obtained as white, compact, rosettes of fine needles, m.p. 41.6–42.0°.

Anal. Calcd. for $C_{30}H_{52}O$: C, 84.04; H, 12.23. Found: C, 84.18; H, 11.92.

1,3-Dimethyl-2-(1-octadecenyl)-5-*t*-butylbenzene (VIII, R = $C_{16}H_{33}$).—The reduction of 1,3-dimethyl-2-*n*-octadecanoyl-5-*t*-butylbenzene (VI, R = $C_{16}H_{33}$) was carried out essentially as described for the corresponding *n*-decyl compound using 256 g. (0.596 mole) of the ketone and 12.3 g. (0.324 mole) of lithium aluminum hydride.

The dehydration was also carried out as described in the *n*-decyl series. It was, however, somewhat slower, requiring a total of ten hours at 184° to complete. By a combination of crystallization from ether and absolute alcohol, and distillation at 1 mm. pressure, a total of 209.8 g. (85%) of 1,3-dimethyl-2-(1-octadecenyl)-5-*t*-butylbenzene (VIII, R = $C_{16}H_{33}$) (m.p. 28.0–30.0°, b.p. approx. 236° at 1 mm.) was obtained.

Anal. Calcd. for $C_{30}H_{52}$: C, 87.30; H, 12.70. Found: C, 87.59; H, 12.46.

1,3-Dimethyl-2-*n*-octadecyl-5-*t*-butylbenzene (IX, R = $C_{16}H_{33}$) was prepared by hydrogenating a suspension of 82.1 g. (0.199 mole) of 1,3-dimethyl-2-(1-octadecenyl)-5-*t*-butylbenzene (VIII, R = $C_{16}H_{33}$) in 100 ml. of glacial acetic acid as described for the *n*-decyl derivative. Crystallization of the product from methanol gave 80.6 g. (98%) of 1,3-dimethyl-2-*n*-octadecyl-5-*t*-butylbenzene (IX, R = $C_{16}H_{33}$), m.p. 35.5–37.0°. One recrystallization from methanol and anhydrous ether gave colorless, waxy needles, m.p. 37.8–38.2°.

Anal. Calcd. for $C_{30}H_{54}$: C, 86.87; H, 13.13. Found: C, 86.96; H, 13.06.

Another sample distilled from 263.2–263.8° (5 mm.) without decomposition. The distillate was water white and solidified as white crystals.

1,3-Dimethyl-2-*n*-octadecylbenzene (XI, R = $C_{16}H_{33}$).—To a complex prepared by dissolving 6.7 g. (0.05 mole) of aluminum chloride in 12.2 g. (0.2 mole) of nitromethane[27] was added 184 g. (2.0 moles) of toluene and 41.5 g. (0.1 mole) of 1,3-dimethyl-2-*n*-octadecyl-5-*t*-butylbenzene (IX, R = $C_{16}H_{33}$). The mixture was warmed to 42° to dissolve the latter and the mixture stirred. The temperature dropped to 28° in 40 minutes, and to 25° in two hours where it remained. Stirring was discontinued after a total of two hours and the mixture let stand at room temperature for an additional 20 hours. The mixture was then shaken with 250 ml. of 3 *N* hydrochloric acid, two 100-ml. portions of 3 *N* potassium hydroxide and with 100 ml. of water. After drying over anhydrous magnesium sulfate, the crude reaction product was distilled through the "zig-zag" column. 1,3-Dimethyl-2-*n*-octadecylbenzene (XI, R = $C_{16}H_{33}$) was collected at 241–243° (5 mm.). After recrystallization from absolute alcohol, it was obtained as 22.2 g. of white crystals melting from 48.5–49.0° (62%, 74% corrected for recovered starting material).

Anal. Calcd. for $C_{26}H_{46}$: C, 87.07; H, 12.93. Found: C, 86.76; H, 12.95.

Two attempts to transfer the *t*-butyl group from 1,3-dimethyl-2-*n*-octadecyl-5-*t*-butylbenzene (IX, R = $C_{16}H_{33}$) to toluene, catalyzed by liquid anhydrous hydrogen fluoride at 0°, gave only a trace of the desired reaction.

