C, 81.87; H, 6.23; N, 11.64; mol. wt.,⁷ 126] is a colorless, thermally unstable, irritating liquid of b.p. 80° (10 mm.). Its infrared spectrum (CCl_4) shows strong $\text{C}=\text{N}$ absorption at 5.74 μ ⁶ and its ultraviolet spectra in cyclohexane and in ethanol show maxima at 239 (13,000) and 242 m μ (13,000), respectively. The n.m.r. spectrum (CCl_4) showed the methylene hydrogens as a sharp line at 8.35 τ and the *meta-para* and *ortho* phenyl hydrogens as multiplets in the regions 2.4 and 2.1 τ , respectively, with intensity ratios of 2:3:2, respectively. Boiling a solution of III in acidic aqueous ethanol resulted in the formation of 2,5-diphenylpyrazine⁸ in 30% yield. These data are consistent with the assigned structure for III.

α -Azidostyrene was prepared as follows: styrene dibromide was treated with one mole of sodium azide in dimethylformamide and the resulting bromoazide dehydrobrominated with potassium tertiary butylate in benzene. The styryl azide was purified by chromatography^{1c} [calcd. for $\text{C}_8\text{H}_7\text{N}_3$: C, 66.19; H, 4.86; N, 28.95. Found: C, 65.96;

H, 4.87; N, 29.18]. The n.m.r. spectrum (CCl_4) showed the non-equivalent methylene hydrogens as two single sharp lines at 5.68 and 4.68 τ and the phenyl hydrogens as a multiplet in the region 2.7 τ . The data confirm the structure of I.

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RECEIVED SEPTEMBER 8, 1961

THE PHOTOLYSIS OF 2-AMINOPYRIDINES AND 2-PYRIDONES

Sir:

A recent report¹ from these laboratories described the irradiation of 2-aminopyridine hydrochloride with sunlight through Pyrex glass to give a photoisomer with very interesting chemical and physical properties, which was considered to possess the valence-bond tautomeric "Dewar" structure Ia. An analogous photo product (Ib) was obtained from the hydrochloride of 2-amino-5-chloropyridine. Reduction of either Ia or Ib gave the same hydrogenation product, considered to be II. In spite of the evidence which strongly supported these structures, we now wish to report that the photo-products are, in fact, dimers (IIIa and b).

Conclusive evidence in favor of these revised structures was obtained by alkaline hydrolysis of the tetrahydro derivative IVa (previously considered to be II) to give a product (V) identical in every respect with the tetrahydro derivative of the photodimer (VIa) of 2-pyridone.² Since n.m.r. studies on IIIb conclusively exclude the possibility that it could be a 3,4-dimer,¹ the conversion of IV to V constitutes convincing proof that the 2-pyridone photodimer (VIa) (and its N-methyl derivative Vlb, to which it has been related by methylation) is also a 3,6- rather than a 3,4- dimer as previously suggested.³ This conclusion is consistent with the observation that N,6-dimethyl-5,6-dihydro-2-pyridone does not dimerize upon irradiation. Of the four 3,6-structures which can be written for the 2-pyridone dimers, only two (VI and VII) are consistent with the negligible dipole moment previously found for Vlb. Of these, VII can be ruled out, since the corresponding structure in the 2-aminopyridine series (VIII) would involve unfavorable proximity of positive charges.

We had previously reported that solution of II (now shown to be IVa) in dilute alkali resulted in the rapid separation of a product which, on the basis of all available evidence, was considered to be *cis*-2-aminocyclobutanecarboxamide (IX). This was not an unreasonable proposal, since II would be expected to undergo a facile hydrolytic ring-cleavage to a less strained system. However, we now have been able to show that this product is actually an extremely stable dihydrate (IVb).

(1) E. C. Taylor, W. W. Paudler and I. Kuntz, Jr., *J. Am. Chem. Soc.*, **83**, 2967 (1961).

(2) E. C. Taylor and W. W. Paudler, *Tetrahedron Letters*, **25**, 1 (1960).

(3) We would like to express our appreciation to Professor P. de Mayo, Department of Chemistry, University of Western Ontario, London, Canada, for revealing to us in advance of publication (*Tetrahedron Letters*, in press) his conclusion that the N-methyl-2-pyridone dimer possesses structure Vlb. In point of time, Professor de Mayo's conclusion on this revised structure preceded our own, and knowledge of his results greatly facilitated our own investigations.

