in 50 ml of water was added. After stirring for 0.5 hr, the deep blue solution was diluted with 3 vol of water, neutralized with HCl, and extracted with ether. The ether solution was then extracted with 5% sodium bicarbonate, and the bicarbonate solution was then carefully neutralized. A light tan solid was obtained which, after recrystallization from aqueous ethanol, melted at 238–240° (lit., *p*-nitrobenzoic acid, mp 242°). The infrared spectrum (mull) coincided with the spectrum of an authentic sample of the acid. A nearly quantitative conversion of *p*-nitrobenzaldehyde to *p*-nitrobenzoic acid was effected.

Esr Studies.—All esr studies were performed with an Alpha esr spectrometer. A 0.01 *M* solution of *o*-dinitrobenzene was prepared in 75-ml of methoxyethanol containing 0.05 mole of sodium hydroxide, 0.05 mole of *p*-nitrobenzaldehyde, and 0.05 mole of potassium cyanide in the presence of air. No free-radical signals were found.

Electrochemical Measurement of Benzoyl Cyanide Hydrolysis.—The rate of hydrolysis of benzoyl cyanide was studied electrochemically at various pH values, using silver and platinum electrodes. The two electrodes were placed into a 0.1 *M* buffer solution of the pH to be studied (Tris or phosphate) and the open-cell voltage between the electrodes was measured using a Keithley electrometer and a Brown recorder. The initial voltage was approximately zero. Then 0.1 ml of a 10^{-2} *M* solution of benzoyl cyanide was added and the rate of change of the voltage with time was automatically recorded. The amount of cyanide liberated was calculated from standard calibration plots of voltage *vs.* log CN^- concentration, and the rate of production of cyanide was indicated by $\Delta E/\Delta t$. At all pH values studied it was found that cyanide was liberated at very fast rates, the yields of cyanide being almost quantitative.

Acknowledgment.—The authors are indebted to Dr. F. Marion Miller for his helpful comments and to Dr. E. Poziomek for obtaining the esr spectra.

The Mechanism of the Disproportionation of Ethylbenzene[1,2]

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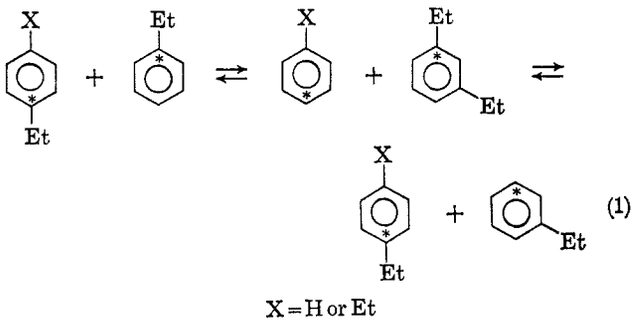
Received July 29, 1965

Ethylbenzene-1-C^{14} was disproportionated with aluminum bromide and hydrogen bromide under the homogeneous conditions of Brown and Smoot to give benzene and di- and triethylbenzenes. A convenient method was developed for the degradation of the recovered ethylbenzene. The activity distribution in the ethylbenzene plus evidence from additional experiments demonstrate that *p*-diethylbenzene is an important intermediate in this disproportionation reaction. The essentially equal labeling in the *ortho* and *meta* positions of recovered ethylbenzene requires that the rate of the intramolecular migration of an ethyl group in ethylbenzene plus one-half of the rate of the reversal of *ortho* alkylation, if any, cannot be greater than one-half of the rate of reversal of any direct *meta* alkylation. All of the evidence and analogies are consistent with *para* alkylation followed by the intramolecular shift of an ethyl group as an important path in the formation of *m*-diethylbenzene, but other possibilities are not rigorously excluded.

