lated from *Saccharomyces cerevisiae*,[20] Q_7 was isolated from Torula yeast,[21] and Q_{10} was isolated from *Rhodospirillum rubrum*.[14] The isolated samples were purified by thin layer chromatography as described previously.[19]

Ubiquinol-6 was prepared from rigorously purified Q_6 as follows. An ether solution of 10 mg of Q_6 was vigorously shaken with an aqueous solution of sodium hydrosulfite. When the color in the organic layer was completely discharged, this layer was carefully removed and evaporated under a stream of nitrogen. The sample was maintained under nitrogen until used, and was then introduced into the spectrometer with a minimum of handling.

Acknowledgment. This research was partially supported by funds from the Merck Sharp and Dohme Research Laboratories, Rahway, N. J. We also express our appreciation to Dr. Max Tishler.

(20) R. L. Lester, F. L. Crane, and Y. Hatefi, *J. Am. Chem. Soc.*, 80, 4751 (1958).

(21) J. Stevenson, P. J. Hayward, F. W. Hemming, and R. A. Morton, *Nature*, 1291 (1962).

Nuclear Magnetic Resonance Studies of Meisenheimer Complexes

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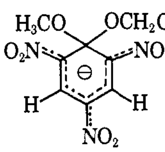
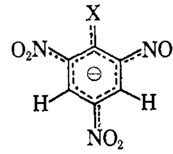
Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007. Received September 14, 1966

Abstract: The addition of methoxide to 1-substituted 2,4,6-trinitrobenzenes has been shown to occur both at the 1 and 3 positions in dimethyl sulfoxide solvent. Similarly, mono-N-substituted 2,4,6-trinitroanilines react both by NH proton loss and by addition at the 3 position. Diethylamine has been shown to react with either 2,4,6-trinitrobenzene or 2,4,6-trinitroanisole in a 2:1 molar ratio to give an ammonium salt of a Meisenheimer type complex. An unusual zwitterionic compound was prepared by the addition of triethylamine to 2,4,6-trinitroanisole.

The structures of the highly colored complexes obtained from the reaction of aromatic nitro compounds with bases have been of interest to chemists for more than 80 years.[2] Despite numerous investigations the structures of many of these compounds remain unsettled.[3] The structure (**1**) proposed by Meisenheimer[4] has been extensively used as a model for the occasionally detectable intermediate[5] in nucleophilic aromatic substitution reactions.[6] In addition, many of the polynitroaromatics have been of interest as acidity indicators where anions of structure **2** are presumed to be formed.[7] Formation of charge-transfer complexes **3** have been proposed to account for the frequent observation of rapidly formed transient intermediates.[8] Direct ionization to form the phenyl anion, **4**, has been suggested to explain the erratically reported[9] deuterium exchange into nitrobenzenes upon treatment with base. Treatment of *m*-dinitrobenzene with base leads to the well-characterized radical anion **5**;[10] similar intermediates have been proposed in the reactions of trinitroaromatics.[11] Zwitterionic intermediates such as **6** have also been proposed to account for the reaction of polynitroaromatics with amine bases.[8a,12]



1



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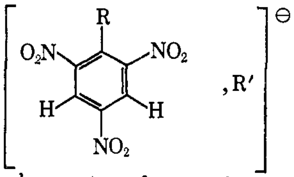
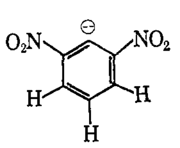


charge–transfer complex

3



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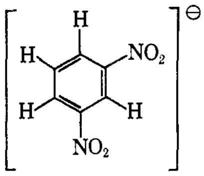

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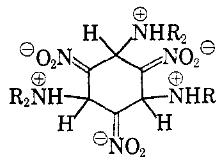

6

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(1) The author gratefully acknowledges support by a grant from the Petroleum Research Fund of the American Chemical Society (PRF-563-G1).

(2) P. Hepp, *Ann. Chem.*, **215**, 345 (1882).

(3) For a review see J. Kapecki, University of Illinois Seminar Abstracts, 1965–1966, p 154; or R. Foster and C. H. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966).

(4) J. Meisenheimer, *Ann.*, **323**, 205 (1902).

(5) J. F. Bunnett and J. J. Randall, *J. Am. Chem. Soc.*, **80**, 6020 (1958).

(6) For recent reviews see: (a) R. Huisgen and J. Sauer, *Angew. Chem.*, 72, 91, 294 (1960); (b) S. D. Ross, *Progr. Phys. Org. Chem.*, 1, 31 (1963).

(7) R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, **18**, 917 (1962); R. Stewart and J. P. O'Donnell, *J. Am. Chem. Soc.*, **84**, 493 (1962).

(8) (a) R. Foster, *J. Chem. Soc.*, 3508 (1959); (b) R. Foster and R. K. Mackie, *ibid.*, 3843 (1962); (c) R. E. Miller and W. F. K. Wynne-Jones, *ibid.*, 2375 (1959); (d) J. B. Ainscough and E. F. Caldin, *ibid.*, 2528, 2540, 2546 (1956); (e) ref 6b, p 44; (f) C. R. Allen, A. J. Brooks, and E. F. Caldin, *J. Chem. Soc.*, 2171 (1961).

(9) (a) R. J. Pollitt and B. C. Saunders, *Proc. Chem. Soc.*, 176 (1962); (b) V. Baliah and B. Ramakrishnan, *Rec. Trav. Chim.*, **87**, 783 (1959); (c) R. Foster and R. K. Mackie, *Tetrahedron* **19**, 691 (1963); (d) J. A. A. Ketelaar, A. Beer, and H. T. Vlaar, *Rec. Trav. Chim.*, **73**, 37 (1954); (e) M. R. Crampton and V. Gold, *J. Chem. Soc., Phys. Org.*, 498 (1966).

