

per electrophoresis¹⁰ (0.1 *M* borate buffer). Under the same conditions maltose readily gave glucose while cellobiose remained unchanged.

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ST. PAUL, MINNESOTA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

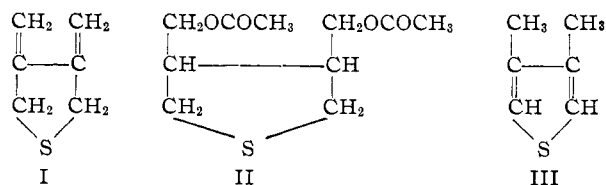
Further Attempts to Prepare 3,4-Dimethylenethiophane and its Sulfone¹

BY C. S. MARVEL, ROBERT M. NOWAK² AND JAMES ECONOMY

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The Hofmann decomposition of the quaternary ammonium hydroxide of 3-methylene-4-dimethylaminomethylthiophane at room temperature and 5 mm. pressure has been found to give the rearranged product 3,4-dimethylthiophene in 21% yield and no 3,4-dimethylenethiophane. It has also been shown that the pyrolysis of 3,4-bis-(acetoxymethyl)-thiophane sulfone at $520 \pm 5^\circ$ does not lead to 3,4-dimethylenethiophane sulfone but causes decomposition with much charring to give poor yields of two products that have been tentatively identified as 3-methylene-4-acetoxymethylthiophane sulfone and 2-methyl-3-acetoxymethyl-1,3-butadiene.

A previous attempt to prepare 3,4-dimethylenethiophane (I) by the pyrolysis of 3,4-bis-(acetoxymethyl)-thiophane (II) yielded only the 3,4-dimethylthiophene (III) and none of the desired



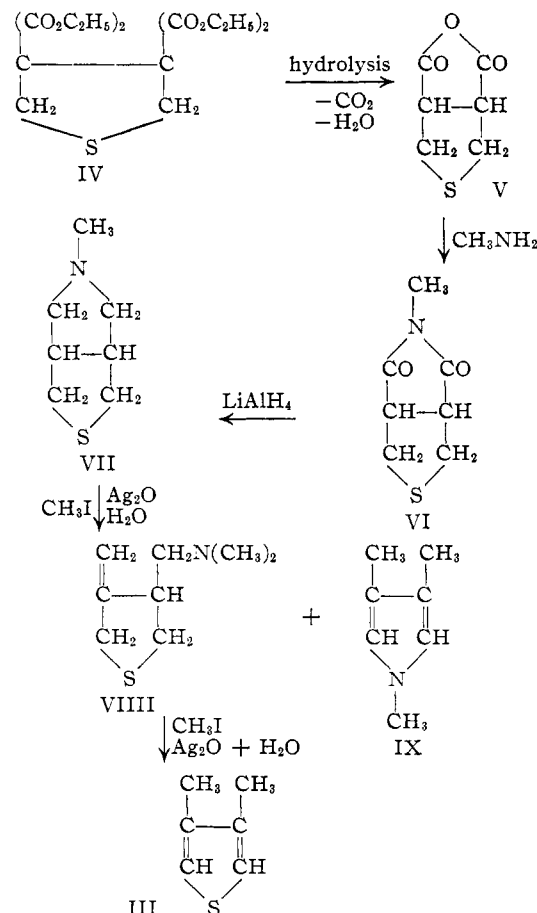
product.³ It was thought that the rearrangement might have been caused by the high temperature encountered during the pyrolysis reaction and that the preparation of the dimethylenethiophane (I) might be accomplished if less vigorous conditions were used. It has now been shown that the Hofmann decomposition of the quaternary ammonium hydroxide of 3-methylene-4-dimethylaminomethylthiophane (VIII) at room temperature also gives the rearranged thiophene isomer III.

The steps involved in the preparation of the required quaternary ammonium hydroxide are outlined in the chart.

In the conversion of the double ring compound VII to the methiodide, some methylation of the sulfur must have occurred since in the decomposition of the quaternary hydroxide in addition to 51.5% yield of the sulfur ring compound VIII there was obtained a 23.5% yield of 1,3,4-trimethylpyrrole (IX). A third product was isolated which, while not completely characterized, appears to be a methyl mercaptan adduct of the olefinic derivative VIII.

