The Isomerization of the Diethylbenzenes Using Zeolite Catalysts[1]

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Partially multivalent metal cation exchanged, partially decationized Type Y zeolites catalyze the isomerization of diethylbenzenes. The absence of stable zeolite catalyst–reactant complexes permits the ready formation of 1,2,4-triethylbenzene through the transalkylation of the diethylbenzenes. This isomer, which has not been reported in previous studies with Lewis acid catalysts, dealkylates to the equilibrium distributions of the diethylbenzene isomers. The formation of complexes between Lewis acid catalysts and alkyl aromatics depends upon the ring position of the alkyl groups and has likely influenced previously reported reaction mechanisms. No isomerization occurs with zeolite catalysts in the absence of transalkylation. The equilibrium product distribution at 170° consists of approximately 50 mol % transalkylate: the diethylbenzene fraction contains about 5% *ortho*, 62% *meta*, and 33% *para* isomers and the triethylbenzene fraction consists of 31% 1,2,4 and 69% 1,3,5 isomers.

Despite the large volume of work published on the isomerization of the diethylbenzenes, it is still not clear what part transalkylation plays in the final isomer distribution. Allen and Yats have demonstrated that the isomerization of alkylaromatics involves both intramolecular and intermolecular rearrangements, the relative contributions of which depend upon the structure of the alkylaromatic.[2,3] Olah, *et al.*, attribute the isomerization of diethylbenzenes solely to a sequence of intramolecular 1,2 shifts even though transalkylation accounts for as much as 40 mol % of the products.[4] On the other hand, Unseren and Wolf have shown that 1,2 shifts can only compete with transalkylation and that ethylbenzene transalkylates more rapidly than it isomerizes.[5] It is important to note that all previous investigations failed to isolate and appreciate the importance of the 1,2,4-trisubstituted isomer in the transalkylation products.

It is generally agreed that the alkylation of aromatic hydrocarbons and the related isomerization and transalkylation of the alkyl-substituted aromatics with acidic catalysts involve electron-deficient intermediates, *i.e.*, carbonium ions. This study was undertaken with the objective of closely following the composition of the transalkylated products during the isomerization of diethylbenzenes with a crystalline catalyst derived from Type Y zeolite. It was hoped that the data would reveal the reaction path of the isomerization and subsequently shed light on the reaction mechanism and the nature of the intermediate species.

Results

Previous work has shown that the catalyst used in this study, partially multivalent cation exchanged, partially decationized Type Y zeolite possesses unusually strong catalytic activity for the alkylation of aromatic hydrocarbons with low molecular weight olefins.[6] Mineral acid promoted and nonpromoted amorphous silica–alumina catalysts require higher temperature for the transalkylation of alkyl-substituted aromatics than for alkylation. On the other hand, the zeolite catalyst is sufficiently active to catalyze isomerization and transalkylation reactions under alkylation conditions. Products rich in the *meta*-substituted isomers are frequently obtained, much the same as with promoted Lewis acid catalysts.

Initial experiments with diethylbenzenes were carried out to determine at what temperature isomerization occurs in the absence of transalkylation. Neither isomerization nor transalkylation of *p*-diethylbenzene occurred at 50°. At 100°, 2 mol % of the diethylbenzene was transalkylated to ethylbenzene and triethylbenzene, but no isomerization occurred even after a reaction time of 24 hr. The triethylbenzene fraction contained only one isomer, the 1,2,4-triethylbenzene. When the temperature was raised to 150° for 16 hr, 30 mol % of the diethylbenzene was transalkylated, accompanied by 10% isomerization of the diethylbenzene fraction. Close examination of the transalkylated products revealed the existence of two trisubstituted isomers, the 1,2,4- and the 1,3,5-triethylbenzenes, and that their relative concentrations varied through the course of the reaction. These initial results showed that isomerization does not take place in the absence of transalkylation and indicated that 1,2,4-triethylbenzene was the principal reaction intermediate. It is significant that this isomer has not been reported in previous investigations of the isomerization and transalkylation of diethylbenzenes.

