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).

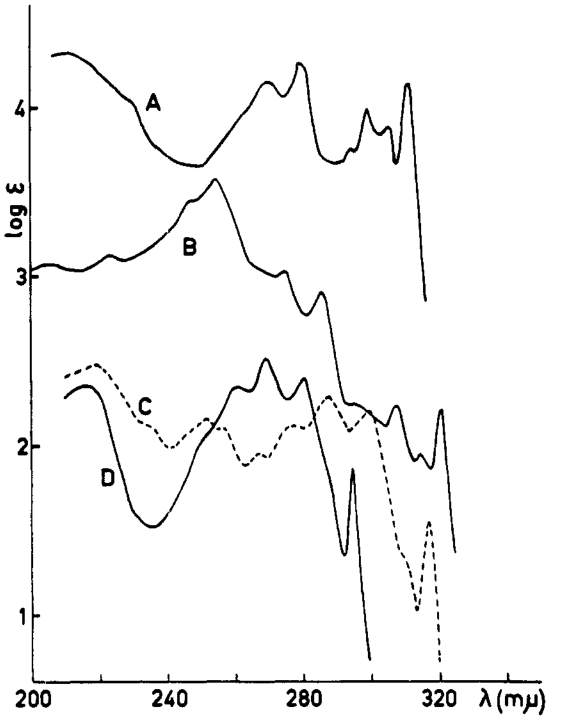


Figure 1.—Ultraviolet spectra of photoproducts taken in cyclohexane solution: curve A, thieno[3,2-*e*]benzofuran (**10**); curve B, benzo[1,2-*b*:3,4-*b*′]dithiophene (**5**); curve C, benzo[1,2-*b*:4,3-*b*′]dithiophene (**4a**); curve D, benzo[1,2-*b*:4,3-*b*′]difuran (**11**). For convenience in plotting, curve B is shifted downward by 1.0 log unit and curves C and D by 2.0 log units.

triene system are obtained from heterocyclic rings should lead to condensed ring systems not easily synthesized by classical methods. The photochemically induced cyclizations of 1-phenyl-2-(2-thienyl)ethene and 1-phenyl-2-(2-thianaphthyl)ethene have been reported.[7] The different isomers of 1,2-di(pyridyl)ethene photocyclize[8] and stilbazoles and related compounds undergo photochemically induced cyclizations.[9,10] The recently reported syntheses of aporphines[11] and dehydroaporphanes[12] provide interesting examples of the synthetic usefulness of these photochemical ring closures.

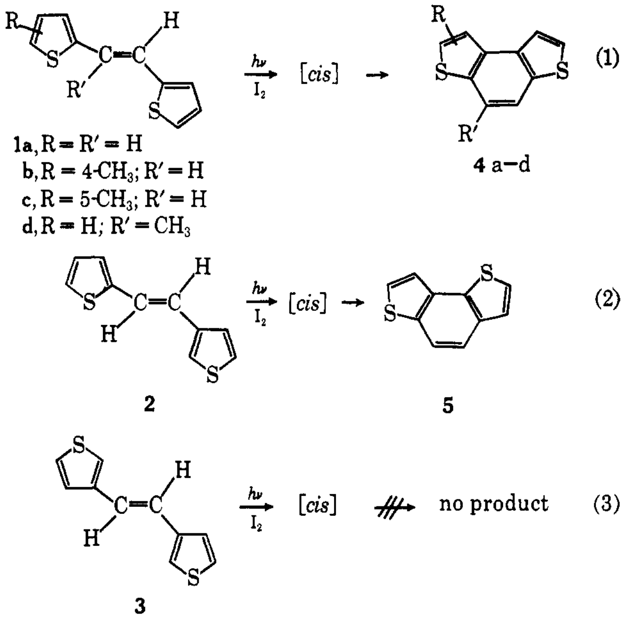
Examples of photochemical ring closures where a double bond of the hexatriene system is replaced by a heteroatom(s) are known but these often seem to involve somewhat different types of excited states. The photocyclizations of azobenzene,[13] Schiff bases,[14] and diphenylamine[15] represent examples of these types of ring closures.[16]

A study of the products and the mechanism of photocyclization of some furyl- and thienylethenes has been carried out by us. Our results indicate practical routes to condensed ring systems otherwise available only by laborious classical syntheses. The mechanistic data accumulated may provide further clarification of the processes involved in photochemical cyclization and subsequent oxidation.

Results

The modification of the Wittig reaction as described by Wadsworth and Emmons[17] for the synthesis of *trans*-stilbene was used to prepare all thienyl- and furylethenes (see Experimental Section).[18] In this manner, the *trans* isomers of 1,2-di(2-thienyl)ethene (**1a**), 1,2-di(2,3′-thienyl)ethene (**2**), and 1,2-di(3-thienyl)ethene (**3**) were prepared.

Photolysis (eq 1) of **1a** with an unfiltered, high pressure mercury lamp in 8×10^{-3} *M* benzene solution in the presence of iodine and air led to the formation in $\sim$3 hr of a material, mp 117–118°, picrate mp 148.5–149.5°. These values agreed with those reported for benzo[1,2-*b*:4,3-*b*′]dithiophene (**4a**) (lit.[19] mp 118°, picrate mp 148–149°). Yields as high as 90% upon work-up were obtained when 350-mμ light was used for irradiation. The product analyzed correctly for $C_{10}H_6S_2$ and had strong ultraviolet absorption with considerable fine structure (Figure 1, curve C). The nmr spectrum in carbon tetrachloride showed a set of doublets, J = 5.5 cps, relative area four protons,



---

(7) (a) W. Carruthers and H. N. M. Stewart, *Tetrahedron Letters*, 301 (1965); (b) W. Carruthers and H. N. M. Stewart, *J. Chem. Soc.*, 6221 (1965).

(8) H. H. Perkampus and G. Kassebeer, *Ann.*, **696**, 1 (1966).

(9) (a) C. E. Loader and C. J. Timmons, *J. Chem. Soc.*, 1078 (1966); (b) P. Bortolus, G. Cauzzo, and G. Galiazzo, *Tetrahedron Letters*, 239 (1966); (c) R. E. Doolittle and C. K. Bradsher, *Chem. Ind.* (London), 1631 (1965); (d) R. E. Doolittle and C. K. Bradsher, *J. Org. Chem.*, **31**, 2616 (1966).

(10) G. Galiazzo, P. Bortolus, and G. Cauzzo, *Tetrahedron Letters*, 3717 (1966).

(11) M. P. Cava, S. C. Havlicet, A. Lindert, and R. J. Spangler, *ibid.*, 2937 (1966).

(12) N. C. Yang, G. R. Lenz, and A. Shani, *ibid.*, 2941 (1966).

(13) See, for example, G. E. Lewis and R. J. Mayfield, *Australian J. Chem.*, **19**, 1445 (1966).

