SYNTHESIS OF 3,6,7-TRIAZABICYCLO[3.3.0]OCTENES BY 1,3-CYCLOADDITION WITH N-ARYLPYRROLIDIN-2-ONES

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The 1,3-dipolar cycloaddition of diazomethane to 1-(4-R-phenyl)-5H-pyrrolidin-2-one was investigated. Some properties of the triazabicyclo[3.3.0]octenes, including the results of an x-ray diffraction analysis, were studied.

In a continuation of our study of 1,3-dipolar cycloaddition in the pyrrolidinone series [1] we studied the reaction of 1-(4-aryl)-5H-pyrrolidin-2-ones Ia, b with diazomethane. The cycloaddition proceeds regioselectively to give adducts IIa, b, which correspond to the "normal" relative orientation of the enone and the dipole in which the methylene groups always react with the most electron-deficient β-carbon atom of the dipolarophile [2, 3].

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\begin{align*}
\text{Ia, b} & \rightarrow \text{IIa, b} & \rightarrow \text{III} & \rightarrow \text{IV, V} \\
\end{align*}
\]

The regiospecificity corresponds to concerted 1,3-dipolar cycloaddition [4].

The reaction is distinguished by cis stereospecificity. The 5-H methylidyne proton shows up in the PMR spectrum of adduct IIa in the form of a multiplet at 5.7 ppm. The second 1-H methylidyne proton also shows up in the form of a multiplet, but it is located at stronger field (2.94 ppm, J_{15} = 9.5 Hz) with a cis orientation of the 5-H and 1-H protons.

It was established by double resonance that the 1-H proton couples with the two 2-H methylene protons (J_{12} = 9.5 Hz, J_{12} = 4.0 Hz), as well as with the 8-H proton (J_{18} = 8.5 Hz, J_{18} = 5.0 Hz). All of the methylene protons are chemically nonequivalent and resonate in different regions [2-H$_1$ at 4.12 ppm, 2-H$_2$ at 3.60 ppm (2J = 10.5 Hz), 8-H$_3$ at 4.92 ppm, and 8-H$_4$ at 4.74 ppm (2J = 18.5 Hz)]; this is due to the asymmetry of the molecule.

The stereochecmical characteristics of the bicyclic system are controlled chiefly by two factors: repulsion of the electron shells of the covalently nonbonded atoms and the effects of n–π conjugation. Thus in the crystalline IIa molecule (Fig. 1) the pyrazoline ring has an "envelope" conformation with a deviation of 14° with respect to the C(8)–C(11) axis, and the
pyrrolidone ring deviates 9.1° with respect to the C(8)-C(10) axis. The angle between the flaps of the envelopes with a base along the C(8)-C(9) bond is 58.7°. The benzene ring is situated in the plane of the base of the "envelope" of the pyrrolidone ring — torsion angle C(7)N(2)C(4)C(5) is equal to 179.4°. The nitro group, in turn, deviates to a small degree from the plane of the benzene ring — torsion angle C(2)C(1)N(1)O(2) is equal to 178.3°. The principal bond distances and some of the bond angles of structure IIa are presented in Tables 1 and 2. The C—H distances range from 0.93 to 1.02 Å. There are no intramolecular interactions, and the intermolecular interactions are limited to van der Waals interactions.

We carried out a number of transformations with the pyrazolines obtained. It is known [5] that Δ1-pyrazolines are unstable: Under the influence of acids and bases they are readily converted to Δ2-pyrazolines. This possibility was checked in the case of IIa. Triethanolamine was used as the base, and 4-oxo-3-(4-nitrophenyl)-3,6,7-triazabicyclo[3.3.0]oct-5-ene (III)

![Fig. 1. X-ray diffraction pattern of crystalline IIa.](image)