under reflux for 3 hr. It was then cooled in an ice bath to 0°, 6 *N* hydrochloric acid (30 ml) was added with stirring and the mixture was refluxed for 6 to 8 hr.

After cooling the layers were separated, and the organic layer was washed with dilute sodium carbonate solution and water. The solvent was removed by distillation and the product was distilled under reduced pressure to yield 5.1 g (49%), bp 81-83° (0.45 mm).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 83.10; H, 7.87.

Rate Determinations.—The iodine monobromide titrimetric method used to follow the disappearance of alkenes has been described previously.[23] A quantitative hydrogenation procedure was used in the case of 4-(*m*-methoxyphenyl)-1-butene and 4-(*p*-methoxyphenyl)-1-butene, since the aromatic ring was brominated by the titrimetric reagent in these instances. Aliquots (2 or 3 ml) were withdrawn from the reacting solutions and injected through a serum cap into the reaction vessel of an atmospheric pressure hydrogenation apparatus, which contained 25 mg of 10% palladium on carbon (presaturated with hydrogen) and 5 ml of acetic acid to quench the reaction of trifluoroacetic acid with the alkene. The reaction vessel and the 10-ml hydrogen buret were jacketed and maintained at 25.0° by water circulated from a constant-temperature bath. Both a "course" (mercury) and "fine" (butyl tartrate) manometer were used to achieve volume readings of high precision. The rate constant for the reaction of 4-phenyl-1-butene with trifluoroacetic acid was measured both by the titrimetric method (10^5k = 25.7 sec^{-1}) and by hydrogenation (10^5k = 25.1 sec^{-1}).

Registry No.—4-(*p*-Bromophenyl)-1-butene, 15451-32-8; 4-(*p*-cyanophenyl)-1-butene, 15451-33-9; 4-(*p*-carbomethoxyphenyl)-1-butene, 15451-34-0; 4-(*p*-carboxyphenyl)-1-butene, 15451-35-1; 4-(*p*-acetylphenyl)-1-butene, 15451-36-2; trifluoroacetic acid, 76-05-1.

Acknowledgment.—We wish to express our deep gratitude to Dr. Michael M. Martin, Department of Chemistry, University of Michigan, who contributed the samples of phenylbutenes having the substituents H, *m*-Cl, *p*-Cl, *m*-CH_3, *p*-CH_3, *m*-OCH_3, and *p*-OCH_3.[24]

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Intermediates in Nucleophilic Aromatic Substitutions. III.[1] Meisenheimer Complexes of 1-Alkoxy-2,4-dinitronaphthalenes

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Received September 11, 1967

The rate constants for the formation and decomposition of the Meisenheimer complex (1) formed by the attack of methoxide ion on 1-methoxy-2,4-dinitronaphthalene (4) in methanolic solution have been determined at 8.10, 25.00, and 35.00°, allowing a determination of K, k_1, k_2, and energies and entropies of activation for the process. These data indicate **1** to be approximately 250 times more stable than the corresponding complex formed from 1-methoxy-2,4-dinitrobenzene but significantly less stable than the corresponding picryl complex. The rate of decomposition of crystalline **1** in methanol and in aqueous buffers has been examined over the pH range 4.97-10.85 at 25.00°; the decomposition is strongly catalyzed by acids. In addition to **1**, the stable crystalline Meisenheimer complexes (**2** and **3**) resulting from the attack of ethoxide ion on **4** and on 1-ethoxy-2,4-dinitronaphthalene (**5**) have been isolated; complex **2** was also prepared by reaction of methoxide ion with **5**. Infrared and proton magnetic resonance spectral studies establish complexes **1-3** to be 1,1-dialkoxy-2,4-dinitro-5,6-benzocyclohexadienylides.

Meisenheimer complexes are brightly colored adducts formed by the attack of a nucleophile at an electron-deficient position of an aromatic ring. The structures and stabilities of these complexes and their role in nucleophilic aromatic substitutions has received considerable attention in recent years.[3] Proton magnetic resonance (pmr) spectra of the 1-alkoxy-2,4,6-trinitrobenzene Meisenheimer complexes showed the two alkoxyl groups to be covalently linked to the same carbon atom.[4] In the preceding paper of this series,[5] we reported the isolation of complexes formed by the attack of alkoxide ions on 2,4-dinitroanisole and 2,4-dinitrophenetole and showed them to be 1,1-dialkoxy-2,4-dinitrocyclohexadienylides by pmr and infrared studies. The equilibrium constant for the formation of the potassium methoxide complex of 2,4-dinitroanisole in methanolic dioxane[5] was found to be several 1000-fold smaller than that for the ethoxyl complex of 2,4,6-trinitroanisole in ethanol.[6]

Dewar has calculated[7] that the formation of cyclohexadienyl intermediates from substituted benzenes requires a 10 kcal mol^{-1} loss inre sonance energy, whereas the resonance energy difference between naphthalene and the 1,1-disubstituted naphthalene intermediate is only 2 kcal mol^{-1}. One would expect, therefore, a smaller activation energy for nucleophilic substitution at a naphthalenoid than at a benzenoid carbon atom. This expectation has been verified by Elias and Parker[8] who found that the energy of activation for the nucleophilic substitutions of 1-chloro-2,4-dinitronaphthalene is approximately 3 kcal mol^{-1} less than that for 1-chloro-2,4-dinitrobenzene. Similarly, one would expect the formation of more stable Meisenheimer complexes with 1-substituted naphthalenes than with the corresponding benzene compounds. Although the formation of the methoxyl complex of 1-methoxyl-2,4-dinitronaphthalene in methanolic so-

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[1] Part II: C. E. Griffin, E. J. Fendler, W. E. Byrne, and J. H. Fendler, *Tetrahedron Lett.*, 4473 (1967).

[2] NASA Postdoctoral Fellow, 1966-1967.

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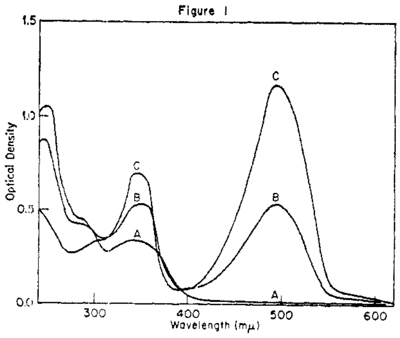
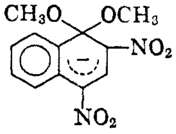
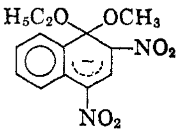


Figure 1.—Absorption spectra of 1-methoxyl-2,4-dinitronaphthalene (5.124×10^{-5} M) in methanolic sodium methoxide at 25.0° using a pair of 1.00-cm matched cells ([$NaOCH_3$]: A, 0; B, 0.00297 M; C, 0.0267 M).

lution[9] and the isolation of a solid from the same system[10,11] have been previously reported, no quantitative studies of this reaction have been undertaken. We wish to report the synthesis, isolation, and chemical and physical properties of the crystalline complexes **1**–**3**, and to present kinetic and thermodynamic data on the formation and decomposition of **1**.



