

## Intermediates in Nucleophilic Aromatic Substitution. IV.<sup>1</sup> Structures and Stabilities of Spiro Meisenheimer Complexes of Dinitro-Substituted Arenes<sup>2</sup>

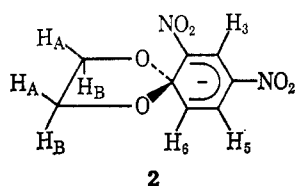
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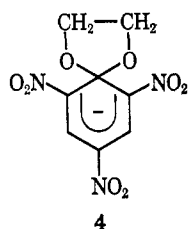
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The rate constants for the formation and decomposition of the spiro Meisenheimer complex **7** formed by the reaction of methoxide ion with 1-( $\beta$ -hydroxyethoxy)-2,4-dinitronaphthalene (**9**) in methanolic solution have been determined at 6.65, 15.00, and 25.00°, allowing a determination of  $K$ ,  $k_1$ , and  $k_2$ , and the energies and entropies of activation for the reactions. These data indicate **7** to be approximately 50% more stable than the analogous acyclic 1,1-dimethoxy-2,4-dinitronaphthalene complex (**10**) and further indicate that the driving force for the formation of **7** is much more entropy dependent than that for **10**. Complex **7** and the analogous spiro complexes of 2,4- (**2**) and 2,6-dinitrobenzene (**6**) systems have been isolated as stable crystalline materials. Studies of the ir and pmr spectra of these complexes substantiate the postulated structures. The anticipated  $A_2B_2$ -type spectra are observed for the dioxolane systems of complexes **2** and **7**.

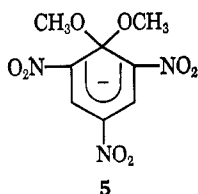
The formation of a bright red coloration ( $\lambda_{\max}$  493  $m\mu$ ) upon the addition of sodium hydroxide to an acetone solution of 1-( $\beta$ -hydroxyethoxy)-2,4-dinitrobenzene (**1**) was first reported by Gitis and Kaminskii,<sup>4</sup> who mistakenly ascribed this observation to the formation of a Janovski complex.<sup>5</sup> In a reinvestigation of this work, Pollitt and Saunders<sup>6</sup> postulated, on the basis of visible and uv spectroscopic studies, that the color was due to the formation of a spiro Meisenheimer complex (**2**). Subsequently, the analogous trinitro



Meisenheimer complex was isolated from the reaction mixtures of 1-( $\beta$ -hydroxyethoxy)-2,4,6-trinitrobenzene (**3**) and sodium<sup>7</sup> or potassium<sup>8</sup> glycolate; the ir and pmr spectra of this complex supported the postulated structure **4**.<sup>7</sup> Furthermore, the rate of decomposition

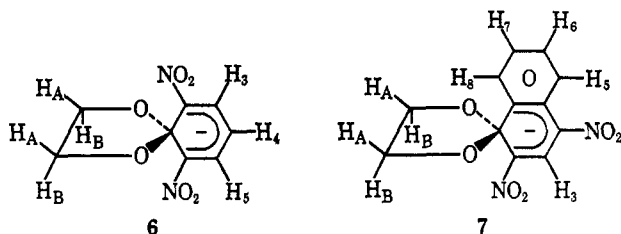


of **4** in aqueous sodium hydroxide solution was observed to be several orders of magnitude slower than that for noncyclic 1,1-dialkoxy Meisenheimer complexes (*e.g.*, **5**),<sup>8</sup> indicative of a greatly enhanced stability for the spiro complexes.



More recently, the pmr spectrum of the complex prepared by the *in situ* reaction of methoxide ion with **1** was examined.<sup>9</sup> The appearance of the low-field portion of the spectrum was consistent with the postulation of structure **2** for the product; the cyclohexadienylidene proton chemical shifts and multiplicities were similar to those observed for 1,1-dialkoxy Meisenheimer complexes of 2,4-dinitrobenzene systems.<sup>9,10</sup> However, the methylene proton equivalence was reported for **2**;<sup>9</sup> this observation is inconsistent with the postulated structure.

The spiro Meisenheimer complexes possess a number of unique features which are relevant to the chemistry, particularly the structures and stabilities, of Meisenheimer complexes and to their role in nucleophilic aromatic substitution. The indicated<sup>8</sup> greater stabilities of the spiro complexes relative to the acyclic complexes should be reflected in the magnitudes of the appropriate kinetic and thermodynamic parameters; entropy effects might be expected to be particularly important for the spiro complexes. A convincing demonstration, lacking in previous studies,<sup>7,9</sup> of the structures of the spiro complexes should provide particularly compelling evidence for the  $sp^3$  hybridization at C-1 of the cyclohexadienyl systems of Meisenheimer complexes. The existence of spiro complexes would require such a hybridization. Accordingly, in this paper we wish to report the synthesis, and isolation, and the determination of the chemical and physical properties of the crystalline complexes **2**, **6**, and **7** and present kinetic and



(5) For a recent review of the chemistry of Meisenheimer and Janovski complexes, see R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966).

