to the following procedure. 1,4-Dithiadiene disulfone was dissolved in acetic acid and slightly more than 2 molar equivalents of the diene were added. The solution was warmed for varying periods of time (see Table I) and the diadducts separated by filtration. The more soluble monoadducts were isolated by evaporating the filtrate to dryness and crystallizing the residue from the appropriate solvent. In most cases, the diadduct proved to be nearly insoluble in all solvents and was found to decompose on attempted sublimation at reduced pressure. The butadiene adduct was prepared by adding butadiene to an acetic acid solution of the sulfone in a Carius tube and heating the sealed tube in a furnace. An attempted Diels–Alder reaction with anthracene, by fusion of the solids gave only reactants as identifiable crystalline solids.

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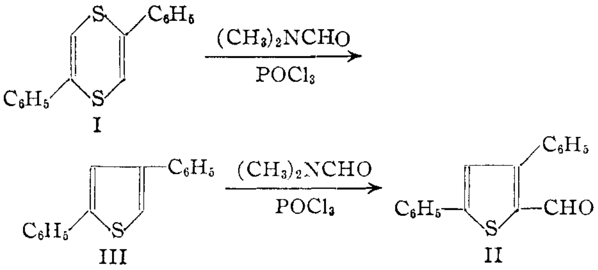
# Heterocyclic Vinyl Ethers. VI. Rearrangements of the 1,4-Dithiadiene Ring System[1]

BY WILLIAM E. PARHAM AND VINCENT J. TRAYNELIS

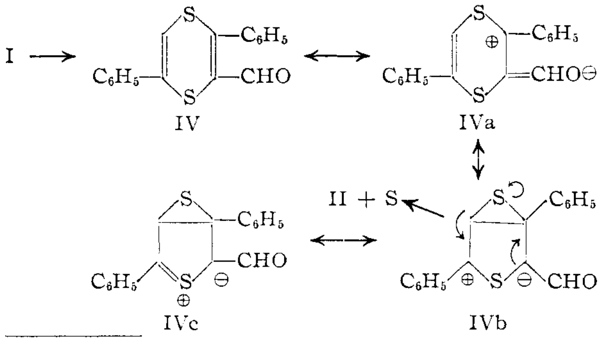
RECEIVED APRIL 30, 1954

New reactions are reported which involve the conversion of 2,5-diphenyl-1,4-dithiadiene into 2,4-diphenylthiophene or derivatives of 2,4-diphenylthiophene.

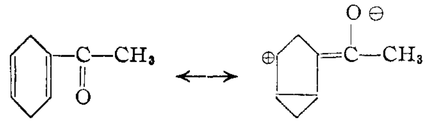
We have investigated the reaction of 2,5-diphenyl-1,4-dithiadiene (I) with dimethylformamide and phosphorus oxychloride (the Vilsmeier reaction), and have shown that the product of this reaction is not 3,5-diphenyl-1,4-dithiadiene-2-carboxaldehyde (IV), the expected aldehyde, but rather 2,4-diphenyl-5-thenaldehyde (II, 32%).



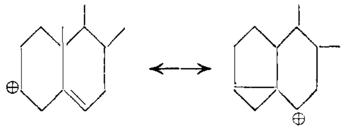
That the aldehyde II was present in substantially greater amounts was shown readily by its isolation, in 48% yield, as the corresponding 2,4-dinitrophenylhydrazone. The structure of the aldehyde was established by independent synthesis (88% yield) from 2,4-diphenylthiophene (III) as summarized in the equations above. The aldehyde obtained from III was shown to be identical to the aldehyde obtained from I, by mixed melting studies of the free aldehydes, the corresponding 2,4-dinitrophenylhydrazones and *p*-nitrophenylhydrazones, and by comparison of the infrared and ultraviolet spectra of the free aldehydes.



