

Intermediates in Nucleophilic Aromatic Substitution. VII.¹ Kinetic, Calorimetric, and Proton Magnetic Resonance Studies of the Formation of Meisenheimer Complexes of the Isomeric 2,4,6-Dicyanonitroanisoles

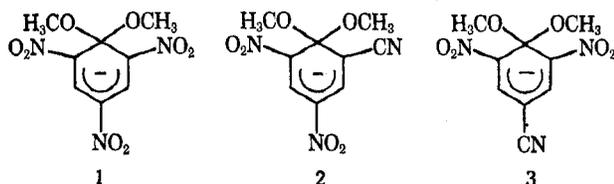
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The rate and equilibrium constants, k_1 and K , for the formation of the 1,1-dimethoxy complexes of 2,6-dicyano-4-nitroanisole (**4**) and 2,4-dicyano-6-nitroanisole (**5**) together with the rate constants for their decomposition, k_2 , have been determined in methanol and methanolic dimethyl sulfoxide solutions. The stabilities of **4** and **5** in methanol ($K_4 = 35 \text{ l. mol}^{-1}$, $K_5 = 101 \text{ l. mol}^{-1}$) are considerably smaller than those for their cyanodinitro- and trinitro-substituted analogs, and replacement of the two nitro groups in the 2 and 4 positions by cyano groups results in a greater decrease in K than the corresponding replacement of the 2- and 6-nitro groups. The observed linear increase in $\log K$ with increasing molarity of DMSO in methanol has been shown to be a composite effect of an increase in k_1 and a decrease in k_2 . The structures of **4** and **5** are substantiated by pmr spectra of both the isolated and *in situ* generated complexes. In the *in situ* generation of **5**, but not of **4**, by the reaction of methanolic methoxide ion with the parent ether in DMSO- d_6 solution, the formation of an unstable transient, 1,3-dimethoxy-2,4-dicyano-6-nitrocyclohexadienylidene ion, is observed by pmr. The formation of this transient also has been observed at low substrate concentrations by calorimetry.

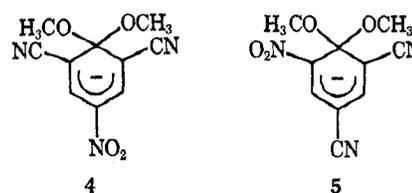
In the preceding part of this series,¹ we reported kinetic and thermodynamic data on the formation and decomposition of the 2,4,6-trinitro- (**1**), 2-cyano-4,6-dinitro- (**2**), and 4-cyano-2,6-dinitro-1,1-dimethoxy-cyclohexadienylidene (**3**). These data indicated that the relative order of complex stabilities is $1 > 2 > 3$ in



methanol, and that the replacement of a *para* nitro group by a cyano group causes a more dramatic decrease in the stability of the complex than the corresponding replacement in the *ortho* position.

In order to substantiate these conclusions, we have prepared, isolated, and studied **4** and **5** as crystalline complexes and report our studies on the effect of replacing two nitro groups by cyano groups on the structure and stability of these complexes. We also wish to present calorimetric and pmr evidence for the forma-

tion of a transient 1,3-dimethoxy complex in the formation of **5**, as well as dimethyl sulfoxide (DMSO) solvent effects on the formation and decomposition of **5** and on the equilibrium constant of **4**.



Experimental Section

The solvents and reagents were prepared, purified, and standardized as previously described.³ Solutions of sodium methoxide in methanolic DMSO were freshly prepared from the purified solvents by the appropriate dilutions.

1-Bromo-2,4-dicyanobenzene (**6**) and 1-bromo-2,6-dicyanobenzene (**7**) were prepared from 4-bromoisophthalic acid (**8**) and 2-bromo-*m*-xylene (**9**), respectively, according to procedures similar to that used by Wallenfels, *et al.*, for the preparation of 1-bromo-2,4,6-tricyanobenzene.⁴ 4-Bromoisophthalamide (**10**) was prepared by refluxing 14.27 g (58 mmol) of **8** in 85 ml of thionyl chloride for 24 hr, followed by removal of the excess thionyl chloride by rotary evaporation. The residue was dissolved

(1) Part VI: J. H. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, **34**, 689 (1969); presented, in part, at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

(2) (a) University of Pittsburgh; (b) Carnegie-Mellon University; (c) The University of Toledo; (d) University of Tennessee.

(3) W. E. Byrne, E. J. Fendler, J. H. Fendler, and C. E. Griffin, *J. Org. Chem.*, **32**, 2506 (1967).

(4) K. Wallenfels, F. Witzler, and K. Friedrich, *Tetrahedron*, **23**, 1353 (1967).

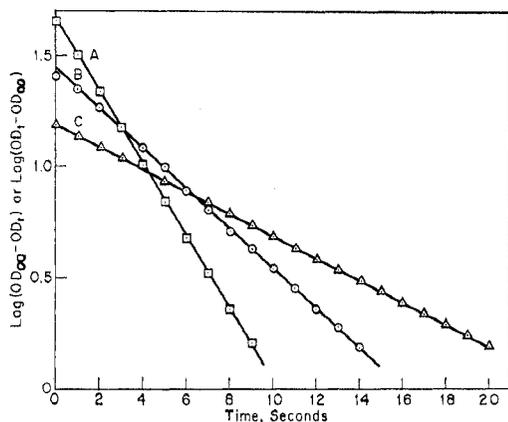


Figure 1.—(A) Plot of $\log(OD_t - OD_\infty)$ against time for the decomposition of 4 in methanol at 25.00°. (B) Plot of $\log(OD_t - OD_\infty)$ against time for the decomposition of 5 in methanol at 25.00°. (C) Plot of $\log(OD_\infty - OD_t)$ against time for the attainment of equilibrium of 5 in DMSO-MeOH, 10:90 (v/v), at 25.00°; $[15] = 9.0 \times 10^{-3}M$, $[NaOCH_3] = 1.86 \times 10^{-3}M$.

in 250 ml of dry benzene and ammonia was bubbled through the stirred reaction mixture for ca. 8 hr. The white precipitate of ammonium chloride and 10 was filtered, dried at 90–100°, and suspended in 200 ml of water. Filtration gave colorless, crystalline 10, which was washed with water and dried at 90–100°, mp 248–249°. The dinitrile 6 was prepared by refluxing a mixture of 10.0 g (41 mmol) of 10, 5.4 g of sodium chloride, and 50 ml of phosphorus oxychloride for 4 hr. The excess phosphorus oxychloride was removed by rotary evaporation at 0.1 mm and the residue was poured into ca. 100 ml of ice water. The precipitate was filtered, washed with water, and dried *in vacuo* over phosphorus pentoxide. After recrystallization from benzene, the colorless crystals of 6 melted at 193–193.5°.

2-Bromoisophthalic acid (11) was prepared by alkaline potassium permanganate oxidation of 9. A mixture of 25 g (135 mmol) of 9, 6.25 g of sodium hydroxide, 132 g of potassium permanganate, and 625 ml of water was refluxed for 15 hr; an additional 50 g of potassium permanganate was added; and the mixture was refluxed for a further 7 hr. The excess potassium permanganate was decomposed with methanol, the hot solution was filtered, and the manganese dioxide precipitate was washed four times with ca. 200-ml portions of hot water. The combined filtrates were concentrated to ca. 250 ml by distillation and acidified with concentrated nitric acid. The precipitate was filtered, washed with cold water, and dried *in vacuo* over phosphorus pentoxide. The colorless crystals of 11 melted at 216–218° (lit.⁵ mp 218°). 2-Bromoisophthalamide (12) was prepared from 11 by a procedure analogous to that described for 10. 7 was prepared by the dehydration of 12 with phosphorus oxychloride as previously described and melted at 190–190.5°.