(6) F. J. Pollitt and B. C. Saunders, *J. Chem. Soc.*, 1132 (1964).

(7) R. Foster, C. A. Fyfe, and J. W. Morris, *Rec. Trav. Chim.*, **84**, 516 (1965).

(8) J. Murto, *Suomen Kemistilehti*, **B39**, 255 (1965).

(1) Part III: J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, **33**, 977 (1968).

(2) Preliminary publication: C. E. Griffin, E. J. Fendler, W. E. Byrne, and J. H. Fendler, *Tetrahedron Lett.*, 4473 (1967).

(3) NASA Postdoctoral Fellow, 1966-1968.

(4) S. S. Gitis and A. Y. Kaminskii, *J. Gen. Chem. USSR*, **30**, 3771 (1960).

(9) R. Foster, C. A. Fyfe, P. H. Emslie, and M. I. Foreman, *Tetrahedron*, **23**, 227 (1967).

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

thermodynamic data on the formation and decomposition of **7** in methanol.

### Experimental Section

The solvents and reagents were prepared, purified, and standardized as previously described.<sup>10</sup> 1-( $\beta$ -Hydroxyethoxy)-2,4-dinitrobenzene (**1**) was obtained from the Hummel Chemical Co.; after recrystallization from aqueous ethanol and drying, **1** melted at 110.5–111°.

1-( $\beta$ -Hydroxyethoxy)-2,6-dinitrobenzene (**8**) was prepared by the addition of 10.95 ml (23 mmol) of freshly prepared 2.10 *M* potassium glycolate in ethylene glycol to a solution of 4.05 g (20 mmol) of 1-chloro-2,6-dinitrobenzene in 11 ml of ethylene glycol at 60°. The reaction mixture was heated at 100° for 2 hr and at 115–123° for 5 hr, cooled, and poured into 150 ml of ice water. After standing for 2 hr, the colorless crystals were removed by filtration and washed with cold water. After drying *in vacuo*, **8** melted at 53–54.5°.

*Anal.*<sup>11</sup> Calcd for C<sub>8</sub>H<sub>7</sub>N<sub>2</sub>O<sub>6</sub>: C, 42.2; H, 3.54; N, 12.3. Found: C, 42.09; H, 3.54; N, 12.40.

1-( $\beta$ -Hydroxyethoxy)-2,4-dinitronaphthalene (**9**) was prepared by the addition of 11.9 ml (25 mmol) of 2.10 *M* potassium glycolate in ethylene glycol to a solution of 5.05 g (20 mmol) of 1-chloro-2,4-dinitronaphthalene in a mixture of 10 ml of ethylene glycol and 5 ml of dioxane at 70°. The reaction mixture was heated at 100–124° for 2.5 hr, poured into 150 ml of ice water, acidified to pH 4, and filtered to remove the product. This material was dissolved in benzene and extracted with aqueous sodium carbonate to remove the solvolysis product, 2,4-dinitro-1-naphthol. The benzene solution was reduced in volume to give light yellow crystals, which were recrystallized from aqueous ethanol: mp 94.5–95.5°.

*Anal.* Calcd for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>6</sub>: C, 51.8; H, 3.63; N, 10.1. Found: C, 51.62; H, 3.70; N, 10.22.

The spiro complex (**2**) of 1-( $\beta$ -hydroxyethoxy)-2,4-dinitrobenzene was prepared by the addition of 2.13 ml (12 mmol) of 5.84 *M* potassium methoxide in methanol to a solution of 2.85 g (12.5 mmol) of **1** in 3 ml of dry dioxane. The bright red solution was flushed with dry nitrogen, cooled to –78°, and then allowed to stand for several hours at 0°. The bright red crystals which were deposited were removed by filtration under dry nitrogen and were washed with benzene and with anhydrous ether. After drying *in vacuo* over phosphorus pentoxide, the product melted at 105° dec.

*Anal.* Calcd for C<sub>8</sub>H<sub>7</sub>N<sub>2</sub>O<sub>6</sub>K: C, 36.1; H, 2.65; N, 10.5; K, 14.7. Calcd for C<sub>8</sub>H<sub>7</sub>N<sub>2</sub>O<sub>6</sub>K · 1/2 C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>: C, 38.7; H, 3.58; N, 9.03; K, 12.6. Found: C, 36.88; H, 3.55; N, 9.22; K, 12.86.

