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Interpretation of Retention Indices in Gas Chromatography for Establishing Structures of Isomeric Products of Alkylarenes Radical Chlorination*

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Abstract—By an example of previously uncharacterized products obtained by alkylarenes radical chlorination was demonstrated that combination of various interpretation methods applied to the retention indices (RI) in the gas chromatography on the standard nonpolar phases (comparison of RI of products and initial compounds, characteristics of succession of the chromatographic elution of the structural isomers with the use of estimation of molecular dynamic parameters, application of the additive schemes to RI calculation, and using of structural analogy $CH_3 \leftrightarrow Cl$ for testing the results obtained) permitted unambiguous identification of the structure even without data of mass spectrometry.

Among the problems of identification of components in mixtures of organic compounds with the use of GC-MS method one of the most difficult cases is structure determination of isomers characterized with insignificant distinctions in the mass spectra (isomeric hydrocarbons in oil, ecotoxic compounds of various classes, in particular, positional isomers of polychlorinated aromatic compounds etc.). The attempts of identification of such objects usually lead to uncertain results and numerous errors. A typical case of this formal approach consists in sometimes occurring description of several different components with the same structure [1]. The risk provided by this uncritical treatment of a long series of identified compounds was indicated already in [2]. In all these cases the reliable identification is possible only with taking into account retention indices of gas chromatography (in formulas *RI*) and the appropriate database. However as was already several times mentioned the volume of the modern databases on chromatography is considerably smaller than that for mass spectrometry. This drawback significantly hampers the practical application of these analytical parameters. Besides when the investigation objects are isomeric components of first obtained reaction mixtures that have not been characterized before either by mass spectra or RI, then the traditional approaches to identification consisting in revealing formal coincidence of analytical parameters are fully unacceptable. In such cases just the chromatographic constants become important since unlike the mass spectra they may be fairly accurately predicted even for previously unstudied compounds classes with the use of additive calculation schemes, principles of structural similarity, calculations based on physicochemical characteristics etc. An example of a new approach to interpretation of RI for the reaction products of ethoxycarbonylcarbene with various substrates with the use of molecular dynamics was demonstrated in [3].

The necessity of application of the chromatographic parameters arises also in characterizing relatively simple classes of organic compounds. For instance, up till now are virtually lacking the analytical data on the products of alkylarenes radical chlorination, although the reactions of this class are extensively studied [4]. The identification problems with chlorinated derivatives of various series are hampered by low structural specificity of their mass spectra that do not permit to locate the position of the halogen atom in the molecule. The most significant characteristic of mass spectra is useful only for group identification: In the molecular ions of compounds containing structural fragments $C(sp^3)$–Cl the prevailing fragmentation consists in elimination of $Cl^{\cdot}$ radical, whereas p-π conjugation in the fragments $C(sp^2)$–Cl causes predominant formation of $[M–R]^+$ ions (R are hydrocarbon radicals) with conservation of chlorine atom [5]. Therefore the spectra of ion series of alkylchloroarenes and (chloroalkyl)arenes should be considerably different; how-

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ever they are lacking in a fairly comprehensive compilation given in [6], and it proves that these compounds are poorly investigated even by mass spectrometry.

RI from gas chromatographic data of some simplest (chloroalkyl)arenes are listed in the handbook [7]. These retention indices are not interlaboratory invariants and cannot serve for identification [8]. The RI of products obtained by radical chlorination of *p*-xylene [9] were measured on nonstandard phases and therefore cannot be compared with the modern data for nonpolar polydimethylsiloxane phases. The above reasons were prerequisite for developing two calculation methods for RI of such chloroderivatives: a) proceeding from structural analogy $CH_3 \leftrightarrow Cl$ and basing on the RI of the corresponding hydrocarbons with the use of statistically processed values of increments $Cl \rightarrow CH_3$ [-61 ± 15 at $C(sp^2)$ and -128 ± 13 index units at $C(sp^3)$] [10], and b) from the boiling points of the structural analogs along the equation $\log RI(X\text{–}Cl) = a \log bp(X\text{–}CH_3) + bA + c$ [11].

Thus the solution of an important practical problem of identification of isomeric products obtained by radical chlorination of substituted aromatic hydrocarbons due to low informative quality of their mass spectra requires first of all an interpretation of their chromatographic parameters in the absence of the necessary reference source. The mass-spectrometrical information in this case is replaced by *a priori* knowledge on the nature of the compounds under investigation (we know the class of the substances) that can be supplemented with characteristics of the influence of the variations in the chlorination conditions on the composition of the reaction mixtures etc. This study contains both experimental measurement of RI of insufficiently characterized (chloroalkyl)arenes, and in extension of the investigation carried out in [3, 12] further development of technique for structure determination of isomer products formed in organic reactions with the use of these data.

The solution of the problem under consideration cannot consist in application of a single "universal" interpretation method of chromatographic data; only combination of various procedures provides a possibility to get an unambiguous answer. This combination should include several versions of IR estimation by additive schemes, the calculation of intramolecular vibrational and rotational energies by molecular dynamics method, and, separately, evaluation only vibrational component of these energies with the use of the simplest models to predict the succession of elution of the isomeric chloroderivatives.