Product distributions obtained in the isomerization of *o*-diethylbenzene at 170°, over a period of 100 hr, are summarized in Table I. The initial products were ethylbenzene and 1,2,4-triethylbenzene. No increase in the amounts of *para* and *meta* isomers occurred, beyond those in the starting material, until the concentration of the 1,2,4 isomer reached about 3–4 mol % of the reaction mixture after a reaction period of about 1–2 hr. During the course of the reaction, the concentration of 1,2,4 isomer in the trisubstituted fraction decreased from 100 to 34%, the balance being the 1,3,5 isomer. The over-all concentration of the former isomer passed through a maximum of 13 mol % of the reaction mixture to its equilibrium value of 9 mol %. The extent of transalkylation at equilibrium was about 50 mol % and was obtained in approximately 24 hr.

The pure *para* isomer transalkylated to about equilibrium distribution (Table II) in about the same time as the pure *ortho* isomer. The initial products were ethylbenzene and, again, the 1,2,4-trisubstituted iso-

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[1] Paper presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[2] R. H. Allen, L. D. Yats, and D. S. Erley, *J. Amer. Chem. Soc.*, **82**, 4853 (1960).

[3] R. H. Allen, *ibid.*, **82**, 4856 (1960).

[4] G. A. Olah, M. W. Meyer, and N. A. Overchuk, *J. Org. Chem.*, **29**, 2313 (1964).

[5] E. Unseren and A. P. Wolf, *ibid.*, **27**, 1509 (1962).

[6] To be published. Paper presented by P. E. Pickert at the Meeting of the American Institute of Chemical Engineers, Columbus, Ohio, May 16, 1966.

TABLE I
THE ISOMERIZATION OF *o*-DIETHYLBENZENE AT 170°

	Product distribution, mol %						Isomer distribution (normalized)				
		Diethylbenzene			Triethylbenzene		Diethylbenzene			Triethylbenzene	
Time	Ethylbenzene	*o*	*m*	*p*	1,2,4	1,3,5	*o*	*m*	*p*	1,2,4	1,3,5
0	0	93.2	5.9	0.9	0	0	93.2	5.9	0.9		
1.5 min	0.6	92.6	5.1	1.1	0.6	0	93.7	5.2	1.1	100	0
5 min	0.8	91.9	5.6	0.8	0.9	0	93.5	5.7	0.8	100	0
20 min	1.4	90.6	5.7	0.4	1.9	0	93.7	5.9	0.4	100	0
40 min	1.6	90.1	5.7	0.7	1.9	0	93.4	5.9	0.7	100	0
60 min	2.5	86.8	6.0	1.8	2.7	0.2	91.8	6.3	1.9	94.3	5.7
2 hr	4.2	81.0	8.5	1.4	4.6	0.4	89.2	9.3	1.5	92.1	7.9
4 hr	8.6	70.8	11.4	1.6	6.7	0.9	84.5	13.6	1.9	88.0	12.0
7 hr	11.8	59.7	14.2	2.2	9.6	2.5	78.4	18.7	2.9	79.5	20.5
23 hr	24.6	12.9	27.8	9.7	13.1	12.0	25.6	55.1	19.3	52.1	47.9
32 hr	23.3	6.5	31.9	12.6	10.9	14.8	12.7	62.5	24.7	42.4	57.6
47 hr	24.5	3.9	31.1	14.8	8.9	16.8	7.8	62.5	29.7	34.6	65.4
71 hr	20.5	3.1	32.8	15.7	9.4	18.4	6.0	63.5	30.4	33.8	66.2
100 hr	20.4	3.1	33.1	15.9	9.2	18.2	6.0	63.4	30.5	33.6	66.4