The same procedure was used to prepare complex **2** by the addition of 2.42 *M* potassium ethoxide in ethanol to a solution of **1** in dioxane and by the addition of 5.24 *M* potassium methoxide in methanol to a solution of **1** in a mixture of 3 ml of benzene and 1.3 ml of methanol. Complex **2** was also isolated by refluxing a solution of **1** in toluene with metallic sodium for 24 hr, followed by heating at 60–80° for 5 days. The dark red crystals were separated by centrifugation and washed twice with anhydrous ether.

The spiro complex (**6**) of 1-( $\beta$ -hydroxyethoxy)-2,6-dinitrobenzene was prepared by the addition of 0.505 ml (3 mmol) of 5.95 *M* potassium methoxide in methanol to a solution of 0.7125 g (3.12 mmol) of **8** in 0.70 ml of dioxane. After evaporation of some of the solvent, purple crystals formed immediately on cooling. These crystals were removed by filtration, washed with benzene and with anhydrous ether, and kept in a vacuum desiccator over phosphorus pentoxide. The purified material melted at 220–230° dec. Complex **6** was also prepared by refluxing a solution of **8** in toluene with metallic sodium.

*Anal.* Calcd for C<sub>8</sub>H<sub>7</sub>N<sub>2</sub>O<sub>6</sub>: C, 36.1; H, 2.65; N, 10.5; K, 14.7. Calcd for C<sub>8</sub>H<sub>7</sub>N<sub>2</sub>O<sub>6</sub>K · 1/2 C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>: C, 38.7; H, 3.58; N, 9.03; K, 12.6. Found: C, 37.19; H, 4.20; N, 7.70; K, 12.37.

The general procedure used for the preparation of **6** was also used to prepare the spiro complex (**7**) of 1-( $\beta$ -hydroxyethoxy)-2,4-dinitronaphthalene. Addition of 0.24 ml (1.41 mmol) of 5.95 *M* potassium methoxide in methanol to a solution of 0.40 g

(1.44 mmol) of **9** in 0.55 ml of dioxane gave **7**, which, after washing and drying, melted at 235° dec.

*Anal.* Calcd for C<sub>12</sub>H<sub>9</sub>N<sub>2</sub>O<sub>6</sub>K: C, 45.6; H, 2.87; N, 8.86; K, 12.4. Found: C, 45.20; H, 2.89; N, 12.14.

The attainment of the equilibrium for the formation of **7** from **9** in dilute methanolic sodium methoxide solutions was followed at 500 m $\mu$  in the thermostated cell compartment of a Beckman DU-2 spectrophotometer. A pair of matched 10.0-mm cells with Teflon stoppers was used. The cell compartment was equipped with a set of Beckman dual thermospeers; the temperature was measured inside the cells and was maintained within  $\pm 0.02^\circ$ . For the faster runs, an energy recording adapter (ERA) was used in conjunction with a Hewlett-Packard recorder. For these runs, rapid mixing was achieved by injecting an appropriate methanolic solution of **9** directly into the cell which contained the sodium methoxide solution. A thermostated Hamilton syringe was used, and the solution was injected through a small bore in the Teflon stopper.

All ir spectra were recorded as Nujol mulls on a Perkin-Elmer Model 221 spectrophotometer.

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*<sub>6</sub> using tetramethylsilane (TMS) as an internal reference; chemical shifts are given on the  $\tau$  scale in parts per million relative to TMS ( $\tau$  10.00 ppm) and are accurate to  $\pm 0.03$  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  $\pm 0.2$  Hz. Frequency swept double-resonance and 100-MHz experiments were carried out with a Varian Associates HA-100 spectrometer.

### Results

The absorbances of  $3.34 \times 10^{-5}$  *M* 1-( $\beta$ -hydroxyethoxy)-2,4-dinitronaphthalene (**9**) in methanol and in methanolic sodium methoxide at 360 and 500 m $\mu$  are given in Table I. The 500-m $\mu$  band, which is absent in

TABLE I  
INTERACTION OF  
1-( $\beta$ -HYDROXYETHOXY)-2,4-DINITRONAPHTHALENE  
( $3.34 \times 10^{-5}$  *M*) WITH METHANOLIC SODIUM METHOXIDE