(14) (a) M. P. Cava and R. H. Schlessinger, *Tetrahedron Letters*, 2109 (1964); (b) G. M. Badger, C. P. Joshua, and G. E. Lewis, *ibid.*, 3711 (1964); (c) F. B. Mallory and C. S. Wood, *ibid.*, 2643 (1965).

(15) See, for example, H. Linschitz and K. Grellmann, *J. Am. Chem. Soc.*, **86**, 303 (1964); W. Carruthers, *Chem. Commun.*, 272 (1966).

(16) Diphenyl sulfide is reported to give only cleavage products: W. Carruthers, *Nature*, **209**, 908 (1966); N. Kharasch and A. I. A. Khodair, *Chem. Commun.*, 98 (1967). Vinyl sulfides, however, have been observed to cyclize: S. H. Groen, R. M. Kellogg, and H. Wynberg, unpublished results.

(17) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

(18) M. J. Handelé, Meeting of the Royal Dutch Chemical Society, Amsterdam, Oct 1965. The synthesis and some properties of the di(thienyl)ethenes will be described in the thesis of M. J. Handelé, Groningen, 1967. We thank Mr. Handelé for making his results available to us.

(19) D. S. Rao and B. D. Tilak [*J. Sci. Ind. Res.* (India), **B16**, 65 (1957); *Chem. Abstr.*, **51**, 13841*i* (1957)] and O. Dann and M. Kokorudz, [*Chem. Ber.*, **91**, 181 (1958)] report a compound which they identify as benzo[1,2-*b*:4,5-*b*′]dithiophene but which has melting point and ultraviolet spectrum identical with those of our **4a**. Their mistaken structure assignment arose from an erroneous assumption of the direction of a ring closure reaction.

centered on 7.38 and 7.56 ppm. A singlet, relative area two protons, at 7.69 ppm composed the rest of the spectrum. The structure of the photolysis product was further confirmed by desulfurization with Raney nickel which yielded *o*-diethylbenzene, the product expected from **4a**.

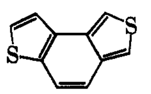
Isomers **1b–d** were subjected to photolysis under the same conditions used for **1a**. The expected methylated derivatives, **4b–d**, were obtained in yields varying from 50 to 70%. The ultraviolet spectra of **4b–d** were almost identical with those of **4a** (see Table I) and the nmr spectra showed the changes expected for methyl substitution; details of the nmr spectra are given in the Experimental Section.

TABLE I

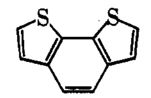
ULTRAVIOLET SPECTRA OF BENZODITHIOPHENES, THIENOBENZOFURAN, AND BENZODIFURAN IN CYCLOHEXANE

Compound	Absorption (log ε), mμ
Benzo[1,2-*b*:4,3-*b*′]-dithiophene (**4a**)	219 (4.47), 234 sh (4.11), 248 sh (4.09), 252 (4.16), 257 (4.10), 268 (3.95), 277 (4.11), 288 (4.29), 300 (4.20), 317 (3.53)
8-Methyl[1,2-*b*:4,3-*b*′]-dithiophene (**4b**)	212 (4.40), 240 (4.14), 247 sh (4.17), 252 (4.24), 257 sh (4.08), 269 (3.90), 282 (4.07), 292 (4.26), 304 (4.16), 319 (3.51)
7-Methyl[1,2-*b*:4,3-*b*′]-dithiophene (**4c**)	219 (4.45), 238 (4.16), 253 (4.19), 258 (4.16), 268 (4.01), 280 (4.15), 290 (4.32), 301 (4.22), 319 (3.59)
4-Methyl[1,2-*b*:4,3-*b*′]-dithiophene (**4d**)	220 (4.46), 236 sh (4.18), 248 sh (4.09), 251 (4.12), 256 sh (4.05), 268 (3.94), 279 (4.10), 289 (4.23), 300 (4.14), 318 (3.55)
Benzo[1,2-*b*:3,4-*b*′]-dithiophene (**5**)	205 (4.08), 223 (4.13), 248 sh (4.48), 255 (4.58), 275 (4.03), 286 (3.90), 296 (3.23), 307 (3.23), 315 (2.93), 320 (3.20)
Thieno[3,2-*e*]benzofuran (**10**)	211 (4.32), 271 (4.17), 280 (4.26), 294 (3.76), 300 (3.98), 305 (3.93), 311 (4.12)
Benzo[1,2-*b*:4,3-*b*′]-difuran (**11**)	215 (4.23), 261 (4.23), 269 (4.39), 279 (4.29), 294 (3.74)

Photocyclization of 1,2-di(2,3′-thienyl)ethene (**2**) could yield benzo[1,2-*b*:3,4-*b*′]dithiophene (**5**) by ring closure in the 2 position of the 3-substituted ring or, alternatively, the much less likely (see Discussion) benzo[1,2-*b*:3,4-*c*′]dithiophene (**6**) by ring closure in the 4 position of the 3-substituted ring. The product of the photolysis of **2** (eq 2) in benzene solution with 5 mole % of iodine was benzo[1,2-*b*:3,4-*b*′]dithiophene (**5**), mp 39.5°, picrate mp 152–153° (lit.[20] mp 43°, picrate mp 149°). The nmr spectrum in deuterioacetone consisted of four sets of doublets, $J = 5.4$ cps, centered at 7.42, 7.60, 7.61, and 7.80 ppm. The set at 7.60 ppm appeared to be slightly split as did the absorptions for the ethylene bridge protons at 7.83 ppm. The spectrum collapsed to three singlets in carbon tetrachloride. The nmr spectrum is thus compatible with structure **5** rather than benzo[1,2-*b*:3,4-*c*′]dithiophene (**6**). In the crude reaction mixture, a second small peak (*ca.* 4%) of slightly longer retention time than **5** was observed; this might possibly be a small amount of **6**, although no proof for this exists. Work-up gave only pure isomer **5**. The ultraviolet spectrum of **5** is shown in Figure 1, curve B.



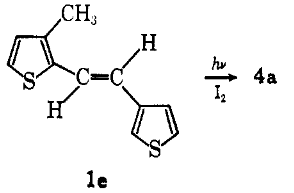
6



7

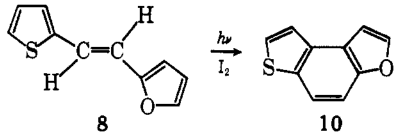
Irradiation of 1,2-di(3-thienyl)ethene (**3**) failed to yield upon work-up the expected benzo[2,1-*b*:3,4-*b*′]dithiophene (**7**) (eq 3). The main reaction observed was slow decomposition to form intractable material. Very small amounts of products were observed in the gas chromatograms but all attempts to isolate these failed. A variety of solvents and oxidizing agents were tried; iodine, oxygen, a mixture of iodine and oxygen, benzophenone, chloranil, selenium, benzoyl peroxide, mercuric oxide, cupric oxide, lead dioxide, and cupric chloride in ethanol[21] were used, but in no case were new products obtained upon working up the reaction mixtures. Increased temperatures failed to aid ring closure.

