# A STUDY OF THE REACTION OF SULFUR WITH ORGANIC COMPOUNDS

## XVII. The Action of Sulfur on 1- and 2-Phenylpolychloropropanes*

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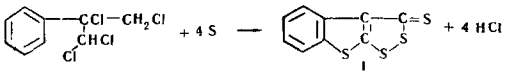
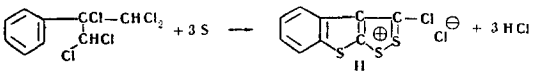
The reaction of sulfur with isomeric exo-polychloro derivatives of iso- and n-propylbenzenes containing from 4 to 6 chlorine atoms in the side chain at 200°–300° C has been studied. The reaction of sulfur with α, β, β, β'-tetrachloro- and α, β, β, β', β'-pentachlorocumenes leads to the formation of the previously unknown thianaphtheno-[2, 3-d]-1, 2-dithiole-3-thione (yield 48%) and thionaphtheno[2,3-d]-3-chloro-1, 2-dithiolium chloride (yield 65%), respectively. The sulfuration reaction of the isomeric exo-tetrachloro- and exo-pentachloro-n-propylbenzenes leads to the formation of 4-chloro-5-phenyl-1, 2-dithiole-3-thione (yield 5–35%). The exo-hexachloro derivatives of iso- and n-bromobenzenes, on being heated with sulfur, form only resinous sulfuration products.

We have previously found [2] that the reaction of sulfur with mono-, di-, and tri-exohalogen derivatives of iso- and n-propylbenzenes leads to the formation of 4- and 5-phenyl-1,2-dithiole-3-thiones, respectively. In the present communication it is shown that with a further increase in the number of halogen atoms in the side chain, the sulfuration reaction changes its direction. The action of sulfur on α,β,β, β'-tetrachlorocumene at 230° C led to the formation of four molecules of hydrogen chloride (three from the hydrogen atoms of the side chain and one from the hydrogen atom in the ortho position with respect to it in the aromatic ring). The reaction product proved to be the previously unknown thianaphtheno[2,3-d]-1,2-dithiole-3-thione (I), formed with a yield of 48% by the following reaction.

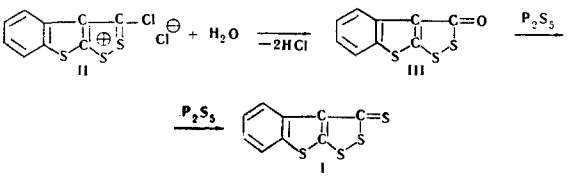


The sulfuration reaction of α,β,β,β',β'-pentachlorocumene led to the formation of thionaphtheno-[2, 3-d]-3-chloro-1,2-dithiolium chloride (II), also previously unknown.



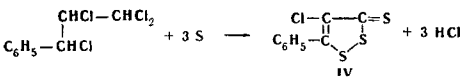
By analogy with this reaction, the action of sulfur on hexachloropropene and pentachloropropane gives 3,4,5-trichloro-1,2-dithiolium chloride [3,4].

On hydrolysis, II is converted into thianaphtheno-[2,3-d]-1,2-dithiol-3-one (III). The latter, in its turn, is converted by the action of phosphorus pentasulfide into the above-described thianaphtheno[2,3-d]-1,2-dithiole-3-thione (I).



Exo-hexachlorocumene [$C_6H_5CCl(CHCl_2)CCl_3$] does not react with sulfur at 200° C, and at 220° C it carbonizes.

The sulfuration of the isomeric exo-tetrachloro-n-propylbenzenes gives rise to the previously unknown 4-chloro-5-phenyl-1,2-dithiole-3-thione (IV).



The yield of IV depends on the arrangement of the chlorine atom in the n-propyl chain (33.7, 5.0, and 11.5% from α,β,γ,γ-, α,β,β,γ-, and β,γ,γ,γ-tetrachloro-n-propylbenzenes, respectively).

The action of sulfur on α,β,β,γ,γ- or β,β,γ,γ,γ-pentachloro-n-propylbenzene gives a low yield of

*For part XVI, see [1].

