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STUDIES ON THE CHEMISTRY OF HETEROCYCLICS. XV. THE SYNTHESIS OF THIOPHENE POLYENES[1]

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The polyenes (1, 2) have been investigated primarily in attempts to synthesize Vitamin A, carotenoids, or related substances occurring in nature. The synthesis of these compounds which contain a multiplicity of linkages provides model substances for the study of the properties of a homologous series and of conjugated double bond systems. In this respect, the main interest has been centered on the correlation of physical and chemical properties with constitution.

The present knowledge of the polyene hydrocarbons is due to the researches of many investigators (2c). In the widely studied diphenyl polyenes, the synthesis of a member containing as many as fifteen conjugated double bonds has been achieved (1, 3).

Polyenes are characterized by their extreme lability towards oxygen and often, to mineral acids. The stability of the higher members is remarkable, so that solubility difficulties have been largely responsible for hindering the further extension of the series. Distillation, especially of higher members, is accompanied by decomposition. Furthermore, the simultaneous production of geometrical isomers frequently inhibits crystallization.

A brief survey of the four most applicable methods indicates the wide variety of chemical techniques which have been employed in these researches.

The 1,2-glycols, such as hydrocinnamoin, when treated with phosphorus diiodide in ether give excellent yields of the diphenyl polyenes (4). The method has now been extended (5) to 1,4-glycols and 1,6-glycols obtained from the condensation of polyenals with acetylenedimagnesium bromide and diacetylenedimagnesium bromide respectively.

Another method involves the dehydration of secondary carbinols formed from the condensation of Grignard reagents with phenylpolyene aldehydes (6, 7).

A novel reaction has been used to extend the series to the members where $n = 11$ and 15. This provides for the replacement of the oxygen atom of polyenals by a sulfur atom from H_2S under suitable conditions. The removal of the sulfur atom is brought about by the action of copper, metal carbonates, or reagents such as pyridine (1, 3).

The early researchers obtained inconsistent and minute yields of diphenyl polyenes from the condensation of aldehydes and sodium succinate (8) or sodium β-benzalpropionate (9) in acetic anhydride. This method was vastly improved and made generally applicable by Kuhn and Winterstein (4). It was found that lead oxide in boiling acetic anhydride forms a homogeneous solution in which

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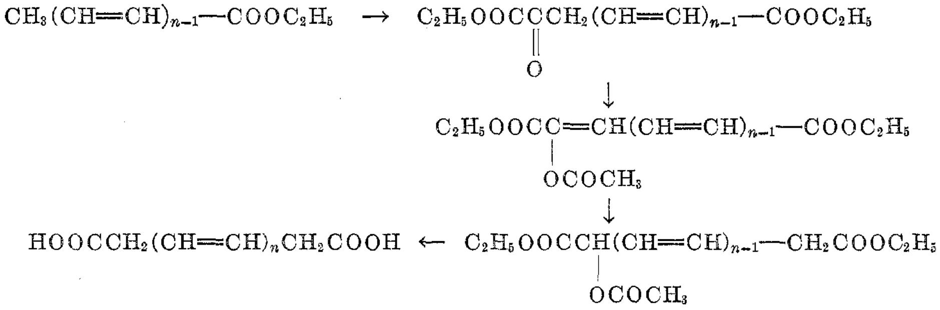
[1] The analyses reported were performed by A. A. Sirotenko of this department.

[2] Abstracted in part from the dissertation presented to the Graduate School of Fordham University, 1951, in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

the aldehyde and sodium succinate readily condense. The yields obtainable range from 4–30%. The synthesis breaks down when applied to members higher than $n = 8$, where n equals the number of double bonds. Dihydromuconic acid and 1,6-hexadiene-2,4-dicarboxylic acid, prepared as indicated in Figure 1, have been substituted for succinic acid.

