trum of carbonate **23** derived from epoxycarbamate **20** showed absorption at 5.71 and 7.91 μ. The nmr ($CDCl_3$) exhibited a multiplet at τ 6.67 (1 H), a singlet at τ 6.17 (3 H), a multiplet at τ 6.15 (1 H), a doublet at τ 4.21 (1 H), and a multiplet at τ 2.61 (9 H).

Registry No.—**2**, 33143-41-8; **3**, 33143-42-9; **4**, 24312-28-5; **5**, 24276-26-4; **13**, 33143-44-1; **17**, 33143-45-2; **19**, 33143-46-3; **20**, 33143-47-4; **22**, 33143-48-5; **23**, 33143-49-6; **24**, 4187-87-5; methyl *trans-N*-(1,3-diphenyl-2-propinyl)carbamate, 33143-50-9; methyl *trans-N*-(3-phenyl-2-propinyl)carbamate, 33143-51-0; methyl *trans-N*-(1-*p*-chlorophenyl-3-phenyl-2,3-epoxypropyl)carbamate, 33213-40-0; methyl *trans-N*-(1,3-diphenyl-1-deuterio-2,3-epoxypropyl)carbamate, 33143-53-2; sodium methoxide, 124-41-4; potassium *tert*-butoxide, 865-47-4.

Acknowledgment.—We gratefully acknowledge support of this work by the National Institutes of Health (Grant No. CA-12195-05).

Intermediates in Nucleophilic Aromatic Substitution. XII.[1,2] Interaction of Alkoxide Ions with 3,5-Dinitrobenzonitrile[3]

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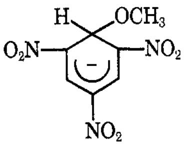
Addition of methanolic methoxide ions to 3,5-dinitrobenzonitrile (**3**) results in the immediate development of an absorption (λ_{max} 490 nm), assigned to the methoxyl σ complex of **3** (**4**), which subsequently decreases rapidly in intensity. The equilibrium constant for the formation of **4** in methanol at 25.00°, $K = 1.9$ l. mol^{-1}, has been obtained from kinetic treatment of the rate of decrease in the absorbance of **4** as a function of methoxide ion concentration. Using the Benesi–Hildebrand equation a value of 1.3 l. mol^{-1} has been obtained for this equilibrium constant under the same conditions. DMSO as a cosolvent increases the stability of **4**. The structure of **4** has been established from the pmr spectra of both the *in situ* generated and isolated complexes. Decomposition of **4** gave 1-methoxy-3-cyano-5-nitrobenzene. Pmr evidence is presented for the *in situ* formation of an analogous complex from 3-cyano-5-nitrobenzonitrile in DMSO-d_6 in the presence of methanolic potassium methoxide. The formation of low concentrations (<1%) of 3,5-dinitrobenzonitrile anion radicals, generated from alkoxide ions and **3** in several dipolar aprotic solvents, has been established using esr spectroscopy. The obtained results are compared to those for related σ, or Meisenheimer, complexes.

1,3,5-Trinitrobenzene has been shown to react extremely rapidly with methoxide ions in methanolic solution to give complex **1**,[6] which subsequently decomposes to produce 3,5-dinitroanisole.[7] The equilibrium constant for the formation of **1** in methanol at 28.0° has been determined to be 15 l. mol^{-1},[7] a value three orders of magnitude smaller than that obtained for the analogous formation of 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide ion (**2**).[8] We have demonstrated recently that substitution of one or two nitro groups by cyano groups in 2,4,6-trinitroanisole profoundly affects the kinetic and thermodynamic parameters for Meisenheimer complex formation.[8,9] More importantly, the unsymmetrical nature of 2-cyano-4,6-dinitroanisole allowed the observation of the preferential initial formation of a 1,3-dimethoxy-2-cyano-4,6-dinitrocyclohexadienylide ion over its 1,5-dimethoxy-2-cyano-4,6-dinitrocyclohexadienylide isomer.[8] As a continuation of our work on the stabilities and structures of Meisenheimer complexes we have, therefore, examined the kinetics for the interaction of methanolic sodium methoxide with 3,5-dinitrobenzonitrile (**3**), isolated crystalline potassium 1-methoxy-2-cyano-4,6-dinitrocyclohexadienylide (**4**) and established its structure together with those of its decomposition products under different conditions. We also wish to report the esr observation of radical anions formed from **3** and alkoxide ions. Pmr parameters for **4** formed *in situ* along with an unspecified amount of 1-hydroxy-2-cyano-4,6-dinitrocyclohexadienylide have been reported recently.[10] However, these authors could not isolate solid salts of **4**.[10]



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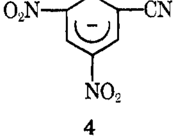

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(2) For recent reviews on Meisenheimer complexes and their relevance in nucleophilic aromatic substitution see (a) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966); (b) E. Buncel, A. R. Norris, and K. E. Russell, *Quart Rev., Chem. Soc.*, **22**, 123 (1968); (c) P. Buck, *Angew. Chem., Int. Ed. Engl.*, **8**, 120 (1969); (d) J. Miller, "Aromatic Nucleophilic Substitutions," Elsevier, Amsterdam, 1968; (e) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969); (f) F. Pietra, *Quart Rev., Chem. Soc.*, **22**, 504 (1969); (g) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

(3) Supported in part by the U. S. Atomic Energy Commission.

(4) (a) Texas A & M University; (b) National Institutes of Health Research Career Development Awardee.

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Experimental Section

The solvents and reagents were prepared, purified, and standardized as previously described.[11] 3,5-Dinitrobenzonitrile (**3**) (Aldrich), mp 129–130°, was checked for purity and used without further purification.

3-Cyano-5-nitrobenzonitrile (**5**) was prepared in good yield from 5-nitroisophthalic acid (J. T. Baker) *via* 5-nitroisophthaloyl chloride and 5-nitroisophthalamide according to the procedure described previously for 1-bromo-2,4,6-tricyanobenzene[1] and 1-bromo-2,4- and -2,6-dicyanobenzenes.[9] After recrystallization from benzene, the white crystals of **5** melted at 209–210°.

