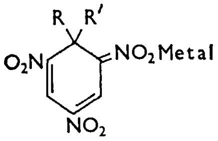
708. *Interaction of Electron Acceptors with Bases. Part IX.*[1] *The Action of Alkoxides on 1,3,5-Trinitrobenzene and on Picryl Ethers.*

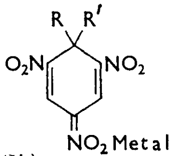
By R. Foster and R. K. Mackie.

The visible spectra of a series of Meisenheimer compounds have been measured and have been compared with the spectrum initially observed of mixtures of 1,3,5-trinitrobenzene and sodium methoxide. The changes in the latter spectrum with time have been measured. The effect of high concentrations of alkoxide on solutions of Meisenheimer compounds has also been determined.

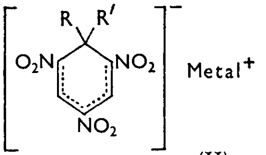
The structures (Ia, Ib; R = OMe, R′ = OEt) suggested by Meisenheimer[2] for the solid obtained from the interaction of 2,4,6-trinitroanisole with potassium or sodium ethoxide have been confirmed by solubility measurements[3,5] and by infrared[4] and ultraviolet spectroscopy.[6] Structures of the type (I) are now represented as (II) and termed " Meisenheimer compounds." Ainscough and Caldin[7] have suggested that in certain reactions of this type an *n*–π intermolecular charge-transfer complex is also formed by a very fast reaction. The orange-yellow solution obtained by mixing dilute ethanol solutions of 1,3,5-trinitrobenzene and sodium ethoxide has a visible absorption which changes with time. A kinetic study of the initial reaction shows only a very fast reaction, thought by Ainscough and Caldin[8] to be analogous to the charge-transfer complex formation observed with 2,4,6-trinitroanisole and ethoxide, although Caldin[9] admits the possibility of σ-bond formation. Because the initial visible spectrum is very similar to that of a Meisenheimer compound we[10] have suggested that this species has the structure (II; R = H, R′ = OEt).



(Ia)



(Ib)



(II)

Caldin and his co-workers[11] have observed two reactions in the interaction of 2,4,6-trinitrotoluene and ethoxide: a very fast reaction, yielding a brown solution, attributed to charge-transfer complex formation, and a slower reaction, giving a purple solution, ascribed to proton transfer. The visible spectrum did not resemble that of a Meisenheimer compound. These results suggest that the solid obtained by Hantzsch and Kissel[12] from potassium methoxide and 2,4,6-trinitrotoluene is the potassium salt of the 2,4,6-trinitrobenzyl anion.

Lobry de Bruyn[13] showed that the end-product of the reaction of sodium methoxide with 1,3,5-trinitrobenzene was 3,5-dinitroanisole. If, as we suppose, the initial product was the Meisenheimer compound (II; R = H, R′ = OMe), then the reaction was not the

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[1] Part VIII, Foster and Mackie, *Tetrahedron*, 1963, **19**, 691.
[2] Meisenheimer, *Annalen*, 1902, **323**, 205.
[3] Jackson and Gazzolo, *Amer. Chem. J.*, 1903, **29**, 89.
[4] Foster and Hammick, *J.*, 1954, 2685.
[5] Dyall, *J.*, 1960, 5160.
[6] Foster, *Nature*, 1955, **176**, 746.
[7] Ainscough and Caldin, *J.*, 1956, 2528.
[8] Ainscough and Caldin, *J.*, 1956, 2540.
[9] Caldin, *J.*, 1959, 3345.
[10] Foster, *Nature*, 1959, **183**, 1042.
[11] Caldin and Long, *Proc. Roy. Soc.*, 1955, *A*, **226**, 263; Ainscough and Caldin, *J.*, 1956, 2546.
[12] Hantzsch and Kissel, *Ber.*, 1899, **32**, 3137.
[13] Lobry de Bruyn, *Rec. Trav. chim.*, 1890, **9**, 208.

