A solution of 434 mg. of VIII in 20 cc. of quinoline was boiled for one hour with 420 mg. of copper chromite catalyst. The solution was then filtered, poured into an ice–HCl mixture and subjected to a continuous ether extraction; yield 302 mg., IX (85%). After two crystallizations from ethanol–water the m.p. was 98–99° (lit.[16] 98–99°). Reduction of this ketone with an equal weight of 10% palladium-on-carbon catalyst in hydrogen at normal pressure produced 1-methylfluorene, m.p. 85–86° (lit.[17] 87°).

Anal. 1.771 ± 0.007 microcurie of carbon-14 per millimole IX.

3-Methoxyfluorene (XI).—3-Methoxyfluorenone, which was prepared by the procedure of Ullmann and Bleier,[18] was reduced to 3-hydroxyfluorene with red phosphorus and hydrochloric acid according to Lothrop's[19] method. 3-Hydroxyfluorene (13.5 g.) was dissolved in 40 ml. of 10% sodium hydroxide solution to which 15 g. of dimethyl sulfate was added. The reaction mixture was stirred at room temperature for three hours. The oily organic layer was extracted with ether and the ether was evaporated in a current of air. The residue of 3-methoxyfluorene was crystallized twice from ligroin; m.p. 101.0–101.5°. The yield was 13 g. (89%).

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.7; H, 6.17. Found: C, 85.5; H, 6.33.

3-Methoxy-9-fluorene-(carboxylic-C^{14}) Acid (XII).—A 90% yield (1.21 g.) of the acid XII was obtained when 1.1 g. of 3-methoxyfluorene was treated with 28 ml. of triphenylmethylsodium solution and 0.056 mole of carbon-C^{14} dioxide.[8] The acid was crystallized twice from toluene; m.p. 190.3–191.2°.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.0; H, 5.04. Found: C, 74.8; H, 5.14; 1.27 microcuries of carbon-14 per millimole of XII.

Methyl 3-Methoxy-9-fluorene-(carboxylate-C^{14}) (XIII).—Esterification of the acid (XII) was accomplished by treating 0.718 g. of it with an excess of diazomethane in ether. A quantitative yield (0.780 g.) of the ester (XIII) was obtained. It was crystallized from ether; m.p. 108–109°.

(16) L. Chardonnens and H. Menert, *Helv. Chim. Acta*, **32**, 2340 (1949).

(17) W. C. Lothrop and P.* A. Goodwin, THIS JOURNAL, **65**, 365 (1943).

(18) F. Ullmann and H. Bleier, *Ber.*, **35**, 4273 (1902).

(19) W. C. Lothrop, THIS JOURNAL, **61**, 2115 (1939).

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.55. Found: C, 75.5; H, 5.40.

3-Methoxyphenanthrene-9,10-C^{14} (XV).—To a solution of the carbinol XIV (0.652 g.) in 15 ml. of xylene was added 4 g. of phosphorus pentoxide. The mixture was heated at reflux temperature for 15 minutes. Water was added to the reaction mixture and the xylene solution was concentrated. A 93.5% yield (0.556 g.) of oily XV was isolated. It could not be caused to solidify.

3-Hydroxyphenanthrene-9,10-C_1^{14} (XVI).—The oily 3-methoxyphenanthrene (XV) (0.556 g.) was heated under a reflux condenser with 20 ml. of 55% hydriodic acid for two hours. The organic material was extracted with ether. The ether solution was then extracted twice with 20 ml. of 4% sodium hydroxide solution to which a trace of sodium thiosulfate had been added. Upon acidification of the basic solution, a white flocculent precipitate of XVI separated. This was extracted with ether and crystallized from light petroleum ether; m.p. 120–121° (lit.[20] 122–123°). The yield was 0.229 g. (44.2%). A mixed melting point of XVI with a sample of 3-hydroxyphenanthrene prepared by the method of May and Mosettig[21] was not depressed.

Anal. 1.25 microcuries of carbon-14 per millimole of XVI.

Oxidation of 3-Hydroxyphenanthrene-9,10-C_1^{14} (XVI).—A mixture of XVI (0.354 g.) and potassium permanganate (2.5 g.) in 40 ml. of water was heated at reflux temperature for one hour. Excess potassium permanganate was decomposed with ethanol. The manganese dioxide was separated from the aqueous solution and was washed with 10 ml. of dilute sodium hydroxide. The basic solution was acidified and extracted continuously with ether for 24 hours. After evaporating the ether, the crystalline residue remaining was washed with chloroform. Impure phthalic acid (XVII) (0.105 g.) remained. This was converted to phthalic dianilide (XVIII) and crystallized three times from ethanol; m.p. 250–251° (lit.[22] 251–252°).

