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ω-HALOALKYL AND ω-AMINOALKYL SULPHIDES

CLEAVAGE OF THE ALKYL–SULPHUR BOND[1]

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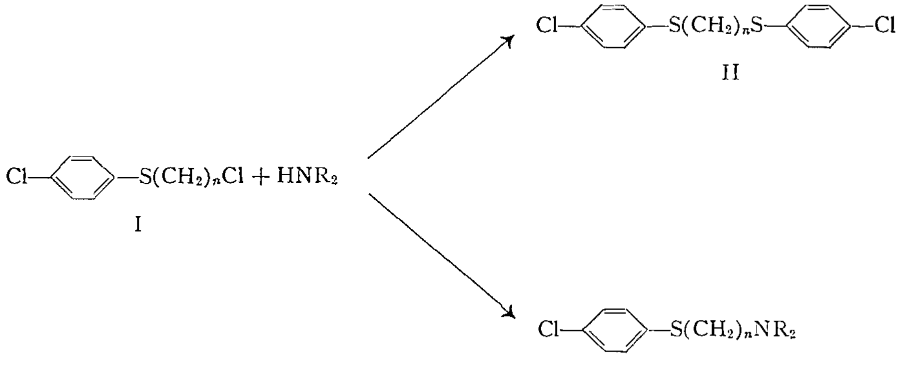
ABSTRACT

In the homologous series of *p*-chlorophenyl ω-chloroalkyl sulphides (I), the first and second members reacted abnormally with amines to yield 1,ω-bis(*p*-chlorophenylmercapto)alkanes (II). The fourth member of the series reacted normally to produce 4-aminobutyl *p*-chlorophenyl sulphide (III). The formation of II is explained on the basis of an alkyl–sulphur bond cleavage. The members of the *p*-chlorobenzyl series (VI) in general reacted with amines to form the expected aminoalkyl sulphides (VII). However, the *p*-chlorobenzyl chloroalkyl sulphides (VI) were thermally labile and decomposed to *p*-chlorobenzyl chloride and a sulphur component. A cyclic sulphur component originated from VI whose chloroalkyl carbon chain was 4, 5, or 6. The thermal degradation of VI is explained through a sulphonium salt cleavage.

INTRODUCTION

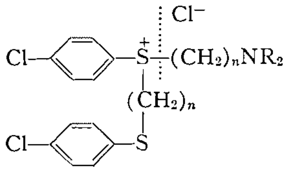
It has been recently shown that *p*-chlorophenyl chloromethyl sulphide (I, $n = 1$) can undergo an unusual bimolecular reaction to form 2,8-dichloro-6H,12H-dibenzo(*b,f*)-1,5-dithiocin (1). Now another anomalous reaction of I has been discovered and is the subject



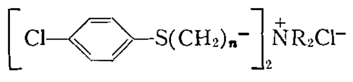
II

I

III



IV



V

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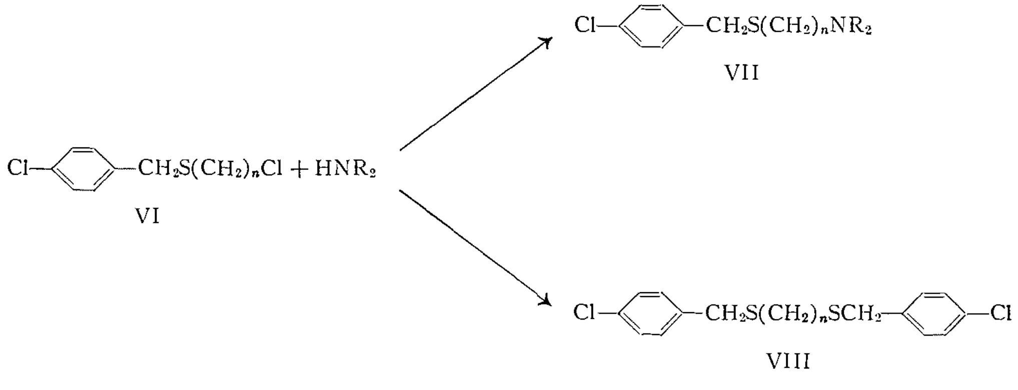
of this paper. When I ($n = 1$) was heated with ammonia, di-*n*-butylamine, or *t*-butylamine, the expected aminomethyl, *p*-chlorophenyl sulphide (III, $n = 1$), was not obtained. Instead, bis(*p*-chlorophenylmercapto)methane (II, $n = 1$) was the product.