The quaternary salt of the olefinic amine (VIII) was prepared, treated with silver oxide in water and allowed to decompose to the olefin at a temperature below 25° . The product, however, proved to be 3,4-dimethylthiophene (III). It is thus obvious

that the rearrangement of the dimethylenethiophane to dimethylthiophene occurs with ease and that the higher temperature involved in the earlier pyrolysis of the diacetate was not necessarily the cause of the rearrangement.



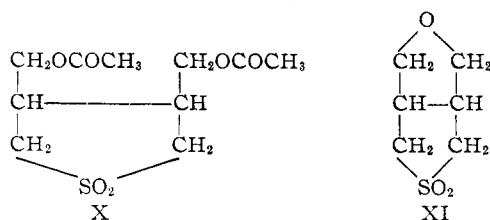
Another approach to a five-membered sulfur ring compound with 3,4-dimethylene substitution was sought. 3,4-Diacetoxymethylthiophane (II) was prepared by modification and improvement of the method used before³ and oxidized with 30% hydrogen peroxide in acetic anhydride to give the

(1) The work discussed herein was performed as a part of the synthetic rubber research project sponsored by the Federal Facilities Corporation and the National Science Foundation.

(2) This paper represents part of a thesis submitted by Robert M. Nowak to the Graduate School, University of Illinois, in partial fulfillment of the degree of Doctor of Philosophy, 1956.

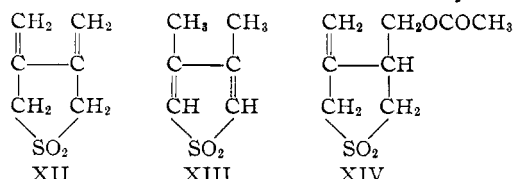
(3) C. S. Marvel and E. E. Ryder, Jr., *THIS JOURNAL*, **77**, 66 (1955).

sulfone X. The yield was only 54% and there was evidence of decomposition with much charring during distillation. A 9% yield of a tetrahydro-

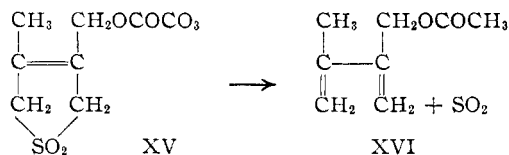


furan derivative XI was isolated from the distillation of the oxidation mixture.

Pyrolysis of the sulfone X at $520 \pm 5^\circ$ gave neither 3,4-dimethylenethiophane sulfone (XII) nor 3,4-dimethylthiophene sulfone (XIII). Instead the molecule was partially deacetylated to give the olefin acetate sulfone XIV in low yield and

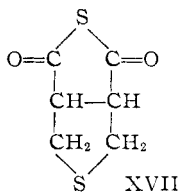


much charring occurred. Further decomposition of this molecule occurred during pyrolysis and resulted in the loss of sulfur dioxide and the apparent formation of a 1,3-diene. This probably occurs by a shift of the double bond to the ring XV and then decomposition to the diene XVI.



Since this sulfur free compound was obtained in only trace amounts, its identification is based mainly on ultraviolet and infrared absorption data.

In seeking a simple process of preparing the anhydride of 3,4-thiophenedicarboxylic acid (V), a sample of the tetraester IV was pyrolyzed. Much decomposition occurred and the only product isolated appeared to be the thioanhydride XVII on the basis of analysis and infrared absorption.



Experimental

Thiophane-3,4-dicarboxylic Acid Anhydride (V).—A solution of 410 g. (1.09 moles) of crude tetraethyl thiophane-3,3,4,4-tetracarboxylate (IV)⁴ in 100 ml. of dioxane and 3300 g. of 11% aqueous sodium hydroxide was refluxed for 27 hr. The solution was made acid to congo red paper, refluxed for 1 hr. and the product then isolated by continuous ether extraction. Distillation gave a 143 g. of mixture of anhydride V and partially hydrolyzed tetraester IV as shown by the infrared spectrum. This mixture was refluxed with 1400 g. of 5.4% aqueous sodium hydroxide for 4 hr. and worked

up exactly as before to give 112 g. (69.5%) of an orange solid, b.p. $144\text{--}150^\circ$ (0.5 mm.). A portion recrystallized from benzene-ether gave white crystals, m.p. $86\text{--}87^\circ$ (the literature lists $87\text{--}87.5^\circ$).⁵