The formation of II from 2,5-diphenyl-1,4-dithiadiene is considered to involve an intramolecular reaction with the elimination of sulfur from the initial reaction product, 3,6-diphenyl-1,4-dithiadiene-2-carboxaldehyde (IV). Resonance hybridization of IV could allow contributions from structures of the type shown in formulas IV–IVc. The formation of II and sulfur can occur as shown in formula IVb. There are a number of arguments in favor of hybridization involving the sulfirane ring (IVb and IVc): (1) There is parallel for three-membered ring hybridization,[2] *i.e.*, the *i*-steroids



*i*-steroids



(2) The boat configuration for 1,4-dithiadiene has been established,[3] and the bond distance between carbon atoms 3 and 5 should be such that interaction is possible; (3) structures involving the sulfirane ring would appear to be favorable ones, since no excessive separation of charge is required (see IVc); furthermore, the phenyl group present on carbon 6 could assist in the delocalization of charge; (4) finally, there is analogy for the interaction of positively polarized carbon atoms with ethylenic systems. The Diels–Alder reaction is such a case, and this reaction can be considered as an intramolecular Diels–Alder reaction.

The action of heat upon I was studied in order to

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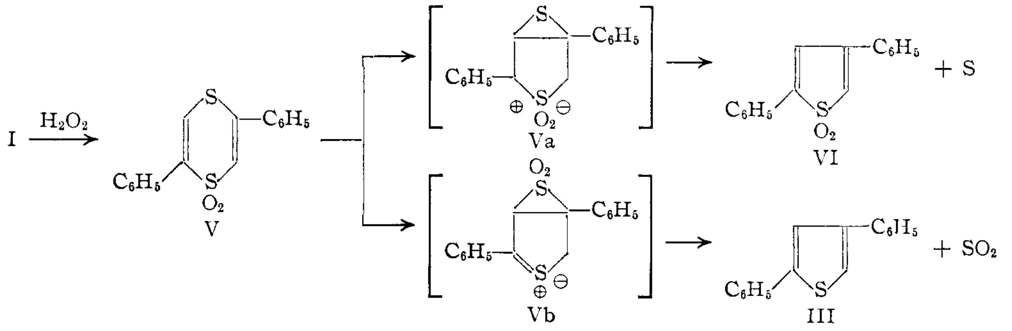
[1] This work was supported by the office of Ordnance Research, Contract No. DA-11-022-ORD-571.

[2] D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5691 (1951), have suggested that a similar spatial electronic interaction is the explanation for the observed shift to longer wave lengths and decrease in intensity of the ultraviolet absorption maximum of 2,5-dihydroacetophenone as compared to 1-acetylcyclohexene.

[3] W. E. Parham, H. Wynberg, W. R. Hasek, P. A. Howell, R. M. Curtis and W. N. Lipscomb, *ibid.*, **76**, 4957 (1954).

gain additional information[4] concerning this novel reaction. It was anticipated that I should eliminate sulfur to give 2,4-diphenylthiophene (III); however, such a transformation should occur at a higher temperature than the analogous reaction with IV, in which there is a bond polarizing carbonyl group present. Such was found to be the case. When 2,5-diphenyl-1,4-dithiadiene (I) was heated to 190° in an inert atmosphere, an exothermic reaction occurred. The products of this reaction were purified by chromatography, and a 67% yield of monoclinic sulfur and a 68% yield of pure 2,4-diphenylthiophene (III) were obtained.

These results directed our attention to the 2,5-diphenyl-1,4-dithiadiene monosulfone (V) system. The sulfone group in this molecule should assist the polarization of the double bonds, and thus lower the energy required for the elimination. In this case, two products (VI and III) appear possible. Although a study of this process proved complicated by experimental limitations, the results indicate strongly the reaction path shown in I → V → Vb → III.



Szmant[5] had previously studied the oxidation of 2,5-diphenyl-1,4-dithiadiene. In addition to the disulfone of I, a second product (m.p. 128–129°), of undetermined structure, was obtained. We have repeated this work and have shown that this product is a molecular compound of 2,5-diphenyl-1,4-dithiadiene (I) and 2,4-diphenylthiophene (III). The structure of this product was established in the following way: (a) the ultraviolet spectrum of this product was essentially identical to the sum of its two components, (b) the product reacts with mercuric chloride to give 5-chloromercuri-2,4-diphenylthiophene (2,5-diphenyl-1,4-dithiadiene does not react with mercuric chloride), (c) the product caused no depression in melting point when mixed with the complex (m.p. 128–129°), obtained in 94% yield, by the recrystallization of an equimolar mixture of I (m.p. 117–118°) and III (m.p. 122–123°).

