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MECHANISM OF FORMATION OF 1,2-DIHYDRO-4H-3,1,-BENZOXAZINE FROM o-AMINOPHENYLDIPHENYLCARBINOL

E. V. Gromachevskaya, I. S. Arustamova,
R. B. Valeev, B. A. Bazhenov,
A. G. Sakhabutdinov, and V. G. Kul'nevich

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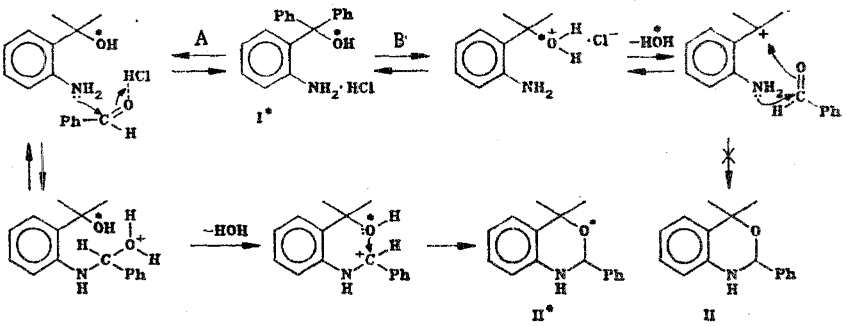
In the reaction of o-aminophenyldiphenylcarbinol with benzaldehyde in the presence of acid the 3,1-oxazine ring can form by two routes: by the electrophilic addition of the carbocation (that forms by dehydration of the alcohol) to the benzaldehyde oxygen (route B), or by initial nucleophilic addition of nitrogen to the benzaldehyde carbonyl oxygen, followed by detachment of a water molecule containing the carbonyl oxygen and heterocyclization to 1,2-dihydro-4H-3,1-benzoxazine (route A).



To determine the route by which the 3,1-oxazine ring is formed we studied the distribution of an isotopic tracer in two benzoxazines. The latter were obtained by the reaction of aminoalcohol hydrochloride I*, containing $O_{(18)}$ in the hydroxyl, with benzaldehyde in boiling absolute benzene (benzoxazine II*), and by the reaction of benzaldehyde enriched in $O_{(18)}$ with untagged aminoalcohol hydrochloride.

The ^{17}O NMR spectrum of II* shows the appropriate signal whereas in the second case this signal is absent. Mass spectrometric data showed that the $O_{(18)}$ of aminoalcohol hydrochloride I* goes entirely into compound II*, whereas in the other variant of the reaction no $O_{(18)}$ of benzaldehyde was observed in the benzoxazine.

According to ^{17}O NMR and mass spectrometry, alcohol oxygen takes part in heterocycle formation under these conditions, but benzaldehyde does not. In this reaction acid catalysis apparently takes place in the dissociation of the ammonium salt, which causes the introduction of the aldehyde. The liberated amino group attacks the carbon of the oxo group; this causes the equilibrium to shift and carries out route A.

Krasnodar Polytechnic Institute, Krasnodar 350700. Institute of Petrochemical and Coal Chemical Synthesis, A. A. Zhdanov State University, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1687-1688, December, 1985. Original article submitted January 7, 1985.