

Homolytic Substitution at Furan and Thiophene: Rate Constants for the Formation and Decay of the Radical Intermediates¹

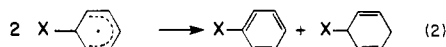
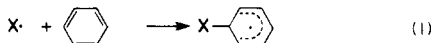
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Absolute rate constants for radical addition to thiophene and furan have been measured by using kinetic EPR spectroscopy and laser flash photolysis. Additions of phenyl, diethoxyphosphonyl, and triethylsilyl radicals are rapid and have rate constants $>10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C in hydrocarbon solvent. Comparison with data for the analogous reactions with benzene and 1-hexene shows that the heterocyclic compounds are generally less reactive than 1-hexene but are substantially more effective as radical scavengers than benzene.

Free radical additions to benzenes and heterocycles are the first steps in homolytic substitution processes, e.g., reaction 1.^{3,4} Some of the radicals thus formed dispropo-



portionate (reaction 2), and lead to the so-called "substitution" products.^{3,4}

Information about these reactions has been gained largely by product studies. However, electron paramagnetic resonance (EPR) spectra of radical intermediates have been detected for additions of a variety of radicals to furan and thiophene⁵ and to substituted benzenes where the resulting cyclohexadienyl radicals were persistent,⁶⁻⁸ and for the addition of hydroxyl to benzene itself.⁹⁻¹¹

In a recent study,¹² rate constants for radical additions to benzene were investigated by monitoring the kinetic behavior of the radical intermediates by use of EPR and optical modulation spectroscopy.¹³⁻¹⁵ The magnitudes of the relative and absolute rate constants were most easily rationalized by simply regarding benzene as being a rather unreactive olefin.¹⁶ The thrust of the present investigation is to set the reactivities of heterocyclic compounds in the context of those for benzene and simple olefins.

Experimental Section

Materials. Thiophene, furan, and pyrrole were purified by distillation under nitrogen, Di-*tert*-butyl peroxide was shaken with aqueous silver nitrate to remove traces of olefin, washed with

water, and dried over magnesium sulfate. Finally, it was passed through alumina so as to remove traces of *tert*-butyl hydroperoxide. All other materials were used as received.

Apparatus. EPR spectra were recorded on a Varian E104 spectrometer. Samples were photolyzed directly in the spectrometer cavity with a 1000-W Xe/Hg arc lamp as the irradiating source. The light from the lamp was filtered through an aqueous cobalt/nickel sulfate solution so as to remove much of the visible and most of the infrared radiation. After filtration, the heating effect of the light at the sample was less than 1 °C.

Kinetic Measurements. EPR experiments were carried out to measure the bimolecular decay kinetics of the radicals under investigation. Radicals were generated repetitively by using pulses (10 mJ; 337 nm; 8 ns) from a Molecron nitrogen laser. The time profile of the growth and decay of the radical signal was obtained by feeding the unfiltered output of the spectrometer into a Nicolet 1170 signal averager. Radical concentrations were measured by a method that has been described previously.¹⁷

Steady-state experiments, analogous to those employed in the study of substitution at benzene,¹² were used to measure rate constants for radical addition to heterocycles.

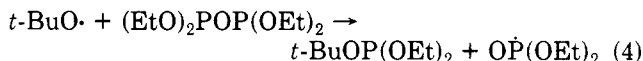
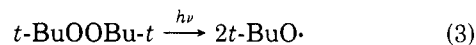
A number of kinetic measurements were made using laser flash photolysis apparatus equipped with optical detection. This apparatus and its associated experimental procedures have been described in detail elsewhere.¹⁸

All experiments were carried out on deoxygenated samples.

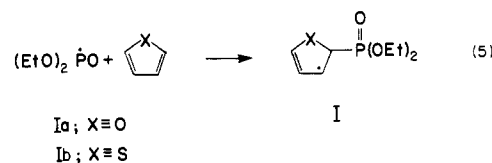
Results and Discussion

In this work, we describe the measurement of rate constants for the addition of a variety of radicals to furan and thiophene.