(10) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964); P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

(11) (a) Reference 8b; (b) R. Foster and R. K. Mackie, *Tetrahedron*, **16**, 119 (1961).

(12) G. N. Lewis and G. T. Seaborg, *J. Am. Chem. Soc.*, **62**, 2122 (1940); M. M. Labes and S. D. Ross, *J. Org. Chem.*, **21**, 1049 (1956).

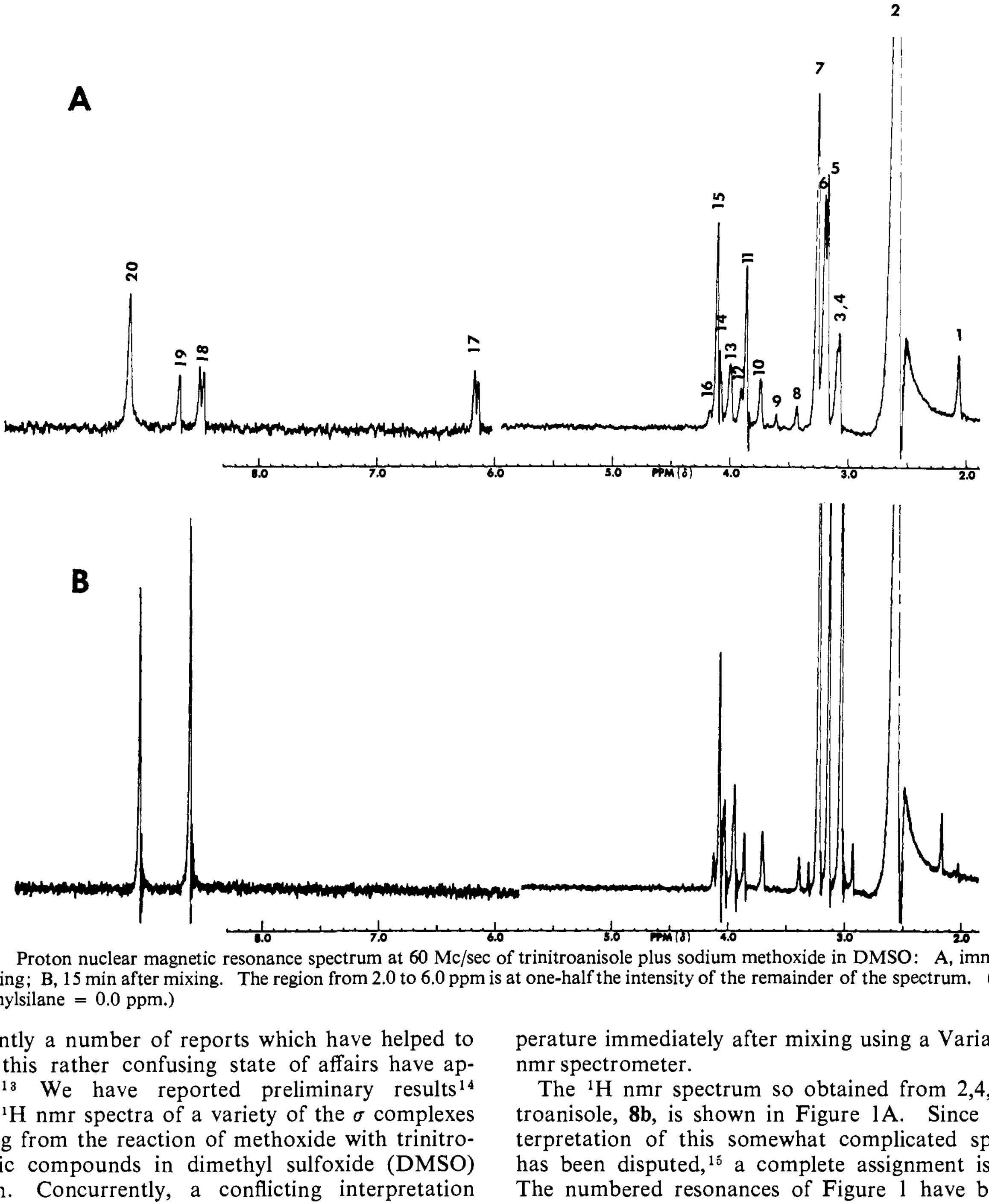


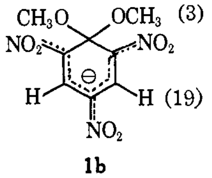
Figure 1. Proton nuclear magnetic resonance spectrum at 60 Mc/sec of trinitroanisole plus sodium methoxide in DMSO: A, immediately after mixing; B, 15 min after mixing. The region from 2.0 to 6.0 ppm is at one-half the intensity of the remainder of the spectrum. (Internal tetramethylsilane = 0.0 ppm.)

Recently a number of reports which have helped to clarify this rather confusing state of affairs have appeared.[13] We have reported preliminary results[14] on the ^1H nmr spectra of a variety of the σ complexes resulting from the reaction of methoxide with trinitroaromatic compounds in dimethyl sulfoxide (DMSO) solution. Concurrently, a conflicting interpretation of similar results appeared.[15] However, further studies by these authors have been reported to completely support our interpretation.[16] In this paper we report the results of our investigations of the reaction of trinitroaromatics with methoxide and amine bases.

