color disappeared very rapidly. After the addition was complete the mixture was heated on a steam bath for 1 hr. and let stand at room temperature for 18 hr. The solvent was removed under reduced pressure and the residue was taken up in chloroform, dried over calcium chloride, filtered, and evaporated. The light yellow oil was chromatographed on a 2.3 × 38 cm. column with acid-washed alumina (Merck) using pentane as eluent. The first fraction contained phenyl disulfide contaminated with a small amount of benzil. This was recrystallized from alcohol, m.p. 60–61° (lit.,[22] 60–61°). There was 1.20 g. of phenyl disulfide representing a yield of 55%. The second and third fraction contained benzil (1.7 g., 85%), m.p. 93–94°,2, 4-DNP, m.p. 187–189°, 2,4-DNP, m.m.p. 187–189°.

Selective Desulfurization of Benzil Diphenylmercaptole (VIII) with Nickel.—The nickel catalyst was prepared as follows: To 4.8 g. (0.02 mole) of nickel(II) chloride hexahydrate in ethanol was added in small portions 0.75 g. (0.02 mole) of sodium borohydride. There was an immediate precipitation of a finely divided black solid. The evolution of hydrogen was brisk. The mixture was stirred for 30 min. and 4.1 g. (0.01 mole) of benzil diphenylmercaptole was added. The mixture was refluxed for 12 hr. and cooled. The solution was filtered through a sintered glass funnel and the solvent removed under reduced pressure. The residue was recrystallized from ethanol to give 2.2 g. (71%) of α-phenylmercaptodesoxybenzoin as white crystals, m.p. 78–79° (lit.,[23] 81°). Infrared spectrum in chloroform shows a strong carbonyl absorption at 5.95 μ. The spectrum of XVIII differed from that of VIII in several respects. Further confirmation of the structure of XVIII was obtained by treating it with additional nickel reagent under like conditions to obtain phenyl benzyl ketone (XIX).

Complete Desulfurization of Benzil Diphenylmercaptole with Nickel.—The reaction was run in the same manner as described above except the ratio of nickel(II) chloride and borohydride to VIII was raised to ten to one. After filtration of the nickel and evaporation of the solvent, 1.2 g. (61%) of phenyl benzyl ketone (XIX), m.p. 55–56° (lit.,[24] 55–56°), 2,4-DNP, m.p. 201–203° (lit.,[21] 204°), was isolated.

Acknowledgment.—This work was supported by the Air Force Office of Scientific Research under contract no. AF-49 (638)-531, and the U. S. Army Research Office under grant no. DA-ARO(D)-31-124-G146.

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[23] W. A. Mitchell and S. Smiles, *J. Chem. Soc.*, 1529 (1933).

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The Intramolecular Cleavage of γ-Alkylmercaptobutyryl Chlorides

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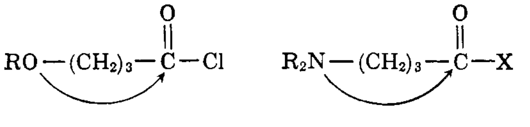
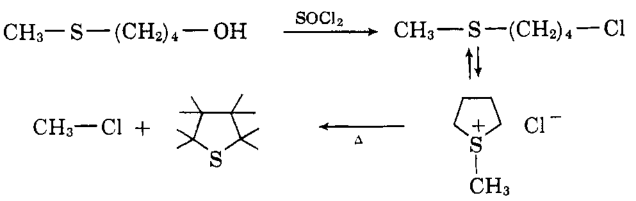
Compounds of the general structure, R—S—$(CH_2)_3COCl$, were cleaved under reflux conditions to give γ-thiolbutyrolactone, alkyl halide (R-Cl), and olefin (isolated when R = 2-octyl). As R was varied from primary to secondary to tertiary alkyl, the yield of thiolactone increased and less vigorous conditions were needed for reaction. When R was the *d*-2-octyl group, the resulting 2-octyl chloride showed net inversion.