Diethoxyphosphonyl Radicals. Diethoxyphosphonyl radicals were generated by photolysis of mixtures containing tetraethyl pyrophosphite (5-10% v/v) and di-*tert*-butyl peroxide (5-10% v/v) in isoctane (reactions 3 and 4).¹⁹



When the photolysis was carried out in the cavity of an EPR spectrometer at -80 °C in the presence of furan or thiophene (5% v/v) the spectra of the adduct radicals Ia and Ib were detected (reaction 5).

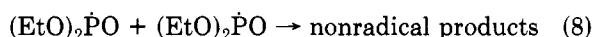
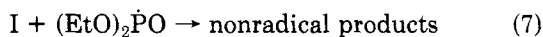
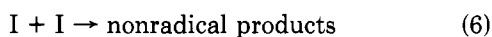


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The above radicals were characterized from the EPR parameters: Ia, $a^{\text{H}_2} = 36.8$ G, $a^{\text{H}_{3,5}} = 13.3$ G, $a^{\text{H}_4} = 2.1$ G, $a^{31\text{P}} = 90.8$ G; Ib, $a^{\text{H}_2} = 32.6$ G, $a^{\text{H}_3} = 12.0$ G,²⁰ $a^{\text{H}_5} = 13.2$ G,²⁰ $a^{\text{H}_4} = 2.5$ G, $a^{31\text{P}} = 79.1$ G (the standard numbering system of heterocyclic chemistry is used). The assignments of the hyperfine splittings were made by analogy with allylic systems²¹ to which the spectra of Ia and Ib show strong similarities. For example, the hyperfine splittings in the allyl radical are $a^{\text{H}_{1,3}} = 14.8$ G (exo), $a^{\text{H}_{1,3}} = 13.9$ G (endo), and $a^{\text{H}_2} = 4.1$ G.²² These results imply that Ia and Ib have electronic structures that are basically allylic and that are essentially unaffected by the presence of the oxygen or sulfur atoms.

Rate constants for addition, k_5 , can be measured by a steady-state, EPR technique if conditions can be adjusted so that I and $(\text{EtO})_2\dot{\text{P}}\text{O}$ can be detected at the same time. Under these circumstances, there is effectively a competition between the pseudo-first-order decay of the phosphonyl radical through reaction 5 and its bimolecular decay through reactions 7 and 8. The kinetic analysis has been



given elsewhere¹⁷ and is summarized in eq 9.

$$\frac{[\text{X}]}{[\text{I}]} = \frac{2k_6}{k_5} \left\{ \frac{[\text{I}]}{[(\text{EtO})_2\dot{\text{P}}\text{O}] + 1} \right\} \quad (9)$$

For furan (0.030 M) at -85 °C, $[(\text{EtO})_2\dot{\text{P}}\text{O}] = 8.4 \times 10^{-8}$ M and $[\text{Ia}] = 4.1 \times 10^{-7}$ M; hence $2k_6/k_5 = 1.2 \times 10^4$. The rate constant, $2k_6$, for the self-reaction of Ia was measured at -85 °C by the standard technique¹⁷ using higher concentrations of furan (0.69 M) so that $(\text{EtO})_2\dot{\text{P}}\text{O}$ could no longer be detected. It was found that the reaction was effectively diffusion controlled since $2k_6 = 1.5 \times 10^9$.²³ Combining these results gives $k_5(\text{Ia}) = 1.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

The rate constant for addition to thiophene, $k_5(\text{Ib})$, was measured by a competitive technique. Diethoxyphosphonyl radicals were generated by continuous photolysis (reactions 3 and 4) in the presence of a mixture of thiophene and furan. Measurement of the relative concentrations of Ia and Ib then yields $k_5(\text{Ia})/k_5(\text{Ib})$ if it is assumed that $2k_6(\text{Ia}) = 2k_6(\text{Ib})$ (eq 10).²⁴ This assumption

$$\frac{k_5(\text{Ia})}{k_5(\text{Ib})} = \frac{[\text{Ib}]}{[\text{Ia}]} \frac{[\text{thiophene}]}{[\text{furan}]} \quad (10)$$

is almost certainly valid since reaction 6 is a diffusion-controlled process (vide supra) and both radicals Ia and Ib are of similar size and molecular weight.²³

At a thiophene:furan molar ratio of 5.52 in isooctane solvent at -85 °C the relative concentrations of Ia:Ib were 0.76 and hence $k_2(\text{Ia})/k_5(\text{Ib}) = 7.26$. Combining this result with the absolute value of $k_5(\text{Ia})$ reported above gives $k_5(\text{Ib}) = 1.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

(20) The assignments of a^{H_3} and a^{H_5} are equivocal and could be reversed.

