

## EFFECT OF CATALYST AND CONDITIONS ON THE COMPOSITION OF BENZENE AND TOLUENE ALKYLATES PRODUCED BY ETHYLATION

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This paper concerns the isomer composition of the diethylbenzene and ethyltoluene fractions obtained in the ethylation of benzene, ethylbenzene, and toluene. The composition was found to be dependent on the catalyst and to be unpredictable by the simple rules of orientation. The isomer composition was determined by infrared spectroscopy.

Three fixed-bed catalysts (alumina-silica, "solid phosphoric acid," and iron phosphate) were studied at superatmospheric pressure, and aluminum chloride was tested at atmospheric pressure. The data in Table I reveal the relative extent of mono- and poly-ethylation as a function of catalyst and molal feed ratio.

The diethylbenzene fraction produced by the ethylation of benzene over the fixed-bed catalysts contained *sec*-butylbenzene; this by-product was not due to C<sub>4</sub>-olefins originally present in the ethylene feed. Mass spectrographic analysis of the ethylene feed showed that its C<sub>4</sub>-hydrocarbon content was less than 0.1 molal-% whereas the amount of *sec*-butylbenzene produced by the iron phosphate catalyst in the ethylation of benzene would have required at least 1.4 molal-% of C<sub>4</sub>-olefin. There was therefore a certain amount of dimerization of the ethylene, the relative amount depending on the catalyst, and the resultant dimer butylated the benzene. The aluminum chloride-catalyzed ethylation of benzene was not accompanied by this side-reaction under the conditions employed. Diethylbenzene alkylate produced in the ethylation of benzene by alumina-silica contained only 5% of *sec*-butylbenzene whereas the alkylates produced by "solid phosphoric acid" and iron phosphate contained 6 and 8.2 times as much, respectively (Table II). The preponderant diethylbenzene isomer in the alumina-silica and aluminum chloride dialkylates was the *m*-isomer, whereas it was the *o*-isomer in the "solid phosphoric acid" and iron phosphate dialkylates (Table II).

In the monoethylation of toluene and of ethylbenzene, as in the diethylation of benzene, alumina-silica and aluminum chloride favored *m*-alkylation, whereas "solid phosphoric acid" and iron phosphate favored *o*-alkylation (Table III). No attempt was made to determine the amount of *sec*-butyltoluene or *sec*-butylethylbenzene produced in the monoethylation of toluene and ethylbenzene, respectively.

### EXPERIMENTAL

*Catalysts.* The alumina-silica catalyst (12% Al<sub>2</sub>O<sub>3</sub>-88% SiO<sub>2</sub>, 16-35 mesh) was a product of the Davison Chemical Company. The "solid phosphoric acid" catalyst was the Universal Oil Products Company catalyst No. 2, employed as 5-10 mesh material. The iron phosphate catalyst was prepared by digesting iron oxide with phosphoric acid at about 250°, drying at 350° and granulating to 5-10 mesh (1).

TABLE I  
DATA ILLUSTRATIVE OF EXTENT OF MONO- AND POLY-ETHYLATION

CATALYST	FEED RATIO <sup>a</sup>	HYDROCARBON ALKYLATE OF		
		Benzene <sup>b</sup>	Ethylbenzene <sup>c</sup>	Toluene <sup>d</sup>
Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> .....	10/1	10/1/0.3	4/1	7/1
H <sub>3</sub> PO <sub>4</sub> .....	10/1	38/1/0.3	4/1	9/1
FePO <sub>4</sub> .....	10/1	25/1/0.3	5/1	10/1
AlCl <sub>3</sub> .....	10/1	35/1/0.8	11/1	17/1
AlCl <sub>3</sub> .....	5/1	19/1/0.4	—	—
AlCl <sub>3</sub> .....	1/1	4/1/0.1	—	—

<sup>a</sup> Aromatic hydrocarbon/ethylene molal feed ratio. <sup>b</sup> Mono-/di-/poly-ethylbenzene molal ratio in product; poly- calculated as tri-. <sup>c</sup> Di-/poly-ethylbenzene molal ratio in product; poly- calculated as tri-. <sup>d</sup> Mono-/poly-ethyltoluene molal ratio in product; poly- calculated as di-.

TABLE II  
MOLAL-% COMPOSITION OF BY-PRODUCT DIETHYLBENZENE<sup>d</sup> ALKYLATE PRODUCED IN THE ETHYLATION OF BENZENE

CATALYST	FEED RATIO <sup>a</sup>	SBB <sup>b</sup>	o-DEB <sup>c</sup>	m-DEB	p-DEB	SBB-FREE BASIS		
						o-DEB	m-DEB	p-DEB
Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> .....	10/1	5	18	56	21	19	59	22
H <sub>3</sub> PO <sub>4</sub> .....	10/1	30	29	24	17	41	34	25
FePO <sub>4</sub> .....	10/1	41	25	20	14	42	34	24
AlCl <sub>3</sub> .....	10/1	0	8	60	32	8	60	32
AlCl <sub>3</sub> .....	5/1	0	4	68	28	4	68	28
AlCl <sub>3</sub> .....	1/1	0	7	64	29	7	64	29

<sup>a</sup> Benzene/ethylene molal feed ratio.