On treatment of higher members of the homologous series of I with amines, it was found the 2-chloroethyl *p*-chlorophenyl sulphide (I, $n = 2$) also reacted abnormally in boiling di-*n*-butylamine to form 1,2-bis(*p*-chlorophenylmercapto)ethane (II, $n = 2$). However, when the temperature of the reaction was lowered to about 120° the only product was N,N-di-*n*-butylaminoethyl *p*-chlorophenyl sulphide (III, $n = 2$). Normal reaction only was indicated with higher members of the homologous series, since *p*-chlorophenyl 4-chlorobutyl sulphide (I, $n = 4$) with boiling di-*n*-butylamine gave *p*-chlorophenyl 4-di-*n*-butylaminobutyl sulphide (III, $n = 4$) in high yield. In this connection it was interesting to note that III ($n = 2$ and 4) forms a hydrochloride which is soluble in benzene and which distills readily without decomposition.

Any mechanism which attempts to explain the formation of II from I must take into account the observation that neither I nor III thermally decomposed to II, but that an equimolecular mixture of I and III on heating at 180° yielded II. This observation suggests two possible intermediates in the mechanism of the reaction, the sulphonium salt IV and the quaternary ammonium salt V, each of which could arise by the reaction of I with III. The dissociation of the sulphonium salt IV (indicated by the dotted line) would lead to II and chloroalkylamine. However, evidence is against this sulphonium salt mechanism since phenyl sulphides in general resist sulphonium chloride formation.

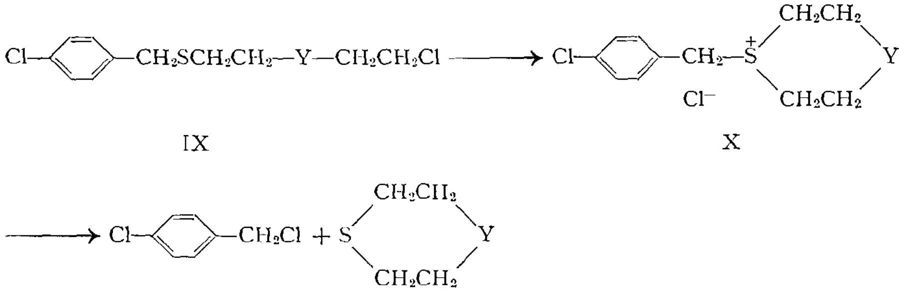
The formation of II ($n = 1$ and 2) from I might be attributed to a side reaction of I with *p*-chlorothiophenol in the presence of the amine. *p*-Chlorothiophenol could arise through an alkyl–sulphur bond cleavage of the quaternary ammonium salt V of I and III. A similar alkyl–sulphur bond cleavage has been experienced previously in the hydrazinolysis of β-*p*-chlorophenylmercapto-ethyl N,N-dimethyldithiocarbamate to *p*-chlorothiophenol (2).

The alkyl–sulphur bond in compounds of the benzyl series VI, unlike that of the phenyl series I, appeared to resist amine cleavage. Thus in the reaction of *p*-chlorobenzyl ω-chloroalkyl sulphides (VI) with amines only the normal products, VII, were formed and little if any of the neutral sulphides VIII could be detected.



However, an alkyl–sulphur bond cleavage of a different nature was encountered in this series. It was found that the *p*-chlorobenzyl ω-haloalkyl sulphides (VI) were thermally labile (unlike the members of the phenyl series I) and cleaved to *p*-chlorobenzyl chloride and a sulphur component. ω-Bromoalkyl *p*-chlorobenzyl sulphides were even more sensitive to heat and yielded *p*-chlorobenzyl bromide.

