amyl alcohol. After filtering and removing the solvent, the residue was washed with water to remove inorganic salts. The residue was extracted with ether and upon removal of this solvent pale yellow needles were deposited. After crystallization from a benzene–petroleum ether solution, 0.24 g. (60%) of colorless hexamethyldiplatinum crystals were obtained. This compound was very soluble in acetone, benzene or ether but insoluble in water and only slightly soluble in cold petroleum ether (b.p. 60–68°).

Considerable difficulty was experienced in the analysis of this compound. It exploded sharply on heating with a brilliant shower of sparks. Analysis for platinum was finally obtained by exploding the compound in a bulb with capillary openings. The capillaries were plugged with about one inch of glass wool to prevent the escape of platinum. After the compound was exploded, a slow current of air was passed through the bulb and it was burned to a constant weight. Analysis for carbon and hydrogen was obtained by scattering a weighed sample of the material over a length of about four inches in the combustion tube and igniting a few particles at a time. A constant series of small explosions accompanied the combustion.

Anal. Calcd. for $C_6H_{18}Pt_2$: Pt, 81.25; C, 14.95; H, 3.76; mol. wt., 480. Found: Pt, 81.13; C, 14.55; H, 3.92; mol. wt., 492.

Tetramethylplatinum.—To a suspension of methylsodium prepared from 4 g. of dimethylmercury in 60 ml. of benzene-free hexanes and 1.5 g. of sodium was added 1 g. of trimethylplatinum iodide. The mixture was stirred for 24 hours, and then hydrolyzed by the addition of 2 ml. of *n*-amyl alcohol followed by ethanol and finally water. The hexane layer was separated, dried over sodium sulfate, filtered, and evaporated to dryness. The residue was covered with 20 ml. of petroleum ether (b.p. 60–68°) and after standing for 30 minutes the mixture was filtered and concentrated slowly. There was deposited 0.32 g. (46%) of a colorless solid which was readily soluble in cold benzene, acetone, ether and petroleum ether (b.p. 60–68°) but less soluble in cold alcohol or chloroform. The compound does not melt but decomposes with a slight explosion when heated in an open flame.

Anal. Calcd. for $C_4H_{12}Pt$: Pt, 76.48; C, 18.80; H, 4.72. Found: Pt, 76.84; C, 18.32; H, 4.31.

When the above reaction was attempted using methyllithium instead of methylsodium, trimethylplatinum iodide was recovered unchanged after a reaction time of ten hours.

Benzoyl Chloride and Tetramethylplatinum.—A solution containing 0.2 g. of tetramethylplatinum and 1 ml. of benzoyl chloride in 10 ml. of benzene was refluxed 100 hours. The tetramethylplatinum was recovered unchanged.

Tetramethylplatinum and Iodine.—A solution containing 0.1 g. of tetramethylplatinum and 0.1 g. of iodine in 10 ml. of chloroform was refluxed 24 hours. The tetramethylplatinum was recovered unchanged.

Tetramethylplatinum and Hydrogen Chloride.—Dry hydrogen chloride was bubbled through a refluxing solution containing 0.1 g. of tetramethylplatinum in 10 ml. of petroleum ether (b.p. 60–68°). White crystals of trimethylplatinum chloride soon began to separate and after 15 minutes the precipitation was complete.

Anal. Calcd. for $(CH_3)_3PtCl$: Pt, 70.75; Cl, 12.90. Found: Pt, 70.20; Cl, 13.10.

AMES, IOWA

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

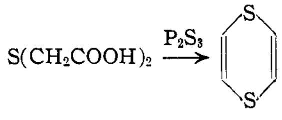
Heterocyclic Vinyl Ethers. III. The Synthesis of 1,4-Dithiadiene and 1,4-Dithiadiene Disulfone[1-3]

BY WILLIAM E. PARHAM, HANS WYNBERG AND FLOYD L. RAMP

RECEIVED DECEMBER 6, 1952

The synthesis and proof of structure of 1,4-dithiadiene and 1,4-dithiadiene disulfone are described.

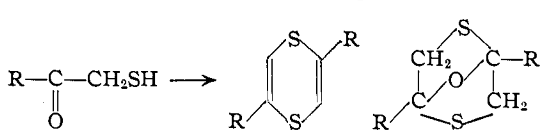
In 1890, Levi[4] reported that the action of phosphorus trisulfide and thiodiglycolic acid resulted in an oil which he formulated as 1,4-dithiadiene (I).