2,4-Dicyanoanisole (13) was prepared by the addition of 2.62 ml (15 mmol) of 5.73 *M* potassium methoxide in methanol to a solution of 1.92 g (10 mmol) of 6 in 20 ml of methanol. The reaction mixture was refluxed for 7 hr, cooled, and poured onto 50 g of ice. The colorless crystals of 13 were filtered, washed with distilled water, and dried *in vacuo* over phosphorus pentoxide, mp 205–206°.

The same procedure was used to prepare 2,6-dicyanoanisole (14), mp 90–90.5°, from 6.93 ml (35 mmol) of 5.05 *M* potassium methoxide in methanol and 5.76 g (30 mmol) of 7 in 30 ml of methanol, with the exception that the reaction mixture was refluxed for 19 hr, cooled, and poured onto 100 g of ice.

2,4-Dicyano-6-nitroanisole (15) was prepared by the addition of 1.75 g of 13 to 35 ml of fuming nitric acid (*d* 1.52). The reaction mixture was stirred at 60–70° for 2 hr and at room temperature for 15 hr, cooled, and poured onto 100 g of ice. The solution was neutralized slowly with rigorous stirring to pH 6 by the addition of concentrated sodium hydroxide at 0°. The colorless, crystalline precipitate was filtered, washed with distilled water, and dried *in vacuo*. After recrystallization from aqueous methanol, the colorless needles of 15 melted at 119–120°.

(5) E. A. Coulson, *J. Chem. Soc.*, 1298 (1937).

*Anal.*⁶ Calcd for $C_9H_5N_3O_3$: C, 53.25; H, 2.48; N, 20.68. Found: C, 53.43; H, 2.48; N, 20.36.

The same procedure and reactant quantities were used to prepare 2,6-dicyano-4-nitroanisole (16) from 14. After recrystallization from methanol, the colorless needles of 16 melted at 148.5–149.5°.

*Anal.*⁶ Calcd for $C_9H_5N_3O_3$: C, 53.25; H, 2.48; N, 20.68. Found: C, 53.41; H, 2.33; N, 20.65.

Potassium 1,1-dimethoxy-2,4-dicyano-6-nitrocyclohexadienylide (5) was prepared by the addition of 0.211 ml (1.07 mmol) of 5.05 *M* potassium methoxide in methanol to a solution of 0.204 g (1.08 mmol) of 15 in 0.25 ml of dry dioxane. The red crystals which formed immediately on slight cooling were filtered under dry nitrogen and were washed with dry benzene and anhydrous ether. The crystalline product did not decompose completely at temperatures <280°. This material contained approximately 0.5 mol of dioxane of crystallization (by pmr integration of dioxane singlet, τ 6.43 ppm³).

*Anal.*⁶ Calcd for $C_{10}H_8N_3O_4K \cdot 0.5C_4H_8O_2$: C, 45.3; H, 4.05; N, 13.2; K, 12.3. Found: C, 40.79; H, 3.58; N, 11.92; K, 16.28.

The same procedures and reactant quantities were used for the preparation of potassium 1,1-dimethoxy-2,6-dicyano-4-nitrocyclohexadienylide (4) from 16 in 0.50 ml of dry dioxane. The yellow crystals, which formed upon evaporation of a small amount of the solvents with dry nitrogen, were filtered and washed with dry benzene and anhydrous ether in an atmosphere of dry nitrogen. The yellow crystals turned red at ca. 140°, but did not decompose completely at temperatures <280°. This material contained approximately 0.34 mol of dioxane of crystallization (pmr integration).

*Anal.*⁶ Calcd for $C_{10}H_8N_3O_4K \cdot 0.3C_4H_8O_2$: C, 44.80; H, 3.49; N, 14.01; K, 13.04. Found: C, 42.03; H, 2.73; N, 13.95; K, 13.02.

The analyses for complexes 5 and 4 are rather poor and duplicate analyses showed a considerable lack of reproducibility which suggests that these results could be due to loss of dioxane or methanol during the analyses or the presence of potassium carbonate in the ash. The purity of these complexes was, however, found to be greater than 98% by pmr integration, and no impurities could be detected in their infrared spectra obtained under conditions of maximum resolution on a Perkin-Elmer 221 spectrophotometer.

The attainment of the equilibrium for the formation of complex 5 and 15 in methanol and in methanolic DMSO was followed at 480 μ in the thermostated cell compartment of a Beckman DU-2 spectrophotometer. The temperature was measured inside the cells and was maintained within $\pm 0.02^\circ$. The mixing techniques for fast reactions have been described previously.¹

The decomposition of complexes 4 and 5 was initiated by injecting a freshly prepared concentrated solution of the complex (50–100 μ l in DMSO) into the thermostated methanol or methanolic DMSO contained in the cell compartment of the spectrophotometer. The rate of color disappearance was followed at the appropriate wavelength. Since the concentration of 15 was kept a hundredfold smaller than that of the sodium methoxide, and since the concentrations of the complexes were in the order of $10^{-4}M$, pseudo-first-order kinetics were observed for both the attainment of the equilibrium for 5 and for the decomposition of complexes 4 and 5. Such first-order plots for typical runs are given in Figure 1.

Rapid mixing techniques¹ were used to determine the absorbance due to the complexes at the various methoxide ion concentrations in methanol and in methanolic DMSO. The blank in each case contained the same concentration of methoxide ion in the corresponding solvent.

Calorimetric studies were carried out with a dual calorimeter similar to that described by Arnett, Bentrude, Burke, and Duggleby.⁷

The apparatus was checked at least once a month by measuring the heat of solution of potassium chloride in water. The values obtained usually agreed within $\pm 1\%$ of the accepted value⁸ and always agreed within $\pm 2\%$.

(6) Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(7) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).

(8) V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," National Bureau of Standards, Washington, D. C., Patent NSRDS-NBS2.

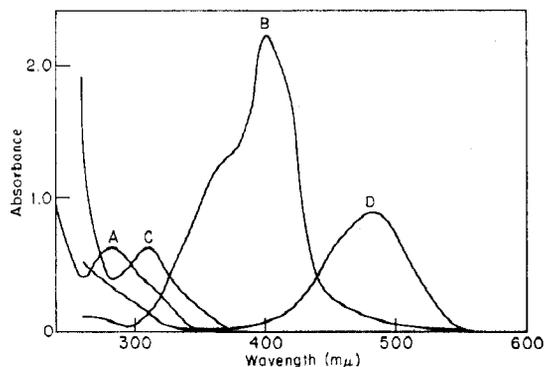


Figure 2.—Absorption spectra of 2,6-dicyano-4-nitroanisole (**16**) ($6.75 \times 10^{-5} M$) in methanol (A) and in 2.99 *M* methanolic sodium methoxide (B). Absorption spectra of 2,4-dicyano-6-nitroanisole (**15**) ($3.96 \times 10^{-5} M$) in methanol (C) and in 2.99 *M* methanolic sodium methoxide (D) (all in matched 1.00-cm cells).

