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Abstract

Full Text

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ON THE CLAISEN REARRANGEMENT IN THE SERIES OF ALLYL ARYL SULFIDES

(Presented by Academician A. V. Topchiev, 24 XII 1956)

The Claisen rearrangement—an isomerization characteristic of allyl aryl ethers—is, in the opinion of a number of investigators (1), also inherent in their sulfur analogs. This conclusion is based on the work of Hurd and Greengard (2), where the authors, carrying out the pyrolysis of allyl phenyl and allyl-*p*-tolyl sulfides, found that in this process *o*-allylthiophenol and 2-allyl-4-methylthiophenol, respectively, are formed in yields of about 25%.

In contrast to (2), we have established that, on boiling allyl phenyl sulfide without solvent, allylthiophenol is practically not formed; rather, isomerization of allyl phenyl sulfide to propenyl phenyl sulfide takes place, an identical product to that isolated by Tarbell and McCall (3) upon the action of an alcoholic solution of sodium ethoxide on allyl phenyl sulfide. Propenyl phenyl sulfide, on standing or on heating, forms condensation products; the compound taken in (2) for *o*-allylthiophenol apparently represented condensation products of propenyl phenyl sulfide containing some amount of monomer and only traces of allylthiophenol, which has not yet been obtained by anyone. Similarly to allyl phenyl sulfide, thermal isomerization of allyl-*o*- and *p*-tolyl sulfides proceeds: in this case, respectively, propenyl-*o*- and *p*-tolyl sulfides are obtained; neither allyl-*p*-thiocresol (contrary to (2)) nor allyl-*o*-thiocresol is formed. Propenyl tolyl sulfides were also obtained by us as a result of heating the corresponding allyl tolyl sulfides with an alcoholic solution of sodium ethoxide by the method of Tarbell and McCall (3). The thermal isomerization of allyl aryl sulfides proceeds according to the scheme

$$\mathrm{ArS{-}CH_2CH{=}CH_2} \xrightarrow{t^\circ} \mathrm{ArSCH{=}CHCH_3}; \quad (\mathrm{Ar} = \mathrm{C_6H_5},\ \text{o-}\mathrm{C_6H_4CH_3} \text{ and } \text{p-}\mathrm{C_6H_4CH_3}).$$

The structure of the products of the thermal isomerization of allyl aryl sulfides was established by hydrodesulfurization over Ni-Raney; in this process propenyl phenyl sulfide is cleaved with formation of propane and benzene, while propenyl tolyl sulfides—with formation of propane and toluene.

In a typical experiment, 150 g of allyl phenyl sulfide was boiled under reflux in a stream of N_2 for 9 h. The mixture was repeatedly treated with 20% NaOH

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solution; the aqueous-alkaline layer contained only traces of mercaptans—after appropriate treatment, 0.19 g of lead mercaptide was obtained. The organic layer, separated from the aqueous-alkaline layer, was diluted with petroleum ether, dried, and distilled on a column of efficiency 25 theoretical plates. 39.7 g of propenyl phenyl sulfide was isolated, yield 36%, based on reacted allyl phenyl sulfide, b.p. 79-80°/3 mm, 225-226°/740 mm,

$$n_D^{20}\ 1.5850; \qquad d_4^{20}\ 1.0328.$$

Found, %:	C 72.04; H 6.68; S 21.32
$C_9H_{10}S$. Calculated, %:	C 72.00; H 6.67; S 21.34

Recovery of allyl phenyl sulfide: 40 g.

5 g of propenyl phenyl sulfide in 75 ml of glacial CH_3COOH was oxidized with a 200% excess of 28% H_2O_2 over the course of 1 h at 100°. The mixture was diluted with water and ex—

paraffin was distilled off to ∼ 50 ml; this operation was repeated five times, after which, on cooling with an ice-salt mixture, propenyl phenyl sulfone precipitated (probably the trans isomer), yield 34.1%, mp 68.5-69° (from alcohol + water in a ratio of 4 : 1).

Found, %:	C 59.36; H 5.46; S 17.70
$C_9H_{10}SO_2$. Calculated, %:	C 59.34; H 5.49; S 17.58

The mother liquors after the trans-propenyl phenyl sulfone were extracted with benzene; the extracts were distilled in vacuo, giving propenyl phenyl sulfone (probably the cis isomer), yield 17.0%, bp 176-180°/3.5 mm (bath temperature), $n_D^{21.5}$ 1.5536.

