1-Oxo-1,2,4,5-tetrahydro-3-benzothiepin 3-Dioxide (VI). Hydrogen peroxide (30%, 16 ml.) was slowly added to 10 g. (0.056 mole) of 1-oxo-1,2,4,5-tetrahydro-3-benzothiepin in 20 ml. of glacial acetic acid cooled in an ice-bath. The solution was allowed to stand 24 hours at room temperature. After scratching the side of the container with a glass rod, 8.3 g. (70% of theory) of 1-oxo-1,2,4,5-tetrahydro-3-benzothiepin 3-dioxide crystallized, m.p. 133–134.5° after recrystallization from ethanol.

Anal. Calcd. for $C_{10}H_{10}SO_3$: C, 57.12; H, 4.71. Found: C, 57.17; H, 4.51.

1-Hydroxy-1,2,4,5-tetrahydro-3-benzothiepin 3-Dioxide (VII).—A mixture of 6 g. (0.0286 mole) of 1-oxo-1,2,4,5-tetrahydro-3-benzothiepin 3-dioxide, 50 ml. of purified dioxane and 2 g. of Raney nickel was shaken under hydrogen at 40 p.s.i. until the theoretical amount of hydrogen was taken up. The Raney nickel was filtered and the dioxane evaporated to yield 6 g. (99% yield) of 1-hydroxy-1,2,4,5-tetrahydro-3-benzothiepin 3-dioxide, m.p. 185.5–187°.

Anal. Calcd. for $C_{10}H_{12}SO_3$: C, 56.57; H, 5.70. Found: C, 56.24; H, 5.66.

1-Bromo-1,2,4,5-tetrahydro-3-benzothiepin 3-Dioxide (VIII).—A mixture of 8.13 g. (0.03 mole) of phosphorus tribromide and 5 g. (0.0236 mole) of 1-hydroxy-1,2,4,5-tetrahydro-3-benzothiepin-3-dioxide was allowed to stand 14 hours at room temperature. The solution was heated on the steam-bath for 1 hour and then poured into a mixture of ice and water. The solid was removed by filtration and recrystallized from methanol to give 5.2 g. (80% yield) of 3-bromo-1,2,4,5-tetrahydro-3-benzothiepin-3-dioxide, m.p. 175–177°.

Anal. Calcd. for $C_{10}H_{11}SO_2Br$; C, 43.62; H, 4.03. Found: C, 43.80; H, 4.20.

1,5-Dibromo-1,2,4,5-tetrahydro-3-benzothiepin 3-Dioxide (IX).—To a refluxing solution of 100 ml. of carbon tetrachloride and 3 g. (0.0109 mole) of 1-bromo-1,2,4,5-tetrahydro-3-benzothiepin-3-dioxide illuminated with a No. 2 photoflood bulb was slowly added (over a 1.5-hour period) 4.3 g. (0.0269 mole) of bromine dissolved in 15 ml. of carbon tetrachloride. The carbon tetrachloride was evaporated with the aid of an air jet and the remaining material was extracted with ethyl ether. Evaporation of the ethyl ether yielded 3.2 g. of red oil. The solid remaining after the ether extraction was boiled with 100 ml. of methanol. The impure 1,5-dibromo-1,2,4,5-tetrahydro-3-benzothiepin 3-dioxide (0.7 g., 18% yield) which did not dissolve was filtered and melted at 188–194°. Evaporation of the methanol extract yielded 0.9 g. of solid melting at 148–155°.

3-Benzothiepin 3-Dioxide (X).—Triethylamine (1.0 g.) was added to 1.0 g. (0.0028 mole) of impure 1,5-dibromo-1,2,4,5-tetrahydro-3-benzothiepin 3-dioxide dissolved in 100 ml. of boiling benzene. After heating the solution for 10 minutes, the triethylamine hydrobromide was filtered and the benzene was evaporated. The residue was washed with water, dried and recrystallized twice from methanol and once from petroleum ether to yield a solid melting at 161.5–163.5°, 0.33 g., 61% yield.

Anal. Calcd. for $C_{10}H_8SO_2$: C, 62.48; H, 4.19; mol. wt., 192. Found: C, 62.80; H, 4.16; mol. wt., 186.

The Reduction of 3-Benzothiepin 3-Dioxide.—A solution of 100 ml. of methanol, 1 g. (0.0052 mole) of 3-benzothiepin 3-dioxide and a catalytic amount of Raney nickel was shaken under hydrogen at 50 p.s.i. until the theoretical amount of hydrogen was taken up. The Raney nickel was filtered and the methanol evaporated to yield 0.8 g. (78%) of 1,2,4,5-tetrahydro-3-benzothiepin 3-dioxide. This material melted at 154–156° after recrystallization from methanol and petroleum ether.

