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SOME ARALKYL AND ARYL ALKYL SULPHIDES AND DISULPHIDES[1]

MARSHALL KULKA AND F. G. VAN STRYK

ABSTRACT

Sixty sulphides and disulphides have been prepared from mercaptans and alkyl and alkylene halides for testing as insecticides.

In a co-operative program of insecticide research, a series of sulphides and disulphides were synthesized in this laboratory and screened for aphicide action at the Ontario Agricultural College by Professor A. J. Musgrave and Mr. I. Kukovica (10). This paper describes the preparation and some reactions of these compounds.

The method of Patterson and du Vigneaud (12), which comprises heating the mercaptan (I) in the presence of alkali with a large excess of ethylene dichloride, was employed in the preparation of the aralkyl 2-chloroethyl sulphides (II) listed in Table I:

$$\underset{\text{I}}{\text{RSH}} + \text{NaOCH}_3 + \text{ClCH}_2\text{CH}_2\text{Cl} \rightarrow \underset{\text{II}}{\text{RSCH}_2\text{CH}_2\text{Cl}} + \text{NaCl} + \text{CH}_3\text{OH}$$

Aralkyl 3-bromopropyl sulphides could not be obtained by this method from 1,3-dibromopropane because at some stage during the reaction with the benzyl mercaptan (I) dehydrohalogenation occurred and the aralkyl allyl sulphide formed. When two moles of the mercaptan (7) and one mole of the alkylene dichloride were allowed to react the product was the disulphide (III) (Table V):

$$2\text{RSH} + 2\text{NaOCH}_3 + \text{Cl(CH}_2)_n\text{Cl} \rightarrow \underset{\text{III}}{\text{RS(CH}_2)_n\text{SR}} + 2\text{NaCl} + 2\text{CH}_3\text{OH}$$

It is known that sodium alkoxides react with trichloroethylene to give α,β-dichlorovinyl ethers (6). Also Cusa and McCombie (4) have provided evidence that the reaction product of thiophenol and trichloroethylene has the α,β-dichlorovinyl sulphide structure (IV).

$$\underset{\text{I}}{\text{RSH}} + \text{NaOCH}_3 + \text{Cl}_2\text{C{=}CHCl} \rightarrow \underset{\text{IV}}{\text{RSCCl{=}CHCl}} + \text{NaCl} + \text{CH}_3\text{OH}$$

On this basis it was concluded that the reaction products of benzyl mercaptans (I) and trichloroethylene recorded in Table IV are α,β-dichlorovinyl benzyl sulphides (IV) and not the β,β-dichlorovinyl sulphides.

2-(*p*-Chlorophenylmercapto) cyclohexanone (V), which was readily obtained from *p*-chlorothiophenol and 2-chlorocyclohexanone, proved to be a good source for ω-*p*-chlorobenzenesulphonylhexanoic acid (VII). The sulphone VI, obtained by hydrogen

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TABLE I

THE PREPARATION OF 2-CHLOROETHYL SULPHIDES, $RSCH_2CH_2Cl$ (II), FROM THE CORRESPONDING MERCAPTANS, RSH (I), AND ETHYLENE DICHLORIDE

$RSCH_2CH_2Cl$ R =	M.p. or b.p.	n_D^{20}	Yield, %	Empirical formula	Analyses Calc. C	Analyses Calc. H	Analyses Found C	Analyses Found H
p-Chlorobenzyl	b_{12} = 163–164	1.5822	80	$C_9H_{10}Cl_2S$	48.87	4.52	49.19	4.49
2,4-Dichlorobenzyl	b_{12} = 182–185	1.5940	85	$C_9H_9Cl_3S$	42.27	3.52	42.50	3.61
3,4-Dichlorobenzyl	b_{13} = 186–189	1.5953	88	$C_9H_9Cl_3S$	42.27	3.52	42.05	3.51
2,4-Dimethylbenzyl	b_{13} = 155–157	1.5573	74	$C_{11}H_{15}ClS$	61.55	7.00	61.27	7.21
4,4′-Dichlorobenzhydryl	$b_{0.1}$ = 165	1.6088	85	$C_{15}H_{13}Cl_3S$	54.32	3.92	54.06	3.99
α-Naphthylmethyl	Not purified							
3-Phenylpropyl	b_{12} = 160–162	1.5500	65	$C_{11}H_{15}ClS$	61.55	6.99	62.59	7.13
3-*p*-Chlorophenylpropyl	b_{13} = 195–200	1.5644	85	$C_{11}H_{14}Cl_2S$	53.01	5.62	53.20	5.55
4-*p*-Chlorophenoxybutyl	b_1 = 165	1.5570	90	$C_{12}H_{16}OCl_2S$	51.61	5.73	51.91	5.59
p-$(ClCH_2CH_2SCH_2)_2C_6H_4$*	m.p. 73–74		40	$C_{12}H_{16}Cl_2S_2$	48.83	5.43	49.11	5.42

