Aromatic Nucleophilic Substitution. I. The Nucleophilic Reactivity of Sodium Phenoxide and Sodium *o*-Cresolate toward 2,4-Dinitrochlorobenzene in Methanol at 35°[1]

CHARLES L. LIOTTA AND RICHARD L. KARELITZ[2]

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received March 16, 1967

A detailed study of the reaction of sodium phenoxide with 2,4-dinitrochlorobenzene in methanol at 35° as a function of phenol concentration is reported. A linear relationship is found between the observed second-order rate coefficient and the ratio $(CH_3OH)/(PhOH)$, except at high concentrations of phenol where the rate of reaction is somewhat suppressed. This rate suppression is attributed to the existence of the biphenoxide ion, $[C_6H_5O\cdots H\cdots OC_6H_5]^-$, a species of low nucleophilicity. A similar study with the sterically hindered *o*-cresolate ion produces no rate suppression at high *o*-cresol concentrations—an observation which lends support to the existence of the biphenoxide ion.

The reaction of phenoxide ion with 2,4-dinitrochlorobenzene has been studied by several workers under a variety of conditions. Bunnett and Davis[3] investigated this reaction in 60% aqueous dioxane and originally obtained a rate coefficient of $1.20 \times 10^{-2}\ M^{-1}$ sec^{-1}. It was recognized, however, that the interaction of phenoxide ion with water would produce the following equilibrium (eq 1). Since this equilibrium

$$C_6H_5O^- + H_2O \rightleftarrows C_6H_5OH + OH^- \qquad (1)$$

would lower the concentration of phenoxide, and since the nucleophilicity of hydroxide is considerably less than that of phenoxide, the above rate coefficient was predicted to be low by about 9%. Because of this, Bunnett and Davis studied the effect of added phenol on the rate. It was found that a plot of rate coefficient *vs.* moles of phenol over moles of sodium hydroxide had a maximum which Bunnett arbitrarily designated as the nucleophilic reactivity of phenoxide ion ($1.27 \times 10^{-2}\ M^{-1}$ sec^{-1}).

Leahy, Liveris, Miller, and Parker[4] studied the reactivity of phenoxide ion toward 2,4-dinitrochlorobenzene in methanol at several temperatures. Aware of the following equilibrium (eq 2), they used a tenfold

$$C_6H_5O^- + CH_3OH \rightleftarrows C_6H_5OH + CH_3O^- \qquad (2)$$

excess of phenol and obtained a rate coefficient of $0.927 \times 10^{-3}\ M^{-1}$ sec^{-1} at 25.2°. Mattaar,[5] on the other hand, reported a rate coefficient of $7.98 \times 10^{-3}\ M^{-1}$ sec^{-1}. This ninefold difference in rate is probably due to the presence of a considerable concentration of methoxide ion in the case reported by Mattaar. It would appear that the rate coefficient obtained by Leahy, *et al.*, better represents the actual nucleophilicity of phenoxide ion. Nevertheless, the use of such a large excess of phenol could possibly change the nature of the solvent and thus change the reactivity of the phenoxide ion. We have thus undertaken a detailed study of the effect of added phenol in the reaction of sodium phenoxide with 2,4-dinitrochlorobenzene in methanol at 35°.

Experimental Section

Materials.—Phenol and *o*-cresol (Baker Analyzed Reagents) were purified by distillation through a spinning-band column containing 23 theoretical plates: phenol, bp 50° (2 mm); *o*-cresol, bp 55° (2 mm). 2,4-Dinitrochlorobenzene (Eastman) was recrystallized twice from 95% ethanol and dried in a vacuum dessicator: mp 51.5–52.5° (observed); 52° (reported[3]). The recrystallized material was stored in a brown screw-cap bottle while not in use. Commercial methanol was purified by distillation from magnesium turnings. In all cases, the phenolic compounds and the methanol were distilled immediately prior to use in a kinetic run. A solution of sodium methoxide in methanol was prepared by treating freshly cut sodium metal (which had been washed with methanol) with freshly distilled absolute methanol. The resulting solution was stored in a glass container fitted with a rubber septum. Standard perchloric acid solutions were prepared by common procedures.

