[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Action of Some Strong Acids on Secondary Phenylpentanes[1]

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Aluminum chloride rapidly racemizes optically active 2-phenylpentane at room temperatures perhaps by a hydride ion transfer chain. Interconversion of 2- and 3-phenylpentane occurs much more slowly and seemingly results from disproportionation to diamylbenzene and benzene followed by reversal of this reaction. The same reactions occur in benzene solution, but direct transalkylation of amyl groups to benzene also occurs. 1,4-Di-3-pentylbenzene and benzene react to give mixtures of 2- and 3-phenylpentane. Transalkylation apparently occurs by transfer of an amyl group as a carbonium ion. With methanesulfonic acid at 140°, racemization is relatively less prominent. In benzene solution, the loss in rotation is largely consequent to transalkylation. Interconversion of 2- and 3-phenylpentane is accompanied by formation of 2-methyl-3-phenylbutane. Transalkylation of the amyl group of 2-phenylpentane to toluene gives amyltoluenes nearly devoid of rotation. In reaction of 2- and 3-phenylpentane with sulfuric acid at room temperatures, sulfonation is fast. The sulfonic acid group then inhibits the other reactions. There is negligible isomerization and little racemization in unsulfonated 2-phenylpentane or in hydrocarbon recovered by hydrolysis of the sulfonic acid.

Work reported in the present paper is an extension of earlier investigations into the action of sulfuric acid and of halosulfonic acids upon optically active alkanes.[2-4]

The present paper reports the action of sulfuric acid, methanesulfonic acid and aluminum chloride upon 3-phenylpentane and upon optically active 2-phenylpentane. The use of the optically active compound is advantageous because it provides a measure of the total extent of reaction and permits one to learn what fraction of the reacting hydrocarbon returns to racemic starting hydrocarbon. Optically active 2-phenylpentane was employed rather than 2-phenylbutane because with the latter, simple isomerization, corresponding to phenyl group migration, would not lead to a new compound.

Experimental

Analysis.—After preliminary fractionation in a microcolumn consisting of an unpacked 6-mm. tubing or in a Piros–Glover column, as appropriate, fractions of interest were examined by infrared spectroscopy. When the Baird double beam instrument was used, one of the pure components, for example 3-phenylpentane, was placed in both the reference and the sample cell and the spectrum recorded. The unknown was then placed in the sample cell and the spectrum rerun. Appropriate synthetic mixtures were then run in the sample cell. This procedure minimizes dependence on Beer's law and it is effective in detecting the presence of minor components. In certain cases, particularly those in which equilibrium compositions were being determined, a synthetic mixture of about the composition of the sample was employed in the reference cell. This results in distinct increase in precision. Many of the earlier determinations were run by a similar comparison technique on the Beckman IR2. In this case several suitable wave lengths were employed.

In determining degree of disproportionation, the strong benzene band at 14.9 μ was very helpful since the alkylbenzenes do not interfere. Analyses for 2- and 3-phenylpentane were primarily based on bands at 8.84, 10.16 and 12.02 microns.

Materials.—Methanesulfonic acid was kindly supplied by the Indoil Chemical Co. After distillation at 3–4 mm. it melted at 13–14°. In earlier experiments this material was used as such. In run 27 *et seq.*, a sample which has been purified by several successive partial crystallizations was employed. The m.p. of this material was about 18.2°. Pure methanesulfonic acid is reported to melt at 19.66°.[5]

3-Phenylpentane was prepared *via* 3-phenyl-3-pentanol which was prepared from ethyl benzoate and ethyl bromide by the Grignard reaction. The carbinol was dehydrated by refluxing with a trace of *p*-toluenesulfonic acid and the resulting 3-phenyl-3-pentene was hydrogenated with platinum oxide. Alkylbenzenes were ordinarily chromatographed on silica gel to remove olefins, hexahydroalkylbenzenes and traces of sulfur compounds. The physical properties of the several fractions employed were in good agreement with those reported by the projects of the American Petroleum Institute.

The preparation of optically active 2-phenylpentane has been described.[6] The optically active material was usually diluted with inactive material to a rotation of 4–5°. This permitted determination of the degree of loss of rotation to about 1%. The racemic compound was prepared by the same method except that allylmagnesium bromide was used rather than allylsodium.

1,4-Di-3-pentylbenzene was obtained through the courtesy of the Whiting Research Laboratories of the Standard Oil Co. (Indiana); b.p. 268° (uncor.) and $n^{20}\text{D}$ 1.4857. We are indebted to Professor Herman Pines for a sample of 2-methyl-3-phenylbutane.

Results Using Aluminum Chloride.—The desired amount of hydrocarbon was weighed into a 16-cc. stainless steel tube fitted with a Teflon gasket and provided with a screw cap. In most runs, 3 to 5 cc. of phenylpentane was employed. Aluminum chloride (Baker and Adamson) was taken from beneath the surface and added to the reaction tube. This procedure was performed with expedition but the aluminum chloride so delivered undoubtedly contained some water. The tube was closed and attached to a vertical piston shaking through a 4-inch stroke at 175 cycles per minute in runs 2, 3, 4, 6 and 7 and at 320 cycles in other runs. Shaking was at ambient temperatures, approximately 25°.