TABLE II
THE ISOMERIZATION OF *p*-DIETHYLBENZENE AT 170°

	Product distribution, mol %						Isomer distribution (normalized)				
		Diethylbenzene			Triethylbenzene		Diethylbenzene			Triethylbenzene	
Time	Ethylbenzene	*o*	*m*	*p*	1,2,4	1,3,5	*o*	*m*	*p*	1,2,4	1,3,5
0	0	0	0	100	0	0					
0.5 min	0.4	0	0	99.5	0.2	0	0	0	100	100	0
2 min	0.3	0	0	99.5	0.3	0	0	0	100	100	0
5 min	0.6	0	0	99.0	0.4	0	0	0	100	100	0
10 min	0.9	0	0	98.4	0.7	0	0	0	100	100	0
20 min	1.3	0	0.1	97.7	1.0	0	0	0.1	99.9	100	0
30 min	2.3	0	0.4	95.6	1.7	0	0	0.4	99.6	100	0
60 min	3.0	0	0.6	93.8	2.6	0	0	0.6	99.4	100	0
2.5 hr	5.7	0.3	1.7	86.3	5.2	0.8	0.3	1.9	97.7	87.5	12.5
4 hr	10.4	0.3	2.7	78.4	7.0	1.2	0.4	3.3	96.3	85.9	14.1
6 hr	11.9	0.7	3.9	73.0	8.4	2.1	0.9	5.0	94.1	79.7	20.3
22 hr	22.7	1.6	15.3	39.0	11.4	10.1	2.9	27.3	69.8	53.1	46.9
46 hr	21.7	3.4	24.8	24.1	10.5	15.4	6.5	47.5	46.0	40.6	59.4
54 hr	22.0	4.1	27.0	21.5	9.7	15.6	7.8	51.2	40.9	38.2	61.8
70 hr	20.9	3.8	30.5	18.1	9.6	17.1	7.2	58.2	34.6	36.1	63.9
100 hr	20.0	2.8	32.9	18.0	8.3	18.1	5.2	61.4	33.5	31.4	68.6

mer; the 1,3,5 isomer appeared only when a substantial amount of the 1,2,4 isomer had been formed. As before, the concentration of the 1,2,4 isomer in the trisubstituted fraction decreased from 100 to 31 mol %, while the over-all concentration passed through a maximum of about 11–12 mol % before reaching its equilibrium concentration of 8 mol %. The close similarity between the transalkylation and isomerization of the *ortho* and *para* isomers suggests that the formation of the 1,2,4 isomer may be the rate-controlling step.

The isomerization of the *meta* isomer (Table III) was considerably more rapid than that of the *ortho* and *para* isomers and was essentially complete after 30 hr yielding the same isomer distributions. The shorter time required to obtain this equilibrium distribution was probably due to starting closer to the final composition, the *meta* isomer constituting over 60% of the mixture. Again transalkylation occurred to the extent of 50 mol % of the diethylbenzenes and led to the appearance of ethylbenzene and triethylbenzenes. However, with the *m*-diethylbenzene, the 1,2,4- and the 1,3,5-triethylbenzenes appeared essentially at the same time and initially closer to their equilibrium distribution. The reversibility of the transalkylation–isomerization reaction was demonstrated by using 1,3,5-triethylbenzene and ethylbenzene as starting materials (Table IV). The products were the diethylbenzene isomers in equilibrium distribution.

That the isomerization mechanism involved the formation of transalkylated products was further shown by repeating the isomerization of the *ortho* isomer in the presence of added ethylbenzene and triethylbenzene (Table V). If transalkylation contributed to isomerization, an increase in rate should result. If, however, the mechanism involved 1,2 shifts, a decrease in rate due to dilution of the reactant should occur. As expected, after 4 hr the disubstituted fraction of the reaction mixture from the pure *ortho* isomer contained 84.5% *ortho*, while that from the reaction mixture with added transalkylation products contained 76.7% *ortho*. Thus the isomerization rate was increased by the presence of the transalkylation products.

