by refluxing in alcoholic potassium hydroxide solution and subsequently neutralizing with hydrochloric acid.

Ethyl 2-ethyl-3-methyl-3-butenoate (II) yielded an acid, b.p. 85° at 4 mm.; n^{20}_D 1.4400; neutralization equivalent calcd. 128, found 130. This acid was isolated with difficulty due to the general tendency of β,γ-unsaturated acids to rearrange to the conjugated α,β-acids in the presence of base.[18] Hydrolysis of (III) yielded a white solid which, on recrystallization from water–ethanol, gave plates melting at 47–48°; b.p. 85° (2 mm.); micro b.p. 218° (741 mm.) with decomposition; neutralization equivalent calcd. 128, found 129.

Summary

Ethyl 3-hydroxy-2-ethyl-3-methylbutanoate has been dehydrated to ethyl 2-ethyl-3-methyl-2-butenoate and ethyl 2-ethyl-3-methyl-3-butenoate. These have been isolated and their physical constants determined.

The structure of these unsaturated esters has been assigned on the basis of the ketones to which they have been degraded.

These unsaturated esters have been hydrolyzed and the corresponding acids isolated.

EAST LANSING, MICHIGAN RECEIVED SEPTEMBER 12, 1947

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[18] Gilman, "Organic Chemistry, An Advanced Treatise," second edition, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 684.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF INDIANA UNIVERSITY]

Some Derivatives of 2-Acylthiophenes[1]

BY E. CAMPAIGNE AND JAMES LOREN DIEDRICH[2]

Several acylthiophenes ranging in side-chain length from two to eighteen carbon atoms[3] have been prepared, usually by some modification of the procedure described by Johnson and May[4] for the preparation of 2-acetylthiophene. The capric acid derivative was prepared by Schleicher,[5] but the homologous 2-hexanoyl, 2-octanoyl, and 2-nonanoylthiophenes have not been synthesized previously.[5a]

The acylthiophenes provide convenient intermediates for the preparation of the corresponding alcohols and alkylthiophenes. The thienyl ketones were readily reduced to the corresponding secondary alcohols by using aluminum isopropoxide in isopropyl alcohol as described by Mowry, Renoll and Huber[6] for 2-acetylthiophene; however, the yields were somewhat lower with the higher molecular weight ketones. The alkylthiophenes were prepared from the ketones by a slight modification of the Clemmensen method described by Fieser and Kennelly.[7]

In addition to the ketones, alcohols and alkylthiophenes, the characteristics of which are summarized in Table I, the oximes, semicarbazones and 2,4-dinitrophenylhydrazones of the ketones, and the 5-chloromercuri derivatives of the alkylthiophenes were prepared and characterized.

An attempt was made to prepare suitable urethans or esters of the secondary alcohols as solid derivatives but the hydroxy group is relatively inactive, apparently due to hindrance of the α-carbon in 2-substituted thiophenes,[8] and no derivatives were isolated.

Experimental

Acylthiophenes.—The procedure used for the ketone preparations was essentially that of Johnson and May[4] for the preparation of acetylthiophene. The thiophene, obtained from the Socony-Vacuum Oil Company, was distilled through a column and the fraction boiling from 82–84° was collected and stored in brown bottles until used. In each acylation freshly distilled stannic chloride was employed. The best yields of the ketones were obtained under the following conditions: 0.5 mole of thiophene and 0.5 mole of the required acid chloride were dissolved in 500 ml. of benzene in a 3-necked flask equipped with a mechanical stirrer, thermometer and dropping funnel, and the mixture was cooled to 0° with stirring. Stannic chloride (0.5 mole) was then added dropwise over a period of one and one-half hours, maintaining the temperature at 0°. When all of the stannic chloride had been added, the cooling bath was removed and stirring was continued for one hour longer. Dilute hydrochloric acid was then added and the benzene layer was separated, washed and dried. The ketone was isolated and purified by distillation.

2-Alkylthiophenes.—The preparation of 2-octylthiophene is typical. A mixture of 125 g. of amalgamated zinc, 225 ml. of 1:1 hydrochloric acid and 26.2 g. (0.125 mole) of 2-octanoylthiophene was allowed to stand in a water-bath at 22° for three and one-half days. To complete the reaction the mixture was refluxed gently for twenty minutes. It was then cooled, extracted several times with ether and the combined ether extracts dried. The ether was removed and the residue distilled at reduced pressure. The yield of colorless oil, b.p. 106–108° at 1 mm., was 13.5 g. (55%).

