

provides 3. Alternatively, cycloaddition of the carbon-sulfur double bond with the carbon-carbon double bond forms a sulfur-bridged bicyclobutane (valene),¹ the implicit symmetry of which fails to rationalize the specific 2-arylthiophene rearrangements.

The observed tendency for 1,2 shifts in benzenoid photorearrangements¹⁰ bears striking similarity to our results and those of Ullman.⁹ The isolation of reasonably stable Dewar,¹¹ prismane, and valene structures¹² with only end ultraviolet absorption leads one to question if these species provide a complete explanation of the rearrangements. The possibility of ring opening has not been considered in the literature. In this connection the formation of a benzene structure by thermal rearrangement of a dicyclopene,¹³ an analog of 3a or Ullman's azirine, is of more than passing interest.

(10) *o*-Xylene gives, in addition to other products, *m*- and *p*-xylene in an 11:1 ratio in the first 20 min of reaction: K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **86**, 2307 (1964). Mesitylene gives 1,2,4-trimethylbenzene: L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *ibid.*, **87**, 675 (1965). *o*-Di-*t*-butylbenzene is reported to give mostly 1,3-di-*t*-butylbenzene in the first 6 hr of reaction: A. W. Burgstahler and P. L. Chien, *ibid.*, **86**, 2940 (1964). In other benzenoid photorearrangements a 1,2 shift cannot be readily distinguished; see, e.g., E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, **50**, 3803 (1964).

(11) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85**, 3297 (1963). The hexamethyl derivative is now commercially available: *Chem. Eng. News*, **44**, No. 28, 20 (1966).

(12) See, for example, K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 4004 (1965).

(13) R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York-London, 1963, pp 243-245. This reaction is also mentioned by E. E. van Tamelen, *Angew. Chem.*, **77**, 759 (1965).

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A New Synthesis of 1,2,4-Oxadiazine Derivatives from 1-Aroylaziridine Oximes

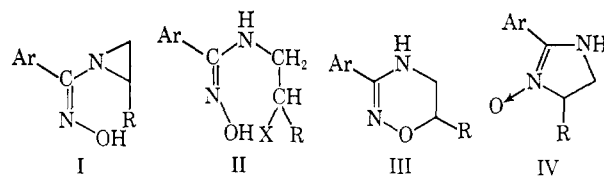
Sir:

The protic and Lewis acid catalyzed isomerization of different types of aziridine derivatives is a well-documented phenomenon.¹

(1) H. W. Heine, *Angew. Chem. Intern. Ed. Engl.*, **1**, 528 (1962), and references cited therein.

We now wish to report on the acid-catalyzed isomerization of 1-aryloxyaziridine oximes, a new class of compounds, leading to the derivatives of the little known 1,2,4-oxadiazine.

The 1-aryloxyaziridine oximes (Ia-e)² were prepared, under conditions where the aziridine ring opening is least likely to occur, by treating equimolar proportions of the appropriate benzonitrile oximes with ethylenimine or propylenimine in ether.



I and IIIa, Ar = 4-chlorophenyl, R = H
b, Ar = phenyl, R = H
c, Ar = 3,4-dichlorophenyl, R = H
d, Ar = phenyl, R = CH₃,
e, Ar = 3-nitrophenyl, R = H
IIa, Ar = 4-chlorophenyl, R = H, X = Cl
b, Ar = 4-chlorophenyl, R = H, X = Br

When 1-(4-chlorobenzoyl)aziridine oxime [Ia; mp 176-178°; infrared spectrum (Nujol): absorptions at 3200 (moderate), 1635 (moderate), 1590 cm⁻¹ (weak); nmr spectrum:³ singlet at δ 2.27 (four protons), multiplet centered at 7.58 (four protons), singlet at 9.7 (one exchangeable proton)] thus prepared was heated for a short period with enough concentrated hydrochloric acid to bring it into solution, the mixture then evaporated to dryness, and the residue dissolved in a minimum quantity of water and rendered strongly alkaline, an isomeric compound (mp 160-162°; molecular weight by mass spectral determination⁴ 196) was isolated. Its infrared spectrum exhibits absorptions at 3300 (moderate) and 1590 cm⁻¹ (strong), and its nmr spectrum³ carries a pair of A₂B₂ multiplets centered at δ 3.57 and 3.93, respectively, a broad singlet at 6.38 (one exchangeable proton), and a multiplet centered at 7.56 (four protons). These physical data would fit in with either of the two structures, IIIa and IV (Ar = 4-chlorophenyl, R = H), possible for this isomeric compound.

Structure IV was eliminated on the following grounds. Treatment of this compound with triphenylphosphine, triethyl phosphite, or phosphorus oxychloride in refluxing benzene left it unchanged, whereas if structure IV (Ar = 4-chlorophenyl, R = H) were correct it should have been smoothly deoxygenated to 2-(4-chlorophenyl)-Δ²-imidazoline. Secondly, if this compound possesses the N-oxide structure IV (Ar = 4-chlorophenyl, R = H), then its mass spectrum should exhibit a peak at *m/e* 180 (M - 16 ion peak) arising from the loss of an oxygen atom.⁵ Actually its mass spectrum contains no peak in the region between *m/e* 153 and 196, and is compatible with the alternate structure IIIa. Finally, IIIa was synthesized by a different method. Condensation of 4-chlorobenzo-

(2) Satisfactory elemental analyses were obtained for all the new compounds reported herein.

(3) A Varian A-60 instrument was used with CD₃COCD₃ as solvent and TMS as internal standard.

(4) We are grateful to Dr. H. Hürzeler of CIBA Ltd., Basle, Switzerland, for the determination and interpretation of the mass spectrum.