N-Methyl-3,4-dicarboximidothiophane (VI).—To 54 g. (0.342 mole) of the thiophane anhydride (V) was added a solution of four drops of concentrated sulfuric acid in 70 ml. of a 40% aqueous solution of monomethylamine. The reaction was slightly exothermic. After all the anhydride had dissolved, the solution was heated with a bunsen burner and the water and excess monomethylamine allowed to escape through an air condenser. When most of the solvents had escaped, the solution was heated to $240\text{--}260^\circ$ for 20 minutes and then to $260\text{--}280^\circ$ for 20 minutes. When cooled, 52 g. (89%) of dark orange product crystallized. An analytical sample was purified with Norite in absolute ethanol and two recrystallizations from a low boiling petroleum ether-ethanol mixture to give a white solid, m.p. $98\text{--}99^\circ$. Infrared spectra on the crude and pure product were identical; $\nu(\text{cm}^{-1})$ C=O 1778 and 1705 in CHCl_3 .

Anal. Calcd. for $\text{C}_7\text{H}_9\text{NO}_2\text{S}$: C, 49.15; H, 5.26; N, 8.18. Found: C, 49.35; H, 5.44; N, 8.29.

N,N'-Dimethyl-3,4-dicarboxamidothiophane.—If the above reaction mixture was kept between $200\text{--}275^\circ$ for only 15 minutes, two solid products were obtained when the mixture was cooled. These products when purified with Norite in ethanol could be separated by hand since they possessed different crystal structures. The major portion melted at $98\text{--}99^\circ$ and proved to be the imide VI by a mixed melting point and infrared analysis. The minor fraction, 25% of the total yield, analyzed for the dimethyldiamide, m.p. $298\text{--}300^\circ$.

Anal. Calcd. for $\text{C}_9\text{H}_{14}\text{N}_2\text{O}_2\text{S}$: C, 47.50; H, 6.94; N, 13.98. Found: C, 47.52; H, 7.12; N, 14.02.

N-Methylthieno[3,4-C]tetrahydropyrrole (VII).—Into a stirred slurry of 28 g. (0.738 mole) of lithium aluminum hydride in 1920 ml. of absolute ether, 23 g. (0.744 mole) of N-methylimide (VI) was introduced slowly by extraction from a Soxhlet extractor by the refluxing ether. The solution was refluxed 20 hours after addition was complete. The excess hydride was decomposed with water, the resulting inorganic precipitate was filtered and the filtrate was dried. The product was isolated by distillation, b.p. 65° (3.5 mm.), n_D^{20} 1.5240. The yield was 30 g. (79%). $\lambda_{\text{max}}^{\text{EtOH}}$ 210 μ ($\log \epsilon$ 3.28), $\nu(\text{cm}^{-1})$ 714, 1357, 1452, 1477.

Anal. Calcd. for $\text{C}_7\text{H}_{13}\text{NS}$: C, 58.81; H, 9.09; N, 9.78. Found: C, 59.17; H, 9.36; N, 9.70.

N-Methylthieno[3,4-C]tetrahydropyrrole Monomethiodide.—To a solution of 10 g. (0.070 mole) of the tetrahydropyrrole VII in 30 ml. of methanol cooled to 10° was added 10 g. (0.070 mole) of methyl iodide. After the ensuing exothermic reaction, which was controlled by means of an ice-bath, had subsided, any excess methyl iodide present was boiled off on a steam-bath. When cooled 19.8 g. (99%) of white crystalline monomethiodide was isolated, m.p. $226\text{--}228^\circ$. An analytical sample was prepared by recrystallization from ethanol-water; m.p. $227\text{--}229^\circ$.

Anal. Calcd. for $\text{C}_8\text{H}_{16}\text{INS}$: C, 33.68; H, 5.61; N, 4.91. Found: C, 33.53; H, 5.68; N, 4.69.

The dimethiodide of VII was prepared by refluxing for 12 hr. a methanolic solution of the monomethiodide with excess methyl iodide. The white solid was recrystallized from water; m.p. $222\text{--}224^\circ$.

Anal. Calcd. for $\text{C}_9\text{H}_{18}\text{I}_2\text{NS}$: C, 25.29; H, 4.44; N, 3.28. Found: C, 25.09; H, 4.38; N, 3.15.

Hofmann Degradation of N-Methylthieno[3,4-C]tetrahydropyrrole Monomethiodide.—To a stirred solution of 101 g. (0.354 mole) of monomethiodide in 300 ml. of water under a nitrogen atmosphere was added the silver oxide prepared as follows. To a stirred solution of 28 g. (0.700 mole) of sodium hydroxide in 150 ml. of water was added a solution of 119 g. (0.700 mole) of silver nitrate in 400 ml. of water. The resulting precipitate of silver oxide was filtered, washed free of sodium hydroxide and added to the methiodide solution.

