

PREPARATION OF SOME TRIMETHYL- AND METHYLETHYLBIPHENYLS AND REACTIVITY OF AROMATIC HYDROCARBONS IN THE GOMBERG REACTION

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Trimethyl- and methylethylbiphenyls with the alkyl groups in the both phenyl rings have been prepared by the Gomberg reaction and identified by the capillary gas-liquid chromatography. Depending on choice of the aromatic hydrocarbon either individual isomers or their mixtures (three at the most) have been obtained which were contaminated with compounds of diarylmethane type in many cases. The methylethylbiphenyls have only been prepared as mixtures contaminated with diarylmethanes. These side products have been prepared by independent syntheses. A method has been developed for isolation and separation of mixtures of trimethyl- and methylethylbiphenyls from the reaction products containing tarry products. The method is suitable for preparation of small amounts of some analytical standards. The HMO method has been used for calculation of values of the radical superdelocalizabilities at individual centres in the molecules of *o*-, *m*- and *p*-xylene, toluene and ethylbenzene, and these values have been compared with composition of the Gomberg reaction products from these hydrocarbons. The competitive technique has been used for comparison of the reactivities of the mentioned aromatic substrates in the Gomberg reactions.

Distillation of tar or liquid fractions of gasoline pyrolysis gives, besides other products, fractions boiling within 250 to 300°C. Attention is given to identification of the aromatic hydrocarbons present in these fractions, because these compounds are of considerable technical importance. The mentioned fractions contain beside others dimethyl- and trimethylnaphthalenes, methyl- and dimethylbiphenyls. Biphenyl and its alkyl derivatives are characterized by high thermal stability.

Literature gives several preparation methods of biphenyl compounds. Besides the usual Gomberg reaction¹⁻³ these compounds can be prepared by a modified Gomberg reaction using arenediazonium salts stabilized with 1-naphthalenesulphonic or 1,5-naphthalenedisulphonic acids⁴ or diazoacetates obtained from diazonium salts by action of solid sodium acetate⁵. The mentioned ways of biphenyl preparation can only be applied to liquid aromatic hydrocarbons, whereas the solid ones can only be used in an inert solvent^{6,7}. Hwang Shu⁸ and Cadogan⁹ carried out the preparation and decomposition of diazonium salt in a single step by addition of *n*-butyl- or *n*-pentyl nitrate to solution of aromatic amine in a boiling hydrocarbon. Abramovitch and Saha¹⁰ prepared biphenyls by decomposition of diazonium tetrafluoroborates in pyridine. These salts can be decomposed into the same products by action of zinc¹¹ or by electrolysis in aprotic

solvents^{1,2}. These hydrocarbons can also be obtained by decomposition of diazonium trifluoroacetates^{1,3}. Whereas for classical arrangement of the Gomberg reaction it is presumed that transient aryl radicals are formed from arenediazonium hydroxide, there exists evidence that in anhydrous media the radicals are formed from the intermediate bisdazo anhydride^{14,15}. A possibility of existence of ionic particles during formation of biaryls by decomposition of arenediazonium fluoroborates was discussed, too¹⁶.

Detailed study of product composition of the Gomberg reaction giving all methyl- and dimethylbiphenyls was enabled¹⁷ by the recent developments in the field of capillary gas-liquid chromatography (GLC). The authors separated the product mixtures by efficient rectification and preparative GLC and obtained pure hydrocarbons. However, none of the hitherto communications deals with identification of trimethyl- and methylethylbiphenyls, with study of methyl or ethyl group effect on rate of the Gomberg reaction, and with comparison of composition of the reaction products with results of quantum-chemical calculations.

The aim of the present communication is to verify possibilities of preparation of polyalkylbiphenyls, *viz* trimethyl- and methylethylbiphenyls with the alkyl groups in the both phenyl rings, by the Gomberg reaction, to identify these compounds, to compare relative composition of mixtures of trimethyl- and methylethylbiphenyls with the values of radical superdelocalizabilities calculated by the HMO method, and by competitive technique to determine relative rate constants and partial rate factors of the aromatic substrates used in the Gomberg reaction. A further aim of the work was to develop a simple preparation method of the mentioned biphenyls as mixed analytical standards.

