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THE ACTION OF SOME STRONG ACIDS
ON
SECONDARY PHENYLPENTANES

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ABSTRACT

Aluminum chloride rapidly racemizes optically active 2-phenylpentane at room temperatures probably by a hydride ion transfer chain. Interisomerization of 2- and 3-phenylpentane occurs very much more slowly and seemingly consequent to disproportionation to diamylbenzene followed by reversal of this reaction. The same reactions occur in benzene solution but transalkylation of amyl groups directly to benzene also occurs. 1,4-Di-3-pentylbenzene and benzene react to give mixtures of 2- and 3-phenylpentane. The transalkylation apparently occurs by transfer of an amyl group as a carbonium ion rather than by bimolecular nucleophilic displacement.

With methanesulfonic acid at 140°, the hydride ion transfer chain is relatively less prominent. In benzene solution, the loss in rotation is largely consequent to transalkylation. Interisomerization of 2- and 3-phenylpentane is accompanied by formation of 2-methyl-3-phenylbutane. Transalkylation of the amyl group of 2-phenylpentane to toluene give amyltoluenes nearly devoid of rotation.

In reaction of 2- and 3-phenylpentane with sulfuric acid at room temperatures, sulfonation is faster than other reactions. 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 which is formed.

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.^{2,3,4}

- (2a) R. L. Burwell, Jr., and G. S. Gordon, III, J. Am. Chem. Soc., 70, 3128 (1948). (2b) Gordon and Burwell, ibid., 71, 2355 (1949).
 (3) Burwell, Robert B. Scott and L. G. Maury, ibid., 76, 0000 (1954).
 (4) Burwell, Maury and Scott, ibid., 76, 0000 (1954).

In the present paper, the action of sulfuric acid, methane-sulfonic acid and aluminum chloride upon 3-phenylpentane and upon optically active 2-phenylpentane is reported. The use of the optically active compound was of great value 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 micro-column 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 Beckmann IR2. In this case several suitable wave lengths were employed.

In determining degree of disproportionation, the strong benzene band at 14.9 microns was very helpful since the alkylbenzenes do not interfere.

Materials.- Methanesulfonic acid was kindly supplied by the Indoil Chemical Company. After distillation at 3-4 mm. it melted at 13-14°. In earlier experiments this material was used as such. In run 59 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

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

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 olefines, 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

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

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 save 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 Company (Indiana); b.p. 268° (uncorr.) and $n_D^{20} = 1.4857$. We are indebted to Professor Herman Pines for a sample of 3-methyl-3-phenylbutane.

Results Using Aluminum Chloride. - The desired amounts of hydrocarbons were 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 Adamsen) 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 20 to 25 or at 320 cycles in later 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 77. - 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, $1.5 \pm 0.5\%$ of the phenylpentane had transalkylated to form benzene and amyltoluenes. The degree of isomerization of the recovered 2-phenylpentane was $0 \pm 1\%$ while the degree of racemization was 99%. In a similar run with inactive 2-phenylpentane carried to 8% dealkylation, isomerization was also undetectable.

Table I

THE ACTION OF ALUMINUM CHLORIDE ON PHENYLPENTANES AT 25°

Run No.	Phenylpentane ^a mole %	Mole ratio ^b catalyst to hydrocarbon	Time min.	Racemization ^c %	Comp. of recovered C ₁₁ H ₁₆ as % 3PP
20	100 2PP	0.050	60	100	16±2 ^d
21	100 3PP	.052	60	—	79±3 ^d
25	100 2PP	.025	15	98.7	1±1 ^d
79	100 2PP	.024	10	62.6	0±1 ^e
23	34.5 2PP	.052	300	—	28±1 ^{d,f}
24	34.5 3PP	.056	300	—	29±1 ^{d,f}
72	34.5 2PP	.013	45	100	29±1
73	34.5 2PP	.013	13	100	17±2
75	34.5 2PP	.0056	10	97	0±1

^aIn last five runs, remainder is benzene. 2PP is 2-phenylpentane.

^bTo total hydrocarbon including benzene. ^cProbable error is 0.5 to 1 percentage units. ^dConsiderable disproportionation to benzene and diamylbenzenes occurred. ^e1.5±0.5 % disproportionation as determined on reaction product by comparison against known mixtures of benzene and 2-phenylpentane. ^fThe distillation residues (diamylbenzenes) were nearly identical as judged by their infrared spectra.

