sodium bicarbonate solution, water and saturated sodium chloride solution. After drying and concentrating, the compound was fractionated through a 10-in. Holtzmann column to produce 1.9 g. of material boiling at 57–59° (55 mm.), $n^{21}\text{D}$ 1.4935. The ultraviolet absorption spectrum of this compound was essentially identical to that observed from the 4,5-dimethylenecyclohexene obtained from the previously mentioned preparation; $\lambda_{\text{max.}}$ 216 mμ; ε 4600 (calcd. for pure diene). For *o*-xylene $\lambda_{\text{max.}}$ 211 mμ; ε 8200.[10]

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[10] Spectrum No. 173, "Catalog of Ultraviolet Spectral Data," American Petroleum Institute Research Project 44, National Bureau of Standards.

URBANA, ILLINOIS

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

Heterocyclic Vinyl Ethers. VII. Rearrangements of the 1,4-Dithiadiene Ring System[1]

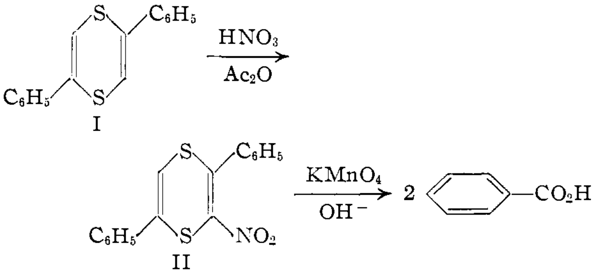
BY WILLIAM E. PARHAM AND VINCENT J. TRAYNELIS

RECEIVED JUNE 4, 1954

The nitration of 2,5-diphenyl-1,4-dithiadiene (I) has been shown to give 2,5-diphenyl-3-nitro-1,4-dithiadiene (II). Reactions are discussed which involve the conversion of the dithiadiene ring system into the thiophene ring system.

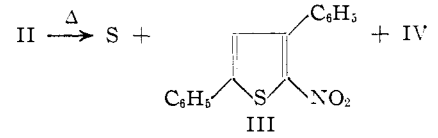
In a previous communication reactions were described which involved the conversion of the dithiadiene ring system to the thiophene ring system.[2] It was assumed by analogy to benzo-1,4-dithiadiene[3] that electrophilic substitution in 2,5-diphenyl-1,4-dithiadiene (I) occurred preferentially in the sulfur-containing ring. This paper describes work pertinent to the orientation of electrophilic substitution in I, and new reactions leading to derivatives of thiophene.

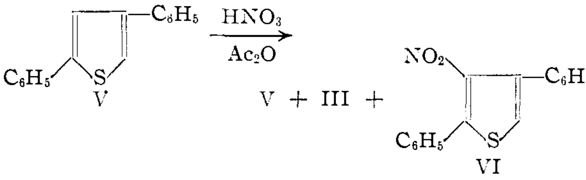
When a weak nitrating agent was added to an acetic anhydride solution of I, a deep red coloration[4] appeared. After a five-minute reaction period, the acetic anhydride was hydrolyzed and a red crystalline material resulted. Recrystallization of the product from ethyl acetate gave 74% yield of 2,5-diphenyl-3-nitro-1,4-dithiadiene (II).



The position of the nitro group was assigned on the basis of potassium permanganate oxidations. Several oxidations were performed and in no experiment was any nitrobenzoic acid found. This observation, along with the isolation of benzoic acid in 67% yield (calculated for 2 moles of acid per mole of II) led to the assignment of structure II for the nitro derivative. The experiments to follow support this assignment of structure.

The pyrolysis of I to give sulfur and 2,4-diphenylthiophene has been reported[2] to proceed at 180°. With the presence of a polarizing nitro group on the dithiadiene ring, the elimination of sulfur should be facilitated. Such was the case, for when II was heated to 135° a vigorous exothermic reaction occurred which resulted in the formation of sulfur (14%), 2-nitro-3,5-diphenylthiophene (III, 20%) and IV (11%). Compound IV was not isomeric with III and is under investigation.





