[CONTRIBUTION FROM THE RESEARCH LABORATORY, DOMINION RUBBER CO. LTD.]

Reactions of Hexachlorobenzene with Mercaptides

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In the reaction of hexachlorobenzene with alkyl mercaptides the chlorine atoms were replaced by alkylmercapto groups two at a time to form either bis(alkylmercapto)tetrachlorobenzene (II) or tetrakis(alkylmercapto)dichlorobenzene (III) depending on conditions used. The orientation in the disubstituted product II was established by degradation to tetrachloro-*p*-benzoquinone (IX). 1,4-Bis(alkylmercapto)-2,3,5,6-tetrachlorobenzenes (II) underwent partial dealkylation to the thiol VI in boiling alcoholic sodium hydrosulfide. One (VII) was converted to the phenol VIII in the presence of alkali.

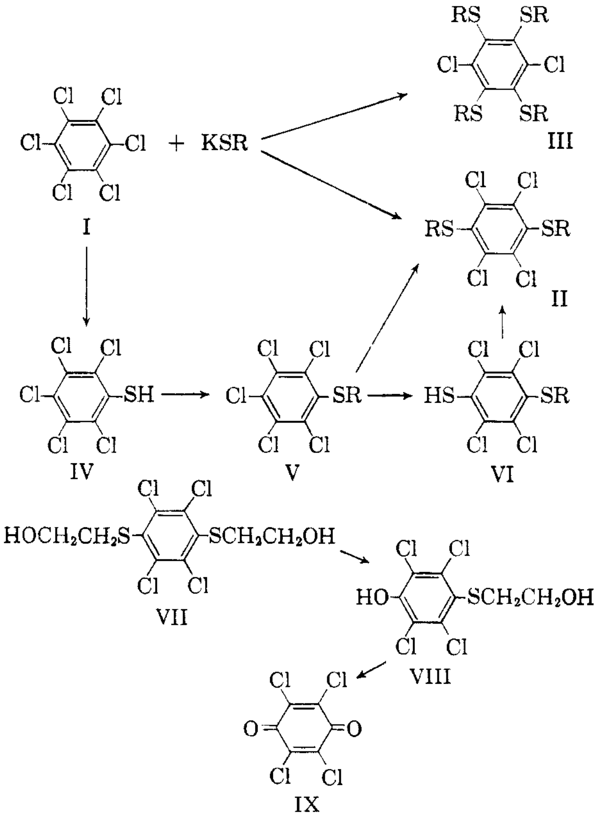
Hexachlorobenzene (I) though regarded as an inert substance does undergo substitution reactions under relatively moderate conditions. It has been pointed out recently that nucleophilic reagents such as alcoholic alkali,[1] alkali alkoxides,[2-4] sodium hydrosulfide or disulfide,[4-6] and amines[4] attack I replacing one chlorine atom.

The thiophenoxide ion is a powerful nucleophilic reagent[7] and therefore would be expected to attack I. Rocklin[4] stated that mercaptides react readily with I in pyridine solution but did not report the isolation of any reaction products.

In this investigation it was found that two chlorine atoms of hexachlorobenzene (I) are attacked by alcoholic alkali mercaptides to form 1,4-bis-(alkylmercapto)tetrachlorobenzenes (II). The reaction was exothermic and when allowed to proceed with excess mercaptide, resulted in further substitution to form tetrakis(alkylmercapto)dichlorobenzene (III). With ethyl mercaptan and 2-mercaptoethanol the conditions of the reaction with I could be controlled so that either the disubstituted product II or the tetrasubstituted product III could be obtained. With amyl mercaptan and *p*-chlorobenzyl mercaptan, although there was evidence for the formation of both substitution products, only the disubstituted compound II was isolated in pure form.

In the case where equimolecular quantities of I and amyl mercaptide were allowed to react the main product was still the disubstituted II. Though none of the monosubstituted compound V could be isolated its formation cannot be excluded.

Some polyhalobenzenes refused to react with mercaptides. Thus *p*-dichlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorophenol, pentachloroanisole, and pentachlorobenzenethiol remained unchanged after prolonged heating with butanolic sodium hydrosulfide or with the potassium salt of 2-mercaptoethanol. However, the blocking of the highly nucleophilic mercapto group of pentachlorobenzenethiol (IV) activated the para chlorine atom so that pentachlorophenyl ethyl sulfide (V) reacted readily with sodium hydrosulfide to form 4-ethylmercapto-2,3,5,6-tetrachlorobenzenethiol (VI). This on ethylation with diethyl sulfate yielded the same 1,4-bis(ethylmercapto)-2,3,5,6-tetrachlorobenzene (II, R = ethyl) as was obtained by the direct reaction I→II. 1,4-bis(Methylmercapto)-2,3,5,6-tetrachlorobenzene (II) did not undergo further substitution reaction when treated with butanolic sodium hydrosulfide. Instead demethylation occurred to form 4-methylmercapto-2,3,5,6-



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(1) P. D. Bartlett, U.S. Patent **2,644,015** (1953); *Chem. Abstr.*, **48**, 5216 (1954).