The solution, which then contained a flocculent precipitate of silver iodide, was stirred and heated on a steam-bath

(5) E. A. Fehnel and M. Carmack, *THIS JOURNAL*, **71**, 84, 232 (1949).

(6) N. J. Leonard and D. M. Locke, *ibid.*, **77**, 437 (1955).

(4) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **123**, 1172 (1923).

at 50–60° for 1 hr. at which time the precipitate was filtered and washed with water. The precipitate was again added to the reaction flask along with 100 ml. of water and heated at 70° for 0.5 hr. after which it was filtered, washed and discarded.

The combined filtrates and washings were evaporated to 250 ml. at 20 mm., after which the solution was transferred to a 300-ml. round-bottomed flask fitted with a Claisen head which in turn was connected to two traps cooled to –78° in acetone–Dry Ice. The remaining water was evaporated at under 5 mm. pressure. Decomposition proceeded smoothly at an oil-bath temperature of 110–130° (0.1 mm.).

The pyrolysates were extracted into ether along with 2 g. of liquid which remained in the decomposition flask. The ether solution was dried and the ether removed. The residue was distilled through a 12-in. Holtzmann column to give three fractions, b.p. 60–63° (approximately 20 mm.), 71–75° (4.1 mm.) and 170–185° (0.5 mm.).

Fraction I. 1,3,4-Trimethylpyrrole (IX).—Refractionation of the low boiling product through a 12-in. Holtzmann column gave 9 g. (23.5%) of a colorless liquid, b.p. 34° (5.5 mm.); n_D^{20} 1.4830; positive Erlich reaction; $\lambda_{\text{max}}^{\text{EtOH}}$ 225 m μ (log ϵ 3.80); $\nu(\text{cm.}^{-1})$ CH 3110, 767, C–CH₃ 1452, 1378 and 1542, 1413, 1166 and 1024.

Anal. Calcd. for C₇H₁₁N: C, 77.06; H, 10.09; N, 12.84. Found: C, 77.13; H, 9.89; N, 12.60.

Fraction II. 3-Methylene-4-dimethylaminomethylthiophane (VIII).—Refractionation of the second fraction through a 12-in. Holtzmann column gave 28.5 g. (51.5%) of colorless liquid, b.p. 75° (4.4 mm.); n_D^{20} 1.5156; $\nu(\text{cm.}^{-1})$ 3050, 1452, 1648 and 891 (the last two bands are indicative of R₁R₂C=CH₂ structure); $\lambda_{\text{max}}^{\text{EtOH}}$ 275 m μ (log ϵ 2.76) 243 shoulder (2.91) 210 (3.45).

Anal. Calcd. for C₉H₁₃NS: C, 61.15; H, 9.55; N, 8.93. Found: C, 60.96; H, 9.77; N, 8.62.

Fraction III.—The high boiling material was fractionated three times through a 12-in. Holtzmann column to give a yellow liquid which boiled at 108° (1.1 mm.); n_D^{20} 1.5358; $\nu(\text{cm.}^{-1})$ 2800, 2750, 1387, 1320 and 705 (no indication of unsaturation); $\lambda_{\text{max}}^{\text{EtOH}}$ 252 m μ (log ϵ 3.05) 211 (3.27). Neither a solid methiodide nor a solid sulfone could be prepared. The above data are most consistent with the structure 3-dimethylaminomethyl-4-methylmercaptomethylthiophane. This structure should probably show no absorption in the ultraviolet above 211 m μ . The yield was 10.5 g. (7.5%) on the basis of this structure.

Anal. Calcd. for C₉H₁₃NS₂: C, 52.68; H, 9.26; N, 6.83; S, 31.22. Found: C, 53.05; H, 9.12; N, 6.65; S, 30.70.

3-Methylene-4-dimethylaminomethylthiophane Monomethiodide.—To a solution of 21.5 g. (0.137 mole) of the 3-methylene compound VIII in 70 ml. of methanol was added 20 g. (0.141 mole) of methyl iodide. The reaction was run as before. The yield was 31.5 g. (77%). A sample was recrystallized from ethanol; m.p. 239–240° (softened at 218–219°).

