from ethyl acetate gave sturdy kernels of XXXIII, the **tetracyanoethylene adduct of methyl 4-methyl-1,3-cyclohexadiene-1-carboxylate**. The substance had m.p. 203–203.5° dec. and showed no absorption maximum above 210 mμ.

Anal. Calcd. for $C_{15}H_{12}N_4O_2$: C, 64.28; H, 4.32; N, 19.99. Found: C, 64.18; H, 4.39; N, 19.93.

After 2 weeks of storage, fraction 10 no longer showed the v.p.c. peak of the original major component. Its ultraviolet spectrum showed λ_{max} 234 mμ.

Fraction 11, 0.35 g., consisted of a mixture of methyl *p*-toluate (75%) and methyl phenylacetate (25%) based on v.p.c., n.m.r., and infrared analyses. It was heated on the steam bath for 15 min. in a solution of 0.2 g. of sodium hydroxide in 4 ml. of 50% aqueous methanol. Most of the methanol was distilled off, ice and 10% sulfuric acid were added, and the resulting tan precipitate (240 mg., m.p. 165–178°) was filtered off and dried. This material was sublimed at about 120° at 25 mm. and then recrystallized from water to give pure ***p*-toluic acid** (120 mg.), m.p. 177–178° alone or mixed with an authentic sample. Its infrared spectrum was superimposable on that of authentic *p*-toluic acid.

Pyrolysis Products Trapped at −80°.—The contents of this trap were allowed to warm to room temperature while the expanding gases were passed through ether. No significant amount of material dissolved in the ether as was shown by v.p.c. The residue in the trap showed a broad ultraviolet absorption maximum in the region 220–230 mμ, similar to that reported for the dimer (XIV) of methyl cyclopentadienecarboxylate, as well as a series of sharp peaks characteristic of benzene. The v.p.c. on both Carbowax and TCEP columns showed peaks with the retention times of benzene and cyclohexene as well as other materials.

Pyrolysis Products Trapped at −127°.—The −127° trap was allowed to warm to room temperature while the expanding gases were bubbled through a 10% solution of bromine in methylene chloride. Concentration on the steam bath gave a liquid residue which was distilled bulb-to-bulb and then had a v.p.c. retention time the same as that of authentic ethylene bromide. The infrared spectrum, except for a very weak extra absorption at 5.7 μ, was superimposable on that of **ethylene bromide**.

Preparation of Authentic Samples.—Methyl cyclopentadienecarboxylate (XIII) was prepared by heating the dimer XIV[16] with a free flame and condensing the distillate in cold benzene. The solution was immediately subjected to v.p.c. analysis and showed, besides the solvent peak, a single peak with the same retention time as that peak in the pyrolysate from Vc which disappears after standing for a few hours.

In another cracking experiment, the distillate was collected in cold ethyl acetate and the solution was immediately hydrogenated over Adams catalyst. The resulting methyl cyclopentanecarboxylate[53] was a colorless liquid which was homogeneous by v.p.c.

Methyl cyclohexylacetate[54] was obtained by esterification (methanol–sulfuric acid) of the product from hydrogenation[55] of phenylacetic acid at room temperature in solvent acetic acid over platinum. The ester was separated from the methyl phenylacetate that accompanied it by preparative v.p.c.

Similarly, the **methyl 4-methylcyclohexanecarboxylates** were prepared from *p*-toluic acid. The product was a mixture of methyl *p*-toluate and the two saturated substances, the latter in the ratio of 2:1.[56]

Methyl 2-methylcyclohexanecarboxylate was prepared similarly from *o*-toluic acid. Its v.p.c. showed only one peak besides the small one due to methyl *o*-toluate.

Methyl 3-methylcyclohexanecarboxylate was prepared by hydrogenation of methyl *m*-toluate (from *m*-toluic acid supplied by Aldrich Chemical Co.) in acetic acid solvent over Adams catalyst. After 30 hr., the catalyst was filtered off and the solution was diluted with ice water and extracted with ether. After having been washed successively with dilute aqueous sodium hydroxide, water, and brine, the ether solution was dried over sodium sulfate and evaporated to give a liquid. This was distilled bulb-to-bulb to give material which showed three v.p.c. peaks, one of which corresponded to methyl *m*-toluate. The two peaks corresponding to the methyl 3-methylcyclohexanecarboxylates were in the intensity ratio 1:5 and had retention times the same as those of the two peaks of methyl 4-methylcyclohexanecarboxylate.

Methyl cycloheptanecarboxylate (XXXVI)[57] was obtained from cycloheptanecarboxylic acid, which in turn was prepared by carbonation of the Grignard reagent from cycloheptyl bromide (Chemicals Procurement Laboratories). The acid was converted *via* the acid chloride to the amide, m.p. 192–193°, reported[58] m.p. 192–193°.

Methyl β-cyclopentylpropionate, prepared from the acid (Fluka), showed a single v.p.c. peak which did not correspond to any of the peaks shown by the hydrogenated pyrolysate from Vc.

Methyl 3-heptanecarboxylate (methyl 2-ethylhexanoate) was obtained from the acid, which was prepared by carbonation of the Grignard reagent from 3-bromoheptane (K and K Laboratories). The major product of this process had a v.p.c. retention time the same as one of the very small peaks in the hydrogenated pyrolysate.