Temp, °C	[NaOCH <sub>3</sub> ], <i>M</i>	Optical density at 360 m $\mu$ <sup>a</sup>	Optical density at 500 m $\mu$ <sup>a</sup>	<i>k</i> <sub>obsd</sub> × 10 <sup>3</sup> , sec <sup>-1</sup>	<i>k</i> <sub>1</sub> , l. mol <sup>-1</sup> sec <sup>-1</sup>	<i>k</i> <sub>2</sub> × 10 <sup>3</sup> , l. mol <sup>-1</sup> sec <sup>-1</sup>	<i>K</i> , l. mol <sup>-1</sup>
6.65	0.00238			1.23			
	0.00594			2.35			
	0.0119			4.56	0.358	0.390	918
	0.0178			6.90			
	0.0238			8.97			
15.00	0.00238			2.58			
	0.00594			4.75			
	0.0119			8.51	0.630	1.02	630
	0.0178			11.8			
25.00	0.0238			16.4			
	0.000	0.111	0.005				
	0.00238	0.182	0.201	6.48			
	0.00594	0.335	0.394	11.3			
	0.0119	0.374	0.660	18.7	1.28	3.60	356
	0.0178	0.398	0.712	26.7			
	0.0238	0.413	0.775	34.0			
	0.0534	0.425	0.900				
	2.11	0.450	0.900				

<sup>a</sup> Using a 1.00-cm cell.

the spectrum of **9** in neutral methanol, increases in intensity with increasing methoxide ion concentration; maximum intensity is reached at a sodium methoxide concentration of  $5.30 \times 10^{-2}$  *M* and the intensity re-

(11) All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

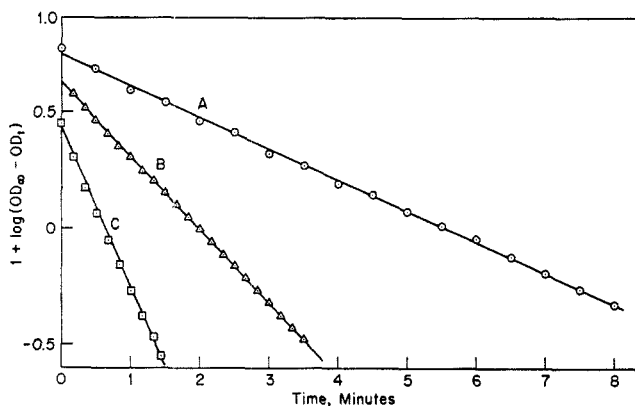
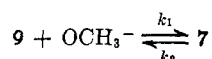


Figure 1.—Plot of  $1 + \log(OD_{\infty} - OD_t)$  vs. time for the attainment of equilibrium in the cyclization of 1-( $\beta$ -hydroxyethoxy)-2,4-dinitronaphthalene (9):  $[9] = 3.34 \times 10^{-4} M$ ; (A)  $[NaOCH_3] = 5.94 \times 10^{-3} M$ ,  $15.00^\circ$ ; (B)  $[NaOCH_3] = 5.94 \times 10^{-3} M$ ,  $25.00^\circ$ ; (C)  $[NaOCH_3] = 17.8 \times 10^{-3} M$ ,  $25.00^\circ$ .

mains constant up to 2.11  $M$ . The constancy of the absorbance over a 40-fold increase in methoxide ion concentration indicates that the equilibrium



is complete at a  $5.30 \times 10^{-2} M$  methoxide ion concentration. A linear Benesi-Hildebrand<sup>12</sup> plot was obtained at  $25.00^\circ$ , from which the extinction coefficient,  $\epsilon$ , and the equilibrium constant,  $K$ , were calculated to be, respectively, 34,500 and 420. The equilibrium constant obtained by this method is in reasonable agreement with that calculated from the rate constants  $k_1$  and  $k_2$  (see Table I). However, owing to the inherent inaccuracies in the Benesi-Hildebrand calculation, the equilibrium constants given in Table I are considered to be appreciably more accurate.

At the lower methoxide ion concentrations, it was possible to follow the rate of attainment of equilibrium by measuring the increase in absorbance at  $500 m\mu$ . A first-order relationship was observed since the concentration of 9 was a 100-fold smaller than that of the methoxide ion. Such first-order plots for typical runs are given in Figure 1. Under the experimental conditions, the observed first-order equilibrium attainment,  $k_{obsd}$ , is expressed by

$$k_{obsd} = k_1[NaOCH_3] + k_2$$

Using the above equation, plots of  $k_{obsd}$  vs. sodium methoxide concentration at 6.65, 15.00, and  $25.00^\circ$  gave good straight lines (Figure 2) whose slopes are  $k_1$  and intercepts are  $k_2$ . The experimental values of  $k_{obsd}$  at the three temperatures are given together with values for  $k_1$ ,  $k_2$ , and  $K$  in Table I. Using the values for  $k_1$  and  $k_2$  at the three different temperatures, linear Arrhenius plots were obtained from which the energies and entropies of activation have been calculated (Table II). Allowing an over-all 5% error in the individual rate constants, at the temperature interval used ( $18.35^\circ$ ), the statistical error in the activation energy is  $\pm 0.8$  kcal/mol and in the activation entropy is  $\pm 2.0$  eu.<sup>13</sup>