The synthesis of dihydromuconic acid and 1,6-hexadiene-2,4-dicarboxylic acid was best effected with potassium ethoxide under anhydrous conditions. Sodium ethoxide did not effect condensation of the unsaturated ester with ethyl oxalate.



$$\begin{array}{l} CH_3(CH{=}CH)_{n-1}{-}COOC_2H_5 \rightarrow C_2H_5OOC\underset{\overset{\|}{O}}{C}CH_2(CH{=}CH)_{n-1}{-}COOC_2H_5 \\ \downarrow \\ C_2H_5OOC\underset{\overset{|}{OCOCH_3}}{C}{=}CH(CH{=}CH)_{n-1}{-}COOC_2H_5 \\ \downarrow \\ HOOCCH_2(CH{=}CH)_nCH_2COOH \leftarrow C_2H_5OOC\underset{\overset{|}{OCOCH_3}}{C}H(CH{=}CH)_{n-1}{-}CH_2COOC_2H_5 \end{array}$$

FIGURE 1. SYNTHESIS OF POLYENE DICARBOXYLIC ACIDS

This reaction is a form of the Claisen condensation (10) involving the acylation of an ester by another ester. The requirement for the acylating ester (in this case ethyl oxalate), is that it does not possess any active α-hydrogen atoms. The ether solution of the second ester is added to a mixture of the ethyl oxalate and potassium ethoxide. This procedure minimizes the self condensation of the unsaturated component. The enol-acetate of the oxaloester is reduced according to Thiele's rule (11). Addition of the hydrogen atoms occurs at the ends of the conjugated system with a resultant rearrangement of the double bonds. Alcoholysis of the ester groups always takes place during the facile 1:x-elimination of acetic acid.

$$\begin{array}{c} \underset{m\,=\,0,\,1}{2R(CH{=}CH)_mCHO} + \underset{n\,=\,0,\,1,\,2}{HOOCCH_2(CH{=}CH)_nCH_2COOH} \\ \downarrow \\ R{-}(CH{=}CH)_{2m+n+2}{-}R \end{array}$$

FIGURE 2. SYNTHESIS OF THIOPHENE POLYENE HYDROCARBONS; R = 2-Thienyl

In order to prepare a series of thiophene polyenes, the lead oxide method was chosen because of its simplicity and general adaptability. The procedure is indicated in Figure 2.

When succinic acid was utilized as the "middle piece" in the lead oxide synthesis, even members of the di-(2-thienyl) polyene series were produced. The use of 1,6-hexadiene-2,4-dicarboxylic acid aided in the synthesis of the higher even members. Dihydromuconic acid, on the other hand, was limited to the preparation of the members having three or five conjugated double bonds.

During the course of this investigation it became necessary to synthesize β-cinnamalpropionic acid. This acid had been reported by Fittig and Batt (8) as a by-product from the reaction of cinnamaldehyde and sodium succinate in the presence of acetic anhydride. In this modification of the Perkin reaction (12), an anhydride salt exchange is known to occur rapidly at 100° such that the position of equilibrium is very far on the side of succinic anhydride and sodium acetate (13).

In an attempt to improve the yield of the acid the use of tertiary amines was investigated (14). Pyridine gave only a trace of β-cinnamalpropionic acid; with triethylamine the yield was increased to 17%. A more convenient and satisfactory synthesis of β-cinnamalpropionic acid utilized the Reformatsky reaction with methyl β-bromopropionate (15).

Saponification of the ester was best accomplished by setting the mixture aside for 48 hours in the presence of methanolic potassium hydroxide. The product formed after acidification consisted predominately of lactonic material (16). In order to convert the sodium carbonate-insoluble material to the desired acid, the mixture was refluxed for a short time with a large volume of water containing a trace of acid. Approximately 30% of this material was recovered unchanged.

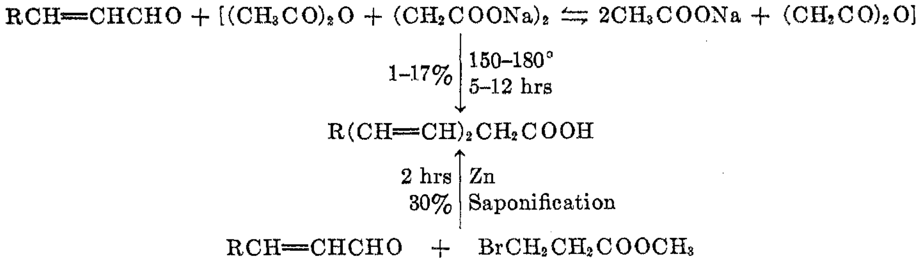
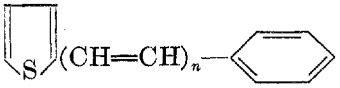


FIGURE 3. SYNTHESIS OF β-CINNAMALPROPIONIC ACID, R = Phenyl

The synthesis of β-cinnamalpropionic acid is shown schematically in Figure 3.

