PREPARATION AND CAPILLARY GAS CHROMATOGRAPHY OF POLYMETHYL- AND ETHYLMETHYLBIPHENYLS AND POLYMETHYLDIPHENYLMETHANES

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Trimethyl-, tetramethyl-, and ethylmethylbiphenyls with the alkyl groups at one aromatic ring have been prepared by the Gomberg reaction and identified by capillary gas chromatography. The products are either chemical individua or mixtures of up to three isomers depending on choice of the aromatic hydrocarbon. The ethylmethylbiphenyls have been prepared as mixed standards only. Most aromatic hydrocarbons used in the Gomberg reaction have been prepared by combination of rectification and sulphonation procedures. The HMO method has been used for calculation of the values of the radical superdelocalizabilities at individual centres of the 1,2,4- and 1,2,3-trimethylbenzene molecules which have been compared with product composition of the Gomberg reactions of these hydrocarbons. Reactivities of the aromatic substrates used in the Gomberg reaction have been compared by the competition technique. Capillary gas chromatography using three columns wetted with non-polar, medium, and polar stationary phases has been used to determine the Kovats indexes of the hydrocarbons prepared and parameters of the linear dependences $I_{\text{Apiez.L}} = k \,.\, I_{\text{stat.phase(2)}} + q$ (with the corresponding correlation coefficients). From the elution data of the isomeric methyl- and ethylbiphenyls the increments have been derived for methyl and ethyl groups, and possibility of prediction and assessment of the Kováts indexes of polyalkylbiphenyls and dimethyldiphenylmethanes is discussed.

Alkyl homologues of biphenyl are present in a number of products of thermal treatment of crude oil and coal, being concentrated into the fractions boiling within the range 255 to 350°C. Due to their high thermal stability, the parent biphenyl and its alkyl homologues are used as components of heat-transfer media (as *e.g.* Dowtherm, Delotherm AD, which is a mixture of isopropyl- and diisopropylbiphenyls, and Gilotherm TH, which is a mixture of non-identified alkylbiphenyls with longer alkyl chain). The preparation methods of the compounds of biphenyl type are summarized in ref.[1]. This report deals with preparation and identification of trimethyl- and ethylmethylbiphenyls with the alkyl groups in both aromatic rings, and another communication[2] brings their detailed identification by means of the Kováts indexes. The authors prepared[2] and identified by capillary gas chromatography[3] methyl-, dimethyl, and ethylbiphenyls. So far, however, no reports have dealt with identifica-

tion of trimethyl-, tetramethyl-, and ethylmethylbiphenyls with the alkyl groups at one aromatic ring and with reactivity of polymethyl- and ethylmethylbenzenes in the classic Gomberg reaction.

The aim of the present work is preparation of trimethyl-, tetramethyl-, and ethylmethylbiphenyls and dimethyldiphenylmethanes with the alkyl groups at one aromatic ring, identification of these compounds by capillary gas chromatography, comparison of relative composition of the biphenyls produced with the values of radical superdelocalizabilities calculated by the HMO method, and determination of the relative rate constants of polymethyl- and ethylmethylbenzenes in the Gomberg reaction.

EXPERIMENTAL

Preparation of the Starting Aromatic Hydrocarbons

The so called Solvent Naphtha I (Urxovy závody, Valašské Meziříčí) containing the following mass fractions of components: 11·4% isopropylbenzene, 14·2% 1,3,5-trimethylbenzene, 20·8% *m*- and *p*-ethyltoluene, 2·9% *o*-ethyltoluene, 11·5% 1,2,4-trimethyl- and 0·6% 1,2,3-trimethylbenzene, and 28·7% indane (the rest up to 100% is formed by cycloalkanes) was repeatedly rectified to give the following aromatic hydrocarbons: 1,2,4-trimethylbenzene (containing 5·0% (m/m) *cis*-perhydroindane), 1,3,5-trimethylbenzene (containing 14·0% (m/m) *o*-ethyltoluene and 8·0% (m/m) cycloalkanes), mixture of 69·8% (m/m) *m*- and 27·0% (m/m) *p*-ethyltoluene (with 3·2% (m/m) cycloalkanes), and mixture of 53·3% *p*- and 42·7% (m/m) *m*-ethyltoluene (with 3·0% (m/m) cycloalkalnes). The Solvent Naphtha I was rectified by means of a glass column of 150 cm length and 3 cm inner diameter packed with constantan helices and electrically heated. The reflux ratio at the column head (efficiency of 70 theor.) plates was adjusted at the value 1 : 80 and controlled electromagnetically.