Anal. 0.030 microcurie of carbon-14 per millimole of XVIII.

(20) P. A. S. Smith and B. Ashby, *ibid.*, **72**, 2503 (1950).

(21) E. L. May and E. Mosettig, *J. Org. Chem.*, **11**, 12 (1946).

(22) S. Hoogewerf and W. A. Van Dorp, *Rec. trav. chim.*, **24**, 343 (1902).

OAK RIDGE, TENN.

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

Heterocyclic Vinyl Ethers. II.[1] Benzo-1,4-dithiadiene

BY WILLIAM E. PARHAM, THOMAS M. RODER[2] AND WILLIAM R. HASEK

The synthesis and proof of structure of benzo-1,4-dithiadiene and benzo-1,4-dithiadiene disulfone are described. The sulfur-containing ring in benzo-1,4-dithiadiene (V) has been shown to undergo electrophilic substitution reactions. The nitration of V gives a 2-nitrobenzo-1,4-dithiadiene (XI), and the reaction of V with N-methylformanilide and phosphorus oxychloride gives benzo-1,4-dithiadiene-2-carboxaldehyde (XIV). The dehydrogenation of benzo-1,4-dithiane constitutes an alternate synthetic route to the benzo-1,4-dithiadiene ring system. Other reactions related to the stability of V are reported.

In the first paper of this series,[3] it was noted that resonance interaction of the sulfur atoms may be sufficient to impart considerable stability to the 1,4-dithiadiene ring system.[4] Some evidence to

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

(2) In part, from the Ph.D. Thesis of Thomas M. Roder, University of Minnesota, 1952.

(3) W. E. Parham, I. Gordon and J. Swalen, THIS JOURNAL, **74**, 1824 (1952). It is of interest to note that dioxadiene does not show aromatic character; therefore it can be concluded that any unusual stability of the 1,4-dithiadiene ring can be attributed to the ability of sulfur to expand its valence shell.

(4) 1,4-Dithiadiene is the isostere of cyclooctatetraene; however, unlike COT, the former may have a planar configuration.

support this possibility was found in the work of Levi[5] who, in 1890, reported that 1,4-dithiadiene undergoes the Friedel–Crafts reaction with acid chloride and aluminum chloride—a reaction atypical of aliphatic vinyl ethers and vinyl sulfides. We have been unable to prepare 1,4-dithiadiene by the condensation of thiodiglycolic acid and phosphorus trisulfide (Levi's procedure); therefore, we have directed our attention to other possible syntheses of the 1,4-dithiadiene ring system, so that a detailed study of the properties and reactions of compounds in this series can be made. This paper is concerned with

(5) L. Levi, *Chem. News*, **62**, 216 (1890).

the synthesis, proof of structure and reactions of benzo-1,4-dithiadiene.

The synthesis of benzo-1,4-dithiadiene (V) was accomplished by the series of reactions which are summarized in the equations
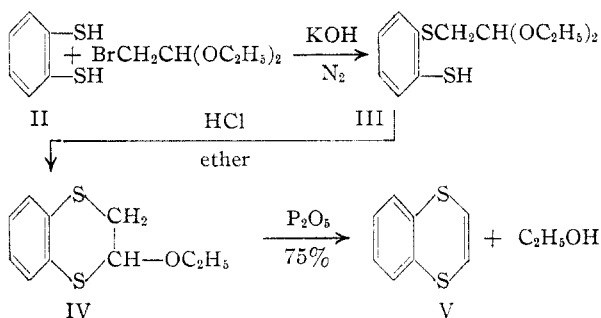
The condensation of dithiocatechol with diethyl bromoacetal was effected in an atmosphere of nitrogen, and the product (III) was converted, without isolation, into 2-ethoxybenzo-1,4-dithiane (IV, 55% yield) by action of hydrogen chloride in ether. The acetal, IV, was characterized by its conversion into a molecular complex with 1,3,5-trinitrobenzene, and by its ultraviolet and infrared absorption spectra.

When the reaction of II with bromoacetal was conducted in the presence of air, the product was high boiling and had the composition calculated for $C_{24}H_{34}S_4O_4$. This product, formulated as VI, was apparently formed by air oxidation of III. The 2,4-dinitrophenylhydrazone (VII) obtained from VI
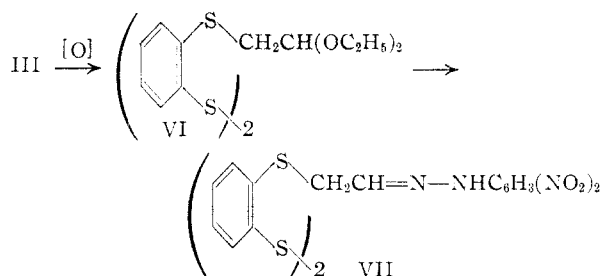

was identical with the product obtained by the acid hydrolysis of IV in the presence of 2,4-dinitrophenylhydrazine.