Rate Measurements.—A methanolic solution of 2,4-dinitrochlorobenzene of known concentration was prepared in a 50-ml volumetric flask suspended in a constant-temperature bath at 35 ± 0.02°, as recorded by an NBS calibrated thermometer. To a known weight of phenolic compound, dissolved in methanol, was added 7 ml of 0.745 *M* (±0.015) sodium methoxide stock solution. The resulting solution was brought up to 50 ml in a volumetric flask at 35°. The flasks and their contents were allowed to equilibrate for at least 30 min after which time 25 ml of each solution was placed in a 50-ml volumetric flask suspended in the constant-temperature bath. The zero time for the reaction was taken at that point when one-half of the second solution had been added. The reaction flask was removed from the bath, quickly shaken, and returned. There was no apparent volume change in the mixing of the two solutions. Five-milliliter samples (six–seven per run) were withdrawn and discharged into either an ice–water mixture or dilute perchloric acid solution. Both methods gave identical results. The time was recorded at the point when the pipet was half-emptied into the quenching medium. The extent of reaction was determined by titration of total base with standard perchloric acid solution. The titrations were followed potentiometrically using a calomel electrode *vs.* a glass electrode cell. The concentration of methanol in a particular kinetic run was determined as follows: 9 ml of the 2,4-dinitrochlorobenzene solution and 9 ml of the sodium phenoxide solution were pipetted into a tared erlenmeyer flask and weighed; from the known weights of the 2,4-dinitrochlorobenzene and phenol that were used to make the solutions, the number of grams of methanol present in 18 ml of the mixed solution was determined and from this the molarity of methanol was calculated.

In all runs the initial concentration of 2,4-dinitrochlorobenzene was always less than that of the nucleophilic reagent (see Tables I and II). Using this procedure, the determination of the difference in base concentration at time zero and at time infinity acted as a check on the initial concentration of 2,4-dinitrochlorobenzene. Rate coefficients were calculated from the slope of the plot of log $(a - x)/(b - x)$ *vs.* time, the slope being equal to $k(a - b)/2.303$. The plots were linear without regular curvature and in most cases covered up to 50% reaction. Slopes were determined by the method of least squares. Duplicate runs agreed with each other to within 3%. The data and plot from a sample run are shown in Table III and Figure 1, respectively.

---

[1] Presented at the 153rd National Meeting of the American Chemical Society, April 1967, Miami, Fla.

[2] Recipient of an NDEA Fellowship.

[3] J. F. Bunnett and G. T. Davis, *J. Am. Chem. Soc.*, **76**, 3011 (1954); **80**, 4337 (1958).

[4] G. D. Leahy, M. Liveris, J. Miller, and A. J. Parker, *Australian J. Chem.*, 382 (1956).

[5] T. J. F. Mattaar [*Rec. Trav. Chim.*, **41**, 103 (1922)] reported $7.15 \times 10^{-3}\ M^{-1}$ sec^{-1}; $7.98 \times 10^{-3}\ M^{-1}$ sec^{-1} is the value at 25.2° approximated by Bunnett and Davis.[3]

Table I

Reaction of Sodium Phenoxide with 2,4-Dinitrochlorobenzene in Methanol at 35°

(PhO^-)	(ArCl)	(PhOH)	(CH_3OH)	(CH_3OH)/ (PhOH)	$k \times 10^3$ M^{-1} sec^{-1}
0.0507	0.0364	0.0855	24.021	280.95	5.49
0.0508	0.0365	0.1035	23.985	231.74	5.24
0.0511	0.0367	0.1071	23.976	223.87	4.86
0.0526	0.0377	0.1324	23.921	180.67	4.77
0.0509	0.0369	0.1413	23.906	169.19	4.81
0.0509	0.0366	0.1926	23.800	123.57	4.15
0.0526	0.0382	0.2153	23.754	110.33	3.93
0.0509	0.0366	0.3678	23.445	63.74	3.64
0.0518	0.0367	0.5392	23.093	43.83	2.81
0.0520	0.0368	0.5307	23.113	43.55	2.78
0.0528	0.0380	0.5328	23.108	43.37	2.80
0.0516	0.0371	0.5894	22.997	39.02	2.55

