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Catalytic Reduction of 2-Acylthiophenes

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This study was initiated to determine the usefulness of cobalt polysulfide as a catalyst for the reduction of certain sulfur compounds. It was found that hydrogenation of 2-acylthiophenes in the presence of sulfur and cobalt polysulfide yields alkyl derivatives of thiophene and/or thiacyclopentanes. Under the conditions used, nitro groups as well as carbonyl groups may be reduced. The hydrogenolysis of the halogen in 2-bromothiophenes has been found to occur simultaneously with the reduction of the carbonyl group. These results indicate that, by using this sulfactive catalyst, it is possible to prepare certain alkyl derivatives of thiacyclopentane, compounds which cannot be readily prepared by other known methods.

I. Introduction

The thiocyclopentanes form a group of sulfur compounds about which relatively little is known. They are interesting because of their natural occurrence in biotin and crude oils. Only the simplest members of the cyclic sulfides have been identified with certainty, for two reasons. First, only the simplest members of the series have been prepared. Secondly, the most useful derivatives are the mercuric chloride complexes, but the sulfides can react with one or two moles of mercuric chloride depending on the condition used. In some cases mixtures are obtained and these can be separated only by repeated crystallizations. The early workers were not always aware of these complications and thus some of their results are doubtful. Derivatives of thiacyclopentane, especially the asymmetric members, are difficult to prepare. Ring closure methods[2–4] are long and tedious and yields are often low. The catalytic transformation of tetrahydrofuran and some of its simple derivatives has been studied by Yur'ev[5] and his associates but these methods also suffer certain disadvantages. Probably the most useful method for the preparation of these compounds is catalytic reduction of thiophenes. Because there are very few catalysts which are not poisoned by sulfur or sulfur compounds there was no suitable method for the catalytic reduction of thiophenes until Mozingo[6] and his associates developed a procedure for the use of palladium catalysts at low pressures. This method, though very useful, has its limitations also. A few years ago Farlow and Signaigo[7] reported that when carbonyl compounds were hydrogenated in the presence of sulfur and certain sulfactive catalysts such as iron and cobalt polysulfides there were obtained the corresponding thiols. Consequently a study of the reduction of certain thiophenes using cobalt polysulfide catalyst was carried out in the hope that a supplementary method of catalytic reduction might be developed. A few preliminary experiments indicated that thiophene and 2-methylthiophene were not reduced at an appreciable rate under the conditions employed. The 2-acylthiophenes were reduced readily, but not to thiols.[8]

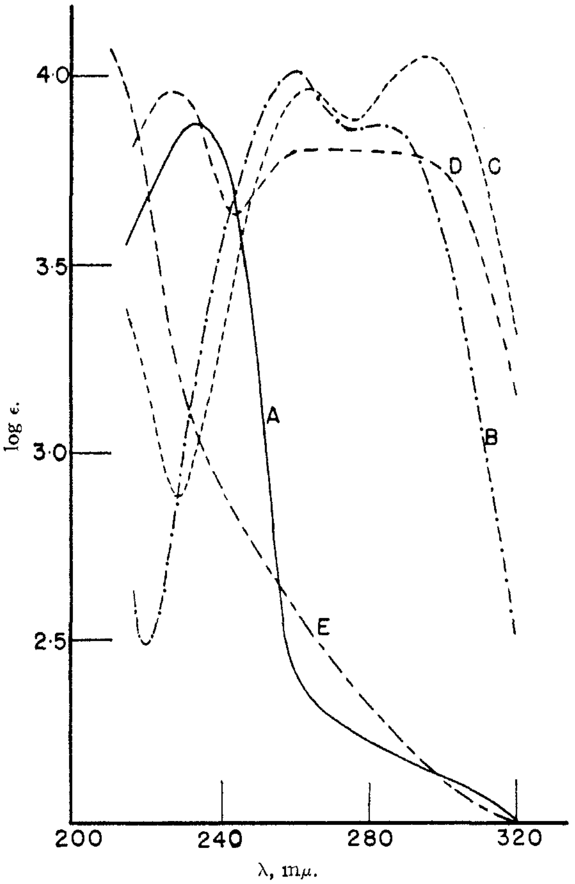

Fig. 1.—Ultraviolet absorption spectra (in 95% ethanol) of thiophene derivatives: A, ——, 2-methylthiophene; B, -·-·, 2-acetylthiophene; C, - - - -, 2-acetyl-5-methylthiophene; D, — — —, 2-benzoylthiophene; E, — - — -, 2-benzyltetramethylene sulfide.

