Tetrahedron, 1965, Vol. 21, pp. 3363 to 3372. Pergamon Press Ltd. Printed in Northern Ireland

INTERACTION OF ELECTRON ACCEPTORS WITH BASES—XVI[1]

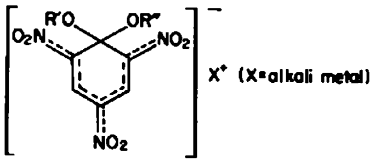
PROTON MAGNETIC RESONANCE SPECTRA OF MEISENHEIMER COMPOUNDS

R. Foster and C. A. Fyfe
Department of Chemistry, Queen's College, University of St. Andrews, Dundee, Scotland

(*Received* 23 *June* 1965; *in revised form* 17 *July* 1965)

Abstract—PMR spectra of several Meisenheimer compounds have been measured in various solvents. Evidence is given that in such products derived from 1,3,5-trinitrobenzene the alkoxy group is readily exchanged in solvolysis by the acetonyl group. Products formed in solution by various concentrations of methoxide on several different polynitroaromatics have also been studied.

Products formed by the action of alkali-metal alkoxides on picryl ethers were described by Meisenheimer.[2] The presently accepted structure for such compounds (I; R′ = alkyl, R″ = alkyl) has been supported by IR[3,4] by visible,[5–7] and recently by NMR spectroscopy.[8,9]



I

We have now extended the NMR study of such compounds.

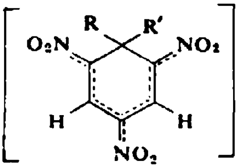
RESULTS AND DISCUSSION

Dialkoxy-Meisenheimer compounds. The data for the NMR spectra of five typical Meisenheimer compounds in various solvents are given in Table 1. The spectra are explicable in terms of structure I. The ring protons show an absorption at low fields, $\delta = -8{\cdot}9$ to $-8{\cdot}7$. The position of this absorption appears to be sufficiently constant to be characteristic of such systems. Crampton and Gold[8] report slightly differing values of $\delta = -8{\cdot}64$ and $\delta = -8{\cdot}78$ for I; R′ = R″ = Me in dimethylsulphoxide and in acetonitrile respectively.

---

[1] Part XV R. Foster and C. A. Fyfe, *Trans. Faraday Soc.* **61**, 1626 (1965).
[2] J. Meisenheimer, *Liebigs Ann.* **323**, 219 (1902).
[3] R. Foster and D. Ll. Hammick, *J. Chem. Soc.* 2153 (1954).
[4] L. K. Dyall, *J. Chem. Soc.* 5160 (1960).
[5] R. Foster, *Nature, Lond.* **176**, 746 (1955).
[6] R. Foster and R. K. Mackie, *J. Chem. Soc.* 3796 (1963).
[7] V. Gold and C. H. Rochester, *J. Chem. Soc.* 1687; 1692 (1964).
[8] M. R. Crampton and V. Gold, *J. Chem. Soc.* 4298 (1964).
[9] R. Foster, C. A. Fyfe and J. W. Morris, *Rec. Trav. Chim.* **84**, 516 (1965).

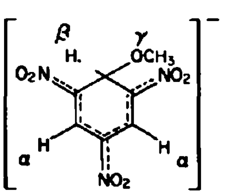
TABLE 1. CHEMICAL SHIFTS IN PPM FROM TETRAMETHYLSILANE OF PROTONS IN MESENHEIMER-LIKE COMPOUNDS IN VARIOUS SOLVENTS[a]

