

**434.** *Some Catalysed Gas-phase Reactions of Aromatic Hydrocarbons. Part IV. The Polymethylbenzenes formed in the Reactions of Dimethyl Ether with Benzene, Toluene, and the Xylenes.*

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The yields and isomeric compositions of the methylbenzenes formed in the methylation of benzene by dimethyl ether over a heated alumina-silica catalyst have been determined. All of the twelve possible isomers, with perhaps the exception of pentamethylbenzene, are formed; a little ethylbenzene is found in the xylene fractions. The corresponding reactions of toluene, *o*-, and *p*-xylene, and a xylene mixture, have also been investigated. Monomethylation is the predominating reaction in all cases, and the yields of polymethylated products fall off rapidly with the number of groups introduced. The compositions of the di- and tri-methylbenzene fractions are shown to correspond closely to the respective thermodynamic equilibrium mixtures. The process is compared with the liquid-phase Friedel-Crafts reaction.

It has been shown (Given and Hammick, *J.*, 1947, 928) that benzene interacts with dimethyl ether on the surface of metal oxide catalysts to yield toluene, xylene, and higher methylbenzenes. Other workers (for references, see Part I, *loc. cit.*) have reported similar gas-phase reactions, but the composition of the polymethylbenzenes formed in such processes has apparently not been investigated. It was therefore thought of interest to determine the yields of the polymethylbenzenes formed in the reaction of benzene, toluene, and each of the three xylenes with dimethyl ether in the presence of an alumina-silica catalyst, and to obtain information concerning the isomeric composition of the C<sub>8</sub>, C<sub>9</sub>, and C<sub>10</sub> fractions.

EXPERIMENTAL.

*Materials.*—The preparation of the benzene, dimethyl ether, and synthetic alumina-silica catalyst (Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> = 1 : 4) has been described (Part I, *loc. cit.*).

**Toluene.** The collected toluene fractions from a number of previous methylations of benzene were fractionated twice through a Podbielniak still; b. p. 110.5°,  $n_D^{20}$  1.4970.

***o*-Xylene.** A sample of "pure" *o*-xylene was fractionated once in a Podbielniak still; b. p. 143.5–144°,  $n_D^{20}$  1.5020, f. p. –28° (cf. values of 144.4°, 1.5052, and –25.2° respectively given by Forziati, Glasgow, Willingham, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 129).

**Mixture of xylene isomers (mainly *m*-).** Commercial xylene ( $n_D^{20}$  1.4925) was freed from sulphur compounds by washing with sulphuric acid, and was then fractionally distilled. The portion of b. p. 137–140° was boiled with dilute nitric acid and freed from aliphatic impurities by sulphonation and separation of unsulphonated material; the hydrocarbon was regenerated by hydrolysis of the acid, and was redistilled.\* The analysis of the product (by ultra-violet spectroscopic method †) was: ethylbenzene, 0.0%; *p*-xylene, 15.7%; *m*-, 73.2%; *o*-, 11.1%.

***p*-Xylene.** A sample of "pure"-grade hydrocarbon was twice partially frozen, the unfrozen residue being neglected; f. p. 13.2°,  $n_D^{20}$  1.4959. Spectroscopic analysis showed the material to be at least 99.4% pure.

**Experimental Method.**—The apparatus and procedure were as described in Part I with the following exceptions: (1) Although the benzene was vapourised by electrical heating as in the previous work, the other hydrocarbons were boiled into the stream of methyl ether over a gas micro-burner. The rate of flow was calculated from the total weight of liquid passed, and the total time of the experiment. (2) The products of the methylation of toluene and the xylenes were immediately fractionated in the Podbielniak still, without the preliminary concentration of the products made in the earlier work.

Between 60 and 150 g. of toluene and the xylenes were passed over the catalyst in each run; but in order to obtain a reasonably large volume of the higher homologues for adequate investigation, 1000 g. of benzene were treated in one run.

