identified as azelaic and sebacic acids by chromatographing a sample of the mixed dicarboxylic acids to which known quantities of azelaic and sebacic acids had been added. The dicarboxylic acids obtained from *cis*-9,10-epoxyoctadecyl acetate consisted of 54.4 mole percent azelaic and 45.6 mole percent sebacic acids.

Application of the above described procedures to the dicarboxylic acids obtained from *cis*-9,10-epoxyoctadecanol showed the mixture to be 54.8 mole percent azelaic and 45.2 mole percent sebacic acids.

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NEW ORLEANS, LA.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF MARQUETTE UNIVERSITY AND IOWA STATE COLLEGE]

Studies in the Synthesis of Long-Chained Hydroxy Acids

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Four long-chained hydroxy acids have been prepared. Included in the group are 6-hydroxyhexacosanoic acid, 4-hydroxytetracosanoic acid, 10-hydroxydotriacontanoic acid, and 10-hydroxyhexacosanoic acid. In each preparation, thiophene was used as a chain extender, the thiophene sulfur ultimately being removed by desulfurization.

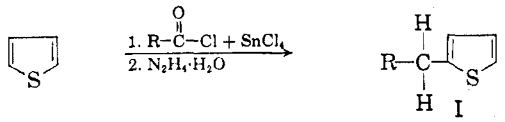
The preparation of hydroxy acids has generally been based upon hydrolysis of the halogenated acid or reduction of the keto acid. Because of the relative unavailability of the starting materials such syntheses have, of necessity, been limited. The present work was thus undertaken to investigate the synthesis of hydroxy acids by Raney nickel catalyzed reduction and desulfurization of selected acidic derivatives of thiophene.

While it has been known for about twenty years that Raney nickel easily and readily desulfurized sulfur-containing organic compounds,[1] it is only during the most recent years that the desulfurization reaction has been used in various synthetic applications. The preparation of an aldehyde from a thiolester[2] is an example.

Of greater importance to the present study is the work which has been carried out on the desulfurization of thiophene derivatives.[3–5] During the past four years a number of investigators[6–10] have reported the synthesis of fatty acids by the desulfurization of substituted thiophenes.

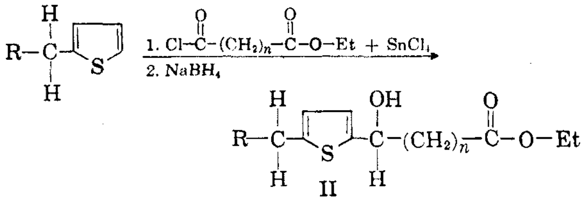
Even more recently the work has been extended by the splendid studies of Wynberg and co-workers[11] to the preparation of long-chain mono- and dicarboxylic acids, ketones, alcohols and hydrocarbons.

The acylation of thiophene by an acyl chloride[9] using anhydrous stannic chloride as catalyst was followed by reduction of the resulting acylthiophene with hydrazine hydrate.[12] The resultant



I

n-alkylthiophene was then acylated with a selected ester-acid chloride, this acylation being followed by reduction of the keto compound to the corresponding hydroxy compound, employing sodium borohydride as the reducing agent.[13–15] Reduction



II

and desulfurization[9,10] of the acidic thiophenes obtained by hydrolysis of the corresponding thienyl esters yielded the desired hydroxy acids.

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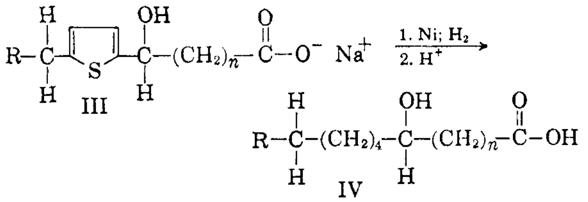

It can thus be seen that, while the total chain-length of the hydroxy acid will be dependent upon both the monobasic and dibasic acid used in the synthesis, the position of the hydroxyl group will be entirely dependent upon the chain-length of the dibasic acid.