Isomer **1e** underwent reaction upon photolysis to form **4a** (eq 4). The reaction was slower than with **1a–d** and proceeded in low yield but gave no other detectable products. The methyl group appeared to be expelled in the aromatization step of the reaction; no **1a** could be observed during photolysis. No attempts were made to trap products derived from the eliminated methyl group.



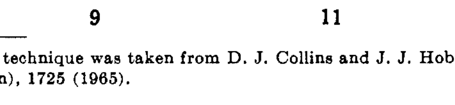
1e (4)

Photolysis of 1-(2-furyl)-2-(2-thienyl)ethene (**8**) in the presence of iodine and oxygen produced in 42% yield thieno[3,2-*e*]benzofuran (**10**) (eq 5). The ultraviolet spectrum of previously unknown **10**, mp 57–58°, is shown in Figure 1, curve A. The nmr spectrum in hexadeuterioacetone showed the protons of the furan ring as a pair of doublets, $J = 2.2$ cps, at 7.20 and 7.88 ppm, the protons of the thienyl ring as a broad singlet at 7.68 ppm, and the protons of the ethylene bridge as a set of doublets, $J = 8.9$ cps, at 7.53 and 7.82 ppm. The doublets from the ethylene bridge proton at 7.53 ppm and the furyl proton doublet at 7.20 ppm exhibited a long-range coupling of 0.8 cps.



8 **10** (5)

First attempts to cyclize 1,2-di(2-furyl)ethene (**9**) resulted in decomposition. It was found, however, that, in ethanol as solvent with cupric chloride as oxidant,[21] photochemical ring closure occurred (eq 6)



9 **11** (6)

---

[20] D. S. Rao and B. D. Tilak, *J. Sci. Ind. Res.* (India), **B13**, 829 (1954); *Chem. Abstr.*, **50**, 933*i* (1956).

[21] This technique was taken from D. J. Collins and J. J. Hobbs, *Chem. Ind.* (London), 1725 (1965).

to form previously unknown benzo[1,2-*b*:4,3-*b*′]difuran, mp 39.5–40°, isolated in 24% yield. The nmr spectrum of **11** in hexadeuterioacetone consisted of two sets of doublets, $J = 2.1$ cps, centered at 7.10 and 7.87 ppm, and a singlet at 7.49 ppm. The integration ratio of the doublets to the singlet was 2:1. The doublet at 7.10 ppm was very slightly broadened. The ultraviolet spectrum of **11** is shown in Figure 1, curve D.[22]

The progress of the reactions could be readily followed by gas chromatography. The reactions of **1a**, **2**, and **3** were examined most carefully. With all three isomers in the beginning period of the photolysis, some of the *trans* isomer disappeared and was approximately accounted for in a peak of shorter retention time assigned to the *cis* isomer. If photolysis was stopped at this point, the new material in the presence of iodine underwent slow thermal reversion to the *trans* isomer. No attempt was made to isolate and characterize the *cis* isomers from **1a**, **2**, and **3**. Attempts along this line are reported elsewhere.[18] Further irradiation of **1a** or **2** led to the formation of a new peak of longer retention time than either the *cis* or *trans* isomers. The retention time of the third peak was identical with that of the isolated ring closure products. Isomer **3** failed to produce in significant amounts a third peak of the retention time estimated from those of **4a** and **5**; only *cis–trans* isomerism was observed.

A transitory yellow color had been noted during photolysis experiments and had been tentatively assigned to dihydro intermediates. Scouting experiments to record the absorption spectrum of the intermediates were carried out with 1,2-di(3-thienyl)ethene (**3**) (which fails to give a phenanthrene derivative upon photolysis). Photolyses were carried out in ultraviolet cells using predominantly 350-mμ light. Brief irradiation of a degassed cyclohexane solution of **3** led to the formation of a yellow solution in which a clearly defined absorption at 420 mμ could be observed. Exposure of the solution to visible light from a table lamp led to rapid disappearance of the yellow color and disappearance of the ultraviolet absorbance. The color could be regenerated by exposure to 350-mμ light. Exposure to air or mild warming caused only a slow decrease in absorption. Solutions of the intermediate were fairly stable for periods of 12–15 hr in the dark. Irradiation of 1,2-di(2,3′-thienyl)ethene (**2**) in degassed cyclohexane solution gave a transitory intermediate with a well-resolved ultraviolet maximum at 390 mμ. This material was also sensitive to visible light but was reasonably stable at room temperature in the dark. Irradiation of a degassed cyclohexane solution of 1,2-di(2-thienyl)ethene (**1a**) led to formation of an intermediate of which only the long wavelength tail was observable. The absorption maximum was estimated to lie at *ca.* 360 mμ. Photolysis of 1-phenyl-2-(2-thienyl)ethene (**12**) gave an intermediate with $\lambda_{\max}$ at 415 mμ.[23] Extended photolysis of the di(thienyl)ethenes led to precipitate formation as did prolonged standing of the intermediates at room temperature.

The ring closure of **1a** was the only reaction which lent itself readily to quantum yield determination. Precipitate formation prevented accurate determination of light absorption in other cases. Under conditions where all light was absorbed during reaction, the quantum yield for the conversion of a 92% *cis*, 8% *trans* photostationary state of **1a** to **4a** at 350 mμ in benzene solution with 5 mole % iodine was calculated to be 0.056 ± 0.003; after correction for absorption by the *trans* isomer, a value of 0.076 was obtained for Φ. The rate of conversion of *cis* **1a** to **4a** was found to be linear through 90% reaction and the value of Φ was found to be independent of the concentration of starting material over the concentration range studied.

Stilbene is known to produce a cyclobutane photodimer at high concentration.[24] This reaction was duplicated by us with a 0.8 *M* solution of stilbene using 350-mμ light. However, under identical conditions no evidence of dimerization could be found with the di(thienyl)ethenes. Attempts to effect cross dimerization between mixtures of stilbene and **4a** likewise failed to yield *any* product. Photodimerization was attempted with 1-phenyl-2-(2-thienyl)ethene (**12**) in which any inhibiting effect of a thienyl group should be lessened, but again no trace of dimerization was observed.