After the reaction period, the sample was washed with cold water and the hydrocarbon layer was dried over potassium hydroxide granules and then calcium chloride. Table I presents results of experiments with phenylpentanes either alone or diluted with benzene. Table II exhibits results of dealkylation of 1,4-di-3-pentylbenzene with benzene. A number of phenylpentane fractions from runs listed in Table I were examined carefully by infrared absorption spectroscopy for possible presence of 2-methyl-3-phenylbutane and *t*-amylbenzene. Neither could be detected. For accurate results in analysis of the phenylpentane mixtures, thorough elimination of benzene was necessary.

Run 1.—A mixture of (+)2-phenylpentane and toluene (mole ratio 0.32) and aluminum chloride (mole ratio to total hydrocarbon 0.0078) was shaken for 10 min. As determined by measurement of the amount of benzene formed, 1.5 ± 0.5% of the phenylpentane had transalkylated to form benzene and amyltoluenes. The degree of isomerization of the recovered 2-phenylpentane was 0 ± 1% while

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(1) Presented at the Symposium on Mechanisms of Homogeneous and Heterogeneous Hydrocarbon Reactions, Kansas City Meeting of the American Chemical Society, March 31, 1954.

(2) (a) R. L. Burwell, Jr., and G. S. Gordon, III, THIS JOURNAL, **70**, 3128 (1948); (b) **71**, 2355 (1949).

(3) R. L. Burwell, Jr., Robert B. Scott, L. G. Maury and A. S. Hussey, *ibid.*, **76**, 5822 (1954).

(4) R. L. Burwell, Jr., L. G. Maury and R. B. Scott, *ibid.*, **76**, 5828 (1954).

(5) R. A. Craig, A. B. Garrett and M. S. Newman, *ibid.*, **72**, 163 (1950).

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

TABLE I

THE ACTION OF ALUMINUM CHLORIDE ON PHENYLPENTANES AT 25°

Run	2-Phenylpentane,[a] mole %	Mole ratio[b] catalyst to hydrocarbon	Time, min.	Racemizn.[c] %	Compn. of recovd. $C_{11}H_{16}$ as % 3-phenylpentane
2	100	0.050	60	100	16 ± 2[d]
3	100[g]	.052	60	...	79 ± 3[d]
4	100	.025	15	98.7	1 ± 1[d]
5	100	.024	10	62.6	0 ± 1[e]
6	34.5	.052	300	...	28 ± 4[d,f]
7	34.5[g]	.056	300	...	29 ± 4[d,f]
8	34.5	.013	45	100	29 ± 1
9	34.5	.013	13	100	17 ± 2
10	34.5	.0056	10	97	0 ± 1

[a] In runs 6 to 10 remainder is benzene. [b] To total hydrocarbon including benzene. [c] Probable error is 0.5 to 1 percentage units. [d] Considerable disproportionation to benzene and diamylbenzenes occurred. [e] 1.5 ± 0.5% disproportionation as determined on reaction product by comparison against known mixtures of benzene and 2-phenylpentane. [f] The distillation residues (diamylbenzenes) of runs 6 and 7 were nearly identical as judged by their infrared spectra. [g] 3-Phenylpentane.

the degree of racemization was 99%. In a similar run with inactive 2-phenylpentane carried to 8% dealkylation, isomerization was also undetectable.

Results Using Methanesulfonic Acid.—Results of the action of methanesulfonic acid on phenylpentanes are presented in Table III. Table II presents results of dealkylation of 1,4-di-3-pentylbenzene.

In runs 24 and 25 (Table III), about 5.4 g. of hydrocarbon was magnetically stirred with the acid in a small flat-bottom flask provided with a Teflon-coated magnetically-operated stirring bar. The flask was connected to the atmosphere through a Dry Ice trap to catch any volatilized benzene. In all other listed runs, 3.5 to 5.0 g. of hydrocarbon and the appropriate amount of acid were sealed in a glass tube which was inserted in a small furnace mounted on a shaking table.

The total reaction product was diluted with water and the hydrocarbon layer removed. The hydrocarbon then was distilled except that in runs 24 and 25 this distillation was preceded by a steam distillation which eliminated those products much higher boiling than diamylbenzene.

TABLE II

THE ACTION OF ALUMINUM CHLORIDE AND OF METHANESULFONIC ACID ON MIXTURES OF 1,4-DI-3-PENTYLBENZENE AND BENZENE

Run	Mole ratio $C_{16}H_{26}/C_6H_6$	Catalyst	Mole ratio catalyst hydrocarbon	Temp., °C.	Time	Dealkylation[a] %	Composition of recovd. $C_{11}H_{16}$ as % 3-phenylpentane
11	0.36	$AlCl_3$	0.061	25	30 min.	33 ± 2	70 ± 2[b]
12	.36	$AlCl_3$	.008	25	25 min.	1.5 ± 0.5	65 ± 15[c]
21	.48	CH_3SO_3H	2.0	143	35 hr.	65 ± 10	60 ± 2[d]
22	.36	CH_3SO_3H	1.8	143	11 hr.	60 ± 5	55 ± 5[d]
23	.36	CH_3SO_3H	2.0	136	8 hr.	28 ± 3	65 ± 2[d,e]

[a] % of 1,4-di-3-pentylbenzene converted to double the moles of phenylpentanes. [b] Infrared examination showed the recovered diamylbenzene to be extensively isomerized and suggested that the *meta* isomer was a major product of isomerization and that tripentylbenzenes, if any, were at best minor constituents. [c] The recovered diamylbenzene was isomerized in the same manner as in run 11 but only to an extent of 3 ± 1% as great. Low precision results from there being too little phenylpentane to isolate as such. The first distillation fractions containing about 10% phenylpentane were employed after freeing from benzene. These were compared in the infrared against dipentylbenzene which distilled in subsequent fractions and to which was added to turn each of the phenylpentanes. [d] % of 3-phenylpentane in sum of 2- and 3-phenylpentanes. [e] The phenylpentane fraction contained 7 ± 2% of 2-methyl-3-phenylbutane.