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(22) Measured at -130 °C in propylene solvent: Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 2635.

(23) For a comprehensive study of diffusion controlled radical-radical reactions see: Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130, 2463.

(24) Benzhydrol was used as a probe molecule for this experiment. See: Paul, H.; Small, R. D., Jr.; Sciano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

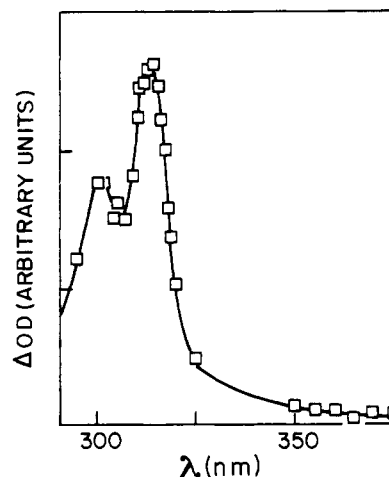
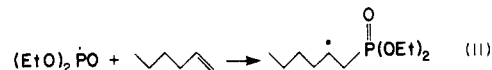


Figure 1. Optical absorption spectrum of the benzyl radical formed in the reaction of diethoxyphosphonyl radicals with benzyl bromide.

Kinetics for the addition of $(\text{EtO})_2\dot{\text{P}}\text{O}$ to 1-hexene were also investigated so that the results for heterocyclic addition could be compared with the rate constant for addition to a normal olefinic double bond (reaction 11).

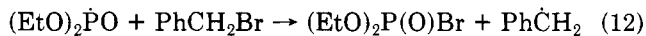


The experimental approach was the same as that used for the measurement on furan. At the concentrations of 1-hexene used in this experiment, 0.017 M, a flow system was required to overcome the effects of sample depletion. With the assumption that the value of $2k_6(\text{Ia})$ can be applied equally in this case (vide supra) the rate constant for addition k_{11} was found to be $1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at -85 °C in isooctane solvent. This rate constant is significantly higher than those measured for the analogous additions to furan and thiophene.

The rate constant for reaction 5 was also measured at 23 °C using laser flash photolysis. In this time-resolved experiment an important requirement was that $(\text{EtO})_2\dot{\text{P}}\text{O}$ could be formed on a submicrosecond timescale.

tert-Butoxyl radicals were found to be scavenged by tetraethyl pyrophosphite with a rate constant of $(2.85 \pm 0.38) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.²⁴ However, we cannot a priori discount the possibility that this reaction gives an intermediate phosphoranil radical which decays slowly to yield $(\text{EtO})_2\dot{\text{P}}\text{O}$. Moreover, since $(\text{EtO})_2\dot{\text{P}}\text{O}$ cannot be detected optically under these conditions, the overall rate of its formation could not be measured directly.

A solution to such difficulties is to add a probe molecule to the system which in its reaction with phosphonyl radicals gives a product that has an easily detectable optical absorption. Benzyl bromide was ideally suited to this purpose since the resulting benzyl radical has a strong absorption at 316 nm¹⁴ (reaction 12, Figure 1). It was



found that the lifetime for the growth of the benzyl radical signal was proportional to the benzyl bromide concentration, indicating that the formation of $(\text{EtO})_2\dot{\text{P}}\text{O}$ must be far more rapid than their subsequent reaction with benzyl bromide. The general kinetic expression which covers this experiment is given in eq 13. Here k_{exptl} is derived from

$$k_{\text{exptl}} = k_0 + k_{12}[\text{PhCH}_2\text{Br}] + k[\text{substrate}] \quad (13)$$

the lifetime for the pseudo-first-order growth of the benzyl radical and k_0 reflects the lifetime of the radical in the