The obtained fractions were refined by sulphonation: 3 mol 1,2,4- or 1,3,5-trimethylbenzene was heated in a 1 l three-necked sulphonation flask under reflux condenser on oil bath at 100 to 120°C. After reaching 90°C with intensive stirring, 7 mol 93% sulphuric acid was added from a dropping funnel during 1 h. The reaction mixture was heated to 110—120°C with intensive stirring and then transferred into a separating funnel, the non-reacted upper layer was separated (in the case of 1,3,5-trimethylbenzene it was repeatedly sulphonated to give *o*-ethyltoluene), the sulphonic acid was transferred into a 2 l flask and treated with 230 ml water. The mixture was submitted to desulphonation by introducing waste steam on a bath heated at 140—150°C. The distilled off fractions were separated in a separating funnel, and the upper organic layer was dried with anhydrous sodium sulphate. Similar procedure was used for the treatment of 4 mol ethyltoluene fraction containing 69·8% (m/m) *m*-ethyltoluene (desulphonation of the obtained sulphonic acid gave *m*-ethyltoluene of 95·1% purity) and for treatment of 4·75 mol mixture containing 53·3% (m/m) *p*-ethyltoluene (from the non-reacted organic layer we obtained *p*-ethyltoluene of 85% purity). *o*-Ethyltoluene of 96·7% purity was obtained by repeated selective sulphonation of 0·5 mol *o*-ethyltoluene from the sulphonation rafination of 1,3,5-trimethylbenzene with 0·5 mol sulphuric acid. Composition of the fractions obtained by the rectification or the sulphonation rafinations was determined by gas chromatography using the columns 1 (analysis of the Solvent Naphtha I), 2 (analysis of *m*- and *p*-ethyltoluene), and 3 (analysis of 1,3,5- and 1,2,4-trimethylbenzenes). Parameters of the columns used are given in Table I.

p-Ethyltoluene of 98% purity (for the kinetic experiments) was prepared by acetylation of tolu-

ene with acetyl chloride catalyzed with anhydrous aluminium chloride[4] and subsequent reduction of the acetyl derivative with zinc amalgam in hydrochloric acid.

The other aromatic hydrocarbons were commercial samples: 1,2,3-trimethylbenzene (Pfalz Bauer, U.S.A.), 1,2,4,5- and 1,2,3,5-, and 1,2,3,4-tetramethylbenzenes (Aldrich Europe, Belgium).

Preparation of Polyalkylbiphenyls and Diarylmethanes

The trimethyl- and ethylmethylbiphenyls were prepared from the above mentioned aromatic hydrocarbons and aniline by the Gomberg reaction and purified according to ref.[1]. The same method was used for the preparation of tetramethylbiphenyls except for purification: as the products are less volatile in steam distillation, the residue after removal of the non-reacted aromatic hydrocarbon was rid of the accompanying tarry substances by addition of 20 g silica gel and filtration. The filtrate was purified by column chromatography (silica gel)[1]. With respect to the state of 1,2,4,5-tetramethylbenzene, the Gomberg reaction was carried out after its dissolution in carbon disulphide at 0 to −3°C. To complete the identification of isomeric ethylmethylbiphenyls, we prepared 2-ethyl-6-methylbiphenyl by the same reaction from 2-ethyl-6-methylaniline and benzene. 4- and 5-phenylindanes and 5- and 6-phenyltetrahydronaphthalenes were prepared from the corresponding isomeric aminoindanes and aminotetrahydronaphthalenes[5]. For elucidation of identification of the Gomberg reaction products from *m*-ethyltoluene, we carried out acetylation of 2-methylbiphenyl (its preparation see ref.[1]) with acetyl chloride with $AlCl_3$ catalysis: 4·7 mmol 2-methylbiphenyl was acetylated with 5 mmol acetyl chloride (Lachema, ČSSR)

TABLE I

The chromatographic columns used for analysis of the aromatic hydrocarbons

Column No	Length m	Inner diameter mm	Stationary phase	Number of theoret. plates	Capacity ratio
1	2	3	polyethyleneglycol adipate[a] (Appl. Sciences, U.S.A.)	—	—
2[b]	45	0·25	squalane (BDH, Great Britain)	70·500	3·4
3[b]	45	0·25	*m*-bis(phenoxyphenoxy)benzene (Perkin–Elmer, U.S.A.)	60·500	9·9
4[c]	58	0·25	Apiezon L (Carlo Erba, Italy)	137·000	3·6
5[c]	45	0·26	*m*-bis(phenoxyphenoxy)benzene	95·000	8·9
6[c]	38	0·26	Carbowax 20M (Appl. Science, U.S.A.)	64·300	2·8

