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Alkylation of Xylenes with Ethylene and Propylene

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With strong alkylation catalysts such as $AlCl_3$, *m*-xylene is selectively monoalkylated to the symmetrical isomer. The other two xylene isomers yield mixed products, part of which are symmetrical. Addition of water to $AlCl_3$ forms a different catalyst system, and the amount of unsymmetrical isomers in the product increases with an increase in added water. $BF_3 \cdot P_2O_5$ is a mild alkylation catalyst which promotes the selective monoalkylation of *m*- and *p*-xylene. The products are 4-alkyl-*m*-xylene and 2-alkyl-*p*-xylene, respectively. This catalyst also promotes selective dialkylation of *m*-xylene. The product is 4,6-dialkyl-*m*-xylene. 2,5-Dialkyl-*p*-xylene can be crystallized from the mixture of dialkylation products of *p*-xylene.

The studies presented are concerned with selective alkylation techniques in which choice of catalyst and reaction conditions are adjusted to produce predominantly a single isomer or a mixture that can be easily resolved by fractionation. The alkylation reaction of olefins and xylenes has been examined using catalysts such as anhydrous $AlCl_3$, $AlCl_3 \cdot H_2O$, $BF_3 \cdot H_3PO_4$, and $BF_3 \cdot P_2O_5$. By use of the latest analytical techniques, analyses of the product mixtures provide a more accurate picture of isomer distribution than has been possible in earlier works.

Alkylation with $AlCl_3$. Strong alkylation catalysts, such as $AlCl_3$, generally promote substitution at positions meta to existing alkyl side chains in aromatic compounds accompanied by isomerization or disproportionation.[1-4] However, by using less than 0.05 mole $AlCl_3$/mole of aromatic and reaction temperatures below 100°, some aromatic hydrocarbons undergo a relatively small amount of isomerization. Experimental data showing the distribution of 1,3,5 and 1,2,4 isomers obtained in the $AlCl_3$ catalyzed alkylation of meta, para, and mixed xylenes are summarized in Table I.

The reaction of *m*-xylene with propylene in the presence of $AlCl_3$ as described results in the predominant production of the 1,3,5 isomer. Reactions in which less than 0.05 mole $AlCl_3$/mole of aromatic was used resulted in 90–99% 1,3-dimethyl-5-isopropylbenzene. The high proportion of the 1,3,5 isomer in the monoalkylate is also independent of the extent of aromatic conversion. Monoalkylation predominates up to 70% xylene conversion; further alkylation results in a diisopropylxylene fraction containing more than one isomer. Ethylation of *m*-xylene under similar reaction conditions yields an ethylxylene fraction containing a lower proportion of the symmetrical 1,3,5 isomer than is obtained by propylation; the fraction contained 47% 1,3-dimethyl-5-ethylbenzene. The differences observed in the distribution of products with these olefins may be the result of "different activity of the attacking species," namely, the olefins, as proposed by Brown and Nelson.[5] A similar relationship in the alkylation of toluene with ethylene and propylene has been reported by Nelson.[6]

In the alkylation of mixed xylenes with propylene, as shown in Table I, a mixture of isomers containing 64% of the 1,3,5 compound is produced. These results can be accounted for by the isomerization of *o*- and *p*-xylenes with accompanying alkylation of the meta isomer. 1,3-Dimethyl-4-isopropylbenzene can be recovered from this mixture in 69% purity by fractionation while 1,3-dimethyl-5-isopropylbenzene of 95% purity can be obtained in a similar manner.