Table II

Reaction of Sodium *o*-Cresolate with 2,4-Dinitrochlorobenzene in Methanol at 35°

$(Ar'O^-)$	(ArCl)	(Ar'OH)	(CH_3OH)	(CH_3OH)/ (Ar'OH)	$k \times 10^3$ M^{-1} sec$^-$
0.0515	0.0385	0.0790	23.995	303.73	9.50
0.0510	0.0378	0.0858	23.978	279.46	8.78
0.0521	0.0376	0.1039	23.930	230.32	7.82
0.0518	0.0368	0.1097	23.920	218.45	7.26
0.0515	0.0373	0.1596	23.913	149.83	5.89
0.0511	0.0391	0.2037	23.675	116.23	4.74
0.0505	0.0359	0.2602	23.533	90.44	4.19
0.0517	0.0327	0.3210	23.375	72.82	3.66
0.0507	0.0369	0.3455	23.320	67.50	3.65
0.0497	0.0340	0.5492	22.800	41.52	2.56
0.0512	0.0370	0.5154	22.888	44.41	2.73
0.0505	0.0356	0.7113	22.390	31.48	2.23

Table III

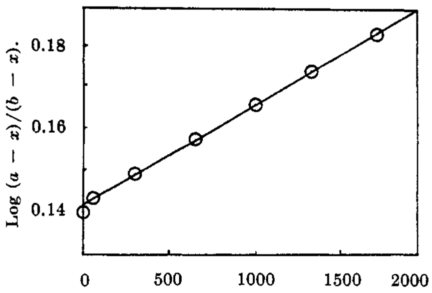
Reaction of Sodium *o*-Cresolate with 2,4-Dinitrochlorobenzene in Methanol at 35°

Sample	0.0270 M $HClO_4$, ml	(Base) = a	(ArCl) = b	Log $(a - x)/(b - x)$	Time, sec
1	9.39	0.0507	0.0369	0.1376	0
2	9.02	0.0487	0.0349	0.1443	57
3	8.69	0.0469	0.0332	0.1508	361
4	8.35	0.0451	0.0313	0.1582	694
5	8.01	0.0433	0.0295	0.1664	1056
6	7.74	0.0418	0.0280	0.1736	1407
7	7.45	0.0402	0.0267	0.1819	1784
8	2.55	0.0138	0.0	...	∞

Product Identification.—The following expected products were isolated from samples of reacting solutions which were allowed to proceed to completion: 2,4-dinitrophenyl ether, mp 69.5–70.0°;[3] 2,4-dinitrophenylanisole, mp 95–96°; 2,4-dinitro-2'-methylphenyl ether, mp 88–89°.

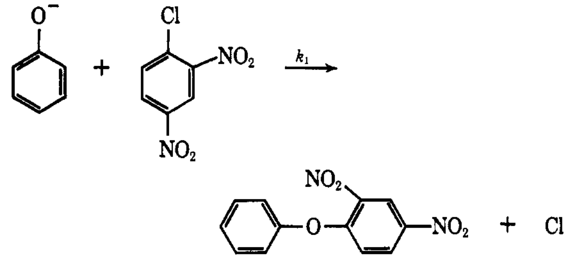
Results and Discussion

The operation of equilibrium 2 produces the methoxide ion which competes with the phenoxide for the 2,4-dinitrochlorobenzene as is shown by eq 3 and 4. Because of its greater nucleophilicity, even small concentrations of the methoxide ion will affect the observed rate constant of the phenoxide ion. In order to determine the actual nucleophilic reactivity of phenoxide, k_1, a series of kinetic investigations were undertaken to study the effect of phenol concentration on the observed rate constant. The reactions were followed by determining the quantity of base consumed. The rate expression 5, which is derived in the appendix, was employed, where (base) is the concentration of phenoxide

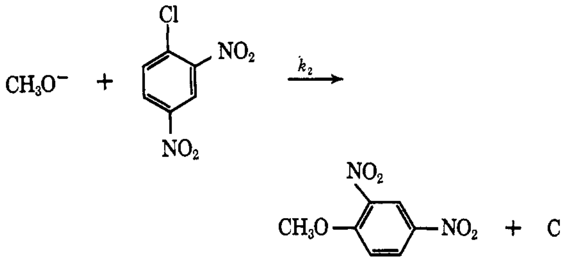


Time, sec, k = 3.65 × 10^{-3} M^{-1} sec^{-1}; $(CH_3OH)/(ArOH)$ = 67.50.