The conversion of IV into benzo-1,4-dithiadiene (V) was accomplished in high yield by dealkoxylation in the presence of phosphorus pentoxide. The dealkoxylation of IV occurred more readily than the dealkoxylation of 2-methoxy-p-oxathiane[3] as evidenced by: (1) shorter time required for dealkoxylation, and (2) formation of V when IV was treated with hot 15% hydrochloric acid. Benzo-1,4-dithiadiene was obtained as a pale yellow-green oil (b.p. 67–70° (0.1 mm.)) possessing a brilliant green fluoresence in ultraviolet light. The unsaturate could be stored without decomposition and distilled essentially unchanged (b.p. 220°) at atmospheric pressure in an atmosphere of nitrogen.

Benzo-1,4-dithiadiene reacted with hydrogen peroxide in glacial acetic acid to give the disulfone X, and with hydrogen in the presence of palladium and charcoal to give the dihydro derivative VIII. Reactions which constitute proof of structure of

benzo-1,4-dithiadiene and the sulfone X are summarized below.
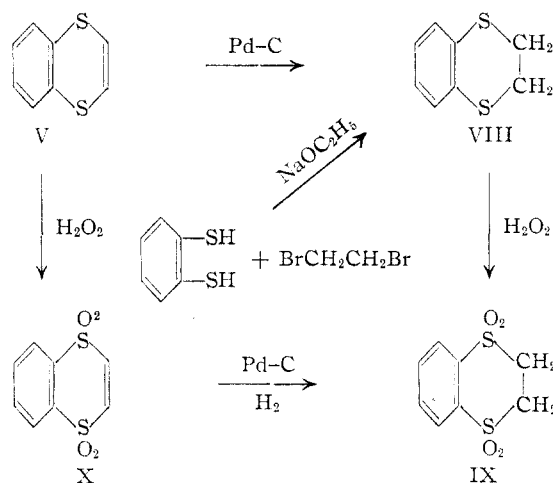
Pertinent to an understanding of the chemical nature of the p-dithiadiene ring, was the knowledge as to whether the benzene or sulfur-containing ring in V undergoes substitution by electrophilic reagents. One might expect, in view of the known orientation of substitution in other heterocyclic systems, such as benzothiophene, that electrophilic substitution in V would lead to products substituted in the p-dithiadiene ring. When V was treated with nitric acid in acetic acid, a single mononitro derivative was formed. This product (m.p. 104–
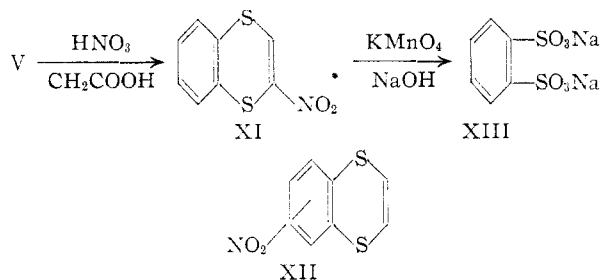
105°) was observed to lose oxides of nitrogen when exposed to light, a fact which suggested that the structure of the product was XI, and not an isomer (XII) with the nitro group in the benzene ring. The structure of the nitro derivative was established as 2-nitrobenzo-1,4-dithiadiene (XI) by oxidation with alkaline permanganate. The product was sodium benzene-o-disulfonate (XIII), which was characterized by conversion to benzene-o-disulfonyl chloride.

The reaction of V with N-methylformanilide and phosphorus oxychloride was studied (1) to confirm the general orientation of electrophilic substitution in V, and (2) to furnish a product useful for other proposed studies in the series. The Vilsmeier reaction was effected according to the procedure described by Weston and Michaels[6] and the crude aldehyde was purified through its bisulfite addition product. Benzo-1,4-dithiadiene-2-carboxyaldehyde (XIV) was obtained as an orange oil in 42% yield.

(6) Thianaphthene gives thianaphthene-3-carboxyaldehyde in 9% yield in the reaction: A. W. Weston and R. J. Michaels, Jr., THIS JOURNAL, 72, 1422 (1950).

