removed by distillation, during which time 200 ml. of hot water was added in small portions. The residual solution was cooled and made acidic with hydrochloric acid. The acidic suspension was extracted with ether. The ether extracts were combined and dried with magnesium sulfate. The ether was removed by evaporation and the residue was heated to 230°. The acid was allowed to cool and then was dissolved in sodium hydroxide solution. The basic solution was filtered and the filtrate was acidified. The solid was removed by filtration and was recrystallized from acetic acid. The solid weighed 16.8 g. and possessed m.p. 110–116°. The analytical sample, colorless platelets from benzene, had m.p. 119.5–120.5°.

Anal. Calcd. for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45. Found: C, 73.05; H, 9.36.

p-Bis(7-carbomethoxyheptyl)benzene (V).—*p*-Bis(7-carboxyheptyl)benzene was treated with methanol, methylene chloride, and sulfuric acid in the manner described for the preparation of IV. From 84.7 g. (0.234 mole) of *p*-bis(7-carboxyheptyl)benzene there was obtained 56.8 g. of V with b.p. 264–269° (4 mm.). The analytical sample, colorless platelets from benzene, had m.p. 51–52°.

Anal. Calcd. for $C_{24}H_{38}O_4$: C, 73.81; H, 9.81. Found: C, 74.01; H, 9.74.

8-Keto[15]paracyclophane (IX).—From 19.52 g. of V was obtained 1.76 g. of IX with m.p. 68.5–69.5° (colorless platelets from methanol).

Anal. Calcd. for $C_{21}H_{32}O$: C, 83.94; H, 10.74; mol. wt., 300.5. Found: C, 83.92; H, 10.68; mol. wt., 303 (Rast, camphor).

Infrared Spectra.—Spectra of the new ketones were recorded with the Perkin–Elmer Model 21 spectrophotometer. A summary of the carbonyl stretching frequencies follows: VIII, 1706 cm.$^{-1}$ (liquid film); IX, 1703 cm.$^{-1}$ (KBr disk); X, 1695 cm.$^{-1}$ (KBr disk); XI, 1705 cm.$^{-1}$ (KBr disk); and XII, 1708 cm.$^{-1}$ (KBr disk). Each spectrum had only one absorption band (located between 1892 cm.$^{-1}$ and 1911 cm.$^{-1}$) in the 1800–2000-cm.$^{-1}$ region, the characteristic display for a *p*-disubstituted benzene.[12] Moreover, each ketone exhibited a characteristic medium-intensity absorption band in the range 794–819 cm.$^{-1}$, confirming the *para* orientation.

Acknowledgment.—Our sincere appreciation is given to the Robert A. Welch Foundation for generous financial support. We are indebted to Dr. J. J. Spurlock for aid with infrared instrumentation.

[12] C. W. Young, R. B. DuVall, and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

The Synthesis and Rearrangement of 2-Hydroxyalkyl 3-Thienyl and 2-Hydroxyalkyl 2-Naphthyl Sulfides

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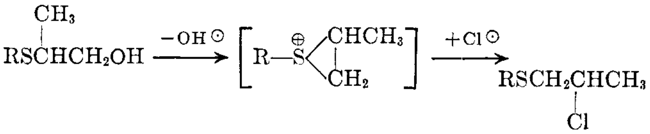
Three 2-hydroxy-*sec*-alkyl 3-thienyl sulfides and a 2-hydroxy-*sec*-alkyl 2-naphthyl sulfide were prepared and converted to their corresponding alkyl chlorides. In the case of the hydroxy heterocyclic sulfides it was found that the chlorides obtained were mixtures of isomers resulting from the intermediate formation of an unsymmetrical sulfonium ion.