The establishing of the structures of the reaction mixtures components is considerably simplified by the fact that simultaneously arise all possible products of the radical chlorination by replacement of nonequivalent hydrogen atoms in the alkyl fragments of molecules. At sufficiently high efficiency of capillary columns it is possible to register the peaks of all these components. In theory it is possible to estimate their relative intensity proportional to $n_H \xi k_{rel}$, where n_H is a number of equivalent hydrogen atoms in the molecule, k_{rel} are the relative rate constants of the radical chlorination (for instance, with alkanes in CCl_4 k_{sec}/k_{prim} amounts to 1.81 ± 0.03, and k_{tert}/k_{prim} to 3.0 ± 0.1 [4]). However such estimates may be used only as provisional since the relative quantities of isomers are changed by secondary processes (dehydrochlorination and formation of polychlorinated derivatives), and the lability of hydrogen atoms in benzyl position of the molecules may be notably unlike that in alkanes.

Among the known processes of radical chlorination of alkylarenes no one excludes the parallel ionic chlorination in the aromatic ring. The fraction of these products is higher for the heterophase process B (see Experimental), and it decreases with growing overall number of carbon atoms in the alkyl substituents. The comparison of the set of chlorination products produced by various procedures turned out to be a very important source of additional information on their chemical nature. It was used for differentiation of the chlorinated substances according to the substitution type.

A preliminary information on the nature of chlorination products obtained from alkylarenes may be gained from comparison of the difference between RI of the products and the initial hydrocarbons (**criterion I**). The values ΔRI corresponding to transformation $H \rightarrow Cl$ differ depending on the degree of substitution of the reaction site and on its hybridization state, namely 189 ± 19 ($ArH \rightarrow ArCl$), 228 ± 14 ($H' \rightarrow Cl'$), 182 ± 22 ($H'' \rightarrow Cl''$) and 175 ± 10 ($H''' \rightarrow Cl'''$) [13]. From these estimates follows that with degree of confidence $\alpha = 0.95$ the value of ΔRI at replacement of the primary hydrogen should be no less than 200 and no more than 256. The larger ΔRI values correspond only to polychlorinated compounds. On the other hand, the value $\Delta RI < 138$ ($\alpha = 0.95$) are excluded for any monochlorinated derivatives, and therefore the criterion $\Delta RI < 105$ permits

unambiguous identification in the reaction mixtures of the principal side products resulting from dehydrochlorination of chloroalkylarenes, conjugated alkenylbenzenes. The above estimates of ΔRI also show that the ranges of these parameters for the *sec*- and *tert*-chloroalkyl derivatives should overlap.

If is fulfilled the above stated the most important condition of the structural interpretation of chromatographic data, registration of the signals of every possible product of radical chlorination, then the unambiguous determination of isomers structure is equivalent to prediction of the succession of their elution from the chromatography column (ranged RI). The analogous feature of the reaction mixtures composition provided a possibility, for instance, to establish the structures of regio- and stereoisomers in the products of Diels–Alder reaction [12] from the estimates of their intramolecular vibrational and rotational energies obtained by computer simulation using the molecular dynamics method. The essence of this approach is based on the fact that for processes resulting in mixtures of isomer compounds of the type $A+B \rightarrow C_1+C_2+\ldots+C_n$ the differences between RI of products and initial reagents $\Delta RI(i) = RI(i)-RI(A)-RI(B)$ are in fair correlation with the corresponding differences of the overall vibrational and rotational energies of the products and reagents $\Delta E(i) = E(i)-E(A)-E(B)$. The observed oppositely directed changes in parameters ΔRI and ΔE can be approximated in quite a few cases by linear equations $\Delta RI = a\Delta E+ b$ $(a<0)$. The coefficients of such relations are calculated from the ΔRI and ΔE values for the known substances; thereafter these relations can be applied for confirming or rejecting the assumed structures of the other products [3]. However this mathematical approach is not the only possible way of using the results of calculations by molecular dynamics method for interpretation of the chromatography data. It is presumable that for practical problems more favorable is a simpler rule (**criterion II**): isomeric products of organic reactions formed for the same precursors are eluted from the chromatograph column in the order of decrease in their dynamic molecular parameters *E*. Just this algorithm of data interpretation was applied to structural assignment of the isomeric adducts arising in [2+4]-cycloaddition [12].

If the main cause of difference in the chromatography parameters of isomers with similar energy of dispersion interaction "sorbate–stationary phase" is the dissimilar molecular dynamic parameters, then simpler models can be suggested taking into account only vibrational components of the intramolecular energy. If the consideration is limited to ordinary bonds C–C and C–X (where X are heteroatoms or structural fragments including cycles and multiple bonds; equal number of C–H bonds in isomers is not taken into account), and each ordinary bond is regarded as a harmonic oscillator, then the overall vibrational energy of molecules should be proportional to the value $U = \Sigma k[M/(m_i m_j)]^{0.5}$, where M is molecular weight, $m_i+ m_j = M$ is the weight of the structural fragments of molecules attached to each bond under consideration. The values of factors k for ordinary bonds may be taken as unity without further differentiation. It was shown by examples of isomeric alkanes, dialkyl sulfides, and alkylamines that E and U values are in good correlation; therefore the estimation of RI in gas chromatography may be performed with the use of an equation of $RI = aU+ b$ $(a<0)$ type [14]. Thus alongside computer simulation by molecular dynamics method it is possible to use simplest estimation of intramolecular vibrational energy U that may be computed even on a microcalculator (**criterion III**).