The purer methanesulfonic acid gave rates several fold greater than the less pure. 2-Methyl-3-phenylbutane was found whenever there was any significant amount of isomerization. The observed % of this component (in the more favorable cases) is listed in Table III. Highest precision obtains in the equilibrium runs, 36 and 37, since these started from fairly near the equilbrium mixture of 2- and 3-phenylpentane and, thus, appearance of 2-methyl-3-phenylbutane had the clearest effect upon the infrared spectrum. No *t*-amylbenzene could be detected in any run. Its rate of formation is at least one-fifth to one-tenth as fast as that of 2-methyl-3-phenylbutane.

TABLE III

THE ACTION OF METHANESULFONIC ACID ON PHENYLPENTANES

Run	2-Phenylpentane,[a] mole %	Mole ratio[b] CH_3SO_3H to hydrocarbon	Temp., °C.	Time, hr.	Loss of rotation, %	Compn.[c] of recovd. $C_{11}H_{16}$ as % 3-phenylpentane
24A[d]	100	2.30	142	12	50.4	3 ± 3
24B	100	1.93	145	30		
25A[d]	100	2.28	142	43	..	78 ± 2[e]
25B	100[i]	1.94	142	25		
31	100	4.61	150	12	..	9.0 ± 1.5[f]
32	100[i]	4.59	150	12	..	17.0 ± 2.0[f]
33	100	5.88	150	13	43	10.5 ± 1.5[g]
27	82.0	7.55	142	8.8	..	35 ± 2
28	67.9	7.92	142	8.8	..	36 ± 2
29	50.0	7.50	145	8	..	45 ± 2
34	60.0	5.40	148	33	..	38 ± 4
35	80.0	5.49	148	33	..	28 ± 4
36	55.0	5.85	148	12	..	42 ± 1.5[h]
37	76.0	6.26	148	12	..	30 ± 1.5[h]

[a] Remainder of phenylpentane is 3-phenylpentane in run 27 and those listed below it. In runs whose run no. is 31 or greater, benzene was added to bring the mole % of total phenylpentane to 34.5%. [b] To total hydrocarbon. [c] Percentage of 2- and 3-phenylpentane present as 3-phenylpentane. [d] Combined with the B part before analysis. [e] Of original phenylpentane, 15 mole % recovered as benzene, 40% as phenylpentanes and 11% as diamylbenzenes, 5% as material which did not steam distill. Of the rest, some represents transfer and distillation losses; some material which boiled above diamylbenzene; and some, presumably, as water-soluble material. A rather similar result was obtained with run 14. [f] About 4% of the phenylpentane was 2-methyl-3-phenylbutane. [g] 7 ± 2% 2-methyl-3-phenylbutane. [h] 6 ± 2% 2-methyl-3-phenylbutane. [i] 3-Phenylpentane.

Run 26.—A mixture of (−)2-phenylpentane and toluene (mole ratio 0.32) was shaken with methanesulfonic acid (mole ratio to total hydrocarbon 1.95) for 72 hr. at 142°. 25% of the phenylpentane was transalkylated to tolylpentanes and benzene. About half as much phenylpentane was consumed by disproportionation. The recovered phenylpentane fraction was isomerized to an extent no greater than 2%, but its loss of rotation was 7%. The rotations of the three amyltoluene fractions lay in the range 3–6% of that of the initial 2-phenylpentane. Considering the difficulty in clean separations, the amyltoluene may be taken as virtually devoid of rotation. An attempt to transalkylate to ethylbenzene failed because of disproportionation of the ethylbenzene.

Results Using Sulfuric Acid.—Results of these experiments are presented in Table IV. After the hydrocarbon-acid mixtures had been either stirred magnetically or shaken, they were diluted with cold water and the hydrocarbon layer removed.

TABLE IV

THE ACTION OF SULFURIC ACID ON PHENYLPENTANES AT 25°

Run	Phenylpentane type	Phenylpentane cc.	Sulfuric acid %	Sulfuric acid cc.	Time, min.	Sulfonation
40	3-	3	92.10	5	60	Slight[a]
41	3-	3	94.55	5	60	One-half[a]
42	3-	3	96.80	5	60	Complete
43	2-	3	95.88	5	35	Two-thirds[a,b]
44	3-	7.3	96.80	10		One-half[a,c]
45	2-	5.8	96.80	10	15	Complete[c,d]
46	2-	6	95.89	10.5	60	One-half[a,e]
47	2-	4.1	96.8	6.0		Complete[c,f]

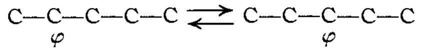
[a] No detectable isomerization of the unsulfonated phenylpentane. [b] Loss of rotation of unsulfonated (−)2-phenylpentane, 3.6%. [c] No detectable isomerization of the phenylpentane obtained by desulfonating the sulfonated material. [d] Loss of rotation of the (−)2-phenylpentane recovered by desulfonating the sulfonated material was 9.7%. [e] 1.9% 3-phenyl-1-pentene added to phenylpentane. [f] 3.19% 4-phenyl-1-pentene added.