1-(2-Thienyl)-alkanols.—The preparation of 1-(2-thienyl)-nonanol is typical. In a 125-ml. three-necked flask equipped with stirrer, distilling column and nitrogen-inlet tube was mixed 5.6 g. (0.025 mole) of 2-nonanoylthiophene and three times the calculated quantity of pure freshly distilled aluminum isopropoxide (5 g., 0.025 mole) in 30 ml. of dry isopropyl alcohol. The mixture was heated under an atmosphere of nitrogen to 100–110°, and acetone and isopropyl alcohol were allowed to distill from the mixture. When 12–13 ml. of distillate had been collected an additional 10 ml. of dry isopropyl alcohol was

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[1] Taken from a thesis submitted by James Loren Diedrich to the Faculty of the Graduate School in partial fulfillment of the requirements for the degree, Master of Arts, in the Department of Chemistry, Indiana University, June, 1947.

[2] The Ohio Oil Company Fellow in Chemistry.

[3] Ralston and Christensen, *Ind. Eng. Chem.*, **29**, 194 (1937).

[4] Johnson and May, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 8.

[5] Schleicher, *Ber.*, **19**, 660 (1886).

[5a] Since this paper was accepted, Cagniant and Deluzarche (*Compt. rend.*, **225**, 455 (1947)) report the preparation of a series of acylthiophenes, including those described here.

[6] Mowry, Renoll and Huber, THIS JOURNAL, **68**, 1105 (1946).

[7] Fieser and Kennelly, *ibid.*, **57**, 1615 (1935).

[8] Chabrier and Tchoubar, *Compt. rend.*, **220**, 284 (1945).

TABLE I

2-SUBSTITUTED THIOPHENES AND DERIVATIVES[a]

	Yield, %	B. p., °C. (1 mm.)	d^{20}_{4}[b]	n^{20}_{D}	Formula	Sulfur, % Calcd.	Sulfur, % Found	Oximes M. p., °C.	Oximes Sulfur, % Calcd.	Oximes Sulfur, % Found
2-Hexanoylthiophene[c]	78	117–119	1.065	1.5301	$C_{10}H_{14}OS$	17.59	17.73	53–54[d]	16.25	16.58
2-Octanoylthiophene[e]	78	140–143	1.005	1.5214	$C_{12}H_{18}OS$	15.24	14.88	56–57[f]	14.23	14.30
2-Nonanoylthiophene[g]	80	155–157	0.970	1.4917	$C_{13}H_{20}OS$	14.29	13.85	(Oil)[h]		
1-(2-thienyl)-hexanol	60	110–112	1.055	1.5155	$C_{10}H_{16}OS$	17.40	17.48			
1-(2-thienyl)-octanol	41	133–135	0.973	1.5203	$C_{12}H_{20}OS$	15.10	15.37			
1-(2-thienyl)-nonanol	47	149–152	.938	1.4902	$C_{13}H_{22}OS$	13.45	13.71	5-Chloromercuri-	Mercury, % Calcd.	Found
2-Hexylthiophene	44	79–82	.946	1.4970	$C_{10}H_{16}S$	19.05	19.02	140–141[i]	49.8	49.3
2-Octylthiophene[j]	55	106–108	.920	1.4824	$C_{12}H_{20}S$	16.33	15.94	136–137[i]	46.5	46.3
2-Nonylthiophene	38	128–131	.906	1.4763	$C_{13}H_{22}S$	15.24	15.11	135–136[i]	45.0	44.6

