can be inferred that a maximum will not be reached in the vicinity of 260 mμ. This is in agreement with the hypothesis of a twinned stilbene-type of resonance structure since this type of structure is not possible for the molecule.

Finally, the possible excitation of twinned stilbene paths would appear to depend upon the extent to which these paths can be excited independent of the carbonyl group. Although no exact measure of this is available, from the infrared studies of Bergmann, *et al.*,[19] and the measurement of dipole moments of tetracyclone[20,21] and several chlorotetracyclones,[21] it does appear that the carbonyl group is not very highly polarized. It seems feasible that for a molecule in which the carbonyl group is not highly polarized, excited states excluding the carbonyl group may be possible.

(19) E. D. Bergmann, J. Berthier. D. Ginsburg, Y. Hirschberg, D. Lavie, S. Pinchas, B. Pullman and A. Pullman, *Bull. soc. chim. France*, **17**, 661 (1951).

(20) E. D. Bergmann and E. Fischer, *ibid.*, **17**, 1084 (1950).

(21) A. Di Giacomo and C. P. Smyth, THIS JOURNAL, **74**, 4441 (1952).

BROOKLYN 1, NEW YORK

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

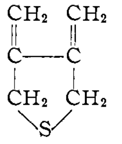
An Attempted Synthesis of 3,4-Dimethylenethiophane[1]

BY C. S. MARVEL AND E. E. RYDER, JR.

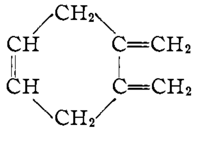
RECEIVED JULY 22, 1954

An attempt to prepare 3,4-dimethylenethiophane by the pyrolysis of 3,4-bis-(acetoxymethyl)-thiophane has given only 3,4-dimethylthiophene.

In the course of an attempt to prepare an all-*cis* polymer we had occasion to undertake the preparation of 3,4-dimethylenethiophane (I). Since Bailey[2] has been able to prepare 4,5-dimethylenecyclohexane (II) by the pyrolysis of the corresponding diacetate, this general method was decided upon as the most promising route to the desired thiophane derivative.

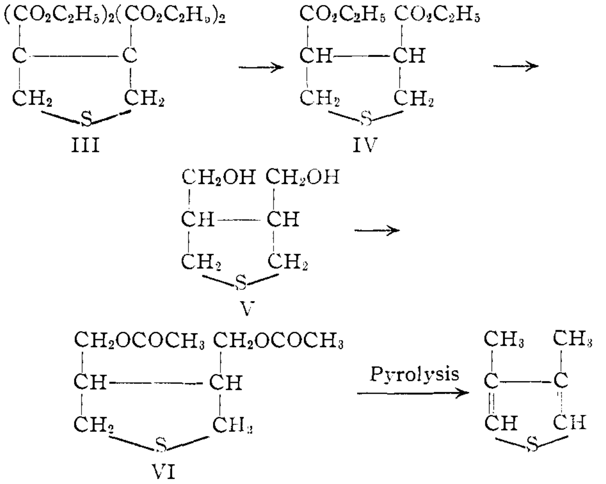


I



II

Accordingly tetraethyl thiophane-3,3,4,4-tetracarboxylate[3] (III) was hydrolyzed, decarboxylated and esterified to yield diethyl thiophane-3,4-dicarboxylate (IV). This ester was reduced to the glycol with lithium aluminum hydride and the glycol V converted to the diacetate VI.



Pyrolysis of the diacetate gave a single product which was established to be 3,4-dimethylthiophene. It was thought that some acidic decomposition products formed on the glass helices during pyrolysis might be responsible for the isomerization of the thiophane to the thiophene. But pyrolysis in the presence of a base (triethylamine) did not change the course of the reaction. Thiophane itself was subjected to pyrolysis under the same conditions used for the diacetate and no appreciable decomposition was noticed. In order to learn if some pyrolytic product might be formed which was responsible for the aromatization of our compound, we pyrolyzed a mixture of a small amount of the thiophane diacetate (VI) and 4,5-bis-(acetoxymethyl)-cyclohexene. The cyclohexene derivative gave Bailey's dimethylenecyclohexene but none was rearranged to *o*-xylene. Thus, none of the thiophane cleavage products seem to be aromatization catalysts. It appears, therefore, that dimethylenethiophane is not stable at the temperatures needed for the pyrolysis of the diacetate.