As a continuation of this study, the mixed polyene hydrocarbons have been



synthesized where $n = 1,2,3$ and 4. The initial members of this series has been previously obtained by Buu-Hoï (6) by the dehydration of the carbinol formed by the condensation of benzylmagnesium chloride and 2-thenaldehyde.

For the synthesis of these members either 2-thenaldehyde or β-2-thienylacrolein have been employed. The benzenoid component has been derived from phenylacetic, β-benzalpropionic, or β-cinnamalpropionic acids.

The data for the di-(2-thienyl)polyenes and the mixed polyenes are recorded in Table I.

As shown in the following graph, a regularity is observed in the melting points for the members of both series. This had been noted earlier by Kuhn and Grundmann (17) for the diphenyl polyene hydrocarbons. Because of the high melting points, it is assumed that these compounds possess a *trans-trans* configuration (6, 17).

TABLE I

Melting Points of Thiophene Polyene Hydrocarbons

COMPOUND	MELTING POINT, °C.
1-Phenyl-2-(2-thienyl)ethylene	111–111.5
1-Phenyl-4-(2-thienyl)butadiene	141.5–142
1-Phenyl-6-(2-thienyl)-1,3,5-hexatriene	174–175
1-Phenyl-8-(2-thienyl)-1,3,5,7-octatetraene	206–207
1,2-Di-(2-thienyl)ethylene	130.5–131
1,4-Di-(2-thienyl)butadiene	164–164.5
1,6-Di-(2-thienyl)-1,3,5-hexatriene	198–199
1,8-Di-(2-thienyl)-1,3,5,7-octatetraene	229–230
1,10-Di(2-thienyl)-1,3,5,7,9-decapentaene	256–257
1,12-Di-(2-thienyl)-1,3,5,7,9,11-dodecahexaene	270–271

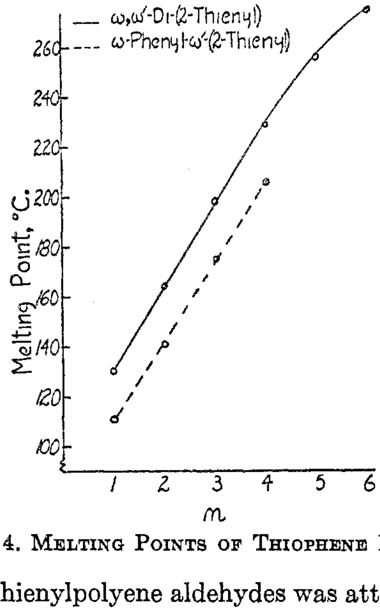


Figure 4. Melting Points of Thiophene Polyenes

The synthesis of 2-thienylpolyene aldehydes was attempted according to the elegant method described by Schmidt (18). This procedure had been successfully applied to the synthesis of both the phenyl (7, 18) and furyl (18, 19) analogs. The reaction mixtures, containing the appropriate thiophene aldehyde and either acetaldehyde or crotonaldehyde, were treated with piperidine acetate under an atmosphere of nitrogen. The reaction was exothermic and evidenced a color change from yellow to red, and finally, to reddish-brown.

In the case of the first two members of the series, the yields of the crude liquid aldehydes were approximately those obtained in analogous reactions; but the yields of the pure compounds were considerably lower. The solid aldehydes were also isolated in amounts appreciably below those reported for this reaction. These solids, moreover, did not sublime and failed to analyze for the expected aldehydes even after repeated crystallizations. The aldehydes appeared to change rapidly into polymeric materials which were non-melting at 350° and insoluble in all the usual organic solvents, including tetrahydrofuran. These polymers, however, possessed the color of the expected aldehydes, which is a function of the number of conjugated double bonds. The qualitative data for the color reactions of these polymers with antimony trichloride in chloroform, and with concentrated sulfuric acid are listed in Table II. The results compare favorably with those given for the corresponding phenyl and furyl polyenals (18).

