[CONTRIBUTION FROM THE DIVISION OF NATURAL SCIENCES, GRINNELL COLLEGE]

The Synthesis of Di- and Terthienyls[1,2]

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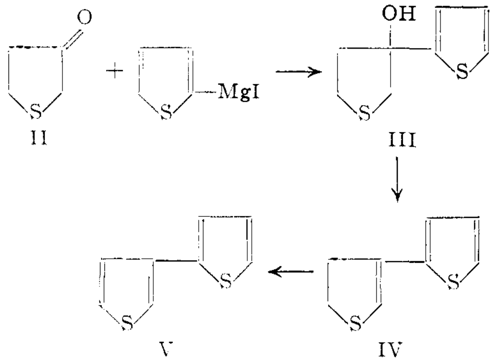
A synthetic route is described which enables the preparation of unsymmetrical di- and terthienyls. The method has been found useful for the synthesis of some simple 3-substituted thiophenes.

In 1947 Zechmeister and Sease[4] reported the isolation from the yellow petals of the African variety of the common marigold (*Tagetes erecta L.*) a yellow substance which they identified as α-terthienyl (I). At the outset of our investigation designed to enlarge our knowledge of polythienyls whose occurrence in nature has no precedent, only two of the three possible dithienyls and one of the fourteen possible terthienyls were known.[5] The Ullmann coupling method used for their preparation does not allow for ready variation to permit the synthesis of unsymmetrical isomers. In addition the coupling method frequently leads to mixtures of polythienyls which can only be separated by chromatography.

I

In this communication we are reporting a rational synthesis of 2,3′-dithienyl (V) as well as two synthetic routes to 2,2′,4′,2″-terthienyl (VII).



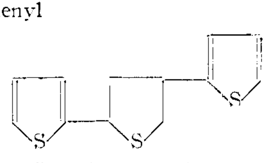
The starting material for the synthesis of V, namely 3-ketotetrahydrothiophene (II), has been adequately described by Woodward.[6] By using the commercially available ethyl mercaptoacetate and methyl acrylate and making minor modifications in the experimental technique this cyclic ketone II is now readily available in improved yield. Karrer[7] had shown that the reaction between the ketone II and methyl- and phenylmagnesium bromide proceeded normally and had indeed isolated a crystalline carbinol (3-methyl-3-hydroxytetrahydrothiophene). We found it expedient to steam distil the Grignard reaction product immediately after acid decomposition of the complex and thus obtained the dihydrothiophene IV in 50–60% yield without isolation of the carbinol. The latter could be dehydrogenated to 2,3′-dithienyl (V) in fair yield using sulfur and in excellent yield using chloranil in boiling ethylene glycol. Finally V could be obtained in an over-all yield of 45–50% by heating the crude Grignard product directly with chloranil in ethylene glycol, thus effecting simultaneous dehydration and dehydrogenation. 2,3′-Dithienyl is a bright yellow solid with a characteristic naphthalene-like odor and high vapor pressure at room temperature. Maximum absorption in the ultraviolet occurs at 283 $m\mu$, a considerable hypsochromic shift from the 301 $m\mu$ maximum exhibited by the 2,2′-dithienyl isomer.[4] This phenomenon of a shift to lower wave length, as compared to the more symmetrical isomer, is again evident when the terthienyls are compared (see Table I) and is undoubtedly due to the interruption of the extended conjugated system found in the completely linear polythienyls.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF POLYTHIENYLS

Compound	λmax, $m\mu$	$E^{\text{mol}}_{\text{cm.}} \times 10^{-4}$	Solvent
2,2′-Dithienyl[4]	301	1.23	Hexane
2,3′-Dithienyl (V)	283	1.19	Ethanol
2,2′:5′,2″-Terthienyl[4]	350	2.31	Hexane
2,2′:4′,2″-Terthienyl[a]	283	2.98	Ethanol

[a] Note added in proof: a third useful synthesis of this terthienyl proved to be the sulfur dehydrogenation in 60% yield of the liquid thiophene trimer, 2,2′-4′,2″-2′,3′,4′,5′-tetrahydroterthienyl



(S. L. Meisel, G. C. Johnson and H. D. Hartough, THIS JOURNAL, 72, 1910 (1950)).