<sup>b</sup> SBB = *sec*-butylbenzene.

<sup>c</sup> DEB = diethylbenzene

<sup>d</sup> B.P., 160-185°/740.

TABLE III  
MOLAL-% COMPOSITION OF ETHYLTOLUENE AND DIETHYLBENZENE PRODUCED IN THE MONOETHYLATION<sup>a</sup> OF TOLUENE AND ETHYLBENZENE, RESPECTIVELY

CATALYST	ETHYLTOLUENES (B.P. 145-175°/740 MM.)			DIETHYLBENZENES (B.P. 160-185°/740 MM.)		
	o-ET <sup>b</sup>	m-ET	p-ET	o-DEB <sup>c</sup>	m-DEB	p-DEB
Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> .....	29	50	21	33	37	30
H <sub>3</sub> PO <sub>4</sub> .....	46	32	22	43	29	28
FePO <sub>4</sub> .....	48	30	22	43	30	27
AlCl <sub>3</sub> .....	11	64	25	3	64	33

<sup>a</sup> Aromatic hydrocarbon/ethylene molal feed ratio = 10/1.

<sup>b</sup> ET = ethyltoluene.

<sup>c</sup> DEB = diethylbenzene.

*Method of ethylation.* Benzene, toluene, and ethylbenzene were ethylated continuously over fixed-bed catalysts (120-hour continuous operation), as previously described (2). The conditions were: 900 p.s.i., 275°, 2 liquid hourly space velocity, and 10/1 aromatic hydrocarbon/ethylene molal feed ratio. The ethylene consumption was about 90%. Ethylation in presence of aluminum chloride was studied batch-wise at atmospheric pressure at about 80° in glass equipment, ethylene being passed into a stirred mixture of aromatic hydrocarbon and 1% catalyst.

*Distillation of alkylates.* The *sec*-butylbenzene-diethylbenzene (so-called diethylbenzene) fraction was separated from the reaction mixture by distillation through a 25-plate packed column, collecting material boiling at 160–185°/740 mm. The ethyltoluene fraction was collected at 145–175°/740 mm.

*Infrared analytical technique.* A Perkin-Elmer Model 12-A infrared spectrometer, equipped with rock salt prism, d. c. breaker type amplifier, and Brown recorder was used. The cells were about 0.08 mm. thick. Concentrations of 0.2 to 1.0 g. of authentic hydrocarbon per 10 g. of isooctane were employed in the calibration of the method; the unknown con-

TABLE IV  
INFRARED ANALYTICAL DATA ON MIXTURES OF KNOWN COMPOSITION CONTAINING  
COMPONENTS OF DIETHYLBENZENE FRACTION

SAMPLE	MOLAR % COMPOSITION							
	Actual				Found <sup>b</sup>			
	SBB	<i>o</i> -DEB	<i>m</i> -DEB	<i>p</i> -DEB	SBB	<i>o</i> -DEB	<i>m</i> -DEB	<i>p</i> -DEB
1	0.0	32.9	33.8	33.3	0.0	31.7	34.8	33.5
2	0.0	39.6	39.3	21.1	0.0	39.3	39.9	21.2
3	24.4	23.8	26.3	25.5	23.7	26.3	27.7	23.7
4 <sup>a</sup>	24.4	23.8	26.3	25.5	24.2	26.3	27.4	24.8
5	4.0	15.4	53.3	27.3	4.6	16.4	51.3	27.7

<sup>a</sup> Analyzed 6 weeks after calibration of method.

<sup>b</sup> Standard deviations  $\left(\pm\sqrt{\frac{\sum d^2}{n-1}}\right)$  of SBB and *o*-, *m*-, and *p*-DEB components were  $\pm 0.7$ ,  $\pm 2.0$ ,  $\pm 1.5$ , and  $\pm 0.6\%$ , respectively.

centrations were 1 to 2 g. per 10 g. of isooctane. A calibration curve (optical density *vs.* concentration) was set up for each component at its key wavelength, and the interference of each component at the key wavelengths of the other components was measured and interference absorption coefficients were calculated. Wavelengths of 13.3, 12.6, 12.1, 14.7, 13.3, 12.8, and 12.3 microns and slit widths of 1.25, 1.00, 0.90, 1.60, 1.16, 1.04, and 0.87 mm. were used in the determination of *o*-, *m*-, *p*-diethylbenzene, *sec*-butylbenzene, *o*-, *m*-, and *p*-ethyltoluene, respectively. Tables IV and V present typical analytical data obtained with mixtures of known composition.