Compound III was prepared independently by nitration of 2,4-diphenylthiophene (V).[5] In this reaction, starting material was recovered in 65% yield; however, an 18% yield of 2-nitro-3,5-diphenylthiophene (III) was obtained. A comparison of infrared and ultraviolet spectra of the two samples of III, and lack of depression in mixture melting points, established the identity of these compounds. Since substitution proceeds readily on the C-2 position in thiophene, structure III was assigned[6] for the major nitro product obtained by nitration of V. Another mononitro product was present in 2% yield; and since some substitution (5%) also occurs in the C-3 position during the nitration of thiophene, this compound was assigned structure VI, 2,4-diphenyl-3-nitrothiophene. Subsequent experiments confirmed the assignment of this structure.

The formation of III (the 2-nitrothiophene) in preference to VI (the 3-nitrothiophene) by the action of heat on II was anticipated from an examination of the possible resonance hybrids of II. The contribution of structure IIa, where the negative charge may be delocalized by the nitro group,

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(1) This work was supported by the Office of Ordnance Research, Contract No. DA-11-022-ORD-571.

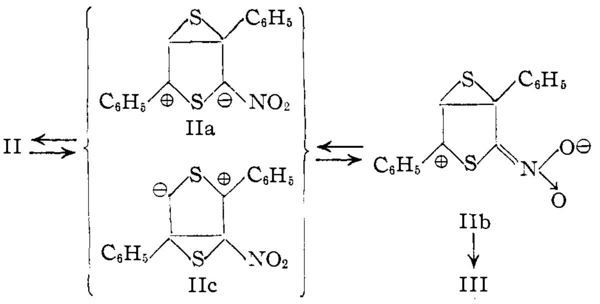
(2) W. E. Parham and V. J. Traynelis, THIS JOURNAL, **76**, 4960 (1954).

(3) W. E. Parham, T. M. Roder and W. R. Hasek, *ibid.*, **75**, 1648 (1953).

(4) Previously, Johnson and co-workers have reported the appearance of a deep red color when I was treated with concentrated nitric acid. *Cf.* T. B. Johnson, R. C. Moran and E. F. Kohmann, *ibid.*, **35**, 451 (1913).

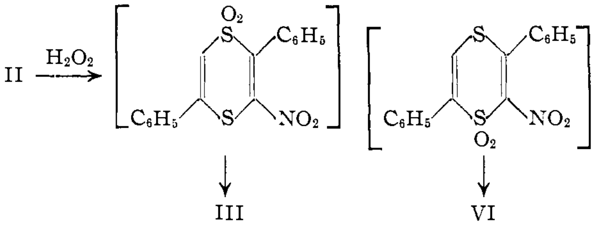
(5) A previous attempt to effect the mononitration of 2,4-diphenylthiophene was unsuccessful; an unidentified mixture was obtained. *Cf.* M. T. Bogert and P. P. Herrera, *ibid.*, **45**, 241 (1923).

(6) The Friedel–Crafts acylation of 2,4-diphenylthiophene is reported to give only 2-thienyl ketones. *Cf.* E. Fromm, P. Fantl and E. Leibsohn, *Ann.*, **457**, 276 (1927).



should be greater than the contribution of IIc. Thus, the favored structures IIa and IIb could eliminate the sulfur from the sulfirane ring, by a mechanism discussed in an earlier paper,[2] to give III.

The monosulfone of I was shown to eliminate sulfur dioxide and give 2,4-diphenylthiophene.[2] The sulfur atoms in II are no longer equivalent and two different monosulfones, and two different nitrothiophenes could result.



A study of the oxidation of II was made and the products isolated were III (31%) and VI (46%). Mixture melting point studies of these compounds and the corresponding nitro compounds obtained from the nitration of V established their identity. Also, the isolation of VI from the oxidation of II afforded evidence which confirmed the assignment of structure for VI.

The reaction of II with phosphorus oxychloride and dimethyl formamide did not introduce an aldehyde group into the molecule; instead, sulfur was eliminated and III was formed in 40% yield.

