860. *The Janovsky Reaction*

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The Janovsky complexes, formed between sodium acetonate and a number of substituted *m*-dinitrobenzenes, have been examined spectroscopically. These complexes differ from the Meisenheimer complexes in a number of ways. A modified structure is proposed for the Janovsky complexes. The complexes formed with methoxide, hydroxide, and ethanethiolate ions, and with the anions derived from ketones, malonate esters, cyclopentadiene, and dialkyl phosphites have also been examined and interpreted in terms of the new structure. The spectra of the Meisenheimer and Janovsky complexes are related to those of the corresponding benzyl anions, and the nature of certain other coloured products is discussed.

THE production of an intense purple coloration when a solution of *m*-dinitrobenzene in acetone is treated with alkali was first noted by Janovsky and Erb in 1886,[1] and is now known as the Janovsky reaction. von Bitto [2] showed that acetone can be replaced by a

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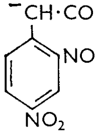
[1] J. V. Janovsky and L. Erb, *Ber.*, 1886, **19**, 2155.

[2] B. von Bitto, *Annalen*, 1892, **269**, 377.

variety of other ketones and aldehydes and the reaction has been widely employed in the detection of aldehydes and ketones having an α-hydrogen atom. The Zimmermann reaction, apparently similar except that the nitro-compound is present in excess, usually in ethanolic solution, is used for the quantitative estimation of ketones, particularly in the steroid field. However, it is now recognised [3,4] that the coloured product obtained in the Zimmermann reaction is the anion (I) from the corresponding 2,4-dinitrobenzyl ketone. This is derived from the original Janovsky complex by oxidation with an excess of the nitro-compound.[5] Fenton's reagent (H_2O_2 and Fe^{2+}) is also effective in this transformation.[6]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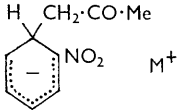
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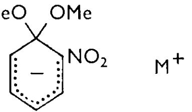
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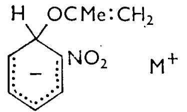
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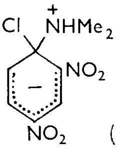
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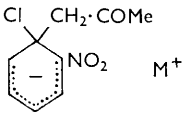
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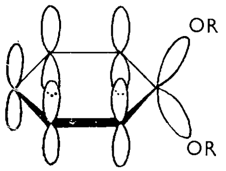
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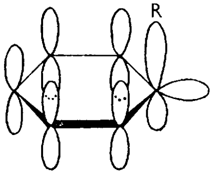
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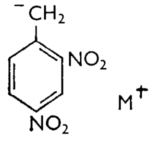
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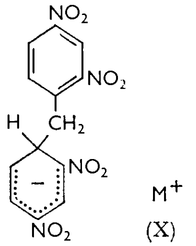
(X)

The coloured product in the Janovsky reaction, that is with the ketone in excess, is formed by the reversible attack of the acetonate ion at one of the ring positions. The complex is usually formulated [4,7] as a direct analogue (II) of the well-known Meisenheimer complexes [8] (III). The alternative formula (IV) was supported by Gitis,[9] but his evidence for this is not valid.[4] The action of acid on the complexes regenerates the parent nitro-compound, but either oxidation [5,6] or reduction [10] gives compounds in which the benzene ring is attached to the methylene group of the original ketone. It is thus almost certain that the structure of the complex approximates to formula (II).

Reactions apparently similar to the Janovsky reaction are given by many substances which are not aldehydes or ketones. Alkyl phosphine oxides give a colour when 30% sodium hydroxide solution is used,[11] as does di-isopropyl ethynylphosphonate.[12] Methylene diphosphonates require less concentrated alkali, as do dialkyl phosphites and other compounds containing the =P(O)H grouping.[13] Alkyltriphenylphosphonium salts, nitromethane, cyclopentadiene, and analogous compounds such as fluorene,[14] quaternary

[3] C. S. Corker, J. K. Norymberski, and R. Thow, *Biochem. J.*, 1962, **83**, 583.
[4] R. Foster and R. K. Mackie, *Tetrahedron*, 1962, **18**, 1131.
[5] T. J. King and C. E. Newall, *J.*, 1962, 367.
[6] M. Akatsuka, *J. Pharm. Soc. Japan*, 1960, **80**, 375.
[7] T. Canback, *Farm. Revy*, 1949, **48**, 153.
[8] R. J. Pollitt and B. C. Saunders, *J.*, 1964, 1132.
[9] S. S. Gitis, *Zhur. obshchei Khim.*, 1957, **27**, 1894.
[10] T. Severin and R. Schwitz, *Angew. Chem. Internat. Edn.*, 1963, **2**, 266.
[11] H. Hecker and F. Hein, *Z. analyt. Chem.*, 1960, **174**, 354.
[12] B. C. Saunders and P. Simpson, *J.*, 1963, 3351.
[13] B. C. Saunders and B. P. Stark, *Tetrahedron*, 1958, **4**, 197.
[14] E. Sawicki, *Analyt. Chem.*, 1952, **24**, 1204.

α- and γ-picolinium compounds,[15] and a number of nitrogen compounds such as pyrrole, and some imides also give apparently similar colours. The colours with diethyl malonate and ethyl acetoacetate fade rapidly through secondary reaction, though by using suitable solvent systems the initial colours can be stabilised. Colours are also obtained with *m*-dinitro-compounds in liquid ammonia,[16] with amines,[17,18] and in dimethylsulphoxide [19] or dimethylformamide (DMF) with bases.[20,21]

In the Janovsky reaction, *m*-dinitrobenzene can be replaced by a variety of other *m*-dinitro-compounds. Under normal conditions *o*- and *p*-dinitro-compounds do not give strong colours.[21] However, violet-purple colours can be obtained by the action of alkali on a solution of *o*- or *p*-dinitrobenzene or 2,2′-dinitrobiphenyl in DMF containing an aldehyde or ketone,[21,22] or a compound containing a cyclopentadiene $=CH_2$ grouping.[21,23] The colour produced depends very much on the nature of the active methylene compound used. For example with *o*-dinitrobenzene, cyclopentadiene gives $\lambda_{max.}$ 570 mμ, indene 650 mμ, and 7*H*-benzo[*c*]fluorene 740 mμ.[23] This is in marked contrast with the Janovsky type of reaction where the range of $\lambda_{max.}$ is relatively small, even for diverse compounds. Possibly some form of condensation reaction occurs, involving the active methylene group and one of the nitro-groups. We have found that dibutyl phosphite, which has no active methylene group, but which gives a good purple colour with *m*-dinitrobenzene and alkali, especially in DMF solution, gives no colour with *o*- or *p*-dinitrobenzene or 2,2′-dinitrobiphenyl under these conditions. Thus, it is apparent that the Janovsky reaction is properly confined (*a*) to compounds with two nitro-groups positioned *meta* to each other, and (*b*) to certain closely related compounds such as 3,3′-dinitroazoxybenzene which give analogous reactions.