The mechanism of the disproportionation (transalkylation) of alkylbenzenes has been widely studied.[5] Lien and McCauley[6] proposed that the reaction proceeded *via* a σ complex, followed by displacement of the alkyl group by an alkylbenzene molecule. To explain the large rate difference between toluene and ethylbenzene, Brown and Smoot[7] suggested a preequilibrium of the σ complex with a localized π complex. The elegant study of Streitwieser and Reif[8] provided strong support for the proposal that the transalkylation proceeds *via* a Bartlett–Condon–Schneider hydride transfer.[9]



Results[5] on the disproportionation of ethylbenzene-1-C^{14} exclude the localized π complex as the major product-determining intermediate, in agreement with the conclusion of Streitwieser and Reif.[8] From the data given in Figure 1, it appeared that direct *meta* alkylation might be taking place, since an excess of radioactivity in the *meta* position compared with the *ortho* can only be reasonably explained by the reversal of *meta* alkylation (eq 1). However, the errors (due to the method of degradation and calculation) in the results[5] were large enough so that a decision on the equality or lack of equality of the activity in the *ortho* and *meta* position could not be made. The ratio of *ortho* to *meta* labeling from these earlier results was 0.6. A ratio of the *ortho* to *meta* activity near to 1 (*i.e.*, essentially equal labeling) might be the result expected if *m*-diethylbenzene were formed by *para* alkylation followed by intramolecular rearrangement (eq 2 and 3). *A priori* the rate of *ortho* alkylation might be expected to be slow owing to steric factors.[10] The intramolecular isomerization of ethylbenzene-1-C^{14} to ethylbenzene-2-C^{14} should take place somewhat more rapidly than the slow intramolecular isomerization of toluene-1-C^{14},[11] and would also give *ortho* labeling. Therefore, equal activity in the *ortho* and *meta* positions would not exlude the possibility of *meta* alkylation, although an ex-

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

(2) Presented at the Southwestern Regional Meeting of the American Chemical Society, Charleston, W. Va., 1964.

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(4) To whom inquiries should be sent.

(5) E. Ünseren and A. P. Wolf, *J. Org. Chem.*, **27**, 1509 (1962), and references therein.

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

(7) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1960).

(8) A. Streitwieser, Jr., and L. Reif, *ibid.*, **82**, 5003 (1960); **86**, 1988 (1964).

(9) P. D. Bartlett, F. E. Condon, and A. Schneider, *ibid.*, **66**, 1531 (1944).

(10) D. A. McCauley, M. C. Hoff, N. Stein, A. S. Couper, and A. P. Lien, *ibid.*, **79**, 5808 (1957).

(11) H. Steinberg and F. L. J. Sixma, *Rec. Trav. Chim.*, **81**, 185 (1962).

SCHEME I

THE DEGRADATION OF ETHYLBENZENE

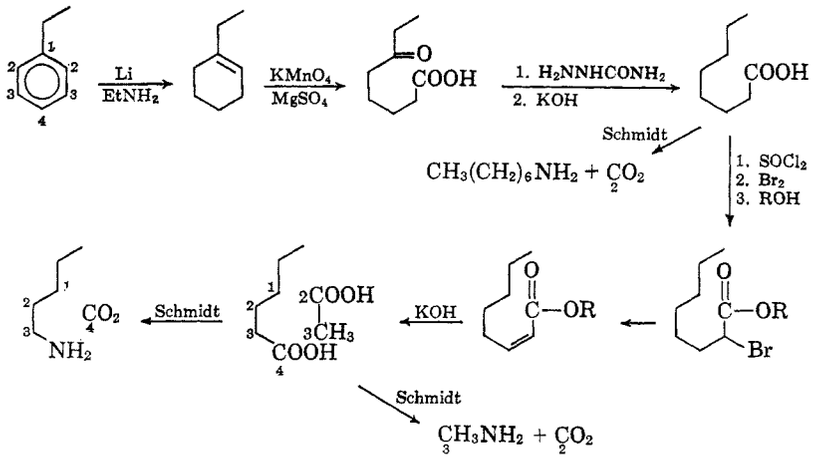
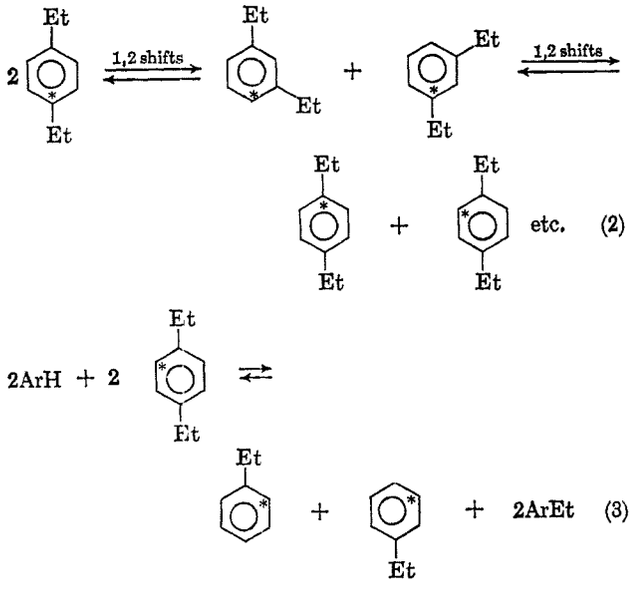