In runs 44, 45 and 47, the sulfuric acid layer was diluted with water and 85% phosphoric acid. The mixture was refluxed in an apparatus which permitted retention of evolved phenylpentane but return of water. Water was removed until the reflux temperature rose to 160 to 180°. After this, water was returned. Desulfonation yields were 60 to 70% of theoretical.

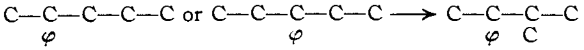
Run 49.—In an effort to determine the fate of the added olefin in runs 46 and 47, a mixture of 15 cc. of α-methylstyrene and 100 cc. of cumene was agitated with concentrated sulfuric acid until the organic layer disappeared (40 min.). The product was desulfonated and distilled. There was no material higher boiling than cumene (31° at 5 mm.). We presume that the alkylate of cumene and α-methylstyrene, $C_{18}H_{22}$, would have distilled from the mixture in analogy to the observed steam distillation of diamylbenzene. This result tentatively suggests that the α-methylstyrene reacted largely by polymerization rather than alkylation.

Discussion

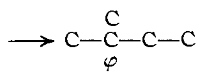
The reactions of phenylpentanes observed in this research can be discussed in terms of the set of reactions



$$\underset{\varphi}{\text{C—C}}\text{—C—C—C} \rightleftarrows \text{C—C—}\underset{\varphi}{\text{C}}\text{—C—C} \quad (1)$$



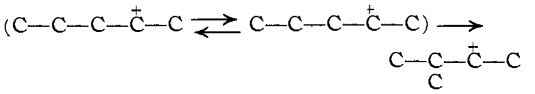
$$\text{C—}\underset{\varphi}{\text{C}}\text{—C—C—C or C—C—}\underset{\varphi}{\text{C}}\text{—C—C} \longrightarrow \text{C—}\underset{\varphi}{\text{C}}\text{—}\underset{\text{C}}{\text{C}}\text{—C} \quad (2)$$



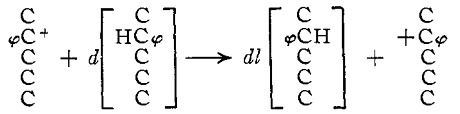
$$\longrightarrow \text{C—}\overset{\text{C}}{\underset{\varphi}{\text{C}}}\text{—C—C} \quad (3)$$

$$2C_6H_5C_5H_{11} \rightleftarrows C_6H_4(C_5H_{11})_2 + C_6H_6 \quad (4)$$

$$C_6H_5C_5H_{11} + C_6H_6 \longrightarrow C_6H_6 + C_5H_{11}C_6H_5 \quad (5)$$



$$(\text{C—C—C—}\overset{+}{\text{C}}\text{—C} \rightleftarrows \text{C—C—C—}\overset{+}{\text{C}}\text{—C}) \longrightarrow \text{C—}\underset{\text{C}}{\text{C}}\text{—}\overset{+}{\text{C}}\text{—C} \quad (6)$$



$$\begin{matrix}\text{C}\\ \varphi\text{C}^+\\ \text{C}\\ \text{C}\\ \text{C}\end{matrix} + d\begin{bmatrix}\text{C}\\ \text{HC}\varphi\\ \text{C}\\ \text{C}\\ \text{C}\end{bmatrix} \longrightarrow dl\begin{bmatrix}\text{C}\\ \varphi\text{CH}\\ \text{C}\\ \text{C}\\ \text{C}\end{bmatrix} + \begin{matrix}\text{C}\\ +\text{C}\varphi\\ \text{C}\\ \text{C}\\ \text{C}\end{matrix} \quad (7)$$

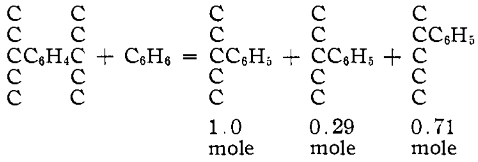
As will appear, the interconversion of 2- and 3-phenylpentane (reaction 1) does not proceed directly but proceeds rather *via* transalkylation reactions (reaction 4 and 5) in which the transalkylated amyl group undergoes isomerization, apparently as a secondary carbonium ion (reaction 6).

Aluminum Chloride.—Aluminum chloride catalyzes the interconversion of 2- and 3-phenylpentane at room temperatures (Table I, runs 2 and 3). Disproportionation (reaction 4) accompanies isomerization and, initially, occurs more rapidly than isomerization (runs 4 and 5). The addition of benzene to the phenylpentane partly decreases the extent of disproportionation as would be expected from reaction 4 (runs 6 and 7). As exhibited by runs 6 and 7, starting from either 2- or 3-phenylpentane, one can reach the equilibrium mixture of these hydrocarbons, 29 ± 4% 3-phenylpentane. This value is consistent with the ratio of 2- and 3-phenylpentane formed by alkylating benzene with 2- and 3-pentyl derivatives.[7,8] Reactions 2 and 3 occur to no detectable extent even in runs protracted to near equilibrium in regard to 2- and 3-phenylpentane, nor were such amylbenzenes reported in alkylation experiments.[7,8]

In the presence of aluminum chloride, 1,4-di-3-pentylbenzene and benzene react to form 2- and 3-phenylpentane (Table II, runs 11 and 12) in a reversal of reaction 4.

