Isomerization of 1-Hexene.—Addition of trifluoroacetic acid 0.125 *M* in sodium trifluoroacetate to 1-hexene (initially 0.5 *M*) was carried out at 35°. Aliquots were removed after 5, 80, 170, and 240 min. and poured into an excess of 2 *M* potassium carbonate. The resulting solutions were extracted with small amounts of diethyl adipate in order to obtain the unchanged hexenes in a nonvolatile solvent. Gas chromatography of the solutions on an adiponitrile-firebrick column gave two peaks attributable to 1-hexene (or a mixture of 1-hexene and *trans*-2-hexene) and *cis*-2-hexene. The approximate amounts of the latter were 0, 10, 10, and 14%, respectively, for the aliquots mentioned above.

Acknowledgment.—We wish to thank Dr. H. B. Donahoe and Dr. Sung Moon for alkene samples and Allied Chemical Corp. for a gift of trifluoroacetic acid.

The Disproportionation of Ethylbenzene-1-C_1^{14} under the Influence of Aluminum Bromide and Hydrogen Bromide[1]

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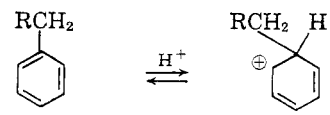
Ethylbenzene-1-C_1^{14} was disproportionated under the influence of aluminum bromide–hydrogen bromide at 0°. The distribution of activity in the benzene ring in ethylbenzene-C_1^{14} isolated from the reaction mixture after partial disproportionation indicates that a rapid prior equilibrium between ethylbenzene and its localized π-complex is not operative. The rearranged activity was found predominantly in the *meta* and *para* positions. A further necessary condition for this observation is that transalkylation (intermolecular shift of an ethyl group) is more rapid than intramolecular isomerization in ethylbenzene.

The general subject of the reactivity of alkyl substituted benzenes in the presence of Lewis acids or strong proton acids toward alkylating agents or in disproportionation studies has received wide interest in the literature. These reactions can all be considered to be examples of intra- or intermolecular alkylations and have numerous features in common.

The particular question of the mechanism of disproportionation reactions in alkylbenzenes has been carefully studied by Lien and McCaulay[3-5] and by Brown and Smoot.[6] Recently Streitwieser and Reif[7] have suggested another mechanism as possibly being operative in disproportionation reactions.

Studies which bear on the different aspects of the mechanism have been carried out by Roberts and co-workers.[8-10] This group has considered the question of rearrangements in the alkyl side chain during disproportionation by using carbon-14-labeled side chains. It had been demonstrated by Kinney[11] that there is no gross isomerization of an *n*-butyl group in the disproportionation of *n*-butylbenzene at 100° using aluminum chloride. The allied subject of "mixed" disproportionation[12] and alkylation[13,14] has been related to the disproportionation reaction in terms of reaction intermediates. Related intermediates can also be found to be suggested in the isomerization reactions of alkylbenzenes.[15-17] The intra- *vs.* intermolecular nature of the isomerization reactions has recently been investigated further by Allen.[18-21]

The mechanism proposed by McCaulay and Lien involved the formation of a sigma complex (stabilized by resonance) by addition of a proton from the strong proton acid HBF_4 (or $HF \cdot BF_3$) (equation 1)



(1)

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) International Coop. Administration Fellow, Brookhaven National Laboratory, 1958–1959.

(3) A. P. Lien and D. A. McCaulay, *J. Am. Chem. Soc.*, **75**, 2407 (1953).

(4) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **75**, 2411 (1953).

(5) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **79**, 5953 (1957).

(6) H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 2176 (1956).

(7) A. Streitwieser, Jr., and L. Reif, *J. Am. Chem. Soc.*, **82**, 5003 (1960).

(8) R. M. Roberts, G. A. Ropp, and O. K. Neville, *J. Am. Chem. Soc.*, **77**, 1764 (1955).

(9) R. M. Roberts and S. G. Brandenberger, *J. Am. Chem. Soc.*, **79**, 5484 (1957).