The intramolecular interactions of the elements, oxygen and nitrogen, with acyl chlorides or carboxylic anhydrides have been demonstrated.[2] Furthermore, in attempts to prepare 1-chloro-4-methylthiobutane from the corresponding alcohol by treatment with thionyl chloride, the sulfonium chloride (I) was obtained, which was pyrolyzed to tetrahydrothiophene.[3] In fact, cyclic sulfonium salts and their degradations have been well studied.[4] Bohme[5] and co-workers have studied the cleavage of mercaptals by acyl chlorides, *e.g.*, treatment of II with acetyl chloride gave methyl thiolacetate and III. Likewise, simple sulfides have been cleaved by acyl bromides and iodides.[6] While thioethers are cleaved by acyl iodides,[6c] the rate of cleavage is very much slower than that of the analogous ethers. The cleavage products from diethyl sulfide and acetyl iodide were ethyl iodide and ethyl thiolacetate. These authors also found that acetyl chloride without catalysts failed completely to cleave diethyl sulfide after seven days at 100°.

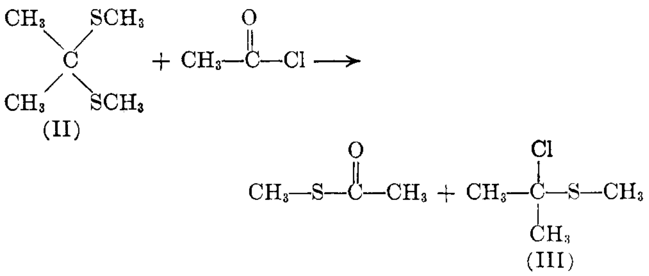


$$RO-(CH_2)_3-\overset{O}{\overset{\|}{C}}-Cl \qquad R_2N-(CH_2)_3-\overset{O}{\overset{\|}{C}}-X$$

(X = chloro and acetoxy)



I



The purpose of this investigation was to determine if sulfur would participate intramolecularly with an

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[1] National Institutes of Health Predoctoral Fellow, 1962–1963.

[2] (a) F. F. Blicke, W. B. Wright, Jr., and M. F. Zienty, *J. Am. Chem. Soc.*, **63**, 2488 (1941); (b) D. S. Noyce and H. I. Weingarten, *ibid.*, **79**, 3093 (1957); (c) J. H. Gardner, N. R. Easton, and J. R. Stevens, *ibid.*, **70**, 2906 (1948); (d) R. L. Clarke, A. Mooradian, P. Lucas, and T. J. Slauson, *ibid.*, **71**, 2821 (1949); (e) F. D. Popp and W. Blount, *J. Org. Chem.*, **26**, 2108 (1961); (f) K. B. Wiberg, *J. Am. Chem. Soc.*, **74**, 3957 (1952); (g) P. A. Cruickshank and J. C. Sheehan, *ibid.*, **83**, 2891 (1961).

[3] W. E. Truce, *et al.*, *J. Org. Chem.*, **27**, 2821 (1962).

[4] (a) G. M. Bennett and H. Gudgeon, *J. Chem. Soc.*, 1891 (1938); (b) G. M. Bennett and E. G. Turner, *ibid.*, 813 (1938); (c) G. M. Bennett, F. Heathcoat, and A. N. Mosses, *ibid.*, 2567(1929); (d) G. M. Bennett and A. L. Hock, *ibid.*, 477 (1927); (e) G. M. Bennett, E. V. Bell, and A. L. Hock, *ibid.*, 1803 (1927);

[5] von H. Bohme and J. Roehr, *Ann.*, **648**, 21 (1962). See this paper for other references.

[6] (a) A. Cahours, *Compt. rend.*, **81**, 1163 (1875); (b) J. Obermeyer, *Ber.*, **20**, 2918 (1887); (c) E. L. Gustus and P. G .Stevens, *J. Am. Chem. Soc.*, **55**, 378 (1933).

acyl chloride group and undergo eventual cleavage to a thiolester. In view of the previous work,[2] the γ-alkylmercaptobutyryl chloride system [$R{-}S{-}(CH_2)_3{-}COCl$] was chosen. Five alkyl groups were used, *i.e.*, methyl, *n*-propyl, *i*-propyl, 2-octyl, and *t*-butyl. As anticipated, these compounds were cleaved, during slow distillation, to give γ-thiobutyrolactone (IV), alkyl halide (RCl), and olefin (obtained from the R=2-octyl group). For example: γ-(2-octylmercapto)-butyryl chloride yielded IV, a mixture of 1- and -2-octenes, and 2-octyl chloride. The thiolactone was synthesized independently from γ-chlorobutyronitrile. It can be seen from Table I that as R is varied from primary to secondary to tertiary alkyl, the yield of IV increases. The acyl chlorides were isolated and purified by distillation under reduced pressure. γ-*t*-Butylmercaptobutyryl chloride could not be purified by distillation under vacuum, but cleaved rapidly under these milder conditions (55° at 3 mm.). The other acyl halides were cleaved under reflux conditions at atmospheric pressure.[7] The acyl chlorides were synthesized from γ-chlorobutyronitrile.[8]