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

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

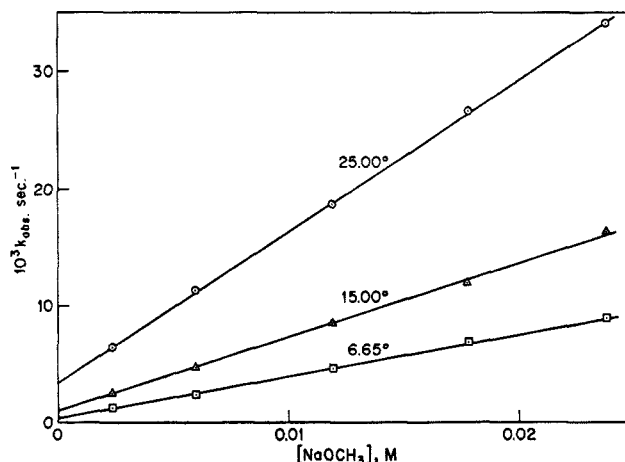
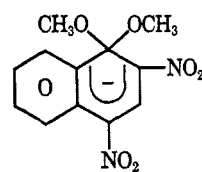


Figure 2.—Plot of  $10^3 k_{obsd}$  for the attainment of equilibrium in the cyclization of 1-( $\beta$ -hydroxyethoxy)-2,4-dinitronaphthalene (9) vs.  $NaOCH_3$  concentration at 25.00, 15.00, and  $6.65^\circ$ .

### Discussion

The order of stability and the ease of formation of spiro Meisenheimer complexes are 2,4-dinitrophenyl  $\ll$  2,4-dinitronaphthyl  $<$  2,4,6-trinitrophenyl. This trend parallels, of course, the electron deficiency of the C-1 carbon atom and the stability of the corresponding noncyclic Meisenheimer complexes.<sup>14</sup> The absorption maximum at the higher wavelength is attributed to the formation of 7 since the isolated solid in DMSO and DMF has an absorption maximum at the same wavelength. The absorption maxima at the lower wavelength for 2, 7, and 4 are 290, 360 and  $414 m\mu$ . Similar bathochromic shifts were observed for the 2,4-dinitrophenyl and 2,4-dinitronaphthyl Meisenheimer complexes<sup>1</sup> and for the 2,4-dinitro-6-X complexes as the electron-withdrawing power of X increased.<sup>6</sup>

The equilibrium constant for the formation of the 1,1-dimethoxy-2,4-dinitronaphthalene Meisenheimer complex (10) was such that it conveniently allowed the kinetic observation of its equilibrium attainment.<sup>1</sup>



10

By analogy, it was expected that 7 would serve as a suitable model compound for a comparison of the rates of formation and decomposition of cyclic and noncyclic Meisenheimer complexes (Table II). The rate constant for the formation of 7 at  $25.00^\circ$  is some 40% higher than the corresponding value for 10, but, more significantly, the greater stability of 7 over 10 is manifested by the values for its equilibrium constant,  $K$ , and its energies of activation,  $E_1$  and  $E_2$ . The equilibrium constant for the formation of 7 at  $25.00^\circ$  is 356 l./mol, a value 50% higher than that for the formation of 10.<sup>1</sup> The formation of 7 requires 2 kcal mol<sup>-1</sup> less; its decomposition requires 4 kcal mol<sup>-1</sup> more energy of activation than the formation and decomposition of 10. All of these results suggest that the rigidly held

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

cyclic structures 2, 4, 6, and 7 are, not unexpectedly, considerably more stable than their noncyclic analogs.