obvious simple nucleophilic substitution of a nitro-group. The action of other bases on 1,3,5-trinitrobenzene has been observed. It gave a red-brown product with aqueous alkali, 3,5-dinitrophenol and 3,3′,5,5′-tetranitroazoxybenzene being two of the products.[13] The latter product has also been obtained by the action of sodium carbonate,[14] sodium polysulphide,[15] and *N*-phenylhydroxylamine.[16] Recently, Izzo[17] has reported a 60—80% yield of 3,5-dinitroanisole by the action of sodium or potassium hydrogen carbonate or sodium carbonate in 76% aqueous methanol. Solutions of 1,3,5-trinitrobenzene plus sodium hydroxide yield coloured solutions which fade—this is increased by exposure to light.[18] The final products include the nitrite ion and ammonia. In the dark, the rate of nitrite formation is smaller than that of fading. This requires at least one intermediate species, which Gold and Rochester[18] suggest should be colourless. In light, the rates of fading and of nitrite formation are about equal, and the final solution contains almost equivalent amounts of nitrite and 3,5-dinitrophenol in about 95% total yield. Lack of deuterium exchange indicates that the interaction of hydroxide ion with 1,3,5-trinitrobenzene does not proceed by proton transfer.[19]

The visible spectra of a series of Meisenheimer compounds have now been measured. The results are compared with those for the reaction between methoxide and 1,3,5-trinitrobenzene. Further changes in the spectra with time, and by increased alkali concentration, have been observed.

RESULTS AND DISCUSSION

Visible Absorption Spectra of Dialkoxy-Meisenheimer Compounds.—The details of the spectra are summarised in Table 1. All the spectra show two maxima in the region 400—800 mμ; the high-energy band is the more intense. The absolute intensities and positions of the bands show little variation with changes in the alkoxy-groups. This is to be expected from structure (II), in which these groups are isolated from the chromophoric trinitropentadienyl anion system. There is a bathochromic shift of the high-energy maxima on altering the solvent from an ether to the more ionising solvent methanol. This behaviour has been related to a π–π * transition.[20] The low-energy band shows a corresponding hypsochromic shift; this is associated with an π–π * transition.[20] Solutions in acetonitrile and acetone are particularly stable; the solvent may in these cases participate in bond formation. Thus, for solutions of *m*-dinitrobenzene,[21] 1,3,5-trinitrobenzene, and their derivatives,[22] in acetone there is evidence of covalent bonding of an acetone moiety in the presence of a strong base.

In dilute methanolic solutions of sodium methoxide, 2,4,6-trinitroanisole has an absorption spectrum virtually identical with that of the corresponding Meisenheimer compound in methanol (Table 2). The intensities of the two bands increase, with increasing concentration of methoxide; above *ca.* 1M-methoxide, the low-energy band appears to shift to shorter wavelengths and the high-energy band decreases in intensity until, above 3M-methoxide, only one maximum is observed (Table 2). These changes can be reversed by the dilution of freshly made solutions. After heating, or prolonged storage, such solutions in concentrated methoxide yield 2,4-dimethoxy-1,3,5-trinitrobenzene. A second product has been isolated from the mixture; it appears to be one of the two compounds

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[14] Lobry de Bruyn and Van Leent, *Rec. Trav. chim.*, 1894, **13**, 148.
[15] Blanksma, *Rec. Trav. chim.*, 1909, **28**, 112.
[16] Meisenheimer, *Ber.*, 1920, **53**, 369.
[17] Izzo, *J. Org. Chem.*, 1959, **24**, 2026.
[18] Gold and Rochester, *Proc. Chem. Soc.*, 1960, 403.
[19] Ketelaar, Bier, and Vlaar, *Rec. Trav. chim.*, 1954, **73**, 37.
[20] McConnell, *J. Chem. Phys.*, 1952, **20**, 700.
[21] Canback, *Farm. Rev.*, 1949, **48**, 153, 217, 234; *Svensk, Farm. Tidskr.*, 1949, **53**, 151; 1950, **54**, 1; Foster and Mackie, *Tetrahedron*, 1962, **18**, 1131.
[22] Kimura, *Pharm. Bull. (Tokyo)*, 1955, **3**, 75.