Figure 1.



(3)



(4)

$$\frac{-\mathrm{d(base)}}{\mathrm{d}t} = \mathrm{(ArCl)(base)}\left[\frac{k_1 + k_2K(CH_3OH)/PhOH)}{1 + K(CH_3OH)/PhOH)}\right] \quad (5)$$

plus methoxide, (ArCl) is the concentration of 2,4-dinitrochlorobenzene, K is the equilibrium constant for reaction 2 at 35°, and k_1 and k_2 are the nucleophilc reactivities of phenoxide and methoxide ions, respectively. At a particular phenol concentration then

$$k_{\mathrm{obsd}} = \left[\frac{k_1 + k_2K(CH_3OH)/(PhOH)}{1 + K(CH_3OH)/(PhOH)}\right] \quad (6)$$

If it is assumed that $K(CH_3OH)/(PhOH)$ is very small compared with unity then eq 6 becomes

$$k_{\mathrm{obsd}} = k_1 + k_2K(CH_3OH)/(PhOH) \quad (7)$$

and a plot of k_{obsd} *vs.* $(CH_3OH)/(PhOH)$ should give a straight line the intercept of which is k_1 and the slope k_2K.[6] Since the rate coefficient of the methoxide ion, k_2, can be obtained from independent experiments, the value of K can be determined. Table I summarizes the experimental data on k_{obsd} at different (CH_3OH)/(PhOH) ratios. The ionic strength was kept fairly constant at 0.0517 M ± 0.0011 while the concentra-

---

[6] The following equation was derived for the system of Bunnett and Davis in 60% dioxane, where k_{obsd}, k_1, k_2, and K have analogous meanings to

$$k_{\mathrm{obsd}} = k_1 + k_2K(H_2O)/(PhOH)$$

the above case. A plot of $(H_2O)/(PhOH)$ *vs.* k_{obsd} produced a scatter of points which appeared to have a maximum at a $(H_2O)/(PhOH)$ ratio of 500. In this approach it is assumed that the concentration of water remains constant. Several "reasonable" straight lines could be drawn the intercepts of which varied from 12.7 to 13.7 × 10^{-3} M^{-1} sec^{-1}. Bunnett's value for the nucleophilic reactivity of phenoxide in dioxane–water appears to represent the lower limit.

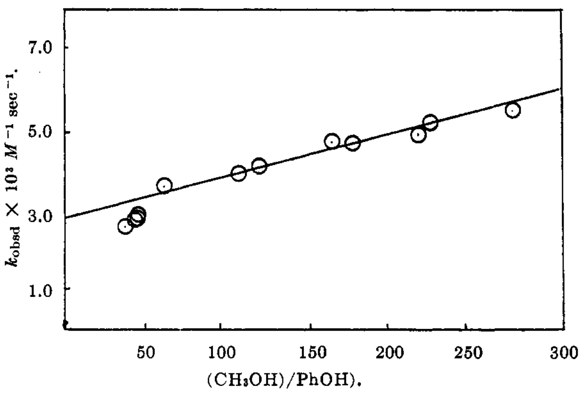


Figure 2.—Reaction of sodium phenoxide with 2,4-dinitrochlorobenzene in methanol at 35°.