This statement was up till now considered in a single study [15], and thus it required additional testing by example of compounds chemically related to the chloroalkylarenes in question. In Table 1 are compared the differences of RI for some chlorine-containing substances (polychlorocompounds included) referred to RI of the isomers with maximal RI on the standard nonpolar phases, and the corresponding differences in U parameters. All the presented data unambiguously show that the succession of chromatographic elution always corresponds to the decrease in U values, similarly to the decrease in the E parameters. Moreover, the ΔRI and ΔU values for all the chlorine-containing compounds listed in Table 1 fit to unique correlation equation $\Delta RI = -(963 \pm 129)\Delta U+(11 \pm 11)$; $r = -0.942$; $s = 15.9$. A similar approach may be extended also to the group of chloroalkylarenes under consideration. However that would be possible only after reliable identification of some compounds belonging to this class. Therefore not to hamper the logical scheme of data interpretation we used here only the criterion of opposite direction in changes of chromatographic RI and absolute values of U parameter. Some distinctions in structure of molecules (e.g. positional isomerism) do not appear in variations of this simple U criterion preventing its application.

The combination of the mentioned three criteria for the structural interpretation of the chromatographic parameters already is sufficient for assigning structures to most of we registered products of alkyl-

Table 1. The dependence of differences in retention indices (ΔRI) of some simple chlorine-containing compounds on variation in Δ*U* parameter

Isomeric chlorine-containing compounds	RI	*U*	ΔRI[b]	Δ*U*[b]
1,2-Dichloroethane	632 ± 9	0.624		
1,1-Dichloroethane	568 ± 7	0.702	–64	0.078
1-Chloropropane	531 ± 5	0.749		
2-Chloropropane	496 ± 5	0.802	–35	0.053
1-Bromo-2-chloromethylbenzene	1244[a]	0.493		
1-Bromomethyl-2-chlorobenzene	1237[a]	0.470	–7	0.023
1-Chlorobutane	637 ± 5	0.930		
2-Methyl-1-chloropropane	604 ± 4	0.988	–33	0.058
2-Chlorobutane	601 ± 3	1.004	–36	0.074
2-Methyl-2-chloropropane	540 ± 4	1.031	–93	0.101
1,3-Dichloropropane	760 ± 12	0.789		
1,2-Dichloropropane	688 ± 11	0.876	–72	0.087
1,1-Dichloropropane	668[a]	0.901	–92	0.112
2,2-Dichloropropane	605 ± 7	0.963	–155	0.179

[a] No published experimental data; the RI presented are estimated along additive schemes.

[b] The differences ΔRI and Δ*U* are given referred to the isomers with maximal retention parameters.

arenes chlorination. However as additional independent test it is useful to apply also an additive scheme including increments of structural transformations $Cl \rightarrow CH_3$ at sp^3- and sp^2-hybridized carbon atoms (–128 ± 13 and –61 ± 15 index units, respectively) [10].

The latter procedure provides a possibility to compare RI of various chlorinated products with the data for isostructural alkyl-substituted arenes with one carbon atom more in the molecule (**criterion IV**). Here we use this criterion at the final stage of the data interpretation in order to check the validity of structural assignments; presumably further applications of this criterion will provide it with more importance.

In conclusion of enumeration of interpretation methods for RI that are used in combination one more additive scheme should be mentioned which does not require preliminary calculation of increments for any structural transformations of molecules. This most traditional element of the majority of additive schemes known in chemistry may be replaced by direct use of informational databases and necessary operations with structural formulas of organic compounds selected by the maximum structural similarity with the characterized object. Up till now this approach was used in calculation of RI for metabolites of polychlorobiphenyls, monohydroxypolychlorobiphenyls (849 congeners, the calculation in any other way virtually impossible) [14], and for nitroanilines in the reversed-phase high resolution liquid chromatography [16]. The specific features of this **criterion V** can be illustrated by an example of RI estimation for two isomers obtained by chlorination of isopropylbenzene.

$$C_6H_5CH_2CH_2Cl + C_6H_5CH(CH_3)_2 - C_6H_5CH_2CH_3 \rightarrow C_6H_5CH(CH_3)CH_2Cl$$
$$1090 \pm 1 + 914 \pm 6 - 854 \pm 9 = 1150 \pm 11$$
(experimental value 1152 ± 1)

$$C_6H_5CH(CH_3)_2 + (CH_3)_3C\_Cl - CH(CH_3)_3 \rightarrow C_6H_5C(CH_3)_2Cl$$
$$914 \pm 6 + 540 \pm 6 - 376 \pm 2 = 1078 \pm 9$$
(experimental value 1070 ± 1)

In the latter case this criterion is more important than the auxiliary condition **IV** that results in unsatisfactory agreement of RI for (1,1-dimethylethyl)-benzene with the published data (Table 2). Using

analogous reasoning it is possible to determine, e.g., the order of elution of isomeric dimethyl-bis-(chloromethyl)benzenes arising in chlorination of 1,2,4,5-tetramethylbenzenes. Another advantage of this criterion compared to the condition **IV** is the use for estimating RI of the data on simple compounds that are usually more accurately characterized than higher homologs.

