Separation of Positional Isomeric Dialkylbenzenes

ALKYLATION-DEALKYLATION

B. B. CORSON, W. J. HEINTZELMAN, R. C. ODIOSO, H. E. TIEFENTHAL, AND F. J. PAVLIK

Multiple Fellowship on Monomers, Koppers Co., Inc., Mellon Institute, Pittsburgh, Pa.

MOST *o-m-p* families of dialkylbenzenes boil too closely together to be separable by distillation. In many cases at least two of the positional isomers boil at essentially the same temperature. For example, the boiling points of the ortho, meta, and para isomers of the following dialkylbenzenes are, respectively: (*1*) dimethylbenzenes, 144.4°, 139.1°, 138.4° C.; methylethylbenzenes, 165.2°, 161.3°, 162.0°; diethylbenzenes, 183.4°, 181.1°, 183.8°; methylisopropylbenzenes, 178.2°, 175.1°, 177.1°; ethylisopropylbenzenes, 193°, 192°, 197°; diisopropylbenzenes, 203.8°, 203.2°, 210.4°; (*6*) methyl-*n*-propylbenzenes, 184.8°, 181.8°, 183.3°; and ethyl-*n*-propylbenzenes, 203°, 201°, 205°.

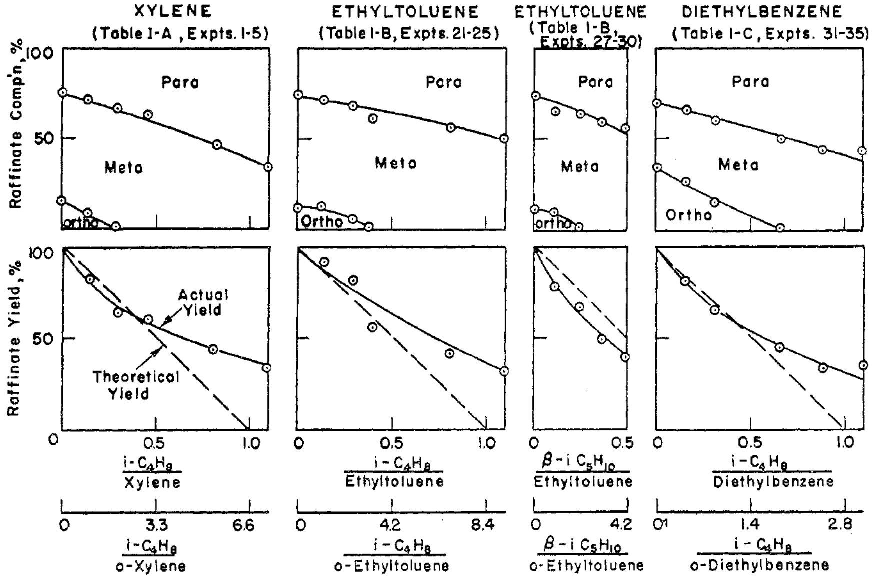


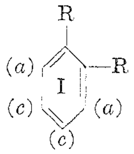
Figure 1. Effect of olefin–aromatic hydrocarbon molal ratio on composition and yield of raffinate

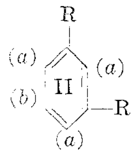
Other methods besides distillation can be used to separate certain of the dialkylbenzenes, the most common being crystallization (*5, 9*) and sulfonation-desulfonation (*14*). These alternative methods have been applied mainly to the separation of *m-p*-xylene mixtures. It is also claimed that the xylenes can be separated by virtue of differential adsorption-desorption, utilizing solid adsorbents (*8*).

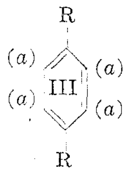
The present paper describes a method of separation involving the alkylation of a mixture of ortho, meta, and para isomers with a bulky alkylating agent in insufficient amount to react with all the isomers, with the result that only the most reactive isomer (or isomers) is alkylated. The reaction product is easily separable by distillation into nonalkylate (raffinate) and selective alkylate. Subsequent dealkylation of the selective alkylate regenerates the most active isomer (or isomers) of the initial mixture. This method was applied successfully to the separation of the xylenes, the ethyltoluenes, and the diethylbenzenes.