1,2,4,5-Tetrahydro-3-benzothiepin 3-Dioxide (XII).—To 100 ml. of ethanol was slowly added a mixture of 5.84 g. (0.02 mole) of o-bis-(β-bromoethyl)-benzene, 4.8 g. (0.0201 mole) of sodium sulfide nonahydrate and 300 ml. of ethanol. The addition was made over an 8-hour period and the solution was allowed to reflux for an additional 84 hours. The ethanol was removed by distillation and the remaining material was extracted with ethyl ether. Evaporation of the ether yielded 2 g. of a viscous liquid. To a solution of this liquid in 10 ml. of glacial acetic acid, 4.5 ml. of 30% hydrogen peroxide was added slowly. The reaction mixture was allowed to stand 24 hours at room temperature and was then poured on ice and water. The solid (2 g., 51% yield) was filtered and dried, m.p. 154–156° after recrystallization from methanol and petroleum ether (90–100°); it produced no melting point depression on admixture with the 1,2,4,5-tetrahydro-3-benzothiepin 3-dioxide prepared by the reduction of 3-benzothiepin 3-dioxide.

Nitro-3-benzothiepin 3-Dioxide.—A solution of 10 ml. of fuming nitric acid and 1.1 g. (0.00573 mole) of 3-benzothiepin 3-dioxide was allowed to react for 2 hours at 0° and 3 more hours at room temperature. The solution was poured into 150 ml. of a mixture of ice and water and the precipitate (1.3 g., 95%) was filtered, washed with water and recrystallized twice from methanol to yield a light yellow crystalline material melting at 173–176°.

Anal. Calcd. for $C_{10}H_7SO_4N$: C, 50.61; H, 2.98. Found: C, 50.73; H, 3.14.

LAFAYETTE, IND.

Heterocyclic Vinyl Ethers. XI. Electrophilic Substitution and Rearrangements of the 1,4-Dithiadiene Ring System[1]

BY WILLIAM E. PARHAM, ISADORE NICHOLSON[2] AND VINCENT J. TRAYNELIS

A study of the reaction of 2,5-diphenyl-1,4-dithiadiene with electrophilic reagents has shown that both mono- and disubstituted products can be obtained in high yield and that substitution occurs exclusively in the sulfur-containing ring. Reactions are discussed which involve the conversion of derivatives of dithiadiene into the corresponding derivatives of thiophene.

Reactions were described in previous communications[3,4] which constitute a new synthesis of thiophenes from[5] the readily available diaryl-1,4-dithiadienes. This paper describes work related to: (a) the orientation of electrophilic substitution of 2,5-diphenyl-1,4-dithiadiene (I), and (b) the structures of thiophenes derived from substituted dithiadienes.

The reaction of equivalent quantities of bromine and I, in acetic acid, afforded a 71% yield of a single monobromo derivative. This product was shown to be 2,5-diphenyl-3-bromo-1,4-dithiadiene (II) by its oxidation with potassium permanganate. A 64% yield of the theoretical amount of benzoic acid was obtained, and there was no evidence for the presence of bromobenzoic acid.

The conversion of II into derivatives of thiophene

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(2) Du Pont Postdoctoral Instructorship, 1954–1955.

(3) W. E. Parham and V. J. Traynelis, THIS JOURNAL, 77, 68 (1955).

(4) W. E. Parham and V. J. Traynelis, *ibid.*, 76, 4960 (1954).

(5) R. H. Baker and C. Barkenbus, *ibid.*, 58, 262 (1936).
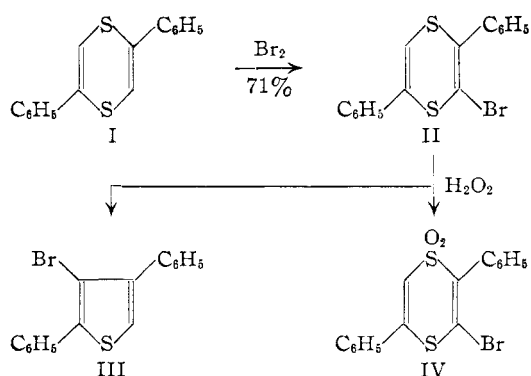
by thermal[3,4] decomposition proved unsatisfactory. Purple tarry products resulted from which no pure products could be obtained by crystallization or by chromatography on alumina. However, two products were isolated when II was treated with hydrogen peroxide in acetic acid. The first of these (14% yield) was the hitherto unknown 2,4-diphenyl-3-bromothiophene (III). The structure of the second product (48% yield) has not been established; however, its composition and spectra[6] suggest that it is a monosulfone of II (tentatively designated in this report as IV). This material melts at 177.5–178.5°, and is thermally stable at temperatures of 200°. The thermal stability of IV is of particular significance since it suggests that monosulfones are not intermediates in the hydrogen peroxide degradation of 2,5-diaryl-1,4-dithiadienes to the corresponding thiophenes.[3,4]