The formation of noncyclic Meisenheimer complexes is accompanied by an increase in the order of these systems, as reflected in their negative entropies of activation. It is to be expected that the rigidity and orderliness of the complexes would be enhanced in the cyclic structures. These effects should be manifested by a decrease in  $\Delta S_1^\ddagger$  and by an increase in  $\Delta S_2^\ddagger$  for 7 in comparison to 10. The experimental results amply bear out this expectation (Table II). From our pre-

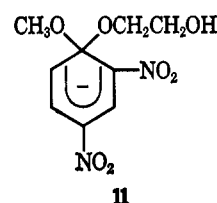
TABLE II  
KINETIC AND THERMODYNAMIC PARAMETERS FOR THE FORMATION AND DECOMPOSITION OF MEISENHEIMER COMPLEXES 7 AND 10 IN METHANOL AT 25.00°

	7	10 <sup>a</sup>
$k_1$ , l. mol <sup>-1</sup> sec <sup>-1</sup>	1.28	0.92
$k_2 \times 10^3$ , sec <sup>-1</sup>	3.60	4.0
$K$ , l. mol <sup>-1</sup>	356	230
$E_1$ , kcal mol <sup>-1</sup>	11.8 ± 0.8	13.8 ± 0.8
$\Delta S_1^\ddagger$ , eu	-20 ± 2 <sup>b,c</sup>	-17 ± 2 <sup>b,c</sup>
$E_2$ , kcal mol <sup>-1</sup>	20.0 ± 0.8	16.5 ± 0.8
$\Delta S_2^\ddagger$ , eu	-5 ± 2 <sup>b,d</sup>	-18 ± 2 <sup>b,d</sup>

<sup>a</sup> Reference 2. <sup>b</sup> Calculated at 25.00°. <sup>c</sup> Calculated by using the second-order rate constants,  $k_1$ . <sup>d</sup> Calculated by using the first-order rate constants,  $k_2$ .

vious work, it has been concluded that the stabilities of 10<sup>1</sup> and the 1,1-dimethoxy-2,4,6-trinitrobenzene complex (5)<sup>15</sup> are dependent to a larger extent on the respective enthalpies than on the entropies of activation. These observations are in good agreement with the results of Miller's calculations.<sup>16</sup> It appears that for the formation of 7 the driving force is much more entropy dependent than that for 10. Furthermore, the values of  $\Delta S_2^\ddagger$  for 7 (-5 ± 2 eu) and 10<sup>1</sup> (-18 ± 2 eu) indicate a greater solvent dependence for the decomposition of the cyclic complex 7 than for 10. The importance of solvent participation has been emphasized previously for the decomposition of 4.<sup>8</sup>

The mechanism of formation of complexes 2, 6, and 7 can best be described in terms of an initial rapid proton removal from the glycol ethers (1, 8, and 9) by the attack of methoxide ion, followed by the rate-determining internal cyclization of the resultant glycolate ions. The formation of 2 from 1 (and also 6 from 8) by the action of metallic sodium in toluene, as well as by the action of potassium ethoxide in dioxane, is not only consistent with this mechanism, but eliminates the possibility of mixed noncyclic Meisenheimer complex formation, e.g., the formation of 11 by the attack of methoxide ion on 1. The possibility of the formation



of such mixed noncyclic complexes has not been eliminated by previous studies.

The postulated structures of complexes 2, 6, and 7 are fully supported by their pmr spectra; in each case, the expected peak multiplicities and relative intensities were observed. The pmr parameters of the cyclohexadienylidene protons (H-3, H-5, and H-6) observed for a solution of the crystalline complex 2 in DMSO-*d*<sub>6</sub> were quite similar to those previously observed for noncyclic Meisenheimer complexes of 2,4-dinitrophenyl ethers.<sup>9,10</sup> The expected AMX pattern was observed with  $\tau_3$  1.45,  $\tau_5$  3.17, and  $\tau_6$  5.70 ppm<sup>17</sup> and  $J_{3,5} = 2.7$  and  $J_{5,6} = 10.7$  Hz. These parameters are in excellent agreement with those reported previously by Foster, *et al.*,<sup>9</sup> for the *in situ* reaction product of 1 and methoxide ion. However, contrary to this earlier report,<sup>9</sup> methylene proton equivalence was not observed in the spectrum of 2. The methylene resonances were observed as a complex multiplet centered at  $\tau$  5.92 ppm (total width 30 Hz), clearly indicative of geminal proton nonequivalence. It would be anticipated that the methylene protons (H<sub>A</sub>) *cis* to the nitro group in 2 would be at low field compared with those protons (H<sub>B</sub>) *trans* to the nitro group. Eighteen of the 24 transitions expected for an A<sub>2</sub>B<sub>2</sub> spectrum were obvious in this multiplet; analysis by the procedure of Abraham<sup>18</sup> gave  $J_{cis} = 7.2$ ,  $J_{trans} = 6.1$ , and  $J_{gem} = 7.6$  Hz and  $\tau_A$  5.87 and  $\tau_B$  5.97 ppm. Computer generated and experimental spectra were in good agreement; the assignments were verified by recording the spectrum at 100 MHz. The methylene groups of 2 are part of a 1,3-dioxolane ring, and the methylene parameters observed for 2 are quite similar to those observed for the model system, 2-methyl-1,3-dioxolane<sup>18</sup> ( $J_{cis} = 7.1$ ,  $J_{trans} = 6.0$ , and  $J_{gem} = 7.5$  Hz). These observations fully substantiate the postulated structure of 2.