Controls.—Methyl *m*-toluate was passed through the pyrolysis chamber under the same conditions used for the pyrolysis of Vc. After twelve passes, it had acquired a faint yellow tinge, but its infrared spectrum was identical with that of the starting methyl *m*-toluate and the v.p.c. showed only one peak.

By the same criteria, methyl *o*-toluate was also stable under the pyrolysis conditions.

(53) K. W. F. Kohlraush and R. Skrabal, *Monatsh.*, **70**, 44 (1937).

(54) P. Sabatier and M. Murat, *Compt. rend.*, **156**, 424 (1913).

(55) R. Adams and J. R. Marshall, *J. Am. Chem. Soc.*, **50**, 1970 (1928).

(56) R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1245 (1939), report the formation of predominantly *cis*-4-methylcyclohexanecarboxylic acid when *p*-toluic acid is hydrogenated at 100° in acetic acid over platinum. It is not clear whether our mixture arises from lack of stereospecificity in hydrogenation or from some epimerization during esterification.

(57) L. Ruzicka, P. Barman, and V. Prelog, *Helv. Chim. Acta*, **34**, 401 (1951).

(58) T. Steadman, *J. Am. Chem. Soc.*, **62**, 1606 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

Mechanism of Transalkylation of Ethylbenzene with Gallium Bromide–Hydrogen Bromide[1]

BY A. STREITWIESER, JR., AND L. REIF

RECEIVED DECEMBER 16, 1963

The kinetics of transalkylation of ethylbenzene-ring-C^{14} in benzene at 50° as followed by loss of radioactivity is first order each in hydrocarbon, gallium bromide, and hydrogen bromide. Reproducibility was good within any one series of kinetic runs but poor from one series to the next. This behavior is consistent with the carbonium ion chain alkylation–dealkylation mechanism for transalkylation that results from the identity of the rates of racemization and of loss of radioactivity with optically active ethylbenzene-α-*d*-ring-C^{14} and the somewhat slower scrambling of deuterium yielding ethylbenzene and ethylbenzene-α-d_2.

Many alkyl-aromatic compounds are known to disproportionate under acidic conditions; the alkyl group transfers from one aromatic ring to another. For secondary alkyl compounds, the transfer seems clearly to involve the essentially free alkyl cation generated from the protonated starting hydrocarbon (σ-complex).[2]

(1) This work was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. This paper is Part XIII of the series "Stereochemistry of the Primary Carbon."

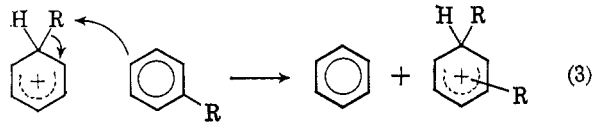
(2) H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 2176 (1956).

The work of Burwell and Shields[3] is especially definitive; they found, for example, that the disproportionation of 2-phenylpentane causes isomerization of the amyl group. Tertiary alkyl groups disproportionate more rapidly than secondary and clearly also involve the free tertiary alkyl cation.[4]

$$ArR + H^+ \rightleftharpoons ArH + R^+ \quad (1)$$

$$R^+ + ArR \rightleftharpoons ArR_2 + H^+ \quad (2)$$

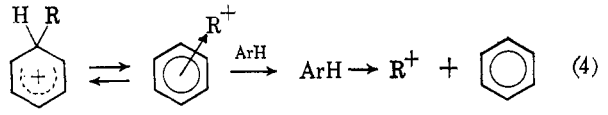
The mechanism of disproportionation of primary alkylarenes, on the other hand, does not involve reactions 1 and 2. Heise and Töhl,[5] in 1892, showed that *n*-propylbenzene and aluminum chloride–hydrogen chloride at 100° gives di-*n*-propylbenzene with no rearrangement. This generality of disproportionation or transalkylation of primary alkylbenzenes with essentially no rearrangement has since been confirmed repeatedly.[2,4a,6] Since a free primary alkyl cation would be expected to rearrange to a more stable secondary cation, McCauley and Lien[4a] suggested an SN2-type of mechanism (3).



(3)

Their finding that neopentylbenzene does not disproportionate with HF–BF_3 under conditions which give rapid disproportionation with ethylbenzene is consistent with this mechanism.

This mechanism is harder to reconcile with the relative rates of disproportionation found by Brown and Smoot[2] with $AlBr_3$–HBr: Me, 10^{-7}; Et, 1; *i*-Pr, 10^2. The difference between toluene and ethylbenzene is unusually large for a direct displacement mechanism.[7] Hence, Brown and Smoot suggested a rapid equilibrium to a "localized π-complex" which is the intermediate in the displacement reaction



(4)

This mechanism has since been invalidated by the findings that ethyltoluene[8] and ethylbenzene[9] do not undergo intramolecular isomerization much faster than intermolecular transalkylation as demanded by the Brown and Smoot mechanism.