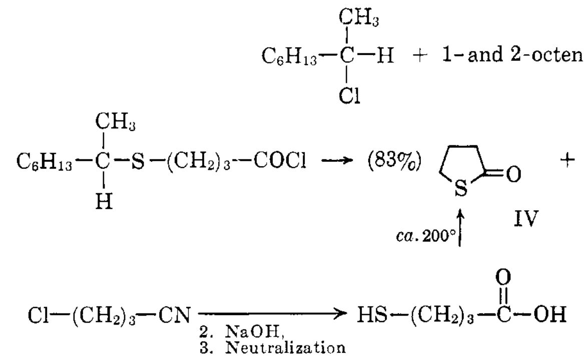
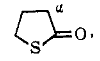


Table I

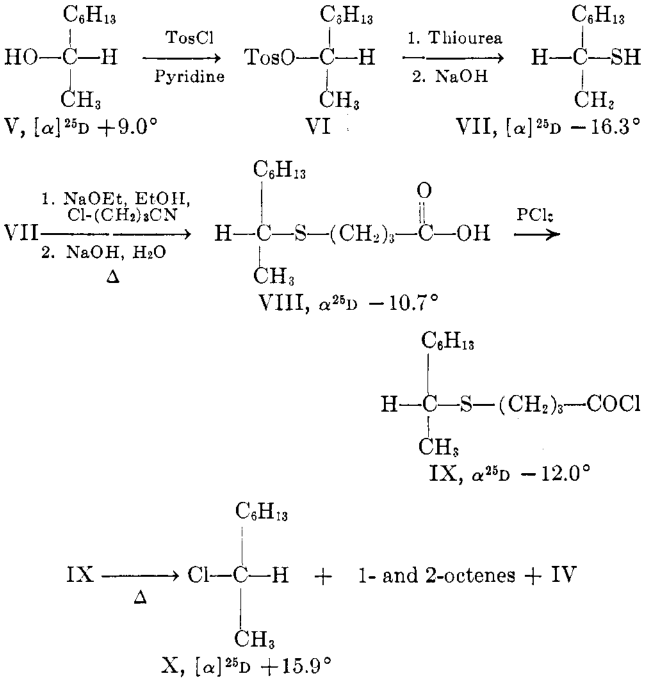
Cleavage of Acyl Chlorides

$R{-}S{-}(CH_2)_3{-}\overset{\overset{O}{\|}}{C}{-}Cl$	 [a], %	R Cl, %	Olefin, %
R = Me	52		
n-Pr	55	27	
i-Pr	87	43	
2-Octyl	82	38	57[b]
t-Butyl	93		

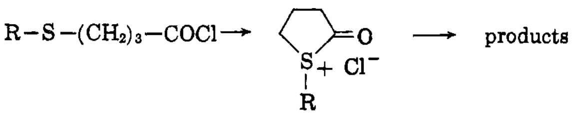
[a] Yields of thiolactone are based on isolated product. [b] 1- and 2-octenes were isolated as a mixture.

$$Cl{-}(CH_2)_3{-}CN \xrightarrow[\text{EtOH} \atop \text{2. NaOH aq.}]{\text{1. R-SNa}} R{-}S{-}(CH_2)_3{-}COOH \xrightarrow{PCl_3} R{-}S{-}(CH_2)_3{-}COCl$$

d-2-Octanol (V)[9] was converted to the tosylate (VI), which was treated with thiourea in dimethylformamide. Hydrolysis produced *l*-2-octyl mercaptan (VII).[10] The sodium salt of VII in ethanol was treated with γ-chlorobutyronitrile and the product was hydrolyzed to *l*-4-(2-octylmercapto)butyric acid (VIII). Then VIII was treated with phosphorus trichloride and the resulting product was distilled under vacuum to give *l*-γ-(2-octylmercapto)butyryl chloride (IX). Upon slow distillation of IX, *d*-2-octyl chloride (X) was isolated.



