[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA]

Heterocyclic Vinyl Ethers. XVIII. Unsymmetrical 2,5-Diaryl-1,4-dithiadienes[1]

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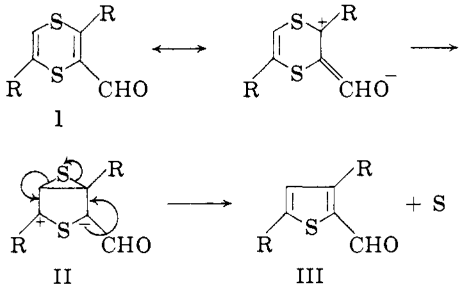
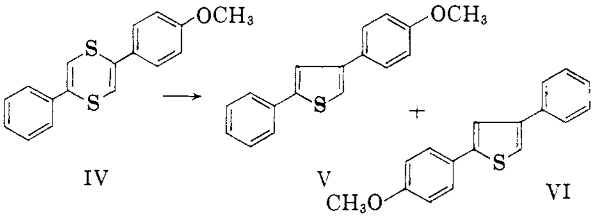
Unsymmetrical 2,5-diaryl-1,4-dithiadienes have been prepared by the acid hydrolysis of mixtures of Bunte salts derived from appropriate phenacyl halides. The product ratios have been determined for the 2,4-diarylthiophenes which are obtained when 2-*p*-methoxyphenyl-5-phenyl-1,4-dithiadiene is decomposed, either thermally or by the action of peracid.

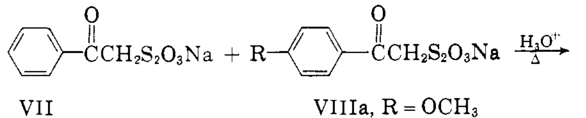
2,5-Diaryl-1,4-dithiadienes are readily converted to 2,4-diarylthiophenes by oxidation with peroxides.[3] Sulfoxides have been shown to be intermediates[4] in these transformations, and high yields of thiophenes are generally obtained. Diaryldithiadienes are also converted to thiophenes by the action of heat.[3] Although little is known concerning the mechanism of this latter process, the reaction sequence has been suggested[3a] to explain: (1) the lower temperature required for such reactions when the dithiadiene ring contains an electron-withdrawing group; (2) the formation of thiophenes such as III instead of isomers with the electron-withdrawing substituent in the 3-position; (3) the importance of the aryl groups,[5] which presumably further stabilize II.

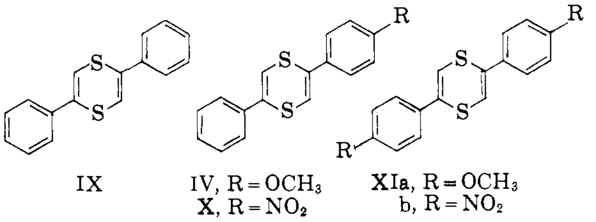


The work described in this paper is concerned with the synthesis of unsymmetrical 2,5-diaryl-1,4-dithiadienes, *e.g.* IV, and the conversion of IV, by oxidation and pyrolysis, into the thiophenes V and VI.

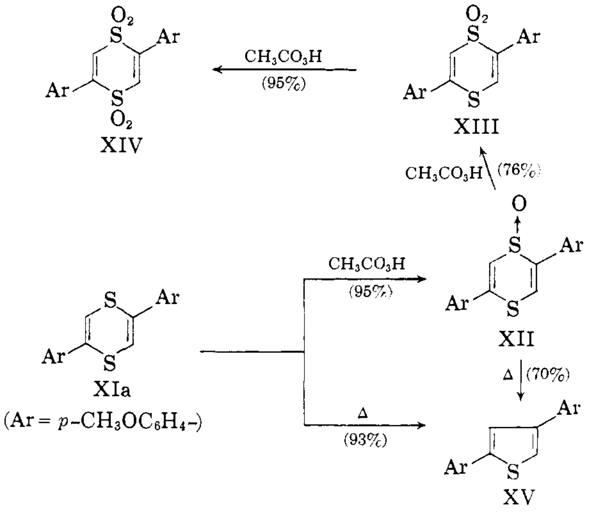


The application of the procedure of Baker and Barkenbus[6] to the synthesis of 2,5-diaryl-1,4-dithiadienes containing different aryl substituents depended on the acid hydrolysis of mixed Bunte salts VII and VIII. Two compounds of the desired type were prepared: 2-*p*-methoxyphenyl-5-phenyl-1,4-dithiadiene (IV) and 2-*p*-nitrophenyl-5-phenyl-1,4-dithiadiene (X). Three dithiadienes (total yield 45–50%) were found in each case and, as judged qualitatively from the weights of chromatographic fractions, the ratio of the three products was nearly statistical (approximately IX/IV/XIa = 1.0/2.2/1.1; IX/X/XIb = 1.0/1.8/$\sim$ 0.8).





