An Adduct Intermediate in the Formation of 3,4-Dimethyl-4-nitrocyclohexa-2,5-dien-1-one

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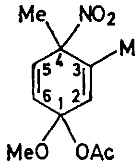
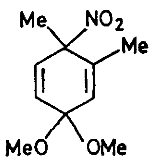
Summary 3,4-Dimethyl-1-methoxy-4-nitro-1,4-dihydrophenyl acetate and the dimethyl acetal of 3,4-dimethyl-4-nitrocyclohexa-2,5-dien-1-one are obtained from the reaction of 3,4-dimethylanisole with nitric acid in acetic anhydride.

There is current interest in non-conventional paths in electrophilic substitution reactions.[1] Reaction of 4-X-*o*-xylene and of 5-X-hemimellitene (X = Br, OAc, OMe) with nitric acid in acetic anhydride gives the dimethyl- and trimethyl-4-nitrocyclohexa-2,5-dien-1-ones, respectively, in addition to the normal substitution products.[2] We report the detection of the adduct (**1**), an intermediate in the formation of the dimethylcyclohexadienone (*cf.* ref. 3).

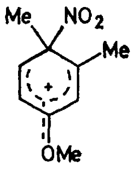
3,4-Dimethylanisole in acetic anhydride was treated with an equivalent amount of nitric acid in acetic anhydride for 44 h at −78°. The reaction was quenched in liquid ammonia and the product chromatographed at −50°. The adducts (**1**) and (**2**) could not be separated, but since they were present in unequal amounts (1 : 3), the n.m.r. peaks [δ(CDCl$_3$)] were readily assigned: (**1**) 1·64 (3H, s, 4-Me), 1·73 [3H, d, *J* (2-H, 3-Me) 1·4 Hz, 3-Me], 2·06 (3H, s, OAc), 3·35 (3H, s, OMe), 5·90 (1H, m, 2-H), 6·12 (2H, m, 5- and 6-H); (**2**) 1·76 (3H, s, 4-Me), 1·86 [3H, d, *J* (2-H, 3-Me) 1·4 Hz, 3-Me], 3·26 (6H, s, OMe), 5·84 (1H, m, 2-H), 6·08 (2H, m, 5- and 6-H). The mixture of (**1**) and (**2**) was labile and at ambient temperature rapidly decomposed to 3,4-dimethyl-4-nitrocyclohexa-2,5-dien-1-one.



(1)



(2)



(3)

The diene (**1**) is the first acetyl nitrate adduct to be obtained which contains a potentially anionic leaving group at the site of addition of the acetate. Formation of the dienone from (**1**) presumably involves the release of methanol and acetic acid. We suggest that (**2**) is formed when the phenonium ion (**3**), obtained on ionization of (**1**) scavenges the methanol. Attack by a nucleophile at the methoxy-methyl group of (**3**) would lead to the dienone, a slower process than the reaction with methanol to form (**2**).

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