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A SPECTROSCOPIC STUDY OF MEISENHEIMER COMPLEXES FROM 1-CHLORO-2,6-DINITRO-4-X-BENZENES

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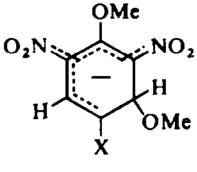
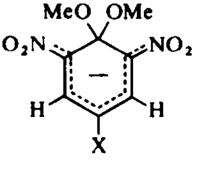
Abstract—The coloured intermediates initially produced on the addition of sodium methoxide, sodium hydroxide or sodium sulphite to picryl chloride in dimethyl sulphoxide have been examined by ^{1}H NMR and visible spectroscopy. The results show that initial addition at a ring carbon carrying hydrogen to give covalently bound Meisenheimer complexes is followed by nucleophilic replacement of chloride ion. Some comparative measurements have been made with 2,6-dinitro-4-X-chlorobenzenes (X = CO_2Me, CF_3, Cl).

Several examples have been reported of the initial formation under kinetic control of 1,3-Meisenheimer complexes (I) from substituted anisoles and sodium methoxide and their subsequent rearrangement to the thermodynamically more stable 1,1-adducts.[1] Thus the fast formation of I (X = NO_2) from 2,4,6-trinitroanisole followed by its conversion to II (X = NO_2) is well documented.[2] Other examples have been reported in the cases of 2-X-4,6-dinitroanisoles and 4-X-2,6-dinitroanisoles.[3]

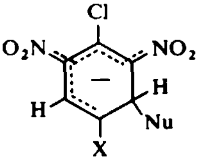


I

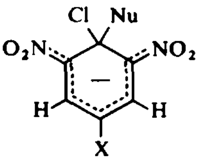


II

The work which we present here indicates a similar type of behaviour with certain activated chlorobenzenes where the mechanism of reaction was thought to be clearly established[4] as direct S_N2 attack at the ring carbon carrying chlorine. Our results using visible and ^{1}H NMR spectroscopy show that the coloured species initially formed on addition of nucleophiles to 1-chloro-2,6-dinitro-4-X-benzenes in dimethyl sulphoxide are of structure type III. However, in this case due to the instability with respect to chloride ion loss of adducts of type IV, rearrangement leads to nucleophilic displacement rather than a stable adduct.



III



IV

RESULTS AND DISCUSSION

Picryl chloride and nucleophiles. The addition of methanolic sodium methoxide to a solution of picryl chloride (2,4,6-trinitrochlorobenzene) in dimethyl sulphoxide gives a red species (λ_{max} 424 and 480 nm). The ^1H NMR spectrum shows in addition to solvent bands two doublets of equal intensity at +6·25 and +8·57 ppm attributed to ring protons and a single band (relative intensity 3) at +3·12 ppm due to methoxyl protons. The large upfield shift of one ring-proton band clearly indicates base addition at this position showing that the complex produced has structure III (X = NO_2, Nu = OMe). With time these bands decreased in intensity and new bands were observed at +9·07 and +4·05 ppm due to the formation of 2,4,6-trinitroanisole. In addition small bands were observed at +8·70 and +8·65 ppm due respectively to the formation of small amounts of II (X = NO_2) and picric acid. The latter compound is probably produced from traces of water in the solvent and is formed slowly from picryl chloride even in the absence of added base. No band was observed attributable to the adduct of structure IV.

TABLE 1. CHEMICAL SHIFTS (δ VALUES, WITH δ = 0·0 FOR TETRAMETHYLSILANE) FOR PARENT COMPOUNDS IN DIMETHYL SULPHOXIDE

	Ring protons	Methoxyl (p.p.m.)	Methoxycarbonyl
1-Chloro-2,6-dinitro-4-X-benzenes			
X = NO_2	9·25		
X = CO_2Me	8·83		3·96
X = CF_3	8·90		
X = Cl	8·65		
1-Methoxy-2,6-dinitro-4-X-benzenes			
X = NO_2	9·07	4·05	
X = CO_2Me	8·72	4·03	3·95
X = CF_3	8·75	4·05	
X = Cl	8·53	3·98	

The NMR bands from the ring protons of the methoxide adduct of picryl chloride are in similar positions (Table 2) but slightly to low field of the bands due to the analogous adduct (I, X = NO_2) from 2,4,6-trinitroanisole. To make absolutely sure that the bands we have attributed to the adduct III (X = NO_2, Nu = OMe) are not in fact due to the formation of I (X = NO_2), which might be produced by methoxide attack on the reaction product, we observed the spectrum of a mixture of 2,4,6-trinitroanisole and picryl chloride containing sodium methoxide. This showed four doublets at the positions expected for the ring protons of the two adducts III (X = NO_2, Nu = OMe) and I (X = NO_2).

