1,4-Migration of a Nitro-group in the Rearomatization of 4,5-Dimethyl-2,4-dinitrocyclohexa-2,5-dienyl Acetate

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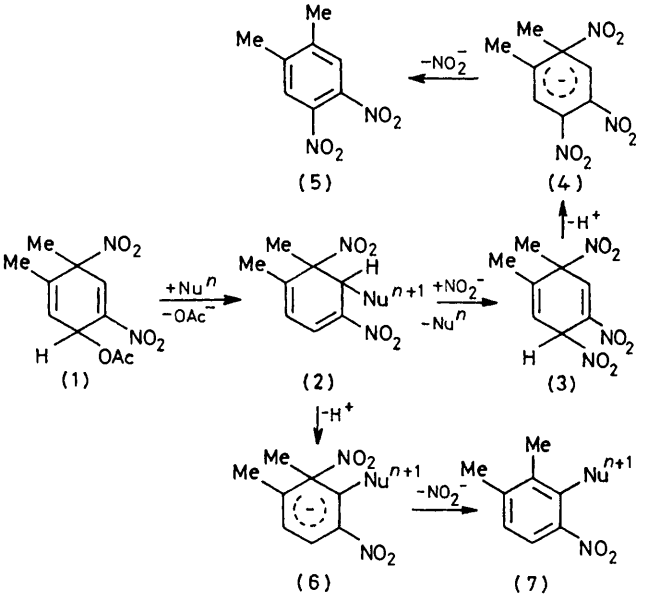
Summary Nitration of 1,2-dimethyl-4-nitrobenzene in a mixture of acetic and trifluoroacetic anhydrides gives the adduct 4,5-dimethyl-2,4-dinitrocyclohexa-2,5-dienyl acetate which reacts with potassium nitrite and other nucleophiles to give 1,2-dimethyl-4,5-dinitrobenzene.

THE formation of nitronium acetate adducts when arenes and appropriate derivatives are nitrated in acetic anhydride is well established.[1-3] Such adducts readily rearomatize in solution. In those cases in which the mechanisms of rearomatization have been established there are two competitive initial steps, both involving a cyclohexadienyl cation intermediate.[4-6] Thus, for 3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate, unimolecular ionization of the nitro group as nitrite (*E*1) produces a 1-acetoxy-3,4-dimethylcyclohexadienyl cation[4] whereas acid-catalysed loss of the acetate group ($A_{AL}1$) produces a 3,4-dimethyl-4-nitrocyclohexadienyl cation.[5] The 1,2-migration of the nitro group in the latter cation, followed by deprotonation, gives 1,2-dimethyl-3-nitrobenzene.[5] A 1,3-migration of a nitro group has also been observed although the mechanism has not been established.[7] We report that 4,5-dimethyl-2,4-dinitrocyclohexa-2,5-dienyl acetate (**1**) obtained in *ca.* 50% yield, together with the three 1,2-dimethyldinitrobenzenes, by nitration of 1,2-dimethyl-4-nitrobenzene in a mixture of trifluoroacetic anhydride and acetic anhydride, exhibits an apparent 1,4-nitro migration on rearomatization to 1,2-dimethyl-4,5-dinitrobenzene (**5**).

Reaction of (**1**) with a variety of nucleophiles, including pyridine, 2,6-lutidine, and nitrite, hydroxide, acetate, fluoride, bromide, and iodide anions gave yields of (**5**) in excess of 90% in the cited cases (anions were used in the form of potassium salts in the presence of 18-crown-6 in acetonitrile solution). Interruption of an incomplete reaction when bromide, iodide, or thiocyanate were used as nucleophiles revealed that an isomer of (**1**), 5,6-dimethyl-2,6-dinitrocyclohexa-2,4-dienyl acetate (**2**, Nu^{n+1} = OAc) was formed as an intermediate. We therefore propose that the apparent 1,4-migration of the nitro group occurs *via* consecutive S_N2' substitutions as indicated in the Scheme (Nu^n is a general nucleophile). For each substitution the normally unreactive vinyl carbon is activated by conjugation of the double bond with the non-migrating nitro group. The proton α to the nitro group in (**3**) is acidic and should be readily removed to form the anion (**4**)



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which in turn should rapidly lose the nitro group as a nitrite anion (which is thereby regenerated) to give (**5**).

Support for the proposed mechanism is provided by the observations that reaction of (**1**) with cyanide ion gives 2,3-dimethyl-6-nitrobenzonitrile whereas reaction of (**2**; Nu^{n+1} = OAc), separately isolated, with cyanide ion gives 4,5-dimethyl-2-nitrobenzonitrile. Reaction of (**1**) with cyanide ion would give initially (**2**; Nu^{n+1} = CN), in which the proton α to the nitrile group is acidic and therefore readily lost to form the anion (**6**; Nu^{n+1} = CN) which in turn would lose the nitro group as nitrite to form (**7**; Nu^{n+1} = CN). Furthermore, cyanide is a poor leaving group and this is a second factor which makes the process (**2**) → (**6**) supersede the normal (**2**) → (**3**) path. Reaction of (**2**; Nu^{n+1} = OAc) with cyanide ion would lead to the cyano analogue of (**3**) and, through the analogue of (**4**), to the observed 4,5-dimethyl-2-nitrobenzonitrile. It is to be noted that, unlike cyanide, nitrite does not apparently compete as a nucleophile in the first step of the reaction with (**1**), although it is a very effective nucleophile towards (**2**). The nitrite anion is subject to greater steric hindrance than the linear cyanide and this is the most likely reason for its apparent failure to attack at the severely hindered 3-position of (**1**). The rate of rearomatization of (**1**) in the presence of pyridine is *ca.* 5 times as rapid as in the presence of 2,6-lutidine, a result also indicative of steric hindrance in (**1**).

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