The 60-MHz pmr spectra were obtained with a Varian Associates A-60 spectrometer at 25° (probe temperature maintained with a V6040 variable-temperature controller). Unless otherwise noted, all spectra were determined on solutions in DMSO-*d*₆ using tetramethylsilane (TMS) as an internal standard; chemical shifts (τ , parts per million) are given relative to TMS (τ 10.00 ppm) and are accurate to ± 0.03 ppm. Chemical-shift data were taken from spectra determined at sweep widths of 500 Hz. The reported coupling constants are the average of at least three determinations at 50-Hz sweep widths and are accurate to ± 0.02 Hz.

Results

The absorption spectra of 2,4-dicyano-6-nitroanisole (**15**) and 2,6-dicyano-4-nitroanisole (**16**) in methanol and in 2.99 *M* methanolic sodium methoxide are shown in Figure 2. The data for the interaction of **15** with sodium methoxide at 25.00° are given in Table I for methanolic solutions and in Table II for methanolic

TABLE I
INTERACTION OF 2,4-DICYANO-6-NITROANISOLE (**15**)
($7.29 \times 10^{-5} M$) WITH METHANOLIC SODIUM
METHOXIDE AT 25.00°

$10^3[\text{NaOCH}_3], M$	Absorbance at 480 $m\mu^a$	$10^3 k_{\text{obsd}}, \text{sec}^{-1}$
0 ^b		1.79
0 ^b		1.81
0 ^b		2.09
0 ^b		2.25
1.03	0.132	2.34
2.06	0.260	2.62
3.09	0.363	3.77
4.12	0.460	2.69
5.18	0.528	2.71

^a Using a pair of matched 10-mm cells. ^b Decomposition of the solid complex **5**.

DMSO. Values and standard deviations of k_1 for **15** in these solvents have been calculated by least-squares treatments of the data. Attempts were made to obtain k_1 values at different temperatures in order to calculate the Arrhenius parameters for the formation of complex **5**. The standard deviations for these kinetic runs were, however, even greater than for those at 25.00°. Similarly, attempts to obtain k_1 values for the reaction of **16** with methoxide ion in methanol or in methanolic DMSO were completely frustrated by irreproducible k_{obsd} values. Kinetic measurements in methanolic DMSO systems yielded better data; the standard deviations in the k_1 values are considerably

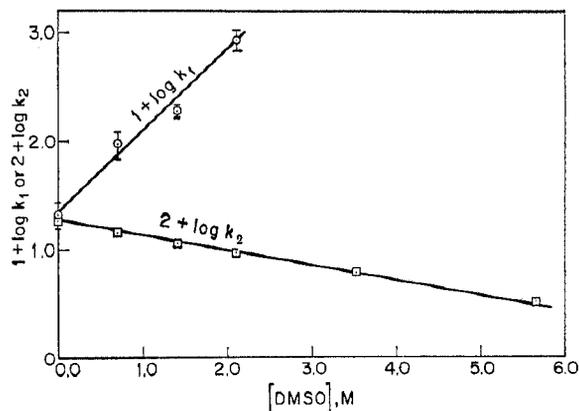


Figure 3.—Plot of $1 + \log k_1$ and $2 + \log k_2$ for **5** in methanolic dimethyl sulfoxide at 25.00°.

TABLE II
INTERACTION OF 2,4-DICYANO-6-NITROANISOLE (**15**) WITH
SODIUM METHOXIDE IN METHANOLIC
DIMETHYL SULFOXIDE AT 25.00°

[DMSO], <i>M</i>	$10^3[\text{NaOCH}_3], M$	$10^3 k_{\text{obsd}}, \text{sec}^{-1}$	$k_1, \text{l. mol}^{-1} \text{sec}^{-1}$	
0			2.06 ± 0.83^a	
0.70 ^b	0 ^c	15.4		
	0 ^c	14.3		
	0 ^c	13.9		
	3.94	17.5		
	7.38	22.5		
	9.85	20.7		
	12.30	25.3		
	14.74	30.4	9.55 ± 1.06	
	1.41 ^b	0 ^c	11.7	
		0 ^c	10.8	
0 ^c		12.0		
1.86		11.7		
2.80		12.4		
3.73		16.3		
4.60		17.3		
9.32		27.1		
11.65		32.7		
16.3		42.5		
2.10 ^d	18.6	45.0	19.1 ± 0.8	
	0 ^c	9.43		
	0 ^c	9.43		
	2.20	16.33		
	4.40	24.2		
	6.60	24.6		
	8.80	58.9		
	11.00	103.5		
	13.2	131.8	87.4 ± 14	

^a For details see Table I. ^b $[\text{15}] = 9.0 \times 10^{-5} M$. ^c Decomposition of the solid complex **5** in the appropriate methanolic DMSO. ^d $[\text{15}] = 8.0 \times 10^{-5} M$.

smaller in 0.70 and 1.41 *M* DMSO in methanol than in pure methanol (Table II). The uncertainty in k_1 values in the 2.10 *M* DMSO system is due to the very high k_{obsd} values. A linear relationship has been found between $\log k_1$ and $\log k_2$ and molar DMSO concentration (Figure 3). Using the absorbance data in Table I and the form of the Benesi-Hildebrand equation⁹ shown

$$\frac{[\text{15}] \text{ or } [\text{16}]}{A} = \frac{1}{\epsilon} + \frac{1}{K\epsilon[\text{NaOCH}_3]} \quad (1)$$

(9) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

TABLE III
DECOMPOSITION OF POTASSIUM 1,1-DIMETHOXY-2,4-DICYANO-6-NITROCYCLOHEXADIENYLIDE (5) IN METHANOLIC DIMETHYL SULFOXIDE

	[DMSO], M			
	0	1.41	2.10	3.52
$10^2 k_2$, sec $^{-1}$ at 25.00°	19.8	11.5	9.43	6.52
$10^2 k_2$, sec $^{-1}$ at 14.45°	9.07	5.51	4.16	2.47
E_2 , kcal mol $^{-1}$	12.4 ± 1.0	11.9 ± 1.0	13.3 ± 1.0	15.7 ± 1.0
ΔS^\ddagger , eu	-22 ± 3	-24 ± 3	-20 ± 3	-13 ± 3

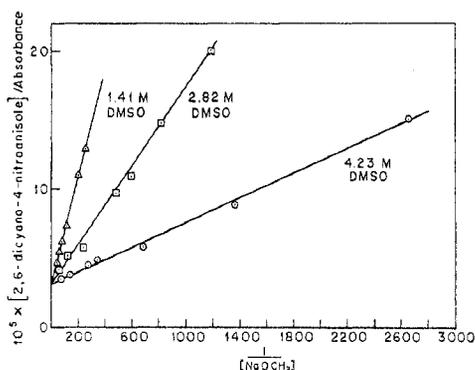


Figure 4.—Benesi-Hildebrand plots for the formation of 4 in methanolic dimethyl sulfoxide.

where A is the absorbance in a 1.0-cm cell, ϵ is the extinction coefficient, and K is the equilibrium constant for the complex, a good linear relationship was obtained on plotting $[15]/A$ vs. $1/[\text{NaOCH}_3]$ indicating that a simple 1:1 equilibrium prevails.^{1,3,10} Since the intercept of the Benesi-Hildebrand plot (*i.e.*, $1/\epsilon$) is susceptible to large errors, ϵ was determined independently by dissolving known amounts of 5 in DMSO and in various DMSO-methanol mixtures and measuring the absorbance (using the appropriate blanks) at 480 m μ . A value of $\epsilon_{480} = (2.1 \pm 0.1) \times 10^4 \text{ cm}^{-1} \text{ l. mol}^{-1}$ represents the mean of five independent measurements and was used in conjunction with eq 1 to obtain $K = 15 \text{ l. mol}^{-1}$. This value is in agreement with that of $K = 10 \pm 5 \text{ l. mol}^{-1}$ obtained from the kinetic data (k_1/k_2 in Table II). Table III contains the kinetic and thermodynamic data for the decomposition of 5 in methanol and methanolic DMSO.