It is known that *o*- and *m*-xylenes can be *tert*-butylated, and it has been reported that *p*-xylene cannot be *tert*-butylated, or is *tert*-butylated with considerable difficulty (*3, 7*). As early as 1929 Nakatasuchi (*10*) described the partial separation of *p*-xylene from a mixture of *m*- and *p*-xylenes by means of selective *tert*-butylation, the raffinate containing 94% of the *p*-xylene content of the initial meta-para mixture. Of the simple alkyl groups, the *tert*-butyl group is the easiest to remove by known means (*4*). Recently there has been a revival of interest (*11–13*) in this separative method, due to the enhanced value of various alkylaromatics, especially *m*- and *p*-xylenes.

It is obvious by inspection of formulas I, II, and III that the (*a*) positions are sterically hindered with respect to alkylation with the bulky *tert*-butyl group, and that the (*b*) position is less active than the (*c*) positions because the (*c*) positions are para to ortho-para directing groups—in conclusion, that the order of ease of alkylation of dialkylbenzenes with the bulky *tert*-butyl group is ortho > meta > para.







The best catalyst for selective alkylation, according to the authors' experiments, is hydrogen fluoride (Table I,A, experiment 11). Concentrated sulfuric acid is probably next in usefulness as alkylating catalyst. The disadvantage of sulfuric acid is the by-product formation of polyisobutene and the loss of aromatic hydrocarbon through sulfonation. The *tert*-butyl chloride–ferric chloride alkylating system gave satisfactory results in some cases, but a certain amount of by-product of unknown composition was usually formed—probably a chlorinated polyisobutene. Aluminum chloride was used as catalyst in a few attempts to obtain selective ethylation. The raffinate showed a decreased amount of ortho isomer, but this decrease was due to isomerization and not to selective ethylation.

Effective groups for the separation of polyalkylbenzenes by selective alkylation are the *tert*-butyl and *tert*-amyl groups. Attempts to obtain selective alkylation by introducing the ethyl, isopropyl, and *s*-butyl groups failed.

Most of the selective alkylation experiments were made in the presence of concentrated sulfuric acid as catalyst. Figure 1 shows the relationship between the amount of *tert*-alkylating agent and the composition of the raffinate. About 2 moles of isobutene (or 2-methyl-2-butene) per mole of ortho isomer was found sufficient to produce ortho-free raffinate. As the amount of olefin was increased considerably beyond this value, the production of raffinate per increment of olefin decreased—presumably because of formation of polyalkylate or high-boiling olefin polymer (Figure 1). In the separation of 50-50 *m*-*p*-xylene by means of hydrogen fluoride–catalyzed *tert*-butylation, 1.5 moles of isobutene per mole of *m*-xylene gave a 90% yield of raffinate of essentially pure *p*-xylene (Table I,A, experiment 11).

The dealkylation of selective alkylate from a mixture of *o*-, *m*-, and *p*-dialkylbenzenes produces regenerated dialkylbenzene high in ortho content (Table I, experiments 1, 22, 26, 31, 32, 33, 35), together with regenerated olefin, whereas the dealkylation of selective alkylate from a mixture of meta and para isomers produces regenerated dialkylbenzene high in meta content (Table I,A, experiments 6 and 11), together with regenerated olefin.

The first attempts to dealkylate selective alkylate involved exchange alkylation in the presence of an acceptor and Filtrol. For example, a stirred mixture of alkylate, *o*-cresol, and Filtrol was heated under a 23-plate column and the regenerated dialkylbenzene was taken overhead as fast as formed. The liberated olefin alkylated the acceptor and remained in the pot. A certain amount of isomerization took place in this type of dealkylation. For example, in the regeneration of xylene from selective alkylate there was some isomerization (*2*) of xylene to ethylbenzene (Table I,A, experiments 1 to 5). Similar results have been reported by Bailey and Bennett (*2*).