The ease of this cleavage of γ-alkylmercaptobutyryl chlorides to form a five-ring thiolactone, shows a marked dependence upon the nature of the alkyl group. The reaction is probably intramolecular in view of the products obtained and by analogy to related systems.[2,4,6c] As R is varied from primary to tertiary, the yield of thiolactone increases and less vigorous conditions are needed for cleavage, presumably because of the increasing ability of the alkyl group to accommodate a positive charge.



XI

The optically active halide, X, obtained from IX has the same absolute configuration[11] as V. In the synthesis of VII from V, inversion is assumed to have occurred.[12] To give X with the same absolute configuration as V, a second inversion must have occurred. The activity of X compared to the literature[13] showed a net inversion of *ca.* 44%. While the degree of inversion can not be definitely stated,[14] the results suggest that the thermal decomposition of IX occurs through the intermediate XI, and that the latter decomposes by a process involving a minimum of 44% inversion of configuration.

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(7) When R was *i*-propyl and 2-octyl, the acyl chloride was also cleaved on the vapor phase chromatographic column. The methyl and *n*-propyl compounds did not appear to do this on the columns which were used.

(8) C. F. H. Allen, *Org. Syn.*, **1**, 156 (1941).

(9) A.I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed., Longmans, Green and Co., New York, N. Y., 1948, p. 505.

(10) Reported: $[\alpha]^{25}D$ −9.3° (?); P. A. Levene and A. L. Mikeska, *J. Biol. Chem.*, **59**, 473 (1924). Their thiol was prepared from an optically impure bromide.

(11) W. Klyne, "Progress in Stereochemistry," Vol. 1, Butterworth Scientific Publications, London, 1954, p. 195.

(12) E. S. Gould, "Mechanism and Structure in Organic Chemistry," N. Holt and Co., New York, N.Y., 1959, p. 265.

(13) N. Brauns, *Rec. trav. chim.*, **65**, 799 (1941); $[\alpha]^{20}D$ −36.15°.

(14) There is the possibility that VII was not formed with 100% inversion. Also the possibilities of racemization taking place in the synthesis of IX from V, and that some X might have formed *via* addition of hydrogen chloride to olefin can not be ruled out.

TABLE II

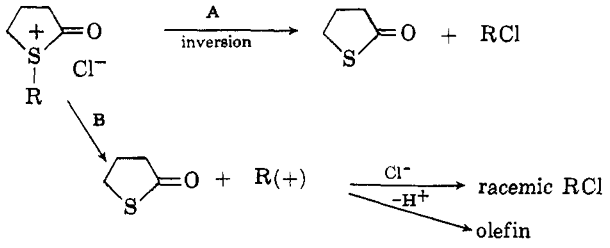
PHYSICAL CONSTANTS OF γ-ALKYLMERCAPTOBUTYRIC ACIDS

$R—S—(CH_2)_3—COOH$

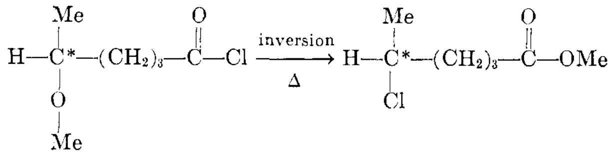
R	% Yield[a]	$n^{25}D$	B.p., °C. (mm.)	Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S
Me-[b]	40	1.4840	107–109 (1.5)						
n-Pr-[c]	73	1.4785	130 (3.0)						
i-Pr-	65	1.4750	124–125 (2.5)	51.85	8.60	19.70	52.15	8.53	20.05
2-Octyl	49	1.4732	147–148 (0.5)	62.07	10.35	13.79	62.51	10.06	13.90
t-Butyl	69	1.4735	125–126 (5.0)	54.54	9.09	18.18	54.69	9.31	17.90

[a] Yields here are for addition of thiolate to γ-chlorobutyronitrile and hydrolysis to the acid (2 steps). [b] Lit. b.p. 130° (9 mm.) and $n^{25}D$ 1.4823, A. Mooradian, *et al.*, *J. Am. Chem. Soc.*, **71,** 3372 (1949). [c] Reported b.p. 141–142° (7 mm.), A. Mooradian, *et al.*, U. S. Patent 2,547,961 (1951); *Chem. Abstr.*, **45,** 8569; and $n^{25}D$ 1.4778, A. Mooradian, *et al.*, *J. Am. Chem. Soc.*, **71,** 3372 (1949).