Equation 1 was used to calculate K for the formation of 4 at 25.00° in methanol and methanolic DMSO. The data are given in Table IV and typical Benesi-Hildebrand plots are shown in Figure 4. The extinction coefficient obtained from the intercept of Figure 4 for 4, $\epsilon_{400} = 3.12 \times 10^4 \text{ cm}^{-1} \text{ l. mol}^{-1}$, is in very good agreement with that of $\epsilon_{400} = (3.1 \pm 0.5) \times 10^4 \text{ cm}^{-1} \text{ l. mol}^{-1}$ obtained from direct measurements by dissolving known amounts of 4 in DMSO and DMSO-methanol mixtures and measuring the absorbance at 400 m μ against the appropriate solvent blanks. A satisfactory linear relationship of $\log K$ vs. $[\text{DMSO}]$, M , for 16 has also been obtained. Table V contains the kinetic and thermodynamic data for the decomposition of 4 in methanol and in methanolic DMSO.

The heats of formation of several Meisenheimer complexes from the corresponding anisoles and sodium methoxide in solution are given in Table VI, together with free energies calculated from the data in Tables II and IV. The heats of formation were obtained by

(10) E. J. Fendler, J. H. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, **33**, 4141 (1968).

TABLE IV
INTERACTION OF 2,6-DICYANO-4-NITROANISOLE (16) WITH SODIUM METHOXIDE IN METHANOLIC DIMETHYL SULFOXIDE AT 25.00°

[DMSO], M	$10^2 [\text{NaOCH}_3]$, M	Absorbance at 400 m μ^a	K , l. mol ^{-1}b	
0°	5.25	0.079		
	10.5	0.136		
	21.0	0.205		
	31.5	0.262		
	42.0	0.316		
	52.5	0.336	33.5	
	1.41 d	9.45	0.332	
		12.18	0.390	
		18.90	0.442	
		23.63	0.548	
28.35		0.515		
37.80		0.560	77.0	
2.82 b		0.84	0.121	
		1.68	0.222	
		2.10	0.249	
		3.60	0.330	
	4.20	0.421		
	8.40	0.468		
	12.6	0.545		
	16.8	0.578		
	21.0	0.618	221	
	4.23 c	0.368	0.109	
0.735		0.200		
1.47		0.278		
2.21		0.325		
2.94		0.336		
3.68		0.362		
7.35		0.428		
14.7		0.477	695	

^a Using a pair of matched 10-mm cells. ^b Obtained from eq 1. ^c $[16] = 1.89 \times 10^{-5} M$. ^d $[16] = 2.43 \times 10^{-5} M$. ^e $[16] = 1.65 \times 10^{-5} M$.

subtracting the heat of solution of the solid substituted anisole in the indicated solvent from the heat of solution of the same compound in the solvent containing sodium methoxide. Concentrations of the reactants were kept below 0.013 M . The above method is applicable only when the equilibrium constant for complex formation is large. When this is not the case, the heat of complex formation (H_f) was calculated from

$$H_f = H_{\text{obsd}}/[c]V$$

where $[c]$ is the concentration of the complex, V is the volume of solution in the calorimeter (210.0 ml), and H_{obsd} is the difference in the heat of solution of the substituted anisole in the pure solvent and in the solvent containing sodium methoxide. The concentration of the complex, $[c]$, was calculated from

$$[c] = \frac{([A] + [B] + 1/K) \pm \sqrt{([A] + [B] + 1/K)^2 - 4[A][B]}}{2}$$

TABLE V
DECOMPOSITION OF POTASSIUM 1,1-DIMETHOXY-2,6-DICYANO-4-NITROCYCLOHEXADIENYLIDE (4) IN
METHANOLIC DIMETHYL SULFOXIDE

	[DMSO], M				
	0	1.41	2.82	4.32	5.64
$10^2 k_2$, sec ⁻¹ at 25.00°	37.3	21.16	12.90	6.30	3.29
$10^2 k_2$, sec ⁻¹ at 14.45°	14.37	6.80	4.37		
$10^2 k_2$, sec ⁻¹ at 7.60°	7.95	3.71	2.29		
E_2 , kcal mol ⁻¹	14.6 ± 0.8	16.7 ± 0.8	16.7 ± 0.8		
ΔS^\ddagger , eu	-20.4 ± 2.0	-6.9 ± 2.0	-7.8 ± 2.0		

TABLE VI
THERMODYNAMIC VALUES FOR FORMATION OF MEISENHEIMER
COMPLEXES AT 25°

Complex	Solvent (vol. % DMSO in methanol)	ΔF , kcal/mol	ΔH , kcal/mol ^a	ΔS , eu
	0	-2.1	Endothermic	
4	20	-3.2	-2.23 ± 0.55	+3.3
	30	-3.9	-2.46 ± 0.64	+4.7
5	15	-3.4	-0.82 ± 0.49	+8.7
19	15		(+3.05 ± 0.64) ^b	
1	0	-5.77	-4.86 ± 0.30	+3.0
18	0		-1.48 ± 0.50 ^c	

^a Errors are standard deviations (σ) from the mean. ^b This is a minimum value calculated assuming that K for the 1,3 complex is the same as K for the 1,1 complex. ^c Calculated assuming that K for the 1,3 complex is large, *i.e.*, that the complex formation is essentially complete.

where [A] and [B] are the initial concentrations of anisole and base and K is the equilibrium constant.