(2) E. A. Kryuger and M. S. Bednova, *J. Gen. Chem. (U.S.S.R.)*, **3**, 67 (1933); *Chem. Abstr.*, **28**, 1593 (1934).

(3) T. Van der Linden, *Rec. trav. chim.*, **57**, 781 (1938); *Chem. Abstr.*, **32**, 6628 (1938).

(4) A. L. Rocklin, *J. Org. Chem.*, **21**, 1478 (1956).

(5) J. Pikl, U.S. Patent **2,765,345** (1956); *Chem. Abstr.*, **51**, 5828 (1957).

(6) F. Lober, O. Bayer, and M. Bögemann, U.S. Patent **2,695,898** (1954); *Chem. Abstr.*, **49**, 3572 (1955).

(7) J. F. Bunnett and W. D. Merritt, *J. Am. Chem. Soc.*, **79**, 5967 (1957).

tetrachlorobenzenethiol (VI). Pentachloroanisole behaved similarly to form pentachlorophenol.

Of the two routes to 1,4-bis(alkylmercapto)-2,3,5,6-tetrachlorobenzenes (II) the direct one (I→II) is more convenient for preparative purposes. However, the indirect route (I→IV→V→II) has the advantage of introducing the sulfur substituents one at a time and therefore lends itself to the preparation of II with mixed alkylmercapto groups.

In order to show that the sulfur substituents of II were located para to each other, an attempt was made to synthesize 2,3,5,6-tetrachlorobenzene-1,4-dithiol by an independent method. Accordingly 1,2,4,5-tetrachlorobenzene was treated with chlorosulfonic acid. The product of the reaction was sulfur free and proved to be hexachlorobenzene. The orientation of the substituents in II was finally demonstrated by degradation and oxidation. 1,4-bis(2-Hydroxyethylmercapto)-2,3,5,6-tetrachlorobenzene (VII) was heated under reflux with potassium hydroxide in ethylene glycol. The resulting product which was obtained in 80% yield, was soluble in alkali, methylated readily with dimethyl sulfate or diazomethane but refused to react with ethylene dichloride in the presence of alkali. This showed that the compound was a phenol and not a thiol. Analytical examination indicated that the product was 4-(2-hydroxyethylmercapto)-2,3,5,6-tetrachlorophenol (VIII). This was presumably formed from VII by replacement of one 2-hydroxyethylmercapto group by a hydroxyl. Finally, the oxidation of VIII with hydrogen peroxide and chromic oxide yielded chloranil (IX), thus proving that the two sulfur substituents are located para to each other. An attempt to replace both the 2-hydroxyethylmercapto groups of VII with hydroxyl groups to form tetrachlorohydroquinone was not successful. Prolonged heating of VII or VIII with alkali in ethylene glycol gave only tars. Methylation of VIII first to the anisole followed by the alkali and ethylene glycol treatment resulted in demethylation and the formation of VIII.

EXPERIMENTAL[8]

1,4-Bis(ethylmercapto)-2,3,5,6-tetrachlorobenzene (II, R = ethyl). (a) *Directly from hexachlorobenzene.* To a cooled solution of potassium hydroxide (18 g.) in ethanol (75 ml.) was added ethyl mercaptan (18 g.) in methyl ethyl ketone (200 ml.). Then hexachlorobenzene (40 g.) was added and the reaction mixture gently warmed until the exothermic reaction commenced. When the reaction became too violent a cooling bath was applied. The exothermic reaction subsided in a few minutes and then the reaction mixture was heated under reflux for 2 hr. The precipitated potassium chloride was filtered from the hot reaction mixture and washed with methyl ethyl ketone. The combined filtrate and washings were concentrated to about 100 ml., a little methanol was added to the concentrate and the solution allowed to cool. The precipitate after filtration and drying melted at 87–89° and weighed 32 g. or 68%. A portion on recrystallization from benzene-methanol yielded white needles melting at 88–89°.

Anal. Calcd. for $C_{10}H_{10}Cl_4S_2$: C, 35.72; H, 2.97. Found: C, 35.26, H, 2.99.