Potassium 1-methoxy-2-cyano-4,6-dinitrocyclohexadienylide (**4**) was prepared by the addition of 1.88 ml (9.5 mmol) of 5.05 M potassium methoxide in methanol to a solution of 1.931 g (10 mmol) of **3** in *ca.* 5 ml of dry dioxane. The dark red solution was flushed with dry nitrogen and then allowed to stand overnight at 0°. After evaporation of some of the solvent with dry nitrogen, the dark purple crystals were removed by filtration under dry nitrogen and were washed four times with dry benzene and anhydrous ether. Pulverization of the dark purple crystals in a drybox resulted in a change in their color to dark red. After drying *in vacuo* over phosphorus pentoxide, **4** decomposed at *ca.* 180°. The structures of the purple and red crystals were shown to be identical from their pmr spectra and to contain 1 mol of dioxane of crystallization (by pmr integration of dioxane singlet, τ 6.43 ppm[11]). In addition the pmr spectrum of **4** in DMSO-d_6 (Table III) was essentially identical with that reported for the *in situ* formation of **4**.[10]

Anal.[12] Calcd for $C_8H_6N_3O_5K \cdot C_4H_8O_2$: C, 40.2; H, 4.05; N, 12.1; K, 11.3. Found: C, 39.9; H, 3.78; N, 12.1; K, 11.1.

The pmr samples of isolated (in methanol, DMSO-d_6, or CD_3CN) or *in situ* generated (in DMSO-d_6 or CD_3CN) **4** were decomposed by pouring the sample into *ca.* 10 ml of water and acidifying the solution to *ca.* pH 2 with 0.1 M HCl. The precipitate was then centrifuged, washed two times with water, and dried *in vacuo* over phosphorus pentoxide. The solutions were tested for the presence of cyanide ion using an Orion cyanide ion selective electrode and for nitrite ion using the method of Rider and Mellon[13] and were found to contain nitrite ion but not cyanide ion. In solutions of **3** in the same solvents in the absence of methoxide ion, no nitrite or cyanide ions could be detected. The structure of the precipitated 1-methoxy-3-cyano-5-nitrobenzene (**6**) was established by pmr and mass spectroscopy and by degradation studies (see Discussion); however, attempted syntheses of **6** by alternate routes were unsuccessful.

The absorption spectra of the transient from **3** and its rate of decay were observed in the thermostated cell compartment of a Beckman DU-2 spectrophotometer, using Teflon stoppered 1-cm cells. An energy recording adaptor (ERA) was used in conjunction with a Hewlett-Packard recorder. The cell compartment was equipped with a set of dual thermospacers; the temperature was measured inside the cells and was maintained within ±0.02°. Runs were started by injecting the appropriate methanolic solution of **3** into a cell containing the sodium methoxide solution in methanol or in methanolic DMSO. A Hamilton syringe was used and the solution was injected through a small bore in the Teflon stopper.

The decomposition of solid **4** was initiated by injecting a freshly prepared concentrated solution of the complex (50–100 μl in DMSO) into the thermostated methanolic DMSO contained in the cell compartment of the spectrophotometer, and the rate of color disappearance was followed at 490 mμ.

Rapid mixing techniques were used to determine the absorbance due to complex **4** 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.

Pmr (60-MHz) spectra were obtained with a Varian Associates A-60 spectrometer at ambient probe temperature (34°) or at 25° (probe temperature maintained with a V-6040 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 are given on the τ scale in parts per million relative to TMS (τ 10.00 ppm) and are accurate to ±0.03 ppm. Chemical shift data were taken from spectra determined at a sweep width of 500 Hz. The reported coupling constants are the average of three determinations at 50-Hz sweep widths and are accurate to ±0.2 Hz. The *in situ* reactions of methoxide ion with **3** and with **5** were followed by examining the pmr spectra of solutions resulting from the dropwise addition of 5.73 M potassium methoxide in methanol to *ca.* 20% solutions of **3** or **5** in DMSO-d_6. The spectrum of each solution was determined immediately after the addition of methoxide ion and the spectrum was scanned repeatedly until no further changes were observed. The process was repeated until sufficient methoxide ion had been added to consume all of the starting **3** or **5**. The 100-MHz spectrum of 3-cyano-5-nitroanisole (**6**) was obtained with a JEOLCO JMN-4H-100 spectrometer. Experimental line frequencies used in the analysis of this spectrum were the averages of four measurements obtained at 50-Hz sweep widths. The general procedure used in analysis has been reported previously;[14] the final fit was made on an LBM 360-44 computer, using the iterative program LAOCN-3.[15]

Esr experiments were performed with an X-band spectrometer constructed in the Radiation Research Laboratories (10-KHz field modulation frequency, Philco L-4154 detector), utilizing a Varian V-4102-3B 12-in. magnet. Magnetic field measurements were made by a field following nmr unit similar to that described by Fessenden and Schuler,[16] with nmr and microwave frequencies measured by a Hewlett-Packard 5246L frequency converter. Phase detection at the second harmonic of the modulation frequency was used to obtain second-derivative spectra. All experiments were done at room temperature using a flat quartz cell, thickness 0.5 mm, and a Varian V-4531 multipurpose cavity. Hyperfine coupling constants were determined by taking appropriate differences in the proton resonance frequency for pairs of lines. Proton resonance frequencies were converted to magnetic field values (gauss) using the factor 0.23487 G/KHz. Values of the coupling constants are estimated to be accurate to ±0.03 G. Estimates of the radical concentrations were made by comparing the spectra of the radical and standard solutions of galvinoxyl at the same instrument settings and in the same solvents and are considered to have a ±50% error.

The radicals were generated by mixing carefully degassed solutions of **3** with methoxide or *tert*-butoxide ions dissolved in the appropriate solvent mixtures in a cell similar to that described by Russell.[17] In some experiments paramagnetic species were obtained by mixing solid **4** placed in one side of the cell with the appropriate alkoxide solution or solvent (see Table II) contained in the other side.

Results

Addition of a *ca.* 10^{-5} M solution of **3** in methanol to a sodium methoxide solution [(3.6–360) × 10^{-4} M], either in methanol or in methanolic DMSO, results in the immediate formation of a red color which rapidly fades. The absorption spectra of the colored adduct (Figure 1) have been obtained, therefore, by linear extrapolation of the absorbance to zero time of mixing. Spectra were recorded at 5-mμ intervals throughout the wavelength region scanned. The absorption maxima at 390 and 490 mμ are assigned to complex **4**, since the spectra of the isolated complex in methanolic DMSO solutions have the same maxima. The formation and subsequent decay of **4** can be described by

$$\mathbf{3} + OCH_3^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathbf{4} \xrightarrow{k_3} \text{product(s)} \quad (1)$$

and we define the formation constant, K, for **4** as

$$K = \frac{[4]}{[3][OCH_3^-]} \quad (2)$$

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

[12] The analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

[13] B. F. Rider and M. G. Mellon, *Anal. Chem.*, **18**, 96 (1946).

