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Studies on the Chemistry of Heterocyclics. XXV. Investigations on Diacetylenes and Diacetylenic Glycols in the Thiophene Series

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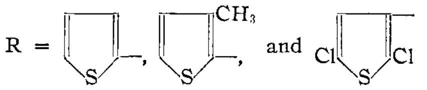
The 2-thienyl- and 3-thienylacetylenes were synthesized using subzero temperatures and sodium amide in liquid ammonia as dehydrohalogenation agent. The acetylenic compounds obtained were oxidized to the corresponding diacetylenes in good yields. Sodium acetylide in liquid ammonia was successfully utilized in converting the thiophene carbonyl compounds to the corresponding secondary and tertiary 2-thienylethynylcarbinols. These were oxidized to the corresponding diacetylenic glycols. The structures of the diacetylenes and diacetylenic glycols were confirmed by hydrogenation to the corresponding butane derivatives and saturated diols, respectively. The ultraviolet absorption data for the conjugated diacetylene chromophore were recorded and compared with those of conjugated phenylacetylene and diene systems.

Using sodium amide as dehydrohalogenation agent at subzero temperatures, a new method was developed giving yields as high as 60–80% of the corresponding 2-thienylacetylenes.[1]

The products so obtained, possessing a triple bond in the side chain of the thiophene nucleus, could be utilized in various reactions. One of these reactions studied in detail was the oxidation to diacetylenic compounds. Furthermore, these investigations were also extended to the study of diacetylenic glycols in the thiophene series.

The formation of diacetylenic compounds by oxidative coupling of metallic derivatives can be represented as

$$2RC{\equiv}CCu \xrightarrow[(OH^-),\ K_3Fe(CN)_6]{(O)} RC{\equiv}C{\cdot}C{\equiv}CR$$



and was observed as early as 1869 by Glaser[2] and subsequently investigated by Salkind and others.[3] There are several alternative procedures which involve mainly oxidation of either cuprous or halogen–magnesium derivatives. We have studied the oxidation of cuprous derivatives of 2-thienyl and substituted 2- and 3-thienylacetylenes by means of air, oxygen, potassium ferricyanide and cupric salts. Cupric acetylides are apparently unstable and in all reactions, in which they should be formed, coupling to diacetylenes takes place. The yields varied from 53–95% and are recorded in Table I.

TABLE I

Compound	Oxidizing agent	pH	Yield, %
2,2′-Dithienyldiacetylene	$K_3Fe(CN)_6$	13–14	53
	(O) $CuCl-NH_4Cl$	8–9	95
	$CuCl_2$	6–7	65
3,3′-Dimethyl-2,2′-dithienyldiacetylene	$K_3Fe(CN)_6$	13–14	55
	(O) $CuCl-NH_4Cl$	8–9	85
	$CuCl_2$	6–7	85
2,5,2′,5′-Tetrachloro-3,3′-dithienyldiacetylene	$K_3Fe(CN)_6$	13–14	55
	(O) $CuCl-NH_4Cl$	8–9	85
	$CuCl_2$	6–7	78

We have found that the yield depends on the pH of the reaction mixture as well as on the oxidizing agent applied. The higher yields were noticed with cuprous chloride and ammonium chloride mixtures at pH 8–9.

When potassium ferricyanide was used as an oxidizing agent, only moderate yields of the corresponding diacetylenes were obtained. Our investigations confirmed the earlier observations that a part of the organic substance is retained in an amorphous cuprous complex from which it cannot be extracted. Consequently, the yields with this oxidizing agent were generally less than 60%. The yields of substituted diacetylenes were somewhat higher, when cupric chloride was used as an oxidizing agent at elevated temperatures (70–80°). In acidic media the strong mineral acids immediately decompose the cuprous derivative with liberation of the true acetylenic compound from which it is formed. Boiling acetic acid, however, dissolves the cuprous derivative of 2-thienylacetylene to give an orange solution containing all the copper in the form of a complex, which could be isolated in an amorphous form by precipitation with ice-water. The cuprous complexes of thienylacetylenes are bright yellow substances, insoluble in ether, alcohol and water and could be readily isolated. They can be kept in dry state without noticeable decomposition at room temperatures.