TABLE 1.

Absorption maxima of some Meisenheimer compounds.

[Structure (II)] R	R′	Cation	Solvent	λ_1 (mμ)	ε_1 (mole^{-1} l. cm.$^{-1}$)	λ_2 (mμ)	ε_2 (mole^{-1} l. cm.$^{-1}$)
MeO	MeO	K$^+$ [a]	Methanol	414	26,000 [b]	487	18,000 [b]
			Acetone	420	29,000	494	19,000
			Acetonitrile	421	29,000	494	19,000
			Dioxan	406	[c]	512	[c]
			EGDME [d]	409	28,000	502	22,000
			THF [e]	407	25,000	504	21,000
MeO	EtO	K$^+$	Acetone	421	29,000	495	19,000
			Acetonitrile	423	27,000	496	18,000
			Dioxan	408	[c]	514	[c]
			EGDME [d]	410	25,000	502	19,000
			THF [e]	409	22,000	505	17,000
EtO	EtO	K$^+$	Ethanol	412	21,000	493	15,000
			Acetone	422	30,000	495	19,000
			Acetonitrile	425	25,000	496	16,000
			Dioxan	408	[c]		[c]
			EGDME [d]	413	26,000	502	20,000
			THF [e]	410	24,000	508	18,000
MeO	Pr^{i}O	K$^+$	Acetone	421	30,000	494	18,000
			Acetonitrile	423	25,000	495	15,000
			Dioxan	408	[c]	517	[c]
			EGDME [d]	411	25,000	504	19,000
			THF [e]	410	24,000	509	20,000
Pr^{i}O	Pr^{i}O	K$^+$	Acetone	427	30,000 [f]	502	19,000 [f]
MeO	MeO	Na$^+$ [a]	Acetone	420	29,000	494	19,000
MeO	MeO	Li$^+$ [a]	Acetone	420	29,000 [f]	494	19,000 [f]

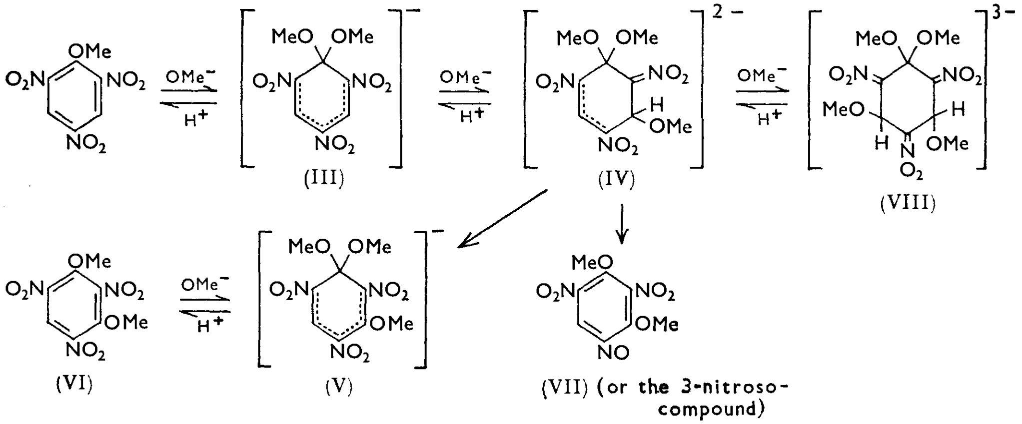
[a] Contains MeOH of crystallisation. [b] Value extrapolated to time of mixing. [c] Solid dissolved slowly and solution faded rapidly, thus it was not possible to determine ε. [d] Ethyleneglycol dimethyl ether. [e] Tetrahydrofuran. [f] Measured by Mr. T. J. Thomson.

TABLE 2.

Absorption Spectra of 2,4,6-trinitroanisole in the presence of sodium methoxide in methanol.