**Prepared from p-xylylene dimercaptan and ethylene dichloride.*

TABLE II

THE PREPARATION OF $RSCH_2CH_2SCN$ BY HEATING $RSCH_2CH_2Cl$ (II) WITH ALCOHOLIC KSCN FOR A FEW HOURS

$RSCH_2CH_2SCN$ R =	B.p. or m.p.	n_D^{20}	Yield, %	Empirical formula	Analyses Calc. C	Analyses Calc. H	Analyses Found C	Analyses Found H
p-Chlorobenzyl	b_1 = 155–158	1.6065	90	$C_{10}H_{10}NClS_2$	49.28	4.11	49.30	4.16
2,4′-Dichlorobenzyl	$b_{0.2}$ = 158–160	1.6200	82	$C_{10}H_9NCl_2S_2$	43.17	3.24	43.29	3.28
3,4-Dichlorobenzyl	$b_{0.2}$ = 165–167	1.6240	85	$C_{10}H_9NCl_2S_2$	43.17	3.24	42.92	3.25
α-Naphthylmethyl	m.p. 62–63			$C_{14}H_{13}NS_2$	64.87	5.02	64.74	4.80
3-Phenylpropyl	$b_{0.5}$ = 138–140	1.5892	70	$C_{12}H_{15}NS_2$	60.76	6.33	60.58	6.56
3-*p*-Chlorophenylpropyl	$b_{0.5}$ = 160–164	1.5960	90	$C_{12}H_{14}NClS_2$	53.04	5.16	53.55	5.30
p-$(NCSCH_2CH_2SCH_2)_2C_6H_4$	m.p. 70–71		86	$C_{14}H_{16}N_2S_4$	49.41	4.70	49.79	4.68
2,5-Dichlorophenyl (1)	b_{12} = 216–219	1.6229	62	$C_9H_7NCl_2S_2$	40.91	2.65	40.50	2.64

TABLE III

PREPARATION OF $RYCH_2CH_2SCH_2CH_2YR$ (XI) FROM BIS-2-CHLOROETHYL SULPHIDE AND PHENOLS OR THIOPHENOLS (RYH)

$RYCH_2CH_2SCH_2CH_2YR$ RY =	M.p.	Yield, %	Empirical formula	Analyses Calc. C	Analyses Calc. H	Analyses Found C	Analyses Found H
p-Chlorophenoxy	56–57	52	$C_{16}H_{16}O_2Cl_2S$	55.98	4.67	56.52	4.90
p-Chlorophenylmercapto	81–82		$C_{16}H_{16}Cl_2S_3$	51.20	4.27	51.22	4.27
p-*t*-Butylphenoxy	41–42	45	$C_{24}H_{34}O_2S_2$	74.61	8.81	74.90	8.51
4-Chloro-2-acetylphenoxy	114–115	60	$C_{20}H_{20}O_4Cl_2S$	56.20	4.68	56.69	4.94
2-Methoxy-4-formylphenoxy	131–132	48	$C_{20}H_{22}O_6S$	61.53	5.64	61.88	5.83
2-Mercaptobenzothiazolyl	71–72	50	$C_{18}H_{16}N_2S_5$	51.44	3.81	51.30	3.84