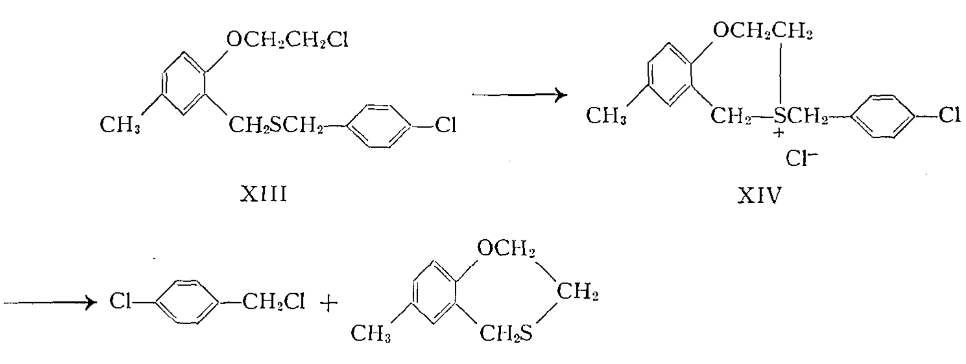
The lower members of the series VI could be distilled *in vacuo* with little if any decomposition but the higher members (n = 4 and 5) were too labile. Thus vacuum distillation of IX (Y = 0), IX (Y = CH_2), IX (Y = S), and IX (Y = 0) yielded *p*-chlorobenzyl chloride (XI) in each case together with tetrahydrothiophene (XII, Y = 0) (not isolated),


IX X
XI XII

pentamethylene sulphide (XII, Y = CH_2), 1,4-dithiane (XII, Y = S), and 1,4-oxathiane (XII, Y = 0) respectively. An attempt to prepare 4-bromo-2-butenyl *p*-chlorobenzyl sulphide from *p*-chlorobenzyl mercaptan and 1,4-dibromo-2-butene resulted in a mixture of *p*-chlorobenzyl bromide and a malodorous liquid which was probably dihydrothiophene.

The explanation for these reactions must involve sulphonium salt formation. Thus intramolecular sulphonium salt cyclization of IX could occur to form the ring X, which by dissociation would yield *p*-chlorobenzyl chloride (XI) and the cyclic sulphur compound (XII). Similar alkyl–sulphur bond cleavages with and without cyclizations have been reported by other workers (3, 4, 5). Bell, Bennett, and Hock (3) showed that mustard gas when heated at 180° yielded *p*-dithiane and ethylene dichloride. They proposed a mechanism for this reaction which consisted of both intermolecular and intramolecular sulphonium salt formation followed by dissociation.

An interesting example is provided of an alkyl–sulphur bond cleavage which must involve a seven-membered sulphonium salt ring (XIV). Thus when 2-β-chloroethoxy-5-methylbenzyl *p*-chlorobenzyl sulphide (XIII) was slowly distilled at 11 mm pressure, a


XIII XIV
XI XV

mixture of low-boiling compounds was obtained. These compounds proved to be *p*-chlorobenzyl chloride (XI) and 2,3-dihydro-7-methylbenzo(*f*)-1,4-oxathiepin (XV) (6).

EXPERIMENTAL

Bis(p-chlorophenylmercapto)methane (II, *n = 1*) *from p-Chlorophenyl Chloromethyl Sulphide* (I, *n = 1*)

To *p*-chlorophenyl chloromethyl sulphide (7) (20 g) was added *t*-butylamine (40 ml) and the solution was heated under reflux for 4 hours. The precipitated *t*-butylamine hydrochloride was filtered off from the cooled reaction mixture and the filtrate freed of excess *t*-butylamine by distillation. The residue was dissolved in benzene, the solution washed with water, and the solvent removed. The residue distilled at 160–162° (0.5 mm) and the distillate (12 g or 77%) when crystallized from methanol melted at 42–43° alone or in admixture with bis(*p*-chlorophenylmercapto)methane (8).

In another experiment *p*-chlorophenyl chloromethyl sulphide was heated in a sealed bomb with excess liquid ammonia at 50–55° for 15 hours. This yielded only bis(*p*-chlorophenylmercapto)methane.

1,2-Bis(p-chlorophenylmercapto)ethane (II, *n = 2*) *from p-Chlorophenyl 2-Chloroethyl Sulphide* (I, *n = 2*)

A solution of *p*-chlorophenyl 2-chloroethyl sulphide (20 g) and di-*n*-butylamine (40 ml) was heated under reflux for 5 hours. The excess di-*n*-butylamine was removed *in vacuo* and the residue was crystallized from methanol. The white prisms (9 g) melted at 92–93° and did not depress the melting point of 1,2-bis(*p*-chlorophenylmercapto)ethane (9).

In another experiment *p*-chlorophenyl 2-chloroethyl sulphide was heated in a sealed bomb with methylamine at 140° for 6 hours. The product was 1,2-bis(*p*-chlorophenylmercapto)ethane.

