Tetrahedron, 1967, Vol. 23, pp. 227 to 237. Pergamon Press Ltd. Printed in Northern Ireland

INTERACTION OF ELECTRON ACCEPTORS WITH BASES—XXI[1]

FURTHER STUDIES OF THE PROTON MAGNETIC RESONANCE SPECTRA OF MEISENHEIMER-LIKE COMPOUNDS

R. Foster, C. A. Fyfe and (in part) P. H. Emslie and M. I. Foreman
Chemistry Dept., Queen's College, University of St. Andrews, Dundee, Scotland

(*Received 6 May 1966; accepted for publication 1 June 1966*)

Abstract—The structures of σ-complexes formed by the reaction of methoxide ion or acetonate ion with various nitroaromatic compounds are confirmed or established from observations of their PMR. The substrates include: 1-x-2,4-dinitrobenzenes; 1-x-2,6-dinitrobenzenes; 1-x-2,4,6-trinitrobenzenes; 1-x-2,4-dinitronaphthalenes; and 9-x-10-nitroanthracenes.

Recently several groups of workers[2-10] have described the PMR spectra of σ-complexes formed by the attack of alkoxides on aromatic nitrocompounds. In nearly all cases the substrate has been 1,3,5-trinitrobenzene or a substituted 1,3,5-trinitrobenzene. The PMR spectra of adducts formed by the attack of methoxide on substituted 1,3-dinitrobenzenes are now described. The results support the conclusions, based on electronic spectra, made by Pollitt and Saunders,[11] that the products are the corresponding dinitro σ-complexes. σ-Complexes of nitronaphthalenes and of nitroanthracenes with methoxide have also been obtained.

The PMR spectra of σ-complexes formed by the action of carbanions derived from ketones on 1,3,5-trinitrobenzene have been described.[10] This work is now extended to reactions with substituted 1,3,5-trinitrobenzenes, 1,3-dinitronaphthalenes and with 9-nitroanthracene.

A recent study by Servis[6] of the interaction of methoxide with 2,4,6-trinitroanisole has caused us to revise our assignment[4] of the PMR spectrum of this system.

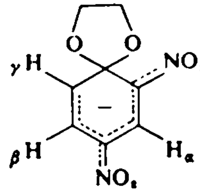
RESULTS AND DISCUSSION

2,4-Dinitrophenyl ether plus alkoxide. Addition of sodium methoxide to 2,4-dinitroanisole in dimethylsulphoxide (DMSO) yields an orange-red solution ($\lambda_{max} = 505$ mμ). Similar solutions are obtained using 2,4-dinitrophenetole with methoxide or ethoxide. Addition of methoxide to 1-(2′-hydroxyethoxy)-2,4-dinitrobenzene yields a solution with a very similar optical spectrum. On the basis of this similarity, Pollitt and Saunders[11] suggested that this product has the spiro structure I corresponding

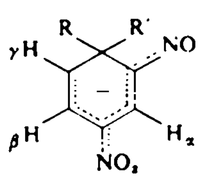
---

[1] Part XX R. Foster and C. A. Fyfe, *Trans. Faraday Soc.* **62**, 1400 (1966).
[2] M. R. Crampton and V. Gold, *J. Chem. Soc.* 4293 (1964).
[3] M. R. Crampton and V. Gold, *Chem. Commun.* 256 (1965).
[4] R. Foster and C. A. Fyfe, *Tetrahedron* **21**, 3363 (1965).
[5] R. Foster, C. A. Fyfe and J. W. Morris, *Rec. Trav. Chim.* **84**, 516 (1965).
[6] K. L. Servis, *J. Amer. Chem. Soc.* **87**, 5495 (1965).
[7] N. E. Brown and R. T. Keys, *J. Org. Chem.* **30**, 2452 (1965).
[8] A. J. Boulton and D. P. Clifford, *J. Chem. Soc.* 5414 (1965).
[9] W. P. Norris and J. Osmundsen, *J. Org. Chem.* **30**, 2407 (1965).
[10] R. Foster and C. A. Fyfe, *J. Chem. Soc.* (B) 53 (1966).
[11] R. J. Pollitt and B. C. Saunders, *J. Chem. Soc.* 1132 (1964).

to structure II (R = R′ = —OMe) for the product formed from 2,4-dinitroanisole and methoxide. The PMR spectra of these products bear a close similarity one to another (Table 1). A typical spectrum is shown in Fig. 1. These spectra amply confirm the structures assigned by Pollitt and Saunders.[11] The H_α proton attached to the



I



II

sp^2-hybridized carbon atom *ortho* to two nitro groups has about the same chemical shift as the protons in a similar environment in the now well-established structures for the corresponding trinitrobenzene σ-complexes. H_α and H_β are weakly coupled. H_β is also coupled with the vicinal H_γ and appears as a double doublet. H_γ absorbs at relatively high fields (Table 1, Fig. 1). This is to be expected since the —M effect of the two nitro-groups has no influence in this position. The PMR spectrum of I in DMSO-d_6 shows the four methylene protons to be equivalent.