Table II

THE ACTION OF ALUMINUM CHLORIDE AND OF METHANESULFONIC ACID

ON MIXTURES OF 1,4-DI-3-PENTYLBENZENE AND BENZENE

Run No.	Mole ratio $C_{10}H_{26}/C_6H_6$	Catalyst	Mole ratio $\frac{\text{catalyst}}{\text{hydrocarbon}}$	Temp. °C	Time	Dealkylation % ^a	Composition of recovered $C_{11}H_{18}$ % 3-phenylpentane
80	0.36	AlCl ₃	.061	25	30 min.	33±2	70±2 ^b
78	.36	AlCl ₃	.008	25	25 min.	1.5±0.5	65±15 ^c
22	.48	CH ₃ SO ₃ H	2.0	143	35 hr.	65±10	60±2 ^d
26	.36	CH ₃ SO ₃ H	1.8	143	11 hr.	60±5	55±5 ^d
27	.36	CH ₃ SO ₃ H	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.

^bInfrared examination showed the recovered diamylbenzene to be extensively isomerized and suggested that the meta-isomer was a major product of isomerization and that triphenylbenzenes, if any, were at best minor constituents.

^cThe recovered diamylbenzene was isomerized in the same manner as in run 80 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 in turn each of the phenylpentanes.

^d% of 3-phenylpentane in sum of 2- and 3-phenylpentanes.

^eThe phenylpentane fraction contained 7±2% of 2-methyl-3-phenylbutane.

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 14 and 15 (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 was then distilled save that in runs 14 and 15 this distillation was preceded by a steam distillation which eliminated products much higher boiling than diamylbenzene.

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, 83 and 84, since these started from fairly near the equilibrium 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 5 to 10 times slower than that of 2-methyl-3-phenylbutane.

Run 19.- 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.

In runs 4, 6 and 9, 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 11. - In an effort to determine the fate of the added olefin in runs 7 and 9, 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 analogous to the observed steam distillation of diamylbenzene. This result tentatively suggests that that the α -methylstyrene reacted largely by polymerization rather than alkylation.

TABLE III

THE ACTION OF METHANESULFONIC ACID ON PHENYLPENTANES

Run no.	Phenylpentane, ^a mole%	Mole ratio ^b CH ₃ SO ₃ H to hydrocarbon	Temp. °	Time hr.	Loss of Rotation %	Composition ^c of recovered C ₁₁ H ₁₆ as % 3VP
14A ^d	100 2VP	2.30	142	12	50.4	3±3
14B	100 2VP	1.93	145	30		
15A ^d	100 3VP	2.28	142	43		78±2 ^e
15B	100 3VP	1.94	142	25		
67	100 2VP	4.61	150	12		9.0±1.5 ^f
68	100 3VP	4.59	150	12		17.0±2.0 ^f
74	100 2VP	5.88	150	13	43	10.5±1.5 ^g
61	82.0 2VP	7.55	142	8.8		35±2
62	67.9 2VP	7.92	142	8.8		36±2
63	50.0 2VP	7.50	145	8		45±2
69	60.0 2VP	5.40	148	33		38±4
70	80.0 2VP	5.49	148	33		28±4
83	55.0 2VP	5.85	148	12		42±1.5 ^h
84	76.0 2VP	6.26	148	12		30±1.5 ^h

^aRemainder of phenylpentane is 3VP in run 61 and those listed below

it. In runs whose run no. is 67 or greater, benzene was added to bring the mole % of total phenylpentane to 34.5%. ^bTo total hydrocarbon.

^cPercent of 2- and 3-phenylpentane present as 3-phenylpentane. ^dCombined with the B part before analysis. ^eOf 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. ^fAbout 4% of the phenylpentane was 2-methyl-3-phenylbutane. ^g7±2% 2-methyl-3-phenylbutane. ^h6±2% 2-methyl-3-phenylbutane.

TABLE IV

THE ACTION OF SULFURIC ACID ON PHENYLPENTANES AT 25°

Run no.	Phenylpentane type	cc.	Sulfuric acid %	cc.	Time min.	Sulfonation
2	3 ψ P	3	92.10	5	60	Slight ^a
3	3 ψ P	3	94.55	5	60	1/2 ^a
1	3 ψ P	3	96.80	5	60	complete
5	2 ψ P	3	95.88	5	35	2/3 ^{a,b}
4	3 ψ P	7.3	96.80	10		1/2 ^{a,c}
6	2 ψ P	5.8	96.80	10	15	complete ^{c,d}
7	2 ψ P	6	95.89	10.5	60	1/2 ^{a,e}
9	2 ψ P	4.1	96.8	6.0		complete ^{c,f}

^aNo detectable isomerization of the unsulfonated phenylpentane.