2-(Di-n-butylamino)ethyl p-Chlorophenyl Sulphide (III, *n = 2*, R = C_4H_9)

A solution of *p*-chlorophenyl 2-chloroethyl sulphide (50 g) and di-*n*-butylamine (100 ml) was heated at 115–125° for 18 hours. The excess di-*n*-butylamine was removed *in vacuo*, the residue dissolved in benzene, and the solution washed with dilute hydrochloric acid. The benzene was removed and the residue distilled yielding a very viscous distillate (52 g) boiling at 160° (0.5 mm). When it was rubbed and warmed, it solidified and the white solid melted at 86–88°. This proved to be the hydrochloride of 2-(di-*n*-butylamino)-ethyl *p*-chlorophenyl sulphide (it is rather unusual that an amine salt should distill and be soluble in benzene). Anal. Calc. for $C_{16}H_{27}NCl_2S$: C, 57.14; H, 8.03. Found: C, 56.68; H, 7.79.

The free base was liberated from the hydrochloride by dissolving the latter in benzene and shaking with aqueous sodium hydroxide. 2-(Di-*n*-butylamino)ethyl *p*-chlorophenyl sulphide boiled at 137–140° (0.5 mm), $n_D^{20} = 1.5350$ and remained a colorless mobile liquid. Anal. Calc. for $C_{16}H_{26}NClS$: C, 64.11; H, 8.68. Found: C, 63.58, 63.27; H, 8.34, 8.52.

In another experiment when *p*-chlorophenyl 2-chloroethyl sulphide was heated with di-*n*-butylamine at 130–150° for 5 hours, a mixture of 2-(di-*n*-butylamino)ethyl *p*-chlorophenyl sulphide and 1,2-bis(*p*-chlorophenylmercapto)ethane was obtained.

4-(Di-n-butylamino)butyl p-Chlorophenyl Sulphide (III, *n = 4*, R = C_4H_9)

A solution of *p*-chlorophenyl 4-chlorobutyl sulphide (1) (17 g) and di-*n*-butylamine

(50 ml) was heated under reflux for 5 hours. The excess amine was removed *in vacuo*, the residue was dissolved in benzene, and the solution washed with aqueous sodium hydroxide and with water. Removal of the solvent and distillation of the residue yielded a colorless liquid (18 g), b.p. = 155° (0.5 mm); $n_D^{22} = 1.5288$. Anal. Calc. for $C_{18}H_{30}NClS$: C, 65.95; H, 9.16. Found: C, 65.43; H, 8.98.

2-(Diethylamino)ethyl p-Chlorophenyl Sulphide (III, $n = 2$, R = C_2H_5)

A solution of *p*-chlorophenyl 2-chloroethyl sulphide (20 g) and 98% diethylamine (35 ml) was heated at 120–130° in a sealed bomb for 6 hours. The product which was worked up as above boiled at 163–165° (11 mm); $n_D^{22} = 1.5535$. The yield was 12 g. Anal. Calc. for $C_{12}H_{18}NClS$: C, 59.14; H, 7.39. Found: C, 58.81, 59.25; H, 7.53, 7.50.

2-Aminoethyl p-Chlorophenyl Sulphide (III, $n = 2$, R = H)

To a solution of sodium hydroxide (10 g) in water (100 ml) was added *p*-chlorothiophenol (16 g) and 2-bromoethylamine hydrobromide (20 g) in water (30 ml). The resulting solution was heated on the steam bath for ½ hour and the precipitated oil was extracted with benzene. The benzene solution was washed with water, the solvent removed, and the residue distilled, b.p. = 152° (11 mm); $n_D^{25} = 1.6025$. The yield was 15 g. Anal. Calc. for $C_8H_{10}NClS$: C, 51.20; H, 5.33. Found: C, 50.27, 50.87; H, 5.25, 5.31.