The first synthesis of the unsymmetrical terthienyl (VII) is based on the observation by Parham and Traynelis[8] that 2,5-diphenyl-1,4-dithiadiene loses sulfur at 200° to form a 2,4-diarylthiophene. Thus 2,5-dithienyl-1,4-dithiadiene (VI) prepared from 2-chloroacetylthiophene *via* the Bunte salt[9] lost sulfur to form the desired terthienyl

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[1] Part of this work was supported by the Office of Ordnance Research, Contract No. DA-11-022-ORD-1579.

[2] Presented in part at the 129th Meeting of the American Chemical Society, Dallas, Texas, April, 1956.

[3] Department of Chemistry, Tulane University, New Orleans, Louisiana.

[4] L. Zechmeister and J. W. Sease, THIS JOURNAL, **69**, 273 (1947).

[5] J. Teste and N. Lozach, *Bull. soc. chim. France*, 492 (1954), have reported the isolation of the missing 2,3′-dithienyl isomer in unspecified yield from the reaction between sulfur and 2-(2-butene-2)-thiophene (see Experimental).

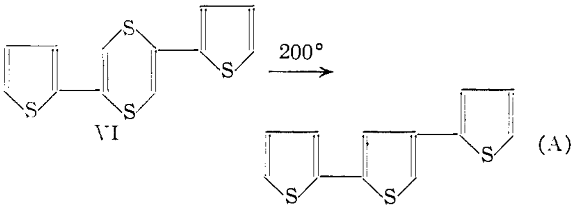
[6] R. B. Woodward and R. H. Eastman, THIS JOURNAL, **68**, 2229 (1946).

[7] P. Karrer and A. Kiese, *Helv. Chim. Acta*, **27**, 1285 (1945).

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

[9] R. H. Baker and C. Barkenbus, *ibid.*, **58**, 262 (1936).

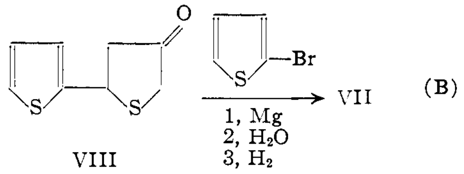
(VII) although the yield was disappointingly low (12%). In order to ensure the correctness of our formulation for this low yield pyrolysis product, the preparation of VII was carried out by another apparently unambiguous route (B)



VI

VII

(A)



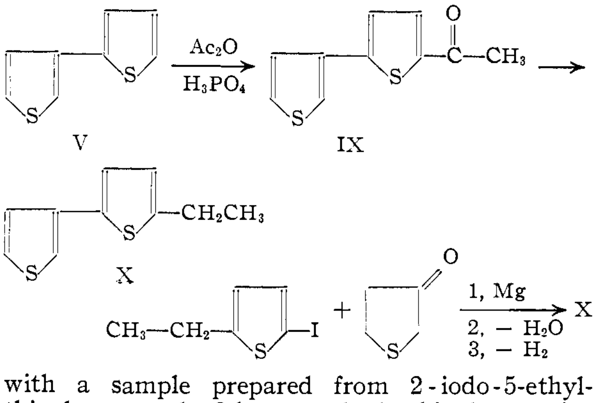
VIII

VII

(B)

The Grignard reaction on the ketone VIII using 2-thienylmagnesium bromide followed by dehydration and dehydrogenation produced the terthienyl (VII) identical with the sample prepared by pyrolysis.

Whereas 2,2'-dithienyl can be mono- and diacetylated[10] with reasonable ease only one mono-acetylated product has thus far been isolated from the reaction between 2,3'-dithienyl (V), acetic anhydride and phosphoric acid at room temperature. The position of the acetyl group was proved by reduction to 5-ethyl-2,3'-dithienyl (X), identical with a sample prepared from 2-iodo-5-ethylthiophene and 3-ketotetrahydrothiophene. Attempts to isolate a diacetyl derivative by using more drastic conditions have led to the formation of tars. This may be due to the lack of resonance stabilization of the unsymmetrical isomer as compared to the symmetrical isomer in support of the spectral observations.