We used a modified procedure for the condensation of bis-chloromethyl sulfide with tetraethyl ethane-1,1,2,2-tetracarboxylate[3] and obtained a better yield than we were able to obtain by the original directions. The tetraester was further characterized by conversion to the sulfone. The anhydride of thiophane-3,4-dicarboxylic acid is also reported.

Experimental[4]

Tetraethyl Thiophane-3,3,4,4-tetracarboxylate.—This compound was prepared by a variation of the method of Mann and Pope.[3] A mixture of 50 g. (2.08 moles) of sodium hydride, 333 g. (1.05 mole) of tetraethyl ethane-1,1,2,2-tetracarboxylate and 2500 ml. of dry dioxane was refluxed with stirring for one hour at which time 138 g. (1.05 mole) of bis-chloromethyl sulfide[3] was added and refluxing continued 24 hours. Following the usual work-up 350 g. of

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(1) The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

(2) W. J. Bailey, *et al.*, THIS JOURNAL, **77**, 73 (1955).

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

(4) All melting points and boiling points are uncorrected.

viscous red oil was obtained. A portion which was purified for analysis showed the properties b.p. 142° (0.1 mm.), $n^{20}\mathrm{D}$ 1.4802.

Anal.[5] Calcd. for $C_{16}H_{24}O_6S$: C, 51.05; H, 6.43; S, 8.52. Found: C, 51.17; H, 6.49; S, 8.70.

The sulfone of this ester was prepared by heating for three hours at steam-bath temperature a mixture of 3.7 g. of ester, 15 ml. of acetic acid and 3.3 g. of 30% hydrogen peroxide. Removal of solvent *in vacuo* left white crystals which melted at 102–103° after recrystallization from absolute ethanol.

Anal. Calcd. for $C_{16}H_{24}O_{10}S$: C, 47.06; H, 5.90; S, 7.85. Found: C, 47.16; H, 5.98; S, 7.95.

Diethyl Thiophane-3,4-dicarboxylate.—The crude tetraester obtained above was refluxed 36 hours with 1200 ml. of water, 208 g. of sodium hydroxide and 100 ml. of ethanol. After cooling and acidification the mixture was continuously extracted with ether for 24 hours. Removal of the ether from this extract left a viscous red oil.

Thiophane-3,4-dicarboxylic acid anhydride was obtained as a yellow solid upon distillation of this material. After recrystallization from benzene–low-boiling petroleum ether and sublimation, white crystals were obtained which melted at 87–87.5°.

Anal. Calcd. for $C_6H_6O_3S$: C, 45.56; H, 3.82; S, 20.37. Found: C, 45.69; H, 3.72; S, 20.20.

The crude acid was mixed with 1500 ml. of dry benzene, 1000 ml. of absolute ethanol and 30 ml. of concentrated sulfuric acid and was refluxed for 48 hours, the water being removed by a Dean–Stark trap. After most of the solvent was removed, the residue was taken up in ether and washed with water and sodium bicarbonate solution. After drying the ether was removed by distillation and the residue was fractionated to yield 94 g. (38.5% based on bis-chloromethyl sulfide) of diethyl thiophane-3,4-dicarboxylate; b.p. 100–110° (0.2 mm.). An analytical sample had a boiling point of 132–132.5° (1.8 mm.), $n^{21}\mathrm{D}$ 1.4821.

Anal. Calcd. for $C_{10}H_{16}O_4S$: C, 51.70; H, 6.94; S, 13.80. Found: C, 51.60; H, 6.97; S, 13.81.

3,4-Bis-(hydroxymethyl)-thiophane.—One hundred grams (0.43 mole) of diethyl thiophane-3,4-dicarboxylate was added to a slurry of 89 g. (2.34 moles) of lithium aluminum hydride, and the mixture was refluxed for 20 hours. Excess reducing agent was decomposed by addition of 335 g. (3.8 moles) of ethyl acetate, after which the residue was added to 2 l. of dilute hydrochloric acid. Continuous extraction with ether was continued for 40 hours. From this extract was obtained 65 g. (100%) of semi-solid 3,4-bis-(hydroxymethyl)-thiophane. A portion which was sublimed three times had a melting point of 90–92° (clear 95°).