TABLE I

ALKYLATION OF XYLENES WITH $AlCl_3$

Aromatic Alkylated	Reaction Temp., °C.	Olefin (Moles/Mole Aromatic)	$AlCl_3$ (Moles/Mole Aromatic)	Monoalkylate, %	
				1,3,5	1,2,4
m-Xylene	30–100	C_3 (0.7)	0.0125	99	1[a]
m-Xylene	85–90	C_2 (1.2)	0.016	47	24[a]
Xylene[b]	90–95	C_3 (0.67)	0.03	64	17
p-Xylene	90–95	C_3 (0.97)	0.0125	44	44[c]

[a] 4-Alkyl-1,3-dimethylbenzene. [b] 21% ortho, 39% meta, and 14% para isomers. [c] 1,4-Dimethyl-2-isopropylbenzene.

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[1] W. C. Howell, U. S. Patent **2,443,247**, June 15, 1948.

[2] A. P. Lien and D. A. McCauley, U. S. Patent **2,564,073**, Aug. 14, 1951.

[3] A. P. Lien, D. A. McCauley, and P. J. Launer, *J. Am. Chem. Soc.*, **76**, 2354 (1954).

[4] D. V. Nightingale and B. J. Carton, *J. Am. Chem. Soc.*, **62**, 281 (1940).

[5] H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

[6] K. L. Nelson, *J. Org. Chem.*, **21**, 145 (1956).

TABLE II

ALKYLATIONS OF XYLENES WITH $BF_3{\cdot}P_2O_5$ AND $BF_3{\cdot}H_3PO_4$

Catalyst	Reaction Temp., °C.	Olefin (Moles/Mole Aromatic)	Aromatic	Monoalkylate[a]	
				1,2,4	1,3,5
$BF_3{\cdot}H_3PO_4$	80–85	C_3 (0.5–1.5)	*m*-Xylene	65–75[b]	21–34
$BF_3{\cdot}P_2O_5$	35–140	C_3 (1.4)	*m*-Xylene	75–82[b]	8–13
$BF_3{\cdot}P_2O_5$	94–97	C_2 (1.0)[c]	*m*-Xylene	80–90[b]	—
$BF_3{\cdot}P_2O_5$	75–80	C_3 (0.8–1.6)	*p*-Xylene	100[d]	0

[a] Yield limits for a number of alkylations. [b] 4-Alkyl-1,3-dimethylbenzene. [c] 350–400 p.s.i.g. ethylene. [d] 1,4-Dimethyl-2-isopropylbenzene.

Alkylation with $BF_3{\cdot}H_3PO_4$ and $BF_3{\cdot}P_2O_5$. Mild alkylation catalysts generally promote ortho-para alkylation without isomerization of the parent aromatics. Such catalysts include HF,[7–10] phosphoric acid,[11] ferric chloride,[12,13] calcium hydrogen phosphate,[14] and sulfuric acid.[15–17]

While BF_3 alone has limited use as an aromatic alkylation catalyst, complexes of BF_3 are numerous and have been extensively used as catalysts.[18] These complexes are generally mild alkylation catalysts except the $HF{\cdot}BF_3$ system which is a strong acid catalyst[19] that often causes extensive isomerization. BF_3 in combination with P_2O_5[20,21] has been reported to be an active catalyst for the alkylation of aromatic compounds with alcohols. A similar type catalyst prepared by passing BF_3 over a pellet bed of P_2O_5 on kieselguhr (UOP polymerization catalyst) was used in these olefin alkylation studies.

Data are presented in Table II showing the distribution of isomers for the alkylation of *m*- and *p*-xylenes using $BF_3{\cdot}P_2O_5$ (solid) and $BF_3{\cdot}H_3PO_4$ (liquid) catalysts. In the propylation of *m*-xylene with the $BF_3{\cdot}P_2O_5$ catalyst, little change in isomer distribution was noted in varying the reaction temperature from 35° to 140°, the olefin charge rate from 0.22 to 0.62 mole/mole of xylene/hour, or the total olefin/xylene molar ratio from 0.16 to 1.5. Only trace amounts of diisopropylxylenes were obtained at olefin/xylene molar ratios below 0.4. While propylene reacts readily with *m*-xylene over solid $BF_3{\cdot}P_2O_5$ at atmospheric pressure, little or no reaction was observed with ethylene under these conditions. However, substantial reaction of *m*-xylene and ethylene occurs at pressures above atmospheric to produce predominantly 1,3-dimethyl-4-ethylbenzene. Data are also included in Table II which compare alkylate compositions obtained with $BF_3{\cdot}H_3PO_4$ and $BF_3{\cdot}P_2O_5$. It can be seen that by using a $BF_3{\cdot}H_8PO_4$ catalyst[22] the ratio of the 1,2,4 isomer to the 1,3-dimethyl-5-isopropylbenzene is approximately 2.5 compared to 7.5 with $BF_3{\cdot}P_2O_5$ catalyst.