TABLE IV

PREPARATION OF SULPHIDES FROM MERCAPTANS AND ALKYL HALIDES

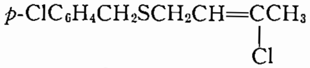
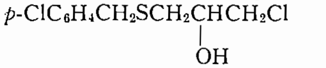
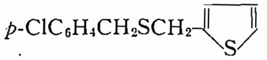
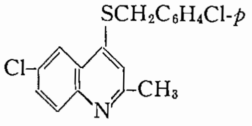
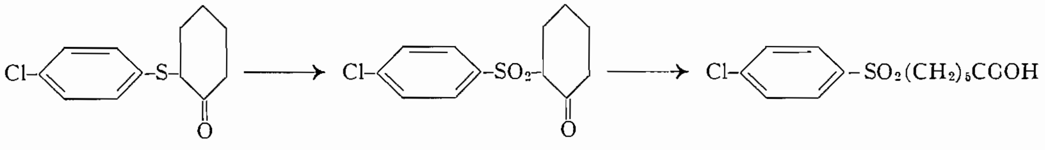
						Analyses			
						Calc.		Found	
Sulphide prepared	Reactants	M.p. or b.p.	n_D^{20}	Yield, %	Empirical formula	C	H	C	H
p-$ClC_6H_4CH_2SCH_2CH{=}CH_2$	p-$ClC_6H_4CH_2SH$ $ClCH_2CH{=}CH_2$	b_{13} = 140	1.5732	88	$C_{10}H_{11}ClS$	60.45	5.54	60.14	5.50
 p-$ClC_6H_4CH_2SCH_2CH{=}\underset{Cl}{C}CH_3$	p-$ClC_6H_4CH_2SH$ $ClCH_2CH{=}CClCH_3$	b_{12} = 176–177	1.5800	92	$C_{11}H_{12}Cl_2S$	53.44	4.86	53.37	4.58
 p-$ClC_6H_4CH_2SCH_2\underset{OH}{CH}CH_2Cl$	p-$ClC_6H_4CH_2SH$ $ClCH_2CHOHCH_2Cl$ (3)	$b_{0.3}$ = 143–145	1.5858	80	$C_{10}H_{12}OCl_2S$	47.81	4.78	48.03	4.50
p-$ClC_6H_4SCH_2CHOHCH_2Cl$	p-ClC_6H_4SH $ClCH_2CHOHCH_2Cl$ (3)	b_{12} = 193–195	1.5975		$C_9H_{10}OCl_2S$	45.57	4.22	45.88	4.04
p-$ClC_6H_4CH_2SCH_2CHOHCH_3$	p-$ClC_6H_4CH_2SH$ $ClCH_2CHOHCH_3$	$b_{0.2}$ = 115	1.5720	94	$C_{10}H_{13}OClS$	55.43	6.00	54.99	5.99
p-$ClC_6H_4CH_2SCCl{=}CHCl$	p-$ClC_6H_4CH_2SH$ $Cl_2C{=}CHCl$	b_{14} = 170–172	1.6040	50	$C_9H_7Cl_3S$	42.60	2.76	42.69	2.94
3,4-$Cl_2C_6H_3CH_2SCCl{=}CHCl$	3,4-$Cl_2C_6H_3CH_2SH$ $Cl_2C{=}CHCl$	b_1 = 140–145	1.6147	65	$C_9H_6Cl_4S$	37.50	2.08	37.65	2.38
2,4-$Cl_2C_6H_3CH_2SCCl{=}CHCl$	2,4-$Cl_2C_6H_3CH_2SH$ $Cl_2C{=}CHCl$	$b_{0.5}$ = 120–123	1.6108	65	$C_9H_6Cl_4S$	37.50	2.08	38.73	2.55
2,4-$(CH_3)_2C_6H_3CH_2SCCl{=}CHCl$	2,4-$(CH_3)_2C_6H_3CH_2SH$ $Cl_2C{=}CHCl$	$b_{0.5}$=105–108	1.5825	70	$C_{11}H_{12}Cl_2S$	53.44	4.86	53.91	5.26
	p-$ClC_6H_4CH_2SH$ thienyl chloride	b_{11} = 206–207	1.6252	90	$C_{12}H_{11}ClS_2$	56.58	4.32	56.22	4.21
p-$ClC_6H_4S{-}C_6H_9O$	p-ClC_6H_4SH 2-Chlorocyclohexanone (11)	b_{11} = 200–202	1.5915	80	$C_{12}H_{13}OClS$	59.88	5.40	59.50	5.27
	p-$ClC_6H_4CH_2SH$ 4,6-dichloroquinaldine	m.p. = 113–114		88	$C_{17}H_{13}NCl_2S$	61.08	3.89	61.70	4.20