(10) R. M. Roberts, S. G. Brandenberger, and S. G. Panayides, *J. Am. Chem. Soc.*, **80**, 2507 (1985).

(11) R. E. Kinney and L. A. Hamilton, *J. Am. Chem. Soc.*, **76**, 786 (1954).

(12) D. A. McCaulay, M. C. Hoff, N. Stein, A. S. Couper, and A. P. Lien, *J. Am. Chem. Soc.*, **79**, 5808 (1957).

(13) H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **78**, 2182 (1956).

(14) H. Jungk, C. R. Smoot, and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 2185 (1956).

(15) G. Baddeley, G. Holt, and G. Voss, *J. Chem. Soc.*, 100 (1952).

(16) (a) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **74**, 6246 (1952). (b) *Cf.* D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951) for relative basicities of the methylbenzenes.

(17) H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **77**, 5579 (1955).

(18) R. H. Allen, A. Turner, Jr., and L. D. Yats, *J. Am. Chem. Soc.*, **81**, 42 (1959).

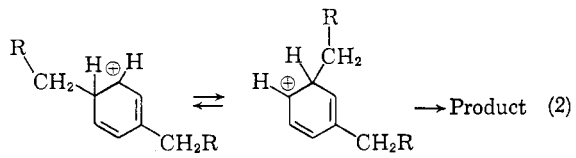
(19) R. H. Allen and L. D. Yats, *J. Am. Chem. Soc.*, **81**, 5289 (1959).

(20) R. H. Allen, L. D. Yats, and D. S. Erley, *J. Am. Chem. Soc.*, **82**, 4853 (1960).

(21) R. H. Allen, *J. Am. Chem. Soc.*, **82**, 4856 (1960).

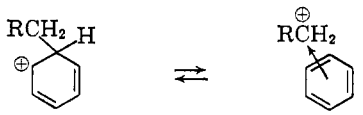
Displacement by an alkylbenzene molecule on the alkyl group of the cation led to a transition state stabilized by hyperconjugation in what was presumed to be the rate-determining step. The stabilization of the transition state by hyperconjugation was invoked to explain the huge rate difference between toluene and ethylbenzene.

It is presumed that the *p*-diethylbenzene sigma complex then isomerizes to the *meta* complex which by loss of a proton leads to the product (equation 2)



(2)

The mechanism suggested by Brown and Smoot[6] differs from this in that the sigma complex (equation 1) is first equilibrated with a localized π-complex of higher energy. This equilibrium is extremely mobile (equation 3)



(3)

The large rate difference between toluene and ethylbenzene is then due to the concentration of the π-complex,[22] since the rate-determining step still involves attack by an uncharged aromatic.

It seemed to us that a possible test for the existence (by inference) of the localized π-complex would be to use one-labeled ethylbenzene. Examination of isotope distribution in the ethylbenzene (remaining after the reaction had proceeded for a short time) might then have something to say about the mobile equilibrium described by equation 3. The labeled ethylbenzene was prepared and the disproportionation carried out.

(22) The concentration of the π-complex for ethylbenzene would be expected to be much larger than that for toluene.

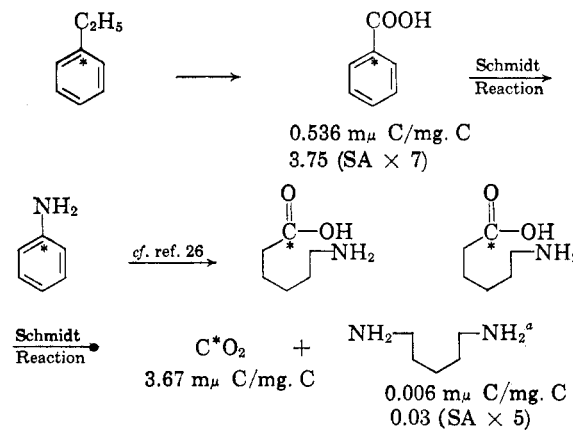
Results

Our first runs were with doubly labeled ethylbenzene, that is ethyl-β-C_1^{14}-benzene-1-C_1^{14}. Our results on rearrangement in the ethyl group were in complete accord with the published results of Roberts.[8]

