Acid-Catalyzed Isomerization of 3-Ethylpentane. Steric Hindrance of Hydride Transfer

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The isomerization of 3-ethylpentane in the presence of sulfuric acid at 25.0° has been studied. 2-Methylhexane and 3-methylhexane are the initial products, with the dimethylpentanes being formed more slowly. The rate of isomerization of 3-ethylpentane is significantly lower than that of 3-methylpentane; this is interpreted as being due to steric hindrance of hydride transfer from 3-ethylpentane. The ratio of the methylhexane isomers formed shows significant variations when different hydrocarbons are present along with 3-ethylpentane in the reaction mixture. This variation also can be rationalized in terms of hydride donating ability of the added substances. Rate constants were calculated for the isomerization of 3-ethylpentane and 3-methylpentane in admixture and for 3-ethylpentane alone. 3-Ethylpentane has been detected as a minor product of isomerization of the methylhexanes in the presence of sulfuric acid.

The isomerization of most of the isomeric heptanes in the presence of sulfuric acid has been studied in some detail.[1-6] In accordance with the behavior of other homologs, isomers having at least one tertiary hydrogen rearrange rapidly by processes involving simple alkyl migration. Reactions which involve a change in degree of branching proceed much more slowly. Thus, 2- and 3-methylhexane are interconverted rapidly as are also 2,3- and 2,4-dimethylpentane. However, the dimethylpentanes are formed only very slowly from the methylhexanes, and 2,2,3-trimethylbutane is formed extremely slowly from the dimethylpentanes.

The isomerization of 3-ethylpentane has received only scant attention. In their study of the H–D exchange between alkanes and deuteriosulfuric acid, Stevenson and co-workers found that the rate was somewhat lower for 3-ethylpentane than for several other singly branched alkanes.[3] Thus, 3.3% of the 3-ethylpentane molecules suffered exchange in 2 hr., whereas with 3-methylhexane, 7% exchange occurred during 40 min. under the same conditions. The nature of the deuterated species formed from 3-ethylpentane deserves mention; d_{12} and d_{15}, with a possible trace of d_9, were the only species present. The unusual feature of these results is the absence of species with lower deuterium content. Mass spectrometric evidence also indicated that the deuterated compounds did not have the 3-ethylpentane skeleton.

Experimental

Materials.—3-Ethylpentane, b.p. 93.0–93.8°, $n^{25}\text{D}$ 1.3907, was obtained by dehydrating 3-ethyl-3-pentanol over alumina at 370°, followed by hydrogenation of the resulting alkene over platinum oxide. This material was fractionated through a 60-cm. column packed with glass helices and then percolated over silica gel. Gas chromatography indicated a purity in excess of 99.9%, with the only contaminant being 3-methylhexane.

3-Methylpentane, b.p. 64.0–64.3°, $n^{25}\text{D}$ 1.3738, was obtained from 3-methyl-3-pentanol by the same sequence of steps as used for 3-ethylpentane. Gas chromatography failed to reveal the presence of impurities.

A single bottle of reagent grade 96.4% sulfuric acid served as a stock solution for all reactions in which acid of this concentration was used. Acids of higher concentration were prepared from this stock solution by adding appropriate amounts of 15% fuming sulfuric acid (C.P. grade). All concentrations were determined by titration with standard sodium hydroxide.

Isomerization Reactions.—In the standard procedure, 0.5 ml. of hydrocarbon and 0.5 ml. of acid were placed in a water-jacketed tube and agitated by the "rapid-stirring" technique of Burwell and co-workers.[5] The water which was circulated through the jacket was maintained at a temperature of 25.0 ±0.1°. At the end of the reaction period, stirring was discontinued, and the mixture was allowed to stand until separation of layers occurred. A portion of the hydrocarbon layer was withdrawn by pipet and placed in a test tube containing a pellet of potassium hydroxide. Duplicate experiments were carried out in each case.

Product Analysis.—The products were analyzed by gas chromatography on a 50-ft. column packed wth β,β'-oxydipropionitrile on Fisher Columpak and maintained at a temperature of 50°. Good resolution was achieved for all isomers encountered in the study, and the areas under the peaks were calculated by triangulation. The per cent composition of synthetic mixtures calculated by this method agreed with the known values to within 0.1.