The combination of all the mentioned modes of RI interpretation was used for establishing structures of chlorination products obtained from 20 alkyl-substituted benzenes listed in Table 2 (in the table was additionally included a representative of another group of compounds, acenaphthene, whose chlorinated derivatives also were not yet characterized). In all cases the variation of reaction conditions (increased excess of chlorine, repeated chlorination of the reaction mixtures) permits registering of various di- and trichloroderivatives; in order to reduce the length of the table this complete information was given only for six hydrocarbons among those presented in the table. However the concepts used in interpretation of the chromatographic parameters of polychlorinated derivatives are the same as the rules recommended and applied to monochlorinated compounds. Only in four cases (for alkylarenes containing alkyls with five or more carbon atoms) we did not find any products of alternative ionic chlorination in the aromatic ring. In six reaction mixtures (mostly with tert-chloroalkylarenes) was observed formation of dehydrochlorination products, 1-alkenylarenes. For each chlorination product in Table 2 is mentioned the procedure of chlorination (A and/or B) that yields this substance in amounts comparable with the other isomers (no less than 0.5–1% from the sum of peak areas of all chlorinated products), are listed the main parameters, and the data applied to isomer structure determination. In brackets are indicated the known now reference data on the RI of the respective products (only for 18 among 118 compounds). Here are also given in decreasing order the values of the dynamic molecular parameters *E* and *U* used in predicting the succession of isomers elution. In all cases but two the decreasing orders for both these values are in agreement. The exceptions are 1,2-dimethyl-4-(1,1-dimethylethyl)-benzene (at close values of *U* is more significant the difference in *E*) and 1,4-dimethyl-2-butylbenzene (here on the contrary is more significant the difference in *U*, and at equal *U* values was considered the decreasing order of *E*). And, finally, the last column of the table includes the results of application of $\Delta RI(\mathrm{Cl} \rightarrow \mathrm{CH_3})$ criterion both to (chloroalkyl) benzenes and to the products chlorinated into the aromatic ring. The auxiliary character of this parameter is due to the fact that the relative elution order of isomeric alkylchlorobenzenes and their structural analogs, alkylmethylbenzenes is usually dissimilar, and thus the average accuracy of this criterion should not exceed the standard deviations in the $\Delta RI(\mathrm{Cl} \rightarrow \mathrm{CH_3})$ values proper. Nonetheless, the mean deviations of the estimated RI of hydrocarbons from the known reference data amount only to 14 ± 10 and 8 ± 6 index units for chloroalkyl- and alkylchlorobenzenes respectively. To our regret, starting from the chlorination products of pentylbenzene isomers this criterion becomes less efficient due to lack of reference data for the majority of hexylbenzene isomers and for more complicated alkylarenes (no data in the last column of Table 2).

Thus just the combination of various methods of interpretation applied to retention indices in gas chromatography gave a possibility to establish structures of over hundred chlorinated aromatic hydrocarbons directly in the reaction mixtures avoiding the preparative isolation of the substances. Now these first obtained new data on RI may be entered into the chromatographic databases and thereafter used for identification along traditional methods by comparison of the measured and reference analytical parameters. Similar combinations of interpretation procedures for the chromatographic parameters may be extended to the other groups of isomeric organic compounds with *a priori* known chemical nature.

EXPERIMENTAL

Gas-chromatographic analysis of the product mixtures obtained by alkylarenes chlorination was carried out on chromatograph Biokhrom-1 equipped with a flame-ionization detector and quartz capillary column 25 m × 0.2 mm (4300 theoretical plates per 1 m), stationary phase OV-101, temperature programmed from 60 to 240°C at a rate 4 deg $\mathrm{min^{-1}}$ carrier gas nitrogen, pressure at input 0.8 atm, split ratio 1 : 30, samples 0.6–0.8 μl. The determination of linear-logarithmic retention indices was performed with the use of a mixture of reference n-alkanes $\mathrm{C_6}$–$\mathrm{C_{18}}$; the retention times were registered by an integrator TR 2213. The indices were calculated according to software published in the supplement to textbook [17].

The calculation of intramolecular vibrational and rotational energies by molecular dynamics methods were carried out by the use of HyperChem 3 software with the same parameters as in [3]: temperature of

Table 2. Results of structural interpretation of retention indices in gas chromatography for chlorination products obtained from alkylaromatic hydrocarbons C_7–C_{12}