The spectra of samples of 2 prepared by different methods (reaction of 1 with potassium methoxide or ethoxide in dioxane, potassium methoxide in benzene, and metallic sodium in toluene) were all identical with the exception of resonances due to solvent (dioxane and benzene) of crystallization.

The postulated structure of the spiro complex 7 formed by the attack of methoxide ion on 9 was similarly supported by its pmr spectrum in DMSO-*d*<sub>6</sub>. For 7, H-3 appeared as a singlet at  $\tau$  0.94, H-8 as a multiplet centered at  $\tau$  1.19, and H-5-H-7 as a broad multiplet centered at  $\tau$  2.60 ppm. As anticipated, the nonequivalent methylene protons gave rise to a multiplet (centered at 5.65 ppm), but the resolution of this multiplet was not sufficient to allow an A<sub>2</sub>B<sub>2</sub> analysis. Apparently, the difference between the chemical shifts

(15) The stability of 5 was estimated by the rates of symmetrical methoxy exchange: J. H. Fendler, *J. Amer. Chem. Soc.*, **88**, 1237 (1966).

(16) D. L. Hill, K. C. Ho, and J. Miller, *J. Chem. Soc. B*, 299 (1966); J. Miller, *J. Amer. Chem. Soc.*, **85**, 1625 (1963); J. Miller, private communication to J. H. Fendler, 1967.

(17) As has been observed in previous studies,<sup>5,9,10</sup> the chemical shifts of the cyclohexadienylidene protons of Meisenheimer complexes are upfield from those of the corresponding aromatic protons of the starting aromatic substrates. This effect is also observed in a comparison of the spectra of 2 and the glycol ether 1 ( $\tau_2$  1.39,  $\tau_3$  1.62,  $\tau_4$  2.49, and  $\tau_{CH_2}$  6.23, 5.67 ppm;  $J_{35} = 3.1$  and  $J_{56} = 9.9$  Hz; spectrum recorded in DMSO-*d*<sub>6</sub>).

(18) R. J. Abraham, *J. Chem. Soc.*, 256 (1965).

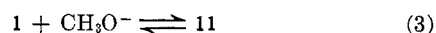
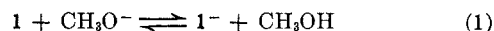
of  $H_A$  and  $H_B$  is significantly less than in the case of 2 as a result of the more nearly comparable anisotropic effects of the 2-nitro and 5,6-benzo groups in 7.<sup>19,20</sup> For the starting ether 9, the following parameters were observed:  $\tau_3$  1.19,  $\tau_{6,7}$  2.00,  $\tau_{5,8}$  1.35,  $\tau_{CH_2}$  6.12, and  $\tau_{OH}$  5.20 ppm. The absolute magnitudes of the parameters observed for 7 and 9 and the chemical-shift differences for H-3 and H-5-H-8 between 7 and 9 are quite similar to those previously observed for 1,1-dialkoxy complexes of the 2,4-dinitronaphthalenes and the parent ethers.<sup>1</sup> The assignments for 7 and 9 were made on the basis of the spectra of these noncyclic reference complexes.<sup>1</sup>

The pmr spectrum of complex 6 in DMSO- $d_6$  was also in full accord with the postulated structure. The expected  $A_2B$  pattern was observed for the cyclohexadienylidene protons with  $\tau_3$  and  $\tau_5$  2.73 and  $\tau_4$  5.22 ppm and  $J_{3,4}$  and  $J_{4,5} = 8.2$  Hz. These parameters are quite similar to those reported by Foster and Fyfe<sup>5</sup> for an *in situ* generated sample of 6. The dioxolane methylene protons of 6 were equivalent as required by the symmetry of the complex; these protons gave rise to a sharp singlet at  $\tau$  6.12 ppm. The parent ether 8 showed an  $A_2M$  aromatic spectrum ( $\tau_3$  and  $\tau_5$  1.72 and  $\tau_4$  2.48 ppm;  $J_{3,4}$  and  $J_{4,5} = 8.9$  Hz); as in the cases of 1 and 9, the methylene groups of 8 possessed different chemical shifts ( $A_2M_2$  pattern;  $\tau$  6.35, 5.89 ppm). The upfield shifts ( $\Delta\delta$ ) observed for the cyclohexadienylidene protons of 6 relative to the corresponding aromatic protons of 8 ( $\Delta\delta_4$  2.74,  $\Delta\delta_{3,5}$  1.01 ppm) are similar in magnitude to those observed in previous studies,<sup>10</sup> indicating a comparable electron density distribution in the cyclohexadienylidene system.