Discussion

Considerable evidence has been assembled which suggests that the mechanism of carbonium ion formation with zeolite catalysts is fundamentally different from that of conventional Lewis acid and Brønsted acid catalysts. It has been postulated that hydrocarbon molecules are polarized by the strong electrostatic fields surrounding positively and negatively charged sites

TABLE III

THE ISOMERIZATION OF *m*-DIETHYLBENZENE AT 170°

	Product distribution, mol %						Isomer distribution (normalized)				
		Diethylbenzene			Triethylbenzene		Diethylbenzene			Triethylbenzene	
Time	Ethylbenzene	*o*	*m*	*p*	1,2,4	1,3,5	*o*	*m*	*p*	1,2,4	1,3,5
0	0	0	100	0	0	0	0	100	0	0	0
2 min	0	0	100	0	0	0	0	100	0	0	0
5 min	0.1	0.1	99.3	0.3	0.2	0	0.1	99.6	0.3	100	0
20 min	0.3	0.2	98.8	0.4	0.2	0.2	0.2	99.4	0.4	50	50
40 min	0.9	0.7	96.5	1.1	0.3	0.6	0.7	98.2	1.1	30.8	69.2
2 hr	0.9	0.7	95.7	1.9	0.3	0.7	0.7	97.4	1.9	27.3	72.4
3 hr	2.7	1.4	90.1	2.4	0.9	3.5	1.5	95.9	2.6	26.8	73.2
20 hr	13.1	2.3	61.0	7.6	4.4	11.6	3.3	86.1	10.7	27.5	72.5
22 hr	15.3	1.8	58.2	8.5	4.3	11.8	2.6	84.9	12.4	26.7	73.3
31 hr	18.2	3.2	35.9	17.6	8.6	16.6	5.6	63.4	31.0	34.0	66.0
76 hr	18.9	2.9	32.9	17.3	8.5	19.5	5.4	62.0	32.6	30.4	69.6

TABLE IV

THE TRANSALKYLATION OF ETHYLBENZENE AND 1,3,5-TRIETHYLBENZENE AT 170°

	Product distribution, mol %						Diethylbenzene isomer distribution (relative)		
	Ethyl-	Diethylbenzene			Triethyl-benzene				
Time	benzene	*o*	*m*	*p*	1,2,4	1,3,5	*o*	*m*	*p*
0 min	48.2	0	0	0	0	51.8			
1 min	48.0	0	0.1	0.2	0	51.8			
2 min	47.7	0	0.6	0.4	0	51.2			
4 min	46.8	0	0.5	0.4	0.1	52.1			
5 min	46.4	0	0.9	0.5	0.3	51.8			
10 min	45.0	0	1.5	1.0	1.5	51.9			
30 min	41.5	0.1	2.9	1.6	1.2	52.7	1	29	16
60 min	37.5	0.3	4.7	2.6	2.0	52.8	1	16	9
2 hr	33.5	0.8	10.7	5.5	3.2	46.4	1	13	7
3 hr	22.0	1.7	24.5	10.9	6.7	34.3	1	14	6
4 hr	15.5	2.4	28.6	13.2	9.1	31.2	1	12	6
5 hr	13.5	2.5	31.5	14.5	10.0	27.9	1	13	6
8 hr	14.3	2.7	32.4	14.3	10.4	25.9	1	12	5
10 hr	13.5	2.5	32.3	14.8	11.1	25.7	1	13	6

TABLE V

THE ISOMERIZATION OF *o*-DIETHYLBENZENE WITH ADDED TRANSALKYLATION PRODUCTS AT 170°

	Product distribution, mol %						Isomer distribution (normalized)				
		Diethylbenzene			Triethylbenzene		Diethylbenzene			Triethylbenzene	
Time	Ethylbenzene	*o*	*m*	*p*	1,2,4	1,3,5	*o*	*m*	*p*	1,2,4	1,3,5
0	7.9	75.9	4.0	0.7	0	11.5	94.2	4.9	0.9	0	100
1 min	9.8	74.1	4.1	0.8	0.3	10.0	93.8	5.2	1.0	2.9	97.1
5 min	10.4	72.8	4.2	0.8	0.7	11.1	93.5	5.4	1.0	5.7	94.3
10 min	10.9	72.5	4.0	0.9	0.7	11.0	93.7	5.2	1.1	6.3	93.7
60 min	10.9	68.9	6.4	1.2	2.6	10.0	90.0	8.4	1.6	20.5	79.5
2 hr	11.8	63.0	8.5	2.0	5.0	9.7	85.7	11.5	2.7	34.0	66.0
4 hr	17.0	48.5	11.9	2.7	10.0	9.7	76.7	18.9	4.3	50.8	49.2
7 hr	18.6	36.3	16.9	3.5	13.4	11.5	64.1	29.8	6.2	53.9	46.1
23 hr	20.8	13.0	27.0	10.1	13.3	15.3	25.7	53.4	19.9	46.4	53.6
30 hr	18.9	9.7	29.8	11.5	12.4	17.8	19.0	58.4	22.6	41.0	59.0
46 hr	20.4	5.7	30.0	14.3	10.4	19.1	11.4	60.0	28.6	35.3	64.7
70 hr	18.8	4.0	30.5	16.1	10.3	20.2	7.9	60.3	31.8	33.8	66.2
94 hr	18.8	2.9	32.2	17.8	9.5	18.8	5.4	60.9	33.6	33.6	66.4