Consequently, it can be stated with certainty that the oxidation of I with hydrogen peroxide does lead to the formation of III. Although it might be anticipated that Vb would make a greater contribution to the structure of V than Va, it is probable that the course of this reaction is directed by the relative stabilities of products formed.

## Experimental

**Formylation of 2,5-Diphenyl-1,4-dithiadiene (I).**—A mixture of 2,5-diphenyl-1,4-dithiadiene[6] (2.7 g., 0.01 mole, m.p. 118–119°), dimethylformamide (1.1 g., 0.015 mole) and phosphorus oxychloride (2.3 g., 0.015 mole) was heated on a steam-bath for one hour. Dimethylformamide (8 ml.) was then added, and the resulting solution was diluted with water. The oil which separated, solidified and was triturated with water, filtered, washed with water and dried *in vacuo*. The crude material was treated with charcoal and recrystallized twice from petroleum ether (60–68°). The yield of aldehyde, m.p. 98–99°, was 0.43 g. The combined mother liquor from the recrystallizations was evaporated, and the residual solid was recrystallized from methanol to give 0.45 g. (17%) of starting material, m.p. 116.5–118°. The methanol mother liquor was evaporated and the residue recrystallized from petroleum ether (60–68°). An addition 0.41 g. (combined yield 32%) of aldehyde, m.p. 97–98°, was obtained. The aldehyde was subsequently shown to be 2,4-diphenyl-5-thenaldehyde (II) Maximum absorption of the aldehyde in the ultraviolet region was: $\lambda^{\max}_{239\ \mathrm{m}\mu}$ $\epsilon$ 13,400, $\lambda^{\max}_{258\ \mathrm{m}\mu}$ $\epsilon$ 17,600, $\lambda^{\mathrm{ax}}_{335\ \mathrm{m}\mu}$ $\epsilon$ 21,000.

*Anal.* Calcd. for $C_{17}H_{12}OS$: C, 77.26; H, 4.58; S, 12.14. Found: C, 77.10; H, 4.87; S, 12.24.

**The 2,4-dinitrophenylhydrazone** of the aldehyde, m.p. 266–267°, was prepared in the usual way and recrystallized from nitromethane. *Anal.* Calcd. for $C_{23}H_{16}N_4O_4S$: C, 62.14; H, 3.63; N, 12.61; S, 7.21. Found: C, 61.75; H, 3.34; N, 12.72; S, 7.29.

**The *p*-nitrophenylhydrazone**, m.p. 244–245°, was recrystallized from nitromethane. *Anal.* Calcd. for $C_{23}H_{17}N_3O_2S$: C, 69.14; H, 4.29; N, 10.52; S, 8.03. Found: C, 68.47; H, 4.43; N, 10.51; S, 7.94.

The experiment above was repeated, but the crude solid obtained from the reaction mixture was dissolved in methanol and treated with an excess of 2,4-dinitrophenylhydrazine reagent. The red derivative was recrystallized from a chloroform–methanol mixture and gave a 48% yield of the corresponding 2,4-dinitrophenylhydrazone, m.p. 265–266°.

**2,4-Diphenylthiophene (III).**—2,4-Diphenylthiophene, m.p. 121.5–123°, was prepared from anhydroacetophenone disulfide, m.p. 111–112°, according to the procedure described by Campaigne.[7] The over-all yield from acetophenone was 52%.

**2,4-Diphenyl-5-thenaldehyde (II).**[8]—The procedure described for the formylation of 2,5-diphenyl-1,4-dithiadiene was employed. From 2,4-diphenylthiophene (1.0 g., 0.0042 mole), dimethylformamide (0.44 g., 0.006 mole) and phosphorus oxychloride (0.92 g., 0.006 mole) there was obtained 1.12 g. of crude aldehyde, m.p. 94–97°. The crude solid was recrystallized from petroleum ether (60–68°) and gave 0.98 g. (88%) of pure 2,4-diphenyl-5-thenaldehyde, m.p. 98–99°. The 2,4-dinitrophenylhydrazone and *p*-nitrophenylhydrazone of this product melted at 266–267° and 244–245°, respectively. The infrared and ultraviolet spectra of II and the aldehyde obtained directly from I were identical; furthermore, mixture of the free aldehydes and mixtures of

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[4] We were unable to demonstrate the presence of elementary sulfur in the product obtained by the conversion of I → II; however, this was not unexpected since sulfur reacts with phosphorus oxychloride.

