$NiCl_2 \cdot (CH_3OCH_2)_2$ or with nickelocene.[29] It was isolated by sublimation at 155° (10^{-4} mm) after extraction with either CS_2 or ether. The yield was 4% from either nickel precursor.

Thus, although pentalene must be very difficult to isolate, and never yet has been, although its 1-methyl derivative recently has at −196°,[30] two of its derivatives are easily prepared and stable under common laboratory conditions: the dianion I and the nickel derivative II.

Acknowledgments. We are grateful to the U. S. Army Research Office—Durham for its support under Grant No. DA-ARO(D)-31-124-G1119.

(29) Allylmagnesium chloride reacts with nickelocene to give π-allyl-π-cyclopentadienylnickel.[15a]

(30) R. Bloch, R. A. Marty, and P. de Mayo, *J. Amer. Chem. Soc.*, 93, 3071 (1971).

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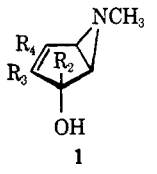
Photohydration of Pyridinium Ions[1]

Sir:

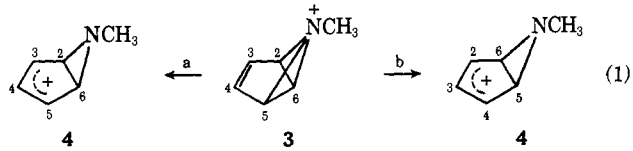
We wish to report that irradiation of methylpyridinium chloride in water at 254 nm yields 6-methylazabicyclo[3.1.0]hex-3-en-2-*exo*-ol (**1a**) with a quantum yield of about 0.1. Its methyl ether **2** is formed by irradiation in methanol. The methochlorides of the picolines and of 3,5-lutidine yield analogous products, **1b–e**. The alcohols are readily isolated by gas chromatography[2] of ethereal extracts. Since the photohydrations occur with appreciable quantum yields and can be carried to completion in basic solutions they provide a convenient route to the 6-azabicyclo[3.1.0]hexenyl system, only one example of which has been reported.[3]

The products are evidently formed by hydration of an azabicyclohexenyl cation **4**, but 1,2 shifts of nitrogen appear to precede formation of this ion in some cases. These shifts are in accord with the intervention of a 1-methylazoniabenzvalene (**3**) (eq 1). Photohydration



	R_2	R_3	R_4
a	H	H	H
b	CH_3	H	H
c	H	H	CH_3
d	H	CH_3	H
e	CH_3	H	CH_3

1



4 **3** **4** (1)

of the pyridinium ion, perforce originating in $\pi-\pi^*$ excitation, is thus completely different from that of pyridine in which $n-\pi^*$ excitation[4] leads to a bicyclic valence isomer ("Dewar pyridine")[5] that is converted by hydration to an open-chain aminoaldehyde.[4,5] It instead resembles that of benzene,[6] in which hydration of the initially formed benzvalene[7-10] yields bicyclo[3.1.0]hex-3-en-2-*exo*-ol (**5**). Unlike the case of benzene, however, there is no indication that the azoniabenzvalene has an appreciable lifetime or that it rearomatizes.[7]

In a typical photolysis, 40 ml of a solution 0.04 *M* in methylpyridinium chloride and 0.05 *M* in KOH was irradiated at room temperature in an annular vessel (2-mm path) with a G8T5 Hg resonance lamp. The uv absorption at 259 nm was reduced to one-half in 1 hr and to one-tenth in 2 hr. An ether extract showed a single gc product peak.[2] The product, **1a**, exhibits only end absorption in the uv; its mass spectrum shows a parent mass of 111 (C_6H_9NO) with a base peak at *m/e* 94. Its nmr spectra in D_2O[11] and CCl_4 are summarized in Table I. The assignment

Table I. 100-MHz Nmr Spectra

Compd	Solvent	Chemical shifts, δ[a] NCH_3	Aziridine	R_2	R_3	R_4
1a	D_2O	2.29	2.61, 2.74[b]	4.47	5.86[c]	6.32
1b	D_2O	2.28	2.43, 2.63[b]	(1.40)	5.67[c]	6.16
1c	D_2O	2.28	2.55, 2.55	4.44	5.42	(1.89)
1d	D_2O	2.22	2.50, 2.50	4.21	(1.68)	5.84
1e	D_2O	2.29	2.38, 2.51[b]	(1.37)	5.25	(1.85)
1a	CCl_4	2.32	~2.3	4.30	5.78	6.15
2[d]	CCl_4	2.23	~2.2	4.00	5.71	6.12