TABLE I

INTERNAL ACTIVITY CHECKS

Degradation products[a]	Positions in molecule accounted for	Run 1 7.5 min	Run 2 11.25 min
n-Heptylamine × 7 + CO_2 (octanoic acid)	Total activity	5.56	...
Acetic acid × 2 + hexanoic acid × 6	Total activity	5.54	9.58
Acetic acid × 2	C-2 + C-3	0.195	0.522
CO_2 (acetic acid) + methylamine	C-2 + C-3	0.198	0.507
CO_2 (hexanoic acid) + *n*-pentylamine × 5	C-1 + C-2 + C-3 + C-4	...	8.34
Hexanoic acid × 6	C-1 + C-2 + C-3 + C-4	5.54	9.06

[a] Specific activities in mμcuries/milligram of C used in calculation.



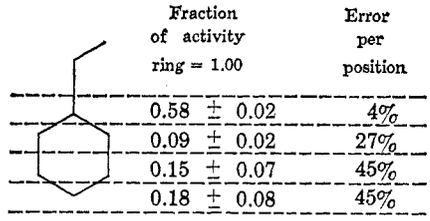


Figure 1.—Distribution of carbon-14 in ethylbenzene obtained in earlier work, using indirect methods for determining the activity per position (*cf.* Table V of ref 5).

cess in the *meta* position would demonstrate this. Also, some change in relative rates would be expected as the reaction proceeds.

Ethylbenzene-1-C^{14} was disproportionated with aluminum bromide and hydrogen bromide according to the procedure of Brown and Smoot[7] and aliquots were quenched in a water–ice mixture. The ethylbenzene was separated and degraded as shown in Scheme I. Ethylbenzene was reduced to 1-ethylcyclohexene by the method of Benkeser, *et al.*,[12] the olefin was oxidized to the keto acid, and a Wolf–Kishner reduction of the semicarbazone gave octanoic acid. The octanoic acid was further degraded by the method of Hunter and Popjak.[13] The degradation gives greatly improved results (*cf.* Figure 1 and Table I), since the activities of the *ortho*, *meta*, and *para* positions are determined uniquely. The errors in the *ortho*, *meta*, and *para* positions are ±27, ±45, and ±45%, respectively, in the earlier work, whereas the present work results in error limits of only ±5% for each of these positions. Valuable internal checks, shown in Table, I, are also provided. The 1-position is determined by difference.

The results of the degradation are summarized in Table II and Figure 2. That the reaction rate varies (runs I and II) with different samples of hydrocarbon or catalyst is well known and consistent with the established mechanism.[8]

These results clearly agree with previous experiments,[5,8] in that a preequilibrium with a localized π complex is not an important product-determining step. The small amount of activity in the *ortho* position shows even more dramatically than previously[5] that a 1,2 shift of an ethyl group in ethylbenzene is slow compared to disproportionation. The fact that the activity

(12) R. A. Benkeser, R. E. Robinson, D. M. Sauve, and H. Thomas, *J. Am. Chem. Soc.*, **77**, 3230 (1955).