All of the reactions of II which have been described, led to the formation of 2,4-diphenylthiophenes with nitro groups on the thiophene ring. Since these reactions involved the elimination of sulfur or sulfur dioxide, the nitro group had to be on the dithiadiene ring to give the nitrothiophenes. Thus, support for the structure of II is found in these reactions.

Experimental

Alcoa Activated Alumina F-20 was used for all the chromatographs.

2,5-Diphenyl-3-nitro-1,4-dithiadiene (II).—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 to 50 ml. with acetic acid. To a solution of 2,5-diphenyl-1,4-dithiadiene[7] (1.0 g., 0.0037 mole) in acetic anhydride (50 ml.) at room temperature was added the above nitrating solution (0.4 ml., 0.004 mole). The resulting red mixture was allowed to stand at room temperature for five minutes. After this time, the solution was poured into an excess of ice-water. The resulting red solid was filtered, washed well with water and dried. Recrystallization of the crude material from ethyl acetate gave 0.86 g. (74%) of deep red needles, m.p. 131–132° dec. An analytical sample of 2,5-diphenyl-3-nitro-1,4-dithiadiene melted at 132–133° dec.

Anal. Calcd. for $C_{16}H_{11}NO_2S_2$: C, 61.32; H, 3.54; N, 4.46. Found: C, 61.09; H, 3.70; N, 4.62.

Oxidation of 2,5-Diphenyl-3-nitro-1,4-dithiadiene.—The procedure of Shriner and Fuson[8] was used for the oxidation of 2,5-diphenyl-3-nitro-1,4-dithiadiene (1.000 g., 0.00319 mole) with potassium permanganate (8.0 g., 0.051 mole). After the reaction mixture was refluxed for nine hours and the manganese dioxide and excess potassium permanganate destroyed, the clear solution was filtered and cooled. The white solid, which crystallized, was filtered and the filtrate extracted twice with 50-ml. portions of ethyl ether. When the ether was removed a white crystalline solid resulted, which combined with the above solid weighed 520 mg. (67%), m.p. 121–122°. Recrystallization of these solids from water gave 436 mg. (55%) of benzoic acid, m.p. 121–122°. A mixture melting point with an authentic sample was not depressed.

This experiment was repeated several times and at no time was any nitrobenzoic acid found.

Pyrolysis of 2,5-Diphenyl-3-nitro-1,4-dithiadiene.—The procedure described in an earlier report[2] was used. 2,5-Diphenyl-3-nitro-1,4-dithiadiene (1.116 g., 0.00357 mole), under an atmosphere of nitrogen was inserted into an oil-bath preheated to 200°. At the melting point (135°) of the red nitro compound a vigorous exothermic reaction took place, which rapidly raised the temperature of the melt to 180°. When the temperature reached 185°, the material was removed from the bath and cooled under nitrogen. The pyrolysate was chromatographed on 80 g. of alumina. Monoclinic sulfur (16 mg., 14%, m.p. 118–121°) was eluted with 10% benzene in petroleum ether (30–60°). A mixture melting point with an authentic sample was not depressed.

The eluant with 40% benzene in petroleum ether (30–60°) contained a bright yellow solid (320 mg., m.p. 104–106°). Recrystallization of the crude material from petroleum ether (60–68°) gave 2-nitro-3,5-diphenylthiophene (200 mg., 20%, m.p. 110–111°). A mixture melting point with the major nitro product from nitration of 2,4-diphenylthiophene was not depressed.

Anal. Calcd. for $C_{16}H_{11}NO_2S$: C, 68.30; H, 3.94. Found: C, 68.42; H, 3.67.

A third compound was eluted with 60 and 70% benzene in petroleum ether (30–60°). This compound was not 2,4-diphenyl-3-nitrothiophene and its structure is under investigation.