Acknowledgment.—The author wishes to acknowledge the invaluable assistance of Mr. R. D. Clark in the interpretation of spectra, Dr. H. Sargent for preparation of some of the intermediates, and Mr. C. D. Cox for general assistance in the laboratory.

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(27) L. Schmerling, *Ind. Eng. Chem.*, **40**, 2072 (1948).

RICHMOND, CALIFORNIA

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

Heterocyclic Vinyl Ethers. V. 1,4-Dithiadiene, Benzo-1,4-dithiadiene and 1,4-Dithiadiene Disulfone[1]

BY WILLIAM E. PARHAM, HANS WYNBERG, WILLIAM R. HASEK,[1b] PETER A. HOWELL, RICHARD M. CURTIS AND WILLIAM N. LIPSCOMB

RECEIVED APRIL 2, 1954

Certain chemical characteristics, such as stability and electrophilic substitution, together with physical characteristics such as geometrical configuration, are discussed in terms of the presence or absence of aromatic character in the dithiadiene ring system. X-Ray diffraction data establish the boat configuration for 1,4-dithiadiene. 1,4-Dithiadiene disulfone has been shown to be an active dienophile.

Since it has been previously established that the dithiadiene ring in benzo-1,4-dithiadiene does undergo certain electrophilic substitution reactions (*i.e.*, nitration and formylation),[2a] it was considered of particular interest to extend our study of this ring system to include the Friedel–Crafts acylation reaction. Attempts to effect the acylation of I with acetyl chloride, benzoyl chloride and acetic anhydride, using conditions and catalysts ($AlCl_3$, $SnCl_4$ and BF_3) that have been successfully employed for the acylation of thiophene and thionaphthene, led to the formation of tarry materials from which no pure ketonic materials could be isolated. It was found, however, that benzo-1,4-dithiadiene could be converted into a methyl ketone (II), in 30% yield, by reaction with acetic anhydride in the presence of 85% phosphoric acid at 110°. The ketone was obtained as a bright yellow solid melting at 55°, and was further characterized by its conversion into the corresponding oxime and 2,4-dinitrophenylhydrazone.

The absorption spectrum of the ketone in the ultraviolet region ($\lambda_{272}^{\max}$ (ϵ 15,300), $\lambda_{234}^{\max}$ (ϵ 13,000)) was quite similar to that of benzo-1,4-dithiadiene-2-carboxaldehyde ($\lambda_{271}^{\max}$ (ϵ 10,700–11,150)), which suggested that the structure of this product was the methyl ketone II, and not an isomer with the acetyl group in the benzene ring. Final confirmation of the structure of the ketone was obtained by a study of its oxidation with hypohalite. Reaction of II with sodium hypoiodite in dioxane gave iodoform and an acidic component (m.p. 132–134°, *ca.* 53%) which did not depress the melting point of the acid obtained by oxidation of benzo-1,4-dithiadiene-2-carboxaldehyde with

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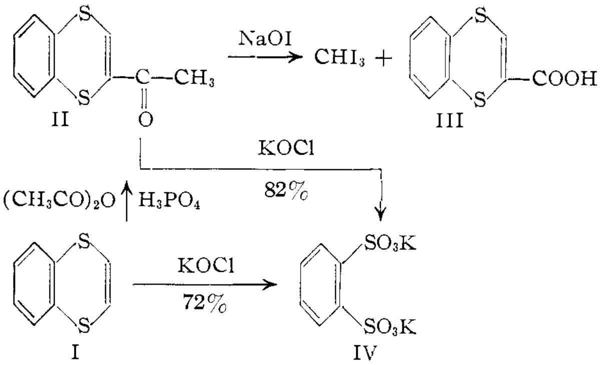
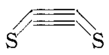
(1) (a) This work was supported by the office of Ordnance Research, Contract Number DA-11-022-ORD-571; (b) National Science Research Fellow 1953–1954.

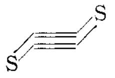
(2) (a) W. E. Parham, T. M. Roder and W. R. Hasek, THIS JOURNAL, **75**, 1647 (1953); (b) W. E. Parham, H. Wynberg and F. L. Ramp, *ibid.*, **75**, 2065 (1953).