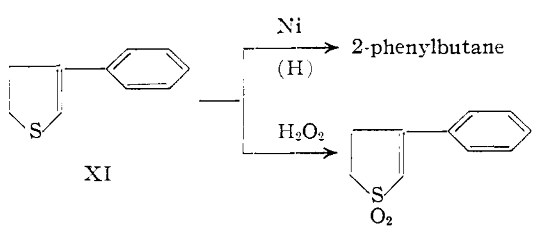
V

IX

X

A limited study was carried out to determine the usefulness of the monocyclic ketone II as an intermediate in the preparation of simple 3-substituted thiophenes. It was found that 3-phenylthiophene and 3-(*n*-butyl)-thiophene could be prepared readily by the route outlined for the synthesis of 2,3'-dithienyl in yields comparable to those recorded.[11]

A more detailed examination was made of the crystalline 3-phenyldihydrothiophene (XI). In contrast to the sodium in liquid ammonia reduction of alkylthiophenes[12] which furnishes a mixture of bond isomers, one isomer apparently predominated in the acid-catalyzed dehydration of the Grignard carbinol.



XI

The position of the double bond is tentatively indicated as shown in XI on the basis of the failure of the sulfone to undergo a reverse Diels–Alder reaction to yield 2-phenylbutadiene. Only 2-phenylbutane (but no olefin) could be isolated from the reaction between XI and Raney nickel.

Acknowledgment.—A Frederick Gardner Cottrell grant from the Research Corporation in support of part of this investigation is gratefully acknowledged.

Experimental[13]

3-Ketotetrahydrothiophene (II).—The following modifications of the described[6] procedure were employed. Using the commercially available methyl acrylate and ethyl mercaptoacetate, the addition in the presence of piperidine yielded the mixed diester sulfide, b.p. 165–179° (20 mm.) in 85–90% yield. Cyclization with sodium methoxide in ether furnished the mixture of the 2- and 4-carbomethoxy- and carboethoxy-3-ketotetrahydrothiophenes, b.p. 146–152° (19 mm.) in 70–72% yield. The hydrolysis and decarboxylation reaction could be shortened from 12 to 1 hour by vigorous stirring. Thus from 85.0 g. of the cyclic keto ester in 650 ml. of 10% sulfuric acid there was obtained 41.0 g. (79%) of the ketone I, b.p. 86–87° (25 mm.) after 75 minutes at 80–85°. Due to the high water solubility of this ketone it was found essential to carry out 8 to 10 hand extractions of 75 ml. of ether each on the reaction mixture which had been carefully saturated with salt.

2,3'-Dithienyl (V).—The Grignard solution prepared from 2-iodothiophene (10.5 g., 0.05 mole) in 75 ml. of anhydrous ether was treated, over a period of 10 minutes, with 3-ketotetrahydrothiophene (5.01 g., 0.049 mole) in 50 ml. of ether. The gummy lump which formed initially was dispersed to a yellow powder by continued stirring at room temperature for 1.5 hours.

A. Direct Conversion to V.—The complex was decomposed with 100 ml. of ice-cold dilute hydrochloric acid, the organic layer washed free of acid with sodium bicarbonate and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 7.46 g. (82%) of viscous oil (presumably mainly the tertiary carbinol). This oil (3.70 g., 0.02 mole) was heated with 0.50 g. of potassium acid sulfate and 0.80 g. of flowers of sulfur. At 150° water began to distil from the reaction mixture and at 160–170° hydrogen sulfide was evolved. Gas evolution ceased after 15 minutes during which time the temperature was slowly raised to 225°. Steam distillation of the reaction mixture yielded 1.80 g. (55%) of lustrous plates, m.p. 65–66°. One crystallization from petroleum ether (b.p. 35°) yielded pure **2,3'-dithienyl**, m.p. 68.0–68.4°.

Anal. Calcd. for $C_8H_6S_2$: C, 57.72; H, 3.64; S, 38.57; mol. wt., 166.25. Found: C, 57.94; H, 3.51; S, 38.49; mol. wt. (ebul. butanone), 169.

B. Stepwise Procedure.—The crude oily carbinol from a similar experiment as above (4.68 g.) was steam distilled

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[10] H. Wynberg and A. Logothetis, THIS JOURNAL, 78, 1958 (1956).

[11] H. Scheibler and F. Rettig, *Ber.*, 59, 1194 (1926); Feldkamp and Tullar, *Org. Syntheses*, 34, 73 (1954); A. Chrzaszcewska, *Roczniki Chem.*, 5, [1], 33 (1925); *C. A.*, 20, 1078 (1926).