1



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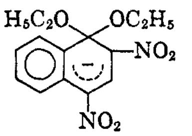

3

Experimental Section

The solvents and reagents were prepared, purified, and standardized as previously described.[5] 1-Chloro-2,4-dinitronaphthalene (Eastman) and 1-methoxy-4-nitronaphthalene (Aldrich) were commercial products.

1-Methoxy-2,4-dinitronaphthalene (4) was prepared by the addition of 8.56 ml of 5.84 M (50 mmol) potassium methoxide in methanol to a warm solution of 10.10 g (40 mmol) of 1-chloro-2,4-dinitronaphthalene in 40 ml of benzene. The reaction mixture was refluxed with stirring for 3 hr, cooled, and extracted with 0.5 M sulfuric acid. The aqueous layer was reextracted with benzene, and the benzene was removed from the combined extracts by rotary evaporation. The light yellow crystals were recrystallized from absolute methanol, mp 97.5–98° (lit.[11] mp 98.5°). The same method was used to prepare **1-ethoxy-2,4-dinitronaphthalene (5)** using 2.42 M potassium ethoxide in ethanol. After recrystallization from absolute ethanol, **5** melted at 91.5–92° (lit. mp 92–93°,[10] 93°,[12a] and 90° [12b]).

The methoxy complex (1) of 1-methoxy-2,4-dinitronaphthalene was prepared by the addition of 0.73 ml (4.25 mmol) of 5.84 M potassium methoxide in methanol to a solution of 1.07 g (4.32 mmoles) of **4** in 1.5 ml of DMSO. After evaporation of some solvent with dry nitrogen, the bright red crystals were filtered under nitrogen, washed with benzene and anhydrous ether, and dried in a vacuum desiccator over P_2O_5, mp 90–92° dec.

Anal.[13] Calcd for $C_{12}H_{11}KN_2O_6 \cdot (CH_3)_2SO$: C, 42.2; H, 4.3; K, 9.8; N, 7.0; S, 8.2. Calcd for $C_{12}H_{11}KN_2O_6 \cdot 2(CH_3)_2SO$: C, 40.5; H, 4.9; K, 8.2; N, 5.9; S, 13.5. Found: C, 39.9; H, 4.6; K, 8.4; N, 6.3; S, 9.3 (the presence of DMSO in this sample was confirmed by pmr spectroscopy).

The same method was used to prepare the **ethoxyl complex (3) of 1-ethoxy-2,4-dinitronaphthalene** from 2.42 M potassium ethoxide in ethanol and **5** in DMSO; **3** melted at 215–218° dec.

Anal. Calcd for $C_{14}H_{15}KN_2O_6$: C, 48.4; H, 4.8; K, 11.3; N, 8.1. Found: C, 47.5; H, 4.75; K, 11.5; N, 7.8.

Complex **1** was also isolated with *ca.* 2 mol of benzene of crystallization by the same procedure with the exception that a solution of **4** in 1.5 ml of dry benzene was used; **1** melted at 189–191° dec. Drying the complex at less than 0.1 mm at 50–60° for 4 hr followed by a further 12-hr drying at 80–90° at the same pressure resulted in no detectable (pmr) loss of benzene.

The same general procedure was used to prepare **1** from a solution of 4.32 mmol of **4** in 1.0 ml of dioxane by the addition of 0.72 ml (4.25 mmol) of 5.95 M potassium methoxide in methanol; the **ethoxyl complex (2a) of 1-methoxy-2,4-dinitronaphthalene** was prepared from a solution of **4** in dioxane with an ethanolic solution of potassium ethoxide; the **methoxyl complex (2b) of 1-ethoxy-2,4-dinitronaphthalene** was prepared from a solution of **5** in dioxane with a methanolic solution of potassium methoxide; and **3** was prepared from a solution of **5** in dioxane with an ethanolic solution of potassium ethoxide. The observed melting points (with decomposition) follow: **1**, 185°; **2a**, 195°; **2b**, 210°; **3**, 205°.

Anal. Calcd for $C_{12}H_{11}KN_2O_6$ (**1**): C, 45.3; H, 3.5; K, 12.3; N, 8.8. Calcd for $C_{12}H_{11}KN_2O_6 \cdot C_4H_8O_2$: C, 47.3; H, 4.7; K, 9.6; N, 6.9. Found: C, 47.3; H, 4.8; K, 8.7; N, 7.0.

Anal. Calcd for $C_{13}H_{13}KN_2O_6$ (**2a**): C, 48.5; N, 3.9; K, 11.8; N, 8.4. Found: C, 47.5; H, 3.95; K, 11.7; N, 8.36.

Anal. Calcd for $C_{13}H_{13}KN_2O_6$ (**2b**): C, 48.5; H, 3.9; K, 11.8; N, 8.4. Found: C, 45.7; H, 4.0; K, 11.6; N, 7.9.

Anal. Calcd for $C_{14}H_{15}KN_2O_6$ (**3**): C, 48.4; H, 4.8; K, 11.3; N, 8.1. Found: C, 48.5; H, 4.5; K, 11.1; N, 8.2.

The presence of *ca.* 1 mol of dioxane of crystallization in this sample of **1** was indicated by its pmr spectrum.

The unsymmetrical complex **2**, mp 210° (with preliminary darkening), was also prepared by the addition of ethanolic potassium ethoxide to a solution of **4** in DMSO; some difficulty was encountered in the crystallization of this material and the addition of benzene to the reaction mixture was necessary. Although the infrared and pmr spectra of the product were essentially identical with those of **2a** and **b**, satisfactory elemental analyses were not obtained.

The visible and ultraviolet spectra of **1** and **4** were obtained on a Beckman DU-2 spectrophotometer; a pair of matched 10.0-mm cells with Teflon stoppers were used. The cell compartment was equipped with a set of Beckman dual thermospacers; the temperature was measured inside the cells and was maintained within ±0.02°. The pH of the buffer solutions used for the studies of the decomposition of **1** was measured at 25.0° by an Orion Model 801 digital pH meter (reproducibility ±0.002 pH). Infrared spectra were recorded on Perkin-Elmer Models 21 and 221 spectrophotometers; all spectra were recorded as Nujol mulls.

Pmr spectra (60 MHz) 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 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 at least three determinations at 50-Hz sweep widths and are accurate to ±0.2 Hz. Frequency swept and 100-MHz double-resonance experiments were carried out with a Varian Associates HA-100 spectrometer.

Results

The absorption spectra of 5.12×10^{-5} M 1-methoxy-2,4-dinitronaphthalene (**4**) in methanol and in methanolic sodium methoxide are given in Figure 1 and Table I. On increasing the concentration of the methoxide ion, a new absorption band appears at 495 mμ which reaches its maximum at a sodium methoxide concentration of $5.3 \times 10^{-2} M$ and remains constant up to 2.94 M. The constancy of the absorbance over a 50-fold increase in methoxide ion concentration indicates that the equilibrium 1 is complete at a methoxide ion

$$4 + OCH_3^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 1 \qquad (1)$$

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[9] R. Foster, C. A. Fyfe, P. M. Emslie, and M. I. Foreman, *Tetrahedron*, **23**, 227 (1963).