Anal. Calcd. for $C_6H_{12}O_2S$: C, 48.62; H, 8.16; S, 21.63. Found: C, 48.34; H, 8.26; S, 21.33.

3,4-Bis-(acetoxymethyl)-thiophane.—A mixture of the crude diol, 132 g. (1.3 moles) of acetic anhydride and 1 ml. of pyridine was allowed to stand at room temperature four days. The acetic acid and excess acetic anhydride were removed at reduced pressure, and the residue was fractionally distilled to give 88 g. (94% based on diethyl thiophane-3,4-dicarboxylate) of 3,4-bis-(acetoxymethyl)-thiophane; b.p. 120° (0.2 mm.). An analytical sample showed the properties b.p. 152° (3.8 mm.), $n^{19}\mathrm{D}$ 1.4933.

Anal. Calcd. for $C_{10}H_{16}O_4S$: C, 51.70; H, 6.94; S, 13.80. Found: C, 51.85; H, 7.13; S, 13.78.

Pyrolysis of 3,4-Bis-(acetoxymethyl)-thiophane.—At a rate of one drop per second 129 g. (0.56 mole) of 3,4-bis-(acetoxymethyl)-thiophane was dropped onto a 3/4 in. Vycor column externally heated to a temperature of 610 ± 5° by a FD303A Hoskins electric furnace and packed to a depth of 10 in. with 1/8 in. Pyrex helices. An inert atmosphere was maintained at all times by introduction of a slow stream of nitrogen at the top of the column. The pyrolysate was collected in a 200-ml. flask cooled in an ice-bath. During the pyrolysis the presence of hydrogen sulfide was detected over the pyrolysate and a considerable deposition of carbon on the helices was noted. When the pyrolysis had been completed, the pyrolysate was connected to a Dry Ice–acetone cooled receiver, and all material was collected which distilled at room temperature at a pressure of 1–4 mm. during ten hours. The residue was recycled four more times in the same manner without purification except that it was distilled between the third and fourth passes. On each occasion the material collected from the Dry Ice-cooled receiver was dissolved in 3 to 4 volumes of peroxide-free ether, and this solution was washed with a 10% sodium bicarbonate solution until a basic wash was obtained, then with water and finally with saturated sodium chloride solution. The products from all pyrolyses were combined, dried, concentrated and fractionally distilled through a 10-in. Holtzmann column to produce 10.5 g. (17%) of material boiling at 70–72° (52 mm.), $n^{20}\mathrm{D}$ 1.5198. Refractionation afforded 8.9 g. of material boiling at 67–68° (4.8 mm.), $n^{21.5}\mathrm{D}$ 1.5188. Literature reports[6] $n^{25}\mathrm{D}$ 1.5187 for 3,4-dimethylthiophene.

Anal. Calcd. for C_6H_8S: C, 64.23; H, 7.19. Found: C, 64.78; H, 7.41.

The infrared absorption spectrum of this product showed bands at 782, 862, 985, 1030, 1110 and 1450 cm.$^{-1}$, identical to that reported for 3,4-dimethylthiophene.[7] The ultraviolet spectrum taken in 95% ethanol showed $\lambda_{max.}$ 238 mμ; ϵ 5370. The spectrum reported for 3,4-dimethylthiophene[8] shows $\lambda_{max.}$ 238 mμ; ϵ 5600 (solvent—isoöctane).

Pyrolysis in the Presence of Triethylamine.—In the same manner as described before 50 g. of 3,4-bis-(acetoxymethyl)-thiophane was added to the pyrolysis column from one dropping funnel simultaneously with 10 g. of triethylamine from another dropping funnel. The pyrolysate was worked up as before, and recycled twice more with appropriate reductions in the amount of triethylamine and with distillation between the second and third passes. The combined products were fractionally distilled through a 10-in. Vigreux column to produce 4 g. of material boiling at 33–38° (9 mm.), $n^{20}\mathrm{D}$ 1.5245. The infrared spectrum of this material indicated identity to 3,4-dimethylthiophene with traces of impurities.

Pyrolysis of Thiophane.—In the same manner as described previously 32.5 g. of thiophane was pyrolyzed at 610 ± 5°. Essentially no decomposition was observed on the column, no hydrogen sulfide evolution was noted, and the pyrolysate collected was a very light yellow. Distillation of the pyrolysate afforded 26 g. (81.5% recovery) of thiophane, $n^{20}\mathrm{D}$ 1.5037, b.p. 119–120°.