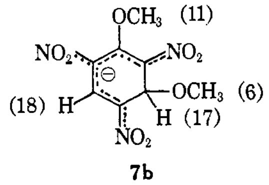
Results

The ^1H nmr spectra of the complexes were obtained from solutions prepared by the addition of sodium methoxide in methanol (7 *M*) to an approximately 1 *M* solution of the aromatic compound in DMSO; the nmr spectra were recorded at ambient probe temperature immediately after mixing using a Varian A-60 nmr spectrometer.

The ^1H nmr spectrum so obtained from 2,4,6-trinitroanisole, **8b**, is shown in Figure 1A. Since our interpretation of this somewhat complicated spectrum has been disputed,[15] a complete assignment is given. The numbered resonances of Figure 1 have been assigned as follows: peak 2, DMSO; peaks 1, 4, and 9, spinning side bands of DMSO (verified by shifts at different spinning rates); peak 10, ^{13}C satellite of DMSO; peaks 5 and 7, doublet of the CH_3 group of methanol; peaks 12, 13, 14, and 16, quartet of the OH group of methanol; peak 15, methoxyl group of trinitroanisole; peak 20, the aromatic hydrogens of trinitroanisole; peak 17, the hydrogen, R_2, of anion **7b** (see below); peak 18, the hydrogen, R_3, of anion **7b**; peak 11, the methoxyl group, R_1, of anion **7b**; peak 6, the methoxyl group at the saturated carbon atom of



1b



7b

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(13) M. R. Crampton and V. Gold, *Chem. Commun.*, 548 (1965); M. R. Crampton and V. Gold, *ibid.*, 256 (1965); M. R. Crampton and V. Gold, *J. Chem. Soc.*, 4293 (1964); R. A. Foster and C. A. Fyfe, *ibid.*, *Phys. Org.*, 53 (1966).

(14) K. L. Servis, *J. Am. Chem. Soc.*, **87**, 5495 (1965).

(15) R. A. Foster and C. A. Fyfe, *Tetrahedron*, **21**, 3363 (1965).

(16) R. A. Foster, personal communication.

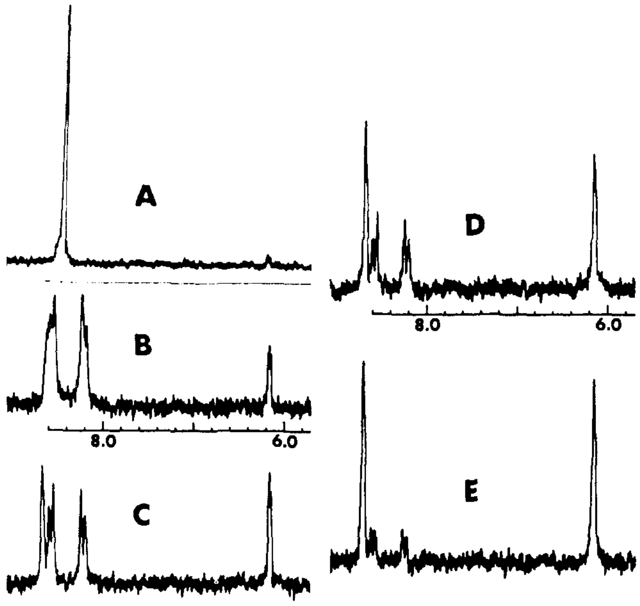
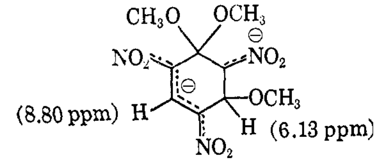


Figure 2. Proton nuclear magnetic resonance spectrum at 60 Mc/sec of N-methyl-2,4,6-trinitroaniline in DMSO: A, 0.8 equiv of sodium methoxide added; B, 1.1 equiv of sodium methoxide added; C, 1.2 equiv of sodium methoxide added; D, 1.5 equiv of sodium methoxide added; E, 1.8 equiv of sodium methoxide added. (Internal tetramethylsilane = 0.0 ppm.)

7b; peak 19, the two equivalent hydrogens, R_1 and R_2, of anion **1b** (see below); peak 3, the two equivalent methoxyl groups of anion **1b**. The spectrum in Figure 1B was obtained 15 min after that in 1A and is of the same solution. The assignments for this spectrum are identical with those outlined above. All of the resonances assigned to anion **7b** have completely disappeared; concurrently, the resonances assigned to **1b** have increased in intensity.

Upon addition of more than 1 equiv of methoxide new resonance at 6.13 and 8.80 ppm in the ratio of 1:1 appear and increase in intensity with increase in methoxide concentration; these resonance have been assigned to the dianion, **9b**.



9b

The ^{1}H nmr spectra of solutions of N-methyl-2,4,6-trinitroaniline (**8d**) and sodium methoxide result from a mixture of the anion obtained by methoxide addition to the 3 position, **7d**, and the anion obtained by proton abstraction from the NH position, **2d** (see Figure 2). As the methoxide concentration is increased, the aromatic proton resonance shifts upfield, and a new doublet (J = 2 cps) appears at 6.2 ppm. When slightly more than 1 equiv of methoxide has been added, the single absorption at 8.5 ppm splits into three closely spaced doublets. The observed change results from a sharp decrease in the rate of rotation around the nitrogen to the ring carbon bond. This rotation occurs in the free amine and when proton exchange between **8d** and **7d** is rapid produces an averaged resonance for the ring protons of amine **8d** and anion **7d**. Formation of dianion **10d** is indicated by the downfield shift of the resonance at 8.5 ppm upon further methoxide addition. Rapid amino-proton exchange is also observed between anion **7d** and dianion **10d** and produces averaged resonances for these two species. These results are summarized in Chart I.