EXPERIMENTAL

Reagents

The aromatic amines (Lachema Brno, except for 2- and 4-ethylanilines and 3,4- and 3,5-dimethylanilines) used for the Gomberg reaction were analyzed by GLC using a Chrom 2 apparatus (3 m column, 3 mm inner diameter, packed with Chromaton N impregnated with 1.3% (m/m) Carbowax 1500, 0.7% (m/m) Carbowax 400 and 1% (m/m) potassium hydroxide, $t_c = 130^\circ\text{C}$, argon flow rate 30 ml. min^{-1}). The total content of impurities in 3,4-dimethylaniline (ICI, Great Britain), 3,5-dimethylaniline (Fluka, Switzerland), 2- and 4-ethylanilines was less than 1% (m/m), in the other amines being less than 2% (m/m). Purity of the starting aromatic hydrocarbons (Lachema, Brno) was checked by GLC using a Fractovap Model GV (Carlo Erba, Milano). The analysis conditions: 2 m column, 3 mm inner diameter, packed with Chromosorb W impregnated with 15% (m/m) polyethylene glycol adipate, $t_c = 90^\circ\text{C}$, $p_{Ar} = 98.06 \text{ kPa}$, flow rate 28 ml Ar per min . All the hydrocarbons contained less than 1% (m/m) of impurities. 2-, 3- and 4-Methylbenzyl chlorides (ICN Pharmaceuticals, USA) were used without purification. Silica gel (Lachema, Brno) grain size 40/100 mesh was purified by repeated (6 times) extraction with freshly distilled acetone. The other chemicals used were of *p.a.* purity grade.

The trimethyl- and methylethylbiphenyls were prepared according to ref.¹⁷ starting from 0.2 mol of the respective aromatic amine. After the reaction was finished, the organic layer was separated, dried with anhydrous calcium chloride, and the starting aromatic hydrocarbon was removed by distillation under normal pressure. The distillate was analyzed by GLC under the same conditions as those used for the starting aromatic hydrocarbons. The distillation residue

was steam-distilled, the distillate was extracted with benzene, the orange extract was separated, dried and benzene along with the rest of the original used aromatic hydrocarbon were removed therefrom by distillation. In one case (preparation of 2,5,2'-trimethylbiphenyl) we tried to separate the mentioned residue by distillation at 666.6 Pa. The product from steam distillation was analyzed by TLC using Silufol plates (elution with n-hexane-benzene 3 : 1 (v/v), detection in UV light), and coloured impurities were removed by column chromatography (silica gel activity 5%, elution with n-hexane-benzene 2 : 1 (v/v)). The biphenyls were present in the colourless fraction eluted from the column before the first coloured fraction. The purified products were rid of the solvents and analyzed by GLC using a Fractovap 2400T apparatus (Carlo Erba, Milano) (the details are given in Table I). The products composition was calculated from the peak areas, the solvent residues being neglected.

The same procedure was used for preparation of 2,3-dimethylbiphenyl from 2,3-dimethylaniline and benzene and for preparation of 2,6,2',4'-tetramethylbiphenyl (as a mixed standard) from 2,4-dimethylaniline and *m*-xylene.

The diarylmethanes were prepared by alkylation of the aromatic hydrocarbons with benzyl chloride or its methyl derivatives using SnCl_4 as catalyst¹⁸, whereas the catalyst AlCl_3 gave transalkylation products besides the main ones¹⁹. The alkylated products were poured into a mixture of ice and hydrochloric acid, the organic layer was separated, dried with calcium chloride, and distilled under the pressure of 666.6 Pa. The obtained diarylmethanes were analyzed by capillary GLC using the columns 1 to 3 under the conditions given in Table I. The mixed diarylethane standard (1-phenyl-1-(4-tolyl)ethane and 1-phenyl-1-(2-tolyl)ethane) was prepared from styrene, toluene and concentrated sulphuric acid according to ref.²⁰. The product was analyzed in the same way as the diarylmethanes.