associated with the crystal lattices to give quasi-carbonium ion intermediates which then react in characteristic fashion.[7] Thus the zeolite catalysts are particularly suitable for alkylbenzene isomerization since the strong complex formation between alkylaromatics and acid catalysts, such as those found with hydrogen halide-promoted Lewis acids, is not observed. These complexes play an important role in alkylation and isomerization reactions with acidic catalysts and likely influence the reaction mechanism significantly. The preponderance of *meta*-substituted products with large, noncatalytic amounts of the halide-containing catalysts has been explained on the basis of the greater stability of the *meta* compared with similar *ortho* and *para* σ complexes.[8,9]

The experimental data obtained in this study show that starting with any one of the three diethylbenzene isomers, the same product distribution was obtained, demonstrating conclusively that equilibrium had been reached. The extent of transalkylation, at equilibrium, was the same for each isomer. The product consisted of about 20 mol % ethylbenzene, 53 mol % diethylbenzenes, and 27 mol % triethylbenzenes. The difference in concentration between the ethylbenzene and triethylbenzene fractions from the theoretical 1:1 molar ratio is explained by the transalkylation of some of the ethylbenzene to diethylbenzenes and benzene; the latter was lost from the system at reaction temperature. The diethylbenzene fraction at equilibrium consisted of about 6% *ortho*, 62% *meta*, and 32% *para* and the trisubstituted fraction of about 32% 1,2,4 and 68% 1,3,5 isomers. That the isomerization of the diethylbenzenes proceeds *via* a transalkylation mechanism is supported by the following observations. (1) Isomerization does not take place in the absence of transalkylation. (2) The rate of isomerization is increased by the addition of transalkylation products. (3) The isomer distribution in the diethylbenzene fraction formed initially

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[7] P. E. Pickert, J. A. Rabo, E. Dempsey, and V. Schomaker, *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, **1**, 714 (1965).

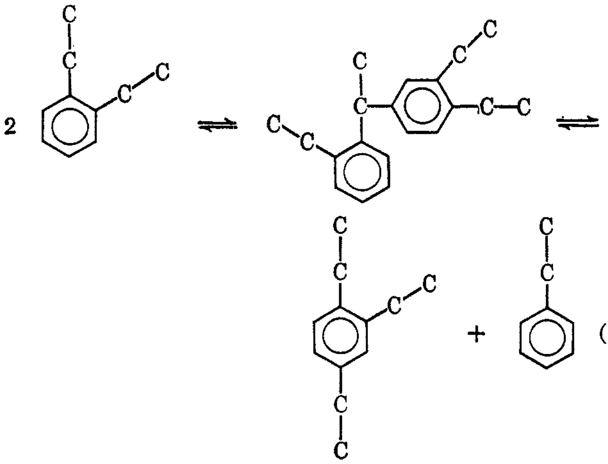
[8] S. U. Choi and H. C. Brown, *J. Amer. Chem. Soc.*, **88**, 903 (1966).

[9] H. C. Brown and J. J. Melchiore, *ibid.*, **87**, 5269 (1965).