Table 1. PMR spectral data of ions with the general formula II (in DMSO)

R	R′	Chemical shifts $(-\delta)$[*]			J(c/s)	
		H_α	H_β	H_γ	$(H_\alpha—H_\beta)$	$(H_\beta—H_\gamma)$
—OCH$_2$CH$_2$O	—	$8{\cdot}5_8$ (D)[*]	$6{\cdot}9_8$ (DD)[*]	$5{\cdot}3_8$ (D)[*]	3	10
—OMe	—OMe	$8{\cdot}6_8$ (D)	$7{\cdot}2_4$ (DD)	$5{\cdot}0_8$ (D)	3	10
—OMe	—OEt	$8{\cdot}7_8$ (D)	$7{\cdot}2_0$ (DD)	5·1 (D)	3	10
—OEt	—OEt	$8{\cdot}6_8$ (D)	$7{\cdot}1_9$ (DD)	$5{\cdot}1_0$ (D)	3	10

[*] Multiplicities are denoted by D = doublet, T = triplet, Q = quartet, M = higher multiplicity than quartet, DD = doublet of doublets.

Earlier we had noted[4] that when large excesses of methoxide were added to solutions of 2,4-dinitroanisole in DMSO, a second set of absorptions were observed in the PMR spectrum. These absorptions increased in intensity with time. We had assigned these absorptions to the ring protons of a di-anion formed by attack of a second methoxide ion on the ion II (R = R′ = —OMe). This second set of absorptions is in fact due to the 2,4-dinitrophenolate anion which appears to be formed by hydrolysis from traces of water present in the solvent.

Additions of methoxide to 1,5-dimethoxy-2,4-dinitrobenzene in DMSO yields a product which shows PMR absorptions[*] at $\delta = -8{\cdot}7_0$ and at $\delta = -6{\cdot}0_3$, compared with $\delta = -8{\cdot}6_0$ and $\delta = -6{\cdot}9_9$ in the parent compound. If the methoxide had attacked at an unsubstituted carbon atom, the chemical shift for that particular proton would have moved considerably up-field as the hybridization of the carbon atom changed from sp^2 to sp^3. No such change is observed. Also the proton absorptions correspond closely to the H_α and H_γ absorptions in I and II. Addition of acetone gives rise to only a slight (solvent) shift. No solvolysis by the acetone is observed.

[*] All chemical shifts measured in ppm from an internal reference of TMS.

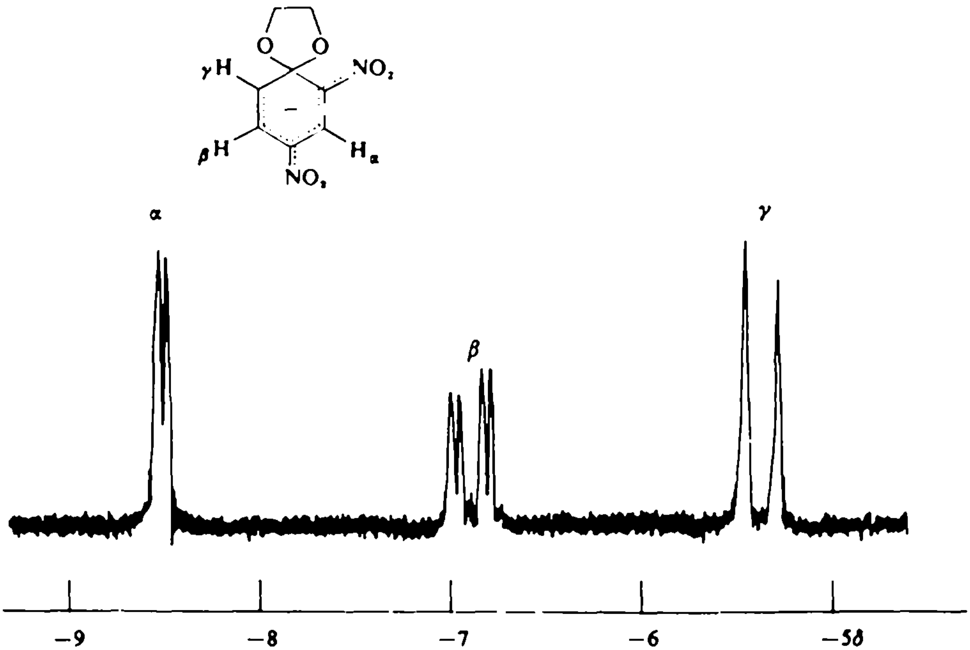
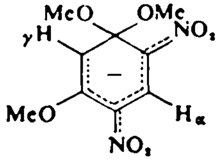


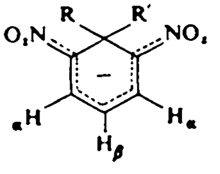
FIG. 1. Partial PMR spectrum of the ion I in DMSO, showing the aromatic ring proton absorptions.