[14] M. P. Williamson, S. Castellano, and C. E. Griffin, *J. Phys. Chem.*, **72**, 175 (1968).

[15] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964). The program is available from Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.

[16] R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

[17] G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964).

TABLE I
INTERACTION OF 3,5-DINITROBENZONITRILE (**3**) WITH SODIUM METHOXIDE IN METHANOL AND IN METHANOLIC DIMETHYL SULFOXIDE AT 25.00°

[DMSO], *M*	10^3[NaOCH$_3$], *M*	Absorbance at 490 mμ[a,b]	$10^3 k_{obsd}$,[b] sec^{-1}	*K*,[c] l. mol^{-1}	*K*,[d] l. mol^{-1}	$10^3 k_3$,[d] sec^{-1}
0[e]	5.25	0.034	3.17	1.3	1.9	32.4
	10.5	0.065	6.21			
	21.0	0.112	12.8			
	31.5	0.171	18.0			
	42.0	0.237	24.6			
	52.5	0.283	30.2			
	105	0.568	54.2			
	208		95.5			
	312		130			
	416		143.3			
	520		158			
1.41[f]	4.62	0.059	3.37	4.4	5.7	12.6
	9.25	0.126	15.9			
	18.5	0.194	12.4			
	27.8	0.356	18.2			
	37.0	0.403	24.0			
	46.2	0.530	27.4			
	46.8		26.2			
	93.6		48.3			
	140.4		62.1			
	187.2		67.8			
	234.0		81.7			
	280.8		78.2			
	329.6		82.8			
2.82[g]	1.26	0.023		15	21	4.55
	2.52	0.051				
	3.36	0.061	3.06			
	4.20	0.105	3.58			
	8.40	0.158	7.20			
	12.6	0.225	10.12			
	16.8	0.276	12.65			
	21.0	0.366	14.95			
	25.2	0.410	17.7			
	29.4	0.420	18.0			
	33.6	0.488	19.1			
	37.8	0.510	20.2			
	42.0		21.9			
	84.0		25.0			
	126		34.0			
	210		35.9			
	252		35.9			
	336		40.5			
	420		41.0			
4.23[h]	0.368	0.023		60	75	1.55
	0.735	0.032				
	1.025	0.051				
	1.47	0.056	1.75			
	1.84	0.058	1.97			
	2.21	0.069	2.49			
	2.57	0.076	2.64			
	3.68	0.092	3.30			
	7.35	0.194	6.05			
	11.02	0.244	7.82			
	14.7	0.286	9.09			
	22.1	0.337	9.60			
	25.7	0.338	10.1			
	36.8		12.0			

[a] Using a 1.00-cm cell. [b] Mean of three runs (each with a ±3% error). [c] Calculated from Benesi–Hildebrand plots (eq 3). [d] Calculated using eq 8. [e] [**3**] = 2.82×10^{-4} *M*. [f] [**3**] = 1.66×10^{-4} *M*. [g] [**3**] = 7.04×10^{-5} *M*. [h] [**3**] = 2.49×10^{-5} *M*.

Using the zero time absorption maxima at 490 mμ, (Table I) and the Benesi–Hildebrand equation[18] form

$$\frac{[\mathbf{3}]}{A} = \frac{1}{\epsilon} + \frac{1}{K[\mathrm{OCH_3^-}]} \qquad (3)$$

where A is the zero time absorbance in a 1.00-cm cell, ϵ is the molar extinction coefficient, and K is the equilibrium constant for the complex, a good linear relationship was obtained on plotting [**3**]/A *vs.* [**1**]/[OCH$_3^-$], indicating that a simple 1:1 equilibrium prevails. Since the intercept of the Benesi–Hildebrand plot

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

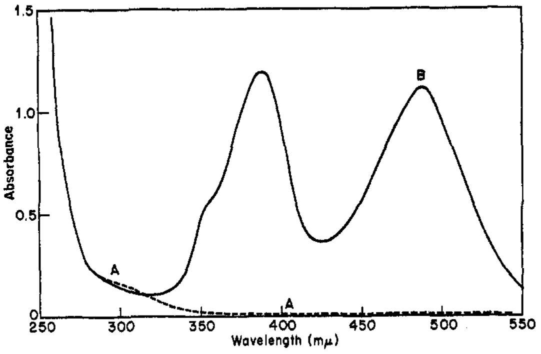


Figure 1.—Absorption spectra of **3** (6.5×10^{-5} M) in methanol (A) and in 0.29 M $NaOCH_3$ in MeOH at zero time (B), using a pair of matched 1.00-cm cells.

(*i.e.*, $1/\epsilon$) is susceptible to large errors, ϵ was determined independently by dissolving known amounts of **4** in DMSO and in DMSO–methanol mixtures and measuring the zero-time absorbances (using the appropriate blank solutions) at 490 mμ. A value of $\epsilon_{490\ m\mu} = (1.8 \pm 0.1) \times 10^4$ cm^{-1} mol^{-1} represents the mean of five independent measurements and was used in conjunction with eq 3 to obtain the K values in methanol and in methanolic DMSO (Table I).