4,5-Dimethylenecyclohexene.[9]—Pyrolysis of 89.5 g. (0.40 mole) of 4,5-bis-(acetoxymethyl)-cyclohexane in the same manner described previously at 580 ± 5° produced, after one fractionation through a 10-in. Holtzmann column, 3.5 g. (22% based on unrecovered acetate) of 4,5-dimethylenecyclohexene; b.p. 56–60° (59 mm.), $n^{21}\mathrm{D}$ 1.4960–1.4970. The infrared absorption spectrum showed bands at 1664 and 1637 cm.$^{-1}$ indicative of an unconjugated cyclohexene bond and a pair of conjugated double bonds. That some *o*-xylene was present was indicated by a slight absorption at 1610 and 1502 cm.$^{-1}$. The ultraviolet absorption spectrum showed $\lambda_{max.}$ 216 mμ; ϵ 4759. Treatment of a small portion of this product with maleic anhydride gave a crystalline solid. After recrystallization from benzene–low-boiling petroleum ether and sublimation, the solid, presumably 1,2,3,4,5,8-hexahydronaphthalene-2,3-dicarboxylic acid anhydride, melted at 145–146°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.55; H, 5.95.

Pyrolysis of 4,5-Bis-(acetoxymethyl)-cyclohexene with 3,4-Bis-(acetoxymethyl)-thiophane.—A mixture of 62.5 g. of 4,5-bis-(acetoxymethyl)-cyclohexene and 22.5 g. of 3,4-bis-(acetoxymethyl)-thiophane was pyrolyzed at 580 ± 5°. The pyrolysate, which was dark red as usual in pyrolyses involving 3,4-bis-(acetoxymethyl)-thiophane, was directly distilled, all material boiling at 41–45° (54–56 mm.) being collected. This liquid was dissolved in ether, washed with

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[5] Analyses were performed by J. Nemeth, E. Fett, K. Pih and E. Chang, Microanalytical Laboratory, University of Illinois.

[6] A. F. Shepard, A. L. Henne and T. Midgley, Jr., THIS JOURNAL, **56**, 1355 (1934).

[7] Spectrum No. 951, "Catalog of Infrared Spectral Data," American Petroleum Institute Research Project 44, National Bureau of Standards.

[8] Spectrum No. 313. "Catalog of Ultraviolet Spectra Data," American Petroleum Institute Research Project 44, National Bureau of Standards.

[9] We are deeply indebted to Dr. W. J. Bailey for an outline of the methods employed in the preparation of 4,5-dimethylenecyclohexene in advance of their publication.

sodium bicarbonate solution, water and saturated sodium chloride solution. After drying and concentrating, the compound was fractionated through a 10-in. Holtzmann column to produce 1.9 g. of material boiling at 57–59° (55 mm.), $n^{21}D$ 1.4935. The ultraviolet absorption spectrum of this compound was essentially identical to that observed from the 4,5-dimethylenecyclohexene obtained from the previously mentioned preparation; $\lambda_{max.}$ 216 mμ; ϵ 4600 (calcd. for pure diene). For *o*-xylene $\lambda_{max.}$ 211 mμ; ϵ 8200.[10]

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[10] Spectrum No. 173, "Catalog of Ultraviolet Spectral Data," American Petroleum Institute Research Project 44, National Bureau of Standards.

URBANA, ILLINOIS

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

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

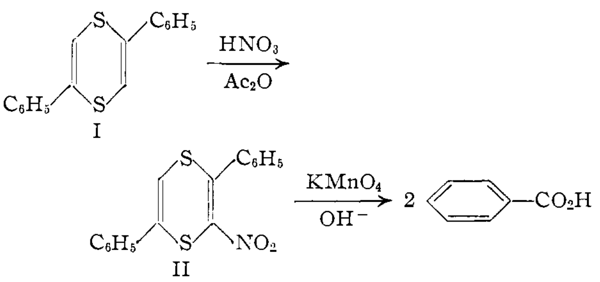
BY WILLIAM E. PARHAM AND VINCENT J. TRAYNELIS

RECEIVED JUNE 4, 1954

The nitration of 2,5-diphenyl-1,4-dithiadiene (I) has been shown to give 2,5-diphenyl-3-nitro-1,4-dithiadiene (II). Reactions are discussed which involve the conversion of the dithiadiene ring system into the thiophene ring system.