Though several workers have examined the Janovsky reactions of a variety of nitro-compounds, the only systematic studies on substituent effects have been those of Gitis *et al.*[24] They have examined the spectra obtained with a number of 4-substituted and 4,6-disubstituted 1,3-dinitro-compounds and have demonstrated that substituents will block the reaction at the ring position concerned. This interpretation appears to have been ignored by some later workers.[16] Gitis *et al.* have also demonstrated that the effect of 6-substituents on the position of the visible band is different for 2- and 4-complexes. They claim [24a] to have shown the existence of 2 : 1 and 3 : 1 complexes of acetonate ion and nitro-compound in solution and Gitis has isolated [9] solid 2 : 1 complexes for *o*-, *m*-, and *p*-dinitrobenzenes and 3 : 1 complexes from 1,3,5-trinitrobenzene derivatives. However, the structure of these complexes does not seem to correspond to that of the complexes in solution as the blocking rules do not apply; even 2,4,6-trinitro-*m*-xylene gives a 3 : 1 complex.

This Paper presents a more thorough examination of the properties of Janovsky complexes and the effect of substituents on the nature of the complexes. A range of analogous reactions is examined and an attempt made to correlate the various properties of these systems.

EXPERIMENTAL AND RESULTS

The visible absorption spectra were taken on a Perkin-Elmer 137 u.v. spectrophotometer scanning at the fast speed (2 min. for 350—750 mμ). For peaks above 750 mμ a Cary 14M-50 spectrophotometer was used. As many of the peaks are broad, and some of the solutions fade

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[15] N. A. Coats and A. R. Katritzky, *J. Org. Chem.*, 1959, **24**, 1836.
[16] R. Foster and R. K. Mackie, *Tetrahedron*, 1962, **18**, 161.
[17] R. Schaal, *J. Chim. phys.*, 1955, **52**, 784.
[18] R. Foster and R. K. Mackie, *Tetrahedron*, 1961, **16**, 119.
[19] J. P. Heotis and J. W. Cavett, *Analyt. Chem.*, 1959, **31**, 1977.
[20] C. C. Porter, *Analyt. Chem.*, 1955, **27**, 805.
[21] E. Sawicki and T. W. Stanley, *Analyt. Chim. Acta*, 1960, **23**, 551.
[22] E. Sawicki, J. Noe, and T. W. Stanley, *Mikrochim. Acta*, 1960, **2**, 286.
[23] E. Sawicki, T. W. Stanley, and J. Noe, *Analyt. Chem.*, 1960, **32**, 816.
[24] (*a*) S. S. Gitis, G. M. Oksengendler, and Ya. Kaminskii, *Zhur. obshchei Khim.*, 1959, **29**, 2983; (*b*) S. S. Gitis and Ya. Kaminskii, *ibid.*, 1960, **30**, 3810.

rapidly, the limit of accuracy of the values given is ±2 mμ. The ratios of extinction coefficients are rounded off to the nearest 0·05. Infrared spectra were taken as Nujol mulls on a Perkin-Elmer No. 21 i.r. spectrophotometer using a sodium chloride prism. The proton magnetic resonance spectrum was taken at 40 Mc./sec using a Perkin-Elmer spectrometer with sample spinning. Positions of reference are quoted as chemical shifts on the τ-scale ($SiMe_4$ = 10·00), using dioxan (τ = 6·43) as an internal reference.

The nitro-compounds were obtained from commercial sources and recrystallised if necessary, or synthesised by known or obvious methods. With the exception of dimethyl 4,6-dinitroisophthalate they had melting points in agreement with literature values. Dimethyl 4,6-dinitroisophthalate had m. p. 157·5—158° (from methanol). Nozoe *et al.*[25] give m. p. 141° but they recrystallised from ethanol and there was the possibility of some ester exchange (Found: C, 42·4; H, 3·0; N, 9·95. Calc. for $C_{10}H_8N_2O_8$: C, 42·3; H, 2·8; N, 9·9%). Dimethylformamide was purified as described previously.[8]

The Janovsky Reaction.—The nitro-compound (2—3 mg.) was dissolved in acetone and 10% sodium hydroxide solution (3—4 drops) added. The coloured acetone layer was then diluted as necessary with acetone and the spectrum taken as soon as possible. The results are presented in Tables 1—4.

TABLE 1

Visible absorption spectra of 1,3-dinitro-5-X-benzenes with acetone and sodium hydroxide

X	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)	λ_3 (mμ)	$\varepsilon_3/\varepsilon_2$
NH_2 [a, b]	—[c]		624	—[d]	
NMe_2 [a]	—[c]		614	—[d]	
OMe	—[c]		590	—[d]	
Me	—[c]		580	—[d]	
H	—[c]		576	692	0·20
Cl	—[c]		563	—[d]	
CO_2^-	380	0·65	568	660[e]	0·40
$CO{\cdot}NH_2$	403	0·85	580[e]	640[e]	0·85
$CO{\cdot}NEt_2$	399[f]	0·95	582[e]	656	1·30
CO_2Me	406	1·35	561	625[e]	0·75
$CO_2C_2H_4OEt$	407	1·45	563	625[e]	0·75
CN[g]	396	1·30	549	631	0·65
NO_2[h]	464	2·45	570[e]		

[a] Complex reluctant to form. [b] Also band at 519 mμ of variable intensity, probably not associated with Janovsky complex. [c] Region where λ_1 expected obscured by end absorption. [d] No band observed. [e] As shoulders on, or closely associated with, another band, $\lambda_{max.}$ subject to uncertainty. [f] This peak may be associated with the 2-complex rather than the 4-complex. [g] Also OH^- complex, 382 and 499 mμ. [h] Also OH^- complex, 439 and 521 mμ.

TABLE 2

Visible absorption spectra of 4-substituted 1,3-dinitrobenzenes with acetone and sodium hydroxide

Substituent	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)	λ_3 (mμ)	$\varepsilon_3/\varepsilon_2$
NH_2[a]	385, 398	1·4, 1·3	529	—[b]	
NMe_2	—[c]		572	—[b]	
OMe	—[c]		576	—[d]	
OEt	—[c]		580	—[d]	
F	—[c]		570	641	1·00
Cl	—[c]		548	666	0·45
Br	—[c]		546	675	0·35
Me	—[c]		580	665	0·65
CO_2Me	—[c]		556	685	0·25
CN	—[c]		548	705	0·15

[a] This spectrum is probably due to the 2,4-dinitroanilide ion. [b] No band observed. [c] Region obscured by end absorption. [d] Expected value of λ_3 very close to λ_2.