2,5-Di-*p*-methoxyphenyl-1,4-dithiadiene (XIa) was also prepared (> 50% yield) by the acid hydrolysis of VIIIa. This new symmetrical diaryldithiadiene was further characterized by its conversion, by successive oxidation with peracetic acid, into the corresponding monosulfoxide (XII, 95%), monosulfone (XIII, 76%) and disulfone (XIV, 95%). 2,5-Di-*p*-methoxyphenyl-1,4-dithiadiene (XIa) decomposed readily at 190° into



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[1] Part of this work was supported by the Office of Ordnance Research, U. S. Army, Contract No. DA-11-022-Ord-2616.

[2] From the Ph.D. Thesis of E. T. Harper, University of Minnesota, 1959.

[3] (a) W. E. Parham and V. J. Traynelis, THIS JOURNAL, **76**, 4960 (1954); (b) W. E. Parham and V. J. Traynelis, *ibid.*, **77**, 68 (1955). (c) W. E. Parham, I. Nicholson and V. J. Traynelis, *ibid.*, **78**, 850 (1956).

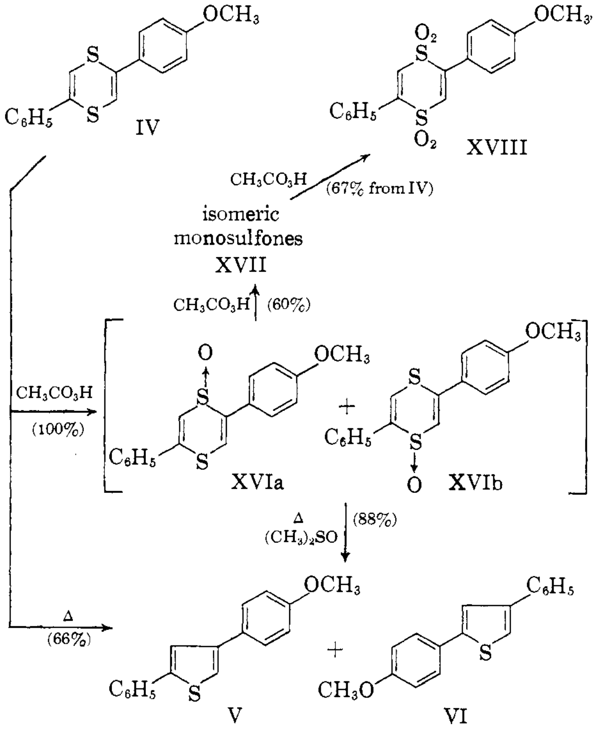
[4] H. H. Szmant and L. J. Alfonso, *ibid.*, **79**, 205 (1957).

[5] W. E. Parham, G. L. O. Mayo and B. Gadsby, *ibid.*, **81**, 5993 (1959).

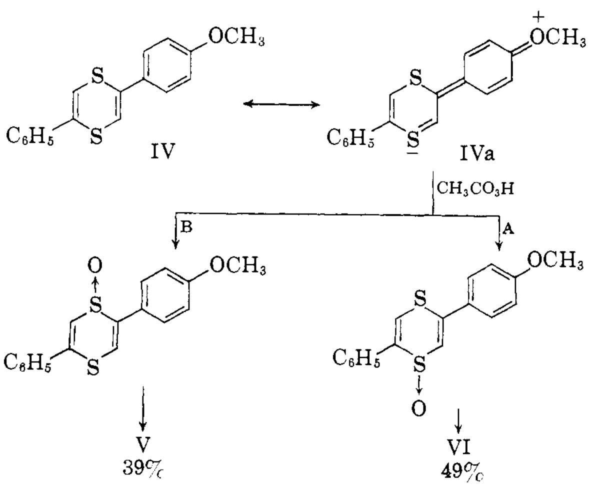
[6] R. H. Baker and C. Barkenbus, *ibid.*, **58**, 262 (1936). We also briefly examined the hydrolysis of xanthates as a method for the synthesis of diaryldithiadienes; however, this method appeared less satisfactory.

sulfur and 2,4-di-*p*-methoxyphenylthiophene (XV, 93% yield). This symmetrical thiophene was also prepared in high yield when the sulfoxide XII was heated in dimethyl sulfoxide.[4]

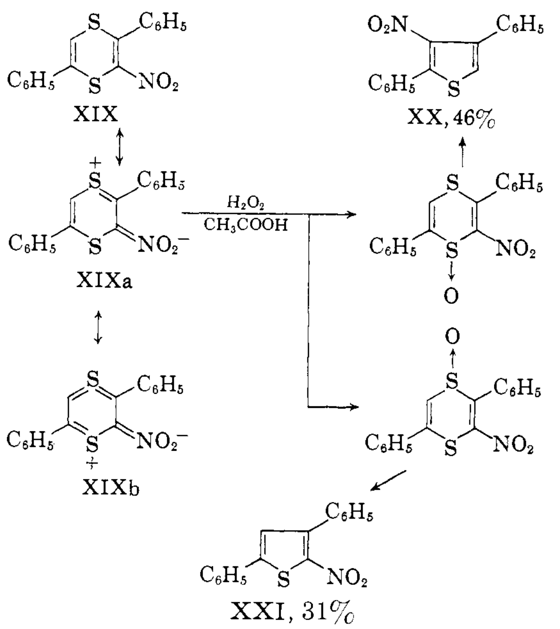
The oxidation of 2-*p*-methoxyphenyl-5-phenyl-1,4-dithiadiene (IV) with peracetic acid gave a mixture of isomeric sulfoxides (XVI) which were relatively unstable and were not separated. Further oxidation of these sulfoxides gave a mixture of monosulfones (XVII) or a single disulfone (XVIII). Either thermal decomposition of IV at 185-215° or decomposition of XVI in dimethyl sulfoxide gave reasonably high yields of a product, m.p. ∼145-150°, which had the composition calculated for the expected thiophenes V and VI ($C_{17}H_{14}OS$).