Reaction of Hydrogen Peroxide with 2,5-Diphenyl-3-nitro-1,4-dithiadiene.—A mixture of 2,5-diphenyl-3-nitro-1,4-dithiadiene (2.0 g., 0.0064 mole) and glacial acetic acid (50 ml.) was heated to 60°, and 30% hydrogen peroxide solution (2.2 g., 0.020 mole) was then added. The reaction mixture was heated between 55–60° for 20 minutes, after which time the red solution became yellow. After the solution was diluted with water, the yellow solid that formed was filtered, washed with water and dried. The crude material was purified by chromatography on 150 g. of alumina. The fraction eluted with 25–30% benzene in petroleum ether (30–60°) contained a pale yellow solid. When this crude material was recrystallized from petroleum ether (60–68°), pure 2,4-diphenyl-3-nitrothiophene (0.83 g., 46%, m.p. 115–116°) was obtained. A mixture melting point with the minor nitro product from nitration of 2,4-diphenylthiophene was not depressed.

Anal. Calcd. for $C_{16}H_{11}NO_2S$: C, 68.30; H, 3.94; N, 4.98. Found: C, 68.70; H, 4.30; N, 4.90.

A bright yellow solid was eluted with 40 and 50% benzene in petroleum ether (30–60°)—this material was obtained from the chromatogram immediately following the 2,4-diphenyl-3-nitrothiophene. Recrystallization of the crude material from petroleum ether (60–68°) gave 2-nitro-3,5-diphenylthiophene (0.55 g., 31%, m.p. 110–111°). A mixture melting point with III was 110–111°.

Reaction of 2,5-Diphenyl-3-nitro-1,4-dithiadiene with Phosphorus Oxychloride in Dimethyl Formamide.—A mixture of 2,5-diphenyl-3-nitro-1,4-dithiadiene (1.0 g., 0.0032 mole), phosphorus oxychloride (0.77 g., 0.005 mole) and dimethyl formamide (1.0 ml.) was heated on a steam-bath for 1.5 hours. To the reaction mixture was then added 10 ml. of dimethyl formamide and the solution poured into ice-

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(7) R. H. Baker and C. Barkenbus, This Journal, **58**, 262 (1936).

(8) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 198.

water. After the aqueous mixture was extracted four times with 100 ml. of ethyl ether, the ether extract was washed with 5% sodium bicarbonate solution and water. The ether was removed and the residue purified by chromatography on 75 g. of alumina. A yellow solid (430 mg.) was eluted with 40% benzene in petroleum ether (30–60°). Recrystallization of the crude material from petroleum ether (60–68°) gave 2-nitro-3,5-diphenylthiophene (360 mg., 40%, m.p. 110–111°). A mixture melting point with III obtained by the nitration of 2,4-diphenylthiophene was not depressed.

Nitration of 2,4-Diphenylthiophene.—2,4-Diphenylthiophene[9] (608 mg., 2.60 mmoles) was dissolved in acetic anhydride (50 ml.) and to this solution was added the nitrating mixture (0.25 ml., 2.5 mmoles) described in the first experiment. The reaction mixture turned yellow and was kept at room temperature for ten minutes. The solution was poured into ice-water and after the acetic anhydride was hydrolyzed, the yellow solid that formed was filtered, washed well with water, dried and chromatographed on 65 g. of alumina. The eluant with 20% benzene in petroleum ether (30–60°) contained unchanged starting material (395 mg., 65%, m.p. 119.5–121°). This material did not depress the melting point of 2,4-diphenylthiophene.

With 30% benzene in petroleum ether (30–60°), a pale yellow solid (21 mg., 3%, m.p. 105–107) was first eluted. Recrystallization of this crude material from petroleum ether (60–68°) gave 2,4-diphenyl-3-nitrothiophene, m.p. 113–115°.

After the 2,4-diphenyl-3-nitrothiophene, a bright yellow solid (180 mg.) was eluted with 30% benzene in petroleum ether (30–60°). Recrystallization of this solid from petroleum ether (60–68°) gave 2-nitro-3,5-diphenylthiophene (135 mg., 18%, m.p. 108–109°). A pure sample melted at 110–111° and the infrared and ultraviolet spectra of this sample were identical to those of III. Also a mixture of the two samples melted at 110–111°.