(b) *From 4-ethylmercapto-2,3,5,6-tetrachlorobenzenethiol* (VI). The thiol VI (see below) was dissolved in excess aqueous alkali and the solution warmed on a steam bath and treated with diethyl sulfate. The reaction mixture was cooled and the precipitate filtered, washed, and dried. It melted at 88–89° alone or in admixture with the product obtained in (a).

1,4-Dichloro-2,3,5,6-tetrakis(ethylmercapto)benzene (III, R = ethyl). To a cooled solution of potassium hydroxide (50 g.) in ethanol (150 ml.) was added a solution of ethyl mercaptan (53 g.) in methyl ethyl ketone (350 ml.). Then hexachlorobenzene (40 g.) was added. After the exothermic reaction subsided, the reaction mixture was heated under reflux for 40 hr. The precipitated potassium chloride (48 g.) was filtered off and the filtrate taken to dryness. The residue distilled at 183–185° (0.5 mm.) and the yellow distillate (49 g.) solidified on standing. It was crystallized from petroleum ether (b.p. 30–60°) twice yielding light yellow prisms (31 g. or 50%) melting at 48–49°.

Anal. Calcd. for $C_{14}H_{20}Cl_2S_4$: C, 43.41; H, 5.16. Found: C, 42.79; H, 5.01.

1,4-Bis(n-amylmercapto)-2,3,5,6-tetrachlorobenzene (II, R = n-amyl) was prepared in 89% from two moles of *n*-amyl mercaptan and hexachlorobenzene in the same manner as was the ethyl analog II (R = ethyl) above. The colorless liquid boiled at 245–255° (12 mm.) or 170–175° (0.5 mm.), $n_D^{20} = 1.5922$.

Anal. Calcd. for $C_{16}H_{22}S_2Cl_4$: C, 45.71; H, 5.24. Found: C, 45.62; H, 5.44.

1,4-Bis(p-chlorobenzylmercapto)-2,3,5,6-tetrachlorobenzene (II, R = $p\text{-}ClC_6H_4CH_2$). This was prepared in 50% yield from two moles of *p*-chlorobenzyl mercaptan and hexachlorobenzene in the same manner as was II (R = ethyl) above except that reaction time was extended to 7 hr. It crystallized from benzene-ethanol yielding white needles melting at 147–148°.

Anal. Calcd. for $C_{20}H_{12}Cl_6S_2$: C, 45.29; H, 2.26. Found: C, 45.18; H, 2.48.

1,4-Bis(2-hydroxyethylmercapto)-2,3,5,6-tetrachlorobenzene (II, R = CH_2CH_2OH). To a stirred suspension of hexachlorobenzene (285 g.), pyridine (1 l.), and methanol (200 ml.) was added dropwise a solution of potassium hydroxide (118 g.), 2-mercaptoethanol (160 ml.) and methanol (100 ml.) over a period of 2.5 hr. The temperature was maintained at 65 to 68° by occasional cooling. The reaction mixture was stirred for an additional hour, let stand overnight, and then filtered. The filtrate was concentrated to a volume of about 350 ml., boiling methanol (350 ml.) added, and the solution allowed to cool. The white precipitate was filtered, washed with methanol, with water, and with methanol and dried. It weighed 265 g. or 72% and melted at 145–147°. Recrystallization from methanol raised the melting point to 151–153°.

Anal. Calcd. for $C_{10}H_{10}O_2Cl_4S_2$: C, 32.62; H, 2.72. Found: C, 32.45; H, 2.94.

1,4-Bis(2-chloroethylmercapto)-2,3,5,6-tetrachlorobenzene. A reaction mixture of 1,4-bis(2-hydroxyethylmercapto)-2,3,5,6-tetrachlorobenzene (II, R = CH_2CH_2OH) (10 g.) and thionyl chloride (25 ml.) was heated under reflux for 0.5 hr. The excess thionyl chloride was distilled off and the residue treated with water. The white solid was filtered, washed, dried, and crystallized twice from benzene, yielding (8.5 g.) microscopic prisms melting at 175–179°.

Anal. Calcd. for $C_{10}H_8Cl_6S_2$: C, 29.63; H, 1.98. Found: C, 29.72; H, 2.02.

1,4-Dichloro-2,3,5,6-tetrakis(2-hydroxyethylmercapto)benzene. To a solution of potassium hydroxide (37 g.) in ethanol (400 ml.) was added hexachlorobenzene (28 g.) and 2-mercaptoethanol (50 ml.) and the reaction mixture was heated

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[8] All melting points are corrected.

under reflux for three days. The potassium chloride (30 g.) was filtered off and the filtrate was taken to dryness *in vacuo*. The residue was crystallized twice from aqueous ethanol yielding (7 g.) of white solid melting at 184–186°.