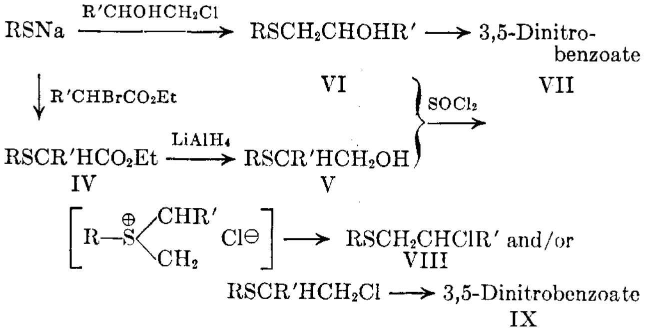
The participation of neighboring sulfur atoms in the rearrangement of 2-hydroxyalkyl sulfides has been reported by Fuson and co-workers.[3–5] Specifically, these investigators showed that nucleophillic displacement of the hydroxy group of 2-hydroxyisopropyl sulfides (I) by chloride ion resulted in rearrangement to the *n*-propyl structure (III). They postulated the rearrangement proceeded through a cyclic sulfonium intermediate (II).[3,5] Formation of the *n*-propyl structure requires that displacement by chloride ion occur at the most substituted carbon atom; *i.e.*, the carbon having the methyl group attached to it.



I II III

R = alkyl or phenyl

The present investigation was undertaken to study some additional cases of displacement–rearrangement reactions involving aromatic and heterocyclic hydroxy sulfides. Four 2-hydroxyalkyl sulfides (V, compounds **5B**, **6B**, **7B**, and **8B**, Table I) were prepared by reduction of the esters, (IV), and the structures of the chlorides, (VIII), obtained from the reaction of these alcohols with thionyl chloride, were investigated. The isomeric 2-hydroxy-*n*-alkyl sulfides (VI, compounds, **9C**, **10C**, **11C**, and **12C**, Table I) were also prepared and converted to the chlorides with thionyl chloride. These chlorides were converted to 3,5-dinitrobenzoate derivatives (IX) and compared with the 3,5-dinitrobenzoates (VII), obtained from the 2-hydroxy-*n*-alkyl sulfides (VI).



R = 3-thienyl or naphthyl; R' = methyl, ethyl or *n*-propyl

Thus, 2-hydroxy-*n*-propyl 3-thienyl sulfide (**9C**) was treated with thionyl chloride in pyridine to obtain 2-chloro-*n*-propyl 3-thienyl sulfide (**13D**). The 3,5-dinitrobenzoate of this chloro sulfide was prepared by reaction of the chloride with sodium 3,5-dinitrobenzoate and was found to be identical with the 3,5-dinitrobenzoate prepared from 2-hydroxy-*n*-propyl 3-thienyl sulfide (**9C**) and 3,5-dinitrobenzoyl chloride.

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[1] Abstracted in part from the Masters thesis of F. J. McCarty, Michigan State University.

[2] The Wm. S. Merrell Company, Cincinnati, Ohio.

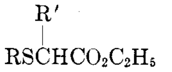
[3] R. C. Fuson, C. C. Price, and D. M. Burness, *J. Org. Chem.*, **11**, 475 (1946).

[4] R. C. Fuson and A. J. Speziale, *J. Am. Chem. Soc.*, **71**, 1582 (1949).

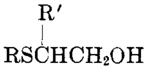
[5] R. C. Fuson and J. H. Koehneke, *J. Org. Chem.*, **14**, 706 (1949).

TABLE I

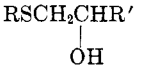
SUBSTITUTED ALKYL SULFIDES AND 3,5-DINITROBENZOATES