[12] S. F. Birch and D. T. McAllen, *J. Chem. Soc.*, 2556, 3411 (1951).

[13] Melting points are corrected; boiling points are uncorrected.

from 10% sulfuric acid and 500 ml. of distillate collected. The solid, obtained from the distillate, weighed 2.35 g. (55%) and melted at 48–49°, after one recrystallization from petroleum ether. It was relatively unstable in air and at room temperature. When 168 mg. (1 millimole) of the **3-thienyldihydrothiophene** (III, R = C_4H_3S), was refluxed for one hour in the presence of 246 mg. of chloranil in 5 ml. of ethylene glycol and the resulting reaction mixture steam distilled from dilute (2%) sodium hydroxide, 150 mg. (90.5%) of pure 2,3′-dithienyl, m.p. 67–68°, was obtained. The reaction between sulfur and 2-(2-butene-2)-thiophene[5] furnished V, m.p. 65–66°, in 5% yield. A mixed m.p. of the dithienyl prepared in this manner with 2,3′-dithienyl described above was undepressed.

3-Phenylthiophene.—Following the procedure as outlined above, an 86% yield of the undistilled 3-hydroxy-3-phenyltetrahydrothiophene was obtained. When 7.45 g. of this carbinol was heated with 1.20 g. of potassium acid sulfate at such a rate that the temperature of the distillate did not exceed 172° (741 mm.), 4.40 g. (67%) of XI, **3-phenyldihydrothiophene**, distilled. The crystalline distillate furnished shiny, fluffy plates, having a characteristic odor, and melting at 78.5–79.6° after recrystallization from petroleum ether. The yield was raised to 72–75% when the carbinol was dehydrated by steam distillation from 10% sulfuric acid.

Anal. Calcd. for $C_{10}H_{10}S$: C, 75.74; H, 6.36. Found: C, 76.01; H, 6.14.[14]

A. Dehydrogenation of 3-Phenyldihydrothiophene Using Sulfur.—When 1.35 g. of crude crystalline dihydrothiophene was heated with 0.261 g. of sulfur until hydrogen sulfide evolution ceased (5–7 minutes at 170–200°), 3-phenylthiophene, 1.19 g. (88%), could be sublimed directly from the reaction mixture. One crystallization from petroleum ether furnished the pure material, m.p. 91.5–92.8° (reported[15] m.p. 92–93°).

B. Dehydrogenation using Chloranil.—Pure 3-phenyldihydrothiophene, m.p. 77–78° (300 mg.), was heated under reflux with 463 mg. of chloranil in 5 ml. of ethylene glycol for one hour. The reaction mixture was diluted with 50 ml. of 5% sodium hydroxide and steam distilled to yield 262 mg. (89%) of pure 3-phenylthiophene, m.p. 92.0–93.4°.

3-Phenyldihydrothiophene Sulfone.—Freshly sublimed (100°, 0.5 mm.) 3-phenyldihydrothiophene (324 mg.) was warmed on the steam-bath for 2 hours with 2 ml. of glacial acetic acid (freshly distilled from potassium permanganate) and 1 ml. of 30% hydrogen peroxide. Precipitation with 20 ml. of water furnished 242 mg. (72%) of crude sulfone, m.p. 132–155°. Several recrystallizations from 95% alcohol gave pure material, m.p. 179.0–180.1°, as shiny platelets.[16]

Anal. Calcd. for $C_{10}H_{10}SO_2$: C, 61.83; H, 5.19. Found: C, 61.71; H, 5.10.

No decomposition took place when the sulfone was heated to 200–225°. Above this temperature the odor of sulfur dioxide was noticed, but neither 2-phenylbutadiene nor its adduct with maleic anhydride could be isolated from the residue.

Structure Proof of 3-Phenyldihydrothiophene.—When 5.2 g. of freshly sublimed 3-phenyldihydrothiophene was refluxed for 6 hours with 50 g. of Raney nickel[17] in 500 ml. of 95% ethanol, an oil was isolated upon removal of catalyst and solvent. Fractional distillation of this oil furnished 4 fractions (total weight 2.81 g., 65%), b.p. 170–175.5°, (738 mm.), $n^{20}\mathrm{D}$ 1.4879–1.4900. The reported constants for 2-phenylbutane are b.p. 173.3° (760 mm.), $n^{20}\mathrm{D}$ 1.4902.