[a] Relative to internal $(CH_3)_3SiCD_2CD_2COONa$ in alkaline D_2O and to TMS in CCl_4; CH_3 resonances in parentheses. [b] $J_{1,5} = 5$ Hz. [c] $J_{3,4} = 6$ Hz. [d] OCH_3 resonance at δ 3.28.

of its structure follows from the observations that there are only two olefinic protons, that the magnitude of the coupling between them is characteristic of a double bond in a C_5 ring, and that the chemical shifts of the bridge protons correspond to those in fused aziridine rings.[12] The stereochemistry at C_2 and the assignment of R_3 and R_4 follow from the similarity of the resonances to those,[13] δ 4.30, 5.47, and 6.13, in the corresponding carbocyclic compound **5**. The structures of the other products are readily deduced from the nmr data in Table I.

(1) Based on work performed under auspices of the U. S. Atomic Energy Commission.

(2) Retentions relative to aniline at 100° on Chromosorb G coated with Carbowax 750 (5%) and KOH (2%) are: **1a**, 1.35; **1b**, 0.48; **1c**, 1.57; **1d**, 1.96; **1e**, 0.59; **2**, 0.16.

(3) A. Mishra, S. N. Rice, and W. Lwowski, *J. Org. Chem.*, 33, 481 (1968).

(4) J. Joussot-Dubien and J. Houdard-Pereyre, *Bull. Soc. Chim. Fr.*, 2619 (1969).

(5) K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, 92, 2178 (1970).

(6) E. Farenhorst and A. F. Bickel, *Tetrahedron Lett.*, 5911 (1966).

(7) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Amer. Chem. Soc.*, 89, 1031 (1967).

(8) J. A. Berson and N. M. Hasty, Jr., *ibid.*, 93, 1549 (1971).

(9) T. J. Katz, E. J. Wang, and N. Acton, *ibid.*, 93, 3782 (1971).

(10) L. Kaplan, L. A. Wendling, and K. E. Wilzbach, *ibid.*, 93, 3821 (1971).

(11) An identical spectrum was observed without processing by irradiating in D_2O containing K_2CO_3. We thank Mrs. Geraldine McDonald for nmr analyses.

(12) A. Hassner, G. J. Matthews, and F. W. Fowler, *J. Amer. Chem. Soc.*, 91, 5046 (1969).

(13) N. M. Hasty, Jr., Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1971. In the endo alcohol the resonance of the proton at C-2 falls at much lower field, δ 5.2. Resonances in the stereoisomeric methyl ethers follow a similar pattern.

The structure and stereochemistry of **1a** suggest[8] that it is formed by solvation of a 6-azabicyclohexenyl cation **4**. The formation of a 2,6 bridge in the excited pyridinium ion would yield **4a** and might be regarded as a plausible path, but results obtained in the photolysis of 3,4,5-trideuterio-1-methylpyridinium chloride[14] are not compatible with this simple origin. The observation that proton resonances in the product appear at R_2 and R_4 as well as in the aziridine positions implies that skeletal rearrangement precedes formation of the bicyclic ion. A plausible intermediate is the 1-azoniabenzvalene **3** which can yield **4b** as well as **4a** (eq *1*). If all of the ions were formed in this way, and isotope effects were negligible, proton areas at R_2 and R_4 would each equal one-third that at each aziridine position. The observed ratio of 1:7 indicates that half the ions result from 2,6 bridging.

Products obtained from photolysis of picoline methochlorides provide further support for the intermediacy of **3** and indicate that methyl groups can exert a strong directive influence on its formation and fate. Photolysis of the 1,4-dimethyl isomer yields **1b**, **1c**, and **1d** in the ratio 1:1:2, whereas only **1d** would be expected from a 2,6-bridged intermediate; the observed result is in accord with statistical opening of its 1-azoniabenzvalene[15] (4-methyl-**3**) by paths a and b and statistical hydration at positions 2 and 4 in the ion corresponding to **4b**. Photolysis of the 1,2 isomer yields only **1b** and **1c**, in approximately equal amounts. The absence of products derived from a 2,6-bridged ion indicates that 2-methyl-**3** is formed to the exclusion of 6-methyl-**3**, and opens only by path b. The 1,3 isomer similarly yields only **1b** and **1c**. Although these products might involve the intermediacy of 2-methyl-**3** or 4-methyl-**3**, they might equally well result from 2,6 bridging. Similar effects are noted in the photolysis of the methochlorides of the lutidines. **1e** is the sole product from the 1,3,5 isomer and the highly predominant product from the 1,2,4 isomer. In the latter case it must be formed by selective ring opening in 2,4-dimethyl-**3**.