2-Aminoethyl Pentachlorophenyl Sulphide

This was prepared in 60% yield from pentachlorobenzenethiol and 2-bromoethylamine hydrobromide as above. The white prisms crystallized from benzene – petroleum ether and melted at 89–90°. Anal. Calc. for $C_8H_6NCl_5S$: C, 29.46; H, 1.81. Found: C, 30.17, 29.81; H, 2.23, 2.12.

p-Chlorobenzyl 2-(Di-n-butylamino)ethyl Sulphide (VII, $n = 2$, R = C_4H_9)

A solution of *p*-chlorobenzyl 2-chloroethyl sulphide (9) (20 g) and di-*n*-butylamine (40 ml) was heated under reflux for 3 hours. The excess amine was removed *in vacuo*, the residue dissolved in benzene and washed with water. The solvent was removed and the residue fractionally distilled. The first fraction consisted of low-boiling material. The second fraction (7 g), which boiled at 137–140° (0.5 mm); $n_D^{27} = 1.5320$, was the required *p*-chlorobenzyl 2-(di-*n*-butylamino)ethyl sulphide. Anal. Calc. for $C_{17}H_{28}NClS$: C, 65.07; H, 8.93. Found: C, 65.26; H, 8.75.

The third fraction (3 g) boiled at 180–210° (0.5 mm) and the distillate on crystallization from methanol yielded white prisms (1.2 g) which melted at 74–76° alone or in admixture with 1,2-bis(*p*-chlorobenzylmercapto)ethane (9).

Pyrolysis of p-Chlorobenzyl 5-Chloropentyl Sulphide (VI, $n = 5$)

The crude *p*-chlorobenzyl 5-chloropentyl sulphide (40 g) (see below) was distilled at 12 mm first, and the distillate was then fractionated.

Fraction 1 consisted of 9 g of colorless malodorous liquid boiling at 140°; $n_D^{20} = 1.5060$. These properties agree with those of pentamethylene sulphide (10, 11). When a portion of fraction 1 was dissolved in acetic acid and treated with 30% hydrogen peroxide, pentamethylene sulphone (12), m.p. 96–97°, was formed.

Fraction 2 consisted of 19 g of colorless lachrymatory liquid; $n_D^{20} = 1.5560$ boiling at 87–89° (11 mm). It solidified on cooling and melted at 29°. Recrystallization from petroleum ether yielded long white needles melting at 29–30° alone or in admixture with *p*-chlorobenzyl chloride.

Pyrolysis of p-Chlorobenzyl 4-Chlorobutyl Sulphide (VI, $n = 4$)

Crude *p*-chlorobenzyl 4-chlorobutyl sulphide was prepared and pyrolyzed as above. *p*-Chlorobenzyl chloride was obtained in 74% yield but no tetrahydrothiophene could be isolated.

Pyrolysis of p-Chlorobenzyl 4-Bromo-2-butenyl Sulphide

To a stirred solution of potassium hydroxide (11 g) in methanol (200 ml) and *p*-chlorobenzyl mercaptan (30 g), cooled to 0°, was added a chilled solution of 1,4-dibromo-2-butene (100 g) in benzene (100 ml). The reaction mixture was stirred with cooling at 5–10° for 1 hour. The precipitated potassium bromide was filtered off and the solvents were removed from the filtrate. The residue was dissolved in benzene, the solution washed with water, and the solvent removed. The residue was distilled at 11 mm and the distillate then fractionated. Fraction 1 was a colorless malodorous liquid boiling at 40–60° (11 mm) and was probably dihydrothiophene. Fraction 2, boiling at 60–95° (11 mm), consisted mainly of 1,4-dibromo-2-butene. Fraction 3 (14 g) boiled at 95–102° (11 mm) and on crystallization from methanol yielded white needles melting at 49–50° alone or in admixture with *p*-chlorobenzyl bromide (13).

β-p-Chlorobenzylmercaptoethyl 2-Hydroxyethyl Sulphide

To a solution of potassium hydroxide (6 g) in methanol (100 ml) was added 2-mercaptoethanol (9 ml) and *p*-chlorobenzyl 2-chloroethyl sulphide (9) (20 g). The resulting solution was heated under reflux for 2 hours and then the methanol distilled off. The residual oil was extracted with benzene, the solution washed with water, and the solvent removed. The residue distilled at 175–178 (0.5 mm) yielding 19 g of a colorless liquid, $n_D^{26} = 1.5992$. Anal. Calc. for $C_{11}H_{15}OClS_2$: C, 50.28; H, 5.71. Found: C, 50.59; H, 5.82.

β-o-Chlorobenzylmercaptoethyl 2-Hydroxyethyl Sulphide

This was prepared in 87% yield from *o*-chlorobenzyl 2-chloroethyl sulphide as above, b.p. = 170–175° (0.5 mm); $n_D^{22} = 1.6020$. Anal. Calc. for $C_{11}H_{15}OClS_2$: C, 50.28; H, 5.71. Found: C, 50.55; H, 5.76.