[a] The content of stationary phase on Chromosorb P was 7% (m/m). [b] Stainless steel capillary columns. [c] Columns of borosilicate glass Simax (Slovak Production of Technical Glass, Bratislava), the inner surface was roughened by etching with methyl 1,1,2-trifluorochloroethyl ether vapours at 350°C (ref.[8]) and deactivated (in the case of column 4) by silanization with a 1 : 2 (v/v) mixture of hexamethyldisilazane and trimethylchlorosilane (both made by Fluka, Switzerland) at 240°C. The capillary columns Nos 2—4 were wetted by dynamic method, the columns 5 and 6 by the mercury plug method[9].

in 5 ml carbon disulphide (Merck, BRD) in the presence of 0·7 g anhydrous aluminium chloride (Lachema, ČSSR). The mixture was refluxed 4 h, poured in 15 ml 20% hydrochloric acid, the organic layer was separated, dried with anhydrous sodium sulphate, and rid of carbon disulphide by distillation. The distillation residue was submitted to reduction with zinc amalgam in a mixture of 15 ml ethanol and 20 ml 35% hydrochloric acid (8 h refluxing). The reaction mixture was diluted with 50 ml water and extracted with 2 × 10 ml benzene (the non-dissolved zinc amalgam was extracted similarly). The benzene extract was concentrated to the minimum volume and analyzed by capillary gas chromatography under the conditions given below. Some diarylmethanes (formed as side products in the Gomberg reaction) were prepared by benzylation of 0·025 mol respective aromatic hydrocarbon with 0·025 mol benzyl chloride catalyzed with 1 g tin tetrachloride (BDH, Great Britain).

Kinetic Measurements

Reactivity of the aromatic hydrocarbons used in the Gomberg reaction was studied by means of the competition technique related to benzene using 4-methylbenzenediazonium chloride as the diazo component[1].

Gas–Liquid Chromatography

The packed column 1 (Table I) was placed in a Fractovap Mod GV chromatograph (Carlo Erba, Italy) equipped with a flame ionisation detector, and the samples were analyzed at t_c = = 110°C at the argon flow rate 28 ml min^{-1}. The polyalkylbiphenyls and diarylmethanes were analyzed on the glass capillary columns (Table I) placed in a Fractovap 2400T chromatograph (Carlo Erba, Italy) equipped with a flame ionisation detector and inlet splitter. The other conditions of the chromatographical analyses: t_c = 170°C, the argon flow rate was 1·0, 0·6, and 1·5 ml min^{-1} in the columns 4, 5, and 6, respectively, the ratio at the inlet splitter was 1 : 100, sample injection 0·05 μl. The dead volume of the used capillary columns under the conditions used was dedetermined by methane sample injection. A mixture of C_{14}—C_{26} n-alkanes was analyzed on all the columns under the same conditions.

The Kováts indexes were calculated from results of three measurements. The increments of methyl and ethyl groups at various positions of the biphenyl molecule and those of methyl group at various positions of diphenylmethane were determined from the Kováts indexes of the corresponding alkyl homologues of biphenyl and diphenylmethane (prepared according to ref.[5]) obtained on the column No 4. With the use of these increments the theoretical Kováts indexes were calculated for ethylmethyl-, trimethyl-, and tetramethylbiphenyls and di- and trimethyldiphenylmethans. The measurement results of the elution indexes on various stationary phases were submitted to statistical treatment.

Quantum-Chemical Calculations

The calculations of radical superdelocalizabilities of 1,2,3- and 1,2,4-trimethylbenzene were carried out by the HMO method.

RESULTS AND DISCUSSION

The trimethyl-, tetramethyl-, and ethylmethylbiphenyls carrying alkyl groups at one aromatic ring were prepared in the yields given in ref.[1]. The identification of the polyalkylbiphenyls was facilitated by the fact that only one isomer was formed

in some cases (*e.g.* 2,4,6-trimethylbiphenyl and all the isomeric tetramethylbiphenyls) and, in other cases, mixtures of two isomers whose elution order could be predicted on the basis of previous experimental findings[1-3]. The ethylmethylbiphenyls were identified in similar way making use of lower reactivity at the positions adjacent to ethyl group in *o*-, *m*-, and *p*-ethyltoluene. Identification of 4-ethyl-2-methylbiphenyl was carried out by its preparation (as a mixed standard) *via* acetylation of 2-methylbiphenyl and subsequent reduction. The product obtained also contained 4-ethyl-2'-methylbiphenyl (which was identified earlier[6]). 2-Ethyl-6-methylbiphenyl was identified in its mixture with 4-ethyl-2-methyl- and 3-ethyl-5-methylbiphenyls by independent synthesis from 2-ethyl-6-methylaniline.