[5] H. H. Szmant and J. Dixon, THIS JOURNAL, **75**, 4354 (1953).

[6] R. H. Barker and C. Barkenbus, *ibid.*, **58**, 262 (1936).

[7] E. Campaigne, *ibid.*, **66**, 684 (1944).

[8] The synthesis of 2,4-diphenyl-5-thenaldehyde was reported by N. P. Buu-Hoï, P. Demerseman and R. Royer, *Compt. rend.*, **237** [2], 397 (1953), after our work was completed.

the corresponding 2,4-dinitrophenylhydrazones and *p*-nitrophenylhydrazones showed no depression in melting points.

**5-Chloromercuri-2,4-diphenylthiophene.**—2,4-Diphenylthiophene (500 mg., 2.1 mmoles) gave a 93% yield of 5-chloromercuri-2,4-diphenylthiophene (m.p. 219.5–221°) by reaction with mercuric chloride and sodium acetate according to the conditions described by Bogert and Herrera.[9]

Chloromercuration of 2,5-diphenyl-1,4-dithiadiene was attempted using the same condition; however, only unchanged starting material was recovered.

**Pyrolysis of 2,5-Diphenyl-1,4-dithiadiene.**—A 6-inch test-tube, with side-arm, was fitted with a stopper, containing a thermometer which extended to the bottom of the tube, and a nitrogen inlet tube. 2,5-Diphenyl-1,4-dithiadiene (997 mg., 3.72 mmoles) was placed in the tube and nitrogen was passed through the system for ten minutes. The tube was inserted into an oil-bath at 200°, and after two minutes (temperature of the melt was 190°) a vigorous reaction took place which caused the temperature of the yellow melt to rise to 250°. The tube was removed from the oil-bath and cooled under a stream of nitrogen. The pyrolysate was purified by chromatography with a 3.5 × 30 cm. column which contained 100 g. of Alcoa Activated Alumina F-20. Petroleum ether (30–60°) eluted 80 mg. (67%) of monoclinic sulfur, m.p. 121–123°. A mixture melting point with with authentic sample was not depressed.

*Anal.* Calcd. for S: S, 100. Found: S, 96.8.

2,4-Diphenylthiophene (598 mg., 69%, m.p. 121–122.5°) was eluted with 10% benzene in petroleum ether (30–60°). The infrared and ultraviolet spectra of this product were identical to those previously obtained for pure III; a mixture melting point with pure III was not depressed.

**Oxidation of 2,5-Diphenyl-1,4-dithiadiene, Compound (I).**[1]—A mixture of 2,5-diphenyl-1,4-dithiadiene (4.0 g., 0.015 mole), 30% hydrogen peroxide (1.8 g., 0.016 mole) and 50 ml. of glacial acetic acid was heated on a steam-bath for one hour. After the solution was diluted with water, the solid was filtered and recrystallized from acetone. The yellow solid (1.5 g., m.p. 126–129°) melted at 127–129° (1.2 g., 33%) after recrystallization from ethyl acetate. This product previously[5] was shown to have the empirical formula $C_{32}H_{24}S_3$.

**The structure of the product** (m.p. 127–129°) **obtained by oxidation of I** was shown to be a molecular complex of 2,4-diphenylthiophene (III) and 2,5-diphenyl-1,4-dithiadiene (I). (a) The ultraviolet spectrum of this product ($\lambda^{\text{max}}_{258\ \text{m}\mu}$ ($\epsilon$ 58,500), $\lambda^{\text{plateau}}_{305\ \text{m}\mu}$ ($\epsilon$ 16,400)) was essentially identical to the sum of the spectra of I ($\lambda^{\text{max}}_{259\ \text{m}\mu}$ ($\epsilon$ 22,100), $\lambda^{\text{max}}_{309}$ ($\epsilon$ 8900)) and III ($\lambda^{\text{max}}_{257\ \text{m}\mu}$ ($\epsilon$ 34,700), $\lambda^{\text{inflection}}_{305}$ ($\epsilon$ 8800)).