EXPERIMENTAL[16]

Acyl and ester-acid chlorides. These were prepared by the action of thionyl chloride on fatty acids and methyl or ethyl hydrogen esters, respectively. In the case of the fatty acids, benzene was employed as solvent. The general procedure was that as described in *Organic Syntheses*.[17,18] All products were obtained in a pure state by vacuum distillation, the distillation being carried out under a nitrogen atmosphere.

Acylthiophenes. A mixture of 40.7 g. hexadecanoyl chloride, 12.5 g. thiophene and 175 ml. anhydrous thiophene-free benzene was cooled to −5° and 16.5 g. anhydrous stannic chloride was added dropwise, with stirring, during 45 min.[19] After removing the ice bath, the mixture was stirred for an additional 4 hr. Decomposition of the reaction mixture was then accomplished by the addition of 100 ml. of 10% hydrochloric acid. After separation, the benzene layer was washed with 10% hydrochloric acid, water, 5% sodium carbonate (aqueous), and water, then dried over calcium chloride. Removal of the solvent and unreacted thiophene afforded 41.0 g. of the product, 2-hexadecanoylthiophene (86.2%), melting at 42° (reported[11] m.p. 42°).

Anal. Calcd. for $C_{20}H_{34}OS$: S, 9.94. Found: S, 9.92.

In a similar manner, 2-octadecanoylthiophene was prepared from octadecanoyl chloride and thiophene in the presence of anhydrous stannic chloride. 2-Octadecanoylthiophene (87.5%) had m.p. 50–51° (reported[11] m.p. 51°).

Anal. Calcd. for $C_{22}H_{38}OS$: S, 9.11. Found: S, 9.00.

2-Dodecanoylthiophene was similarly prepared using dodecanoyl chloride and thiophene (stannic chloride). 2-Dodecanoylthiophene had b.p. 187–190° (1.4 mm.).

n-Alkylthiophenes. 2-Hexadecanoylthiophene (41.0 g.), 30 ml. 85% aqueous hydrazine hydrate and 375 ml. diethylene glycol were heated to 190° and maintained at that temperature until the water and excess hydrazine hydrate had distilled off. After cooling the mixture to 80°, 25 g. of potassium hydroxide was added, the temperature then being raised to, and maintained at, 180° for 2 hr. After cooling, the mixture was poured into cold water, acidified with hydrochloric acid and the aqueous solution extracted with benzene. Following drying of the benzene extracts (calcium chloride) and removal of the solvent, 2-*n*-hexadecylthiophene (30.0 g.; 81.3%) was obtained by vacuum distillation, the product boiling at 147–147.5° at 0.2 mm. (reported[11] b.p. 147° at 0.2 mm.).

Following the above procedure, reduction of 2-octadecanoylthiophene was accomplished with hydrazine hydrate. 2-*n*-Octadecylthiophene (88.3%) had b.p. 183° at 0.8 mm. (reported[11] b.p. 182° at 0.6 mm.) and crystallized very slowly to a solid of m.p. 30–31°.

2-Dodecanoylthiophene was similarly reduced to the corresponding *n*-alkylthiophene by using hydrazine hydrate. 2-*n*-Dodecylthiophene (87.2%) had b.p. 153–155° (2 mm.).

Anal. Calcd. for $C_{16}H_{28}S$: S, 12.75. Found: S, 12.69.

n-Alkylthenoyl esters. These were prepared by a method analogous to that used for the acylthiophenes described previously.

Thus, ethyl 5-(5-hexadecyl-2-thenoyl)valerate was prepared from 5-carbethoxyvaleryl chloride and 2-*n*-hexadecylthiophene. Recrystallization from methanol yielded the pure material (66%; m.p. 39–40°).

Anal. Calcd. for $C_{28}H_{48}O_3S$: C, 72.37; H, 10.41; S, 6.90. Found: C, 72.17; H, 10.58; S, 6.85.