2,5-Diphenyl-3-bromo-1,4-dithiadiene (II) readily undergoes further bromination or nitration, and it has been shown that such substitution occurs exclusively in the dithiadiene ring. Similarly, it was found that 2,5-diphenyl-3-nitro-1,4-dithiadiene[3] (VII) undergoes facile bromination or nitration,
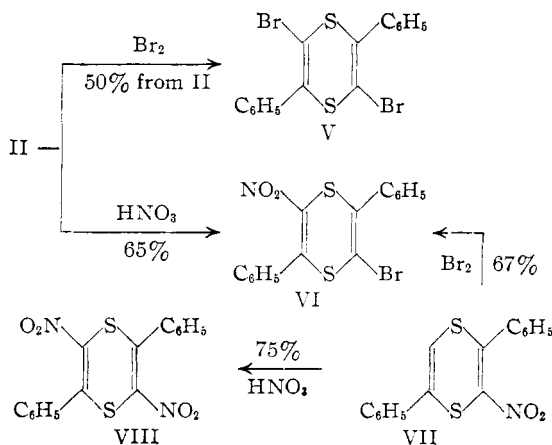

and, here again, only the dithiadiene ring is involved.

The structure of VI was immediately established by its formation from II and VII. The structure of VIII was established by its oxidation with potassium permanganate. A 50% yield of the theoretical amount of benzoic acid was obtained, and there was no nitrobenzoic acid formed.

(6) The infrared spectrum (KBr disc) of this product showed characteristic sulfone absorption at 1130 cm.$^{-1}$ and 1310 cm.$^{-1}$.

Confirmation of structures V and VI was obtained by their conversion into derivatives of thiophene by reaction with hydrogen peroxide in acetic acid.

The reaction of 2,5-diphenyl-3,6-dibromo-1,4-dithiadiene (V) with hydrogen peroxide gave a 76% yield of 2,4-diphenyl-3,5-dibromothiophene (X). This thiophene derivative, together with unknown reference compounds, was prepared as summarized in these equations
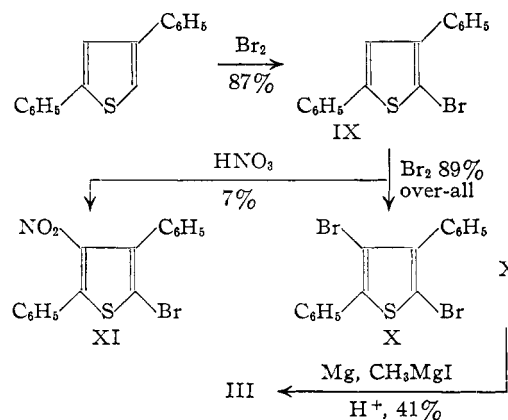
The reaction of 2,5-diphenyl-3-nitro-6-bromo-1,4-dithiadiene (VI) with hydrogen peroxide, similarly, yielded predominately a single product (>50% yield). This material was shown to be 2,4-diphenyl-3-nitro-5-bromothiophene (XI), instead of the possible 3-bromo-5-nitro isomer, by its independent synthesis from IX, as shown in the equations above. It is interesting to note that the 3-nitro isomer is also the principal product when 2,5-diphenyl-3-nitro-1,4-dithiadiene (VII) is oxidized with hydrogen peroxide.[3]

The reaction of 2,5-diphenyl-3,6-dinitro-1,4-dithiadiene (VIII) with hydrogen peroxide gave, as a principal product (25% yield), 2,4-diphenyl-3,5-dinitrothiophene (XII).
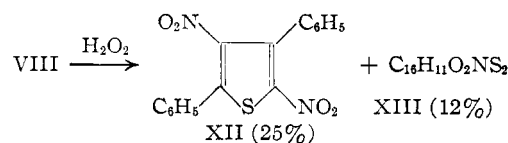
A second product of this reaction, XIII, isolated in 12% yield, was a solid melting at 231–232°. This material is isomeric with 2,5-diphenyl-3-nitro-1,4-dithiadiene (VII, m.p. 131–132°), and had previously been isolated[3] as a minor product of the thermal decomposition of VII. When VIII was thermally decomposed, in boiling benzene, oxides of nitrogen were evolved, and XIII was isolated as the principal product (43% yield). Our efforts to elucidate the structure of this compound have been unsuccessful; however, we do know that the compound is stable to hot, aqueous, alkaline permanganate, and that its reductive acetylation gives 2,4-diphenyl-5-acetylaminothiophene (XIV, 41% yield). An authentic sample of XIV was prepared by the reductive acetylation of the corresponding nitrothiophene.[3]

Experimental

2,5-Diphenyl-3-bromo-1,4-dithiadiene (II).—2,5-Diphenyl-1,4-dithiadiene (2.0 g., 0.0074 mole) was dissolved in

acetic anhydride (100 ml.) and bromine (1.2 g., 0.0075 mole) in acetic acid (5 ml.) was added dropwise. The mixture was allowed to stand for ten minutes and then poured onto ice. After the acetic anhydride had hydrolyzed the mixture was filtered, and the solid was washed with water and recrystallized from 95% ethanol. The product weighed 1.8 g. and melted at 85–86°. An additional 0.15 g. of product (m.p. 85–86°) was obtained from the mother liquors (combined weight 1.95 g., 75% yield).