	CD_3COCD_3				CH_3COCH_3		CH_3CN		CH_3SOCH_3	
	α[b]	β	γ	δ	α	β	α	β	α	β
R = OMe R' = OMe	$-8{\cdot}8_8$	—	$-3{\cdot}1_4$	—	$-8{\cdot}9_0$	—	$-8{\cdot}8_6$	—	$-8{\cdot}7_1$	—
R = OEt R' = OEt	$-8{\cdot}8_4$	—	$-3{\cdot}3_0$ (Q)	$-1{\cdot}1_6$ (T)	$-8{\cdot}8_9$	—	$-8{\cdot}8_2$	—	$-8{\cdot}7_4$	—
R = OMe R' = OEt	$-8{\cdot}8_7$	—	$-3{\cdot}1_2$ $-3{\cdot}3_0$ (Q)	$-1{\cdot}1_5$ (T)	$-8{\cdot}8_8$	—	$-8{\cdot}8_0$	—	$-8{\cdot}6_9$	
R = OBu^n R' = OBu^n	$-8{\cdot}8_6$	—	(M)		$-8{\cdot}8_8$	—	$-8{\cdot}7_9$	—	$-8{\cdot}6_8$	—
R = OMe R' = OPr^i	$-8{\cdot}8_7$	—	(M) $-3{\cdot}1_1$	$-1{\cdot}0_8$	$-8{\cdot}8_9$	—	$-8{\cdot}8_4$	—	$-8{\cdot}6_8$	—
R = H R' = OMe	$-8{\cdot}6_7$ (D)	$-6{\cdot}3_0$ (T)	$-3{\cdot}3_0$	—	$-8{\cdot}6_6$ (D)	$-6{\cdot}3_3$ (T)	$-8{\cdot}6_5$ (D)	$-6{\cdot}3_2$ (T)	$-8{\cdot}5_2$ (D)	$-6{\cdot}2_3$ (T)
R = H R' = OEt	$-8{\cdot}5_8$ (D)	$-6{\cdot}3_0$ (T)	$-3{\cdot}6_8$ (Q)	$-1{\cdot}1_3$ (T)	$-8{\cdot}5_5$ (D)	$-6{\cdot}4_4$ (T)			$-8{\cdot}4_1$ (D)	$-6{\cdot}2_6$ (T)
R = H R' = CH_3COCH_3	$-8{\cdot}4_0$	$-5{\cdot}2_0$ (T)	$-2{\cdot}8_7$	$-2{\cdot}6_5$ (D)	$-8{\cdot}4_5$	$-5{\cdot}1_8$ (T)	$-8{\cdot}4_1$	$-5{\cdot}1_0$ (T)	$-8{\cdot}3_2$	$-5{\cdot}0_5$ (T)

[a] Band multiplicities are denoted: (D) = doublet; (T) = triplet; (Q) = quartet; (M) = higher multiplicity than four.

[b] The nomenclature α, β, γ, δ is defined in a footnote.

The Meisenheimer compounds derived from 1,3,5-*trinitrobenzene plus methoxide ions.* Lobry de Bruyn and Van Leent[10] obtained a solid product by addition of aqueous potassium hydroxide to a methanolic solution of 1,3,5-trinitrobenzene. This has a visible and IR spectrum[6] commensurate with structure II. This compound has been



[*]

II

---

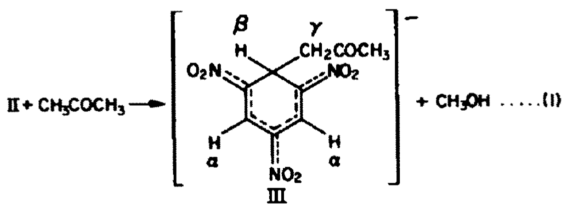
[*] In the following discussion when reference is made to a particular Meisenheimer compound, only the anion is considered. The spectra, both NMR and visible, appear to be little affected by the particular cation in the salt. "Aromatic" ring protons are labelled α, "aliphatic" ring protons are labelled β, other protons are labelled γ, δ and are marked in this and following formulae.

reprepared. A product has also been obtained by the action of methanolic sodium methoxide on methanolic 1,3,5-trinitrobenzene, both by spontaneous crystallization and by precipitation with dry ether. The superficial appearance of the product varies with the mode of preparation, and may in preparations from aqueous solvents include some water of crystallization. Nevertheless, although the product has been obtained in the form of green fluorescent plates, green needles and as a red-brown powder, all form red powders on grinding and have identical visible and NMR spectra in solution, and have satisfactory analyses. The NMR spectrum of this product in various solvents has been described recently by Crampton and Gold.[8] They reported the line at $\delta = -6{\cdot}2$ to be broad and suggested that this is an unresolved triplet, the result of spin-spin coupling of the β-proton by the two equivalent α-protons. This has been resolved as a triplet, $J(H\alpha\text{-}H\beta) \simeq 1$ c/s.

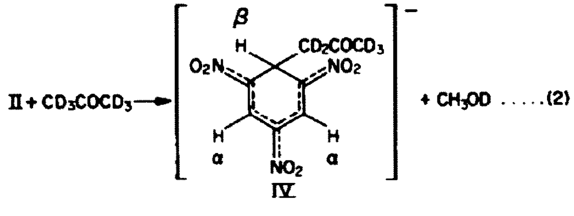
We have observed an alteration in the NMR spectrum of II in acetone with time (Fig. 1). The absorption at $\delta = -8{\cdot}66$ (doublet, $J \simeq 1$ c/s) assigned to Hα in structure II decreases with the increase of a new band, $\delta = -8{\cdot}47$ (doublet $J < 1$ c/s), and the absorption at $\delta = -6{\cdot}33$ (triplet, $J \simeq 1$ c/s) assigned to Hβ is gradually replaced by a band $\delta = -5{\cdot}18$ (triplet, $J \simeq 9$ c/s). The sum of the intensities of these lines remains constant throughout the change. This suggests that the same number of ring protons is involved in both the reactant and the product.