TABLE II

COLOR REACTIONS OF THIOPHENE POLYENALS

REAGENT \ *n*	2	3	4	5	6
—	Lemon-yellow	Yellow-orange	Orange-red	Brown-red	Violet
$SbCl_3$	—	Blue-red	Green	Olive-green	Dark green
H_2SO_4	—	Grey	Red-blue	Violet	Blue-violet

EXPERIMENTAL

Materials. Tetrahydrofuran was generously supplied by the Electrochemicals Division, E. I. du Pont de Nemours, Co. The crotonaldehyde was donated by the Carbide and Carbon Chemical Corp. The thiophene was kindly furnished by the Socony-Vacuum Oil Company. The thiophene aldehyde was prepared according to Reference (20); the procedure of Doebner (21) was used to synthesize sorbic acid.

β-Benzalpropionic acid was synthesized by the method reported previously (22). A solution of 50.0 g. (0.48 mole) of malonic acid, 60.0 g. (0.5 mole) of freshly distilled phenylacetaldehyde, and ten drops of diethylamine in 130 cc. of absolute ethanol were refluxed for six hours. The mixture was poured into an excess of 2 *N* sodium carbonate, extracted with ether, and acidified. The yield was 45.4 g. (56%); m.p. 85–86°.[3]

The 2-thienylacetic acid was prepared from 2-thienylacetonitrile (obtained from 2-thenyl chloride as previously described (23) by hydrolysis with alcoholic potassium hydroxide for 18 hours. The acid melted at 63.5–64°.

β-2-Thienylacrolein. The directions of Keskin, Miller, and Nord (24) were followed. Alternatively, 40.0 g. (0.35 mole) of 2-thenaldehyde, 30.0 g. (excess) of acetaldehyde, and 10.0 g. of piperidine acetate were reacted in 100 cc. of 70% ethanol for eight days at room temperature. The product (15.2 g., 36.5%) distilled at 108–112°/5 mm.

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[3] Melting points were obtained with a Fisher-Johns apparatus.

Dihydromuconic acid. Potassium ethoxide was prepared from 7.5 g. of potassium metal, 55 cc. of ether, and 35 cc. of ethanol. To the ice-cold mixture 14.0 g. (0.08 mole) of ethyl oxalate in 10 cc. of ether was added in small portions with shaking. After 15 minutes, 12.0 g. (0.085 mole) of ethyl crotonate in 10 cc. of ether was added slowly with shaking. The mixture was allowed to stand 24 hours in the ice-box. The yellow potassium salt of ethyl oxalocrotonate (14.0 g.) was filtered, washed rapidly with ether, and dried.

The dry salt was refluxed with 40 cc. of acetic anhydride for one hour. The mixture was filtered, ether was added, and the ether extract washed thoroughly with water. The ether was evaporated and the remaining oil was distilled. The α-acetoxymuconic diethyl ester distilled at 150–153°/2 mm. The yield was 8.9 g.

The α-acetoxy ester was reduced with 20.0 g. of aluminum amalgam in 300 cc. of moist ether for three hours. The crude α-acetoxy-α,δ-dihydromuconic diethyl ester was saponified, after evaporation of the ether, in 200 cc. of methanol with 200 cc. of 20% potassium hydroxide for four hours. Following reduction with sodium amalgam and acidification, the *trans-trans* dihydromuconic acid (4.3 g., 76.0%) melted at 294.5–295° (17, 25).

1,6-Hexadiene-2,4-dicarboxylic acid was obtained in a similar fashion from ethyl sorbate (17). The diethyl α-acetoxyhexatrienate (10.0 g.) had m.p. 46–46.5°.

After reduction with aluminum amalgam, the mixture was shaken with aluminum oxide which absorbed the dihydro compound. The 1-acetoxy-hexadiene-2,4-dicarboxylic diethyl ester was eluted with methanol-ether and after evaporating the solvent, was distilled; b.p. 158–160°/1 mm., yield: 6.6 g.

Saponification yielded the 1,6-hexadiene-2,4-dicarboxylic acid (4.3 g., 80.0%). After reduction with sodium amalgam and acidifying, this product was recrystallized from 50% ethanol; m.p. 190–191°.

β-Cinnamalpropionic acid. Cinnamaldehyde (20.0 g., 0.15 mole), sodium succinate (24.0 g., 0.15 mole), and acetic anhydride (25.0 g., 0.25 mole) were refluxed at 125–130° for six hours. The mixture was poured into boiling water and the strongly acid solution was extracted with ether and washed thoroughly with a sodium carbonate solution. The alkaline washings upon acidification yielded 2.0 g. (7.1%) of β-cinnamalpropionic acid, m.p. 113–114° (8).