To prove the structure of 2,2′-dithienyldiacetylenes and substituted 2,2′- and 3,3′-dithienyldiacetylenes, the compounds were hydrogenated to the corresponding 2,2′-dithienyl- and 3,3′-dithienylbutanes, respectively, with palladium-on-charcoal as catalyst. In all cases 4 moles of hydrogen was consumed thus indicating the presence of two triple bonds in the molecule. The hydrogenation products were isolated and their composition confirmed by elemental analysis.

Furthermore, the structures of 2,2′- and 3,3′-dithienylacetylenes were confirmed by studying their ultraviolet absorption and comparing the data with those of the corresponding phenyl derivatives and diene systems. The absorption spectrum of gaseous diacetylene in the near ultraviolet was examined by Woo and Chu.[4]

A few years ago Schlubach[5] and more recently Jones[6] have studied the ultraviolet absorption

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(1) A. Vaitiekunas and F. F. Nord, *J. Org. Chem.*, **19**, no. 6 (1954).

(2) L. Glaser, *Ber.*, **2**, 522 (1869).

(3) J. S. Salkind, *J. Gen. Chem. U.S.S.R.*, **7**, 227 (1937); *ibid.*, **9**, 971 and 1725 (1939); *Ber.*, **69**, 128 (1936).

(4) Sho-Chow Woo and T. C. Chu, *J. Chem. Phys.*, **3**, 541 (1935); **5**, 786 (1937).

(5) H. Schlubach and V. Franzen, *Ann.*, **573**, 110 (1951).

(6) J. B. Armitage, C. C. Cook, N. Ernstwistle, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1998 (1952).

TABLE II

ULTRAVIOLET ABSORPTION DATA OF DIACETYLENIC COMPOUNDS AND POLYENES

Compound	Thiophene nucleus λ, mμ	ε	Band at the longest wave length λ, mμ	ε	2nd absorption band λ, mμ	ε	3rd absorption band λ, mμ	ε
2,2′-Dithienyldiacetylene	235	16,500	334	18,600	287	20,900	268	18,600
3,3′-Dimethyl-2,2′-dithienyldiacetylene	241	15,300	345	20,300	325	17,800	297	24,300
2,5,2′,5′-Tetrachloro-3,3′-dithienyldiacetylene	226	44,500	341	14,200	319	14,800	286	12,400
Diphenyldiacetylene	. . .	. . . .	326	30,000	304	30,000	287	31,000
Diphenylpolyene[a] $Ph(CH{=}CH)_2Ph$	. . .	. . . .	352	60,000	339	94,000	316	84,000

[a] K. W. Hausser, R. Kuhn and A. Smekala, *Z. physik. Chem.*, **B29**, 384 (1935).

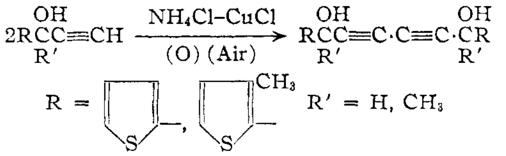
spectra of several diacetylenes and polyacetylenes. With increasing numbers of acetylenic chromophores, they noticed a shift of the first, second and third absorption bands to the visible. Our and earlier studies with phenyl derivatives and 2,2′- and 3,3′-dithienyl compounds reveal that the substitution of 2- and 3-thienyl or phenyl for hydrogen in the diacetylenes shifts the absorption bands appreciably to the visible. The values for the molar extinction at λ_{max} as compared with polyenes are recorded in Table II.

When compared with the corresponding phenyl derivatives, the 2,2′-dithienyldiacetylenes as well as 3,3′-dithienyldiacetylenes show somewhat lower intensities. The pronounced peaks at 233 mμ are attributed to the thiophene molecule.