3-(*n*-Butyl)-thiophene.—The Grignard reaction product from 5.10 g. of II and 7.00 g. of *n*-butyl bromide was carefully decomposed with cold dilute sulfuric acid to furnish 5.45 g. of oily carbinol. When this was heated with 1.10 g. of sulfur and 0.2 g. of potassium acid sulfate to 200° in 15 minutes then slowly distilled with a free flame, 2.70 g. (57%) of distillate, $n^{20}\mathrm{D}$ 1.5125, was collected. Upon redistillation **3-*n*-butylthiophene**, distilling at 176–178° (739 mm.), $n^{20}\mathrm{D}$ 1.5114, was collected (reported[11] b.p. 181–183° (760 mm.); $n^{20}\mathrm{D}$ 1.5101).

Acylation of 2,3′-Dithienyl.—A mixture of 0.860 g. (0.005 mole) of 2,3′-dithienyl (V), 0.65 ml. (0.0065 mole) of acetic anhydride and one drop of sirupy phosphoric acid (85%) was allowed to stand at room temperature for 24–30 hours while protected from moisture. Steam distillation of the reaction mixture furnished 0.415 g. (48%) of starting material, m.p. 59–62°. The residue from the steam distillation was extracted with ether. Upon removal of the ether 0.403 g. (39%) of light yellow crystals of 5-acetyl-2,3′-dithienyl (IX) was obtained which melted at 121.5–122.5° after one crystallization from methanol.

Anal. Calcd. for $C_{10}H_8OS_2$: C, 57.66; H, 3.87. Found: C, 57.89; H, 3.93.

Proof of Structure of IX. A. Reduction of 5-Acetyl-2,3′-dithienyl.—A mixture of 1.4 g. of IX, 350 g. of amalgamated mossy zinc, 550 ml. of water, 25 ml. of concentrated hydrochloric acid, 10 ml. of acetic acid and 30 ml. of dioxane was allowed to stand at room temperature for two days while 30 ml. of concentrated hydrochloric acid was added at intervals in 5-ml. portions. The organic material was separated with ether. After washing, drying and removal of the solvent an oil, $n^{20}\mathrm{D}$ 1.6291, m.p. 21.7–23.7°, remained.

B. 5-Ethyl-2,3′-dithienyl.—A Grignard reagent was prepared from 25.10 g. (0.105 mole) of 2-ethyl-5-iodothiophene (b.p. 117–120° (20–25 mm.)), 2.55 g. (0.105 mole) of magnesium turnings and 150 ml. of anhydrous ether. To this reagent was added over a period of 30 minutes a solution of 12.7 g. (0.120 mole) of 3-ketotetrahydrothiophene (II) in 60 ml. of anhydrous ether. The complex was hydrolyzed after an additional hour with 130 ml. of 10% ammonium chloride. Ether extraction furnished 20.8 g. (72%) of crude carbinol which was dehydrated and dehydrogenated by adding 30 ml. of ethylene glycol and 26 g. of chloranil and allowing this mixture to stand at room temperature for 42 hours. After an additional 4 minutes of heating under reflux the mixture was steam distilled from 10% sodium hydroxide solution to furnish 4.4 g. of 5-ethyl-2,3′-dithienyl. Low temperature crystallization of the oil from methanol furnished white plates, m.p. 21–23.9°, b.p. 99° (0.28 mm.), $n^{20}\mathrm{D}$ 1.6309 (as supercooled liquid).

Anal. Calcd. for $C_{10}H_{10}S_2$: C, 61.81; H, 5.19; S, 33.00. Found: C, 62.19; H, 5.12; S, 32.84.

Three mixed melting points of X prepared as described above with the material obtained by reduction of 5-acetyl-2,3′-dithienyl in approximate ratios of 1:4, 1:1 and 4:1 melted at 21.8–23.3°, 22–23.0° and 22.0–23.3°, respectively.

