Acknowledgment. We are indebted to the Royal Society (London) for generous financial support.

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(15) Imperial Chemical Industries Fellow.

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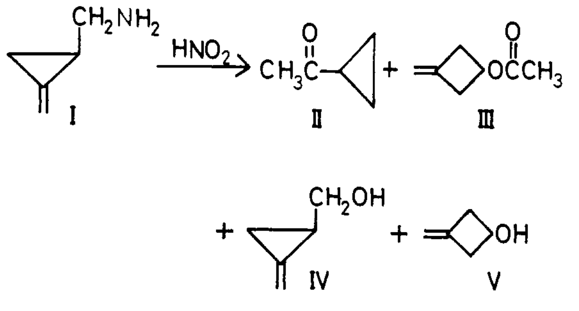
Deamination of Methylenecyclopropylcarbinylamine

Sir:

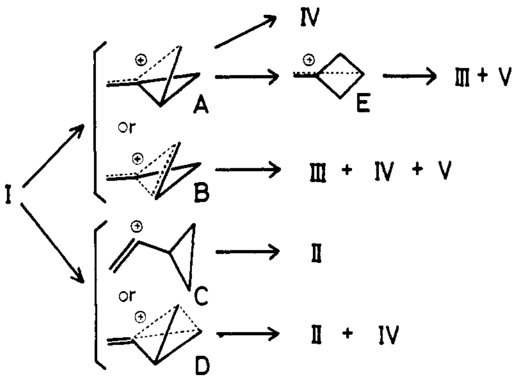
The current interest on reactions involving vinyl cation intermediates[1] prompts us to report the deamination of methylenecyclopropylcarbinylamine (I), which suggests that a vinyl cation is formed by cleavage of a carbon–carbon bond.

Amine I was prepared by the ammonolysis of ethyl methylenecyclopropanecarboxylate[2] followed by the lithium aluminum hydride reduction of the resulting amide. Its infrared spectrum shows bands at 3360 and 3295 cm^{-1} for the amino group, 3065, 1745, and 886 cm^{-1} for the terminal methylene group, and 3040 and 1019 cm^{-1} for the cyclopropane group. Its nmr spectrum exhibits a multiplet centered at τ 4.90 (2 H, terminal methylene), a doublet at 7.52 (2 H, methylene group adjacent to the amino group), and a broad multiplet at 8.30–9.46 with a sharp singlet at 9.09 (5 H, ring protons and amino group). The phenyl isothiocyanate adduct melted at 70–71°.

The treatment of I with sodium nitrite in 20% aqueous acetic acid gave acetylcyclopropane (II), 3-methylenecyclobutyl acetate (III), methylenecyclopropylcarbinol (IV), and 3-methylenecyclobutanol (V) with a vpc peak area ratio of 2.3:1.0:1.6:16.4, along with three other minor components.[3] Compound II was identified by comparison of its mass and infrared spectra and vpc retention time with those of an authentic sample,[4] and the carbinol V was identified by comparison of its infrared and nmr spectra with the reported value.[5] The infrared spectrum of the acetate III exhibits bands at 3080, 1740, 1240, 1070, 1032, and 882 cm,$^{-1}$ showing the presence of an ester group and a terminal methylene group. Its nmr spectrum is very similar to that of V except that the peak of the hydroxyl proton is replaced by a sharp singlet of an acetoxy group at τ 8.15. The acetylation of V gave III, and the lithium aluminum hydride reduction of III gave V. The nmr and infrared spectra and vpc retention time of IV are the same as those of an authentic sample of IV prepared by the lithium aluminum hydride reduction of ethyl methylenecyclopropanecarboxylate.[2]



The formation of III and V as the major products and the absence of 2-methylenecyclobutanol in the deamination products suggest a considerable interaction between the π electrons of the double bond and the nearby situated cationic center, such as is shown in A or B.[6] Of special interest is the formation of acetylcyclopropane,



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(1) M. Hanack and J. Haeffner, *Tetrahedron Letters*, 2191 (1964); M. Hanack, J. Haeffner, and I. Herterich, *ibid.*, 875 (1965); M. Hanack and I. Herterich, *ibid.*, 3847 (1966); M. Hanack and J. Haeffner, *Chem. Ber.*, **99**, 1077 (1966); W. D. Clossen and S. A. Roman, *Tetrahedron Letters*, 6015 (1966); M. Bertrand and M. Santelli, *Compt. Rend.*, **259**, 2251 (1964); H. R. Ward and P. D. Sherman, Jr., *J. Am. Chem. Soc.*, **89**, 1963 (1967); D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *ibid.*, **87**, 2295 (1965); P. E. Peterson and R. J. Kamat, *ibid.*, **88**, 3152 (1966); P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966); W. M. Jones and F. W. Miller, *ibid.*, **89**, 1960 (1967).

