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INTERACTION OF ELECTRON ACCEPTORS WITH BASES—VIII[1]

FURTHER CONSIDERATIONS OF THE JANOVSKY REACTION

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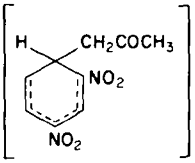
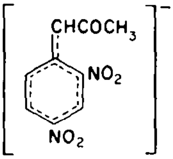
Abstract—Deuterium exchange is observed in methanolic solutions of *m*-dinitrobenzene in the presence of the methoxide ion. No visible absorption characteristic of the Janovsky reaction is observed in this system. Consequently there appears to be little support for the suggestion (based on similar exchange reactions) that the blue colour obtained with the same system in dimethylformamide or dimethylsulphoxide is necessarily due to the dinitrophenyl anion.

Many compounds which have weakly acidic hydrogen atoms appear to be effective in the Janovsky reaction.

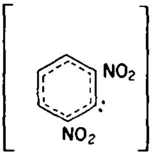
RECENTLY[2] evidence was adduced to support the σ-complex structure I for the coloured product formed by *m*-dinitrobenzene in acetone solution in the presence of a base (the Janovsky reaction), a structure which had previously been suggested by other workers.[3] The product formed in the related Zimmermann reaction appears to have structure II. The medium for this reaction is usually an ethanolic solution of sodium ethoxide.[2]



I



II



III

Pollitt and Saunders[4] have now suggested that in certain cases it is the ion III which is responsible for the colour in Janovsky-like reactions. The previous objection to this had been that no deuterium exchange is observed with 1,3,5-trinitrobenzene in the presence of 8N sodium hydroxide.[5,6] However Pollitt and Saunders have shown that deuterium exchange does occur in *m*-dinitrobenzene in dimethylformamide in the presence of 0·005 N sodium hydroxide, which system shows an intense Janovsky-like colour.

RESULTS AND DISCUSSION

Solutions of *m*-dinitrobenzene in methanolic sodium hydroxide show exchange with added deuterium oxide. Such solutions show no visible absorption which

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[1] Part 7. R. Foster and T. J. Thomson, *Trans. Faraday Soc.* Accepted for publication.

[2] R. Foster and R. K. Mackie, *Tetrahedron*, **18**, 1131 (1962).

[3] E. g. T. Canback, *Farm. Revy.* **48**, 153, 217, 234 (1949); *Svensk. Farm. Tid.* **53**, 151 (1949); **54**, 1 (1950).

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

[5] J. A. A. Ketelaar, A. Bier and H. T. Vlaar, *Rec. Trav. Chim.* **73**, 37 (1954).

[6] R. E. Miller and W. K. F. Wynne-Jones, *J. Chem. Soc.* 2375 (1959).

corresponds with the "Janovsky" colour. Pollitt and Saunders[4] explanation in terms of the ion III would require the ion to be short lived in methanolic solution, but long lived in acetone. An alternative explanation is also tenable, namely that such an ion, if it is formed, is short lived in either solvent and is not responsible for the characteristic visible absorption.

It would appear that many compounds which contain a hydrogen atom of within a certain range of acidity, and not merely ketones, will give a positive Janovsky reaction. For example it is reported that nitromethane[7,8] and indene[8] give positive reactions.

We have now observed this reaction with a wide range of such compounds. (Table 1). The original Janovsky reaction required the ketone to serve as the solvent. Several of the substances listed in Table 1 are in fact solid at room temperature; for these solutions in ethanol were used. The ratio of substrate to base was made very high in order to minimize hydrogen abstraction by the Zimmermann reaction.[2] It would appear from Table 1 that if the conjugate base ion of the substrate is sufficiently

