Identification of the higher-boiling products resulting from chlorination of isobutylene

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Di- and trichloro derivatives, identified by infrared spectroscopy, elemental analysis and physical data, were isolated from the technical product of isobutylene chlorination by means of preparative chromatography.

The main product of substitution chlorination of isobutylene was found to be methylallyl chloride. Further saturated and unsaturated mono- to trichloro derivatives are the products of side reactions. To optimize the conditions of methylallyl chloride synthesis, it was necessary to analyze qualitatively and quantitatively the technical reaction product. Various methods were used to identify the by-products: monochloro derivatives by gas chromatography using reference substances, di- and trichloro derivatives by elemental analysis, physical constants and interpretation of infrared spectra.

Experimental

The technical product was analyzed gas-chromatographically under the specified conditions:

Apparatus — Chrom I (Laboratorní přístroje, Praha) with flame-ionization detector adapted for direct introduction of the air into the burner.

Column — length 3 m, diameter 3 mm; packing 3% triglycol dibenzoate on Chezasorb II (Lachema, Brno).

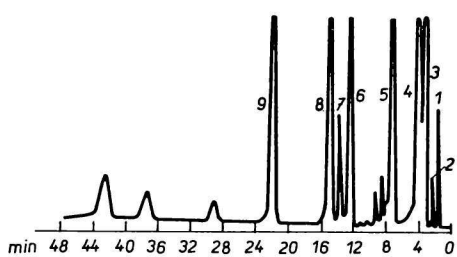

Fig. 1. The chromatogram of crude methylallyl chloride.
1. isobutene; *2.* *tert*-butyl chloride; *3.* 1-chloro-2-methyl-1-propene; *4.* methylallyl chloride; *5.* 1,2-dichloro-2-methylpropane; *6.* lower-boiling 1,3-dichloro-2-methyl-1-propene; *7.* higher-boiling 1,3-dichloro-2-methyl-1-propene; *8.* 3-chloro-2-chloromethyl-1-propene; *9.* 1,2,3-trichloro-2-methylpropane.

Gas flow — nitrogen 21 ml/min; hydrogen 29 ml/min; air 500 ml/min.

Infrared spectra were measured with a double-beam UR-10 (Zeiss, Jena) spectrophotometer.

Boiling point was determined according to Karr—Childers' micromethod [1].

Elemental analysis was done with a Hewlett—Packard CHN-Analyzer.

Pure components isolated from the technical product by means of preparative chromatography (Chromatograph Giede) under conditions of analytical separation consisted of di- and trichloro derivatives, which eluated after methylallyl chloride (the last of monochloro derivatives). The chromatogram is seen in Fig. 1.

Physicochemical constants are consistent with those reported.

Results and discussion

1,2-Dichloro-2-methylpropane

The spectrum of substance which eluates immediately after methylallyl chloride (peak *5*) reveals strong absorption band within 700—800 cm^{-1} belonging to symmetric

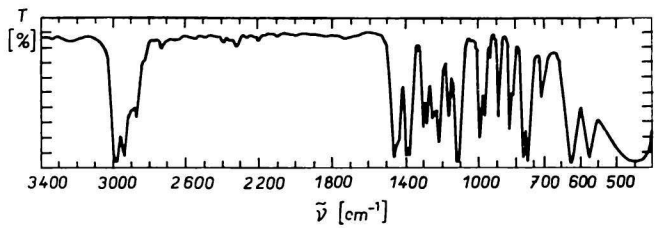

Fig. 2. Infrared spectrum of 1,2-dichloro-2-methylpropane. Slit programme 8, cell 0.02 mm KBr.

and asymmetric stretching C—Cl vibrations. The band at 1380 cm^{-1} is split due to two methyl groups attached to one carbon atom ($\delta_s(CH_3)$ doublet at 1380 cm^{-1}). This assumption is also supported by the appearance of a peak at 1220 cm^{-1} associated with the skeletal vibration $CH_3—C—CH_3$ [2—4].

Fig. 3. Infrared spectrum of 1,2-dichloro-2-methylpropane. Slit programme 4, cell 0.05 mm KBr.

Better resolution (programme *4*) showed that the band at 1470 cm^{-1} consisted of two bands at 1445 cm^{-1} ($\delta_{as}(CH_3)$) and 1465 cm^{-1} (CH_2 scissor); Figs. 2 and 3.

B.p. 106.5°C, n_D^{20} 1.4373, No. *5*.