Reactions in DMF.—The above procedure was followed except that acetone was replaced by a solution (usually 5%) of the reagent in DMF and the coloured solutions were diluted into pure DMF. Results obtained with acetone and sodium hydroxide in DMF are presented in Table 5. Table 6 gives the initial visible absorption spectra of complexes of nitro-compounds with sodium hydroxide, sodium methoxide, and sodium ethanethiolate. Sodium hydroxide

[25] T. Nozoe, Y. Kitahara, K. Yamane, and K. Yamaki, *Proc. Japan Acad.*, 1950, **26**, 14.

Table 3

Visible absorption spectra of 2-substituted 1,3-dinitrobenzenes with acetone and sodium hydroxide[a]

Substituents	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)	Substituents	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)
2-OMe	—[b]		521	2-Cl	—[b]		545
2-OMe, 5-Cl	—[b]		508	2-Cl, 5-Cl	—[b]		536
2-OMe, 5-CO_2Me	405	0·90	501	2-Cl, 5-CO_2Me	408	1·15	522
2-OMe, 5-CN	394	0·80	494	2-Cl, 5-CN	396	1·05	512
2-Me	—[b]		555	2-Cl, 5-CO·NH_2	384	0·85	526

[a] The λ_3 band is not seen with these compounds. [b] Region obscured by end absorption.

Table 4

Visible absorption spectra of 4,6-disubstituted 1,3-dinitrobenzenes with acetone and sodium hydroxide

Substituents	λ_2 (mμ)	λ_3 (mμ)	Substituents	λ_2 (mμ)	λ_3 (mμ)	$\varepsilon_3/\varepsilon_2$
Cl, Cl	—[a]	634	CO_2Me, CO_2Me	562	685	2·85
OMe, Me	—[a]	598	CO_2Me, Me	560	675	2·25
OMe, OMe	—[a]	556	Me, Me	—[a]	651	—
Cl, NMe_2	—[a]	560	Me, Cl	—[a]	658	—

[a] No band observed.

Table 5

Visible absorption spectra of substituted 1,3-dinitrobenzenes with acetone and sodium hydroxide in DMF

Substituent	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)	λ_3 (mμ)	$\varepsilon_3/\varepsilon_2$
5-NMe_2	377	1·00	625	—[a]	
5-OMe	360, 376	0·50	603	—[a]	
5-CH_3	360, 372sh	0·60, 0·50	588	—[b]	
5-H[c]	360, 372sh	0·50, 0·40	580	700	0·35
5-Cl	365, 379sh	0·60, 0·50	570	726	0·10
5-CO_2^-	406	1·15	580	640	0·90
5-CO·NH_2[d]	404	—	580	650sh	
5-CO_2Me[d]	407	1·05	572	630sh	0·50
4,6-Di-CO_2Me	—		560	690	1·75
4-CN	370	0·55	551	—[a]	
4-CO_2Me	358	0·55	552	695	0·30
4-CO_2^-	—		575	670sh	

[a] No band observed. [b] Very faint band present, wavelength uncertain. [c] Using dry acetone and sodium hydride as base, *m*-dinitrobenzene gives $\lambda_{max.}$ 358 mμ, with shoulder 360, and 578 mμ. [d] Mixed with OH^- complex.

Table 6

Initial[a] absorption spectra of substituted 1,3-dinitrobenzenes with sodium hydroxide, sodium methoxide, or sodium ethanethiolate

	Sodium hydroxide			Sodium methoxide			Sodium ethanethiolate		
Substituent	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)
5-NMe_2	376[b]	1·30	601	374[b]	1·20	594	395[b]	1·50	635
5-OMe	351 363sh	0·60 0·50	560	351 363	0·65 0·60	548	342	—[c]	570
5-H	352 362	0·55 0·50	536	350 362sh	0·55 0·50	531	370[d]	0·55	566
5-Cl	360 370	0·65 0·65	524	357 370	0·60 0·55	514	376	0·65	560
5-CO_2^-	—		542	366	0·80	537	—[e]		575
5-CO·NH_2	392	0·95	531	384	0·95	525	403	0·90	555
5-CO_2Me	394	1·00	503	380	0·95	508	412	1·05	542[f]
5-CN	379	0·90	502	392[g]	0·95	498	410	1·05	540
5-NO_2	435	1·30	518	431	1·40	516	465	2·05	570
4,6-Di-CO_2Me	—[e]		506[h]	356	0·85	505[i]			—[j]

[a] Secondary changes occur rapidly in the hydroxide and methoxide systems. [b] This intense λ_1 band probably does not correspond to the other λ_1 bands. [c] Rapidly fading, $\varepsilon_1/\varepsilon_2$ not determined. [d] With slight shoulder. [e] Obscured by end absorption. [f] λ_3 610sh, $\varepsilon_3/\varepsilon_2$ 0·25. [g] With slightly lower shoulder at 380 mμ compared with the corresponding Meisenheimer complex. [h] Initial spectrum has $\lambda_{max.}$ 615 mμ; slowly changes to 506 mμ. [i] Initial spectrum has $\lambda_{max.}$ 620 mμ; changes rapidly to 505 mμ. Acidification gives starting material. [j] Yellow colour only.

and sodium methoxide were added to solutions of the nitro-compounds in DMF as aqueous and methanolic solutions, respectively. The ethanethiolate complexes were obtained by using a solution of ethanethiol in DMF and adding a very small drop (0·05 ml.) of 5% sodium hydroxide solution when the colours developed very rapidly. With these reagents halogen and ether groups are rapidly replaced, and with strong bases methyl groups often give colours by a different mechanism. Similar limitations apply to the diethyl malonate and diethyl methylmalonate systems (Table 7). Spectra obtained in DMF with cyclopentanone and cyclohexanone are

TABLE 7

Visible absorption spectra of substituted 1,3-dinitrobenzenes with diethyl malonate or diethyl methylmalonate and sodium hydroxide in DMF [a]

	$CH_2(CO_2Et)_2$			$Me{\cdot}CH(CO_2Et)_2$		
Substituent	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)
5-NMe_2 [b]	—		—	—		—
5-OMe	—[c]		594	—[c]		590
5-H	365	0·60	570	360	0·75	563
5-Cl	363	0·55	556	365	0·60	552
5-CO_2^-	—[c]		568	—[c]		561
5-$CO{\cdot}NH_2$	398	0·75	552	397	0·70	547
5-CO_2Me	406	1·10	542	402	0·95	528
5-CN	404	1·00	536	404	0·95	525
5-NO_2	460	2·05	568	454	1·80	538
4,6-Di-CO_2Me	365	0·50	548	—[c]		546

[a] λ_3 Band not observed in any of these systems. [b] Only yellow colour obtained. [c] Obscured by end absorption.