Since the concentration of **3** is considerably smaller than that of $NaOCH_3$, good pseudo-first-order plots were obtained for the rate of absorbance decrease due to the decay of **4**. Figure 2 illustrates such first-order plots together with that observed when solid **4** was dissolved in methanolic sodium methoxide. The good agreement between k_{obsd} for absorbance decay for the *in situ* generated complex (line A) with that of the decay of solid **4** in the same concentration of methoxide ion (line B) is self-evident. The observed pseudo-first-order rate constant k_{obsd} represents a change in the concentration of **4**.

$$k_{obsd} = -\frac{d(\ln[\mathbf{4}])}{dt} \tag{4}$$

The formation of products in eq 1 can be defined by

$$\frac{d([\text{product}])}{dt} = k_3[\mathbf{4}] \tag{5}$$

and also by eq 6, if **3** and **4** are rapidly interconvertible.

$$\frac{d([\text{products}])}{dt} = \frac{d([\mathbf{3} + \mathbf{4}])}{dt} \tag{6}$$

Combination of eq 2, 4, 5, and 6 leads to

$$k_{obsd} = \frac{Kk_3[OCH_3^-]}{1 + K[OCH_3^-]} \tag{7}$$

and rearrangement of eq 7 gives

$$\frac{[OCH_3^-]}{k_{obsd}} = \frac{1}{Kk_3} + \frac{[OCH_3^-]}{k_3} \tag{8}$$

which suggests that plots of $[OCH_3^-]/k_{obsd}$ *vs.* $[OCH_3^-]$ should give straight lines whose slopes are $1/k_3$ and whose intercepts are $1/Kk_3$. Figure 3 illustrates such plots of eq 8 for reaction 1 in methanol and methanolic dimethyl sulfoxide solutions containing, respectively, 1.41 and 2.82 M DMSO in methanol. Values for K and k_3 are given in Table I. Considering the uncertainties involved in obtaining the equilibrium constants from eq 3 and 8, the agreement between the two sets of independently obtained values is considered to be good (Table I).

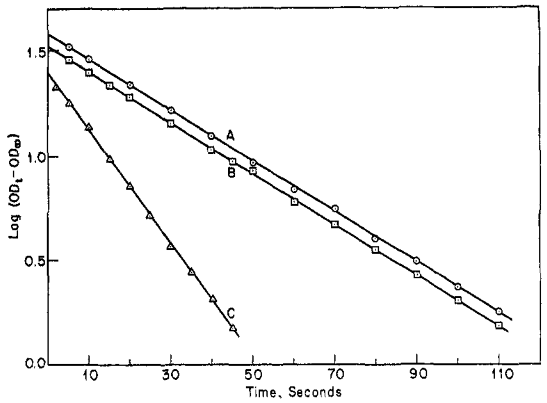


Figure 2.—Plots of log ($OD_t - OD_\infty$) against time for the fading of **4** at 25.00°. (A) [**3**] = 2.81×10^{-4} M, [$NaOCH_3$] = 5.25×10^{-2} M, solvent = MeOH. (B) Solid **4** dissolved in 5.25×10^{-2} M methanolic sodium methoxide. (C) [**3**] = 4.0×10^{-5} M, [$NaOCH_3$] = 0.187 M, solvent = MeOH-DMSO, 10:90 (v/v).

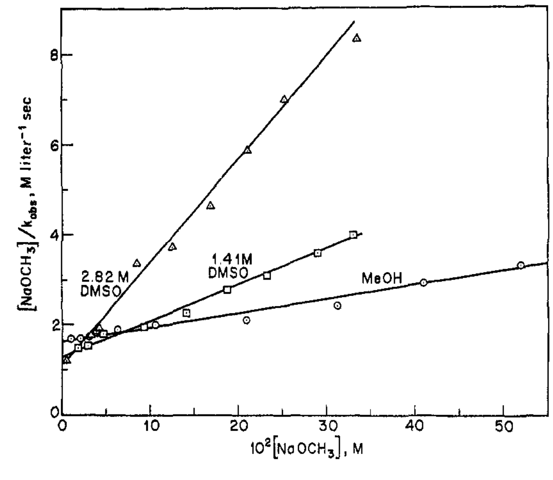


Figure 3.—Plots of [$NaOCH_3$], M/k_{obsd} against [$NaOCH_3$], M, in MeOH and in 1.42 M and 2.84 M DMSO in MeOH.

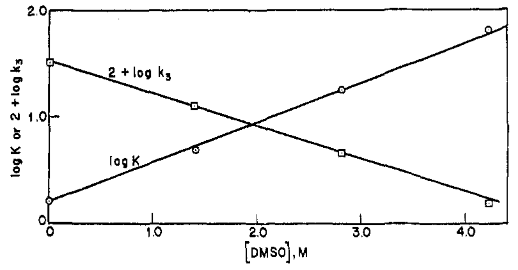


Figure 4.—Plot of log K and 2 + log k_3 against [DMSO], M.

Solid **4** decomposed instantaneously in methanol and all attempts to follow the kinetics for this process have failed. Good linear relationships between log K and log k_3 *vs.* [DMSO], M, are illustrated in Figure 4.

Anion radicals were formed from **3** in several base–solvent systems. In each case the esr spectrum could be observed 3 min after mixing and was generally found to increase slowly in intensity for a period of between 30 and 90 min before decaying. A summary of the conditions leading to the production of radicals, their estimated concentrations, and the hyperfine coupling constants of their esr spectra are given in Table II. Additional lines of weaker intensity were observed in the spectra from systems A, B, and C, and in B the coupling constants for this second species were deduced and are also given in Table II.

TABLE II

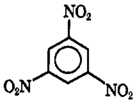
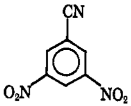
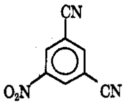
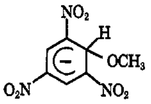
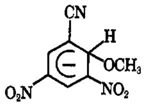
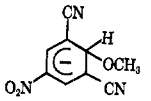
ESR PARAMETERS FOR RADICAL ANIONS DERIVED FROM **3** AND ALKOXIDE IONS[a]

System	[**3**], *M*	[Alkoxide], *M*	Solvent	Coupling constants, G			
A	0.085	2.5[b]	MeOH	$a_N^{NO_2} = 9.76$	$a_H(2) = 4.13$	$a_H = 3.36$	
B	0.085	2.5[b]	75% MeOH–25% DMSO[e]	$a_N^{NO_2} = 9.12$	$a_H(2) = 4.24$	$a_H = 3.31$	
				$a_N^{NO_2} = 10.92$[f]	$a_H(2) = 3.75$[f]	$a_H = 3.06$[f]	
C	0.024	0.094[c]	20% MeOH–80% DMSO[e]	$a_N^{NO_2} = 9.62$	$a_H(2) = 3.84$	$a_H = 2.98$	
D	0.042	0.027[d]	*tert*-BuOH	$a_N^{NO_2} = 9.71$	$a_H(2) = 3.43$	$a_H = 4.71$	
E	0.041	0.029[d]	20% *tert*-BuOH–80% DMF[e]	$a_N^{NO_2}(2) = 3.41$	$a_H(2) = 3.43$	$a_H = 4.74$	$a_N^{CN} < 0.3$
	0.005	Electrochemical[g] reduction	DMF	$a_N^{NO_2}(2) = 3.00$	$a_H(2) = 2.84$	$a_H = 5.00$	$a_N^{CN} < 0.3$

[a] The concentration of paramagnetic species in all cases was estimated to be (2.0–4.0) × 10^{-4} *M*. [b] CH_3OK. [c] CH_3ONa. [d] *tert*-BuOK. [e] Volume per cent. [f] Secondary species. [g] Taken from ref 36.