Anal. Calcd. for $C_{16}H_{11}BrS_2$: C, 55.34; H, 3.20. Found: C, 55.45; H, 3.24.

The Oxidation of 2,5-Diphenyl-3-bromo-1,4-dithiadiene (II).—A mixture of II (0.62 g., 0.0018 mole), potassium permanganate (2.07 g., 0.0131 mole), acetone (70 ml.) and water (30 ml.) was stirred at room temperature for 11 hours. The resulting mixture was filtered with diatomaceous filter aid and the solid was washed with hot water. The combined acetone–water filtrate and wash was extracted with ether, neutralized to *p*H 2–3 with hydrochloric acid and the liberated benzoic acid extracted with ether (continual extraction). The ethereal extract from the continual extraction was concentrated and bromine-free acid (m.p. 120–122°) was obtained. This product was recrystallized from water to give 0.28 g. (64.3% yield) of pure benzoic acid (m.p. and mixed m.p. 122–122.5°).

The Reaction of 2,5-Diphenyl-3-bromo-1,4-dithiadiene (II) with Hydrogen Peroxide. 2,4-Diphenyl-3-bromothiophene and a Sulfone of II.—A solution of 30% hydrogen peroxide (2.20 g., 0.0194 mole) in acetic acid (10 ml.) was added to a solution of 2,5-diphenyl-3-bromo-1,4-dithiadiene (2.22 g., 0.00640 mole) in acetic acid (50 ml.), and the resulting solution was maintained at 87° for 80 minutes. The mixture was then poured into water (100 ml.), and the resulting emulsion was extracted with benzene and with ether. The organic extract was washed with aqueous bicarbonate, dried, and the solvents were removed. The resulting tan crystalline residue (1.65 g.) was chromatographed on neutralized Merck alumina. The column was developed first with petroleum ether–benzene (20%) which afforded 0.28 g. (13.9% yield) of slightly impure 2,4-diphenyl-3-bromothiophene (III). This product was purified, with little loss, by recrystallization from ethanol. The pure material melted at 120–121.5° and caused no depression in melting point when admixed with authentic III.

The column was then eluted with petroleum ether–diethyl ether. Little material was eluted until the concentration of diethyl ether was 70–100%. From these fractions 1.16 g. (47.8%) of a colorless solid was obtained, most of which melted at 173–177°. This material was further purified (m.p. 176.5–178.5) with little loss by recrystallization from ethyl acetate. This product has been tentatively designated as a monosulfone of II (IV?).

Anal. Calcd. for $C_{16}H_{11}O_2S_2Br$: C, 50.70; H, 2.92; S, 16.89; Br, 21.07. Found: C, 51.17; H, 2.95; S, 17.24; Br, 21.20.

This product was thermally quite stable and was recovered in 63.5% yield after being maintained at 200° for 40 minutes.

2,5-Diphenyl-3,6-dibromo-1,4-dithiadiene (VI) (a).— 2,5-Diphenyl-1,4-dithiadiene (2.0 g., 0.0074 mole) in acetic anhydride (50 ml.) was treated dropwise with bromine (2.4 g., 0.015 mole) in acetic acid (3 ml.). The resulting solution was cooled, and the white solid that separated weighed 2.0 g. (m.p. 161–162° dec.) after being washed with methanol. An additional quantity of this solid was obtained from the acetic anhydride solution by a procedure similar to that described above for other brominations in acetic anhydride. The combined product was recrystallized from ethyl acetate and weighed 1.6 g. (50% yield, m.p. 165–166°).

Anal. Calcd. for $C_{16}H_{10}Br_2S_2$: C, 45.10; H, 2.37. Found: C, 45.39; H, 2.58.

(b).—2,5-Diphenyl-3-bromo-1,4-dithiadiene (940 mg., 2.70 moles) was brominated with bromine (0.5 g., 3.1 mmoles) in acetic anhydride (25 ml.). The mixture was processed as described in a, above, and 368 mg. (32% yield) of pure 2,5-diphenyl-3,6-dibromo-1,4-dithiadiene was obtained.

Nitration of 2,5-Diphenyl-3-bromo-1,4-dithiadiene. 2,5-Diphenyl-3-bromo-6-nitro-1,4-dithiadiene (VI).—2,5-Diphenyl-3-bromo-1,4-dithiadiene (1.018 g., 2.96 moles) was dissolved in acetic anhydride (25 ml.) and the nitrating solution (0.4 ml., 4 mmole) prepared as previously described[3] was added dropwise. The mixture was allowed to stand at room temperature for five minutes, and was then cooled. The orange needles that separated were collected and washed with 95% ethanol. This material weighed 700 mg. and melted at 143–144°. The acetic anhydride solution was hydrolyzed with water, and the solid, thus obtained, was recrystallized from ethyl acetate. The combined product weighed 754 mg. (65% yield) and melted at 143–144°.

Anal. Calcd. for $C_{16}H_{10}BrNO_2S_2$: C, 48.99; H, 2.57. Found: C, 49.04; H, 2.75.