If attack had occurred at an unsubstituted position such a solvolysis would have been expected.[10] The visible spectrum is very similar to II (R = R′ = —OMe) and acidification yields the original nitrocompound. All these observations are consistent with the structure III.

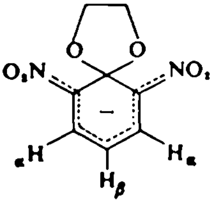


III

2,6-*Dinitrophenyl ethers plus alkoxide*. Addition of methoxide to 2,6-dinitroanisole in DMSO gives a blue solution (λ_{max} = 585 mμ). The PMR spectrum of 2,6-dinitroanisole alone in DMSO shows an anticipated AX_2 spectrum for the ring protons. The product formed by the addition of methoxide also has an AX_2 PMR spectrum (Table 2). This strongly suggests that the methoxide attacks at the 1-position to yield



IV



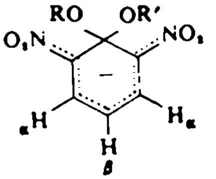
V

the ion IV (R = R′ = —OMe), since attack at the 4-position is unlikely on electronic grounds and attack at the 3-position would not yield a product which would show an AX_2 pattern in its PMR spectrum. Confirmation of structure IV (R = R′ = —OMe) is given by the close resemblance of this PMR spectrum (Fig. 2) to the spectrum of the product formed by the addition of base to 1-(2′-hydroxyethoxy)-2,6-dinitrobenzene (Table 2). If this occurs through an intramolecular cyclization, then attack must be at the 1-position to form the spiro-compound V. The spectrum in DMSO-d_6 shows that the four methylene protons are equivalent as are required by structure V. The visible spectrum of V in DMSO (λ_{max} = 585 mμ) is nearly identical with that of IV (R = R′ = —OMe).

Table 2. PMR spectral data of ions with the general formula IV (in DMSO)

		Chemical shifts (−δ)		J(c/s)
R	R′	H_α	H_β	H_α—H_β
—OCH_2CH_2O	—	$7 \cdot 6_7$ (D)	$5 \cdot 0_9$ (T)	8
—OMe	—OMe	$7 \cdot 9_8$ (D)	$5 \cdot 0_3$ (T)	8
—OMe	—OEt	$7 \cdot 8_4$ (D)	$4 \cdot 9_8$ (T)	8

Thus for all the alkoxy-substituted 1,3-dinitrobenzenes studied, the attack by alkoxide always occurs at a carbon atom substituted by an alkoxyl group. Addition of alkoxide to 3,5-dinitroanisole gives free radicals.



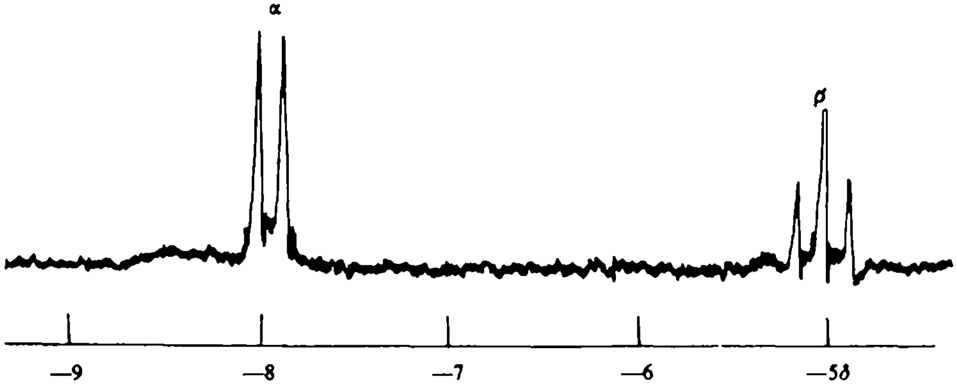
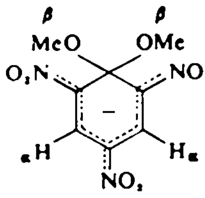
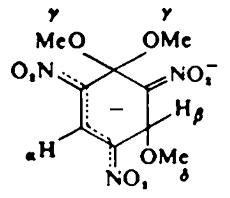


Fig. 2. Partial PMR spectrum of the ion IV (R = R′ = —OMe) in DMSO, showing the aromatic ring proton absorptions.