Results

The results of the isomerization studies are summarized in Table I. As expected, 2- and 3-methylhexane were found to be the initial products of isomerization; the ratios of the concentration of these isomers in the products are listed in col. 5 of Table I. The reason for presenting the data in this fashion will become apparent below. The dimethylpentanes are formed at a much slower rate. For example, in experiment 15, approximately 0.1% of 2,4-dimethylpentane, and 0.05% of 2,3-dimethylpentane were formed, whereas the methylhexanes were present to the extent of 4.3%. Disproportionation products were not detected.

Mixtures of 3-ethylpentane and 3-methylpentane were used in the initial experiments (1–8) so that the rate for the former could be compared with that of a "methyl-shift" compound. Experiments 10–15 were conducted with 3-ethylpentane as the sole hydrocarbon to determine if the 3-methylpentane exerted a significant effect on the rate of isomerization of the former. The effect of a trace of olefin is illustrated by experiment 9, in which a small amount of 3-methyl-2-pentene was present.

The effect of doubling and tripling the acid to hydrocarbon ratio is illustrated by experiments 16 and 17. In experiment 18, a trace of 3-methyl-2-pentene was added to the 3-ethylpentane, and samples were withdrawn for analysis at the times indicated. The effect of methylcyclopentane on the rate of isomerization of 3-

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[1] G. S. Gordon, III, and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **71**, 2355 (1949).

[2] V. I. Komarewsky and W. E. Ruther, *ibid.*, **72**, 2501 (1950).

[3] D. P. Stevenson, C. D. Wagner, O. Beeck, and T. W. Otvos, *ibid.*, **74**, 3269 (1952).

[4] A. K. Roebuck and B. L. Evering, *ibid.*, **75**, 1631 (1953).

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

[6] L. G. Maury, R. L. Burwell, Jr., and R. H. Tuxworth, *ibid.*, **76**, 5831 (1954).

TABLE I[a]

ISOMERIZATION OF 3-ETHYLPENTANE AT 25.0°

Expt. no.	Alkane	Time, hr.	% isomerization of 3 EP	Ratio of 2MH/3MH in product	% isomerization of 3 MP
			96.4% acid		
1	3EP, 3MP	1.0	0.8		2.3
2		1.5	1.3	1.2	3.9
3		2.0	1.8	1.2	5.5
4		2.5	2.3	1.2	6.6
5		3.0	2.7	1.2	7.5
6		3.5	3.4	1.3	9.6
7		4.0	4.0	1.3	11.3
8		5.0	4.8	1.3	13.0
9[b]		2.0	19.6	1.2	37.6
10	3EP	1.0	0.6	2.1	
11		2.0	1.5	1.9	
12		3.0	1.9	1.9	
13		4.0	2.8	1.9	
14		5.0	3.8	2.0	
15		6.0	4.4	2.0	
16[c]		2.0	2.8	2.1	
17[d]		2.0	3.9	2.1	
18[b,e]		0.25	0.9	1.1	
		0.50	3.3	1.5	
		1.0	9.3	1.7	
		1.5	12.2	1.7	
19[f]	3EP, MCP	18.0	1.5	0.2	
20[g]		5.0	0.3	0.5	
21[h]		5.0	0.4	0.7	
			98.7% acid		
22	3EP, 3MP	0.25	3.6	1.0	6.0
23		0.50	6.7	1.0	11.8
24		0.75	9.9	1.0	16.2
25		1.0	13.6	1.0	20.6
26		1.5	20.8	1.1	28.2
			99.4% acid		
27	3EP, 3MP	0.50	28.7	1.1	37.6

[a] These abbreviations are used: 3EP for 3-ethylpentane, 2MH and 3MH for 2- and 3-methylhexane, 3MP for 3-methylpentane, and MCP for methylcyclopentane. [b] One microliter of 3-methyl-2-pentene was added. [c] Acid–hydrocarbon volume ratio, 2:1. [d] Acid–hydrocarbon volume ratio, 3:1. [e] Samples were removed from reaction mixture at times indicated. [f] 50:50 mixture of 3EP and MCP by volume. [g] 10:1 mixture of 3EP and MCP by volume. [h] 20:1 mixture of 3EP and MCP by volume.