The mixture of thiophenes obtained by oxidation of IV was found[7] to contain V in 39% yield and VI in 49% yield (product ratio V/VI is 1/1.3). Since oxidation by peracetic acid (electrophilic attack[8]) should be more rapid at the sulfur atom possessing the higher electron density, the preferential oxidation of the 4-sulfur atom in IV (scheme A preferred over scheme B) is consistent with a small sulfur 3d orbital resonance effect as indicated in IVa.



It is of interest to note, in this connection, that oxidation of 3-nitro-2,5-diphenyl-1,4-dithiadiene (XIX)[8b] gives the thiophenes XX and XXI in respective yields of 46% and 31% (product ratio XX/XXI is 1.5/1). This observation suggests that the nitro group withdraws electrons, presumably by conjugation with sulfur 3p orbital electrons (XIXa), somewhat more effectively from the 1-sulfur atom of XIX than from the 4-sulfur atom.



These observations are consistent with the interpretation that: (a) sulfur 3p orbital conjugation is inhibited by the non-planarity[9a] of the dithiadiene ring which reduces the conjugative effect of the nitro group and (b) sulfur 3d orbital conjugation, while not dependent upon planarity of the ring,[9b] is relatively unimportant. The possibility cannot be excluded, however, that the substituents exert a significant conjugative effect on *both* sulfur atoms as shown in XIXb.

The thermal decomposition of IV produced, in addition to sulfur, the thiophenes V and VI in 39% and 27% yields, respectively. This distribution of products is difficult to interpret in view of uncertainties concerning the mechanism of the pyrolysis reaction. However, the product ratio of near unity (V/VI = 1.4/1) does not seem consistent with a simple polar mechanism of the type postulated in I → III. The *p*-methoxyphenyl group of IV would be expected to exert a more profound effect upon such a polar transition state and to have a greater influence on the product distribution.

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(7) The independent synthesis of the thiophenes V (m.p. 163.5–165.0°) and VI (m.p. 144.5–145.5°) and the method for determining the composition of mixtures containing V, VI and also IV is described in the accompanying paper by W. E. Parham and E. T. Harper, This Journal, **82**, 4936 (1960).

(8) C. G. Overberger and R. W. Cummins, *ibid.*, **75**, 4250 (1953).

(9) (a) P. A. Howell, R. M. Curtis and W. N. Lipscomb, *Acta Cryst.*, **7**, 498 (1954); (b) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

Experimental

2,5-Di-*p*-methoxyphenyl-1,4-dithiadiene (XIa).—A hot solution obtained by heating (1 hr.) a mixture of *p*-methoxyphenacyl chloride[10] (18.0 g., 0.0978 mole), sodium thiosulfate pentahydrate (24.5 g., 0.0988 mole) and distilled water (30 ml.) was diluted with 95% ethanol (50 ml.). The white Bunte salt, which crystallized when the solution was cooled, was dissolved in a mixture of methanol (60 ml.) and distilled water (30 ml.). Concentrated hydrochloric acid (60 ml.) was added to this solution at room temperature, and the resulting mixture was stirred and heated at the reflux temperature for 21 hr.

The reaction mixture was cooled in an ice-bath, and the yellow solid (13.07 g., 79% yield, m.p. 138–162°) was collected and recrystallized from acetic acid. There was obtained 8.97 g. (54%) of 2,5-di-*p*-methoxyphenyl-1,4-dithiadiene (XIa), m.p. 161–166°. An additional quantity (2.73 g.) of XIa was obtained when the acetic acid mother liquor was diluted with water, but this material was not processed further. A sample of XIa (m.p. 161–166°) was chromatographed on alumina and recrystallized from methylene chloride–petroleum ether (b.p. 30–60°); the pure product melted at 167–169°.

Anal. Calcd. for $C_{18}H_{16}O_2S_2$: C, 65.82; H, 4.91. Found: C, 65.73; H, 4.93.