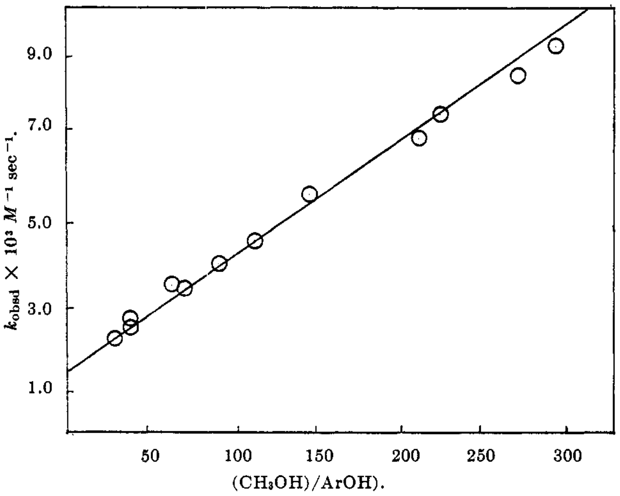


Figure 3.—Reaction of sodium *o*-cresolate with 2,4-dinitrochlorobenzene in methanol at 35°.

TABLE IV

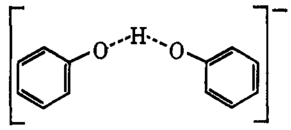
REACTION OF SODIUM METHOXIDE WITH 2,4-DINITROCHLOROBENZENE IN METHANOL AT 35°

(CH_3O^-)	(ArCl)	$k \times 10^3$ M^{-1} sec^{-1}
0.0472	0.0384	7.77
0.0523	0.0383	7.50
0.0750	0.0374	7.80
0.0423	0.0281	7.59
0.0300	0.0371	7.49
	Average =	7.63

tion of phenol (and thus the ratio of $(CH_3OH)/(PhOH)$) was varied over a sevenfold range. Table IV summarizes the data for the reaction of sodium methoxide with 2,4-dinitrochlorobenzene in methanol at 35°. The reaction was studied over an ionic strength range of 0.0300 to 0.0750 *M*. Only a 2% variation in rate was observed. This observed insensitivity of reaction rate to changes in ionic strength is compatible with the results of Reinheimer, *et al.*,[7] who studied the reaction at 24.90°.

Figure 2 shows a plot of k_{obsd} *vs.* $(CH_3OH)/(PhOH)$. All points, except those at high phenol concentrations, fall on a straight line. This bears out the assumption that the term $K(CH_3OH)/(PhOH)$ is small compared with unity within the concentration range studied. A value of $2.80 \pm 0.15 \times 10^{-3}\ M^{-1}\ sec^{-1}$ is obtained for k_1 and a value of $1.46 \pm 0.11 \times 10^{-4}$ is obtained for K. A rigorous approach to the determination of k_1 and K can be accomplished directly from eq 6. Since there are only two unknown quantities in this equation, k_1 and K, by solving simultaneous equations for all possible combinations of the data points, with the exception of those at high phenol concentrations, these quantities can be determined. The values of k_1 and K are found to be identical with those obtained by the graphical method. Leahy, *et al.*,[3] reported a rate coefficient of $2.50 \times 10^{-3}\ M^{-1}\ sec^{-1}$ at 35°; however, careful examination of the work reveals that their experiments were conducted at a concentration of phenol which would put them in the anomalous portion of Figure 2, and, consequently, the closeness of their rate constant to ours appears to be purely fortuitous.

The rate suppression at high phenol concentration could be due to a general medium effect or perhaps to some specific interaction of the excess phenol with one or both of the reactants. For instance the phenol might be forming a charge-transfer complex with the 2,4-dinitrochlorobenzene thus decreasing the effective concentration of this reactant and the over-all rate of reaction. Evidence for the formation of charge-transfer complexes in aromatic nucleophilic substitution was presented by Ross and Kuntz,[8] who observed that the rate of condensation of aniline with 2,4-dinitrochlorobenzene is decelerated as the concentration of aniline was increased. Bunnett and Davis[2] have observed a rate decrease in the reaction of phenoxide with 2,4-dinitrochlorobenzene in 60% aqueous dioxane in the presence of a high concentration of phenol. They attributed this behavior to the formation of the biphenoxide ion (shown below), a species of low nucleophilicity. This same species could also account for the observed rate suppression in methanol.