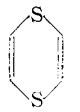


silver oxide. This acid was not appreciably stable; however, its composition was in reasonable agreement with that calculated for the expected acid III. Oxidation of the methyl ketone with excess potassium hypochlorite gave a high yield of potassium benzene-*o*-disulfonate (IV, isolated in 82% yield as the disulfonyl chloride). Although complete degradation of the dithiadiene ring was not expected under these conditions, it was subsequently shown that the parent ring, benzo-1,4-dithiadiene (I), is degraded similarly upon reaction with excess hypochlorite.

A boat Va, chair Vb and planar Vc configuration can be written for 1,4-dithiadiene.


Va

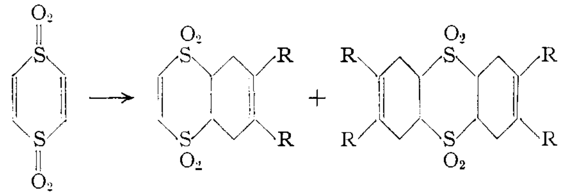

Vb


Vc

It would be unsafe to conclude on *a priori* structural grounds that any one of these proposed structures is necessarily the correct one. If the molecule is nonplanar, Va might be favored over Vb in view of expected planarity of the S—C═C—S group. On the other hand, aromatic resonance might be sufficient to stabilize the planar configuration Vc. The properties of the dithiadiene ring in benzo-1,4-dithiadiene (I) parallel those generally associated with aromatic character; however, the data now accumulated concerning the parent heterocycle, 1,4-dithiadiene (V), seem sufficient to warrant classification of the latter as aliphatic in character. These data include: (1) the facile conversion of 1,4-dithiadiene to the corresponding monosulfilimine (84% yield) and disulfone (72% yield), (2) the facile polymerization of 1,4-dithiadiene by action of Lewis acids, (3) the failure of 1,4-dithiadiene to give ketones in Friedel–Crafts type reactions,[3] and (4) its geometrical configuration as established by X-ray diffraction methods.[4]

The unit cell of 1,4-dithiadiene was found to be orthorhombic, with $a = 11.28$, $b = 6.41$ and $c = 7.36$ Å. and the space group is $Cmc2_1$. The structure was solved uniquely by the use of Patterson projections, and refined by use of projections along *a*, *b* and *c*. The final value of $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ is 16.5% for the 123 observed reflections. The observed molecular structure indicates the "boat" configuration as shown in formula Va, unlike other six-membered rings, but consistent with the C–S–C bond angle of about 100° and with ethylenic hybridization in the double bond. The angle ϕ between the two planes in Va is 137°. Molecular dimensions have not been determined accurately, but they strongly suggest that the isolated molecule has C_{2v} symmetry. Bond lengths and average deviations for the C_{2v} model are C–S = 1.78 ± 0.05 Å. and C═C = 1.29 ± 0.05 Å., while bond angles are C═C—S = 124° and C–S–C = 100°. Distances are to be considered correct to about ±0.05 Å. There appears to be a slight systematic shortening below the normal covalent distances[5] of C–S = 1.81 and C═C = 1.33 Å., due possibly to resonance in the molecule, but at least partly to the incompleteness of our diffraction data. The angles are probably correct to ±3°. Hence the non-planarity and the "boat" configuration may be considered as established. It thus appears that resonance structures involving multiple bonds from sulfur are of small consequence.[6]

Since it has been previously established[7] that open chain bis-disulfonylethylenes serve as active dienophiles, it was considered of interest to study the reaction of 1,4-dithiadiene disulfone (VI) with dienes.



VI VII VIII

Mono- and diadducts (VII and VIII) were obtained by reaction of VI with 2,3-dimethylbutadiene, butadiene, cyclopentadiene and 2-methylbutadiene. Details of this work are found in the Experimental section of this report.

Experimental

2-Acetylbenzo-1,4-dithiadiene (II).—A stirred mixture of benzo-1,4-dithiadiene[2a] (5.00 g., 0.03 mole) and acetic anhydride (3.30 g., 0.03 mole) was heated to 76°, and four drops (approx. 0.24 g.) of 85% orthophosphoric acid was added. The reaction mixture was heated rapidly to 110° and maintained at that temperature (±5°) for two hours. The cooled (20°) reaction mixture was diluted with ether (16 ml.) and treated with water (6 ml.). The ether layer was extracted with aqueous 5% sodium carbonate (until the aqueous extract was alkaline), and then with water. The residual oil, obtained from the dry ($MgSO_4$) ethereal solution, was distilled from a small Claisen flask having a two-inch side arm packed with glass helices. The lower boiling product (1.86 g., b.p. 70–76° (0.14–0.19 mm.), $n^{25}D$ 1.6753) was unchanged benzo-