[NaOMe] (M)	λ_1 (mμ)	ε_1 (mole^{-1} l. cm.$^{-1}$)	λ_2 (mμ)	ε_2 (mole^{-1} l. cm.$^{-1}$)
0·14	412	27,000	488	19,000
0·5	412	34,000	489	24,000
1·0	412	36,000	489	25,000
2·7	416	10,000	482	24,000
2·9	420sh	8,000sh	482	24,000
3·3	—	—	482	19,000

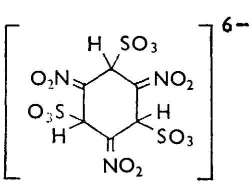
2,4-dimethoxy-1,3(5)-dinitro-5(3)-nitrosobenzene. These observations may be explained by the following scheme:



(III) (IV) (VIII)

(VI) (V) (VII) (or the 3-nitroso-compound)

The Meisenheimer compound (III), formed in low concentrations of methoxide, is converted into (V) by reaction with a second methoxide ion at higher concentrations. The decrease in extinction coefficient of the band at 482 mμ [assigned to (IV)] at very high concentrations of methoxide (Table 2) suggests that a 1 : 3 adduct (VIII) may be formed under these conditions. On heating, or prolonged storage, nucleophilic substitution occurs at C-3 to form (V). Elimination of OMe^- and OH^- gives (VII). 2,4-Dimethoxy-1,3,5-trinitrobenzene gives an orange solution in methanolic methoxide ($\lambda_{max.} = 465$ mμ, $\varepsilon = 21,000$). Since this absorption is unaffected by changes in the methoxide concentration, it is probable that only the univalent Meisenheimer compound (V) is formed. Addition of acid regenerates (VI). The absorption spectrum of the nitroso-compound (VII) is unaffected by the presence of methoxide ion; it is likely, therefore, that the nitroso-compound (VII) is present in the reaction mixture as the uncomplexed molecule shown. Structures corresponding to (IV) have been suggested by Cuta and Pisecky [23] and by Abe [24] for the products of the reaction between 1,3,5-trinitrobenzene and concentrated sodium hydroxide, and by Cuta and Beranek [25] for the action of concentrated cyanide, sulphite, or sulphide on 1,3,5-trinitrobenzene. Indeed, in very concentrated solutions of sulphite, for example, the sexavalent ion (IX) has been suggested. Henry [26] has recently isolated a solid which may be the corresponding 2 : 1 adduct.



(IX)

Visible Absorption Spectra of Methanolic Solutions of 1,3,5-*Trinitrobenzene plus Methoxide*.—The preparation of the solid obtained by Lobry de Bruyn and Van Leent [27] from potassium hydroxide and 1,3,5-trinitrobenzene in methanol has been repeated. The absorption spectrum of a methanolic solution is identical with that of 1,3,5-trinitrobenzene in the presence of low concentrations of methoxide. Within a few minutes, however, the spectra alter considerably. The initial spectrum closely resembles those of the dialkoxy-Meisenheimer compounds. This is very marked with acetone solutions (Table 3). The solid also has a similar visible spectrum. Furthermore the infrared spectrum of the solid bears a considerable resemblance to that of a typical Meisenheimer compound. The series of bands between 1225 and 1040 cm.$^{-1}$ noted by Dyall [5] is observed, as is the absence of the strong asymmetric N–O stretching band at 1552 cm.$^{-1}$. The strong broad band observed near 1300 cm.$^{-1}$ has been previously assigned to the nitro-groups carrying an increased negative charge.[4,5] This evidence suggests that the initial species involved in methanolic solutions of 1,3,5-trinitrobenzene, in the presence of methoxide, is the Meisenheimer compound (II; R = H, R′ = OMe).

TABLE 3.

Absorption maxima of: Adduct from 1,3,5-trinitrobenzene, potassium hydroxide and methanol; 1,3,5-trinitrobenzene + methoxide in methanol; and of a typical dialkoxy-Meisenheimer compound.