The use of higher temperatures and/or longer reaction periods did not improve the yield. The substitution of succinic anhydride for acetic anhydride offered no significant improvement.

When cinnamaldehyde (13.2 g., 0.1 mole) succinic anhydride (5.0 g., 0.05 mole), acetic anhydride (40.8 g., 0.4 mole), and pyridine (15.8 g., 0.2 mole) were heated for five hours at 150° (14) the acid was obtained in *ca.* 1% yield.

The cinnamaldehyde, succinic, and acetic anhydrides were treated with 12.0 g. (0.2 mole) of triethylamine for six hours at 180°. The yield of the acid amounted to 3.3 g. (17.0%).

The Reformatsky reaction for the preparation of this acid was as follows: A few cc. of a solution of 20.0 g. (0.15 mole) of cinnamaldehyde and 30.0 g. (0.18 mole) of methyl β-bromopropionate dissolved in 100 cc. of a 1:1 mixture of dry benzene and tetrahydrofuran were run into a three-necked flask containing 20.0 g. of magnesium turnings and 0.5 g. of mercuric chloride. The reaction was initiated on a steam-bath and the stirrer was started. The remainder of the solution was added over a 45-minute period at a rate sufficient to maintain gentle refluxing. The mixture, after refluxing for an additional hour, was cooled and hydrolyzed with dilute acid. The mixture was extracted with ether, the ether was evaporated, and the unreacted aldehyde and bromoester were distilled off. The crude methyl ester was saponified at room temperature for 48 hours with 50 cc. of 5% methanolic potassium hydroxide. Upon acidification 9.4 g. (33%) of β-cinnamalpropionic acid were obtained; m.p 112.5–113°.

Anal. Calc'd for $C_{12}H_{12}O_2$: C, 76.60; H, 6.38.
Found: C, 76.59; H, 6.21.

Thiophene polyenes. General method. In a round-bottomed flask equipped with a reflux condenser protected from moisture were placed the freshly distilled aldehyde and the acid.

Acetic anhydride was added and the solution was heated. To the warm solution litharge was added with continual shaking. When the lead oxide was in solution the mixture was boiled five hours. The contents were then poured, while still hot, into a beaker and allowed to stand overnight. The semi-solid contents were stirred to a mush and filtered. The solid was washed with several portions of ethanol, transferred to a beaker, stirred with a further portion of ethanol, and again filtered.

For purification the solid was dissolved in benzene, boiled with Norit, and filtered while hot. The filtrate was treated with hot ethanol and cooled rapidly in an ice-bath. The higher members were recrystallized from chloroform.

1-Phenyl-2-(2-thienyl)ethylene. (a). Phenylacetic acid (14.0 g., 0.103 mole), 2-thenaldehyde (11.0 g., 0.1 mole), and 30.0 g. of acetic anhydride were refluxed with 10.0 g. of litharge. The ethylene (4.6 g., 25.0%) melted at 110–111°.[4]

(b) Activated magnesium was covered with 10 cc. of ether and a solution of 21.0 g. (0.12 mole) of benzyl bromide in 50 cc. of ether was allowed to drop in. After the reaction had subsided, the mixture was heated 15 minutes on a steam-bath. The mixture was cooled and 12.0 g. (0.107 mole) of 2-thenaldehyde was added dropwise. After hydrolysis with cold dilute hydrochloric acid, the ether extracts were washed with bisulfite solution, 10% sodium carbonate, and water. The ether was evaporated and the oil distilled at 175–181°/11 mm. Recrystallization from ethanol gave 9.0 g. (45.3%) of the product, m.p. 111–111.5°.

Anal. Calc'd for $C_{12}H_{10}S$: C, 77.48; H, 5.38.
Found: C, 77.53; H, 5.06.

1-Phenyl-4-(2-thienyl)butadiene. (a) A solution of 13.8 g. (0.1 mole) of β-2-thienylacrolein, 14.0 g. (0.103 mole) of phenylacetic acid, 10.0 g. of litharge, and 30.0 g. of acetic anhydride was heated five hours. The yield of butadiene was 6.1 g. (29.0%), m.p. 141.5–142°.