**Analysis of the Products.**—The yields of the sets of C<sub>7</sub>, C<sub>8</sub>, C<sub>9</sub>, and C<sub>10</sub> hydrocarbons were determined by distillation in the Podbielniak still, which consisted of a vacuum-jacketed column 1 m. long and 0.55 cm. in diameter, packed with a wire spiral. Direct tests with known mixtures showed that the sets of C<sub>7</sub>, C<sub>8</sub>, C<sub>9</sub>, and C<sub>10</sub> hydrocarbons could be separated in the still with a maximum uncertainty in the analysis of ±0.3 c.c. The weight of starting material used in the various experiments was such that this uncertainty in the volumes resulted in a maximum uncertainty of about 4% in the percentages of C<sub>7</sub>, C<sub>8</sub>, and C<sub>9</sub> cuts in Table I, and about 10% in the C<sub>10</sub> cuts; the uncertainty in many of the figures is considerably less than the maximum.

The penta- and hexa-methylbenzenes were determined by difference; some information about their relative proportions was obtained by the distillation of the collected high-boiling residues from a number of previous methylations of benzene.

Analyses of the C<sub>8</sub> and C<sub>9</sub> hydrocarbons obtained by methylation of benzene have been made spectroscopically; and the recovered xylene fractions from the xylene methylations have been analysed in the same way. In addition, the C<sub>8</sub> and C<sub>9</sub> cuts from every run were carefully refractionated to effect a partial separation between the isomers (a complete separation cannot be achieved in the type of Podbielniak still used). The b. p.s and f. p.s, and the m. p.s if above –78°, and also the refractive indices of the fractions, were determined. These data provided some further and confirmatory information.

In the analysis of the tetramethylbenzenes, use was made of the freezing point–composition curve for the binary system, durené–isodurené, reported by Smith and Macdougall (*J. Amer. Chem. Soc.*, 1929, **51**, 3001). The semi-solid distillate from the primary analysis was filtered off and sucked dry, and the weights of durené on the filter and of the liquid in the filter-flask were observed. Using the solubility of durené in isodurené at the temperature of the filtration estimated from the freezing-point curve, the total weight of durené was then calculated (the presence of a small amount of prehnitene should not affect the solubility greatly). The filtrates from the products of all methylation experiments described below were mixed, cooled to –15° to remove a further quantity of durené, and distilled through the Podbielniak still. An estimate of the average proportions of the three tetramethylbenzenes was thus obtained.

**Results.**—The yields of the sets of methylbenzenes obtained in the various experiments, expressed as moles of product per 100 moles of reactant passed, are given in Table I. The volume of the packed catalyst space was 470 c.c., and it contained 294 g. of catalyst.

**The xylenes.** The spectroscopic analyses of the C<sub>8</sub> cuts are given in Table II. All the xylene fractions obtained (including those recovered from the methylations of a single isomer) had a refractive index  $n_D^{20}$  1.4979–1.4981, and all except that recovered from the methylation of the *o*-isomer showed similar behaviour on refractionation. The initial f. p. of the recovered *p*-xylene was –20°, and the other samples began to freeze at about –40° to –50°; none of the fractions was completely frozen at –75°.

**The trimethylbenzenes.** Spectroscopic analysis of the trimethylbenzenes from the methylation of benzene gave the following results: 1:3:5-isomer, 20.6%; 1:2:4-, 59.5%; 1:2:3-, 19.1%. The refractionation of the trimethylbenzene fractions from the various methylations showed that they were all of similar composition, that *ψ*-cumene was the main constituent, but that the other two isomers were both present. The data in Table III, relating to the trimethylbenzenes formed in the methylation of *p*-xylene, are typical specimens of the results.

**The tetramethylbenzenes.** The yields of durené, as percentages of the total C<sub>10</sub> cut, are given below:

Substance methylated .....	Benzene.	<i>p</i> -Xylene.	<i>m</i> -Xylene.	<i>o</i> -Xylene.
Durené, % by weight .....	56	34	53	42

\* The method of purification was that of Clarke and Taylor (*J. Amer. Chem. Soc.*, 1923, **45**, 831) who have claimed that it yields pure *m*-xylene from the commercial mixture.