2,5-Di-*p*-nitrophenyl-1,4-dithiadiene (XIb).—A mixture of *p*-nitrophenacyl chloride[11] (m.p. 89–91°, 6.7 g., 0.034 mole), sodium thiosulfate pentahydrate (8.4 g., 0.034 mole) and water (15 ml.) was stirred vigorously and heated at the reflux temperature for thirty minutes. The aqueous solution of the Bunte salt was cooled slightly, diluted with absolute ethanol (10 ml.), and concentrated hydrochloric acid (20 ml.) was added slowly. This mixture was stirred and heated at the reflux temperature for 3 hr. A rust-colored solid (m.p. 147–167° dec., 5.93 g., 99% yield) was obtained when the solution was cooled. Considerable loss accompanied the purification of this product by recrystallization from dioxane (16% recovery of material melting at 200–202.5° dec.). Pure XIb melted at 205.5–207° dec.

Anal. Calcd. for $C_{16}H_{10}N_2O_4S_2$: C, 53.62; H, 2.81. Found: C, 53.92; H, 3.08.

Pyrolysis of 2,5-Di-*p*-methoxyphenyl-1,4-dithiadiene (XIa). 2,4-Di-*p*-methoxyphenylthiophene (XV).—A sample of XIa (672 mg.) was placed in a side-arm test-tube fitted with a two-hole rubber stopper which supported a thermometer and a gas inlet tube. The tube was flushed with nitrogen and immersed in an oil-bath which was slowly heated to 235°. The pyrolyszate was cooled, suspended in benzene and chromatographed on a 15 × 450 mm. column of alumina packed in petroleum ether (b.p. 60–68°).

An oily yellow solid (50 mg., 76% calcd. as pure sulfur) was eluted with petroleum ether. 2,4-Di-*p*-methoxyphenylthiophene (566 mg., 93% yield, white crystals, m.p. 200–218°) was eluted with solutions of benzene (37–50%) in petroleum ether (b.p. 60–68°). The melting point of this product was raised to 214–219° (79% recovery) by one recrystallization from carbon tetrachloride and to 218–219° by further recrystallization from carbon tetrachloride.

Anal. Calcd. for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44. Found: C, 72.66; H, 5.65.

2,5-Di-*p*-methoxyphenyl-1,4-dithiadiene-1-oxide (XII).—The procedure of Szmant and Alfonso[4] was modified slightly. To a solution of 2,5-bis-*p*-methoxyphenyl-1,4-dithiadiene (XIa), 0.57 g., 1.7 mmoles) in methylene chloride (25 ml.) was added a solution of 40% peracetic acid[12] (0.66 ml., 4.0 mmoles) in ethyl acetate (6 ml.). After one minute, the mixture was extracted with water (3 × 25 ml.). The organic layer was dried ($CaCl_2$), cooled and filtered. There was obtained 0.50 g. (probably wet weight, 85% yield) of product, m.p. 141–144° dec. An additional 0.32 g. (54%) of product (m.p. 138–145° dec.) was isolated by dilution of the mother liquor with petroleum ether (b.p. 30–60°) and by concentration of the solution. An almost quantitative yield of product melting at 141–145° dec. was obtained by further recrystallization of the crude sulfoxide from methylene chloride–petroleum ether (b.p. 30–60°).

Anal. Calcd. for $C_{18}H_{16}O_3S_2$: C, 62.76; H, 4.68. Found: C, 62.50; H, 4.76.

The infrared spectrum of the product in Nujol mull showed strong absorption at 1025 cm.$^{-1}$, characteristic of the sulfoxide group.[13]

2,5-Di-*p*-methoxyphenyl-1,4-dithiadiene-1,1-dioxide (XIII).—A solution prepared from the sulfoxide XII (0.32 g., 0.93 mmole, m.p. 138–145°) in methylene chloride (35 ml.) and 40% peracetic acid (0.47 ml., 2.9 mmoles) in ethyl acetate (5 ml.) was allowed to stand at room temperature for 20 hr. The solution was extracted with water (3 × 25 ml.), the organic layer was dried and the solvent was removed. The crude monosulfone (0.25 g., 76% yield, m.p. 199–204°) was recrystallized from benzene. Pure XIII melted at 204.5–205.5°.

Anal. Calcd. for $C_{18}H_{16}O_4S_2$: C, 59.98; H, 4.48. Found: C, 60.10; H, 4.61.

The infrared spectrum of the monosulfone showed absorptions characteristic[13] of sulfones: 1315, 1120 cm.$^{-1}$ (Nujol); 1305, 1125 cm.$^{-1}$ (chloroform).

2,5-Di-*p*-methoxyphenyl-1,4-dithiadiene-1,1,4,4-tetroxide (XIV).—A solution of the monosulfone XIII (400 mg., 1.11 mmoles) and 40% peracetic acid (5 ml., 30 mmoles) in acetic acid (80 ml.) was heated on the steam-bath for 2 hr. The yield of crude disulfone (m.p. 249–254°) obtained from the reaction mixture was 95% (415 mg.). The melting point was raised to 252–255° by recrystallization of the product from acetic acid.

Anal. Calcd. for $C_{18}H_{16}O_6S_2$: C, 55.09; H, 4.11. Found: C, 54.83; H, 4.20.