TABLE 1. REACTION OF VARIOUS SUBSTRATES WITH *m*-DINITROBENZENE IN THE PRESENCE OF OH^- OR OEt^- UNDER JANOVSKY-LIKE CONDITIONS

	p*Ka*[a]	Reaction	λ_{max} (mμ)
Nitromethane	10·2[b]	+[7,8]	542
Nitroethane	8·5[b]	−	
Acetylacetone	9[b]	−[8]	
Acetonylacetone	18·7[c]	+[8]	567
Di-isopropylketone		+	561
t-Butylphenylketone		−	
Biacetyl		−	
Dimedone		−	
2-Pyrrolidone		+	525
γ-Butrolactone		+	555
Malononitrile	11·2[b]	−	
Ethyl cyanoacetate	9[b]	+[8]	557
Diethyl malonate	13·3[b]	+[8]	556[e,f]
Acetylene	26[d]	−	
Phenylacetylene	21[g]	+	550
Indene	21[g]	+[8]	500
Fluorene	25[g]	+	552
Xanthene	29[g]	+	550[e]
Triphenylmethane	33[g]	+	480[e]
2-Nitrotoluene		+	548
4-Nitrotoluene		+	508

[a] Approximate p*Ka* values.
[b] R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.* **75**, 2439 (1953).
[c] R. P. Bell, *Trans. Farad. Soc.* **39**, 253 (1943).
[d] W. S. Wooding and W. C. E. Higginson, *J. Chem. Soc.* 774 (1952).
[e] Very weak absorption.
[f] Second maximum at 472 mμ.
[g] W. K. McEwen, *J. Amer. Chem. Soc.* **58**, 1124 (1936).

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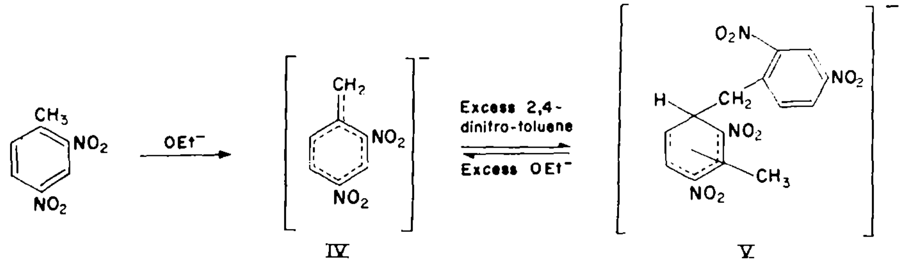
[7] T. Urbanski, *Bull. Acad. Polon. de Sciences* **9**, 321 (1961).

[8] J. Gough, *Part II Thesis, Oxford University* (1953).

stable then no coloured complex is formed. This would account for the lack of reaction by nitroethane. Such a relationship was first suggested by Gough.[8]



An interesting situation occurs with 2,4-dinitrotoluene. As 2- and 4-nitrotoluenes give Janovsky reactions with *m*-dinitrobenzene, 2,4-dinitrotoluene might be expected to act in the roles of both *m*-dinitro-compound and the substrate to yield a σ-complex.