† The authors wish to acknowledge gratefully the kindness of Dr. Powell of Anglo-Iranian Oil Co. Ltd. in performing all the spectroscopic analyses quoted in this paper. His method is described by Gordon and Powell, *J. Inst. Pet.*, 1945, **31**, 428.

TABLE I.

Reactant: Benzene.	Toluene.				Xylenes:		
	1.	2.	3.	4.	<i>p.</i>	<i>o.</i>	mixture (mainly <i>m.</i> )
Run.					5.	6.	7.
Rate of flow of hydrocarbon, g./hr.	29.6	33.6	42.5	50	60	51.5	51.5
Rate of flow of ether, g./hr. ....	10.9	15.3	15.3	15.3	15.3	15.3	15.3
Flow of hydrocarbon, vol. liq./vol. catalyst/hr. ....	0.072	0.082	0.10	0.12	0.15	0.13	0.13
Mol. ratio, hydrocarbon/ether ...	1.6	1.1	1.4	1.6	1.7	1.5	1.5
Yields (moles %).							
Benzene .....	61	3.0	2.6	—	0	0	0.4
Toluene .....	11.6	—	—	—	4.7	3.9	3.8
Xylene .....	3.9	22.3	20.8	19.0	52	51	54.4
Trimethylbenzene .....	1.6	8.7	7.9	6.2	22.1	21.9	23.4
Tetramethylbenzene .....	0.3	1.05	0.8	1.2	6.1	6.0	6.8
Penta- + hexa-methylbenzene ...	0.4	2.2	1.7	1.4	3.6	3.6	3.0
Total methylation per pass (%) ...	15.8	34.3	31.2	27.8	31.8	29.5	33.2
Monomethylated product calc. on hydrocarbon consumed * .....	29.7	—	—	—	46	45	51

\* The "hydrocarbon consumed" is the difference between hydrocarbon passed and hydrocarbon recovered.

TABLE II.

Substance methylated.	Weight, %, of:			
	$C_6H_5Et.$	<i>p</i> - $C_6H_4Me_2.$	<i>m</i> - $C_6H_4Me_2.$	<i>o</i> - $C_6H_4Me_2.$
Benzene .....	0.4	24.2	54.3	21.1
<i>p</i> -Xylene .....	0.8	33.8	46.1	19.3
<i>m</i> -Xylene .....	3.0	23.2	52.6	21.4
<i>o</i> -Xylene .....	0	17.0	45.6	37.4

TABLE III.

*Distillation of trimethylbenzenes from p-xylene.*

Fraction.	Vol., c.c.	B.p.	$n_D^{20}$ .	Fraction.	Vol., c.c.	B.p.	$n_D^{20}$ .
1	2.0	165—169°	1.5024	3	3.8	170—172°	1.5064
2	25.0	169—170	1.5040				

Fraction 2 froze within the range  $-58^\circ$  to  $-69^\circ$ .

The durenene, crystallised twice from alcohol, had m. p.  $79^\circ$ . The combined liquids after removal of the solid durenene were fractionated with the results given in Table IV.

TABLE IV.

*Distillation of combined liquid tetramethylbenzenes.*

Fraction.	Vol., c.c.	B.p.	F.p.	M.p.	$n_D^{20}$ .	Fraction.	Vol., c.c.	B.p.	F.p.	M.p.	$n_D^{20}$ .
1	3.3	194—198°	—	—	1.5124	3	4.2	198—199°	$-16^\circ$	$-35^\circ$	1.5138
2	4.7	198	—	—	1.5131	4	3.4	199—203	$-11^\circ$	$-35^\circ$	1.5149

Comparison of these figures with the data for the pure tetramethylbenzenes (see Smith *et al.*, *J. Amer. Chem. Soc.*, 1932, **54**, 1614, and references given therein; Francis, *Chem. Reviews*, 1948, **42**, 107) shows, after durenene has been removed, the residue is mainly *isodurenene*, but some *prehnitene* is present.