Table 1

Sulfuration Conditions for exo-Polychloro Derivatives of Iso- and n-Propylbenzenes

| Initial chloro derivative (V) | Molar ratio, V:S:$C_6H_4Cl_2$ | Reaction temperature | Reaction time, hr | Reaction product, yield, % |
|---|---|---|---|---|
| $C_6H_5CCl(CH_2Cl)CHCl_2$ | 1 : 4 : 1 | 225—235 | 5 | I (47.5) |
| $C_6H_5CCl(CHCl_2)_2$ | 1 : 3 : 1 | 200—205 | 10 | II (64.5) |
| $C_6H_5CCl(CHCl_2)CCl_3$ | 1 : 3 : 1 | 200—202 | 5 | No reaction |
| | | 210—220 | 3 | Resin |
| $C_6H_5CHClCHClCHCl_2$ | 1 : 3 : 1 | 210—230 | 5 | IV (33.7) |
| $C_6H_5CHClCCl_2CH_2Cl$ | 1 : 3 : 1 | 200—203 | 8 | IV (5.0) |
| $C_6H_5CH_2CHClCCl_3$ | 1 : 3 : 1 | 218—225 | 4 | IV (11.5) |
| $C_6H_5CHClCCl_2CHCl_2$ | 1 : 3 : 1 | 215—220 | 4 | IV (13.5) |
| $C_6H_5CH_2CCl_2CCl_3$ | 1 : 3 : 1 | 210—220 | 4 | IV (8.0) |
| $C_6H_5CCl_2CCl_2CHCl_2$ | 1 : 3 : 1 | 190—200 | 8 | Resin |

Table 2

Initial exo-Chloro Derivatives of Iso- and n-Propylbenzenes

| Chloro derivatives | Mp, ° C | Bp, ° C (pressure, mm) | $n_D^{20}$ | Yield, % |
|---|---|---|---|---|
| $C_6H_5CCl(CH_2Cl)CHCl_2$ | — | 154—157 (12) | 1.5740 | 39.7 |
| $C_6H_5CCl(CHCl_2)_2$[5] | — | 138—141 (2) | 1.5845 | 65.3 |
| $C_6H_5CCl(CHCl_2)CCl_3$[5] | 71.5 | — | — | 20.0 |
| $C_6H_5CHClCHClCHCl_2$* | 91 | — | — | 79.0 |
| $C_6H_5CHClCCl_2CH_2Cl$* | — | 158—160 (12) | 1.5677 | 62.5 |
| $C_6H_5CH_2CHClCCl_3$[6, 7] | — | 111—112 (2) | 1.5534 | 57.0 |
| $C_6H_5CHClCCl_2CHCl_2$* | — | 157—159 (5) | 1.5772 | 76.0 |
| $C_6H_5CH_2CCl_2CCl_3$[6, 7] | 75 | — | — | 26.1 |
| $C_6H_5CCl_2CCl_2CHCl_2$* | 88 | — | — | 17.5 |

*New compound

IV. It was impossible to isolate other sulfuration products. On being heated with sulfur, exo-hexachloro-n-propylbenzene [1,1,2,2,3,3-hexachloro-n-propylbenzene] forms only resinous sulfuration products.

Data on the conditions of performing the sulfuration reactions and the yields of the products are given in Table 1.

## EXPERIMENTAL

### STARTING MATERIALS

**α, β, β, β'-Tetrachlorocumene** was obtained by the photochlorination of cumene with sulfuryl chloride [2].

**α, β, β, β', β'-Pentachlorocumene.** A quartz flask fitted with a gas-inlet tube, a thermometer, and a reflux condenser, was charged with 51.6 g (0.02 mole) of α, β, β, β'-tetrachlorocumene and 0.5 g of $PCl_3$. Dry chlorine was passed through the mixture with illumination by a PRK-4 mercury lamp (12 hr at 140° C and 13 hr at 180° C). After the elimination of the excess of chlorine with a current of dry air, the reaction mixture was distilled in vacuum. Yield 38.2 g (65.3%); bp 138°–141° C (2 mm); $n_D^{20}$ 1.5845. According to the literature [5], bp 173°–176° C (15 mm); mp 45°–46° C. Found, %: C 36.57; H 2.42; Cl 60.33. Calculated for $C_9H_7Cl_5$, %: C 36.96; H 2.41; Cl 60.62. The same derivative was obtained by the condensation of benzene with 1, 1, 3, 3-tetrachloroacetone in the presence of $AlCl_3$ [5].