V + C₆H₅N—CH₃ [below: CHO] $\xrightarrow{POCl_3}$ $\xrightarrow{[O]}$ XIII

XIV
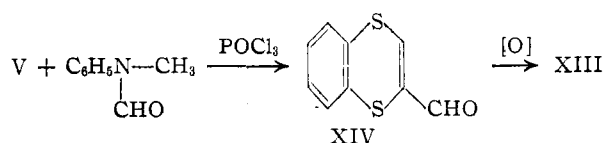
The aldehyde was characterized by its conversion to the corresponding phenylhydrazone (unstable, m.p. 139–140°) and oxime (m.p. 166–169°). The structure of XIV was confirmed by its oxidation to sodium o-benzenedisulfonate.

Alkanes, alkenes and hydroaromatic compounds. can be dehydrogenated with the appropriate catalyst; however, low temperature dehydrogenations using chloranil have only been reported for reactions giving products which are stabilized by conjugation.[7] When benzo-1,4-dithiane (VIII) was treated with chloranil in xylene at 140°, it was converted into benzo-1,4-dithiadiene in 38% yield. The product was identified by its ultraviolet and infrared spectra,[3] and by its conversion into XI.

VIII   O
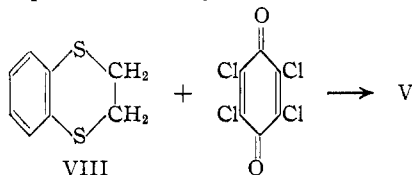
Attempts to dehydrogenate VIII to V with sulfur at 200° were unsuccessful; however, subsequent experiments established that the expected product, V, was unstable under conditions used for the reactions.

Other experiments were conducted to test the stability of the Δ²-double bond of benzo-1,4-dithiadiene. The distillable oil (about 80% recovery) obtained after prolonged action of V and hot 2.5 N hydrogen chloride in ethanol, was 87% unchanged V and 13% 2-ethoxybenzo-1,4-dithiane. Attempts to hydrolyze V in the presence of acid and 2,4-dinitrophenylhydrazine were unsuccessful.

Reactions of X, XI, XIV, and other derivatives of V are currently being examined.

Experimental[8]

2-Ethoxybenzo-1,4-dithiane (IV).—Oxygen-free nitrogen was swept through a 300-ml. flask and then dithiocatechol[9] (20.0 g., 0.14 mole), absolute ethanol (150 ml.), potassium hydroxide (9.27 g., 0.14 mole) and diethyl bromoacetal (27.7 g., 0.14 mole) were added. The mixture was heated at the reflux temperature for 1.5 hours in an atmosphere of nitrogen. Anhydrous magnesium sulfate was added to the cooled mixture to remove water and the solids were separated by filtration. Most of the ethanol was distilled from the filtrate (stream of nitrogen) and the residue was dissolved in 200 ml. of anhydrous ether. The ethereal solution was made just acidic with a saturated solution of hydrogen chloride in ether, and an additional 2 ml. of the ethereal hydrogen chloride was added. The acidic solution was allowed to stand for 16 hours and solid sodium carbonate was added until the solution was basic to moist litmus. The mixture was poured into water, the ether layer was separated, and the water solution was extracted twice with ether. The combined ether solutions were dried and the ether was removed. 2-Ethoxybenzo-1,4-dithiane (16.3 g., 55% yield, $n^{25}D$ 1.6229) was collected at 124–125° (0.9 mm.), and had the following characteristic absorption in

the ultraviolet region[10]: $\lambda^{95\% \ ethanol}_{max}$ 241 mμ (E 18,800), λmax 265 mμ (E 5600).

Anal. Calcd. for $C_{10}H_{12}OS_2$: C, 56.57; H, 5.70. Found: C, 56.80; H, 5.67.

IV (0.25 g.) was treated with 2,4-dinitrophenylhydrazine according to the procedure described by Shriner and Fuson.[11] The solution was heated at the reflux temperature for 15 minutes and allowed to stand for two days. Orange crystals (m.p. 126–134°) were separated mechanically from the tarry product and recrystallized from ethyl acetate and finally from ethanol. The product melted at 161.5–162.5°.

When dithiocatechol was allowed to react with diethyl bromoacetal and potassium hydroxide in the absence of nitrogen the product was high boiling and was formulated as VI.

Anal. Calcd. for $C_{24}H_{34}S_4O_4$: C, 55.99; H, 6.66. Found: C, 56.00; H, 6.44.

The 2,4-dinitrophenylhydrazone of the disulfide (VII) melted at 163.5–164.5° (from ethanol).

Anal. Calcd. for $C_{28}H_{22}N_8O_8S_4$: C, 46.27; H, 3.05; N, 15.42. Found: C, 46.48; H, 3.53; N, 15.22.

A mixed melting point of this hydrazone and that obtained from IV was 162–164°.