TABLE V

PREPARATION OF DISULPHIDES FROM ALKYLENE DIHALIDES AND *p*-CHLOROBENZYL MERCAPTAN OR *p*-CHLOROTHIOPHENOL

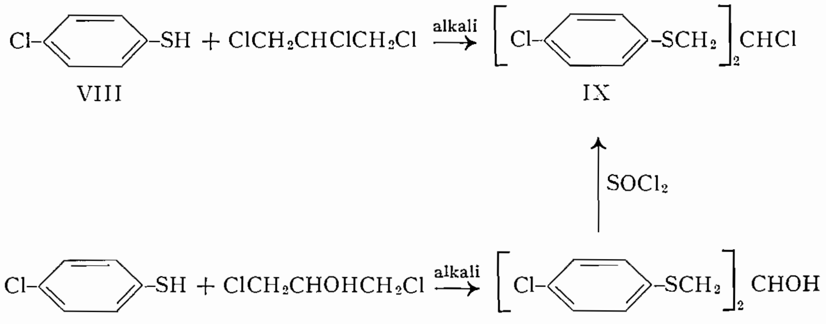
Disulphides prepared R = *p*-ClC_6H_4-	Reactants R = *p*-ClC_6H_4-	M.p.	Yield, %	Empirical formula	Analyses Calc. C	Analyses Calc. H	Analyses Found C	Analyses Found H
$[RCH_2SCH_2CH{=}]_2$	RCH_2SH and $BrCH_2CH{=}CHCH_2Br$	71–72	87	$C_{18}H_{18}Cl_2S_2$	58.54	4.88	58.55	4.63
$RSCH_2SR$ (9)	RSH and CH_2Cl_2	43–44	85	$C_{13}H_{10}Cl_2S_2$				
$RSCH_2CH_2SR$	RSH and $ClCH_2CH_2Cl$	92–93	32	$C_{14}H_{12}Cl_2S_2$	53.33	3.81	53.31	3.56
$RSCH_2CH_2CH_2SR$	RSH and $ClCH_2CH_2CH_2Cl$	36–37	12	$C_{15}H_{14}Cl_2S_2$	54.71	4.26	54.57	4.19
$RSCH_2CH_2CH_2CH_2SR$	RSH and $Cl(CH_2)_4Cl$	67–68	55	$C_{16}H_{16}Cl_2S_2$	55.98	4.67	55.95	4.61
$RSCH_2CH_2CH_2CH_2CH_2SR$	RSH and $Cl(CH_2)_5Cl$	51–52	35	$C_{17}H_{18}Cl_2S_2$	57.14	5.04	57.23	5.07
$RCH_2SCH_2SCH_2R$	RCH_2SH and CH_2Cl_2	53–54	30	$C_{15}H_{14}Cl_2S_2$	54.71	4.26	54.77	4.21
$RCH_2S(CH_2)_2SCH_2R$	RCH_2SH and $Cl(CH_2)_2Cl$	76–77	32	$C_{16}H_{16}Cl_2S_2$	55.98	4.67	56.02	4.66
$RCH_2S(CH_2)_3SCH_2R$	RCH_2SH and $Cl(CH_2)_3Cl$	23–24	31	$C_{17}H_{18}Cl_2S_2$	57.14	5.04	57.03	4.96
$RCH_2S(CH_2)_4SCH_2R$	RCH_2SH and $Cl(CH_2)_4Cl$	54–55	12	$C_{18}H_{20}Cl_2S_2$	58.22	5.39	58.30	5.45
$RCH_2S(CH_2)_5SCH_2R$	RCH_2SH and $Cl(CH_2)_5Cl$	37–38	18	$C_{19}H_{22}Cl_2S_2$	59.22	5.71	59.06	5.65
$RSCH_2CHOHCH_2SR$	RSH and $ClCH_2CHOHCH_2Cl$	46–47	61	$C_{15}H_{14}OCl_2S_2$	52.18	4.05	51.93	3.81
$RSCH_2CHClCH_2SR$	RSH and $ClCH_2CHClCH_2Cl$	85–86	30	$C_{15}H_{13}Cl_3S_2$	49.53	3.57	49.66	3.45
$RSCH_2COCH_2SR$	RSH and $ClCH_2COCH_2Cl$ (2)	80–81	87	$C_{15}H_{12}OCl_2S_2$	52.48	3.50	52.43	3.45
$RS(CH_2)_3CO(CH_2)_3SR$	RSH and $Cl(CH_2)_3CO(CH_2)_3Cl$ (5)	63–64	80	$C_{19}H_{20}OCl_2S_2$	57.28	5.02	57.45	4.86

peroxide oxidation of the sulphide V, behaved like a typical β-ketosulphone (8) and gave VII in high yield when treated with dilute alkali.