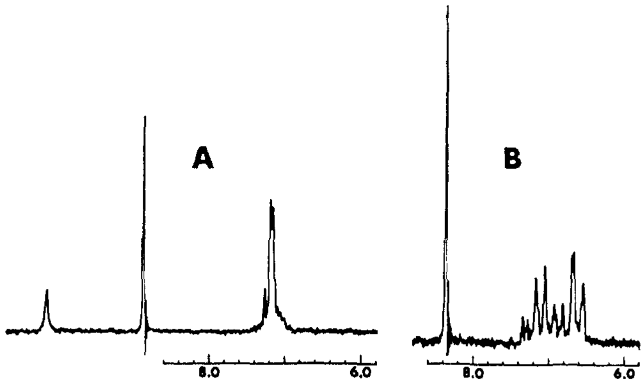
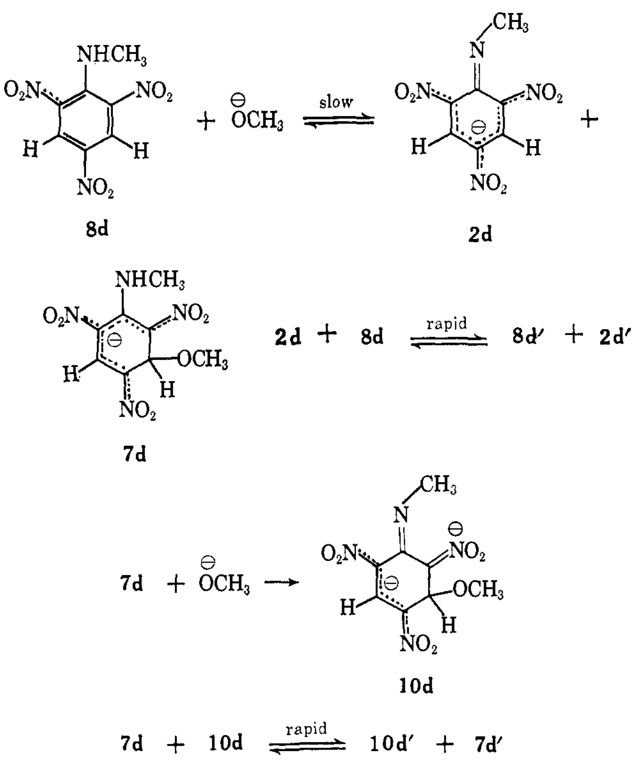


Figure 3. Proton nuclear magnetic resonance spectrum at 60 Mc/sec of N-phenyl-2,4,6-trinitroaniline in DMSO: A, before addition of methoxide; B, 1 equiv of sodium methoxide added. (Internal tetramethylsilane = 0.0 ppm.)

Chart I



As previously reported, N-phenyl-2,4,6-trinitroaniline reacts with methoxide in DMSO to give a single anion of structure **2e** whose ^{1}H nmr spectrum is shown in Figure 3. Arguments supporting this structure have been previously presented.[14] The equivalence of the two nitro ring proton absorptions probably arises from a more rapid reversible proton exchange; however, rapid rotation around the nitrogen to ring carbon bond in **2e** cannot be ruled out. Reaction with more than 1 equiv of methoxide appears to give the unstable dianion **10e**.

The ^{1}H nmr spectrum obtained upon reaction of 2,4,6-trinitroaniline with NaOMe (Figure 4) indicates the presence of two anions, **7c** and **2c**. The structural assignments follow from a comparison with those discussed above. In contrast to the N-methyl compound,

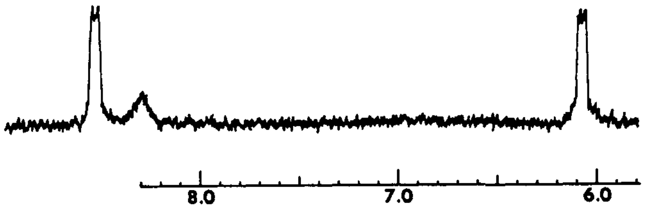
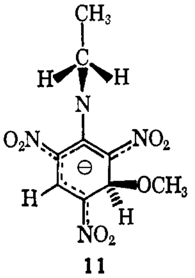


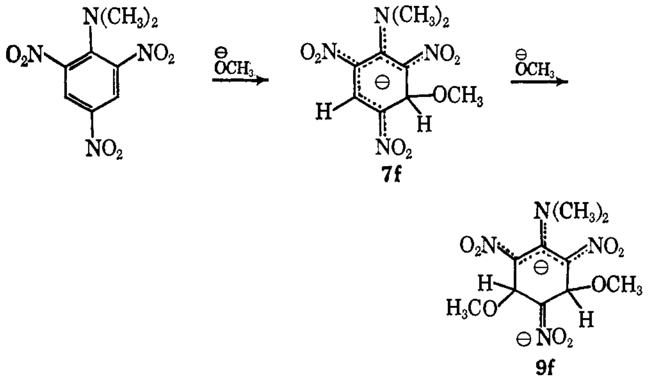
Figure 4. Proton nuclear magnetic resonance spectrum at 60 Mc/sec of 2,4,6-trinitroaniline plus 1 equiv of sodium methoxide in DMSO. (Internal tetramethylsilane = 0.0 ppm.)

2,4,6-trinitroaniline yields predominantly the σ complex, **7c**.