Discussion

The mechanism of these photochemical ring closures is probably akin to those discussed by Mallory[4a] for the liquid-phase ring closure of stilbenes. With representative isomer **1a**, the *trans* isomer is photochemically isomerized to the *cis* isomer which has been tentatively identified in the photolysis mixtures (see Results). The *cis* isomer upon further photochemical excitation undergoes ring closure, probably in the first excited singlet state, to form a dihydrophenanthrene derivative. This dihydrophenanthrene may photochemically or possibly thermally revert to the *cis* isomer or, in the presence of an oxidizing agent, one allylic hydrogen may be abstracted followed by the loss of the second hydrogen atom to form the phenanthrene derivative. The mechanism may be schematically represented as in eq 7. The thermal stability of the intermediates (Results) indicates that the rate of thermal conversion of the intermediate back to *cis* is negligibly small compared with the photochemical rate, k_{-1}.

$$\textit{trans} \rightleftharpoons \textit{cis} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{diH} \xrightarrow{k_{\text{oxidn}}} \text{product} \tag{7}$$

The mechanism set forth in eq 7 for the conversion **1a** → **4a** indicates that the quantum yield for formation of product is a function of the three rate constants, k_1, k_{-1}, and k_{oxidn}.[4d] If the rate of photochemical conversion of the intermediate back to *cis* is of a comparable magnitude with k_{oxidn}, the "quantum" yield for the conversion of *cis* to product will be a variable of the concentration of *cis* isomer. This conclusion is readily derived from steady-state kinetics. Srinivasan and Powers[5] have reported a concentration dependence for stilbene cyclization at 254 and 313 mμ in solution at concentrations near 10^{-3} *M;* Stegemeyer[4e] does not report such an effect at 313 mμ at concentrations near 10^{-5} *M*. No concentration effect is noted in our limited data (see

---

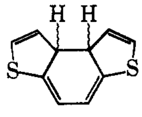
[22] The new condensed ring systems described here have been submitted for pharmacological testing.

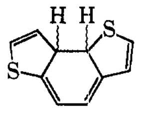
[23] The cyclization of this compound has been reported.[7]

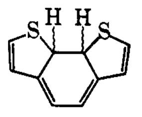
[24] H. Schechter, W. J. Link, and G. V. D. Tiers, *J. Am. Chem. Soc.*, **85**, 1601 (1963).

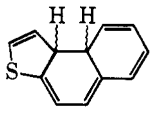
Experimental Section). This, coupled with the observation that the disappearance of *cis* isomer was zero order through 90% reaction, suggests that in our system k_{oxidn} is much larger than k_{-1} and that the quantum yield found accurately approximates the photoefficiency of *cis* ring closure. The value obtained, 0.076 (after correction for *trans* absorption), is close to Stegemeyer's[4e] value for stilbene at 313 mμ, 0.071. This agreement is, however, only fortuitous. The cyclization of **1a** is thus approximately as efficient as that of *cis*-stilbene; it can, however, proceed at a longer wavelength at a reasonable rate owing to the red shift of absorption of **1a** compared with stilbene. Cyclizations of the other compounds mentioned in this publication proceeded at roughly the same rate as that of **1a**.

Transitory species in the photocyclizations of stilbene and stilbene derivatives have often been observed by ultraviolet spectroscopy. These spectra have been assigned to the dihydrophenanthrene intermediates.[4a,c,d] Substantial support for this assignment has recently been obtained by the direct observation by nmr as well as ultraviolet spectroscopy of an analogous intermediate bearing methyls in place of hydrogens at the 9,10 positions.[25] Analogously, the transitory intermediates observed by us in the cyclizations of **1a**, **2**, **3**, and **12** are very likely the dihydro derivatives **13**, **14**, **15**, and **16**. Alternative structures derived by cyclization across the 4 position of the 3-substituted thiophene ring(s) are possible for **14** and **15**. The structure proposed for **14** is supported by the shift of the absorption maximum to longer wavelength over **13** (longer conjugated system) and by the derived product, **5**. The shift to still longer absorption wavelengths in the intermediate derived from **4** strongly supports structure **15** rather than any structure derived from cyclization across the 3,4 positions of the thiophene ring.[26,27] *trans* stereochemistry of the bridge hydrogens in dihydrophenanthrene intermediates has been postulated from analogy with vitamin D work;[1,4] this assignment may well have theoretical justification.[28] Our results allow no new conclusions concerning stereochemistry of the intermediates.[29]


13

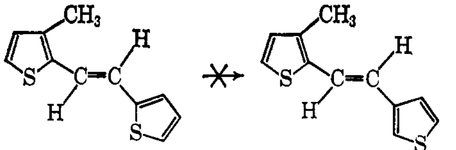

14


15


16

When the ethylenic bond is attached to the 3 position of the thiophene nucleus, the yields of cyclization products decrease. Thus **1a** gives a virtually quantitative yield of product, **2** gives only a 47% yield on cyclization, and **3**, where both thiophene rings are substituted in the 3 position, fails to yield any phenanthrene derivative. Since all of these di(thienyl)ethenes form a dihydro derivative on irradiation, the failure to obtain products must come from a problem in the oxidation step. Examination of the structures of the dihydro intermediates coupled with a consideration of the mechanism of oxidation provides a ready explanation of these observations. The mechanism of oxidation must involve abstraction of a hydrogen atom from the dihydro intermediate followed by either β elimination of the second hydrogen atom or a second abstraction reaction.[4a,30] This process can occur with **13** with no difficulty. However, in intermediate **15** which yields no cyclization product, abstraction of a hydrogen leads to a β-thio-substituted radical. These types of radicals undergo very ready elimination of the sulfur as a thiyl radical.[31] In this case the formation of a benzenoid system and the concomitant loss of strain would serve as powerful driving forces for elimination. The radical obtained upon elimination, a vinylthiyl radical, could directly polymerize or form an extremely unstable vinyl sulfide (or thioaldehyde) which would be expected to be very short-lived under the reaction conditions. These species are probably the precursors of the intractable material formed during photolysis. A similar situation exists with intermediate **14** derived from **2**. If the hydrogen α to sulfur is abstracted, elimination cannot occur and product **5** is obtained. However, if the proton β to the sulfur is abstracted, elimination and formation of polymer is to be expected. This prediction is seen in the lowered yield of product.[32]

The extremely involved photoisomerizations that occur with arylthiophenes and dithienyls, which have been extensively studied by us,[27] prompted our very close examination of the di(thienyl)ethenes for any evidence of similar rearrangements. The closest gas chromatographic examination of the photolyses of **1a–d**, **2**, or **3** under conditions capable of separating these three isomers failed to provide any evidence for rearrangement from one isomer to another. Isomer **1e** was synthesized in the hope that blocking one of the positions at which ring closure must occur would perhaps force a rearrangement (eq 8). No evidence of rearrangement was obtained but rather the only reaction seemed to be ring closure to **4a** with expulsion of the



1e (8)

---

[25] K. A. Muszkat, D. Gegiou, and E. Fischer, *Chem. Commun.*, 447 (1965).

[26] Ring closure across the 3,4 positions of the 3-substituted rings in either **2** or **3** would not only produce a shorter conjugated system but would require a stable intermediate having an expanded valence shell for sulfur or, alternatively, a "Dewar" structure for the thiophene ring. Such an intermediate would not be expected, on the basis of current information,[27] to display such stability.