Studies have also been made in which reaction conditions were adjusted to maximize the production of tetraalkylbenzenes. Such data are summarized in Table III for the alkylation of a number of aromatic compounds using $BF_3{\cdot}P_2O_5$ as a catalyst. The tetraalkylbenzene yields with the liquid $BF_3{\cdot}H_3PO_4$ catalyst were similar.

TABLE III

PREPARATION OF TETRAALKYLBENZENES WITH $BF_3{\cdot}P_2O_5$ CATALYST

Reactants		
Olefin (Moles/Mole Aromatic)	Aromatic	Tetraalkylbenzene Fraction[a]
C_3 (0.5–4.0)	*m*-Xylene	83–92% 1,2,4,5 Isomer[b]
C_2 (5–6)	*m*-Xylene	Mix[c]
C_3 (3–5)	*p*-Xylene	50–60% 1,2,4,5 Isomer[d]
C_3 (0.7)	Pseudocumene	Mix[c]
C_3 (0.7)	1,3,5-Isopropylxylene	Mix[c]

[a] Yield limits for a number of alkylations. [b] 4,6-Diisopropyl 1,3-dimethylbenzene. [c] The mixtures obtained in these experiments were not separated and could not be analyzed by infrared absorption spectroscopy due to lack of pure reference samples. Two or more isomers appear to be present, and no single isomer was formed in major proportions. [d] 2,5-Diisopropyl-1,4-dimethylbenzene.

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(7) F. M. Smith, U. S. Patent **2,507,765**, May 16, 1950.

(8) F. E. Condon and M. P. Matuszak, *J. Am. Chem. Soc.*, **70**, 2539 (1948).

(9) J. H. Simons and S. Archer, *J. Am. Chem. Soc.*, **62**, 1623 (1940).

(10) F. M. Smith and R. S. Hanmer, U. S. Patent **2,507,766**, May 16, 1950.

(11) V. N. Ipatieff, H. Pines, and V. I. Kowarewsky, *Ind. Eng. Chem.*, **28**, 222 (1936).

(12) D. V. Nightingale and J. R. Jones, *J. Am. Chem. Soc.*, **66**, 154 (1944).

(13) L. Schmerling, U. S. Patent **2,402,847**, June 25, 1946.

(14) R. E. Schaad, U. S. Patent **2,290,211**, July 21, 1942.

(15) S. J. Slanina, F. J. Sowa, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **57**, 1547 (1935).

(16) V. N. Ipatieff, B. B. Corson, and H. Pines, *J. Am. Chem. Soc.*, **58**, 919 (1936).

(17) V. N. Ipatieff, H. Pines, and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940).

(18) H. S. Booth and D. R. Martin, *BF_3 and Its Derivatives*, John Wiley and Sons, New York, 1949.

(19) A. P. Lien and D. A. McCauley, *J. Am. Chem. Soc.*, **75**, 2411 (1953).

(20) C. E. Welsh and G. F. Hennion, *J. Am. Chem. Soc.*, **63**, 2603 (1941).

(21) N. F. Toussaint and G. F. Hennion, *J. Am. Chem. Soc.*, **62**, 1145 (1940).

(22) W. N. Axe, U. S. Patent **2,412,595**, Dec. 17, 1946.