Bromination of 2,5-Diphenyl-3-nitro-1,4-dithiadiene. 2,5-Diphenyl-3-bromo-6-nitro-1,4-dithiadiene (VI).—2,5-Diphenyl-3-nitro-1,4-dithiadiene (VII)[3] (1.0 g., 0.0032 mole) was suspended in acetic anhydride (40 ml.), and a solution of bromine (0.6 g., 0.0075 mole) in acetic acid (2 ml.) was added dropwise. The resulting solution was heated at 50° for 2 minutes. The orange needles that separated (0.25 g., m.p. 143–144°) were collected, and the filtrate was reheated to 55° for ten minutes and then cooled. An additional 0.58 g. of solid (m.p. 143–144°) was obtained. The mother liquor was hydrolyzed with water, and the solid thus obtained was recrystallized from ethyl acetate affording an additional 0.01 g. of product melting at 143–144°. The combined product weighed 0.84 g. (67% yield) and caused no depression in melting point when admixed with the product prepared by the nitration of 2,5-diphenyl-3-bromo-1,4-dithiadiene.

2,5-Diphenyl-3,6-dinitro-1,4-dithiadiene (VIII). (a).—A 10 *M* nitrating solution was prepared by mixing concentrated nitric acid (31.6 ml., 0.5 mole), urea (0.5 g.) and diluting the solution in 50 ml. with acetic acid. 2,5-Diphenyl-3-nitro-1,4-dithiadiene[3] (1.0 g., 0.0032 mole) was dissolved in acetic anhydride, and the nitrating solution (0.7 ml., 0.007 mole) was added dropwise. The mixture was cooled in an ice-bath, and the solid that formed was collected and washed with acetic anhydride and then with methanol. The product weighed 0.75 g. and melted at 136° dec. The filtrate was poured onto ice-water and an additional 0.2 g. of material (m.p. 127–129° dec.) was obtained which was purified by recrystallization from chloroform–petroleum ether (the combined weight was 0.86 g., 75% yield, melting at 136.5° dec.).

Anal. Calcd. for $C_{16}H_{10}N_2O_4S_2$: C, 53.63; H, 2.82; N, 7.82. Found: C, 53.31; H, 2.78; N, 7.78.

(b).—2,5-Diphenyl-1,4-dithiadiene (0.0075 mole) was nitrated with the nitrating mixture (0.025 mole) by a procedure essentially identical to that described in a, above. The yield of pure 2,5-diphenyl-3,6-dinitro-1,4-dithiadiene was 57%.

Oxidation of 2,5-Diphenyl-3,6-dinitro-1,4-dithiadiene (VIII).—A mixture of 2,5-diphenyl-3,6-dinitro-1,4-dithiadiene (999 mg., 2.79 mmoles), potassium permanganate (8 g., 0.051 mole), water (80 ml.) and 10% sodium hydroxide solution (1 ml.) was refluxed for 5.5 hours. A second portion of potassium permanganate (3.0 g.) was then added to the reaction mixture and the refluxing was continued for six additional hours. The mixture was acidified with concd. sulfuric acid and refluxed for 20 minutes. Finally, the mixture was clarified with sodium bisulfite, cooled and extracted with ether. Ether was removed from the ethereal extract, and a nitrogen-free acid was obtained (339 mg., m.p. 120.5–122°, 50% yield). This material caused no depression in melting point when admixed with authentic benzoic acid. An insoluble, neutral product was also formed in this reaction. This was identified as XIII.

Attempted Oxidation of 2,5-Diphenyl-3,6-dibromo-1,4-dithiadiene.—The procedures used were essentially identical to those described for the oxidation of II and VIII. Starting material was recovered in yields of 60–65%.

2,4-Diphenyl-5-bromothiophene (IX).—A solution of 2,4-diphenylthiophene[3] (1.52 g., 0.00644 mole) in carbon tetrachloride (100 ml.) was treated dropwise with a solution of bromine (1.00 g., 0.00625 mole) in carbon tetrachloride (10 ml.). The solvent and hydrogen bromide were removed by distillation (reduced pressure), and the oily residue solidified (2.14 g.). This product was recrystallized from absolute ethanol to give 1.65 g. (81% yield) of colorless product melting at 51.5–53°. The product was further purified, with only small loss, by chromatography on Merck alumina using petroleum ether as eluent. Pure 2,4-diphenyl-5-bromothiophene melts at 55–56.5°.

Anal. Calcd. for $C_{16}H_{11}SBr$: C, 61.00; H, 3.53. Found: C, 61.23; H, 3.51.