^bLoss of rotation of unsulfonated (-)2 ψ P, 3.6%. ^cNo detectable isomerization of the phenylpentane obtained by desulfonating the sulfonated material. ^dLoss of rotation of the (-)2 ψ P recovered by desulfonating the sulfonated material was 9.7%. ^e1.9% 3-phenyl-1-pentene added to phenylpentane. ^f3.19% 4-phenyl-1-pentene added.

^g3.2% 3-phenyl-1-pentene added. ^hLoss of rotation of unsulfonated 2 ψ P, 16%.

Discussion

Aluminum chloride. - Aluminum chloride catalyses the interisomerization of 2- and 3-phenylpentane at room temperatures (Table I, runs 20 and 21). Accompanying the isomerization is disproportionation in the sense of



Such disproportionation seems initially to occur more rapidly than isomerization (runs 25 and 79). The addition of benzene to the phenylpentane largely, but not completely (runs 23 and 24), suppresses disproportionation as would be expected from Equation (1). As exhibited by runs 23 and 24, starting from either 2- or 3-phenylpentane, one can reach the equilibrium mixture of these alkylaromatic hydrocarbons, $29 \pm 4\%$ 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} There is no detectable formation

(7) H. Pines, W. D. Huntsman and V. N. Ipatieff, *ibid.*, 73, 4343, 4483 (1951).

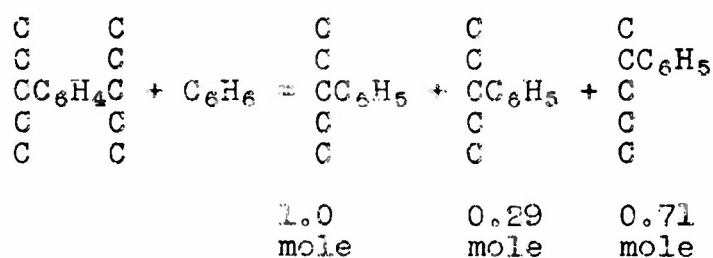
(8) R. L. Burwell, Jr., L. M. Elkin and A. D. Shields, *ibid.*, 74, 4570 (1952).

of either 2-methyl-3-phenylbutane or *t*-amylbenzene even in runs protracted to near equilibrium in regard to 2- and 3-phenylpentane. Nor, were such amylbenzenes formed in the 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 78 and 80). This constitutes a reversal of Equation (1). Unreacted diamylbenzene is isomerized, primarily, probably by formation of the meta-isomer. This isomerization does not occur by reversal of the dealkylation reaction at least initially since the ratio of 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 an secondary pentyl group from one benzene ring to another results in interisomerization of the 2-pentyl and the 3-pentyl groups. This isomerization proceeds so rapidly that 2- and 3-phenylpentane are formed in nearly their equilibrium ratio as shown by runs 78 and 80. In this reaction



according to this proposal, the first phenylpentane molecule on the right side of the equation is one left by removal of an amyl group. It should be 3-phenylpentane. The transferred amyl group would lead to 2- and 3-phenylpentane in the ratio 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_N^1 or by S_N^2 processes.^{9,10,11}

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

(10) H. C. Brown and M. Grayson, J. Am. Chem. Soc., **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).

By the product criterion, the occurrence of isomerization demonstrates that the transalkylation is not S_N^2 but is to be classified as a carbonium ion process.^{7,8}

Isomerization of a phenylpentane occurs, then, by disproportionation in the sense of Equation (1) followed by its reversal. Alternatively,

once some benzene has accumulated, an amyl group may transalkylate directly to benzene. 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 amyl carbonium which, under the conditions studied, rapidly isomerizes 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 fluoride¹²

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

or when using aluminum chloride.¹³ With aluminum chloride, and as will

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

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 would seem better interpreted as carbonium ion processes rather than as S_N2 processes¹² as has been suggested.

The ionic intermediate given above can presumably lead to

intramolecular para-meta isomerization as has been suggested.^{14, 15}

(14) G. Baddeley, G. Holt and D. Voss, J. Chem. Soc., 1011 (1952).

G. Baddeley, ibid., 994 (1950).

(15) D.A. McCauley and A. P. Lien, J. Am. Chem. Soc., 74, 6246(1952).