Reaction of methoxide with either N,N-dimethyl or N,N-diethyl-2,4,6-trinitroaniline produces none of the Meisenheimer type complexes but only the σ complexes **7f** and **7g**. After 45 days at room temperature, anion **7f** has partially decomposed to give what appears to be **1b**, but no rearrangement to the Meisenheimer type complex, **1f**, is evident. The N-ethyl resonances of anion **7g** (Figure 5) are characteristic of an ABX_3 spin system.[17] The AB methylene group undoubtedly arises from the asymmetric environment induced by the methoxyl group in a preferred conformation such as **11.**



11



9f

Since the two N-methyl groups of **7f** and the two CH_3 portions of the N-ethyl groups of **7g** are both chemical shift equivalent, rotation around the nitrogen to ring carbon bond must be rapid.

Upon addition of methoxide to a solution of anion **7f**, new resonances at 2.97, 3.14, and 6.04 ppm in the ratio 3:3:1 appear in the nmr spectrum, indicating the formation of the dianion **9f**. Although *cis* and *trans* isomers of **9f** are conceivable, no evidence as to this occurrence is available from the observed spectra.

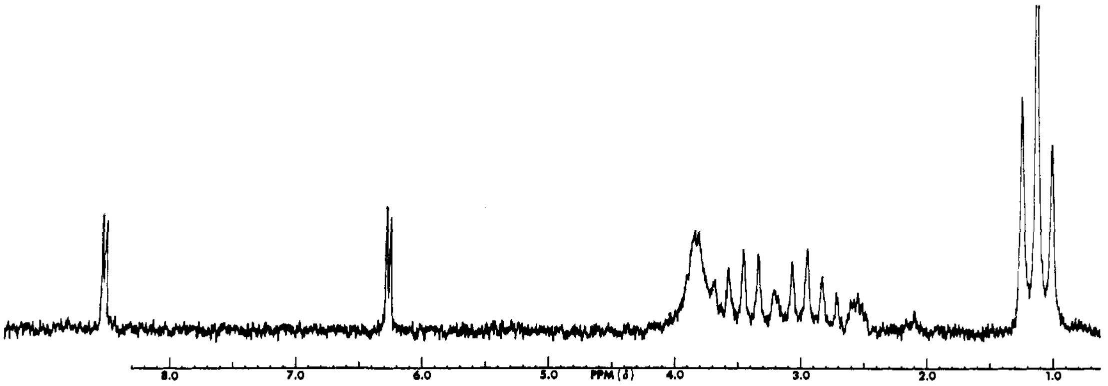


Figure 5. Proton nuclear magnetic resonance spectrum at 60 Mc/sec of N,N-diethyl-2,4,6-trinitroaniline plus 1 equiv of $NaOCD_3$ in DMSO-d_6. (Internal tetramethylsilane = 0.0 ppm.)

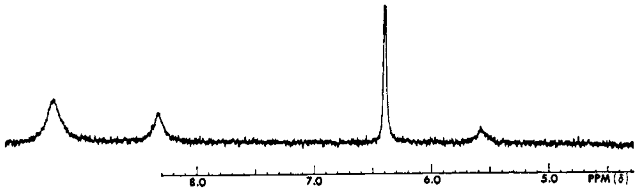
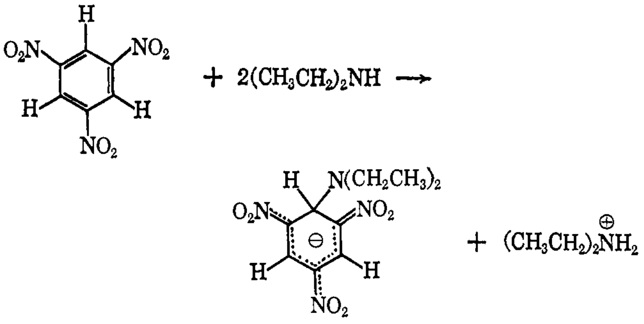


Figure 6. Proton nuclear magnetic resonance spectrum at 60 Mc/sec of 1,3,5-trinitrobenzene plus diethylamine in DMSO. (Internal tetramethylsilane = 0.0 ppm.)

Trinitrobenzene reacts with methoxide in DMSO to generate the anion **1a**. In agreement with the report of Foster and Fyfe we find that anion **1a** reacts further to give the dianion **9a**. Diethylamine also reacts with 2,4,6-trinitrobenzene in DMSO as follows.



Despite careful purification, the ${}^1H$ nmr spectrum of these solutions always exhibited broad resonances (Figure 6). This may be due to the low concentration of radicals previously detected in this system.[11b,18] No reaction is observed with triethylamine.

The 2,4,6-trinitroanilines do not react with either secondary or tertiary amines in DMSO. However, 2,4,6-trinitroanisole reacts with both types of amines. The ${}^1H$ nmr spectrum of 2,4,6-trinitroanisole plus excess diethylamine in DMSO-d_6 is shown in Figure 7. Addition occurs at the 1 position to generate a Meisenheimer type complex as follows.

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[17] G. M. Whitesides, F. Kaplan, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **48**, 1113 (1962).

[18] V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1692 (1964).