The infrared spectrum of the disulfone showed absorptions characteristic[13] of sulfones: 1330, 1315 cm.$^{-1}$ (doublet), 1120 cm.$^{-1}$ (Nujol mull); 1335, 1310 cm.$^{-1}$ (doublet), 1130 cm.$^{-1}$ (chloroform solution).

2,4-Di-*p*-methoxyphenylthiophene (XV) *via* the Sulfoxide XII.—2,5-Di-*p*-methoxyphenyl-1,4-dithiadiene-1-oxide (XII, 117 mg.) was dissolved in dimethyl sulfoxide (10 ml.), and the solution was heated on the steam-bath for 1 hr.[4] The mixture was diluted with water (100 ml.) and cooled, and slightly impure XV (90 mg., 90%, m.p. 167–213°) was collected. Recrystallization of this product from carbon tetrachloride gave 70 mg. (70% yield) of yellowish needles, m.p. 216–220°, which had an infrared spectrum essentially identical with that of an authentic sample of XV. The melting point was raised to 217–219° by repeated recrystallization of the product from carbon tetrachloride (including decolorization with charcoal). The resulting product was shown to be identical, by mixed melting point and comparison of infrared spectra, to 2,4-di-*p*-methoxyphenylthiophene obtained by pyrolysis of XIa.

Unsymmetrical 2,5-Diaryl-1,4-dithiadienes from Bunte Salts. A. 2-*p*-Methoxyphenyl-5-phenyl-1,4-dithiadiene (IV).—A solution of sodium *p*-methoxyphenacyl thiosulfate (VIIIa) was obtained when a mixture of *p*-methoxyphenacyl chloride[10] (4.6 g., 0.025 mole), sodium thiosulfate pentahydrate (6.3 g., 0.025 mole) and water (12.5 ml.) was stirred vigorously at 75–85° for 30 minutes. An aqueous solution of sodium phenacyl thiosulfate (VII) was prepared[6] from phenacyl chloride (3.9 g., 0.025 mole), sodium thiosulfate pentahydrate (6.3 g., 0.025 mole) and water (7.5 ml.). To these combined aqueous solutions was added absolute ethanol (15 ml.) and, slowly, concd. hydrochloric acid (30 ml.). The resulting mixture was stirred and heated at reflux for 4 hr. The tacky solid that separated as the solution was cooled to room temperature was collected, washed with water and dissolved in a 50% solution (200 ml.) of benzene in petroleum ether (b.p. 30–60°) before chromatography on a 35-mm. column containing 250 g. of alumina.

Three products were isolated by chromatography. The first of these, 2,5-diphenyl-1,4-dithiadiene (IX, 0.53 g., 16% yield, m.p. 95–117°; recrystallized from acetic acid, 0.33 g., 10%, m.p. and mixed m.p. with authentic IX[6] 116–118°), was eluted with a 50% solution of benzene in petroleum ether (b.p. 30–60°). The second product, eluted with 50 and 60% solutions of benzene in petroleum ether (b.p. 30–60°), was 2-*p*-methoxyphenyl-5-phenyl-1,4-

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[10] Prepared in 55% yield (m.p. 96.5–98.5°) by the procedure of A. L. Wilds and T. L. Johnson, THIS JOURNAL, **67**, 287 (1945).

[11] P. Karrer and J. Schukri, *Helv. Chim. Acta*, **28**, 823 (1945).

[12] Becco Chemical Division, Food Machinery and Chemical Corp., Buffalo 7, N. Y.

[13] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

dithiadiene (IV, 1.44 g., 19% yield, m.p. 107–117°; 0.92 g. from acetic acid, 12% yield, m.p. 112–119°). Pure IV melted at 119–120° after further recrystallization from acetic acid.

Anal. Calcd. for $C_{17}H_{14}OS_2$: C, 68.42; H, 4.73. Found: C, 68.12; H, 4.86.

The third component, eluted with a 70% solution of benzene in petroleum ether (b.p. 30–60°) was 2,5-di-*p*-methoxyphenyl-1,4-dithiadiene (XIa, 1.00 g., 24% yield, m.p. 125–157°). This product was recrystallized from carbon tetrachloride–ethyl acetate, and the product thus obtained (m.p. 160–161°) caused no depression in melting point when mixed with authentic XIa.

The reaction was carried out three times, and the average ratios of the products, as judged from the slightly impure fractions obtained by chromatography, was IX/IV/XIa = 1.0/2.2/1.1.

B. **2-*p*-Nitrophenyl-5-phenyl-1,4-dithiadiene (X).**—A solution of the Bunte salt VIIIb, prepared as described earlier, from *p*-nitrophenacyl chloride (4.96 g., 0.0249 mole), sodium thiosulfate pentahydrate (6.25 g., 0.0252 mole) and water (35 ml.), was cooled. The crystalline Bunte salt, assumed[6] to be the monohydrate, was collected and recrystallized from ethanol (6.36 g. of pale yellow solid, 81% yield). A hot solution of sodium phenacyl thiosulfate, prepared[6] from phenacyl chloride (3.85 g., 0.0249 mole), was diluted with hot ethanol until turbid. The solution was cooled and 5.66 g. (83% yield) of VII was collected as shiny white plates.

