Studies on Nitroaromatic Compounds. Part VII.[1] A Nuclear Magnetic Resonance Study of the Reaction of [$^2H_3$]Methoxide Ion with Some Polynitrodimethylnaphthalenes

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The interaction of 1,8-dimethyl-2,4,5,7-tetranitro- (I), 1,5-dimethyl-2,4,6,8-tetranitro- (II), and 1,5-dimethyl-2,4,8-trinitro-naphthalene (III) with [$^2H_3$]methoxide ion in [$^2H_6$]dimethyl sulphoxide has been investigated by ^1H n.m.r. spectroscopy. The major initial reaction is proton abstraction from a methyl group of (I)—(III) to give a resonance stabilised benzyl-type anion. The anions from (I) and (III) are stable, whereas the anion from (II) undergoes isomerisation to give a stable product. The anion from (III), unlike those from (I) and (II), can react with [$^2H_3$]methoxide ion to give a dianionic species. In the case of (I), addition of base to a nuclear position in the parent nitro-compound competes with proton abstraction.

THE reactions of nitroaromatic compounds with base are well documented [2-5] and, of these, the reactions of 2,4,6-trinitrotoluene (TNT) with both weak and strong base have received considerable attention. In a number of systems the reaction of TNT with base has been postulated as proceeding *via* the intermediacy of the 2,4,6-trinitrobenzyl anion (TNT$^-$).[6-10]

Whereas in many cases, ^1H n.m.r. spectroscopy has provided direct evidence in establishing the structures of intermediates and products in the reactions of alkoxide with nitroaromatic compounds,[2-5] it has not proved possible to obtain n.m.r. spectra relating to the reaction of alkoxide with TNT, owing probably to the presence of free radicals in these systems.[4,11] Hence it has not been possible to gain direct structural evidence for the existence of the TNT$^-$ anion. We have investigated the reaction of [$^2H_3$]methoxide ion with some polynitrodimethylnaphthalenes which are structurally related to TNT, and now report on n.m.r. evidence for the formation of benzyl-type anions in the systems studied.

RESULTS AND DISCUSSION

As can be seen from Figure 1, there are notable differences between the ^1H n.m.r. spectrum of 1,8-dimethyl-2,4,5,7-tetranitronaphthalene (I) in [$^2H_6$]dimethyl sulphoxide and the n.m.r. spectrum of a 1 : 1 mixture of (I) and sodium [$^2H_3$]methoxide in the same medium. The most noticeable effect of addition of sodium [$^2H_3$]methoxide is the splitting of the aromatic proton resonance of (I) into two resonances at τ 1.43 and 1.72, the halving in relative intensity of the methyl proton resonance at τ 7.31, and the appearance of two new resonances at τ 3.84 and 4.69 [see Figure 1(b)]. The integral ratio of these resonances (from low to high field) is 1 : 1 : 1 : 1 : 3. The broad resonance at τ *ca.* 6.0 and the multiplet resonance centred at 7.50 were present in all spectra after addition of base and can be assigned to CD_3OH and CD_2HSOCD_3 respectively. Other features are the appearance of somewhat weaker resonances close to τ 7.0 and 8.0 and in the region τ 1—2.

The spectrum of Figure 1(b) indicates that reaction with [$^2H_3$]methoxide occurs at a methyl group of (I) and that this involves loss of a proton to give a structure in which the remaining two protons resonate in the midfield region of the spectrum. The main features of the spectrum can be explained in terms of a resonance stabilised benzyl-type anion of which two canonical forms (IV) and (V) are shown in Scheme 1. The observation of two resonances in the midfield region indicates that structure (V), and other similar canonical forms involving charge