[10] S. S. Gitis and A. I. Glaz, *J. Gen. Chem. USSR*, **33**, 888 (1963).

[11] D. S. Gilbert, Thesis, Leicester College of Technology, Leicester, England, 1963.

[12] (a) P. Hiermann, *J. Prakt. Chem.*, **44**, 243 (1891); (b) F. Ullmann and W. Bruck, *Ber.*, **41**, 3932 (1908).

[13] All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

TABLE I

INTERACTION OF 1-METHOXY-2,4-DINITRONAPHTHALENE (5.124×10^{-5} M) WITH METHANOLIC SODIUM METHOXIDE

Temp, °C	[$NaOCH_3$], M	Optical density at 350 mμ[a]	Optical density at 495 mμ[a]	α	K,[b] l. mol^{-1}	10^3k_{obsd}, sec^{-1}	k_1,[c] l. mol^{-1} sec^{-1}	k_1,[d] l. mol^{-1} sec^{-1}	10^3k_2,[c] sec^{-1}	10^3k_2,[d] sec^{-1}
8.10	0.000	0.310	0.000							
	0.000742	0.366	0.221	0.17	275	0.92	0.213		0.76	
	0.00148	0.449	0.376	0.29	280	1.10	0.217		0.79	
	0.00267	0.517	0.600	0.46	330	1.34	0.214	0.215	0.77	0.77
	0.327	0.542	1.308	1.00						
	1.635	0.583	1.310							
25.00	0.000	0.330	0.000							
	0.000742	0.384	0.173	0.13	204	4.33	0.82		3.7	
	0.00148	0.418	0.307	0.23	200	5.52	0.92		4.2	
	0.00222	0.475	0.426	0.32	214	5.98	0.88		4.0	
	0.00297	0.525	0.535	0.40	230	6.74	0.89	0.95	4.1	3.95
	0.00594	0.580	0.778	0.58	237					
	0.0148	0.665	1.043	0.78	245					
	0.0267	0.700	1.172	0.84	210					
	0.0534	0.720	1.326	1.00						
	0.327	0.745	1.328							
	1.635	0.735	1.328							
	2.943	0.800	1.310							
35.00	0.000	0.320	0.000							
	0.000742	0.367	0.138	0.104	160	11.8	1.82		10.5	
	0.00148	0.368	0.267	0.20	171	13.5	1.86		10.8	
	0.00222	0.444	0.365	0.28	174	14.7	1.83		10.7	
	0.00267	0.419	0.453	0.31	169	15.6	1.84	1.70	11.0	10.8
	0.00742	0.563	0.771	0.58	183					
	0.0148	0.635	0.970	0.73	181					
	0.327	0.750	1.328	1.00						
	1.635	0.820	1.328							

$E_1 = 13.8 \pm 0.8$ kcal mol^{-1} $\Delta S_1^{\ddagger} = -17 \pm 2$ eu[e,f]

$E_2 = 16.5 \pm 0.8$ kcal mol^{-1} $\Delta S_2^{\ddagger} = -18 \pm 2$ eu[e,g]

[a] Using a 1.00-cm cell. [b] Calculated by using eq 2. [c] Calculated by using eq 4. [d] Calculated by using eq 3. [e] Calculated at 25.00°. [f] Calculated by using the second-order rate constants, k_1. [g] Calculated by using the first-order rate constants, k_2.

concentration of 5.3×10^{-2} M. The fraction (α) of **4** converted into the complex **1** can therefore be evaluated at lower methoxide ion concentrations by dividing the optical densities at 495 mμ by 1.328 (see Table I). From the α values the equilibrium constant K can be readily calculated by using the expression given in eq 2

$$K = \frac{\alpha}{([NaOCH_3] - \alpha[\mathbf{4}])(1 - \alpha)} \qquad (2)$$

(assuming that $[NaOCH_3] \gg [\mathbf{4}]$). Plots of [**4**]/absorbance at 495 mμ *vs.* $1/[NaOCH_3]$ gave good straight lines at all three temperatures indicating that the equilibrium in eq 1 prevails without any complications. Using the Benesi–Hildebrand equation,[14a] the following values for ϵ and K were obtained, respectively, at 8.10, 25.00 and 35.00°: 35,500, 185; 29,400, 175; and 23,700, 185. The equilibrium constants obtained by this method are in reasonable agreement with those calculated by the use of eq 2 (Table I). Owing to the very nature of the calculation and to the high extinction coefficients involved, this method inevitably leads to less accurate equilibrium constants than those presented in Table I. At the lower methoxide ion concentrations, the red color was not formed immediately and the attainment of the equilibrium could be followed by measuring the increase of absorbance at 495 mμ. Since the concentration of **4** was by some 100-fold smaller than that of the methoxide ion, a first-order relationship was observed. Such first-order plots for typical runs are given in Figure 2. Since the rate of equilibrium attainment is proportional to the distance from equilibrium, the observed first-order rate of attainment of the equilibrium, k_{obsd}, is expressed by eq 3 or 4. Using eq 3, plots of k_{obsd}

$$k_{obsd} = k_1[NaOCH_3] + k_2 \qquad (3)$$

$$k_{obsd} = k_1([NaOCH_3] + 1/K) \qquad (4)$$

against sodium methoxide concentration at 8.10, 25.00, and 35.00° gave good straight lines whose slope is k_1 and whose intercept is k_2. Equation 4 permits independent calculation of k_1 and k_2 by using k_{obsd} and the corresponding equilibrium constants (obtained from eq 2). The results of both sets of calculations are given in Table I. From the rate constants obtained from eq 3 we have calculated the equilibrium constants at 8.10, 25.00, and 35.00° to be 278, 240, and 167, respectively. The agreement between the two sets of rate and equilibrium constants is excellent. Using the two sets of k_1 and k_2 values at the three temperatures, linear Arrhenius plots were obtained from which the energies and entropies of activation have been calculated (Table I). Allowing an over-all $\pm 7\%$ error in the individual rate constants at the temperature interval used (26.90°), the statistical error in E is ± 0.8 kcal mole^{-1} and in ΔS is $\pm$ 2.0 eu.[15]

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(14) (a) The Benesi–Hildebrand equation[14b] for the present case is 2a

$$\frac{[\mathbf{4}]}{A} = \frac{1}{\epsilon} + \frac{1}{K\epsilon[NaOCH_3]} \qquad (2a)$$

where A is the absorbance and ϵ is the extinction coefficient for complex **1**. (b) H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

(15) L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*, **1**, 1 (1963).

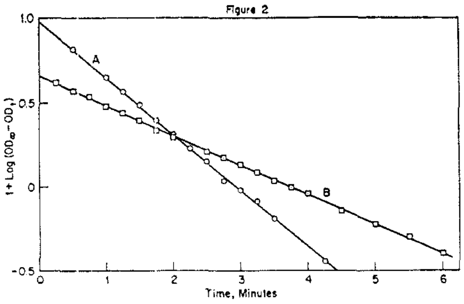

Figure 2.—Plot of 1 + log (OD ∞ − OD$_t$) against time for the attainment of equilibrium of 1 [4] = 5.12 × 10^{-5} *M*: A, [NaOCH$_3$] = 2.222 × 10^{-3} *M*, 35.00°; B, [NaOCH$_3$] = 2.93 × 10^{-3} *M*, 25.00°.