If the reaction is carried out in CD_3COCD_3 a broad band, instead of the triplet with acetone, is observed at $\delta = -5{\cdot}18$.

All these observations are consistent with the following solvolyses:



.....(1)



.....(2)

There is no evidence of deuterium exchange of the ring protons in reaction 2. The increased coupling constant for the absorption of the β-proton in III is consistent with the stronger coupling by the γ-methylene protons than the α-β coupling which give rise to a value of $J = 1$ c/s in II. Likewise the effect of the deuterons in the methylene group of IV accounts for the broadening of the absorption due to the β-proton in this compound. Kimura[11] has adduced chemical evidence in support of

[10] C. A. Lobry de Bruyn and F. W. Van Leent, *Rec. Trav. Chim.* **14**, 150 (1895).

[11] M. Kimura, *J. Pharm. Soc. Japan* **73**, 1219 (1953).

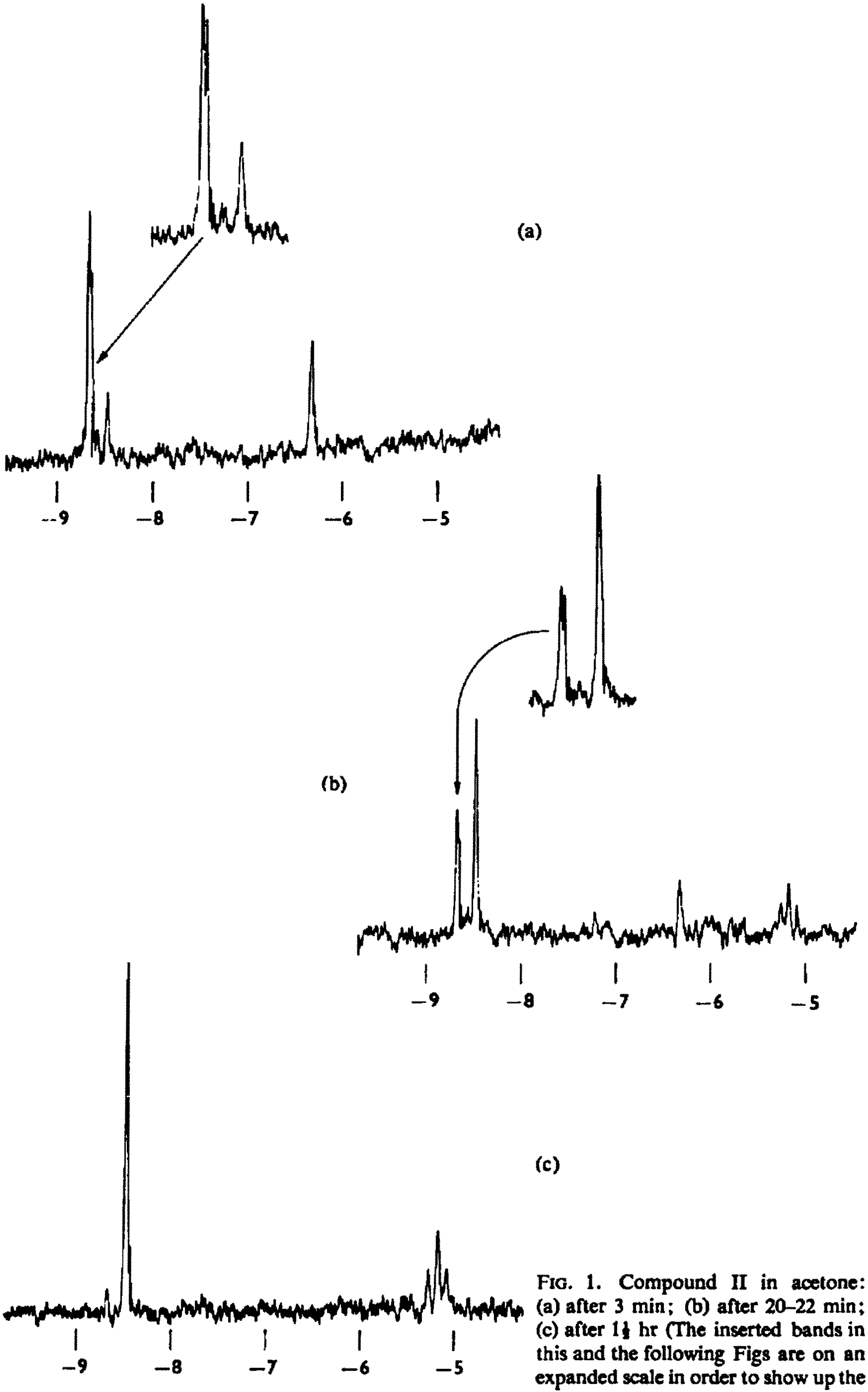


FIG. 1. Compound II in acetone: (a) after 3 min; (b) after 20–22 min; (c) after 1½ hr (The inserted bands in this and the following Figs are on an expanded scale in order to show up the particular band multiplicities).

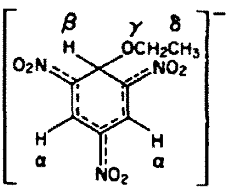
structure III for the product formed by the action of alkoxides on acetone solutions of 1,3,5-trinitrobenzene. Further support has been given from the work of Severin.[12]

When dimethylsulphoxide is used as solvent, again the spectrum is observed to alter with time. The doublet at $\delta = -8{\cdot}52$ shifts to $\delta = -8{\cdot}39$ and the triplet at $\delta = -6{\cdot}22$ moves slightly to $\delta = -6{\cdot}25$. In both reactant and product, $J(H\alpha\text{-}H\beta) \simeq 1$ c/s. This suggests that the product has a structure in which the bonding occurs through the sulphur or oxygen, since a linkage via a methylene group in the manner suggested above for acetone would give rise to a much larger coupling constant for the $H(\beta\text{-}\gamma)$ splitting as is the case for acetone.

Solutions in acetonitrile appeared to be stable for at least one week.

The Meisenheimer compound derived from 1,3,5-*trinitrobenzene and ethoxide ion.* By the action of potassium ethoxide on ethanolic solutions of 1,3,5-trinitrobenzene a product superficially similar to II is obtained.