(b) 2-Thenaldehyde (11.0 g., 0.1 mole), 16.2 g. (0.1 mole) of β-benzalpropionic acid, 12.0 g. of litharge, and 35.0 g. of acetic anhydride were refluxed. The yield was 5.6 g. (26.4%); mixed melting point showed no depression.

Anal. Calc'd for $C_{14}H_{12}S$: C, 79.30; H, 5.66.
Found: C, 79.04; H, 5.47.

1-Phenyl-6-(2-thienyl)-Δ^4-tetrahydrophthalic anhydride. A mixture of 2.5 g. (0.011 mole) of 1-phenyl-4-(2-thienyl) butadiene and 4.0 g. (0.408 mole) of maleic anhydride was cautiously heated over a free flame. The mixture formed a dark-colored liquid which was heated gently for 15 minutes longer. The melt was allowed to cool. An almost theoretical yield of the tetrahydro compound was obtained. Recrystallized from benzene it had a m.p. 186.5–187.5°.

Anal. Calc'd for $C_{18}H_{14}O_3S$: C, 69.75; H, 4.52.
Found: C, 69.28; H, 4.38.

1-Phenyl-6-(2-thienyl)-1,3,5-hexatriene. (a) β-2-Thienylacrolein (13.8 g., 0.1 mole) and 16.2 g. (0.1 mole) of β-benzalpropionic acid dissolved in 38.0 g. of acetic anhydride were treated with 15.0 g. of lead oxide. The yellow colored hexatriene was obtained in 30.0% yield (7.1 g.) m.p. 174–175°.

(b) β-Cinnamalpropionic acid (1.8 g., 0.01 mole) and 1.1 g. (0.01 mole) of 2-thenaldehyde were refluxed in 3.1 cc. of acetic anhydride with 2.3 g. of litharge. The product melted at 174–175°. A mixed melting point showed no depression. The yield was 0.47 g. (30.0%).

Anal. Calc'd for $C_{16}H_{14}S$: C, 80.73; H, 5.88.
Found: C, 80.71; H, 5.68.

1-Phenyl-8-(2-thienyl)-1,3,5,7-octatetraene. The orange colored octatetraene was obtained from 1.4 g. (0.01 mole) of β-2-thienylacrolein, 1.8 g. (0.01 mole) of β-cinnamalpropionic acid, 2.3 g. of litharge, and 3.3 cc. of acetic anhydride. The yield was 0.5 g. (18.9%); m.p. 206–207°.

Anal. Calc'd for $C_{18}H_{16}S$: C, 81.89; H, 6.34.
Found: C, 81.70; H, 5.98.

1,2-Di-(2-thienyl)ethylene. The 2-thenaldehyde (11.0 g., 0.1 mole) and 2-thienylacetic

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[4] Buu-Hoï, Hoán, and Lavit (5) report m.p. 111°.

acid (14.0 g., 0.1 mole) were refluxed with 15.0 g. of lead oxide dissolved in 30.0 g. of acetic anhydride. The product had a tan color. Yield: 5.2 g. (27%); melting point 130.5–131°.[5]

Anal. Calc'd for $C_{10}H_8S_2$: C, 62.55; H, 4.17.
Found: C, 62.62; H, 4.25.

1,4-Di-(2-thienyl)butadiene. (a) Succinic acid (11.8 g., 0.1 mole), 2-thenaldehyde (22.0 g., 0.2 mole), 33.0 g. of lead oxide, and 30.0 g. (0.3 mole) of acetic anhydride were boiled five hours. The butadiene was obtained in 20.6% yield (4.5 g.); melting point 164.5–165°.

(b) The 2-thienylacetic acid (14.2 g., 0.1 mole) and 13.8 g. (0.1 mole) of β-2-thienylacrolein dissolved in 30.0 g. of acetic anhydride were refluxed for five hours with 15.0 g. of lead oxide. The yellow butadiene melted at 163.5–164.5°. The yield was 5.1 g. (22.4%).

Anal. Calc'd for $C_{12}H_{10}S_2$: C, 66.11; H, 4.59.
Found: C, 66.41; H, 4.58.