Initial alkylarene (n[a])	RI[b]	RI of reaction products (synthesis method)	ΔIR[c]	Structure assigned[d]	Parameters for structure assignement[e]	Criterion ΔI ($Cl \leftrightarrow CH_3$)
Toluene (1)	760 ± 9	986 ± 7	226	**Benzyl chloride**	ΔIU > 200	858 (854)
Ethylbenzene (2)	854 ± 9	1028 ± 1 (B)	174	1-Chloro-4-ethylbenzene	[1031 ± 7]	967 (951)
		1044 ± 1 (A, B)	190	**(1-Chloroethyl)benzene**	[1043 ± 7], *U* 0.638	916 (914)
		1090 ± 1 (A)	236	**(2-Chloroethyl)benzene**	[1076 ± 14], (70.542, ΔIU > 200	962 (945)
o-Xylene (1)	885 ± 9	1046 ± 1 (B)	161	1,2-Dimethyl-3-chlorobenzene	[1060 ± 9]	985 (1011)
		1073 ± 1 (A, B)	188	1,2-Dimethyl-4-chlorobenzene	[1071 ± 10]	1012 (984)
		1098 ± 2 (A)	213	**1-Methyl-2-chloromethylbenzene**	[1088 ± 14], ΔIU > 200	970 (967)
				Polychloro derivatives		
		1248 ± 1 (B)		1-Methyl-4-chloro-2-chloromethylbenzene	[f]	1059 (1067)
		1296 ± 1 (A)	2×206	**1,2-Bis(chloromethyl)benzene**		1040 (1040)
		1434 ± 2 (B)		1-Chloro-3,4-bis(chloromethyl)benzene	[f]	1117 (1149)
m-Xylene (1)	865 ± 8	1054 ± 2 (A, B)	189	1,3-Dimethyl-4-chlorobenzene	[1045 ± 8]	993 (984)
		1098 ± 1 (A)	233	**1-Methyl-3-chloromethylbenzene**	ΔIU > 200	970 (950)
				Polychloro derivatives		
		1230 ± 1 (B)		1-Methyl-2-chloro-5-chloromethylbenzene	*E* 41.5	1041 (1074)
		1238 ± 1 (B)		1-Methyl-4-chloro-3-chloromethylbenzene	*E* 41.2	1049 (1064)
p-Xylene (1)	863 ± 8	1044 ± 2 (A, B)	181	1,4-Dimethyl-2-chlorobenzene	[1045 ± 17]	983 (984)
		1098 ± 2 (A)	235	**1-Methyl-4-chloromethylbenzene**	ΔIU > 200	970 (951)
				Polychloro derivatives		
		1213 ± 1 (B)		1-Methyl-2-chloro-4-chloromethylbenzene	[f]	1024 (1074)
		1437 ± 1 (B)		2-Chloro-1,4-bis(chloromethyl)benzene	1120 (1145)	
Propylbenzene (3)	945 ± 9	1111 ± 1 (B)	166	1-Propyl-4-chlorobenzene	[1132 ± 6]	1050 (1042)
		1133 ± 1 (A, B)	188	**(1-Chloropropyl)benzene**	*E* 47.3, *U* 0.831	1005 (1003)
		1138 ± 1 (A, B)	193	**(2-Chloropropyl)benzene**	*E* 46.7, *U* 0.789	1010 (997)
		1164 ± 1 (A, B)	219	**(3-Chloropropyl)benzene**	*E* 46.5, *U* 0.690, ΔIU > 200	1036 (1046)
Isopropylbenzene (2)	914 ± 6	965 ± 1 (A, B)	51	(1-Methylethenyl)benzene	[966 ± 6]	
		1070 ± 1 (A)	156	**(1-Methyl-1-chloroethyl)benzene**	*E* 50.4, *U* 0.893,[g]	942 (984)
		1080 ± 1 (B)	166	1-(1-Methylethyl)-4-chlorobenzene	[1101]	1019 (1013)
		1102 ± 1 (B)	188	1-(1-Methylethyl)-2-chlorobenzene	[1097 ± 20]	1041 (1024)
		1152 ± 1 (A)	238	**(1-Methyl-2-chloroethyl)benzene**	*E* 47.9, *U* 0.643, ΔIU > 200,[g]	1024 (1003)

Table 2. (Contd.)

Initial alkylarene (n[a])	RI[b]	RI of reaction products (synthesis method)	ΔIR[c]	Structure assigned[d]	Parameters for structure assignement[e]	Criterion ΔI ($Cl \leftrightarrow CH_3$)
1,2,4-Trimethyl-benzene (3)	984 ± 10	1177 ± 1 (A, B)	193	1,2,4-Trimethyl-5-chlorobenzene	[f]	1116 (1003)
		1182 ± 2 (A, B)	198	1,2,4-Trimethyl-3-chlorobenzene	[f]	1121 (1137)
		1200 ± 1 (A)	216	**1,2-Dimethyl-4-chloromethylbenzene**	*E* 49.0, ΔIU > 200	1072 (1074)
		1208 ± 1 (A)	224	**1,3-Dimethyl-4-chloromethylbenzene**	*E* 48.2, ΔIU > 200	1080 (1067)
		1228 ± 1 (A)	244	**1,4-Dimethyl-2-chloromethylbenzene**	*E* 47.8, ΔIU > 200	1100 (1064)
				Polychloro derivatives		
		1364 ± 1 (B)		Dimethylchloro(chloromethyl)benzene	Structure was not found	1175
		1368 ± 2 (A, B)		Dimethylchloro(chloromethyl)benzene	Structure was not found	1179
		1392 ± 2 (A, B)		**1-Methyl-2,5-bis(chloromethyl)benzene**	*E* 49.1	1136 (1145)
		1399 ± 1 (A)	2 × 204	**1-Methyl-2,4-bis(chloromethyl)benzene**	*E* 49.1	1152 (1149)
		1411 ± 1 (A)	2 × 208	**1-Methyl-3,4-bis(chloromethyl)benzene**	*E* 48.2	1155 (1149)
		1533 ± 1 (A)	2 × 214	Dichloro(chloromethyl)benzene	Structure was not found	1283
		1574 ± 1 (B)		Chlorobis(chloromethyl)benzene	Structure was not found	1257
		1599 ± 1 (A)	3 × 205	**1,2,4-Tris(chloromethyl)benzene**		1215 (1227)
1,3,5-Trimethyl-benzene (1)	963 ± 13	1152 ± 1 (A, B)	189	1,3,5-Trimethyl-2-chlorobenzene	1092 (1107)	
		1196 ± 1 (A)	233	**1,3-Dimethyl-5-chloromethylbenzene**	ΔIU > 200	1068 (1045)
				Polychloro derivatives		
		1344 ± 2 (A, B)		1,3-Dimethyl-2-chloro-5-chloromethylbenzene	*E* 49.5	1155 (1194)
		1348 ± 1 (A)		1,3-Dimethyl-4-chloro-5-(chloromethyl)benzene	*E* 43.3	1159 (1184)
		1402 ± 1 (A)	2 × 220	**1-Methyl-3,5-bis(chloromethyl)benzene**		1146 (1129)
		1525 ± 1 (B)		1,3-Dimhyl-2,3-dichloro-5-(chloromethyl)benzene	[f]	1275
		1566 ± 1 (A)		1-Methyl-2-chloro-3,5-bis(chloromethyl)benzene	[f]	1249
		1596 ± 2 (A)	3 × 211	**1,3,5-Tris(chloromethyl)benzene**		1212 (1203)
Butylbenzene (4)	1046 ± 5	1111 ± 1 (A, B)	65	(*Z*)-1-Butenylbenzene	[f]	1050 (1138)
		1213 ± 1 (B)	167	1-Butyl-4-chlorobenzene	*E* 53.7, *U* 0.996	1100 (1081)
		1228 ± 1 (A, B)	182	**(1-Chlorobutyl)benzene**	*E* 53.7, *U* 0.974	1104 (1105)
		1232 ± 2 (A, B)	186	**(2-Chlorobutyl)benzene**	*E* 53.4, *U* 0.930	1112 (1112)
		1240 ± 1 (A, B)	194	**(3-Chlorobutyl)benzene**	*E* 53.1, *U* 0.829	1128 (1143)
		1256 ± 2 (A)	210	**(4-Chlorobutyl)benzene**	*E* 53.1, *U* 0.829	1128 (1143)
p-Cymene (3)	1013 ± 5	1076 ± 1 (A, B)	63	1-Methyl-4-(1-methylethenyl)benzene	[1073 ± 8]	
		1189 ± 1 (B)	176	Mixture:	[1188] (I)l [1190] (II)	1128
				1-Methyl-4-(1-methylethyl)-3-chlorobenzene (I)	I (1124)	
				1-Methyl-4-(1-methylethyl)-2-chlorobenzene (II)	II (1128)	
		1199 ± 1 (A, B)	186	**1-Methyl-4-(1-methyl-1-chloroethyl)benzene**	*E* 55.7, *U* 1.156	1071 (1078)
		1252 ± 2 (A, B)	239	**1-(1-Methylethyl)-4-chloromethylbenzene**	*E* 54.3, *U* 1.078, ΔIU > 200	1124 (1107)
		1258 ± 2 (A, B)	245	**1-Methyl-4-(1-methyl-3-chloroethyl)benzene**	*E* 54.3, *U* 1.056, ΔIU > 200	1130 (1101)