Our investigations were also extended to the diacetylenic glycols in the thiophene series. The diacetylenic glycols are of particular importance and interest, since they provide convenient synthetic routes to bifunctional compounds difficult to prepare by other means.

As has been shown earlier[7] the secondary ethynyl carbinols could be obtained in yields as high as 60%. However, the yields of the corresponding tertiary ethynyl carbinols were low (5–10%) even when sodium acetylide was applied in great excess (in a ratio of 1:4), and the separation from the starting material was rather cumbersome.

It has been reported by Salkind[3] that oxidation of the cuprous acetylides of tertiary ethynyl carbinols with air gave good yields of the corresponding diacetylenic glycols; however, secondary ethynylcarbinols furnished the corresponding glycols in very low yields. In all these reactions two molecules of the ethynylcarbinols are linked together directly to give a symmetrical product as



$$2R\overset{OH}{\underset{R'}{C}}C{\equiv}CH \xrightarrow[(O)\,(Air)]{NH_4Cl\text{-}CuCl} R\overset{OH}{\underset{R'}{C}}C{\equiv}C{\cdot}C{\equiv}C{\cdot}\overset{OH}{\underset{R'}{C}}R$$

R′ = H, CH_3

This reaction usually takes place under milder conditions than those of alternative coupling and usually gives high yields of the corresponding diacetylenic glycols. When it was applied to the corresponding 2-thienylethynylcarbinols, it progressed with difficulty. Upon elevating the oxidation temperature to 45–55° and keeping the *p*H of the reaction mixture at 3 the starting materials were polymerized and decomposed to a great extent, and the isolated products were not the expected diacetylenic glycols, but trimeric compounds. On the other hand, at room temperature the oxidation proceeded so slowly that the starting material was recovered almost quantitatively.

In earlier work strongly acid conditions[6] were used for the coupling of acetylenic alcohols, whereas hydrocarbons, as mentioned above, have usually been coupled in alkaline medium. Our investigations in the thiophene series revealed that the *p*H of the reaction mixture as well as the oxidation time exerted an influence on the yields of the diacetylenic glycols as recorded in Table III.

TABLE III

YIELDS OF THE DIACETYLENIC GLYCOLS IN THE THIOPHENE SERIES

Compound	*p*H	Oxidizing agent	Time, hr.	Yield, %
1,6-(2,2′-Dithienyl)-hexa-2,4′-diyne-1,6-diol	6	Oxygen	6	2
	6	Oxygen	24	0
	5	Oxygen	6	4
	3	Oxygen	6	20[a]
1,6-(3,3′-Dimethyl-2,2′-diethienyl)-hexa-2,4-diyne-1,6-diol	6	Air at 55°	3	0
	5	Oxygen	6	15
	3	Oxygen	6	6
1,6-(2,2′-Dithienyl)-1,6-dimethylhexa-2,4-diyne-1,6-diol	5	Oxygen	6	2
	3	Oxygen	6	12

[a] Several attempts to repeat this original experiment gave yields of only 2-4%.

The yields were very low, and the isolation of the monomeric compounds could be accomplished only by applying chromatographic separation, *e.g.*, adsorption on alumina usually from benzene solution and subsequent elution with petroleum ether and benzene. It seems that the 2-thienylethynylcarbinols polymerize more readily than the corresponding phenyl derivatives.

Salkind[3] stated that the utilization of oxygen instead of air increased the rate of coupling of ethynyldimethylcarbinol about sixfold. Further examination[6] of the effect of oxygen in the case of secondary ethynylcarbinols with the standard procedure gave very low yields. However, it was observed that by using oxygen and providing an intimate contact between the two phases, such alcohols couple quite readily. Applying oxygen in a hydrogenation apparatus with 2-thienyl derivatives, the yields of the corresponding diacetylenic glycols could be slightly increased. However, the products of isolation were mostly trimers the structure of which could not be determined with certainty. The 3-methylthiophene derivative polymerized more readily.