TABLE 8

Visible absorption spectra of substituted 1,3-dinitrobenzenes with cyclopentanone or cyclohexanone and sodium hydroxide in DMF

	Cyclopentanone					Cyclohexanone				
Substituent	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)	λ_3 (mμ)	$\varepsilon_3/\varepsilon_2$	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)	λ_3 (mμ)	$\varepsilon_3/\varepsilon_2$
5-NMe_2	378	0·85	625	—[a]		378		625	—[a]	
5-OMe	356	0·60	605[b]	—[a]		—[a]		604	—[a]	
5-H	358 372sh	0·50 0·45	585[b]	705	0·05	360 370sh	0·50 0·45	585	—[a]	
5-Cl	364	0·60	573[b]	—[a]		365 380sh	0·60 0·55	570	—[a]	
5-CO_2^-	406	1·25	570	640[c]	0·75	386	0·80	580	660[c]	0·60
5-$CO{\cdot}NH_2$	398	0·80	570	650[c]	0·15	401	0·90	580	—[a]	
5-CO_2Me	408	1·25	560	638	0·55	403	1·20	550	—[a]	
5-CN	—[d]		550[d]	650[d]	0·85	—[e]		—[e]	—[e]	
4,6-Di-CO_2Me	360		550	694	0·85	—[a]		549	660	0·70
4,6-Di-Cl	—[a]		—[a]	618		—[a]		—[a]	613	
4,6-Di-OMe	—[a]		—[a]	552		—[a]		—[a]	542	
2-OMe	—[a]		529	—		—[a]		525	—	

[a] No band observed. [b] With shoulders on short-wavelength side. [c] Closely associated with λ_2 band, wavelength uncertain. [d] Mixed with OH^- complex. [e] Largely OH^- complex formed.

TABLE 9

Visible absorption spectra of substituted 1,3-dinitrobenzenes with cyclopentadiene and sodium hydroxide in DMF

Substituent	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)	Substituent	λ_1 (mμ)	λ_2 (mμ)
5-NMe_2	385		635[a]	4,6-Di-Cl	—[d]	584
5-OMe	362	0·50	600	4,6-Di-OMe	—[e]	572
5-H	359, 372sh	0·65	579	4-Cl, 6-Me	—[e]	592
5-Cl	366	0·50	563	4-OMe, 6-Me	—[e]	592
5-CO_2^-	377	0·70	582	4-Me	—[e]	588
5-$CO{\cdot}NH_2$	405	0·90	559[b]	4-Cl	—[e]	600
5-CO_2Me	410	1·05	550[c]	4-Cl, 6-NMe_2	—[e]	587
5-CN	406	0·90	545	4-NMe_2	—[e]	584
5-NO_2	468	2·10	570	2-OMe	—[e]	524
4,6-Di-CO_2Me	365	0·55	552	2-Cl	—[e]	560

[a] Also a band at 513 mμ, possibly a decomposition product. [b] With shoulder at 650 mμ. [c] With shoulder at 630 mμ. [d] Weak band at 337 mμ. [e] No band present in λ_1 region.

TABLE 10

Visible absorption spectra of substituted 1,3-dinitrobenzenes with di-n-butyl phosphite and sodium hydroxide in DMF

Substituent	λ_1 (mμ)	$\varepsilon_1/\varepsilon_2$	λ_2 (mμ)	λ_3 (mμ)	$\varepsilon_3/\varepsilon_2$
5-NH_2	382	0·85	634	—	
5-NMe_2	378	0·85	632	—	
5-OMe	358	0·45	601	—	
5-Me	362, 374sh	0·50	587	—	
5-H	363	0·50	586	715	1·20
5-Cl	367	0·65	566	—	
5-CO_2^-	400	0·95	588	650	0·70
5-CO·NH_2	406[a]	1·40	595sh	667	1·50
5-CO_2Me	409[a, b]	1·50	600sh	642	1·15
5-CN	400[a, c]	1·65	580sh	652	1·25
5-NO_2	473	2·40	580	—	
4-Cl, 5-CN	396	2·10	550	624	1·25
2-Cl, 5-CN	405	1·20	528	—	
2-Cl, 5-CO_2Me	412	1·00	533	—	
2-OMe, 5-CO_2Me	406	0·70	507	—	
2-OMe, 5-NO_2	454	2·40	544	—	
2-Cl, 5-NO_2	459	2·10	535	—	
4,6-Di-CO_2Me	—[d]		546	700	0·05[e]
4,6-Di-Cl	328			658	
4,6-Di-OMe	335			561	

[a] Probably associated with λ_3. [b] Shoulder at 400 mμ. [c] Shoulder at 420 mμ. [d] Region obscured by end absorption. [e] Very intense at first, rapidly fades.

TABLE 11

Visible absorption spectra of 4,6-disubstituted and 2,4,6-trisubstituted 1,3-dinitrobenzenes with dibutyl phosphite and sodium hydroxide in DMF

Substituents	$\lambda_{\text{max.}}$ (mμ)	Substituents	$\lambda_{\text{max.}}$ (mμ)
2,4,6-Tri-F	591	4,6-Di-F	590
2,4,6-Tri-Cl	328, 365sh, 558	4,6-Di-Cl	328, 365sh, 658
2-Cl, 4,6-Di-OMe	335, 561	4,6-Di-OMe	335, 561
2,4,6-Tri-Br	580, 710	—	—

TABLE 12

Visible absorption spectra of 1,3-dinitrobenzene derivatives in DMF and sodium hydroxide

Substituent	$\lambda_{\text{max.}}$ (mμ)	Substituent	$\lambda_{\text{max.}}$ (mμ)
2-NH_2	535sh, 560	2-NMe_2	—[a]
4-NH_2	387, 400sh, 540	4-NMe_2	570
5-NH_2	378,[b] 507, 610sh[b]	5-NMe_2	376, 610
2-Me	553;[c] 795, 835[d]	2-Me, 5-NO_2	369, 510sh, 532, 645
4-Me	407, 420sh, 648	4,6-Di-Me	415, 664

[a] No definite colour. [b] Reaction of OH^- at the 4-position. [c] With excess of sodium hydroxide. [d] With excess of nitro-compound; fades very rapidly.

summarised in Table 8, with cyclopentadiene in Table 9, and with di-n-butyl phosphite in Tables 10 and 11. Table 12 gives the spectra of a number of amino- and methyl-substituted nitro-compounds in DMF with aqueous sodium hydroxide solution.