Subsequently, vapor phase dealkylation over Filtrol at 350° to 450° C. was tried in the absence of acceptor. The yield of regenerated aromatic hydrocarbon was high, but part of the regenerated isobutene was isomerized and disproportionated to give a mixture of 80% isobutene, 15% 2-butene, and 5% isobutane. In addition, the regenerated dialkylbenzene was probably partially isomerized, as passage of a nonequilibrium mixture of ethyltoluene over Filtrol under conditions employed in dealkylation resulted in isomerization (Table II).

The best dealkylation procedure was to pass selective alkylate over Attapulgus clay at 375° to 475° C. at a liquid hourly space velocity of 1 to 2. Under these conditions the per pass yield of aromatic hydrocarbon and olefin ranged from 54 to 90%. The regenerated isobutene was 98% pure. Passage of a nonequilibrium mixture of ethyltoluene over Attapulgus clay under dealkylating conditions caused very little isomerization (Table II).

The extent of separation and recovery of isomers which can be obtained under optimal conditions is illustrated by two results obtained with a 50-50 mixture of *m*- and *p*-xylenes. Ferric chloride–catalyzed *tert*-butylation of 50-50 *m*-*p*-xylene gave a 44 mole % yield of raffinate whose *o*-*m*-*p* composition was 0-1-99 plus a 43 mole % yield of selective alkylate which on dealkyla-