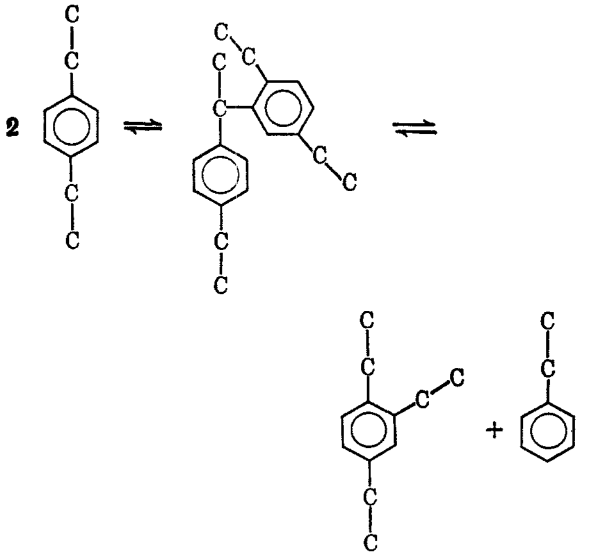
from the reaction of 1,3,5-triethylbenzene and ethylbenzene is that found in the final isomer distribution.

The intermolecular isomerization of the diethylbenzenes can be satisfactorily explained by a 1,1-diphenylethane-type intermediate. Such an intermediate, proposed by Streitwieser[10] and Pines,[11] would not be at variance with the data of Unseren[5] and its existence was substantiated by the recent[12] isolation of diarylalkanes from the disproportionation products of alkylbenzenes. No catalyst aging was observed in our studies which precludes the presence of ethylene as an intermediate. If ethylene were an intermediate, *sec*-butylbenzenes would have been formed with similar zeolite catalysts containing 0.5 wt % Pd as is found in the alkylation of benzene with ethylene using such catalysts. The presence of diarylalkane intermediates provides a satisfactory explanation of the experimental results obtained in our studies.

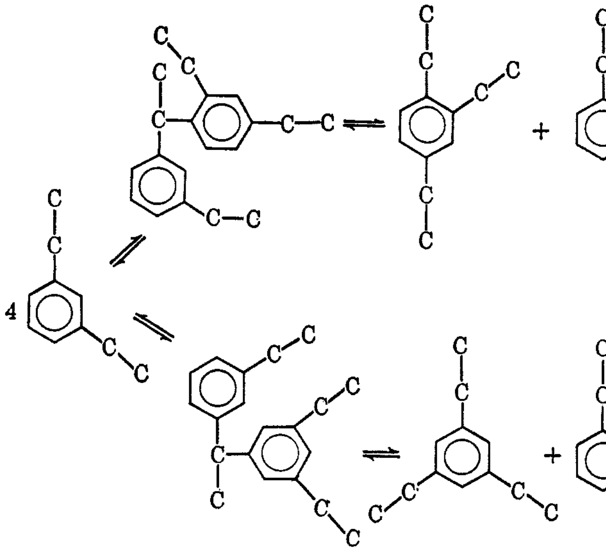
The only possible products from the transalkylation of *o*-diethylbenzene with a diarylalkane-type intermediate are 1,2,4-triethylbenzene and ethylbenzene as shown in eq 1. The absence of the 1,2,3 isomer is presumably due to steric considerations and the remaining positions on the aromatic ring are equivalent. From the *para* isomer (eq 2) it can be seen that the only products are again ethylbenzene and 1,2,4-triethylbenzene, since all four unoccupied positions on the aromatic nucleus are equivalent. This is consistent with the experimental data shown in Tables I and II. Starting with the *ortho* and *para* isomers, the trisubstituted fraction initially consists exclusively of the 1,2,4-triethylbenzene. However, it is important to note that with the *meta* isomer both the 1,2,4- and the 1,3,5-triethylbenzenes can be formed as illustrated in eq 3. Two of the three available positions on the aromatic ring of the *meta* isomer are equivalent and lead to the formation of the 1,2,4-triethylbenzene, while the third position accounts for the formation of the 1,3,5-substituted product. The data from the experiment starting with the *meta* isomer (Table III) showed both trisubstituted isomers appearing at approximately the same time. The concentration of the 1,3,5 isomer in the triethylbenzene fraction increased more rapidly starting with the *m*-diethylbenzene than with the *ortho* and *para* isomers. Starting with *o*- and *p*-diethylbenzenes, no 1,3,5 isomer appeared before a significant amount of *m*-diethylbenzene had been formed. Both these points indicate that the 1,3,5 isomer is directly derived from the *m*-diethylbenzene, although the rate of transalkylation was significantly more rapid with the *ortho* and *para* isomers. After about 2 hr with this latter compound, approximately 5% of the reaction mixture consisted of triethylbenzenes, whereas 1% was formed from the *m*-diethylbenzene.