The NMR spectrum suggests that, although slightly impure, the product has structure V. The position of the absorptions in the various solvents are given in Table 1. The absorptions due to the H_γ and H_δ protons could not be observed in acetone, dimethylsulphoxide or acetonitrile because of solvent absorption. The coupling constant $J(H\alpha\text{-}H\beta) \simeq 1$ c/s is similar to that observed for II. These lines combined with the absorption characteristic of the ethyl group observed in CD_3COCD_3 are in agreement with structure V. Further, the spectrum of this compound in acetone or CD_3COCD_3 changes with time in exactly the same manner as solutions of II to yield final spectra which are identical.



V

Confirmation that the compound III is eventually formed in the reaction of acetone solutions of II or V has been obtained by the isolation of the same solid product from six-hour-old solutions of either II or V in acetone by precipitation with dry ether. The spectrum of this solid in acetone is identical with that obtained from an aged solution of either II or V in acetone. The details of the spectrum of III in various solvents are given in Table 1.

The addition of methoxide ions to 1,3,5-*trinitrobenzene in acetone.* Spectra similar to those described in the previous section were also obtained without isolating the intermediate product. Addition of sodium methoxide to a solution of 1,3,5-trinitrobenzene in acetone causes a broadening and decrease and finally the disappearance of the line at $\delta = -9{\cdot}1$ due to 1,3,5-trinitrobenzene; a doublet at $\delta = -8{\cdot}57$ ($J \simeq 1$ c/s) and a triplet at $\delta = -6{\cdot}24$ ($J \simeq 1$ c/s) and a further small peak at $\delta = -8{\cdot}40$ appear. With time this last peak increases at the expense of the other two lines and a triplet appears at $\delta = -5{\cdot}12$ ($J = 5$ c/s). These results are in agreement with those given above for the formation of II and III.

---

[12] T. Severin and R. Schmitz, *Angew. Chem.* **75**, 420 (1963); T. Severin, R. Schmitz and H-L. Temme, *Chem. Ber.* **97**, 467 (1964).