Pyrolysis of β-p-(IX, Y = S) *and β-o-Chlorobenzylmercaptoethyl 2-Chloroethyl Sulphide*

A solution of *β-o*-chlorobenzylmercaptoethyl 2-hydroxyethyl sulphide (30 g), benzene (100 ml), and thionyl chloride (12 ml) was heated under reflux for 2 hours. The benzene and excess thionyl chloride were removed *in vacuo* and the residue was slowly distilled at 11 mm. The distillate was cooled and the white malodorous precipitate (6 g) filtered, washed with cold methanol, and dried. It sublimed readily and melted at 111–112°. This was *p*-dithiane (14).

The filtrate on distillation yielded *o*-chlorobenzyl chloride.

When *β-p*-chlorobenzylmercaptoethyl 2-hydroxyethyl sulphide was converted to the 2-chloroethyl derivative IX, (Y = S) with thionyl chloride and treated as above, a separable mixture of *p*-dithiane and *p*-chlorobenzyl chloride was obtained.

Pyrolysis of β-p-Chlorobenzylmercaptoethyl 2-Chloroethyl Ether (IX, Y = 0)

β-p-Chlorobenzylmercaptoethyl 2-chloroethyl ether (10 g) (see below) was heated at 160–170° for 7 hours. A malodorous liquid (3 g) distilled into the receiver which on redistillation boiled at 147–150°; $n_D^{22} = 1.5070$. The properties of this compound are in agreement with those given for 1,4-oxathiane (15, 16).

The residue on distillation yielded 5 g of *p*-chlorobenzyl chloride.

Pyrolysis of 2-β-Chloroethoxy-5-methylbenzyl p-Chlorobenzyl Sulphide (XIII)

To a solution of potassium hydroxide (5 g) in methanol (100 ml) was added *p*-chlorobenzyl mercaptan (11 g) and 2-β-chloroethoxy-5-methylbenzyl chloride (6) (15 g) in that order. The resulting reaction mixture was heated under reflux for 15 minutes. The methanol was removed, the residue dissolved in benzene, the solution washed with water, and the solvent removed. The residue was distilled slowly at 11 mm pressure up to 200° and the distillate was fractionated. Fraction 1 (5 g) which boiled at 80–135° (11 mm) was treated with thiourea in ethanol. The resulting isothiuronium salt melted at 205–207° and did not depress the melting point of the isothiuronium salt of *p*-chlorobenzyl chloride. Fraction 2 (9 g) boiled at 135–150° (11 mm) and when crystallized from methanol yielded white prisms melting at 45–46° alone or in admixture with 2,3-dihydro-7-methylbenzo(*f*)-1,4-oxathiepin (XV) (6).

Preparation of ω-Chloroalkyl Sulphides

These were prepared by the method used for 2-chloroethyl aryl and aralkyl sulphides previously described (9).

(*a*) *p-Chlorobenzyl 3-chloropropyl sulphide* (VI, $n = 3$) was obtained in 87% yield from 1,3-dichloropropane and *p*-chlorobenzyl mercaptan, b.p. = 115–118 (0.5 mm); $n_D^{22} = 1.5720$. Anal. Calc. for $C_{10}H_{12}Cl_2S$: C, 51.06; H, 5.10. Found: C, 50.63, 50.91; H, 4.89, 4.64.

(*b*) *p-Chlorobenzyl 3-bromopropyl sulphide* was prepared in 60% yield from 1,3-dibromopropane and *p*-chlorobenzyl mercaptan, b.p. = 120–125° (0.5 mm); $n_D^{22} = 1.5884$. Anal. Calc. for $C_{10}H_{12}ClBrS$: C, 42.93; H, 4.29. Found: C, 42.21, 42.27; H, 3.39, 3.50.

(*c*) *p-Chlorobenzyl 2-bromoethyl sulphide* could not be prepared in pure form because pyrolysis occurred during distillation to form *p*-chlorobenzyl bromide.

(*d*) *n-Amyl 4-chlorobutyl sulphide* was prepared in 20% yield from *n*-amyl mercaptan and 1,4-dichlorobutane, b.p. = 120–130° (11 mm); $n_D^{23} = 1.4775$. Anal. Calc. for $C_9H_{19}ClS$: C, 55.53; H, 9.76. Found: C, 56.33, 56.74; H, 9.75, 9.84.

