STUDY OF THE REACTION OF SULFUR WITH ORGANIC COMPOUNDS

XIII. Reaction of Sulfur with Mono-, Di-, and Tri-exo-Halogen-Substituted iso- and n-Propylbenzenes*

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A study is made of the action of sulfur on halogen derivatives of iso- and n-propylbenzene, with 1–3 chlorine or bromine atoms at various places in the side chain. Reaction of sulfur with α-chlorocumene, α, β-dichlorocumene, and α, β, β-trichlorocumene and mixtures of these, proves to be a new convenient method of preparing 4-phenyl-1, 2-dithio-3-thione (40% yield). Sulfuration of mono-, di- and tri-exo-halogen derivatives of n-propylbenzene gives 5-phenyl-1, 2-dithiol-3-thione in 11–18% yield.

Hitherto 4-phenyl- and 5-phenyl-1, 2-dithiol-3-thione, recently used as starting materials for synthesizing compounds with fungicidal activity [2–4], have been obtained by the action of sulfur and phosphorus pentasulfide on esters of cinnamic or β-keto-carboxylic acids [5–7], and by sulfurating 1- and 2-phenylpropenes, cinnamyl alcohol, or cinnamaldehyde [8, 9]. However the practical possibilities offered by these methods are limited, as they necessitate use of not easily accessible and expensive starting compounds, and the yields of the resultant dithiothiones were not over 40%. In 1955 it was found that 4-phenyl-1, 2-dithiol-3-thione (I) is formed by the action of sulfur on cumene in the presence of basic catalysts [10]. However, unlike cumene derivatives with a substituent in the aromatic ring [10, 11], cumene itself reacts with sulfur very slowly (to obtain a 60% yield of crude I the reactants must be heated together for over 170 hr). An attempt to prepare 5-phenyl-1, 2-dithio-3-thione (II) similarly, by the action of sulfur on n-propylbenzene, was unsuccessful [10]. Obviously in both cases the very low rate of the sulfuration reaction, or its virtual absence, is due to the reaction temperature being too low.

It was previously shown [1, 12–14], that introduction of a halogen into the side chain of alkylbenzenes increases their reactivities towards sulfur sharply. Thus it was found that the action of sulfur and phosphorus pentasulfide on halogenated ketones gave yields of 1, 2-dithiol-3-thiones almost 10 times those obtained using the actual ketone (40% and 4% respectively) [15].

It was possible to obtain compounds containing a 1, 2-dithiol heterocyclic ring by reacting sulfur with halogenated propenes and propanes [16, 17].

All this gave reason to assume that reaction of sulfur with exo-halogen-substituted iso- and n-propylbenzenes must give the corresponding phenyl-1, 2-dithiol-3-thiones I, II). With this in mind, we made a study of the reaction of sulfur with cumene and n-propyl-benzene, having 1–3 atoms of chlorine or bromine at various positions in the side chains. This

Table 1

Conditions for the Reaction between exo-Halogen-Substituted iso- and n-Propylbenzenes.

Starting halogen derivative	Mole ratio halogen: :S:solvent	Reaction temperature, °C	Reaction time, hr	Yield of 1,2-dithiol-3-thione (on the starting halogen derivative), %
$C_6H_5CCl(CH_3)_2$	1 : 5 : 0	200—220	4	39.0 (I)
"	1 : 5 : 2*	214—216	8	36.3 (I)
$C_6H_5CH(CH_3)CH_2Cl$	1 : 5 : 0	210—220	6	16.5 (I)
"	1 : 5 : 2*	205—207	10	20.0 (I)
$C_6H_5CCl(CH_3)CH_2Cl$	1 : 4 : 0	200—220	3	39.5 (I)
$C_6H_5CCl(CH_3)CHCl_2$	1 : 3 : 0.5**	204—206	6	39.9 (I)
$C_6H_5CBr(CH_3)_2$	1 : 5 : 2*	214—216	6	15.3 (I)
$C_6H_5CH(CH_3)CH_2Br$	1 : 5 : 2*	214—216	8	30.8 (I)
$C_6H_5CHClCH_2CH_3$	1 : 5 : 0	200—220	2	11.6 (II)
$C_6H_5CH_2CHClCH_3$	1 : 5 : 0	200—215	6	12.3 (II)
$C_6H_5CH_2CH_2CH_2Cl$	1 : 5 : 2*	213—216	8	17.7 (II)
$C_6H_5CH_2CHClCH_2Cl$	1 : 4 : 0	215—220	4.5	13.5 (II)
"	1 : 4 : 0.5**	217—219	10	12.7 (II)
$C_6H_5CHClCHClCH_2Cl$	1 : 3 : 0.7**	222—224	8	10.9 (II)
$C_6H_5CH_2CHBrCH_2Br$	1 : 4 : 1**	190—195	8	11.1 (II)