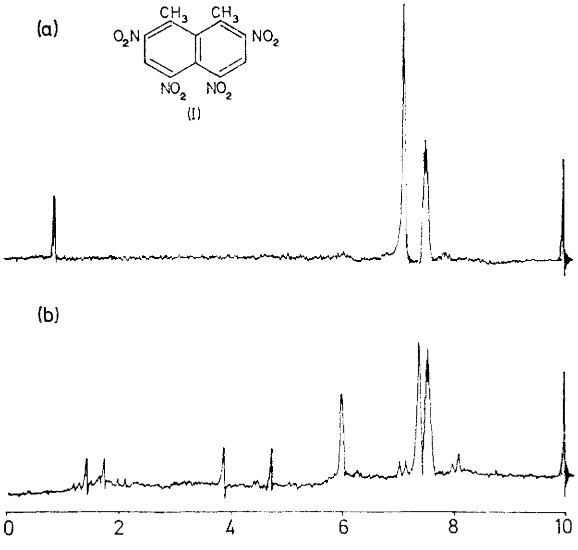

FIGURE 1 ^1H N.m.r. spectra of 1,8-dimethyl-2,4,5,7-tetranitronaphthalene in [$^2H_6$]dimethyl sulphoxide containing sodium [$^2H_3$]methoxide; mole ratio [CD_3O^-] : [nitroaromatic] is (a) 0.0 and (b) 1.0

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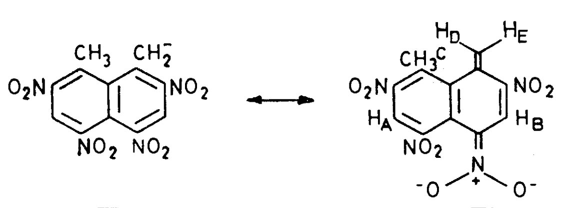
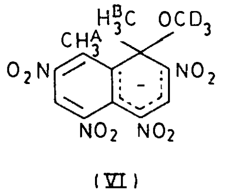
localisation at a nitro-group, represent the charge distribution in the anion more closely than structure (IV). Thus the resonances at τ 1.43, 1.72, and 7.31 can be assigned to protons H_A, H_B, and H_C of anion (V) respectively, while the resonances at τ 3.84 and 4.69 can be assigned to protons H_D and H_E. It is not possible to assign unambiguously the resonance for H_D and H_E as their relative chemical shifts will depend upon the orientation of the 2-nitro-group and the associated shielding cone with respect to the aromatic ring system. The absence of observable coupling between the geminal protons H_D and H_E is consistent with the n.m.r. spectra of other compounds in which the exocyclic olefinic group is part of a conjugated system.[12,13] Further evidence of hydrogen abstraction having occured from (I) was obtained by adding a sample exhibiting the n.m.r. spectrum of Figure 1(b) to deuteriochloric acid–heavy water whence 1,8-dimethyl-2,4,5,7-tetranitro[^{2}H]naphthalene was precipitated.

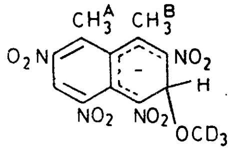


(IV) (V)

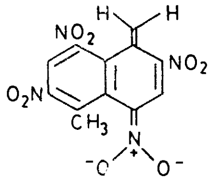
Scheme 1



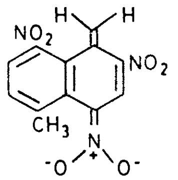
(VI)



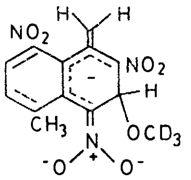
(VII)



(VIII)



(X)



(XI)

The signals in the spectrum of anion (V) decreased in intensity with time and were not detectable after 24 h; no new signals were detectable however. The change in spectrum does not arise because of reaction of anion (V) with [$^2H_3$]methoxide ion since addition of two equivalents of sodium [$^2H_3$]methoxide to a sample exhibiting the spectrum of anion (V) did not cause any alteration in the spectrum.

The weak resonances in the spectrum of Figure 1(b) most probably arise from the 1 : 1 adducts (VI) and (VII) formed by σ-addition of the [$^2H_3$]methoxide ion at the C-1 and -3 positions of (I) respectively. On this basis, the resonances at τ 6.96 and 7.08 can be assigned to the H_A protons of (VI) and (VII), whilst the resonances at τ 7.92 and 8.04 can be assigned to the H_B protons of (VI) and (VII). The weak singlet resonances in the region of τ 1—2 may be attributed to the aromatic protons of (VI) and (VII). The sum of the integrals for the H_A resonances of (VI) and (VII) amounted to *ca.* 15% that of the integral for the H_C protons of (V). It is thus apparent that the reaction of [$^2H_3$]methoxide ion with (I) involves competitive proton abstraction and σ-addition processes, and that under the conditions employed in the present study, compound (I) undergoes *ca.* 85% methyl proton abstraction to 15% σ-addition. This contrasts to the reaction of methoxide with 2,4,6-trinitroaniline where, in a 1 : 1 methanol–dimethyl sulphoxide solvent system, the nitroaromatic compound undergoes *ca.* 20% NH proton abstraction and 80% σ-addition.[11,14]