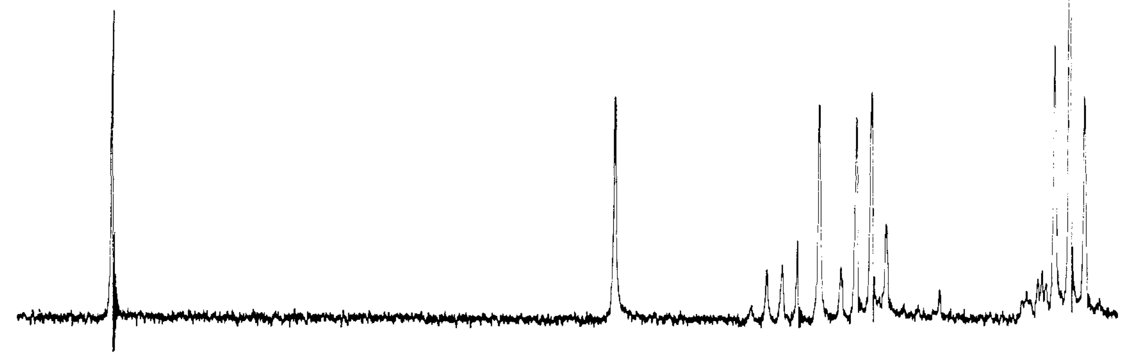


Figure 7. Proton nuclear magnetic resonance spectrum at 60 Mc/sec of 2,4,6-trinitroanisole plus excess diethylamine in DMSO-d_6. (Internal tetramethylsilane = 0.0 ppm.)

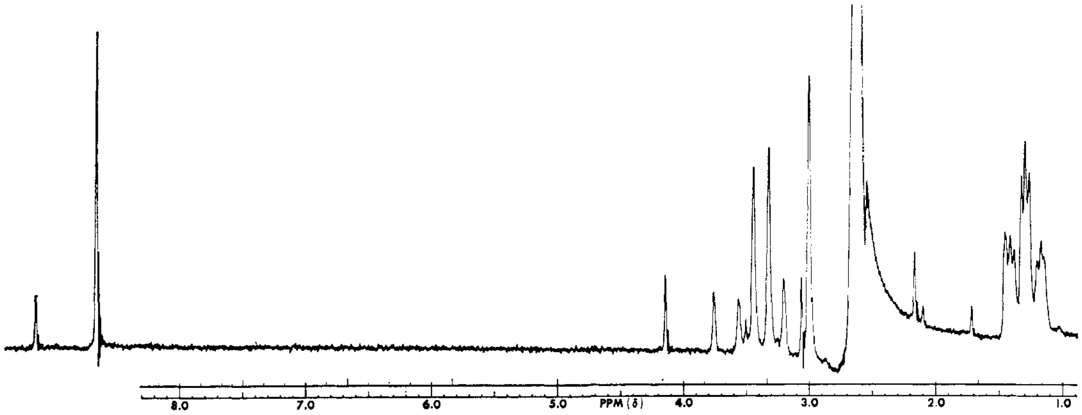
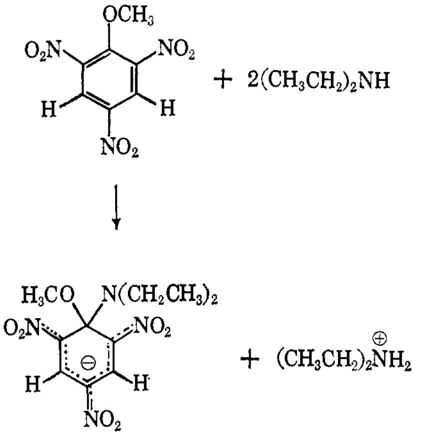
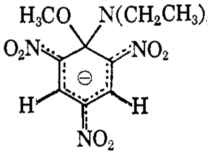


Figure 8. Proton nuclear magnetic resonance spectrum at 60 Mc/sec of 2,4,6-trinitroanisole plus 0.8 equiv of triethylamine in DMSO. (Internal tetramethylsilane = 0.0 ppm.)



Somewhat surprisingly, triethylamine in DMSO also reacts with 2,4,6-trinitroanisole to generate the zwitterionic complex, **1h**, whose ^1H nmr spectrum is shown in Figure 8. The assignment of resonances not due to unreacted trinitroanisole (9.07 and 4.13 ppm) or solvent (1.7, 2.2, 2.6, 3.1, 3.5, and 3.8 ppm) corresponds to those expected from **1h** as shown in Table I.



1h

Addition of base to solutions of 2,4,6-trinitrotoluene in a variety of solvents leads to a complete disappearance of the resonance absorptions of the aromatic protons. The nmr spectral properties of the observed anions are summarized in Table I.

Discussion

In the numerous cases studied, addition of an anion to a solution of a trinitroaromatic compound produces either a σ complex of the general type proposed by Meisenheimer or a σ complex formed by addition at the 3 position. If the nitroaromatic contains an acidic proton, then ionization to the conjugate base occurs in competition with σ-complex formation, the relative amounts depending on the detailed structure of the reactant. For the 2,4,6-trinitroanilines, the ratio of conjugate base to σ complex increases in the series NH_2, $NHCH_3$, NHC_6H_5. The phenyl substituent has the expected acid-strengthening effect. Although the N-methyl group might have been expected to decrease the acidity of the NH proton (in analogy with alkyl group effects on the acidity of hydrocarbons[19]), the observed effect is to increase the stability of the conjugate base relative to that of the σ complex. As evidenced by the nmr spectrum of anion **2d**, the nitrogen to ring carbon bond has a high degree of double bond character and consequently may be expected to have a relatively low negative charge density on the nitrogen atom. The methyl group effect reflects the normal increased stabilization which results from alkyl substitution on unsaturated centers.[20]

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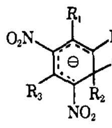
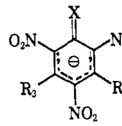
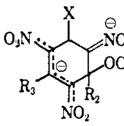
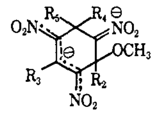
(19) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, p 417.

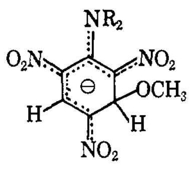
(20) See, for example, E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, Inc., New York, N. Y., 1959, p 49.