Deuterium Exchange in m-*Dinitrobenzene.*—*m*-Dinitrobenzene (0·20 g.) was dissolved in a mixture of DMF (2·0 ml.) and 0·1N-sodium hydroxide (0·10 g.) in D_2O. The solution was pale purple. After 24 hr. at room temperature in the dark, the solution, which was still purple, was acidified with 4N-HCl (in H_2O) and water was added to precipitate the nitro-compound. The dry crude product had m. p. 89·5—90·5° (hot-stage). A sample was sublimed for analysis (Found: C, 42·9; N, 16·3. Calc. for $C_6H_3DN_2O_4$: C, 42·6; N, 16·55%. The sample gave 2·1% H_2O/D_2O; Calc. 2·2%). The ultraviolet spectrum in ethanol had $\lambda_{\text{max.}}$ 235 mμ (ε 17,400) and was identical with that of *m*-dinitrobenzene. The infrared spectrum had the following new peaks (values in cm.$^{-1}$): 2313, 1087, 987, 925, 768, and 689, and had the following peaks missing or reduced in intensity 1092, 1068, 913, 904, 817, and 712. The proton magnetic resonance spectrum showed a weak triplet centred at 0·98 owing to residual 2-protons. The remaining protons gave peaks at τ 1·20, 1·24, 1·42, 1·86, 2·04, 2·10, and 2·26. About 70% of the 2-protons had been replaced by deuterium.

Competition Between Janovsky and Meisenheimer Reactions.—To a solution of 2,4-dinitroanisole in DMF containing 5% (v/v) each of acetone and methanol was added a drop (0·1 ml.) of N-sodium hydroxide solution. The initial colour was the salmon-pink of the Meisenheimer complex, but this was rapidly replaced by the intense purple-blue of the Janovsky complex, with virtually no absorption around 500 mμ attributable to residual Meisenheimer complex.

m-*Dinitrobenzene with Di-n-butyl Sodiophosphite in Ether.*—The spectra summarised in Tables 10 and 11 were obtained in DMF using an excess of di-n-butyl phosphite. This reaction was also carried out in dry ether. A solution of di-n-butyl phosphite (9·7 g., 0·05 mole) in dry ether (100 ml.) was treated with an excess of granulated sodium and the mixture heated gently under reflux in nitrogen until the evolution of gas was complete. The solution of the sodio-derivative was decanted from unreacted sodium and added dropwise under nitrogen to a solution of *m*-dinitrobenzene (4·2 g., 0·025 mole) in dry ether (250 ml.). On the addition of the first few drops of sodio-derivative solution a purple colour was obtained, but this rapidly changed to bright green ($\lambda_{max.}$ 425 and 705 mμ). The addition was continued with stirring and ice–salt cooling and the fine precipitate collected on a sintered glass filter in a dry-box under nitrogen, washed with ether, and dried *in vacuo* at room temperature. The product was a fine black powder with a greenish tinge. The *complex* was extremely hygroscopic giving an intense green syrup, which soon turned brown. Analysis agreed more closely with a 2 : 1 than 1 : 1 complex of dibutyl sodiophosphite and *m*-dinitrobenzene, but the hygroscopic nature and instability of the product made accurate determination difficult (Found: N, 5·5. $C_{22}H_{40}N_2Na_2O_{10}P_2$ requires N, 4·7; $C_{14}H_{22}N_2NaO_7P$ requires N, 7·3%).

If there was much unchanged di-n-butyl phosphite in the ether solution the formation of the green product was inhibited and a purple solution was obtained.

DISCUSSION

The Janovsky Complexes.—The Janovsky complexes of 5-substituted 1,3-dinitro-compounds (Table 1) often show two peaks (λ_2 and λ_3) in the visible region. These are due to complexes formed by reaction at the 4- and 2-positions, respectively. As in the corresponding Meisenheimer complexes,[8] the 4-complex has a visible band at shorter wavelengths than the 2-complex and in both the 2- and 4-complexes the visible band moves to shorter wavelengths on the introduction of electronegative 5-substituents. The ratio in which the two complexes are formed varies somewhat with the exact conditions used, but usually the 4-complex predominates. As the 5-substituent is made more electronegative the value of $\varepsilon_3/\varepsilon_2$ increases since the 2- and 4-positions become more nearly equivalent. The high $\varepsilon_3/\varepsilon_2$ value seen with *NN*-diethyl-3,5-dinitrobenzamide is probably due to steric hindrance at the 4-position.

As in the Meisenheimer complexes a short-wavelength band (λ_1) is present, and in most cases is associated with the 4-complex. Using acetone as solvent, this band is seen only with the more-electronegative nitro-compounds, since with the less-electronegative nitro-compounds the band is less intense and lies at shorter wavelengths, and there is increased end-absorption due to unchanged nitro-compound. Using DMF as solvent (Table 5), complex formation is enhanced and the λ_1 band is visible in nearly all cases. Direct comparison is possible with the Meisenheimer complexes studied in this solvent.[8] The doublet structure of the λ_1 band in a number of 2,4-dinitroanisole Meisenheimer complexes is seen also with some of the Janovsky complexes (Figure 1) and the unexpectedly high value of λ_2 in the 4-chloro-2,6-dinitroanisole Meisenheimer complex is paralleled in the high value of λ_3 for the Janovsky reaction of 3,5-dinitrochlorobenzene in DMF.

Unfortunately, in DMF selectivity is reduced and the direct attack of OH^- on the nitro-compound (Table 6) interferes so that the Janovsky spectra cannot be distinguished with certainty with the more-electronegative nitro-compounds. The same reaction occurs to some extent in acetone. The three bands that Gitis *et al.*[24a] observed and ascribed to 1 : 1, 2 : 1, and 3 : 1 complexes of sodium acetonate and 1,3,5-trinitrobenzene were λ_2 and λ_1 of the Janovsky complex and λ_2 of the OH^- complex (or possibly a band due to a secondary product), respectively. The close resemblance of the Janovsky spectra to those of the corresponding Meisenheimer complexes suggests that under the conditions used here only 1 : 1 complexes are formed.

The effects of substitution at the 4- or the 2-position of a 1,3-dinitro-compound are shown by the results in Tables 2 and 3. It is not possible to separate clearly steric from electronic effects, but there is a general correlation between the electronegativity ($-M$ effect) of the substituent and the band position. It is probable that all substituents produce a general shift to shorter wavelengths by twisting the nitro-groups from the plane of the ring, since, for nearly all the 4-substituted nitro-compounds examined, λ_3 is found at shorter wavelengths than for *m*-dinitrobenzene itself.

The substituent effects may be summarised:

Position of complex formation	2	4	4
Position of substituent	4	2	6
Effect on wavelength of $+M$ group	Shortens	Shortens	Lengthens
Magnitude of effect	Large	Large	Small

The effect of some of these 4-substituents on band position has previously been noted by Gitis and his co-workers.[24b]

4,6-Disubstituted 1,3-dinitrobenzene derivatives (Table 4) in general show only one band. The position of this and the effects of substituents on it show clearly that it is due to the 2-complex, as would be expected from the blocking phenomenon discovered by Gitis *et al.* However, this blocking is not absolute, as both the compounds with methoxycarbonyl groups as 4-substituent show a small λ_2 band. The cyclic ketones, cyclopentanone and cyclohexanone, where ring formation has reduced steric interaction, show (Table 8) increased reaction at the 4-position of 4,6-di(methoxycarbonyl)-1,3-dinitrobenzene (Figure 2). This increase is realised in spite of the fact that in both these cases the donating atom is secondary whereas in acetone it is primary. Otherwise the spectra resemble those similarly obtained with acetone.