These data show the dialkylation of *m*-xylene is selective in that 83–92% of the diisopropylated material is 4,6-diisopropyl-1,3-dimethylbenzene. The dialkylate from *p*-xylene contains two isomers and a trace of a third. One of these isomers has been separated by freezing and appears to be 2,5-diisopropyl-1,4-dimethylbenzene. Data are also presented for the alkylation of two trialkyl benzenes to tetraalkyl isomers. Mixtures were obtained in both these cases which could not be separated.

Alkylation with $AlCl_3 \cdot H_2O$. Xylene alkylation studies were made with a catalyst of $AlCl_3$ modified with small amounts of water. Data are presented in Fig. 1 for a series of experiments in which *m*-xylene was alkylated with propylene at 90–95° with 0.0125 mole of $AlCl_3$/mole of xylene. The product distribution is shown to be a function of the amount of water present. The ratio of 1,2,4- to 1,3,5-isopropylxylene changes from approximately 0.01 with anhydrous $AlCl_3$ to 0.44 for a system containing equal molar quantities of water and $AlCl_3$ (considered to be monomolecular for this calculation).

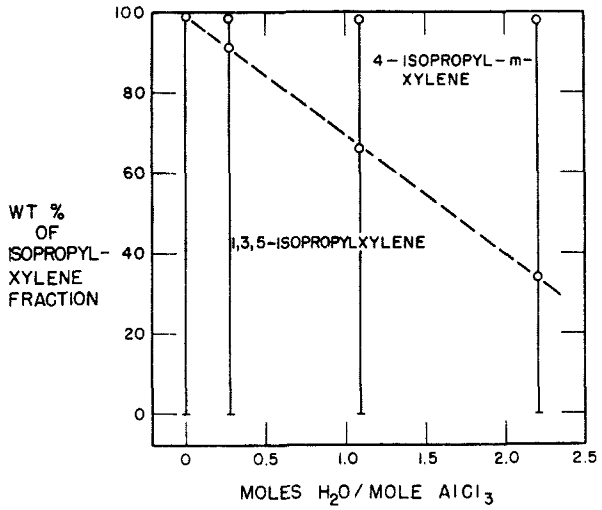

Fig. 1. Propylation of *m*-xylene with $AlCl_3$-H_2O catalysts

While the xylene conversion is observed to decrease somewhat as the amount of water is increased, a marked decline in propylation reaction is shown, in Fig. 2, to occur only with catalyst systems containing more than one mole of water/mole of $AlCl_3$. Water seems to have a somewhat greater effect on the conversion of xylene for reaction with ethylene.

These data clearly indicate the marked effect of water in altering product distribution for an $AlCl_3$ alkylation. The product variation is not equivalent to the results obtained with a lowered catalyst concentration such as might be assumed to result from destruction of part of the $AlCl_3$. The marked shift in isomer distribution resulting from the addition of water indicates a different catalyst system is formed by the reaction of water with $AlCl_3$ in xylene. The results also substantiate further the conclusion of Brown and Nelson[5] that there is no sharp division between meta-directed substitutions and reactions that produce high proportions of ortho- and para-substituted products. As noted by Brown, *et al.*,[23] the effect of water on $AlCl_3$ catalyst likely is the case of part or all of the discrepancies in previous publications regarding alkylation isomer distribution.