It can be estimated that the average composition of the various tetramethylbenzene fractions is: durenene (1 : 2 : 4 : 5), 50%; *isodurenene* (1 : 2 : 3 : 5), 42%; *prehnitene* (1 : 2 : 3 : 4), 8%.

*Penta- and hexa-methylbenzenes.* As stated above, no attempt was made to determine these substances directly in the routine analyses of the reaction products. The presence of hexamethylbenzene was demonstrated in the following manner. The residues from the analyses of the products of a number of methylations of benzene were distilled without a fractionating column. The temperature rose rapidly to  $260^\circ$  without pausing at either  $232^\circ$  or  $255^\circ$  (the b. p.s of pentamethylbenzene and diphenyl, respectively). A liquid distilled at  $260$ — $265^\circ$ , and rapidly solidified in the condenser. The solid was crystallised from alcohol, m. p.  $164$ — $165^\circ$  (corr.) (Found: C, 88.8; H, 11.1. Calc. for  $C_{12}H_{18}$ : C, 88.8; H, 11.2%). Hence the residual reaction products, after removal of the  $C_6$  to  $C_{10}$  hydrocarbons, consist mainly of hexamethylbenzene; little, if any, pentamethylbenzene is formed. Diphenyl, which could conceivably be formed in side reactions, evidently is not present to any significant extent.

## DISCUSSION.

The spectroscopic analyses given in Table II show that small amounts of ethylbenzene were present in the  $C_8$  cuts recovered from the methylations of benzene, *p*-xylene, and the xylene

mixture. The benzene and toluene used in our experiments were carefully fractionated before use, and contained no ethylbenzene, and spectroscopic analyses of the *p*-xylene and the xylene mixture showed the absence of this hydrocarbon initially. (The spectroscopic analysis of the C<sub>8</sub> products of the methylation of the *o*-isomer revealed no ethylbenzene, so that the purity of the starting material is not in question in this case.)

Taylor, Wagman, Williams, Pitzer, and Rossini (*J. Res. Nat. Bur. Stand.*, 1946, **37**, 95) have calculated the equilibria among the four C<sub>8</sub> hydrocarbons in the vapour state over the temperature range, 298·16—1500° K.; it may be shown from their data that at 723° K. (450° C.) the equilibrium mixture contains: 9% ethylbenzene; 21·2% *p*-xylene; 47·3% *m*-; 22·5% *o*-. Comparison of these figures with the experimentally determined compositions of the C<sub>8</sub> cuts given in Table II shows that the proportion of *m*-xylene in all the four samples analysed agrees with the equilibrium value within the limits of experimental error; so also do the proportions of *o*- and *p*-xylene in the cuts separated from the methylations of benzene and the xylene mixture (the latter contained initially 73·2% *m*-, 11·1% *o*-, and 15·7% *p*-xylene). It is evident that *o*- and *p*-xylene do not isomerise all the way to the equilibrium mixture in a single passage over the catalyst (under our conditions) since the recovered fractions contain the respective starting materials in greater than equilibrium proportions. The proportion of ethylbenzene found is in all cases less than the equilibrium value; but one would perhaps expect the rate of isomerisation of one xylene into another to be much higher than the rate of isomerisation of a xylene into ethylbenzene.

Thus we conclude that the C<sub>8</sub> cut obtained as a product of the interaction of benzene and dimethyl ether under the conditions we have used is substantially the thermodynamic equilibrium mixture; and under the same conditions any xylene isomerises to a considerable extent towards the equilibrium mixture.

Rossini *et al.* (*loc. cit.*) have also calculated the equilibria among the eight C<sub>9</sub>H<sub>12</sub> alkylbenzenes in the gas phase at temperatures of 298·16—1500° K. From their data we may deduce that the proportions of the three trimethylbenzenes in equilibrium with each other would be: mesitylene (1 : 3 : 5), 22·0% *ψ*-cumene (1 : 2 : 4), 62·3%; hemimellitene (1 : 2 : 3), 15·7%. The trimethylbenzenes formed in the methylation of benzene had substantially this composition, within the limits of experimental error. Sufficient data are not available for a similar comparison to be instituted for the tetramethylbenzenes.