Table 2. (Contd.)

Initial alkylarene (n[a])	RI[b]	RI of reaction products (synthesis method)	ΔIR[c]	Structure assigned[d]	Parameters for structure assignement[e]	Criterion ΔI ($Cl \leftrightarrow CH_3$)
1,2,4,5-Tetramethyl-benzene (1)	1103 ± 4	1267 ± 1 (A, B)	164	1,2,4,5-Tetramethyl-3-chlorobenzene	[1262 ± 5]	1206 (1259)
		1319 ± 1 (A, B)	216	**1,2,4-Trimethyl-5-chloromethylbenzene**	ΔIU > 200	1191 (1173)
				Polychloro derivatives		
		1497 ± 1 (B)		Trimethylchloro(chloromethyl)benzene	Structure was not found	
		1530 ± 1 (B)	2 × 214	**1,2-Dimethyl-4,5-bis(chloromethyl)benzene**	[g]	1274 (1264)
		1561 ± 1 (B)	2 × 229	Mixture:	[g]	1305 (-)
				1,3-Dimethyl-4,6-bis(chloromethyl)benzene		
				1,4-Dimethyl-2,5-bis(chloromethyl)benzene		
Pentylbenzene (5)	1143 ± 9	1322 ± 2 (A, B)	179	**(1-Chloropentyl)benzene**	*U* 1.145	1194 (1169)
		1328 ± 1 (A, B)	185	**(2-Chloropentyl)benzene**	*U* 1.133	1200 (1191)
		1334 ± 1 (A, B)	191	**(3-Chloropentyl)benzene**	*U* 1.108	1206 (-)
		1342 ± 1 (A, B)	199	**(4-Chloropentyl)benzene**	*U* 1.062	1214 (1187)
		1353 ± 1 (A, B)	210	**(5-Chloropentyl)benzene**	*U* 0.959, ΔIU > 200	1225 (1240)
2-Phenylpentane (5) (2 diastereomer pairs)	1081 ± 10	1184 ± 3 (A, B)	103	(*E*)-(1-Methyl-1-butenyl)benzene		
		1245 ± 1 (A)	164	1-(1-Methylbutyl)-4-chlorobenzene	[f]	1117 (-)
		1254 ± 1 (A, B)	173	**(1-Methyl-1-chlorobutyl)benzene**	*U* 1.254	1126 (-)
		1279 ± 2 (A, B)	198	**(1-Methyl-2-chlorobutyl)benzene**[h]	*U* 1.236	1151 (-)
		1286 ± 2 (A, B)	205	**(1-Methyl-3-chlorobutyl)benzene**[h]	*U* 1.200	1158 (-)
		1308 ± 4 (A, B)	227	**(1-Chloromethylbutyl)benzene**	*U* 1.152, ΔIU > 200	1180 (-)
		1318 ± 4 (A, B)	237	**(1-Methyl-4-chlorobutyl)benzene**	*U* 1.081, ΔIU > 200	1190 (-)
3-Phenylpentane (3) (1 diastereomer pair)	1076 ± 12	1155 ± 2 (A, B)	79	(*E*)-(1-Ethyl-1-propenyl)benzene		
		1171 ± 1 (A, B)	95	(*Z*)-(1-Ethyl-1-propenyl)benzene		
		1259 ± 1 (A, B)	183	**(1-Ethyl-1-chloropropyl)benzene**	*E* 64.6	1131 (-)
		1276 ± 2 (A, B)	200	**(1-Ethyl-2-chloropropyl)benzene**[h]	*E* 62.7	1148 (-)
		1282 ± 2 (A, B)	206	**(1-Ethyl-2-chloropropyl)benzene**[h]	*E* 62.7	1154 (-)
		1310 ± 2 (A, B)	234	**(1-Ethyl-3-chloropropyl)benzene**	*E* 59.9, ΔIU > 200	1182 (-)
3-Methylbutylbenzene (4) (1 diastereomer pair)	1112 ± 7	1279 ± 2 (A, B)	167	**(3-Methyl-1-chlorobutyl)benzene**	*U* 1.212	1151 (-)
		1303 ± 1 (A, B)	191	**(3-Methylbutyl)-4-chlorobenzene**	[f]	1242 (-)
		1314 ± 2 (A, B)	202	**(3-Methyl-2-chlorobutyl)benzene**	*U* 1.200	1186 (-)
		1326 ± 3 (A, B)	214	**(3-Methyl-3-chlorobutyl)benzene**	*U* 1.175	1198 (-)
		1342 ± 2 (A, B)	230	**(3-Methyl-4-chlorobutyl)benzene**	*U* 1.073, ΔIU > 200	1214 (-)