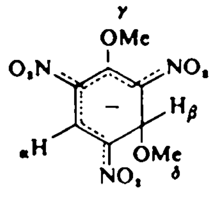
2,4,6-Trinitrophenyl ethers plus alkoxide. The product formed by the addition of methoxide to 2,4,6-trinitroanisole in DMSO shows in its PMR spectrum a singlet at δ = −8·6 and two doublets at δ = −8·36 and δ = −6·06. We originally assigned the singlet to H_α in VI and the two doublets to H_α and H_β respectively in VII. That the relative intensities of these two doublets increase as the methoxide concentration



VI



VII

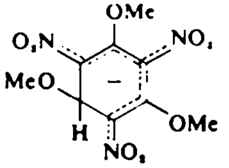


VIII

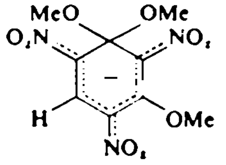
is increased appeared to substantiate the hypothesis of a doubly-charged ion. Servis[8] has argued from similar spectra that the ion VIII is first formed which then isomerises to VI.

We have now remeasured the spectra in DMSO-d_6, this has enabled the relative intensities of the methoxyl-protons to be measured. The methoxide was methanol-free. This has the effect of slowing down the conversion of the first product to the second.[8] The results confirm Servis's conclusions. The absorptions of the two species may be assigned to VI: H_α, $\delta = -8{\cdot}65$ (1); H_β, $\delta = -3{\cdot}06$ (3); and to VIII; H_α, $\delta = -8{\cdot}47$(1); H_β, $\delta = -6{\cdot}15$(1); H_γ, $\delta = -3{\cdot}85$(3); H_δ, $\delta = -3{\cdot}18$ (3). The relative intensities, which are given in parentheses (not on a common scale), are those initially observed. With time, traces of water in the solvent react with VI to yield picric acid (or picrate ion), which absorbs close to H_α in VI.

Addition of methoxide to 1,3-dimethoxy-2,4,6-trinitrobenzene in DMSO gives a product which has a PMR absorption at $\delta = -6{\cdot}0_9$ compared with $\delta = -8{\cdot}9_9$ in the parent molecule. This large shift up-field suggests that the hybridization of the carbon atom to which this ring proton is attached has altered from sp^2 to an sp^3 state. This absorption is similar in position to that of H_β in VIII. This can only occur if the methoxide has attacked at this carbon atom to yield the ion IX. With time the spectrum alters and a new absorption develops at $\delta = -8{\cdot}8_6$ at the expense of the initial absorption. The position of this absorption is characteristic of a proton attached to an sp^2-hybridized carbon atom which is between two nitro-substituted carbon atoms in such σ-complexes, and would therefore be accounted for by the formation of the ion X from IX. This rearrangement (presumably intermolecular) is analogous to that proposed by Servis[8] for the reaction of 2,4,6-trinitroanisole with methoxide.



IX

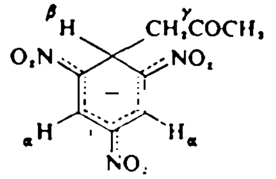


X

1-*x-Substituted*-2,4,6-*trinitrobenzenes plus acetonate ion*. Previous work[10] has shown that addition of a base such as OR^-, OH^- or an aliphatic tertiary amine to an acetone solution of 1,3,5-trinitrobenzene gives rise to the formation of the ion XI through attack by the acetonate anion, e.g.:

$$NEt_3 + CH_3COCH_3 \rightleftharpoons NHEt_3^+ + CH_3COCH_2^-$$

The assignments of the PMR absorptions of XI are given in Table 3. Corresponding studies have now been made by adding triethylamine to acetone solutions of substituted