Similarly, methyl 3-(5-hexadecyl-2-thenoyl)propionate was prepared from 3-carbomethoxypropionyl chloride and 2-*n*-hexadecylthiophene. Methanol recrystallization afforded the pure compound (80.0%; m.p. 30°).

Anal. Calcd. for $C_{26}H_{44}O_3S$: S, 7.34. Found: S, 7.36.

Using 2-*n*-octadecylthiophene and 9-carbethoxynonanoyl chloride, ethyl 9-(5-octadecyl-2-thenoyl)nonanoate was prepared in 79.5% yield. Recrystallization from methanol yielded the pure product, m.p. 58–59°.

Anal. Calcd. for $C_{34}H_{60}O_3S$: S, 5.85. Found: S, 5.79.

Ethyl 9-(5-dodecyl-2-thenoyl)nonanoate was obtained from 2-*n*-dodecylthiophene and 9-carbethoxynonanoyl chloride in 73.8% yield. The pure material, obtained by methanol recrystallization, had m.p. 44–45°.

Anal. Calcd. for $C_{28}H_{48}O_3S$: S, 6.90. Found: S, 6.92.

Reduction of the keto esters by sodium borohydride yielded the corresponding hydroxy esters (II). The following relative amounts were used: 0.0431 mole keto ester; 0.013 mole sodium borohydride (20% excess) and 150 ml. ethanol; the solution being stirred at 70–75° for 2 hr. After the addition of water and hydrochloric acid, the product was solvent-extracted, the extracts water-washed and dried, and the solvent evaporated. Recrystallization of the residue from dilute alcohol afforded the pure esters. The results are summarized in Table I.

TABLE I

PREPARATION OF HYDROXY ESTERS[a] (II)

Ester	% Yield	Sapon. Equiv. Calcd.	Sapon. Equiv. Found	M.P.
Ethyl 6-hydroxy-6-(5-hexadecyl-2-thienyl)hexanoate	92.5	466.7	465.9	28–29
Methyl 4-hydroxy-4-(5-hexadecyl-2-thienyl)butyrate	85.6	438.7	437.9	20–21
Ethyl 10-hydroxy-10-(5-octadecyl-2-thienyl)decanoate	79.5	549.9	549.1	44–45
Ethyl 10-hydroxy-10-(5-dodecyl-2-thienyl)-decanoate	86.4	465.7	464.8	...

[a] All esters prepared were negative toward phenylhydrazine, *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine.

The free acids were obtained from the above esters by saponification with alcoholic potassium hydroxide followed by acidification with hydrochloric acid. After extraction with ether and drying (magnesium sulfate), the solvent was evaporated to afford the impure acid, which was then recrystallized from aqueous acetone to yield the pure material.

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(16) All melting and boiling points are uncorrected.

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TABLE II

HYDROXY-THIO ACIDS

Acid	Neut. Equiv. Calcd.	Found	M.P.
6-Hydroxy-6-(5-hexadecyl-2-thienyl)hexanoic acid[a]	438.7	438.0	84–85
4-Hydroxy-4-(5-hexadecyl-2-thienyl)butyric acid[b]	410.7	410.1	78–79
10-Hydroxy-10-(5-octadecyl-2-thienyl)decanoic acid	522.9	523.1	68–69
10-Hydroxy-10-(5-dodecyl-2-thienyl)decanoic acid	437.7	438.9	31–32[c]

[a] *Anal.* Calcd. for $C_{26}H_{46}O_3S$: C, 71.18; H, 10.57; S, 7.29. Found: C, 71.30; H, 10.41; S, 7.13. [b] Product obtained as lactone which was converted to free acid. [c] Crystallized very slowly.