System	State	Maxima (mμ) [a]		
Adduct	Solid	408 ± 2	510sh	550 ± 5
Meisenheimer (II; R = R′ = OMe) K$^+$	Solid	414 ± 2	500sh	545 ± 6
Adduct	Methanol soln.	427 ↓	473 ↑	500 ↓
1,3,5-Trinitrobenzene + NaOMe	Methanol soln.	427 ↓	473 ↑	500 ↓
Adduct	Acetone soln.	428	490sh	513
Meisenheimer (II; R = R′ = OMe) K$^+$	Acetone soln.	420	470sh	494

[a] ↓ Indicates maximum which decreases in intensity with time; ↑ maximum which increases in intensity with time.

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[23] Cuta and Pisecky, *Chem. Listy*, 1957, **51**, 433; *Coll. Czech. Chem. Comm.*, 1958, **23**, 628.

[24] Abe, *Bull. Chem. Soc. Japan*, 1960, **33**, 41.

[25] Cuta and Beranek, *Chem. Listy*, 1957, **51**, 1669; *Coll. Czech. Chem. Comm.*, 1958, **23**, 1501.

[26] Henry, *J. Org. Chem.*, 1962, **27**, 2637.

[27] Lobry de Bruyn and Van Leent, *Rec. Trav. chim.*, 1895, **14**, 150.

The spectra of methanolic solutions of 1,3,5-trinitrobenzene, in the presence of 0·03M-methoxide, fade with time. The rate of fading is considerably increased by exposure to light; this agrees with the observations, referred to above, by Gold and Rochester [18] for the 1,3,5-trinitrobenzene–hydroxide system. However, neither light nor the addition of small quantities of water affects the profile of the spectrum. The initial Meisenheimer-like spectrum ($\lambda_{max.} = 427$, 500 mμ) alters with time; in dilute methoxide a maximum appears at 473 mμ, but in concentrated solutions this band is not observed. After a considerable time, in all cases, a single maximum is observed at about 510 mμ. In the early stages of the reaction, the colour is completely discharged by acid, but in the later stages a band at 480 mμ is obtained on acidification. Under the conditions used in the preparation of 3,5-dinitroanisole, two maxima (429, 503 mμ) are observed initially. On boiling the solution for 15 min. the colour fades and a new absorption band appears at 342 mμ; this band corresponds to the absorption of 3,5-dinitroanisole in the above environment. It appears that the initial Meisenheimer compound decomposes to give first a species with $\lambda_{max.} = 473$ mμ and then a species with $\lambda_{max.} \sim 510$ mμ, the final product being 3,5-dinitroanisole. Neither of these bands can be attributed to complexed 3,5-dinitroanisole, which only shows a weak absorption band ($\lambda_{max.} = 525$ mμ, $\varepsilon = 1600$) in the presence of *ca.* 5M-methoxide; no absorption is observed in 0·5M-methoxide. Also, 3,3′5,5′-tetranitroazoxybenzene, in alkaline solution does not have an absorption at these wavelengths. Thus the nature of the intermediate species remains undetermined.

EXPERIMENTAL

Materials.—1,3,5-Trinitrobenzene, recrystallised four times from ethanol and twice from carbon tetrachloride, had m. p. 123°. 2,4,6-Trinitroanisole, prepared by Borsche's method [28] and recrystallised from methanol, had m. p. 68°. 2,4,6-Trinitrophenetole, prepared by Willgerodt's method [29] and recrystallised from ethanol, had m. p. 78°. 2,4-Dimethoxy-1,3,5-trinitrobenzene, prepared by Sudborough and Picton's method [30] and recrystallised from methanol, had m. p. 127°. 3,3′,5,5′-Tetranitroazoxybenzene, prepared by Lobry de Bruyn and Van Leent's method [14] and recrystallised from chloroform, and then from concentrated nitric acid, had m. p. 187°.

Meisenheimer Compounds. These were prepared substantially as described by Dyall.[5] In agreement with Dyall, it was found that the action of potassium methoxide on phenyl picrate yielded potassium methyl 1-methoxypicrate. It was possible to prepare potassium isopropyl 1-isopropoxypicrate by the action of potassium isopropoxide on picryl chloride, a reaction reported by Dyall to give a tar. This compound was also prepared by the action of potassium isopropoxide on isopropyl picrate.