[27] (a) H. Wynberg and H. van Driel, *J. Am. Chem. Soc.*, **87**, 3998 (1965); (b) H. Wynberg and H. van Driel, *Chem. Commun.*, 204 (1966); (c) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Am. Chem. Soc.*, **88**, 5047 (1966).

[28] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965), and subsequent publications. The suggestion that these rules might apply in stilbene photocyclizations was first made by Mallory.[14c]

[29] The thermal and oxidative stability of our dihydro derivatives suggests that fairly high concentrations could be built up in the absence of visible light. Direct observation and assignment of stereochemistry by nmr spectroscopy might be possible with properly designed systems. Experiments in this direction are being carried out.

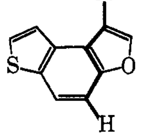
[30] Combination of a radical with I· followed by concerted elimination of HI is a possibility which cannot be eliminated on the basis of the present evidence.

[31] For studies of thiyl radical eliminations, see E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, **31**, 3366 (1966); J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *J. Am. Chem. Soc.*, **88**, 1257 (1966). For typical references on the reversible additions of thiyl radicals, see C. Walling and W. Helmreich, *ibid.*, **81**, 1144 (1959); E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, **30**, 2867 (1965).

[32] It is true that in **13** derived from **1a** there is a sulfur atom β to the radical generated. However, elimination of this radical would lead to a severely strained cyclic allene. This reaction would not be expected and does not occur to a significant extent.

methyl substituent. This particular type of alkyl expulsion has been reported with *o*-methyl-substituted 2-styrylthiophenes and 3-styryl benzothiophenes,[7a,b] with 2-styryl-3-methylpyridine,[9b] and with *o*-methyl-substituted azobenzenes.[13] The reaction is reported not to take place with *o*-methyl or halo-substituted stilbenes but may occur to a small extent with *o*-methoxystilbenes.[6] The most probable mechanism of elimination is abstraction of the tertiary allylic hydrogen followed by β elimination of the methyl group from the resultant radical.[33] The alkyl group is virtually parallel to the π lobe of the radical and is in a perfect conformation for elimination; moreover, the loss of strain may serve as further driving force. It is possible that aromatization of dihydro derivatives may at least partially occur by a similar elimination of the second hydrogen atom.

Some properties of the condensed ring systems obtained are suggested by their nmr spectra. The chemical shifts of individual protons were quite solvent sensitive and better separated spectra were usually obtained in hexadeuterioacetone rather than carbon tetrachloride. Examination of all the unsubstituted ring systems formed in this study (**4a**, **5**, **10**, and **11**) indicates that no appreciable change occurs in the coupling constants in the thienyl or furyl rings upon cyclization. Coupling constants for the protons in the thienyl ring of **4a**, **5**, and **10** vary from 5.2 to 5.5 cps, in excellent agreement with the value of 4.90–5.80 cps for J_{23} coupling in thiophene derivatives.[34] A value of J_{23} = 1.8–2.0 cps is given for furan and substituted furans[35] again corresponding well with the values of 2.2 cps found in **10** and 2.1 cps in **11** for the furyl rings. Interestingly, in the one compound where it is observable, **10**, the two protons of the ethylenic bridge couple to the extent of 8.9 cps, a value of comparable magnitude to normal *ortho* coupling in a benzene ring;[35] this may suggest considerable benzenoid character of the center ring. The long-range coupling observed in **10** between presumably one proton of the furan ring with a proton of the ethylene bridge is apparently related to the long-range coupling reported in benzofuran,[36a,b] benzothiophene,[36a] indene,[36a] indole,[36a] and isoquinoline.[36b] The highest field peak of **10** virtually reproduced the published spectrum of the 3-proton of benzofuran.[36b] The 0.98-cps coupling in benzofuran has been proved to be due to 3,7 coupling[36b] and undoubtedly a similar effect is responsible for the long-range coupling in **10**. A similar coupling of 0.7–0.9 cps has been reported for benzothiophene[36c] and substituted benzothiophenes,[36a] but interestingly enough the coupling is only observed with the furyl ring in **10**. Such an effect might be operative in **5** which did show broadening of one doublet plus the ethylene bridge absorbances; no accurate estimation of the coupling could be made. Long-range coupling cannot be observed in **11** or **4a** because of symmetry effects. In methyl-substituted isomers **4b–d** allylic couplings (see Experimental Section) of the methyl protons with ring protons of 0.9, 1.6, and 0.9 cps, respectively, were seen. These are of a similar magnitude to those reported for methylthiophenes.[37]



10

$J_{H,H}$ = 0.8 cps

The ultraviolet spectra of the different systems as shown in Figure 1 are of considerable interest. The spectra of **5** (curve B) and phenanthrene (not shown) resemble each other in the shape and nature of fine structure. On the other hand, **10** (curve A) bears resemblance to that of benzothiophene (not shown). The inclusion of an extra ring seems only to distort the spectrum shape. Neither phenanthrene nor benzothiophene serve as models for **4a** or **11**. The spectra of these two compounds resemble each other somewhat; no good comparison compound presents itself. No marked correlation with the published spectrum of benzofuran[38] appears to exist.

Further work on the synthetic applications of photochemical ring closures as well as the chemistry of some of the systems described in this paper is being carried out in these laboratories.

Experimental Section

Ultraviolet spectra were determined with a Zeiss PMQ II and are reported in millimicrons. Nmr spectra were obtained with a Varian A-60 using tetramethylsilane (TMS) as an internal standard. Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. Gas chromatography was done with a F & M Model 810 gas chromatograph. Merck activity 1 alumina was used for column chromatography.

Photolyses were carried out with a Hanau Q-700 unfiltered high pressure mercury lamp equipped with a quartz jacket or with a smaller Hanau S-81 unfiltered high pressure mercury lamp. About 500–600 ml of solution could be irradiated with the Q-700 and 100–125 ml with the S-81. The apparatus was designed so that solutions could be effectively stirred and reactions could be run under nitrogen if desired. Temperatures were maintained at 20°. Good results were also obtained using a Rayonet commercial reactor equipped with a battery of lamps giving a relatively narrow emission band with maximum emission at 350 mμ. For some experiments, lamps with 254-mμ maximal output were used in the same reactor. Temperatures were maintained at *ca.* 40°.

Preparation of Phosphonates.—Michaelis–Arbuzov reaction[39] of 2-chloromethylthiophene[40] with neat trimethyl- and triethylphosphite for *ca.* 5 hr gave, respectively, upon distillation **dimethyl-2-thienylphosphonate** (**17**), bp 152–154° (10 mm), $n^{20}{}_D$ 1.5200, and **diethyl-2-thienylphospnhoate** (**18**), bp 180–184° (31 mm), $n^{20}{}_D$ 1.5037. Similarly, reaction of 3-bromomethylthiophene[41] and chloromethylfuran[42] with trimethylphosphite gave **dimethyl-3-thienylphosphonate** (**19**), bp 164–172° (24 mm),

---

(33) C. Walling, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 440–447.

