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MEISENHEIMER-TYPE COMPOUNDS FROM AZA-ACTIVATED SUBSTRATES

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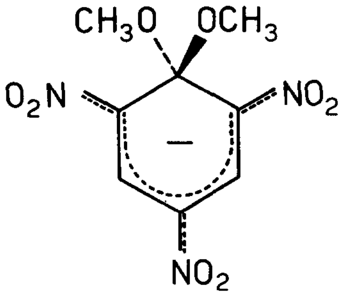
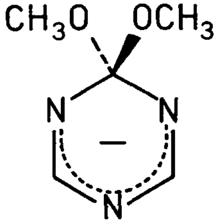
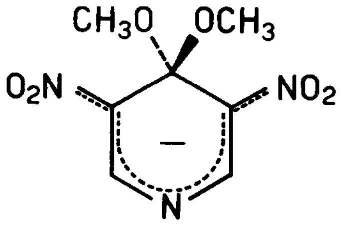
The detection of σ-complexes of type I as reaction intermediates in the nucleophilic aromatic substitution of nitro-activated benzenoid substrates is considered an important piece of evidence in favor of the two-stage mechanism of the over-all reaction. It has been noted (1) that similar information on reaction intermediates of type II, as possibly involved in N-heteroaromatic substitution, is needed.

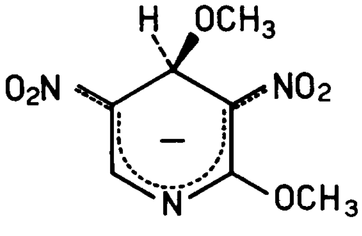

I


II

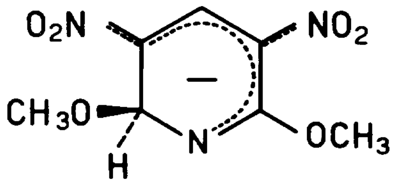
Such aza-activated substrates as sym-triazine derivatives are very reactive and methoxytriazine has been found to undergo rapid methoxyl group exchange with methoxide ion in methanol solution (2). While the detection of complex II proved to be difficult under standard conditions and is still the object of our current studies, structures involving gradual transition from trinitrobenzene- to triazine-type activation have been examined as starting substrates. Such structures include the isomeric pairs 2- and 4-methoxy-3,5-dinitropyridines and 2- and 4-methoxy-5-nitropyrimidines. Out of these the most stable complex was obtained in the case of 4-methoxy-3,5-dinitropyridine. Accordingly, complex III was isolated upon the action of methoxide ion with the pyridine substrate in methanol solution, and its structure was proved by elemental analysis and visible, i.r., and n.m.r. spectral evidence. In particular, in DMSO-$\underline{d}_6$ solution only two singlets were found, their τ values being 1.22 and 7.08, with relative intensities 1 and 3, respectively.



III



IV



V

For the other substrates only spectral evidence in solution was obtained. In DMSO-$\underline{d}_6$ solution a 1 : 1 adduct is formed from 2-methoxy-3,5-dinitropyridine whose n.m.r. spectrum consists of two doublets ($J \simeq 1$ Hz) in the low-field region (τ, 1.41 and 4.01) and two singlets in the higher field region (τ, 6.23 and 6.74). These data and the relative intensities, i.e., 1, 1, 3 and 3, respectively, are consistent with a Meisenheimer-type complex of type IV or V and involve the attack of methoxide ion to a hydrogen-bearing, rather than to a methoxyl-bearing, ring position. Thus, the general point of attack (CH-position) does not differ from the case of 3,5-dinitropyridine, where no methoxyl group is present (3). Although complexes involving geminal hydrogen, such as IV and V, are less stable than complexes with a ketal functional group, such as III, and eventually rearrange to the more stable ones (4), in our case any further reaction was obscured by a demethylation reaction promoted by the methoxide ion itself.

The two isomeric methoxynitropyrimidines also undergo attack by methoxide ion at a CH-position. The n.m.r. spectrum of the DMSO solution shows two doublets in the low-field region, whose chemical shifts have τ values equal to 1.65 and 4.16 (2-methoxy isomer) and to 1.57 and 4.24 (4-methoxy isomer) and are thus analogous to the complex obtained from 2-methoxy-3,5-dinitropyridine.

The electronic spectrum in methanol solution consists of an absorption band of similar intensity in all complexes (ε in the order of 10^4) at λ_{max} values of 455 (methoxydinitropyridines), 394 (2-methoxy-5-nitropyrimidine), and 352 mμ (4-methoxy-6-nitropyrimidines). The spectrophotometric determination of the equilibrium constants in the same solvent shows that whenever attack of the methoxide ion on a CH-position occurs the resulting complex is less stable than complex III by a factor of 10^3. This relationship is completely analogous to that found among the complexes obtained from trinitrobenzene derivatives (4).

A full account of this work will be published elsewhere.

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