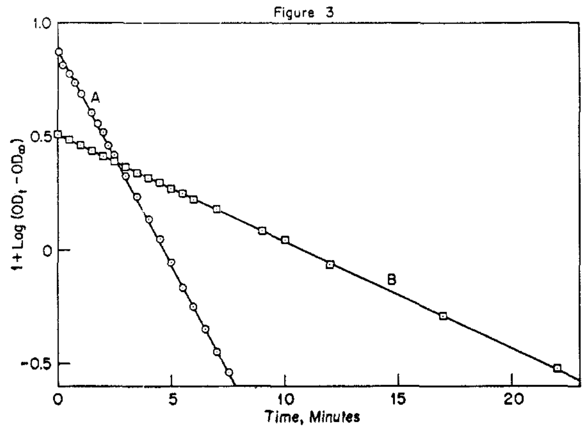

Figure 3.—Plot of 1 + log (OD$_t$ — OD ∞) against time for the decomposition of 1 in aqueous buffers at 25.00° (A, pH = 6.64; B, pH = 8.80).

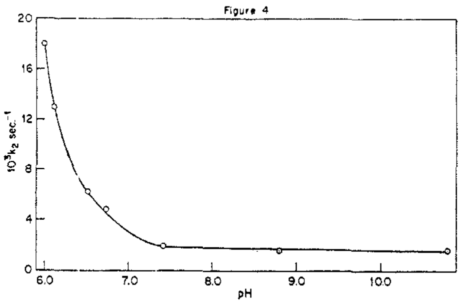

Figure 4.—pH–Rate profile for the decomposition of 1 at 25.00°.

The bright red crystalline Meisenheimer complexes of 1-alkoxy-2,4-dinitronaphthalenes are fairly stable in the solid state. They are soluble and reasonably stable in DMSO, DMF, dioxane, acetone, and acetonitrile, and in water, methanol, and ethanol but slowly decompose in these latter polar protic solvents.

The rates of decomposition of the solid 1 in methanol and in aqueous buffers at different pH values have been obtained by following the decrease in optical densities at 495 mμ in a thermostated cell compartment of a Beckman DU-2 spectrophotometer. Plots of typical runs are given in Figure 3, and the data are given in Table II. Figure 4 shows the pH–rate profile for the decomposition of 1. In methanol, 4 undergoes solvolytic exchange to yield the naphthol; the half-life of this "solvolysis" is, however, 1000 hr at 35°.[11] Similarly the decomposition of 1 at high pH ultimately gives the naphthol. The naphthol does not, however, absorb at 495 mμ; thus the observed rate constant corresponds to k_2.

Table II

Decomposition of the Methoxyl Complex of 1-Methoxyl-2,4-dinitronaphthalene in Methanol and in Water at 25.00°

pH[a]	10^3k_2, sec^{-1}	$10^{-4}k_2^{H^+}$, l. mol^{-1} sec^{-1} [b]
Abs MeOH	4.16	
5.97	18.0	1.52
6.11	13.0	1.46
6.21	11.0	1.48
6.52	6.40	1.53
6.64	4.98	1.43
7.42	1.97	
8.80[c]	1.76	
10.85[d]	1.76	

[a] 0.01 KH$_2$PO$_4$ buffer, except where stated otherwise. [b] $k_2^{H^+}$ = (k_2 (measured) − $k_2°$)/[H$^+$], where $k_2°$ = 1.76 × 10^{-3} sec^{-1}. [c] 0.01 *M* KHC$_8$H$_4$O$_4$ buffer. [d] 0.01 *M* K$_2$HPO$_4$ buffer.

The infrared absorption data for the complexes and the parent ethers are given in Table III, and the pmr parameters for the same compounds are given in Table IV.

Discussion

The methoxyl Meisenheimer complex (1) of 1-methoxy-2,4-dinitronaphthalene forms very readily upon mixing a dilute solution (5 × 10^{-5} *M*) of the ether (4) with a 15-fold excess of sodium methoxide in methanol. The absorption maximum at 495 mμ is attributed to the formation of 1 since the absorption maximum of the isolated solid 1 in methanol occurs at this wavelength. The increased absorption relative to 4 at 350 mμ with increasing methoxide ion concentration is possibly due to the formation of another species, the formation of which is favored by high methoxide ion concentration (see Table I). A similar situation exists with the interaction between methoxide ion and 2,4-dinitroanisole.[5] However, the methoxyl complex of 2,4-dinitroanisole forms considerably less readily than its naphthalene analog (1). Indeed, at the methoxide ion concentrations used it was found necessary to use polar cosolvents to enhance the stability of the methoxyl-2,4-dinitroanisole complex.[5] The absorption maxima due to 4 plus a second complex have shifted to a longer wavelength in relation to the 2,4-dinitroanisole complex (from 316 to 350 mμ). Similar bathochromatic shifts were observed in the 2,4-dinitroanisole–6X complexes as the electron-withdrawing power of X was increased.[16] This observation is in accord with the fact that an additional phenyl ring in the naphthalene system increases the electronegativity of the C-1 carbon atom.

The stability of 1 is also evident from its equilibrium constant which is approximately 250 times greater than that for its benzene analog. The equilibrium constant for the formation of the methoxyl Meisenheimer complex of 2,4,6-trinitroanisole is 7700,[17] while that for 1 is 230 at 25.0°. The magnitude of the equilibrium constant for the formation of 1 facilitated calculation of the rate constants for the formation and decomposition of 1 at the three different temperatures (Table I). The validity of the assumptions used in

[16] R. J. Pollitt and B. C. Saunders, *J. Chem. Soc.*, 1132 (1964).
[17] V. Gold and C. H. Rochester, *ibid.*, 1687 (1964).

TABLE III

INFRARED SPECTRA[a] OF 1-METHOXY-2,4-DINITRONAPHTHALENE, 1-ETHOXY-2,4-DINITRONAPHTHALENE, AND THEIR MEISENHEIMER COMPLEXES