Table I. Rate Constants for the Reactions of Various Radicals with Furan, Thiophene, 1-Hexene, and Benzene in Hydrocarbon Solvent at 25 or -85 °C

substrate	rate constants, M ⁻¹ s ⁻¹			
	(EtO) ₂ P ^o O		Ph [•] , 25 °C	Et ₃ Si, ^a 25 °C
	25 °C	-85 °C		
furan	1.3 × 10 ⁶	1.3 × 10 ⁵	2.7 × 10 ⁶	1.4 × 10 ⁶
thiophene	1.7 × 10 ⁶	1.7 × 10 ⁴	6.4 × 10 ⁶	5.0 × 10 ⁶
1-hexene	8.7 × 10 ⁶	1.4 × 10 ⁶	2.8 × 10 ⁸ ^b	4.8 × 10 ⁶
benzene	2.9 × 10 ³ ^c		4.5 × 10 ⁵ ^b	4.6 × 10 ⁵

^a Reference 31. ^b Reference 27. ^c Reference 12.

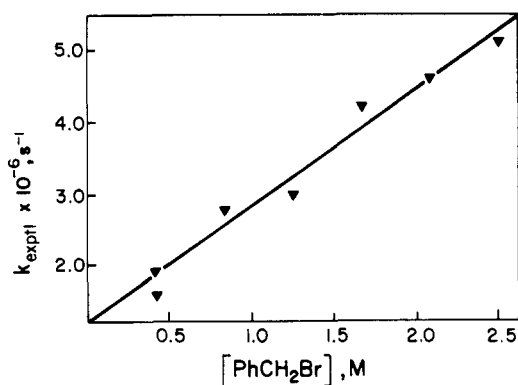


Figure 2. Plot of k_{exptl} vs. $[\text{PhCH}_2\text{Br}]$ for the growth of benzyl radicals formed in reaction 12.

absence of benzyl bromide. In experiments where no additional substrate was present, k_{12} was found to be $(1.64 \pm 0.26) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 2), in good agreement with the value of $1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ obtained in a competitive EPR experiment.²⁵

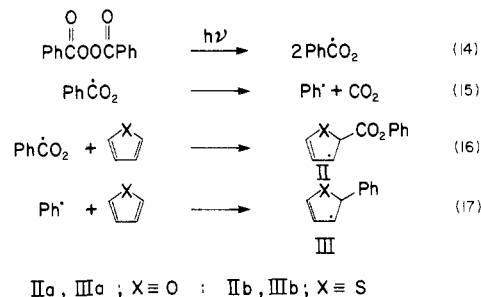
Equation 12 can also be used in measurements of the rate constants for reactions of diethoxyphosphonyl radicals with other substrates. At a constant concentration of benzyl bromide (0.04 M), k_{exptl} is directly proportional to the substrate concentration and is again measured by measuring the growth of the benzyl radicals that now serve simply as a probe of the lifetime of the phosphonyl radical.

When the above approach was used, k_5 was measured for furan and thiophene while k_{11} was determined for 1-hexene at 25 °C in isooctane as solvent. The results are reported in the Table I. Combination of these results with those obtained by EPR leads to the following *A* factors and activation energies: $10^{(7.8 \pm 1.0)} \text{ M}^{-1} \text{ s}^{-1}$ and $(2.3 \pm 1.0) \text{ kcal mol}^{-1}$ (furan), $10^{(9.8 \pm 1.0)} \text{ M}^{-1} \text{ s}^{-1}$ and $(4.8 \pm 1.0) \text{ kcal mol}^{-1}$ (thiophene), and $10^{(8.4 \pm 1.0)} \text{ M}^{-1} \text{ s}^{-1}$ and $(1.9 \pm 1.0) \text{ kcal mol}^{-1}$ (1-hexene). The error limits represent a combination of the experimental errors on the individual rate constants. These Arrhenius parameters cannot be extremely reliable since they depend upon only two experimental points (albeit that they are well separated in temperature), yet the *A* factors obtained are in accord with expectations for a simple bimolecular process.²⁶

No optical spectra due to these radicals could be detected down to 310 nm by laser flash photolysis or optical modulation spectroscopy. In addition, EPR and optical experiments using pyrrole and *N*-methylpyrrole as substrates were frustrated by the rapid discoloration of samples on photolysis which could not be overcome by the use of flow systems.

