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Abstract

Full Text

CHEMISTRY

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FREE-RADICAL ISOMERIZATION OF ACETONE DIPHENYLMERCAPTAL

Rearrangements of radicals in solution are one of the youngest and most actively developing areas of radical chemistry. At present, rearrangements of radicals in solution with migration of aryls, chlorine, and hydrogen are known. Examples are known of rearrangements of radicals with migration of an alkyl group; these rearrangements, however, require severe conditions (1). In continuation of studies in which a series of rearrangements of radicals in solution was investigated ([1–3]), we undertook a search for rearrangements of radicals with migration of an arylthio group.

Considering that one of the driving forces of rearrangement is the transition to more stable radicals, we chose as the object of study primary radicals of the structure $CH_3C(SC_6H_5)_2\dot{C}H_2$ (A), whose rearrangement should lead to the formation of more stable secondary radicals of the structure $CH_3\dot{C}(SC_6H_5)CH_2SC_6H_5$ (B). To obtain radicals A, we acted with tert-butyl peroxide on acetone diphenylmercaptal in chlorobenzene at 130°; in this process the isomeric 1,2-diphenylthiopropane was formed, along with some amount of diphenyl disulfide and phenylisopropenyl sulfide. In an experiment carried out in the absence of peroxide, the reaction does not proceed, which indicates the radical character of the observed isomerization.

We assume that the reaction under study can be described by Scheme I.

Scheme I

$$CH_3C(SC_6H_5)_2CH_3 \xrightarrow[a]{\text{initiator}} CH_3C(SC_6H_5)_2\dot{C}H_2 \quad A$$

$$CH_3C(SC_6H_5)_2\dot{C}H_2 \xrightarrow[b]{\text{rearrangement}} CH_3\dot{C}(SC_6H_5)CH_2SC_6H_5 \quad B$$

$$CH_3C(SC_6H_5)_2\dot{C}H_2 \xrightarrow{c} CH_3C(SC_6H_5)=CH_2 + C_6H_5\dot{S}$$

$$CH_3\dot{C}(SC_6H_5)CH_2SC_6H_5 + CH_3C(SC_6H_5)_2CH_3 \xrightarrow{g} CH_3CH(SC_6H_5)CH_2SC_6H_5 + A \quad \text{(chain)}$$

$$2C_6H_5\dot{S} \xrightarrow{d} C_6H_5S{-}SC_6H_5$$

The radicals A formed according to this scheme at stage a rearrange into radicals B (stage b); the latter, on interaction with the starting mercaptal (stage g), form 1,2-diphenylthiopropane and radicals A, which continue the chain. Radicals A are also capable of eliminating phenylthio groups (stage c) with the formation of phenylisopropenyl sulfide. Recombination of phenylthio radicals leads to diphenyl disulfide. Elimination of arylthio groups from radicals containing the grouping

$$> C - \dot{C} < \qquad \overset{|}{S}R$$

has been described many times (4). The structure of 1,2-diphenylthiopropane was proved by its independent synthesis from 1,2-dibromopropane and sodium thiophenolate. Identification of both substances was carried out by gas-liquid chromatography. The sulfones obtained from both samples also proved to be identical.

Identification of phenylisopropenyl sulfide with an authentic sample (obtained by the interaction of phenylsulfenyl chloride with isopropenyllithium) was carried out by gas-liquid chromatography.

Experimental Part

1. Isomerization of diphenylmercaptol of acetone. To a solution of 15 g of crystalline diphenylmercaptol of acetone in 22 ml of chlorobenzene, under reflux for 10 h, 3.3 g of tert-butyl peroxide (40 mole %) was added. After distillation of the solvent, the residue was fractionated in vacuum. Obtained:

a) 2.8 g (19% of theory) of 1,2-diphenylthiopropane, which after repeated distillation had b.p. 166-167° at 2 mm, n_D^{20} 1.6220, d_4^{20} 1.1281. Found MR 81.17, $C_{15}H_{16}S_2$ |=, calculated* 81.06.

Found %: C 69.17; 69.11; H 6.14; 6.16; S 24.68; 24.74
Calculated %: C 69.25; H 6.16; S 24.60

On oxidation of 0.4 g of the substance with hydrogen peroxide in glacial acetic acid, 0.3 g (60% of theory) of the sulfone with m.p. 111-112° (from alcohol) was obtained. A mixed-melting-point test with deliberately prepared 1,2-diphenylsulfonylpropane gave no depression of the melting point.

b) 1.9 g of a fraction boiling at ~ 51° at 2 mm, n_D^{20} 1.5545, d_4^{20} 1.0059. According to gas-liquid chromatography, this fraction contains ~ 90% of the main substance, identical with known phenylisopropenyl sulfide.

c) 8.4 g of a solid mixture, from which 2.7 g of diphenyl disulfide was isolated. In addition, the starting mercaptol was isolated from this mixture.

2. Heating a solution of diphenylmercaptol of acetone in the absence of peroxide. A solution of 5.8 g of diphenylmercaptol of acetone in 9 ml of chlorobenzene was boiled for 10 h. After distillation of the solvent, 5.3 g of the starting substance was isolated, identified by the absence of melting-point depression in a mixed sample with an authentic specimen.

3. Synthesis of 1,2-diphenylthiopropane. From 10 g of 1,2-dibromopropane, 2.5 g of sodium, and 12.1 g of thiophenol in absolute alcohol solution, 9 g of 1,2-diphenylthiopropane was obtained (yield 76.8% of theory), b.p. 167-168° at 2 mm, n_D^{20} 1.6252; d_4^{20} 1.1323. Found MR 81.20, $C_{15}H_{16}S_2$ |=, calculated 81.06.

Found %: C 69.17; 68.87; H 5.84; 6.08; S 24.37; 24.38
Calculated %: C 69.25; H 6.16; S 24.60

On oxidation of 0.5 g of the substance with hydrogen peroxide in glacial acetic acid, 0.5 g of 1,2-diphenylsulfonylpropane was obtained (yield 80.5% of theory), with m.p. 111-112° (from alcohol).

Found %: C 56.00; 55.71; H 4.86; 4.79; S 19.90; 19.63
Calculated %: C 55.70; H 4.94; S 19.75

4. Synthesis of phenylisopropenyl sulfide. From 20 g of isopropenyl bromide and 2 g of lithium in absolute ether solution, a solution of isopropenyllithium was obtained, to which 24 g of phenylsulfenyl chloride in 20 ml of absolute ether was added at 7-8°. After decomposition with water, the reaction mixture was extracted with ether. After distillation of the ether, the residue was fractionated. Obtained 7.3 g (~ 34% of theory) of phenylisopropenyl sulfide with b.p. 50° at 2 mm, n_D^{20} 1.5680; d_4^{20} 1.0226. Found MR 47.98; $C_9H_{10}S$ |=, calculated 48.09 (literature data[6]: n_D^{20} 1.5690; d_4^{20} 1.0162).

Found %: C 71.44; 71.63; H 6.86; 6.69
Calculated %: C 71.94; H 6.72

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* The increment of atomic refraction for sulfur was taken as equal to 8.4 (5).

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