2,5-Dithienyl-1,4-dithiadiene (VI).—A mixture of 42.30 g. of 2-chloroacetylthiophene,[18] 220 g. of sodium thiosulfate and 250 ml. of water was stirred mechanically at 60° for 2 hours then an additional hour without external heating. Upon cooling in an ice-bath 57.0 g. (82%) of crude Bunte salt crystallized as yellow plates. Recrystallization from ethanol furnished 26.5 g. of the pure white salt.[19] Ten grams of this salt was refluxed for 3.5 hours with 40 ml. each of water, concentrated hydrochloric acid and ethanol. Upon cooling the oil was taken up in benzene and the organic layer washed free of acid with 5% sodium bicarbonate. Removal of the solvent left an oil which was purified by passage through 60 g. of alumina (Merck F-20) using first petroleum ether (b.p. 30–60°), then benzene–petroleum ether, 1:2.5, as eluents. This process furnished 0.681 g. (12.7%) of yellow crystals, m.p. 129–131°. An analytical sample of **2,5-dithienyl-1,4-dithiadiene** prepared by crystallization from acetic acid melted at 135–136°.

Anal. Calcd. for $C_{12}H_8S_4$: C, 51.53; H, 3.13. Found: C, 51.79; H, 2.95.

2,2′;4′,2″-Terthienyl.—A test-tube fitted with thermometer and gas inlet tube and containing 0.717 g. of 2,5-dithienyl-1,4-dithiadiene was flushed with nitrogen and lowered into an oil-bath held at 200°. After 2 minutes a vigorous reaction ensued raising the internal temperature to 225°. The remaining black oil was chromatographed on 60 g. of alumina (F-20) using petroleum ether (30–60°).

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(14) The calculated values for the fully aromatic compound $C_{10}H_8S$ are: C, 75.0; H, 5.0.

(15) E. Bamberger, *Ber.*, **30**, 366 (1897).

(16) H. J. Backer and J. Strating, *Rec. trav. chim.*, **53**, 525 (1934), record a m.p. of 166–167° for this sulfone.

(17) R. Mozingo, D. W. Wolf, S. A. Harris and K. Folkers, THIS JOURNAL, **65**, 1013 (1943).

(18) W. G. Emerson and T. M. Patrick, *J. Org. Chem.*, **13**, 722 (1948).

(19) It was found advantageous to purify the Bunte salt before cyclization.

The first 50 ml. of eluate furnished 0.078 g. of yellow crystals, m.p. 50–52°. Evaporative sublimation at 50° (0.05 mm.) gave pure 2,2′;4′,2″-terthienyl, m.p. 53–54°.

Anal. Calcd. for $C_{12}H_8S_3$: C, 58.03; H, 3.25; S, 38.73. Found: C, 58.20; H, 3.27; S, 38.64.

A mixed m.p. with a sample of VIII prepared as described below was undepressed.

Methyl 2-Thienylacrylate.—2-Thienylacrylic acid[20] (61.7 g.) was converted to the methyl ester by refluxing for 4.5 hours with 150 ml. of absolute methanol and 33 g. of concentrated sulfuric acid. The ester, 54.3 g., melted at 48–49° after one crystallization from aqueous methanol.

Anal. Calcd. for $C_8H_8O_2S$: S, 19.06. Found: S, 19.10.

2-Thienyl-4-ketotetrahydrothiophene (VIII).—A mixture of 25.2 g. (0.15 mole) of methyl 2-thienylacrylate, 25.0 g. (0.20 mole) of ethyl mercaptoacetate and 1–2 ml. of piperidine was heated at 80–90° for 6 hours, then allowed to stand overnight. Distillation of the reaction mixture furnished 35.6 g. (82%) of mixed diester, b.p. 168–170 (0.6 mm.), n_D^{23} 1.5300. When 53.90 g. of diester sulfide was cyclized in the same manner as described for the preparation of II using 30.0 g. of sodium methoxide in 500 ml. of absolute ether, 17.0 g. (36%) of mixed cyclic ketoesters, b.p. 165–172° (1.0 mm.), was isolated. Decarboalkoxylation of 19.6 g. of ketoester by heating and stirring at 100° in the presence of 200 ml. of 15% sulfuric acid for 4.5 hours furnished 12.85 g. (61%) of 2-thienyl-4-ketotetrahydrothiophene, m.p. 59–60°, after recrystallization from petroleum ether (b.p. 90–100°) followed by ethyl alcohol.

Anal. Calcd. for $C_8H_8S_2O$: C, 52.14; H, 4.38; S, 34.80. Found: C, 52.43; H, 4.66; S, 34.62.