TABLE II

RATE CONSTANTS FOR ISOMERIZATION OF 3-ETHYLPENTANE AND 3-METHYLPENTANE IN ADMIXTURE, 25.0°

	k_1, hr.$^{-1}$[a] 96.4% acid	k_1, hr.$^{-1}$[a] 98.7% acid
3-Ethylpentane	0.0105 ± 0.0002	0.158 ± 0.004
3-Methylpentane	0.0308 ± 0.0008	0.238 ± 0.002

[a] The isomerization of 3-ethylpentane was treated as an irreversible reaction; that of 3-methylpentane was treated as a reversible reaction with equilibrium concentrations of 69% 2- and 31% 3-methylpentane (see ref. 4).

ethylpentane and on the ratio of the methylhexanes formed is illustrated by experiments 19–21. In agreement with the findings of others,[3] we did not detect isomerization of methylcyclopentane to cyclohexane.

Discussion

It is apparent from experiments 1–8 that 3-ethylpentane isomerizes at a decidedly lower rate than 3-methylpentane. Both reactions follow first-order kinetics, and rate constants, calculated by a least squares treatment of the data, are given in Table II. It has been shown that the rate of isomerization of isoparaffins depends greatly on the acid concentration.[4] Rate constants for reactions carried out with 98.7% acid (experiments 22–26) also are presented in Table II where it is seen that the proportional increase is greater for 3-ethylpentane than for 3-methylpentane. The possibility that, at a sufficiently high acid concentration, the rate for 3-ethylpentane might surpass that for 3-methylpentane is rendered unlikely by the results of experiment 27 where it is seen that, with 99.4% acid, 3-methylpentane still isomerizes at a substantially greater rate.

Although an exact comparison cannot be made, it does appear that our rate constants for 3-methylpentane are somewhat larger than those that Roebuck and Evering found.[4] Thus, from the curve presented by these authors, one estimates $k_1 \simeq 0.15$ hr.$^{-1}$ for 98.7% acid, as compared with our value of 0.24 hr.$^{-1}$. The discrepancy is believed to be due to more efficient stirring of the reaction mixtures in the present study.[7]

When 3-ethylpentane alone is treated with sulfuric acid (experiments 10–15), the rate of isomerization, $k_1 = 0.0081 \pm 0.008$ hr.$^{-1}$, is slightly lower than when 3-methylpentane is present. The difference is small, how-

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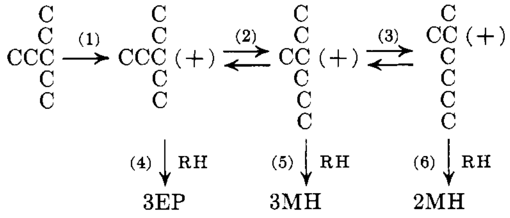
(7) Roebuck and Evering observed a decline in value of the first-order rate constants at increasing conversions. Burwell, *et al.*,[5] found that this did not occur with the "rapid-stirring" technique.

ever, and it may be concluded that 3-methylpentane does not exert a significant influence on the rate of isomerization of 3-ethylpentane.

The essential steps of the carbonium ion mechanism of isomerization of 3-ethylpentane are as follows. This scheme differs from the one presented by Burwell, *et al.*,[5] for the methylhexanes only in that ethyl as well as methyl migration is included. In step 1, the chain-initiating step, oxidation of 3-ethylpentane to the carbonium ion state by sulfuric acid occurs, and, in steps 4, 5, and 6, the chain-carrying step, a new carbonium ion (not shown) is formed from RH, the hydride donor.



Stevenson, *et al.*, suggested that the absence of deuterated species with preserved carbon skeleton when 3-ethylpentane was treated with deuteriosulfuric acid might be due to (a) rapid migration of ethyl groups in the 3-ethylpentyl ion, or (b) an unusually long period of ionic residence, due perhaps to steric hindrance in the chain-carrying step.[3] The results of our study can be rationalized readily in terms of the latter postulate, *viz.*, the low reactivity of 3-ethylpentane as a hydride donor. This would result in a lowered rate for the chain-initiating and chain-propagating steps and an over-all reduction in rate of isomerization of 3-ethylpentane compared to 3-methylpentane.