Kinetic measurements: 0.125 mol *p*-toluidine (purified by crystallization from ethanol) was dissolved in warm 75 ml 5M-HCl, and the suspension of *p*-toluidine hydrochloride was diazotised by addition of 20 ml 6.25M- NaNO_2 at -5 to -3°C . The diazonium salt solution (15 ml) was added quickly drop by drop into a stirred emulsion of 5 ml 6M-NaOH in 0.1 mol benzene and 0.2 mol of further aromatic hydrocarbon (toluene, ethylbenzene, *o*-, *m*- or *p*-xylene) at -1 to $+1^\circ\text{C}$, and the reaction mixture was stirred at the same temperature for further 30 min. The organic layer was processed in the same way as that in the preparation of trimethylbiphenyls. Both the original product and that rid of coloured impurities by column chromatography were analyzed by capillary GLC (the former once, the latter three times) on the column 2 under the conditions given in Table I.

TABLE I

Capillary Columns and the Conditions Used in Analyses of Products

The column temperature 170°C , the separation ratio 1 : 100, feed 0.05 μl .

| No | Stationary phase | <i>L</i> m | <i>d_c</i> mm | <i>F_m</i> (Ar) ml min ⁻¹ | <i>p_{Ar}</i> kPa |
|----|--|---------------|----------------------------|---|------------------------------|
| 1 | Apiezon L (C. Erba) | 50 | 0.28 | 0.35 | 98.06 |
| 2 | BPB ^a -6 rings (Perkin-Elmer) | 23 | 0.35 | 1.08 | 58.84 |
| 3 | Reoplex 400 (Applied Science) | 41 | 0.28 | 0.54 | 93.16 |

^a *m*-Bis(*m*-phenoxyphenoxy)benzene.

The quantum-chemical calculations of radical superdelocalizabilities of *o*-, *m*- and *p*-xylene, ethylbenzene and toluene were carried out by the HMO method.

RESULTS AND DISCUSSION

Tables II and III give yields and composition of the trimethyl- and methylethylbiphenyls prepared by the Gomberg reaction. Identification of the individual isomers was enabled by the fact that in the case of mixtures of trimethyl- and methylethylbiphenyls either all or at least two out of three possible isomers were present in further mixed products prepared by independent syntheses. Thus suitable combination of starting anilines and aromatic hydrocarbons made it possible to identify all the isomers. The yields of the purified products agree well with literature data¹⁷ for methyl- and dimethylbiphenyls. Purification of the products by steam distillation and subsequent column chromatography appears to be a better method for preparation of small samples of individual or mixed standards as compared with the procedure given in ref.¹⁷ which necessitates greater charges and relatively complicated rectification apparatus. The method is suitable for preparation of dimethylbiphenyls, too (2,3-dimethylbiphenyl of 98% (m/m) purity was prepared in this way with the yield of 16%). Mere vacuum distillation of the Gomberg reaction products gave products of intensive red colour. The method has a disadvantage in being unable to remove the impurities of diarylmethane or diarylethane type formed by side reactions¹⁷. The mentioned side reaction products (which were entrained in the main products) were prepared by independent syntheses either as individual isomers or mixed standards and were identified in the same way as trimethyl- and methylethylbiphenyls by comparison of elution data from three capillary columns²¹ and percentage of the individual components peaks (Table IV). It was necessary to use this identification method, because mere combination of capillary GLC and mass spectrometry cannot give sufficient information about position of alkyl groups in molecules of aromatic hydrocarbons. From the table it follows that the presence of an alkyl group at 2-position of aniline or in the same position with respect to the second methyl group in the molecule of aromatic hydrocarbon results in substantial increase of content of side impurities of diarylmethane or diarylethane types. This fact agrees with the experimental results given in ref.¹⁷ concerning preparation of methyl- and dimethylbiphenyls. The capillary GLC excluded the possibility of a rearrangement of *o*-tolyl radical into benzyl radical with subsequent reaction with aromatic hydrocarbon to give diarylmethane. Otherwise the combination A (Table II) would have to give the same diarylmethanes as the combinations J and K. The rearrangements can also be excluded on the basis of the fact that no 2-methyldiphenylmethane is formed during preparation of 2,3-dimethylbiphenyl. Toluene (3.2% (m/m)) was proved by GLC in the *o*-xylene distilled from the reaction mixtures. In this case the following reaction also takes place:

TABLE II
Composition of Products of the Gomborg Reaction

| Notation | Combination $\text{ArNH}_2\text{-Ar}^{\text{H}}$ | Content of TMBF ^a in products | | Content of DMDFM ^b in products | | Relative amounts of trimethylbiphenyls | | | Content of further side products % m/m | Yield ^c % m/m |
|----------------|--|--|-------|---|-------|--|-------|--------|--|--------------------------------|
| | | % m/m | % m/m | % m/m | % m/m | % m/m | % m/m | % m/m | | |
| A | <i>o</i> -toluidine- <i>o</i> -xylene | 37.4 | 39.8 | 2.2' | 56.1 | 2.3,2' | 43.9 | 3.4,2' | 6.0 2-methylbiphenyl | 12.1 |
| B _d | <i>m</i> -toluidine- <i>o</i> -xylene | 70.8 | 9.8 | 2.3' | 72.8 | 2.3,3' | 27.2 | 3.4,3' | 16.8 3-methylbiphenyl | 13.9 |
| C | <i>p</i> -toluidine- <i>o</i> -xylene | 82.1 | 12.7 | 2.4' | 72.0 | 2.3,4' | 28.0 | 3.4,4' | 5.2 unidentified | 12.9 |
| D | <i>o</i> -toluidine- <i>m</i> -xylene | 97.3 | 0.3 | 2.3' | 50.1 | 2.6,2' | 44.3 | 2.4,2' | 2.4 unidentified | 14.1 |
| E | <i>m</i> -toluidine- <i>m</i> -xylene | 97.5 | 0.4 | 3.3' | 58.8 | 2.6,3' | 34.2 | 2.4,3' | 2.1 unidentified | 14.2 |
| F | <i>p</i> -toluidine- <i>m</i> -xylene | 97.1 | 0.4 | 3.4' | 69.1 | 2.6,4' | 28.4 | 2.4,4' | 2.5 unidentified | 13.7 |
| G | <i>o</i> -toluidine- <i>p</i> -xylene | 97.9 | 0.4 | 2.4' | 100.0 | 2.5,2' | | | 1.7 unidentified | 14.0 |
| H | <i>m</i> -toluidine- <i>p</i> -xylene | 92.3 | 0.5 | 3.4' | 100.0 | 2.5,3' | | | 6.5 3,3'-DMBF ^d | 14.2 |
| | | | | | | | | | 0.7 unidentified | |
| I | <i>p</i> -toluidine- <i>p</i> -xylene | 96.8 | 1.4 | 4.4' | 100.0 | 2.5,4' | | | 1.8 unidentified | 12.9 |
| J | 2,3-dimethylaniline- -toluene | 53.6 | 21.3 | 2.3' | 53.0 | 2.3,2' | 30.7 | 2.3,3' | 18.7 3,4-DMDFM ^b | 13.5 |
| | | | | | | | | | 6.4 unidentified | |
| K | 3,4-dimethylaniline- -toluene | 95.9 | 1.8 | 3.4 | 60.6 | 3.4,2' | 26.0 | 3.4,3' | 2.3 unidentified | 14.3 |
| L | 2,4-dimethylaniline- -toluene | 63.1 | 7.3 | 2.4 | 60.0 | 2.4,2' | 27.5 | 2.4,3' | 4.6 2,6,4'-TMBF ^a | 13.3 |
| | | | | | | | | | 16.2 2,6,2',4'-tetra methylbiphenyl | |
| M | 3,5-dimethylaniline- -toluene | 70.0 | 15.8 | 3.5 | 74.2 | 3.5,2' | 17.9 | 3.5,3' | 8.8 unidentified | 14.4 |
| | | | | | | | | | 14.2 2,6,2',4'-tetra- methylbiphenyl | |

^a TMBF Trimethylbiphenyl, ^b DMDFM Dimethyldiphenylmethane, ^c the yield relative to ArNH_2 , ^d DMBF dimethylbiphenyl.