A solution containing the two Bunte salts, water (15 ml.), 95% ethanol (15 ml.) and concd. hydrochloric acid (30 ml.) was stirred and heated at the reflux temperature for 4 hr. The crude, partly granular gum (5.5–6.0 g., 87–95% yield) obtained from the cooled reaction mixture was dissolved in benzene and chromatographed on a 35-mm. column containing 250 g. of alumina packed in a solution of benzene (25%) and petroleum ether (b.p. 60–68°).

Three products were again isolated. The first product, eluted with a solution of 25% benzene in petroleum ether, was principally 2,5-diphenyl-1,4-dithiadiene (IX, 0.05 g., 18% yield, m.p. 98–115°). The second product, eluted with a solution of 50% benzene in petroleum ether, was slightly impure 2-*p*-nitrophenyl-5-phenyl-1,4-dithiadiene (X, 0.99 g., m.p. 128–139°). Pure X (m.p. 138.5–139.0°) was obtained with little loss by recrystallization of the crude product from acetic acid.

Anal. Calcd. for $C_{16}H_{11}NO_2S_2$: C, 61.32; H, 3.54. Found: C, 61.33; H, 3.89.

A series of red oils, which hardened to glasses, was eluted with a solution of 50% benzene in petroleum ether and with benzene. A third impure solid (0.54 g., 15% yield, m.p. 65–180°) was eluted with benzene. This solid contained XIb but was not purified.

The ratio of products, as judged from the weights of the fractions obtained from the chromatogram, was approximately IX/X/XIb = 1.0/1.8/0.8.

The Isomeric Sulfoxides (XVI) and Isomeric Sulfones (XVII) Derived from 2-*p*-Methoxyphenyl-5-phenyl-1,4-dithiadiene (IV).—A solution of 34% peracetic acid[14] (0.10 ml., 0.49 mmole) in ethyl acetate (5 ml.) was added to a solution of IV (110 mg., 0.369 mmole) in methylene chloride (25 ml.). After one minute, the mixture was extracted with water (3 × 25 ml.), the organic layer was dried ($CaCl_2$) and the dried extract was concentrated in a rotating evaporator to 7 ml. This solution was diluted with an equal volume of petroleum ether (b.p. 30–60°) and an essentially quantitative yield of product (m.p. 118–126° dec.) was obtained from the cold mixture.

Anal. Calcd. for $C_{17}H_{14}O_2S_2$: C, 64.94; H, 4.49. Found: C, 64.66; H, 4.20.

The infrared spectrum of the product showed absorption at 1025 cm.$^{-1}$, characteristic[13] of the sulfoxide group.

A mixture prepared from the above mixed sulfoxides (0.41 g., 1.3 mmoles) in methylene chloride (20 ml.) and 40% peracetic acid (0.7 ml., 4 mmoles) in ethyl acetate (5 ml.) was allowed to stand for 29 hr. at room temperature. The reaction mixture was processed as described above, and the mixture of crude monosulfones was recrystallized from benzene. The product (0.26 g., 60% yield) was a mixture containing tufts melting at 117–130° and prisms melting at 140–150°. Recystallization of this product from ethanol gave a white crystalline powder melting at 129–130°, with an isolated rod melting at 149°. *Anal.* Calcd. for $C_{17}H_{14}O_3S_2$: C, 61.79; H, 4.27. Found: C, 61.41; H, 4.19.

The infrared spectrum of this product showed absorptions characteristic[13] of sulfones: 1300 and 1120 cm.$^{-1}$.

2-*p*-Methoxyphenyl-5-phenyl-1,1,4,4-tetroxide (XVIII).—A solution prepared from 2-*p*-methoxyphenyl-5-phenyl-1,4-dithiadiene (IV, 0.49 g., 1.6 mmoles), methylene chloride (10 ml.), 40% peracetic acid (2 ml., 12.0 mmoles) and acetic acid (5–10 ml.) was allowed to stand at room temperature for two days and then was heated on a steam-bath for 1 hr. The crude disulfone (0.36 g., 67% yield, m.p. 209–213°) was recrystallized from acetic acid. (An additional 0.11 g. of crude product, m.p. 178–213°, was not processed.) The disulfone melted at 215–219° and showed infrared absorptions consistent with the proposed structure: 1330, 1320 cm.$^{-1}$ (doublet), 1130 cm.$^{-1}$ (Nujol mull); and 1335, 1315 cm.$^{-1}$ (doublet), 1130 cm.$^{-1}$ (chloroform solution).

Anal. Calcd. for $C_{17}H_{14}O_5S_2$: C, 56.34; H, 3.89. Found: C, 56.24; H, 3.92.