Desulfurization.[20]

TABLE III

DESULFURIZATION OF DERIVATIVES

Derivative III		Product	
R	n	Acid	% Yield
n-pentadecyl	4	6-Hydroxyhexacosanoic	63.9
n-pentadecyl	2	4-Hydroxytetracosanoic	68.0
n-heptadecyl	8	10-Hydroxydotriacontanoic	75.0
n-undecyl	8	10-Hydroxyhexacosanoic	74.7

To a suspension of Raney nickel catalyst (dissolved and digested as described by Bilicka and Adkins)[21] in 900 ml. distilled water was added 5 g. 6-hydroxy-6-(5-hexadecyl-2-thienyl)hexanoic acid in 10% sodium carbonate (aqueous). The resultant mixture was stirred at 80 ± 3° for 3 hr., the catalyst was filtered off, the filtrate acidified (hydrochloric acid) and extracted with ether. The spent catalyst was dissolved in 15% hydrochloric acid and the solution extracted with ether. The ether extracts were combined, washed, dried (magnesium sulfate), and the solvent evaporated. Recrystallization of the residue (benzene-ethanol) gave pure 6-hydroxyhexacosanoic acid (63.9%), m.p. 89.5–90.5°.

Anal. Calcd. for $C_{26}H_{52}O_3$: C, 75.66; H, 12.65; OH, 4.12; Neut. Equiv., 412.7. Found: C, 75.53; H, 12.73; OH, 4.03; Neut. Equiv., 412.0.

Desulfurization of 4-hydroxy-4-(5-hexadecyl-2-thienyl)-butyric acid by the above procedure yielded 4-hydroxytetracosanoic acid (68.0%). The pure material, obtained from the lactone, had m.p. 80–82°.

Anal. Calcd. for $C_{24}H_{48}O_3$: OH, 4.42; Neut. Equiv., 384.6. Found: OH, 4.33; Neut. Equiv., 384.1.

In a similar manner, 10-hydroxydotriacontanoic acid was obtained by the desulfurization of 10-hydroxy-10-(5-octadecyl-2-thienyl)decanoic acid. Recrystallization from ethanol at −5° afforded the pure material (75%) of m.p. 81–83°.

Anal. Calcd. for $C_{32}H_{64}O_3$: OH, 3.42; Neut. Equiv., 496.6. Found: OH, 3.38; Neut. Equiv., 496.3.

10-Hydroxyhexacosanoic acid was likewise obtained by the desulfurization of 10-hydroxy-10-(5-dodecyl-2-thienyl)-decanoic acid. The pure product (74.7%), obtained by recrystallization from ethanol, had m.p. 93–95°.

Anal. Calcd. for $C_{26}H_{52}O_3$: OH, 4.12; Neut. Equiv., 412.7. Found: OH, 4.10; Neut. Equiv., 409.3.

The hydroxyl analysis mentioned in each of the above four desulfurizations was carried out according to the general procedure described by Smith and Shriner.[22]

Acknowledgment. The authors are indebted to the Sharples Chemicals Inc. for a generous sample of thiophene.

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AMES, IOWA

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[20] The weights of all thio-acids used were based on the introduction of 125 g. Raney nickel-aluminum alloy powder, the alloy being present in excess.

[21] H. R. Bilicka and H. Adkins, *Org. Syntheses,* **Coll. Vol. III,** 176 (1955).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reactions of Triphenylsilyllithium with Some Halides and Related Compounds of Group V Elements

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Whereas the reactions of triphenylsilyllithium with phosphorus trichloride, phosphorus tribromide, and phosphorus oxychloride give hexaphenyldisilane as the chief product, the reaction with tributyl phosphate gives *n*-butyltriphenylsilane. Arsenic trichloride, antimony trichloride, and bismuth trichloride give hexaphenyldisilane and the corresponding metals when allowed to react with triphenylsilyllithium. A possible explanation for the high yield of hexaphenyldisilane is given.

In the course of the past few years a study has been carried out in this Laboratory to ascertain the usefulness of triphenylsilyllithium as a synthetic tool for the preparation of various organosilicon compounds. Successful preparations of this reagent in a suitable solvent like tetrahydrofuran, by the lithium cleavage of hexaphenyldisilane[1] and by the direct reaction of chlorotriphenylsilane and lithium[2] have greatly increased the scope of this study.

The object of the present investigation was to study possible approaches to the synthesis of organosilylmetallic compounds containing some

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