$RS\overset{R'}{C}HCO_2C_2H_5$

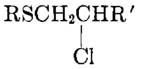
A


$RS\overset{R'}{C}HCH_2OH$

B


$RSCH_2\underset{OH}{C}HR'$

C


$RSCH_2\underset{Cl}{C}HR'$

D

No.	R	R′	Method	Yield, %	B.p., °C.	$n^{25}D$	d^{25}_{25}	Formula	Sulfur, %		MRD	
									Calcd.	Found	Calcd.	Found
1A	3-Thienyl	Methyl	a	85	115–116 (1 mm.)	1.5410	1.1645	$C_9H_{12}O_2S_2$[b]	14.81	14.83	58.23	58.55
2A	3-Thienyl	Ethyl	a	83	116–118 (0.5 mm.)	1.5357	1.1469	$C_{10}H_{14}O_2S_2$	13.91	14.05	62.85	62.78
3A	3-Thienyl	*n*-Propyl	a	66	120–122 (0.5 mm.)	1.5293	1.1202	$C_{11}H_{16}O_2S_2$	13.11	13.22	67.47	67.51
4A	2-Naphthyl	Methyl	a	77	150–151 (0.5 mm.)	1.5991	1.1304	$C_{15}H_{16}O_2S$	12.30	12.28		
5B	3-Thienyl	Methyl	b	87	120–123[c] (1 mm.)	1.5864	1.2073	$C_7H_{10}OS_2$[d]	18.40	18.42	48.78	48.62
6B	3-Thienyl	Ethyl	b	84	122–124 (0.5 mm.)	1.5747	1.1743	$C_8H_{12}OS_2$	17.01	17.40	53.49	53.12
7B	3-Thienyl	*n*-Propyl	b	82	133–135 (0.5 mm.)	1.5632	1.1394	$C_9H_{14}OS_2$	15.83	16.02	58.11	57.86
8B	2-Naphthyl	Methyl	b	83	160–162 (0.5 mm.)			$C_{13}H_{14}OS$	14.67	15.10		
9C	3-Thienyl	Methyl	c	85	116–117 (5 mm.)	1.5783	1.2011	$C_7H_{10}OS_2$	18.40	18.40	48.87	48.31
10C	3-Thienyl	Ethyl	c[e]	53	115–118 (0.5 mm.)	1.5755	1.1751	$C_8H_{12}OS_2$	17.02	17.29	53.49	53.15
11C	3-Thienyl	*n*-Propyl	c	71	125–127 (0.5 mm.)	1.5636	1.1397	$C_9H_{14}OS_2$	15.82	16.11	58.11	57.88
12C	2-Naphthyl	Methyl	c	87				$C_{13}H_{14}OS$	14.67	15.10		
13D	3-Thienyl	Methyl	[f]	37	92–94 (1 mm.)	1.5794	1.2304	$C_7H_9ClS_2$	16.62	16.84	52.21	52.35
14D	2-Naphthyl	Methyl	[g]	80	140–141 (0.5 mm.)	1.6366	1.1711	$C_{13}H_{13}ClS$	13.52	13.91		
15D	2-Naphthyl	Methyl	[h]	79		1.6360		$C_{13}H_{13}ClS$	13.52	13.78		

[a] The sulfide sulfur was determined by the back titration method of R. D. Schuetz and W. H. Houff *Anal. Chem.*, **25,** 1258 (1953). [b] *Anal.* Calcd: C, 49.97; H, 5.59. Found: C, 49.89; H, 5.85. [c] R. D. Schuetz and W. H. Houff, *J. Am. Chem. Soc.*, **75,** 2072 (1953); b.p. 111° (4 mm.). [d] *Anal.* Calcd: C, 48.26; H, 5.79. Found: C, 47.83; H, 5.84. [e] Previously reported by R. D. Schuetz and W. H. Houff, *Anal. Chem.*, **25,** 1258 (1953). [f] Prepared from **9C**. [g] Prepared from **12C**. [h] Prepared from **8B**.

The reaction of 1-methyl-2-hydroxyethyl 3-thienyl sulfide (**5B**) with thionyl chloride in chloroform resulted in a product which was also converted, in low yield, to the 3,5-dinitrobenzoate of **9C**. Therefore, in the latter case it appeared that rearrangement of the isopropyl structure to a *n*-propyl structure had taken place. However, the n.m.r. spectrum[6] of the chloride obtained from **5B** showed it to be a mixture of 2-chloro-*n*-propyl 3-thienyl sulfide and 1-methyl-2-chloroethyl 3-thienyl sulfide. Two doublets ($\delta = 1.35$ p.p.m. and $\delta = 1.56$ p.p.m., $\tau = 6$ c.p.s.) each representing three protons of the isomeric methyl groups were present. The integral curve was consistent with a total of 18 protons and showed the isomers to be present in a 3:2 ratio. It is presumed that the doublet at 1.35 p.p.m. with a relative intensity of 3 represents the methyl protons of 2-chloro-*n*-propyl 3-thienyl sulfide.