Reaction of 1,3,5-Trinitrobenzene with IV.—Trinitrobenzene (0.25 g.) and IV (0.25 g.) were dissolved in ethanol (15 ml.) and the solution was warmed for a few moments. The solution was cooled and 0.44 g. of orange crystals (m.p. 102–103°) was collected. The product was recrystallized from ethanol; m.p. 103.5–104°.

Anal. Calcd. for $C_{16}H_{15}O_7N_3S_2$: C, 45.17; H, 3.55; N, 9.88. Found: C, 45.40; H, 3.78; N, 9.82.

Benzo-1,4-dithiadiene (V).—The dealkoxylation of IV was carried out in an atmosphere of nitrogen. A small quantity (30 mg.) of phosphorus pentoxide was added to 15 g. (0.07 mole) of IV and the mixture was placed in an oil-bath heated to 125°. The bath temperature was increased to 170–175° and ethanol was collected in a cooled graduated cylinder. The bath was maintained at 170–175° for two hours during which time 2 ml. (75%) of ethanol was collected. If the elimination of ethanol was unduly slow during the heating period an additional 30 mg. of phosphorus pentoxide was added. The reaction mixture was then distilled at reduced pressure (75–90° (0.1 mm.)). Redistillation of the distillate gave 8.5 g. (72% yield, $n^{25}D$ 1.6748–1.6754) of V, boiling at 67–70° (0.1 mm.). A sample, $n^{25}D$ 1.6754, had the following composition.

Anal. Calcd. for $C_8H_6S_2$: C, 57.79; H, 3.64; S, 38.57; MD 48.82. Found: C, 57.85; H, 3.73; S, 38.68; MD 48.86; d^{20}_4 1.2799.

V has a yellow green fluorescence in visible light and a brilliant green fluorescence in ultraviolet light. V had the following characteristic absorption in the ultraviolet region: $\lambda^{95\% \ ethanol}_{max}$ 253 mμ (E 16,800), shoulder λ 262 mμ (E 6450), λmax 301 mμ (E 810).

Reaction of 2-Ethoxybenzo-1,4-dithiane (IV) with Dilute HCl.—A mixture containing 2.2 g. of IV, 15 ml. of water and 10 ml. of concentrated hydrochloric acid was heated to reflux for one hour, and then 20 ml. of distillate was collected. The distillate contained 0.2 g. of oil which possessed a brilliant green fluorescence in ultraviolet light. The product was shown to contain appreciable quantities of V by determination of the ultraviolet spectra (strong peak at 253 mμ, smaller peak of undetermined origin at 233 mμ). The oil remaining after the steam distillation was not examined further.

Benzo-1,4-dithiane (VIII).—A solution of 24.4 g. (0.172 mole) of dithiocatechol and 32.3 g. (0.172 mole) of ethylene bromide in 150 ml. of absolute ethanol was placed in a 500-ml. three-necked flask equipped with a condenser, gas inlet tube and dropping funnel. Oxygen-free nitrogen was slowly passed through the flask and a solution prepared from 12 g. (0.52 atom) of sodium in 200 ml. of absolute ethanol was added to the refluxing solution over a period of 2 hours. The reaction mixture was refluxed for 18 additional hours without further nitrogen flow. Sodium bro-

(7) R. T. Arnold and C. J. Collins, THIS JOURNAL, **61**, 1407 (1939).

(8) M.p.'s and b.p.'s are uncorrected.

(9) Prepared from orthanilic acid by extensive modifications of the combined procedures reported by A. F. Holleman, *Rec. trav. chim.*, **40**, 446 (1921), and T. Zincke and O. Kruger, *Ber.*, **45**, 3471 (1912).

(10) E = O.D./C in (moles per liter) × d (in cm.).

(11) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

mide was removed by filtration and most of the alcohol was evaporated under reduced pressure. The alkaline solution, resulting from the addition of 300 ml. of water to the residue, was extracted four times with ether. The ether solutions were combined, washed with water and dried over magnesium sulfate. The ether was evaporated, and the residue distilled through a small Vigreux column. Benzo-1,4-dithiane (19.8 g., 69%, n^{25}D 1.6713) was collected at 82.5–85° (0.18 mm.) and had the following characteristic absorption in the ultraviolet region: $\lambda_{max}^{95\% \text{ ethanol}}$ 243 mμ (E 22,300), λ_{max} 273 mμ (E 5340).

Anal. Calcd. for $C_8H_8S_2$: C, 57.10; H, 4.79. Found: C, 57.07; H, 4.91.

The Disulfone of Benzo-1,4-dithiane (IX).—This was prepared in the usual way from VII (0.2 g.) and H_2O_2 (30%, 1 g.) in glacial acetic acid (5 ml.). The crude sulfone (93% yield) melted at 271–272° and after three recrystallizations from acetone the product melted at 269°.