Unreacted diamylbenzene is isomerized. A large portion of the isomeric product is apparently the *meta* isomer. This isomerization does not occur by reversal of the dealkylation reaction, at least initially, since the relative extents of dealkylation and isomerization of 1,4-di-3-pentylbenzene are nearly the same at 1.5 and at 33% dealkylation.

Apparently, then, transfer of a secondary pentyl group from one benzene ring to another results in interconversion of the 2-pentyl and the 3-pentyl groups. The isomerization of the group being transalkylated proceeds so rapidly that 2- and 3-phenylpentane are formed in nearly their equilibrium ratio as shown by runs 11 and 12. According to this proposal, in the transalkylation of di-3-pentylbenzene, the first phenylpentane molecule



$$\begin{matrix}\text{C} & & \text{C}\\ \text{C} & & \text{C}\\ \text{C} & C_6H_4 & \text{C}\\ \text{C} & & \text{C}\\ \text{C} & & \text{C}\end{matrix} + C_6H_6 = \underset{\substack{1.0\\ \text{mole}}}{\begin{matrix}\text{C}\\ \text{C}\\ \text{C}C_6H_5\\ \text{C}\\ \text{C}\end{matrix}} + \underset{\substack{0.29\\ \text{mole}}}{\begin{matrix}\text{C}\\ \text{C}\\ \text{C}C_6H_5\\ \text{C}\\ \text{C}\end{matrix}} + \underset{\substack{0.71\\ \text{mole}}}{\begin{matrix}\text{C}\\ \text{C}C_6H_5\\ \text{C}\\ \text{C}\\ \text{C}\end{matrix}} \quad (8)$$

on the right side of the equation is the one formed by removal of an amyl group. It should be 3-phenylpentane. The transferred amyl group would lead to 2- and 3-phenylpentane in their equilibrium ratio as shown. Accordingly one would expect the composition of the phenylpentane initially formed to be 65% 3-phenylpentane in reasonable agreement with the results.

According to current mechanistic views, *this* transfer might, *a priori*, have occurred either by S_N1[9] or by S_N2 processes.[10,11] By the product criterion, the occurrence of isomerization demonstrates

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[7] H. Pines, W. D. Huntsman and V. N. Ipatieff, THIS JOURNAL, **73**, 4343, 4483 (1951).

[8] R. L. Burwell, Jr., L. M. Elkin and A. D. Shields, *ibid.*, **74**, 4570 (1952).

[9] C. C. Price, *Chem. Revs.*, **29**, 37 (1941).

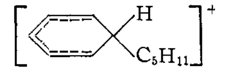
[10] H. C. Brown and M. Grayson, THIS JOURNAL, **75**, 6285 (1953); H. C. Brown, H. W. Pearsall, L. P. Eddy, W. J. Wallace, M. Grayson and K. L. Nelson, *Ind. Eng. Chem.*, **45**, 1462 (1953).

[11] L. Schmerling, *ibid.*, **45**, 1447 (1953).

that the transalkylation is not S_N2 but that it is to be classified as a carbonium ion process.[7,8]

Isomerization of a phenylpentane occurs, then, by disproportionation in the sense of reaction 4 followed by its reversal. Alternatively, once some benzene has accumulated, an amyl group may transalkylate directly to benzene (reaction 5). Initial addition of benzene favors this latter process. With a phenylpentane alone, the disproportionation reaction should proceed to some extent before detectable appearance of isomeric phenylpentane.

Whether aluminum chloride acts as a Lewis acid or, since it is undoubtedly partly hydrated, as a proton acid is not clear. Taking the latter view for simplicity, the following intermediate is first formed.



This loses an amylcarbonium ion which, under the conditions studied, rapidly isomerizes (reaction 6) and adds to a benzene molecule.

It has been shown that transalkylation of primary groups occurs by an S_N2 process when using boron trifluoride and hydrogen fluoride[12] or when using aluminum chloride.[13] With aluminum chloride and, as will be seen, with methanesulfonic acid, the transfer of secondary groups is clearly S_N1. With hydrogen fluoride plus boron trifluoride, transalkylation of secondary and tertiary alkyl groups might be interpreted as carbonium ion processes rather than as S_N2 processes as has been suggested.[12]

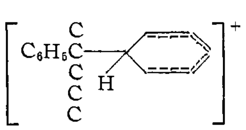
The ionic intermediate given above can presumably lead to intramolecular *para–meta* isomerization.[14,15] Although with xylenes[16] intramolecular migration is much faster than transalkylation, with *sec*-amylbenzenes the two rates are similar (runs 11 and 12).

The transalkylation sequence as applied to optically active 2-phenylpentane would lead to the formation of the 3-phenylpentane and racemic 2-phenylpentane. However, racemization of 2-phenylpentane is so fast compared to isomerization that this type of transalkylation cannot contribute significantly to the racemization. Whenever racemization was even slightly incomplete, isomerization was undetectable (Table I, runs 4, 5 and 10). As described in run 1 in the Experimental section, in transalkylation between (+)2-phenylpentane and toluene, recovered phenylpentane was 99% racemized but negligibly isomerized when transalkylation had proceeded to but 1.5%.