Although the cleavage reaction has some carbonium ion character, the ion may have definite restrictions as to its freedom, *e.g.*, the carbonium ion may be shielded by the leaving group so that the incoming reagent is more likely to attack the ion on the "unshielded" side. The most stable and long-lived carbonium ions would be expected to undergo complete or nearly complete racemization. Possibly, as the alkyl group is changed from primary to tertiary, the mechanism shifts from SN2 to SN1 or from path A to B. Some olefin may result from an E_2 elimination, in spite of the presence of only weak bases in the system.



Wiberg[2f] has observed that inversion occurs in the oxygen series, as in the following equation.



$$H—\overset{\overset{Me}{|}}{\underset{\underset{\underset{Me}{|}}{O}}{\underset{|}{C^*}}}—(CH_2)_3—\overset{\overset{O}{\|}}{C}—Cl \xrightarrow[\Delta]{\text{inversion}} H—\overset{\overset{Me}{|}}{\underset{\underset{Cl}{|}}{C^*}}—(CH_2)_3—\overset{\overset{O}{\|}}{C}—OMe$$

In this respect, the present system is similar to the oxygen system.

Experimental

General Synthesis of γ-Alkylmercaptobutyric Acids.—In a 500-ml. flask were placed 200 ml. of absolute ethanol and 7.7 g. (0.33 g.-atom) of sodium. To this cooled solution were added 0.33 mole of alkylmercaptan and 33.8 g. (0.32 mole) of γ-chlorobutyronitrile.[7] The sodium chloride precipitated immediately and the reaction mixture was refluxed for 2–3 hr. The sodium chloride was filtered off and the solvent evaporated to give the crude mercaptonitrile. This crude nitrile was placed in a 500-ml. flask and 60.0 g. (1.5 moles) of sodium hydroxide in 300 ml. of water was added. The resulting mixture was refluxed until there was a homogeneous system with no further evolution of ammonia. This time varied from 8–38 hr. See Table II for physical constants and analysis.

General Synthesis of γ-Alkylmercaptobutyryl Chlorides.—The 4-alkylmercaptobutyric acid was placed in a 100-ml. flask and a twofold excess by weight of phosphorus trichloride was added. The resulting solution was left to stand at room temperature for ca. 20 hr. The clear liquid was decanted from the flask leaving a sirupy viscous material behind. The excess phosphorus trichloride was removed from the acyl halide portion by vacuum and collected in a Dry Ice–acetone trap. The acyl halide was then distilled under vacuum. All acyl halides could be purified by distillation except the γ-*t*-butylmercaptobutyryl chloride which cleaved under distillation at 3 mm. and *ca.* 55°. (See Table III.)

TABLE III

PHYSICAL CONSTANTS OF γ-ALKYLMERCAPTOBUTYRYL CHLORIDES

$R—S—(CH_2)_3—COCl$

R	% Yield	$n^{25}D$	B.p., °C. (mm.)
Me	89	1.4892[a]	64–65 (2.5)
n-Pr	94	1.4835	74–76 (1.0)
i-Pr	86	1.4810	64–65 (1.5)
2-Octyl	93	1.4771	124–126 (0.5)

[a] Reported $n^{25}D$ 1.4898, A. Mooradian, *et al.*, *J. Am. Chem. Soc.*, **71,** 3372 (1949).

Cleavage of γ-Alkylmercaptobutyryl Chlorides.—The acyl chlorides were placed in a distillation pot fitted with a distillation head and cutter or in some cases distilled through a Todd column. The low boiling alkyl halides were trapped in a Dry Ice–acetone bath along with some hydrogen chloride and olefins that formed. After removal of the above products, the system was placed under vacuum and the γ-thiolbutyrolactone was distilled (usually around 55° at 3 mm.).

Anal. Calcd. for C_4H_6SO: C, 47.05; H, 5.88; S, 31.37. Found: C, 47.17; H, 6.17; S, 31.08.