(b) The oxidation product (288 mg., 0.57 mmole) readily gave 5-chloromercuri-2,4-diphenylthiophene (98 mg., 36%, m.p. and mixed m.p. 219.5–221°) by reaction (6 days at room temperature) with saturated aqueous mercuric chloride (25 g.) and sodium acetate (5 g., 33% in water) in 95% ethanol (150 ml.). The precipitate that originally formed was washed with petroleum ether (60–68°) and the insoluble chloromercuri derivative was recrystallized from 95% ethanol. From the petroleum ether extract there was obtained 86 mg. (30%) of unchanged starting material (m.p. 126–127°).

(c) An equimolar mixture of I (m.p. 118–119°) and III (m.p. 121.5–123°) was recrystallized from ethyl acetate. The product (94% yield) melted at 128–129° and caused no depression in melting point when admixed with the product obtained by oxidation of I. The ultraviolet spectrum of this product ($\lambda^{\text{max}}_{258\ \text{m}\mu}$ ($\epsilon$ 56,400), $\lambda^{\text{max}}_{305\ \text{m}\mu}$ ($\epsilon$ 16,200)) was essentially identical to the product obtained by oxidation of I.

*Anal.* Calcd. for $C_{32}H_{24}S_3$: C, 76.14; H, 4.79. Found: C, 75.97; H, 5.05.

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[9] M. T. Bogert and P. P. Herrera, THIS JOURNAL, **45**, 240 (1923).

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

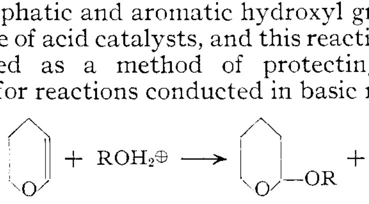
# Protection of Hydroxyl Groups. II. Preferential Pyranylation

BY WILLIAM E. PARHAM AND DALE M. DELAITSCH[1]

RECEIVED APRIL 28, 1954

The approximate rate of addition of phenol, ethyl mercaptan and thiophenol to dihydropyran has been determined and the following order of reactivity has been established: $C_6H_5OH >>> C_2H_5SH > C_6H_5SH$. Although thiophenol reacts at an appreciably slower rate with dihydropyran than does phenol, the latter serves as a catalyst for the pyranylation of the former, and, consequently, thiophenol is preferentially pyranylated in competitive reactions with phenol. Studies of the monopyranylation of 4-substituted pyrocatechols show that a carbethoxy group, but not a methyl group, in the 4-position, causes preferential pyranylation of the least acidic hydroxyl group.

Dihydropyran (I), a typical vinyl ether, readily adds aliphatic and aromatic hydroxyl groups in the presence of acid catalysts, and this reaction has been employed as a method of protecting hydroxyl groups for reactions conducted in basic media.[2]



I

In order that additional information concerning this reaction might be gained, the relative rates of reaction of I with phenol, ethyl mercaptan, and thiophenol have been determined. Also, a study has been made of the monopyranylation of 4-substituted pyrocatechols.

For the reactions of I with ethanol, phenol, ethyl mercaptan and thiophenol identical experimental conditions were employed.[3] It was observed that the rate of reaction of dihydropyran with compounds containing hydroxyl groups was much more rapid than with compounds containing sulfhydryl groups. Furthermore, ethanol appeared[4] to react more rapidly than did phenol.

It can be seen from Tables I, II and III (Experimental section) that phenol was 50% consumed in less than seven minutes, whereas ethyl mercaptan and thiophenol were 50% consumed in approximately eight and twenty-one hours, respectively. Under the conditions employed, the rates of reaction were related to the basicity of the addendum—the most basic compounds reacting the fastest.

Although thiophenol reacts at an appreciably

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[1] From the Ph.D. Thesis of D. M. DeLaitsch, University of Minnesota, 1950.

[2] *Cf.* W. E. Parham and E. L. Anderson, THIS JOURNAL, **70**, 4187 (1948).

[3] RXH (0.25 mole), I (0.50 mole), hydrogen chloride (0.00058 mole) in ether (0.50 ml.) at 28°.

[4] The reaction with ethanol was studied qualitatively only; however, the reaction was very fast and an 82% yield of addition product was isolated after the reaction had progressed for seven minutes.