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Abstract

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REARRANGEMENT OF RADICALS IN THE COURSE OF REACTIONS OF THIOLS WITH POLYHALOPROPENES

Two of the authors of the present article, together with co-workers, discovered the rearrangement of radicals of type A into radicals of type B in solution ([1]):

$$\dot{X}CCl_2-\dot{C}Y-CH_2Z \overset{\circ}{\longrightarrow} \dot{X}CCl-CYCl-CH_2Z$$

(A) (B)

$$X = Cl, F, H, CH_3; \quad Y = H, Cl, Br, CH_3; \quad Z = Br, Cl, CCl_3$$

In our preceding communication ([2]) an analogous rearrangement was presented, occurring in the course of the reaction of thiophenol and benzyl mercaptan with 1,1,1-trichloropropene, which we described by Scheme 1:

$$\dot{S}R + CCl_3{-}CH{=}CH_2 \longrightarrow CCl_3{-}\dot{C}H{-}CH_2SR \overset{\circ}{\longrightarrow} CCl_2{-}CHCl{-}CH_2SR$$

(A) (B)

$$CCl_2{-}CHCl{-}CH_2SR + HSR \begin{cases} \xrightarrow{a} HCCl_2{-}CHCl{-}CH_2SR + \dot{S}R & \text{(I)} \\ \xrightarrow{b} CCl_2{=}CH{-}CH_2SR + HCl + \dot{S}R & \text{(II)} \end{cases}$$

In the case of thiophenol, pathway *a* predominates; in the case of benzyl mercaptan, pathway *b*. In the present investigation we studied the interaction of certain thiols with 1,1,1-trichloropropene and 1,1,1-trichloro-2-bromopropene.

In the interaction of *n*-hexyl mercaptan with 1,1,1-trichloropropene it was possible to isolate only an unsaturated product of the structure $CCl_2{=}CHCH_2SC_6H_{13}$-n (pathway *b*, Scheme 1). Since thiophenol has a

considerably higher transfer constant (in the polymerization of styrene) than alkyl mercaptans ([3]), it seems natural to associate the predominance of pathway *a* in the case of thiophenol and of pathway *b* in the case of benzyl and, in particular, *n*-hexyl mercaptans with the greater effectiveness of thiophenol as a chain-transfer agent in the reaction.

A less effective chain-transfer agent, by increasing the lifetime of radical A (or B), promotes stabilization of the radical by elimination of a chlorine atom.

Using the reaction of thiophenol with 1,1,1-trichloro-2-bromopropene as an example, it was possible to show that radicals containing the grouping $\dot{C}Cl_2CBrCH <$ react even with such a vigorous chain-transfer agent as thiophenol along pathway *b* (Scheme 1), with elimination of bromine and formation of unsaturated—

compounds. Thiophenol reacts with 1,1,1-trichloro-2-bromopropene according to scheme 2:

$$2.\quad \underset{\text{(III)}}{CCl_3CBr{=}CH_2} + HSC_6H_5 \rightarrow \underset{\text{(IV)}}{CCl_2{=}CClCH_2SC_6H_5}.$$

As was shown earlier by two of the authors of the present article and by V. N. Kost ([4]), 1,1,1-trichloro-2-bromopropene, upon irradiation with ultraviolet light (or upon storage in diffuse light), isomerizes to 1,1,2-trichloro-3-bromopropene-1:

$$CCl_3CBr{=}CH_2 \xrightarrow{h} CCl_2{=}CClCH_2Br.$$

A chain radical mechanism of this reaction was demonstrated, and the following scheme was proposed to describe the isomerization:

$$3.\quad \underset{\text{A}}{\dot{B}r + CCl_3CBr{=}CH_2} \rightarrow \underset{\text{B}}{CCl_3\dot{C}BrCH_2Br} \xrightarrow{\text{isomerization}} CCl_2CCl\dot{B}rCH_2Br$$

$$\downarrow$$

$$\underset{\text{(V)}}{CCl_2{=}CClCH_2Br}$$

$$\uparrow$$

$$\dot{B}r+$$

It may be asserted that the formation of unsaturated sulfide IV (scheme 2) is not due to prior isomerization of the trichlorobromopropene according

to scheme 3, followed by substitution of allylic bromine in 1,1,2-trichloro-3-bromopropene-1 by the group RS. In a specially conducted experiment, in which 1,1,1-trichloro-2-bromopropene did not react completely with thiophenol, it was shown that the unreacted trichlorobromopropene has the structure of 1,1,1-trichloro-2-bromopropene.