2-*p*-Methoxyphenyl-4-phenylthiophene (VI) and 2-Phenyl-4-*p*-methoxyphenylthiophene (V) by Oxidation of IV.—A solution of 34% peracetic acid[14] (0.28 ml., 1.5 mmoles) in ethyl acetate (5 ml.) was added to a solution of IV (257 mg., 0.862 mmole) in methylene chloride (25 ml.) at room temperature. After one minute, the solution was extracted with water (3 × 25 ml.), and the organic layer was separated, dried ($CaCl_2$) and evaporated to dryness (rotating evaporator, 25°, 15 mm. pressure). The light yellow residue (XVI) was dissolved in dimethyl sulfoxide (50 ml.), and this solution was heated on the steam-bath for 2 hr. and then poured into distilled water. The precipitate was allowed to coagulate at 25° for 18 hr. and was then collected. The nearly white crystals (212 mg., 93% yield) melted at 143–148.5°. This material was shown, by infrared analysis,[7] to contain 53% of VI (49% yield) and 42% of V (39% yield). The distribution of products was not changed appreciably by recrystallization of the product from petroleum ether (b.p. 60–68°) (73% recovery, m.p. 145–147°, 54% VI/47% V) or methanol (67% recovery, m.p. 144–147.5°, 51% VI/48% V).

Attempts to effect separation of either the thiophenes V and VI or the sulfoxides XVI by chromatography on alumina were unsuccessful.

Pyrolysis of 2-*p*-Methoxyphenyl-5-phenyl-1,4-dithiadiene (IV).—(a) The reaction was carried out as previously described for the pyrolysis of XIa. The melt was maintained at 205° for 1 hr. and at 215° for 1 hr. The pyrolyzate was cooled and made homogeneous by solution in methylene chloride. The solvent was removed and the residue was analyzed.

1. The crude product was found, by infrared analysis,[7] to contain 2-*p*-methoxyphenyl-4-phenylthiophene (VI, 27% yield), 2-phenyl-4-*p*-methoxyphenylthiophene (V, 39% yield) and less than 5% of starting material.

2. Chromatography of the crude product (455 mg.) on a 15 × 360 mm. column of alumina (activated at 250° for 36 hr.) packed in petroleum ether (b.p. 60–68°) yielded fractions (88% recovery) which were analyzed as follows. The yields and ratio of V and VI matched those found for the crude product.

Fract.	Wt., mg.	M.p., °C.	% VI	% V	% Yield VI	% Yield V
1	69	80–135	27	15	4	2
2	291	125–147	35	52	22	33
3	14	Oily	5	20	0	1
4	28	Oil	Infrared spectrum unsuitable for analysis			

3. Recrystallization of fraction 2 from petroleum ether (b.p. 60–68°) (71% recovery, m.p. 146–149°, 36% VI/57% V) or from methanol (57% recovery, m.p. 147–150°, 36% VI/56% V) did not appreciably alter the product distribution.

(b) The reaction was carried out as described[3a] for the pyrolysis of 2,5-diphenyl-1,4-dithiadiene (IX): a side-arm test tube containing IV (606 mg.) was immersed in a hot oil-bath (195–200°) for 10 minutes. The pyrolysate was chromatographed on a 15 × 470 mm.

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[14] Titrated according to the procedure of F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

column of alumina (activated at 200° for 18 hr.) packed in petroleum ether (b.p. 60–68°). Sulfur (35 mg., 54% yield, m.p. 107–109°, mixed m.p. with authentic (m.p. 115–116°) sulfur, 113–116°) was eluted from the column with petroleum ether. Further elution of the column with 19-20% solutions of methylene chloride in petroleum ether (b.p. 60–68°) gave the principal fractions (466 mg., m.p. 65-139°, 77% recovery) which were shown[7] to contain 21% of VI (18% yield), 29% of V (25% yield) and 43% of starting material (IV, 33% recovery). The ratio VI/V was essentially identical to that found in the previous experiment, and the composition of the mixture was again unchanged by recrystallization from petroleum ether (b.p. 60–68°) (85% recovery, m.p. 134–139°, 23% VI/33% V/44% IV) or methanol (75% recovery, m.p. 135--145°, 23% VI/32% V/46% IV).

Ethyl *p*-Methoxyphenacyl Xanthate.—A stirred solution of *p*-methoxyphenacyl chloride (5.6 g., 0.030 mole) in dry acetone (10 ml.) was added dropwise to a suspension of potassium ethyl xanthate (4.83 g., 0.030 mole) in dry acetone (100 ml.). The precipitated potassium chloride was removed by filtration, the solvent was removed by distillation at reduced pressure and the residue was recrystallized from ethanol. There was obtained 6.08 g. (80% yield) of ethyl *p*-methoxyphenacyl xanthate (m.p. 60–64°). Further recrystallization of this product from ether–petroleum ether (b.p. 30–60°) gave yellow transparent plates melting at 67.5–68.0°.

Anal. Calcd. for $C_{12}H_{14}O_3S_2$: C, 53.31; H, 5.22. Found: C, 53.36; H, 5.58.

Ethyl *p*-nitrophenacyl xanthate was prepared from *p*-nitrophenacyl chloride (6.00 g., 0.030 mole) by a procedure similar to that described above for ethyl *p*-methoxyphenacyl xanthate. The crude product (7.52 g., 93% yield, m.p. 84–87°) was purified by recrystallization from ether–petroleum ether (b.p. 30–60°) and the pure xanthate was obtained as fine white needles melting at 88–89°.