Table 2. (Contd.)

Initial alkylarene (n[a])	RI[b]	RI of reaction products (synthesis method)	ΔIR[c]	Structure assigned[d]	Parameters for structure assignement[e]	Criterion ΔI ($Cl \leftrightarrow CH_3$)
1-Methyl-4-(1,1-dimethylethyl)benzene (2)	1078 ± 4	1260 ± 1 (B)	182	1-Methyl-4-(1,1-dimethylethyl)-3-chlorobenzene		1199 (1168)
		1262 ± 1 (B)	184	1-Methyl-4-(1,1-dimethylethyl)-2-chlorobenzene		1201 (1191)
		1326 ± 2 (A, B)	248	**1-(1,1-Dimethylethyl)-4-chloromethylbenzene**	*E* 64.8, ΔIU > 200	1198 (1169)
		1353 ± 1 (A, B)	275	**1-Methyl-4-(1-methyl-1-chloromethylethyl)-benzene**	*E* 64.3, ΔIU > 200	1225 (1184)
3-Methyl-2-phenylbutane (4) (1 diastereomer pair)	1068 ± 2	1262 ± 2 (A, B)	194	**(1,2-Dimethyl-1-chloropropyl)benzene**	*E* 66.5	1134 (-)
		1279 ± 2 (A, B)	211	**(1,2-Dimethyl-2-chloropropyl)benzene**	*E* 64.8	1151 (-)
		1296 ± 1 (B)	231	**(1,2-Dimethyl-3-chloropropyl)benzene**[h]	*E* 63.2, ΔIU > 200	1168 (-)
		1311 ± 2 (B)	243	**(1,2-Dimethyl-3-chloropropyl)benzene**[h]	*E* 63.2, ΔIU > 200	1183 (-)
1,2-Dimethyl-4-(1,1-dimethylethyl)benzene (3)	1196 ± 3	1388 ± 1 (A, B)	192	**(2-Methyl-1-chloromethylpropyl)benzene**	*E* 62.1, ΔIU > 200	1188 (-)
		1316 ± 2 (A, B)	248	**1,2-Dimethyl-4-(1,1-dimethylethyl)chloro benzene**	Structure was not found	1327
		1392 ± 1 (A, B)	196	**1,2-Dimethyl-4-(1,1-dimethylethyl)chloro-benzene**	Structure was not found	1331
		1400 ± 1 (A, B)	204	**1,2-Dimethyl-4-(1,1-dimethylethyl)chloro benzene**	Structure was not found	1339
		1410 ± 1 (B)	214	**1,2-Dimethyl-4-(1,1-dimethyl-2-chloroethyl)-benzene**	*U* 1.569, *E* 75.1[i]	1282 (-)
		1420 ± 2 (A, B)	224	**1-Methyl-2-chlorometyl-4-(1,1-dimethylethyl) benzene**	*U* 1.577, *E* 73.2[i]	1292 (-)
		1442 ± 2 (A, B)	246	**1-Methyl-2-chlorometyl-5-(1,1-dimethylethyl)-benzene**	*U* 1.577, *E* 72.9[i]	1314 (-)
1,4-Dimethyl-2-butylbenzene (6)	1246 ± 2	1420 ± 1 (A, B)	174	**1,4-Dimethyl-2-(1-chlorobutyl)benzene**	*U* 1.510, *E* 71.4	1292 (-)
		1426 ± 1 (A, B)	180	**1,4-Dimethyl-2-(2-chlorobutyl)benzene**	*U* 1.483, *E* 68.6	1298 (-)
		1446 ± 2 (A, B)	200	**1,4-Dimethyl-2-(3-chlorobutyl)benzene**	*U* 1.434, *E* 68.5	1318 (-)
		1452 ± 1 (A)	206	**1-Methyl-2-butyl-4-chloromethylbenzene**	*U* 1.420, *E* 67.9[i], ΔIU > 200	1324 (-)
		1462 ± 1 (A, B)	216	**1-Methyl-3-butyl-4-chloromethylbenzene**	*U* 1.420, *E* 67.0[i], ΔIU > 200	1334 (-)
		1490 ± 2 (A, B)	244	**1,4-Dimethyl-2-(4-chlorobutyl)benzene**	*U* 1.331, *E* 68.3[i], ΔIU > 200	1362 (-)

Table 2. (Contd.)