The behavior of 2,4,6-trinitroanisole (17) and 15 toward sodium methoxide in methanol and in 15% (v/v) DMSO in methanol indicates that a complex forms prior to the formation of the more stable 1,1 complex. Two typical calorimetric runs are superimposed in Figure 5. Curve 1 is typical of the injection of solid 17 into pure methanol. Curve 2 reproduces an injection of the same amount of 17 into methanol containing 0.01 M sodium methoxide. Normally, one-step complex formation yields a curve identical with 1 but displaced along the enthalpy axis. Extrapolation of the lines on opposite sides of the peak yields an intersection point considerably below the displacement due to the endothermic solution of 17 in methanol. With 15, the curve is displaced in an endothermic direction from the curve generated by the dissolution of the anisole in the solvent. In both cases, the calorimeter results indicate formation of a transient. In contrast, 16 gives no evidence for transient formation. As shown by curve 2, the transients are converted in an exothermic process into the final products, the 1,1 complexes. The rate of formation of the 1,1 complex 1 from the transient calculated from curve 2 is in fair agreement with the rate reported by Gold¹¹ (4 l. mol⁻¹ sec⁻¹). The first-order rate of formation of 5 from the transient in 0.01517 M sodium methoxide in methanol is roughly $k = 0.20$ sec⁻¹. This is too fast to enable an accurate determination using the calorimeter. The method of Bolles and Drago¹² has been applied to the calorimetric data yielding values of K in rough agreement with those obtained from absorption spectroscopy. Using this method¹² the values of K obtained for the 1,1 and 1,3 complexes were the same within a rather large experi-

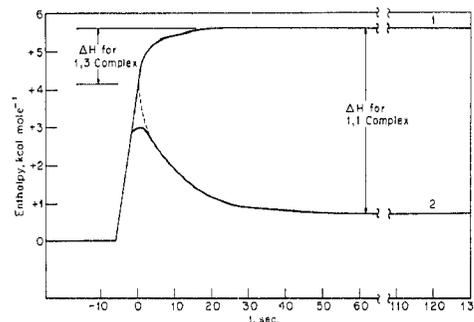


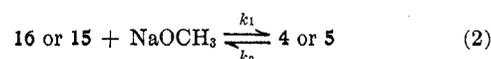
Figure 5.—Plots of enthalpy, ΔH , vs. time for solid 17 in pure methanol (curve 1) and the same amount of 17 in 0.01 M methanolic sodium methoxide (curve 2).

mental error. This result indicates that the two K values are at least of the same order of magnitude.

Table VII allows an intercomparison of kinetic and thermodynamic data for the formation and decomposition of complexes 1 and 5 in methanol at 25.00°. The pmr data for the dicyanonitroanisoles and the 1,3- and 1,1-dimethoxycyclohexadienylides are given in Table VIII.

Discussion

The absorption maxima of 15 and 16 in methanolic sodium methoxide at 400 and 480 μ are assigned to complexes 4 and 5 since the spectra of the isolated complexes have the same maxima. In each case the absorption maximum is reached at approximately 10^{-1} M sodium methoxide and remains essentially constant at higher concentrations; *i.e.*, the equilibria given in eq 2



prevail. As in the case of the Meisenheimer complex formations previously studied,¹ the increase of absorbance at 480 μ for 5 at lower methoxide ion concentrations was followed as a function of time. Under the experimental conditions, the observed first-order rate constant, k_{obsd} , for equilibrium attainment is given by¹

$$k_{\text{obsd}} = k_1[\text{NaOCH}_3] + k_2 \quad (3)$$

where k_1 is the second-order rate constant for the formation of the complex and k_2 is the first-order rate constant for its decomposition. We have successfully used eq 3 previously for calculating k_1 and k_2 values for a number of Meisenheimer complexes.^{1,3,10} However, plots of k_{obsd} against sodium methoxide concentration for 15 showed considerable scatter. The reason for these difficulties lies mainly in the unfavorably small equilibrium constants. With the present technique, it appears that optimum conditions for obtaining k_1 and k_2 values prevail when K is reasonably high and when

(11) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1987 (1964).

(12) T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, **87**, 5015 (1965).

TABLE VII
KINETIC AND THERMODYNAMIC PARAMETERS FOR THE FORMATION AND DECOMPOSITION OF TRINITRO-,
CYANODINITRO-, AND DICYANONITRO-SUBSTITUTED MEISENHEIMER COMPLEXES IN METHANOL AT 25.00°

	1 ^a	2 ^a	3 ^a	4	5
k_1 , l. mol ⁻¹ sec ⁻¹	17.3	18.8	6.1	~12 ^b	2.0
10 ³ k_2 , sec ⁻¹	1.04	7.20	22.0	373	198
K , l. mol ⁻¹	17,000	2600	280	34	10
E_1 , kcal mol ⁻¹	13.5 ± 1.0	17.8 ± 0.8	13.9 ± 0.8		
ΔS_1^\ddagger , eu	-9.4 ± 2.0	+5.0 ± 2.0	-10.4 ± 2.0		
E_2 , kcal mol ⁻¹	19.0 ± 1.0	14.4 ± 0.8	9.6 ± 0.8	14.6 ± 0.9	12.4 ± 1.0
ΔS_2^\ddagger , eu	-4.8 ± 2.0	-20 ± 2.0	-32.0 ± 2.0	-20.4 ± 2.5	-22.0 ± 3.0

^a Data obtained in ref 1. ^b Calculated from k_2 and K .

TABLE VIII
PMR SPECTRA OF DICYANONITROANISOLES AND THE CORRESPONDING 1,3- AND 1,1-DIMETHOXYCYCLOHEXADIENYLIDES^a

	16	4 ^b	15	5 ^b	19 ^c
τ_1 (OCH ₃)	5.53	7.02	5.78	7.08	5.78
τ_3 (OCH ₃)				7.03	
τ_3 (H)	1.00	2.10	1.24	2.70	4.88
τ_5 (H)	1.00	2.10	1.14	2.00	2.12
J_{35}			2.7	2.3	2 ^d

^a Except where noted, spectra determined in DMSO-*d*₆ at 25°. Details of method are given in Experimental Section. ^b Spectra determined on samples of isolated complexes. ^c Spectrum determined in MeOH-DMSO-*d*₆ mixtures. ^d J_{35} estimated from 500-Hz sweep width spectra.

the methoxide ion concentration is kept in the region of 10⁻²-10⁻³ *M*. Carbon dioxide may interfere at lower methoxide ion concentrations and changes in ion activities introduce uncertainties at higher concentrations.

The order of stabilities of the 2,4,6-trisubstituted Meisenheimer complexes parallels the electron-withdrawing power of the substituents at these positions. The stabilities of the trinitro- (1),¹ cyanodinitro- (2, 3),¹ and dicyanonitro- (4, 5) substituted Meisenheimer complexes are best expressed by the equilibrium constants of their formation in methanol at 25.00°: $K_1 > K_2 > K_3 > K_4 > K_5$. Replacing two nitro groups in the 2 and 4 positions by cyano groups results in a greater effect on K than replacing two nitro groups in the 2 and 6 positions: $K_1/K_4 = 500$, $K_1/K_5 = 1700$. The present results substantiate our earlier¹ findings of $K_1/K_2 = 6.5$ and $K_1/K_3 = 60$, and those of others who observed greater activating power for *p*-nitro compared with *o*-nitro groups for methoxydehalogenations.¹³ Molecular orbital calculations have also demonstrated that the *para* substituent carries the bulk of the negative charge in Meisenheimer complexes.¹⁴

Changes in the equilibrium constants for complexes 1-5 are dependent to a greater extent on the changes in k_2 than those in k_1 (Table VI). A similar situation has been encountered in comparisons of the k_1 and k_2 values for the methoxyl complexes of 1-methoxy-2,4-dinitronaphthalene¹⁰ and 2,4-dinitroanisole.¹⁵ Lack of experimental data does not allow the comprehensive discussion of the Arrhenius parameters for complexes 4 and 5 which was possible for complexes 1-3.¹

It has been known for some time that dipolar aprotic

solvents enhance the stability of Meisenheimer complexes.³ Indeed, this fact has been used extensively to facilitate the isolation of crystalline potassium or sodium cyclohexadienylides.^{1,3,10,16} Kinetic results on the interaction of 15 and 16 with sodium methoxide in methanol and methanolic DMSO (Tables II and IV, Figure 3) allows a quantitative treatment of this observation. The similarity of the dielectric constants of methanol (30) and DMSO (47)¹⁷ renders this solvent pair particularly useful for kinetic studies. The equilibrium constant for the formation of 4 is higher by a factor of approximately 20 in 4.23 *M* DMSO in methanol (DMSO-MeOH, 30-70 v/v) than in pure methanol. Furthermore, this increase in the equilibrium constant with increasing amounts of DMSO in the solvent pair is a composite effect of an increase in k_1 and a decrease in k_2 (Table II and Figure 3).