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(3) In ref. 2b attention was called to the fact that 1,4-dithiadiene did not give ketones under the specific conditions previously reported by Levi. As part of this work, a detailed study of the acylation of 1,4-dithiadiene with acetyl chloride, benzoyl chloride and acetic anhydride, using conditions and catalyst ($AlCl_3$, $SnCl_4$, BF_3, H_3PO_4) that have been successfully employed for the acylation of thiophene, furan, and/or benzo-1,4-dithiadiene was made. The products were either polymer or tarry and no ketonic material was isolated.

(4) The low temperature techniques employed were essentially those described by T. B. Reed and W. N. Lipscomb, *Acta Cryst.*, **6**, 45 (1953). This portion of the work was supported by ONR.

(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1942, pp. 79, 84 and 164.

(6) Details of the X-ray diffraction studies will appear in "Acta Crystallographica."

(7) H. R. Snyder and D. P. Hallada, THIS JOURNAL, **74**, 5595 (1952).

TABLE I

DIELS–ALDER REACTIONS WITH 1,4-DITHIADIENE DISULFONE

Diene	Product	T, °C.	Time, hr.	Yield, %	M.p., °C.	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
Butadiene	VII	100	3	22	195.5–200[a]	41.01	40.51	4.30	4.37
	VIII	150	5	38	>350 dec.	49.98	49.34	5.59	5.09
Dimethylbutadiene	VII	80	17	60	152–153[b]	45.78	45.54	5.38	5.03
	VIII	80	17	15.5	304–306	55.78	55.12	7.02	7.39
Isoprene	VII	52	17	20	153–154[c]	43.53	43.76	4.87	4.84
Cyclopentadiene	VIII	100	1	43	>370	53.82	53.90	5.16	5.43

Solvents: [a] ethanol, [b] petroleum ether, [c] chloroform–petroleum ether.

1,4-dithiadiene. The higher boiling fraction (bright orange-yellow, 1.13 g., b.p. 126-137° (0.14–0.42 mm.), n^{25}_{D} 1.6845, 30% based upon starting material consumed) had the composition (C and H) calculated for 2-acetylbenzo-1,4-dithiadiene. The ketonic products obtained from several such experiments were combined and distilled (with essentially no loss) through a ten-inch column containing a spiral nichrome wire packing. The distillate b.p. 124–127° (0.08 mm.) solidified in the receiver, and the bright yellow crystals melted at 55–55.5° after two recrystallizations from petroleum ether (b.p. 60–68°).

Anal. Calcd. for $C_{10}H_8OS_2$: C, 57.66; H, 3.87. Found: C, 57.76 (oil), 57.37 (solid); H, 4.15 (oil), 3.77 (solid).

2-Acetylbenzo-1,4-dithiadiene exhibits two strong maxima in the ultraviolet region: 234 mμ (ϵ 13000) and 272 mμ (ϵ 15300). The carbonyl band in the infrared spectrum appears at 1685 cm.$^{-1}$.

The oxime of 2-acetylbenzo-1,4-dithiadiene was prepared in absolute ethanol and pyridine. The solvents were evaporated with a jet of air and the residual solid was recrystallized from ethanol. The pale-yellow oxime melted at 169–170°.

Anal. Calcd. for $C_{10}H_9ONS_2$: C, 53.78; H, 4.06. Found: C, 53.84; H, 4.09.

The 2,4-dinitrophenylhydrazone of 2-acetylbenzo-1,4-dithiadiene was recrystallized from chloroform–methanol; deep red, m.p. 248–248.5°.

Anal. Calcd. for $C_{16}H_{12}O_4N_4S_2$: C, 49.47; H, 3.12; N, 14.43. Found: C, 49.77; H, 3.15; N, 14.54.