In order to get a clearer insight into what is happening at the higher phenol concentrations, the reaction of sodium *o*-cresolate with 2,4-dinitrochlorobenzene in methanol was investigated at different concentrations of *o*-cresol. The data are summarized in Table II and Figure 3 shows a plot of k_{obsd} *vs.* $(CH_3OH)/(ArOH)$. The assumption that $K(CH_3OH)/(ArOH)$ is small compared with unity is again born out by the linearity of the plot. A value of $1.42 \pm 0.15 \times 10^{-3}\ M^{-1}\ sec^{-1}$ is obtained for k_1, the nucleophilic reactivity of *o*-cresolate ion, and a value of $4.05 \pm 0.19 \times 10^{-4}$ for K. Identical values of k_1 and K were obtained by employing eq 6 and solving simultaneous equations for all possible combinations of the data points.

If the formation of charge-transfer complexes was responsible for the rate suppression observed at high phenol concentrations one would expect a similar effect with *o*-cresol. It is true that an *ortho*-methyl group should sterically hinder the formation of a charge-transfer complex; yet, from electronic considerations, the methyl group should increase the electron

---

(7) J. D. Reinheimer, W. F. Kieffer, S. W. Frey, J. C. Cochran, and E. W. Barr, *J. Am. Chem. Soc.*, **80**, 164 (1958).

(8) S. D. Ross and I. Kuntz, *ibid.*, **76**, 3000 (1954).

density of the ring and this should work in opposition to the steric effect. It has been shown by Ross, *et al.*,[9] both spectrophotometrically and kinetically, that hexamethylbenzene forms complexes with picryl chloride. In this case the steric requirements are much greater than those for the *o*-cresolate and it would appear that the electronic effects override the steric influence of a group as small as methyl. This argument does not mean that charge-transfer complexes are not formed in solution. It simply indicates that these complexes cannot be used to explain the rate suppression at high phenol concentrations.

As far as general medium effects are concerned, one would anticipate phenol and *o*-cresol to have a similar influence on the dielectric properties of the medium and also on the degree of dissociation of the sodium salts. As a consequence both should exhibit similar behavior at high concentrations of the phenolic compound. Thus dielectric effects cannot be used to explain the rate suppression.

From a steric point of view, one would predict that the bi-*o*-cresolate ion would be a species of somewhat higher energy than the biphenoxide ion and that, if the biphenoxide ion were the species responsible for the rate suppression at high phenol concentrations, little or no rate suppression should be observed at high *o*-cresol concentrations. Examination of Figure 3 reveals that this is the case.

Appendix

Derivation of Kinetic Equation.—Since the extent of reaction was determined by the quantity of total base consumed, where total base is equal to the concentration of phenoxide ion and methoxide ion, then

$$\frac{-\mathrm{d(base)}}{\mathrm{d}t} = k_1(\mathrm{PhO^-})(\mathrm{ArCl}) + k_2(\mathrm{CH_3O^-})(\mathrm{ArCl}) \qquad (8)$$

The equilibrium expression for eq 2 is

$$K = \frac{(\mathrm{CH_3O^-})(\mathrm{PhOH})}{(\mathrm{PhO^-})(\mathrm{CH_3OH})} \qquad (9)$$

Substitution of eq 9 in eq 8 results in the following expression.

$$\frac{-\mathrm{d(base)}}{\mathrm{d}t} = (\mathrm{PhO^-})(\mathrm{ArCl})\,[k_1 + k_2K(\mathrm{CH_3OH})/(\mathrm{PhOH})] \qquad (10)$$

Since

$$(\mathrm{PhO^-}) = \frac{(\mathrm{base})}{1 + K(\mathrm{CH_3OH})/(\mathrm{PhOH})} \qquad (11)$$

then

$$\frac{-\mathrm{d(base)}}{\mathrm{d}t} = (\mathrm{ArCl})(\mathrm{base})\left[\frac{k_1 + k_2K(\mathrm{CH_3OH})/(\mathrm{PhOH})}{1 + K(\mathrm{CH_3OH})/(\mathrm{PhOH})}\right]$$

Registry No.—Sodium phenoxide, 139-02-6; sodium *o*-cresolate, 4549-71-8; 2,4-dinitrochlorobenzene, 97-00-7; methanol, 67-56-1; sodium methoxide, 124-41-4.