Table I. Separation of Dialkylbenzenes by Alkylation-Dealkylation

	Selective Alkylation of Isomer Mixture							Dealkylation of Selective Alkylate		
	Dialkylbenzene Charged				Raffinate			Recovered Aromatic Hydrocarbon		
Expt.	Moles	*o*-*m*-*p* Compn., %	Catalyst, Moles	Alkylating agent, moles	Yield, mole %	*o*-*m*-*p* compn., %	Selective alkylate yield, mole %	Yield, mole %	*o*-*m*-*p* compn., %	Method
				A. Xylenes						
1	1	15-59-26	96% H_2SO_4, 0.5	i-C_4H_8, 0.14	83	9-62-29	6	92	82-11-1[a]	A
2	1	15-59-26	96% H_2SO_4, 0.5	i-C_4H_8, 0.29	64	1-65-34	18	94	59-31-1[a]	A
3	1	15-59-26	96% H_2SO_4, 0.5	i-C_4H_8, 0.46	60	0-63-37	22	88	52-37-1[a]	A
4	1	15-59-26	96% H_2SO_4, 0.5	i-C_4H_8, 0.82	44	0-46-54	34	96	31-60-4[a]	A
5	1	15-59-26	96% H_2SO_4, 0.5	i-C_4H_8, 1.10	33	0-34-66	45	92	27-64-7[a]	A
6	1	0-50-50	$FeCl_3$, 0.07	*t*-C_4H_9Cl, 1.0	44	0-1-99	43	84	0-98-2	B (400° C., 2 l.h.s.v.)[b]
7	1	0-50-50	$FeCl_3$, 0.07	i-C_4H_8, 1.0	78	0-51-49	0			
8	1	0-50-50	$FeCl_3$, 0.07	i-C_4H_8, 1.0 + HCl[c]	45	0-6-94	39			
9	1	0-50-50	$FeCl_3$, 0.07	i-C_4H_8, 1.0 + HCl[d]	77	0-42-58	4			
10	1	0-50-50	85% H_2SO_4, 3.5	*t*-C_4H_9OH, 1.0	77	0-42-58	22			
11	1.25	0-50-50	HF, 3.2	i-C_4H_8, 0.76	45	0-3-97	48	90	0-96-4	B (475° C., 1 l.h.s.v.)
				B. Ethyltoluenes						
12	2.6	18-52-30	$AlCl_3$, 0.1	C_2H_5Br, 0.7	69	12-60-28	18			
13	2.5	16-49-35	$AlCl_3$, 0.1	C_2H_5Br, 1.2[e]	56	10-60-30	34			
14	2.5	16-49-35	$AlCl_3$, 0.8	C_2H_5Br, 1.5	35	10-62-28	48			
15	1	16-49-35	96% H_2SO_4, 0.62	C_3H_6, 0.16	67	18-51-31	6			
16	1	16-49-35	96% H_2SO_4, 0.62	C_3H_6, 0.32	67	16-54-30	14			
17	1	16-49-35	96% H_2SO_4, 0.62	C_3H_6, 0.48	61	15-55-30	21			
18	1	16-49-35	96% H_2SO_4, 0.62	C_3H_6, 0.64	53	18-49-33	27			
19	1	12-62-26	96% H_2SO_4, 0.69	1-C_4H_8, 0.24	68	14-51-35	23			
20	1	12-62-26	96% H_2SO_4, 0.69	1-C_4H_8, 0.48	48	12-54-34	32			
21	1	12-62-26	96% H_2SO_4, 0.62	i-C_4H_8, 0.14	92	13-58-29	2			
22	1	12-62-26	96% H_2SO_4, 0.62	i-C_4H_8, 0.29	81	6-62-32	8	86	79-21-0	A
23	1	12-62-26	96% H_2SO_4, 0.62	i-C_4H_8, 0.40	55	0-61-39	20	85	54-46-0	A
24	1	12-62-26	96% H_2SO_4, 0.62	i-C_4H_8, 0.82	42	0-57-43	29	84	42-58-0	A
25	1	12-62-26	96% H_2SO_4, 0.62	i-C_4H_8, 1.1	32	0-50-50	30	86	36-54-0	A
26	5	22-48-30	96% H_2SO_4, 3.0	i-C_4H_8, 2.8	49	0-49-51	32	89	63-37-0	C (400° C., 2 l.h.s.v.)
								54	73-27-0	B (375° C., 2 l.h.s.v.)
27	1	12-62-26	96% H_2SO_4, 0.75	i-C_5H_{10}, 0.12	78	10-55-35	7			
28	1	12-62-26	96% H_2SO_4, 0.75	i-C_5H_{10}, 0.24	66	2-62-36	15			
29	1	12-62-26	96% H_2SO_4, 0.75	i-C_5H_{10}, 0.36	49	0-60-40	22			
30	1	12-62-26	96% H_2SO_4, 0.75	i-C_5H_{10}, 0.48	40	0-57-43	27			
				C. Diethylbenzenes						
31	1	35-36-29	96% H_2SO_4, 0.56	i-C_4H_8, 0.16	81	27-39-34	8	86	92-8-0	A
32	1	35-36-29	96% H_2SO_4, 0.56	i-C_4H_8, 0.32	65	16-45-39	18	70	89-11-0	A
33	1	35-36-29	96% H_2SO_4, 0.56	i-C_4H_8, 0.66	45	2-48-50	31	85	81-19-0	A
34	1	35-36-29	96% H_2SO_4, 0.56	i-C_4H_8, 0.88	33	0-45-55	31			
35	1	35-36-29	96% H_2SO_4, 0.56	i-C_4H_8, 1.1	35	0-45-55	37	77	75-25-0	A

[a] This regenerated xylene contained about 5% of ethylbenzene.
[b] l.h.s.v. = liquid hourly space velocity (volume of liquid per volume of catalyst per hour).
[c] Xylene was first saturated with hydrogen chloride; isobutylene was then added.
[d] Hydrogen chloride and isobutylene were added simultaneously.
[e] Alkylation was run at 50°; stirred for 1 hour.

tion gave an 84 mole % yield of xylene whose *o-m-p* composition was 0-98-2 (Table I,A, experiment 6). This corresponds to an 88% recovery of *p*-xylene of 99% purity and a 72% recovery of *m*-xylene of 98% purity. With hydrogen fluoride as alkylating catalyst, the recovery of 97% pure *p*-xylene was 90% and that of 96% pure *m*-xylene was 86% (Table I,A, experiment 11).