(1)

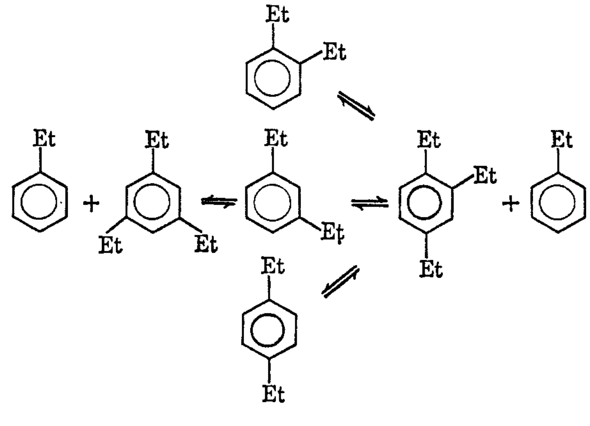


(2)



(3)

It is now possible to describe an isomerization reaction scheme, based on a transalkylation mechanism, consistent with the experimental data and which does not require a 1,2-shift step. This scheme is summarized in eq 4.



(4)

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[10] A. Streitwieser and L. Rief, *J. Amer. Chem. Soc.*, **86**, 1988 (1964).

[11] H. Pines and J. T. Arrigo, *ibid.*, **80**, 4369 (1958).

[12] R. M. Roberts, E. K. Baylis, and G. J. Fonken, *ibid.*, **85**, 3454 (1963).

The data in Table V show that, in the reaction (transalkylation) of the 1,3,5-triethylbenzene and ethylbenzene, the amount of the *m*-diethylbenzene was greater than that of the 1,2,4-triethylbenzene. This indicates that *m*-diethylbenzene was the precursor of this latter compound in this reaction. The diethylbenzene fraction was initially richer in the *meta* isomer than the final equilibrium distributions of 1:12:6, *ortho–meta–para,* since it is the only product of the dealkylation of the 1,3,5 compound as indicated in eq 4. The products obtained from the transfer of an ethyl group to the ethylbenzene reactant should be in equilibrium distribution, which is again richer in the *meta* isomer. The experimental results support these conclusions within the accuracy of the analytical measurements.

That the 1,2,4-triethylbenzene has not previously been reported[4,13] as one of the products of transalkylation using metallic halide catalysts is simply explained by the greater stability of catalyst complexes of *meta* derivatives. For example, the equilibrium leading to the formation of the 1,3,5-triethylbenzene as shown in eq 5 is shifted far to the right,[13] particularly when large, noncatalytic amounts of Lewis acid catalysts are employed.

$$(1,2,4\text{-}Et_3C_6H_3\cdot H)^+\cdot BF_4^- \rightleftharpoons 1,2,4\text{-}Et_3C_6H_3 \rightleftharpoons 1,3,5\text{-}Et_3C_6H_3 \rightleftharpoons (1,3,5\text{-}Et_3C_6H_3\cdot H)^+BF_4^- \quad (5)$$

The product distributions of both the isomerization and transalkylation reactions always agree with calculated thermodynamic equilibria with the molecular sieve zeolite catalyst. This indicates the absence of the stable catalyst–reactant intermediate complex frequently observed with conventional acid catalysts.