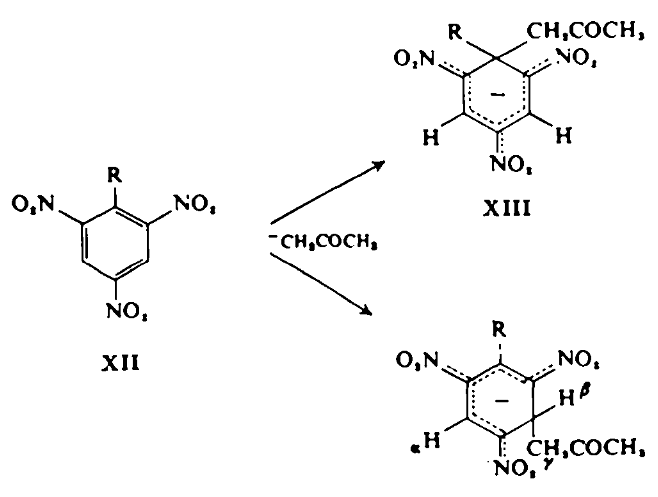
XI

1,3,5-trinitrobenzenes, (XII, R = —Cl, —OEt, —OC$_6$H$_5$, —NMe$_2$) and measuring the PMR spectra which develop. Nucleophilic attack may occur either at the substituted position to yield XIII, or at an unsubstituted position to give XIV. Based on small differences in the electronic spectra, Kimura[13] had suggested that attack by the acetonate carbanion occurs at both positions for the compound XII (R = —OPh) to yield a mixture of XIII and XIV, whereas for XII (R = —Cl, —OEt, and NEt$_2$) only the product XIV is formed. The PMR absorptions for the ring protons of the products from the various substrates are only slightly dependent on the nature of R in XII (Table 3). The absorption at $\delta \approx -8{\cdot}4$ is very close to that assigned to H$_\alpha$

TABLE 3. PMR SPECTRAL DATA OF IONS WITH THE GENERAL FORMULA XIV (IN ACETONE)

R	Chemical shifts (−δ)		J(c/s)	
	H_α	H_β	(H_α—H_β)	(H_β—H_γ)
—H	$8{\cdot}3_6$ (D)	$5{\cdot}0_8$ (T)*	<1	5·5
—Cl	$8{\cdot}4_8$ (D)	$5{\cdot}2_1$ (T)	~2	6
—OEt	$8{\cdot}3_6$ (D)	$5{\cdot}3_1$ (T)	~2	6
—OC$_6$H$_5$	$8{\cdot}5_6$ (D)	$5{\cdot}2_7$ (T)	~2	6
—NMe$_2$	$8{\cdot}3_7$ (D)	$5{\cdot}3_6$ (T)	~1	7

* Splitting by H_α is not observed.



XII

XIII

XIV

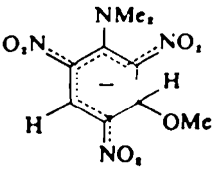
---

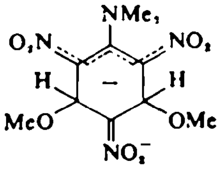
[13] M. Kimura, *Pharm. Bull., Tokyo* 3, 75 (1955).

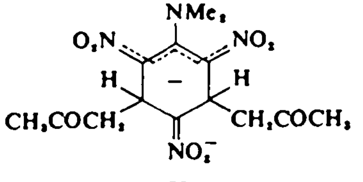
in XI and the absorption at $\delta \approx -5{\cdot}2$ is similar to that assigned to H_f in XI; the coupling constants are also similar (Table 3). These PMR spectra are consistent with structure XIV. The spectra cannot be explained in terms of an ion with the structure XIII: such species would show only one singlet at low fields.

When methylamine is added to solutions containing XII (R = —OPh, —OEt or —Cl) in acetone, simultaneously with the formation of the σ-complex a further absorption appears at $\delta = -8{\cdot}6_7$. This intensifies with time. It appears to be due to the picrate ion formed by hydrolysis from traces of water present. In acid solution the corresponding absorption increases in intensity when picric acid is added.

Crampton and Gold,[3] have shown that the anion XV is formed by the addition of one equivalent of methoxide to a solution of XII (R = $-NMe_2$) in DMSO. Subsequent addition of acetone to this solution yields XIV (R = $-NMe_2$). Ions corresponding to XV derived from XII (R = —Cl, —OEt, —Oph) are too short-lived for this acetonolysis to be carried out under our experimental conditions (probe temp


XV


XVI

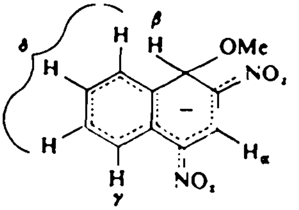

XVII

33·5°). Crampton and Gold[3] have shown that the addition of a second equivalent of methoxide to XII (R = $-NMe_2$) gives XVI which has one singlet absorption at low fields. Addition of acetone to solutions of this ion in DMSO yields the product XVII which shows a triplet absorption at $\delta = -4{\cdot}7_4$, (J = 7 c/s). The splitting results from coupling with the methylene protons of the acetonyl group. The ion XVII is also formed when an acetone solution of XII (R = $-NMe_2$) containing a large excess of triethylamine is allowed to stand for two days at room temperature.

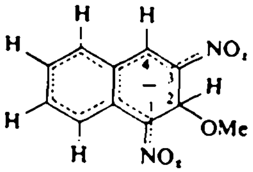
Addition of triethylamine to an acetone solution of picric acid gives only the picrate ion.