**α, β, β, β, β', β'-Hexachlorocumene** was obtained by the dehydrochlorination and subsequent chlorination of pentachlorocumene. Bp 71.5°—72.5° C [5]).

**α, β, γ, γ-Tetrachloro-n-propylbenzene.** Dry chlorine was passed 0° C into a solution of 66.0 g (0.5 mole) of cinnamaldehyde in 100 ml of chloroform. After the elimination of the excess of chlorine with a current of dry air, vacuum distillation yielded 92.0 g (91.0%) of 2, 3-dichloro-3-phenylpropanal with bp 144°–148° C (30 mm); $n_D^{20}$ 1.5540. This was dissolved in 100 ml of dry chloroform, and over an hour this solution was added in drops to 95.0 g (0.45 mole) of $PCl_5$. The reaction mixture was heated in the water bath for another half an hour, the $POCl_3$ formed and the solvent were distilled off, and the residue was recrystallized from ethanol. Yield 93.0 g (79.0%), mp 91° C. Found, %: C 41.53; H 3.21; Cl 54.55. Calculated for $C_9H_8Cl_4$, %: C 41.85; H 3.21; Cl 54.68.

**α, β, β, γ-Tetrachloro-n-propylbenzene.** A solution of 13 g of KOH in 100 ml of ethanol was added to a solution of 50.5 g (0.22 mole) of α, β, γ-trichloro-n-propylbenzene in 100 ml of ethanol. The precipitate of KCl that deposited was filtered off and the solution was evaporated. The residue, consisting mainly of dichloropropenylbenzene, was dissolved in 100 ml of chloroform, and dry chlorine was passed through the solution at 0° C. After the excess of chlorine had been driven off, the reaction mixture was distilled in vacuum. Yield 35.9 g (62.5%). Bp 141°–143° C, (12 mm); $n_D^{20}$ 1.5677. Found, %: C 42.18; H 3.44; Cl 54.18. Calculated for $C_9H_8Cl_4$, %: C 41.85; H 3.21; Cl 54.68.

**β, γ, γ, γ-Tetrachloro-n-propylbenzene** was obtained by condensing benzene with 1, 1, 1-trichloropropene in the presence of sulfuric acid with subsequent chlorination of the 1, 1-dichloro-3-phenyl-1-propene formed. Bp 111°–112° C (2 mm); $n_D^{20}$ 1.5534 ($n_D^{20}$ 1.5535 [6, 7]).

**β, β, γ, γ, γ-Pentachloro-n-propylbenzene** was prepared by the dehydrochlorination of β, γ, γ, γ-tetrachloropropylbenzene and the chlorination of the resulting 1, 1, 2-trichloro-3-phenyl-1-propene. Mp 75° C (76° C [6, 7]).

**α, β, β, γ, γ-Pentachloro-n-propylbenzene.** Dry chlorine was passed into a boiling solution of 50.0 g (0.2 mole) of α, β, γ, γ-tetrachloro-n-propylbenzene and 0.5 g of $PCl_3$ in 100 ml of $CCl_4$ with ultraviolet irradiation for 12 hr. The excess of chlorine was eliminated with a current of dry air, the solvent was driven off, and the residue was distilled in vacuum. Yield 46.1 g (76.0%). Bp 157°–159° C (5 mm); $n_D^{20}$ 1.5755. Found, %: C 36.39; H 2.53; Cl 60.12. Calculated for $C_9H_7Cl_5$, %: C 36.96; H 2.41; Cl 60.62.