All this leaves the theory of disproportionation in an unsatisfactory state. We hoped to provide useful information by a study of the stereochemistry of the reaction by using optically active ethylbenzene-α-*d*-ring-C^{14}. Preliminary studies showed that ethylbenzene-ring-C^{14} lost radioactivity at a convenient rate in benzene with gallium bromide–hydrogen bromide at 50°. This loss of C^{14}, k^*, measures the rate of transfer of the ethyl group to an inactive benzene molecule. In principle, we could follow simultaneously the loss of optical activity, k_{rac}, of the deuterated compound. If the transalkylation occurs with complete racemization, $k_{rac} = k^*$. A displacement reaction with inversion of configuration requires $k_{rac} = 2k^*$.[10] The deuterium serves as an additional label to check other possible reactions at the α-carbon. The transalkylation in homogeneous benzene solution was chosen to avoid the problems inherent in the mixture of diethylbenzenes obtained by a normal disproportionation. We would expect any findings for transalkylation to benzene to apply as well for transalkylation to ethylbenzene.

Results and Discussion

Ethylbenzene-α-*d*-ring-C^{14} was prepared by acetylation of benzene-C^{14} and reduction to the alcohol. The α-phenethyl-ring-C^{14} alcohol was resolved, converted to the chloride, and treated with lithium deuteride–lithium aluminum deuteride to give optically active ethylbenzene-α-*d*-ring-C^{14}. This route was adapted from earlier preparations of the optically active but nonradioactive hydrocarbon.[11,12] Ethylbenzene-ring-C^{14} was prepared similarly for use in preliminary kinetic studies to determine the best conditions for the stereochemical studies. The actual kinetic study was more extensive than we had originally anticipated and gave interesting results by itself.

In these studies, purified and dried reagents were used in a kinetic procedure that used syringing techniques and serum-capped vessels. This method allowed considerable care in making up the solution but clearly does not approach the care permitted by thoroughgoing vacuum line techniques. Dilute solutions (~2%) of ethylbenzene in benzene were used to avoid producing important amounts of diethylbenzenes. The kinetic solutions were made up with gallium bromide and hydrogen bromide, and, after thermostating at 50°, aliquots were syringed out at intervals. Ethylbenzene was isolated using a preparative gas chromatograph, and its radioactivity was measured by liquid scintillation counting. When plotted on semilog paper *vs.* time, the radioactivity does not fall off linearly as expected for a pseudo-first-order reaction. Instead, the fall-off is usually somewhat more rapid. If sufficient points were taken during the first 20–30% of reaction, a good straight line could usually be defined for the initial rate (Fig. 1). In some cases when the points were poorly spaced, integrated first-order rate constants could be extrapolated to zero time.

In early kinetic runs, disconcerting nonreproducibility was observed in rates, particularly between the optically active and inactive ethylbenzenes. Consequently, the kinetic studies were made in series in which a freshly prepared kinetic solution was distributed among two or more vessels and additional reagents were syringed in as desired. After thermostating, ethylbenzene was syringed into each vessel to start the reactions.

(3) R. L. Burwell, Jr., and A. D. Shields, *J. Am. Chem. Soc.*, **77**, 2766 (1955).

(4) (a) D. A. McCauley and A. P. Lien, *ibid.*, **75**, 2411 (1953); (b) see also G. Dallinga and G. Ter Maten, *Rec. trav. chim.*, **79**, 737 (1960).

(5) R. Heise and A. Töhl, *Ann.*, **270**, 155 (1892).

(6) G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303 (1935); D. V. Nightingale and J. M. Shackelford, *J. Am. Chem. Soc.*, **76**, 5767 (1954); **78**, 1225 (1956); R. E. Kinney and L. A. Hamilton, *ibid.*, **76**, 786 (1954); R. M. Roberts, G. A. Ropp, and O. K. Neville, *ibid.*, **77**, 1764 (1955).

(7) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 13.

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

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

(10) E. D. Hughes, F. Juliusberger, S. Masterman, B. Topley, and J. Weiss, *J. Chem. Soc.*, 1525 (1935).

(11) E. Eliel, *J. Am. Chem. Soc.*, **71**, 3970 (1949).

(12) H. J. Dauben, Jr., and L. L. McCoy, *ibid.*, **81**, 5404 (1959).

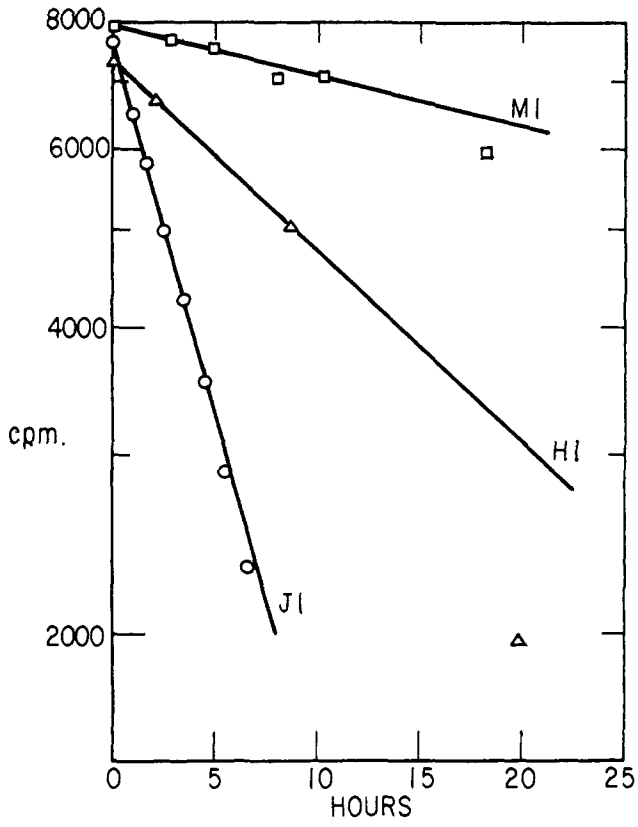


Fig. 1.—Some typical kinetic plots for three runs included in *Table I*.

