Intermediates in Aromatic Nucleophilic Substitution Reactions: Meisenheimer Complexes from 1-Chloro-2,6-dinitro-4-X-benzenes

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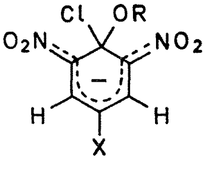
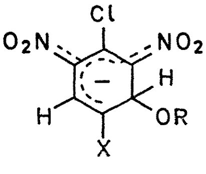
Summary The coloured intermediates initially produced on the addition of sodium methoxide to 1-chloro-2,6-dinitro-4-X-benzenes in dimethyl sulphoxide are shown to result from base addition at a ring carbon carrying hydrogen rather than at the chloro-substituted position.

ACCORDING to the well-known S_N2 mechanism,[1] substitution of chlorine by alkoxides or hydroxide in activated aromatic substrates proceeds through intermediates of finite stability of structure (I; R = H, alkyl). Indeed, the colour observed in solutions of picryl chloride in aqueous sodium hydroxide has been ascribed[2] to such an intermediate (I; R = H; X = NO_2). We report here results based on visible and ^1H n.m.r. spectroscopy which show that the coloured species initially produced from three activated chlorobenzenes are of structure type (II) rather than (I).



(I)



(II)

In the case of substituted anisoles several examples have previously been reported[3,4] of the initial formation under kinetic control of 1,3-Meisenheimer complexes (such as III) and their subsequent rearrangement to the thermodynamically more stable 1,1-complexes (such as IV). The present work indicates a similar type of behaviour for the 1-chloro-2,6-dinitro-4-X-benzenes with addition at C-3 being kinetically favoured. However, in this case, due to the instability with respect to loss of chloride ion of adducts of type (I), rearrangement will lead to nucleophilic subsitution rather than a stable adduct.

^{1}H *N.m.r. and visible spectral data for adducts with sodium methoxide*

	Chemical shifts[a] (p.p.m.)				Visible spectrum
	Ring protons[b]		Methoxyl protons		λ_{max} (nm)
Adduct (II)					
$X = NO_2$, R = Me	6·25	8·57	3·12		424 (480sh)
$X = CO_2Me$, R = Me ..	5·87	8·15	3·07[c]		485
X = Cl, R = Me	5·52	7·22	3·11		504
Adduct (III)					
$X = NO_2$	6·13	8·48	3·17	3·83	418, 485
$X = CO_2Me$	5·80	8·07	not measured		470
X = Cl	5·45	7·17	3·10	3·81	480
Adduct IV					
$X = NO_2$	8·65		3·02		420, 490
$X = CO_2Me$	8·45		2·97[c]		533
X = Cl	7·85		3·00		610

[a] Downfield from internal tetramethylsilane.

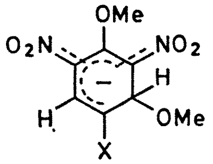
[b] The ring protons in compounds of structure types (II) and (III) give spin-coupled bands, *J ca.* 1·5 Hz.

[c] CO_2Me protons give a singlet at 3·70 p.p.m.

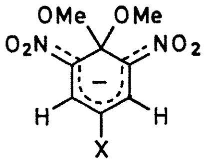
N.m.r. data are collected in the Table for the species initially formed on the addition of slightly less than 1 equiv. of sodium methoxide to solutions of the parent chloro-compounds in dimethyl sulphoxide containing a little methanol at 15°. In each case the ring protons are differentiated in the complex; one band is shifted considerably to high field, indicating methoxide addition at this position. The added methoxy protons give a singlet at *ca.* 3·10 p.p.m. The spectra are consistent only with adducts of structure (II), which are formed in high yield. No bands attributable to adducts of structure (I) were observed, and we estimate that 5% would be detectable.

The situation is complicated in that the products of nucleophilic substitution, the 1-methoxy-2,6-dinitro-4-X-benzenes themselves interact with methoxide. The fast formation of (III; $X = NO_2$) from 2,4,6-trinitroanisole followed by its conversion into (IV; $X = NO_2$) is well documented[3] and the analogous transformation (III; X = Cl) to (IV; X = Cl) has been studied.[4] For the sake of completeness we have measured the spectra produced on addition of methoxide to solutions of the anisoles. Data are in the Table. The positions of the bands due to ring protons in the n.m.r. spectra of the adducts (III) are similar but slightly to high field of those due to the adducts (II). To confirm beyond doubt that the bands we have attributed to the adducts (II) are not due to adducts of structure (III), we measured the n.m.r. spectrum of a mixture of picryl chloride and 2,4,6-trinitroanisole in the presence of sodium methoxide. This spectrum showed four doublets corresponding to ring protons due to the expected adducts (II; $X = NO_2$, R = Me) and (III; $X = NO_2$).

Evidence for the fast formation of adducts of structure (II) also comes from the visible spectra. In the presence of an excess of sodium methoxide in methanolic dimethyl sulphoxide, the 4-CO_2Me compound gives a yellow colour which quickly becomes red. The corresponding colour change for the 4-chloro-substituted compound is from red to blue. These results indicate the fast formation of (II, R = Me, $X = CO_2Me$ or Cl) followed by ultimate conversion in excess of methoxide, into (IV; $X = CO_2Me$ or Cl). The shift to longer wavelength can be attributed[5] to the fact that the group *para* to the position of addition is less electron-withdrawing in (IV; $X = CO_2Me$, Cl) than in (II). In media containing nearly 100% dimethyl sulphoxide there is evidence for some incursion of a reaction other than replacement of chlorine by methoxide, whose nature we are investigating. The visible maxima of the adducts of structure (III; $X = CO_2Me$, Cl) initially produced on base addition to the corresponding anisoles are at slightly shorter wavelength than those of the corresponding adducts of structure (II).



(III)



(IV)

Additionally, we find that the n.m.r. spectrum initially produced on addition of aqueous sodium hydroxide to picryl chloride in dimethyl sulphoxide gives two bands at 8·4 and 6·2 p.p.m. downfield from tetramethylsilane, attributed to the ring protons of (II; $X = NO_2$, R = H).

We think it likely that the substitution of chlorine by base proceeds through species of structure type (I) which are intermediates rather than transition states. However, in the systems we have studied the observable coloured species are of structure type (II).

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