Although intramolecular migration is much faster than transalkylation
with xylenes,¹⁶ with s-amylbenzenes the two rates are similar

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

(runs 78 and 80).

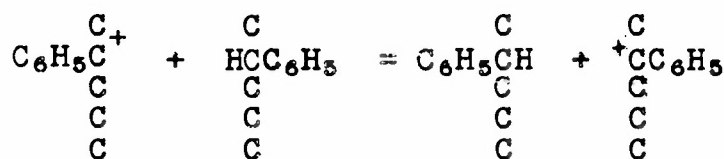
The transalkylation sequence as applied to optically active 2-phenylpentane would lead to the formation of the racemic compound. However, racemization of 2-phenylpentane is so fast compared to isomerization that transalkylation cannot contribute significantly to the racemization. Whenever racemization was even slightly incomplete, isomerization was undetectable (Table I, runs 25, 79 and 75). As described in run 77 in the experimental section, in transalkylation between (+)2-phenylpentane and toluene, recovered phenylpentane is 99% racemized but negligibly isomerized when transalkylation had proceeded to but 1.5%.

Since transalkylation and intramolecular migration occur at comparable rates (runs 78 and 80), the latter process is presumably not important in racemization. The reaction seems, then, to proceed by the usual carbonium ion chain reaction obtaining in isomerization^{17,2}

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

and racemization^{2, 18} of alkanes.

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

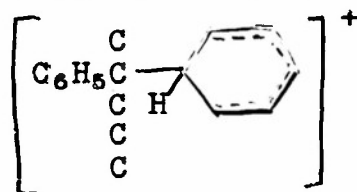


If this view is accepted, the rate of interisomerization of ions derived from 2- and 3-phenylpentane is very slow compared to the rate of propagation of the hydride ion transfer chain.

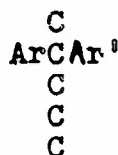
The rate of addition of the isopropyl carbonium ion to benzene is many times faster than that of hydride ion transfer to this carbonium ion from isobutane.¹⁹ With the compounds studied in this research,

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

such addition would yield an intermediate of the form,



If such was 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

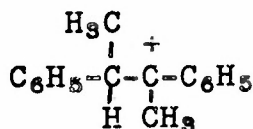


would be formed. While this might be presumed to dealkylate rapidly, such a sequence would lead to disproportionation occurring at a rate comparable to that of racemization in the case of 2-phenylpentane alone. Runs 25 and 79 exclude this possibility as does run 77 for 2-phenylpentane and toluene.

The reactions reported in the present paper are closely related to some reported by Somerville and Spoerr.²⁰ Aluminum chloride

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

causes the isomerization of d,l-2,3-diphenylbutane dissolved in a large excess of benzene to the meso-isomer. The reaction was 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



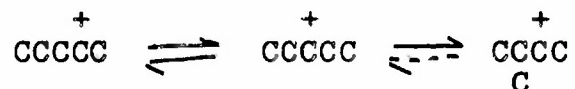
was involved in the epimerization is equivalent to the proposal we make for the racemization of 2-phenylpentane. No skeletal isomerization accompanied the epimerization. On the contrary, 2-methyl-1,2-diphenylpropane is isomerized to meso-2,3-diphenylbutane although this seems to proceed via a dealkylation mechanism²⁰ 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 14 and 15, 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 interisomerization since 2-methyl-3-phenylbutane is also formed.

The equilibrium ratio of 2- and 3-amylbenzene was estimated at 148° by direct approach to equilibrium from each side. Mixtures whose composition lay near the estimated equilibrium composition were used

to minimize the effect of side reactions (Table III, runs 61, 62, 63 without added benzene and runs 69, 70, 83 and 84 with added benzene). The % 2-phenylpentane in the estimated equilibrium mixture of 2- and 3-phenylpentane is 63 ± 5 . During transalkylation, the amyl carbonium ion comes substantially to equilibrium in regard to the two species at the left:



Thus in transalkylation between 1,4-di-3-pentylbenzene and benzene one would expect from one mole of diamylbenzene, one mole 3-phenylpentane + 0.63 mole 2-phenylpentane + 0.37 mole 3-phenylpentane, or, overall, 68% 3-phenylpentane, in good agreement with the results of Table II, run 27. If such equilibrium obtains the relative initial extents of isomerization of 3- and 2-phenylpentane should stand in the ratio 63/37.⁸ Runs 67 and 68 show this to be so.