As a first approximation, the enhancement of k_1 obtained by an enrichment of the solvent in DMSO can be attributed to the difference in the hydrogen-bonding power of these solvents. It has been generally recognized that such strong hydrogen-bond acceptors as methoxide ions become considerably less solvated in dipolar aprotic than in protic solvents.¹⁸ The methoxide ion in the DMSO-rich solvent is, therefore, less extensively hydrogen bonded and can consequently become a stronger nucleophile than in pure methanol. A similar rationalization can be extended to the effect of DMSO as a cosolvent on k_2 . Since the negative charge is delocalized in the Meisenheimer complex, the aprotic DMSO solvates this large ionic species to a greater

(16) G. S. Gitis, A. I. Glaz, and A. Ya. Kaminskii, *J. Gen. Chem. USSR*, **33**, 3229, (1963); S. Nagakura, *Tetrahedron Suppl.*, **19**, 361 (1963).

(17) D. Martin, A. Weise, and H.-J. Niclas, *Angew. Chem. Intern. Ed. Engl.*, **6**, 318 (1967), and references cited therein.

(13) J. F. Bunnett and R. J. Morath, *J. Amer. Chem. Soc.*, **77**, 5051 (1955); W. Greizerstein and J. A. Brioux, *ibid.*, **84**, 1032 (1962).

(14) P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller, and H. Zolinger, *Helv. Chim. Acta*, **50**, 848 (1967).

(15) C. F. Bernasconi, *J. Amer. Chem. Soc.*, **90**, 4982 (1968).

(18) A. J. Parker, *Quart. Rev. (London)*, **163** (1962); *Advan. Org. Chem.*, **5**, 1 (1965); *Advan. Phys. Org. Chem.*, **5**, 173 (1967); *Chem. Rev.*, **69**, 1 (1969).

extent than methanol and hence enhances its stability.

The arguments presented so far are, however, gross oversimplifications. Any serious consideration of solvent effects on rates has to include changes in the activity coefficients of the reactants and of the transition state as a function of solvent changes. The pioneering work of Parker and his coworkers has laid the foundation for this type of treatment.¹⁹ From solubility and electrochemical measurements these workers have demonstrated quantitatively that polar reactants and large polarizable S_NAr transition states are more, but small negative ions are less, solvated by DMSO than by methanol. This conclusion qualitatively fits our data, but quantitative treatment must wait until activity coefficient data are available for **15** and **16** or similar aromatic ethers. It is realized that "solvent sorting" could possibly occur in mixed solvents such as methanolic DMSO. This "solvent sorting" would result in further complications by producing cybotactic regions whose composition is different from that of the bulk solvent.²⁰ Such a situation is more likely to occur in DMSO-rich solvents (>95% DMSO) where the effects of extensive ion pairing of the methoxide ion also need to be considered.²¹

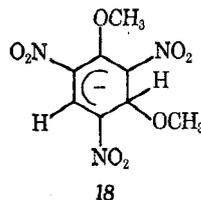
Linear correlations have been obtained between $\log k_1$, $\log k_2$, and $\log K$ vs. molar DMSO concentration for compounds **15** and **16** (Figure 3). Similar results have been found for the reactions of alkoxides and amines with 4-fluoronitrobenzene and 2,4-dinitrochlorobenzene in methanolic DMSO.²² Kingsbury observed that the slopes of $\log k$ vs. [DMSO], M , have a fairly constant value of 0.275 and concluded that the DMSO "catalysis" is relatively independent of the system involved.²² Values of 0.75 and -0.14 for the slopes of $\log k_1$ and $\log k_2$ vs. [DMSO], M , for the reaction of **15** with methoxide ion clearly render this conclusion untenable. In the light of the numerous parameters influencing the solvent effects (*vide supra*), it is unwarranted to attach any mechanistic significance to the linearity of this type of plot. Once such linearity has been established, however, this relationship may be used profitably to obtain K values in methanol for such nucleophilic aromatic substitutions where $k_1/k_2 < 1$. We have successfully used this method for estimating the equilibrium constant for the interaction of methoxide ion with tricyanoanisole in methanol from the data obtained in various methanolic DMSO solutions.²³

A large body of experimental evidence for nucleophilic aromatic substitutions where the rate-determining step is the formation of the intermediate complex indicates that dipolar aprotic solvents more strongly affect the enthalpy than the entropy of activation.¹⁸ Unfortunately, the lack of data on the temperature effect on k_1 for the reaction of methoxide ion with **15** and the large uncertainties in the calorimetric determination of ΔH values for **4** do not allow us to substan-

tiate this generalization. The decomposition of Meisenheimer complexes (k_2) in different methanolic DMSO mixtures are governed to a greater extent by entropy changes (Tables III and V). Increasing the DMSO concentration caused an increase in ΔS^\ddagger . This is explicable in terms of a greater solvation difference between the ground and transition states in methanol than in DMSO.

The structures of the 1,1-dimethoxy complexes **4** and **5** are confirmed by their pmr spectra (Table VIII). The observed parameters are in full accord with expectations based on the spectra of the corresponding cyanodinitro¹ (**2** and **3**) and trinitro^{1,24} (**1**) complexes. Since the salient characteristics and structural implications of the pmr spectra of Meisenheimer complexes have been discussed in detail elsewhere,^{1,8,10,24,25} no further comments on the spectra of **4** and **5** are warranted.

Calorimetric studies indicate the formation of transients in the reactions leading to **1** and **5**; however, no conclusions regarding structures can be drawn on the basis of calorimetric studies. In the light of previous work,^{1,24,26} it appears most likely that the transients detected are 1,3 complexes, formed by rapid attack of methoxide ion at the 3 position of the anisoles. Servis²⁴ has provided pmr evidence for the formation of **18** as a transient in the reaction of 2,4,6-trinitroanisole with methoxide ion; **18** undergoes rapid conversion into the



1,1 complex **1**.²⁷ Pmr studies of the *in situ* generation of **5** from **15** and potassium methoxide confirm the calorimetric detection of a transient and provide evidence for its structure. Addition of 1 drop of 5.73 M potassium methoxide in methanol to a solution of **15** in DMSO- d_6 at 25° results in a broadening²⁸ of the protons of **15** and the development of weak doublets of equal intensities at τ 2.12 and 4.88 ppm at the expense of the signals attributable to **15**. Within 18 min of the addition of the potassium methoxide, the transient doublets are undetectable and only the multiplet due to **15** and the doublets at τ 2.00 and 2.70 ppm are observable. Similar behavior is observed on the addition of the second and third drops of 5.73 M potassium methoxide. The rate of disappearance of the transient signals

(24) K. L. Servis, *J. Amer. Chem. Soc.*, **89**, 1508 (1967).