Anal. Calcd. for $C_{14}H_{20}O_4Cl_2S_4$: C, 37.15; H, 4.44. Found: C, 37.49; H, 4.49.

1,4-Dichloro-2,3,5,6-tetrakis(2-chloroethylmercapto)benzene. A reaction mixture of 1,4-dichloro-2,3,5,6-tetrakis (2-hydroxyethylmercapto)benzene (5 g.) and thionyl chloride (20 ml.) was heated under reflux for 0.5 hr. The excess thionyl chloride was removed *in vacuo* and the residue crystallized from benzene. This yielded 5 g. of white needles melting at 184–185°.

Anal. Calcd. for $C_{14}H_{16}Cl_6S_4$: C, 32.00; H, 3.05. Found: C, 32.30; H, 2.95.

Methyl pentachlorophenyl sulfide. Pentachlorobenzenethiol (60 g.)[4-6] was dissolved in a solution of sodium hydroxide (20 g.) and water (300 ml.), heated on a steam bath and treated with excess dimethyl sulfate. The reaction mixture was cooled, the white solid (60 g.) filtered, washed, and crystallized from benzene-methanol, m.p. 93–94°.

Anal. Calcd. for $C_7H_3Cl_5S$: C, 28.33; H, 1.01. Found: C, 28.25; H, 1.00.

Ethyl pentachlorophenyl sulfide. This was prepared in 90% yield by ethylation of pentachlorobenzenethiol with diethyl sulfate and alkali as above. It crystallized from methanol in the form of white needles melting at 51–52°. Tadros and Saad[9] give a melting point of 42–44°.

Anal. Calcd. for $C_8H_5Cl_5S$: C, 30.92; H, 1.61. Found: C, 30.96; H, 1.50.

2-Chloroethyl pentachlorophenyl sulfide. To a solution of potassium hydroxide (4 g.) in methanol (50 ml.) was added pentachlorobenzenethiol (14 g.) and ethylene dichloride (250 ml.) and the reaction mixture was heated under reflux for one hour. This was cooled, washed with water, and the residue crystallized from benzene. The white prisms (13 g.) melted at 132–134°.

Anal. Calcd. for $C_8H_4Cl_6S$: C, 27.83; H, 1.16. Found: C, 28.25; H, 1.25.

4-Methylmercapto-2,3,5,6-tetrachlorobenzenethiol (VI, R = CH_3). A reaction mixture of technical sodium hydrosulfide (36 g.), methyl pentachlorophenyl sulfide (55 g.), and butanol (300 ml.) was heated under reflux for 16 hr. The butanol was distilled off *in vacuo*, the residue treated with water and the aqueous solution was extracted with benzene in order to remove unreacted material. The aqueous solution was acidified, extracted with benzene, and the organic solvent removed. The residue distilled at 150–155° (0.5 mm.) and the distillate on crystallization from acetone-methanol yielded 36 g. or 65% of almost white plates melting at 82–84°.

Anal. Calcd. for $C_7H_4Cl_4S_2$: C, 28.57; H, 1.36. Found: C, 28.73; H, 1.58.

4-Ethylmercapto-2,3,5,6-tetrachlorobenzenethiol (VI, R = C_2H_5). This was prepared in 60% yield from ethyl pentachlorophenyl sulfide and sodium hydrosulfide as described above for 4-methylmercapto-2,3,5,6-tetrachlorobenzenethiol. The yellow prisms melted at 58–59°. An aqueous alkaline solution of this when treated with diethyl sulfate yielded a product melting at 88–89° alone or in admixture with 1,4-bis(ethylmercapto)-2,3,5,6-tetrachlorobenzene (see above).

1,4-Bis(methylmercapto)-2,3,5,6-tetrachlorobenzene. This was prepared in 90% yield by the methylation of 4-methylmercapto-2,3,5,6-tetrachlorobenzenethiol with dimethyl sulfate and alkali. The white needles melted at 132–134°.

Anal. Calcd. for $C_8H_6Cl_4S_2$: C, 31.17; H, 1.95. Found: 30.90; H, 2.12.

1-(Methylmercapto)-4-(2-chloroethylmercapto)-2,3,5,6-tetrachlorobenzene. This was prepared in 90% yield from 4-methylmercapto-2,3,5,6-tetrachlorobenzenethiol and ethylene dichloride in the same manner as was 2-chloroethyl pentachlorophenyl sulfide (above). The white product after crystallization from acetone-methanol melted at 104–106°.

Anal. Calcd. for $C_9H_7Cl_5S_2$: C, 30.30; H, 1.96. Found: C, 30.04; H, 1.81.