In accordance with the published results[1] it can be stated that tin tetrachloride is a suitable catalyst of the Friedel-Crafts benzylation reactions using some of the isomeric trimethyl- or ethylmethylbenzenes as the aromatic substrates, because the obtained products contain (according to the capillary GLC) no transalkylation products. The identification of the mentioned diarylmethanes was carried out on the basis of chromatographical elution data and different reactivities at individual positions of unsymmetric aromatic hydrocarbons during electrophilic aromatic substitution.

The capillary GLC with the columns wetted with stationary phases of various polarities represents a suitable method for identification of the prepared polyalkylbiphenyls and diarylmethanes. With respect to close boiling points of the components to be separated, the inlet splitter was used for injection without causing any distortion of relative proportions of the individual isomers. Tables II and III give the elution data of the hydrocarbons prepared (the accuracy is ± 3 elution units for all the columns used). From the results of Table II and the experimentally found[6] Kováts indexes for Apiezon L as the stationary phase it follows that the elution indexes of isomeric trimethyl- and ethylmethylbiphenyls having the alkyl groups at two aromatic rings are comparable with those carrying the alkyl groups at one aromatic ring. Obviously, the elution behaviour on non-polar stationary phases and, hence, boiling point of these hydrocarbons are not substantially affected by the fact that the molecule contains all its alkyl groups in one aromatic ring or in the both rings. Substantially larger differences in the elution behaviour of the said type of biphenyls can be observed with the capillary column wetted with a stationary phase of medium polarity. Introduction of a methyl group into an aromatic ring carrying already two other methyl groups results in a more marked change of polarity of the molecule than the introduction into the non-substituted ring. This fact could possibly be utilized also for basic differentiation between the two types of trimethylbiphenyls. As in ref.[6] it can be stated that the fastest elution takes place with trimethyl- and ethylmethylbiphenyls having the alkyl groups at 2 and 6 positions, whereas those with the alkyl groups at 3 and 4 positions are retained more. The presence of 2- and 6-methyl groups, *e.g.*, causes the elution shift of 2,3,5,6- and 2,3,4,6-tetramethyl-

biphenyls before 3,4,5-trimethylbiphenyl and two other isomeric ethylmethylbiphenyls. Similarly, 4-phenylindane is retained (in all the three capillary columns) more than 3-ethyl-2-methyl- and 2-ethyl-3-methybiphenyls, the same being true, for comparison, of 5-phenylindane with 4-ethyl-3-methyl- and 3-ethyl-4-methylbiphenyls. In the both cases this fact can be ascribed to the effect of five-membered ring in these aromatic hydrocarbons which probably increases their boiling point and overall polarity. The capillary GLC with the said stationary phases, however, enabled no separation of 2,4,6-trimethylbiphenyl from 3-ethyl-2-methylbiphenyl, and 5-ethyl--2-methyl- from 2-ethyl-4-methylbiphenyl. As the pairs of these aromatic hydrocarbons were prepared by independent syntheses from different starting compounds, their identification cannot be considered wrong. 2-Ethyl-3-methylbiphenyl and 2,4,5-trimethylbiphenyl are eluted simultaneously from the polar stationary phase, but they were perfectly separated on the non-polar stationary phase, in contrast to the pair 2,3,4-trimethyl- and 2,3,5,6-tetramethylbiphenyls which was successfully separated on the stationary phase of medium polarity.

From the elution data on isomeric methyl-, dimethyl-, and trimethyldiphenylmethanes it follows that, in contrast to the isomeric methylbiphenyls, 3-methyldiphenylmethane is eluted before 2-methyldiphenylmethane on both non-polar and polar stationary phases. An exception represents the stationary phase of medium polarity, where the two components are eluted simultaneously. This phenomenon, however, was not observed with isomeric ethyldiphenylmethanes which are eluted from all the three columns in the same order as the isomeric ethylbiphenyls. The elution order of isomeric dimethyldiphenylmethanes with methyl groups at one aromatic ring is identical with that of the corresponding dimethylbiphenyls on the stationary phases Apiezon L and m-bis(*m*-phenoxyphenoxy)benzene[6], and it can be presumed that the same will be true for the polar stationary phases, too.