Since transalkylation and intramolecular migration occur at comparable rates (runs 11 and 12), the latter process is presumably not important in racemization. The reaction may, then, proceed by the usual carbonium ion chain reaction obtaining in isomerization[2,17] and racemization[2,18] of alkanes (reaction 7).

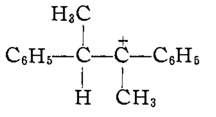
If this view is accepted, the rate of interconversion of ions derived from 2- and 3-phenylpentane is very slow compared to the rate of propagation of the hydride ion transfer chain.

The rate of addition of the isopropylcarbonium ion to benzene is many times faster than that of hydride ion transfer to this carbonium ion from isobutane.[19] With the compounds studied in this research, such addition would yield an intermediate of the form



If such is formed at any significant rate, the rate of loss of a proton must be small compared with the rate of departure of the entering group. Otherwise the compound  $\overset{Ar'}{\underset{Ar}{CCCCC}}$ would be formed. While this might be presumed to dealkylate rapidly, such a sequence would lead to disproportionation occurring at a rate comparable to that of racemization in the case of 2-phenylpentane alone. Runs 4 and 5 exclude this possibility as does run 1 for 2-phenylpentane and toluene.

The reactions reported in the present paper are closely related to some reported by Somerville and Spoerri.[20] Aluminum chloride causes the isomerization of *dl*-2,3-diphenylbutane dissolved in a large excess of benzene to the *meso* isomer. The reaction is considerably slower at larger proportions of aluminum chloride than the rates in the present work. It is likely that the aluminum chloride had become more extensively hydrated in the present work. The proposal of Somerville and Spoerri, that the ion



$$C_6H_5-\overset{H_3C}{\underset{H}{C}}-\overset{+}{\underset{CH_3}{C}}-C_6H_5$$

is involved in the epimerization is equivalent to the proposal we make for the racemization of 2-phenylpentane. No skeletal isomerization accompanies the epimerization. On the contrary, 2-methyl-1,2-diphenylpropane is isomerized to *meso*-2,3-diphenylbutane although this seems to proceed *via* a dealkylation mechanism[20] similar to the one proposed here for the phenylpentanes.

Methanesulfonic Acid.—The action of this material at 140° exhibits some differences from that of aluminum chloride. The reaction is less clean at given degrees of conversion (runs 24 and 25, Table III), perhaps in part owing to sulfonation by methanesulfonic acid and to slow decomposition of the acid at this temperature.

Isomerization occurs by transalkylation as with aluminum chloride. However, isomerization is not restricted to 2- and 3-amyl interconversion since 2-methyl-3-phenylbutane also is formed (reaction 2).

The equilibrium ratio of 2- and 3-amylbenzene was estimated at 148° by direct approach to equilib-

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(12) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **75**, 2411 (1953).

(13) R. E. Kinney and L. A. Hamilton, *ibid.*, **76**, 786 (1954).

(14) G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 100 (1952); G. Baddeley, *ibid.*, 994 (1950).

(15) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **74**, 6246 (1952).

(16) A. P. Lien and D. A. McCaulay, *ibid.*, **75**, 2407 (1953).

(17) H. S. Bloch, H. Pines and L. Schmerling, *ibid.*, **68**, 153 (1946).

(18) H. E. Heller, *ibid.*, **74**, 4858 (1952).

(19) F. E. Condon and M. P. Matuszak, *ibid.*, **70**, 2539 (1948).

(20) W. T. Somerville and P. E. Spoerri, *ibid.*, **74**, 3803 (1952).

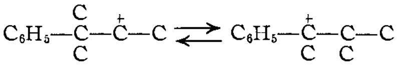
rium from each side. Mixtures whose composition lay near the estimated equilibrium composition were used to minimize the effect of side reactions (Table III, runs 27, 28 and 29 without added benzene and runs 34, 35, 36 and 37 with added benzene). The percentage 2-phenylpentane in the estimated equilibrium mixture of 2- and 3-phenylpentane is 63 ± 5. During the transalkylation, the amylcarbonium ion comes substantially to equilibrium in regard to the two species at the left of reaction 6. Thus in transalkylation between 1,4-di-3-pentylbenzene and benzene as in reaction 8, one would expect from one mole of diamylbenzene, one mole of 3-phenylpentane + 0.63 mole of 2-phenylpentane + 0.37 mole of 3-phenylpentane, or, over-all, 68% 3-phenylpentane, in good agreement with the results of Table II, run 23. If equilibrium between the secondary amylcarbonium ions obtains the relative initial extents of isomerization of 3- and 2-phenylpentane should stand in the ratio 63/37.[3] Runs 31 and 32 show this to be so.

In run 23, 7% of the phenylpentane product was 2-methyl-3-phenylbutane. Allowing for the 50% formed as unchanged 3-phenylpentane, about one molecule out of seven transalkylated appears as the skeletal isomer. This is consistent with runs reported in Table III. We do not have data to decide whether the degree of skeletal isomerization is rate limited or equilibrium limited.