1-Methoxy-2,4-dinitronaphthalene (4)	1-Ethoxy-2,4-dinitronaphthalene (5)	Potassium methoxide complex of 1-methoxy-2,4-dinitronaphthalene (1)	Potassium ethoxide complex of 1-methoxy-2,4-dinitronaphthalene (2a)	Potassium methoxide complex of 1-ethoxy-2,4-dinitronaphthalene (2b)	Potassium ethoxide complex of 1-ethoxy-2,4-dinitronaphthalene (3)
1581 vs, sh	1583 vs, sh	1581 vs, sh	1581 vs, sh	1580 vs, sh	1580 vs, sh
1545 w	1545 w	1550 s, sh	1550 s, sh	1550 s, sh	1545 s, b
1525 m, sh	1526 m, sh				
1515 m, sh	1516 m, sh	1512 w	1512 w	1511 w	1510 w
1493 m, sh	1496 w	1493 m, sh	1493 m, sh	1494 m, sh	1503 s
		1451 w	1451 w	1451 w	1454 w
		1448 vw	1448 vw	1448 vw	1450 w
1415 s	1416 m	1411 s	1421 m	1419 m	1419 m
	1400 w				
1345 s	1335 s, b	1358 m	1358 m	1357 m	1360 s
		1325 m	1326 m	1326 m	1329 m
		1287 w			1297 w
1270 m	1262 s	1263 s	1263 s	1262 s	1265 s
1243 m	1230 w	1230 m	1230 m	1320 m	1230 m
1212 w	1220 w	1218 m	1210 m	1210 m	
	1200 vw				1190 m
1172 m	1155 m	1172 m			
		1122 s, b	1135 s, b	1135 s, b	1140 s, b
1100 s	1092 s	1090 m	1105 m, b	1105 m, b	1100 m, b
1048 w	1038 w	1058 m, b	1050 m, b	1049 m, b	1050 m
		1027 m			
1000 m	1015 s		1005 w	1005 w	1005 m
962 s	968 vw	957 w	956 w	956 w	959 m
		941 m	941 m		942 m
919 m	923 m	923 s	923 s	923 s	923 s
905 s	905 s				
		885 w			
	869 s	872 s			875 w
837 s	830 s	815 s	817 s	818 s	818 s, sh
805 s	793 s	796 m	792 m	791 m	790 m
789 m	789 m				
772 vs	773 s	770 s			
753 vs	760 s	762 m	762 s	761 s	762 s, sh
743 w		738 m	735 m	733 m	736 m
723 m	724 m	703 s	713 s	713 s	715 s
682 m	684 m	660 s	660 s, b	660 s, b	663 s

[a] Frequencies (cm^{-1}) and intensities of observed bands (vs = very strong, s = strong, m = medium, w = weak, vw = very weak s = shoulder on neighboring band, b = broad).

this treatment (see Results) is amply verified by the excellent agreement between the k_2 values calculated from the attainment of the equilibrium for **1** using K (Table I) and those determined directly at 25.00° (Table II).

The stability of **1** is further demonstrated by its observable rate of decomposition in water in the 5.97–10.85 pH region (Table II and Figure 4). The decomposition is catalyzed very strongly by acids. Decreasing the pH from 8.00 to 5.97 results in a tenfold increase in the decomposition rate. Similar decomposition studies on the 1,1-dialkoxypicrylic Meisenheimer complexes in aqueous buffer solutions have been reported.[18] The rate constant for the spontaneous decomposition of **1**, $k_2°$, at 25.00° is six times greater than that for the methoxyl complex of 2,4,6-trinitroanisole. The second-order rate constant for the acid-catalyzed decomposition of the methoxyl 2,4,6-trinitroanisole complex at 25.00° is 1.2×10^4 l. mol^{-1} sec^{-1}. The corresponding value for the decomposition of **1** is 1.5×10^4 l. mol^{-1} sec^{-1} (Table II), indicating that the acid catalysis is more pronounced for the decomposition of **1** than for the picrylic complex.

The energies of activation for the formation and decomposition of **1** (Table I) are best illustrated by potential energy diagrams. For purposes of comparison, corresponding diagrams for the 2,4-dinitroanisole[19] and 2,4,6-trinitroanisole[19,20] complexes are also included (Figure 5).

It can be seen readily that the stabilities of these Meisenheimer complexes are in the order 2,4-dinitroanisole < **4** < 2,4,6-trinitroanisole. It was suggested that an activation energy of 12–18 kcal mol^{-1} (E_2 in Figure 5) is needed in order to isolate an adduct formed in a nucleophilic aromatic substitution reaction.[21] This requirement is clearly met even for the 2,4-dinitroanisole complex, whose isolation we reported previously.[5] The fact that the saddle of the potential energy diagram for the formation of **1** lies below that of the initial state (**4**) suggests that in symmetrical methoxyl exchange reactions between methoxide ion

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(18) J. Murto and J. Vainionpää, *Suomen Kemistilehti*, **B39**, 133 (1966).

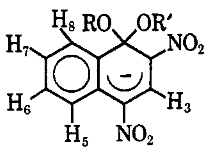
(19) J. H. Fendler, *J. Amer. Chem. Soc.*, **88**, 1237 (1966).

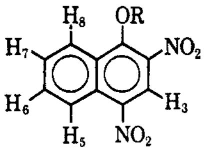
(20) J. Murto and E. Kohrakha, *Soumen Kemistilehti*, **B39**, 128 (1966).

(21) R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 294 (1960).

TABLE IV

PMR SPECTRA OF MEISENHEIMER COMPLEXES AND PARENT 2,4-DINITRONAPHTHYL ETHERS[a]


1-3


4, 5

Compd	Source[b]	R	R′	τ 3	τ 5	τ 8	τ 6,7	τ OCH_3	τ OCH_2	τ CCH_3	Solvent[c]	J_{56}	J_{57}	J_{68}	J_{78}
1	A	CH_3	CH_3	0.67	2.25	1.24	2.70	7.22			7.45 (2.6)	7.4	2.7	2.2	7.8
1	B	CH_3	CH_3	0.67	2.25	1.24	2.70	7.20			6.40 (0.98)	7.6	2.7	2.2	7.8
2a	A	CH_3	CH_2CH_3	0.77	2.23	1.25	2.73	7.29	7.09	9.04	None	7.5	2.7	2.3	7.9
2a	B	CH_3	CH_2CH_3	0.72	2.23	1.23	2.73	7.29	7.03	9.04	6.44 (0.075)	7.4	2.7	2.3	7.9
2b	B	CH_3	CH_2CH_3	0.75	2.22	1.23	2.70	7.24	7.09	9.02	6.44 (0.03)	7.4	2.7	2.3	7.9
3	A	CH_2CH_3	CH_2CH_3	0.79	2.23	1.27	2.72		7.17	9.04	7.44 (0.59)	7.4	2.7	2.5	7.8
3	B	CH_2CH_3	CH_2CH_3	0.77	2.23	1.27	2.73		7.15	9.04	6.44 (0.13)	7.4	2.7	2.4	7.9
Multiplicity				1	2 × 2	2 × 2	m	1	m	3					
4		CH_3		1.34	1.68		2.17	5.87							
5		CH_2CH_3		1.22	1.59		2.06		5.67	8.49					
Multiplicity				1	m		m	1	4	3					

[a] All spectra are recorded in DMSO-d_6 at 25°. Chemical shifts are given on the τ scale in parts per million relative to internal TMS; coupling constants are given in Hz. For details, see Experimental Section. [b] Solvent used in preparation: A = DMSO; B = dioxane. [c] Solvent of crystallization was as in source. Number of moles of solvent per mole of complex is indicated in parentheses; integrals for DMSO include solvent DMSO-d_5.