(13) G. D. Hunter and G. Popjak, *Biochem. J.*, **50**, 163 (1951).

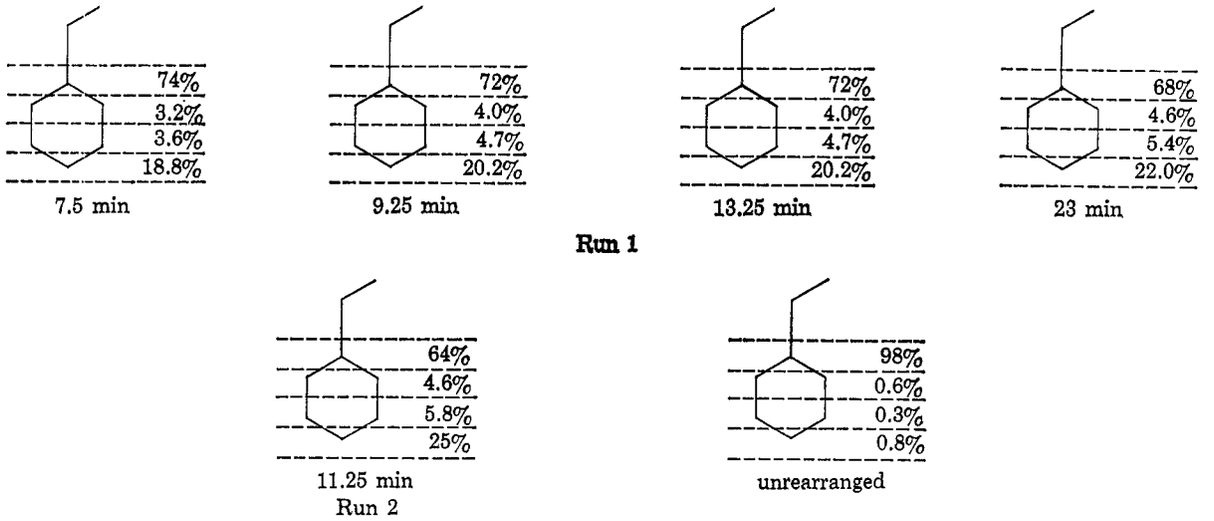


Figure 2.—Distribution of activity in ethylbenzene in per cent where the total ring activity equals 100%.

TABLE II

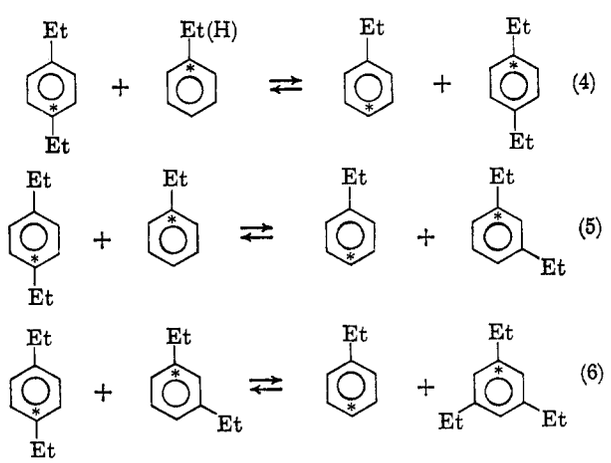
RADIOASSAYS FOR THE ETHYLBENZENE DEGRADATION[a]