Anal. Calcd. for $C_{11}H_{11}O_4NS_2$: C, 46.30; H, 3.89. Found: C, 46.80; H, 3.79.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA]

Heterocyclic Vinyl Ethers. XIX. Unsymmetrical 2,4-Diarylthiophenes[1]

BY WILLIAM E. PARHAM AND EDWIN T. HARPER[2]

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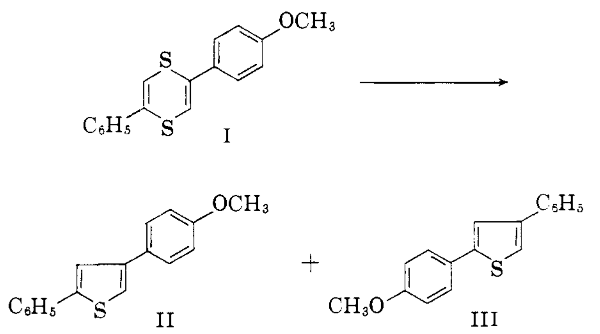
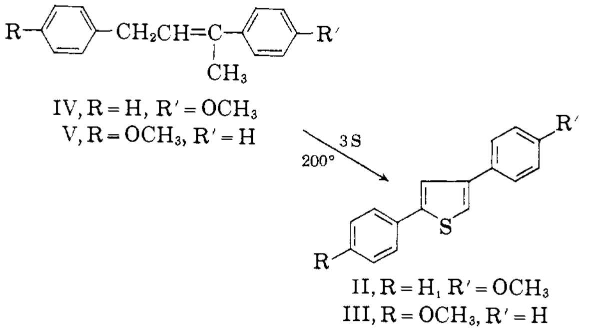
The synthesis of 2-phenyl-4-*p*-methoxyphenylthiophene (II) and 2-*p*-methoxyphenyl-4-phenylthiophene (III) is described by procedures which involve the high temperature sulfuration of appropriate olefins. A by-product, believed to be 2-(*p*-methoxyphenyl)-thieno[2,3-b]thianaphthene (X), was isolated from the reaction of 1-phenyl-3-*p*-methoxyphenyl-2-butene (IV) and sulfur. The composition of mixtures of the isomeric thiophenes, either alone or containing 2-*p*-methoxyphenyl-5-phenyl-1,4-dithiadiene (I), can be determined conveniently by infrared spectroscopic analysis.

As part of our study[3] of the formation of 2,4-diarylthiophenes from 2,5-diaryl-1,4-dithiadienes (such as I), it became necessary to prepare 2-phenyl-4-*p*-methoxyphenylthiophene (II) and 2-*p*-methoxyphenyl-4-phenylthiophene (III) and to devise a method for determining the composition of mixtures of I, II and III.



The synthesis of 2,4-diarylthiophenes has been studied in detail,[4] but these methods have been generally limited to thiophenes in which the aryl substituents are identical. Schmitt[5] and co-workers recently have reported the synthesis of 2-*p*-methoxyphenyl-4-phenylthiophene (III) by the reaction of V with sulfur, and we have employed this procedure (reaction of IV and V, respectively, with sulfur) for the preparation of the isomeric thiophenes II and III. It became evident that the product obtained by Schmitt was not 2-*p*-methoxyphenyl-4-phenylthiophene (III) as described, but more probably the isomeric thiophene II.[5b]



The olefins, 1-phenyl-3-*p*-methoxyphenyl-2-butene (IV) and 1-*p*-methoxyphenyl-3-phenyl-2-butene (V) were synthesized, in 37% and 56% yields, respectively, by Grignard reactions.

The dehydration of the alcohols VII and IX could logically give olefins with structures corresponding to A, B or C. Structure A (*cis*-2-butene) was assigned to olefin V (Ar = *p*-$CH_3OC_6H_4$-, Ar′ = C_6H_5) in the following way. Structure C was eliminated on the basis of the infrared spectrum of

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[2] From the Ph.D. Thesis of E. T. Harper, University of Minnesota, 1959.

[3] W. E. Parham and E. T. Harper, THIS JOURNAL, **82**, 4932 (1960).

[4] (a) E. Campaigne, *ibid.*, **66**, 684 (1944). (b) P. Demerseman, Ng. Buu-Hoï, R. Royer and A. Cheutin, *J. Chem. Soc.*, 2720 (1954).

[5] (a) J. Schmitt, R. Fallard and M. Suquet, *Bull. soc. chim. France*, **2**, 1147 (1956). (b) These workers reported their starting ketone, β-*p*-methoxyphenylpropiophenone, to melt at 99-100° and the thiophene (III) to melt at 162°. Neither of these melting points are correct. β-*p*-Methoxyphenylpropiophenone melts at 59–60°, and the thiophene III melts at 145°. It is reasonable to assume that Schmitt and co-workers started with the isomeric ketone β-phenyl-*p*-methoxypropiophenone (m.p. 97°) and prepared thiophene II (m.p. 163°).