Found, %:	C 59.31; H 5.55; S 17.54
$C_9H_{10}SO_2$. Calculated, %:	C 59.34; H 5.49; S 17.58

Allyl *o*-tolyl sulfide was obtained from *o*-thiocresol by the method recommended ([2]) for allyl phenyl sulfide, in 90% yield, bp 96-97°/5 mm, n_D^{20} 1.5707, d_4^{20} 1.0125.

Found, %:	C 73.17; H 7.42; S 19.04
$C_{10}H_{12}S$. Calculated, %:	C 73.17; H 7.32; S 19.51

6 g of allyl *o*-tolyl sulfide was oxidized with H_2O_2 analogously to the preceding compound; after extraction with benzene and distillation in vacuo, allyl *o*-tolyl sulfone was isolated, yield 61%, bp 168-170°/8 mm, n_D^{20} 1.5492, d_4^{20} 1.1673.

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Found, %:	C 61.42; H 6.17; S 16.17
$C_{10}H_{12}SO_2$. Calculated, %:	C 61.22; H 6.12; S 16.32

12 g of allyl *o*-tolyl sulfide was boiled under reflux in a stream of N_2 for 3 h. The reaction mixture was worked up as in the case of allyl phenyl sulfide. After repeated distillation from a Claisen flask, 6.15 g (51.2% of theory) of propenyl *o*-tolyl sulfide was isolated, bp 129-133°/25 mm, n_D^{20} 1.5762, d_4^{20} 1.0175.

Found, %:	C 73.32; H 7.29; S 19.91
$C_{10}H_{12}S$. Calculated, %:	C 73.17; H 7.32; S 19.51

3 g of propenyl *o*-tolyl sulfide was oxidized with H_2O_2 in CH_3COOH analogously to the preceding compound. Propenyl *o*-tolyl sulfone was obtained, yield 2.5 g, bp 173-175°/7 mm, n_D^{20} 1.5551, d_4^{20} 1.1741.

Found, %:	C 61.24; H 6.15; S 16.43
$C_{10}H_{12}SO_2$. Calculated, %:	C 61.22; H 6.12; S 16.32

7.2 g of allyl *p*-tolyl sulfide was boiled under reflux in a stream of N_2 for 3 h. Partial decomposition was observed—∼ 0.33 g of propylene was isolated. The reaction mixture was worked up as in the case of the *o*-isomer; propenyl *p*-tolyl sulfide was isolated, yield 36.8% of theory, bp 131-136°/25 mm, n_D^{20} 1.5746, d_4^{20} 1.0119.

Found, %:	C 73.24; H 7.32; S 19.43
$C_{10}H_{12}S$. Calculated, %:	C 73.17; H 7.32; S 19.51

The product gives no precipitate with a solution of $Pb(CH_3COO)_2$ in alcohol; the fore-fractions and the residue after distillation contain only traces of compounds with an SH group.

2.0 g of propenyl phenyl sulfide in 112 ml of alcohol was boiled with stirring for 8 h with Raney Ni, prepared according to ([4]) from 70 g of Raney alloy. The evolved gases were collected in a Mariotte bottle and analyzed; 278 ml of propane was obtained—96% of theoretical. The reaction mixture was diluted with 50 ml of water and distilled off from Ni and NiS. The distillate was distilled on a column 38 cm high with a fine Levin metal packing. Fractions with bp 64.5-77°

(containing the azeotropic mixture) were diluted with water; 0.5 ml of benzene was isolated (42% of theory), identified from its absorption spectrum in the ultraviolet region.

On reduction of 5 g of propenyl-*o*-tolyl sulfide with Raney nickel (from 140 g of Raney alloy) in 280 ml of alcohol (12 h boiling), similarly to the preceding

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experiment, 1.9 g (78% of theory) of toluene was isolated, b.p. 107–109°, n_D^{21} 1.4910.

6 g of propenyl-*p*-tolyl sulfide were reduced with Raney nickel (from 160 g of alloy) in 300 ml of alcohol, as described above. 654 ml of propane were obtained (81% of theory) and 1.4 g of toluene (44% of theory), b.p. 105–109°, $n_D^{22.5}$ 1.4779.

For the propenyl aryl sulfides studied by us, a characteristic color reaction with sulfuric acid is observed: to a drop of propenyl aryl sulfide two drops of concentrated H_2SO_4 are added—the appearance of a red coloration is observed, rapidly turning brown. Allyl aryl sulfides, on addition of concentrated H_2SO_4, only turn faintly yellow.

The data obtained by us make it possible to conclude that, for allyl aryl thioethers, in contrast to the corresponding oxygen compounds, the Claisen rearrangement practically does not occur. On heating, allyl aryl thioethers isomerize into the corresponding propenyl aryl sulfides.

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