The addition of methoxide ions to 1,3,5-*trinitrobenzene in dimethylsulphoxide.* Addition of methoxide causes the broadening and decrease in intensity of the absorption at $\delta = -9{\cdot}2$ due to 1,3,5-trinitrobenzene and the appearance of a doublet ($\delta = -8{\cdot}44$; $J \simeq 1$ c/s) and a triplet ($\delta = -6{\cdot}15$; $J \simeq 1$ c/s) identifiable from the above spectra as II. Addition of more methoxide causes the complete collapse of the band at $\delta = -9{\cdot}2$ and the replacement of the band assigned to Hα in structure II by a band at $\delta = -8{\cdot}6$. Further addition of methoxide causes a broadening of the displaced Hα band and a decrease in its intensity and a gradual increase in intensity of the Hβ band (Fig. 2). The additions were made rapidly to avoid significant

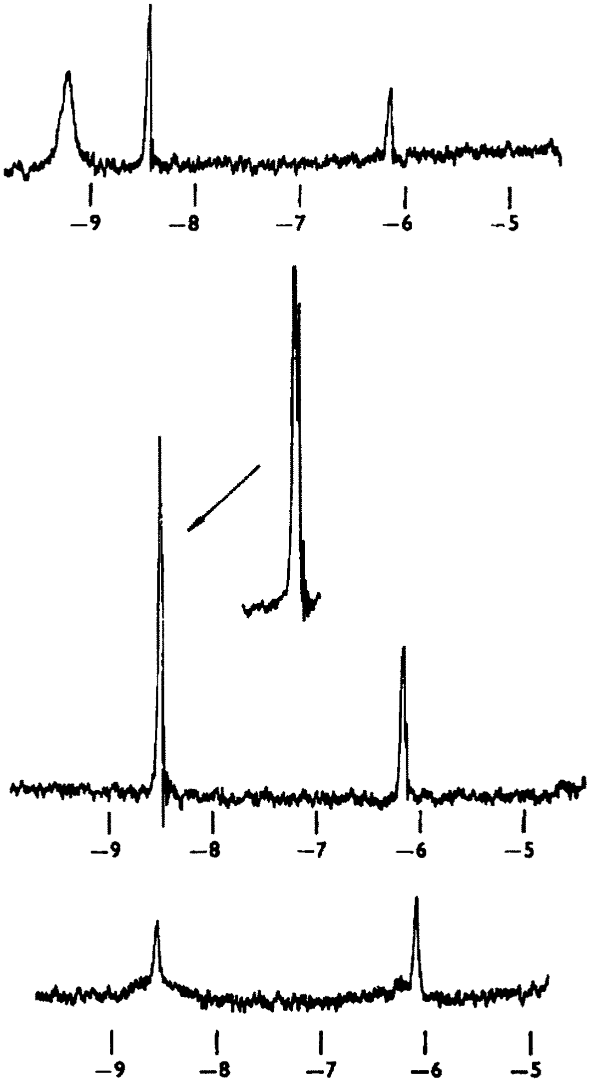
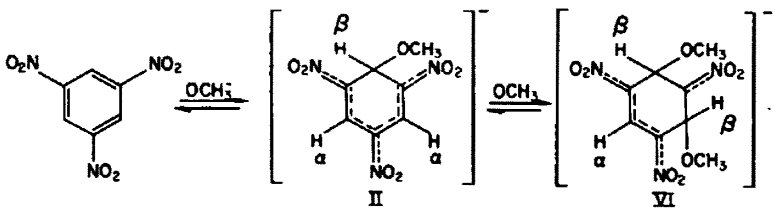


Fig. 2. 1,3,5-Trinitrobenzene in dimethylsulphoxide, with increasing concentration of added OCH$_3^-$.

concentrations of products formed by the slow solvolysis referred to above. The observations are consistent with the scheme:



.....(3)

which corresponds to the first two steps in the reaction of methoxide with 1,3,5-trinitrobenzene in methanolic solution proposed on the basis of the visible absorption spectra.[8]