(*e*) *β-p-Chlorobenzylmercaptoethyl 2-chloroethyl ether* (IX, Y = 0) was prepared in 75% yield from *p*-chlorobenzyl mercaptan and excess β,β′-dichloroethyl ether, b.p. = 137–140° (0.5 mm); $n_D^{22} = 1.5618$. Anal. Calc. for $C_{11}H_{14}OCl_2S$: C, 49.81; H, 5.28. Found: C, 49.94, 49.82; H, 5.08, 5.12.

(*f*) *p-Chlorobenzyl 5-chloropentyl sulphide* (VI, $n = 5$) was prepared from *p*-chlorobenzyl mercaptan and 1,5-dichloropentane (17). No attempt was made to distill the crude product because it pyrolyzed very readily.

(*g*) *Crude p-chlorobenzyl 4-chlorobutyl sulphide* (VI, $n = 4$) was prepared similarly.

o-Chlorobenzyl 2-Hydroxyethyl Sulphide

To a stirred mixture of sodium hydroxide (70 g) in 2-mercaptoethanol (200 ml) and benzene (200 ml) was added, over $\frac{1}{2}$ hour, a solution of *o*-chlorobenzyl chloride (250 g) in benzene (150 ml). The reaction mixture boiled vigorously. It was heated under reflux for 2 hours, washed with water, the solvent removed, and the residue distilled, b.p. = 175–178° (11 mm); $n_D^{20} = 1.5832$. The yield was 293 g. Anal. Calc. for $C_9H_{11}OClS$: C, 53.33; H, 5.43. Found: C, 53.73; H, 5.58.

o-Chlorobenzyl 2-Chloroethyl Sulphide

To a stirred solution of *o*-chlorobenzyl 2-hydroxyethyl sulphide (200 g) in benzene (250 ml) was added, over $\frac{1}{2}$ hour, thionyl chloride (125 g) with cooling. The reaction mixture was heated under reflux for 1 hour, the solvent removed, and the residual oil distilled, b.p. = 155–158° (11 mm); n_D^{23} = 1.5827. The yield was 190 g. Anal. Calc. for $C_9H_{10}Cl_2S$: C, 48.87; H, 4.52. Found: C, 48.76; H, 4.05.

β-p-t-Butylphenoxyethyl 2-Hydroxyethyl Sulphide

This was prepared in 90% yield from *p-t*-butylphenyl 2-chloroethyl ether and 2-mercaptoethanol in the same way as was *o*-chlorobenzyl 2-hydroxyethyl sulphide above. The colorless liquid boiled at 205–210° (11 mm); n_D^{23} = 1.5410. Anal. Calc. for $C_{14}H_{22}O_2S$: C, 66.14; H, 8.66. Found: C, 65.49; H, 8.86.

β-p-t-Butylphenoxyethyl 2-Chloroethyl Sulphide

This was prepared in 94% yield by treatment of *β-p-t*-butylphenoxyethyl 2-hydroxyethyl sulphide with thionyl chloride. It distilled at 145–148° (0.5 mm) as a colorless liquid, n_D^{22} = 1.5400. Anal. Calc. for $C_{14}H_{21}OClS$: C, 61.65; H, 7.70. Found: C, 61.83; H, 7.79.

Preparation of the Aminoalkyl Sulphides

These were prepared by the same method as was (*a*).

(*a*) *p-Chlorobenzyl 2-aminoethyl sulphide* (VII, $n = 2$, R = H) was prepared by the addition of liquid ammonia (about 100 ml) to 30 g *p*-chlorobenzyl 2-chloroethyl sulphide cooled by dry ice, and the reaction mixture was sealed in a hydrogenation bomb and heated at 135–140° for 6 hours. The excess ammonia was allowed to evaporate, the residue treated with aqueous sodium hydroxide and extracted with benzene. The benzene solution was washed with water, the solvent removed, and the residue distilled. Most of it (20 g) distilled at 103–105° (0.2 mm) as a colorless liquid; n_D^{25} = 1.5850. Anal. Calc. for $C_9H_{12}NClS$: C, 53.59; H, 5.95. Found: C, 52.83, 53.01; H, 5.83, 6.02. The residue from the distillation on treatment with hydrochloric acid and crystallization from methanol yielded 3 g of bis(*β-p*-chlorobenzylmercaptoethyl)amine hydrochloride melting at 140–141°. Anal. Calc. for $C_{18}H_{21}NCl_2S_2$: C, 51.07; H, 5.20. Found: C, 51.22, 51.32; H, 5.26, 5.36.

