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A MEISENHEIMER COMPLEX OF 3,5,6,8-TETRANITROACENAPHTHENE

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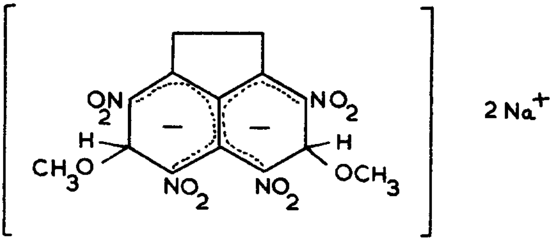
Meisenheimer complexes are formed by nucleophilic attack at electron - deficient sites in aromatic molecules and are of importance in regard to their role as intermediates in nucleophilic aromatic substitution reactions (1). The reactions of nucleophiles with polynitroaromatic compounds have been extensively studied and the results reviewed in detail (2,3). Although many 1-substituted polynitrobenzenoid compounds react with nucleophiles to give the expected Meisenheimer complexes α - trinitrotoluene is an exception and the reactions of this compound with base are more complicated due to the possibility of proton abstraction from the methyl group (4). 3,5,6,8-tetranitroacenaphthene bears a structural resemblance to α - trinitrotoluene in that it contains nitro substituents symmetrically disposed ortho and para to an aliphatic group. However, unlike α - trinitrotoluene, 3,5,6,8-tetranitroacenaphthene yields an isolatable Meisenheimer complex on reaction with methoxide ion.

Treatment of 3,5,6,8-tetranitroacenaphthene in dry dichloromethane, under a blanket of nitrogen, with sodium methoxide resulted in a bright red solution. Cooling to 0° caused the precipitation of a brown solid which was filtered off under nitrogen and identified as the Meisenheimer complex, I, shown below. (Found: C, 37.5; H, 2.4; N, 13.1; Na, 10.6. $C_{14}H_{12}N_4O_{10}Na_2$ requires C, 38.0;



(I)

H, 2.7; N, 12.7; Na, 10.4%); n.m.r. spectrum in $(CD_3)_2SO$: singlet (2H) τ3.80, singlet (4H) τ5.82, and a singlet (6H) τ6.79.

The upfield shift of the aromatic resonance representing two protons from τ0.80 in 3,5,6,8-tetranitroacenaphthene to τ3.80 in the complex indicates that the ring protons are bonded to the carbon atoms at which attack of the anion takes place (2). The resonance at τ5.82 corresponds to four protons and arises from the methylene bridge protons in the complex. The integrated intensity of this resonance and the small shift from the resonance position (τ5.83) in 3,5,6,8-tetranitroacenaphthene provides evidence that the attack of the methoxy ion occurs by substitution in the ring system and not by proton abstraction from the methylene bridge. The sharp resonance at τ6.79 representing six protons indicates that the methoxyl groups are equivalent and are in an environment which corresponds more closely to an aliphatic ether than to an aromatic ether.

An interesting feature of the Meisenheimer complex, I, is that it is stabilised by two nitro groups per negative charge whereas normally for complexes to be isolatable three nitro groups per negative charge are required. This is especially significant since steric interaction between the nitro groups at the 5- and 6- positions forces them out of the plane of the ring and diminishes the Lewis acid effect of these groups.

Structure I will be of high energy and the expected instability of complexes with this type of structure is borne out by the fact that the complex isolated from the reaction of ethoxide ion with 3,5,6,8-tetranitroacenaphthene detonated on touch.

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