Various 2-acylthiophenes, all of which were prepared by known methods (see Table I), were subjected to hydrogenation under 100–150 atmospheres pressure up to 225° in the presence of cobalt polysulfide and sulfur with glacial acetic as solvent (see Table II for conditions). An attempt was made to characterize the products by preparing certain solid derivatives (Table III) and by determining the ultraviolet absorption spectra of the

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(1) Taken from a thesis submitted in partial fulfillment of the requirements for the degree, Doctor of Philosophy, at Indiana University by James L. Diedrich in June, 1949.

(2) W. Steinkopf, "Die Chemie des Thiophens," Edwards Brothers, Inc., Ann Arbor, Mich., 1941, p. 104.

(3) P. Karrer and H. Schmid, *Helv. Chim. Acta*, **27**, 1275 (1944).

(4) S. A. Harris, *et al.*, THIS JOURNAL, **66**, 1756 (1944).

(5) Y. K. Yur'ev, *et al.*, *J. Gen. Chem.* (*U. S. S. R.*), **11**, 344 (1941).

(6) R. Mozingo, S. A. Harris, D. E. Wolf, C. E. Hoffhine, Jr., N. R. Easton and K. Folkers, THIS JOURNAL, **67**, 2092 (1945).

(7) (a) M. W. Farlow and F. K. Signaigo, U. S. Patent 2,402,613 (1946); *C. A.*, **40**, 5758 (1946). (b) See also M. W. Farlow, W. A. Lazier and F. K. Signaigo, *Ind. Eng. Chem.*, **42**, 2457 (1950).

(8) A referee has called our attention to the fact that acetophenone under these drastic conditions yields ethylbenzene (7b), but at lower temperatures some thiol is obtained. Therefore, it is not surprising that complete reduction of the side-chain occurred in these experiments, and it is possible that under milder conditions of temperature some thiols could be produced from acylthiophenes.

TABLE I

STARTING MATERIALS

Thiophene prepared	Yield, %	B.p. or m.p.^{a} Found °C.	Found Mm.	Reported °C.	Reported Mm.	Derivative	M.p.^{a} (°C.) Found	M.p.^{a} (°C.) Rptd.
2-Formyl-^{b} (thenaldehyde)	65	82–84	10	66–67	4^{b}	Oxime	111	111–112^{c}
2-Acetyl-^{d}	83	65–68	1	77	4^{e}	2,4-DNP^{f}	254	.....^{g}
2-Acetyl-5-bromo-^{h}	50	M.p. 95		94^{i}		....	...	.....
2-Acetyl-5-methyl-^{j}	79	95–97	10	85	2^{k}	Oxime	124	125^{k}
2-Propanoyl-^{d}	69	85–87	3	88	7^{k}	2,4-DNP	220	.....^{l}
2-Butanoyl-^{d}	57	90–95	2	87-92	3^{k}	2,4-DNP	167	.....^{m}
2-Hexanoyl-^{d}	82	114–117	1	117–119	1^{n}	2,4-DNP	156	153^{n}
2-β-Carboxypropanoyl-^{o}	67	M.p. 120		120.5		......	...	.....
2-Benzoyl-^{d}	62	M.p. 50		55.5–56^{p}		......	...	.....
2-Methyl-3-nitro-5-acetyl-^{q}	62	M.p. 123		123^{q}		......	...	.....

