

Preparation and determination of isomeric chloromethylation products of C₆—C₈ aromatics

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A mixture of isomeric chloromethylated aromatic hydrocarbons resulting from the chloromethylation of individual C₆—C₈ aromatics was separated by vacuum distillation and the obtained monochloromethyl aromatics were analyzed by gas chromatography using di-*n*-decyl phthalate and Carbowax 1450-coated capillary columns at 100°C. The individual monochloromethyl derivatives were characterized by means of their i.r. spectra and Kovats' indices.

Смеси хлорметилпроизводных ароматических углеводородов полученные хлорметилированием индивидуальных ароматических соединений C₆—C₈ были разделены вакуумной дистилляцией, и фракция монохлорметилпроизводных ароматических углеводородов была анализирована хроматографией на капиллярных колоннах наполненных ди-*n*-децилфталатом и Карбоваксом 1450 при температуре 100°C. Отдельные монохлорпроизводные были характеризованы ИК спектрами и индексами по Коватцу.

Chloromethylation of C₇—C₈ aromatics gives, in addition to a negligible amount of *m*-isomers, mainly *p*- and *o*-substituted derivatives. A higher content of the *m*-isomer (~15% wt.) was found to be present only in the reaction mixture of the chloromethylation of benzyl chloride [1]. The ratio of the isomeric products depends on the reaction conditions and the used catalysts.

The analytical methods suitable for the determination of the isomeric aromatic chloromethyl derivatives are rather laborious. A viscometric method for the determination of toluene-chloromethylation products was described by *Rabjohn* [2]. *Hill* and *Short* [3] used thermal analysis of a mixture of alcohols obtained *via* acetates and *Nazarov et al.* [1, 4] applied a semiquantitative method of oxidation with chromium trioxide taking advantage of the fact that only *p*- and *m*-isomers are oxidized by this reagent while the *o*-isomer decomposes.

Johnson et al. [5] investigated the hydrogenolysis of alkyl chlorides with lithium aluminium hydride in tetrahydrofuran. Chlorine can be substituted with hydrogen also catalytically under high pressure [6], which was used by *Shacklett* and *Smith* [7]

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in the synthesis of polymethylbenzenes from chloromethyl aromatics. The obtained aromatic hydrocarbons can be analyzed by current methods *e.g.* gas chromatography.

A direct analysis by gas chromatography on poly(ethylene glycol adipate)-coated capillary column was for the first time applied by *Mironov et al.* [8] for the determination of the relative velocities of the chloromethylation in a series of aromatics. The authors, however, failed to give the operating conditions of their analysis. An indirect procedure for the determination of chloromethylated alkyl aromatics bearing a long side chain has been described by *Lyushin et al.* [9]. The method comprised conversion of the chloromethyl derivatives into the corresponding acetates which were analyzed by gas chromatography on Apiezon L and by i.r. spectrometry.

Another indirect determination of isomeric chloromethylation products of 1,2,4-trimethylbenzene [10] was based on the analysis of the corresponding methoxymethyl-trimethylbenzenes on a semicapillary column packed with SE 301 on Chromosorb P and on SE 30 on Chromosorb W. Good results and short time of the analysis were reported by this procedure.

In the present work we report on data obtained for chloromethylated aromatic hydrocarbons and on a direct determination of isomers of this class which have not been described previously.

Experimental

Gas chromatography was performed using a Chrom 3 instrument equipped with a flame-ionization detector. Nitrogen (2.5 kp/cm²) was used as a carrier gas. The separation of 0.2–0.4 μ l samples was carried out at 100°C on a 45 m capillary column (I.D. 0.25 mm). Coating with di-*n*-decyl phthalate or Carbowax 1450 was done using the dynamic method proposed by *Ettre* [11]. The i.r. spectra of the monochloromethyl aromatics were measured at 2000–200 cm⁻¹ on a Perkin–Elmer spectrometer Model 225 using potassium bromide cells (0.05 mm). In the range of very intense absorption bands (C–H and C–Cl vibrations) neat-film technique was applied.

The pertinent i.r. spectral data, Kovats' indices, and the composition of the isomeric monochloromethyl derivatives resulting from the individual C₆–C₈ aromatics are given in Table 1.

Chloromethylation was accomplished by passing dry hydrogen chloride into a stirred mixture of benzene, toluene or ethylbenzene (4 moles), paraformaldehyde (1 mole), freshly fused zinc chloride (100 g), and glacial acetic acid (100 ml) at 60°C for 20–60 min. The mixture was cooled and the organic layer was washed with water, a solution of sodium carbonate, and water. After drying with anhydrous calcium chloride the product was decolorized, filtered, and distilled first at atmospheric and then at a reduced pressure.