*1,2,4-trichlorobenzene
**1,2-dichlorobenzene

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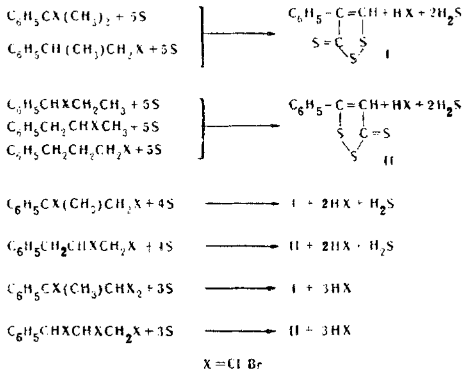
*For Part XII see [1].

Table 2

Starting exo-Halogen-Substituted iso- and n-Propylbenzenes

Halogen derivative	Bp °C (pressure, mm)	n_D^{20}	Yield, %
$C_6H_5CCl(CH_3)_2$	81.5—83.5 (10)	1.5398	59.0
$C_6H_5CH(CH_3)CH_2Cl$	86—88 (15)	1.5232	10.5
$C_6H_5CHCl(CH_3)CH_2Cl$	98—100 (3)	1.5570	10.0
$C_6H_5CHCl(CH_3)CHCl_2$	137—141 (13)	1.5640	34.0
$C_6H_5CBr(CH_3)_2$	102—104 (10)	1.5873	55.0
$C_6H_5CH(CH_3)CH_2Br$	109--111 (18)	1.5481	—
$C_6H_5CHClCH_2CH_3$	75—77 (10)	1.5241	85.0
$C_6H_5CH_2CHClCH_3$	81—83 (10)	1.5185	22.0
$C_6H_5CH_2CH_2CH_2Cl$	153—155 (30)	1.5220	85.0
$C_6H_5CH_2CHClCH_2Cl$	118—120 (15)	1.5430	80.0
$C_6H_5CHClCHClCH_2Cl$	140—142 (12)	1.5590	68.0
$C_6H_5CH_2CHBrCH_2Br$	139—141 (12)	1.5856	76.0

work showed that on reaction with sulfur, all the halogen derivatives investigated give I or II in up to 40% yield after 2–10 hr. In the absence of catalysts the equations for the reactions investigated are:



The nature and position of the halogen atom greatly affects the rate of the process and the yields (Table 1).

The maximum yield of I is obtained from α-chlorocumene, α, β-dichlorocumene, α, β, β-trichlorocumene, and mixtures of these. When these chlorine derivatives are heated at 190° with sulfur, hydrogen chloride begins to evolve. Then when the temperature reaches 210°, hydrogen sulfide starts to come off along with the hydrogen chloride (no hydrogen sulfide was observed with the trihalogen derivatives). The reaction stops after 2–4 hr. Use of solvents (1, 2, 4-trichlorobenzene, 1, 2-dichlorbenzene) facilitates isolation and purification of I, and somewhat hinders the formation of a resin, but increases the time of the process to 8–10 hours.

On the other hand β-chlorocumene splits off hydrogen chloride with difficulty when boiled with sulfur, thus lengthening the process and cutting the yield of I because of resin formation.

α-Bromocumene starts decomposing vigorously even at 160° when heated with sulfur, giving mainly resinification products, the yield of I not exceeding 15%.

β-Bromocumene reacts more smoothly with sulfur and the yield of I is only slightly slower than for α-chlorocumene.

α-Chloro-n-propylbenzene, like α-bromocumene is quite stable under the reaction conditions, leading to considerable resin formation and a low yield of II (11%).

The highest yield of II (up to 17%) is obtained from γ-chloro-n-propylbenzene. A somewhat lower yield of II (13–14%) is obtained from β-chloro-n-propylbenzene or β, γ-dichloro-n-propylbenzene. Low yields of II (11%) result from reaction of sulfur with β, γ-dibromo-n-propylbenzene and α, β, γ-trichloro-n-propylbenzene.

Thus the action of sulfur on exo-halogen derivatives of n-propyl-benzene gives II with a yield not over 17%. So the previously suggested way of preparing this compound by the action of sulfur on 1-phenyl-prop-1-ene [8, 9] is still the most economic.