The data summarized in Table I show that results *within a series* are reproducible (compare E1 and E2, H1 and H2, J1 and J3). When gallium bromide is held constant within a run, the initial rates show a first-order dependence on [HBr] (runs F1 and F2, H1,2 and H3). Similarly, when hydrogen bromide is constant within a series, the initial rates are first order in [$GaBr_3$] (runs G1 and G2, H1,2 and H4). The initial rates follow the third-order relation

$$\text{initial rate} = k_3[C_6H_5C_2H_5{}^*][GaBr_3][HBr] \qquad (5)$$

The initial third-order rates are also summarized in Table I. For many of the runs, these constants are satisfactorily reproduced, but for others, substantial variation is apparent. Increasing the ethylbenzene concentration (runs M1 and M2, N1 and N3) or adding diethylbenzenes to the amount present at equilibrium (M1 and M3, T1,2 and T3) did not affect the rate significantly. A solution of gallium bromide and hydrogen bromide in benzene is known to be unstable—after several days, the solution discolored and a tar deposited.[13] In series N and P, the benzene–$GaBr_3$–HBr solution was allowed to stand for 1 or more days before adding the ethylbenzene. The initial rates were increased substantially. These results show that this decomposition produces a significant catalyst for the transalkylation of ethylbenzene and are difficult to rationalize by the displacement mechanisms. On the other hand, the tar precipitated during the reaction was shown in series R to have no significant effect on the reaction.

The comparisons of k^* for ethylbenzene-ring-C^{14} and of k_{rac} for ethylbenzene-α-*d* in runs B1 and B2, C1 and C2, would mean at face value a partial net retention of configuration during transalkylation. This result is at variance with the later runs using ethylbenzene-α-*d* ring-C^{14}, in which k^* and k_{rac} are measured during the same run for the same compound and found to be equal. Instead, there seems to be some dependence of k_3 on the source of ethylbenzene. The runs through G2 used one preparation of ethylbenzene-ring-C^{14}, H1 through J3 used a second; of a third preparation, runs M1-P1 used one fraction, P2-T2 used a second fraction. Note also the comparison of J1 and J3 with J2. It appears that different samples of ethylbenzene can cause ~6-fold rate variations, and it seems possible that a sample could change with age. Furthermore, although not clearly evident in our data, it is possible that some of

(13) Note the similar behavior of benzene containing aluminum bromide and hydrogen bromide; ref. 2.

TABLE I

KINETICS OF TRANSALKYLATION OF ETHYLBENZENE WITH $GaBr_3$–HBr

Temp. 50°, $[EtC_6H_5]$ = 0.177 mole/l.

Series	$[GaBr_3]$, mole/l.	[HBr], mole/l.	Initial k × 10^{-5}, sec.$^{-1}$	10^3k_2, l.^{2}/mole^2 sec.
B1	0.389	0.033	3.6	2.8
2[a]	.389	.033	~0.6	
C1	.314	.028	1.9	2.2
2[a]	.314	.028	~0.5	
D	.302	.081	8.4	3.4
E1	.292	.017	1.2	2.4
2	.292	.017	1.2	2.4
F1	.261	.013	0.75	2.2
2	.261	.043	2.75	2.4
G1	.110	.013	0.21	1.5
2	.183	.012	0.42	1.9
H1	.313	.019	1.2	2.0
2	.313	.019	1.1	1.8
3	.313	.034	1.9	1.8
4	.608	.019	1.8	1.6
I	.311	.025	1.5	1.9
J1	.259	.082	4.9	2.3
2[b]	.259	.082	1.9	
3	.259	.082	4.6	2.2
K[c]	.221	~ .08[d]	0.67	
M1	.263	.026	.36	0.52
2[e]	.260	.026	.36	.53
3[f]	.263	.026	.42	.61
N1	.290	.130	~3	~ .8
2[g]	.290	.130	26	
3[e]	.287	.129	3.9	1.1
4[h]	.290	.130	11	
P1	.258	.039	0.44	0.44
2[h]	.258	.039	1.0	
R[i]	.23	.049	0.47	0.42
S1	.299	.079	~0.9[j]	~ .4
2	.299	.079	1.9	.8
T1	.325	.064	..[k]	
2	.325	.064	1.8	.9
3[l]	.325	.064	2.5	1.2

[a] Optically active $C_6H_5CHDCH_3$ was used; k is that for racemization. [b] Ethylbenzene-α-*d*-ring-C^{14} was used; $k_{rac} \cong 2 \times 10^{-5}$ sec.$^{-1}$. [c] Ethylbenzene-α-*d*-ring-C^{14} was used; $k_{rac} = 0.69 \times 10^{-5}$ sec.$^{-1}$. [d] An unknown amount of HBr was lost during this run. [e] $[EtC_6H_5] = 0.263$ mole/l. [f] The ethylbenzene used contained 2.9% of diethylbenzenes. [g] $GaBr_3$–HBr solution was allowed to stand several days before start of reaction. [h] $GaBr_3$–HBr solution was allowed to stand 1 day before start of reaction. [i] After 28% reaction, a portion of the contents was centrifuged. In the several points taken thereafter, there was no significant difference in radioactivity between the uncentrifuged aliquot, the clear centrifugate, and the centrifugate containing the centrifuged tar. [j] Ethylbenzene-α-*d*-ring-C^{14} was used; $k_{rac} \cong 1.1 \times 10^{-5}$ sec.$^{-1}$. [k] See Table II. [l] Ethylbenzene contained 1.6% of diethylbenzenes.

the variations between series are associated with the other reagents.