TABLE III

PMR SPECTRA OF 1,3,5-TRINITRO-, CYANODINITRO-, AND DICYANONITROBENZENES AND THEIR METHOXYL COMPLEXES[a]

		 **3**	 **5**	 **1**	 **4**	 **10**
τ_2	0.80	0.84	1.14	3.86,[b] 3.78,[c] 3.88[d]	4.40	
	0.79[b]			(4.05)	(4.53) (4.6, broad)[e]	(5.74)
τ_4	0.80	0.92	1.29	1.58,[b,d] 1.48[c]	1.52	
	0.79[b]			(1.72)	(1.72) (1.92)[e]	(3.13)
τ_6	0.80	0.84	1.14	1.58,[b,d] 1.48[c]	2.23	
	0.79[b]			(1.72)	(2.41) (2.65)[e]	(3.13)
τOCH_3				6.90,[b] 6.78[d]	6.92	
				(6.88)	(6.95)	(7.20)
J_{24}		1.8	1.5	~1,[c] 1.5[f]	1.2	
				(1.2)	(1.2) (2)[e]	
J_{46}					2.2	
					(2.2	

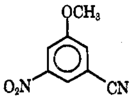
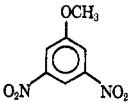
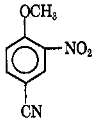
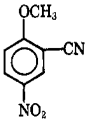
[a] Values in parentheses have been obtained from formation of the complex *in situ* by the dropwise addition of 5.73 *M* potassium methoxide in methanol to a solution of the parent substituted benzene in DMSO-d_6. [b] Values taken from ref 6. [c] Values taken from R. Foster and C. A. Fyfe, *Tetrahedron*, **21**, 3363 (1965). [d] Values taken from K. L. Servis, *J. Amer. Chem. Soc.*, **89**, 1508 (1967). [e] Values taken from ref 9. [f] Values taken from M. R. Crampton in ref 2.

Pmr parameters for 1,3,5-trinitrobenzene, **3**, **5**, and their methoxyl complexes in DMSO-d_6 solutions are given in Table III and those for the decomposition product (**6**) of **4** and certain reference compounds in dioxane are collected in Table IV.

TABLE IV

PMR SPECTRA OF

DINITRO- AND CYANONITROANISOLES IN DIOXANE[a]

	 **6**			
τ_2	2.57	1.93		
τ_3			1.71	1.39
τ_4	2.40	1.47		
τ_5			2.12	1.56
τ_6	2.55	1.93	2.72	2.77
J_{24}	1.91	2.0		
J_{26}	2.37			
J_{35}			2.1	2.8
J_{56}			8.9	9.3
J_{36}				0.5
J_{46}	1.84			

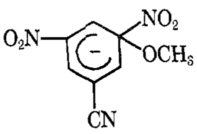
[a] The spectrum of **6** was recorded at 100 MHz; other spectra were recorded at 60 MHz.

Discussion

The interaction of methoxide ions with 3,5-dinitrobenzonitrile (**3**) resembles, at least qualitatively, the formation of the methoxyl complex (**7**) of 2-cyano-4,6-dinitroanisole. Both complexes **4** and **7** have a shorter (380 mμ for **7**,[8] 390 mμ for **4**) and a longer (470 mμ for **7**,[8] 490 mμ for **4**) wavelength absorption maximum which is absent in their parent aromatic compounds. The structures of the isolated complexes **4** and **7** are also similar in that they both involve sp^2–sp^3 rehybridization of the carbon atom at the point of attack with respect to their parent aromatic compounds. Considerable quantitative differences exist, however, between the rates and equilibrium constants for the formation of complexes **4** and **7**. The attainment of the equilibrium for **7** was measurable and allowed the calculation of the equilibrium constant. Its value in methanol at 25.00° was found to be 2600 l. mol^{-1},[8] a value more than three orders of magnitude greater than that obtained for **4**. The instantaneous formation of **4** implies that k_1 for this process is considerably faster than that for the formation of **7**. Essentially similar kinetic behavior has been observed in the interaction of 1,3,5-trinitrobenzene with methanolic sodium methoxide.[7] The equilibrium constant for the formation of **1** in methanol has been reported to be 15.4 l. mol^{-1},[7] a value also three orders of magnitude smaller than that for the formation of 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide ion (**2**).[8] It is reassuring to observe that replacing an *o*-nitro group by a cyano group in trinitrobenzene causes an almost identical decrease in the equilibrium constant for complex formation as that observed in comparing K_2 with K_7 ($K_1/K_4 = 9.6$ and $K_2/K_7 = 6.6$). The differences between the stabilities of trinitro and cyanodinitro Meisenheimer complexes reflect, of course, the smaller electron-withdrawing power of the cyano group.

The greater stability of the 1,1-dimethoxycyclohexadienylides (**2** and **7**) over the 1-methoxycyclohexadienylides (**1** and **4**) is largely explicable in terms of steric considerations. The methoxyl group in both 2,4,6-trinitroanisole and 2-cyano-4,6-dinitroanisole is sterically compressed by the neighboring nitro and cyano groups. The formation of the methoxyl complexes of these anisoles (**2** and **5**) results in structures in which both methoxyl groups lie out of the plane of the aromatic ring,[19-21] thereby relieving the crowding present in the parent ethers. No comparable steric compression exists for either 3,5-dinitrobenzonitrile (**3**) or 3-cyano-5-nitrobenzonitrile (**5**).