The reaction of 2-hydroxy-*n*-butyl 3-thienyl sulfide (**10C**) or 1-ethyl-2-hydroxyethyl 3-thienyl sulfide (**6B**) with thionyl chloride in carbon tetrachloride apparently resulted, in each instance, in the formation of an identical mixture of the isomeric chlorides, 2-chloro-*n*-butyl 3-thienyl sulfide and 1-ethyl-2-chloroethyl 3-thienyl sulfide. The mixture of chloride products from each of the initial reactions of the hydroxy sulfide with thionyl chloride on treatment with sodium 3,5-dinitrobenzoate formed a mixture of the corresponding 3,5-dinitrobenzoates of **10C** and **6B**, as determined by mixed melting point data.

Similar results were obtained when 2-hydroxy-*n*-pentyl 3-thienyl sulfide (**11C**) or 1-(*n*-propyl)-2-hydroxyethyl 3-thienyl sulfide (**7B**) were allowed to interact with thionyl chloride in carbon tetrachloride. Again, in each instance, an identical mixture of the isomeric chlorides, 2-chloro-*n*-pentyl 3-thienyl sulfide and 1-(*n*-propyl)-2-chloroethyl 3-thienyl sulfide, was obtained. Each mixture of chlorides on treatment with sodium 3,5-dinitrobenzoate formed an identical mixture of the 3,5-dinitrobenzoates of **11C** and **7B**, as demonstrated by mixed melting point determination. In order to obtain further evidence that a mixture of chlorides had been obtained, initially, the 3,5-dinitrobenzoate mixture was hydrolyzed with alcoholic potassium hydroxide to produce a mixture of the hydroxy sulfides, 2-hydroxy-*n*-pentyl 3-thienyl sulfide (**11C**) and 1-(*n*-propyl)-2-hydroxyethyl 3-thienyl sulfide (**7B**). The infrared spectrum of the mixture of hydroxy sulfides showed the carbon–oxygen stretching absorption of the primary alcohol at 9.56 μ and of the secondary alcohol at 8.92 μ. From their relative intensities in the mixture compared to their intensities in the spectrum of the pure isomers (**11C** and **7B**), it was estimated (Beer's law) that the mixture was composed of 40% of **11C** and 60% of **7B**.

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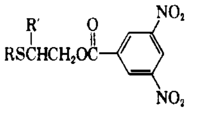
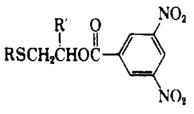
(6) Determined by D. Klinke of these laboratories, in CCl_4, with 60-Mc. Varian A-60 instrument, using tetramethylsilane as internal standard.

TABLE II


E


F

No.	R	R′	Method	M.p., °C	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
16E	3-Thienyl	Methyl	d	88–89	$C_{14}H_{12}N_2O_6S_2$	45.64	45.67	3.28	3.11			7.61	7.39
17E	3-Thienyl	Ethyl	d	120–121	$C_{15}H_{14}N_2O_6S_2$					8.38	8.48		
18E	3-Thienyl	*n*-Propyl	d	97–98	$C_{16}H_{16}N_2O_6S_2$					8.08	8.19		
19E	2-Naphthyl	Methyl	d	144–145	$C_{20}H_{16}N_2O_6S$	58.45	58.36	3.88	4.08				
20F	3-Thienyl	Methyl	d	82–84	$C_{14}H_{12}N_2O_6S_2$	45.64	45.81	3.28	3.27			7.61	7.53
21F	3-Thienyl	Ethyl	d	104–105	$C_{15}H_{14}N_2O_6S_2$					8.38	8.48		
22F	3-Thienyl	*n*-Propyl	d	94–95	$C_{16}H_{16}N_2O_6S_2$					8.08	8.13		
23F	2-Naphthyl	Methyl	d	189–190	$C_{20}H_{16}N_2O_6S$	58.45	58.36	3.88	3.99				

When 2-hydroxy-*n*-propyl 2-naphthyl sulfide (**12C**) or 1-methyl-2-hydroxyethyl 2-naphthyl sulfide (**8B**) was allowed to react with thionyl chloride in chloroform, 2-chloro-*n*-propyl 2-naphthyl sulfide, **14D** and **15D**, respectively, were formed. The 3,5-dinitrobenzoates derived from **14D** and **15D** were both identical with the 3,5-dinitrobenzoate prepared from 2-hydroxy-*n*-propyl 2-naphthyl sulfide (**12C**). In this instance, as in the preceding examples, it would be expected that a common sulfonium ion intermediate would result in the formation of the same chloride or the same isomeric chloride mixture. However, in this case, it was not determined if the products were contaminated with the isomeric primary chloride.