All of these subtle influences are difficult to fit to the mechanisms already discussed—rather, they are more typical of reactions of the radical-chain type. Nevertheless, the definitive results come from the studies with optically active ethylbenzene-α-d-ring-C^{14}. In runs J2 and K, $k^* = k_{rac}$. Similarly, in runs S1 and T1, optical activity is lost at about the same rate as radioactivity (Table II). In these runs also, the deuterium content was determined by mass spectral analyses[14]; we find progressive conversion of ethylbenzene-d to ethylbenzene and ethylbenzene-d_2. The fact that no trideuterio compound could be found suggests strongly that the dideuterioethylbenzene present is ethylbenzene α-d_2. The rate at which the deuterium scrambling occurs is clearly slower than the transalkylation but is of the same order of magnitude.

TABLE II

TRANSALKYLATION OF ETHYLBENZENE-α-d-RING C^{14}

Run	Time, hr.	Rotation ±0.01–0.02°	Rotation % reacn.	Radioactivity C.p.m.	Radioactivity % reacn.	Deuterium content, % D_0	D_1	D_2
S1	0	0.441		16970		4.8	95.0	0.2
	2.4	.386	13	15281	10	10.2	88.2	1.6
	7.1	.224	49	9784	42	13.2	79.9	6.9
	14.0	.057	87	3332	84	23.5	61.1	15.4
T1	0	.405		17075		4.8	95.0	0.2
	3.0	.339	16	13839	19	9.0	87.8	3.2
	11.8	.104	74	4362	74	21.9	63.9	14.2
	19.9	...		731		36.4	38.9	24.7[a]

[a] Product contained no detectable D_3.

The deuterium scrambling is undoubtedly due to a hydride transfer to carbonium ions of the Bartlett–Condon–Schneider[15] type

$$C_6H_5CHDCH_3 + C_6H_5\overset{+}{C}HCH_3 \longrightarrow C_6H_5\overset{+}{C}DCH_3 + C_6H_5CH_2CH_3 \quad (6)$$

$$\longrightarrow C_6H_5\overset{+}{C}HCH_3 + C_6H_5CHDCH_3 \quad (7)$$

$$C_6H_5CHDCH_3 + C_6H_5\overset{+}{C}DCH_3 \longrightarrow C_6H_5\overset{+}{C}DCH_3 + C_6H_5CHDCH_3 \quad (8)$$

$$\longrightarrow C_6H_5\overset{+}{C}HCH_3 + C_6H_5CD_2CH_3 \quad (9)$$

This type of hydride transfer has been demonstrated earlier for secondary alkylbenzenes[3,16] and has been suggested for ethylbenzene-α-d.[16] Consider the case that this process occurs independently of transalkylation. Each of the reactions 6–9 should result in racemized material. Because of the reactions 7 and 8, which result in racemization but not scrambling, the rate of racemization by hydride transfer should be greater than the rate of deuterium scrambling. Any remaining rate of racemization is then associated with the transalkylation; the results of runs J2, K, S1, and T1 then mean that the rate of racemization must be substantially less than the rate of transalkylation as measured by loss of radioactivity. For such to be the case, the transalkylation must occur largely with *retention* of configuration. This conclusion is not consistent with any plausible mechanism for disproportionation or transalkylation.

Alternatively, all three processes have the same rate-determining step. One such mechanism is

$$^*C_6H_5\overset{+}{C}H(D)CH_3 + C_6H_6 \longrightarrow C_6H_5C(H(D))(^*C_6H_5)CH_3 \quad (10)$$

$$C_6H_5C(H(D))(^*C_6H_5)CH_3 \longrightarrow C_6H_6 + {}^*C_6H_5\overset{+}{C}H(D)CH_3 \quad (11)$$

$$\longrightarrow C_6H_6^* + C_6H_5\overset{+}{C}H(D)CH_3 \quad (12)$$

$$C_6H_5\overset{+}{C}H(D)CH_3 + {}^*C_6H_5CHDCH_3 \longrightarrow C_6H_5C(H(D))(H(D))CH_3 + {}^*C_6H_5\overset{+}{C}H(D)CH_3 \quad (13)$$

Reactions 10, 11, and 12 are postulated to be rapid; step 13 is the rate-determining step. This mechanism involves a cation chain reaction whose rate depends on the steady state concentration of α-phenethyl cation. In part, this cation could derive from traces of styrene present

$$C_6H_5CH{=}CH_2 + HBr + GaBr_3 \rightleftarrows C_6H_5\overset{+}{C}HCH_3\ GaBr_4^- \quad (14)$$