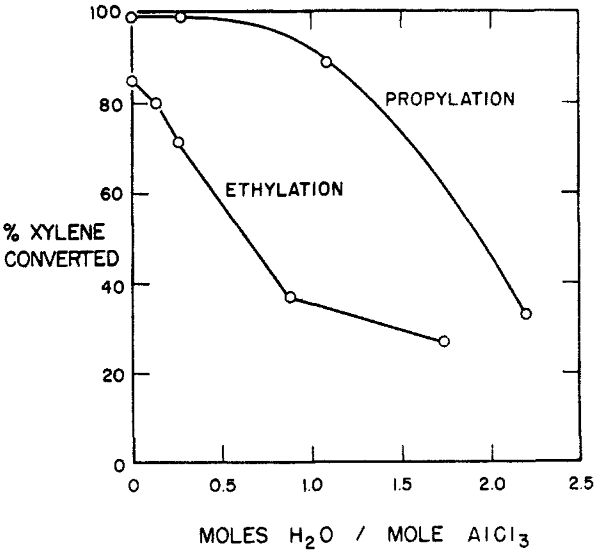

Fig. 2 *m*-Xylene conversion with $AlCl_3$-H_2O catalyst

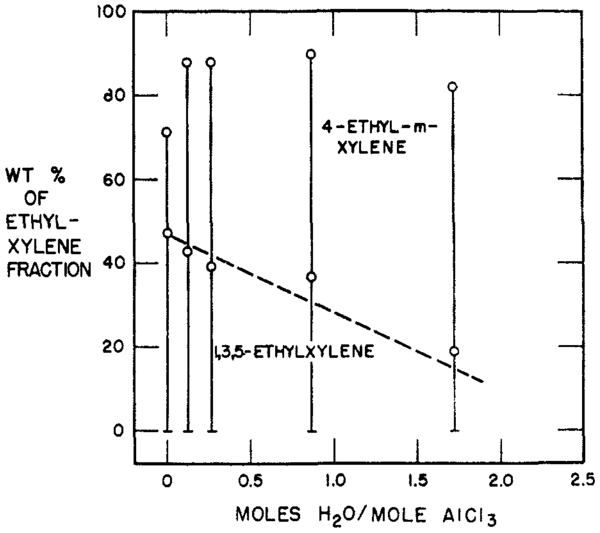

Fig. 3. Ethylation of *m*-xylene $AlCl_3$ catalyst, modified with H_2O

Similar data are supplied for the ethylation of *m*-xylene in Figs. 2 and 3. These results indicate that such catalyst systems are less selective for ethylation as compared with propylation and that

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(23) H. C. Brown, H. W. Pearsall, L. P. Eddy, E. J. Wallace, M. Grayson, and K. L. Nelson, *Ind. Eng. Chem.*, **45,** 1462 (1953).

product distribution is also altered less by varying the amount of water added.

Purification and properties of alkylxylenes. Physical properties of the alkylated xylenes prepared in this work are listed in Table IV. The physical properties which have been reported in the literature[24,25] are also included.

TABLE IV

PHYSICAL PROPERTIES OF ALKYLXYLENES

	B.P., °C.	F.P., °C.[a]	d_{25}	n_D^{25}
1,3,5-Ethylxylene				
Experimental	—	—	—	—
Literature[24]	183.8	−84	0.8608	1.4958
4-Ethyl-1,3-dimethylbenzene				
Experimental	186–187	−62.5	—	1.5012
Literature[24]	188.4	−63	0.8723	1.5016
1,3,5-Isopropylxylene				
Experimental	194.6	−70	0.8593	1.4926
Literature[24]	194.5	—	0.858	1.493
4-Isopropyl-1,3-dimethylbenzene				
Experimental	199.0	−82	0.8707	1.4982
Literature[24]	199.1	—	0.869	1.498
1,4-Dimethyl-2-Isopropylylbenzene				
Experimental	196.2	—	0.8721	1.4990
Literature[24]	196.2	—	0.8699	1.4988
4,6-Diisopropyl-1,3-dimethylbenzene				
Experimental	236.4	16.8	0.8668	1.4957
2,5-Diisopropyl-1,4-dimethylbenzene				
Experimental	243.8	37.2	0.8612[b]	1.4945[b]
Literature[25]	—	37.2	—	1.4917[c]

[a] Freezing data for alkyl xylene are only approximate since all tend to form glasses. F.P. for dialkyl xylenes was determined from freezing curves. The accuracy of these is about 16.8 ± 0.3° and 37.2 ± 0.1°. [b] These measurements made at 45.1°. [c] At 50°.