Initial alkylarene (n[a])	RI[b]	RI of reaction products (synthesis method)	ΔIR	Structure assigned[d]	Parameters for structure assignement[e]	Criterion ΔI ($Cl \leftrightarrow CH_3$)
1,3,5-Trimethyl-2-(1-methylethyl)benzene (4)	1240 ± 3	1311 ± 1 (A, B)		1,3,5-Trimethyl-2-(1-methylethenyl)benzene		
		1389 ± 3 (A, B)	159	**1,3,5-Trimethyl-2-(1-methyl-1-chloroethyl)-benzene**	*U* 1.676	1267 (-)
		1447 ± 2 (A, B)	207	**1,3-Dimethyl-2-(1-methylethyl)-5-chloromethyl-benzene**	*U* 1.599	1319 (-)
		1470 ± 1 (A)	230	**1,3,5-Trimethyl-2-(1-methyl-2-chloroethyl)-benzene**	*U* 1.572	1342 (-)
Acenaphthene (1)	1461 ± 15	1639 ± 1 (B)	178	5-Chloroacenaphthene	*E* 63.7	
		1647 ± 1 (B)	186	4-Chloroacenaphthene	*E* 63.2	
		1668 ± 1 (B)	207	3-Chloroacenaphthene	*E* 63.1	
		1706 ± 1 (B)	245	**1-Chloroacenaphthene**		1578 (-)

[a] Number of isomers due to substitution of nonequivalent hydrogen atoms in the molecule by a single chlorine atom.

[b] Averaged published data.

[c] Differences between retention indices of chlorinated products and the initial compounds here and hereinafter are given only for monochlorinated alkylarenes derivatives and in some cases also for di- and trichlorinated substances.

[d] The names of the products of radical chlorination into the alkyl substituents are set off by bold type.

[e] In brackets are given experimental or calculated reference data on retention indices.

[f] The indicated isomer is the more probable from two (more seldom from more)possible structural isomers.

[g] The estimations by additive scheme were used.

[h] Compounds exist as a pair of diastereomers.

[i] The estimations of elution order by *E* and *U* values are contradictory (the value used in determination of the chromatographic elution order is underlined).

simulation 300 K, averaging step 0.0003 ps, relaxation time 0.1 ps, overall simulation time (no more than 20 ps) was selected as required the attainment of the desired precision in estimation of *E* parameters (no more than 1 rel%, commonly less than 1 kJ mol^{-1}. The molecular geometry was preliminary optimized by MM+ method. To accelerate the attainment of the desired precision in *E* estimation the initial period of simulation (about 1 ps) equivalent to heating the molecule to the given temperature 300 K was excluded, and the calculations were restarted with command RESTART. The calculation of *U* parameters was performed with a simple routine (QBasic).

The initial alkylbenzenes were characterized by comparison f their two independent constants, refraction index n_D^{20} and retention index on the standard nonpolar polydimethylsiloxanes (Table 2) with data from reference books. At homophase chlorination of alkylarenes in water-free medium (procedure A) to 20–40 μl of the hydrocarbon (depending on its molecular weight) in a flask or ampule of 2 ml capacity was added 1 ml of 0.4 M chlorine solution in CCl_4, the mixture was maintained for 3–5 min in the light on incandescent lamp (100 W) placed at 10 cm from the reactor, then if needed the excess unreacted chlorine was removed by adding 0.5 ml of 10% sodium sulfite solution, the solution was evaporated to the volume of the organic layer approximately of 100 μl, and thereto was added 20 μl of the reference mixture of n-alkanes.

The heterophase chlorination (procedure B) in the presence of water was used as comparative method resulting in greater amounts of products originating from ionic reactions of hydrogen replacement in the benzene ring. This method was formerly recommended for microanalytical chlorination of phenols and hydroxybiphenyls [14]. The procedure is based on relatively high (more than unity) distribution factors of molecular chlorine between organic and water phases. Into a two-phase system consisting of 2 ml of concn. HCl and 20–40 μl of hydrocarbon in a flask of 7 ml capacity within 5 min was added 100 mg of $KMnO_4$ by portions of 10–20 mg; the flask was under the light similar to that used in the procedure A; the content of the flask was shaken from time to time. After 5 min from completion of $KMnO_4$ addition the reaction was stopped with 2 ml of 10% sodium sulfite solution, then was added 0.5 ml of n-heptane, and 20 μl of the reference n-alkanes mixture.

In both chlorination procedures the unreacted chlorine can be removed by bringing the samples to boiling of CCl_4 (A) or water (B); however this treatment results in increased content of dehydrochlorination products formed from *sec*- and *tert*-(chloroalkyl)arenes. The degree of alkylarenes conversion in both procedures did not exceed 10% as estimated from the areas of the peaks on chromatograms.

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