(34) S. Gronowitz, *Advan. Heterocyclic Chem.*, **1**, 8 (1963), and references cited therein.

(35) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press Ltd., London, p 789.

(36) (a) J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 590 (1963); 981 (1964); (b) P. J. Black and M. L. Hefferman, *Australian J. Chem.*, **18**, 353 (1965); **19**, 1287 (1966); (c) K. Takahashi, I. Ito, and Y. Matsuki, *J. Chem. Soc. Japan*, **39**, 2316 (1966).

(37) R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, **16**, 563 (1960).

(38) G. M. Badger, B. J. Christie, H. J. Rodda, and J. M. Pryke, *J. Chem. Soc.*, 1179 (1958).

(39) G. M. Kosolapoff, "Organic Phosphorus Compounds," 1st ed, John Wiley and Sons, Inc., New York, N. Y., 1950.

(40) K. B. Wiberg and H. F. McShane, *Org. Syn.*, **29**, 31 (1949).

(41) E. Campaigne and B. F. Tullar, *ibid.*, **33**, 96 (1953).

(42) R. Lukeš and V. Dienstbierová, *Chem. Listy*, **48**, 280 (1954); *Chem. Abstr.*, **49**, 2422*g* (1953).

$n^{20}\mathrm{D}$ 1.5206, and **dimethyl-2-furylphosphonate (20)**, bp 135–138°, (12 mm), $n^{20}\mathrm{D}$ 1.4768, respectively. Yields were from 25 to 70%.

General Procedure for Synthesis of Thienyl- and Furylethylenes.—The appropriate aldehyde (0.05 mole) and phosphonic ester (0.05 mole) and 50 ml of sodium dried dimethoxyethane were put in a 100-ml flask. Sodium hydride (2.4 g, 0.05 mole) as a 50% suspension in mineral oil was added and a reflux condenser attached to the flask. Evolution of hydrogen began immediately upon warming to 60° and the reaction was completed by allowing it to reflux 0.5 hr. After cooling, the reaction mixture was poured in 500 ml of water. In most cases the product precipitated and was collected by filtration. In a few cases an oil formed and extraction with ether was necessary. Removal of the ether left a solid product. Crude products were recrystallized from ethanol. Steam distillation, column chromatography, and sublimation were occasionally used as further purification techniques where necessary.

***trans*-1,2-Di(2-thienyl)ethene (1a)** was prepared from the reaction of **18** with 2-thienoaldehyde. The product, mp 133–134° (lit.[43] 132–133.5°), ultraviolet (cyclohexane), λ_{max} 338 (log ε 4.45), was obtained in 68% yield.

Anal. Calcd for $C_{10}H_8S_2$: C, 62.46; H, 4.19; S, 33.35. Found: C, 62.47; H, 4.27; S, 33.56.

***trans*-1-(2-Thienyl)-2-(4-methyl-2-thienyl)ethene (1b)** was prepared from reaction of **17** with 4-methyl-2-thienoaldehyde.[44] The product, mp 101–101.5°, ultraviolet (cyclohexane), λ_{max} 334 (log ε 4.44), was obtained in 41% yield.

Anal. Calcd for $C_{11}H_{10}S_2$: C, 64.03; H, 4.89; S, 31.08. Found: C, 64.29; H, 5.02; S, 31.15.

***trans*-1-(2-Thienyl)-2-(5-methyl-2-thienyl)ethene (1c)** was prepared from the reaction of **17** with 5-methyl-2-thienoaldehyde.[45] The product, mp 61.5–62.5°, ultraviolet (cyclohexane), λ_{max} 346 (log ε 4.43), was obtained in 60% yield.

Anal. Calcd for $C_{11}H_{10}S_2$: C, 64.03; H, 4.89; S, 31.08. Found: C, 64.32; H, 4.93; S, 31.43.

1,2-Di(2-thienyl)propene-1 (1d) was synthesized in 14–25% yield as a *cis–trans* mixture by reaction of **17** with 2-acetylthiophene. The major reaction product was a phosphonate-containing material. Synthesis by ordinary Wittig techniques as described in the literature[43] gave a *cis–trans* mixture in 40% yield. This mixture was used for cyclization reactions. For identification purposes a pure isomer, presumably with the thienyl groups *trans*,[18] was crystallized out by cooling the *cis–trans* mixture in a pentane solution to −80°. Material, mp 42–42.5°, ultraviolet (cyclohexane), λ_{max} 327 (log ε 4.34), was obtained.

Anal. Calcd for $C_{11}H_{10}S_2$: C, 64.03; H, 4.89; S, 31.08. Found: C, 64.24; H, 4.91; S, 31.30.

***trans*-1-(2-Thienyl)-2-(3-methyl-2-thienyl)ethene (1e)** was prepared from the reaction of **18** with 3-methyl-2-thienoaldehyde.[46] The product, mp 60–60.5°, ultraviolet (cyclohexane), λ_{max} 346 (log ε 4.43), was obtained in 40% yield.

Anal. Calcd for $C_{11}H_{10}S_2$: C, 64.03; H, 4.89; S, 31.08. Found: C. 64.42; H, 4.85; S, 30.21.

***trans*-1,2-Di(2,3′-thienyl)ethene (2)** was prepared from the reaction of **17** with 3-thienoaldehyde.[46] The product, mp 137–137.5°, ultraviolet (cyclohexane), λ_{max} 316 (log ε 4.45), was obtained in 40% yield.

Anal. Calcd for $C_{10}H_8S_2$: C, 62.46; H, 4.19; S, 33.35. Found: C, 62.83; H, 4.20; S, 33.43.

***trans*-1,2-Di(3-thienyl)ethene (3)** was obtained from the reaction of **19** with 3-thienoaldehyde. The product, mp 166.5–167°, ultraviolet (cyclohexane), λ_{max} 291 (log ε 4.50), 304 (4.38), was obtained in 46% yield.

Anal. Calcd for $C_{10}H_8S_2$: C, 62.46; H, 4.19; S, 33.35. Found: C, 62.48; H, 4.23; S, 33.26.

***trans*-1-(2-Furyl)-2-(2-thienyl)ethene (8)**[43] was obtained from the reaction of **17** with 2-furylaldehyde. The product, mp 78–79° (lit.[43] 79.5–80°), ultraviolet (cyclohexane), λ_{max} 333, (log ε 4.39), was obtained in 43–65% yield.