Table I. Chemical Shift of Anions and Dianions from 1-Substituted 2,4,6-Trinitrobenzenes in Dimethyl Sulfoxide

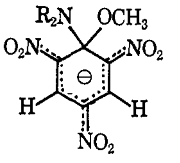
		Compound				Chemical shifts, ppm[a]				
		R_1	R_2	R_3		R_1	R_2	R_3	OCH_3	
	**1a**	H	H	H		8.42	6.12	8.42	3.22	
	7b	OCH_3	H	H		3.45	6.17	8.42	3.20	
	7c	NH_2	H	H		*b*	6.09	8.48	*b*	
	7d	$NHCH_3$	H	H		3.23	6.18	8.50	*b*	
	7f	$N(CH_3)_2$	H	H		2.85	6.18	8.49	3.19	
	7g	$N(CH_2CH_3)_2$	H	H		*c*	6.28	8.50	3.20	
	1b	H	OCH_3	H		8.67	3.06	8.67	3.06	
	1g	H	$N(CH_2CH_3)_2$	H		8.65	*d*	8.65	3.08	
	1h	H	$^{\oplus}N(CH_2CH_3)_3$	H		8.64	*e*	8.64	2.97	
		X	R_2	R_3		X	R_2	R_3		
	**2c**	NH	H	H		*b*	8.37	8.37		
	2d	NCH_3	H	H		2.85	8.54	8.20		
	2e	NC_6H_5	H	H		*f*	8.37	8.37		
		Compound				Chemical shifts, ppm[a]				
		R_2	R_3	R_4	R_5	R_2	R_3	R_4	R_5	OCH_3
	**9a**	H	H	H	OCH_3	6.11	8.60	6.11	3.40	3.40
	9f	H	$N(CH_3)_2$	H	OCH_3	6.04	2.97	6.04	3.14	3.14
	9b	H	H	OCH_3	OCH_3	6.13	8.80	*b*	*b*	*b*
		X	R_2	R_3		X	R_2	R_3	OCH_3	
	**10d**	NCH_3	H	H		*b*	6.16	8.70	*b*	
	10e	NC_6H_5	H	H		*b*	6.17	8.71	3.40	
	10c	NH	H	H		*b*	6.06	8.67	*b*	

[a] Relative to tetramethylsilane internal standard = 0.0 ppm. [b] Not observed. [c] $N(CH_AH_BCH_3)_2$, $\nu_A = 2.85$; $\nu_B = 3.56$; $J_{AB} = 14$ cps; $\nu_{CH_3} = 1.14$; $J_{AX} = J_{BX} = 7$ cps (see text). [d] This is an A_2X_3 system: $\nu_A = 3.43$; $\nu_X = 1.34$; $J_{AX} = 7$ cps ($J_{^{14}NX} = 2$). [e] This is an A_2X_3 system: $\nu_A = 3.35$; $\nu_X = 1.26$; $J_{AX} = 7$ cps ($J_{^{14}NX} = 2$). [f] The resonance extends from 6.57 to 7.40 ppm; for N-phenyl-2,4,6-trinitroaniline the resonance extends from 7.09 to 7.34 ppm.

The N,N-dialkyl-2,4,6-trinitroanilines present a rather perplexing problem. Addition of methoxide to the aniline yields the 3-substituted σ complexes (**7f** and **7g**), while addition of the amine to the anisole yields the 1-substituted Meisenheimer complexes (**1f** and **1g**).



7f, R = CH_3
7g, R = CH_2CH_3



1f, R = CH_3
1g, R = CH_2CH_3

All attempts to equilibrate the anions were unsuccessful owing to competing side reactions which occur in these systems. The anion with structure **7** is expected to be the initial kinetic product while the anion of structure **1** should be the thermodynamic product (*vide infra*). The rate of formation of **1g** from N,N-diethyl-2,4,6-trinitroaniline may be unusually slow owing to steric shielding of the 1-carbon by the ethyl groups in conformations such as **11**. The corresponding transition state to **1g** from 2,4,6-trinitroanisole should not suffer the same limitations.

Miller has proposed a semiempirical quantitative approach to nucleophilic aromatic substitution reactions.[21] Considering the numerous assumptions inherent in the calculations, the method has in general been remarkably successful.[22] The calculated reaction coordinate diagram for the reaction of methoxide with 2,4,6-trinitroanisole is shown in Figure 9. The portion corresponding to addition at the 1 position has been taken directly from the original paper.[21] The portion corresponding to addition at the 3 position was calculated using the same parameters except that a "series term" of +74 kcal was used.[23] Obviously no α-substituent effect need be applied to the calculation of the transition-state energy. These calculations

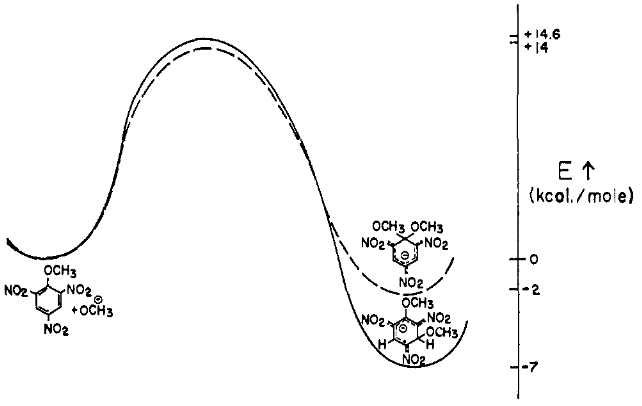


Figure 9. Schematic representation of the calculated energetics for the reaction of methoxide with 2,4,6-trinitroanisole.