The formation of 3-cyano-5-nitroanisole (**6**) from solutions containing **4** must involve a species such as **8** either as a short-lived intermediate or as a transition state. A structure similar to **8** has been considered in the interaction of methoxide ion with 1,3,5-trinitrobenzene[7] and with *N-tert*-butyl-2,4,6-trinitrobenzamide.[22] The lifetimes of **4** and **8** depend on the magnitude of the equilibrium constants for their formation (k_1/k_2 and K for $4 \rightleftharpoons 8$). In this sense either **4** or **8** or both can be transition states or intermediates of finite stability. The isolation of complexes on a preparative scale does not constitute an unambiguous proof that the same complexes are intermediates in the kinetic solutions involving generally 10^{-4}–10^{-5} M substrates. Proof for intermediates must be substantiated by obtaining thermodynamic parameters for the rates and hence for the equilibrium constants for their formation. We have provided such measurements and coupled them with structural analysis of the isolated complexes for several aromatic ethers.[8,23] The instantaneous formation of **4** did not allow, under our experimental conditions, meaningful kinetic determinations of the free energies of activation for its formation and decomposition. In spite of our isolation of solid **4** (under preparative conditions) we cannot, therefore, ascertain **4** to be an intermediate in reaction 1. Indeed, it is more likely that the product is formed *via* path A (rather than *via* path B as indicated in eq 1) through **8** as a transition state or as an intermediate which is undetectable under our experimental conditions. If **3** and methoxide ion are in rapid equilibrium with **4**, as in the present case, formation of the product *via* path A is kinetically indistinguishable from that *via* path B.[24] It is apparent from our investigations[8,23] that the electron-withdrawing power of the substituents on the parent aromatic compounds, specific ground- and transition-state steric and solvation requirements, and the nucleophilic and basic strength of the attacking alkoxide ion all influence these equilibria. The stability of the 1,1-dimethoxy-2,4,6-trinitrocyclohexadienylide (**2**) is so great (K = 17,000 l. mol^{-1})[8] that any subsequent rearrangement of it is extremely unlikely. On the other hand, the instability of 1,1-dimethoxy-2,4-dinitrocyclohexadienylide ($K = 2.5 \times 10^{-5}$ l. mol^{-1})[25] allowed us to study its rearrangement, by pmr spectroscopy, to a relatively more stable 1,2-dimethoxy-2,4-dinitrocyclohexadienylide (**9**).[26]



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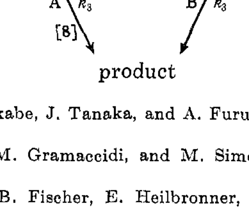

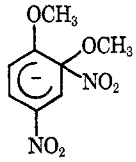

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Since the stability of **4** (K = 1.6 l. mol^{-1}) is several orders of magnitude greater than that of 1,1-dimethoxy-2,4-dinitrocyclohexadienylide, one would expect its decomposition involving **8** to be extremely rapid. This is indeed the case, since all our attempts to follow the rates of this process in dilute solution have been unsuccessful.

It has been demonstrated previously that dipolar aprotic solvents enhance the stability of Meisenheimer complexes,[1,9,27] and we had hoped that a DMSO-rich methanolic solvent system might stabilize **4** to such an extent that the rate for its equilibrium attainment could be determined. Although the equilibrium constant for the formation of **4** was found to be some 40 times greater in 4.23 M DMSO (DMSO:MeOH = 30:70, v/v) than in pure methanol (Table I), its rate of equilibrium attainment was still unmeasurably fast by our technique. The increase in the equilibrium constant for the formation of the methoxyl complex of 2,4-dicyano-6-nitroanisole with increasing DMSO concentration was demonstrated to be a composite effect of an increase in k_1 and a decrease in k_2.[9] It is likely that the increase in K_4 with increasing DMSO concentration is also a composite effect and originates from changes in the activity coefficients of the reactants and of the transition states as a function of solvent composition.[9,28] In view of the numerous parameters involved in the solvent effects,[28,29] undue mechanistic significance cannot be attributed to the obtained linear correlation be-

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[20] R. Destro, C. M. Gramaccidi, and M. Simonetta, *ibid.*, **215**, 390 (1967).

[21] P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller, and H. Zollinger, *Helv. Chim. Acta*, **50**, 848 (1967).

[22] E. J. Fendler, D. M. Camaioni, and J. H. Fendler, *J. Org. Chem.*, **36**, 1544 (1971).

[23] J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *ibid.*, **33**, 977 (1968).

[24] L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, pp 150–151.

[25] C. F. Bernasconi, *J. Amer. Chem. Soc.*, **90**, 4982 (1968).

[26] W. E. Byrne, E. J. Fendler, J. H. Fendler, and C. E. Griffin, unpublished results.

[27] G. S. Gitis, A. I. Glaz, and A. Ya. Kaminskii, *J. Gen. Chem. USSR*, **33**, 3229 (1963); S. Nagakura, *Tetrahedron Suppl.*, **19**, No. 2, 361 (1963).

[28] J. H. Fendler and J. W. Larsen, *J. Org. Chem.*, in press.

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

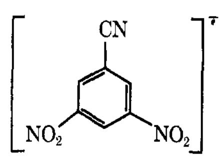
tween the logarithm of the rate and equilibrium constants for **4** and the molar DMSO concentration (Figure 4).

Pmr spectroscopy has been utilized both to establish the structures of the methoxyl complexes of **3** and **5** and their decomposition products and to detect any relatively long-lived transients involved in complex formation or decomposition. The pmr parameters for the isolated and *in situ* generated complexes (**1** and **4**) and their parent aromatics (1,3,5-trinitrobenzene and **3**) as well as for 1-methoxy-2,6-dicyano-4-nitrocyclohexadienylide (**10**) and its parent aromatic (**5**) are summarized in Table III. The spectra (*i.e.*, the chemical shift, multiplicities, coupling constants, and relative intensities) of both the *in situ* generated and isolated **4** are completely consistent with the postulated structures and the parameters are in good accord with those reported by Foreman and Foster[10] (Table III) considering the "water impurity" and the absence of methanol in their medium.[30,31] In addition, the chemical shifts and the absence of discernible coupling constants in the spectra obtained from the *in situ* reaction of **5** with methanolic potassium methoxide (Table III) are consistent with the postulated structure of the complex,[33] *i.e.*, **10**. These spectra unambiguously eliminate, particularly through the upfield shift for H-2, alternative formulations, *e.g.*, **8**, for complexes **4** and **10**. The pmr criteria for the structures have been discussed and reviewed[34] extensively elsewhere and will not be reiterated here. The chemical shifts and coupling constants observed for **4** are unremarkable, with the exception of the coupling of the methine proton, H-2, to H-4 (J_{24} = 1.2 Hz) but not to H-6 ($J_{24} < 0.4$ Hz). We have observed similar behavior in the case of the 1,3-dimethoxy-4-cyano-2,6-dinitro- and 2-cyano-4,6-dinitrocyclohexadienylides for which the methine proton ortho to a cyano and a nitro group is coupled to a meta aromatic proton ortho to two nitro groups but not to that ortho to a cyano and a nitro group.[8] These observations are also consistent with the postulated structure for the methoxyl complex of **5** (**10**) since coupling of the methine proton to H-4,6 is undiscernible.