Phenyl Radicals. EPR experiments have shown that photolysis of benzoyl peroxide in the presence of thiophene

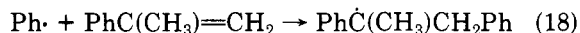
or furan at low temperatures leads to the spectra of both benzoyloxy and phenyl adducts (II and III, reactions 14–17).⁵



The trapping of benzoyloxy at low temperatures is not inconsistent with a rate constant for its decomposition of $\geq 10^8 \text{ S}^{-1}$ at 25 °C²⁷ since this process could well have a substantial activation energy.²⁸ Moreover, product studies^{29,30} indicate increased yields for benzoyloxy substitution when reagents are present that can scavenge II, implying that reaction 16 is readily reversible at room temperature and above. Both of these factors explain why the benzoyloxy adducts are not detected by EPR above ca. -30 °C.

Despite these considerations, it has been demonstrated²⁷ that the lifetime of the free benzoyloxy radical at room temperature is $\leq 10 \text{ ns}$ and hence it is possible to measure addition by phenyl radicals using benzoyl peroxide as a precursor.

Rate constants for addition of phenyl to thiophene and furan were measured by using a laser flash photolysis technique²⁷ which makes use of β -methylstyrene to probe the lifetime of the phenyl radical (reaction 18), in the same



way that benzyl bromide was used to probe the lifetime of diethoxyphosphonyl (vide supra). The rate constants obtained are reported in Table I.

Triethylsilyl Radicals. Rate constants for addition of triethylsilyl radicals to furan and thiophene have been measured by using benzil as a probe molecule,³¹ and the adducts obtained in these reactions have been characterized by EPR spectroscopy.⁵ The results are given in Table I.

Other Radicals. Several other radicals which did not add readily to thiophene or furan were investigated. For example, while thiol and alkoxy radicals add to these substrates at temperatures below -100 °C,⁵ there was no sign of addition at room temperature, indicating that these

(27) Sciano, J. C.; Stewart, L. C.; *J. Am. Chem. Soc.* **1983**, *105*, 3609.

(28) It must also be admitted that the benzoyloxy adducts could be formed by photolysis of a complex consisting of substrate molecule and benzoyl peroxide.

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(30) Minisci, F.; Porta, O. *Adv. Heterocycl. Chem.* **1974**, *16*, 123.

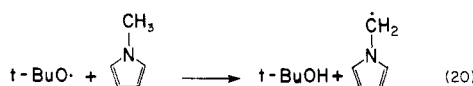
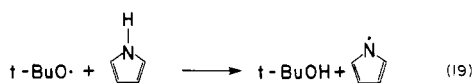
(31) We thank Dr. C. Chatgililoglu for carrying out these measurements. Chatgililoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 3292.

(25) Anpo, M.; Sutcliffe, R.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 3580.

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reactions are readily reversible. No EPR signals were detected when pyrrole or *N*-methylpyrrole were used. This was most probably due to the fact that on photolysis peroxide/pyrrole mixtures quickly went brown, thus screening further photodecomposition.

In laser flash photolysis experiments where sample discoloration presents less significant problems both pyrrole and *N*-methylpyrrole were found to react with *tert*-butoxyl radicals. While the reaction products have not been identified, because of discoloration during preparative photolysis, it seems likely that hydrogen abstraction is the dominant reaction since the experience with thiophene and furan suggests that additions to the double bonds are slow or rapidly reversible (reactions 19 and 20).



The rate constants for these reactions were measured by using benzhydrol as a probe molecule²⁴ and were found to be $k_{19} = 8.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{20} = 4.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

These rate constants are similar to those for the reaction of *tert*-butoxyl with dimethylamine where the rate constant for N-H abstraction is $1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ while that for C-H abstraction is $6.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.³²

Optical signals due to phenylthiyl radicals generated from diphenyldisulfide were not quenched by addition of thiophene, furan, or pyrrole, indicating that the addition of this radical must be relatively slow ($<10^5 \text{ M}^{-1} \text{ s}^{-1}$) or readily reversible.

Summary

The kinetic data obtained in this work indicate that thiophene and furan have reactivities toward radical addition that are intermediate between those of normal olefins and benzene.