MINNEAPOLIS, MINNESOTA

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[9] E. Campaigne, THIS JOURNAL, **66**, 684 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

Orientation in Aromatic Substitution by the Benzenesulfonimido Radical[1]

BY O. C. DERMER AND M. T. EDMISON[2]

RECEIVED JUNE 5, 1954

The thermal decomposition of benzenesulfonyl azide in solution yields radicals capable of initiating vinyl polymerization. The action of these radicals on various monofunctional derivatives of benzene and hydrolysis of the resulting substituted benzenesulfonanilides gives a mixture of isomeric substituted anilines. Spectrophotometric determination of these anilines showed that groups *ortho–para* directing in ordinary electrophilic substitution produce *ortho–meta–para* orientation of the benzenesulfonimido group in a ratio roughly approaching 4:1:2.

The orientation in substitution of radicals on aromatic nuclei already bearing other groups is of value in the elucidation of mechanism of radical reactions. The reaction described by Curtius and co-workers,[3] in which the thermal decomposition of arenesulfonyl azides in aromatic liquids gave simple and N-substituted arenesulfonamides, appears to have involved radicals, as he thought, although it is not discussed by Waters.[4] Curtius' finding that *p*-toluenesulfonyl azide and dimethylaniline thus yield *p*-toluenesulfonamidodimethylanilines in the isomeric ratio of 2 *ortho* to 1 *para* is particularly interesting in view of recently published results of phenylation and hydroxylation experiments.

Methyl acrylate and especially acrylonitrile were found to polymerize at 110° in the presence of small amounts of decomposing benzenesulfonyl azide; this is taken as good evidence[5] of the presence of radicals. Furthermore, such polymerization of acrylonitrile was inhibited by the presence of traces of hydroquinone or *p*-benzoquinone.

According to the method of Curtius,[3] benzenesulfonyl azide was decomposed at 105–120° in various monosubstituted benzenes to yield nitrogen, benzenesulfonamide, and isomeric benzenesulfonanilides. The solid sulfonamide–sulfonanilide mixture was isolated and hydrolyzed in 25% hydrochloric acid and the substituted anilines were extracted, usually after steam distillation from alkaline solution. The extract was analyzed spectrophotometrically for the *ortho*, *meta* and *para* isomeric forms of the substituted anilines by the method of Vaughn and Stearn.[6]

The quantitative results are shown in Table I.

TABLE I

ISOMER RATIOS IN SUBSTITUTED ANILINES

Aromatic substrate	Ratio of isomeric anilines, % *ortho*	*meta*	*para*
Toluene	60,61	12,11	28,28
Chlorobenzene	54,57	18,13	28,30
Bromobenzene	54,61	14,6	32,33
Anisole	48,60	26,17	26,33
Phenol	58	20	22

Experiments with benzoyl chloride, benzonitrile and methyl benzoate as substrates all yielded mixed aminobenzoic acids as final products, but these could not be isolated for spectrophotometric analysis without disturbing the isomer ratio in the mixture, as shown by knowns. Unfortunately chromatographic separation was not tested. The results were sufficient only to indicate that *ortho* substitution was predominant in the reaction of these derivatives of benzoic acid. The reaction of benzenesulfonyl azide with nitrobenzene gave an intractable tar, as reported by Curtius, and nitric oxide, evidently by an unexpected reaction with the nitro group. The preferential attack on a nitro

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[1] Abstracted from the Ph.D. dissertation of M. T. Edmison, May, 1952. Presented in part at the 7th Southwest Regional Meeting of the American Chemical Society, December, 1951.

[2] University of Arkansas, Fayetteville, Arkansas.

[3] T. Curtius, *J. prakt. Chem.*, **125**, 303 (1930).

[4] W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, New York, N. Y., 1946.

[5] K. Ziegler, W. Deparade and H. Kuhlhorn, *Ann.*, **567**, 151 (1950); K. Ziegler, W. Deparade and W. Meye, *ibid.*, **567**, 141 (1950).

[6] R. T. Vaughn and A. E. Stearn, *Anal. Chem.*, **21**, 1361 (1949).