Anal. Calcd. for C₉H₁₃INS: C, 36.12; H, 6.02; N, 4.68; I, 42.48. Found: C, 36.15; H, 6.34; N, 4.81; I, 42.50.

3-Methylene-4-dimethylaminomethylthiophane Hydrochloride.—Dry hydrogen chloride gas was bubbled through an ethereal solution of the base VIII. The resulting white solid was filtered and recrystallized successively from ethanol, chloroform and isopropyl alcohol; m.p. 220–221°.

Anal. Calcd. for C₉H₁₃ClNS: C, 49.61; H, 8.27; N, 7.24. Found: C, 49.40; H, 8.21; N, 6.91.

Hofmann Degradation of 3-Methylene-4-dimethylaminomethylthiophane Monomethiodide.—The decomposition of 76.5 g. (0.256 mole) of the monomethiodide of this base was carried out in the same manner as the previous decomposition, except that no heat was applied during the actual decomposition of the quaternary hydroxide. The conditions during the reaction were kept at 25° (5 mm.). The combined products from the cold traps were worked up as before. The product was fractionated through a 12-in. Holtzmann column to give 6 g. (21.4%) of a yellow liquid, b.p. 70–71° (55 mm.); n_D^{20} 1.5206 (reported⁸ n_D^{20} 1.5187);

$\lambda_{\text{max}}^{\text{EtOH}}$ 238 m μ (log ϵ 3.75) (identical to reported^{8,9} value) $\nu(\text{cm.}^{-1})$ 1450, 1110, 1030, 985, 862 and 782 (identical to reported spectrum).¹⁰ The nuclear magnetic resonance spectrum indicates 3,4-dimethylthiophene (III) at the compound rather than 3,4-dimethylenethiophene (I).

Anal. Calcd. for C₈H₈S: C, 64.23; H, 7.19. Found: C, 63.71; H, 7.24.

3,4-Bis-(acetoxymethyl)-thiophane Sulfone (X).—To a solution of 40 g. (0.172 mole) of 3,4-bis-(acetoxymethyl)-thiophane (II) in 52 ml. of glacial acetic acid was added slowly while cooling in an ice-bath 95 g. (0.837 mole) of 30% hydrogen peroxide. After the exothermic reaction which ensued had subsided, the solution was refluxed for 8 hr. The solvents were removed by distillation at 0.05 mm. to ensure complete removal and the colorless sirup which remained was reacylated by adding 50 ml. of acetic anhydride. The solution was allowed to stand 12 hr. after which another 30 ml. of acetic anhydride was added. The solution was refluxed 4 hr. and the solvents then removed by distillation. The residue was fractionated through a 12-in. Holtzmann column to give two fractions, b.p. 125–138° (0.015 mm.), 191–194° (0.05 mm.). The residue consisted of 10 g. (25% of the starting material) of charred material. From the residue 0.1 g. of a white solid was isolated by manual separation.

Fraction I. Thieno[3,4-C]tetrahydrofuran Sulfone (XI).—The low boiling fraction solidified when cooled and was purified by recrystallization from ethanol–low boiling petroleum ether to give 2.6 g. (9%) of white solid, m.p. 99–99.5; $\nu(\text{cm.}^{-1})$ SO₂ 1315, 1150, THF ring 1096 in CHCl₃ (no C=O, C=C or –OH absorption); mol. wt. (Rast), 171.

Infrared analysis on the crude sulfone diacetate X before distillation fails to show even a trace of the 1096 cm.^{–1} band which indicates that the tetrahydrofuran sulfone XI is formed during the distillation of the sulfone diacetate X. Formation of this ether XI must come from the *cis*-isomer of X.

Anal. Calcd. for C₆H₁₀O₃S: C, 44.50; H, 6.50; S, 19.77. Found: C, 44.75; H, 6.51; S, 19.84.

Fraction II. 3,4-Bis-(acetoxymethyl)-thiophane Sulfone (X).—The second fraction consisted of 24 g. (54%) of viscous yellow liquid which was not purified further, $\nu(\text{cm.}^{-1})$ SO₂ 1309, 1125, C=O 1737, 1240, 1042 (probable) and C–CH₃ 1369.

Anal. Calcd. for C₁₀H₁₆O₆S: C, 45.42; H, 6.07; S, 12.12. Found: C, 45.07; H, 6.13; S, 12.46.