TABLE III
Composition of the Methylbiphenyls Obtained by Gomberg Reaction

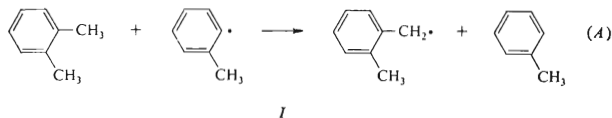
| Notation | Combination ArNH ₂ -ArH | | Content of MEBF ^a in products | | Content of MDFE ^b in products | | Relative amounts of methyl-ethylbiphenyls | | Content of further side products | | Yield ^c % m/m | | |
|----------|------------------------------------|-------|--|-------------------|--|-------|---|-------|----------------------------------|-------|--------------------------------|--------------------------|------|
| | % m/m | % m/m | % m/m | % m/m | % m/m | % m/m | % m/m | % m/m | % m/m | | | | |
| N | <i>o</i> -toluidine-ethylbenzene | 34.9 | 34.8 | 2- | 49.1 | 2,2'- | 23.9 | 2,3'- | 27.0 | 2,4'- | 14.2 | 2-ethyl-diphenyl-methyne | 12.8 |
| O | <i>m</i> -toluidine-ethylbenzene | 71.6 | 7.3 | 3- | 51.4 | 3,2'- | 30.7 | 3,3'- | 17.9 | 3,4'- | 16.1 | unidentified | 13.6 |
| P | <i>p</i> -toluidine-ethylbenzene | 91.2 | 7.8 | 4- | 58.9 | 4,2'- | 28.4 | 4,3'- | 12.7 | 4,4'- | 11.1 | unidentified | 13.8 |
| R | <i>o</i> -ethylamine-toluene | 43.2 | 36.7 | 2-Et ^d | 61.0 | 2,2'- | 22.7 | 3,2'- | 16.3 | 4,2'- | 20.1 | unidentified | 12.7 |
| S | <i>p</i> -ethylamine-toluene | 91.5 | 1.2 | 4-Et ^e | 69.2 | 2,4'- | 19.2 | 3,4'- | 11.6 | 4,4'- | 7.3 | unidentified | 14.1 |

^a MEBF methyl-ethylbiphenyls, ^b MDFE methyldiphenylethanes, ^c the yield of products related to ArNH₂ charge, ^d 2-ethyl-diphenylmethane, ^e 4-ethyl-diphenylmethane.

TABLE IV
Composition of Diarylmethanes and Diarylethanes

| Starting components | Composition of products, % m/m | Yield ^a , % m/m |
|--------------------------------------|--|----------------------------|
| Toluene-benzyl chloride ^b | 8.9 DFM ^c ; 37.6 MDFM ^{d,e} ; 53.5 DMDFM ^f | 53.0 |
| Toluene-benzyl chloride | 47.2 2-MDFM; 1.1 3-MDFM; 51.7 4-MDFM | 58.5 |
| <i>o</i> -Xylene-benzyl chloride | 46.1 2,3-DMDFM; 53.9 3,4-DMDFM | 60.0 |
| <i>m</i> -Xylene-benzyl chloride | 77.3 2,4-DMDFM; 21.7 2,6-DMDFM; 1.0 3,5-DMDFM | 59.2 |
| <i>p</i> -Xylene-benzyl chloride | 100.0 2,5-DMDFM | 56.0 |
| Toluene-2-methylbenzyl chloride | 46.9 2,2'-DMDFM; 0.9 2,3'-DMDFM; 52.2 2,4'-DMDFM | 55.7 |
| Toluene-3-methylbenzyl chloride | 47.8 2,3'-DMDFM; 0.9 3,3'-DMDFM; 51.3 3,4'-DMDFM | 57.0 |
| Toluene-4-methylbenzyl chloride | 48.2 2,4'-DMDFM; 1.0 3,4'-DMDFM; 50.8 4,4'-DMDFM | 59.0 |
| Toluene-styrene ^g | 4.1 1-phenyl-1-(2-tolyl)ethane; 31.5 1-phenyl-1-(4-tolyl)ethane; 59.6 1-methyl-3-phenylindane | 17.0 |

^a The yield related to ArCH₂Cl, ^b catalyzed with anhydrous AlCl₃, ^c DFM diphenylmethane, ^d content of all the isomers, ^e MDFM methyl-diphenylmethane, ^f DMDFM dimethyldiphenylmethane, ^g catalyzed with concentrated sulphuric acid. Conditions of the chromatographical analyses: the columns 1 and 2; for further conditions see Table I.