[a] All melting points corrected. [b] Method of W. J. King and F. F. Nord, *J. Org. Chem.*, **13**, 635 (1948). [c] W. Steinkopf, "Die Chemie des Thiophens," Edwards Brothers, Inc., Ann Arbor, Mich., 1941, p. 67. [d] "Organic Syntheses," Coll. Vol. II, 1943, p. 8. [e] H. D. Hartough and L. G. Conley, THIS JOURNAL, **69**, 3096 (1947). [f] 2,4-Dinitrophenylhydrazone. [g] *Anal.* Calcd. for $C_{12}H_{10}N_4O_4S$: S, 10.47. Found: S, 10.59. [h] 2-Bromothiophene was prepared by method of E. Krause and G. Renwanz, *Ber.*, **62**, 1710 (1929), and acetylated. [i] L. Gattermann and M. Romer, *ibid.*, 19, 688 (1886). [j] By acetylation of 2-methylthiophene. [k] H. D. Hartough and A. I. Kosak, THIS JOURNAL, **69**, 3093 (1947). [l] *Anal.* Calcd. for $C_{13}H_{12}N_4O_4S$: S, 10.01; found: S, 9.95. [m] *Anal.* Calcd. for $C_{14}H_{14}N_4O_4S$: S, 9.59. Found: S, 9.71. [n] E. Campaigne and J. L. Diedrich, THIS JOURNAL, **70**, 391 (1948). [o] Method of D. Papa, E. Schwenk and H. Hankin, *ibid.*, **69**, 3018 (1947). [p] W. Steinkopf, "Die Chemie des Thiophens," Edwards Brothers, Inc., Ann Arbor, Mich., 1941, p. 76. [q] H. Grose, Ph.D. Thesis, Indiana University, 1951.

TABLE II

CONDITIONS AND PRODUCTS

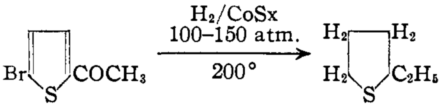
	Conditions^{a}				Principal products							
							Constants				Constants	
Thiophene reduced	Amt., g.	Solvent,^{b} g.	Time, hr.	Yield, g.	Thiophene	Yield,^{c} %	B.p., °C.	$n^{20}D$	Thiacyclopentane	Yield,^{c} %	B.p., °C.	$n^{20}D$
2-Formyl-	28^{d}	50	5	0	....				....			
2-Acetyl	64^{e}	50	2	29	2-Ethyl	50	134–136^{f}	....	2-Ethyl	50	137–139^{g}	1.4862
2-Acetyl-5-bromo	51^{d}	500	6	15	2-Ethyl	25	134–136^{f}	....	2-Ethyl	75	136–139^{g}	1.4871^{g}
2-Acetyl-5-methyl	35^{d}	0	3	18	2-Ethyl-5-methyl	80	173–177	1.5015	2-Ethyl-5-methyl-	15	.....^{h}	....^{h}
2-Propanoyl	70^{e}	0	3	20	2-Propyl-	100	157–159	1.4930	....	0	.....	....
2-β-Carboxypropanoyl	46^{d}	400	6	21	2-β-Carboxypropyl	100	138–140 (2 mm.)	1.5394	....	0	.....	....
2-Butanoyl-	39^{d}	500	13	23	2-Butyl	65	185–189	1.4914	2-Butyl	30	.....^{i}	....^{i}
2-Hexanoyl-	45^{d}	300	5	17	2-Hexyl	95	90–93 (6 mm.)	1.4919	....	0		
2-Benzoyl-	47^{d}	100	4	23	....	0	.....	....	2-Benzyl	95	M.p. 51^{j}	
2-Methyl-3-nitro-5-acetyl	23^{k}	500	4	13	2-Methyl-3-acetamino-5-ethyl-	100	M.p. 101^{l}		....	0	.....	....