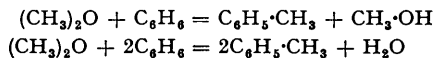
A comparison of the products of the gas-phase reaction described here with those of the liquid-phase Friedel-Crafts reaction may be made. In the former, the yield of the product formed by the introduction of one methyl group into toluene or xylene is about double the yield of the corresponding reaction of benzene (see Table I). Nevertheless, introduction of only one methyl group is the predominating reaction whatever the starting material, and the yields of polymethylbenzenes fall off rapidly with the number of groups introduced; the ratio of mono- to poly-methylation is rather insensitive to variations in the hydrocarbon : dimethyl ether ratio (see Part I, *loc. cit.*, p. 932). On the other hand, Smith and Dobrolovny (*J. Amer. Chem. Soc.*, 1926, **48**, 1413) found that in the Friedel-Crafts reaction of methyl chloride with xylene in the presence of aluminium chloride, the yield of disubstituted was high compared with monosubstituted products, whatever the proportion of methylating agent used; and considerably more penta- than hexa-methylbenzene was formed. The first of these results is a well-known characteristic of the Friedel-Crafts reaction (see Calloway, *Chem. Reviews*, 1935, **17**, 327).

In the interaction, under our conditions, of dimethyl ether with benzene and its homologues, substantial amounts of the vicinal substituted products (*o*-xylene, hemimellitene, prehnitene) are formed. In the Friedel-Crafts reaction, *o*-disubstituted products are often not found (see, e.g., Ador and Rilliet, *Ber.*, 1878, **11**, 1627; 1879, **12**, 329; Moyle and Smith, *J. Org. Chem.*, 1937, **2**, 114; Shoosmith and McGechee, *J.*, 1930, 2231). Smith and Cass (*J. Amer. Chem. Soc.*, 1932, **54**, 1603, 1609) showed that in the methylation of xylene with methyl chloride in the presence of aluminium chloride, no hemimellitene or prehnitene is formed (*i.e.*, less than 1%).

The differences between the two types of reaction must be ascribed partly to differences in the equilibria, and partly to the relatively higher rates of the isomerisation reactions at the higher temperature used in the reactions of dimethyl ether.

A number of authors (see "Organic Reactions", ed. Adams, Wiley, 1946, Price, Vol. 1*a*, p. 10) have remarked on the fact that the xylene obtained by the Friedel-Crafts reaction consists largely of the *m*-isomer; Price and Ciskowski (*J. Amer. Chem. Soc.*, 1938, **60**, 2499) have suggested that the expected *o*- and *p*-xylenes are formed first, these are methylated further to 1 : 2 : 4-trimethylbenzene, and that then a proton replaces a methyl group; substitution rules lead one to expect that *m*-xylene would be formed in this reverse reaction. This may be the mechanism by

which the *m*-isomer is formed in methylations with methyl chloride and aluminium chloride, but a similar course is impossible in the dimethyl ether gas-phase reaction, since thermodynamic data (see Part I, *loc. cit.*) show that the reactions :



are not reversible to any significant extent (the corresponding equilibria for the homologues will not differ greatly). In any case it is clear that the basic reason for the predominance of the *m*-isomer in both reactions is its superior stability. It is perhaps of interest to note that the compositions of coal-tar xylenes, although they vary somewhat with the source and method of preparation, are always fairly close to the equilibrium composition; certainly the *m*-isomer always predominates (Kishner and Krasova, *J. Gen. Chem. Russia*, 1936, 6, 748, have given analyses of typical coal-tar xylenes). It is unlikely that the coal-tar xylenes, however they are produced, are formed in equilibrium proportions, or that isomerisation occurs in the gas phase, and so it appears that coal during carbonisation (presumably at temperatures of 600—1100°) catalyses the isomerisation.

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