SYNTHESIS AND X-RAY DIFFRACTION ANALYSIS OF 1-METHYL-5-(METHOXYCARBONYLMETHYL)-4,6-DIOXA-1-AZONIABICYCLO[3.3.0]OCTANE BROMIDE

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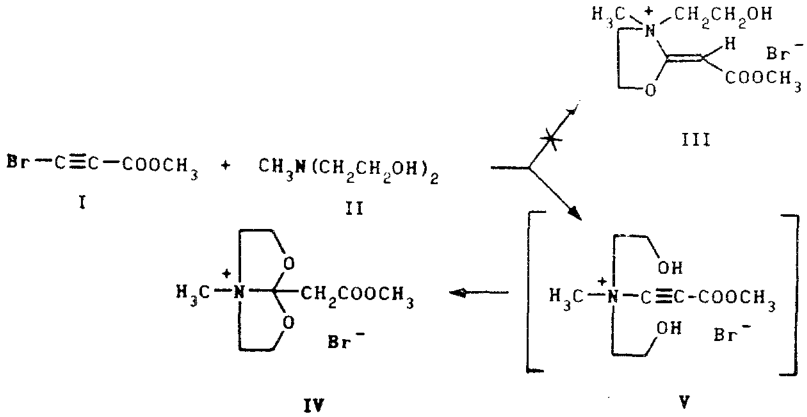
The reaction of methyl bromopropiolate with diethanolmethylamine gave a quaternized 5-(methoxycarbonylmethyl)-4,6-dioxa-1-azabicyclo[3.3.0]octane, the structure and conformation of which were studied by x-ray diffraction analysis.

The reaction of methyl bromopropiolate with β-amino alcohols, as a result of which 2-functionally substituted Δ^2-1,3-oxazolines and 1,3-oxazolidines were synthesized, was studied in [1]. In a continuation of this research we have studied the reaction of methyl bromopropiolate with a polyatomic amino alcohol — diethanolmethylamine.

Considering the results obtained in [1], in carrying out this reaction one might have expected the formation of 1-hydroxyethyl-1-methyl-2-(methoxycarbonylmethylene)-1,3-oxazolidinium bromide (III). However, it was found that the only reaction product is a bicyclic system — 1-methyl-5-(methoxycarbonylmethyl)-4,6-dioxa-1-azoniabicyclo[3.3.0]octane bromide (IV):



The IR spectrum of IV does not contain absorption bands of a double bond and hydroxy groups but does contain an absorption band of an unconjugated carboxy group at 1733 cm^{-1}. The PMR spectral data do not contradict the proposed structure.

5-Unsubstituted 4,6-dioxa-1-azabicyclo[3.3.0]octane was previously obtained by the reaction of dimethylformamide acetal with diethanolamine [2] and was converted to the corresponding salt by quaternization with dimethyl sulfate. However, this salt proved to be hygroscopic, which made it impossible to carry out x-ray diffraction analysis. Bicyclic system IV is a stable crystalline compound. To confirm the structure of the bicyclic system and establish its conformation we therefore carried out x-ray diffraction analysis.

In conformity with Fig. 1, both five-membered rings of IV have an envelope conformation; the $C_{(3)}$ and $C_{(7)}$ atoms deviate from the planes formed by the remaining four atoms by an average of 0.51 Å toward one another. The substituents

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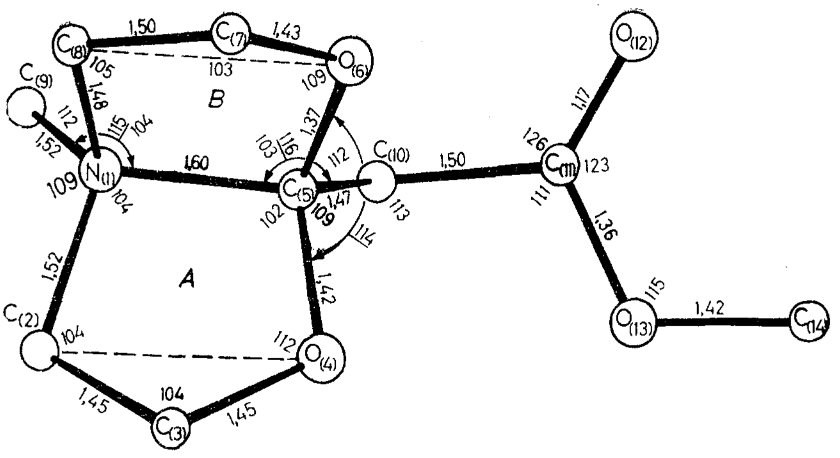

Fig. 1. Geometry of the molecular ion of IV.

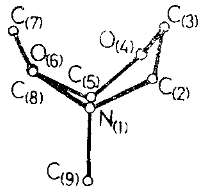

Fig. 2. Conformation of the molecular ion of bicyclic system IV.