[a] Temp., 200–225°; initial press., 1400–1500 p.s.i.; sulfur, 15–16 g.; catalyst, CoSx paste, 20–25 g. [b] Glacial acetic acid. [c] % of product obtained based on yield of $HgCl_2$ derivatives. Where sum of the two columns is less than 100%, the balance is considered to be starting material. [d] One-quarter mole. [e] One-half mole. [f] Steinkopf, Frommel and Leo, *Ann.*, **546**, 199 (1941), report 132–134°. [g] Yur'ev[5] reports b.p. 155.5–156.5° (753 mm.), $n^{20}D$ 1.4896 for this sulfide. [h] Isolated as the di-mercuric chloride addition product. [i] Isolated as the mono-mercuric chloride addition product. [j] *Anal.* Calcd. for $C_{11}H_{14}S$: S, 18.09. Found: S, 18.04. [k] One-eighth mole. [l] *Anal.* Calcd. for $C_9H_{13}NOS$: C, 59.01; H, 7.10; N, 7.65. Found: C, 59.35; H, 7.25; N, 7.95.

starting materials and products (refer to Table IV for absorption maxima and to Fig. 1 for typical absorption curves). Most of the crude products isolated after reduction were mixtures which could not be separated by distillation. Samples of each mixture were added to acetone solutions of mercuric chloride. If a thiacyclopentane was present precipitation occurred after a few minutes standing, but thiophene derivatives did not react under those conditions. The latter were isolated from the mixtures through the formation of chloromercuric derivatives.

II. Discussion

It was found that the principal product in the case of 2-acetyl-, 2-acetyl-5-bromo- and 2-benzoylthiophene was the corresponding alkyl derivative of thiacyclopentane. In the case of the bromo derivative the reduction was accompanied by hydrogenolysis of the bromine atom. The other



2-acylthiophenes yielded the corresponding 2-alkylthiophenes as principal products with some 2-alkylthiacyclopentanes being formed. The only product isolated after the reduction of 2-thenaldehyde was a small amount of viscous oil which has not been identified.

TABLE III

MERCURIC CHLORIDE DERIVATIVES

A. Thiophenes	Derivative Chloromercuri	M.p.,[a] °C.	Formula	Hg, % Calcd.	Hg, % Found
2-Ethyl-	Mono	147–148[b]	$C_6H_{11}ClHgS$	...	...
2-Ethyl-5-methyl-	Mono	200	C_7H_9ClHgS	8.8[c]	8.6[c]
2-Propyl-	Di	240	$C_7H_9Cl_2Hg_2S$	67.2	67.1
2-Hexyl-	Di	270	$C_{10}H_{14}Cl_2Hg_2S$	62.8	62.5
B. Thiacyclopentanes	Mercuric chloride				
2-Ethyl-	Mono	100[d]	$C_6H_{12}Cl_2HgS$	8.3[c]	8.4[c]
	Di	210	$C_6H_{12}Cl_4Hg_2S$	60.8	60.6
2-Ethyl-5-methyl-	Di	146–148	$C_7H_{14}Cl_4Hg_2S$	59.6	59.6
2-Butyl-	Mono	100–101	$C_6H_{16}Cl_2HgS$	48.3	48.3
2-Benzyl-	Mono	174–175	$C_{11}H_{14}Cl_2HgS$	44.6	44.5

[a] All melting points corrected. [b] M.p. 148°, W. Steinkopf, *Ann.*, **424**, 23 (1920), [c] % S. [d] In agreement with Yur'ev.[5]

TABLE IV

ULTRAVIOLET ABSORPTION SPECTRA[a]