We note in passing that the methoxyl protons at C-1 of the adduct I (X = NO_2) from 2,4,6-trinitroanisole show absorption at 3·83 ppm and not 3·45 ppm as previously stated.[1b, 2a, 3a]

In order to compare qualitatively the rates of rearrangement of the initially formed C-3 adducts from picryl chloride and 2,4,6-trinitroanisole we measured in separate experiments the rates of disappearance of the characteristic doublets due to ring protons. In a solvent of dimethyl sulphoxide-methanol (80–20 v/v) with sodium methoxide 0·4 M and nitrocompounds 0·5 M the half-times for rearrangement were *ca* 6 minutes for 2,4,6-trinitroanisole and *ca* 10 minutes for picryl chloride. The slightly slower rate in the latter case may result from the greater thermodynamic stability of the C-3 adduct of picryl chloride compared with the adduct from 2,4,6-trinitroanisole, or a smaller rate constant for nucleophilic attack by methoxide at C-1 of picryl chloride than at C-1 of 2,4,6-trinitroanisole.

A behaviour pattern similar to that observed with sodium methoxide was observed on the addition of other nucleophiles to picryl chloride in dimethyl sulphoxide. Thus the addition of aqueous sodium hydroxide gave initially NMR bands at 8·4 and 6·2 ppm due to the ring protons of III ($X = NO_2$, Nu = OH) with the eventual formation of picric acid (resonance at 8·65 ppm). The addition of aqueous sodium sulphite gave visible and NMR spectra consistent with the production of III ($X = NO_2$, $Nu = SO_3^-$) with the eventual replacement of chlorine by sulphite to give 2,4,6-trinitrobenzenesulphonate (resonance at 8·87 ppm).

2,6-*Dinitro*-4-X-*chlorobenzenes and sodium methoxide*. The addition of methanolic sodium methoxide to solutions of the parent compounds ($X = CF_3$, CO_2Me, Cl) in dimethyl sulphoxide gave intensely coloured species which were shown from NMR spectra to result from base addition at C-3. Eventually nucleophilic replacement of chloride ion occurred. Again no bands attributable to species of structure IV were observed. The visible spectra recorded in more dilute solutions containing excess sodium methoxide showed initially bands due to adducts of structure III. With time these decreased in intensity and new bands appeared due to the symmetrical adducts of structure II which were formed no doubt by the reaction of excess sodium methoxide with the product anisoles. In the case of the 4-CO_2Me compound the colour change was from yellow to red while with the 4-Cl compound the change was from red to blue. The shift to longer wavelength is due[9] to the fact that the group *para* to the position of addition is less electron withdrawing in these adducts of structure II than of structure III.

For completeness we include in Table 2 data for the corresponding adducts formed from similarly activated anisoles.

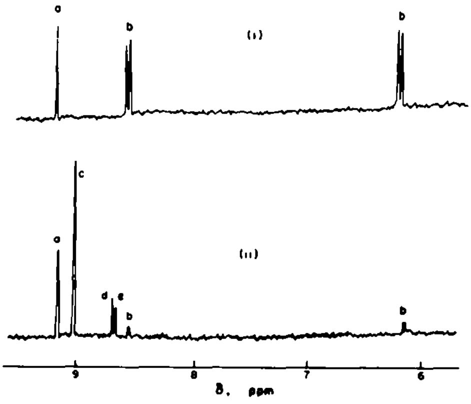
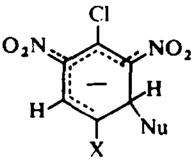
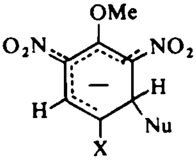
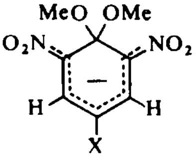


FIG 1. ^1H NMR spectra of picryl chloride (0·4 M) and sodium methoxide (0·3 M) in methanolic dimethyl sulphoxide, (i) initially after mixing and (ii) after 20 minutes. Bands labelled 'a' are due to unchanged picryl chloride, 'b' to the ring protons of complex III ($X = NO_2$, Nu = OMe), 'c' to ring protons of 2,4,6-trinitroanisole, 'd' to ring protons of adduct II ($X = NO_2$) and 'e' to picric acid.