Anal. Calcd. for $C_8H_8O_4S_2$: C, 41.37; H, 3.47. Found: C, 41.50; H, 3.64.

Reduction of V.—A mixture containing V (0.5 g., 0.003 mole), methanol (150 ml.), sulfuric acid (1.4 ml.) and 4 g. of 30% palladium-on-charcoal was agitated for one hour under a pressure of 50 p.s.i. of hydrogen. The catalyst was removed and sodium carbonate, sufficient to neutralize the sulfuric acid, was added. The alcohol and salts were removed and the residue was dissolved in 12 ml. of glacial acetic acid. Hydrogen peroxide (2.5 g. of 30%) was added and 0.35 g. of benzo-1,4-dithiane disulfone was isolated; m.p. and mixed m.p. 269°.

The Disulfone of Benzo-1,4-dithiadiene (X).—This was prepared in the usual way from V (0.5 g., 0.003 mole) and 4.7 g. (0.041 mole) of 30% hydrogen peroxide in 7.5 ml. of glacial acetic acid. The crude product weighed 0.5 g. and melted at 188–202°. After several recrystallizations from absolute ethanol the product melted at 221.5–222.5°.

Anal. Calcd. for $C_8H_6O_4S_2$: C, 41.73; H, 2.63. Found: C, 41.53; H, 2.60.

The reduction of X was effected in absolute ethanol using 30% palladium and charcoal as a catalyst. A pressure of 45 p.s.i. of hydrogen and a reaction time of 2.5 hours were employed. The product melted at 270.5° and did not depress the melting point of IX.

Nitration of V.—A solution containing 2.6 g. (0.156 mole) of V in 10 ml. of glacial acetic was cooled to 18°, and 1.67 ml. of dilute nitric acid (25 ml. of solution prepared from glacial acetic acid, 70% nitric acid (18.3 ml.) and urea (0.5 g.)) was added dropwise. The mixture was poured onto 200 g. of ice and the resulting mixture was allowed to stand for several hours. The dry product (1.52 g., 46% yield) melted at 102–106°. The nitro derivative was recrystallized from petroleum ether (60–80°) or aqueous ethanol and was obtained as long red needles melting at 104.5–105.5°.

Anal. Calcd. for $C_8H_5S_2O_2N$: C, 45.48; H, 2.39; N, 6.63. Found: C, 45.60; H, 2.65; N, 6.68.

Oxidation and Proof of Structure of 2-Nitrobenzo-1,4-dithiadiene (XI).—A mixture of XI (0.6 g.), 50 ml. of 5% aqueous potassium permanganate and 1 ml. of 10% sodium hydroxide was heated at the reflux temperature for five hours. The excess permanganate was decomposed with ethanol and the clear solution, obtained by filtering the mixture, was boiled to dryness. The residue (1.9 g.) was ground with 5 g. of phosphorus pentachloride. Phosphorus oxychloride (5 ml.) was added to the mixture of XIII and phosphorus pentachloride and the resulting mixture was heated at 130° for four hours, and then poured onto ice and water. The mixture was stirred until the phosphorus oxychloride was destroyed and the resulting solid was collected and recrystallized from benzene–petroleum ether. The product (white needles) melted at 143–144° and did not depress the melting point of an authentic sample of benzene-*o*-disulfonyl chloride (m.p. 143–144°). The X-ray diffraction[12] pattern of the product and of an authentic sample of benzene-*o*-disulfonyl chloride confirmed the identity of the two samples.

The reaction V with N-methylformanilide and phosphorus oxychloride was carried out according to the procedure described by Weston and Michaels.[6] The tarry material, ob-

tained when the product from 4.5 g. of V was poured into water, was extracted with ether (200 ml.) and with chloroform (200 ml.). The volume of the combined neutral extracts was concentrated to about 20 ml., and 40 ml. of saturated sodium bisulfite was added. The precipitate (12.44 g.), containing the bisulfite adduct, was washed with ether and decomposed with aqueous potassium carbonate. The aldehyde was obtained as an orange oil in 42% yield (2.2 g.). A small quantity was distilled at low pressure with no change in color. The index of refraction of XIV was greater than 1.7. XIV showed the following absorption in the ultraviolet region: $\lambda_{max}^{95\% \text{ ethanol}}$ 271 mμ (E 14,300), λ_{min} 249 mμ (E 5,150), broad absorption band from λ 210–233 mμ (E 10,700–11,150).

Anal. Calcd. for $C_9H_6OS_2$: C, 55.65; H, 3.11. Found: C, 55.58; H, 3.39.

A yellow oxime was prepared from XIV which, after recrystallization from ethanol, melted at 166–169°.