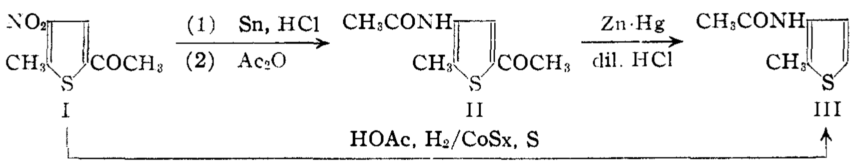
Compound	Source[b]	Maxima mμ	log ε
Thiophene	1	230	3.85
A. 2-Alkylthiophenes			
Methylthiophene	1	232	3.87
Propylthiophene	2	234	3.88
γ-Carboxypropylthiophene	3	234	3.81
Hexylthiophene	4	234	3.91
B. 2-Acylthiophenes			
Acetylthiophene	1	260	4.01
		283	3.87
Propanoylthiophene	5	260	3.99
		282	3.88
β-Carboxypropanoylthiophene	6	260	3.97
		282	3.86
Butanoylthiophene	5	260	4.07
		282	3.95
Hexanoylthiophene	5	260	3.99
		283	3.88
Benzoylthiophene	5	260–290[c]	3.80
		226	3.96
C. 2,5-Disubstituted thiophenes			
2-Acetyl-5-methylthiophene	7	264	3.96
		295	4.05
2-Acetyl-5-bromothiophene	8	268	3.91
		294	4.08

[a] All spectra were determined with 95% ethanol. Source references: (1) purified commercial material; (2) catalytic reduction of 2-propanoylthiophene over cobalt polysulfide; (3) catalytic reduction of 2-β-carboxypropanoylthiophene over cobalt polysulfide; (4) Clemmensen reduction of 2-hexanoylthiophene; (5) acylation of thiophene; (6) acylation of thiophene using β-carbomethoxypropanoyl chloride; (7) acetylation of 2-methylthiophene; (8) acetylation of 2-bromothiophene. [c] Plateau.

2-Ethylthiacyclopentane exhibited the properties of an aliphatic sulfide; that is, it formed addition products with mercuric salts and a sulfonium iodide with methyl iodide. It reacted readily with bromine but the product was unstable, as were the mercuric iodide complex and sulfonium salts. Furthermore, the sulfide exhibited strong absorption in the ultraviolet region near 210 mμ. This is a characteristic of aliphatic sulfides as shown by the report of Fehnel and Carmack.[9] For comparison, 2-ethylthiacyclopentane was prepared by the following method. 2-Acetylthiophene was reduced to 2-ethylthiophene by a modified Clemmensen reduction, and the ring reduced by low-pressure hydrogenation over a palladium catalyst. The monomercuric chloride complex of this sulfide exhibited the same melting point, 100°, as the corresponding complex from the cobalt polysulfide-catalyzed reduction product of 2-acetylthiophene, and a mixture of the two showed no depression. It should be noted that 2-ethylthiacyclopentane also forms a complex containing two molecules of mercuric chloride which melts at 210°.

Likewise, 2-benzylthiacyclopentane showed the properties of a sulfide. It formed a mercuric chloride complex and absorbed light strongly in the lower region of the ultraviolet spectrum (Fig. 1). Oxidation of this sulfide with alkaline permanganate yielded the corresponding sulfone.

Hydrogenation of 2-methyl-3-nitro-5-acetylthiophene (I) gave a solid which appeared to be the acetyl derivative of 2-methyl-3-amino-5-ethylthiophene (III). An authentic sample was prepared from I for comparison. Reduction with tin and hydrochloric acid followed by acetylation gave 2-methyl-3-acetamino-5-acetylthiophene (II) which yielded (III) upon reduction with amalgamated zinc and dilute hydrochloric acid.



The results of these experiments indicate that, while there may be some limitations to the reaction, cobalt polysulfide is a useful catalyst for the preparation of alkyl derivatives of thiophene and thiacyclopentane by hydrogenation procedures. It appears that the keto group is reduced more readily than the ring but ring reduction proceeds only when the ring unsaturation is part of the conjugated system which includes the carbonyl system. The behavior of nitro and halogen derivatives followed the same pattern observed for these thiophene derivatives by Mozingo[6] and his associates using palladium catalysts at low pressures. The nitro group was reduced readily, as in the benzene series,[10] and the bromine atom at the 2-position expelled. In the case of thiophene itself there was no sign of reduction. Likewise, 2-thenoic acid was unchanged.