(25) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966); M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969).

(26) E. Bunel, A. R. Norris, and K. E. Russell, *Quart. Rev. (London)*, **22**, 123 (1968).

(27) Throughout this paper we have referred to the 1,3-dimethylcyclohexadienylidene complexes as transients. However, by the use of this terminology in the formation of the 1,1 complexes, we do not intend to imply that the 1,3 complexes are direct precursors of the 1,1 complexes. Indeed, it is more probable that concurrent equilibria exist and that the 1,1 complexes are formed via the aromatic ethers or similar ion-paired species, formed by the dissociation of the 1,3 complexes.

(28) This effect is most probably the result of the formation of a paramagnetic species, although this postulate has not been verified experimentally. The formation of the anion radical of 3,5-dinitrobenzonitrile by reaction of that aromatic with methoxide ion in methanol has been demonstrated recently.²⁹

(29) N. L. Arthur, E. J. Fendler, J. H. Fendler, and C. E. Griffin, unpublished results.

(19) A. J. Parker and R. Alexander, *J. Amer. Chem. Soc.*, **90**, 3313 (1968); R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *ibid.*, **90**, 5049 (1968).

(20) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956); J. B. Hyne, R. Willis, and R. E. Wonkka, *ibid.*, **84**, 2914 (1962).

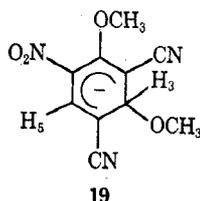
(21) E. C. Steiner, R. O. Trucks, J. D. Starkey, and J. H. Exner, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. POLY-18.

(22) C. A. Kingsbury, *J. Org. Chem.*, **29**, 3262 (1964).

(23) W. G. Ernsberger, E. J. Fendler, J. H. Fendler, and C. E. Griffin, unpublished results.

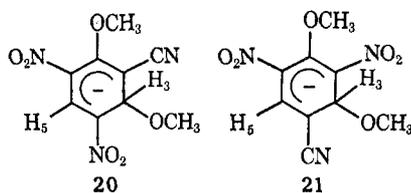
increases with increasing concentrations of methanol and methoxide ion. Thus, after the addition of the third drop of methanolic potassium methoxide, the transient signals disappear within 3 min. The intensity of the signals due to **15** decrease with successive methoxide additions, disappearing after the addition of the third drop. The persistent spectrum is identical with that obtained for the isolated complex **5**, *i.e.*, doublets at τ 2.00 and 2.70 ppm.

Similar evidence for the formation of a transient species is obtained by examination of the high-field portion of the spectrum. Addition of potassium methoxide to a solution of **15** results in a reduction in the intensity of the methoxyl singlet of **15**, τ 5.78 ppm, and the appearance of a singlet at τ 7.03 ppm. The intensity of the latter singlet is three times the intensity of either the 2.12- or 4.88-ppm doublet at the same elapsed time after methoxide addition. With time, the 7.03-ppm singlet decreases in intensity with the simultaneous development of a singlet at τ 7.08 ppm. Ultimately, the lower field singlet completely disappears. The intensity of the 7.08-ppm singlet is three times that of either the 2.00- or 2.70-ppm doublet. The rates of disappearance and appearance of these singlets parallels the behavior of the lower field resonances. The same behavior is observed on the addition of the second and third drops of potassium methoxide solutions; the rate of disappearance of the 7.03-ppm singlet increases with successive additions. After the addition of the third drop of methoxide solution, the 5.78-ppm signal disappears and the persistent spectrum is that of the isolated complex **5**, namely a singlet at 7.08 ppm. In addition, resonances due to methanol and DMSO- d_6 are observed in this region of the spectrum. The transient signals consisted of a two-proton AX system (τ 2.12, 4.88 ppm, $J_{AX} = 2$ Hz) and a methoxyl singlet at τ 7.03 ppm, assignable as the H-5, H-3, and C-3 methoxyl signals, respectively, of 1,3-dimethoxy-2,4-dicyano-6-nitrocyclohexadienylide (**19**).³⁰ These as-



19

signments are based on the chemical shifts previously reported for the 1,3-dimethoxycyclohexadienylides **18**, **20**, and **21**¹ formed by the reactions of methoxide ion



20

21

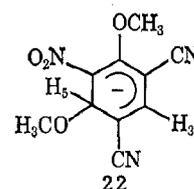
with methyl picrate, 2-cyano-4,6-dinitroanisole, and 4-cyano-2,6-dinitroanisole, respectively. These com-

(30) The C-1 methoxyl signal of **19** has approximately the same chemical shift as the methoxyl of **15** (τ 5.78 ppm) and is not resolved. Similar chemical-shift behavior has been observed for the C-1 methoxyl signals of **18**, **20**, and **21** and the C-1 methoxyl signals of the starting anisoles.

parisons unequivocally establish the transient to be a 1,3-dimethoxycyclohexadienylide.

The 1,3-dimethoxycyclohexadienylides **18** and **19** have also been observed calorimetrically in solutions containing low concentrations of reactants and DMSO (Results and Table VI), indicating that 1,3 complex formation does not require either the high concentrations of reactants or the use of dipolar aprotic solvents previously employed.^{1,24,25,31} In the light of these calorimetric results, the rapidly formed species, presumed to be a charge-transfer complex, observed in a kinetic investigation of **17** and ethanolic sodium ethoxide prior to 1,1 complex formation³² might, in fact, be the 1,3 complex.

However, **15** is unsymmetrical with respect to attack by methoxide ion at the unsubstituted ring positions and two isomeric complexes **19** and **22** could be formed. The spectrum of complex **22** would possess the same



22

gross features as **19**, but a consideration of chemical shifts supports the latter structure. In **22** the environment of H-5 is identical with that of H-3 in both **20** and **21** and would consequently be expected to display the same chemical shift, *i.e.*, τ 4.50–4.52 ppm.¹ However, the proton bonded to sp^3 -hybridized carbon in the transient is more strongly shielded, τ 4.88 ppm. This shielding effect is consistent with the environment of H-3 in **19** since it has been shown that the deshielding effect of cyano groups is considerably less than that of nitro groups on the ring protons (attached to either sp^2 - or sp^3 -hybridized carbons) of Meisenheimer complexes.¹ A consideration of the chemical shift of the lower field proton of the transient similarly supports structure **19**. The shift (τ 2.12 ppm) of this proton, H-5 of **19**, is very similar to that of H-5 of **21** (τ 2.25 ppm), reflecting their essentially identical environments. H-3 of **22** is flanked by two cyano groups and would be expected to be much more strongly shielded.³³ Thus, the structure **19** is established for the transient.

The selectivity observed in the reaction of methoxide ion with **15** to yield the 1,3 complex **19**, rather than the isomeric **22**, is further evidence for the greater stabilizing effect of nitro groups compared with cyano groups in Meisenheimer complex chemistry (*vide supra*). In **19**, the entering methoxy group is *para* to the nitro function, while an *ortho* relationship is present in **22**. This selectivity now appears to be quite general for the formation of complexes from nitro cyano aromatics, and is manifested by the relative stabilities of complexes **4** and **5**, and **2** and **3**,¹ by the selectivity observed in the formation of the 1,3-dimethoxycyclohexadienylide precursors (**20** and **21**) of **2** and **3**,¹ and in the attack of

(31) M. R. Crampton and V. Gold, *J. Chem. Soc., B*, 893 (1966).