The elution index increment due to the presence of methylene group (calculated from difference between the elution indexes of the corresponding dimethylbiphenyls and dimethyldiphenylmethanes) varies, on the non-polar stationary phase, from 170 elution units for 2,6-dimethyldiphenylmethane to the value of 8 elution units for 3,4-dimethyldiphenylmethane. A similar trend can be observed also on the stationary phase of medium polarity. In this case, too, the presence of 2- and 6-methyl groups causes the most significant shift of the elution indexes to lower values. All the obtained isomeric dimethyldiphenylmethanes are eluted after the corresponding dimethylbiphenyls, the elution difference, however, evidently decreases with increasing distance of the methyl groups from the methylene group. These facts could be used for mutual differentiation of the isomeric dimethylbiphenyls from the corresponding dimethyldiphenylmethanes. Similar elution behaviour is also observed with the prepared trimethyldiphenylmethanes. These elution data were used for calculation of the increments of methyl and ethyl groups at the individual positions of biphenyl and diphenylmethane. The following facts must be respected in the

TABLE II

The experimentally measured and theoretically calculated Kováts elution indexes of some polyalkylbiphenyls

Isomer	I_{APL} [a]		I_{BPB} [b]		I_{CWX} [c]		Calculation method of the index
	exp.	theor.	exp.	theor.	exp.	theor.	
				Trimethylbiphenyls			
2,4,6-	1 556	1 558	1 774	1 777	1 963	1 970	$I_{2,6-}$ [d] + ΔI_{4-} [e]
2,3,6-	1 574	1 568	1 803	1 800	1 996	2 000	$I_{2,6-}$ + ΔI_{3-}^{kor} [f]
2,3,5-	1 642	1 639	1 882	1 889	2091	2 096	$I_{2,3-}$ + ΔI_{3-}
2,4,5-	1 655	1 654	1 894	1 901	2 108	2 115	$I_{3,4-}$ + ΔI_{2-}
2,3,4-	1 673	1 677	1 932	1 933	2 154	2 157	$I_{2,3-}$ + ΔI_{4-}^{kor}
3,4,5-	1 797	1 778	2 057	2 050	2 314	2 308	$I_{3,4-}$ + ΔI_{3-}^{kor}
				Ethylmethylbiphenyls			
2,6-	1 510	1 502	1 732	1 716	1 916	1 907	$I_{2,6-}$ + ΔI_{2-CH_2}
3,2-	1 556	1 586	1 774	1 833	1 963	2 031	I_{2-Me} + ΔI_{3-Et}
2,5-	1 570	1 564	1 799	1 804	1 997	2 003	I_{2-Et} + ΔI_{3-Me}
5,2-	1 595	1 590	1 832	1 823	2 025	2 031	I_{2-Me} + ΔI_{3-Et}
2,4-	1 595	1 585	1 832	1 813	2 023	2 014	I_{2-Et} + ΔI_{4-Me}
4,2-	1 611	1 613	1 849	1 859	2 047	2 056	I_{2-Me} + ΔI_{4-Et}
2,3-	1 637	1 599	1 898	1 836	2 108	2 044	I_{2-Et} + ΔI_{3-Me}
3,5-	1 697	1 695	1 941	1 949	2 169	2 182	I_{3-Me} + ΔI_{3-Et}
3,4-	1 743	1 733	2 021	1 994	2 258	2 242	I_{3-Et} + ΔI_{4-Me}^{kor}
4,3-	1 745	1 742	2 024	2 007	2 262	2 249	I_{4-Et} + ΔI_{3-Me}^{kor}
				Tetramethylbiphenyls			
2,3,5,6-	1 672	1 662	1 898	1 896	2 115	2 092	$I_{2,3,6-}$ + ΔI_{3-Me}
2,3,4,6-	1 709	1 707	1 938	1 940	2 145	2 152	$I_{2,3,6-}$ + ΔI_{4-Me}^{kor}
2,3,4,5-	1 812	1 791	2 068	2 061	2 297	2 287	$I_{2,3,4-}$ + ΔI_{3-Me}^{kor}
				Phenylindanes [g]			
4-	1 737	—	2 013	—	2 248	—	—
5-	1 831	—	2 110	—	2 368	—	—
				Phenyltetrahydronaphthalenes [g]			
5-	1 818	—	2 096	—	2 321	—	—
6-	2 029	—	2 252	—	2 529	—	—

The Kováts elution indexes obtained with a column wetted with: [a] Apiezon L, [b] *m*-bis(*m*-phenoxyphenoxy)benzene, [c] Carbowax 20M. [d] The Kováts elution index $I_{x,y}$ of dimethylbiphenyl. [e] The increment of methyl group at *z*-position, where $z = 2-4$. [f] The corrected increment of methyl