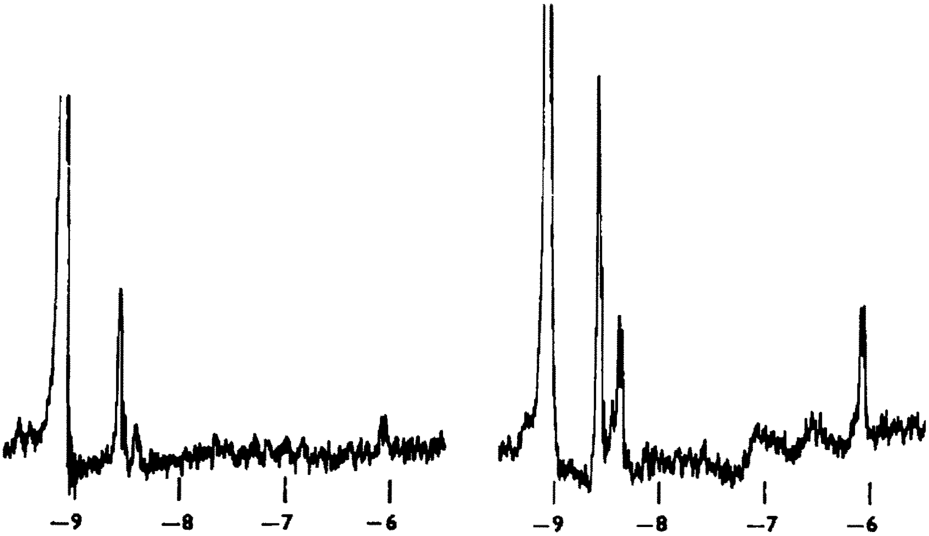
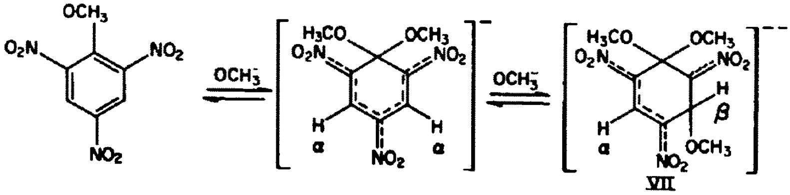


FIG. 3. 2,4,6-Trinitroanisole in dimethylsulphoxide, with increasing concentration of added OCH_3^-.

Addition of methoxide ions to 2,4,6-trinitroanisole in dimethylsulphoxide. Addition of small amounts of sodium methoxide to 2,4,6-trinitroanisole in dimethylsulphoxide causes the collapse of the trinitroanisole band at $\delta = -9{\cdot}2$ and the appearance of a singlet at $\delta = -8{\cdot}6$ and two small doublets at $\delta = -8{\cdot}36$ and $\delta = -6{\cdot}06$ ($J \simeq 2$ c/s). These absorptions increase as the concentration of methoxide is increased (Fig. 3). These have $J = 2$ c/s, and are of equal intensity. These successive spectra are consistent with the scheme:

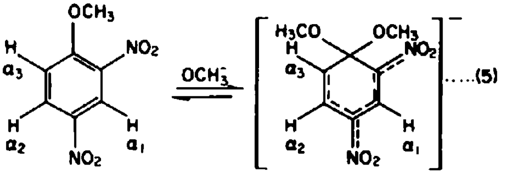


.....(4)

A species with structure VII has been proposed[6] for one of the products formed in methanolic solution by the action of concentrated methoxide on 2,4,6-trinitroanisole. A solid obtained by ether precipitation from the system in dimethylsulphoxide in the presence of a large excess of methoxide was shown by analysis to be the monovalent ion salt.

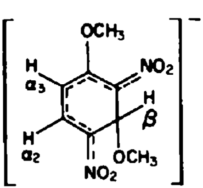
Addition of methoxide ions to 2,4,6-*trinitroanisole in acetonitrile.* When methoxide is added to such solutions, the absorption due to free 2,4,6-trinitroanisole ($\delta = -8{\cdot}98$) decreases and a singlet appears at $\delta = -8{\cdot}77$. This line intensifies and shifts slightly to $\delta = -8{\cdot}81$ as the methoxide is further increased until a point is reached where precipitation occurs. The absorption observed is consistent with the formation of the first product in reaction (4).

Addition of methoxide ions to 2,4-*dinitroanisole in dimethylsulphoxide.* The NMR spectrum of 2,4-dinitroanisole VIII in dimethylsulphoxide is given in Fig. 4. Gradual addition of methoxide reduces and broadens the lines due to VIII whilst a quartet appears at $\delta = -7{\cdot}26$ (J = 3 c/s; J = 10 c/s) and a doublet at $\delta = -5{\cdot}12$ (J = 10 c/s). (Fig. 4). These absorptions have been assigned to $H\alpha_2$ and $H\alpha_3$ in structure IX. The absorption of the protons $H\alpha_1$ in the product, corresponding to the absorptions $H\alpha_1$ in VIII at $\delta = -8{\cdot}79$, is not evident. One reason for believing it to be hidden under the absorption due to free VIII is that the $H\alpha_2$ proton absorption is split with approximately the same coupling constant as in VIII. Other evidence in support of $H\alpha_1$ being hidden is given below. Although the spectrum of the product is consistent with the structure IX, consideration should be given to structures X and XI. Evidence against these structures is that, at least for the corresponding trinitrobenzene compounds, the $H\beta$ absorption occurs at $\delta \simeq -6{\cdot}2$ which should be observable. Also in the trinitro compounds the value of $J(H\alpha\text{-}H\beta) \simeq 1$ c/s whereas in the present case J = 3 c/s. Further, attack by the nucleophile is at C_1 in 2,4,6-trinitroanisole: there seems no reason why attack should not be in the same position in the dinitro compound.