Then, presumably, the radical *I* reacts with toluene to give X,X'-dimethyldiphenylmethane, *i.e.* the same product as that which can be formed also by a direct attack of one methyl group in *o*-xylene by *o*-tolyl radical. The experimental results do not allow any explanation of the considerable amount of isomeric methylbiphenyls formed in the combinations A and B. The relatively high content of 3,3'-dimethylbiphenyl in the combination Z is obviously due to recombination of unstable *m*-tolyl radical. The presence of 2,6,4'-trimethylbiphenyl in the combination L can be ascribed to rearrangement and stabilization of 2,4-xylyl radical to 2,6-xylyl radical. The high content of 2,6,2',4'-tetramethylbiphenyl formed obviously from the *m*-xylene produced in the reaction (1) from 2,3-xylyl radical is due to higher reactivity of *m*-xylene. *m*-Xylene was proved chromatographically in the toluene distilled off from the reaction mixture (4.7% (m/m)). Similar reaction is encountered in the combination M, too.

Thus the Gomberg reaction as a method for preparation of trimethyl- and methylethylbiphenyls (individual isomers or mixed standards) is applicable in those cases only in which 2-alkylanilines are not used. Then the required compounds form at least 70% (m/m) of the product. In the opposite case preparation of the pure hydrocarbons would necessitate the procedure¹⁷ with greater charges. Increasing number of alkyl groups in the aromatic ring of both aniline and hydrocarbon increases the risk of side reactions leading to formation of diarylmethanes.

The side products of the Gomberg reaction were prepared by independent synthesis. Application of AlCl₃ as the catalyst for the reaction of benzyl chloride with toluene resulted in formation of products of transalkylation reactions (Table IV), and therefore, its use was avoided in the other cases. Identification of isomeric dimethyldiphenylmethanes was enabled by their presence among the products of both the Friedel-Crafts and the Gomberg reactions. The preparation of 1-phenyl-1-(4-tolyl)ethane was complicated by the presence of 1-phenyl-1-(2-tolyl)ethane and 1-methyl-3-phenylindane resulting from dimerization reaction of styrene.

The relative amounts of isomers in the mixtures of trimethylbiphenyls agree well with the values of radical superdelocalizabilities given in Table V. Hence the HMO method can be used for the reactivity assessment of alkyl- and dialkylbenzenes in the radical reactions.

For determination of relative rate constants and partial rate factors in the Gomberg reaction we chose intentionally combinations of aromatic hydrocarbons with respect to the minimum content of the side reaction products. In addition, the steric effect of methyl group is excluded. Determination of real rate constants of the Gomberg

reaction was prevented by heterogeneousness of the reaction medium. The results are given in Table V. The relative response factor of trimethylbiphenyls and methyl-ethylbiphenyls with respect to 4-methylbiphenyl, which was determined by calculation²² (0.989), was neglected in the same way as that of dimethylbiphenyls (0.994), because the error introduced by this neglect lies within the standard deviation of the measurement (Table V). By capillary GLC it was found that no changes in relative percentage of biphenyls and diarylmethanes (or -ethanes) occurred during the purification of the Gomberg reaction products by column chromatography. With respect to limited service life of capillary columns the analyses were repeated only in the cases of the products purified on a silica gel column.

From Table V it follows that *m*-xylene is the most reactive hydrocarbon due to high reactivity of the 2-position activated by two neighbouring methyl groups. The 4-position, which is activated by one *ortho* and one *para* methyl group, is less reactive (almost 3 times). In spite of that, this position is almost 3.6 times more reactive than the corresponding position in toluene, which is obviously due to activation by two groups in alternating positions. On the contrary, the presence of two methyl groups affects negatively the reactivity of the 5-position of *m*-xylene molecule, whereas the influence of a single methyl (or ethyl) group is slightly positive (the 3-position in toluene and ethylbenzene molecules) or negligible (as in the 4-position of *o*-xylene molecule). From comparison of reactivities of one ring position of *p*-xylene