In the second run, ethylbenzene-1-C_1^{14} was prepared from commercially available benzoic

TABLE I

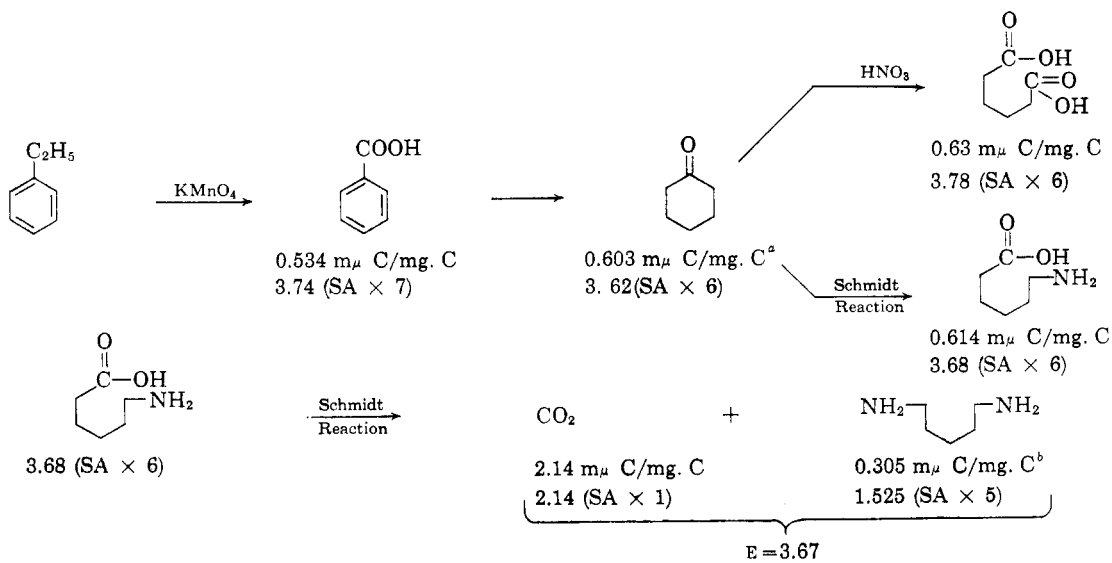
DEGRADATION OF CONTROL MATERIAL



[a] Assayed as dibenzamide; activity corrected for dilution by inactive carbon from compound used to form derivative.

TABLE II

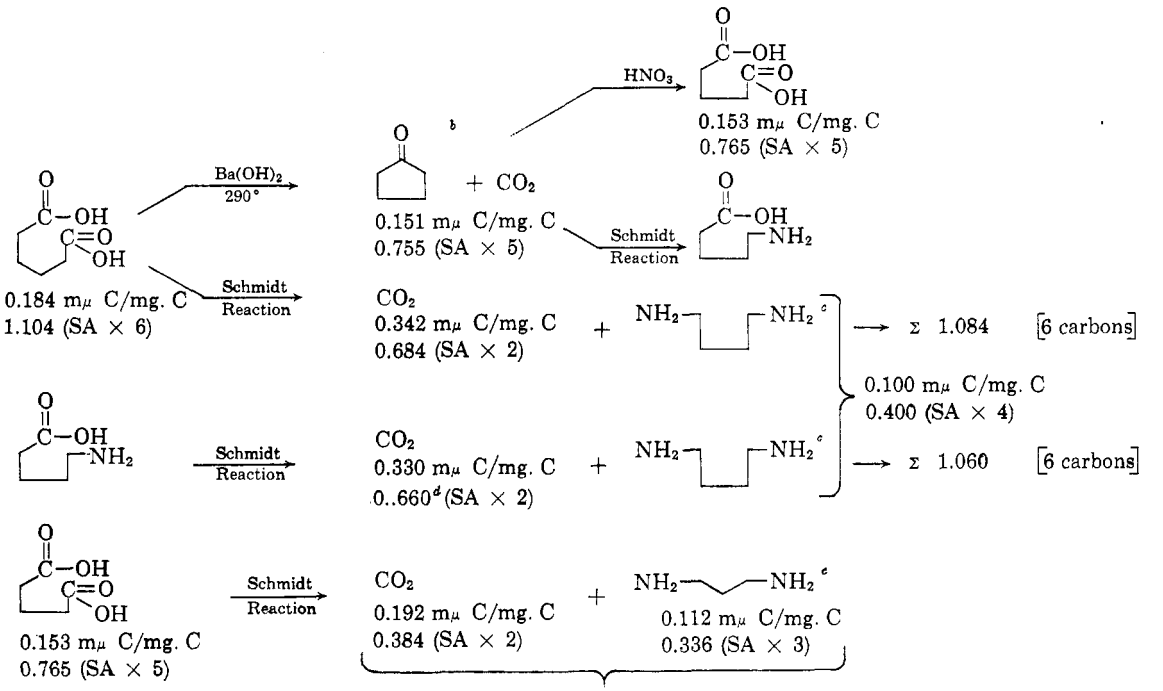
DEGRADATION OF ETHYLBENZENE-C_1^{14}: PART I