V VI VII

It is interesting to note that 1,2,3-trichloropropane reacted with two moles of *p*-chlorothiophenol to yield 1,3-bis-*p*-chlorophenylmercapto-2-chloropropane (IX) as the main product, and the alkyl chlorine of IX was so inert that it failed to react with potassium thiocyanate, alkali mercaptides, and sodium N,N-dimethyldithiocarbamate. This is surprising in view of the fact that sodium N,N-dimethyldithiocarbamate has been found to react easily with many aliphatic and some aromatic halides (7). That this reaction product of VIII and 1,2,3-trichloropropane has the structure IX and is not the 1,2-isomer was indicated by the fact that 1,3-bis-(*p*-chlorophenylmercapto)-2-propanol (X) (obtained from VIII and 1,3-dichloro-2-propanol) could be converted to IX by thionyl chloride.



VIII IX X VIII

EXPERIMENTAL

Preparation of 2-Chloroethyl Aryl and Aralkyl Sulphides (Table I)

To a solution of sodium (0.2 mole) in methanol (50 ml.) was added the mercaptan (RSH, R = aralkyl) (0.2 mole). The resulting solution was cooled, ethylene dichloride (300 ml.) was added, and the reaction mixture heated under reflux for ½ hour. The reaction was only slightly exothermic. The reaction mixture containing precipitated sodium chloride was washed with water, the excess ethylene dichloride removed, and the residue distilled. Methanolic potassium hydroxide may be used instead of sodium and methanol with equally good results.

Preparation of the Bis-(aryloxyethyl) and Bis-(arylmercaptoethyl) Sulphides ($RYCH_2CH_2SCH_2CH_2YR$) (XI) from Bis-(2-chloroethyl) Sulphide (Table III)

To a solution of sodium (0.2 mole) in methanol (200 ml.) was added the phenol or the thiophenol (0.2 mole) followed by bis-(2-chloroethyl) sulphide (0.1 mole), and the reaction mixture was heated under reflux for 3 hours. The methanol solution was decanted from the precipitated salt, the solvent removed, the residue dissolved in benzene, and the benzene solution washed with aqueous sodium hydroxide and with water. The solvent was removed from the benzene solution and the residue crystallized from methanol or benzene.

Preparation of the Sulphides Listed in Table IV

These sulphides were prepared by the same method as were the 2-chloroalkyl aralkyl sulphides (II) of Table I (above) using excess alkyl halide where possible. In those cases where the boiling point of the alkyl halide was over 100° an excess was not used. Instead, benzene or methyl ethyl ketone was employed as solvent. With less reactive halides such as trichloroethylene the reaction time had to be extended to 5 hours.

Preparation of the Disulphides from Alkylene Dihalides (Table V)

The method used here was essentially the same as that employed in the preparation of 1,3-bis-(*p*-chlorophenylmercapto)-2-propanol except that distillation of the final product was not necessary (see p. 526).

p-Chlorobenzyl 2-Chloroethyl Sulphone

To a solution of *p*-chlorobenzyl 2-chloroethyl sulphide (5 g.) (Table I) in acetic acid (15 ml.) was added 30% hydrogen peroxide (15 ml.) and the solution heated on the steam bath for ½ hour with occasional cooling in order to keep the temperature below 100°. The resulting solution was diluted with a few milliliters of water and allowed to cool. White needles (5.4 g. or 95%) precipitated and melted at 119–120°. Anal. calc. for $C_9H_{10}O_2Cl_2S$: C, 42.69; H, 3.96. Found: C, 42.60, 43.17; H, 3.91, 4.11.

p-Chlorobenzyl α,β-Dichlorovinyl Sulphone

This was prepared in poor yield by the above method from *p*-chlorobenzyl α,β-dichlorovinyl sulphide (Table IV), m.p. 70–72°. Anal. calc. for $C_9H_7O_2Cl_3S$: C, 37.83; H, 2.45. Found: C, 37.97, 38.15; H, 2.63, 2.90.