Experimental Section

The di- and triethylbenzenes were obtained from the Aldrich Chemical Co., Milwaukee, Wis., and were used without further purification. The *o*-diethylbenzene contained 93% *ortho,* 6% *meta,* and 1% *para;* the *m*- and *p*-diethylbenzenes and the 1,3,5-triethylbenzene were all 99% pure.

The reactions were carried out in a 100-ml flask, fitted with a water-cooled condenser and a magnetic stirrer. The crystalline catalyst was synthesized from Type Y zeolite with a SiO_2/Al_2O_3 molar ratio of 5.0 by partial multivalent cation exchange (40% Ce^{3+}) and partial decationization (50%). The balance of the cations was sodium. The preparation and pertinent properties of this material have been previously reported.[6] Five grams of catalyst were used/0.5 mol of reactant and the reaction temperatures were maintained using a constant-temperature oil bath. Samples were removed periodically and analyzed on a Perkin-Elmer 154 D vapor fractometer. The fractometer was equipped with a 150-ft *m*-bis(*m*-phenoxyphenoxy)benzene-coated (modified by 20% Apiezon L) capillary column and a hydrogen flame ionization detector. The 1,2,4-trialkylbenzene was characterized by both ir and uv analyses.

Retention times of ethylbenzene, diethylbenzenes, and triethylbenzenes are given in Table VI.

TABLE VI

RETENTION TIMES OF ETHYLBENZENE, DIETHYLBENZENES, AND TRIETHYLBENZENES

Compd	Retention time,[a] min
Ethylbenzene	3.7
o-Diethylbenzene	5.8
m-Diethylbenzene	5.5
p-Diethylbenzene	5.6
1,2,4-Triethylbenzene	11.2
1,3,5-Triethylbenzene	10.0

[a] At 150°; He, 30 psi.

Registry No.—Ethylbenzene, 100-41-4; *o*-diethylbenzene, 135-01-3; *m*-diethylbenzene, 141-93-5; *p*-diethylbenzene, 105-05-5; 1,2,4-triethylbenzene, 877-44-1; 1,3,5-triethylbenzene, 102-25-0.

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Long-Range Effects in the Alkylation of Benzene with Dichloroalkanes[1]

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The results obtained from alkylation reactions on benzene with two series of primary chloro-containing dichloroalkanes are interpreted on the basis of a long-range effect of the reference primary chloro group on the reaction of the second chloro group. Benzene was alkylated with 1,X-dichlorooctane (*i.e.*, a mixture of the 1,1 through 1,8 isomers) using a boron trifluoride–hydrogen fluoride catalyst (a system specific for alkylation of secondary halides). The relative reaction rates for the 1,3, 1,4, 1,5, 1,6, and 1,7 isomers and the composite rate for the secondary monochlorooctanes were 1, 9.9, 23.2, 36.8, 49, and 73, respectively. The products were 7-, 6-, 5-, and 4-phenyl-1-chlorooctanes in a ratio 53:29:14:4, which was independent of the degree of dichloride conversion. The 1,1, 1,2, and 1,8 isomers did not react. The aluminum chloride catalyzed alkylation of benzene with a series of α,ω-dichloroalkanes was also examined. The rate of reaction was in the order of 1,4-dichlorobutane > 1,6-dichlorohexane > 1,5-dichloropentane > 1,3-dichloropropane and was generally slower than that of 1-chlorohexane. The higher members of this series gave the greatest amount of rearranged products from the initial reaction, but this was always less than the corresponding 1-chloroalkane. 1,4-Dichlorobutane is a special case in which anchimeric assistance by one chloro group in the ionization of the other is responsible for an increased reaction rate.

In our previously reported work on the alkylation of benzene with 1,2-dichloroalkanes using aluminum chloride, it was observed that the adjacent primary chloride had a profound effect in determining the products of reaction.[2] This report describes our work on systems in which the two chloro groups are farther apart. We have studied the effect of one chloro group on the reaction rate and products from reaction of the second chloro group. Special emphasis has been placed on the change of the effect with distance between the two chloro groups and on a comparison with the monochloroalkane reaction. Two alkylation systems have been used in this work. The alkylation of benzene with

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[1] Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

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