EXPERIMENTAL

Starting materials. α-Chlorocumene was prepared in 59% yield by chlorinating cumene with SO_2Cl_2 in the presence of azoisobutyronitrile [8]. A 10% yield of α, β-dichlorocumene is obtained from the reaction.

β-Chlorocumene is prepared by chloroalkylating benzene with allyl chloride in the presence of sulfuric acid [19, 20].

α, β, β-Trichlorocumene and α, β, β-tetrachlorocumene. 72.0 g (0.6 mole) Cumene, 337.5 g (2.5 mole) SO_2Cl_2 and 5.0 g PCl_3 were placed in a quartz flask fitted with a reflux condenser and thermometer. The reaction mixture was held at 80–90° (towards the end of the chlorination the temperature was raised to 115°) and illuminated with UV light from a PRK-4 lamp 20 cm from the flask, for 25 hr. After blowing dry air through the reaction products to remove a slight excess of SO_2Cl_2, they were distilled twice through a column. Yield of α, β, β-trichlorocumene by 137–141° (13 mm), d_4^{20} 1.3288, 45.5 g (33.9%). Found: C 48.36; H 4.06; Cl 47.58%; MR_D 54.72, calculated for $C_9H_9Cl_3$: C 48.56; H 3.85; Cl 47.69%; MR_D 54.93.

Also obtained was 61.5 g (39.7%) α, β, β, β'-tetrachlorocumene, bp 154–157° (12 mm); d_4^{20} 1.4342. Found: C 41.90; H 3.12; Cl 54.97%; MR_D 59.35, calculated for $C_9H_8Cl_4$: C 41.85; H 3.21; Cl 54.68%; MR_D 59.77.

α-Bromocumene. 180.0 g (1.5 mole) Cumene was placed in a quartz flask fitted with reflux condenser, boiled gently, irradiated with UV light, and 80.0 g (0.5 mole) bromine added. When all the bromine had been added, and the mixture decolorized, the products were vacuum fractionated, yield of α-bromocumene by 102–104° (10 mm), 54.7 g (55.0%).

β-Bromocumene. The commercially available product was purified by distilling through a column.

α-Chloro-n-propylbenzene was obtained in 85% yield by chlorinating n-propylbenzene with SO_2Cl_2 in the presence of azoisobutyronitrile [18].

β-Chloro-n-propylbenzene was synthesized by condensing benzene with allyl chloride in the presence of ferric chloride [21].

γ-Chloro-n-propylbenzene was prepared by treating phenylpropyl alcohol with PCl_5 [22].

β, γ-dichloro-n-propylbenzene and β, γ-dibromo-n-propylbenzene were prepared from halogenated allylbenzene [23, 24].

α, β, γ-Trichloro-n-propylbenzene was synthesized by chlorinating cinnamyl chloride in $CHCl_3$ at 0°. Cinnamyl chloride was, in turn, obtained by the action of thionyl chloride on cinnamyl alcohol in the presence of pyridine [25].

Physical constants and yield of the starting halogen compounds after purification by column distillation are given in Table 2.

4-Phenyl-1, 2-dithio-3-thione (I). 10.0 g (0.06 mole) α-Chlorocumene, 10.0 g (0.31 g-at) S, and 20 ml 1, 2, 4-trichlorobenzene were heated together for 8 hr at 214–216°. On cooling crystals of I came down and these were filtered off, washed with hexane-benzene (2:1), and recrystallized from AcOH. Yield 5.3 g, or 39.0%, calculated on the starting α-chlorocumene. Mp 120.3°. Found: C 50.92; H 2.80; S 45.86%, calculated for $C_9H_6S_3$: C 51.39; H 2.87; S 45.73%. With MeI it forms yellow needles of methiodide, mp 193°. Found: I 36.16%, calculated for $C_{10}H_9S_3I$: I 36.10%. The literature gives [10] mp 122.0°, methiodide mp 194°.

5-Phenyl-1, 2-dithiol-3-thione (II). 10.0 g (0.06 mole) α-Chloro-n-propylbenzene and 10.0 g (0.31 g-at) S were heated together for 2 hr at 200–220°. II was extracted from the reaction products with isopropanol. Yield 1.6 g or 11.6%, calculated on the starting α-chloro-n-propylbenzene, mp 122.5°. Found: C 51.49; H 3.07; S 45.50%, calculated for $C_9H_6S_3$: C 51.39; H 2.87; S 45.73%. With MeI forms red glistening plates of methiodide, mp 156°. Found: I 36.28%, calculated for $C_{10}H_9S_3I$: I 36.1%. The literature gives [9] mp 126.6°, methiodide mp 154–155°.

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