I

Evidence cited for the structure of I was: (1) sulfur analysis, (2) positive indophene test with isatin and sulfuric acid, and (3) conversion of I, by procedures involving Friedel–Crafts reactions with aluminum chloride, into the corresponding methyl ketone[5] (b.p. above 300°, phenylhydrazone m.p. 128°) and phenylketone[5] (b.p. 241°, mononitro derivative, m.p. 112°). With the exception of the boiling point (165–170°), no physical properties of I were reported. Other attempts to prepare 1,4-dithiadiene by Levi's procedure have been unsuccessful.[6,7] In our laboratories Levi's procedure was modified by the use of P_4S_7 and P_2S_5 in place of P_2S_3, by the use of petroleum ether and absolute ether in place of U.S.P. diethyl ether, and further by temperature variations. Only small quantities of distillable oils were obtained, which in no case gave derivatives as reported by Levi.[7]

With the exception of the thianthrenes (dibenzo-1,4-dithiadienes), there have been relatively few compounds prepared which contain the 1,4-dithiadiene ring system. A series of 2,5-diaryl-1,4-dithiadienes (III) have been prepared[8] by the self-condensation of α-mercaptoketones; however, this scheme is apparently not applicable to reactions in which R is aliphatic. The compound reported to



II III IV

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(1) This work was supported by the Office of Ordnance Research, Contract Number DA-11-022-ORD-571.

(2) Presented at the 122nd Meeting of the American Chemical Society, September, 1952.

(3) For the preceding paper of this series, see W. E. Parham, T. M. Roder and W. R. Hasek, THIS JOURNAL, **75**, 1647 (1953).

(4) L. E. Levi, *Chem. News*, **62**, 216 (1890). Levi called his product biophene. *Cf.* R. K. Summerbell and R. R. Umhoefer, THIS JOURNAL, **61**, 3020 (1939), for a discussion of 1,4-dioxadiene.

(5) Analytical data were not reported for the ketones.

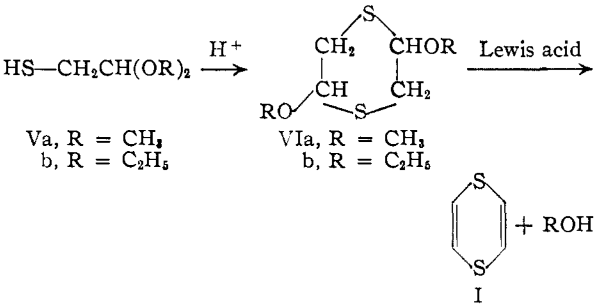
(6) *Cf.* O. Hromatka and E. Engel, *Monatsh.*, **78**, 28 (1948).

(7) The study of Levi's procedure was carried out, in part, by Dr. Irving Gordon, University of Minnesota, 1950.

(8) T. B. Johnson, J. C. Moran and E. I. Kohmann, THIS JOURNAL, **35**, 447 (1913); (b) B. Groth, *Chem. Zentr.*, **95**, I, 1036 (1924); (c) R. H. Baker and C. Barkenbus, THIS JOURNAL, **58**, 262 (1936).

be 2,5-dimethyl-1,4-dithiadiene was shown by Hromatka and Engel[6] to be 2,5-dimethyl-2,5-endoxy-1,4-dithiane (IV). The self-condensation of ethyl γ-mercaptoacetoacetate to give 2,5-dicarboethoxymethyl-1,4-dithiadiene in low yield has been reported by Steude.[9a] No definite conclusion can be drawn as to the correctness of this formulation, but the ultraviolet absorption spectrum[9b] ($\lambda^{95\%\ \text{EtOH}}_{\text{max}}$ 291 mμ, E 25,000) suggests the 1,4-dithiadiene structure.

In view of the successful preparation of benzo-1,4-dithiadiene,[3] of proven structure, by the acid-catalyzed dealkoxylation of benzo-2-ethoxy-1,4-dithiane, it appeared that a similar dealkoxylation of 2,5-dialkoxy-1,4-dithiane (VI) would yield the desired 1,4-dithiadiene.



The preparation of diethyl mercaptoacetal (Vb) by the action of potassium hydrosulfide and diethyl bromoacetal has hitherto failed or resulted in a product of doubtful purity.[10] The isolation of mercaptoacetal, prepared by this procedure, has been complicated by the similar physical[11,12] properties of bromoacetal and mercaptoacetal. We have been able to prepare Vb[11] of high purity (better than 98%), and Va of analytical purity, using this procedure. The reaction was allowed to proceed to the point where all of the bromoacetal was converted to a mixture of mercaptoacetal and bis-(2,2-dialkoxyethyl) sulfide.

Three alternative preparations of dimethyl mercaptoacetal (Va) have been developed, which proceed in good yield from readily available starting material. These syntheses are summarized in equations 1,[12] 2 and 3. The synthesis of mercaptans by the reduction of mixture of polysulfides with sodium and liquid ammonia (equation 3), is apparently new. We have found this reaction the method of choice for the synthesis of Va and Vb.

The cyclization of diethyl mercaptoacetal (Vb) with ethereal hydrogen chloride gave varying yields of a solid product, m.p. 91–92°, which was formulated as VIb on the basis of its composition and molecular weight. Hesse[12] has recently prepared the same product by allowing diethyl mercaptoacetal to stand for six weeks in an atmosphere of carbon dioxide. The cyclization of dimethyl mercaptoacetal (Va) can be accomplished in reproducible yields of 50–55% in a refluxing benzene solution containing catalytic amounts of *p*-toluenesulfonic acid. The mixture of *cis*- and *trans*-2,5-dimethoxy-1,4-dithiane (VIa) produced in this manner was used successfully in the next step. One crystalline isomer of VIa was obtained pure (α-isomer, m.p. 84–85°), but neither chromatography nor fractional distillation yielded the other isomer in a pure state.