[a] Assayed as semicarbazone; activity corrected for inactive carbon from derivatizing agent. [b] Assayed as dibenzamide; activity corrected for inactive carbon from derivatizing agent.

TABLE III

DEGRADATION OF DILUTED[a] ADIPIC ACID: PART II



[a] In order to compare the activities listed in this table with those in the previous table, all activities must be multiplied by the dilution factor of 3.423. [b] Assayed as semicarbazone; activity corrected for inactive carbon from derivatizing agent. [c] Assayed as the dibenzamide; activity corrected for inactive carbon from derivatizing agent. [d] The carbon dioxide from this compound is composed of 50% 1-position and 50% *ortho* position. The specific activity should therefore be the same as that found for the carbon dioxide from the adipic acid. The specific activity of the carbon dioxide from δ-aminovaleric acid is therefore multiplied by 2 as a weighting factor to allow comparison between the results for both degradations to give 1,4-tetramethylenediamine.

acid-1-C_1^{14}. The acid was reduced to benzyl alcohol from which benzyl chloride was prepared. Treatment of the Grignard of this material with dimethyl sulfate gave a final over-all yield of ethylbenzene-1-C_1^{14} of about 60%.

Degradation of this material is portrayed in Table I. It is clear from this table that at least 98% of the activity is in the 1-position.

The disproportionation was carried out at 0° in the manner described by Brown and Smoot.[6] The reaction mixture was quenched by pouring over ice after a seventeen-minute contact time with the catalysts.

The results of the degradation of the ethylbenzene-C_1^{14} isolated from the disproportionation reaction are given in Tables II and III.

It can be seen from the degradative scheme that specific carbons are obtained in some cases, and in others, one obtains activities which are the sum of varying proportions of the different positions. Table IV is a summary of the degradations.

The specific activities for the 1-position, the *ortho* positions and the *meta* positions can be calculated from the carbon dioxide values. Using these data, the *para* position value must be obtained by difference. The specific activities for the *ortho*, *meta*, and *para* positions can be calculated by using the following three equations based on values for the derivatives

$$0.4\,o + 0.4\,m + 0.2\,p = 0.0891 \quad (4)$$

$$0.25\,o + 0.5\,m + 0.25\,p = 0.100 \quad (5)$$

$$0.166\,o + 0.5\,m + 0.333\,p = 0.112 \quad (6)$$

These results are summarized in Table V.

There can be little question that there has been rearrangement in the recovered ethylbenzene-C_1^{14}. If one makes no assumptions about mechanism it is obvious that a minimum of 41.6% of the activity originally in the 1-position is now in the *ortho*, *meta*, and *para* positions. These results leave little doubt that the bulk of the rearranged activity is now in the *meta* and *para* positions. The distribution based on the diamine results is given in Fig. 1.