III. Experimental

Nitration of 2-Acetyl-5-methylthiophene.[11]—A solution of 10 ml. of fuming nitric acid in 50 ml. each of acetic anhy-

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[9] E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 84 (1949).

[10] W. V. Freed and F. K. Signaigo, U. S. Patent 2,344,244 (1944); *C. A.*, **38**, 3663 (1944); F. K. Signaigo, U. S. Patent 2,402,686 (1946); *C. A.*, **40**, 5766 (1946).

[11] H. Grose, Ph.D. Thesis, Indiana University, 1951, p. 73.

dride and acetic acid was cooled to −10° in a three-necked flask equipped with thermometer, stirrer and separatory funnel. To the cold solution was added dropwise 7 g. (0.05 mole) of 2-acetyl-5-methylthiophene in 10 ml. of acetic anhydride with the temperature maintained at −5 to −10°. Toward the end of the addition a white precipitate separated from solution. The solid was collected, washed with dilute bicarbonate and then with water. The yield of 2-methyl-3-nitro-5-acetylthiophene, m.p. 123°, was 3.3 g. Another 2.5 g. was obtained from the filtrate to give a total yield of 5.8 g. (62%).

Anal. Calcd. for $C_7H_7O_3NS$: S, 17.31; N, 7.56. Found: S, 16.84; N, 7.78.

Cobalt Polysulfide Catalyst.[7]—About 100 g. of sodium sulfide and 28 g. of sulfur in 300 ml. of water was added rapidly to a solution of 74 g. of cobalt chloride hexahydrate in 170 ml. of water. The black precipitate was filtered on a large büchner funnel and washed with water, then with dioxane and stored as a paste in a glass-stoppered wide-mouth bottle.

Hydrogenation Apparatus.—The apparatus was obtained from the American Instrument Company of Silver Springs, Maryland. The volume of bomb was approximately 2.5 liters. A dial pressure gage calibrated to 5000 p.s.i. was connected to the bomb head through a two-way needle valve. Temperature control was accomplished by means of an electrically heated jacket, a thermocouple, a relay, an indicating and controlling potentiometer, a rheostat, an ammeter and suitable switches and connections. The charged bomb was agitated by a rocking mechanism.

General Procedure for Hydrogenation Over Cobalt Polysulfide.—The bomb was charged with the compound to be reduced, sulfur, cobalt polysulfide paste and solvent. After sealing the bomb carefully hydrogen was introduced under a pressure of 100 atmospheres. The mixture was heated to about 200° and shaken at constant temperature. The cooled bomb was opened and the contents emptied. The vessel was rinsed with ether and the washings added to the reaction mixture. After filtering off the catalyst and gummy residue the filtrate was diluted with water and extracted with ether. The ether was distilled from the dried extracts and the residue distilled.

Mercuric Chloride Complexes.—One ml. of the reduction product was added to a solution of 2.7 g. of mercuric chloride in 25 ml. of acetone. The precipitate was separated on a Hirsch funnel and recrystallized from acetone.

Chloromercuric Derivatives.[12]—The thiophene derivative (0.01 mole) was dissolved in 50 ml. of glacial acetic acid, warmed, and added to a warm solution of mercuric acetate (6.4 g., 0.02 mole) in 40 ml. of 50% acetic acid. After warming the mixture on the steam-bath for one hour a solution of sodium chloride (2 g., 0.03 mole) in 200 ml. of water was added. The precipitate was digested for an hour on the steam-bath, then separated by filtration and washed with water and alcohol. The product was purified by dissolving in pyridine, filtering, and reprecipitating with water.

Clemmensen Reduction of 2-Acetylthiophene.—Amalgamated zinc, prepared from 125 g. of mossy zinc, was placed in a 500-ml. round-bottom flask and covered with 225 ml. of 1:1 hydrochloric acid solution. About 12 g. (0.1 mole) of acetylthiophene was added and the mixture warmed for 20 minutes. Heating was discontinued and the reaction allowed to proceed at room temperature for several hours. Then the mixture was extracted with ether. The dried extract was partially evaporated and the residue distilled to give 2.7 g. (27%) of 2-ethylthiophene, b.p. 134–36°. 2-Ethyl-5-chloromercurithiophene was found to melt at 147°.