FIGURE 5

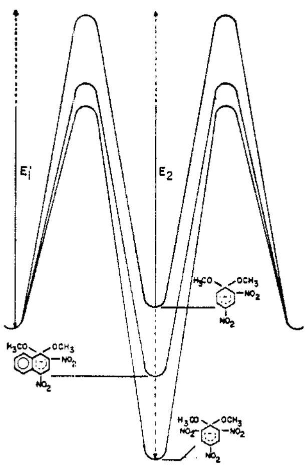


Figure 5.—Potential energy diagrams for the formation and decomposition of dialkoxy Meisenheimer complexes.

and **4**, the decomposition of **1** should be the rate-determining step. This is indeed the case, as has been verified by experimental data.[11] Similarly the rate-determining step for the methoxyl exchange reaction between methoxide ion and 2,4,6-trinitroanisole is the decomposition of the intermediate complex.[19]

The formation of complex **1** from **4** and methoxide ion results in an increase in the order of the system. This is reflected by the negative entropy of activation ($\Delta S_1^{\ddagger}$ in Table I). Using a rate constant of 4.0 l. mol^{-1} sec^{-1} [17] and an energy of activation of 13 kcal mol^{-1} [19] for the formation of the methoxyl 2,4,6-trinitroanisole complex, we calculate the entropy of activation for this reaction to be −14 eu. Similarly comparing values from the literature,[17,19] we obtain −11 eu for $\Delta S_2^{\ddagger}$ for the decomposition of the methyl picrate complex. However, it is difficult to compare $\Delta S_1^{\ddagger}$ with $\Delta S_2^{\ddagger}$ since their standard states are different. Nevertheless, their magnitude and direction are consistent within the series of compounds studied so far. Furthermore, it appears that the rates of symmetrical methoxyl exchange reactions, and hence the stabilities of the Meisenheimer complexes in this series, are dependent to a larger extent on the respective enthalpies rather than on the entropies of activation. This is in good agreement with the thermodynamic parameters of other nucleophilic aromatic substitutions.[22] Using electron affinities and bond and solvation energies, Miller calculated the energy levels of the initial, transition, and intermediate states of numerous nucleophilic aromatic substitutions.[22,23] From this data he estimated the energies and entropies of activation for these reactions and found that the calculated and experimentally obtained values agreed well and that the entropies of activation varied little in comparison with changes in the activation energies.[22]

Furthermore, using this treatment Miller estimated the thermodynamic parameters for the formation and decomposition of **1** and found them to be in excellent agreement with the experimental values in Table I.[24]

We continue to use infrared and proton magnetic resonance spectroscopic techniques to confirm the postulated structures of intermediates **1-3**. The infrared spectra of charge transfer complexes closely resemble those of their parent ethers with the addition of the internal vibration frequencies of the added alkoxyl groups.[25] The presence of the additional ketal

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(22) D. L. Hill, K. C. Ho, and J. Miller, *J. Chem. Soc., Sect. B*, 299 (1966).

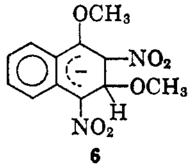
(23) J. Miller, *J. Amer. Chem. Soc.*, **85**, 1628 (1963).

(24) J. Miller, private communication, 1967.

(25) (a) R. A. Friedel, *J. Phys. Chem.*, **62**, 1341 (1959); (b) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

bands[26] at 1126–1058 cm^{-1} (Table III) are consistent with the proposed covalent structure of the complexes. In our previous paper[5] we reported the isolation of complexes from the reaction of 2,4-dinitroanisole and potassium ethoxide and, separately, from 2,4-dinitrophenetole and potassium methoxide and showed them to be identical by infrared and pmr spectroscopy. We have now prepared the 1-methoxy-1-ethoxy-2,4-dinitronaphthalene complexes (**2a** and **2b**) by these two routes and found their spectra (Tables III and IV) to be identical.

The pmr parameters observed for complexes **1**–**3** and the parent ethers **4** and **5** are given in Table IV; the spectra of a representative complex parent ether pair (**3** and **5**) are given in Figure 6. The spectra are completely in accord with the postulated structures (1,1 complexes) and eliminate alternate formulations, *i.e.*, those involving attack of alkoxide ion at positions other than C-1 of **4** or **5**. For example, formation of the 3 complex (**6**) would require methoxyl nonequivalence and a marked upfield shift for H-3,[4] observations clearly inconsistent with the experimental observations. Only 1,1 complexes could account for the observation of alkoxyl equivalence for **1** and **3**, single methoxyl and ethoxyl resonances for **2** and the five aromatic resonances for **1**–**3**. The spectra of the various complexes prepared by different routes, *e.g.*, **1** from both DMSO and dioxane solutions and **2** from both **4** and **5**, were identical within experimental error, with the exception of the peaks due to solvent of crystallization; satisfactory integrated intensities were obtained for all resonances. The only previous report of pmr data for naphthalene Meisenheimer complexes is that of Foster, *et al.*,[9] who have reported aromatic proton chemical shift data for complex **1** prepared by the *in situ* reaction of methoxide ion and **4**. The chemical shifts reported for H-3 and H-5 are essentially identical with those observed in this study; Foster, *et al.*, did not, however, observe separation of the H-8 resonance from the H-6, H-7 multiplet.



6

The pmr criteria for the structure of Meisenheimer complexes have been summarized previously[4,5] and need not be reiterated here in detail. In addition to the structural support provided by the gross appearance of the spectra as cited above, alkoxyl and aromatic proton chemical shifts provide more detailed confirmation of structure. It has been shown that the transition from the sp^2 hybrid C-1 of the parent ethers to the sp^3 hybrid C-1 of the 1,1 complexes in the di- and trinitrobenzene series[3-5,9,27] results in an upfield shift for alkoxyl proton resonances: methoxyl complexes, $\Delta\delta$ 1.20 ppm; ethoxyl complexes, $\Delta\delta_{OCH_2}$ 1.21–1.33 ppm, $\Delta\delta_{C-CH_3}$ 0.33–0.37 ppm.[1] Closely comparable upfield alkoxyl shifts are observed for the complexes **1**–**3**: $\Delta\delta_{OCH_3}$ 1.33–1.42 ppm, $\Delta\delta_{OCH_2}$ 1.36–1.50 ppm, $\Delta\delta_{C-CH_3}$ 0.53–0.55 ppm. As required by the postulated structures, the methoxyl resonances of **1** and **2** are singlets. However, the methylene resonance of the diethoxy complex **3** was considerably more complex than the expected quartet; a 50-Hz sweep width spectrum of this region showed thirteen resolved transitions downfield from the DMSO-d_5 resonance. The complexity of this multiplet is greater than would be expected if the two ethoxyl groups were in different magnetic environments as in **6** (two quartets would be anticipated) and is most probably due to methylene proton nonequivalence resulting from a restriction of rotation about the carbon–oxygen bonds of the ethoxyl groups. If such a nonequivalence were involved, the methylene resonance would comprise the AB portion of an ABX_3 system and a total of 16 transitions should be observable; a first-order analysis of this multiplet supported this postulation. The A portion of the resonance (two quartets with J_{AB} = 9.4 and J_{AX} = 7.5 Hz and τ_A 6.97 ppm) was cleanly resolved. Five transitions of the B portion were observed from which J_{BX} = 7.3 Hz could be obtained and, using the value of J_{AB} from the A portion, τ_B could be estimated as 7.17 ppm. This assignment was confirmed by a double-resonance experiment at 100 MHz; irradiation of the methyl triplet at τ 9.04 ppm resulted in collapse of the methylene resonance to an AB quartet (the most upfield transition of this quartet was partially obscured by the DMSO-d_5 peak.) A value of J_{AB} = 9.4 Hz was obtained from the decoupled spectrum. Kaplan and Roberts have reported a geminal coupling of −9.3 Hz for the methylene protons of diethyl acetal.[28] The methyl triplet of **3** showed no further splitting. A similar methylene nonequivalence was apparent in the spectra of the mixed complex **2**, but could not be fully resolved because of overlap with the methoxyl singlet.