Oxidation of 2-Acetylbenzo-1,4-dithiadiene with Hypoiodite.—A solution of iodine (0.888 g., 0.0035 mole) and posssium iodide (1.776 g., 0.0107 mole) in water (7 ml.) was added to a solution prepared from 2-acetylbenzo-1,4-dithiadiene (0.207 g., 0.00099 mole), sodium hydroxide (0.30 g., 0.0075 mole), dioxane (10 ml.) and water (2 ml. added dropwise). The stirred solution was heated to 60° for five minutes, cooled, and was then diluted to three times its volume with water. The resulting mixture was cooled (15°) overnight. The brown solid that formed (0.90 g., m.p. 80–120°) was shown to be principally iodoform (m.p. and mixed m.p. 119–120°).

Sodium bisulfite (0.2 g.) was added to the basic filtrate, and the solution was then acidified with dilute hydrochloric acid and cooled (overnight at 0°). The brown acidic material that separated melted at 119–126° and weighed 0.111 g. (53% yield of III). The melting point of the acid was 132–134° after two recrystallizations from ethanol–water. A mixture of benzo-1,4-dithiadiene-2-carboxylic acid (m.p. 134–137°) and this acid melted at 132–135°.

Oxidation of Benzo-1,4-dithiadiene-2-carboxaldehyde with Silver Oxide.—The oxidation of the aldehyde[2a] (1.00 g., 0.00513 mole) was carried out in alcohol with aqueous (30 ml.) silver nitrate (2.62 g., 0.0154 mole) and aqueous (40 ml.) sodium hydroxide (1.85 g., 0.0462 mole) according to directions previously described.[8] The acidic component weighed 0.71 g. (70% yield) and was obtained as a dark yellow solid melting at 115–126° with softening at 107°. The solid was dissolved in benzene and chromatographed on silica gel using benzene–chloroform (200 ml. 1:1), chloroform–alcohol (300 ml. 3:1) as eluants. From the second fraction there was obtained 0.62 g. of a yellow solid (acid) melting at 125–134°. This material appeared unstable and was difficult to purify by recrystallization. A sample melting at 134–137° (from benzene–petroleum ether) had the following composition.

Anal. Calcd. for $C_9H_6O_2S_2$: C, 51.44; H, 2.88. Found: C, 52.04; H, 2.60.

Oxidation of 2-Acetylbenzo-1,4-dithiadiene with Potassium Hypochlorite.—A heterogeneous mixture prepared from 2-acetylbenzo-1,4-dithiadiene (0.96 g., 0.0046 mole), dioxane (20 ml.) and aqueous potassium hypochlorite (20 ml., 0.092 mole of hypochlorite[9]) was stirred and heated on a steam-bath. When the temperature of the reaction mixture reached 90° a vigorous reaction occurred. An additional 20 ml. of aqueous hypochlorite (0.092 mole) was added to the hot (90°) mixture and when the exothermic reaction subsided sodium bisulfite (0.2 g.) was added to destroy the excess hypochlorite. The small quantity (0.2 g.) of pale yellow solid that had formed was separated and the filtrate was acidified with hydrochloric acid. The clear solution that resulted was made alkaline with aqueous sodium hydroxide, and the resulting solution was evaporated to dryness. The sodium and/or potassium benzene-*o*-disulfonate (contaminated with sodium chloride) thus obtained was converted to benzene-*o*-disulfonyl chloride (1.04 g., m.p. and mixed m.p. with an authentic sample 143–144°, 82% yield from II) by reaction with phosphorus pentoxide (10.0 g.) in phosphorus oxychloride (20 ml.).[10]

The Oxidation of Benzo-1,4-dithiadiene with Potassium Hypochlorite.—The oxidation of benzo-1,4-dithiadiene (0.50 g., 0.003 mole) with potassium hypochlorite (0.138 mole) was carried out by a procedure essentially identical to that described above for the oxidation of 2-acetylbenzo-1,4-dithiadiene. The principal product of the reaction, potassium benzene-*o*-disulfonate, was converted to benzene-*o*-disulfonyl chloride (0.60 g., 72.5% yield, m.p. and mixed m.p. 143–144°) by reaction with phosphorus pentoxide (5.0 g.) in phosphorus oxychloride (15 ml.).[10]

The Monosulfilimine Derivative of 1,4-Dithiadiene (V).—1,4-Dithiadiene (0.122 g., 0.001 mole),[2b] in methanol (2.5 ml.), was added to a solution prepared from Chloramine-T (0.75 g., 0.003 mole), water (5 ml.) and methanol (5 ml.). The resulting mixture was heated on a steam-bath for several minutes, then allowed to cool to room temperature, and finally maintained at 15° overnight. The product (0.240 g., 84% yield, m.p. 151–153° dec.) melted at 155–156° after recrystallization from methanol.