Anal. Calcd. for $C_9H_7S_2NO$: C, 51.65; H, 3.37; N, 6.69. Found: C, 51.96, 51.52; H, 3.51, 3.50; N, 6.62.

XIV gave a yellow phenylhydrazone which, after recrystallization from ethanol, melted at 138.8–139.4°. This product was unstable, as evidenced by the rapid change of color and melting point.

Anal. Calcd. for $C_{15}H_{12}S_2N_2$: C, 63.34; H, 4.25. Found: C, 63.74; H, 4.48.

The oxidation and proof of structure of XIV was carried out as described for XI. The benzene-*o*-disulfonyl chloride obtained from 0.64 g. of XIV weighed 0.5 g., and melted at 143–144°.

The reaction of VIII and sulfur at 200° resulted in the formation of hydrogen sulfide, tar and a green fluorescent liquid (54%) composed chiefly of unchanged VIII (λ_{max} 243 mμ). When the reaction was carried out at 230–240°, the distillable oil contained VIII, and an unidentified product having an absorption maximum at 235 mμ. It was subsequently shown that V decomposes in air at temperatures higher than 200°.

Dehydrogenation of VIII with Chloranil.—A mixture of 3 g. (0.018 mole) of VIII, 5 g. (0.02 mole) of chloranil and 9 ml. of *o*-xylene was heated at the reflux temperature for 20 hours. The product was processed in the usual way,[7] and two arbitrary fractions were collected: (1) 0.46 g. boiling at 75–79° (0.22 mm.), and (2) 0.83 g. boiling at 79° (0.22 mm.). Both fractions possessed the green fluorescence in ultraviolet light typical of V.

The ultraviolet absorption spectrum of fraction 1 (λ_{max} 253 mμ) was nearly identical to that of pure V. Fraction 2 exhibited a broad maximum at 248 mμ which is between the maxima of V and VIII.[13] The equation, $OD = C_1E_1 + C_2E_2$, was solved for C_1 and C_2, and fraction 2 was found to contain 76–81% of V.[14]

The infrared spectra of fractions 1 and 2 were determined on the undiluted liquids. Quantitative analyses made from the curves were less accurate than those obtained from the ultraviolet spectra; however, the results were in fair agreement. The infrared analysis indicated that fraction 1 was 85 ± 5% V, and fraction 2 was 62 ± 15% V.

The yield of V was, therefore, approximately 37% based on the quantity of VIII employed. The presence of V was confirmed by its conversion to XI (m.p. and mixed m.p. 104.5–105°).

Reaction of V with Ethanol and Hydrogen Chloride.—A mixture containing 2 g. of V (n^{25}D 1.6764), 5 ml. of dry ethanol and 2 drops of 7.5 N hydrogen chloride in ethanol was allowed to stand at room temperature for three days. The mixture was then heated to reflux for five minutes and neutralized with sodium ethoxide. Distillation of the residue gave 1.56 g. (n^{25}D 1.6769) of unchanged benzo-1,4-dithiadiene. The infrared spectum of the recovered product was identical to that of the starting material.

A mixture containing 2.5 g. of V (n^{25}D 1.6764) and 15 ml. of 2.5 N hydrogen chloride in ethanol was heated at the reflux temperature for four hours, and processed as described above. The distillate (2 g.) was fractionated and four frac-

(12) The samples were run as powders using a General Electric XRD-3 unit with Geiger counter recording.

(13) A synthetic mixture of V and VIII possessed a similar spectrum.

(14) A plot of the equation $OD/E_1 = C_1 + (E_2C_2/E_1)$ was a straight line, showing that the mixture was binary. The slope and intercept of the line gives C_1 and C_2.

tions were collected (n^{25}D 1.6716−1.6493). Fractions 1–3 contained principally unchanged starting material. The infrared spectrum of fraction 3 was identical to that of the starting material. Analysis of the ultraviolet spectra of V, 2-ethoxy-1,4-benzodithiane, and fraction 4 revealed that fraction 4 had a composition[13] corresponding to 57% V and 43% 2-ethoxy-1,4-benzodithiane. Thus, the yield of recovered V was 87% of the distillable liquid.

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Side-chain Sulfonation of Phenylalkanoic Acids[1]

BY WILLIAM E. TRUCE AND CECIL E. OLSON

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Several ω-phenylalkanoic acids have been directly sulfonated to α-sulfo-ω-phenylalkanoic acids. ω-Phenylbutyric acid reacts abnormally, undergoing cyclization as well as sulfonation. α-Phenylbutyric acid can be sulfonated by this method, but only in poor yield. Diphenylacetic acid and α-cyclohexylphenylacetic acid do not react with dioxane sulfur trioxide under the conditions employed. A possible explanation for the unreactivity of these acids and a mechanism for the sulfonation reaction is suggested.