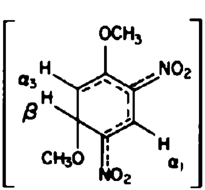


VIII IX

.....(5)



X



XI

As the concentration of methoxide is increased, there is complete disappearance of the absorption due to free 2,4-dinitroanisole. An absorption does remain in this region however (Fig. 4), which may be assigned to the $H\alpha_1$ proton in structure IX, which, it was suggested, might be hidden by the 2,4-dinitroanisole. In addition to the

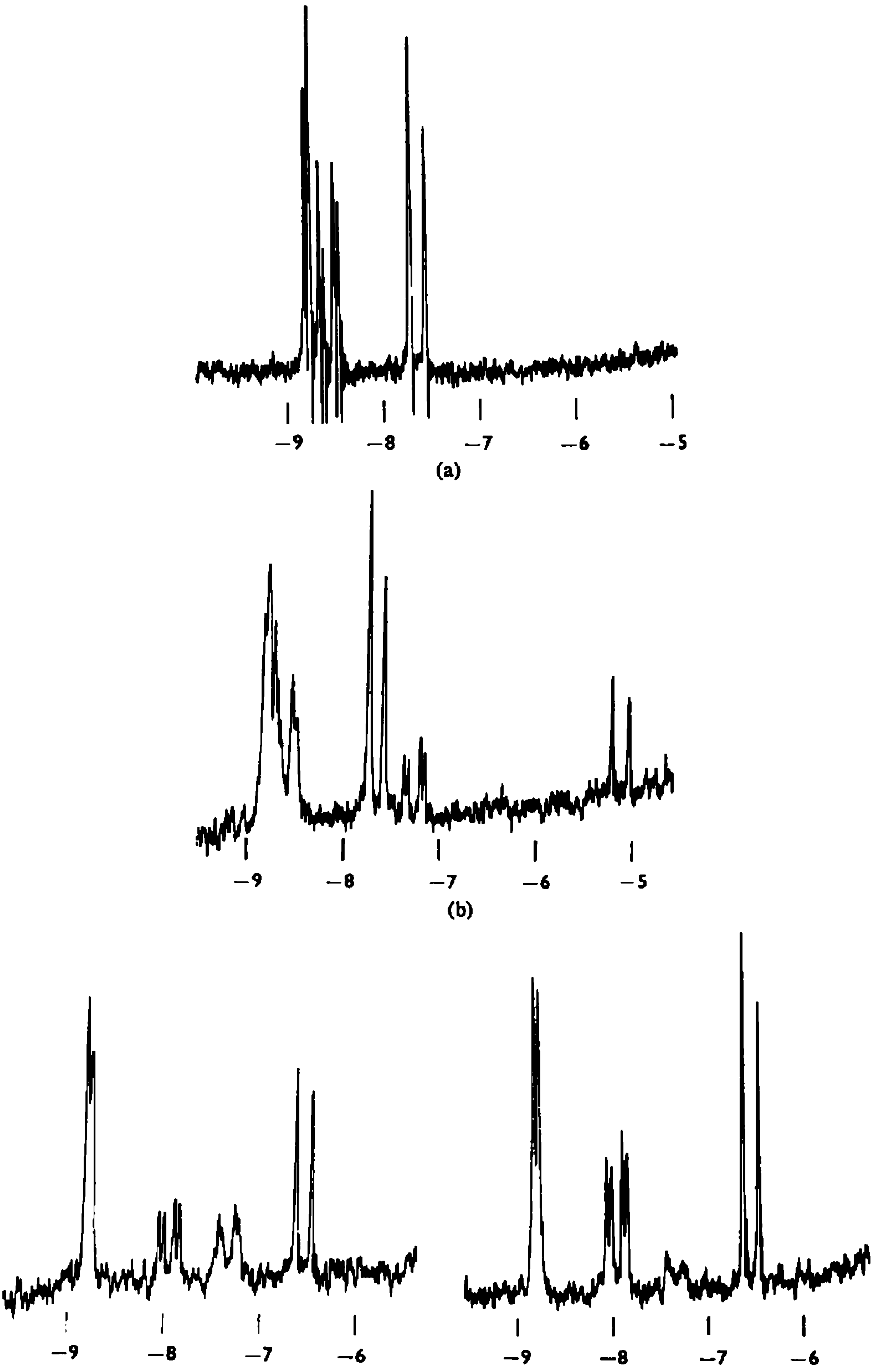
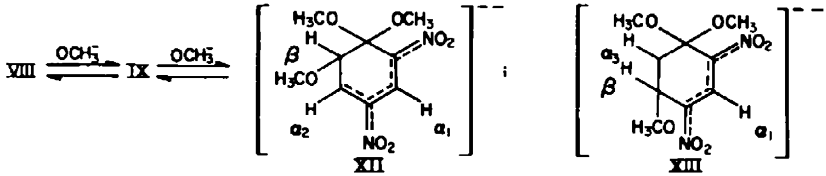