Experimental

General Procedures.—The structures of the products obtained by experimental Methods a–c are shown in Table I; d is shown in Table II. The capital letter following each compound number (first column, Tables I and II) indicates the general formula (**A**, **B**, **C**, or **D** in the heading of Table I) or **E** and **F** in the heading of Table II) to which the compound conforms. Variations in the general experimental procedures are described separately under each method.

Method a. 1-Carbethoxyalkyl 3-Thienyl Sulfides (1A, 2A, 3A).—3-Thiophenethiol,[7] 34.8 g., 0.30 mole, was added to a solution prepared from 6.9 g., 0.30 g.-atom, of sodium and 120 ml. of absolute ethanol. The basic mixture was heated to its reflux temperature and the α-bromo ester, 0.33 mole, was added, dropwise, during a 45-min. period. The reaction mixture was kept at its reflux temperature for 2 hr., cooled, and filtered. The filtrate was concentrated under vacuum and extracted with 300 ml. of ether. This in turn was extracted with 5% sodium hydroxide solution and then with water. The solvent was removed from the dried extract and the product was distilled.

1-Carbethoxyethyl 2-Naphthyl Sulfide (4A).—Method a was modified as follows. A solution of 32 g., 0.2 mole, of 2-naphthalenethiol dissolved in 250 ml. of absolute ethanol was stirred in a nitrogen atmosphere while a solution prepared from 4.6 g., 0.2 g.-atom, of sodium and 100 ml. of absolute ethanol was added. The basic mixture was heated to its reflux temperature and 41.5 g., 0.23 mole, of ethyl α-bromopropionate was added during 0.5 hr. The reaction mixture was kept at its reflux temperature for 1.5 hr. and then filtered. The filtrate, on cooling, precipitated 1.5 g. of 2,2′-dinaphthyl disulfide, m.p. 150°. The filtrate was concentrated *in vacuo* and 60 ml. of water was added. The mixture was extracted with 200 ml. of benzene; the benzene solution was in turn extracted with water, decolorized (Norite), and dried over anhydrous sodium sulfate. After removal of the benzene, the crude product was distilled.

Method b. 1-Alkyl-2-Hydroxyalkyl 3-Thienyl and 2-Naphthyl Sulfides (5B, 6B, 7B, 8B).—A solution of the ester, 0.16 mole, dissolved in 100 ml. of dry ether was added, dropwise, during 0.5 hr. to a stirred mixture of 9.1 g., 0.24 mole, of lithium aluminum hydride and 235 ml. of dry ether. The reduction mixture was stirred for 1 hr., cooled, and 25 ml. of ethyl acetate was added, dropwise. The reaction mixture was poured into 700 ml. of cold 10% sulfuric acid solution. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether layers were extracted with 10% sodium bicarbonate solution, then with water, and dried with anhydrous sodium sulfate. After removal of the ether the product was distilled.

Compound 5B.—An alternative procedure was also used to prepare this compound. A mixture of 29 g., 0.25 mole, of 3-thiophenethiol, 17.4 g., 0.3 mole, of freshly distilled allyl alcohol and 0.25 g. of sulfur was heated at its reflux temperature in a nitrogen atmosphere for a day. The reaction mixture was dissolved in 50 ml. of ether; the ether solution was extracted with 5% sodium hydroxide solution and then with water. The ether was removed and the product was distilled; b.p. 123–125° (1 mm.); yield 13 g. (30%); $n^{25}\text{D}$ 1.5852; d^{25}_{25} 1.2078.

Anal. Calcd. for $C_7H_{10}OS_2$[8]: S, 18.40; Found: S, 17.96.

