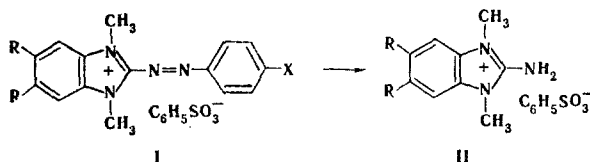


UNUSUAL CLEAVAGE OF HETEROCYCLIC AZO COMPOUNDS UNDER THE INFLUENCE
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UDC 547.785.5:542.924

The ability of the N=N bond of aromatic azo compounds to undergo cleavage in the absence of a reducing agent has not been previously observed. We have found that brief heating of azobenzimidazolium salts I with excess primary or secondary amines leads to cleavage of the azo group to give 2-aminobenzimidazolium salts II in 60-90% yields. Resinification of the reaction mixtures is simultaneously observed.

I, II R=H, CH₃; X=H, OCH₃, OC₂H₅, N(CH₃)₂

A mixture of 10 mmole of azo compound I and a fourfold to sixfold excess of amine was heated at 70-80°C until the violet color of the mixture vanished. It was then triturated with two to three portions of dry ether, and the residue was crystallized from alcohol-ether. The identical character of salts II (and the 1,3-dimethyl-2-iminobenzimidazolines obtained from them) and authentic samples was established by UV and IR spectroscopy and from the absence of melting-point depressions of mixtures of the compounds. The ease of cleavage depends on the basicity of the amine: The reaction proceeds readily with piperidine and benzylamine but with greater difficulty with morpholine; virtually no reaction is observed with aromatic amines. Monitoring of the course of the reaction by means of thin-layer chromatography makes it possible to assume that cleavage of the azo group precedes replacement of the X group in I by an amino group. The mesomeric cation of the resulting azo compound is evidently attacked by the amine at the β-N atom with subsequent cleavage of the N-N bond.