The most striking difference between the experiments in which 3-methylpentane was present in the reaction mixture and those in which 3-ethylpentane alone was used is the difference in the relative amounts of the methylhexanes formed. The ratio of 2- to 3-methylhexane was approximately 1.25 when 3-methylpentane was present and 1.95 when it was absent. The postulation of low hydride donor tendency for 3-ethylpentane also provides an explanation for these differing ratios. The relative amounts of the methylhexanes formed would be expected to depend on the nature of the hydride donors present in the reaction mixture. When only reluctant donors are present—the situation that exists in the early stages of reactions involving 3-ethylpentane alone—a smaller fraction of the 3-methylhexyl ions will be converted to 3-methylhexane (step 5) than when a more efficient donor, *e.g.*, 3-methylpentane, is present.

It seems most likely that steric factors are responsible for the low hydride donor activity of 3-ethylpentane, and the situation is reminiscent of the findings of Brown and Taylor on the basicity of amines toward trimethylboron.[8] It was observed that basicity decreases in the series $EtNH_2 > Et_2NH \gg Et_3N$. Brown and Taylor proposed that at least one of the methyl groups of triethyl amine is held in a conformation in which it protrudes in front of the nitrogen, thus interfering with salt formation. A comparable situation may exist in 3-ethylpentane in which the methyl groups interfere with removal of the tertiary hydrogen. In support of this hypothesis may be cited the data on the exchange of ethylcyclopentane with deuteriosulfuric acid. This hydrocarbon exchanges very rapidly—35% in 2 hr. with 95% acid—as contrasted with 3.3% exchange for 3-ethylpentane in the same period of time.[3] Ethylcyclopentane can be visualized as an analog of 3-ethylpentane in which the accumulation of atoms in the region around the tertiary hydrogen has been reduced by tying two of the ethyl groups behind the carbon. The enhanced basicity of quinuclidine over that of triethylamine has been rationalized by a similar argument.[8]

To gain additional evidence concerning the relationship between the nature of the hydride donors present and the ratio of methylhexanes formed, experiments were carried out in which mixtures of methylcyclopentane and 3-ethylpentane were used (experiments 19–21). Methylcyclopentane, which can be considered as a cyclic analog of 3-methylpentane in which congestion around the tertiary hydrogen has been reduced by ring formation, has been shown to exchange very rapidly with deuteriosulfuric acid, *e.g.*, 9.5% in 40 min. and 63% in 120 min.[3] The presence of methylcyclopentane caused a marked reduction in the ratio of 2- to 3-methylhexane, *e.g.*, to a value of 0.2 when a 50:50 mixture was used. The ratio increased when smaller amounts of methylcyclopentane were used, but, even with a mixture of one part methylcyclopentane to twenty 3-ethylpentane, the ratio was only 0.7. Thus, these results support the postulate of the relationship between hydride donor ability and ratio of methylhexanes.

It is interesting to note the drastic reduction of rate of isomerization brought about by methylcyclopentane, *e.g.*, only 1.5% isomerization occurred in 18 hr. when a 50:50 mixture was used. This also may be related to the tendency of methylcyclopentane to donate hydride to an open-chain carbonium ion and thus decrease the rate of the chain-carrying step.

The methylhexane ratio is not affected greatly by the concentration of acid, although it does appear to be slightly lower at higher acid concentrations. Thus, for mixtures of 3-ethylpentane and 3-methylpentane with 98.7% acid, the ratio was approximately 1.0, and with 99.4% acid, the value was 1.1. The significance of the latter value can be questioned on the grounds that an extensive amount of isomerization occurred. The fact that the ratios do appear to be slightly lower for higher acid concentrations may reflect a higher concentration of hydride donors in the acid phase.

One experiment (no. 18) was performed in which a trace of 3-methyl-2-pentene was added to 3-ethylpentane, and the methylhexane ratio was determined periodically during the early stages of the reaction. Initially, the ratio was quite small, for 1.1 after 0.9% isomerization had occurred, but increased to a value of 1.7 after 9% isomerization. The low values observed initially are believed to result from a higher-than-usual concentration of hydride donors, *e.g.*, alkene, in the acid phase. As the reaction proceeds, the extra concentration diminishes because of polymerization, etc., and a corresponding increase in the methylhexane ratio is observed.

Small amounts of 3-ethylpentane are formed by isomerization of the methylhexanes, but the rate of formation is very low. For example, 3-ethylpentane was not detected after 4 hr. treatment with 96.4% acid, and less than 1.0% was present after 28 hr. with 98.7% acid.

(8) H. C. Brown, and M. D. Taylor, *J. Am. Chem. Soc.*, **69**, 1332 (1947).