In run 27, 7% of the phenylpentane product was 2-methyl-3-phenylpentane. 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 other runs reported in Table III. We do not have data to decide whether this is rate limited or equilibrium limited.

The appearance of the new type of isomerization compared to the simpler isomerization given by aluminum chloride at 25° may largely result 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 system.⁴

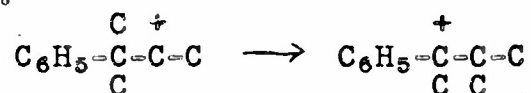
No formation of t-amylbenzene could be detected. This accords with recent work^{21,22} which establishes that alkylation via aluminum

(21) L. Schmerling and J.P. West, ibid., 76, 1917 (1954).

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

chloride of tertiary amyl and hexyl halides leads predominantly to s-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 tertiary halides and aluminum chloride, it was proposed²¹ that the tertiary carbonium ion first formed added to benzene to form a tertiary alkylbenzene. This was then supposed to react with an alkyl carbonium ion by hydride ion transfer to form a carbonium ion of the following type:



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



The position of equilibrium should lie heavily to the left and addition of this mixture of ions might heavily form a tertiary alkylbenzene. However, the rate of dealkylation of the tertiary alkylbenzene would be very much more rapid than that of the secondary so that continued transalkylation could lead to but slight net formation of tertiary alkylbenzenes. Although in alkane isomerization by aluminum chloride,

it is necessary to assume that tertiary carbonium ions can isomerize to primary ones, with sulfuric acid, for example, one must assume that this is impossible.⁸ One may correlate the formation of tertiary alkylbenzenes with weaker alkylating agents²¹ with this difference.

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 silico-phosphoric acid at 200 to 300° gives a mixture of both s- and t-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

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

isomerization proceeds by a transalkylation mechanism much like those reported in this paper.

In run 19 (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 amyl toluene 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 slow compared to transalkylation.

Racemization is also slow compared to isomerization when benzene and 2-phenylpentane are agitated with methanesulfonic acid as shown by run 74, Table III. Ignoring reverse isomerization, one would expect that in transalkylating a total of thirty-five s-amyl groups, 10.5 would 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 74. 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 computation with allowance for approach to equilibrium⁸ will not change the picture much. Thus, unlike the situation with aluminum chloride, a large share of the loss of rotation occurs via the transalkylation process.

When no benzene is added (run 14) the situation is somewhat different. Here, the loss of rotation considerably exceeds isomerization. This excess loss of rotation probably results from a hydride ion transfer chain as in aluminum chloride. The addition of benzene depresses the rate of the hydride ion transfer reaction. It also makes it unnecessary for disproportionation to diamylbenzene and benzene to occur to a considerable extent before transalkylation can return isomerized amylbenzene to the system.

Sulfuric acid.— Sulfuric acid behaves very differently. Phenylpentane is from slightly to completely sulfonated upon agitation with sulfuric acid for one hour at room temperatures as the acid concentration increases from 92 to 97% (Table IV, runs 2, 3 and 1). 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 4 and 6). With 2-phenylpentane, the total loss in rotation occurring during sulfonation and desulfonation was but 9.7%.

Thus, sulfonation is substantially faster than other chemical reactions. 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 the tetramethyl- and tetraethylbenzenesulfonic acids which undergo the Jacobsen reaction.²⁴

(24) L.I. Smith, "Organic Reactions", Vol. 1, Chapter 12, R. Adams, Editor-in-chief, John Wiley and Sons, New York, 1942.

Trimethyl- and triethylbenzenesulfonic acids, however, are stable in the presence of sulfuric acid.²³ 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 dealkyl-

(25) V.N. Ipatieff and B.B. Corson, J. Am. Chem. Soc., 59, 1417(1937).

ation 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

Cram²⁶ reported that action of sulfuric acid on 2-phenylpentane

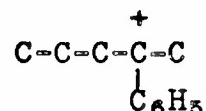
(26) D.J. Cram, ibid., 74, 2152 (1952).

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 rapidly removed, apparently largely by polymerization (run 11, experimental section).

Runs 7 and 9 show that olefin does not induce isomerization.

Thus the ion



must be assumed to isomerize at a rate negligible in comparison to hydride ion transfer. This accords with the similar conclusion reached with aluminum chloride.

Slow epimerization of d,l-2,3-diphenylbutane to the meso-isomer²⁰ accompanied by much more rapid sulfonation has been reported.

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