Anal.. Calcd. for $C_{11}H_{11}O_2NS_3$: C, 46.29; H, 3.89. Found: C, 46.27; H, 3.84.

1,4-Dithiadiene Disulfone.—The following procedure was found to be superior to that previously reported.[2b] Hydrogen peroxide (30%, 50 ml.) was added dropwise (90 min.) to a solution of 1,4-dithiadiene (8.1 g., 0.07 mole) in glacial acetic acid (250 ml.). The resulting mixture was heated at 70° for 17 hours, and then maintained at 15° for one hour. The product was collected and washed successively with water and 95% ethanol. 1,4-Dithiadiene disulfone (8.35 g., 66% yield, m.p. 241° dec.) was obtained in a high state of purity by this procedure. The filtrate was evaporated to dryness and the resulting solid was treated (20 minutes) with hot (steam-bath) acetic acid (25 ml.) and hydrogen peroxide (5 ml.). From this solution an additional 0.8 g. of the disulfone was obtained (combined yield 72%).

Diels–Alder Adducts of 1,4-Dithiadiene Disulfone.—Except for butadiene, the adducts were prepared according

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(8) *Cf.* J. C. Sheehan and C. A. Robinson, THIS JOURNAL, **73**, 1207 (1951); H. Fiesselmann, *Ber.*, **75**, 881 (1942).

(9) M. S. Newman and H. L. Holmes, "Organic Syntheses," second edition, Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 429.

(10) See reference 2a for the isolation of benzene-*o*-disulfonyl chloride from the oxidation products of benzo-1,4-dithiadiene-2-carboxaldehyde.

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.

MINNEAPOLIS, MINNESOTA

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

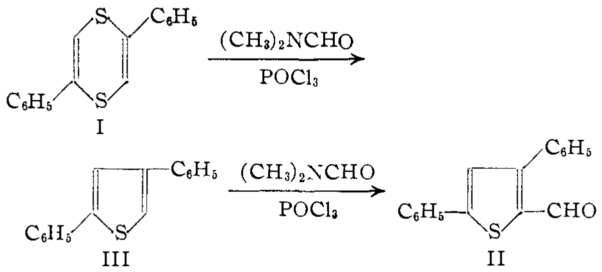
Heterocyclic Vinyl Ethers. VI. Rearrangements of the 1,4-Dithiadiene Ring System[1]

BY WILLIAM E. PARHAM AND VINCENT J. TRAYNELIS

RECEIVED APRIL 30, 1954

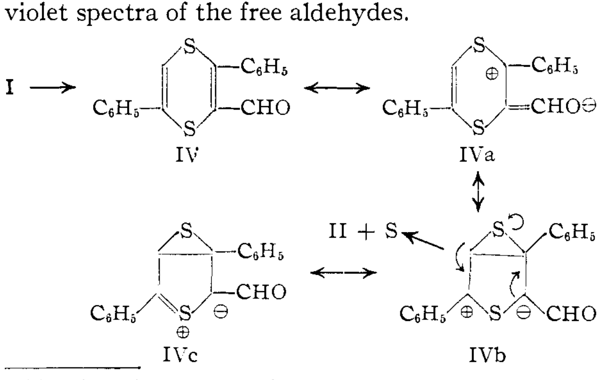
New reactions are reported which involve the conversion of 2,5-diphenyl-1,4-dithiadiene into 2,4-diphenylthiophene or derivatives of 2,4-diphenylthiophene.

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%).



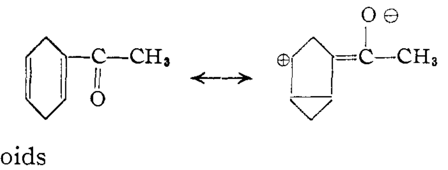
I III II

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.

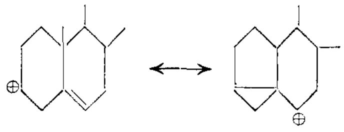


IV IVa IVb IVc

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).