TABLE III

The experimentally measured and theoretically calculated Kováts elution indexes of some polymethyldiphenylmethanes

Isomer	I_{APL}[a]		I_{BPB}[b]		I_{CWX}[c]		Calculation method of the index
	exp.	theor.	exp.	theor.	exp.	theor.	
				Dimethyldiphenylmethanes			
2,6-	1 631	1 649	1 879	1 904	2 098	2 126	I_{2-}[d] $+ \Delta I_{2-Me}$
2,5-	1 639	1 644	1 895	1 905	2 112	2 121	$I_{2-} + \Delta I_{3-Me}$
2,4-	1 662	1 662	1 908	1 916	2 132	2 135	$I_{2-} + \Delta I_{4-Me}$
2,3-	1 682	1 674	1 944	1 935	2 173	2 164	$I_{2-} + \Delta I^{kor}_{3-Me}$[f]
3,4-	1 687		1 946		2 173		
				Trimethyldiphenylmethanes			
2,4,6-	1 728	1 732	1 978	1 983	2 192	2 194	$I_{2,3-} + \Delta I_{4-Me}$
2,3,6-	1 748	1 744	2 006	2 001	2 227	2 222	$I_{2,6-} + \Delta I^{kor}_{3-Me}$
2,3,5-	1 758	1 752	2 021	2 009	2 244	2 236	$I_{2,5-} + \Delta I^{kor}_{3-Me}$
2,4,5-	1 764	1 770	2 023	2 021	2 247	2 250	$I_{2,5-} + \Delta I^{kor}_{4-Me}$
2,3,4-	1 800	1 813	2 074	2 078	2 306	2 311	$I_{2,3-} + \Delta I^{kor}_{4-Me}$
3,4,5-	1 815	1 800	2 084	2 068	2 320	2 297	$I_{3,4-} + \Delta I^{kor}_{3-Me}$

[a–f] For the footnotes see Table II.

calculation of the theoretical Kováts indexes of the biphenyl and diphenylmethane homologues: *1*) The calculated elution index of trimethylbiphenyl approaches most closely to the experimental value if the increment of methyl group at the given position is added to the experimental elution index of 2,3-, 3,4-, or 2,6-dimethylbiphenyl. *2*) Only in the calculation of elution index of 2,4,6-trimethylbiphenyl it is possible to add the increment of methyl group ΔI_{4-Me} calculated from 4-methylbiphenyl to that of 2,6-dimethylbiphenyl, since in this case the theoretical elution index is not affected by mutual polar action of the methyl groups present in *ortho* positions. *3*) In the other cases the corrected increments ΔI^{corr}_{x-Me} (where $x = 3$ or 4), calculated from the elution indexes of 2,3- and 3,4-dimethylbiphenyls and 2- and 3-methylbiphenyls, resp. (which respect the increment change of methyl group due

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group with respect to steric and polar effect of the neighbouring alkyl group. [g] The theoretical elution indexes of phenylindanes and phenyltetrahydronaphthalenes were not determined.