Spectra.—These were measured with an Optica CF4DR recording spectrophotometer. For evaluation of extinction coefficients the optical densities at the maxima were remeasured with an Optica CF4 manually-operated spectrophotometer. Spectra of solids were measured on Nujol mulls sandwiched between microscope slides.

The Action of Potassium Hydroxide on a Methanolic Solution of 1,3,5-*Trinitrobenzene.*—A solution of 1,3,5-trinitrobenzene (5 g.) in methanol (120 ml.) was added to concentrated aqueous potassium hydroxide (1·3 g.). After 1 hr., the solution was filtered and the precipitate then washed with methanol followed by ether, and dried (P_2O_5) (Found: C, 29·1; H, 2·6. Calc. for $C_7H_6N_3OK,\frac{1}{2}H_2O$: C, 28·8; H, 2·4%).

The Action of Sodium Methoxide on 2,4,6-*Trinitroanisole.*—The products obtained by acidification of solutions from reactions carried out under various conditions are given in Table 4. The 2,4-dimethoxy-1,3,5-trinitrobenzene obtained had m. p. and mixed m. p. 127°; the infra-red spectra were also identical. 2,4-*Dimethoxy*-1,3(5)-*dinitro*-5(3)-*nitrosobenzene* was isolated by washing the precipitate, obtained on acidification, with methanol in which it is only slightly soluble. It was then recrystallised from methanol–benzene as pale yellow needles, m. p. 189° (decomp.) (Found: C, 37·2; H, 3·0; N, 16·6; O, 43·2. $C_8H_7N_3O_4$ requires C, 37·4; H, 2·7;

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[28] Borsche, *Ber.*, 1923, **56**, 1941.
[29] Willgerodt, *Ber.*, 1879, **12**, 1277.
[30] Sudborough and Picton, *J.*, 1906, **89**, 592.

TABLE 4.

Products of reaction of 2,4,6-Trinitroanisole (TNA) with sodium methoxide in methanol.

[NaOMe] (M)	Conditions	Recovered products on acidification
1	Room temp. 96 hr.	100% TNA
1	Reflux 1 hr.	100% TNA
2	Reflux 2 hr.	50% TNA + 5% nitroso-compound
3	Reflux 15 min.	30% (VI)
3	Reflux 15 min., set aside for further 30 min.	20% (VII)
3	Room temp. 96 hr.	30% (VI)
3[a]	Reflux 15 min.	10% (VII)

[a] Solution prepared by dissolving sodium hydroxide in methanol.

N, 16·3; O, 43·6%). The infrared spectrum closely resembles that of 2,4-dimethoxy-1,3,5-trinitrobenzene. Solutions in benzene or chloroform are green, due to a weak absorption band (784 mμ in benzene, 781 mμ in chloroform). This is characteristic of nitroso-compounds.[31] The absorption is concentration dependent; in benzene $\varepsilon = 25$, at 784 mμ, for a 10^{-2}M-solution, and $\varepsilon = 33$, at 784 mμ, for a 10^{-3}M-solution. The corresponding change for chloroform solutions is from 15 to 33. The extinction coefficient increases with temperature; for a 10^{-3}M-solution in chloroform, $\varepsilon = 29$ at 784 mμ and 12°, 32 at 17°, 36 at 25°, and 41 at 31°. The above changes correspond to the dissociation of the colourless dimer to the monomer with increased dilution and with elevated temperature.[32]

This work was carried out during the tenure, by R. K. M., of a Postgraduate Scholarship, Queen's College, University of St. Andrews, and of a supplementary award of the University of St. Andrews.

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[*Received, November 26th*, 1962.]

[31] Gowenlock and Lüttke, *Quart. Rev.*, 1958, **12**, 325.

[32] Ingold and Piggott, *J.*, 1924, **125**, 168; Lüttke, *Angew. Chem.*, 1958, **70**, 442; Keussler and Lüttke, *Z. Electrochem.*, 1959, **63**, 614.