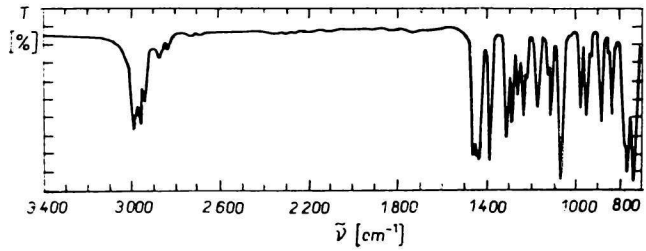

Fig. 4. Infrared spectrum of lower boiling 1,3-dichloro-2-methyl-1-propene. Slit programme 4, cell 0.05 mm NaCl.

Lower-boiling 1,3-dichloro-2-methyl-1-propene

The absorptions in the 1650, 3020, and 3070 cm^{-1} region indicate the presence of an unsaturated bond (Fig. 4). Other absorption bands could be ascribed to $\delta_{as}(CH_3)$ (and probably also CH_2 scissor) at 1450 cm^{-1}, $\delta_s(CH_3)$ at 1380 cm^{-1} and $\tilde{\nu}(C-Cl)$ at 790—820 cm^{-1}.

B.p. 129.5°C, n_D^{20} 1.4706, No. *6*.

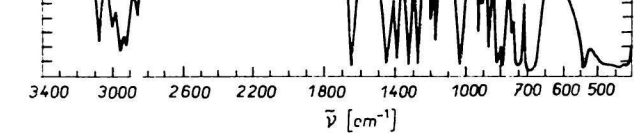

Fig. 5. Infrared spectrum of higher-boiling 1,3-dichloro-2-methyl-1-propene. Slit programme 4, cell 0.05 mm KBr.

Higher-boiling 1,3-dichloro-2-methyl-1-propene

As apparent from the spectrum (Fig. 5), the component is a chlorinated hydrocarbon possessing besides an unsaturated bond (1645, 3000, and 3070 cm^{-1}) also a methyl group (1380 cm^{-1}). Both the infrared spectrum and the physical constants were not reliable enough because the reported data satisfy two compounds: 3,3,3-trichloro-2-methyl-1-propene and the higher-boiling 1,3-dichloro-2-methyl-1-propene.

Decisive was the elemental analysis which undoubtedly showed the compound to be 1,3-dichloro-2-methyl-1-propene.

Found: 38.4% C, 5.18% H, 56.42% Cl.

B.p. 132.5°C, n_D^{20} 1.4765, No. *7*.

3-Chloro-2-chloromethyl-1-propene

The infrared spectrum (Fig. 6) provides the fundamental information referring to the character of the substance. As there is no methyl group in the spectrum, only 3-chloro-2-chloromethyl-1-propene can be concerned of compounds assumed.

B.p. 137.5°C, n_D^{25} 1.4740, No. *8*.

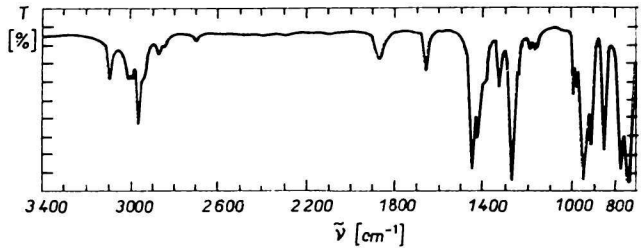

Fig. 6. Infrared spectrum of 3-chloro-2-chloromethyl-1-propene.
Slit programme 4, cell 0.05 mm NaCl.

1,2,3-Trichloro-2-methylpropane

The infrared spectrum (Fig. 7) of this substance is indicative of a saturated methyl group possessing chlorinated hydrocarbon. Elemental analysis fits the calculated requirements.

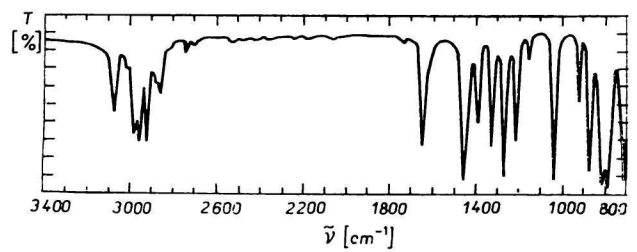

Fig. 7. Infrared spectrum of 1,2,3-trichloro-2-methylpropane.
Slit programme 4, cell 0.05 mm NaCl.

B.p. 163°C, n_D^{20} 1.4759, No. *9*.

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