Fraction III.—The solid isolated from the residue was purified by three recrystallizations from methanol to give a white solid, m.p. 153–154°, $\nu(\text{cm.}^{-1})$ 1773 in Nujol, many sharp bands between 975–1500 cm.^{–1} so as to make specific functional group identification impossible. The product has not been characterized completely.

Anal. Found: C, 41.47; H, 5.07; S, 18.51.

Pyrolysis of 3,4-Bis-(acetoxymethyl)-thiophane Sulfone (X).—A 36-in. Fenske column was dry-packed with one-eighth inch Pyrex helices to a height of 11 inches and suspended vertically in the center of a Hoskins FD303A electric furnace. A pressure equalizing dropping funnel was placed on top of the column. The pyrolysate was caught in a 500-ml. round-bottomed flask with a side-arm which was connected by means of a 9 inch length of Tygon tubing to a trap cooled to –78° in an acetone–Dry Ice mixture. The temperature of the column was maintained at 520 ± 3°, and the apparatus was flushed with a slow stream of nitrogen during pyrolysis.

The optimum temperature of 520° was arrived at by pyrolyzing 10-g. samples of diacetate at 600, 540 and 520° and titrating the per cent. of acetic acid split out; the respective amounts were 100, 85 and 67%.¹¹ These values will be too high if sulfur dioxide splits from the molecule during pyroly-

(8) A. F. Shepard, A. L. Henne and T. Midgley, *THIS JOURNAL*, **56**, 1355 (1934).

(9) Spectrum No. 313, "Catalog of Ultraviolet Spectral Data," American Petroleum Institute Research Project 44, National Bureau of Standards.

(10) Spectrum No. 951, "Catalog of Infrared Spectral Data," American Petroleum Institute Research Project 44, National Bureau of Standards.

(11) W. J. Bailey and H. R. Golden, *THIS JOURNAL*, **75**, 4780 (1953).

(7) H. Fischer and H. Orth, "Die Chemie Des Pyrrols," Akademische Verlagsgesellschaft m.b.H., Leipzig, 1934, p. 66.

sis and dissolves in the solution to be titrated. It is unlikely that any appreciable amount will dissolve, however.

After the preliminary pyrolyses the dropping funnel was charged with 126 g. (0.477 mole) of sulfone diacetate X and dropped through the column at a rate of 1 drop per 2 seconds. Due to excessive charring on the column, the column was replaced with a clean one after one-half of the diacetate had been pyrolyzed.

The pyrolysate was washed with four 20-ml. portions of water. Each fraction was titrated for acetic acid; a total value of 53% was obtained which is considered low since the fourth washing still contained a considerable amount of acid. A closer approximation would be 60–65%. The washings were combined and filtered to give 3 g. (4.2%) of a brown solid which was shown to be starting material X. Three recrystallizations from ethanol–ether gave a white solid, m.p. 89.5–92.5° (repeated recrystallizations did not narrow this range); saponification equivalent 130 (calculated 132); ebullioscopic molecular weight 277 (calculated 264); infrared spectrum of the solid in CHCl_3 is identical to the spectrum of the liquid reported as the sulfone diacetate X. This was the first solid sample of X obtained.

Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_6\text{S}$: C, 45.42; H, 6.07; S, 12.12. Found: C, 45.78; H, 6.15; S, 12.50.

After the aqueous washings were filtered they were extracted seven times with 50-ml. portions of ether. The combined ether washings and neutralized organic layer from pyrolysis were dried. Two fractions were isolated by distillation.

Fraction I.—The first fraction was fractionated through a 12-in. Holtzmann column to give 1 g. of yellow liquid, b.p. 79° (0.1–0.3 mm.); n_D^{20} 1.4761; $\lambda_{\text{Diox}}^{227-232}$ μ (no max. obtained¹²); $\nu(\text{cm}^{-1})$ $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$ 890, conj. 1605, $\text{C}=\text{O}$ 1740, 1237, 1039 (probable), $\text{C}-\text{CH}_3$ 1367. The above data were consistent with 2-methyl-3-acetoxymethyl-1,3-butadiene (XVI). An analytically pure sample was not obtained.

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{O}_2$: C, 68.57; H, 8.57. Found: C, 71.73; H, 9.11.

(12) R. B. Woodward, *THIS JOURNAL*, **63**, 1123 (1941); **64**, 76 (1942).