Method c. 2-Hydroxyalkyl 3-Thienyl Sulfides (10C and 11C).—To a stirred solution of sodium 3-thienyl mercaptide prepared from 0.18 g.-atom of sodium, 0.18 mole of 3-thiophenethiol and 150 ml. of absolute ethanol was added 0.18 mole of 1-chloro-2-alkanol[9], dropwise, during 0.25 hr. The reaction mixture was heated at its reflux temperature for 1.5 hr., cooled, filtered, concentrated under vacuum, and extracted with ether. The ether solution was in turn extracted with 5% sodium hydroxide solution and then with water. The solvent was removed from the dried extract and the product was distilled.

Compound 9C.—A mixture of 46.4 g., 0.40 mole, of 3-thiophenethiol and 120 ml. of 20% sodium hydroxide solution was stirred while 45.6 g., 0.48 mole, of 1-chloro-2-propanol was added to it during 0.5 hr. The reaction mixture was heated at its reflux temperature for 1 hr. The crude product was extracted with ether; solvent was removed from the dried extract and the product was distilled.

Compound 12C.—In this synthesis, 2-naphthalenethiol and 1-chloro-2-propanol were used, as described in the procedures for **10C** and **11C**. The reaction was conducted in a nitrogen atmosphere. After removal of the ethanol from the reaction mixture, the crude product crystallized. It was recrystallized from 50% ethanol.

Method d. 3,5-Dinitrobenzoate Derivatives of Hydroxyalkyl 3-Thienyl and 2-Naphthyl Sulfides.—A mixture of 0.02 mole of the alcohol, 0.02 mole of 3,5-dinitrobenzoyl chloride and 20 ml. of dry pyridine was heated at 40–50° for 10 min. The reaction mixture was poured into 100 ml. of cold 10% hydrochloric acid solution. The crude product was extracted with ether; the ether solution was extracted in turn with 10% sodium carbonate solution and then with water. The ether was removed and the product was crystallized from ethanol.

Method e. 3,5-Dinitrobenzoate Derivatives of Chloroalkyl 3-Thienyl and 2-Naphthyl Sulfides.—A mixture of 0.02 mole of the chloroalkane, 0.02 mole of sodium 3,5-dinitrobenzoate, and

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[7] A crude sample was supplied by the Socony Vacuum Oil Company. This was extracted with sodium hydroxide solution; the extract was acidified with hydrochloric acid; and mercaptan was purified by distillation, b.p. 61° (15 mm.).

[8] Footnote *c*, Table I.

[9] 1-Chloro-2-butanol was prepared as described by B. Helferick and J. A. Speidel, *Ber.*, **54**, 2634 (1921). 1-Chloro-2-pentanol was prepared by the same method by P. A. Levene and H. L. Haller, *J. Biol. Chem.*, **77**, 560 (1928).

30 ml. of absolute ethanol was heated at its reflux temperature for 2 hr. The mixture was filtered and the alcohol was removed under vacuum. The residue was extracted with benzene. The benzene solution was extracted in turn with 10% sodium carbonate and then with water. The benzene was removed and the product was crystallized from ethanol.

2-Chloro-*n*-propyl 3-Thienyl Sulfide (13D).—Thionyl chloride[10], 20.6 g., 0.17 mole, was added, dropwise, during 1 hr. to a stirred solution of 25 g., 0.14 mole, of **9C** dissolved in 15 ml. of dry pyridine. The reaction mixture was stirred for a 0.5 hr., 80 ml. of ether was added, the ether solution was extracted with water, and dried over sodium sulfate. The ether was removed from the dried extract and the product (**13D**) was distilled.

Its 3,5-dinitrobenzoate was prepared by Method e and melted at 82–84°; m.m.p. with **20F**, 82–84°.