(1)(a) G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4717 (1960); (b) *ibid.*, **83**, 2489 (1961); (c) *J. Org. Chem.*, **26**, 4108 (1961).

(2) D. H. R. Barton and L. R. Morgan, Jr., *Proc. Chem. Soc.*, 206 (1961).

(3) F. Eloy, *J. Org. Chem.*, **26**, 952 (1961).

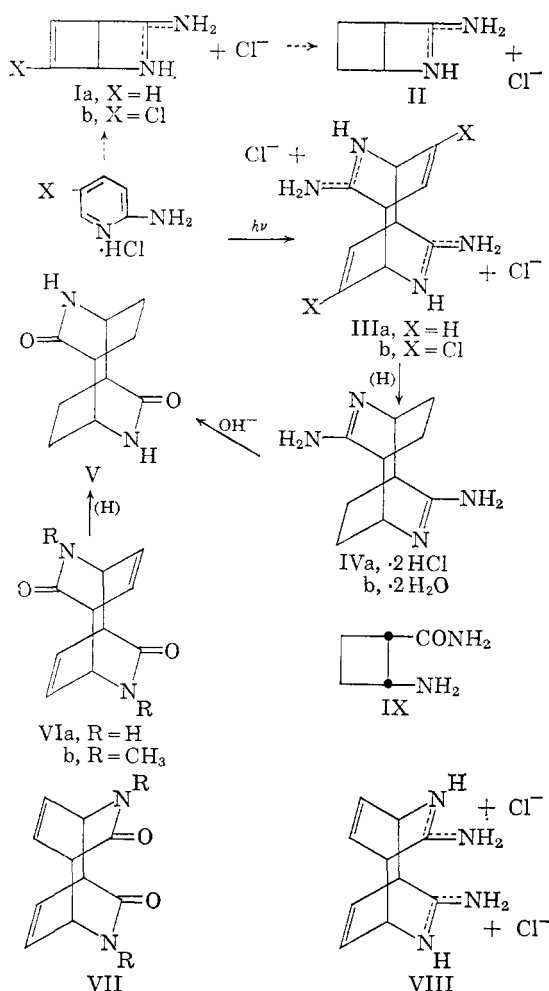
(4) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 2015 (1961).

(5) P. W. Neber and A. Burgard, *Ann.*, **493**, 281 (1932); P. W. Neber and G. Huh, *ibid.*, **515**, 283 (1935).

(6) D. J. Cram and M. J. Hatch, *J. Am. Chem. Soc.*, **75**, 33 (1953).

(7) Cryoscopic determination in cyclohexane.

(8) Identity of this material established by comparison with an authentic sample.



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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RECEIVED OCTOBER 2, 1961

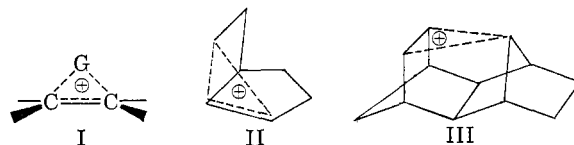
THE π -ROUTE TO A BICYCLOOCTYL NON-CLASSICAL CATION¹

Sir:

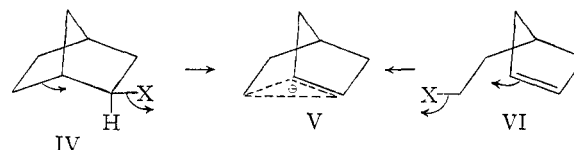
Many cationic reaction intermediates possess the three-center bonding indicated by formula I.

(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.

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 cation² V, species³ II which is related to the 7-norbornyl and *trans*-2-bicyclo[3.2.0]-heptyl systems, and the octahydrodimethanonaphthyl cation⁴ 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.* 10^8 and which leads exclusively to racemic



exo-norbornyl acetate² (*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 10^3 , 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, Walborsky⁶ had concluded that the bicyclo[2.2.2]-octyl cation was classical. However, it is impossible to account for the behavior of the bicyclooctyl systems in solvolysis on the basis of classical cationic intermediates. Thus, Le Ny⁷ and Goering and Sloan⁸ have reported that acetolysis of Δ^4 -cycloheptenylmethyl bromobenzenesulfonate⁷ (VII) or *cis*-bicyclo[3.2.1]octyl toluenesulfonate⁸ (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 -cycloheptenylmethyl and *cis*-bicyclo[3.2.1]octyl esters VII and

(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. Gadiant, 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.*, **261**, 1526 (1960).

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