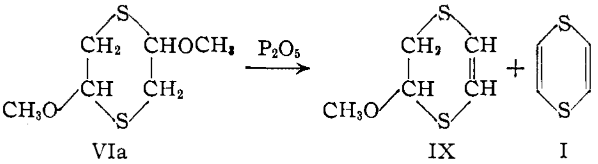
$$\mathrm{ClCH_2CH(OCH_3)_2 + C_6H_5CH_2SNa \xrightarrow{89\%} \underset{\text{VII}}{C_6H_5CH_2S{-}CH_2CH(OCH_3)_2} \xrightarrow[60\text{–}70\%]{\text{Na, NH}_3} \underset{\text{Va}}{HSCH_2CH(COH_3)_2}} \quad (1)$$

$$\mathrm{ClCH_2CH(OCH_3)_2 + Na_2S_2 \xrightarrow{53\%} \underset{\text{VIII}}{(CH_3O)_2CHCH_2S{-}S{-}CH_2CH(OCH_3)_2}}$$

$$\begin{tikzcd}
\text{Va} & \text{VIII} \arrow[l, "\text{LiAlH}_4"', "57\%"] \arrow[r, "\text{Na, NH}_3", "50\%"'] & \text{Va} \quad (2) \\
 & & \mathrm{[(CH_3O)_2CHCH_2{-}S_n{-}CH_2CH(OCH_3)_2]} \arrow[u, "\text{Na, NH}_3\ 67\%\ \text{from chloroacetal}"']
\end{tikzcd}$$

$$\mathrm{ClCH_2CH(OCH_3)_2 + Na_2S_x \longrightarrow [(CH_3O)_2CHCH_2{-}S_n{-}CH_2CH(OCH_3)_2]} \quad (3)$$

Dealkoxylation of the the mixture of *cis*- and *trans*-2,5-dimethoxy-1,4-dithiane (VIa) with phosphorus pentoxide at 100–120° gave methanol and the monoölefin, 2-methoxy-1,4-dithiene-5 (IX, 45% yield). When the reaction temperature was increased to 180–200°, extensive decomposition occurred. The product, obtained in low yield, had the composition calculated for a mixture of dithiene (IX) and dithiadiene.



The vapor phase dealkoxylation of *cis*–*trans*-2,5-dimethoxy-1,4-dithiane (VIa) over alumina at 300° occurred readily to give methanol and 1,4-dithiadiene (I, 40–45% yield, b.p. 80° (27 mm.), $n^{30}\mathrm{D}$ 1.6288). Although this material had the composition calculated for $C_4H_4S_2$, subsequent experiments showed that 1,4-dithiadiene, obtained in this way, was contaminated with an evil-smelling impurity which could readily be removed by chromatography over alumina (83% recovery after redistillation). Pure 1,4-dithiadiene has a pleasant, olefinic odor and has the following physical characteristics: b.p. 80° (27 mm.), 181° dec. (735 mm.), $n^{30}\mathrm{D}$ 1.6319.

Oxidation of 1,4-dithiadiene with two equivalents of hydrogen peroxide at room temperature gave a product, m.p. 99–100°, which had the composition

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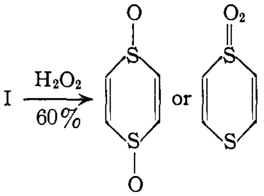
(9) (a) M. Steude, *Ann.*, **261**, 22 (1891); (b) the ultraviolet spectrum was determined in this Laboratory.

(10) E. Fisher, *Ber.*, **42**, 1070 (1909); (b) T. Curtius and N. Kyriacou, *J. prakt. Chem.*, **95**, 370 (1917), were unsuccessful in their attempt to prepare Vb by the hydrosulfide method using diethyl chloroacetal; (c) C. A. Grob and H. von Sprechen, *Helv. Chim. Acta*, **35**, 885 (1952), reported the preparation of Va and Vb using bromoacetal and potassium hydrosulfide after our work was completed; however, their products were characterized through the crystalline mercury derivatives. The purity of their mercaptoacetal remains in doubt.

(11) From the Ph.D. thesis of Floyd L. Ramp, University of Minnesota, 1950.

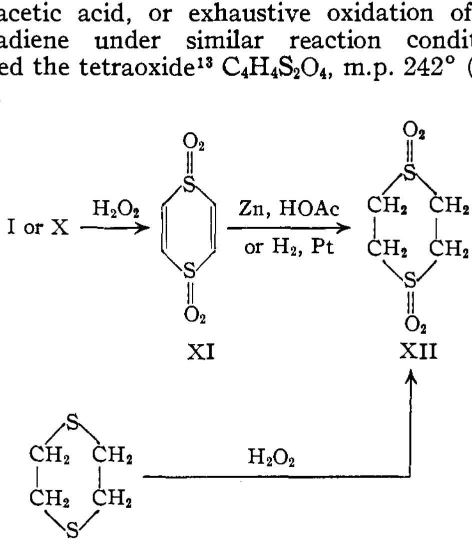
(12) G. Hesse and I. Jorder, *Ber.*, **85**, 924 (1952); G. Hesse, *Angew. Chem.*, **63**, 97 (1951). The former publication, received after our work was completed, reports the preparation of Vb by method 1.

calculated for the dioxide, $C_4H_4S_2O_2$. Whether this product was the disulfoxide (Xa) or the monosulfone (Xb) has not as yet been established.