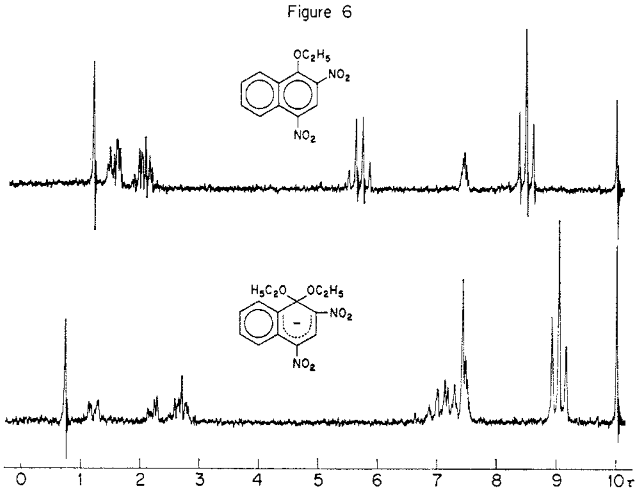


Figure 6.—Proton magnetic resonance spectra of 1-ethoxy-2-4-dinitronaphthalene (**5**) and its ethoxy complex (**3a**) in DMSO-d_6.

It has been shown previously that the aromatic protons of Meisenheimer complexes are relatively strongly shielded as compared with the corresponding protons of the parent ethers.[4,5,9,27] The magnitude of this upfield shift ($\Delta\delta$) has been shown to be positionally dependent for the 1,1 complexes (**7**) of 2,4-dinitrophenyl ethers,[5] reflecting relative charge densities at the various positions, *i.e.*, H-3, 0.04–0.07; H-5, 1.26–1.40; H-6, 2.50–2.57 ppm. The greater de-

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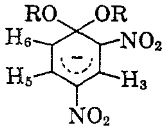
(26) E. D. Bergmann and S. Pinchas, *Rec. Trav. Chim.*, **71**, 161 (1952).

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

(28) F. K. Kaplan and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 4666 (1961); P. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci.*, **47**, 49 (1961).

shielding of H-6 would be expected since conventional canonical structures for the ions would place the maximum charge density at H-2, -4, and 6. An interpretation of aromatic proton chemical shifts in naphthalene complexes **1**–**3** is somewhat less straightforward. Among other factors, the interpretation is complicated by the fact that the four aromatic protons of the unsubstituted ring of the naphthalene complexes comprise an ABCD system,[29] while the previously examined complexes (**7**)[5] contain a more readily interpretable ABX system.



7

The aromatic proton resonances of 1-ethoxy-2,4-dinitronaphthalene (**5**) consist of a one-proton singlet (H-3) at τ 1.22 and two pseudo-symmetric two-proton multiplets centered at τ 1.59 and 2.06 ppm (Table IV and Figure 6). The chemical shift observed for H-3 is quite similar to those observed for the comparable resonances in other 2,4-dinitro-substituted naphthalenes.[30] The downfield (τ 1.59 ppm) multiplet is assigned to H-5 and H-8, while the upfield multiplet is assigned to H-6 and H-7. The symmetry of these multiplets indicates that the chemical shifts of the protons comprising the multiplets are almost identical, a conclusion confirmed by the observation that the structure of the multiplets was unchanged at 100 MHz. Similar ABCD spectra have been observed for indole and benzofuran[29b] and for 1-methyl-4-nitronaphthalene.[31] The low field assignment for H-5 and H-8 is based on the well-established deshielding effect of *peri* substituents in naphthalene systems;[30–32] the chemical shifts for all four protons are quite closely comparable with those reported for model structures.[30,32] The assignment was confirmed by a double resonance experiment at 100 MHz; irradiation of the upfield multiplet caused collapse of the 1.59-ppm multiplet to two partially resolved singlets at τ 1.53 and 1.60 ppm. Essentially identical spectra in terms of multiplicity structure were observed for the corresponding methyl ether **4** and for the ABCD system of 1-methoxy-4-nitronaphthalene. No separations of these resonances were achieved by solvent changes (DMSO-d_6 acetone, trifluoroacetic acid); the line separations and relative intensities of the transitions of the multiplets were essentially unaffected by these changes.[33]

The appearance of the aromatic resonances of the diethoxy complex **3** is markedly altered in terms of both multiplicity and chemical shifts from that of ether **5**. The H-3 resonance remains a singlet, but is shifted downfield ($\Delta\delta$ −0.45) to 0.77 ppm; H-8 also shows a downfield shift ($\Delta\delta$ −0.32) to 1.27 ppm. However, the H-5, H-6, and H-7 resonances show the expected upfield shifts: H-5, τ 2.23 ($\Delta\delta$ 0.64); H-6 and H-7, 2.73 ppm ($\Delta\delta$ 0.66). As cited previously, all three ring protons of the benzene complexes (**7**) show upfield shifts and of considerably larger magnitudes than the maxima observed for **3**; smaller shifts might be anticipated for **3** since the negative charge is delocalized over more atoms than in the case of **7**. These shifts indicate a significant decrease in electron density at the 3 and 8 positions of the complex relative to the parent ether with an increase in electron density at the 5, 6, and 7 positions. On the basis of canonical contributions, the increase at H-5 and H-7 is expected, although the similarity in increase for H-6 and H-7 and the actual decrease in electron density at H-3 and H-8 is not readily explicable. The deshielding at H-8 is probably due in part to the change in hybridization at C-1. In the starting ether, H-8 undergoes *peri* shielding as a result of the anisotropic effect of the C-1 ethoxyl group, whereas in the complex **3**, two ethoxyl groups are present at C-1 and it might be expected that the combined anisotropic effect of these two carbon–oxygen bonds might be sufficient to overcompensate for any shielding due to increased charge density at H-8. An examination of models of **3** and **5** indicates the changes in geometry at C-1 (vectors from center of carbon–oxygen bond to H-8) should produce an increase in anisotropic deshielding for H-8. Recently, HMO calculations of π-electron densities in **4** and the symmetrical complex **1** have been reported.[34] These calculations indicate that in the formation of **1** from **4** there is a slight increase in electron density in the unsubstituted ring, but that most of the accumulation of negative charge is in the nitro groups; pertinent to the observations above, however, is the conclusion that electron density should decrease to a marked extent in the substituted ring, *i.e.*, at H-3. In this regard, the experimentally observed $\Delta\delta$ values are in qualitative accord with the results of HMO calculations. Similar changes are observed in the aromatic resonances for complexes **1** and **2**.