***trans*-1,2-Di(2-furyl)ethene (9)** was prepared in 52% yield from the reaction of **20** with 2-furylaldehyde.[43] The material had mp 99–101° (lit.[43] 99.5–100°), ultraviolet (cyclohexane), λ_{max} 321 (log ε 4.56), 338 (4.52).

Photocyclizations of 1,2-di(2-thienyl)ethene (1a) and derivatives (1b–d) were carried out at 20° in the Q-700 reactor. Approximately 5 mmoles of the di(thienyl)ethene was dissolved in 550 ml of benzene with *ca.* 1 mole % I_2 and irradiated under an air atmosphere with vigorous stirring for 2–3 hr. The progress of the reaction was followed by glpc (4-ft Apiezon L, 270°) or ultraviolet spectroscopy. The purple color of the iodine was still present after reaction. The solvent was evaporated and the product purified by chromatography over Al_2O_3 with petroleum ether (bp 40–60°) containing increasing amounts of benzene as eluent. Further purification was accomplished by sublimation under vacuum for higher melting compounds or recrystallization from petroleum ether for lower melting isomers.

Benzo[1,2-*b*:4,3-*b*′]dithiophene (4a) was obtained in 70% yield from cyclization of **1a** in the Q-700 reactor; a yield of 90% after work-up was obtained using the Rayonet reactor with a 350-mμ lamp. The product had mp 117–118°, picrate 148.5–149.5° (lit.[19] 117–118°, picrate 148–149°). The nmr spectrum is reported in the Results and the ultraviolet spectrum in Figure 1 and Table I.

Anal. Calcd for $C_{10}H_6S_2$: C, 63.12; H, 3.18; S, 33.77. Found: C, 63.21; H, 3.41; S, 32.80.

The cyclization product (0.5 g) was treated with 10 g of Raney nickel in 25 ml of refluxing ethanol for 45 min. The reaction mixture was filtered and diluted with 100 ml of water. The aqueous solution was extracted three times with chloroform, the chloroform layer dried over $MgSO_4$, and the chloroform removed to yield 0.18 g of liquid with an infrared spectrum identical with that of *o*-diethylbenzene.

8-Methylbenzo[1,2-*b*:4,3-*b*′]dithiophene (4b) was obtained in 69% yield from **1b**. The product had mp 100–102°, picrate 157–158°. The nmr spectrum in CCl_4 consisted of a set of doublets, J = 5.5 cps, at 7.37 and 7.80 ppm, a broadened singlet (area 1 proton) at 6.99 ppm, a sharp singlet at 7.61 ppm (2 protons, ethylene bridge), and the methyl protons at 2.77 ppm as a doublet, J = 1.6 cps. The ultraviolet spectrum is reported in Table I.

Anal. Calcd for $C_{11}H_8S_2$: C, 64.66; H, 3.95; S, 31.39. Found: C, 64.63; H, 3.97; S, 31.08.

7-Methylbenzo[1,2-*b*:4,3-*b*′]dithiophene (4c) was obtained in 68% yield from **1c**. The product had mp 79–80°, picrate 119–120°. The nmr spectrum in CCl_4 consisted of a set of doublets, J = 5.5 cps, at 7.29 and 7.45 ppm, a broad singlet at 7.14 ppm (1 proton), the ethylene bridge protons as sharp singlet at 7.61 ppm, and the methyl group as a doublet, J = 0.9 cps, at 2.56 ppm. The ultraviolet spectrum is reported in Table I.

Anal. Calcd for $C_{11}H_8S_2$: C, 64.66; H, 3.95; S, 31.39. Found: C, 65.05; H, 4.04; S, 31.24.

4-Methylbenzo[1,2-*b*:4,3-*b*′]dithiophene (4d) was obtained in 50% yield from the *cis–trans* mixture of **1d**. The product had mp 82–82.5°, picrate 148–150°. The nmr spectrum in hexadeuterioacetone consisted of four sharp sets of doublets, J = 5.2 cps, at 7.51, 7.61, 7.71, and 7.77 ppm. A broadened singlet (one proton) was observed for the ethylene bridge proton at 7.55 ppm and the methyl group gave a doublet, J = 0.9 cps, at 2.55 ppm. The ultraviolet spectrum is reported in Table I.

Anal. Calcd for $C_{11}H_8S_2$: C, 64.66; H, 3.95; S, 31.39. Found: C, 64.55; H, 4.02; S, 31.33.

Benzo[1,2-*b*:3,4-*b*′]dithiophene (5) was obtained in 32% yield from photolysis of **2** in the general method described above. The product was obtained in 47% yield when 1 mmole was irradiated in 125 ml of benzene with 5 mole % I_2 at 20° under degassed conditions in the S-81 lamp for 4 hr. The product had mp 39.5–40°, picrate 151–153° (lit.[20] 43°, picrate 149°). The nmr spectrum is reported in the Results and the ultraviolet spectrum in Figure 1 and Table I.

Anal. Calcd for $C_{10}H_6S_2$: C, 63.12; H, 3.18; S, 33.70. Found: C, 63.27; H, 3.31; S, 33.27.

Attempted cyclization of 1,2-di(3-thienyl)ethene (3) was carried out with 100–200-mg quantities of **3** in 130 ml of benzene. Oxidation was attempted using as oxidizing agents 7 mg of I_2, 100 mg of quinone, 140 mg of chloranil, 50 mg of benzophenone, 200 mg of benzoyl peroxide, 200 mg of mercuric oxide, 200 mg of lead dioxide, 200 mg of cuprous oxide, and 40 mg of selenium, respectively. Oxidations were attempted with cyclohexane as solvent and iodine as oxidant and also with cupric chloride in ethanol. Examination of reaction mixtures by glpc showed *trans–cis* isomerization with establishment of a photostationary state of *ca.* 75% *cis* isomer. Traces of products could be seen in the gas chromatograms but no product was isolable. Irradiation

---

(43) Y. K. Yur'ev and D. Eckhardt, *Zh. Obshch. Khim.*, **31**, 3526 (1961); *Chem. Abstr.*, **57**, 4621*b* (1962).

(44) J. Sicé, *J. Org. Chem.*, **19**, 70 (1954).

(45) W. J. King and F. F. Nord, *ibid.*, **13**, 235 (1948).

(46) S. Gronowitz, P. Moses, A. Hörnfeldt, and R. Håkansson, *Arkiv Kemi*, **17**, 165 (1961).

of a solution of 800 mg of **3** in 550 ml of benzene with 80 mg of selenium for 2 hr in the Q-700 reactor gave a large amount of decomposition products. Work-up gave 135 mg of a *cis–trans* mixture of starting material and no other isolable products.

Photocyclization of 1-(2-thienyl)-2-(3-methyl-2-thienyl)ethene was carried out at 20° with the S-81 lamp with 1 mmole dissolved in 125 ml of benzene without added I_2 (to attempt to induce rearrangement, see Discussion) for 23 hr. Glpc (4-ft Apiezon L, 270°) showed one new product besides starting material and *cis* isomer. Isolation by column chromatography gave in 6% yield product, mp 117–118°, which was identical in all respects with benzo[1,2-*b*:4,3-*b*′]dithiophene (**4a**).