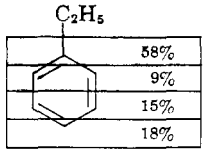


Fig. 1.—Activity distribution in recovered ethylbenzene

TABLE IV
SUMMARY OF ACTIVITIES IN VARIOUS POSITIONS[a]

Compound	Source of Activity Relative to Position in Benzene Ring	Value
A. Control on unchanged starting material		
1. Benzoic acid[b]	All positions	0.156 mμ C/mg. C
2. CO_2 from ε-amino-caproic acid	100% #1	1.07 mμ C/mg. C
3. 1,5-Pentamethyl-enediamine	40% *ortho* 40% *meta* 20% *para*	0.002 mμ C/mg. C
B. Degradation of ethylbenzene-C_1^{14} recovered from reaction mixture		
1. Benzoic acid[b]	All positions	0.156 mμ C/mg. C
2. CO_2 from ε-amino-caproic acid	100% #1	0.625 mμ C/mg. C
3. CO_2 from adipic acid	50% #1 50% *ortho*	0.342 mμ C/mg. C
4. CO_2 from δ-amino-valeric acid	50% #1 50% *ortho*	0.330 mμ C/mg. C
5. CO_2 from glutaric acid	25% #1 50% *ortho* 25% *meta*	0.192 mμ C/mg. C
6. 1,5-Pentamethyl-enediamine	40% *ortho* 40% *meta* 20% *para*	0.0891 mμ C/mg. C
7. 1,4-Tetramethyl-enediamine	25% *ortho* 50% *meta* 25% *para*	0.100 mμ C/mg. C
8. 1,3-Trimethylene-diamine	16.6% *ortho* 50% *meta* 33.3% *para*	0.112 mμ C/mg. C

[a] All activities are related to the diluted values indicated in Table III. [b] Obtained by oxidation of ethylbenzene.

TABLE V
SPECIFIC ACTIVITIES FOR EACH RING POSITION

Position	Source	Value	Estimated Error
#1	CO_2	0.625[a] mμ C/mg. C	4%
ortho	CO_2	0.048[b] mμ C/mg. C	27%
meta	CO_2	0.048 mμ C/mg. C	73%
ortho	Diamine	0.046[a] mμ C/mg. C	42%
meta	Diamine	0.082[a] mμ C/mg. C	45%
para	Diamine	0.190[a] mμ C/mg. C	

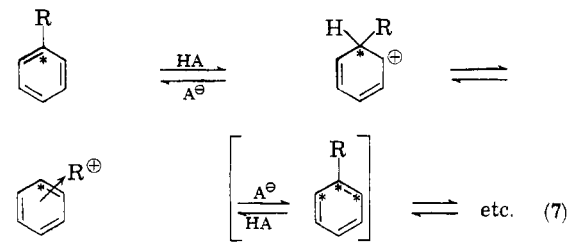
[a] These values were used in calculating isotope distribution in Fig. 1. [b] An average.

The large errors in the values for the *ortho*, *meta*, and *para* positions and particularly for the *meta* and *para* positions is, of course, due to the fact that the calculations involve small differences in large numbers. The errors, however, do not vitiate the conclusion stated in the previous paragraph.

The question may also be raised as to what bearing the isotope effect might have on the results. Clearly, the breaking of a carbon-12–carbon-14 bond is involved in many of the steps. No systematic investigation of how this would affect our results was made in this case. It is interesting to note, however, that 1,4-tetramethylenediamine is produced in two ways, *via* adipic acid and *via* δ-aminovaleric acid produced from cyclopentanone which in turn was produced from the adipic acid.[23] The assays on the diamines from each source are the same as are the carbon dioxide values within the precision of our method. Sequential and additive isotope effects would probably have altered the assay values significantly.

