

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL CO. (INDIANA)]

Disproportionation of Alkylbenzenes. V. Ethylbenzene Interaction with Xylenes

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Ethylbenzene, in the presence of a xylene isomer, disproportionates under the influence of hydrogen fluoride plus excess boron trifluoride, into products that are dependent upon reaction conditions and the nature of the particular xylene isomer. At low temperatures and short contact times ethylbenzene and *o*-xylene yield benzene and 1,2-dimethyl-4-ethylbenzene. However, ethylbenzene and *p*-xylene or *m*-xylene give only benzene and 1,3-diethylbenzene. The inactivity of *p*-xylene is attributed to the steric blocking of all alkylation positions by an adjacent methyl group; that of *m*-xylene to the formation of a positively charged ion. At higher temperatures or longer times, 1,3,5-ethylxylene forms as the equilibrium-favored product and the xylenes are isomerized to the *meta* isomer. A mixture of the four 8-carbon alkylbenzenes can thereby be converted into three pure compounds—benzene, *m*-xylene and 1,3,5-ethylxylene—which are readily separable by distillation.

Ethylbenzene, under the influence of hydrogen fluoride plus boron trifluoride, disproportionates readily by transalkylation into benzene and diethylbenzene. Because ethylbenzene usually occurs in admixture with the isomeric xylenes, it was of interest to determine how the presence of xylenes affects this reaction. At temperatures below 80°, the xylenes are inert to HF-BF₃ in the sense that methyl groups do not move from ring to ring.¹ Therefore, when mixed with ethylbenzene under transalkylating conditions, the xylenes do not donate methyl groups but merely accept migrating ethyl groups. The only additional product, then, is ethylxylene. In this study mixtures of ethylbenzene with each of the individual xylenes were stirred with hydrogen fluoride plus excess boron trifluoride for various times and temperatures. The object was to determine the first-formed products and the final equilibrium composition.

Experimental

Ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene were purchased from Eastman Kodak Co. (White Label Grade). Commercial grades of hydrogen fluoride, 99.6% pure, and boron trifluoride, about 99% pure, were obtained from the Harshaw Chemical Co.

Hydrocarbon, hydrogen fluoride and boron trifluoride were charged to a 1000-ml. Hastelloy autoclave and the mixture was stirred at a controlled temperature. After reaction, the contents were withdrawn into crushed ice and the hydrocarbon layer was separated from the aqueous acid phase. The hydrocarbon product was distilled into successive carbon number fractions. The eight-carbon fraction was analyzed by ultraviolet absorption and the ten-carbon fraction by infrared absorption.

Discussion

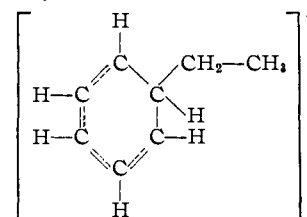
Table I summarizes the results. Mixtures of ethylbenzene and *m*-xylene behave much like ethylbenzene alone.² In the presence of hydrogen fluoride plus excess boron trifluoride, the *m*-xylene, because it is tied up as a positively charged ion, accepts a migrating positively charged ethyl group more slowly than does ethylbenzene. Hence, the primary product is diethylbenzene and the rate of formation of ethylxylene is slow. If reaction time is lengthened or if all reactions are accelerated by an increase in temperature, 1,3,5-ethylxylene forms as the equilibrium-favored product.

Even at room temperature *o*- and *p*-xylene slowly

isomerize to *m*-xylene. At long contact times any mixture of xylenes with ethylbenzene is almost completely converted into benzene, *m*-xylene and 1,3,5-ethylxylene. But the isomerization reaction is slow enough at room temperature to permit some of the primary disproportionation products to be observed. *o*-Xylene and *p*-xylene are much less basic than *m*-xylene, are not tied up to the same extent as positive ions, and hence are free to take on a migrating ethyl group.

In agreement with this concept, *o*-xylene rapidly accepts an ethyl group to form 1,2-dimethyl-4-ethylbenzene.

On the other hand, *p*-xylene does not accept an ethyl group—diethylbenzene rather than 1,4-dimethyl-2-ethylbenzene is formed. This lack of reactivity of *p*-xylene probably is due to steric hindrance; there are no positions in *p*-xylene which are not blocked by a vicinal methyl group. Schlatter and Clark³ have shown that the addition of a bulky alkylating group, such as *t*-butyl, to a position adjacent to a methyl group is difficult. Thus *o*-*t*-butyltoluene is not produced from toluene; also *o*- and *m*-xylene are *t*-butylated in preference to *p*-xylene. The disproportionation reaction is actually transalkylation in which the alkylating agent is the ethylbenzene cation¹



This ion is at least as bulky as the *t*-butyl group and therefore does not readily add to a position adjacent to a methyl group.