TABLE 1. Coordinates of the Nonhydrogen Atoms in the IV Molecule

Atom	x	y	z	Atom	x	y	z
BP	0,1155(1)	0,17754(9)	0,10503(0)	$C_{(8)}$	0,206(1)	−0,105(1)	0,153(2)
$N_{(1)}$	0,1304(9)	−0,1326(8)	0,006(1)	$C_{(9)}$	0,194(1)	−0,113(1)	−0,161(2)
$C_{(2)}$	0,009(1)	−0,0794(9)	0,005(2)	$C_{(10)}$	0,110(1)	−0,3186(9)	−0,105(2)
$C_{(3)}$	−0,064(1)	−0,1402(9)	0,117(3)	$C_{(11)}$	0,103(1)	−0,4282(9)	−0,057(2)
$O_{(4)}$	−0,0252(6)	−0,2439(5)	0,086(2)	$O_{(12)}$	0,1839(9)	−0,4817(7)	−0,027(2)
$C_{(5)}$	0,097(1)	−0,2493(9)	0,041(2)	$O_{(13)}$	−0,0119(8)	−0,4631(6)	−0,063(1)
$O_{(6)}$	0,1714(9)	−0,2753(7)	0,172(1)	$C_{(14)}$	−0,027(1)	−0,5677(9)	−0,031(2)
$C_{(7)}$	0,190(1)	−0,189(1)	0,279(2)				

attached to the $N_{(1)}$ and $C_{(5)}$ atoms are cis-oriented relative to one another, and the five-membered rings correspondingly are cis-fused.

Thus bicyclic system IV has a slightly distorted boat conformation (Fig. 2). The dihedral angle between planes A and B (see Fig. 1) is 118°. It is interesting that the bicyclic system is unsymmetrical relative to the plane passing through the $N_{(1)}$, $C_{(5)}$, $C_{(10)}$, and $C_{(11)}$ atoms. This plane forms angles of 110° and 131° with planes A and B.

The $N_{(1)}$—$C_{(5)}$ bond (1.60 Å) is anomalously elongated as compared with the standard value for the C_{sp^3}—N^+ bond (1.485 Å) [3], which is evidently associated with the peculiar electron state of the $C_{(5)}$ atom.

The intramolecular contacts of the $O_{(4)}\cdots O_{(13)}$ (3.11 Å) and $O_{(6)}\cdots O_{(12)}$ (3.14 Å) atoms are no smaller than the sums of their van der Waals radii.

The formation of bicyclic system IV can be conceived of as being the result of a double cyclization with the participation of the hydroxy groups in intermediate V, while the reaction of methyl bromopropiolate with diethanolmethylamine can be thought of as a new method for the synthesis of a quaternized 4,6-dioxa-1-azabicyclo[3.3.0]octane.

EXPERIMENTAL

The IR spectra of suspensions in Nujol were recorded with a Perkin—Elmer 580-B spectrometer. The PMR spectra of solutions in d_6-DMSO were recorded with a Bruker WH-90 spectrometer with tetramethylsilane (TMS) as the internal standard.

The crystals obtained from IV had the composition $C_9H_{16}BrNO_4$, were rhombic, and had the following parameters: a = 11.158(2), b = 13.166(2), c = 7.867(1) Å, V = 1155.8(5) Å^3, d_{calc} = 1.62 g/cm^3, Z = 4, space group Pna2_1. The cell parameters and the intensities of 1053 nonzero reflections were measured with a Syntex R2_1 automatic diffractometer (Mo K_α emission, $\theta/2\theta$ scanning, θ_{max} = 30°). The structure was decoded by the Paterson method and was refined by the method of least squares within the complete-matrix approximation anisotropically for the nonhydrogen atoms up to R = 0.067. The hydrogen atoms were obtained from differential synthesis and were not included in the refinement. The accuracies in the determination of the bond lengths and bond angles were 0.015 Å and 1.5°, respectively. The geometry of the molecular ion is presented in Fig. 1, while the coordinates of the atoms are given in Table 1.

The results of elementary analysis for C, H, and N for IV were in agreement with the calculated values.

1-Methyl-5-(methoxycarbonylmethyl)-4,6-dioxa-1-azoniabicyclo[3.3.0]octaneBromide(IV,$C_9H_{16}BrNO_4$). A0.73-g (6.1 mmole) sample of II in 10 ml of THF was added with stirring at 0°C to 1.0 g (6.1 mmole) of I in 20 ml of absolute THF, after which the reaction mixture was stirred for 24 h at 20°C. The resulting precipitate was removed by filtration, dissolved in ethanol, and precipitated with ether. The precipitate was removed by filtration and dried to give 1.34 g (78%) of a colorless crystalline product. Single crystals of IV were grown from a solution in ethanol and had mp 128-130°C. IR spectrum: 1733 cm^{-1} (C=O). PMR spectrum: 3.33 (3H, s, $\overset{+}{N}CH_3$), 3.42 (2H, s, CH_2), 3.60 (3H, s, OCH_3), 3.7-4.1 (4H, m, NCH_2), 4.30 ppm (4H, m, OCH_2).

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