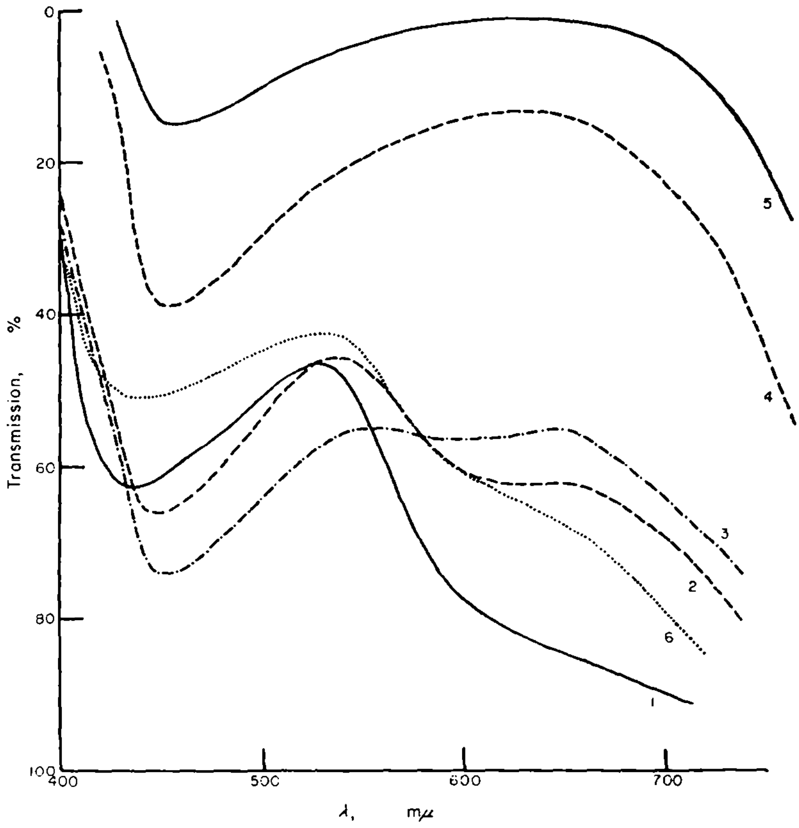


FIG. 1. Visible absorption spectra of ethanolic solutions of 2,4-dinitrotoluene (A) in the presence of sodium ethoxide (B). All spectra save (6) have been measured at 17°C. (1) [A] = 1·3 × 10^{-2} M, [B] = 1·2 × 10^{-2} M; (2) [A] = 0·96 × 10^{-3} M, [B] = 6·1 × 10^{-2} M; (3) [A] = 2·25 × 10^{-3} M, [B] = 0·18 M; (4) [A] = 2·7 × 10^{-3} M, [B] = 0·50 M; (5) [A] = 4·5 × 10^{-3} M, [B] = 0·41 M; (6) Same concentrations as solution (5), −70°C.

In the presence of relatively low concentrations of base, ethanolic solutions of 2,4-dinitrotoluene have an absorption maxium at 520 mμ. As the concentration of ethoxide is increased, a second broad maximum grows at ~660 mμ at the expense of the higher energy band. At sufficiently high base concentration only the 660 mμ band is observed (Fig.1). It is suggested that the band at 520 mμ results from the Janovsky complex such as V (the particular ring carbon which is attacked by the dinitrobenzyl ion has not yet been determined). Excess ethoxide would favour the formation of IV. Evidence that the species which absorbs at 660 mμ is not the product of an irreversible Zimmermann reaction is that the absorption at 660 mμ is reversible. Thus on dilution this band disappears and the band at 520 mμ reappears. Similarly solutions which show the absorption at 660 mμ at room temperature, show only the 520 mμ band when cooled to $-70°$. The original spectrum reappears when the solution returns to room temperature (Fig. 1).

EXPERIMENTAL

Deuterium exchange in m-*dinitrobenzene.* A solution of *m*-dinitrobenzene (0·07 g) in 4 ml 0·2 N sodium methoxide in methanol to which 1 ml deuterium oxide had been added was allowed to stand for 24 hr. No coloration was observed. The mixture was acidified with a solution of conc sulphuric acid in deuterium oxide (1:10). The methanol was removed by evaporation at room temp, the solid removed by filtration, extracted with carbon tetrachloride, which solution was evaporated to dryness. Recovery was about 100%. The product had exchanged 40% hydrogen for deuterium as estimated by mass spectrometry. New infra-red bands are observed at 2313, 926, 766 and 691 cm^{-1}. The bands at 2313 and 766 cm^{-1} correspond with those assigned by Pollitt and Saunders[4] to C–D stretching and C–D in-plane vibrations respectively.

Janovsky reaction. Solutions were prepared by dissolving about 0·5 mg *m*-dinitrobenzene in 25 ml substrate. This was shaken with 25 ml 10 N sodium hydroxide for 2 min and the organic layer separated. For Janovsky-type reactions which involved solid substrates, the *m*-dinitrobenzene was dissolved in 0·2 N sodium ethoxide in ethanol and a large excess of the substrate was added.

The visible spectra were measured using an Optica CF4R recording spectrophotometer.

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