Further confirmation that attack by the acetonate anion only occurs at an unsubstituted position is given by the following observations. Addition of triethylamine to an acetone solution of 1,3-difluoro-2,4,6-trinitrobenzene causes the ring proton absorption to move from the "aromatic" value of $\delta = -9{\cdot}3_4$ to $\delta = -5{\cdot}1_1$, J(H—F) = 9·5 c/s, J(H—H) = 6 c/s characteristic of a proton attached to an sp^3-hybridised carbon atom in such systems. The solution shows an optical absorption in acetone at $\lambda_{max} = 450$ mμ. No reaction is observed when triethylamine is added to an acetone solution of 1,3,5-trichloro-2,4,6-trinitrobenzene.

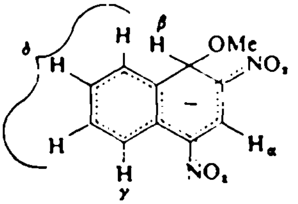
1,3-Dinitronaphthalene plus anion. When sodium methoxide is added to a solution of 1,3-dinitronaphthalene in DMSO, a deep purple-red solution is obtained (λ_{max} = 520 mμ). The PMR spectrum (Fig. 3) of the product is very different from that of 1,3-dinitronaphthalene which has absorptions at $\delta = -9{\cdot}2$; $-8{\cdot}7_5$; $-8{\cdot}3$ and $-7{\cdot}8_5$, the last two being multiplets. The PMR absorption spectrum of the product is in agreement with the structure XVIII, (Table 4). The chemical shift of H_a in XVIII ($\delta = -8{\cdot}9_0$) is consistent with the value of the corresponding proton in the ion II (R = R′ = —OMe), namely $\delta = -8{\cdot}6_8$. If the attack had occurred at the 2-position



XVIII



XIX



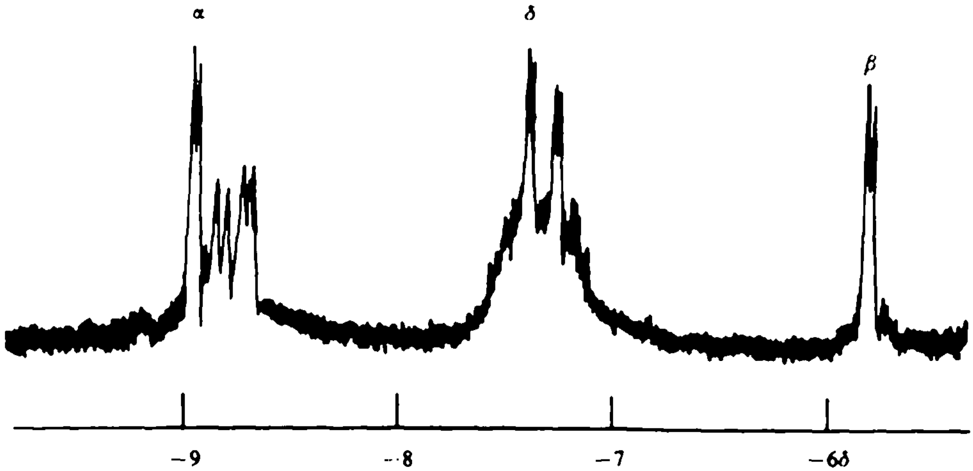


Fig. 3. Partial PMR spectrum of the ion XVIII in DMSO, showing the aromatic ring proton absorptions.

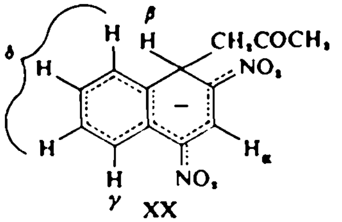
Table 4. PMR spectral data of anions derived from 1,3-dinitronaphthalene, 9-nitroanthracene and their alkoxy derivatives

	Chemical shifts ($-\delta$)				J(c/s)	
Formula	H_α	H_β	H_γ	H_δ	H_α—H_β	(H_β—CH_3)
XVIII	$8{\cdot}9_0$ (D)	$5{\cdot}7_5$ (D)	$8{\cdot}7_8$ (DD)[a]	$7{\cdot}3_0$ (M)	1·5	—[b]
XX	$8{\cdot}7_6$ (D)	$4{\cdot}8_1$ (T)	$8{\cdot}5_9$ (DD)	$7{\cdot}1_4$ (M)	~1	6[c]
				$7{\cdot}3_5$ (M)		
XXI	$9{\cdot}3_8$	—	$8{\cdot}8_1$ (DD)	$7{\cdot}7_8$ (M)	--	—[b]
XXII						
(R = —OMe)	—	$4{\cdot}9_6$	$8{\cdot}8_1$ (DD)	$7{\cdot}1_6$ (M)	—	—[b]
XXII						
(R = —CH_2COCH_3)	--	$4{\cdot}2_9$ (T)	$8{\cdot}7_2$ (DD)	$7{\cdot}0_6$ (M)	—	7[c]
				$7{\cdot}4_5$ (M)		
XXIII	--	--	$8{\cdot}9_3$ (DD)	$7{\cdot}1_3$ (M)	--	—[b]

[a] Doublet of doublets. [b] In DMSO. [c] In acetone.