The salient ir absorption characteristics of complexes 2, 6, and 7 were quite similar to those observed for previously studied Meisenheimer complexes.<sup>1,10</sup> In particular, the covalent nature of the bonding at C-1 of the complexes was supported by the observation of very strong and broad ketal bands centered at 1110  $cm^{-1}$  for the benzenoid complexes 2 and 6 and at 1140  $cm^{-1}$  for the naphthalenoid complex 7. Previously studied complexes have been characterized by similar ketal bands at 1178–1176  $cm^{-1}$  (2,4-dinitrophenyl systems<sup>10</sup>) and at 1126–1058  $cm^{-1}$  (2,4-dinitronaphthyl systems<sup>1</sup>). The remaining features of the spectra are quite similar to those reported for the analogous 1,1-dialkoxy complexes.<sup>1,10,21</sup> Both asymmetric and symmetric nitro group stretching frequencies (1549–1542

and 1340–1330  $cm^{-1}$ )<sup>22</sup> and asymmetric and symmetric C–O–C stretching frequencies (1274–1230 and 1071–1050  $cm^{-1}$ )<sup>23</sup> are observable in the spectra of the complexes.

No evidence was obtained in the studies of the spectra of complexes 2, 6, and 7, regardless of the reagents employed in their preparation, for the formation of mixed noncyclic complexes, e.g., 11. The *in situ* formation of complex 2 by the gradual addition of an equivalent of potassium methoxide to a solution of 1 in DMSO- $d_6$  was followed by pmr spectroscopy; the appearance of resonances attributable to the mixed complex 11 were not observed during the formation of 2. Throughout the reaction, the observed spectrum of the reaction mixture was a superposition of the spectra of 1 and 2. On the addition of methoxide ion or other base to a nitroaryl glycol ether (e.g., methoxide ion plus 1), three basic equilibrium processes are possible: (1) proton removal from 1 to yield the glycolate ion (1<sup>-</sup>) and methanol, (2) internal cyclization of 1<sup>-</sup> to yield the spiro complex 2, and (3) direct attack by methoxide ion at C-1 of 1 to yield the noncyclic mixed complex 11.



It is apparent from the preceding studies that reaction 2 is highly favored over reaction 3 on both thermodynamic and kinetic grounds; the enhanced stability of the spiro complexes results in their essentially exclusive formation at the expense of the noncyclic mixed complexes. The enhanced stability of the spiro complexes is also shown by their failure to undergo rearrangement or deuterium exchange with solvent; solutions of the complexes in DMSO- $d_6$  do not show detectable pmr changes over a period of months. It has been shown previously that 1,1-dialkoxy complexes of 2,4-dinitrobenzenes undergo both rearrangement to 1,2 complexes and exchange of cyclohexadienylidene protons for solvent deuterium.<sup>1,10,24</sup> Also, in the presence of excess methoxide ion, 1,1-dialkoxy complexes of 2,4-dinitronaphthalene systems undergo rapid and complete exchange of ring protons with solvent (DMSO- $d_6$ ) deuterium;<sup>1</sup> no comparable reaction is observed with the more stable spiro complex 7.

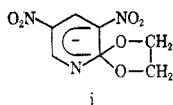
**Registry No.**—2, 12296-65-0; 6, 12296-66-1; 7, 12296-67-2; 8, 17512-03-7; 9, 17512-18-4.

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(22) R. D. Kross and V. A. Fassel, *J. Amer. Chem. Soc.*, **78**, 4225 (1956)

(23) A. Katritzky and H. A. Coats, *J. Chem. Soc.*, 2062 (1959).

(19) A similar, but more exaggerated, effect has been observed in the spectrum of the complex (i) formed by the reaction of sodium methoxide with



2-( $\beta$ -hydroxyethoxy)-3,5-dinitropyridine.<sup>20</sup> Although the lack of symmetry of i would require geminal proton nonequivalence for the dioxolane protons, a singlet was observed for these protons.

(20) C. A. Fyfe, *Tetrahedron Lett.*, 659 (1968).

(21) Copies of the ir spectra of complexes 2, 6, and 7 and the starting ethers 1, 8, and 9 are available on request.