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[7] A. Vaitiekunas, R. E. Miller and F. F. Nord, *J. Org. Chem.*, **16**, 1603 (1951).

The structures of the monomeric 2,2′-dithienyl diacetylenic glycols obtained were confirmed by hydrogenation to the corresponding saturated diols using palladium-on-charcoal as catalyst. The ultraviolet absorption data were also recorded and are summarized in Table IV.

TABLE IV

ULTRAVIOLET ABSORPTION DATA OF 2,2′-DITHIENYLDIACETYLENIC GLYCOLS

	λ_{max}	ϵ	λ_{max}	ϵ
1,6-(2,2′-Dithienyl)-hexa-2,4-diyne-1,6-diol	247	1120	265	870
1,6-(3,3′-Dimethyl-2,2′-dithienyl)-hexa-2,4-diyne-1,6-diol	245	940	262	810
1,6-(2,2-Dithienyl)-1,6-dimethyl-hexa-2,4-diyne-1,6-diol	244	1500	256	1480

The aromatic diacetylenic glycols, as observed by earlier workers,[6] show light absorption properties which appreciably deviate from those which might be predicted on the basis of the chromophores present. Analogous results have been obtained in the thiophene series. Perhaps these effects are the result of an electronic interaction of the type

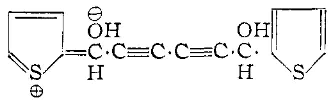

TABLE V

PHYSICAL PROPERTIES, YIELDS AND ELEMENTAL ANALYSES OF DITHIENYLDIACETYLENES

Compound	M.p., °C.	Yield, %	Calcd. C	Calcd. H	Calcd. Cl	Calcd. S	Found C	Found H	Found Cl	Found S
2,2′-Dithienyldiacetylene	88–89	53	67.25	3.3	..		67.15	3.1	..	
3,3′-Dimethyl-2,2′-dithienyldiacetylene	62–63	53	69.5	4.15	..	26.4	69.4	4.0	..	25.9
2,5,2′,5′-Tetrachloro-3,3′-dithienyldiacetylene	69–70	55	41.0	0.6	40.3		41.2	0.95	40.7	

Experimental

Materials.—The thiophene used in this work was obtained through the courtesy of Drs. C. A. Hochwalt and O. J. Weinkauff of the Monsanto Chemical Co., St. Louis, Mo. 2-Chlorothiophene and 2,5-dichlorothiophene were furnished by the Jefferson Chemical Co., Inc., New York 22, N. Y. Acetyl-2-thiophene and substituted acetylthiophenes were prepared as usual, while the 2-thienylacetylenes and substituted 2-thienyl- and 3-thienylacetylenes were prepared according to earlier methods developed in our laboratories.

General Procedure for the Preparation of 2,2′-Dithienyldiacetylenes and Substituted 2,2′-Dithienyl- and 3,3′-Dithienyldiacetylenes by Means of Potassium Ferricyanide in Alkaline Solution or Cupric Chloride ($CuCl_2$) in Aqueous Solution as Oxidizing Agents.—The preparation of substituted 2,2′-dithienyl- and 3,3′-dithienyldiacetylenes while using potassium ferricyanide in alkaline solution as oxidizing agent is essentially the same as described below for the preparation of 2,2′-dithienyldiacetylene.

2,2′-Dithienyldiacetylene.—2-Thienylacetylene (5 g., 0.048 mole) was dissolved in 100 ml. of absolute alcohol and added under continuous stirring to the ammoniacal cuprous chloride solution. The latter was prepared by dissolving cuprous chloride (15 g., 0.152 mole) in 50 ml. of concentrated ammonium carbonate solution. A voluminous precipitate was obtained which was filtered off, washed with dilute ammonium hydroxide, then with water, ethanol and finally three times with ether. The yellow precipitate was dried *in vacuo* over anhydrous sodium sulfate.