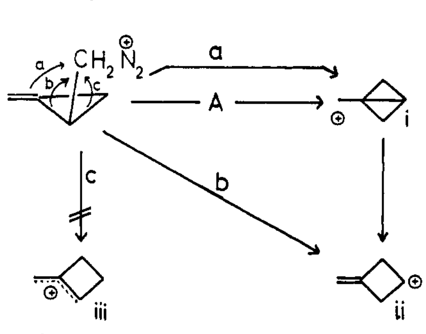
(2) J. A. Carbon, W. B. Martin, and L. R. Swett, *ibid.*, **80**, 1002 (1958); E. F. Ullman and W. J. Fanshawe, *ibid.*, **83**, 2379 (1961).

(3) These four components, II–V, constituted 87% of the total products in the peak area ratio.

(4) G. W. Cannon, R. C. Ellis, and J. R. Leal, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 597.

(5) D. E. Applequist and G. F. Fanta, *J. Am. Chem. Soc.*, **82**, 6393 (1960).

(6) A referee has suggested that structures A, B, D, and E may only be transition states rather than intermediates. The lack of kinetic data prevents us from speculating on the exact nature of the intermediates. The use of nonclassical structures in this report is primarily for simplicity of representation and does not at present have any mechanistic significance. Thus, with respect to structure E, for example, the formation of III and V may well be explained *via* classical intermediates i and ii (pathway a)[7] or even by direct ring expansion to ii (pathway b). In the last case, the absence of 2-methylenecyclobutanol (pathway c) in the reaction products may be taken as an example of a vinyl group being a good migrating group[8] and/or an example of the steric inhibition of normal allylic stabilization in the transition state from I to iii.[9]



(7) E. F. Kiefer and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 784 (1962); K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965). See, however, the unpublished results of Martin and Anderson cited in the paper of Applequist and Fanta.[5]

(8) W. Herz and G. Caple, *J. Org. Chem.*, **29**, 1691 (1964); R. S. Bly and R. T. Swindell, *ibid.*, 30, 10 (1965). We are indebted to the anonymous referee for bringing our attention to these reports.

(9) P. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **84**, 3411 (1962); W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, 7, 397 (1966); M. R. Willcott and E. Goerland, *Tetrahedron Letters*, 6341 (1966); J. A. Berson and R. S. Wood, *J. Am. Chem. Soc.*, **89**, 1043 (1967).

because it requires the formation of vinyl cation C or D as the precursor. Such a mode of generation of a vinyl cation by cleavage or loosening of a C–C bond has no precedence to the best of our knowledge. Work is now under progress to further elucidate the nature of the intermediate.

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Aromatic Halogenation. III. Kinetics of Iodination of Azulene. Amplification of Isotope Effects by Steric Hindrance[1]

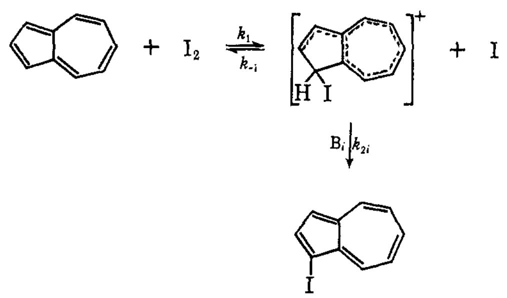
Sir:

Azulene reacts with iodine at 25° in dilute aqueous solutions of sodium iodide (0.1 *M*) to give 1-iodoazulene in good yield[2] and at a convenient rate for determination of the velocity of the reaction from spectroscopic measurement of the triiodide concentration. Since 1-iodoazulene reacts with additional iodine to give diiodoazulene at a rate which is about one-tenth that of monoiodination, a threefold or greater molar excess of azulene over iodine was employed in the present kinetic measurements to ensure monoiodination. Under these conditions iodination was found to obey the rate law

$$\frac{d[\mathrm{AzI}]}{dt} = \frac{[\mathrm{AzH}][\mathrm{I_2}]}{[\mathrm{I^-}]}\sum_i k_i[\mathrm{B}_i]$$