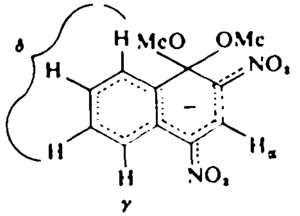
to form XIX, then the proton in the 4-position in XIX might be expected to absorb at about $\delta = -7\cdot8$ corresponding to similarly orientated protons in IV.*

Dilution of a solution of XVIII in DMSO with acetone results in a solvolysis similar to that obtained in the trinitrobenzene analogue. The PMR spectrum of the product (Table 4) is similar to that of XVIII except that the proton assigned to H_β in XVIII now appears as a triplet. The spectrum is accounted for in terms of the ion XX. The triplet arises from the coupling of H_β with the methylene protons of the acetonyl group.



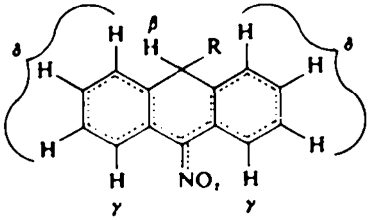
XX

Further support for structure XVIII is given by the PMR spectrum of the product formed by the action of methoxide on 2,4-dinitro-1-methoxynaphthalene. The red-coloured product absorbs at $\delta = -9\cdot3_2$, $-8\cdot8_1$ and $-7\cdot7_2$ in DMSO. These absorptions are assigned to the protons H_α, H_γ and H_δ respectively in structure XXI. Apart from the slight downfield shift of H_α, and the expected absence of an absorption corresponding to H_β in XVIII, the spectrum closely resembles that of XVIII. The correspondence with the H_γ and H_δ protons of XXII is nearly exact (*vide infra*).



XXI

9-Nitroanthracene plus anion. The PMR absorption spectrum of 9-nitroanthracene alone in DMSO shows a singlet ($\delta = -8\cdot9_3$) due to the proton in the 10-position together with three multiplets centred at $\delta = -8\cdot2$, $-7\cdot8$ and $-7\cdot7$ respectively. On addition of methoxide the solution becomes deep red ($\lambda_{max} = 505$ mμ). In the PMR spectrum (Fig. 4) the greatest change is in the absorption of the proton in the 10-position which moves to $\delta = -4\cdot9_6$. The remaining ring protons show a pattern very similar



XXII

---

* A referee has pointed out that a lower screening would be expected in XVIII or XIX, than in the analogous single-ring compounds II or IV, due to the second aromatic ring.

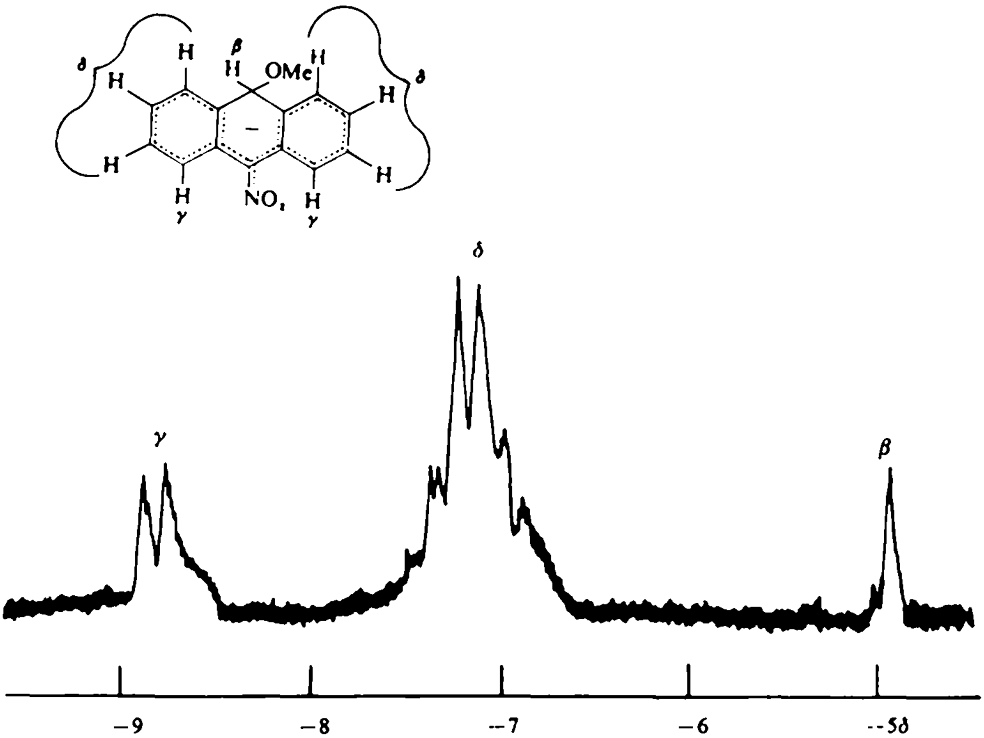
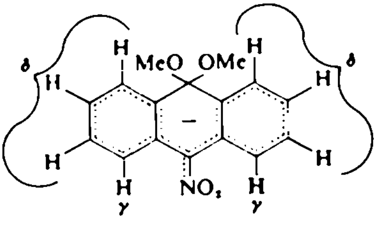