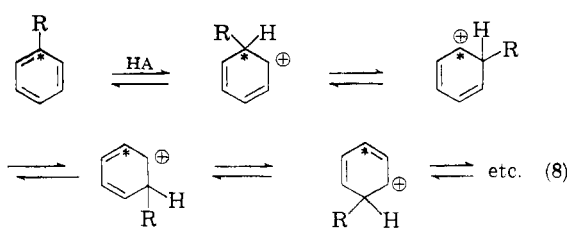
Discussion

It is clear from the large body of work that has been done on the isomerization and disproportionation reactions that product distribution at equilibrium is a function of catalyst concentration (particularly those catalysts which can form stable complexes with some of the products), structure of the alkyl side chain, and the temperature at which the reaction is carried out. What is considerably more complex and perhaps less clear is the kinetic interrelationship of the various products and intermediates. The consequences of a mobile pre-equilibrium[6] would imply a rapid distribution of activity into the *ortho* position and then more slowly into the *meta* and *para* positions. This postulate is not in accord with the results obtained by using ethylbenzene-1-C_1^{14}. While the mechanism of Brown and Smoot[6] involving a localized π-complex is attractive, it cannot be the major product determining reaction operative under these conditions. The results indicate that a rapid pre-equilibrium of the first formed sigma complex to a π-complex (equation 7) or a rapid isomerization of the sigma complex (equation 8) (whether *via* a π-complex or not) cannot be the



exclusive reaction taking place prior to disproportionation under the reaction conditions used here.

It is further interesting to note that the isomerization (for example, a series of rapid stepwise carbonium ion rearrangements, equation 8) of ethylbenzene with respect to the isotope cannot be faster than the disproportionation. At best it can only be competing with the disproportionation.



(23) An isotope effect was not observed in this reaction when barium adipate-1-C^{13} was used. J. Bigeleisen, A. A. Bothner-By, and L. Friedman, *J. Am. Chem. Soc.*, **75**, 2908 (1953).

The elegant work of Allen, Yats, and co-workers[18-21] on the isomerization of alkyl aromatics has shown among other things that the *resulting* proportions of product isomers can be due to both intra- and intermolecular reactions, the percentage "responsibility" in any given case being a function of the structure of the alkyl aromatic (*cf.*, ref. 20 and 21). It is clear from our results that ethylbenzene transalkylates more rapidly than it isomerizes. This presumes that the buildup of activity in the *para* position is due to an intermolecular reaction. One could postulate 1,3 or 1,4-intramolecular ethyl group shifts in order to accommodate the results, but these seem less likely on mechanistic grounds.

The results suggest that the disproportionation may involve dialkyl intermediates which are powerful alkylating agents. For example, the rapid formation of *p*-diethylbenzene, which then alkylates ethylbenzene more rapidly than the ethylbenzene alkylates itself, might account for the growth of activity in the *para* position of ethylbenzene. It is, of course, possible that isomerization (with respect to the isotope) in ethylbenzene and in diethylbenzene (with respect to *p-m* conversion *vs. m-p* conversion) is going on concurrently. The mechanism suggested by Streitwieser[7] involving oxidation to a 1-phenylethyl carbonium ion as a first step represents a different aspect of this reaction and is not at variance with our results. The mechanism, however, was not sufficiently detailed[7] with respect to the disproportionation *vs.* transalkylation *vs.* isomerization to allow a prediction (relating to isotope distribution in jeopardized starting material) to be made.

The detailed nature of the intermediates and their interrelation is not resolved in these experiments. Further work on this system is currently underway in our laboratory.

Experimental

No attempt is made in this Experimental section to give detailed descriptions or physical constants except where the authors deemed this pertinent. All procedures are conventional and all intermediates are well known and well characterized. We felt it superfluous to supply this readily available information.

Ethylbenzene-1-C_1^{14}.—Benzoic acid-1-C_1^{14} was reduced to benzyl alcohol-1-C_1^{14} with lithium aluminum hydride. Benzylchloride-1-C_1^{14} was prepared by treating the alcohol with thionyl chloride. A Grignard reagent prepared from the chloride was allowed to react with dimethyl sulfate to give ethylbenzene-1-C_1^{14} in an over-all yield of 60%. All procedures were conventional.