Table II. Isomerization of Ethyltoluene

Experiment	1	2	3	4
Catalyst	Filtrol X-358c		Attapulgus clay	
Temperature, ° C.	400	400	375	425
L.H.S.V.	2	4	1	1
Compn. liquid product, wt. %				
Light ends	4.7	4.3	0	0
Ethyltoluene	95.3	95.7	100	100
Isomer compn. (*o-m-p*)	41-48-11	49-44-7	65-35-0	64-36-0
Ethyltoluene charge (*o-m-p*)	69-30-1	69-30-1	69-30-1	69-30-1

EXPERIMENTAL

Materials. The propylene, 1-butene, and isobutene were C.P. grade hydrocarbons obtained from the Matheson Co., Inc. The 2-methyl-2-butene was prepared by heating a mixture of 800 grams (9.1 moles) of *tert*-amyl alcohol, 500 ml. of 96% sulfuric acid, and 1000 ml. of water, and distilling off the hydrocarbon as formed. Redistillation of the olefin through a 27-plate column at 10 to 1 reflux ratio gave 405 grams (64% yield) of 2-methyl-2-butene, boiling point 37° to 39° C. at atmospheric pressure. The Filtrol catalysts were obtained from Filtrol Corp., Los Angeles, Calif.; the Attapulgus clay from Attapulgus Minerals and Chemicals Corp., Philadelphia, Pa.

Selective Alkylation in Presence of Sulfuric Acid. Olefin (propylene, isobutene, 1-butene, or 2-methyl-2-butene) was passed into a cold (0° to 10° C.) stirred mixture of aromatic hydrocarbon (xylene, ethyltoluene, or diethylbenzene) and 96% sulfuric acid until the required amount of olefin had been absorbed. The reaction product was poured onto crushed ice, and the hydrocarbon layer was washed with water, refluxed for 1 hour with 10% aqueous NaOH, washed with water, and distilled (Table I,A, 1 to 5; I,B, 15 to 30; I,C, 31 to 35).

***tert*-Butylation of 50-50 *m-p*-Xylene with *tert*-Butyl Chloride in Presence of Ferric Chloride.** To a stirred mixture of 106 grams (1 mole) of 50-50 *m-p*-xylene and 12 grams (0.07 mole) of ferric chloride was added, at 0° to 10° C. during 0.5 hour, 82.5 grams (1 mole) of *tert*-butyl chloride. After 2.5 hours of additional stirring at 0° to 10° C., the reaction product was stirred into a mixture of 100 grams of concentrated hydrochloric acid and 100 grams of crushed ice. The hydrocarbon layer was separated, washed successively with water, 10% aqueous sodium hydroxide, and water, and distilled (Table I,A, experiment 6).

***tert*-Butylation of 50-50 *m-p*-Xylene with Isobutene in Presence of Ferric Chloride.** Isobutene (56 grams, 1 mole) was passed into a stirred mixture of 106 grams (1 mole) of 50-50 *m-p*-xylene and 12 grams (0.07 mole) of ferric chloride at 0° to 10° C. during 1.5 hours. The reaction product was stirred into a mixture of 150 ml. of concentrated hydrochloric acid and 100 grams of crushed ice. The hydrocarbon layer was separated, washed with 10% aqueous NaOH, and water, and distilled (Table I,A, 7 to 9).

***tert*-Butylation of 50-50 *m-p*-Xylene with *tert*-Butyl Alcohol in Presence of 85% Sulfuric Acid.** To a stirred mixture of 106 grams (1 mole) of 50–50 *m-p*-xylene and 74 grams (1 mole) of *tert*-butyl alcohol was added, at 0° to 10° C. during 1 hour, 210 ml. (3.5 moles) of 85% sulfuric acid. After 14 additional hours of stirring at room temperature, the hydrocarbon layer was separated, washed with water, and distilled (Table I,A, 10).

Selective *tert*-Butylation in Presence of Hydrogen Fluoride. A mixture of 106 grams (1 mole) of 50-50 *m-p*-xylene and 50 grams (2.6 moles) of HF was stirred at 0° to 5° C. in a copper flask while 37 grams (0.7 mole) of isobutene was passed into the mixture during 1.5 hours. The reaction product was poured onto 400 grams of crushed ice (precooled with dry ice), and the hydrocarbon layer was separated, washed with water, dilute aqueous NaOH, and water, and distilled (Table I,A, 11).