1-(Ethylmercapto)-4-(2-chloroethylmercapto)-2,3,5,6-tetrachlorobenzene. This was prepared in 90% yield from 4-ethylmercapto-2,3,5,6-tetrachlorobenzenethiol and ethylene dichloride in the same manner as described above. It crystallized as white needles and melted at 102–103°.

Anal. Calcd. for $C_{10}H_9Cl_5S_2$: C, 32.39; H, 2.43. Found: C, 31.91; H, 2.55.

Reaction of 1,2,4,5-tetrachlorobenzene with chlorosulfonic acid. A reaction mixture of 1,2,4,5-tetrachlorobenzene (35 g.) and chlorosulfonic acid (150 ml.) was heated at 140–145° for 20 hr. The cooled reaction mixture was cautiously added to cracked ice. The precipitate was filtered, washed with cold water, dried, and crystallized from benzene. The product (35 g.) melted at 231–233° and did not depress the melting point of *hexachlorobenzene.*

4-(2-Hydroxyethylmercapto)-2,3,5,6-tetrachlorophenol (VIII). A solution of potassium hydroxide (25 g.) in ethylene glycol (150 ml.) and 1,4-bis(2-hydroxyethylmercapto)-2,3,5,6-tetrachlorobenzene (VII) (25 g.) was heated under reflux for 3 hr. The amber solution was concentrated *in vacuo* until most of the glycol was removed. The residue was dissolved in water, filtered, and the filtrate acidified. The precipitate was filtered, washed, dried, and then distilled from a large Späthe bulb, b.p. (1 mm.) 180–220°. The distillate on crystallization from benzene-methanol yielded 17 g. or 80% of white prisms which melted at 168–169°.

Anal. Calcd. for $C_8H_6O_2Cl_4S$: C, 31.17; H, 1.95; S, 10.4. Found: C, 31.13; H, 2.00; S, 11.1.

This compound did not react with ethylene dichloride in the presence of alkali showing that it is not a thiol.

4-(2-Hydroxyethylmercapto)-2,3,5,6-tetrachloroanisole. This was prepared in almost quantitative yield by methylation of 4-(2-hydroxyethylmercapto)-2,3,5,6-tetrachlorophenol with diazomethane. Methylation with dimethyl sulfate gave poor yields because the alkyl hydroxyl group was also attacked. The product crystallized from benzene as white needles and melted at 100–101°.

Anal. Calcd. for $C_9H_8O_2Cl_4S$: C, 33.54; H, 2.49. Found: C, 33.99; H, 2.93.

4-(2-Chloroethylmercapto)-2,3,5,6-tetrachloroanisole. 4-(2-Hydroxyethylmercapto)-2,3,5,6-tetrachloroanisole (4 g.) and thionyl chloride (20 ml.) were heated under reflux for 0.5 hr. and then the excess thionyl chloride was removed *in vacuo*. The residue on crystallization from methanol yielded white prisms (2.5 g.) melting at 107–108°.

Anal. Calcd. for $C_9H_7OCl_5S$: C, 31.76; H, 2.06. Found: C, 31.81; H, 2.34.

4-(2-Chloroethylmercapto)-2,3,5,6-tetrachlorophenol. This was prepared in 70% yield from 4-(2-hydroxyethylmercapto)-2,3,5,6-tetrachlorophenol (VIII) and thionyl chloride in the usual manner. After crystallization from benzene the white prisms melted at 134–135°.

Anal. Calcd. for $C_8H_5Cl_5OS$: C, 29.41; H, 1.53. Found: C, 29.21; H, 1.69.

Oxidation of 4-(2-hydroxyethylmercapto)-2,3,5,6-tetrachlorophenol (VIII) *to 2,3,5,6-tetrachloro-1,4-benzoquinone* (IX). To 4-(2-hydroxyethylmercapto)-2,3,5,6-tetrachlorophenol (VIII) (1 g.) in acetic acid (20 ml.) was added 30% hydrogen peroxide (5 ml.) and the resulting solution was heated on the steam bath for 1 hr. To this was added dropwise with stirring a solution of chromic oxide (3 g.) in water (2 ml.) and acetic acid (20 ml.) over about 5 min. The dark solution was diluted with water, the yellow precipitate filtered, washed, dried, and crystallized from benzene. The yellow crystals (0.18 g. or 20%) melted at 290–292° alone or in admixture with 2,3,5,6-tetrachloro-1,4-benzoquinone.

GUELPH, ONT.

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(9) W. Tadros and E. Saad, *J. Chem. Soc.*, 1155 (1954).