Xa Xb

Further oxidation of X with hydrogen peroxide in hot acetic acid, or exhaustive oxidation of 1,4-dithiadiene under similar reaction conditions, yielded the tetraoxide[13] $C_4H_4S_2O_4$, m.p. 242° (dec.) (XI).



Final confirmation of the structure of 1,4-dithiadiene, and the disulfone XI, was obtained by reduction of XI with zinc and acetic acid, or hydrogen with platinum catalyst, to dithiane disulfone. The identity of XII and an authentic sample of 1,4-dithiane disulfone was established by a comparison of the X-ray powder diffraction patterns[14] and infrared[15] spectra of the two samples.

Whether 1,4-dithiadiene is identical to the product reported by Levi is not as yet evident; however, the following comparisons are of interest. Levi purified biophene by distillation at atmospheric pressure (b.p. 165–170°). We have found that 1,4-dithiadiene decomposes at its boiling point (181° (735 mm.)). Levi reported that biophene gives a violet indophine test. Our samples of 1,4-dithiadiene gave an orange color with sulfuric acid and an orange-cherry color with sulfuric acid and isatin. Levi prepared the corresponding methyl and phenyl ketone from biophene from the appropriate acid chloride and aluminum chloride. As yet, we have been unable to isolate these ketones from the reaction products obtained when 1,4-dithiadiene was treated with acetyl chloride or benzoyl chloride and aluminum chloride under the conditions described by Levi.

It is hoped that thermochemical studies (resonance energy), X-ray diffraction studies (planar or non-planar configuration)[16] and studies of substitution of I by electrophilic reagents, will furnish information as to the effect of the resonance interaction of the sulfur atoms in the parent member of the 1,4-dithiadiene ring system.

Experimental

Benzyl-(1,1-dimethoxyethyl) Sulfide (VII).—The procedure used was essentially that previously described for the corresponding ethyl acetal.[17] There was obtained, from sodium (18.5 g., 0.805 atom), absolute ethanol (400 ml.), potassium iodide (5.0 g.), benzyl mercaptan (100 g., 0.805 mole), and dimethyl chloroacetal (101.0 g., 0.805 mole), 143.8 g. (89%) of VII (b.p. 90–95° (3–4 mm.), n^{30}_{D} 1.5299).

Anal. Calcd. for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60. Found: C, 62.11; H, 7.91.

1,1,1′,1′-Tetramethoxyethyl Disulfide (VIII).—Dimethyl chloroacetal (82.5 g., 0.667 mole) and potassium iodide (5 g.) were added to a solution prepared from sodium sulfide nonahydrate (120 g., 0.5 mole) and sulfur (24 g., 0.75 atom)[18] in 500 ml. of 95% ethanol, and the resulting mixture was heated at the reflux temperature for 16 hours. Most of the alcohol was then removed by distillation at atmospheric pressure, water (500 ml.) was added, and the product isolated by extraction with ether. Removal of the ether left 61.7 g. of light yellow oil (n^{20}_{D} 1.4930) which was distilled to give 32.9 g. (53%) of the disulfide (b.p. 100–105° (0.6 mm.), n^{27}_{D} 1.4880). The forerun, 8.0 g., b.p. 79–99° (0.6 mm.), n^{27}_{D} 1.4620, represented approximately a 13% conversion to sulfide, and the residue, 20.7 g., n^{27}_{D} 1.5220, represented 34% conversion to tri- and polysulfide. A sample of fraction 1, b.p. 85° (1 mm.), n^{25}_{D} 1.4569, has the following composition.

Anal. Calcd. for $C_8H_{18}O_4S$: C, 45.79;. H, 8.63. Found: C, 45.66; H, 8.71.

A sample of disulfide, b.p. 102 (0.6 mm.), n^{27}_{D} 1.4876.

Anal. Calcd. for $C_8H_{18}O_4S_2$: C, 39.65; H, 7.49. Found: C, 39.63; H, 7.57.

When the above procedure was carried out using 32 g. (1 gram atom) of sulfur the crude sulfide mixture, n^{25}_{D} 1.5292, weighed 83.3 g. The best yields of Va were obtained by reduction of this mixture.