The appearance of skeletal isomerization in contrast to its absence with aluminum chloride at 25° may result largely from relative temperature coefficients of the rates of the two types of isomerization. A similar phenomenon occurs with temperature in the action on alkanes of the sulfuric acid–chlorosulfonic acid mixtures.[4]

No *t*-amylbenzene (reaction 3) could be detected. This accords with recent work[21,22] which establishes that alkylation *via* aluminum chloride of tertiary amyl and hexyl halides leads predominantly to *sec*-alkylbenzenes of the type of 2-methyl-3-phenylbutane rather than of *t*-alkylbenzenes. Thus, *t*-alkylbenzenes are not favored at equilibrium.

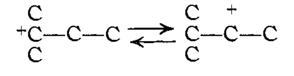
To account for the formation of branched-chain secondary alkylbenzenes from *t*-halides and aluminum chloride, it was proposed[21] that the *t*-carbonium ion first formed added to benzene to form a *t*-alkylbenzene which then reacted with an alkylcarbonium ion by hydride ion transfer to form a carbonium ion, A



$$C_6H_5-\underset{C}{\overset{C}{C}}-\overset{+}{C}-C \rightleftarrows C_6H_5-\underset{C}{\overset{+}{C}}-\underset{C}{C}-C$$

A B

which then is presumed to isomerize as shown and to continue a hydride ion transfer chain. However, from the present work, the reaction well may occur by transalkylation accompanied by isomerization of the migrating amylcarbonium ion



$$^{+}\underset{C}{\overset{C}{C}}-C-C \rightleftarrows \underset{C}{\overset{C}{C}}-\overset{+}{C}-C$$

The position of equilibrium should lie heavily to the left and addition of this mixture of ions might predominately form a *t*-alkylbenzene. However, the rate of dealkylation of the *t*-alkylbenzene would be very much more rapid than that of the secondary so that continued transalkylation could lead to but slight net formation of *t*-alkylbenzenes.

Isomerization during alkylation or transalkylation from a straight-chain secondary to a branched-chain structure apparently occurs only under rather drastic conditions. Alkylation of benzene by either butylene or isobutylene on silicophosphoric acid at 200 to 300° gives a mixture of both *sec*- and butylbenzene, although in both cases the isomerization stops well short of equilibrium. Similarly, either alkylbenzene is partially isomerized when it is passed over the catalyst with benzene, or more slowly and accompanied by disproportionation when alone.[23] Apparently, this heterogeneous, catalytic isomerization proceeds by a transalkylation mechanism much like those reported in this paper.

In run 26 (Experimental section), the amyl group of (−)2-phenylpentane was transalkylated to toluene. The amyltoluene fraction was substantially devoid of rotation which indicates that drastic racemization occurred during transalkylation (barring the unlikely possibility that one of the position isomers had a sign of rotation opposite that of the others and to such degree that the amyltoluene mixture had nearly zero rotation). The unreacted phenylpentane had suffered a loss of rotation of but 7%. Thus, unlike the results with aluminum chloride, racemization is not rapid compared to transalkylation.

A similar relationship between racemization and isomerization is observed when benzene and 2-phenylpentane are agitated with methanesulfonic acid as shown by run 33, Table III. In transalkylating a total of 35 *sec*-amyl groups, 10.5 should appear as 3-phenylpentane, 19.5 as 2-phenylpentane and 5 as 2-methyl-3-phenylbutane. These figures are chosen to give 10.5% isomerization to 3-phenylpentane as in run 33. Thus, about 35% of the molecules would react to produce 10.5% isomerization to 3-phenylpentane. These would all be optically inactive. The actual loss of rotation is 43%. The performing of these computations with allowance for approach to equilibrium will not change the picture much. Thus, unlike the situation with aluminum chloride, the loss of rotation occurs predominately *via* the transalkylation process.

When no benzene is added (run 24), the loss of rotation considerably exceeds isomerization. This excess loss of rotation probably results from a process like that in aluminum chloride, possibly a hydride ion transfer chain. The addition of benzene would depress the rate of reaction 7 by a dilution effect and greatly augment the rate of reaction 5 thus making it unnecessary for reaction 4 to occur to a considerable extent before transalkylation can return isomerized amylbenzene to the system.

Sulfuric Acid.—Sulfuric acid behaves very differently. Phenylpentane is sulfonated from slightly to completely upon agitation with sulfuric acid for

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[21] L. Schmerling and J. P. West, THIS JOURNAL, **76**, 1917 (1954).

[22] M. Inatome, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **74**, 292 (1952).

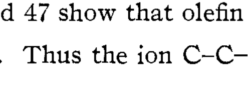
[23] H. Pines, J. D. LaZerte and V. N. Ipatieff, *ibid.*, **72**, 2850 (1950).

one hour at room temperature as the acid concentration increases from 92 to 97% (Table IV, runs 40, 41 and 42). Recovered unsulfonated hydrocarbon is negligibly isomerized. With (−)2-phenylpentane at two-thirds sulfonation the recovered hydrocarbon exhibits a slight loss of rotation, 3.6%, but no isomerization. If either 2- or 3-phenylpentane is sulfonated, and the sulfonic acid is then desulfonated by hydrolysis with phosphoric acid at 170°, unisomerized phenylpentane results (runs 44 and 45). With 2-phenylpentane, the total loss in rotation occurring during sulfonation and desulfonation was but 9.7%.