(5) T. A. Bryce and J. R. Maxwell, *Chem. Commun.*, 206 (1965); A. Chatterjee, P. L. Majumder, and A. B. Ray, *Tetrahedron Letters*, 159 (1965).

nitrile oxide with 2-bromoethylamine (freshly liberated from its hydrobromide at low temperatures) yielded the bromo amidoxime (IIb), which, when treated with concentrated aqueous sodium hydroxide, furnished a compound identical in all respects with IIIa.

In trying to establish whether the formation of IIIa from Ia proceeded in a single step or through two discrete steps, we were able to isolate the intermediate chloro amidoxime (IIa) as its hydrochloride and cyclize it to IIIa with base. Hence, this reaction cannot be termed a rearrangement in the formal sense of the term.

Since the 1-arylozaziridine oximes Ib-e can also be converted, in a similar fashion, into compounds IIIb-e, this sequence of reactions constitutes a new method for the synthesis of 1,2,4-oxadiazine derivatives.

It is pertinent to mention here that the 1-arylozaziridine oximes (Ia-e) do not undergo any type of isomerization in the presence of the nucleophilic iodide ion.¹

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Microwave Spectrum, Dipole Moment, and Structure of Bicyclo[1.1.0]butane

Sir:

Since bicyclo[1.1.0]butane was first synthesized in 1963,^{1,2} many of the physical and chemical properties of this interesting bicyclic species have been elucidated. Wiberg³ has given a good review of much of this work. It is particularly interesting that the molecule has the largest strain energy per carbon atom of any known molecule.³ In this regard, it is of interest to know, also, the geometrical structure and electronic distribution of bicyclobutane. Haller and Srinivasan⁴ obtained some structural information from the analysis of partially resolved infrared vibration-rotation bands, but the method cannot be expected to give results of high accuracy. In order to obtain accurate values of the structural parameters, we have begun an investigation of the microwave (rotational) spectrum of bicyclobutane. In this article we wish to report microwave spectroscopic measurements of the dipole moment and some preliminary structural calculations based on the normal isotopic species, ¹²C₄H₆.

The sample used in this study was prepared by the method of Wiberg and Lampman.⁵ An infrared spectrum of the gas agreed well with that reported by Haller and Srinivasan.⁴ The microwave spectrum of

(1) D. M. Lemal, F. Menger, and G. W. Clark, *J. Am. Chem. Soc.*, **85**, 2529 (1963).

(2) R. Srinivasan, *ibid.*, **85**, 4045 (1963).

(3) K. B. Wiberg, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **26**, 143 (1965).

(4) I. Haller and R. Srinivasan, *J. Chem. Phys.*, **41**, 2745 (1964).

(5) K. B. Wiberg and G. M. Lampman, *Tetrahedron Letters*, 2173 (1963).

Table I. Rotational Transitions and Rotational Constants of Bicyclobutane

Transition	Observed ^a	Calculated
0 ₀₀ → 1 ₁₀	26,625.55	26,625.50
1 ₁₀ → 2 ₀₂	26,420.63	26,420.72
2 ₁₁ → 2 ₂₁	23,995.38	23,995.40
3 ₁₂ → 3 ₂₂	22,664.28	22,664.27
4 ₁₃ → 4 ₂₃	20,927.71	20,927.74
2 ₁₂ → 2 ₂₀	26,830.19	26,830.27
	A 17,311.98 Mc/sec	
	B 9,313.51 Mc/sec	
	C 8,393.52 Mc/sec	

^a Observed and calculated frequencies have units of Mc/sec. Estimated uncertainty of observed frequencies is less than ±0.1 Mc/sec.

the normal isotopic species has been studied, the most startling feature of this spectrum being the relatively high intensity of the observed absorption lines. Table I lists some of the observed rotational transitions and the rotational constants which were obtained by the usual rigid rotor analysis.⁶ The goodness of the fit may be seen in Table I by comparing the observed frequencies with those calculated from the derived rotational constants. All the observed lines were *c* type; that is, their intensities are proportional to the square of the component of the molecular dipole moment along the inertial *c* axis. No *a*- or *b*-type transitions were observed, which is in accord with the C_{2v} symmetry of the molecule.⁴ It should be mentioned that the rotational constants reported by Haller and Srinivasan⁴ are in remarkably good agreement with those given in Table I considering the difficulties encountered in analyzing partially resolved vibration-rotation bands.

The dipole moment of the molecule has been determined by studying the shifts, Δ*ν*, of the 0₀₀ → 1₁₀ and 2₁₁ → 2₂₁ (*M* = 2) transitions as a function of electric field, *E* (the quadratic Stark effect). The experimental values of Δ*ν*/*E*², 2.198 × 10⁻⁶ and 1.140 × 10⁻⁶ Mc/sec (v/cm)², respectively, give, by use of the theory of Golden and Wilson,⁷ the value 0.675 ± 0.01 D. for the dipole moment of the molecule (along the C₂ axis). This value agrees well with that obtained by similar, but less accurate, measurements on the 1₁₀ → 2₀₂ transition.

It is difficult to account in a simple way for such a large dipole moment in this saturated hydrocarbon. Since it is unlikely that the entire dipole moment can be produced by the heteropolar C-H bond dipoles (cancellations of methylene and bridgehead C-H dipoles should be effective), electronic charge must be distributed unequally in or near the homopolar C-C bonds. Relatively small differences in hybridization of the bridgehead and ring C-C bonds may produce an appreciable skeletal dipole moment by means of the atomic dipole and overlap moments discussed by Coulson and Rogers.⁸

The rotational constants obtained in this study are not sufficient for a complete structural analysis. If, however, all parameters needed to locate the hydrogen nuclei relative to the carbon skeleton are assumed,

(6) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(7) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

(8) C. A. Coulson and M. T. Rogers, *ibid.*, **35**, 593 (1961).