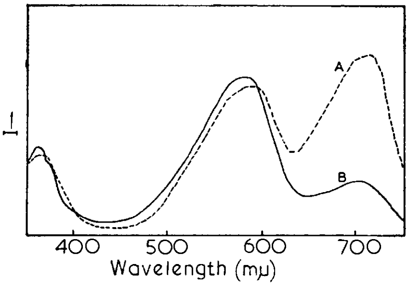

FIGURE 1. Visible absorption spectra of *m*-dinitrobenzene in DMF with sodium hydroxide and (A) dibutyl phosphite, (B) acetone

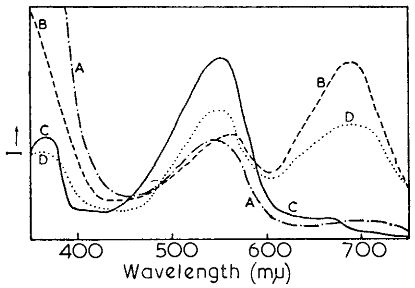

FIGURE 2. Visible absorption spectra of 4,6-di(methoxycarbonyl)-1,3-dinitrobenzene in DMF with sodium hydroxide and (A) dibutyl phosphite, (B) acetone, (C) cyclopentadiene, (D) cyclopentanone

Complexes with Hydroxide, Methoxide, Ethanethiolate, Diethyl Malonate, and Diethyl Methylmalonate Ions.—The reactions of 1,3,5-trinitrobenzene with hydroxide and methoxide ions have recently been thoroughly investigated by Gold and Rochester.[26] The spectra we obtained for the initial trinitrobenzene–OH^- and trinitrobenzene–OMe^- complexes in DMF resemble the spectrum of the 1 : 1 complex that Gold and Rochester observed with trinitrobenzene and methanolic sodium methoxide. In aqueous sodium hydroxide their 1 : 1 complex with trinitrobenzene has only a single broad peak, but it was suggested that

[26] V. Gold and C. H. Rochester, *J.*, 1964, 1692, 1710.

this might be two peaks overlapping. The spectra with other nitro-compounds and hydroxide or methoxide ions are also of the general Janovsky–Meisenheimer type, with λ_2 situated at fairly short wavelengths. With 4,6-di(methoxycarbonyl)-1,3-dinitrobenzene the 4-complexes are more stable than the 2-complexes, though the latter are formed faster. In the EtS^- complexes, λ_2 occurs at longer wavelengths than in the OH^- and OMe^- complexes, and the complexes are somewhat more readily formed. The diethyl malonate and diethyl methylmalonate complexes, too, give spectra intermediate between the Janovsky and the Meisenheimer type. As the malonate esters are relatively strongly acidic, the direct OH^- interaction does not interfere, but even so they are poor reagents and give colours reluctantly with the less-electronegative nitro-compounds. Diethyl methylmalonate is less reactive than diethyl malonate and also λ_2 is at shorter wavelengths. None of the anions in this section gives significant quantities of 2-complex and [except in the 4,6-di(methoxycarbonyl) complexes] the λ_3 band is absent.

Complexes with Cyclopentadiene and Base in DMF.—The spectra of the complexes with 5-substituted 1,3-dinitrobenzenes show that cyclopentadiene acts as a typical Janovsky reagent with alkali in DMF and gives values of λ_1 and λ_2 very close to those obtained with acetone. However, the doubly blocked 4,6-derivatives do not show the spectra expected for 2-complexes, and some of the spectra produced by 4-substituted 1,3-dinitrobenzenes are exceptional. (Compare with Tables 2 and 4.) The cyclopentadienyl anion is planar and it is quite easy to envisage it escaping normal blocking effects either by lying over the benzene ring itself or by virtue of its greatly reduced steric interaction with the ring substituents.

Complexes with Di-n-butyl Phosphite and Base in DMF.—Unlike the reaction of dibutyl sodiophosphite in ether with *m*-dinitrobenzene, which initially gives a purple colour, the reaction in DMF and in the presence of excess of dibutyl phosphite (Table 10) gives a deep blue solution with a prominent absorption peak at 715 mμ (Figure 1). However, there is no absorption around 420 mμ as there is in the ? 2 : 1 complex obtained in ether, and it appears that the major species is the normal 2-complex. The predominance of the 2-complex under these conditions may be explained by the acidity of the dibutyl phosphite, combined with the high reactivity of the phosphonate anion, promoting a rapid exchange reaction; it is known [27] that the trinitro-Meisenheimer complexes are decomposed by both dissociated and undissociated acids. It must be assumed that reaction is more rapid at the 2-position, though the 4-complex is the more stable. This effect of an exchange reaction can also explain why the proportion of 2- and 4-complex formed by some other reagents varies slightly with the conditions used.

The other spectra in the Table confirm that the normal 1 : 1 complexes are formed, but that there is a strong tendency for reaction at the 2-position. This reaction is blocked by 2-substituents. Blocking by methoxycarbonyl groups in the 4- and 6-positions is again incomplete and the initial 2-complex is rapidly replaced by the 4-complex (Figure 2).

The ease of complex formation with dibutyl phosphite, together with its high acidity, makes it a suitable compound for the study of 1,3,5-trinitro-complexes, where it is seen that both chlorine and methoxy-groups shorten the wavelength of λ_2 and that the chlorine does so more than the methoxy-group. This is in contrast with the effect of these substituents in the 2-position of a 4-complex of 1,3-dinitrobenzene (Table 5) when the methoxy-shortens the wavelength of λ_2 much more than does the chloro-group. This difference may simply reflect the greater crowding of the substituents round the ring in the trinitro-derivatives, but is more likely to be due to the dual character of the λ_2 transition in the trinitro-complexes,[8] since whereas a 6-methoxy-group will increase the wavelength of λ_2 for a 4-complex, a 6-chloro-group will lower it.

Comparison.—(a) *Spectra.* While the numerous points of similarity in the spectra of the Meisenheimer and Janovsky complexes indicate a basic similarity in structure,

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[27] J. B. Ainscough and E. F. Caldin, *J.*, 1956, 2528.

the positions of the absorption maxima are surprisingly different. Thus, for the 4-complexes, the change in $\lambda_{max.}$ on changing the 5-substituent from CO_2Me to OMe is only 44 mμ for the Meisenheimer complexes and 31 mμ for the Janovsky complexes (both in DMF), but on changing from the Meisenheimer to the corresponing Janovsky complex the shift is in the region of 75—85 mμ, depending on the case.