FIG. 4. Partial PMR spectrum of the ion XXII (R = —OMe) in DMSO, showing the aromatic ring proton absorptions.

to the absorption assigned to the protons marked γ, δ in XVIII and in XXI. These observations are consistent with the structure XXII (R = —OMe). The assignments are given in Table 4. Meisenheimer[13] described the isolation of a salt the anion of which we would now write as XXII (R = —OMe). Attempts to repeat the isolation have not been successful. Addition of acetone to XXII (R = —OMe) in DMSO yields the corresponding acetonyl δ-complex XXII (R = $-CH_2COCH_3$) (Table 4). Further confirmation for the structure XXII is obtained from the product formed by the action of methoxide on 9-nitro-10-methoxyanthracene. This has a PMR spectrum (Table 4) showing ring proton absorptions which are nearly identical with those of XXII (R = —OMe or $-CH_2COCH_3$) except that the absorption corresponding to the proton β in XXII is absent. This is to be expected on the basis of the assignments given if attack in this last case occurs at the 10-position to yield XXIII.



XXIII

---

[13] J. Meisenheimer, *Liebigs Ann.* 323, 205 (1902).

EXPERIMENTAL

NMR spectra 60 mc/s, 33·5°, using a Perkin–Elmer R10 spectrometer; using TMS as an internal reference.

2,4-Dinitroanisole was recrystallized twice from MeOH and once from CCl_4, m.p. 88°. 2,4-Dinitrophenetole was recrystallized from CCl_4, m.p. 85–86°. 1-(2′-Hydroxyethoxy)-2,4-dinitrobenzene was recrystallized twice from CCl_4, m.p. 111°. 2,6-Dinitroanisole was recrystallized twice from CCl_4, m.p. 118°. 1-(2′-Hydroxyethoxy)-2,6-dinitrobenzene was obtained only as a viscous oil. 1,3-Dinitrobenzene was recrystallized twice from EtOH, m.p. 148°. 1-Methoxy-2,4-dinitrobenzene was recrystallized twice from MeOH, m.p. 97°. 9-Nitroanthracene was recrystallized twice from glacial AcOH, m.p. 145–146°. 9-Methoxy-10-nitroanthracene was recrystallized twice from EtOH m.p. 156°. 2,4,6-Trinitrophenetole was recrystallized twice from EtOH, m.p. 78·5°. 2,4,6-Trinitro-N,N-dimethylaniline was recrystallized once from EtOH, m.p. 138°. 2,4,6-Trinitrodiphenyl ether was recrystallized twice from benzene–EtOH m.p. 153°. Picryl chloride was recrystallized twice from EtOH and once from CCl_4, m.p. 83°. 1,3-Dimethoxy-2,4,6-trinitrobenzene was recrystallized twice from EtOH, m.p. 125°. 1,3-Difluoro-2,4,6-trinitrobenzene was recrystallized twice from CCl_4, m.p. 147°. 1,3,5-Trichloro-2,4,6-trinitrobenzene was recrystallized twice from EtOH, m.p. 197°. 1,5-Dimethoxy-2,4-dinitrobenzene was recrystallized twice from MeOH, m.p. 158°. Dimethylsulphoxide (B.D.H.) was distilled from CaH_2, and stored over a molecular sieve (Linde Air Products, type 5A).

Acknowledgements—The authors wish to thank the Medical Research Council and the Science Research Council for financial support, also Fundamental Research Co. Ltd. Berkeley, California, for a gift of 1,3-dinitronaphthalene.

Note added in proof—In the reactions of polynitroaromatics with tertiary amines in ketonic solutions we have previously (Ref. 10) and in this paper suggested that the ketonic adducts are formed by attack of the ketonate anion on the polynitroaromatic substrate, the ketonate ion being formed initially by proton transfer to the amine. In fact we have no evidence that this is the mechanism. The interaction of the amine with the polynitroaromatic to form a complex (unspecified) at low concentration, followed by very fast solvolysis to yield the ketonate adduct is an alternative possibility.