The pmr parameters in dioxane solution for 3-cyano-5-nitroanisole (**6**) obtained from the decomposition of **4** and dinitro- and cyanonitroanisoles are given in Table IV. A tightly coupled ABC spectrum was observed for **6** at both 60 and 100 MHz, but a satisfactory fit of the observed transitions was obtained by an interative program.[15] The calculated coupling constants are of the expected order for meta J_{HH}. However, the marked shielding of all three ring protons relative to the shifts observed for 3,5-dinitroanisole (Table IV), and the accidental equivalence of τ_2 and τ_6 were unexpected. Presumably, the shielding effect is a reflection of the replacement of a nitro by a less strongly electron-withdrawing cyano group. This effect is apparent in other cyanonitroanisoles, but is most marked in the case of **6**. Similar accidental chemical shift equivalences for ring protons have been observed in other cyanonitroanisoles, *e.g.*, 2-cyano-4,6-dinitroanisole.[8,35]

A linear relationship between the chemical shifts of the H-3,5 protons of the complex in DMSO-d_6 and the equilibrium constant, *K*, for its formation in methanol has been found for **1**, **4**, the cyano complex of 1,3,5-trinitrobenzene, and the methoxyl complex of *N-tert*-butyl-2,4,6-trinitrobenzamide. An analogous relationship has been observed for the isomeric 2,4,6-substituted nitro- and cyanoanisoles.[1] Indeed, the sensitivity of the equilibrium constants to the chemical shifts (or vice versa) appears to be identical within experimental error. By extrapolation from this relationship an equilibrium constant for the formation of **10** of 1.4×10^{-3} l. mol^{-1} has been estimated. This value can only be considered to be accurate within an order of magnitude; however, the ratio of the equilibrium constants for the dicyanonitroanisoles to this value obtained for **10** is the same order of magnitude as the corresponding ratios for **1** and **4** ($K_2/K_1 \sim K_7/K_4 \sim 10^3$).

Paramagnetic species have been observed in the interaction of alkoxide ions with solutions of **3** in several solvent systems (Table II). The esr spectrum from system E, consisting of 27 lines, analyzes for two equivalent nitrogens, two equivalent protons, and a third proton (Figure 5), and is attributed to the 3,5-dinitrobenzonitrile radical anion (**11**). The similarity of the observed splitting constants to those of **11** produced by electrolysis of **3** in DMF[36] (Table II) allows the following assignments: $A_3^N = A_5^N = 3.41$, $A_2^H = A_6^H = 3.43$, $A_4^H = 4.74$. The larger value of $A_{NO_2}^N$ found in this work is due to the *tert*-BuOH cosolvent. Differential solvation of the nitro group has been shown to alter its spin density and hence $A_{NO_2}^N$.[36]



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The esr spectra generated in A, B, C, and D show only one nitrogen hyperfine interaction. The radical anions of *m*-dinitrobenzene,[37-39] 2,6-dinitrotoluene,[40] and 3,5-dinitroanisole also give spectra of this type. However, high-resolution studies of the *m*-dinitroben-

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[30] These authors observed, in addition to the methoxyl complex **4**, a species in "smaller abundance" (τ_2 = 4.5, τ_4 = 1.79, and τ_6 = 2.48 ppm), assigned as the hydroxyl complex, in the *in situ* reaction of **3** in DMSO with solid sodium methoxide. We, therefore, examined the pmr parameters for the *in situ* reaction of 5.00 *M* potassium hydroxide with **3** in DMSO-d_6. The parameters obtained for the hydroxyl complex (τ_2 = 4.52, τ_4 = 1.73, τ_6 = 2.48 ppm; $J_{24} < 0.5$ Hz, and $J_{46} \approx 2.2$ Hz) confirm the structure of this species.

[31] Subsequent to submission of this manuscript, Terrier and coworkers[32] reported the observation of **4** in 100-MHz pmr spectra obtained by the addition of potassium methoxide to a solution of **3** in DMSO-d_6. Resonances for a species in 5% abundance also were observed and were ascribed to the methoxyl complex resulting from attack of methoxide ion at the 4 position of **3**.

[32] F. Terrier, F. Millot, and M.-P Simonnin, *Tetrahedron Lett.*, 2933 (1971).

[33] In this case, however, coincidence of the resonance frequencies for the H-3 and H-5 protons of 1-methoxy-2,4-dicyano-6-nitrocyclohexadienylide would result in a similar spectrum.

[34] See ref 1 and 2 and references cited therein.

[35] In order to provide an unambiguous assignment of the structure of **6**, the compound was reduced with lithium aluminum hydride and converted *via* diazotization to 3-hydroxy-5-methoxybenzyl alcohol (i). Methylation of i gave 3,5-dimethoxybenzyl alcohol (ii). Pmr spectra provided an unambiguous demonstration of the 1,3,5 relationship of the substituents in i and ii. These data, coupled with the mass spectrum of **6** (appropriate M peak), conclusively establish the structure of **6**.

[36] P. A. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 683 (1963).

[37] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963).

[38] C. J. W. Gutch and W. A. Waters, *Chem. Commun.*, 39 (1966).

[39] C. Corvaja and G. Giacometti, *J. Amer. Chem. Soc.*, **86**, 2736 (1965).

