Tetrahedron Letters No. 19, pp. 691-695, 1961. Pergamon Press Ltd. Printed in Great Britain.

THE DISPROPORTIONATION OF ETHYLBENZENE-1-C_1^{14} UNDER THE INFLUENCE OF ALUMINUM BROMIDE AND HYDROGEN BROMIDE[1]

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(Received 29 September 1961)

It is known[3] that the disproportionation[4] of ethylbenzene to give benzene and a mixture of di- and triethylbenzenes catalyzed by hydrogen bromide promoted aluminum bromide is much faster than the corresponding disproportionation of toluene. McCaulay and Lien[3] have explained the huge rate difference on the basis of hyperconjugative stabilization of the transition state in the case of ethylbenzene. Brown and Smoot[5] modified this mechanism by suggesting that the first formed sigma complex rapidly isomerized to a π-complex, which complex was in mobile equilibrium with the starting material. Thus according to this concept, the rate determining step involving two molecules of alkyl benzene depends on the concentration of this π-complex which could reasonably be expected to be significantly higher than the corresponding π-complex derived from toluene.

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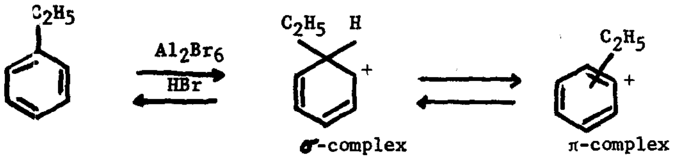
[1] Research performed under the auspices of the U.S. Atomic Energy Commission.

[2] International Cooperation Administration Fellow, Brookhaven National Laboratory, 1958-1959.

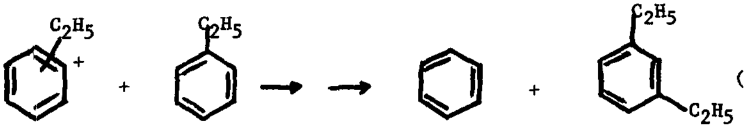
[3] D. A. McCaulay and A. P. Lien, J. Amer. Chem. Soc. 75, 2411 (1953).

[4] This term means primarily transalkylation but actually embraces intramolecular isomerization and isomerization resulting from intermolecular reactions, all of which are occurring at varying rates under the usual reaction conditions for "disproportionation."

[5] H. C. Brown and C. R. Smoot, J. Amer. Chem. Soc. 78, 2176 (1956)



(1)



(2)

Streitwieser and Reif[6] have suggested another mechanism involving oxidation to the α-phenethyl cation as being operative. Recent work by Douglass and Roberts[7] and by Nenitzescu *et al.*[8] also bears on this problem.

In an effort to provide more detailed information on the disproportionation reaction we studied the reaction using ethylbenzene-1-C_1^{14}. The use of one-labeled material bears on the existence of a π-complex as a transitory intermediate and on the relation of isomerization to transalkylation. Ethylbenzene-1-C_1^{14} was prepared from commercially available benzoic acid-1-C_1^{14}. The acid was reduced to benzyl alcohol from which benzyl chloride was prepared. Treatment of this material with dimethyl sulfate gave ethylbenzene-1-C_1^{14} in 60% overall yield.

The reaction was carried out without solvent under conditions similar to those of Brown and Smoot.[5] The reaction was quenched after a contact time of about seventeen minutes. Use was made of the degradation scheme of J. D. Roberts *et al.* Adipic acid was also prepared from the cyclohexanone

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[6] A. Streitwieser Jr. and L. Reif, *J. Amer. Chem. Soc.* **82**, 5003 (1960).

[7] J. E. Douglass and R. M. Roberts, *Chem. and Ind.* 926 (1959).

[8] C. D. Nenitzescu, I. Necsoiu, A. Glatz and M. Zalman, *Chem. Ber.* **92**, 10 (1959).

[9] J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr. and L. A. Carlsmith, *J. Amer. Chem. Soc.* **78**, 601 (1956).

intermediate and this was degraded via Schmidt reactions. In addition glutaric acid was prepared via cyclopentanone prepared from the adipic acid. Glutaric acid and δ-aminovaleric acid were prepared from the cyclopentanone. These acids were also degraded via Schmidt reactions. The results of the degradations are given in Table I.

Calculations using the CO_2 value for the one position and using the diamine values in simultaneous equations gave the specific activities for each position. These are listed in Table II. Larger errors are involved if the CO_2 values alone are used. Both methods involve considerable error since one is dealing with small differences in large numbers. Ring distribution is shown in Fig. 1.

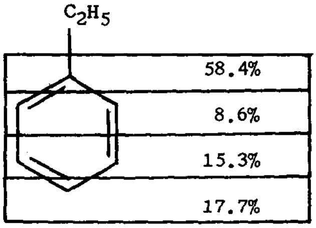

Fig. 1. Activity distribution in recovered ethylbenzene

Clearly rearrangement with respect to the specifically labeled position has taken place. It is further evident that the bulk of the rearranged activity is now in the <u>meta</u> and <u>para</u> positions (the errors involved notwithstanding). This consequence unequivocally eliminates a localized π-complex as a major intermediate which is involved in a prior equilibrium in this reaction (cf. equations 1 and 2).

The fact that the specific activity of the <u>ortho</u> position is lower than that specific activity of the para position clearly shows that trans-

Table I. Summary of Activities in Various Positions

Compound[a] Assayed	Source of Activity Relative to Position in Benzene Ring	Value
1. benzoic acid	all positions	0.156 mμc/mgC
2. CO_2; ε-aminocaproic acid	100% #1	0.625 mμc/mgC
3. CO_2; adipic acid	0.5 #1; 0.5 *o*	0.342 mμc/mgC
4. CO_2; δ-aminovaleric acid	0.5 #1; 0.5 *o*	0.330 mμc/mgC
5. CO_2; glutaric acid	0.25 #1; 0.5 *o*; 0.25 *m*	0.192 mμc/mgC
6. 1,5-pentamethylenediamine	0.4 *o*; 0.4 *m*; 0.2 *p*	0.0891 mμc/mgC
7. 1,4-pentamethylenediamine	0.25 *o*; 0.5 *m*; 0.25 *p*	0.100 mμc/mgC
8. 1,3-trimethylenediamine	0.166 *o*; 0.5 *m*; 0.333 *p*	0.112 mμc/mgC

[a] Control degradations on unreacted starting material indicated at least 98% of the activity to be in the one position.

alkylation (or intermolecular migration of an ethyl group) must occur more rapidly than a succession of 1-2 intramolecular ethyl group shifts.[10] These results would tend to support the view that rapid transalkylation to give p-diethylbenzene occurs, which compound then can isomerize and/or transalkylate further. Studies to determine the relative rates of transalkylation and isomerization of the ethylbenzenes are in progress in this laboratory.

Table II. Specific Activities for Each Ring Position

Position	Source	Value	Error
#1	CO_2	0.625 mμc/mgC	± 4%
ortho	diamine	0.046 mμc/mgC	±42%
meta	diamine	0.082 mμc/mgC	±45%
para	diamine	0.190 mμc/mgC	±45%
ortho	CO_2	0.048 mμc/mgC	±27%

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[10] Bridged intermediates or transition states involving 1,3 or 1,4 shifts will not be considered in this short communication.