Sigmatropic Rearrangement of Adducts from *ipso*-Nitration: Formation of Adducts containing a Secondary Nitro-group

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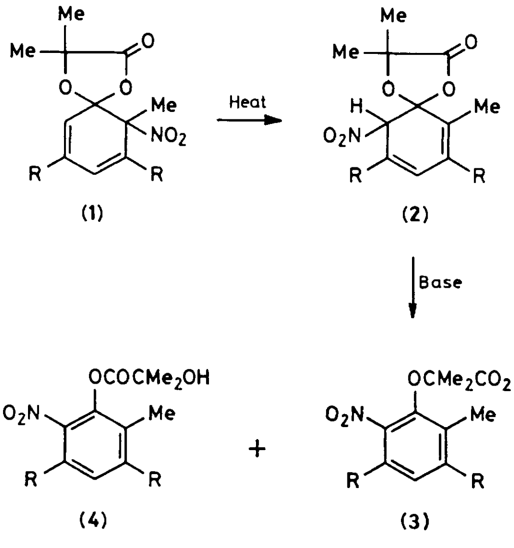
The regiospecific and stereospecific rearrangement of 3-chloro-6-methyl-6-nitrocyclohexa-2,4-dienyl acetate (and related adducts) to 5-chloro-2-methyl-6-nitrocyclohexa-2,4-dienyl acetate (and analogues) and of 2-cyano-4,5-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate (and its 3,4-dimethyl isomer) to 2-cyano-4,5-dimethyl-6-nitrocyclohexa-2,4-dienyl acetate (and its 3,4-dimethyl isomer) appear to involve [1,5] and [1,3] sigmatropic nitro-shifts, respectively.

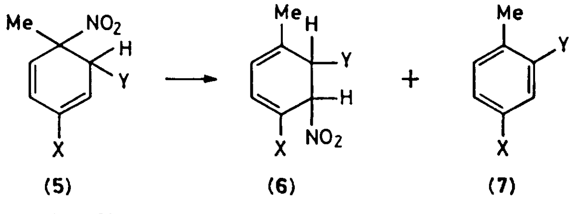
Nitration of appropriately substituted aromatic compounds, *e.g.* *p*-xylene, in acetic anhydride gives nitronium acetate adducts.[1–3] All such reported adducts have the nitro-group *ipso* to a substituent, *e.g.* a methyl group, reflecting the fact that the deprotonation of the nitrocyclohexadienyl cation, formed by addition of nitronium ion to an unsubstituted position of the aromatic substrate, is preferred over addition of a nucleophile to form the adduct. In this communication we report the facile rearrangement of a number of nitronium acetate adducts to isomers in which the nitro-group is attached to a carbon bearing a hydrogen, producing a novel class of compounds.



a; R = H
b; R = Me

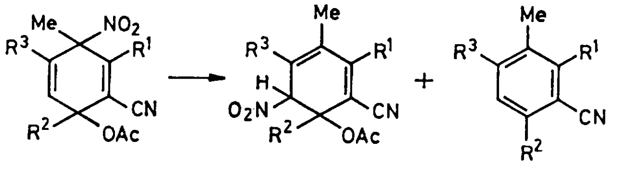
Scheme 1

We have observed nitro-shifts in compounds (**1**), (**5**), (**6a, b**), and (**8**). When a solution of diene (**1a**) was heated at 50 °C (**2a**) was obtained in greater than 95% yield (Scheme 1). The isomerization was regiospecific: the 4-nitro-isomer was not obtained. The reaction occurred at the same rate in carbon tetrachloride, benzene, acetonitrile, and tetrahydrofuran. At ambient temperature $t_{\frac{1}{2}}$ = 7 days and at 50 °C $t_{\frac{1}{2}}$ = 5 h. The reaction was unaffected by light. The isomerization was stereospecific: (*Z*)-(**1a**) gave one of (*Z*)- or (*E*)-(**2a**) [presumably (*Z*)] and (*E*)-(**1a**) gave the other of (*E*)- or (*Z*)-(**2a**) [presumably (*E*)]. Treatment of each product with aqueous sodium hydrogen carbonate solution gave (**3a**) (80%) and (**4a**) (20%). The isomerization was not suppressed in the presence of *p*-cresol as would be expected if the mechanism involved a radical dissociation–recombination process with free NO_2 formed. 2-Methyl-2-(*o*-tolyloxy)propanoyl nitrate is a possible intermediate in a dissociation–recombination pathway from (**1a**) to (**2a**). We generated this compound by reaction of the propanoyl chloride with silver nitrate in acetonitrile but no (**2a**) was obtained. Only (**1a**), (**3a**), and the 4-nitro-isomer of (**3a**) were formed. We therefore propose that (**1**) isomerizes to (**2**) by a [1,5] sigmatropic nitro-shift. Previous reports of sigmatropic nitro-shifts are rare and all involve shifts from a



a; X = Cl, Y = OAc
b; X = Br, Y = OAc
c; X = F, Y = OAc
d; X = OMe, Y = OAc
e; X = Bu^t, Y = OAc
f; X = Cl, Y = Cl
g; X = Cl, Y = OMe