Palladium-Catalyzed Reduction of 2-Ethylthiophene.—The catalyst for this experiment was prepared[6] and tested by reducing 0.4 g. of thiophene.

Ten grams of palladium on Darco catalyst was reduced in 200 ml. of methanol with hydrogen at 50 pounds pressure. To the reduced catalyst and methanol were added 1.4 ml. of concentrated sulfuric acid and 0.5 g. (0.005 mole) of 2-ethylthiophene. The mixture was shaken under 50 pounds of hydrogen for 12 hours. At the end of that time the drop in pressure was only about 0.3 pound (as compared with 0.8–1.0 pound for an equivalent amount of thiophene). The catalyst was removed by filtration and the filtrate warmed with 2.7 g. of mercuric chloride at 45°. Shortly after diluting the warm mixture with water, fine needles precipitated from the solution. The precipitate was collected on a filter and washed. The yield of mercuric chloride addition product, m.p. 100°, was 0.9 g. (46%).

2-Benzylthiacyclopentane-1,1-dioxide.—About 2 g. of the product obtained by reduction of 2-benzoylthiophene was added to 100 ml. of 50% alcohol. Then 8 g. of potassium permanganate and 1 ml. of 25% sodium hydroxide were added and the mixture diluted to 200 ml. After refluxing the mixture for an hour, another 5 g. of permanganate was added and the refluxing continued one hour. The mixture was cooled, acidified and the manganese dioxide removed by the addition of bisulfite solution. The solid substance which remained was separated by filtration and washed with water. The sulfone, after one crystallization from water, melted at 188–189°.

Anal. Calcd. for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71; S, 15.25. Found: C, 62.60; H, 6.97; S, 14.90.

2-Methyl-3-acetamino-5-acetylthiophene.—To 45 ml. of concentrated hydrochloric acid and 3.7 g. (0.02 mole) of 2-methyl-3-nitro-5-acetylthiophene at 40–45° was added with stirring 4.5 g. of tin. Stirring was continued until all the metal was in solution, after which the mixture was filtered and the precipitate washed with a little alcohol and ether. A solution containing 3 g. of the tin salt in 9 ml. of water was covered with a mixture of 2.5 g. of acetic anhydride and 2.5 ml. of ether. The whole mixture was added with shaking and cooling to a solution of 4 g. of sodium hydroxide in 4 ml. of water. The precipitate was separated by filtration, washed and recrystallized from water. The yield of 2-methyl-3-acetamino-5-acetylthiophene, m.p. 167°, was 1.5 g. (65%).

Anal. Calcd. for $C_9H_{11}O_2NS$: N, 7.10. Found: N, 6.77.

2-Methyl-3-acetamino-5-ethylthiophene.—One gram (0.005 mole) of the ketone from the preceding experiment was allowed to stand with 25 ml. of 1:1 hydrochloric acid over amalgamated zinc. The mixture was shaken occasionally and every few hours another 15 ml. of 1:1 acid was added. After 10 hours the solution was filtered, one ml. of acetic anhydride added and the solution neutralized with sodium hydroxide solution. The precipitate, which was crystallized from water, melted at 101°. A mixed-melting point determination showed this compound to be identical with that obtained by the cobalt polysulfide-catalyzed reduction of 2-methyl-3-nitro-5-acetylthiophene in glacial acetic acid.

Ultraviolet Absorption Measurements.—All the spectrophotometric measurements referred to in this report were made with a Beckman quartz spectrophotometer, model DU, using a spectral band width of 1 m. and 95% ethanol as solvent.

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BLOOMINGTON, INDIANA RECEIVED MARCH 10, 1951

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(12) C. D. Hurd and H. M. Priestley, THIS JOURNAL, **69**, 859 (1947).