Mercaptoacetal (V). **A. Vb by the KSH Method.**—Diethyl bromoacetal (98.5 g., 0.5 mole) and potassium iodide (5.0 g.) were added to a solution prepared from 66 g. of potassium hydroxide in 300 ml. of 95% ethanol which was saturated with hydrogen sulfide. The reaction mixture was allowed to stand for seven days, during which time a slow stream of hydrogen sulfide was passed into the solution. Most of the alcohol was removed by distillation at atmospheric pressure, water (100 ml.) was added, and the solution was saturated with carbon dioxide (to *p*H 7.8) and then extracted with ether. Distillation of the dried ether extract gave 22.1 g. (29.5%) of Vb, b.p. 68–72° (17 mm.), n^{25}_{D} 1.4392.

Anal. Calcd. for $C_6H_{14}O_2S$: C, 47.94; H, 9.39; SH, 22.0. Found: C, 47.24, 48.40; H, 9.66, 9.70; SH, 22.3.[19]

After two weeks the refractive index of Vb was n^{25}_{D} 1.4400. Vb was characterized by conversion to the following derivatives.

1. **The 2,4-dinitrophenylhydrazone** of **mercaptoacetaldehyde** was recrystallized from ethyl acetate; m.p. 204.5–206.5°.

Anal. Calcd. for $C_8H_8O_4N_4S$: C, 38.00; H, 3.12. Found: C, 38.32; H, 3.40.

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[13] *Cf.* H. P. Koch and W. E. Moffett, *Trans. Faraday Soc.*, **47**, 7 (1951). A study of the reactions of 1,4-dithiadiene disulfone has been initiated in order to gain additional information concerning conjugation in cyclic α,β-unsaturated sulfones.

[14] The samples were run as powders using a General Electric XRD-3 unit with Geiger counter recording.

[15] The infrared spectra were determined by the Department of Physical Chemistry, University of Minnesota, using a Perkin-Elmer single beam instrument. A detailed study of the infrared and Raman spectra of 1,4-dithiadiene is in progress.

[16] A single crystal study of 1,4-dithiadiene by the X-ray diffraction method is being carried out by Dr. William Lipscomb, Department of Physical Chemistry, University of Minnesota.

[17] C. G. Hutchinson and S. Smiles, *Ber.*, **47**, 805 (1914).

[18] The use of an equivalent amount of sulfur resulted in a product which contained 43% disulfide and 20% sulfide.

[19] Method of J. R. Sampey and E. E. Reid, THIS JOURNAL, **54**, 3404 (1932).

2. **The 2,4-Dinitrophenylhydrazone of *n*-Butylthioacetaldehyde.**—A mixture prepared from Vb (1 g.), ethanol (10 ml.), sodium ethoxide (from 0.23 g. of sodium) and butyl bromide (1.5 ml.) was heated for 1.5 hours. The solution was made acidic with hydrochloric acid and treated with 2,4-dinitrophenylhydrazine. The crude hydrazone (1.15 g.), m.p. 67–69.5°, was recrystallized from ethanol to give a product melting at 68.5–70°.

Anal. Calcd. for $C_{12}H_{16}O_4N_4S$: C, 46.14; H, 5.16. Found: C, 46.28; H, 5.21.

3. **2,4-Dinitrophenylhydrazone of (1-Phenyl-2-nitroethylthio)-acetaldehyde.**—A solution containing ω-nitrostyrene (1.49 g.), Vb (1.5 g.) and three drops of pyridine in 55 ml. of absolute ethanol was allowed to stand three days at room temperature. Treatment of an aliquot of the solution with 2,4-dinitrophenylhydrazine and acid gave the crude hydrazone (30%), m.p. 122–125°. A sample recrystallized from chloroform melted at 139–139.5°.

Anal. Calcd. for $C_{16}H_{15}O_6N_5S$: C, 47.40; H, 3.71. Found: C, 47.20; H, 3.86.

B. **Va by the KSH Method.**—Dimethyl mercaptoacetal was prepared from dimethyl bromoacetal by a procedure essentially as described for Vb above; however, the reaction was not carried out at room temperature. The reactants were heated at 40–50° for one hour, and then at 80° for 0.5 hour. Va was obtained in 23% yield, b.p. 81–82° (80 mm.), $n^{30}\mathrm{D}$ 1.4463.

Anal. Calcd. for $C_4H_{10}O_2S$: C, 39.32; H, 8.25; SH, 27.0. Found: C, 39.31; H, 8.06; SH, 26.5.[19]

C. **Va from VII.**—A 319-g. (1.5 moles) sample of the benzyl sulfide, b.p. 90–95° (3 mm.), $n^{30}\mathrm{D}$ 1.5297, was reduced essentially according to the method described by du Vigneaud,[20] using 1500 ml. of ether, 3750 ml. of liquid ammonia and 100 g. (4.35 atom) of sodium. The blue solution was stirred for 45 minutes, poured upon 200 ml. of absolute methanol, and the ammonia was allowed to evaporate. The dry sodium salts were washed free of toluene with ether, water was added and the mercaptoacetal was separated by carbonation and extraction. Distillation of the extract gave 121 g. (66%) of Va, b.p. 83–84° (84 mm.), $n^{30}\mathrm{D}$ 1.4463, thiol content 26.5% (calcd. 27.0%).