Scheme 2



(8) **(9)**

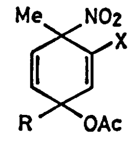
a; $R^1 = R^2 = H, R^3 = Me$
b; $R^1 = Me, R^2 = R^3 = H$
c; $R^1 = R^3 = H, R^2 = Me$

Scheme 3

nitrogen centre in hetrocycles such as triazoles[4] and pyrazoles[5] ([1,5] shifts) or in *N*-nitroenamines[6] ([1,3] shift). Orbital symmetry rules require a thermal [1,5] shift to involve retention of configuration, and a [1,3] shift inversion of configuration, at the nitro-group.

The isomerization of the dienes (**5f**) and (**5g**) to give (**6f**) and (**6g**), respectively, were similarly regiospecific and stereospecific and presumably follow the same mechanistic pathway as that of (**1**) (Scheme 2). Some rearomatization by elimination of nitrous acid to form (**7**) also occurred. However, the isomerizations of the dienes (**5a**—**e**) were regiospecific but not stereospecific, both diastereoisomers of the products (**6a**—**e**) being formed. Isomerization of (**5a**) was investigated in detail and was shown to become stereospecific in the presence of *p*-cresol and other radical trapping agents. The nitro-group migration was reversible. The rearranged compound (**6**) gave a mixture of the original adduct (**5**) and (**6**). These results indicate that dienes (**5a**—**e**) rearrange (reversibly) by the same [1,5] sigmatropic nitro-shift proposed for (**1**) and (**5f**, **g**). However, there is in addition a radical epimerization reaction.

The regiospecificity of the rearrangement in the conjugated dienes (**1**) and (**5**) can be understood in terms of a preference for a transition state involving the maximum number of electrons.[7] The [1,5] shift observed requires a transition state involving six electrons whereas the alternative [1,3] shift would require four electrons. We also examined the behaviour of some non-conjugated dienes in which only a [1,3] shift is possible. Compounds (**8**) exhibited regiospecific and stereospecific nitro-shifts (Scheme 3) while (**10**) did not isomerize. The rearrangement products (**9**) have extended conjugation involving three multiple bonds and this provides a driving force for the rearrangement of (**8**). This difference is demonstrated by comparison of (**8c**) and (**10a**). These two adducts differ only in the location of the cyano-group and only (**8c**), which leads to (**9c**), the product with the extended conjugaion, isomerizes. The isomerization of (**8**) to (**9**) is accompanied by rearomatization in which the acetyl nitrate is eliminated and the dimethylbenzonitrile is formed.



(10)

a; $X = CN, R = Me$
b; $X = H, R = Bu^t$
c; $X = H, R = Me$
d; $X = Me, R = H$

Several of the novel compounds described in this communication have been isolated and characterized.† Others not yet isolated have been observed in solution by ^{1}H n.m.r. and, in some cases, by ^{13}C n.m.r. spectroscopy.

Received, 6th October 1982; Com. 1175

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† Both diastereoisomers of (**1a**) were obtained from nitration of 2-methyl-2-(*o*-tolyloxy)propanoic acid and one diastereoisomer of (**1b**) was obtained similarly. Both diastereoisomers of (**2b**) were isolated and characterized. One diastereoisomer of each of (**5a**—**e**) has been reported previously (ref. 3 and A. Fischer and R. Röderer, *Can. J. Chem.*, 1976, **54**, 3978). The second diastereoisomer of (**5a**) and that of (**5b**) have been isolated and characterized in the present work. Compound (**5f**) was obtained by reaction of (**5a**) with hydrogen chloride and (**5g**) by reaction of (**5f**) with silver nitrate in methanol. The diastereoisomers of (**6a**), (**6b**), and (**6e**) were isolated and characterized. One diastereoisomer of each of (**8a**) and (**8b**) has been reported (A. Fischer and C. C. Greig, *Can. J. Chem.*, 1974, **52**, 1231). The second diastereoisomer of each has been isolated from the nitration reaction mixtures (D. L. Fyles, G. N. Henderson, and S. Sankararaman, unpublished work) Compounds (**8c**) and (**10a**) were obtained by nitration of 2,5-dimethylbenzonitrile (W. V. Nykodym, unpublished work). One diastereoisomer of (**9a**) was isolated and characterized.