Ethylbenzene-1-C_1^{14} Disproportionation.—The method of Brown and Smoot[6] was followed. Freshly distilled aluminum bromide was used. The reaction mixture was kept in the ice bath for 17 min. from the beginning of hydrogen bromide addition and then quenched. Starting with 60.1 g. of ethylbenzene-1-C_1^{14}, we obtained 10.6 g. benzene-C_1^{14}, b.p. 80–82°, 27.3 g. ethylbenzene-C_1^{14}, b.p. 130–134°, and 14.9 g. of diethylbenzene-C_1^{14}. Fractionation was discontinued at this point.

Benzoic Acid-C_1^{14}.—Two batches of ethylbenzene-C_1^{14} of 12.6 g. each were oxidized using 90 g. of potassium permanganate 2 l. of water and 5 g. of sodium hydroxide. These mixtures were refluxed for 24 hr. Benzoic acid-C_1^{14}, 17.9 g., m.p. 122°, was obtained in 62% yield.

Cyclohexanone-C_1^{14}.—This ketone was prepared by the method of Roberts.[25]

ϵ-Aminocaproic Acid-C_1^{14}.—This acid was prepared as the hydrochloride by the method of Doering and Denney.[26] The free acid was prepared by treating the hydrochloride with silver carbonate. Degradiations were carried out on both the hydrochloride and on the free acid, the latter giving better results.

Adipic Acid-C_1^{14}.—This acid was prepared from cyclohexanol-C_1^{14} by the method described in *Organic Syntheses*.[27] Cyclohexanol-C_1^{14} was prepared as described by Roberts.[25]

Cyclopentanone-C_1^{14}.—This ketone was prepared from adipic acid-C_1^{14} by the procedure described in *Organic Syntheses*.[28]

Glutaric Acid-C_1^{14}.—This acid was prepared from cyclopentanone-C_1^{14} by the method described in Vogel.[29]

δ-Aminovaleric Acid-C_1^{14}.—This acid was prepared from cyclopentanone-C_1^{14} in a manner entirely analogous to that described for ϵ-aminocaproic acid-C_1^{14}.

Decarboxylations and Derivatizations.—All decarboxylations, whether on amino acids, on dicarboxylic acids, or on benzoic acid were carried out by the micro method of Anderson and Wolf.[30] The carbon dioxide was collected, transferred to gas counters, and then assayed.[24] Derivatives of the amines produced in the decarboxylation reactions were made in the manner described by Doering and Denney.[26] Monoamines were assayed as the monobenzamide, diamines as the dibenzamide. Ketones were assayed as the semicarbazides. Amino acids were assayed neat or as the hydrochlorides. The results of assays on all pertinent compounds are given in Tables I–IV.

Control Ethylbenzene-1-C_1^{14}.—Ethylbenzene-1-C_1^{14} not used in the disproportionation run was degraded as described above and shown to have almost all its activity in the 1 position (see Table I).

Acknowledgment.—The authors wish to thank Miss Beatrice Bonné for developing the synthesis of labeled ethylbenzene while a participant in the Brookhaven Summer Student Program in 1956. We also wish to thank Miss C. S. Redvanly for her help in carrying out a number of the Schmidt degradations. In addition we are indebted to Dr. D. Christman and Mrs. C. T. Paul for doing the carbon-14 radioassays.[24]

(24) The method of D. R. Christman, N. E. Day, P. R. Hansell, and R. C. Anderson, *Anal. Chem.*, **27**, 1935 (1955) was used.

(25) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Am. Chem. Soc.*, **78**, 601 (1956).

(26) W. von E. Doering and D. B. Denney, *J. Am. Chem. Soc.*, **77**, 4619 (1955).

(27) H. Gilman and A. H. Blatt, *Org. Syntheses*, **I**, 18 (1941).

(28) See ref. 27, p. 192.

(29) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 477.

(30) R. C. Anderson and A. P. Wolf, Brookhaven National Laboratory Report 3222. This is a modification of the method of E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 173 (1951).