[40] P. H. Rieger and J. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

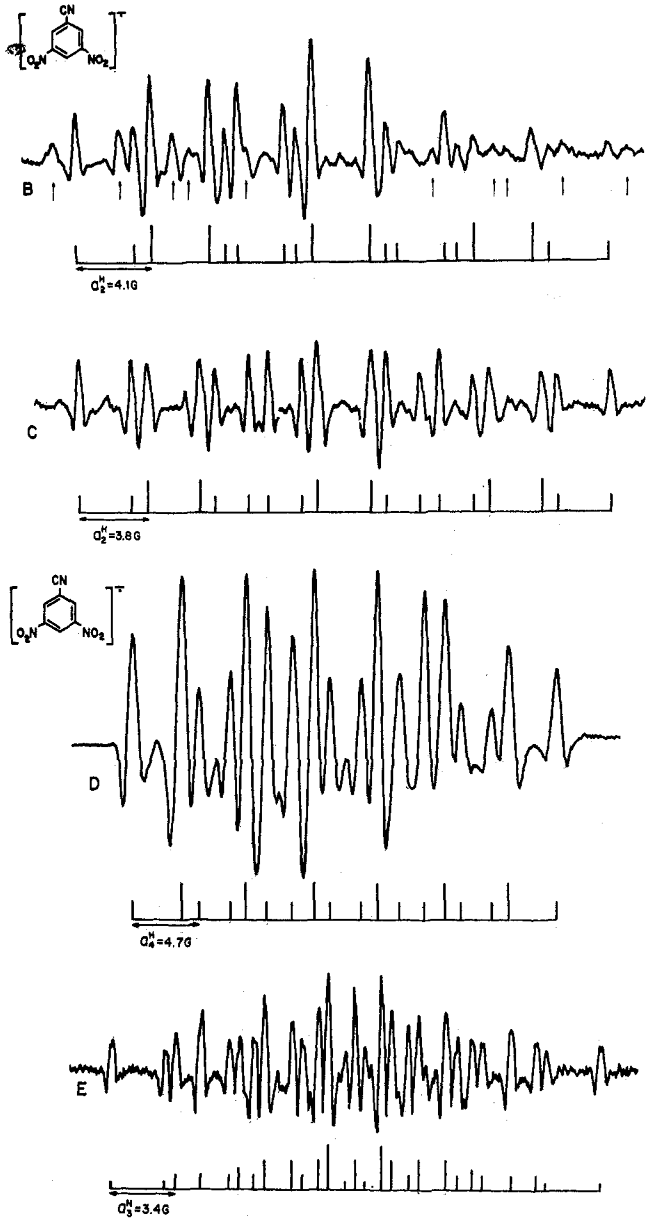

Figure 5.—Esr spectra of radical anions derived from **3** and alkoxide ions in systems B, C, D, and E.

zene radical anion, prepared by alkali metal reduction in ethanol, suggested the presence of a very small interaction with the second nitrogen.[41] The large difference between A_3^N and A_5^N was ascribed to a strong ion-pair type of interaction between one of the nitro groups and an alkali metal cation. Freed and Fraenkel have proposed a more general explanation of these one-nitrogen spectra in terms of an alternating line-width effect.[42] The spectrum from two equivalent nitrogen nuclei consists of five lines with intensities in the ratio 1:2:3:2:1 corresponding to $M_N = 2, 1, 0, -1, -2$, where M_N is the sum of the Z components of the spin angular momenta of the two nuclei. Any time-dependent process which results in a momentary inequality of the two nitrogen couplings can lead to broadening of the lines corresponding to $M_N = \pm 1$ and two components of the line corresponding to $M_N = 0$. In the limit, these lines would no longer be observed, leaving the lines corresponding to $M_N = \pm 2$ and 0 of equal intensity. Freed and Fraenkel regard their model as providing a basis for representing Ward's long-lived anion radical–alkali metal complex. The spectra due to **11** formed in systems A, B, C, and D which show only one nitrogen hyperfine splitting are considered to be examples of this type.[42] They show pronounced line-width variations, the high field lines being wider than those at low field. This is due to anisotropic *g* tensor and dipolar interactions resulting from the very viscous solvent. This phenomenon has been observed previously in nitro-substituted aromatic radical anions.[42,43]

The observed esr spectra in systems A, B, C, and D could alternatively represent 3-cyano-5-nitrophenol or 3-cyano-5-nitroanisole radical anions produced by nucleophilic replacement of the nitro group by alkoxyl or hydroxyl groups. The significant differences in coupling constants between the methoxyl- and hydroxyl-[44] substituted nitroarenes and those of **11** (Table II), however, renders this interpretation unlikely. The second radical species detected in these systems may indicate the presence of radicals formed from the "solvolysis" of **3** or possibly from other species present in reaction 1.

Absence of free radicals in solutions of 1,3,5-trinitrobenzene or 2,4,6-trinitroanisole in methanolic sodium methoxide or in ethanolic sodium ethoxide[7] reflects the greater stability of Meisenheimer complexes **1** and **2** as compared to **4**. Since the estimated concentration of the paramagnetic species in reaction 1 is less than 1% of that of **3**, radical processes constitute only a minor part of the overall reaction. The inherent complexity of the system[2,17] does not allow a distinction among the alkoxide ion, the methylsulfinyl carbanion (present in the DMSO–BuO$^-$K$^+$–*tert*-BuOH system), or **4** as the possible electron donor. Indeed all of these species can concurrently or consecutively transfer their charges to **3**. The fact that the radical concentration increases as a function of time and that identical radicals were observed in the *in situ* generation of **4** and in the decomposition of solid **4** in methanolic sodium methoxide solutions tend to suggest that **4** is, at least partially, involved in the radical formation.

Registry No.—**1**, 12244-65-4; **3**, 4110-35-4; **4**, 29661-06-1; **5**, 33224-18-9; **6**, 33224-19-0; **10**, 33293-81-1; sodium methoxide, 124-41-4; methanol, 67-56-1; DMSO, 67-68-5; potassium methoxide, 865-33-8; *tert*-BuOK, 865-47-4; 3,5-dinitroanisole, 5327-44-6; 4-cyano-2-nitroanisole, 33224-23-6; 2-cyano-4-nitroanisole, 10496-75-0.

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[41] R. L. Ward, *J. Chem. Phys.*, **36**, 1405 (1962).

[42] G. H. Freed and G. K. Fraenkel, *ibid.*, **41**, 699 (1964).

[43] G. H. Freed and G. K. Fraenkel, *ibid.*, **40**, 1815 (1964).

[44] L. H. Pietter, P. Ludwig, and R. N. Adams, *J. Amer. Chem. Soc.*, **84**, 4212 (1962).