# FORMATION OF 2- AND 3-CHLOROTHIOPHENE BY PYROLYSIS OF BIS(β-CHLOROVINYL) SULFIDE

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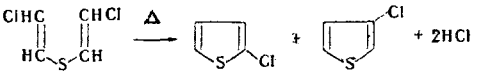
The pyrolysis of 12 g of bis(β-chlorovinyl) sulfide (I) (a mixture of spatial isomers: 43% trans,trans, 14% cis,cis, and 43% cis,trans) by passage at a rate of 12 ml/h in a nitrogen atmosphere (v = 2 liters/h) through a hollow quartz tube (d = 30 mm, l = 650 mm) heated to 440-460°C leads to the formation of 7 g of a condensate consisting, according to the data from gas–liquid chromatography (with an LKhM-8MD chromatograph under conditions of linear programming of the temperature of the column from 25 to 160°C; the liquid phase was 5% lukopren on Chromaton HMDS, the column length was 2 m, and the carrier gas was helium), of 66.6% starting sulfide I and a mixture of 5.23% and 12.56% 2- (II) and 3-chlorothiophene (III), respectively. The preparative yield of II was 16.3%, the preparative yield of III was 6.6% and the conversion of bis(β-chlorvinyl) sulfide (I) was 61.5%.




I II III

The isomeric composition of the recovered I changed: 46% trans,trans, 43% cis,cis and 11% cis,trans. This indicates thermal conversion of the cis,trans isomer of I to the cis, cis isomer. The subsequent pyrolysis of 9 g of this recovered bis(β-chlorovinyl) sulfide (I) under similar conditions leads to 7.6 g of condensate containing 46.1% I, 16.1% II, and 7.4% III, but with a higher preparative yield of chlorothiophenes II and III — 27.2 and 16.7%, respectively; the conversion of starting I was 61.1%. The percentage of the trans,trans isomer in the recovered I decreased sharply to 19% (55% cis,cis and 23% cis,trans), evidently due to the primary heterocyclization of precisely this isomer.

The isomers of sulfide I were isolated from the mixture (bp 70-75°C (12 mm)) with a preparative chromatograph of the PAKhV type; the liquid phase was 5% lukopren on Chromaton HMDS, the column was 3-m long, and the temperature was 160°C. Found: Cl 44.9; S 20.2%. $C_4H_4Cl_2S$. Calculated: Cl 45.8; S 20.6%. PMR spectrum (in $CCl_4$, internal standard hexamethyldisiloxane): trans,trans 6.08 and 6.36 ppm, J = 13.0 Hz; cis,cis 6.01 and 6.36 ppm, J = 7.5 Hz; cis,trans 6.47, 6.01, and 6.16 ppm, $J_1$ = 12.0 and $J_2$ = 6.0 Hz. A mixture of chlorothiophenes II and III was isolated by fractionation of the condensate and had bp 126°C (720 mm).

The mechanism of the formation of not only 3-chlorothiophene but also 2-chlorothiophene is now under study.

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