As indicated above, the formation of the complex **3** from ether **5** results in an increase in the chemical-shift difference of H-5 and H-8 so that both resonances are the expected first-order multiplets (doublets of doublets); *i.e.*, H-5 is coupled to both H-6 and H-7. The following coupling constants are observed: J_{56} = 7.4, J_{57} = 2.7, J_{78} = 7.8, and J_{68} = 2.5 Hz. The magnitudes of these coupling constants are comparable with those observed in related naphthalene systems.[30a,35] The singlet structure of the H-3 resonance of **5** is unchanged in the complex; the same symmetry is observed for the H-6, H-7 multiplet in both the starting ether and the complex. The aromatic resonances of complexes **1** and **2** are essentially identical in character.

In order to establish that the 1,1 complexes (**1**–**3**) were the initially formed species in the reaction of alkoxide ions with **4** and **5** and not the result of rearrangement of some less stable species, as in the case of the picryl complexes,[3,4] the *in situ* generation of **1** was examined. Treatment of a 1 *M* solution of **4** in DMSO-d_6 with 1 equiv of potassium methoxide in methanol led to the immediate development of the

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[29] (a) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964); (b) P. J. Black and M. L. Heffernan, *Australian J. Chem.*, **18**, 353 (1965).

[30] (a) P. R. Wells, *J. Chem. Soc.*, 1967 (1963); (b) F. Bell and K. R. Buck, *ibid., Sect. C*, 904 (1966).

[31] P. R. Wells and P. G. E. Alcorn, *Australian J. Chem.*, **16**, 1108 (1963).

[32] A. Zweig, J. E. Lancaster, and M. T. Neglia, *Tetrahedron*, **23**, 2577 (1967).

[33] The low-field portion of the AB signal for H-2 and H-3 of 1-methoxy-4-nitronaphthalene overlaps the H-5, H-8 signal; the chemical shift of this doublet does show a solvent dependence.

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

[35] J.-C. Richer and C. Lamarre, *Can. J. Chem.*, **43**, 715 (1965).

spectrum of 1. In a similar experiment, the potassium methoxide solution was added dropwise with the spectrum recorded after each addition of methoxide. The development of peaks ascribable to 1 and the disappearance of those due to 4 were observed; after the addition of 1 equiv of base, only the peaks due to the complex were observed. In neither experiment were peaks ascribable to any third species observed; the initial observations of the spectra of these solutions were made within 20 sec of the time of addition of methoxide ion. No changes were observed in the spectra of solutions of complexes 1–3 which had been allowed to stand at room temperature for extended periods of time. This solution behavior is one manifestation of the greater stability of these complexes as compared to those of the 2,4-dinitrophenyl ethers which undergo a relatively rapid rearrangement to the isomeric 1,2 complexes.[5,36] No exchange of ring protons with solvent deuterons (from DMSO-d_6) was observed for solutions of 1–3, but, in the presence of excess base, exchange is rapid and complete. Addition of a large excess of potassium methoxide in methanol to a solution of 4 in DMSO-d_6 led to the immediate development of the spectrum of 1, but the intensities of the aromatic resonances of 1 underwent a rapid decrease and after 3–5 min all of the aromatic protons appeared to have exchanged with a concomitant increase in the intensity of the DMSO-d_5 peak.

Registry No.—4, 13772-69-5; 5, 15352-94-0.

Acknowledgment.—We are indebted to Drs. S. Castellano and J. J. Burke for helpful discussions and to Dr. B. D. Martin for assistance in the determination of pmr spectra. This work was supported, in part, by the U. S. Atomic Energy Commission and instrumentation provided by a grant (FR 00292) from the National Institutes of Health was used.

(36) E. J. Fendler, W. E. Byrne, J. H. Fendler, and C. E. Griffin, unpublished results.

Nucleophilic Addition–Elimination Reactions of 1,2-Di-*p*-toluenesulfonylethene[1]

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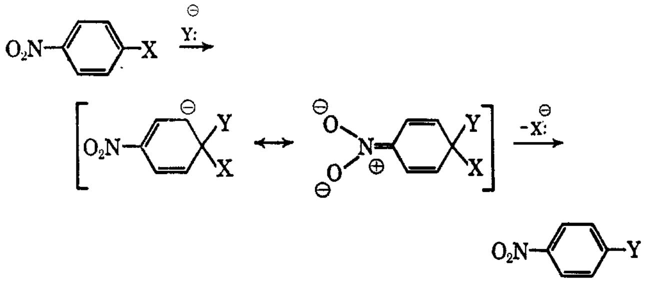
Received September 20, 1967

The addition–elimination reactions of *cis*- and *trans*-1,2-di-*p*-toluenesulfonylethene (1 and 2 in text) with azide, methoxide, and thiophenoxide ions occur with a high degree of retention of configuration of the substrate. Trimethyl phosphite reacts with both 1 and 2 to yield dimethyl *trans*-2-*p*-toluenesulfonylethenephosphonate and methyl *p*-toluenesulfinate. With cyclohexylamine, the *trans*-addition–elimination product is obtained with both 1 and 2. Ethylenimine gives an adduct with 1 and 2 plus the expected addition–elimination product. Phenylmagnesium bromide reacts with 1 to give *trans*-β-styryl *p*-tolyl sulfone. *cis*-1,2-Di-*p*-toluenesulfonylethene reacts with diazomethane to give 3(5)-*p*-toluenesulfonylpyrazole. Sodium azide reacts with 1 in dimethyl sulfoxide to give 4(5)-*p*-toluenesulfonyltriazole which has been shown to arise from the cyclization of *trans*-2-azidovinyl *p*-tolyl sulfone under basic conditions.

Although nucleophilic substitution reactions at aryl carbon atoms are generally difficult, they occur readily when electron-withdrawing groups are substituted *ortho* or *para* to the leaving group, owing to the stabilization of the transition state (or in some cases, an intermediate).[3]



Similarly, the replacement of vinylic halides is facilitated by electron-withdrawing groups β to the site of substitution. Addition–elimination reactions of this type have been reviewed by Patai and Rappaport,[4] and nucleophilic substitution reactions of β-halovinyl ketones,[5] β-chloroacrylonitrile,[6] β-halovinyl sulfones,[7] and β-halovinyl fluorides[8] are well documented in the literature. However, disulfonylethenes where the sulfone group is both the activating and leaving group have received scant attention. The only nucleophilic addition–elimination reactions so far reported are those of *cis*- and *trans*-1,2-dibenzenesulfonylethene, 1,2-di-*p*-nitrobenzenesulfonylethene, and 1-benzenesulfonyl-2-*p*-nitrobenzenesulfonylethene with cyclohexylamine and piperidine.[9] In order to extend the scope of these reactions *cis*- and *trans*-1,2-di-*p*-toluenesulfonylethene (1 and 2) were chosen for study.

Results and Discussion

Scheme I summarizes the reaction products without specifying stereochemistry. In the stereochemical studies the reactions of both 1 and 2 were carried out

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(1) This paper was presented in part at the 153rd National Meeting of the American Chemical Society, April 1967, Miami, Beach, Fla.

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