Thieno[3,2-*e*]benzofuran was obtained in 42% yield when 1 mmole of **8** dissolved in 125 ml of benzene with 5 mole % I_2 was irradiated for 4 hr under degassed conditions with the S-81 lamp. A yield of 33% was obtained when 5 mmoles in 550 ml of benzene with 1 mole % I_2 was irradiated in the Q-700. The product had mp 57–58°; the nmr spectrum is reported in the Results and the ultraviolet spectrum in Figure 1 and Table I.

Anal. Calcd for $C_{10}H_6SO$: C, 68.94; H, 3.47; S, 18.41. Found: C, 68.71; H, 3.54; S, 18.15.

Photocyclization of 1,2-di(2-furyl)ethene (**9**) failed to occur in good yield when I_2 was used as oxidant. Better results were obtained when **9** (3.7 mmoles) was dissolved in 550 ml of absolute ethanol with anhydrous $CuCl_2$ (1.26 g, 9.6 mmoles) and I_2 (0.04 g, 0.32 mmole) and irradiated 5.5 hr in the Q-700.[21] The solvent was carefully removed, avoiding excessive warming of the product. Water was added and the solution extracted with petroleum ether and the organic layer dried over $MgSO_4$. After careful removal of the petroleum ether, an oil remained which was chromatographed over Al_2O_3 in the usual manner. A colorless crystalline product (140 mg, 24% yield) was obtained, mp 39.5–40° after recrystallization from pentane. The material was identified as benzo[1,2-*b*:4,3-*b*′]difuran by the nmr spectrum (Results) and ultraviolet spectrum (Figure 1 and Table I).

Anal. Calcd for $C_{10}H_6O_2$: C, 75.94; H, 3.82. Found: C, 75.30; H, 3.78.

Attempted Photodimerizations.—Saturated solutions (*ca.* 130 g/l., 0.8 *M*) of *trans*-stilbene, **1a**, **3**, and **12** were irradiated in benzene solution. Quartz tubes were filled with *ca.* 4 ml of solution and irradiated for 24 hr with 350-mμ light. Stilbene was converted to dimers in high yield under these conditions but **1a**, **3**, and **12** yielded only a mixture of *trans–cis* isomers and small amounts of cyclization products.

Determination of quantum yields at 350 mμ were carried out using the photochemical transformation of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid as an actinometer.[47] A solution of pure *o*-nitrobenzaldehyde (1 g, 1.32×10^{-2} *M*) was dissolved in 500 ml of absolute ethanol and sulfolane (which was independently shown to be unreactive to photolysis) was added as an internal standard. The well-stirred solutions were irradiated at *ca.* 40° using 350-mμ commercial lamps. Samples were taken at 5-min intervals and the rate of disappearance of aldehyde followed by gas chromatography (diethylene glycolsuccinate, 170°, or SE-30 at 150°). Reaction rates were determined by extrapolation to zero time (curves were linear through *ca.* 20% reaction). A quantum yield of 0.5 was taken in calculating the intensity of absorbed light.

Photolysis of **1a** in 500 ml of benzene with 50 wt % sulfolane (based on **1a**) and 5 mole % I_2 was carried out under conditions identical with those used for the actinometer. Samples were taken at 10–20-min intervals and analyzed by glpc (DEGS, 190°). A period of *ca.* 15 min was necessary to establish the photostationary state of 92% *cis* to 8% *trans* (the same photostationary state was formed with or without iodine; in the presence of iodine the *cis* slowly reverted thermally to the *trans*). After this time a plot of disappearance of *cis* (or appearance of **4a**) was absolutely linear through 90% reaction. Calculation of quantum yield was made assuming direct conversion of *cis* to **4a** (see Results for comments on this technique). The values obtained are given in Table II. A correction factor for absorption by *trans* isomer was made by taking into account the absorption of the *cis* isomer (obtained by subtracting the known absorption of the 8% of *trans* isomer at the photostationary state) and the pure *trans* isomer together with the spectral distribution of the lamps as reported by the manufacturer. In this manner it was calculated that 26% of the incident light was absorbed by the *trans* isomer. This gives a corrected value of Φ = 0.076. This correction is nearly accurate because all light is absorbed by the system during photolysis and the same stationary state is maintained.

TABLE II

$M \times 10^3$	Φ
10.0	0.055
3.74	0.057
2.50	0.060
1.38	0.050
Av	0.056

Detection of dihydro intermediates was done with 0.005 *M* solutions of the appropriate compound in cyclohexane. An ultraviolet cell equipped with a gas-tight Teflon plug was filled with solution and degassed by five freeze–thaw cycles. The degassed cell was irradiated in the Rayonet reactor with 350-mμ light for *ca.* 10 min. The solutions were yellow after this time and a new peak appeared in the ultraviolet region. The color and ultraviolet absorption rapidly disappeared upon exposure to visible light. Exposure to oxygen caused only a very slow decrease in absorption and solutions could be kept overnight with little absorption change, although a precipitate slowly formed in some cases. A solution of the dihydro derivative from 1,2-di(3-thienyl)ethene prepared in larger volume was concentrated at low temperature by evaporation of solvent. Little change in extinction was noted. With 1,2-di(3-thienyl)ethene a peak was observed with λ_{max} at 420 mμ (*A* = 0.26), with 1,2-di(2,3′-thienyl)ethene λ_{max} was at 390 mμ (*A* = 0.19), and with 1-phenyl 2-(2-thienyl)ethene λ_{max} was at 415 mμ (*A* = 0.14). With 1,2-di(2-thienyl)ethene only the end absorption of the new peak could be observed because of overlap with the spectrum of the starting compound. The position of the maximum was estimated to be at *ca.* 360 mμ.

Registry No.—**1a**, 13640-78-3; **1b**, 13640-79-4; **1c**, 13640-80-7; **1d**, 13640-81-8; **1e**, 13640-82-9; **2**, 13640-83-0; **3**, 13640-84-1; **4a**, 210-80-0; **4b**, 13640-86-3; **4c**, 13640-87-4; **4d**, 13640-88-5; **5**, 211-02-9; **8**, 13640-90-9; **9**, 1439-19-6; **10**, 438-27-7; **11**, 210-79-7; **17**, 13640-94-3; **18**, 16340-95-4; **19**, 13640-96-5; **20**, 13640-97-6.

---

[47] P. A. Leighton and F. A. Lucy, *J. Chem. Phys.*, **2**, 756 (1934); J. N. Pitts, Jr., J. K. S. Wan, and E. A. Schuck, *J. Am. Chem. Soc.*, **86**, 3606 (1964).