

3-Methyl-6-methylene-3-nitrocyclohexa-1,4-diene and (4-Methyl-4-nitrocyclohexa-2,5-dienylidene)acetonitrile, Intermediates in the Rearomatizations of 1,4-Dimethyl-4-nitrocyclohexa-2,5-dienyl Acetate and (1-Acetoxy-4-methyl-4-nitrocyclohexa-2,5-dienyl)acetonitrile

Alfred Fischer* and Alok Goel

Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

4-Methyl-4-nitro-1-trimethylsilylmethyl- (**1e**) and 4-methyl-4-nitro-1-cyanomethyl-cyclohexa-2,5-dienol (**1c**) in acidified acetic anhydride give 3-methyl-6-methylene-3-nitrocyclohexa-1,4-diene (**3a**) and (4-methyl-4-nitrocyclohexa-2,5-dienylidene)acetonitrile (**3c**), respectively.

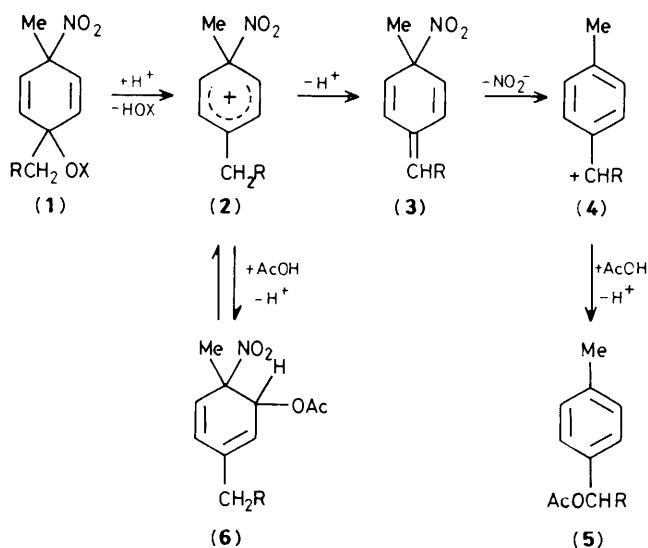
Nitration of *p*-xylene and polymethylbenzenes containing 1,4-methyl groups commonly gives side-chain derivatives.^{1,2} The same arenes, when nitrated in acetic anhydride, give 1,4-nitronium acetate adducts formed by addition of nitronium ion *ipso* to one methyl group followed by the addition of acetate to the *para* position.³ Such adducts on treatment with acids in moderately basic solvents give the same or similar side-chain derivatives as those obtained directly by nitration and their formation has been explained in terms of the sequence shown in Scheme 1, (1)—(5).^{1,3b-c,4,5} None of the intermediates between the *p*-xylene and the side-chain derivative have been observed directly. Robinson⁶ suggested that a compound isolated from the nitration of 1,4-dimethylnaphthalene⁷ might be a methylenecyclohexadiene but this is unlikely.^{1,3b} In this communication we report results for three systems, including the parent 1,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate (**1b**),^{3a,d,4,5} in which we have observed the formation of a methylenecyclohexadiene intermediate in the conversion of a diene adduct to a side-chain derivative.

Reaction of dienol (**1e**) with chlorosulphonic acid (0.05%—0.2%) in acetic anhydride at -78°C gave (**3a**) [^1H n.m.r. δ_{H} (-70°C) 1.79 (3H, s, Me), 5.43 (2H, br. s, C=CH₂), 6.17 (2H, d, *J* 9 Hz, 2-, 6-H or 3-, 5-H), 6.64 (2H, d, *J* 9 Hz, 3-, 5-H or 2-, 6-H); ^{13}C n.m.r. δ_{C} 27.4 (Me), 87.3 (C-3), 121.7 (C=CH₂),

127.7 and 130.8 (C-1 and C-5, and C-2 and C-4), 135.9 (C-6)]. Triene (**3a**) started to disappear when the temperature of the reaction mixture was raised to -30°C and, at -20°C , disappeared completely over 10 min to form a mixture of benzylic derivatives in which *p*-methylbenzyl acetate (**5a**) and *p*-tolylnitromethane predominated.

Reactions of the dienol (**1c**)⁸ and acetate (**1d**) with chlorosulphonic acid in acetic anhydride were identical and the substrates could be used interchangeably. Reaction of (**1d**) with 1% acid at -5°C gave (**5c**) (100%). When the reaction was repeated with (**1c**) using 4% acid, preparing the reaction solution at -78°C , and observing the ^1H and ^{13}C n.m.r. spectra at -50°C , a mixture of (**3c**) [δ_{H} 1.80 (3H, s, Me), 5.60 (1H, br. s, C=CHCN), 6.56 (2H, d, *J* 9 Hz, 2-, 6-H), 6.84 (2H, d, *J* 9 Hz, 3-, 5-H); δ_{C} 26.5 (Me), 86.9 (C-4), 99.9 (C=CHCN), 117.6 (CN), 125.9, 128.7, 133.7, 134.8 (C-2, C-3, C-5, C-6), 145.6 (C=CHCN)] (85%) and (**6c**) (15%) was obtained. After 30 min (**3c**) (78%), (**6c**) (15%), and (**5c**) (7%) were present. When the reaction was carried out with 2% acid at -40°C a mixture of (**6c**) (44%), (**3c**) (22%), and (**5c**) (34%) was obtained when (**1c**) had reacted completely. A higher concentration of acid and a lower temperature enhances formation of the triene before it reacts further.

Identification of (**3a**) allowed us to recognize its presence in



Scheme 1. a; R = H, X = H
 b; R = H, X = Ac
 c; R = CN, X = H
 d; R = CN, X = Ac
 e; R = SiMe₃, X = H

minor amounts as an intermediate in the reaction of (1b). When (1b) was reacted with 2% chlorosulphonic acid in acetic anhydride at -78°C triene (3a) (~35%) and acetate (5a) (~35%) were formed. With 1% acid at -40°C the substrate disappeared over 30 min and (3a) (~30%) was then present as well as the benzylic derivatives. Formation of (3c) from (1c) occurs with less competition from the subsequent reactions of (3c) than in the case of (3a). The cyano group increases the acidity of the α -protons in (2c) and thus increases the rate of formation of (3c). It also destabilizes the carbocation (4c) and thus inhibits the ionization of nitrite from (3c). Generation of the silylmethyl cation (2e) leads to the formation of a major

amount of (3a) since the bond to silicon is readily broken and the loss of the incipient silyl cation is much more facile than the deprotonation of (2a). Loss of the elements of trimethylsilanol is a general method for the introduction of an alkene double bond.⁹

Diene (6d) [(6c)] is favoured in the quasi-equilibrium between (1d) and (6d). Other electron-withdrawing α -substituents have been shown to facilitate the isomerization of (1) to (6).¹⁰

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