In addition, it was shown that authentic 1,1,2-trichloro-3-bromopropene-1 does not interact with thiophenol under conditions analogous to the reaction of thiophenol with 1,1,1-trichloro-2-bromopropene.

It may be thought that thiophenol inhibits the isomerization according to scheme 3 by binding bromine, and the reaction proceeds entirely according to scheme 1b.

Investigation of the reaction of thiols with 1,1,1-trichloropropene does not make it possible to determine whether unsaturated sulfides II (scheme 1) are formed from rearranged radicals (path b) or from unrearranged radicals (path c). In contrast, in the reaction of thiophenol with 1,1,1-trichloro-2-bromopropene, the unsaturated sulfide IV (scheme 2) could be formed only from rearranged radicals.

If the reaction of 1,1,1-trichloro-2-bromopropene with thiophenol is carried out in the presence of elemental sulfur (which, as is known, is an inhibitor of homolytic and a catalyst of heterolytic addition of thiols to unsaturated compounds ([5])), then addition occurs without rearrangement according to scheme 4:

$$4.\quad CCl_3{-}CBr{=}CH_2 + C_6H_5SH \xrightarrow{S} CCl_3{-}CHBr{-}CH_2SC_6H_5$$

(VI)

analogously to what takes place in the case of the reaction of thiophenol with 1,1,1-trichloropropene ([2]).

The mode of addition of thiophenol to bromotrichloropropene is confirmed by the absence, in the IR spectrum of substance VI, of absorption bands characteristic of a methyl group.

1. Interaction of thiophenol with 1,1,1-trichloro-2-bromopropene. a) A mixture of 25 g (0.11 mole) of 1,1,1-trichloro-2-bromopropene and 15 g (0.14 mole) of thiophenol was irradiated with an incandescent lamp (150 W) at 105-110° for 3 h. The reaction mixture was then washed with soda solution and water and dried. After distillation of the starting products, 15.6 g of 2,3,3-trichloropropen-2-yl phenyl sulfide was obtained, b.p. 112° at 1 mm, n_D^{20} 1.5995, d_4^{20} 1.3888. Found: MR 62.40. $C_9H_7Cl_3S$. Calculated: 62.36 (yield 55% of theory).

On oxidation of the sulfide with hydrogen peroxide in glacial acetic acid, 2,3,3-trichloropropen-2-yl phenyl sulfone with m.p. 93-94° was obtained. A mixed-

melting-point test with a sample obtained by an unambiguous method (see experiment 6) gave no depression of the melting point.

b) The experiment was carried out analogously to the preceding one, but without illumination. After distillation, fractions were obtained: I, b.p. up to 55° at 10 mm, 7.8 g; II, b.p. 120° at 1.5 mm, 12.9 g, n_D^{20} 1.5993, d_4^{20} 1.3917 (yield 46% of theory).

The substance of fraction I was boiled for 2 hours with 7 g of diethylamine in 15 ml of methanol. After the usual work-up, 2.9 g of 3,3-dichloro-2-bromopropen-2-yl diethylamine was obtained, with b.p. 54.5–55° at 0.5 mm, n_D^{20} 1.5093, d_4^{20} 1.4080. Hydrochloride, m.p. 144°. Literature data [4]: b.p. 68–69° at 2 mm, n_D^{20} 1.5080, d_4^{20} 1.4060. Hydrochloride, m.p. 144°.

Part of the product of fraction II was oxidized with hydrogen peroxide in glacial acetic acid. 2,3,3-Trichloropropen-2-yl phenyl sulfone was obtained, with m.p. 93–94°. A mixed-melting-point test with a sample obtained by an unambiguous method gave no depression of the melting point.