The effect of sodium [$^2H_3$]methoxide on the n.m.r. spectrum of 1,5-dimethyl-2,4,6,8-tetranitronaphthalene-(II) is shown in Figure 2. The spectrum of Figure 2(b), obtained shortly after addition of one equivalent of sodium [$^2H_3$]methoxide, is similar to that of Figure 1(b) both in terms of chemical shift positions and relative integral ratios of the observed resonances. Thus it would appear that a resonance stabilised benzyl-type anion (VIII) is formed by proton abstraction from (II).

Unlike (V), the anion (VIII) is not stable and within 30 min the spectrum of (VIII) is replaced by that shown in Figure 2(c). In this latter spectrum, the olefinic resonances of (VIII) in the midfield region have been replaced by two resonances of the same intensity in the low field region. With regard to this, it is interesting to note that a downfield shift has been observed for the amino protons in 2,4,6-trinitroaniline on reaction of 2,4,6-trinitroaniline with base.[15] This shift was ascribed to

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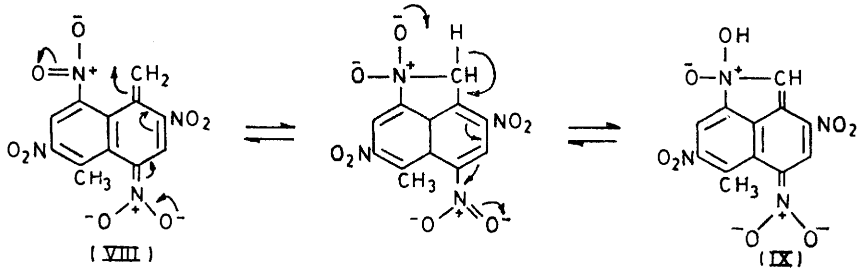
increased hydrogen bonding between the amino-protons and the adjacent nitro-groups in the anion as compared to that in the parent molecule. The time scale of the present process excludes hydrogen bonding as the cause of the change but indicates, instead, some form of chemical reaction. The disappearance with time of the olefinic resonances of (VIII), coupled with the observation that anion (V) is stable and does not react in this way, suggests that the reaction proceeds *via* the nitro-group at the 8-position. A reaction product of structure (IX) could account for the observed n.m.r. spectrum. The formation of this product can be rationalised in terms of the mechanism tentatively proposed in Scheme 2. As might be expected, the reaction sequence (II) ⟶ (VIII) ⟶ (IX) is reversed under acid conditions. Thus, addition of a solution exhibiting the n.m.r. spectrum of Figure 2(C) to deuteriochloric acid–heavy water gave 1,5-dimethyl-2,4,6,8-tetranitro[^{2}H]naphthalene.



SCHEME 2

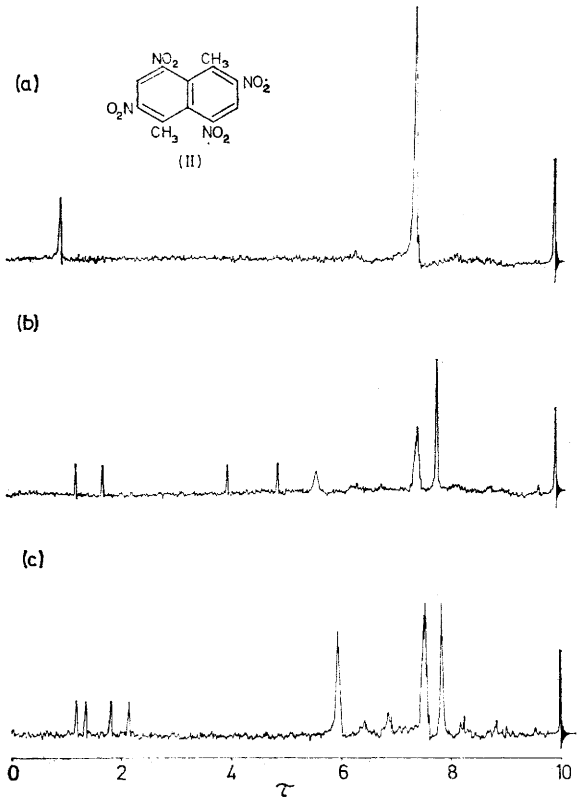


FIGURE 2 ^{1}H N.m.r. spectra of 1,5-dimethyl-2,4,6,8-tetranitronaphthalene in [$^2H_6$]dimethyl sulphoxide containing sodium [$^2H_3$]methoxide; mole ratio [CD_3O^-] : [nitroaromatic] is (a) 0.0, (b) 1.0, spectrum after 2 min, (c) 1.0, spectrum after 30 min