	Activity, mμcuries/mg of C					
		Run 1				Run 2
Source of Activity	Unrearranged	7.5 min	9.25 min	13.25 min	23 min	11.25 min
CO_2 (octanoic acid)	...	0.0918	0.113	0.113	0.136	...
n-Heptylamine[b]	...	0.796	...	0.803	...	...
CO_2 (acetic acid)	0.0076	0.0950	0.111	0.115	0.128	0.225
Methylamine[b]	0.0144	0.103	0.136	0.135	0.153	0.282
CO_2 (hexanoic acid)	0.036	1.07	1.15	1.15	1.25	2.49[c]
Acetic acid[d]	0.0122	0.0973	0.126	...	0.137	0.261
Hexanoic acid	...	0.923	0.903	0.817	0.843	1.51
n-Pentylamine[e]	1.17[c]	...	...	...	0.767	1.17[c]

[a] About half of the assays are averages of duplicates. [b] Assayed as phenylthioureas and corrected for inactive carbon in the derivatizing agent. [c] Corrected for dilution. [d] Assayed neat or as thallium salts. [e] Assayed as chloroplatinates.

in the *meta* position is consistently a little higher than in the *ortho* position is indicative of at least a small amount of direct *meta* alkylation, although the difference is very close to the estimated 5% error in each position. (A systematic error would appear to have been more likely in the opposite direction, since the *meta* position was determined by derivatization of a volatile radioactive substance with an inactive reagent.) Four possible explanations of these results can be envisioned: (1) that by chance the activity due to a 1,2 shift of an ethyl group in ethylbenzene and *ortho* alkylation give approximately the same amount of *ortho* labeling as the reversal of direct *meta* alkylation gives *meta* labeling; (2) that the reactions suggested under (1) are relatively unimportant and that the equality is mainly due to *para* alkylation followed by a 1,2 shift of an ethyl group; (3) the label in *m*-diethylbenzene becomes randomized much more rapidly than in ethylbenzene; or (4) some combination of the above. The possibility that this near equality in *ortho* and *meta* labeling is a result of a much faster alkylation of benzene than the reverse reaction of *m*-diethylbenzene to give ethylbenzene seems excluded by labeling experiments[14] at the apparent equilibrium concentrations. These labeling experiments show these two rates are of the same magnitude. The essentially equal labeling in the *ortho* and *meta* positions does require that the rate of the 1,2 shift of an ethyl group in ethylbenzene plus one-half of the rate of the reversal of *ortho* alkylation, if any, be not greater than one-half of the rate of the reversal of any direct *meta* alkylation. Ideally, only half of the reversals of direct *meta* alkylation (eq 1) give *meta* labeling, while every 1,2 shift of an ethyl group in ethylbenzene gives *ortho* labeling. If, in fact, the label in *m*-diethylbenzene were randomized, an even lower limit could be placed upon this relative rate.

Several "net" reactions (eq 4–6) are suggested as possibly contributing to the strikingly large amount of



para labeling. This labeling requires that the ion produced from *p*-diethylbenzene be an important alkylating reagent in this reaction. Although alkylation by

(14) G. Moore and A. P. Wolf, unpublished data.

the intermediate diphenylalkanes[8,15a] would give the same result, this does not seem to be energetically favorable owing to steric strain. Similarly, *p*-xylene seems to be a better alkylating agent than the other xylene isomers.[15b]

In order to place a limit on the ratios of initial *meta* and *para* attack, the disproportionation reaction was carried out at short contact time in a flow system. The catalyst in benzene was mixed with ethylbenzene and rapidly quenched.[16] When 3% *net reaction* had occurred, the *meta*:*para* ratio of diethylbenzenes was 1.8:1.0, showing that *para* attack is at least slightly favored per position. This result is in the direction expected on the basis of electronic effects in electrophilic substitution. Even though the value is far from the apparent equilibrium ratio for the *m*- and *p*-diethylbenzenes of 11:1 under these conditions, there is no good reason to believe that this is close to the correct value of the selectivity of the ions involved. Without additional information, using the activity in the *meta* and *para* positions as a rough measure of the selectivity of the alkylating ion[8] is questionable, even though the value of 8–10 obtained here is not too far from the value of 4 obtained by Brown[17] for the alkylation of toluene with benzyl bromide.[17] Among the many complicating reactions involved here, it is quite conceivable that a significant fraction of the *meta* labeling is a result of *para* attack (eq 2 and 3). These data, combined with the conclusion of Allen,[18] that *p*-ethyltoluene isomerizes largely intramolecularly, provides further support for the importance of *para* alkylation as a prior step in the formation of *m*-diethylbenzene. This explanation requires that the intramolecular isomerization of ethylbenzene be considerably slower than the intramolecular isomerization of *p*-diethylbenzene. This is not unreasonable in view of the fact that *p*-xylene is 100 times and *m*-xylene is 300 times as basic as toluene.[19] Similarly, the rearrangement of diphenyl is not unexpected.[20]