2,4-Diphenyl-3,5-dibromothiophene (X).—A solution of bromine (1.92 g., 0.0120 mole) in acetic acid (5 ml.) was added dropwise to a suspension of 2,4-diphenylthiophene[3,4] (1.18 g., 0.005 mole) in acetic anhydride (40 ml.). The resulting solution was stirred for two hours, filtered, and then water (100 ml.) was added. The resulting solution was stirred for two hours during which time a heavy tan oil separated. The resulting mixture was extracted with ether, and from the ethereal extract there was obtained 1.92 g. of amorphous solid. This product was chromatographed on neutralized Merck alumina using petroleum ether to develop the column. The crude product (1.88 g., m.p. 67–72°, 95.6% yield) was recrystallized from petroleum ether and 1.75 g. (89% yield) of pure X (m.p. 75–76.5°) was obtained.

Anal. Calcd. for $C_{16}H_{10}SBr_2$: C, 48.80; H, 2.56. Found: C, 48.54; H, 2.37.

2,4-Diphenyl-3-bromothiophene (III).—To a solution of 2,4-diphenyl-3,5-dibromothiophene (0.478 g., 0.00121 mole) in ether (10 ml.) was added magnesium turnings (0.0315 g., 0.00130 g. atom), and the mixture was heated to the reflux temperature. A solution of methylmagnesium iodide (from 0.006 mole of methyl iodide) in ether was added to the stirred solution, and the resulting mixture was stirred and heated at the reflux temperature for one hour. Saturated ammonium chloride (20 ml.) was then added to the cold reaction mixture, the ethereal layer was separated, dried and concentrated. The resulting solid (0.394 g.) was recrystallized from petroleum ether to give 0.158 g. (41% yield) of colorless plates melting at 117–120°. The melting point was raised to 120–121.5° by further recrystallizations from methanol.

Anal. Calcd. for $C_{16}H_{11}BrS$: C, 61.00; H, 3.53; S, 10.17; Br, 25.35. Found: C, 61.27; H, 3.57; S, 10.29; Br, 25.40.

2,4-Diphenyl-3-nitro-5-bromothiophene (XI).—A solution of 2,4-diphenyl-5-bromothiophene (0.239 g., 0.000759 mole), in acetic anhydride (20 ml.), was maintained at 0–5° while a solution of nitric acid (0.107 g., 0.00119 mole) in acetic anhydride (10 ml.) was added (15 min.). The resulting solution was stirred at 5° for two hours and quenched with water (50 ml.). The resulting solution was extracted with ether after the acetic anhydride had hydrolyzed. The ethereal extract was then dried, and the ether was removed. The gummy product was chromatographed on neutralized Merck alumina using petroleum ether, petroleum ether–diethyl ether (5–7%), petroleum ether–diethyl ether (10%), petroleum ether–diethyl ether (20%) as eluents. The initial fractions contained a colorless oil, and the fraction obtained with petroleum ether–diethyl ether (10%) contained yellow needles (19 mg., 7% yield, m.p. 101.5–103.5°). The melting point was raised to 103–103.5° by further recrystallization from methanol.

Anal. Calcd. for $C_{16}H_{10}NO_2SBr$: C, 53.36; H, 2.80; N, 3.90. Found: C, 53.67, 53.71; H, 3.05, 2.90; N, 3.96.

2,4-Diphenyl-5-acetylaminothiophene (XIV).—A mixture containing 2,4-diphenyl-5-nitrothiophene[3] (637 mg., 2.26 mmoles), acetic acid (40 ml.), acetic anhydride (20 ml.), Raney nickel (one-half teaspoon) and hydrogen (39 p.s.i.) was shaken for 15 minutes at room temperature. The resulting mixture was filtered and the filtrate was diluted with water (100 ml.). The white solid that separated was recrystallized from 95% ethanol to give 290 mg. (44% yield) of 2,4-diphenyl-5-acetylaminothiophene melting at 162–163°.

Anal. Calcd. for $C_{18}H_{15}NOS$: C, 73.69; H, 5.15. Found: C, 73.55; H, 5.37.

The Reaction of 2,5-Diphenyl-3,6-dibromo-1,4-dithiadiene (V) with Hydrogen Peroxide. 2,4-Diphenyl-3,5-dibromothiophene.—A solution of V (0.512 g., 0.00120 mole) in glacial acetic acid (45 ml.) was heated to 65°, and 30% hydrogen peroxide (0.451 g., 0.00397 mole) was added. The reaction mixture was then maintained at 95° for 70 minutes and then poured into 60 ml. of water. The resulting emulsion was extracted with benzene, and the benzene extract was concentrated to give 0.49 g. of amber gum. The gum was chromatographed on neutralized Merck alumina using petroleum ether and petroleum ether–diethyl ether as eluents. The principal product (0.362 g., 76.7% yield,

m.p. 73–74°) was obtained from the petroleum ether–diethyl ether (10%) fraction. This was the first fraction employing diethyl ether. The product, 2,4-diphenyl-3,5-bromothiophene, melted at 75–76° after recrystallization from petroleum ether and caused no depression in melting point when admixed with authentic X.