*Spectrographic hydrocarbon standards.* *sec*-Butylbenzene was separated from the diethylbenzene fraction from the ethylation of benzene over iron phosphate by fractionation through a Podbielniak Hyper-Cal column at reflux ratio of 20 to 1. The melting points of its mono- and di-acetamino derivatives (3) were 125–126° and 191–192°, respectively. *o*-Diethylbenzene was obtained from the National Bureau of Standards. *m*-Diethylbenzene was separated from a mixture of isomeric diethylbenzenes by sulfonation, followed by purification and hydrolysis of barium *m*-diethylbenzene sulfonate (4), the regenerated hydrocarbon being distilled through a 45-plate packed column at 10 to 1 reflux ratio. *p*-Diethylbenzene was prepared by the following synthetic route: ethylbenzene, *p*-ethylacetophenone,

TABLE V  
INFRARED ANALYTICAL DATA ON MIXTURES OF KNOWN COMPOSITION CONTAINING  
*o*-, *m*-, AND *p*-ETHYLTOLUENES

SAMPLE	MOLAL-% COMPOSITION					
	Actual			Found <sup>b</sup>		
	<i>o</i> -ET	<i>m</i> -ET	<i>p</i> -ET	<i>o</i> -ET	<i>m</i> -ET	<i>p</i> -ET
1	23.2	52.0	24.8	22.8	53.2	23.7
2 <sup>a</sup>	23.2	52.0	24.8	22.6	53.2	24.1
3	33.2	26.8	40.0	32.5	25.3	42.2
4 <sup>a</sup>	33.2	26.8	40.0	32.3	26.2	41.5

<sup>a</sup> Analyzed 4 weeks after calibration of method.

<sup>b</sup> Standard deviations ( $\pm \sqrt{\frac{\sum d^2}{n-1}}$ ) of *o*-, *m*-, and *p*-isomers were  $\pm 0.8$ ,  $\pm 1.4$ , and  $\pm 1.7\%$ , respectively.

TABLE VI  
CONSTANTS OF SPECTROGRAPHIC HYDROCARBON STANDARDS

HYDROCARBON	B.P., °C. <sup>a</sup>	$n_D^{20}$	$d_4^{20}$
<i>sec</i> -Butylbenzene.....	173	1.4901	0.8608
<i>o</i> -Diethylbenzene <sup>b</sup> .....	—	—	—
<i>m</i> -Diethylbenzene.....	182	1.4960	.8638
<i>p</i> -Diethylbenzene.....	184	1.4951	.8620
<i>o</i> -Ethyltoluene.....	165	1.5049	.8804
<i>m</i> -Ethyltoluene.....	161	1.4968	.8643
<i>p</i> -Ethyltoluene.....	162	1.4952	.8609

<sup>a</sup> Distillation temperatures at 760 mm.

<sup>b</sup> Standard sample (0.05  $\pm$  0.03 mole % impurity), National Bureau of Standards.

TABLE VII  
CONSTANTS OF CERTAIN INTERMEDIATES

INTERMEDIATE	B.P., °C. <sup>a</sup>	$n_D^{20}$	$d_4^{20}$
<i>o</i> -Ethylphenethyl alcohol.....	127.5	1.5357	1.0116
<i>m</i> -Ethylphenethyl alcohol.....	125	1.5291	0.9986
<i>p</i> -Ethylphenethyl alcohol.....	125	1.5275	.9935
<i>o</i> -Methylstyrene.....	66	1.5450	.9106
<i>m</i> -Methylstyrene.....	67	1.5419	.8989
<i>p</i> -Methylstyrene.....	67	1.5428	.8760

<sup>a</sup> Distillation temperatures at 20 mm.

*p*-ethyl- $\alpha$ -hydroxyethylbenzene, *p*-ethylstyrene (5), *p*-diethylbenzene (hydrogenation at 30° and 70 atmospheres with nickel, and distillation through a 45-plate packed column at 10 to 1 reflux ratio). The general procedure for the preparation of the *ethyltoluene* isomers follows. The Grignard reagent from the appropriate bromotoluene was reacted with ethereal

ethylene oxide and the product was hydrolyzed by ice and sulfuric acid. The alcohol ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OH}$ ) was distilled through a 27-plate packed column at 20 mm. and subsequently dehydrated by heating at about  $220^\circ$  in an oil-bath with solid potassium hydroxide (6). The crude vinyltoluene was hydrogenated at  $30^\circ$  and 70 atmospheres with nickel and the resulting ethyltoluene was distilled through a 45-plate packed column at 10 to 1 reflux ratio. The physical constants (Table VI) compared favorably with recent data (7, 8, 9, 10). Table VII lists data on certain intermediates.

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#### SUMMARY

1. The isomer compositions of diethylbenzene and of ethyltoluene alkylates were found to be dependent on the catalyst. Alumina-silica and aluminum chloride favored the production of *m*-isomers, whereas iron phosphate and "solid phosphoric acid" catalysts favored the *o*-isomers.

2. A diethylbenzene cut obtained as by-product in the monoalkylation of benzene by ethylene over the three fixed-bed catalysts contained *sec*-butylbenzene resulting from dimerization of the ethylene and subsequent alkylation of the benzene by the ethylene dimer.

3. "Solid phosphoric acid" and iron phosphate catalysts produced more *sec*-butylbenzene than did alumina-silica; aluminum chloride alkylate did not contain *sec*-butylbenzene.

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