Pure isopropylxylenes were obtained by fractionation through a 4′ × 1″ Hypercal column at 80/1 reflux ratio. Pure 1,3,5-ethylxylene was obtained from the National Bureau of Standards. 4-Ethyl-*m*-xylene was synthesized by hydrogenation (Clemmenson method) of 2,4-dimethylacetophenone. The ketone was prepared by reaction of *m*-xylene and acetyl chloride (Friedel-Crafts reaction) with aluminum chloride catalyst. Fractionation of the hydrogenation product gave pure hydrocarbon.

Two pure diisopropylxylenes have been obtained. 4,6-Diisopropyl-*m*-xylene was purified by fractionation of the reaction product. A freezing curve showed the material to be pure, m.p. 16.8° ± 0.3°. Pure 2,5-diisopropyl-*p*-xylene could not be separated from a close boiling isomer by fractionation. However, the compound crystallized from the contaminating isomer and recrystallized nicely from *n*-pentane. A freezing curve of the recrystallized material showed it to be quite pure, m.p. 37.2° ± 0.1°. The physical properties of this material agree with those published by Kooyman and Strang[25] for 2,5-diisopropyl-*p*-xylene.

The two diisopropylxylenes prepared in this work are believed to have the 1,2,4,5 structure because: (1) The relatively high melting points are characteristic of symmetrical tetraalkyl benzenes; (2) the infrared absorption spectrum is similar to spectra of known 1,2,4,5-tetraalkyl benzenes; and (3) each is prepared, with nonisomerizing catalysts and reaction conditions, from the corresponding isopropyxylene. In addition, vapor phase oxidation of pure 4,6-diisopropyl-*m*-xylene has yielded pyromellitic acid. Kooyman and Strang[25] reported the ultraviolet spectrum of a 2,5-diisopropyl-*p*-xylene, which has the same physical properties as our material, to indicate the structure as given.

EXPERIMENTAL

Alkylations using $BF_3 \cdot P_2O_5$ on kieselguhr (solid) were carried out in a vertical glass tube reactor, 30″ × 2″, equipped with an electrical heater. Cylindrical pellets, 1/4″ × 1/4″, were added to the reactor to make a catalyst bed 13″ × 2″. The P_2O_5-kieselguhr pellets were saturated with xylene and a known weight of the aromatic was charged. The catalyst and xylene were then saturated with BF_3 over a 30-min. period by introducing BF_3 at a rate of 80 cc./min. (room temperature and atmospheric pressure). Gaseous olefin was introduced into the reactor after heating to the desired temperature. The gases were dispersed at the bottom of the reactor by means of a fritted glass disk. In order to maintain catalyst activity, BF_3 was introduced continuously with the olefin charge during alkylation. The reaction product was washed free of catalyst, dried, and distilled.

The $BF_3 \cdot H_3PO_4$, which is a liquid, was prepared by saturating 86% phosphoric acid with BF_3 resulting in a catalyst having a mole ratio of $H_3PO_4/H_2O/BF_3$ of 6.9/6.0/13.0. The alkylations with this catalyst were carried out in the same glass reactor mentioned above. While aromatic hydrocarbons are not miscible with such a catalyst, adequate mixing was obtained by introducing the olefin charge through a fritted glass disk at the bottom of the reactor tube.

Detailed information regarding reaction conditions and product distribution for $BF_3 \cdot P_2O_5$ and $BF_3 \cdot H_3PO_4$ catalyzed reactions are summarized in Table V.

$AlCl_3$ catalyzed alkylations were carried out in conventional flasks equipped with suitable stirrers. Catalyst was removed from the reaction products by washing with dilute HCl, followed by drying and distilling.