to the presence of another methyl group in *ortho* position), must be added to the elution indexes of the said dimethylbiphenyls. This increase of the increment is about 25% of its original value for both 3- and 4-methyl groups on the stationary phases Apiezon L and *m*-bis(phenoxyphenoxy)benzene, and about 31·5% on Carbowax 20M. *4*) The elution indexes of the ethylmethylbiphenyls in which the alkyl groups do not stand in mutual *ortho* position can be determined in similar way as that of 2,4,6-trimethylbiphenyl. The calculation must start from the experimental elution index of 2-alkylbiphenyl (methyl or ethyl) and the increment of the alkyl group at 3 or 4 position calculated from experimental indexes of the respective 3- or 4-alkylbiphenyls. In the case of 2-ethyl-6-methylbiphenyl it is possible (except for *m*-bis(phenoxyphenoxy)benzene) to predict the elution index by addition of ΔI_{2-CH_2} (given by lengthtening of the 2-alkyl chain by one methylene unit). This lenghtening results in polarity decrease of the molecule (Table IV), which makes itself felt by decrease in the increment value when going from non-polar to polar stationary phase. *5*) None of the above-mentioned procedures, however, can predict with sufficient accuracy (max. 10 elution units) the elution indexes of ethylmethylbiphenyls with the alkyl groups at 2,3- or 3,4-positions, which can be explained by probably selective influence of the two alkyl groups. *6*) In similar way (see the points 2 through 4) it is possible to predict with sufficient accuracy the elution indexes of dimethyl- and trimethyldiphenylmethanes having the alkyl groups at one aromatic ring. The elution index of 3,4-dimethyldiphenylmethane was not determined theoretically, since the experimental value was used for the calculation of the corrected increments of 3- and 4-methyl groups. *7*) The corrected elution increments of methyl groups on the stationary phases Apiezon L and *m*-bis(phenoxyphenoxy)benzene are, in the case of dimethyldiphenylmethanes, greater for 3- and 4-positions by about 30 elution units, which is comparable with the corresponding values for biphenyls. On the column wetted with Carbowax 20M the increase in the elution index is (as with the biphenyls) greater by about 12 elution units, which indicates polar character of the mutual influence of the two methyl groups. With respect to the finding given ad 2) through 4) it is possible to predict (with the accuracy of ± 10 elution units) the indexes of about 75% of the isomeric trimethyl-, tetramethyl- and ethylmethylbiphenyls and di- and trimethyldiphenylmethanes carrying the alkyl groups at one aromatic ring on the columns wetted with stationary phases of various polarity. The Kováts elution indexes of methyl-, ethyl-, and some dimethylbiphenyls and those of methyl- and ethyldiphenylmethanes are given in Table IV along with the increments. Parameters of the linear dependences $I_{\text{Apiez.L}} = k \,.\, I_{\text{stat.phase(2)}} + q$ are summarized in Table V along with the correlation coefficients.

As the Gomberg reaction takes place in heterogeneous system, the reactivity of the aromatic hydrocarbons had to be studied by competition arrangement of the kinetic experiments allowing determination of the relative rate constants and partial rate factors related to benzene or another atomatic hydrocarbon. Results of these experi-

TABLE IV

The Kováts elution indexes and increments of these indexes of some alkylbiphenyls and alkyldiphenylmethanes

Isomer	Stationary phase					
	Apiezon L		BPB		Carbowax 20M	
	I	ΔI	I	ΔI	I	ΔI
Biphenyl	1 439		1 683		1 930	
diphenylmethane	1 473		1 720		1 954	
Methylbiphenyls						
2-	1 425	−14	1 663	−20	1 871	−59
3-	1 527	88	1 780	97	2 022	92
4-	1 539	100	1 788	105	2 033	103
Ethylbiphenyls						
2-[a]	1 472	47	1 707	44	1 911	40
3-	1 600	161	1 852	170	2 090	160
4-	1 624	185	1 878	196	2 115	185
Dimethylbiphenyls						
2,6-	1 450	—	1 672	—	1 867	—
2,5-	1 519	—	1 756	—	1 960	—
2,4-	1 529	—	1 767	—	1 975	—
2,3-[b]	1 544	118	1 792	129	2 004	133
3,5-	1 620	—	1 873	—	2 113	—
3,4-[c]	1 660	133	1 921	141	2 174	152
Methyldiphenylmethanes						
2-	1 561	88	1 813	92	2 040	86
3-	1 556	83	1 813	92	2 035	82
4-	1 574	101	1 824	104	2 049	96
Ethyldiphenylmethanes						
2-	1 614	141	1 872	152	2 087	134
3-	1 617	144	1 880	160	2 088	135
4-	1 654	181	1 912	192	2 129	176

[a] $\Delta I = I_{2-\text{Etbiph}} - I_{2-\text{Mebiph}}$, [b] $\Delta I^{\text{corr}}_{3-\text{Me}} = I_{2,3-\text{diMebiph}} - I_{2-\text{Mebiph}}$, [c] $\Delta I^{\text{corr}}_{4-\text{Me}} = I_{3,4\text{diMebiph}} - I_{3-\text{Mebiph}}$.