1,6-Di-(2-thienyl)-1,3,5-hexatriene. Dihydromuconic acid (4.0 g., 0.032 mole) was refluxed with 7.3 g. (0.055 mole) of 2-thenaldehyde, 9.2 g. of acetic anhydride, and 4.4 g. of litharge. The yield of the yellow hexatriene was 1.0 g. (12.8%); m.p. 198–199°.

Anal. Calc'd for $C_{14}H_{12}S_2$: C, 68.90; H, 4.92.
Found: C, 69.30; H, 5.00.

1,8-Di-(2-thienyl)-1,3,5,7-octatetraene. (a) A solution of 4.0 g. (0.026 mole) of dihydrohexatrienic acid, 6.2 g. (0.055 mole) of 2-thenaldehyde, 4.0 g. of litharge, and 9.0 g. of acetic anhydride was refluxed for five hours. The tetraene melted at 229–230°. The yield was 1.1 g. (15.9%).

(b) Succinic acid (11.8 g., 0.1 mole), β-2-thienylacrolein (13.8 g., 0.1 mole), and 15.0 g. of litharge were dissolved in 30.0 g. of acetic anhydride and the solution was boiled for five hours. Isolation in the usual way gave 6.0 g. (23.6%) of the product. No depression was observed in the mixed melting point.

Anal. Calc'd for $C_{16}H_{14}S_2$: C, 71.16; H, 5.19.
Found: C, 70.85; H, 4.93.

1,10-Di-(2-thienyl)-1,3,5,7,9-decapentaene. The β-2-thienylacrolein (8.0 g., 0.058 mole) was refluxed for five hours with 9.0 g. of acetic anhydride, 4.5 g. of litharge, and 4.1 g. (0.028 mole) of dihydromuconic acid. Recrystallization from chloroform gave 0.62 g. (15.0%) of the pentaene, m.p. 256–257°.

Anal. Calc'd for $C_{18}H_{16}S_2$: C, 72.99; H, 5.40.
Found: C, 73.16; H, 5.42.

1,12-Di-(2-thienyl)-1,3,5,7,9,11-dodecahexaene. A solution of 6.0 g. (0.039 mole) of dihydrohexatrienic acid, 11.0 g. (0.08 mole) of β-2-thienylacrolein, 6.0 g. of lead oxide, and 30.0 g. of acetic anhydride was heated for five hours. The hexaene (0.88 g., 7.1%) was a reddish color and melted at 270–272°.

Anal. Calc'd for $C_{20}H_{18}S_2$: C, 74.53; H, 5.59.
Found: C, 74.29; H, 5.53.

5-(2-Thienyl)-2,4-pentadienal. The 2-thenaldehyde (20.0 g., 0.178 mole) and crotonaldehyde (12.5 g., 0.178 mole) were mixed in 100 cc. of 70% ethanol with strong cooling. The mixture was decomposed with 10.0 g. of piperidine acetate (5.0 g. of piperidine + 5.0 g. of acetic acid) under an atmosphere of nitrogen. The mixture was allowed to stand eight days at room temperature. The precipitated solid was filtered and washed several times with ethanol-water. The aqueous ethanol solution was extracted with ether, dried, and the solvent evaporated. The pale yellow dienal, b.p. 134–136°/2 mm., weighted 10.5 g. (36%). After repeated distillations, the liquid crystallized, m.p. 44–45°.

The dienal (3.5 g., 12.0%) was also obtained as a co-product from the reaction of 2-thenaldehyde with acetaldehyde as described above.

Anal. Calc'd for C_9H_8OS: C, 65.84; H, 4.91.
Found: C, 65.72; H, 4.80.

9-(2-Thienyl)-2,4,6,8-nonatetraenal. The solid which was filtered from the reaction of

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[5] Steinkopf and Jacob (26) give m.p. 132°.

2-thenaldehyde and crotonaldehyde was recrystallized repeatedly from boiling benzene. The orange tetraenal (0.6 g., 15.6%) had m.p. 153–154°.

Anal. Calc'd for $C_{13}H_{12}OS$: C, 72.29; H, 5.54.
Found: C, 72.61; H, 5.37.

SUMMARY

1. A series of ω,ω'-di-(2-thienyl) and ω-phenyl-ω'-(2-thienyl) polyene hydrocarbons have been prepared.

2. Several methods available for the synthesis of β-cinnamalpropionic acid have been evaluated.

3. The attempted preparation of thiophene polyenals is described.

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