Detailed experimental data and product distribution for $AlCl_3$ and $AlCl_3 \cdot H_2O$ alkylations are summarized in Table VI.

The aromatic hydrocarbons were analyzed by infrared absorption spectroscopy, using Perkin-Elmer No. 12-B and No. 21 recording spectrometers. High purity alkylxylene isomers were separated by fractionation through a 4′ × 1″ Hypercal column operating at 80/1 reflux ratio. The di-

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(24) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, 1953.

(25) E. C. Kooyman and A. Strang, *Rec. trav. chim.*, **72**, 329 (1953).

TABLE V

ALKYLATION DATA FOR BF_3 COMPLEXES

Reactants		Reaction Conditions			Products, Mole % of Aromatic Charge				Monoalkylate Analysis, Wt. %	
Hydrocarbon charge	Catalyst[a]	Temp., °C.	Duration, hours	Olefin/arom. mole ratio	Arom. converted	Monoalkylate	Dialkylate	Bottoms[b]	1,2,4 Isomer	1,3,5 Isomer
p-Xylene-C_3	$BF_3 \cdot P_2O_5$(s)	75– 80	5.0	1.6	88	45	32.4	11.0	100	0
o-Xylene-C_3	$BF_3 \cdot P_2O_5$(s)	75– 80	3.0	1.1	55	25.7	10.3	7.0	Ca 50	—
m-Xylene-C_3	P_2O_5	75– 80	4.0	0.9	—	0	0	3.5	—	—
m-Xylene-C_3	$BF_3 \cdot P_2O_5$(s)	35– 40	2.5	0.9	77	42	12.0	8.0	79	10
m-Xylene-C_3	$BF_3 \cdot P_2O_5$(s)	75– 80	3.0	0.9	63	42	4.0	12.0	78	13
m-Xylene-C_3	$BF_3 \cdot P_2O_5$(s)	95–100	2.0	0.9	79	45	9.0	8.0	76	13
m-Xylene-C_3	$BF_3 \cdot P_2O_5$(s)	125–130	2.5	0.9	75	47	6.0	7.0	75	14
m-Xylene-C_3	$BF_3 \cdot P_2O_5$(s)	75– 80	1.0	0.2	32	14	0	5.0	78	10
m-Xylene-C_3	$BF_3 \cdot P_2O_5$(s)	75– 80	3.0	0.5	44	24	3.0	3.7	80	12
m-Xylene-C_3	$BF_3 \cdot P_2O_5$(s)	75– 80	4.0	0.7	64	37	10.0	4.0	80	13
m-Xylene-C_3	$BF_3 \cdot H_3PO_4$(l)	80– 85	1.8	0.5	45	24	4.0	5.0	65	34
m-Xylene-C_3	$BF_3 \cdot H_3PO_4$(l)	80– 85	5.0	1.5	91	48	28.0	9.0	75	21
Pseudocumene-C_3	$BF_3 \cdot P_2O_5$(s)	75– 80	2.0	0.7	62	34	0	10.0	—	—
1,3,5-Isopropylxylene[c]-C_3	$BF_3 \cdot P_2O_5$(s)	75– 80	2.0	0.7	48	43	—	15.0	5[d]	95[d]
m-Xylene-C_3	$BF_3 \cdot Al_2O_3$[e]	75– 80	2.5	1.5	77	25	36.0	12.0	75	20
m-Xylene-C_2[f]	$BF_3 \cdot P_2O_5$(s)	150–156	6.3	0.5	Ca 25	14	2.0	5.0	Ca 85	—
m-Xylene-C_2[f]	$BF_3 \cdot P_2O_5$(s)	94– 97	5.3	1.0	Ca 60	23	4.0	15.0	Ca 85	—

[a] The (s) designates the supported $BF_3 \cdot P_2O_5$ on kieselguhr. The (l) designates the liquid $BF_3 \cdot H_3PO_4$ made as per Axe, U. S. Patent 2,412,595. [b] This value given as wt. % of aromatic charged. [c] 90% pure, also contained 6% 4-isopropyl-m-xylene. [d] This analysis is for the recovered isopropylxylene. [e] BF_3 added to alumina (Alcoa F-1 grade, 8–14 mesh). The solid contained 20% BF_3, by weight. [f] 350–450 p.s.i.g.