Va from VIII. 1.—When 3.95 g. (0.016 mole) of pure VIII, b.p. 101° (0.6 mm.), $n^{30}\mathrm{D}$ 1.4868, was reduced for one hour with 1.9 g. (0.05 mole) of lithium aluminum hydride in 50 ml. of ether,[21] a 57% yield of Va, b.p. 79–80° (80 mm.), $n^{30}\mathrm{D}$ 1.4463 was obtained.

2.—When 4.61 g. (0.019 mole) of pure VIII, b.p. 101° (0.6 mm), was reduced with sodium (1 g.) in 60 ml. of liquid ammonia there was obtained 2.32 g. (50%) of Va, b.p. 80–81° (77–80 mm.), $n^{25}\mathrm{D}$ 1.4472.

3.—When 50 g. (0.21 mole) of mixed sulfide, disulfide and polysulfides (prepared from Na_2S_3 as described in synthesis of VIII), $n^{26}\mathrm{D}$ 1.5292, was reduced with sodium (20 g., 0.87 gram atom) and liquid ammonia (600 ml.), there was obtained 33.3 g. of Va (b.p. 72° (50 mm.), $n^{30}\mathrm{D}$ 1.4458). This represents a 67% yield of Va from chloroacetal. When the same procedure was used with the mixed sulfides, $n^{29}\mathrm{D}$ 1.4930, the yield of Va from chloroacetal was 45%.

Preparation of 2,5-Dialkoxy-1,4-dithiane (VI). 1. **Reaction of Vb with Ethereal Hydrogen Chloride.**—A solution containing 1.5 g. of diethyl mercaptoacetal (Vb), 10 ml. of anhydrous ether and a trace of dry hydrogen chloride was refluxed for 1 hour. The ether was removed by distillation and the residue was sublimed at reduced pressure to give 0.48 g. (46%) of white crystals, m.p. 87–92°. This material was recrystallized from ethanol to give a product melting at 90–92°.

Anal. Calcd. for $C_8H_{16}O_2S_2$: C, 46.14; H, 7.67; mol. wt. (benzene), 208. Found: C, 46.35; H, 7.76; mol. wt., 210, 191.

2. **Reaction of Va with *p*-Toluenesulfonic Acid.**—A solution containing 50.0 g. of Va, 1.6 g. of *p*-toluenesulfonic acid, and 1000 ml. of anhydrous benzene was refluxed for 2 hr. The solution was cooled, extracted with three 50-ml. portions of 10% sodium hydroxide solution, and distilled to yield 20.0 g. (55%) of semi-crystalline 2,5-dimethoxy-1,4-dithiane (VIa), b.p. 79–84° (1 mm.).

Anal. Calcd. for $C_6H_{12}O_2S_2$: C, 39.97; H, 6.71. Found: C, 40.28, 40.47; H, 7.12, 6.78.

This mixture was used without further purification for subsequent dealkoxylations to I. The mixture of *cis*- and *trans*-2,5-dimethoxy-1,4-dithiane was filtered and the solid product was washed with ether. The α-isomer, obtained in this way, melted at 84–85°.[12]

Anal. Calcd. for $C_6H_{12}O_2S_2$: C, 39.97; H, 6.71. Found: C, 40.05; H, 6.74.

3. **Reaction of Vb with *p*-Toluenesulfonic Acid.**—Vb (90.0 g.) was treated with *p*-toluenesulfonic acid (2.0 g.) in benzene (1500 ml.), as described for Va above. *cis–trans*-2,5-Diethoxy-1,4-dithiane (VIb, 40.5 g., 65%) was obtained as a semi-crystalline solid, b.p. 93–111° (4 mm.). This mixture was used for subsequent dealkoxylation to I. The pure α-isomer, m.p. 90–92°, was easily separated by a procedure similar to that described for VIa in the preceding experiment.

Dealkoxylation of VI, Using Phosphorus Pentoxide. Preparation of 2-Methoxy-1,4-dithiene-5 (IX).—An 8.5-g. sample of *cis–trans*-2,5-dimethoxy-1,4-dithiane, b.p. 93–95° (3–4 mm.), was heated for 1.5 hours at 110° with 0.1 g. of phosphorus pentoxide in a 25-ml. Claisen flask. The distillate was identified as methanol by conversion to methyl 3,5-dinitrobenzoate (m.p. and mixed m.p. 106–107°). The residue was distilled to give 3.09 g. (46%) of IX as a nearly colorless liquid, b.p. 61–62° (4–5 mm.). Distillation through a spiral-wire column gave a colorless, odorless liquid, b.p. 63.1–63.2° (4 mm.), $n^{28.5}\mathrm{D}$ 1.5942, $\lambda^{95\%\ \mathrm{EtOH}}_{\mathrm{max}}$ 221 mμ (*E* 3300), λ 272 mμ (*E* 4580), λ_{min} 246 mμ (*E* 2160).

Anal. Calcd. for $C_5H_8OS_2$: C, 40.51; H, 5.44. Found: C, 40.72; H, 5.73.