Chloromethylation of *o*-, *m*-, and *p*-xylene (1 mole) was carried out by heating their mixture with paraformaldehyde (1.3 mole) freshly fused zinc chloride (30 g), glacial acetic acid (200 ml), concentrated hydrochloric acid (250 ml) under stirring at 60°C for 1–4 hrs. The reaction was terminated by the addition of petroleum ether (250 ml) and the organic layer was processed as described above.

Results and discussion

The products of chloromethylation are summarized in Table 1.

The ratio of the products of chloromethylation of toluene under different reaction conditions has been investigated by several authors [2, 12–16]. Except [16] where

Table 1

Infrared data, elution indices, and the ratio of chloromethyl C₆-C₈ aromatics

Starting hydrocarbon	Product	Combination vibrations at 2000-1600 cm ⁻¹	Deformation (out of plane) vibrations ArH	Deformation (scissoring) vibrations of CH ₂ in the chloromethyl group	Stretching vibrations C-Cl	Elution index		Composition of the isomers mole %	
						I _{DDP} ¹⁰⁰	I _{CBX} ¹⁰⁰	DDP	CBX
Benzene	Benzyl chloride	1945, 1880, 1800	760 (S), 690	1258 (S)	670 (S)	1126.3	1536.3	100	100
Toluene	3-Methylbenzyl chloride	—	—	—	—	1228.8	1619.8	2	1.5
	2-Methylbenzyl chloride	1950, 1835	835, 738 (S)	1258 (S)	666 (S)	1233.7	1626.1	98	42.1
Ethylbenzene	4-Methylbenzyl chloride	1900, 1792	795 (S)	1258 (S)	666 (S)	—	1632.3	—	56.4
	4-Ethylbenzyl chloride	1905, 1795	800 (S)	1260 (S)	665 (S)	1306.5	1695.5	67.9	67.3
	3-Ethylbenzyl chloride	—	—	—	—	—	—	—	—
<i>p</i> -Xylene	2-Ethylbenzyl chloride	1955, 1840	840, 740 (S)	1260 (S)	665 (S)	1322.2	1712.8	32.1	32.7
	2,5-Dimethylbenzyl chloride	1895, 1832, 1750	805 (S), 875	1255 (S)	662 (S)	1329.4	1714.4	100	100
<i>m</i> -Xylene	3,5-Dimethylbenzyl chloride	—	—	—	—	1330.4	1718.7	3.8	5.2
	2,6-Dimethylbenzyl chloride	1925, 1850, 1785	762 (S), 715	1255 (S)	660 (S)	1334.4	1725.4	13.6	11
<i>o</i> -Xylene	2,4-Dimethylbenzyl chloride	1892, 1825, 1750	815 (S), 872	1255 (S)	660 (S)	1338.5	1732.6	82.6	83.8
	3,4-Dimethylbenzyl chloride	1880, 1750	812 (S), 875	1260 (S)	670 (S)	1359.5	1762.0	63.5	67.4
	2,3-Dimethylbenzyl chloride	1920, 1840	780 (S), 712	1260 (S)	670 (S)	1362.4	1772.5	36.5	32.6

S — intense absorption band.

it was claimed that the chloromethylation according to *Blanc* gave exclusively the *p*-isomer, the reported amount of this substance in the reaction mixtures was 47–80%. The corresponding *m*-isomer has been found only rarely, *i.e.* in [14].

Under our conditions of the chloromethylation the formed amounts of *p*-, *o*-, and *m*-isomers, as found on Carbowax-coated columns, were 56.4, 42.1, and 1.5 mole %, respectively.

The columns coated with di-*n*-decyl phthalate, not separating the *o*- from the *p*-isomer, gave unsatisfactory results.

The chloromethylation of ethylbenzene has not been studied to such an extent as that of toluene. The presence of the ethyl group makes the substitution at the *o*-position more difficult and thus the content of the *p*-isomer in the reaction mixture increases. As found by *Nazarov et al.* [1], the exchange of a methyl group on benzene with an ethyl group results in an increase of the *p*-isomer produced from 48.3 to 70%, which is in agreement with the observation we made during this work. The separation of the two produced isomers was good on both columns used and the presence of the *m*-isomer was not observed.

By chloromethylation of *m*-xylene all three isomers were formed and these could be satisfactorily separated on both columns. Predominantly, the 2,4-derivative was produced.

Chloromethylation of *o*-xylene gave two isomers and the separation on both columns was good.

The analysis of the products of chloromethylation of 1,2,4-trimethylbenzene, carried out capillary columns, was not quite as good. The elution times observed were long and the substances gave broadened peaks. At temperatures above 100°C the decomposition of the substances, irreversible adsorption of the decomposition products on the column and corrosion becomes more probable. In this case, the use of packed columns or indirect methods of the analysis appeared to be more advantageous.

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