Isomer Separation

The results obtained in these transalkylation reactions demonstrate that a mixture of the eight-carbon alkylbenzene isomers can be converted by HF-BF₃ into different products, depending on the conditions chosen. At high temperatures or prolonged reaction times the sole products are benzene, *m*-xylene and 1,3,5-ethylxylene—all of which are readily separable by distillation. If the eight-carbon mixture is first fractionated to remove the

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(2) D. A. McCaulay and A. P. Lien, *ibid.*, **79**, Nov. 20 (1957).

(3) M. J. Schlatter and R. D. Clark, *ibid.*, **75**, 361 (1953).

TABLE I
DISPROPORTIONATION OF ETHYLBENZENE IN THE PRESENCE OF XYLENE AND 150 VOLUME % HF

Feed composition, mole %									
<i>o</i> -Xylene	0	0	0	20	20	75	75	75	0
<i>m</i> -Xylene	67	33	75	40	40	0	0	0	0
<i>p</i> -Xylene	0	34	0	20	20	0	0	0	50
Ethylbenzene	33	33	25	20	20	25	25	25	50
Temp., °C.	24	24	63	25	50	0	20	65	20
Reaction time, min.	30	30	30	4160	240	90	60	60	90
Moles BF ₃ per mole aromatic	1.5	1.1	1.0	1.6	2.0	1.1	1.1	1.1	1.1
Product distribution, mole %									
Benzene	15	15.5	22	20	19	12.5	18	24	21
C ₈ Fraction	70	69	56	60	62	74	63	52	58
C ₁₀ Fraction	15	15.5	22	20	19	13.5	19	24	21
Composition of C ₈ fraction, %									
<i>o</i> -Xylene	0	0	4	0	1	69	16	1	0
<i>m</i> -Xylene	77	71	83	98	95	15	73	95	64
<i>p</i> -Xylene	2	18	7	1	3	0	0	0	17
Ethylbenzene	10	11	6	Trace	1	16	11	4	19
Composition of C ₁₀ fraction, %									
1,3-Diethylbenzene	85	90	0	0	0	10	Trace	0	93
1,3-Dimethyl-5-ethylbenzene	15	10	100	100	100	Trace	20	100	7
1,2-Dimethyl-4-ethylbenzene	0	0	0	0	0	90	80	0	0
1,4-Dimethyl-4-ethylbenzene	0	0	0	0	0	0	0	0	0
1,3-Dimethyl-4-ethylbenzene	0	0	0	0	0	0	0	0	0
Ethylbenzene converted, %	85	90	88	99+	97	60	75	96	75

higher boiling *o*-xylene, then the lower-boiling fraction—ethylbenzene, *m*- and *p*-xylene—can be transformed under mild conditions into benzene, *m*- and *p*-xylene and 1,3-diethylbenzene. Also, under mild conditions, the *o*-xylene can be con-

verted by transalkylation with ethylbenzene into 1,2-dimethyl-4-ethylbenzene, another pure ten-carbon alkylbenzene not readily obtained by direct alkylation.

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[CONTRIBUTION FROM THE WALKER LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

The Metalation and Addition Reactions of Allylbenzene and Propenylbenzene with Butyllithium and Lithium Amide

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1-Phenylallyllithium has been prepared in liquid ammonia and in ether. Its reactions with proton donors and with carbon dioxide are very similar to those of 1-phenylallylsodium and cinnamylsodium leading to the conclusion that the compound is probably ionic in both solvents, albeit existing as ion pairs or higher aggregates in ether. A possible explanation is offered for the formation of propenylbenzene from the quenching of 1-phenylallyllithium in a kinetically controlled reaction. Propenylbenzene undergoes addition reactions with butyllithium and is quite unreactive to lithium amide.

Although a number of examples have appeared of allylic rearrangements of organolithium compounds,¹ those which have been reported do not afford a good basis for comparison with allylic rearrangements of other organometallic compounds. The most extensive studies of allylic rearrangements of organometallic compounds have been concerned with the cinnamyl and butenyl Grignard reagents² and cinnamylsodium^{3a,b} as well as 1-phenylallylsodium.^{3a,c} Other reactions of allylic derivatives of so-

dium,^{3b,c,4} potassium⁵ and cesium⁶ also have been reported.

That the inorganic alkali metal cation can have an effect on the behavior of the organic anion has been emphasized.⁷ In view of the marked differ-

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