Acknowledgment. We thank Dr. J. C. Scaiano of these laboratories for the use of the laser flash photolysis equipment.

Registry No. Ia, 86885-42-9; Ib, 86885-43-0; (EtO)₂P=O, 31682-65-2; Ph₂, 2396-01-2; Et₃Si₂, 24669-77-0; furan, 110-00-9; thiophene, 110-02-1; 1-hexene, 592-41-6; benzene, 71-43-2.

(32) Nazran, A. S.; Griller, D. *J. Am. Chem. Soc.* 1983, 105, 1970.

Neighboring Group Participation in Organic Redox Reactions. 8.¹ Kinetics and Products of the Aqueous Iodine Oxidation of 3-Hydroxy- and 3-Methoxy-1,5-dithiacyclooctanes

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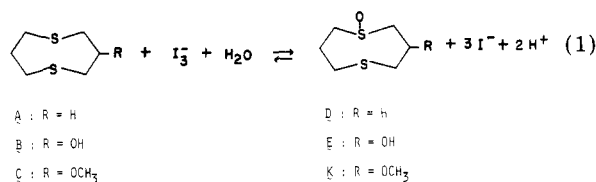
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The aqueous iodine oxidation of 3-hydroxy- and 3-methoxy-1,5-dithiacyclooctanes (B and C) occurs about 10^4 times faster than the similar reaction of thiacyclooctane but about 10^2 times slower than the oxidation of the parent compound 1,5-dithiacyclooctane (A). These observations are consistent with the formation of a dicationic intermediate. The *cis*- and *trans*-sulfoxides are formed in roughly equal amounts. Single-crystal X-ray diffraction of *trans*-3-methoxy-1,5-dithiacyclooctane 1-oxide (*trans*-K) and of *cis*-3-hydroxy-1,5-dithiacyclooctane 1-oxide (*cis*-E) reveals a transannular sulfur-sulfur close contact of 3.175 (2) and 3.135 (2) Å, respectively, and S...S-O angles of 176.9 (1) and 175.4 (1)°. As predicted by the S...S-O alignment, the reverse reaction, the HI reduction of *trans*-3-methoxy-1,5-dithiacyclooctane 1-oxide (*trans*-K), is accelerated over that of a simple sulfoxide but is ca. 10 times slower than the reduction of 1,5-dithiacyclooctane 1-oxide. The equilibrium constant is ca. 150 for the reaction $\text{K} + 2\text{H}^+ + 3\text{I}^- \rightleftharpoons \text{H}_2\text{O} + \text{I}_3^- + \text{C}$. Cyclic voltammetric measurements show that both B and C have low oxidation potentials but that, although the oxidation of B is reversible, that of C is quasi-reversible.

Introduction

We previously reported the remarkable redox characteristics of the eight-membered ring dithioether 1,5-dithiacyclooctane (A). For example, A forms both a long-lived cation radical and dication on treatment with NOBF₄,^{2a} its oxidation potential is almost a volt lower than that of the cyclic monothioether 1-thiacyclooctane, and it exhibits a completely reversible cyclic voltammogram in acetonitrile.^{2b} As shown in eq 1, A is oxidized with aqueous iodine to the monosulfoxide D reversibly^{3a} and at a rate



that is about one million times faster than that of 1-thiacyclooctane. This unusual behavior can be attributed to the facile transannular oxidative coupling reaction between the two thioether groups to give intermediates containing a sulfur-sulfur bond.

(1) For paper 7 in this series: deLeeuw, D. L.; Goodrow, M. H.; Olmstead, M. M.; Musker, W. K.; Doi, J. T. *J. Org. Chem.* 1983, 48, 2371.
(2) (a) Musker, W. K.; Wolford, T. L.; Roush, P. B. *J. Am. Chem. Soc.* 1978, 100, 6416. (b) Wilson, G. S.; Swanson, D. D.; Klug, J. T.; Glass, R. S.; Ryan, M. D.; Musker, W. K. *Ibid.* 1979, 101, 1040-1042.

(3) (a) Doi, J. T.; Musker, W. K. *J. Am. Chem. Soc.* 1981, 103, 1159.
(b) Doi, J. T.; Musker, W. K. *Ibid.* 1978, 100, 3533.