Mixture of 2-Chloro-*n*-propyl 3-Thienyl Sulfide and 1-Methyl-2-chloroethyl 3-Thienyl Sulfide.—Thionyl chloride,[10] 14.3 g., 0.12 mole, was added, dropwise, during 45 min. to a stirred solution of 17.4 g., 0.1 mole, of **5B** dissolved in 75 ml. of dry chloroform. The reaction mixture was heated at its reflux temperature for 1 hr.; chloroform was removed *in vacuo* and the residual oil was dissolved in ether. The ether solution was extracted with water, ether was removed from the dried solution, and the crude product was distilled; b.p. 94–96° (1 mm.) yield 13.1 g. (68%); $n^{25}\text{D}$ 1.5793.

Anal. Calcd. for $C_7H_9ClS_2$[9]: C, 43.62; H, 4.71; S, 16.62. Found: C, 43.77; H, 4.64; S, 16.66.

Their 3,5-dinitrobenzoates were prepared by Method e and melted at 82–84°; m.m.p. with **20F**, 82–84°.

Mixture of 2-Chloro-*n*-butyl 3-Thienyl Sulfide and 1-Ethyl-2-chloroethyl 3-Thienyl Sulfide. (a) Preparation from 2-Hydroxy-*n*-butyl 3-Thienyl Sulfide (10C).—A solution of 10 g., 0.053 mole, of **10C** dissolved in 30 ml. of dry carbon tetrachloride was stirred while 7.1 g., 0.06 mole, of thionyl chloride[10] was added to it during 10 min. The reaction mixture was heated to its reflux temperature, refluxed for 45 min., cooled, and extracted with ether. The ether solution was extracted in turn with water, dried, and the ether was removed. The mixture of isomeric chlorides was distilled; b.p. 92–94° (0.5 mm.); yield 11 g. (50%); $n^{25}\text{D}$ 1.5711; d^{25}_{25} 1.2005; MRD calcd: 56.83; found: 56.76.

Anal. Calcd. for $C_8H_{11}ClS_2$[8]: S, 15.50; Found: S, 15.67.

The mixture of 3,5-dinitrobenzoates, of the chlorides prepared by Method e, melted at 103–105°; m. m.p. with **21F**, 96–98°; m. m.p. with **17E**, 101–115°. A mixture of equal parts of **17E** and **21F** melted at 95–97°.

Anal. Calcd. for $C_{15}H_{14}N_2O_6S_2$: C, 47.12; H, 3.66; N, 7.33; S, 16.75. Found: C, 47.26; H, 3.64; N, 7.35; S, 16.79.

(b) **Preparation from 1-Ethyl-2-hydroxyethyl 3-Thienyl Sulfide (6B).**—The procedure used was the same as described in the preceding reaction except that **6B** was substituted for **10C**. The mixture of isomeric chlorides was distilled; b.p. 94–96° (0.5 mm.); yield 13 g. (63%); $n^{25}\text{D}$ 1.5712; d^{25}_{25} 1.2008; MRD calcd.: 56.83. Found: 56.76.

Anal. Calcd. for $C_8H_{11}ClS_2$[8]: S, 15.50. Found: S, 15.77.

The mixture of 3,5-dinitrobenzoates of the chlorides prepared by Method e, melted at 103–105°; m.m.p. with the mixture obtained in part (a), 103–105°; m.m.p. with **21F**, 96–98°.

Anal. Calcd. for $C_{15}H_{14}N_2O_6S_2$: C, 47.12; H, 3.66; N, 7.33; S, 16.75. Found: C, 47.21; H, 3.56; N, 7.43, S, 16.79.

Mixture of 2 Chloro-*n*-pentyl 3-Thienyl Sulfide and 1-(*n*-Propyl)-2-chloroethyl 3-Thienyl Sulfide. (a) Preparation from 2-Hydroxy-*n*-pentyl 3-Thienyl Sulfide (11C).—Thionyl chloride,[10] 10.7 g., 0.09 mole, was added during 10 min. to a solution of 16 g., 0.08 mole, of **11C** dissolved in 35 ml. of dry carbon tetrachloride. The experimental procedure was the same as that described in part (a) of the preceding example. The mixture of isomeric chlorides was distilled; b.p. 110–112° (0.5 mm.); yield 10 g. (57%); $n^{25}\text{D}$ 1.5600; d^{25}_{25} 1.1593; MRD calcd.: 61.45; found: 61.75.