To further demonstrate the importance of *p*-diethylbenzene as an alkylating agent, the disproportionation reaction was carried out using inactive ethylbenzene with *p*-diethylbenzene-1-C^{14} added. As seen in Table III, the activities of the ethylbenzene and *p*-diethylbenzene became identical within experimental error in 1.5 min. Hoff[21] suggested that *m*-diethylbenzene, not ethylbenzene, was the source of the ethyl group in the reaction of ethylbenzene with xylenes in the presence of excess hydrogen fluoride and boron trifluoride. This suggestion was made on the basis of the slow increase of the diethylbenzene concentration, indicating that some of the product was diverted. Although the alkylation of xylenes, at least at lower temperatures, shows that *m*-diethylbenzene is formed more readily than the ethylxylenes,[10] it is possible that *p*-diethylbenzene is an important alkylating agent in this system also.

TABLE III

DISPROPORTIONATION WITH ACTIVE *p*-DIETHYLBENZENE ADDED

Time 1.5 min

Ph-X	Mole %[a]	mμcurie/mmole
Et	70	0.77
m-Et_2	26.5	...
p-Et_2	3.8	0.79
sym-Et_3	>1	...
as-Et_3	...	...
H	...	...

[a] Mole per cent excludes benzene throughout the table.

Experimental Section

Ethylbenzene-1-C^{14}.—Benzoic acid-1-C^{14} was converted to ethylbenzene-1-C^{14} by a sequence of conventional reactions[5] and purified by vpc to remove a small amount of toluene-1-C^{14}.

Disproportionation of Ethylbenzene-1-C^{14}.—The method used was essentially that of Brown and Smoot.[7] Freshly prepared aluminum bromide[16] was redistilled into a three-necked 500-ml Morton flask. The flask was fitted with a stirrer, a thermometer, an outlet with a drying tube of phosphorus pentoxide, and a tube extending to the bottom of the flask. After ethylbenzene-1-C^{14} (167.5 g) was added, hydrogen bromide, dried over phosphorus pentoxide, was metered in with cooling over a 2-min period at $-12 \pm 5°$. The reaction mixture was warmed to 0° (1.5 min required) and held at that temperature. Samples were removed under nitrogen pressure and quenched in a water–ice mixture at 7.5, 9.33, 13.5, and 23 min from the beginning of the hydrogen bromide addition. Each organic layer was separated, dried over anhydrous sodium carbonate, and distilled through a short packed column to give the labeled ethylbenzenes, bp 132–138°.

In a similar run the addition of hydrogen bromide over a 2-min period was begun at −20° and warmed from 16 to 0° in an additional 2 min. A sample was taken at 11.25 min after the beginning of the hydrogen bromide addition.

Degradation of Ethylbenzene.—The method used is somewhat similar to that published by Koptyug and co-workers.[22,23]

Reduction of Ethylbenzene.—The reduction was carried out as described by Benkeser, *et al.*,[12] at −5 to −10° in ethylamine containing 10% diethylamine to give a 50–55% yield (70% of organic material recovered) of 1-ethylcyclohexene.