Traces of styrene are probably present in most samples of ethylbenzene and may well explain the rate variations observed. Unfortunately, we have only limited data on the amount of styrene present in our samples. From ultraviolet spectra in ethanol solutions, we estimate that the ethylbenzene in runs J2, K, S1, and T1 contained styrene to the extent of 0.1, 0.006, 0.006, and 0.029%, respectively. There seems to be some tendency for increased styrene to increase the reaction rate, but these limited data are not definitive. It should be noted that the effect of styrene may be moderated by the postulated rapid reactions 10, 11, and 12 which constitute an equilibrium with 1,1-diphenylethane. Indeed, the formulation of this equilibrium shows how the steady state cation is dependent on [HBr] and [$GaBr_3$] and is consistent with the observed kinetics

$$C_6H_5\overset{+}{C}HCH_3\ GaBr_4^- + C_6H_6 \rightleftarrows (C_6H_5)_2CHCH_3 + HBr + GaBr_3 \quad (15)$$

A necessary corollary of this mechanism is that 1,1-diphenylethane should cleave rapidly with gallium bromide and hydrogen bromide. This corollary has been demonstrated: 1,1-di-p-tolylethane in benzene containing gallium bromide and hydrogen bromide is converted within seconds to 1,1-diphenylethane and toluene.[17]

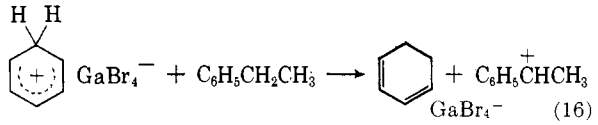
Oxidation of ethylbenzene during the course of reaction would account for the autocatalytic character of the reaction. One possible source of increased α-phenethyl cation is a hydride transfer to a protonated σ-complex of benzene or other aromatic compounds formed in side reactions.

(14) These analyses were performed by Dr. R. M. Teeter of the California Research Corp., Richmond, Calif., to whom we express our gratitude.

(15) P. D. Bartlett, F. E. Condon, and A. Schneider, *J. Am. Chem. Soc.*, **66**, 1531 (1944).

(16) E. L. Eliel, P. H. Wilken, and F. T. Fang, *J. Org. Chem.*, **22**, 231 (1957).

(17) A. Streitwieser, Jr., and W. J. Downs, *ibid.*, **27**, 625 (1962).



(16)

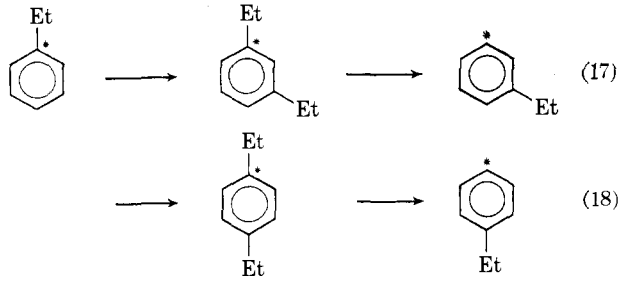
The small amounts of deuterium lost from the deuterated ethylbenzenes in runs S1 and T1 may, in part, be due to such hydride transfers. Once removed from the α-position of ethylbenzene, the deuterium enters the total aromatic hydrogen pool. An experiment in which benzene-d_6 in benzene was treated with $GaBr_3$–HBr under our reaction conditions showed complete conversion to benzene-d by the time the first kinetic aliquot was taken (24 sec.). In several runs, we noticed a small amount of by-product having the same retention time as bromobenzene. Oxidation–reduction processes leading to free bromine could lead also to increased levels of catalytic carbonium ions.

We should also point out that our mechanisms have been formulated in terms of $GaBr_3$ and $GaBr_4^-$. If an additional $GaBr_3$ is involved—that is, if the species present are Ga_2Br_6 and $Ga_2Br_7^-$ [18]—the kinetics are unchanged.

The proposed mechanism represents a complete departure from the SN2-type mechanisms which had generally been accepted for disproportionation reactions of primary alkylarenes. Similar mechanisms have been suggested earlier to account for some disproportionation results in the presence of high concentrations of hydrogen acceptors,[19] but we may go a step further and show that the new mechanism is consistent as well with all of the other known features of the reaction.

The very low relative rate of disproportionation of toluene (*vide supra*) is now understandable. Toluene is less likely to contain traces of alkenes which can generate chain carrying carbonium ions. Hydride transfer of toluene to yield benzyl cation, a *primary* cation, should be much more difficult than the similar conversion of other primary alkylbenzenes to *secondary* benzylic cations. Neopentylbenzene (*vide supra*) is also an understandable exception, since phenyl-*t*-butylcarbinyl cation is destabilized by steric hindrance to coplanarity.

The mechanism is also completely consistent with the results of Unseren and Wolf[9] who found that after disproportionation of ethylbenzene-1-C^{14} with aluminum bromide and gallium bromide, the recovered ethylbenzene had the C^{14}-distribution: *o*-, 9%; *m*-, 15%; *p*-, 18%. According to the present mechanism, rearrangement of the C^{14}-label would be accomplished by successive alkylations and dealkylations of α-phenylethyl cation with the net result

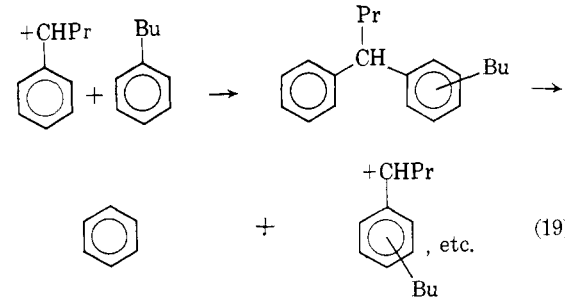


(17)