2. Interaction of thiophenol with 1,1,1-trichloro-2-bromopropene in the presence of sulfur. The experiment was carried out analogously to the preceding one, but with the addition of 2 g of elemental sulfur. 14 g of 3,3,3-trichloro-2-bromopropyl phenyl sulfide was obtained, with b.p. 155° at 2 mm. The yield of crude sulfide (which, apparently, was contaminated with elemental sulfur) was 38% of theory. The product was purified and identified in the form of the sulfone; 3 g of sulfide was oxidized with hydrogen peroxide in glacial acetic acid; 2 g of 3,3,3-trichloro-2-bromopropyl phenyl sulfone was obtained (yield 61% of theory), m.p. 85° (from alcohol).

Found, %: C 29.81; 29.69; H 2.22; 2.16;
$C_9H_8Cl_3BrSO_2$. Calculated, %: C 29.45; H 2.18

3. Interaction of 1,1,1-trichloropropene with *n*-hexyl mercaptan. A mixture of 22 g (0.15 mole) of 1,1,1-trichloropropene and 11.8 g (0.10 mole) of hexyl mercaptan was irradiated with an incandescent lamp (100 W) at 100° for 15 hours. After removal of the starting materials by distillation, 6.6 g (yield 30% of theory) of 3,3-dichloropropen-2-yl hexyl sulfide was obtained, with b.p. 100° at 2 mm, n_D^{20} 1.4996, d_4^{20} 1.0853. Found MR 61.48. $C_9H_{16}Cl_2S$. Calculated 61.10.

Found, %: C 47.78; 47.85; H 7.49; 7.53; Cl 31.00; 31.10
Calculated, %: C 47.57; H 7.05; Cl 31.27

4. Interaction of 1,1,1-trichloropropene with thiophenol. A mixture of 22 g (0.15 mole) of 1,1,1-trichloropropene and 16.5 g (0.15 mole) of thiophenol was irradiated with an incandescent lamp (150 W) for 5 hours at 110° in a stream of nitrogen. After the usual work-up, the following were obtained:

I. 3.5 g of 3,3-dichloropropen-2-yl phenyl sulfide, with b.p. 111–113° at 3 mm, n_D^{20} 1.5930, d_4^{20} 1.2755. Found MR 58.17. $C_9H_8Cl_2S$. Calculated 57.49. Yield

10.6% of theory. Sulfone, m.p. 89° (from alcohol). A mixed-melting-point test with deliberately obtained 3,3-dichloropropen-2-yl phenyl sulfone (see experiment 5) gave no depression of the melting point.

II. 11.6 g of 2,3,3-trichloropropyl phenyl sulfide, described by us earlier [2] (yield 30% of theory).

5. Interaction of sodium thiophenolate with 1,1,3-trichloropropene-1. From 21 g of 1,1,3-trichloropropene-1 (0.15 mole) and sodium thiophenolate (from 11 g (0.10 mole) of thiophenol and 2.3 g of metallic sodium) in absolute alcohol, 16.9 g (76% of theory) of 3,3-dichloropropen-2-yl phenyl sulfide was obtained, with b.p. 102–103° at 1 mm, n_D^{20} 1.5948, d_4^{20} 1.2776. Found MR 58.23. $C_9H_8Cl_2S$. Calculated 57.49.

Found, %: C 49.18; 46.31; H 3.76; 3.64
$C_9H_8Cl_2S$. Calculated, %: C 49.31; H 3.65

Sulfone, mp 88.5–89° (from alcohol).

Found %:		C 42.84; 42.93; H 3.15; 3.24; Cl 28.27; 28.27
$C_9H_8Cl_2SO_2$.	Calculated %:	C 43.02; H 3.18; Cl 28.28

6. Reaction of sodium thiophenolate with 1,1,2-trichloro-3-bromopropene-1. From 12.5 g (0.06 mole) of 1,1,2-trichloro-3-bromopropene-1 and sodium thiophenolate, 8.1 g of 2,3,3-trichloropropen-2-yl phenyl sulfide was obtained (yield 57%), bp 109° at 1 mm, n_D^{20} 1.5998, d_4^{20} 1.3811. Found MR 62.80. $C_9H_7Cl_3S4E$. Calculated 62.36.

Found %:	C 42.54; 42.46; H 2.82; 2.91
Calculated %:	C 42.60; H 2.76

Sulfone, mp 92–93° (from alcohol).

Found %:		C 37.87; 37.76; H 2.46; 2.50
$C_9H_7Cl_3SO_2$.	Calculated %:	C 37.86; H 2.46

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Note: Figure translations are in progress. See original paper for figures.