Anal. Calcd. for $C_9H_{13}ClS_2$[9]: S, 14.50. Found: S, 14.78.

The mixture of 3,5-dinitrobenzoates, the chlorides prepared by method E, melted at 79–81°; m.m.p. with **18E** or **22F**, 80–86°. A mixture of equal parts of **18E** and **22F** melted at 80–82°.

Anal. Calcd. for $C_{16}H_{16}N_2O_6S_2$: C, 48.73; H, 4.04; N, 7.07; S, 16.16. Found: C, 48.73; H, 4.27; N, 7.12; S, 16.20.

(b) **Preparation from 1-(*n*-Propyl)-2-hydroxyethyl 3-Thienyl Sulfide (7B).**—The experimental procedure was the same as described in part (a) except that **7B** was substituted for **11C**. The mixture of isomeric chlorides was distilled,; b.p. 112–118° (0.5 mm.); yield 16 g. (73%); $n^{25}\text{D}$ 1.5603; d^{25}_{25} 1.1594; MR calcd.: 61.45. Found: 61.78.

Anal. Calcd. for $C_9H_{13}ClS_2$[8]: S, 14.50. Found: S, 14.75.

The mixture of 3,5-dinitrobenzoates of the chlorides prepared by Method e, melted at 79–81°; m.m.p. with the mixture obtained in part (a), 78–80°.

Anal. Calcd. for $C_{16}H_{16}N_2O_6S_2$: C, 48.73; H, 4.04; N, 7.07; S, 16.16. Found: C, 48.77; H, 4.17; N, 7.08; S, 16.40.

Mixture of 2-Hydroxy-*n*-pentyl 3-Thienyl Sulfide and 1-(*n*-Propyl)-2-hydroxyethyl-3-Thienyl Sulfide.—A mixture of 300 ml. of absolute ethanol and 20 g. of potassium hydroxide was stirred for 0.5 hr. The solution was decanted and added to 13 g., 0.033 mole, of the mixture of 3,5-dinitrobenzoates obtained in part (b) of the preceding reaction. The reaction mixture was heated at its reflux temperature for 1.5 hr. and concentrated under reduced pressure. The residue was extracted with ether and the ether solution was extracted in turn with water. After drying, the ether was removed and the residual oil was distilled; b.p. 129–136° (0.5 mm.); yield 3 g. (45%); $n^{25}\text{D}$ 1.5617.

Anal. Calcd. for $C_9H_{14}OS_2$[8]: S, 15.83; Found: S, 16.01.

The mixture of 3,5-dinitrobenzoates, prepared from the alcohols by Method d, melted at 81–83°.

2-Chloro-*n*-propyl 2-Naphthyl Sulfide (14D and 15D). (a) Preparation from 2-Hydroxy-*n*-propyl 2-Naphthyl Sulfide (12C).—To a stirred solution of 4 g., 0.02 mole, of **12C** dissolved in 15 ml. of dry chloroform was added, dropwise, 2.5 g. (0.02 mole) of thionyl chloride.[10] The reaction mixture was heated at its reflux temperature for 10 min. and dissolved in 50 ml. of ether. After the ether solution had been extracted with water and dried, the ether was removed and the product (**14D**) was distilled.

The 3,5-dinitrobenzoate of the chlorides prepared by Method e, melted at 189–190°; m.m.p. with **23F**, 189–190°.

(b) **Preparation from 1-Methyl-2-hydroxyethyl 2-Naphthyl Sulfide (8B).**—To a stirred solution of 7 g., 0.03 mole, of **8B** dissolved in 25 ml. of dry chloroform was added, dropwise, 4.2 g. (0.03 mole) of thionyl chloride.[10] The reaction mixture was heated at its reflux temperature for 10 min. and dissolved in 80 ml. of ether. The ether solution was extracted with water, dried, and treated with Norite. The mixture was filtered, the ether removed, and the residual oil (**15D**) was purified by heating on a steam bath for 1 hr. under a vacuum of 0.5 mm.

Its 3,5-dinitrobenzoate, prepared by Method e, melted at 186–187°; m.m.p. with **23F**, 186–188°.

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[10] Purified by distillation from quinoline, and then from linseed oil.