**α, α, β, β, γ, γ-Hexachloro-n-propylbenzene** was obtained by chlorinating a boiling solution of 50.0 g (0.17 mole) of α, β, β, γ, γ-pentachlorobenzene and 0.5 g of $PCl_3$ in 100 ml of dichlorobenzene with ultraviolet irradiation. Yield 12.1 g (26.0%). After recrystallization from methanol, mp 88° C. Found, %: C 32.59; H 1.77; Cl 65.47. Calculated for $C_9H_6Cl_6$, %: C 32.97; H 1.84; Cl 65.18%.

The physical constants and yields of the initial chloro derivatives purified by columm distillation or by recrystallization are given in Table 2.

### REACTION OF SULFUR WITH EXO-POLYCHLOROPHENYLPROPANES

**Thianaphtheno[2, 3-d]-1, 2-dithiole-3-thione (I).** A mixture of 10.4 g (0.04 mole) of α, β, β, β'-tetrachlorocumene, 5.0 g (0.16 g-atom) of sulfur, and 4 ml of o-dichlorobenzene was heated at 225°–235° C for 5 hr. When the reaction mixture was cooled, it deposited crystals of I, which were filtered off with suction, washed with benzene, and recrystallized from chlorobenzene. Yield 4.4 g (47.5%). Mp 211° C. Found, %: C 45.06; H 2.08; S 53.04; mol. wt. 237.7. Calculated for $C_9H_4S_4$, %: C 44.96; H 1.68; S 53.35%; mol. wt. 240.4.

**Thianaphtheno[2, 3-d]-3-chloro-1, 2-dithiolium chloride (II).** A mixture of 15.0 g (0.05 mole) of α, β, β, β', β'-pentachlorocumene, 5.0 g (0.15 g-atom) of sulfur, and 5 ml of o-dichlorobenzene was heated at 200°–205° C for 10 hr. The precipitate of II that deposited on cooling was filtered off with suction and washed with hot benzene. Yield 9.2 g (64.5%). Mp 272.5° C (from o-dichlorobenzene). Found, %: C 38.88; H 1.48; S 34.65. Calculated for $C_9H_4S_3Cl_2$, %: C 38.90; H 1.44; S 34.51.

**Hydrolysis of 3-chlorothianaphtheno[2, 3-d]-1, 2-dithiolium chloride.** 3.0 g (0.01 mole) of II was heated in 50 ml of boiling 70% acetic acid for 4 hr, by which time the II had dissolved almost completely. The hot solution was filtered. On cooling, it deposited bright yellow needle-like crystals of thianaphtheno[2, 3-d]-1, 2-dithiol-3-one (III). Yield 1.5 g (62.5%). Mp 128°–128.5° C (from ethanol). Found, %: C 47.46; H 1.68; S 42.66. Calculated for $C_9H_4S_3O$, %: C 48.19; H 1.79; S 42.88.

**Sulfuration of thianaphtheno[2, 3-d]-1, 2-dithiol-3-one.** A mixture of 1.0 g of III and 4.0 g of $P_2S_5$ was heated in boiling xylene for 1 hr. The hot solution was filtered. On cooling, it deposited orange needle-like crystals of thianaphtheno[2, 3-d]-1, 2-dithiole-2-thione (I) with

mp 207°–208° C. A mixture with the I obtained previously gave no depression of the melting point.

**4-Chloro-5-phenyl-1, 2-dithiole-3-thione (IV).** A mixture of 10.0 g (0.04 mole) of α, β, γ, γ-tetrachloro-n-propylbenzene, 4.0 g (0.12 g-atom) of sulfur, and 4 ml of o-dichlorobenzene was heated at 210°–230° C for 5 hr. The crystals of IV that deposited on cooling were filtered off with suction, washed with a mixture of hexane and benzene (2:1), and recrystallized from 80% ethanol. Yield 3.2 g (33.7%); mp 115° C. Found, %: C 44.08; H 2.26; S 39.93; Cl 14.37. Calculated for $C_9H_5S_3Cl$, %: C 44.16; H 2.06; S 39.29; Cl 14.48.

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