The Reaction of 2,5-Diphenyl-3-bromo-6-nitro-1,4-dithiadiene (VI) with Hydrogen Peroxide. 2,4-Diphenyl-3-nitro-5-bromothiophene (XI).—A suspension of VI (0.516 g., 0.00132 mole) in acetic acid (45 ml.) was oxidized with 30% hydrogen peroxide (0.450 g., 0.00397 mole) by a procedure essentially identical to that described above. The crude orange semi-solid product (0.43 g.) was chromatographed on neutralized Merck alumina, using petroleum ether and petroleum ether–diethyl ether as eluents. The main product (57% yield) was eluted in several fractions with diethyl ether concentrations of 12–16%. This product (m.p. 98–103°) was further purified, with little loss of material, by crystallization from methanol. The pure product, m.p. 103–103.5°, caused no depression in melting point when admixed with authentic 2,4-diphenyl-3-nitro-5-bromothiophene (XI).

The fraction (44 mg.) eluted with 40% diethyl ether in petroleum ether was crystallized from benzene–methanol to give a small quantity of lemon-yellow solid that melted at 223–226°; however, this material was not further examined.

The Reaction of 2,5-Diphenyl-3,6-dinitro-1,4-dithiadiene (VIII) with Hydrogen Peroxide. 2,4-Diphenyl-3,5-dinitrothiophene (XII) and Compound XIII.—A suspension of VIII (1.006 g., 2.81 mmoles), 30% hydrogen peroxide (1.0 g., 8.6 mmoles) and acetic acid (50 ml.) was heated on a steam-bath for 35 minutes, and the resulting solution was diluted with water (100 ml.). The orange solid that separated was dried and chromatographed on Alcoa activated alumina (70 g.). The column was developed with 3 l. of petroleum ether–benzene mixtures in which the benzene content was increased from 40 to 90%. Two products were isolated. The first to be eluted (265 mg., m.p. 110–112°) was recrystallized from petroleum ether to give a yellow solid (233 mg., 25% yield, m.p. 124.5–125.5°). This product has been assigned the structure 2,4-diphenyl-3,5-dinitrothiophene (XII).

Anal. Calcd. for $C_{16}H_{10}O_4N_2S$: C, 58.90; H, 3.10. Found: C, 58.96; H, 3.21.

The second product to be eluted was recrystallized from benzene–petroleum ether. This material weighed 103 mg. (12% yield, m.p. and mixed m.p. 231–232° dec.) and was shown to be compound XIII.

Thermal Decomposition of 2,5-Diphenyl-3,6-dinitro-1,4-dithiadiene (VIII).—A solution of VIII (3.0 g., 0.0084 mole) in benzene (100 ml.), was heated at the reflux temperature for 45 minutes. During this time the evolution of oxides of nitrogen was evident. The benzene solution was then cooled, diluted with petroleum ether (80 ml.), and the resulting solution was chromatographed on Alcoa activated alumina (250 g.). The column was developed with the following solvents: benzene (60)–petroleum ether (40) (500 ml.), benzene (70)–petroleum ether (30) (500 ml.), benzene (80)–petroleum ether (20) (500 ml.), benzene (1500 ml.).

A small quantity (146 mg.) of yellow solid was isolated from the earlier fractions. This material melted at 133–134° subsequent to recrystallization from petroleum ether.

Anal. Calcd. for $C_{16}H_{11}O_2SN$: C, 68.30; H, 3.94. Found: C, 68.04; H, 4.11.

This material has the composition calculated for 2,4-diphenylmononitrothiophene; however, it was not identical to either the 2-isomer (m.p. 108–109°)[3] or the 3-isomer (m.p. 113–115°),[3] and has not, as yet, been identified.

The principal fraction was eluted in the latter fractions from the column. This material was recrystallized from benzene–petroleum ether (1.13 g. (43%), m.p. 231–232° dec.).

Anal. Calcd. for $C_{16}H_{11}O_2NS_2$: C, 61.32; H, 3.54; N, 4.47; S, 20.45; mol. wt., 313. Found: C, 61.43, 61.61, 61.95; H, 3.53, 3.66, 3.98; N, 4.35; S, 21.35; mol. wt. (ebullioscopic benzene), 322–333.

This compound proved to be identical with the third compound[3] obtained upon pyrolysis of 2,5-diphenyl-3-nitro-1,4-dithiadiene (VII). The composition of this compound suggests that it is isomeric with 2,5-diphenyl-3-nitro-1,4-dithiadiene (VII). This unknown product, unlike its

isomer VII, was resistant to the action of alkaline permanganate in water (96% recovery).

Reductive Acylation of XIII.—A mixture containing compound XIII (849 mg., 2.71 mmoles), acetic acid (25 ml.), acetic anhydride (12 ml.), Raney nickel (one teaspoon) and hydrogen (39 p.s.i.), was shaken for 15 minutes at 25°. The resulting mixture was filtered (solid washed with acetic acid) and the filtrate was diluted with water (100 ml.).

The white·solid that separated was collected, washed with water and recrystallized from 95% ethanol. 2,4-Diphenyl-5-acetylaminothiophene (XIV) (m.p. and mixed m.p. 162–163°) was obtained in 41% yield (324 mg.). This material caused no depression in melting point when admixed with authentic XIII.