Fig. 4. (a) 2,4-Dinitroanisole in dimethylsulphoxide; (b), (c) with increasing concentration of added OCH_3^-; (d) solution (c) after 30 min.

three multiplets due to IX, there also appears a doublet at $\delta = -6{\cdot}48$ and a quartet at $\delta = -7{\cdot}9$. After standing for $\frac{1}{2}$ hour the absorption due to IX disappears, and there remains the spectrum of the second product (Fig. 4), to which we assign the structure XII in the sequence:



XII XIII

By analogy with the structure postulated for the dianion formed from 2,4,6-trinitroanisole, the dianion in the case of 2,4-dinitroanisole might be expected to have the structure XIII. This is contrary to the NMR spectrum. Three bands of equal intensity are observed, these are assigned a doublet, $H\alpha_1$ $\delta = -8{\cdot}80$ (J = 3 c/s); a quartet, $H\alpha_2$, $\delta = -7{\cdot}95$, (J = 3 c/s, J = 10 c/s); and a doublet $H\beta$, $\delta = -6{\cdot}55$ (J = 10 c/s). If there are no large changes in the chemical shift values for the various types of proton in the doubly charged ion compared with the singly charged ion (IX), which for the corresponding trinitroanisole derivatives appears to be the case, then it is reasonable to assign $H\alpha_1$ to the low field resonance, and the high field shift at $\delta = -6{\cdot}55$ to the "aliphatic" ring proton $H\beta$. Since the other "aromatic" ring proton is split by both $H\beta$ and $H\alpha$, this proton must be α_2 in structure XII; it could not be α_3 in structure XIII.

Addition of methoxide ions to 1,3-*dinitrobenzene in dimethylsulphoxide.* As the methoxide concentration is increased in this system, the NMR absorption due to 1,3-dinitrobenzene disappears and no other absorption is observed. This may be related to the observation by Pollitt and Saunders[13] of the formation of a free radical under these conditions.

EXPERIMENTAL

NMR spectra were measured at 60 mc/s, 33·5° using a Perkin-Elmer R10 spectrometer. All shifts are measured from the internal reference tetramethylsilane. *Dialkoxy Meisenheimer compounds* were prepared as described previously.[4,6]

Meisenheimer compounds from 1,3,5-*trinitrobenzene.* The potassium salt of II was prepared by adding a methanolic solution of 1,3,5-trinitrobenzene (2·5 g in 60 ml) to a solution containing 0·65 g KOH in 10 ml water. After 1 hr the mixture was filtered and the precipitate washed with a little MeOH and copious amounts of dry ether. (Found: C, 29·63; H, 2·54; N, 14·80. $C_7H_6N_3O_7K$ requires: C, 29·68; H, 2·13; N, 14·85%.) Further amounts were obtained by the addition of dry ether to the filtrate from the above preparation. (Found: C, 29·69; H, 2·63; N, 14·67. $C_7H_6N_3O_7K$ requires: C, 29·68; H, 2·13; N, 14·85%.) This compound was also prepared by the addition of MeOK (from 0·45 g K in 10 ml MeOH) to 1,3,5-trinitrobenzene (2·5 g) in MeOH (60 ml). The product was obtained by precipitation with dry ether. (Found: C, 29·67; H, 2·38; N, 14·78. $C_7H_6N_3O_7K$ requires: C, 29·68; H, 2·13; N, 14·85%.) The corresponding ethoxy compound decomposed before an analysis could be performed.

The acetonyl compound III was prepared as the potassium salt by dissolving the potassium salt of II in excess acetone and stirring slowly for 6 hr. Dry ether was then added when a dark-red crystalline material precipitated. (Found: C, 34·41; H, 2·62; N, 13·26. $C_9H_8N_3O_7K$ requires: C, 34·95; H, 2·61; N, 13·59%.)

Acknowledgement—The authors wish to thank the Medical Research Council for financial assistance.

[13] R. J. Pollitt and B. C. Saunders, *Proc. Chem. Soc.* 176 (1962).