(18)

The observed activity in the *m*- and *p*-positions should be a rough measure of the "selectivity"[20] of α-phenethyl cation under these conditions. The measure is rather crude because of the several reactions involved—a sequence of two transalkylations is required to rearrange the label in ethylbenzene, alkylation of the benzene produced gives evenly labeled ethylbenzene, and some of the diethylbenzenes are diverted to triethylbenzenes; nevertheless, the observed value of $2p\text{-}/m\text{-}$, $18 \times {}^2/_{15} = 2.4$, is qualitatively similar to the value, 4, obtained for alkylation of toluene with benzyl bromide and gallium bromide.[21] Reaction at the *o*-position could well be inhibited by steric hindrance as observed.

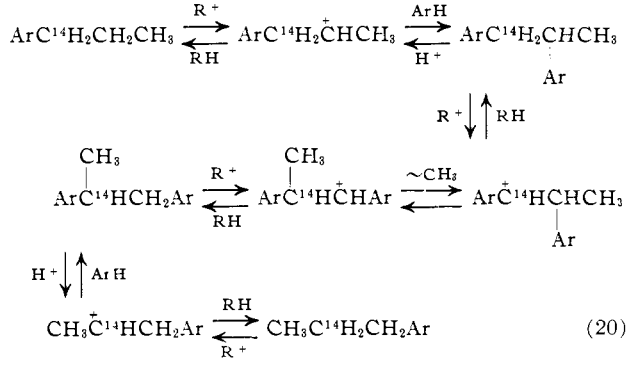
The lack of rearrangement in disproportionation of the higher primary alkylbenzenes is also understandable. For *n*-butylbenzene, for example, the key step in the process is



(19)

Under more vigorous conditions, rearrangements have been observed. These conditions (for example, $AlCl_3$ at 100°) are such that rearrangements and hydride transfers among secondary and benzylic cations should be facile and the observed rearrangements can generally be interpreted by such reactions.[22,23] Some of the rearrangements, however, have apparently required the intervention of primary carbonium ions or bridged phenonium ions, one such case being the rearrangement of 1-phenylpropane-1-C^{14} to 1-phenylpropane-2 C^{14}.[24]

The facile alkylation–dealkylation demonstrated in our work suggests the following alternative mechanism which avoids the involvement of primary carbonium ions



(20)

(18) *Cf.* S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 2596 (1963); E. A. Roth, Dissertation, Purdue University, 1961.

(19) H. Pines and J. T. Arrigo, *J. Am. Chem. Soc.*, **80**, 4369 (1958); L. Schmerling, J. P. Luvisi, and R. W. Welch, *ibid.*, **81**, 2718 (1959).

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The Ar groups are interconvertible between phenyl and substituted phenyl groups by further alkylation–dealkylation reactions. Mechanisms of the type 20 involving diarylalkanes can account completely for all of the observed rearrangements. This proposal receives additional credence from the recent isolation of diarylalkanes in such reactions by Roberts, *et al.*,[25] and the beautiful demonstration of Karabatsos, *et al.*,[26] that rearrangements of aliphatic hydrocarbons avoid involvement of primary carbonium ions by comparable bimolecular reactions.

Experimental

α-Phenethyl Alcohol.—The conventional resolution by fractional crystallization of the brucine salt of the hydrogen phthalate[27] is laborious; the "rapid" method of Kantor and Hauser[28] was found to be convenient for the preparation of material of high but not complete optical purity. In a typical preparation, 101.2 g. (0.38 mole) of α-phenethyl hydrogen phthalate was mixed well with 148 g. (0.38 mole) of brucine and the mixture was refluxed with 1045 ml. of acetone for 24 hr. Complete solution does not occur. Hot filtration gave 58.2 g. of brucine salt which, on treatment with hydrochloric acid, gave hydrogen phthalate having $[\alpha]^{21.4}D$ +30.4° (EtOH). On standing, the mother liquor deposited a second crop (43.5 g.) of brucine salt which gave ester having $[\alpha]^{21.4}D$ +26.6° (EtOH). Optically pure ester is reported[27] to have $[\alpha]^{25}D$ +36.5° (EtOH).

Further resolution could be achieved by grinding a brucine salt crop in a mortar, refluxing with insufficient acetone to cause solution, and filtering hot. In this way, material was obtained having optical purities of over 90%.

Regeneration of alcohol from hydrogen phthalate was best achieved by saponification with 25% aqueous sodium hydroxide followed by steam distillation. Other procedures (*e.g.*, lithium aluminum hydride reduction of hydrogen phthalate or of the brucine salt) gave lower yields.