When the dealkoxylation of VIa was attempted with phosphorus pentoxide at 180–185°, methanol was again identified in the distillate by means of the 3,5-dinitrobenzoate, m.p. 106.0–106.5°. Upon distillation of the residue a small amount of straw-colored liquid was obtained. The analysis suggested that it contained both IX and I.

Anal. Calcd. for $C_4H_4S_2$ (I): C, 41.35; H, 3.47. Calcd. for $C_5H_8OS_2$ (IX): C, 40.51; H, 5.44. Found: C, 40.90; H, 5.29.

Dealkoxylation of VI with Alumina. Preparation of 1,4-Dithiadiene (I). 1. **Dealkoxylation of VIa.**—Sixty grams of alumina pellets (The Harshaw Chemical Co., T 1/8") were heated for 40 hours at 360° in a vertical glass tube (2 × 29 cm.). The temperature was lowered to 310° and 5 ml. of absolute methanol was passed through the tube with dry, oxygen-free, nitrogen gas (rate of flow 0.5 l. per minute). A solution prepared from VIa (9.94 g., 0.055 mole) and 20 ml. of methanol[22] was passed through the tube at a rate of 10–15 drops per minute, while the nitrogen flow was kept at 0.5 l. per minute. The crude product, which had collected in a trap cooled with Dry Ice, was diluted with water and extracted with ether. The combined ether extracts were washed with water, saturated sodium chloride, and dried over calcium chloride. Distillation of the residue through an 8" spiral-wire column gave 2.9 g. (45%) of I as a straw-colored, unpleasant-smelling liquid, b.p. 85–88° (30 mm.). This material was further purified by chromatography, using 20 g. of alumina and 50 ml. of 1:1 ether–petroleum ether (60–80°). The combined eluate was distilled to give 2.40 g. (83% recovery) of pure 1,4-dithiadiene. 1,4-Dithiadiene was obtained as a light yellow, pleasant-smelling oil; b.p. 77 (17 mm.), $n^{30}\mathrm{D}$ 1.6319, $\lambda^{95\%\ \mathrm{EtOH}}_{\mathrm{max}}$ 262 mμ (*E* 5400), $\lambda_{\mathrm{shoulder}}$ 266–270 mμ (*E* 4480), λ_{min} 245 mμ (*E* 3560).

Anal. Calcd. for $C_4H_4S_2$: C, 41.35; H, 3.47; S, 55.18. Found: C, 41.36; H, 3.62; S, 55.40.

1,4-Dithiadiene, obtained previous to chromatography, had the following physical properties; $n^{30}\mathrm{D}$ 1.6288, $\lambda^{96\%\ \mathrm{EtHO}}_{\mathrm{max}}$ 262 mμ (*E* 5000), $\lambda_{\mathrm{shoulder}}$ 266–270 mμ (*E* 4300), λ_{min} 240 mμ (*E* 2520).

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[21] R. C. Arnold, A. P. Lien and R. M. Alm, THIS JOURNAL, **72**, 731 (1950).

[22] In another run methanol was not used to condition the tube or as a diluent. The yield of I (b.p. 96.5–97° (42–44 mm.), $n^{28}\mathrm{D}$ 1.6266) was 39%. Methanol was isolated in 53% yield and identified by conversion to methyl 3,5-dinitrobenzoate (m.p. and mixed m.p. 106–107°).

Anal.[23] Calcd. for $C_4H_4S_2$: C, 41.35; H, 3.47; S, 55.18. Found: C, 41.59, 41.63; H, 3.69, 3.71; S, 55.40.

2. **Dealkoxylation of VIb.**—VIb (17 g.), in absolute ethanol (17 ml.), was passed over alumina according to the procedure described for VIa above. There was obtained: (1) 3.76 g. (40%) of 1,4-dithiadiene, b.p. 66° (10 mm.), $n^{30}D$ 1.6285–1.6304; and (2) 3.58 g. (27.2%) of 2-ethoxy-1,4-dithiene-5, b.p. 68–72° (2 mm.), $n^{25}D$ 1.5731. Fraction 1 had the pleasant odor of pure I.

Anal. of fraction 2. Calcd. for $C_6H_{10}OS_2$: C, 44.41; H, 6.42. Found: C, 44.62; H, 6.21.

Preparation of 1,4-Dithiadiene Dioxide (X).—A solution of 1.12 g. (9.65 mmoles) of I in 40 ml. of glacial acetic acid was cooled to 20° and 2.5 ml. of 30% hydrogen peroxide was added. The temperature was kept below 20° for 30 minutes. The solution was allowed to stand at room temperature for 20 hours, then concentrated to 5 ml. at reduced pressure. Water (50 ml.) was added and the solution was again concentrated to a small (2 ml.) volume. Benzene (50 ml.) was added and the last traces of water were removed by azeotropic distillation at atmospheric pressure. When about 25 ml. of benzene had been distilled, 10 ml. of petroleum ether (b.p. 60–68°) was added at the boiling point, and the solution was allowed to cool slowly. The solid, 615 mg. (m.p. 95–98°), was removed by filtration. The filtrate yielded an additional 240 mg. of crystalline material to bring the total yield to 60%. A sample of this product was sublimed at 0.6 mm. and 120° to give colorless stout rods, m.p. 99.0–100.0°.