5-Keto-*n*-octanoic Acid.—The mixture from the reduction of ethylbenzene, 1-ethylcyclohexene (8.3 g, 0.078 mole), isomeric olefin, and ethylcyclohexane, and 200-ml of ethanol were placed in a three-necked 1-l. flask fitted with a stirrer, thermometer, and an addition funnel. Potassium permanganate (50 g, 0.32 mole) and magnesium sulfate (27 g) in 600 ml of water were added at 0° with stirring. After saturation with a salt and acidifying with hydrochloric acid, the oily layer was taken up in ether and the water layer was extracted twice more with ether. The combined extracts were dried over magnesium sulfate, and the ether was removed. To the residue was added 45 ml of ethanol, 35 ml of water, 12 g of sodium acetate, and 8.5 g of semicarbazide hydrochloride. After heating on the steam bath and cooling, the semicarbazone was collected to give 8.0 g (50%) of crude product, mp 180–185° (lit.[24] mp 190°). The yield of purified material was 30–35%.

Octanoic Acid.—The semicarbazone (4.6 g) and potassium hydroxide (8.3 g) in 50 ml of diethylene glycol were heated on an oil bath at 190° for 6 hr. The mixture was acidified with hydrochloric acid and ether extracted. After the ether was dried and removed, the residue was distilled to give 4.0–4.2 g (90–95%) of octanoic acid.

Acetic and Caproic Acids.—The octanoic acid was degraded by the method of Hunter and Popjak[13] to give acetic and caproic acids. The acids were separated by benzene–water partition followed by vpc.

Decarboxylations and Derivatizations.—All decarboxylations were carried out by the micromethod of Anderson and Wolf.[25]

(15) (a) R. M. Roberts, A. A. Khalaf, and R. N. Greene, *J. Am. Chem. Soc.*, **86**, 2846 (1964); (b) R. H. Allen and L. D. Yats, *ibid.*, **81**, 5289 (1959).
(16) H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955).
(17) H. C. Brown and B. A. Bolto, *ibid.*, **81**, 3320 (1959).
(18) R. H. Allen, *ibid.*, **82**, 4856 (1960).
(19) D. A. McCauley and A. P. Lien, *ibid.*, **73**, 2013 (1951).
(20) H. Wynberg and A. P. Wolf, *ibid.*, **85**, 3308 (1963).
(21) M. C. Hoff, *ibid.*, **80**, 6046 (1958).
(22) V. A. Koptyug, I. S. Isaev, and N. N. Vorozhtsov, *Dokl. Akad. Nauk SSSR*, **137**, 866 (1961).
(23) *Cf.* also H. Steinberg and F. L. J. Sixma, *Rec. Trav. Chim.*, **79**, 679 (1960); J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Am. Chem. Soc.*, **78**, 601 (1956).
(24) E. E. Blaise and A. Koehler, *Bull. Soc. Chim. France*, **7**, 223 (1910).

The CO_2 was collected, transferred to gas counters, and then assayed by the method of Christman, *et al.*[26] The amines produced were assayed as their phenylthioureas or chloroplatinates. The 1-position was determined by difference.

Control Ethylbenzene-1-C^{14}.—Unreacted ethylbenzene-1-C^{14} was degraded as described above and shown to have almost all of its activity in the 1-position (see Table III).

The Disproportionation of Ethylbenzene at Short Contact Times.—The reactions were carried out in a flow system according to the procedure of Brown and Jungk.[16] The benzene–catalyst mixture (35 ml) and ethylbenzene (50 ml) were allowed to react for about 0.005 sec, quenched, and analyzed on a Carbowax capillary vpc column. The ratio of *m*-:*p*-diethylbenzene was 1.8:1.0 when 3% of the ethylbenzene had reacted. The peaks were calibrated with an authentic mixture of pure isomers.

The Preparation of *p*-Diethylbenzene-1-C^{14}.—The method of Mowry, *et al.*,[27] was used to prepare *p*-ethylacetophenone-4-C^{14} from ethylbenzene-1-C^{14}. The semicarbazone, mp 190° (lit.[28] mp 191°), was prepared and reduced as above to give *p*-diethylbenzene-1-C^{14} containing 0.5% of the *meta* isomer.