The cuprous complex (2.7 g., approx. 0.016 mole) of 2-thienylacetylene was mixed with 0.033 mole of potassium ferricyanide while adding 1.6 g. (0.028 mole) of potassium hydroxide dissolved in 25 ml. of water. Under occasional stirring the mixture was allowed to stand for 24 hours at room temperature.

The precipitate was filtered off and extracted three times with hot acetone. The solvent was allowed to evaporate and the residue extracted with ether. 2,2′-Dithienyldiacetylene (0.89 g.) was isolated as colorless needles which, when recrystallized from methanol, melted at 88–89°, yield 53%. The elemental analysis, yields and physical data of the diacetylenic compounds prepared are recorded in Table V.

The oxidation of the cuprous complexes of 2-thienylacetylene and substituted 2- and 3-thienylacetylenes by means of cupric chloride in aqueous solution were carried out in a manner analogous to that given for 2,5-dichloro-3-thienylacetylene: The dry cuprous complex of 2,5-dichloro-3-thienylacetylene (5 g., 0.025 mole) was carefully mixed with cupric chloride (8 g., 0.06 mole) in 10 ml. of water and heated for 5 hours at 70–80° on a water-bath with occasional shaking. After 3 hours a brown oil usually separated which froze on cooling. It was filtered off, washed with dilute ammonium hydroxide and extracted with boiling methyl alcohol. There was obtained 3.8 g. of 2,5,2′,5′-tetrachloro-3,3′-dithienylacetylene, yield 78%. When recrystallized from methyl alcohol it melted at 69°. The elemental analysis of this compound is recorded in Table V. The yields of 2,2′-dithienylacetylene and 3,3′-dimethyl-2,2′-dithienyldiacetylene are recorded in Table I.

General Procedure for the Preparation of 2,2′-Dithienyldiacetylene and Substituted Derivatives by Means of Cuprous Chloride–Ammonium Chloride and Oxygen or Air.—The oxidation of the cuprous complexes of the substituted 2- and 3-thienylacetylenes was carried out in a manner as described for 2,2′-dithienyldiacetylene: 2-thienylacetylene (5 g., 0.048 mole) was dissolved in 50 ml. of 95% ethanol and added to the suspension of 15 g. (0.15 mole) of cuprous chloride and 25 g. of ammonium carbonate in 50 ml. of water. Sufficient quantity of ammonium hydroxide was added to render the mixture of *p*H 8–9. The mixture was shaken in an oxygen atmosphere for 24 hours. On neutralization with dilute hydrochloric acid (0.1 *N*) the product usually crystallized out on the surface and could be extracted with ether. Isolation and recrystallization in the usual manner furnished the 2,2′-dithienyldiacetylene, m.p. 89°, yield 4.65 g. (95%). When oxygen was substituted by air, the shaking had to be prolonged for several days in order to obtain the same high yields of the corresponding diacetylenic compound. Yields of the substituted 2,2′- and 3,3′-dithienyldiacetylenes obtained are recorded in Table I in the discussion part of this paper.

Hydrogenation of 2,2′-Dithienyldiacetylenes and Substituted 2,2′- and 3,3′-Dithienyldiacetylenes to the Corresponding Dithienylbutanes.—These hydrogenations were carried out in the usual manner. The corresponding dithienyldiacetylenes were dissolved in anhydrous ether, the palladium catalyst added (5%) and the reaction mixture shaken in the apparatus, until the hydrogen uptake amounted to 4 moles. The isolation of the hydrogenated products furnished the corresponding dithienylbutanes. The elemental analyses and physical properties of these compounds are recorded in Table VI.

Preparation of 2-(2-Thienyl)-3-butyn-2-ol.—To sodium acetylide (0.8 mole) in 500 ml. of liquid ammonia under continuous stirring there was added 25 g. (0.195 mole) of 2-acetylthiophene. The reaction mixture was stirred for 3 additional hours and decomposed with ammonium chloride. Upon isolation in the usual manner we obtained 4.5 g. of the desired ethynylcarbinol, which gave the positive acetylene test with the Ilosvay solution, yield 15%. There was recovered 14 g. of 2-acetylthiophene. The product boiled at 110–115° (33 mm.).[8]

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(8) G. T. Gmitter and F. L. Benton, THIS JOURNAL, **72**, 4586 (1950).