[a] All boiling and melting points uncorrected. [b] All density measurements made with a Fisher–Davidson Gravitometer. [c] Semicarbazone, m. p. 133–134°; % S, calcd.,13.40; found, 13.59. 2,4-DNP (2,4-dinitrophenylhydrazone), m. p. 152–153°; % S, calcd., 8.85; found, 9.10. [d] Yield, 83% on 0.1 mole run. [e] Semicarbazone, m. p. 127–129°; % S, calcd., 11.99; found, 12.27. 2,4-DNP, m. p. 123–125; % S, calcd., 8.21; found, 8.40. [f] Mixed m. p. with 2-hexanoylthiophene oxime, 48–51°. [g] Semicarbazone, m. p. 134–135 (mixed m. p. with 2-hexanoylthiophene semicarbazone, 103–109°). % S, calcd., 11.40; found, 11.50. 2,4-DNP, m. p. 108–109°. % S, calcd., 7.93; found, 7.73. [h] An intractable oil, not isolated. [i] Mixture of all possible pairs of these three derivatives melted about 40° lower and over a 20° range, *i. e.*, about 95–120°. [j] Prepared by Schweinitz (*Ber.*, 19, 644 (1886)) by a Wurtz–Fittig reaction, b. p. 257–259°.

added to the reaction mixture and distillation continued until 25 ml. of distillate had been collected. The residue was decomposed with dilute acid, extracted with ether and the ether extracts washed and dried over potassium carbonate. Distillation of the ether-free residue yielded 2.8 g. (47%) of 1-(2-thienyl)-nonanol, b.p. 150–156° at 2 mm.

Acknowledgment.—We are deeply indebted to the Ohio Oil Company for the financial support of this research.

Summary

A number of thiophenes having alkyl, 1-alkanol and acyl groups substituted in the 2-position have been synthesized and characterized. Some solid derivatives of these compounds have also been made.

BLOOMINGTON, INDIANA RECEIVED AUGUST 15, 1947

[CONTRIBUTION FROM THE DIVISION OF FUEL TECHNOLOGY, THE PENNSYLVANIA STATE COLLEGE]

The Distribution of Nitrogen in the Oxidation Products of Coals and Selected Nitrogen Compounds[1]

BY C. R. KINNEY, J. W. ECKERD, PAULINE REXFORD AND H. B. CHARMBURY

The chemical nature of the nitrogen occurring in coals is little understood, although it is agreed that its source is the proteins of the plants, animals, and microörganisms that inhabited the coal-swamps. In a peat, as much as 78.5% of the nitrogen can be extracted by dilute acid[2] but the percentage of the nitrogen extracted from coals rapidly falls with increasing rank; lignite, 21.8%; bituminous coal, 5.4%; anthracite, 2.6%. The nitrogen compounds which are extracted are largely amino acids among which present-day acids have been identified. The decrease in extractability of nitrogen compounds from the higher rank fuels indicates that the proteins or the amino acids present in the original starting material have undergone condensation reactions, possibly of the type suggested by Maillard.[3]

A knowledge of the chemical nature of the nitrogen in coal might be of particular value in the coking industry because of the possibility of making changes in the yields of nitrogen products and it might also be of importance in the hydrogenation of coal because of the amines which may be obtained. When coal is coked, 50% or more of the nitrogen remains in the coke,[4,5] about 15–20% is evolved as ammonia and 25–30% as free nitrogen. The formation of a variety of nitrogen-containing products strongly suggests that more than one nitrogen structure occurs in coal.

On the hydrogenolysis of coal[6] a considerable part of the nitrogen is evolved as ammonia. At moderate temperatures, less than 500°, the maxi-

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[1] Presented before the Division of Gas and Fuels, Atlantic City Meeting of the American Chemical Society, April 17, 1947.

[2] Shacklock and Drakely, *J. Soc. Chem. Ind.*, **46**, 478–81T (1927).

[3] Maillard, *Ann. chim.*, **7**, 113–152 (1917); for a discussion of this work see "Chemistry of Coal Utilization," H. H. Lowry, Editor, John Wiley and Sons. Inc., New York, N. Y., 1945, chapter 13, W. R. Kirner, page 452.

[4] In the older literature low nitrogen analyses of cokes were reported because the ordinary Kjeldahl procedure failed to obtain all of the nitrogen from cokes and to obtain a material balance the difference was often ascribed to a larger yield of gaseous nitrogen.

[5] Lowry, Landan and Naugle, *Trans. A. I. M. E.*, **149**, 297–330 (1942), have published average percentages of nitrogen distributed among the carbonization products of a number of coals. Using these data it can be calculated that the average per cent. of the nitrogen remaining in 1000°-coke is 56.6%.

[6] Storch, Hirst, Fisher and Sprunk, *U. S. Bur. Mines Tech. Paper* **622**, 53, Table 24 (1941).