In the cases of methyl- and *n*-propylmercaptobutyryl chlorides, other higher boiling fractions were obtained. These seemed to be a complex mixture of products, one of which was the acid derivative of the acyl chloride. The γ-*n*-propylmercaptobutyryl chloride cleavage produced besides the *n*-propyl chloride and thiolactone a compound the composition of which is in reasonable agreement for $CH_3—(CH_2)_2—S—(CH_2)_3—\overset{\overset{O}{\|}}{C}—S—(CH_2)_2\text{-}CH_3$. The infrared spectra suggested this also but no rigorous proof of structure was effected. This compound distilled at 110° at 2 mm. and amounted to a 6% yield. The γ-*t*-butylmercaptobutyryl chloride could not be distilled under vacuum but was cleaved to give the thiolactone in a 93% yield (see Table I).

Anal. Calcd. for $CH_3—(CH_2)_2—S—(CH_2)_3—\overset{\overset{O}{\|}}{C}—S—(CH_2)_2\text{-}CH_3$: C, 55.17; H, 9.37; S, 28.81. Found: C, 54.60; H, 9.09; S, 29.09.

Independent Synthesis of γ-Thiolbutyrolactone.—In a 1-l. flask were placed 30.0 g. (0.29 mole) of γ-chlorobutyronitrile, 22.0 g. (0.29 mole) of thiourea, and 100 ml. of water. This mixture was refluxed for 2.5 hr. Then 60 g. (1.5 moles) of sodium hydroxide in 250 ml. of water was added slowly. This solution was refluxed overnight with no further evolution of ammonia observed in the morning. The solution was extracted with ether to remove insoluble organic impurities and the aqueous layer neutralyzed with concd. hydrochloric acid. Oil was extracted from the aqueous layer with ether, the ether dried and removed by distillation. The oil was distilled slowly with water distilling at 90–120°. The oil distilled at 194–206° and was removed from some of the water by extraction with ether. The ether was dried with calcium chloride and the solvent evaporated. The liquid remaining was distilled at 53 to 54° at 3 mm. ($n^{25}D$ 1.5200) and yielded 15.3 g. (52% yield over-all reactions) of γ-thiolbutyrolactone. The infrared spectrum was identical to that obtained from the cleavages and retention times by v.p.c. were also identical. Mixed samples of synthetic and cleavage products only produced one peak on the v.p.c. spectrum.

Optical Studies.—All rotations were taken neat in a 1-dm. cell at 25°. The optically active *d*-2-octanol[8] was obtained and had a rotation $[\alpha]^{25}\text{D}$ +8.97° compared to $[\alpha]^{25}\text{D}$ +9.5° for optically pure material.[15]

Preparation of *l*-2-Mercaptoöctane.—In a 300-ml. flask were placed 28.0 g. (0.22 mole) of *d*-2-octyl alcohol and 70 ml. of dry pyridine. The solution was cooled in an ice bath and 45.0 g. (0.24 mole) of *p*-toluenesulfonyl chloride was added. The mixture solidified and was placed in an ice box for 3 hr. Water, 100 ml., was added very slowly while keeping the mixture cold. The solution was extracted with ether, and the ether extracted with two 125-ml. portions of hydrochloric acid (1:1 with water). The ether was separated, washed with water, and dried with anhydrous calcium chloride. The solution was filtered and the ether was distilled to give the crude tosylate oil.

In a 250-ml. flask were placed the crude tosylate and 50 ml. of dimethylformamide. To this was added 19.0 g. (0.25 mole) of thiourea and the solution heated on a steam bath for 2 hr. To the solution was added 13.5 g. (0.33 mole) of sodium hydroxide. The solution was refluxed on the steam bath for 1 hr. where the crude thiol separated to the top of the solution. Upon separation, the mercaptan weighed 28.8 g. This material was distilled to give 16.4 g. of material boiling at 179–183°. The rotations for three fractions taken were $[\alpha]^{25}\text{D}$ −12.2°, −14.0°, −16.3° and, respectively, $n^{25}\text{D}$ were 1.4372, 1.4402, and 1.4420.[10,16]