(32) J. B. Ainscough and E. F. Caldin, *ibid.*, 2528 (1956).

(33) H-5 of **18** and **20** (τ 1.47–1.59 ppm)^{1,24} is more strongly deshielded than H-5 of **21** (τ 2.25 ppm).¹ The replacement of one flanking nitro group by a cyano group thus produces a shielding effect of *ca.* 0.75 ppm. It might be argued that similar replacement of the second nitro group would produce a similar shielding effect to give τ 3.00 ppm for H-3 of **22**.

methoxide ion on 3,5-dinitrobenzonitrile.^{20,24} The failure to observe formation of a transient species by either pmr or calorimetric probes in the reaction of methoxide ion with **16** is also consistent with this reactivity and stability pattern. In the symmetrical anisole **16**, attack is directed to the 1 position (*para* to nitro) to yield the 1,1 complex **4** as both the kinetic and thermodynamic product of the reaction. From these and our preceding studies,¹ it is clear that the same substitutional factors which determine the relative stabilities of the thermodynamically stable 1,1 complexes also determine the occurrence and position of attack in the formation of 1,3 complexes.

(34) M. I. Foreman and R. Foster, *Can. J. Chem.*, **47**, 729 (1969).

Registry No.—**4**, 12384-95-1; **5**, 12384-96-2; **6**, 22433-89-2; **7**, 22433-90-5; **10**, 22487-60-1; **11**, 22433-91-6; **13**, 22433-92-7; **14**, 22433-93-8; **15**, 22414-19-3; **16**, 22433-95-0; **18**, 12244-75-6; **19**, 12384-97-3; sodium methoxide, 124-41-4.

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Oxidation of Nitronates with Persulfate and with Silver Ions

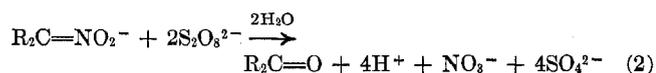
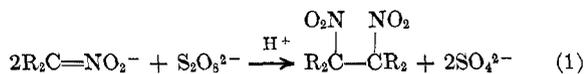
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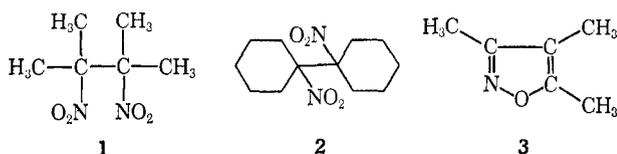
Received June 6, 1969

Sodium or ammonium persulfates convert salts of primary nitro compounds into secondary vicinal dinitro compounds ($R_2CHNO_2CHNO_2R$) and aldehydes. Silver ion catalyzes the oxidation-reduction reactions, and advantageous specific procedures using buffers and heterogeneous extractants are described for effecting oxidative dimerization. Experimental methods have been developed which minimize transformation of the oxidative dimers to conjugated nitro olefins and their addition products. Salts of phenylnitromethane, 1-nitropropane, 1-nitrobutane, and 2-methyl-1-nitropropane are converted by persulfates into their corresponding vicinal dinitro derivatives. In the absence of an extractant, ammonium persulfate oxidizes sodium phenylmethanenitronate to *cis*- α -nitrostilbene, α,β,γ -triphenyl- α -nitropropene, 3,4,5-triphenylisoxazoline oxide, and 3,4,5-triphenylisoxazole, along with benzaldehyde. Sodium 1-phenyl-1-ethanenitronate, sodium 9-fluorenenitronate, and sodium 1-(1-cyclohexenyl)-1-ethanenitronate, secondary nitronates having conjugating unsaturated centers, are converted effectively into acetophenone, fluorenone, and 1-cyclohexenyl methyl ketone, respectively. Potassium 1-nitropentane-1-nitronate and ammonium persulfate yield pentanoic acid and pentanamide. Various mechanisms for oxidation of nitronates by persulfates have been considered. An effective method for oxidizing secondary nitronates to tertiary vicinal dinitro compounds ($R_2CNO_2CNO_2R_2$) by reaction with equivalent quantities of silver nitrate in aqueous dimethyl sulfoxide or acetonitrile has been developed. 9-Nitrofluorene, 1-phenyl-1-nitroethane, nitrocyclohexane, and 2-nitropropane have thus been oxidized advantageously to 9,9'-dinitro-9,9'-bifluorenyl, 2,3-dinitro-2,3-diphenylbutanes, 1,1'-dinitrobicyclohexyl, and 2,3-dimethyl-2,3-dinitrobutane. Oxidative dimerization of silver salts of primary nitro compounds to secondary vicinal dinitro compounds is complicated by competitive oxidative nitration of the silver nitronates by silver nitrite to primary geminal dinitro alkanes.

Salts of secondary nitro compounds are oxidized by persulfates in the pH range of 9.5–7.0 at 0–5° to vicinal tertiary dinitro compounds (eq 1) and ketones (eq 2).¹



Thus alkaline solutions of 2-nitropropane, 2-nitrobutane, and nitrocyclohexane, respectively, with ammonium or sodium persulfates yield 2,3-dimethyl-2,3-dinitrobutane (**1**, 51–62%) and acetone (8–27%), 3,4-dimethyl-3,4-dinitrohexane² (**3**, 37%) and 2-butanone (48%), and 1,1'-dinitrobicyclohexyl (**2**, 14–30%) and



(1) H. Shechter and R. B. Kaplan, *J. Amer. Chem. Soc.*, **75**, 3980 (1953).
 (2) The stereochemistry of the 3,4-dimethyl-3,4-dinitrohexane is not known.

cyclohexanone (67%). Oxidation of salts of primary nitro compounds by persulfates has been limited to nitroethane, which results ultimately in 3,4,5-trimethylisoxazole (**3**, ca. 25%),¹ and to phenylnitromethane² (**4**), which gives *meso*- (**5**, 5%) and *dl*- (**6**, 33%) 1,2-dinitro-1,2-diphenylethanes along with benzaldehyde (**7**).

The present investigation was initiated to determine the reactions of persulfates with salts of primary nitroalkanes, unsaturated primary and secondary nitro compounds, and 1,1-dinitro alkanes. The study was expanded to include the catalytic effects of silver ion on oxidation of salts of primary and secondary nitro compounds with persulfates. These efforts led to investigation of the actions of stoichiometric quantities of silver ion on representative alkane nitronates and to development of an advantageous method for converting silver salts of secondary nitro alkanes into their vicinal oxidative dimers.

Oxidation of phenylnitromethane (**4**) by ammonium

(3) (a) A. Dornow and K. Fust, *Chem. Ber.*, **90**, 1774 (1957). (b) Reference 3a describes the oxidative dimers of **4** as α - and β -1,2-dinitro-1,2-diphenylethanes. The α and β oxidative dimers are **5** and **6**, respectively. The stereochemistry of **6** is established upon its partial resolution by less than 1 equiv of brucine: H. Shechter, J. J. Gardikes, and A. H. Pagano, *J. Amer. Chem. Soc.*, **81**, 5420 (1959).