2-p-Chlorobenzenesulphonylcyclohexanone (VI)

This could not be prepared by the above method because the reaction in this case was very exothermic and could not be controlled. To a cold solution of 2-*p*-chlorophenylmercaptocyclohexanone (V) (Table IV) (10 g.) in acetic acid (50 ml.) was added 30% hydrogen peroxide (25 ml.) and the resulting solution was allowed to stand at room temperature for 3 days with occasional cooling on the first day in order to keep the temperature below 30°. The product was worked up as above and when recrystallized from aqueous methanol it melted at 78–80°. The yield was 70%. Anal. calc. for $C_{12}H_{13}O_3ClS$: C, 52.94; H, 4.78. Found: C, 53.25, 53.29; H, 5.07, 4.88.

ω-p-Chlorobenzenesulphonylhexanoic Acid (VII)

To a solution of sodium hydroxide (3 g.) in water (50 ml.) was added 2-*p*-chlorobenzenesulphonylcyclohexanone (1 g.) and the reaction mixture heated on the steam bath for 1 hour. The resulting solution was cooled, acidified with concentrated hydrochloric acid, and the white precipitate (0.80 g. or 78%) filtered, washed, and dried, m.p. 109–110°. It is soluble in aqueous sodium bicarbonate. Anal. calc. for $C_{12}H_{15}O_4ClS$: C, 49.58; H, 5.16. Found: C, 50.00, 49.98; H, 5.22, 5.33.

p-Chlorobenzyl 2-Chloropropyl Sulphide

This was prepared in 90% yield from *p*-chlorobenzyl 2-hydroxypropyl sulphide (Table IV) and thionyl chloride in the usual manner. The colorless liquid boiled at 165°

at 13 mm. pressure, $n_D^{20} = 1.5692$. Anal. calc. for $C_{10}H_{12}Cl_2S$: C, 51.06; H, 5.11. Found: C, 51.29, 51.69; H, 5.07, 5.35.

p-Chlorobenzyl 2,3-Dichloropropyl Sulphide

This was prepared in 90% yield from *p*-chlorobenzyl 2-hydroxy-3-chloropropyl sulphide (Table IV) and thionyl chloride. The colorless liquid boiled at 135–137° at 0.2 mm. pressure, $n_D^{20} = 1.5845$. Anal. calc. for $C_{10}H_{11}Cl_3S_2$: C, 44.53; H, 4.08. Found: C, 44.96; H, 4.29.

p-Chlorobenzyl 2-Thiocyanatopropyl Sulphide

A solution of *p*-chlorobenzyl 2-chloropropyl sulphide (10 g.), sodium thiocyanate (4 g.), and ethanol (75 ml.) was heated under reflux for 2 hours. The ethanol was distilled off, benzene and water were added to the residue, and the whole shaken. The benzene layer was washed, the solvent removed, and the residue distilled, b.p. (0.1 mm.) = 151–153°, yielding 9 g. of colorless liquid, $n_D^{20} = 1.6010$. Anal. calc. for $C_{11}H_{12}NClS_2$: C, 51.26; H, 4.66. Found: C, 51.23; H, 4.76.

1,3-Bis-(p-chlorophenylmercapto)-2-propanol (X)

To a solution of potassium hydroxide (24 g.) in methanol (100 ml.) was added *p*-chlorothiophenol (58 g.), benzene (100 ml.), and 1,3-dichloro-2-propanol (26 g.) and the reaction mixture was heated under reflux for 5 hours. Water was then added, the benzene layer separated and washed with water, the solvent removed, and the residue distilled. The fraction boiling at 205–208° at 0.5 mm. pressure was collected and allowed to solidify. It was pulverized, washed with petroleum ether (b.p. 30–60°), and dried. The white powder (42 g. or 61%) melted at 46–47°. Anal. calc. for $C_{15}H_{14}OCl_2S_2$: C, 52.18; H, 4.05. Found: C, 51.90, 51.93; H, 3.86, 3.81.

1,3-Bis-(p-chlorophenylmercapto)-2-chloropropane (IX)

A solution of 1,3-bis-(*p*-chlorophenylmercapto)-2-propanol (X) (20 g.), thionyl chloride (20 ml.), and dry benzene (50 ml.) was heated under reflux for 3 hours. The excess thionyl chloride and benzene were removed *in vacuo* and the residue distilled at 195–220° at 0.5–1 mm. pressure. The distillate on crystallization from methanol yielded white needles (13 g. or 60%) which melted at 86–87° alone or in admixture with the product obtained from 1,2,3-trichloropropane and *p*-chlorothiophenol (Table V).

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