The Grignard Reaction with VIII.—To a Grignard reagent prepared from 4.45 g. of 2-bromothiophene, 1.0 g. of magnesium turnings and 40 ml. of anhydrous ether was added 5.00 g. of 2-thienyl-4-ketotetrahydrothiophene in 30 ml. of ether at such a rate that rapid refluxing was maintained. After decomposition of the complex with dilute sulfuric acid in the usual manner, the organic residue was heated briefly with 10 ml. of 20% sulfuric acid in order to complete the dehydration of the carbinol. The remaining oil (2.85 g.) was heated under reflux for 20 minutes with 3.4 g. of chloranil in 15 ml. of ethylene glycol. The reaction mixture was diluted with 100 ml. of 5% sodium hydroxide solution and extracted with benzene. The benzene extracts were washed with dilute hydrochloric acid and water. Removal of the solvent furnished 1.30 g. (20% from II) of 2,2′;4′,2″-terthienyl, m.p. 53–54°, after several recrystallizations from petroleum ether. A mixed m.p. with the terthienyl obtained by pyrolysis was undepressed.

GRINNELL, IOWA

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[20] W. J. King and F. F. Nord, *J. Org. Chem.*, **14**, 405 (1949).

[CONTRIBUTION FROM THE NUTRITION AND PHYSIOLOGY SECTION, RESEARCH DIVISION, AMERICAN CYANAMID CO., LEDERLE LABORATORIES]

Synthesis of Thioctic Acid and 8-Methylthioctic Acid

BY MILON W. BULLOCK, JOHN J. HAND AND E. L. R. STOKSTAD

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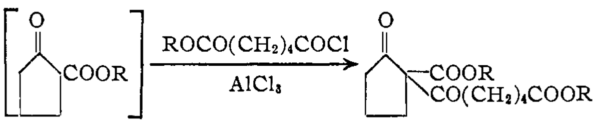
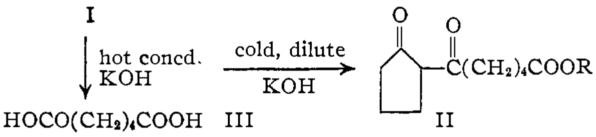
Improved methods are described for the preparation of thioctic acid, 8-methylthioctic acid and intermediates. The condensation of methyl and ethyl 5-chloroformylvalerate with ethylene, propylene and isobutylene have been improved to yield easily purified unsaturated ketoesters. The addition of thioacetic acid to the unsaturated ketones is described as is the reduction of the addition products to the corresponding alcohol.

Several methods for the preparation of thioctic acid have been described.[1–6] Some of the more useful methods require as an intermediate the condensation product of ethyl 5-chloroformylvalerate and ethylene. The initial condensation product, ethyl 8-chloro-6-oxoöctanoate has been dehydrohalogenated thermally to yield the desired ethyl 6-oxo-7-octenoate.[1] We have found that the yields in the condensation and dehydrohalogenation reaction are greatly improved if the condensation is done in ethylene chloride and the intermediate β-chloroketone dehydrohalogenated with sodium acetate. Vigorous stirring is essential during the addition of ethylene. The stirrer should be of the propeller type and should be turning at a sufficiently high speed so that the ethylene is suspended in the reaction mixture as fine bubbles. A side reaction occurring to the extent of 10–15% when ethylene is employed as the olefin is the self condensation of the acid chloride to form ultimately the cyclopentanone derivative I.



The structure of the by-product I has been partially confirmed by the degradation reactions



The degradation product II was obtained from partial saponification of the methyl ester with cold potassium hydroxide. It was isolated as the di-2,4-dinitrophenylhydrazone. Product II was also obtained by redistillation of an old sample of I which had been stored with a trace of hydrogen chloride. The ester gave a pale orange color with ferric chloride solution. Strong hydrolysis of the ethyl ester I with methanolic potassium hydroxide gave 69% yield of adipic acid (III). No readily purified products were obtained by acid hydrolysis.

When propylene or isobutylene was substituted

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[1] M. W. Bullock, J. A. Brockman, Jr., E. L. Patterson, J. V. Pierce, M. H. von Saltza, F. Sanders and E. L. R. Stokstad, THIS JOURNAL, **76**, 1828 (1954).

[2] Q. F. Soper, W. E. Buting, J. W. Cochran, Jr., and A. Pohland, *ibid.*, **76**, 4109 (1954).

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