TABLE VI

ALKYLATION WITH $AlCl_3$

Reactants		Reaction Conditions			Products, Mole % of Aromatic Charge				Monoalkylate Analysis, Wt. %	
Hydrocarbon charge	$AlCl_3$ mole/mole arom. (H_2O, mole/mole arom.)	Temp., °C.	Duration, hours	Olefin arom. mole ratio	Arom. converted	Monoalkylate	Dialkylate	Bottoms[a]	1,2,4 Isomer	1,3,5 Isomer
Xylene[b]-C_3	0.0076	90– 95	2.0	0.63	55	43.0	0	7.5	20	62
Xylene[b]-C_3	0.030	90– 95	2.0	0.68	63	42.3	0	8.7	17	64
p-Xylene-C_3	0.0128	90– 95	2.8	1.0	86	54.0	12.5	4.0	44[c]	41
m-Xylene-C_3	0.0128	30– 35	5.5	1.5	99	46.5	41.0	3.5	11	88
m-Xylene-C_3	0.0128	90 –95	5.0	1.5	99	53.1	34.2	5.5	1	99
m-Xylene-C_3	0.0128	125–130	4.7	1.5	100	63.7	26.2	12.0	9	81
m-Xylene-C_3	0.0128	90– 95	2.7	1.5	100	41.0	38.3	4.5	4	96
m-Xylene-C_3	0.0128	90– 95	5.0	1.0	79	68.0	0	5.5	9	84
m-Xylene-C_3	0.0063	90– 95	2.3	0.7	24	15.8	0	4.0	10	90
m-Xylene-C_3	0.013 (0.0035)	90 –95	5.7	1.5	99	49.3	28.6	11.5	6	92
m-Xylene-C_3	0.013 (0.014)	90– 95	4.7	1.3	88	50.1	22.6	8.0	32	66
m-Xylene-C_3	0.013 (0.028)	90– 95	5.0	1.4	33	16.4	Tr	3.0	64	34
m-Xylene-C_2	0.016	85– 90	4.0	1.3	85	41.8	13.8	13.0	24[d]	47[e]
m-Xylene-C_2	0.016 (0.002)	85– 90	4.0	1.2	80	42.7	15.8	15.0	45[d]	43[e]
m-Xylene-C_2	0.016 (0.004)	85– 90	4.0	1.2	71	36.1	13.6	18.0	49[d]	39[e]
m-Xylene-C_2	0.015 (0.014)	85– 90	4.0	1.2	37	12.2	1.0	5.8	53[d]	37[e]
m-Xylene-C_2	0.016 (0.028)	85– 90	4.0	1.2	27	2.5	0	6.2	63[d]	19[e]

[a] High boiling residue measured as wt. % of aromatic charged. [b] 21% o-, 39% m-, and 14% p-xylene. [c] This fraction is 2-isopropyl-p-xylene. [d] 4-Ethyl-m-xylene. [e] 1,3,5-Ethylxylene.

isopropylxylenes were purified by fractionation and recrystallization. After isolation and identification, the high purity products were used as calibrating standards for conventional infrared quantitative analyses.

All hydrocarbons used were obtained from chemical supply companies and were at least 95% pure. The P_2O_5 in kieselguhr catalyst was conventional UOP No. 2 polymerization catalyst and was supplied by Universal Oil Products Company. In those reactions in which anhydrous $AlCl_3$ was used, precautions were taken to avoid contamination by atmospheric moisture. Water was carefully measured and added to systems in which $AlCl_3 \cdot H_2O$ was employed as the catalyst.

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