Reaction of sodium [$^2H_3$]methoxide with 1,5-dimethyl-2,4,8-trinitronaphthalene (III) in 1 : 1 mole ratio gives the n.m.r. spectrum shown in Figure 3(b). It is apparent that an anion of similar structure to (V) and (VIII) is formed. Comparison of this spectrum with that of (III) in Figure 3(a) shows clearly that the olefinic resonances of the anion are derived from one of the methyl

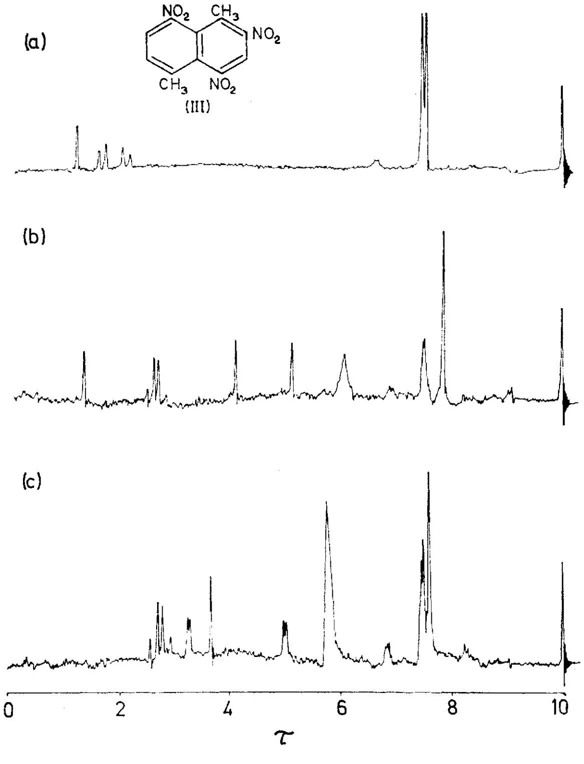


FIGURE 3 ^{1}H N.m.r. spectra of 1,5-dimethyl-2,4,8-trinitronaphthalene in [$^2H_6$]dimethyl sulphoxide containing sodium [$^2H_3$]methoxide; mole ratio [CD_3O^-] : [nitroaromatic] is (a) 0.0, (b) 1.0, and (c) 3.0

group resonances of (III). Since proton abstraction is more likely to occur from the methyl group at the 1-position in (III), the anion would be expected to have structure (X). Deuteriation of (X) in deuteriochloric acid–heavy water yielded 1,5-dimethyl-2,4,8-trinitro-[^{2}H]naphthalene.

The spectrum of Figure 3(b) does not change with time, but further addition of sodium deuteriomethoxide results in the spectrum of Figure 3(c). The resonances in the latter spectrum may be assigned on the basis of addition of methoxide at C-3 in (X) to give the adduct (XI). As would be expected, addition at C-3 causes the resonance for the proton at this site to shift upfield; from τ 1.25 to 3.68 in this case. Interestingly, coupling between the exocyclic olefinic protons is observed when conjugation between the olefinic linkage and the C-2–C-3 bond is broken by σ addition at C-3.

EXPERIMENTAL

The nitroaromatic compounds were prepared and purified as previously described.[1] [$^2H_6$]Dimethyl sulphoxide and [$^2H_4$] methanol were dried over molecular sieve.

^{1}H N.m.r. spectra were recorded at 31° on a Perkin-Elmer R10 spectrometer operating at 60 MHz. Chemical shifts were measured relative to internal tetramethylsilane as reference. Solutions were prepared immediately prior to use, and the initial n.m.r. spectra recorded within 2—4 min after preparation. Deuteriated products were prepared by drowning out samples, after recording their n.m.r. spectra, in deuteriochloric acid–heavy water mixtures. The precipitated product was filtered off, dried *in vacuo*, and the mass spectrum of the product recorded using an A.E.I. MS9 spectrometer.

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