ments are given in Table VI along with the radical superdelocalizabilities. From the Table it follows that out of three isomeric trimethylbenzenes the highest reactivity is exhibited by the symmetrical 1,3,5-trimethylbenzene, which is obviously due to the fact that each of the free positions in the aromatic ring is activated by methyl groups at the alternating positions. In the less reactive 1,2,4-trimethylbenzene the highest reactivity is found at the 3 position, *i.e.* again one activated by two methyl groups at the neighbouring positions. Also the least reactive 1,2,3-trimethylbenzene has the 4 position more reactive than 5, the former being activated by one methyl in adjacent position. Among the isomeric ethyltoluenes meta isomer is more reactive than *para*, which agrees with the results[1] for *m*- and *p*-xylene. *o*-Ethyltoluene was not evaluated because of its contamination with 1,3,5-trimethylbenzene. In the case of *m*- and *p*--ethyltoluene, obviously, an increased steric effect of ethyl group is operating, which results in the reactivity order of the positions 2 < 3 and 6 < 4 in *p*- and *m*-ethyltoluene, respectively. In *m*-ethyltoluene (as in *m*-xylene[1]) 2 position is more reactive for the above-given reasons, its reactivity being comparable with that of 3 position of 1,2,4-trimethylbenzene. The relatively low reactivity of 1,2,3,4- and 1,2,3,5-tetramethylbenzenes can obviously be explained by sterical reasons which are especially marked in the later compound. Indane and tetrahydronaphthalene show about the same reactivity (relatively higher than that of *o*-xylene) in the Gomberg reaction In contrast to *o*-xylene, in which 3 position is more reactive than 4, the reactivity order of the corresponding positions of indane and tetrahydronaphthalene is 5 < 4 and 6 < 5, respectively.

TABLE V

Parameters of the linear relation $I_{APL} = k \cdot I_{stat.phase(2)} + q$ and the corresponding correlation coefficients *r*

Aromatic hydrocarbons	Stationary phase 2					
	m-bis(*m* phenoxyphenoxy) benzene			Carbowax 20M		
	k	*q*	*r*	*k*	*q*	*r*
Trimethylbiphenyls	0·8597	26·68	0·9995	0·6840	210·48	0·9979
Ethylmethylbiphenyls	0·7948	139·41	0·9961	0·6628	249·06	0·9966
Tetramethylbiphenyls	0·8113	134·51	0·9996	0·7357	123·14	0·9952
Methyldiphenylmethanes	1·8547	801·73	0·9631	1·5379	575·67	0·9994
Dimethyldiphenylmethanes	0·7900	149·18	0·9900	0·7189	124·11	0·9885
Trimethyldiphenylmethanes	0·7987	146·62	0·9967	0·6713	254·29	0·9972
Ethyldiphenylmethanes	1·0382	328·90	0·9951	1·0109	495·93	0·9996

The values of partial rate factors agree qualitatively with those of the radical superdelocalizabilities calculated by the EHT method[7] for indane and tetrahydronaphthalene, and by the HMO method for the other hydrocarbons, which indicates that these quantum-chemical methods can serve for qualitative evaluation of reactivity of the individual positions in the given hydrocarbons during the Gomberg reaction. From the kinetic measurements it also follows that the said reaction was complicated by formation of compounds of diarylmethane type, however, the table shows no distinct connection between number and position of alkyl groups and the presence of diarylmethanes.

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TABLE VI

Relative rate constants, partial rate factors and radical superdelocalizabilities of aromatic hydrocarbons in the Gomberg reaction

Aromatic hydrocarbon	$k^a_{rel.tot.}$	$k^b_{rel.arom.}$	position	f^c	s^d
m-Ethyltoluene	4·419 ± 0·191	4·419 ± 0·191	2-:	13·367	0·8558
			6-:	6·335	0·8539
			4-:	4·595	0·8539
			5-:	2·215	0·8321
p-Ethyltoluene	4·238 ± 0·187	3·881 ± 0·189	2-:	7·232	0·8321
			5-:	—	0·8321
1,2,3-Trimethylbenzene	1·892 ± 0·085	1·640 ± 0·086	4-:	4·027	0·8532
			5-:	1·796	0·8419
1,2,4-Trimethylbenzene	3·997 ± 0·165	3·997 ± 0·165	3-:	13·389	0·8551
			5-:	6·178	0·8550
			6-:	4·417	0·8438
1,3,5-Trimethylbenzene	9·854 ± 0·264	8·014 ± 0·273	2-:	16·027	—
1,2,3,4-Tetramethylbenzene	3·633 ± 0·287	3·633 ± 0·287	5-:	10·900	—
1,2,3,5-Tetramethylbenzene	1·681 ± 0·151	1·681 ± 0·151	4-:	1·681	—
Indane[e]	1·795 ± 0·149	1·795 ± 0·149	4-:	1·694	0·3645[f]
			5-:	2·376	0·3776[f]
Tetrahydronaphthalene[e]	1·662 ± 0·143	1·662 ± 0·143	5-:	1·441	0·1581[f]
			6-:	2·640	0·2266[f]

[a] The total relative rate constant, [b] the relative rate constant of the substitution in the aromatic ring. The both constants are related to benzene. [c] The partial rate factors, [d] the radical superdelocalizabilites, [e] the relative rate constants related to *o*-xylene, [f] calculated by the EHT method[7].

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