Fraction II.—This material was twice fractionated through a 12-in. Holtzmann column to give an orange liquid, b.p. 132–135° (0.04 mm.); n_D^{20} 1.500; $\lambda_{\text{Diox}}^{211}$ μ ($\log \epsilon$ 3.005¹³); $\nu(\text{cm}^{-1})$ $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$ 1655, 916, $\text{C}=\text{O}$ 1735, 1240, 1040 (probable), SO_2 1313, 1130, $\text{C}-\text{CH}_3$ 1369. The data are consistent with 3-methylene-4-acetoxymethylthiophane sulfone (XIV). The yield after the first fractionation was 3 g. (3.1%).

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{O}_4\text{S}$: C, 47.06; H, 5.88; S, 15.67. Found: C, 47.44; H, 6.01; S, 15.60.

Pyrolysis of Tetraethyl Thiophane-3,3,4,4-tetracarboxylate (IV).—The procedure and apparatus for pyrolysis were identical to that previously described. An average drop rate of 1 drop per 1.5 seconds was used, and the column was heated to $565 \pm 5^\circ$ during pyrolysis.

Through the Fenske column was dropped 20 g. (0.053 mole) of tetraester IV. The column was badly charred after pyrolysis and the pyrolysate was a dark brown liquid. The only product isolated was a brown solid which was recrystallized from benzene–acetone to give 0.2 g. (2.2%) of a white crystalline solid which analyzed for the thioanhydride XVII, m.p. 159–160°; $\nu(\text{cm}^{-1})$ 1727, 1687, 817 and 688.

Anal. Calcd. for $\text{C}_8\text{H}_6\text{O}_2\text{S}_2$: C, 41.38; H, 3.45; S, 36.80. Found: C, 41.52; H, 3.49; S, 36.98.

Acknowledgments.—Microanalytical work was done by J. Nemeth, E. Fett, L. Chang and M. Benassi of the Microanalytical Laboratory of the University of Illinois; Clark Microanalytical Laboratory, Urbana, Illinois; and Micro-Tech Laboratory, Skokie, Illinois. Infrared spectra were run by J. Brader. Ultraviolet spectra were run by G. Meerman. Nuclear magnetic resonance spectrum and interpretation was done by A. Saika.

(13) H. P. Koch, *J. Chem. Soc.*, 387, 408 (1949).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

Dimerization Reactions in Sunlight. IV.¹ Photodimerization of Thianaphthene-1,1-dioxide and its Substituted Derivatives and of 3-Benzylidene-6,7-benzophthalide

BY AHMED MUSTAFA AND SALAH MOHAMED ABDEL DAYEM ZAYED

RECEIVED JULY 23, 1956

Investigation of our previous finding that thianaphthene-1,1-dioxide and its 3-methyl derivative undergo photodimerization in sunlight now has been extended. 2-Methyl-, 2-bromo-, 5-methyl-, 6-methyl-, 7-methyl- and 7-chlorothianaphthene-1,1-dioxides similarly give high-melting crystalline dimers, which are considered to contain a central cyclobutane structure, as in IV or V. 3-Methoxy- and 5-methyl-3-acetoxithianaphthene-1,1-dioxides proved to be stable toward the action of sunlight under similar conditions. 3-Benzylidene-6,7-benzophthalide forms a photodimer analogous to those from arylidene phthalides. This dimer gave the monomer when heated.

(a) **Photodimerization of Thianaphthene-1,1-dioxide and its Substituted Derivatives.**—Recently it was shown^{1c} that the 2,3-double bond in thianaphthene-1,1-dioxide (Ia) undergoes a photodimerization reaction, analogous to that of the similarly situated bond in indone derivatives, for example 2-methyl-3-phenylindone.² Thus when a benzene solution of Ia is exposed to sunlight for three days (July), it forms the difficultly soluble photodimer IVa or Va. While the work was in progress, Davies and James³ reported similar re-

sults on exposure of Ia to sunlight for 20 days. The photodimer sublimes readily at 300° under reduced pressure, a fact which excludes the possibility that it could be regarded as a Diels–Alder dimerization adduct⁴ II. Similar to that of Davies and James,³ our photodimer is stable toward the action of potassium permanganate in boiling acetone and/or the action of lithium aluminum hydride in boiling benzene.

The rejection of the theoretically possible structures II and III,³ analogy with the photodimers previously⁵ reviewed and the formal analogy with

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(3) W. Davies and F. C. James, *J. Chem. Soc.*, 314 (1955).

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