α-Phenethyl Chloride.—A number of preparations were tried (*e.g.*, $SOCl_2$ with and without solvent), but the best method was found to be that of Burwell, Shields, and Hart.[29] In a typical preparation, 27.1 g. (0.74 mole) of hydrogen chloride was passed into 150 ml. of pyridine. To the mixture, cooled to −10°, was added 44.5 g. (0.27 mole) of α-phenethyl alcohol, $[\alpha]^{21.4}D$ −40.8° (neat) in 356 ml. of chloroform in one portion followed by 45 ml. (0.49 mole) of phosphorus oxychloride slowly. The reaction mixture was allowed to warm to room temperature overnight, decomposed with ice, and extracted with chloroform. Washing, drying, and distilling gave 38.1 g. (74%) of α-phenethyl chloride, b.p. 57–66° (5 mm.), $[\alpha]^{19.6}D$ +85.8° (88% inversion).[30]

Ethylbenzene-α-*d*.—A mixture of 3.6 g. of lithium deuteride, 1.0 g. of lithium aluminum deuteride, and 38.1 g. (0.27 mole) of α-phenethyl chloride, $[\alpha]^{19.6}D$ +85.8° (neat), in 75 ml. of purified tetrahydrofuran was refluxed for 12 hr. A further 0.1 g. of lithium aluminum deuteride was added, and after 3 days of refluxing, an additional 1.0 g. of lithium aluminum deuteride, 1.4 g. of lithium deuteride, and 15 ml. of tetrahydrofuran was added. After 2 more days of refluxing, the mixture was cooled, decomposed with water and dilute sulfuric acid, and extracted with pentane. Distillation of the washed and dried extract gave 21.8 g. (75%) of ethylbenzene-α-*d*, b.p. 135–136°, $n^{21.2}D$ 1.4949, $[\alpha]^{21.2}D$ +0.561° (neat). In Table III are summarized several experiments from which the rotation of optically pure ethylbenzene-α-*d* is computed. This rotation would appear to be about 0.70°.

TABLE III

OPTICAL ACTIVITY OF ETHYLBENZENE-α-*d*

Starting $[\alpha]D$	α-Phenethyl choride opt. purity,[a] %	Ethylbenzene-α-*d* $[\alpha]D$ of product	Ethylbenzene-α-*d* $[\alpha]D$ calcd. for opt. pure	Ref.
59.4°	57.2	0.39°	0.68°	This work
77.8	74.9	.62	.83	This work
85.8	82.6	.56	.68	This work
79.1	76.1	.45	.59	This work
−49.2	47.4	−.30	.63	11
−43.6	42.0	−.29	.69[b]	12

[a] Based on 103.9° for 100% optical purity. [b] Corrected to −0.70° by presence of 1% of undeuterated hydrocarbon.

Radioactive Materials.—Benzene-C^{14} was acetylated with acetic anhydride and aluminum chloride to give acetophenone-ring-C^{14} which was reduced with lithium aluminum hydride to α-phenethyl-ring-C^{14} alcohol. This material was mixed with optically active alcohol to prepare optically active ethylbenzene-α-*d*-ring-C^{14} or was diluted with inactive alcohol, converted to chloride, and reduced to prepare ethylbenzene-ring-C^{14}. The final products had activity levels of ~6000 c.p.m. for 50 λ samples and were counted on a Packard Tri-Carb automatic liquid scintillation counter, Model 314X.

Gallium Bromide.—Gallium metal (McKay Co., 99.99% pure) was converted to the bromide following Smoot and Brown.[31] The gallium bromide was kept in a long segmented sealed Pyrex tube. As needed, the compound was sublimed into the top segment and sealed off.

Kinetics.—Preliminary studies showed that gallium bromide–hydrogen bromide stock solutions in benzene were not stable; hence, such stock solutions were prepared immediately before each series of runs. Benzene was distilled from lithium aluminum hydride as needed or stored over sodium. For each kinetic series, a measured amount was placed in the stock solution flask, a 300-ml. or 500-ml. flask carrying a sidearm with a stopcock closed with a serum cap. A previously weighed ampoule of gallium bromide was broken and transferred rapidly to the flask which was then stoppered. When the gallium bromide had dissolved, hydrogen bromide was admitted with a hypodermic needle inserted into the serum cap with the stopcock opened. The amount of hydrogen bromide introduced was determined by weighing the flask on a large scale analytical balance. Desired amounts of this stock solution were syringed into one or more of the previously prepared reaction flasks. These flasks were tubes sealed by a stopcock and serum cap and were cleaned and baked out before use. Because of pressure built up in these flasks, the stopcocks were retained by heavy spring clamps and the serum caps were wired on. In use, the stopcocks were opened only when materials were syringed in or aliquots were syringed out in order to avoid undue contact of vapors with the serum caps. To each reaction flask in a series was added additional reagents as desired. The series was placed in the thermostat and after about 1 hr. reaction was initiated by injecting the ethylbenzene. Aliquots of about 8 ml. were removed at intervals and quenched with water. The washed and dried benzene layer was put through a preparative g.c. column (8 ft. × 0.75 in. silicone on Chromosorb) and the ethylbenzene peak was collected. Further g.c. analysis showed typically only ~2% of benzene in the ethylbenzene thus isolated. The product was counted on the liquid scintillation counter as above and portions of the optically active samples, in addition, were saved for mass spectrometric analyses[14] and for optical activity measurement. Rotations were taken on the pure liquid in a 1-dm., 1.6-mm. bore tube; the average of at least 10 readings was used.

Initially, each run was prepared individually, but in later runs when nonreproducibility was established, two or three runs were prepared frequently from a given stock solution.

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(29) R. L. Burwell, A. D. Shields, and H. Hart, *ibid.*, **76**, 908 (1954).

(30) $[\alpha]D$ 43.5 and 103.9° taken as rotations of optically pure carbinol and halide, respectively, ref. 12.

(31) C. R. Smoot and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6245 (1956).