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(21) J. Miller, *J. Am. Chem. Soc.*, **85**, 1628 (1963).

(22) D. L. Hill, K. E. Ho, and J. Miller, *J. Chem. Soc., Phys. Org.*, 299 (1966).

(23) No correction appears to be necessary for the change in C_1–OCH_3 bond strength on going from the 3-substituted complex to trinitroanisole.

predict that addition at the 1 position should lead to the kinetically controlled product but that addition to the 3 position should lead to the thermodynamically controlled product. These predictions are in complete disagreement with our observations; we find that the initially formed complex arises from addition at the 3 position while the equilibrium product arises from addition at the 1 position.[24] A similar discrepancy is found between the calculated and observed reactivities of methoxide toward the 1 and 5 positions of 2,4-dinitroanisole.[26] This appears to be a general problem with Miller's method of calculation.

Methoxide in DMSO reacts with 1,3-dinitrobenzene by an electron-transfer reaction to yield the corresponding radical anion, **5**,[27] while 1,3,5-trinitrobenzene reacts under similar conditions to form the σ complex. A ready explanation for this change in behavior comes from a consideration of the simple Hückel molecular orbital description of aromatic molecules. Owing to the symmetry of the antibonding molecular orbitals,[28] the third nitro group should add very little to the stability of the radical anion but should make a large contribution to the stability of the cyclohexadienide-type anion. 2,4-Dinitroanisole also gives σ-complex formation rather than electron transfer on treatment with methoxide. The explanation for this is undoubtedly connected with the stabilizing effect of methoxyl on the anions **1b** and **7b** and may be due to a bond-strengthening α-substituent effect.

Although 2,4,6-trinitrotoluene has been reported to react with base forming a benzyl-type anion,[29] this now appears very unlikely. Amines are known to be on the order of 10^{10} more acidic than the corresponding hydrocarbons.[30] By comparison with 2,4,6-trinitroaniline, one would predict that 2,4,6-trinitrotoluene would not suffer proton loss to methoxide but instead would undergo addition at the 3 position. No evidence was found for this reaction. The observed results do hint at radical formation in this system, and studies are in progress to test the validity of this proposal.[32]

Experimental Section

Dimethyl sulfoxide (Matheson Coleman and Bell) was stored over calcium hydride and distilled at reduced pressure immediately before use. Anhydrous methanol (Mallinckrodt) was distilled from magnesium methoxide. Diethylamine and triethylamine (Matheson Coleman and Bell) were refluxed over potassium hydroxide and fractionally distilled through a 30-cm, wire-spiral column.

2,4,6-Trinitrotoluene, 2,4,6-trinitroanisole, 1,3,5-trinitrobenzene, and 2,4,6-trinitroaniline were obtained from Eastman Organic Chemicals. N-Methyl-, N,N-dimethyl-, N,N-diethyl-, and N-phenyl-2,4,6-trinitroaniline were prepared by reaction of picryl chloride (Matheson Coleman and Bell) with the appropriate amine. All of the trinitroaromatics were recrystallized and sublimed before use to give the materials whose melting points are given in Table II.

Table II. Physical Properties of 1-Substituted 2,4,6-Trinitrobenzenes

	Mp, °C	
	Obsd[a]	Lit.
1,3,5-$(NO_2)_3C_6H_3$	123.0–123.6	122.1–122.4[b]
2,4,6-$(NO_2)_3C_6H_2CH_3$	80.2–80.7	81.1[b]
2,4,6-$(NO_2)_3C_6H_2OCH_3$	67.3–67.5	67–68[c]
2,4,6-$(NO_2)_3C_6H_2NH_2$	190.6–191.0	190–191[d]
2,4,6-$(NO_2)_3C_6H_2NHCH_3$	112.9–113.4	110.4–110.8[b]
2,4,6-$(NO_2)_3C_6H_2NHC_6H_5$	178.2–179.2	179.5–180[e]
2,4,6-$(NO_2)_3C_6H_2N(CH_3)_2$	139.3–140.0	138[f]
2,4,6-$(NO_2)_3C_6H_2N(CH_2CH_3)_2$	166.6–167.0	163–164[f]

[a] Corrected. [b] W. E. Garner and C. L. Abernathy, *Proc. Roy. Soc.* (London), **99A**, 219 (1921). [c] E. Chapman, A. G. Perkins, and R. Robinson, *J. Chem. Soc.*, 3030 (1927). [d] W. Borsche, *Chem. Ber.*, **56**, 1939 (1923). [e] T. I. Davis and A. A. Ashdown, *J. Am. Chem. Soc.*, **46**, 1054 (1924). [f] P. Van Romburgh, *Rec. Trav. Chim.*, **2**, 105 (1883).

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(24) The reported activation energies for ethoxide addition are 10.4 and 13.1 kcal/mole, respectively, while the equilibrium constants for formation of the Meisenheimer complex from methoxide is 7.7×10^3 l./mole.[25]

(25) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1687 (1964).

(26) R. Foster and C. A. Fyfe, in press.

(27) G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962).

(28) K. Higasi, H. Baba, and A. Rembaum, "Quantum Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1965, p 64.

(29) K. G. Shipp and L. A. Kaplan, *J. Org. Chem.*, **31**, 857 (1966); E. F. Caldin and G. Long, *Proc. Roy. Soc.* (London), **238A**, 263 (1955).

(30) The reported pK_a's of aniline and toluene are 27 and 37, respectively.[31]

(31) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 4 and 17.

(32) Radicals have been detected in the reaction of trinitrotoluene with potassium *t*-butoxide in DMSO.[27]