MINNEAPOLIS, MINNESOTA

Conjugative Effects in Divalent Sulfur Groupings[1]

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From measurements of the acidity constants of m- and p-substituted benzoic acids and phenols it is concluded that the order of electron-pair donor type conjugation is $(CH_3)_2N > CH_3O > CH_3S$, and $CH_3CONH > CH_3COO > CH_3COS$. This order also expresses the relative activating influence of the groups in aromatic substitution. Acidity constant and ultraviolet absorption spectral measurements indicate that electron-pair acceptor conjugation for SH, SCH_3, $SCOCH_3$ and SCN groups with groups like p-OCH_3 or p-O^- is slight. It is concluded that the presence of a powerful electron-donor, such as a carbanion, is necessary to evoke a clearly recognizable electron pair acceptor type conjugation in divalent sulfur groups.

It seemed desirable to extend the acidity constant method, which has revealed electron-pair acceptor conjugative effects for sulfone,[3] sulfonium,[4] sulfoxide[5] and sulfonate[6] groups, to groups containing divalent sulfur. The present paper reports such a study and includes some related work on ultraviolet absorption spectra and aromatic substitution reactions.

Electron-pair Releasing Conjugative Effects. Acidity Constant Measurements.—Evidence for the relative ability of CH_3S, CH_3O and $(CH_3)_2N$ groups to release electrons in conjugative interactions with the carboxyl groups was obtained by examining the acidity constants of m- and p-substituted benzoic acids and phenols. The electronic effects of the groups may be expressed as Hammett sigma (σ) constants.[7] Since conjugative interactions should be absent between *meta* groups, and since differences in inductive effects between *meta* and *para* positions are small, the differences $\sigma_{para} - \sigma_{meta}$ of benzoic acids gives an approximate measure of conjugative effects. These groups should not conjugate with the hydroxyl group in phenols, so differences between the σ_{para}-constants of substituted benzoic acids and phenols should also be a rough measure of conjugation in the benzoic acids. Pertinent data have been compiled in Table I.

The greater the $\sigma_p - \sigma_m$ difference for benzoic acids, the higher is the order of conjugative ability of the electron-releasing group with the carboxyl group. From Table I the order is seen to be $(CH_3)_2N = H_2N > CH_3O = HO > CH_3S$. This is

TABLE I

HAMMETT σ-CONSTANTS CALCULATED FROM ACIDITY CONSTANTS OF m- AND p-SUBSTITUTED BENZOIC ACIDS AND PHENOLS

Substituents	Benzoic acids		Phenols	
	σ	$\sigma_p - \sigma_m$	σ	$\sigma_p - \sigma_m$
m-$(CH_3)_2N$	-0.16^a		$+0.04^f$	
p-$(CH_3)_2N$	$-.72^a$	-0.56	$-.12^f$	-0.16
m-H_2N	$-.16^b$		$+.03^g$	
p-H_2N	$-.66^b$	$-.50$	$-.15^g$	$-.18$
m-CH_3O	$+.11^b$		$+.13^e$	
p-CH_3O	$-.27^b$	$-.38$	$-.11^e$	$-.24$
m-HO	$+.06^c$		$+.06^g$	
p-HO	$-.31^d$	$-.37$	$-.17^g$	$-.23$
m-CH_3S	$+.14^e$		$+.23^f$	
p-CH_3S	$-.01^e$	$-.15^h$	$+.21^f$	$-.03$

[a] C. C. Price and D. C. Lincoln, THIS JOURNAL, **73**, 5838 (1951). [b] Ref. 7. [c] J. D. Roberts and W. T. Moreland, THIS JOURNAL, **75**, 2267 (1953). [d] J. F. G. Dippy, *Chem. Revs.*, **25**, 207 (1939). [e] Ref. 3a. [f] Present investigation, see Experimental section. [g] A. Kuhn and A. Wasserman, *Helv. Chim. Acta*, **11**, 23 (1928). [h] This difference agrees well with the difference of -0.17 obtained by C. C. Price and J. J. Hydock, THIS JOURNAL, **74**, 1945 (1952). from the saponification of substituted ethyl benzoates.

the order predicted by Ingold[8] and that found by Baker, Barrett and Tweed[9] using a method different from that of the present investigation.

Since conjugative effects are not expected in the phenols the $\sigma_p - \sigma_m$ differences here should be constant. Table I reveals that this is true for the most part, only the difference for the CH_3S group being out of line.

The σ_{meta}-constants for a given group should be the same whether determined from benzoic acids or phenols if the interactions are purely inductive. This is true for m-CH_3O and m-HO groups and the difference for m-CH_3S is not much greater than the experimental error. The differences for m-H_2N and m-$(CH_3)_2N$ appear to be definitely outside of experimental error, however, and suggest a disturb-

(1) This investigation was supported in part by the American Petroleum Institute as part of Project 48B.

(2) Texas Company Research Fellow 1952–1954.

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