where AzI and AzH represent iodoazulene and azulene, respectively, B_i is a general base, and the quantities in brackets refer to the actual concentration of the species indicated. Similar kinetic expressions have been found previously for the iodination of phenol,[3] 4-nitrophenol,[1] and aniline,[4,5] except that for the neutral hydrocarbon azulene the extent of protonation of the reactant does not complicate the kinetics at the low acidities (pH 5.2–7.5) used nor does the azulene molecule function as an effective general base. In accord with the proposed mechanism of iodination of 4-nitrophenol[1] and aniline,[5] the mechanism in Scheme I seems likely for azulene. This mechanism can be shown to be in agreement with the observed kinetics provided that the steady-state approximation is applicable to the intermediate iodoazulenium cation and provided that $k_{-1}[\mathrm{I^-}] \gg \Sigma k_{2i}[\mathrm{B}_i]$; under these conditions, the individual catalytic constant k_i in the experimental rate expression corresponds to the product k_1k_{2i}/k_{-1} in the derived mechanism. The indicated inequality of the rates of the step k_{-1} *vs.* step k_{2i} is found to hold at [I⁻] of 0.04–0.20 *M* with the solvent water as general base and at 0.1 *M* [I⁻] with up to 0.15 *M* of a general base such as chloroacetate anion.

Scheme I



Since the mechanism of electrophilic aromatic substitution upon azulene has been studied in detail previously only for proton exchange,[6] we deemed it of interest to study iodination in more detail. Azulene-1,3-d_2 (>95% of the theoretical deuterium content according to analysis by nmr) was prepared from azulene by deuterium exchange with 1 *M* D_2SO_4 in a modification of the procedure of Gruen and Long.[6] The iodination of this material was performed under the same conditions as those of the protium compound. The catalytic constants $(k_i)_H$ for the protium compound and the ratios of the catalytic constant of protium compound to those of the deuterium compound $(k_i)_H/(k_i)_D$ are recorded in Table I for various bases along with literature values for the acidity of the conjugate acids of these bases. It is immediately obvious that the iodination of azulene has an appreciable isotope effect of sufficient size to be classified as a primary isotope effect. The general mechanism of iodination suggested above is therefore confirmed; in particular, cleavage of the C–H bond is part of the rate-determining step. Moreover, the position of iodination is confirmed since the location of deuterium in the reactant is well established by nmr analysis[7] and only if deuterium is being replaced would such a large isotope effect be expected.

Table I. Catalytic Constants for Iodination of Azulene and Azulene-1,3-d_2 in Aqueous Solution at 25.0°, μ = 0.3

Base	pK_a of base	$(k_i)_H$, M^{-1} sec^{-1}	$(k_i)_H/(k_i)_D$
Water	−1.7[a]	6.1[a]	3.2 ± 0.1
Chloracetate	2.85	4.4×10^3	3.0 ± 0.3
Acetate	4.75	3.1×10^4	3.0 ± 0.1
Pyridine	5.23	2.9×10^4	2.0 ± 0.2
HPO_4^{2-}	7.21	2.5×10^5	3.2 ± 0.1
2,4,6-Trimethylpyridine	7.59	5.0×10^3	6.5 ± 1.3

[a] Based on the assumption that the effective concentration of H_2O in water is 55.6 *M*.

Table I further shows that the catalytic constant depends upon the nature of the base. A Brønsted plot of

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[1] Part II: E. Grovenstein and N. S. Aprahamian, *J. Am. Chem. Soc.*, 84, 212 (1962).

[2] The yield of iodoazulene was determined by vapor phase chromatography with an Apiezon L on Chromosorb column; it was assumed that the product of slightly longer retention time than 1-iodonaphthalene was 1-iodoazulene. The ultraviolet absorption spectrum of this product was very similar to that of 1-chloroazulene [F. A. Long and J. Schulze, *ibid.*, **86**, 327 (1964)]. Attempts to isolate pure 1-iodoazulene resulted in a green-black product of very different ultraviolet spectrum which appears to be a polymer of iodoazulene. For a similar report of an unsuccessful attempt to isolate pure 1-bromoazulene see A. G. Anderson, J. A. Nelson, and J. J. Tazuma, *ibid.*, **75**, 4980 (1953).

[3] F. G. Soper and G. F. Smith, *J. Chem. Soc.*, 2757 (1927); B. S. Painter and F. G. Soper, *ibid.*, 342 (1947); E. Berliner, *J. Am. Chem. Soc.*, **73**, 4307 (1951).

[4] E. Berliner, *ibid.*, 72, 4003 (1950).

[5] F. M. Vainstein, E. I. Tomilenko, and E. A. Shilov, *Kinetika i Kataliz*, 4, 357 (1963).

[6] L. C. Gruen and F. A. Long, *J. Am. Chem. Soc.*, **89**, 1287 (1967).

[7] The doublet assigned [W. G. Schneider, H. J. Bernstein, and J. A. Pople, *ibid.*, **80**, 3497 (1958)] to H_1 and H_3 in azulene is absent and the triplet assigned to H_2 is reduced to a singlet, as expected in azulene-1,3-d_2.