The Disproportionation of Ethylbenzene with Added *p*-Diethylbenzene-1-C^{14}.—Ethylbenzene (33 ml) containing 2 wt % of *p*-diethylbenzene-1-C^{14} was disproportionated as above at +10 ± 5° and quenched immediately after the proper amount of hydrogen bromide was added (1.5 min). The mixture was analyzed at 125° by vpc on a 0.25-in. column packed with 12% by weight of Bentone 34 on firebrick.[29] The *m*- and *p*-diethylbenzenes were completely separated in 7 min on this column. The *meta*:*para* ratio was 5.3:1.0 and 30% of the ethylbenzene had disproportionated. To collect samples for radioassay, a 0.5-in. column was used (see Figure 2).

Acknowledgment.—The authors wish to thank Miss C. S. Redvanly for her help in carrying out most of the Schmidt degradations. We also are indebted to Dr. D. R. Christman and Mrs. C. T. Paul for the carbon-14 radioassays. A generous supply of Bentone 34 was provided by the National Lead Company.

(25) 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).

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The Mechanism of the Prins Reaction. V. The Prins Reaction of Styrenes[1]

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Received September 7, 1965

The stereochemistry of the products from the Prins reaction with *cis*- and *trans*-1-phenylpropene, *cis*- and *trans*-β-bromostyrene, and *cis*- and *trans*-β-chlorostyrene is reported. In no case was the reaction stereospecific, in contrast to previous reports. The Prins reaction of *cis*- and *trans*-1-phenylpropene appears to proceed predominantly *via* a simple symmetrically solvated carbonium ion intermediate. However, the Prins reaction with the β-halostyrenes is more complex.

The acid-catalyzed condensation of formaldehyde with various styrenes has been the subject of several investigations.[3-7] These studies have been concentrated on the stereochemistry of the reaction. One fact emerges from these studies; *cis* addition accounts for a large fraction of the products, whereas *trans* addition is the normal result with acyclic and aliphatic compounds.[8-12] Since most of the previous studies were carried out on cyclic styrenes or styrenes which would yield very stable intermediate carbonium ions, it seemed desirable to study a simple case, *cis*- and *trans*-1-phenylpropene. The Prins reaction of the *cis*- and *trans*-β-bromostyrenes was also of interest since it has been examined three times previously with various results. Bernardi and Leone[6] report only the formation of *trans*-5-bromo-4-phenyl-1,3-dioxane from both *cis*- and *trans*-β-bromostyrene, whereas Terada[4] reports the formation of both stereoisomeric 5-bromo-4-phenyl-1,3-dioxanes, and Hsing and co-workers[3] report two products, both liquids, although pure *cis*-4-phenyl-5-bromo-1,3-dioxane is crystalline.

In the present study we have determined the stereochemistry of the Prins reaction with three pairs of isomeric substituted styrenes; *cis*- and *trans*-β-bromostyrene, *cis*- and *trans*-β-chlorostyrene, and *cis*- and *trans*-1-phenylpropene. We find that the Prins reaction is not stereospecific with any of these olefins. The results of our study are summarized in Table I.

The olefins used in the study were pure isomers as shown by their spectroscopic and chromatographic behavior. *cis*-β-Chlorostyrene was the most difficult of the styrenes to prepare in pure form. The mixture of *cis*- and *trans*-β-chlorostyrenes obtained by the method of Biltz[13] was partially separated by fractional distillation, and pure *cis*-β-chlorostyrene was obtained by chromatography over alumina. Pure *trans*-β-chlorostyrene was obtained from mixtures of *cis* and *trans* material by destroying the *cis* isomer with sodium hydroxide in dimethyl sulfoxide. *cis*-β-Bromostyrene was prepared by the method of Cristol and Norris,[14] and *trans*-β-bromostyrene was obtained from mixtures of the *cis* and *trans* isomers by destroying the *cis* material with sodium hydroxide in 2-propanol. Pure *cis*-

(1) Supported by a grant from the Petroleum Research Fund of the American Chemical Society, Grant No. 915-A4.

(2) Alfred P. Sloan Research Fellow.

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