Thus, sulfonation is substantially faster than reactions 1 to 5. Once the sulfonic acid group is added, it induces a positive charge on the aromatic ring which stabilizes it against proton addition and presumably against formation of a benzylic carbonium ion. Such phenylpentanesulfonic acids are more stable than tetramethyl- and tetraethylbenzenesulfonic acids since these undergo the Jacobsen reaction.[24] Trimethyl- and triethylbenzenesulfonic acids, however, are stable in the presence of sulfuric acid.[24] On the other hand, di-*t*-butylbenzene and benzene react in the presence of sulfuric acid to form *t*-butylbenzene and *t*-butylbenzenesulfonic acid.[25] Greater ease of dealkylation of *t*-butyl groups and, perhaps, steric resistance to sulfonation may be involved. The possibility of intramolecular isomerization of the di-*t*-butylbenzene was not examined.[25]

Cram[26] reported that action of sulfuric acid on 2-phenylpentane caused a loss of rotation of 2% under conditions where sulfonation seems to have proceeded to about 10%.

If oxidation of the phenylpentane to form a benzylic carbonium ion is slow compared to sulfonation, it might be possible to augment racemization by addition of olefin, the addition of a proton to which would form a suitable carbonium ion. Indeed, Cram observed that addition of about 20% of olefins of the same skeleton to a mixture of 2- and 3-phenylpentane resulted in a 23% loss of rotation. Olefin is effective only during the first few moments since it is removed rapidly, apparently largely by polymerization (run 49, Experimental section).

Runs 46 and 47 show that olefin does not induce isomerization. Thus the ion  $\mathrm{C{-}C{-}C{-}\underset{C_6H_5}{\overset{+}{C}}{-}C}$ must be assumed to isomerize at a rate negligible in comparison to that of hydride ion transfer. This accords with the similar conclusion reached with aluminum chloride.

Slow epimerization of *dl*-2,3-diphenylbutane to the *meso* isomer accompanied by much more rapid sulfonation has been reported.[20]

Acknowledgment.—This work was supported by the Office of Naval Research.

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[24] L. I. Smith, "Organic Reactions," Vol. 1, R. Adams, Editor-in-chief, John Wiley and Sons, Inc., New York, N. Y., 1942, Chapter 12.

[25] V. N. Ipatieff and B. B. Corson, THIS JOURNAL, **59**, 1417 (1937).

[26] D. J. Cram, *ibid.*, **74**, 2152 (1952).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF OBERLIN COLLEGE]

A Kinetic Study of the Aminolysis and Hydrolysis of α-Naphthyl Acetate

BY PETER J. HAWKINS AND IVAN PISCALNIKOW

RECEIVED OCTOBER 13, 1954

A kinetic study of the reaction of *n*-butylamine with α-naphthyl acetate in aqueous solution is reported. The rate of disappearance of ester by simultaneous aminolysis and hydrolysis is in agreement with the equation $-\mathrm{d(ester)}/\mathrm{d}t = k_4(\mathrm{ester})(\mathrm{RNH}^-) + k_5(\mathrm{ester})(\mathrm{RNH_2})(\mathrm{H}^+) + k_2(\mathrm{ester})(\mathrm{OH}^-)$ (1). The similarity of aminolysis and hydrolysis in the form of their kinetic equations is indicated.

A kinetic study of the aminolysis of two thiol esters in aqueous solution has previously been reported[1] and it was shown that an equation involving at least the following terms was applicable

$$\mathrm{rate} = k(\mathrm{ester})(\mathrm{RNH_2})(\mathrm{OH}^-) + k(\mathrm{ester})(\mathrm{OH}^-) \quad (1)$$

The first term was identified with the aminolysis and the second with the hydrolysis of the ester.

It was the purpose of the work presently reported to extend the investigation to oxygen esters, to demonstrate the third-order reaction previously observed and to confirm, if possible, the inclusion of the hydroxide ion concentration by the introduction of hydroxide ion from a source other than that of the hydrolysis of the amine.

The problems of defining the concentrations of kinetically significant species were met firstly, by the use of aqueous solutions for which the constants governing the interaction of amine and solvent are known and secondly by determining pseudo first-order rate factors under conditions where the amine was in large excess and could be assumed to remain essentially constant during the course of reaction. In view of the low concentrations necessary to retain a reasonable rate of reaction a spectrophotometric method of analysis was used to follow the course of the reaction. The ester α-naphthyl acetate was chosen because of its susceptibility to this method of analysis.

Previous investigations[2] of the aminolysis of oxygen esters have been largely confined to non-aqueous or part-aqueous solutions and in consequence some ambiguity must remain where the equilib-

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[1] P. J. Hawkins and D. S. Tarbell, THIS JOURNAL, **75**, 2982 (1953).

[2] (a) R. L. Betts and L. P. Hammett, *ibid.*, **59**, 1569 (1937); (b) M. Gordon, J. G. Miller and A. R. Day, *ibid.*, **70**, 1946 (1948); (c) E. M. Arnett, J. G. Miller and A. R. Day, *ibid.*, **72**, 5635 (1950); (d) R. Baltzly, I. M. Berger and A. A. Rothstein, *ibid.*, **72**, 4149 (1950); (e) T. A. Koch, J. G. Miller and A. R. Day, *ibid.*, **75**, 953 (1953).