(b) *Blocking effect.* The Meisenheimer complexes are formed by attack of OR^- at a position already occupied by OR in preference to positions occupied by hydrogen, whereas in the Janovsky reaction attack at unsubstituted ring-positions is favoured. By the use of 4,6-disubstituted nitro-compounds the site of the Janovsky reaction can thus be changed from the preferred 4- to the 2-position. Of the substituents examined the methoxycarbonyl group shows the least complete blocking action, and the results with the three ketones indicate that this action is of a steric nature. However, these steric factors are not constant from one type of donor to another, as the malonate esters react exclusively at the 4-position of 4,6-di(methoxycarbonyl)-1,3-dinitrobenzene even though the substituents round the donating atom are more bulky than those in acetone, whereas the hydroxide ion attacks the 2-position readily and only slowly changes to the 4-position. These differences are probably due to the differing electronic requirements both of the various donors and of the types of complex they form. In terms of the models proposed below, Meisenheimer complex formation involves changing the type of bond to the ring substituent, whereas Janovsky complex formation does not. Different ring substituents will vary in the energy which this change requires, and different attacking ions in the energy differential between the 2- and 4-positions.

(c) *Stability.* The Janovsky complexes have much smaller dissociation constants than the corresponding Meisenheimer complexes. This is shown both by the competitive reaction described above and by the general ease with which the complexes are formed in the test-tube. Thus, fairly concentrated solutions of sodium methoxide are needed to give colorations with dinitroanisoles in methanolic solution, yet the concentration of acetonate ions present under Janovsky conditions must be quite low, and intense colours are produced even with dilute solutions of nitro-compound. Gold and Rochester [26] have shown that the 2,4,6-trinitroanisole Meisenheimer complex is more stable than the corresponding complex of OMe^- and 1,3,5-trinitrobenzene so that stability is obviously not related directly to the position of the absorption maximum (λ_2). However, there is a general tendency, with the complexes examined, that those which are formed most readily (*i.e.*, require less nitro-compound and less base to give a strong coloration) have λ_2 at longer wavelengths, and *vice versa*.

It is clear from these points of difference that the Janovsky type of complex cannot be regarded simply as a direct analogue of the Meisenheimer complexes as implied in formula (II). In the latter, the effect on $\lambda_{max.}$ of the substituents at the saturated ring position should be slight compared with that of substituents at the 5-positions (nitro-groups 1,3), as their effect should be an inductive one on the adjacent unsaturated ring atoms. Further, the blocking of the Janovsky reaction by ring substituents such as chlorine is difficult to justify in terms of the accepted structures. Examination of molecular models shows that there is no undue crowding in this case, and intermediates having the approximate geometry of the Meisenheimer complexes are regarded [28] as participating in many activated nucleophilic aromatic substitution reactions. Many of these intermediates, for example (V), would be no less crowded than the corresponding Janovsky complex (VI). The surprising ease of the Janovsky reaction remains unexplained.

As a preliminary hypothesis we propose that, while the Meisenheimer complex be represented by the accepted structure (VII), the Janovsky complex be represented by the structure (VIII; $R = CH_2{\cdot}CO{\cdot}CH_3$) in which the acetonate ion is situated above one of the ring carbon atoms and is donating the lone pair on the methylene group to the lowest

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[28] J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1.

available π^*-orbital of the benzene ring to form a dative σ-bond. The hydrogen atom at the ring position concerned is still in or near its original position, and the basic π-structure is not grossly disturbed. This sort of structure could provide a basis for rationalising the different spectra of the Meisenheimer and Janovsky products and the relative ease of the Janovsky reaction. The fact that the bond angle between the original substituent and the donating methylene group in structure (VIII) is only 90° as opposed to 108° in the tetrahedral structure accounts for the blocking effect of ring substituents. Further steric specificity would be introduced if the substituent around the donating methylene group were planar, but there is no evidence that this is so. Electron spin resonance studies of the *m*-dinitrobenzene radical-ion show [29] that the lowest vacant π^*-orbital has its greatest density at the 4-position, and a somewhat lower density at the 2-position, which is in accord with the relative stabilities of the complexes at these two positions. It is interesting to note in connection with the spectra of dinitroanilines (below) that the e.s.r. spectrum shows that the lowest π^*-orbital has a small but definite density on the 5-position.

Methyl and Amino-group Ionisation.—(Table 12) Caldin and his co-workers [18,30] have suggested that the purple colour obtained by the action of ethanolic alkali on 2,4,6-trinitrotoluene is due to the corresponding 2,4-6-trinitrobenzyl anion. In DMF, 2,4,6-trinitrotoluene gives an intense purple colour without addition of base; the spectrum corresponds closely to that recorded by Caldin and his co-workers, and also to that of Schaal [17] for the compound in ethylenediamine.

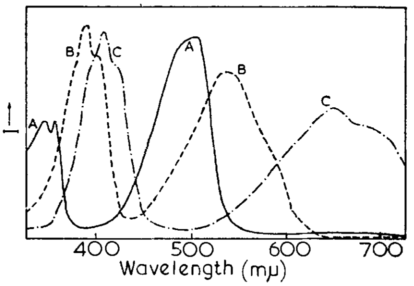

FIGURE 3. Visible absorption spectra in DMF with sodium hydroxide of (A) glycol 2,4-dinitrophenyl ether, (B) 2,4-dinitroaniline, (C) 2,4-dinitrotoluene

In the dinitro-series, a similar ionisation of the methyl protons must be postulated to account for the anomalous spectra in DMF with sodium hydroxide. The spectrum of the 2,4-dinitrobenzyl anion (IX) (Figure 3) resembles that of a Meisenheimer–Janovsky type of complex.

The nature of the coloured species in these solutions is in little doubt. Deuterium exchange is known to occur rapidly in the methyl groups of various nitrotoluenes under basic conditions, and a considerable number of base-catalysed condensations with aldehydes are recorded. In these reactions the methyl group of the nitro-compound must first lose a proton to form the benzyl anion, and this is followed by attack of the electrophile. Foster and Mackie [31] interpret colours obtained with 2,4-dinitrotoluene in ethanol in terms of two structures (IX) and (X). The structure (IX) is ascribed to the red colour formed with excess of OEt^-, and the structure (X) to the green colour when the nitro-compound is in excess. The spectrum of the green complex corresponds closely to that which we have ascribed to the 2,4-dinitrobenzyl anion (IX). If the interpretation of Foster and Mackie were correct, and assuming the normal blocking rules to apply, then the spectrum obtained with 4,6-dimethyl-1,3-dinitrobenzene (4,6-dinitro-*m*-xylene) would be expected to have a much higher value of $\lambda_{max.}$ than that with 4-methyl-1,3-dinitrobenzene (2,4-dinitrotoluene) as the reaction would be in the 2-position. Further, the rather characteristic shoulder on

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[29] A. H. Maki and D. H. Geske, *J. Chem. Phys.*, 1960, **33**, 825.
[30] J. B. Ainscough and E. F. Caldin, *J.*, 1956, 2546.
[31] R. Foster and R. K. Mackie, *Tetrahedron*, 1963, **19**, 691.

the λ_1 band is in general seen only when the 4-position of a 1,3-dinitro-compound is involved [8] so the alternative explanation of the spectral similarities that the 2-complex is responsible for the colours in both cases is unlikely. The red colour is possibly due to attack of OEt^- at the 5-position of 2,4-dinitrotoluene.