Ethylation of Ethyltoluene. A mixture of isomeric ethyltoluenes, ethyl bromide, and aluminum chloride was stirred for 20 hours at 0° to 10° C. The reaction product was poured into iced HCl, and hydrocarbon layer separated, washed with water, 10% aqueous NaOH, and water, and distilled (Table I,B, 12 to 14).

Isomerization of Ethyltoluene. The small change in isomer composition produced by the above ethylation experiments was probably due to isomerization and not to selective ethylation, as shown by the following experiment. A mixture of 240 grams (2 moles) of ethyltoluene (*o-m-p*-18-55-27), 46 grams (0.5 mole) of toluene, 124 grams (0.84 mole) of diethyltoluene, and 10.3 grams (0.08 mole) of anhydrous aluminum chloride was stirred for 24 hours at 27° C., and then poured into ice water. The hydrocarbon layer was dried and distilled to give 216 grams (90% yield) of ethyltoluene; *o-m-p* composition 11-63-26.

***tert*-Butyl-*o*-xylene and *tert*-Butyl-*m*-xylene.** Into a stirred 0° to 10° C. mixture of 109 grams (1.03 moles) of *o*- or *m*-xylene and 37 grams (0.36 mole) of 96% sulfuric acid was passed 58 grams (1.03 moles) of isobutene during 1 hour. The hydrocarbon layer was separated, washed with water, refluxed for 1 hour with 20% aqueous sodium hydroxide, and distilled at atmospheric pressure. The *tert*-butyl-*o*-xylene (129 grams, 77% yield) was collected at 206° to 212° C.; n_D^{25} 1.4965. The *tert*-butyl-*m*-xylene (71 grams, 44% yield) distilled at 205° to 206° C.; n_D^{25} 1.4926. The infrared spectra of the alkylates showed *tert*-butyl-*o*-xylene to be a 1,2,4-trisubstituted benzene and *tert*-butyl-*m*-xylene to be a 1,3,5-trisubstituted benzene.

Liquid Phase Debutylation of Selective Alkylate in Presence of Filtrol as Catalyst and Cresol as Acceptor (Method A). A stirred mixture of 0.4 mole of selective alkylate, 3.9 moles of *o*-cresol, and 49 grams of Filtrol X-202 was heated under a 27-plate column; liberated aromatic hydrocarbon was removed overhead as formed (Table I,A, 1 to 5; I,B, 22 to 25; I,C, 31 to 33, 35).

Vapor Phase Debutylation of Selective Alkylate over Attapulgus Clay (Method B) and Filtrol (Method C). Selective alkylate was passed over catalysts and liberated gas and debutylated aromatic hydrocarbon (after distillation) were analyzed by infrared spectroscopy (Table I,A, 6, 11; I,B, 26).

Distillation of Products. The alkylation and dealkylation catalyzates were distilled through a 27-plate column at atmospheric pressure and 5 to 1 reflux ratio. The fractions were collected as follows: xylenes, 130° to 145° C.; ethyltoluenes, 152° to 168°; diethylbenzenes, 170° to 185°; diethyltoluenes, 185° to 202°; *tert*-butylxylenes, 200° to 215°; isopropylethyltoluenes, 204° to 225°; *tert*-butylethyltoluenes, 212° to 225°; *s*-butylethyltoluenes, 215° to 226°; *tert*-amylethyltoluenes, 215° to 230°; *tert*-butyldiethylbenzenes, 226° to 237°.

Isomerization of Ethyltoluene under Conditions Employed in Dealkylation of Selective Alkylate. Two samples of a mixture of ethyltoluenes were passed separately over Filtrol and Attapulgus clay. Light ends were removed by topping through a 45-plate column at 10 to 1 reflux ratio, and the bottoms were analyzed by infrared spectroscopy (Table II).

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