TABLE 2. SPECTRAL DATA FOR COMPLEXES[a]

	Chemical Shifts (δ) Ring protons[b]	Chemical Shifts (δ) Methoxyl protons	Visible spectrum λ_{max} (nm)
X = NO_2, Nu = OMe	6·27 8·57	3·12	424 (480 sh)
X = NO_2, Nu = OH	6·2 8·4		
X = NO_2, Nu = SO_3^-	6·1 8·45		470
X = CF_3, Nu = OMe	5·77 7·78	3·07	
X = CO_2Me, Nu = OMe	5·87 8·15	3·07[c]	485
X = Cl, Nu = OMe	5·52 7·22	3·11	504
			
X = NO_2, Nu = OMe	6·15 8·48	3·17 3·83	418 (485 sh)
X = NO_2, Nu = OH	6·0 8·2[d]		
X = NO_2, Nu = SO_3^-	6·05 8·35[e]	3·85	462
X = CF_3, Nu = OMe	5·64 7·65		465
X = CO_2Me, Nu = OMe	5·80 8·07		470
X = Cl, Nu = OMe	5·45 7·17	3·10 3·81	480
			
X = NO_2	8·70	3·02	422 (494 sh)
X = CF_3	8·07	3·02	545
X = CO_2Me	8·43	2·98[c]	533
X = Cl	7·85	3·00	610

[a] The solvent is dimethyl sulphoxide, containing a little methanol when Nu = OMe, or a little water when Nu = OH or SO_3^-.

[b] The ring protons in complexes formed by addition at C-3 give spin-coupled bands, J *ca* 2 Hz.

[c] CO_2Me protons give a singlet at 3·70 ppm

[d] Ref[1a]

[e] Ref[8]

CONCLUSIONS

Our results show that addition of nucleophiles at C-3 of the parent chloro-compounds is kinetically favoured relative to addition at the chlorosubstituted position. In this respect the chloro compounds are similar to substituted anisoles,[3] 1,2,3,5-tetranitrobenzene[10] and 2,4,6-trinitroanilines[2b] where in each case addition occurs first at a ring carbon carrying hydrogen. The faster addition at the unsubstituted positions in these compounds may result from steric effects[2b] which inhibit addition at the crowded 1-position.

These results were obtained in media consisting largely of dimethyl sulphoxide. In hydroxylic media transient colours have sometimes been observed during nucleophilic substitutions. Thus Gaboriaud and Schaal[11] who studied the reaction of picryl chloride with aqueous sodium hydroxide observed a coloured species which was thought to have structure IV (Nu = OH, X = NO_2). In fact their kinetic analysis requires that hydroxide ion is a better leaving group than chloride ion which is unlikely.[1b] In the light of our results it is probable that here too the coloured species results from hydroxide addition at an unsubstituted position to give III (Nu = OH, X = NO_2) or possibly from the addition of two hydroxide ions.[12] Similarly Bowden and Cook[13] in a kinetic study of the reactions of 1-substituted-2,4-dinitrobenzenes with base in aqueous dimethyl sulphoxide have observed coloured species which were thought to result from hydroxide addition at a ring-carbon carrying hydrogen. Our results add to the likelihood of this possibility.

EXPERIMENTAL

Picryl chloride (m.p. 83°, lit. 83°,[5]) was a recrystallised commercial specimen. The preparation of other nitro compounds and the purification of solvents was carried out as before.[6,7] ^1H NMR measurements were made on solutions (*ca* 0·2 M) with a Varian A56/60 instrument using TMS as internal reference. In order to study more easily the initial interactions solutions were in some cases cooled to 10° in order to slow down subsequent reactions. Visible spectra were recorded with a Unicam SP800 instrument on samples with concentrations *ca* 10^{-4} M.

Acknowledgement—We thank the Libyan Government for financial assistance to M. El G.

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