Acknowledgment.—The authors wish to acknowledge useful discussions of these results with Professor Henry M. Neumann.

---

(9) S. D. Ross, M. Bassin, M. Finkelstein, and W. A. Leach, *J. Am. Chem. Soc.*, **87**, 69 (1954); S. D. Ross and I. Kuntz, *ibid.*, **76**, 74 (1954).

Photochemically Induced Cyclization of Some Furyl- and Thienylethenes

Richard M. Kellogg, M. B. Groen, and Hans Wynberg

Department of Chemistry, Bloemsingel 10, Groningen, The Netherlands

Received April 7, 1967

Photolysis of a number of 1,2-di(thienyl)ethenes in the presence of oxidizing agents produced condensed ring systems derived from cyclization followed by oxidation. Photolysis of 1,2-di(2-thienyl)ethene in the presence of iodine gave benzo[1,2-*b*:4,3-*b*′]dithiophene in nearly quantitative yield. Methylated derivatives of this compound underwent similar ring closures; 1-(2-thienyl)-2-(3-methyl-2-thienyl)ethene cyclized with concomitant loss of the methyl substituent. Photolysis of 1,2-di(2,3′-dithienyl)ethene yielded benzo[1,2-*b*:3,4-*b*′]dithiophene, 1-(2-furyl)-2-(2-thienyl)ethene gave thieno[3,2-*e*]benzofuran, and 1,2-di(2-furyl)ethene gave benzo[1,2-*b*:4,3-*b*′]difuran. Interesting long-range coupling effects were observed in the nmr spectra of the coddensed ring systems. The dihydro intermediates involved in the cyclization of the di(thienyl)ethenes have been observed by ultraviolet spectroscopy. The quantum yield for cyclization of 1,2-di(2-thienyl)ethene was found to be 0.076. All attempts to photocyclize 1,2-di(3-thienyl)ethene failed, although formation of the dihydro intermediate occurred readily upon photolysis. Failure to obtain products is attributed to the expulsion of a thiyl radical during the oxidation process.

A well-studied and recognized type of photochemical reaction is the reversible ring closure of 1,3,5-hexatrienes to 1,3-cyclohexadienes. This reaction has been extensively studied by Havinga and co-workers in the ergosterol system[1] and by Srinivasan for the unsubstituted system.[2] An interesting and valuable variation of this reaction occurs when one or more double bonds of the hexatriene system are derived from an aromatic ring. The photochemically induced cyclization of *cis*-stilbene, which in the presence of an oxidizing agent yields phenanthrene in high yield, has been studied thoroughly by Mallory[3] and his students. The mechanistic aspects of the stilbene ring closure have been extensively discussed[4,5] as well as the synthetic potentials.[6] Analogous systems in which double bonds of the hexa-

---

(1) E. Havinga, R. J. de Kock, and M. P. Rappoldt, *Tetrahedron*, **11**, 276 (1960), and earlier references.

(2) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 2806 (1961). For a review, see R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966).

(3) (a) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, *J. Am. Chem. Soc.*, **84**, 4361 (1962). For earlier reports, see (b) C. O. Parker and P. E. Spoerri, *Nature*, **166**, 603 (1950); (c) R. E. Buckles, *J. Am. Chem. Soc.*, **77**, 1040 (1955); (d) D. G. Coe, R. W. Garnish, M. M. Gale, and C. J. Timmons, *Chem. Ind.* (London), 665 (1957).

(4) (a) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964); (b) F. B. Mallory, J. T. Gordon, and C. S. Wood, *ibid.*, **85**, 828 (1963); (c) W. M. Moore, D. D. Morgan, and F. R. Stermitz, *ibid.*, **85**, 829 (1963); (d) J. Cornelisse, Thesis, University of Leiden, The Netherlands, 1965; (e) H. Stegemeyer, *Z. Naturforsch.*, **B17**, 153 (1962).

(5) The gas phase reactions have been studied: (a) R. Srinivasan and J. C. Powers, Jr., *J. Am. Chem. Soc.*, **85**, 1355 (1963); (b) *J. Chem. Phys.*, **39**, 580 (1963).

(6) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).