In the absence of added base the photohydrations occur with comparable (initial) quantum yield, but as the solution becomes acidic the products slowly re-form pyridinium ions. Nmr studies of the aromatization of isolated **1a–e** in D_2O indicate that both rearrangement and hydrogen exchange occur during the process: R_2, R_3, and R_4 appear at α, β, and γ positions, respectively, in the ions, and resonances for β protons are absent. In the case of **1d**, where aromatization occurs even at pH 7, the accompanying formation and disappearance of 370-nm absorption suggests the intermediacy of an open-chain aminoaldehyde. In the case of **1e**, where a lower pH is required, the intermediacy of a 1,2-dihydropyridin-2-ol is suggested by the formation and disappearance of 240-nm absorption.

A corresponding photohydration of protonated pyridines is suggested by the observation that 3,5-lutidine irradiated in acidic D_2O disappears with $\Phi \sim 0.1$, and that 2,4-lutidine-d_2 is subsequently formed.

(14) Prepared by exchange of methylpyridinium-d_5 chloride with aqueous NaOH.

(15) Formation of **1d** *via* a simple 2,6-bridged intermediate is not precluded if ring opening of the azoniabenzvalene occurs preferentially by path b. Formation of **1b** and **1c** did not involve prior formation of 1,3-dimethylpyridinium ion, either by rearrangement of the 1,4 isomer or by dehydration of **1d**, since its characteristic uv absorption was not observed during photolysis.

(16) University of Wisconsin—River Falls, River Falls, Wis., Faculty Research Participant, Summer 1971.

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*Book Reviews**

Mechanisms of Molecular Migrations. Volume 4. Edited by B. S. THYAGARAJAN (University of Idaho). Wiley-Interscience, New York, N. Y. 1971. xv + 326 pp. $22.50.

The latest volume in this continuing series contains four chapters, the first two of which are much concerned with orbital symmetry considerations. Joseph J. Gajewski discusses *thermal degenerate rearrangements of hydrocarbons*, a subject that embraces those transformations in which the product has the same structure as the reactant (for example, the rearrangements of bullvalene to itself, and 1,3-hydrogen shift in propene). M. J. Perkins and P. Ward write about *dienyl rearrangements:* electrocyclic and sigmatropic rearrangements of dienyl cations, anions, and radicals. The growth of this new field is indicated by the fact that although the references are drawn almost entirely from the last ten years, there are 137 of them. A. Fry writes about *acid-catalyzed rearrangements of ketones*, a field whose long history begins with the conversion of camphor to carvenone in hot sulfuric acid by Delalande in 1839. Finally, R. T. Conley and S. Ghosh discuss *abnormal Beckmann rearrangements:* the Beckmann fragmentation, the Semmler–Wolff aromatization, and the Neber rearrangement.

The chapters give thorough treatments to the subjects, and cover both mechanism and applications but do not include comprehensive tables of reported examples. Coverage of the literature appears to extend well into 1970. Besides author and subject indexes, this volume includes a cumulative index to the chapter titles in Volumes 1 to 4.

Fused Pyrimidines. Edited by D. J. BROWN. **Part II. Purines.** By J. H. LISTER, R. L. JONES, and P. D. LAWLEY (Chester Beatty Research Institute, London) and G. H. HITCHINGS and G. B. ELION (Wellcome Research Laboratories). Wiley-Interscience, New York, N. Y. 1971. xxiv + 655 pp. $49.50.

This book constitutes Volume 24, Part 2, of the series "The Chemistry of Heterocyclic Compounds," under the general editorship of A. Weissberger and E. C. Taylor. The chemistry of pyrimidines has become so extensive that the subject is now separated into four volumes, of which two are yet to come. The authors follow the customary emphasis of this series on a critical, yet exhaustive treatment of the practical aspects, with theoretical aspects being treated in outline. There must be several thousand references. An 81-page appendix lists nearly 3000 purine derivatives in tabular form with melting points and references. The literature has been

* Unsigned book reviews are by the Book Review Editor.