The protons on amino-groups are more acidic than the corresponding methyl-group protons, and the ability of 2,4,6-trinitroaniline (picramide) to form potassium salts is well established. The brilliant colours obtained with some dinitroanilines in alkali were noted [32] as long ago as 1872. Comparison of the spectra of the 2,4-, 2,6-, and 3,5-dinitroanilines with the corresponding *NN*-dimethyl compounds suggests that *N*-proton ionisation occurs in all three cases. The 2,4-dinitroaniline spectrum (Figure 3) resembles the Janovsky–Meisenheimer complex spectra.

The general resemblance of the benzyl spectra to the spectra of the Janovsky and Meisenheimer complexes is satisfactory, as Janovsky complex formation can be regarded as extending the conjugated system by a further atom at the ring position concerned, much in the same way as the transition state in the reaction of benzene with a methyl radical may be treated like a benzyl radical.[33a] Further, examination of the Meisenheimer structure (VIII) shows that the geometry of the two σ-orbitals joining the OR groups to the ring is such as to enable some residual interaction with the rest of the π-system. Such an interaction, resulting in less disruption of the ring π-system than has previously been supposed, would make the stability of these complexes less surprising and also lessens the abruptness of the change from the Meisenheimer to the Janovsky type complexes. The ethylenephenonium ion, which has a geometry analogous to that of the Meisenheimer complex, can thus be treated as a modified benzyl cation,[33b] and there seems to be no reason why the Meisenheimer complexes should not be treated analogously as modified benzyl anions. Indeed such a treatment has been independently suggested [34] for the transition state in the attack of methoxide ion on *p*-chloronitrobenzene. Intermediate types of complex, such as the malonate complexes, can be derived from the two structures [(VII) and (VIII)] by similar vectorial addition of the orbitals concerned.

Halogen-displacement Reaction.—In an attempt to force the Janovsky reaction at a substituted position we examined complex formation with 2,4,6-trihalogeno-1,3-dinitro-compounds. Anomalous results were obtained. Thus, 2,4,6-trichloro-1,3-dinitrobenzene-does not give a colour with acetone and sodium hydroxide solution, whereas the corresponding tribromo-compound slowly develops an intense blue colour, $\lambda_{max.}$ 640 mμ. This might be due to reaction at the 5-position, but it is difficult to explain the difference between the two compounds in this way. The reaction with dibutyl phosphite in DMF proved helpful in elucidating this phenomenon, and gave good colorations with a number of compounds with a halogen in the 2-position. From the results set out in Table 11 it can be seen that there is a striking resemblance between the spectrum obtained with the nitro-compound and dibutyl phosphite, and the spectrum similarly obtained from the corresponding nitro-compound with 2-position unsubstituted. The halogen in the 2-position has been replaced by hydrogen and a Janovsky type reaction has then occurred in the normal way. The spectrum obtained with 2,4,6-tribromo-1,3-dinitrobenzene resembles that expected from 4-bromo-1,3-dinitrobenzene indicating that bromine can be displaced even from the 4-position. 2,4,6-Trimethoxy-1,3-dinitrobenzene does not give a colour with dibutyl phosphite and sodium hydroxide in DMF so it appears that methoxyl groups cannot be removed in this way.

Precedents for this type of removal are found in the literature. Jackson *et al.*[35] allowed 1,3-dinitro-2,4,6-tribromobenzene to react with methanolic sodium methoxide and isolated

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[32] H. Salkowski, *Annalen*, 1872, **163**, 1.

[33] A. Streitweiser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, 1961, (*a*) p. 403, (*b*) p. 382.

[34] M. Simonetta and S. Carra, *Tetrahedron*, 1963, **19** Supp. 2, 467.

[35] C. L. Jackson and W. P. Cohoe, *Amer. Chem. J.*, 1901, **26**, 1; C. L. Jackson and R. B. Earle, *ibid.*, p. 46.

a small quantity of 4,6-dimethoxy-1,3-dinitrobenzene from the reaction mixture. Heating 1,3-dinitro-2,4,6-tribromobenzene with sodium sulphite in methanol under reflux also replaces the 2-bromine atom by hydrogen.[36] Diethyl sodiomalonate with 5-bromo-2,4,6-tri-iodo-1,3-dinitrobenzene gives 5-bromo-4,6-di-iodo-1,3-dinitrobenzene and tetraethyl ethanetetracarboxylate.[36] Jackson concludes that for this type of reaction to occur, the halogen must be flanked by two nitro-groups.

Deuterium Exchange.—The action of sodium hydroxide on *m*-dinitrobenzene in DMF gives spectra which do not appear to be due solely to the direct OH^- complex, or to a complex with dimethylamine. The initial spectrum (Table 6) is slowly replaced by another, with peaks at 316 and 556 mμ. There is also a peak at 695 mμ which becomes less intense with time. The spectrum of 3,5-dinitrobenzoic acid and sodium hydroxide in DMF changes similarly, though the rate of change is very dependent on the conditions. The nature of these secondary reactions has not been established, but a possibility we considered was that the coloured species were ions formed by loss of a proton from the benzene ring. A serious objection to this theory is that deuterium exchange does not occur with 1,3,5-trinitrobenzene in 8N-sodium hydroxide solution[37] or in pyridine.[38] However, we have shown[39] that *m*-dinitrobenzene undergoes ready deuterium exchange in DMF–D_2O solution under very mild conditions. The major exchange occurs at the 2-position, whereas the spectra are more readily explained in terms of proton loss from the 4-position. However, it may well be that, as with the complexes of dibutyl phosphite, the 2-position is the more reactive whereas attack at the 4-position gives the more stable product. 1,3,5-Trinitrobenzene undergoes very little deuterium exchange under these conditions[39] and does not give secondary products with maxima on the long-wavelength side of the original λ_2 band.

It is possible that the deuterium-exchange reaction and the halogen-removal reaction proceed by similar mechanisms, as the relative ease of the latter reaction (Br > Cl) suggests removal as a positive halogen ion.

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[36] C. L. Jackson and J. F. Langmaid, *Amer. Chem. J.*, 1904, **32**, 297; C. L. Jackson and H. E. Bigelow, *ibid.*, 1909, **42**, 1868.

[37] J. A. A. Ketelaar, A. Bier, and H. T. Vlaar, *Rec. Trav. chim.*, 1954, **73**, 37.

[38] R. E. Miller and W. F. K. Wynne-Jones, *J.*, 1959, 2375.

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