TABLE VI

PHYSICAL PROPERTIES AND ELEMENTAL ANALYSES OF DITHIENYLBUTANES

Compound	M.p.,[a] °C.	Elemental analyses, % Calcd. C	H	Cl	S	Found C	H	Cl	S
2,2′-Dithienylbutane	48	65.1	6.4	. . .	28.7	65.3	6.7	. .	28.4
3,3′-Dimethyl-2,2′-dithienylbutane	44	67.0	7.2	. . .	. .	66.7	7.5	. .	
2,5,2′,5′-Tetrachloro-3′,3′-dithienylbutane	29–32	40.2	2.78	39.55		39.8	2.5	39.8	

[a] The melting points are not corrected and were taken on a Fisher–Johns apparatus.

Anal. Calcd. for C_8H_8OS: C, 63.2; H, 5.3. Found: C, 63.7; H, 5.2.

Preparation of 2-(5-Chloro-2-thienyl)-3-butyn-2-ol.—Seven and two-tenths gram (0.32 mole) of metallic sodium was converted to sodium acetylide in 500 ml. of liquid ammonia and to that solution 13.4 g. (0.12 mole) of 5-chloro-2-acetothienone dissolved in threefold volume of absolute ether was added in the course of 30 minutes. The isolation of the product in the usual manner gave 1.6 g. of slightly yellowish needles melting at 137°. It gave the acetylene test with the Ilosvay solution; yield 10%.

Anal. Calcd. for C_8H_7ClOS: C, 51.5; H, 3.7; Cl, 19.3. Found: C, 51.3; H, 3.33; Cl, 20.0.

1,6-(2,2′-Dithienyl)-hexa-2,4-diyne-1,6-diol.—To a mixture of 20 g. (0.37 mole) of ammonium chloride, 50 ml. of water, 12.5 g. (0.128 mole) of cuprous chloride and 6.25 ml. of ammonium hydroxide (21%) in a three-necked flask there was added 5 g. (0.036 mole) of 2-thienylethynylcarbinol dissolved in 30 ml. of 95° ethanol, and the contents of the flask were shaken in an atmosphere of oxygen for 6 hours. The resultant blue-green suspension was extracted (6 × 100 ml.) with ether without preliminary filtration, which is unnecessary and rather difficult. The extract was dried over anhydrous sodium sulfate and the solvent allowed to evaporate. There was obtained a brown viscous oil which froze on cooling. Using chromatographic adsorption on alumina and subsequent elution with benzene and light petroleum ether (b.p. 50–60°), a substance melting at 153° (0.1 g., yield 2%) was isolated from this oil. When recrystallized from benzene it gave colorless needles, m.p. 153°.

Anal. Calcd. for $C_{14}H_{10}O_2S_2$: C, 61.4; H, 3.63; S, 23.4. Found: C, 61.25; H, 3.9; S, 22.9; mol. wt., 310.

1,6-(2,2′-Dithienyl)-hexane-1,6-diol.—Five-tenths gram of monomeric 1,6-(2,2′-dithienyl)-hexa-2,4-diyne-1,6-diol was dissolved in 50 ml. of methanol and 0.03 g. (5%) of palladium-on-charcoal was added. The reaction mixture was shaken in a hydrogenation apparatus at atmospheric pressure. The hydrogen uptake amounted to 198 ml. at 25° (750 mm.) thus indicating two triple bonds in the above compound. Filtration and isolation furnished a slightly yellowish substance melting at 110–115°.

Anal. Calcd. for $C_{14}H_{18}O_2S_2$: C, 59.5; H, 6.35; S, 22.8. Found: C, 60.0; H, 6.2; S, 22.4.