(*b*) *o-Chlorobenzyl 2-aminoethyl sulphide* was prepared from *o*-chlorobenzyl 2-chloroethyl sulphide in 76% yield. The almost colorless liquid boiled at 160–165° (13 mm); n_D^{24} = 1.5862. Anal. Calc. for $C_9H_{12}NClS$: C, 53.59; H, 5.95. Found: C, 53.86, 53.38; H, 5.56, 5.93.

(*c*) *β-p-Chlorobenzylmercaptoethyl 2-aminoethyl ether* was prepared from *β-p*-chlorobenzylmercaptoethyl 2-chloroethyl ether in 45% yield. It distilled as a colorless liquid boiling at 135–137° (0.5 mm); n_D^{22} = 1.5640. Anal. Calc. for $C_{11}H_{16}NOClS$: C, 53.77; H, 6.42. Found: C, 53.68, 52.97; H, 6.25, 6.21.

(*d*) *p-Chlorobenzyl 5-aminopentyl sulphide* (VII, $n = 5$, R = H) was prepared in 25% yield from crude *p*-chlorobenzyl 5-chloropentyl sulphide. It distilled at 145–150° (0.5 mm); n_D^{25} = 1.5580. Anal. Calc. for $C_{12}H_{18}NClS$: C, 59.14; H, 7.39. Found: C, 58.94, 59.41; H, 7.10, 7.14.

(*e*) *p-Chlorobenzyl 3-amino-2-hydroxypropyl sulphide* was prepared from *p*-chlorobenzyl 3-chloro-2-hydroxypropyl sulphide (9) in 68% yield. It distilled at 170–175° (0.5 mm) and crystallized from ether containing a little methanol as white prisms which melted at 85–86°. Anal. Calc. for $C_{10}H_{14}NOClS$: C, 51.84; H, 6.04. Found: C, 51.96; H, 5.80. The residue from the distillation crystallized from methanol to yield bis(1-*p*-chlorobenzylmercapto-2-hydroxypropyl)amine melting at 97–100°. Anal. Calc. for $C_{20}H_{25}NO_2Cl_2S_2$: C, 53.81; H, 5.60. Found: C, 54.25, 53.85; H, 5.47, 5.31.

(*f*) *p-Chlorobenzyl 3-aminopropyl sulphide* (VII, $n = 3$, R = H) was prepared from *p*-chlorobenzyl 3-chloropropyl sulphide in 67% yield. It distilled as a colorless liquid with b.p. = 112–115° (0.5 mm); $n_D^{22} = 1.5754$. Anal. Calc. for $C_{10}H_{14}NClS$: C, 55.68; H, 6.49. Found: C, 54.91, 55.13; H, 6.47, 5.99.

(*g*) *n-Amyl 4-aminobutyl sulphide* was prepared from *n*-amyl 4-chlorobutyl sulphide in 42% yield. It distilled as a colorless liquid with b.p. = 112° (11 mm); $n_D^{23} = 1.4790$. Anal. Calc. for $C_9H_{21}NS$: C, 61.71; H, 12.00. Found: C, 60.99, 61.17; H, 11.91, 12.17.

(*h*) *n-Dodecyl 2-aminoethyl sulphide* was prepared from *n*-dodecyl 2-chloroethyl sulphide (18) in 50% yield. It distilled as a yellow liquid with b.p. = 120–123° (0.5 mm); $n_D^{23} = 1.4755$. Anal. Calc. for $C_{14}H_{31}NS$: C, 68.57; H, 12.65. Found: C, 68.56, 68.76; H, 12.21, 12.62.

(*i*) *β-p-t-Butylphenoxyethyl 2-aminoethyl sulphide* was prepared from *β-p-t*-butylphenoxyethyl 2-chloroethyl sulphide in 73% yield. It distilled as an almost colorless liquid with b.p. = 138–140° (0.5 mm); $n_D^{24} = 1.5400$. Anal. Calc. for $C_{14}H_{23}NOS$: C, 66.40; H, 9.09. Found: C, 66.44; H, 9.16.

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