Anal. Calcd. for $C_4H_4S_2O_2$: C, 32.42; H, 2.72. Found: C, 32.33; H, 2.93.

Preparation of 1,4-Dithiadiene Tetraoxide (XI).—A 315-mg. sample of the dioxide (X), m.p. 95–98°, was refluxed for 1.5 hours in 15 ml. of glacial acetic acid containing 5 ml. of 30% hydrogen peroxide. The solution was allowed to stand overnight and 235 mg. (61%) of colorless crystalline disulfone (XI) was removed by filtration. A further 18 mg. (5%) of (XI) was obtained by concentration of the filtrate. The combined product was recrystallized from acetic acid (1 ml. for every 10 mg. of compound) to give colorless stout prisms, m.p. 241.5–242.5° (dec.) with darkening at 236° (capillary).

Anal. Calcd. for $C_4H_4S_2O_4$: C, 26.66; H, 2.44. Found: C, 26.77; H, 2.32.

A 44% yield of XI was obtained by allowing 1,4-dithiadiene to stand for 1 hour at room temperature with 2 equivalents of hydrogen peroxide in acetic acid, followed by refluxing the solution for 1.5 hours with an additional 2.5 equivalents of hydrogen peroxide.

Reduction of 1,4-Dithiadiene Tetraoxide. A.—A 95-mg. sample of XI was dissolved in 5 ml. of glacial acetic acid and 200 mg. of zinc dust was added carefully. The solution was refluxed for 1 hour and the solids were removed by filtration. These solids were washed with warm water to remove zinc salts and treated with 5 ml. of hot diluted (1:2) hydrochloric acid to remove excess zinc. The white solid remaining (57 mg., 59% yield) was recrystallized from 2 ml. of concentrated nitric acid to give 40 mg. of essentially pure 1,4-dithiane disulfone (XII). This material was obtained as a microcrystalline powder which did not melt below 370°, but decomposed slowly from 330 to 370°.

Anal. Calcd. for $C_4H_8S_2O_4$: C, 26.08; H, 4.38. Found: C, 26.11; H, 4.07.

B.—A mixture containing XI (108 mg.), glacial acetic acid (5 ml.), and prereduced platinum oxide (150 mg.) was stirred in an atmosphere of hydrogen for 20 hours at room temperature. A total of 32.5 ml. of hydrogen was absorbed (calculated for 2 equivalents 30.4 ml.). The mixture of catalyst and solid was removed by filtration and the catalyst was dissolved in hot nitric acid. The remaining solid was recrystallized from hot nitric acid to give 1,4-dithiane disulfone (dec. above 330°; identical X-ray powder diffraction pattern and infrared spectrum to authentic material).

Authentic 1,4-dithiane disulfone[24] was prepared by oxidation of 1,4-dithiane[25] with hydrogen peroxide. This product was purified by crystallization from concentrated nitric acid and showed the same melting characteristics as those reported for the reduction product of XI. The identity of this material to that obtained from 1,4-dithiadiene was established by comparing the X-ray powder diffraction patterns[14] and the infrared spectra of the two samples.

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[23] The first analysis was performed by the Clark Laboratory, Urbana, Ill. All other analyses were performed by the Microanalytical Laboratory, University of Minnesota.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Rearrangements in the Reactions of 2-(4-Substituted)-phenylethylamines-1-C^{14} with Nitrous Acid[1,2]

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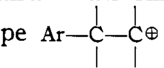
Treatment of a series of C^{14}-labeled 2-(4-substituted)-phenylethylamines (X——$CH_2C^{14}H_2NH_2$) with nitrous acid in water and acetic acid has been found to yield more or less of the isotope-position rearrangement products (X——$C^{14}H_2CH_2Y$; Y = -OH or -OAc) depending on the solvent and the nature of X. With X = $-OCH_3$, -H and $-NO_2$, the most rearrangement (45%) was observed in acetic acid with X = $-OCH_3$, and the least (~5%) rearrangement when X = $-NO_2$ in water or acetic acid.

Considerable stereochemical[3,4] and kinetic[4,5] evidence has recently been accumulated for stabilization by the π-electron system of an aromatic ring of cationic intermediates of the type  $Ar—C—C^{\oplus}$ (I). The stereochemical studies have led to the suggestion that symmetrical non-classical "phenonium" structures (II) are involved.[3] In the present research, the isotopic tracer technique[6] has been employed to detect rearrangements in the reactions

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[2] Supported in part by the program of research of the U. S. Atomic Energy Commission.

[3] (a) D. J. Cram, THIS JOURNAL, **71**, 3863, 3883 (1949); (b) **74**, 2129 (1952).

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[5] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *ibid.*, **74**, 1113 (1952).

[6] (a) J. D. Roberts, R. E. McMahon, W. Bennett and E. W. Holroyd, Jr., *ibid.*, **74**, 4283 (1952); J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5943 (1952).