Trimer of 1,6-(2,2′-Dithienyl)-hexa-2,4-diyne-1,6-diol.—On prolonged oxidation and on oxidation at elevated temperatures (40–50°) most of the reaction product was isolated as a brown substance, which was soluble only in benzene and decomposed at 290°.

Anal. Calcd. for $C_{14}H_{10}O_2S_2$: C, 61.4; H, 3.63; S, 23.4. Found: C, 61.2; H, 3.9; S, 23.6; mol. wt., 788.

1,6-(3,3′-Dimethyl-2,2′-dithienyl)-hexa-2,4-diyne-1,6-diol.—The experimental procedure is analogous to that described for 1,6-(2,2′-dithienyl)-hexa-2,4-diyne-1,6-diol. From 5 g. (0.033 mole) of the 3-methyl-2-thienylethynylcarbinol 0.3 g. (6%) of the corresponding diacetylenic glycol was isolated by means of chromatographic adsorption from benzene solution on alumina. When recrystallized from benzene–petrol ether it had a m.p. 89–102°.

Anal. Calcd. for $C_{16}H_{14}O_2S_2$: C, 63.5; H, 4.7. Found: C, 63.8; H, 4.85; mol. wt., 350.

1,6-(3,3′-Dimethyl-2,2′-dithienyl)-hexane-1,6-diol.—0.639 g. of the 1,6-(3,3′-dimethyl-2,2′-dithienyl)-hexa-2,4-diyne-1,6-diol was dissolved in 50 ml. of methanol. Hydrogenation and isolation in the usual manner furnished a slightly yellowish product which melted at 78–82°.

Anal. Calcd. for $C_{16}H_{22}O_2S_2$: C, 61.8; H, 7.08; S, 20.8. Found: C, 62.3; H, 7.0; S, 20.2.

Trimer of 1,6-(3,3′-Dimethyl-2,2′-dithienyl)-hexa-2,4-diyne-1,6-diol.—Most of the oxidation product, especially when the oxidation was prolonged for considerable time, was isolated as a trimer which was soluble in benzene and decomposed at 280–290°.

Anal. Calcd. for $C_{16}H_{14}O_2S_2$: C, 63.9; H, 4.64. Found: C, 63.5; H, 4.1; mol. wt., 849.

1,6-(2,2′-Dithienyl)-1,6-dimethylhexa-2,4-diyne-1,6-diol.—The experimental procedure is essentially analogous to that described for 1,6-(2,2′-dithienyl)hexa-2,4-diyne-1,6-diol. From 5 g. (0.033 mole) of the 3-(2-thienyl)-3-methylprop-1-yne-3-ol there was isolated 0.1 g. of the corresponding glycol, yield 2%. When recrystallized from benzene and petroleum ether (30–60°) it melted at 90–95°.

Anal. Calcd. for $C_{16}H_{14}O_2S_2$: C, 63.9; H, 4.6; S, 21.2. Found: C, 63.7; H, 4.6; S, 20.9; mol. wt., 300.

1,6-(2,2′-Dithienyl)-1,6-dimethylhexa-2,4-diyne-1,6-diol.—The hydrogenation is analogous to that described for 1,6-(2,2′-dithienyl)-hexane-1,6-diol. The saturated diol obtained melted at 60–63°.

Anal. Calcd. for $C_{16}H_{22}O_2S_2$: C, 61.8; H, 7.08; S, 20.6. Found: C, 62.3; H, 7.0; S, 20.2.

Trimer of 1,6-(2,2′-Dithienyl)-1,6-dimethylhexa-2,4-diyne-1,6-diol.—On prolonged oxidation at elevated temperatures of the corresponding ethynylcarbinol a brown product melting with decomposition at 290° was always isolated. However, its molecular weight could not be determined with certainty and its elemental analysis was unsatisfactory. From analogy, however, it is believed that the brown product obtained on isolation was the trimer which was, as usually observed, soluble in benzene.

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