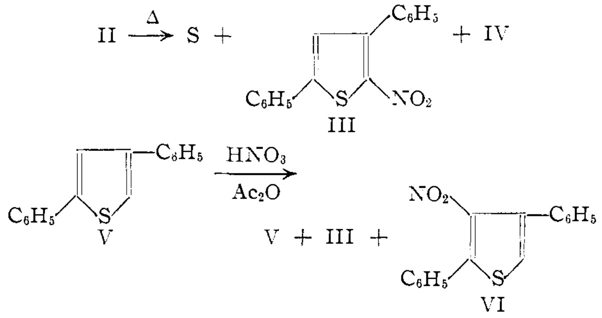
In a previous communication reactions were described which involved the conversion of the dithiadiene ring system to the thiophene ring system.[2] It was assumed by analogy to benzo-1,4-dithiadiene[3] that electrophilic substitution in 2,5-diphenyl-1,4-dithiadiene (I) occurred preferentially in the sulfur-containing ring. This paper describes work pertinent to the orientation of electrophilic substitution in I, and new reactions leading to derivatives of thiophene.

When a weak nitrating agent was added to an acetic anhydride solution of I, a deep red coloration[4] appeared. After a five-minute reaction period, the acetic anhydride was hydrolyzed and a red crystalline material resulted. Recrystallization of the product from ethyl acetate gave 74% yield of 2,5-diphenyl-3-nitro-1,4-dithiadiene (II).



The position of the nitro group was assigned on the basis of potassium permanganate oxidations. Several oxidations were performed and in no experiment was any nitrobenzoic acid found. This observation, along with the isolation of benzoic acid in 67% yield (calculated for 2 moles of acid per mole of II) led to the assignment of structure II for the nitro derivative. The experiments to follow support this assignment of structure.

The pyrolysis of I to give sulfur and 2,4-diphenylthiophene has been reported[2] to proceed at 180°. With the presence of a polarizing nitro group on the dithiadiene ring, the elimination of sulfur should be facilitated. Such was the case, for when II was heated to 135° a vigorous exothermic reaction occurred which resulted in the formation of sulfur (14%), 2-nitro-3,5-diphenylthiophene (III, 20%) and IV (11%). Compound IV was not isomeric with III and is under investigation.



Compound III was prepared independently by nitration of 2,4-diphenylthiophene (V).[5] In this reaction, starting material was recovered in 65% yield; however, an 18% yield of 2-nitro-3,5-diphenylthiophene (III) was obtained. A comparison of infrared and ultraviolet spectra of the two samples of III, and lack of depression in mixture melting points, established the identity of these compounds. Since substitution proceeds readily on the C-2 position in thiophene, structure III was assigned[6] for the major nitro product obtained by nitration of V. Another mononitro product was present in 2% yield; and since some substitution (5%) also occurs in the C-3 position during the nitration of thiophene, this compound was assigned structure VI, 2,4-diphenyl-3-nitrothiophene. Subsequent experiments confirmed the assignment of this structure.

The formation of III (the 2-nitrothiophene) in preference to VI (the 3-nitrothiophene) by the action of heat on II was anticipated from an examination of the possible resonance hybrids of II. The contribution of structure IIa, where the negative charge may be delocalized by the nitro group,

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

[2] W. E. Parham and V. J. Traynelis, THIS JOURNAL, **76**, 4960 (1954).

[3] W. E. Parham, T. M. Roder and W. R. Hasek, *ibid.*, **75**, 1648 (1953).

[4] Previously, Johnson and co-workers have reported the appearance of a deep red color when I was treated with concentrated nitric acid. *Cf.* T. B. Johnson, R. C. Moran and E. F. Kohmann, *ibid.*, **35**, 451 (1913).

[5] A previous attempt to effect the mononitration of 2,4-diphenylthiophene was unsuccessful; an unidentified mixture was obtained. *Cf.* M. T. Bogert and P. P. Herrera, *ibid.*, **45**, 241 (1923).

[6] The Friedel–Crafts acylation of 2,4-diphenylthiophene is reported to give only 2-thienyl ketones. *Cf.* E. Fromm, P. Fantl and E. Leibsohn, *Ann.*, **457**, 276 (1927).