The direct sulfonation of phenylalkanoic acids has been reported to result in nuclear sulfonation only. Phenylacetic acid has been sulfonated with concentrated sulfuric acid,[2] chlorosulfonic acid[3] and sulfur trioxide[4] to give o- and p-sulfophenylacetic acids. Analogous results have been obtained with β-phenylpropionic acid.[5]

Recently, acetophenone has been sulfonated with dioxane sulfur trioxide to give ω-acetophenonesulfonic acid in good yield.[6] In view of some structural similarity, it seemed of interest to employ this reagent with phenylalkanoic acids in the attempt to achieve side-chain sulfonation. This paper reports on the reaction of phenylalkanoic acids with dioxane sulfur trioxide leading to α-sulfo-ω-phenylalkanoic acids in good yield. Phenylacetic acid, β-phenylpropionic acid and ω-phenylcaproic acid were converted by this reagent to phenylsulfoacetic acid, β-phenyl-α-sulfopropionic acid and ω-phenyl-α-sulfocaproic acid, respectively.

The mechanism for the side-chain sulfonation of phenylalkanoic acids with dioxane sulfur trioxide is probably related to the mechanisms proposed for the acid-catalyzed bromination[7] and the sulfonation[6] of ketones.
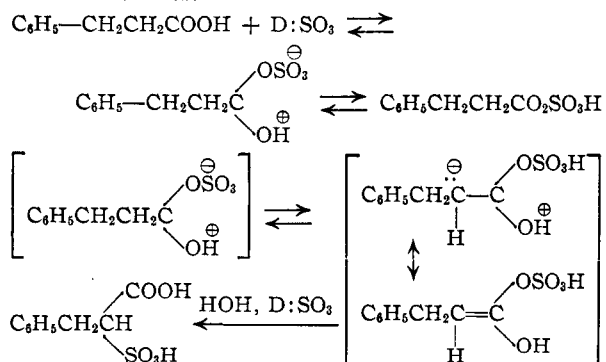
where D = dioxane

(1) Presented at the Atlantic City Meeting of the American Chemical Society, September 15, 1952.

(2) J. Hausman, German Patent 289,028; Chem. Zentr., 87, 194 (1916).

(3) J. Stewart, J. Chem. Soc., 121, 2555 (1922).

(4) J. Brust, Rec. trav. chim., 47, 153 (1928).

(5) J. B. Senderens and J. Abouienc, Compt. rend., 186, 1497 (1928).

(6) W. E. Truce and C. C. Alfieri, THIS JOURNAL, 72, 2740 (1950).

(7) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 96.

The first step involves polarization of the carboxyl group by coördination with sulfur trioxide. This is followed by the loss of an α-hydrogen to a sulfate ion, dioxane or other Lewis base, giving rise to an active enolate-type intermediate, which would be attacked by the reagent to give the product.

The fact that diphenylacetic acid did not react with dioxane sulfur trioxide can be explained on the basis of steric factors. In the Fisher–Hirschfelder molecular model of α-sulfodiphenylacetic acid, before the sulfur trioxide group can be attached to the α-carbon, the two phenyl rings must be turned to specific positions. Even then, the entering group must be oriented in a certain manner before it can be connected. These special requirements in orientation of the two reacting groups would hinder the reaction.

To determine whether an electronic effect is also operative in determining the unreactivity of diphenylacetic acid, α-cyclohexylphenylacetic acid was considered. In this molecule a cyclohexyl group replaces a phenyl radical and results in greater steric hindrance at the α-carbon than in diphenylacetic acid. However, the electronic effect of the cyclohexyl group is such that the resulting intermediate would be even more susceptible to attack at the α-carbon by an electrophilic agent. α-Cyclohexylphenylacetic acid did not react with dioxane sulfur trioxide, the unchanged acid being recovered nearly quantitatively. These results demonstrate the importance of steric hindrance by phenyl and cyclohexyl substituents at the α-carbon in the sulfonation reaction.

Related results were obtained in the sulfonation of α-phenylbutyric acid. On the basis of Fisher–Hirschfelder models, this compound should be subject to nearly the same steric hindrance toward sulfonation as diphenylacetic acid, but would have the electron-supplying ethyl group in place of one of the phenyl groups. Treatment of this acid with dioxane sulfur trioxide gave sulfonation but in poor yield (14–20%). More than half of the unreacted acid was recovered in each reaction.

Sulfonation of γ-phenylbutyric acid with dioxane sulfur trioxide produced β-sulfo-α-tetralone and a small amount of γ-phenyl-α-sulfobutyric acid.