TABLE V

Relative Rate Constants, Partial Rate Factors and Radical Superdelocalizabilities of the Aromatic Hydrocarbons Used in the Gomberg Reaction

| Aromatic hydrocarbon | $k_{rel.total}^a$ | $k_{rel.arom.}^b$ | Partial rate factors (superdelocalizabilities) |
|----------------------|-------------------|-------------------|--|
| Toluene | 1.765 ± 0.041 | 1.736 ± 0.045 | 2-: 3.482 (0.8449); 3-: 1.088 (0.8327); 4-: 1.280 (0.8416) |
| Ethylbenzene | 1.785 ± 0.033 | 1.708 ± 0.038 | 2-: 2.725 (0.8558); 3-: 1.414 (0.8322); 4-: 1.859 (0.8498) |
| <i>o</i> -Xylene | 1.490 ± 0.026 | 1.343 ± 0.013 | 3-: 2.776 (0.8437); 4-: 1.246 (0.841 <i>p</i>) |
| <i>m</i> -Xylene | 3.384 ± 0.056 | 3.319 ± 0.048 | 2-: 12.000 (0.8558); 4-: 3.557 (0.8539); 5-: 0.867 (0.8321) |
| <i>p</i> -Xylene | 2.995 ± 0.021 | 2.884 ± 0.023 | 2-: 4.331 (0.8451) |

^a Relative rate constant of the reaction in the aromatic ring of the hydrocarbon, ^b total relative rate constant of the reaction. The both constants are related to benzene.

molecule and 3-position of *o*-xylene molecule (in *p*-xylene it is higher by a factor of approximately 1.5) it follows that the two reaction centres do not show equal reactivities in spite of being activated by one *ortho* and one *meta* methyl group in the both case. Hence the overall structure and symmetry of hydrocarbons must be taken into account when evaluating their reactivity. The reactivity differences between the corresponding positions of toluene and ethylbenzene can be ascribed probably to higher sterical requirements of ethyl group.

REFERENCES

1. Gomberg M., Bachmann W. E.: J. Amer. Chem. Soc. 46, 2339 (1924).
2. Gomberg M., Pernet J. C.: J. Amer. Chem. Soc. 48, 1372 (1926).
3. Bachmann W. E., Hoffman R. A.: Org. React. 2, 224 (1944).
4. Hodgson H. H., Marsden E.: J. Chem. Soc. 1940, 208.
5. Ellas J., Haworth J. W., Hey D. H.: J. Chem. Soc. 1940, 1284.
6. Grieve W. S. M., Hey D. H.: J. Chem. Soc. 1934, 1938.
7. Grieve W. S. M., Hey D. H.: J. Chem. Soc. 1938, 108.
8. Hwang Shu: Acta Chim. Sinica 25, 171 (1959); Chem. Abstr. 54, 4489.
9. Cadogan J. I. G.: J. Chem. Soc. 1962, 4257.
10. Abramovitch R. A., Saha J. G.: Tetrahedron 21, 297 (1965).
11. Norman R. O. C., Waters W. A.: J. Chem. Soc. 1958, 167.
12. Gadallah F. F., Elofson R. M.: J. Org. Chem. 34, 3335 (1969).
13. Petit M. R., Tatlow J. C.: J. Chem. Soc. 1954, 1941.
14. Grieve W. S. M., Hey D. H.: J. Chem. Soc. 1934, 1797.
15. Röchardt C., Merz E.: Tetrahedron Lett. 36, 2431 (1964).
16. Makarova I. G.: Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci. 1958, 565, 693, 1939.
17. Kříž J., Hála S., Popl M., Mostecký J.: Chem. Prům. 25, 75 (1975).
18. Zonew N. S.: Chem. Zentrabl. 1923 I, 1497.
19. Friedel C., Crafts J. M.: Ann. Chim. Phys. 6, 1, 480 (1884).
20. Kraemer G., Spilker A.: Chem. Ber. 24, 2788 (1891).
21. Novrocík J., Novrocíková M.: This Journal, in press.
22. Purnell H.: *Plynová chromatografie*, p. 315. Published by SNTL, Prague 1966.

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