Preparation of *l*-γ-(2-Octylmercapto)butyric Acid.—In a 250-ml. flask fitted with a reflux condenser were placed 75 ml. of absolute ethanol and 2.54 g. (0.11 g.-atom) of sodium. To this solution, after cooling, was added 16.0 g. (0.11 mole) of the *l*-2-octanethiol. The mixture was cooled in an ice bath and 11.4 g. (0.12 mole) of chlorobutyronitrile was added. The mixture warmed to room temperature and was refluxed on the steam bath for 1.5 hr. The sodium chloride was filtered off and the ethanol distilled from the crude nitrile. This crude oil was placed into a 250-ml. flask and 10 g. (0.25 mole) of sodium hydroxide in 75 ml. of water was added. This solution was refluxed with stirring for 36 hr. during which time 15 g. (0.38 mole) of sodium hydroxide in 75 ml. of water was added. Ammonia was no longer evolved and the organic layer had dissolved in the water layer. The solution was cooled and concd. hydrochloric acid was added slowly until the solution was acidic to litmus. Then a 20-ml. excess portion of concentrated hydrochloric acid was added. The organic acid was separated from the water solution and washed with three portions of water. The combined water extracts were extracted three times with diethyl ether and the ether combined with the crude, acid. This resulting solution was dried with calcium chloride, filtered, and the acid distilled at 147–148° at 0.5 mm. This gave 12.6 g. of acid with $n^{25}\text{D}$ 1.4732 and α −10.73° and −10.68° for the two main fractions.

Preparation of *l*-γ-(2-Octylmercapto)butyryl Chloride.—In a 50-ml. flask fitted with a calcium chloride drying tube were placed 12.0 g. (0.052 mole) of *l*-γ-(2-octylmercapto)butyric acid and 35 ml. of phosphorus trichloride. The solution was left to stand at room temperature for 21 hr. The mixture was decanted from the viscous material and the phosphorus trichloride was removed under vacuum and received in a Dry Ice–acetone bath. The acyl chloride was then distilled at 124–126° at 0.5 mm. to give 12.2 g. with rotation $\alpha^{25}\text{D}$ = −12.03°.

Cleavage of *l*-γ-(2-Octylmercapto butyryl Chloride.—In a 50-ml. flask was placed 12.0 g. (0.048 mole) of the *l*-γ-(2-octylmercapto)butyryl chloride. The acyl halide was distilled slowly in a micro apparatus fitted with a distillation head and cutter. The following fractions were taken and v.p.c. analysis was used for identification.

Fraction	Weight	B.p., °C.	V.p.c.
1	0.22 g.	121–122	Mixture of 2 octenes
2	.25	121–122	...
3	.73	121–122	...
4	.73	123–125	...
5	.65	125–130	—
6	.69	130–152	—
7	.48	163–176	—
8	1.0	178–181	70% 2-Chloroöctane $\alpha^{25}\text{D}$ +8.91°
9	1.1	182–185	69% 2-Chloroöctane $\alpha^{25}\text{D}$ +9.03°
10	4.0	54–55 (3 mm.)	γ-Thiolbutyrolactone

If fractions 8 and 9 are corrected for 100% purity in 2-chloroöctane (+8.91°/.70 and +9.03°/.69) the $\alpha^{25}\text{D}$ becomes +12.1° and +13.2°, respectively. Fractions 8 and 9 were placed through an Aerograph with an R-column at 175°. A 0.1335-g. fraction of pure active 2-chloroöctane was collected and this mixed with 0.3798 g. of inactive 2-chloroöctane. The rotation recorded was +3.37° which if corrected (3.37 × 0.5133/0.1335) gives $\alpha^{25}\text{D}$ +12.95°. When this was converted to specific rotation and corrected for a 95% purity of starting alcohol, $[\alpha]^{25}\text{D}$ = +15.9° was obtained. The yield of γ-thiolbutyrolactone obtained was 4.0 g. or 82%. The yield of olefins obtained amounts to 57%. No attempt was made to separate the octenes, the retention time being identical to a commercial mixture which gave only one peak on the v.p.c. spectrum at 175°. The infrared spectrum was identical with the commercial octene mixture.

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(15) J. Kenyon and R. H. Pickard, *J. Chem. Soc.*, **99**, 45 (1911).

(16) Reported b.p. 186.4° and $n^{25}\text{D}$ 1.4481, L. M. Ellis, Jr., and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 1674 (1932).