at the C–O bond of a β-hydroxy group. Finally, evidence is presented which shows that isomerization of the erythritols takes place at 165° over a copper–chromium oxide catalyst. The interrelationships of these reactions are briefly discussed and some of the pioneering concepts of Adkins and his co-workers are confirmed and extended.

Rahway, New Jersey Received November 26, 1948

[Contribution from the Chemical Laboratory of Northwestern University]

The Action of Sulfuric Acid, Ethanesulfonic Acid and Chlorosulfonic Acid on Aliphatic Hydrocarbons

By George S. Gordon III[1] and Robert L. Burwell, Jr.

In a recent investigation of the action of sulfuric acid on (+)3-methylheptane,[2] it was found that sulfuric acid-d_2 caused hydrogen exchange, racemization and isomerization to occur at rates strongly influenced by the water content of the acid. With 80 mole per cent. sulfuric acid, the reactions proceeded at convenient rates at 60° with relative rates of 30:2:1. The rate of exchange of 2-methylheptane was about the same as that of 3-methylheptane but that of octane was over a hundred-fold slower.

It was proposed that these reactions involve an intermediate formed by the oxidation of the hydrocarbon, and that this intermediate acts as a chain initiator for a reaction of a chain length of about twenty.

It appeared desirable to extend these experiments to hydrocarbons of lower and higher molecular weight, to study the effect of the addition of materials which might be presumed to act as initiators and to investigate the action of some other acids. The results of these experiments are reported in the present paper.

Experimental

Materials.—(+)4-Methyl-2-hexanol (the diastereoisomeric pair in unknown ratio) was prepared from (+)2-methyl-1-bromobutane[2] and acetaldehyde by the Grignard reaction and distilled in a 25-plate Stedman column to give a 77% yield in a 0.8-mole run, $[\alpha]^{25}\mathrm{D}$ +11.7°, b. p. 150–151°. The bromide, d^{25}_{4} 1.2173 and $n^{20}\mathrm{D}$ 1.4452, had been prepared as previously described[2] from protracted action of phosphorus tribromide on active amyl alcohol and had not been distilled. Its rotation, $[\alpha]^{25}\mathrm{D}$ +3.89° was less than that of the probable maximum value of 4.05° consistent with the work of Marckwald[3] and Brauns[4] and confirmed in this research on a fractionated sample prepared by the action of phosphorus tribromide in the conventional way.

(+)3-Methylhexane was prepared from (+)4-methyl-2-hexanol in two ways. The latter compound was converted into the bromide by the method previously described[2] in 96% yield. This (0.46 mole) was converted to the Grignard reagent, hydrolyzed with 20% sulfuric acid, washed with concentrated sulfuric acid and fractionated to give a 30% yield based on the carbinol, $[\alpha]^{25}\mathrm{D}$ +9.10°. In the second method, the alcohol was dehydrated by passage over activated alumina (Puralox, Harshaw Chemical Company) at 450° at a rate of one cc. of alcohol per cc. of catalyst per hour. The resulting heptylene ($\alpha^{26}\mathrm{D}$ +13.70°, 1 dm.) was hydrogenated in methanol with the Adams platinum oxide catalyst to give an over-all yield of 55%, $[\alpha]^{25}\mathrm{D}$ +9.12°; d^{25}_{4} 0.6824 and $n^{20}\mathrm{D}$ 1.3889.[5]

(+)3-Methylhendecane was made via the Grignard reaction between (+)2-methyl-1-bromobutane and heptanal, dehydration of the resulting carbinol and hydrogenation of the resulting dodecylene by the methods described above, $[\alpha]^{25}\mathrm{D}$ +7.45°, $n^{20}\mathrm{D}$ 1.4229.

2,2-Dimethylhexane was obtained from the American Petroleum Institute Research Project 45 at The Ohio State University through the kindness of Dr. Kenneth Greenlee. Its purity was estimated as 99.58 ± 0.13% by A. P. I. project 6 at the National Bureau of Standards.

2-Methylpentane was prepared by hydrogenating, with the platinum oxide catalyst, 2-methylpentadiene from the Commercial Solvents Corporation. After distillation (b. p. 59.8–60.0°, 750 mm.), this showed $n^{20}\mathrm{D}$ 1.3717.

The preparation of (+)3-methylheptane, *n*-octane and sulfuric acid-d_2 has been described.[2] A sample of triply distilled ethanesulfonic acid from the Standard Oil Company (Indiana) was mixed with 99.8% deuterium oxide and dehydrated by warming under vacuum. Upon analysis of the water produced by neutralization with sodium hydroxide, 45.8% of the acidic hydrogen was found to have been replaced by deuterium. The ethanesulfonic acid was free from sulfuric acid to the degree detectable by barium chloride.

Vacuum distillation of a solution of sulfuric acid whose deuterium content was 25 mole per cent. and chlorosulfonic acid gave chlorosulfonic acid of 11.5% deuterium content.

Apparatus and Procedure.—The former apparatus[2] was employed. The reactants were stirred together at a fixed temperature under an atmosphere of nitrogen. The hydrocarbon layer was then removed by distillation under vacuum at low temperatures for examination in the polarimeter and infrared spectrograph and for combustion to permit deuterium analysis. However, where the hydrocarbon had too low a vapor pressure (3-methylhendecane) or the acid had too high a vapor pressure (chlorosulfonic acid), the products were pipetted directly from the reaction vessel to a graduated tube and were immediately washed to remove acidic impurities. Save as otherwise indicated, 4.2 cc. of acid and 3.0 cc. of hydrocarbon were used. Stirring corresponding to that of the higher speed of the previous paper[2] was used save as otherwise specified.

Experimental Results

The former experiments with (+)3-methylheptane and sulfuric acid have been extended to an investigation of the effects of the addition of small amounts of butylene and of sodium *s*-butyl sulfate. A temperature of 60° and 95.3% sulfuric acid was employed. Results are given in Table I.

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[1] Standard Oil Company (Indiana) Fellow, 1946–1948. Present address, General Electric Company, Pittsfield, Massachusetts.

[2] Burwell and Gordon, This Journal, **70**, 3128 (1948).

[3] Marckwald and Nolda, *Ber.*, **42**, 1583 (1909).

[4] Brauns, *J. Research Nat. Bur. Standards*, **18**, 315 (1937).

[5] American Petroleum Institute, Research Project 44 at the National Bureau of Standards, Selected Values of Properties of Hydrocarbons, Table 2a (part 2) gives $n^{20}\mathrm{D}$ 1.38865 and d^{25}_{4} 0.6828.

TABLE I

EFFECT OF CERTAIN ADDITIVES ON RACEMIZATION OF (+)3-METHYLHEPTANE BY SULFURIC ACID

Time, hr.	Loss in rotation $\Delta\alpha/\alpha$.	Additive
2.2	0.156	None
0.5	.077	None
2.2	.171	0.10 g. $NaSO_4C_4H_9$
0.5	.106	0.26 g. $NaSO_4C_4H_9$
2.2	.359	.384 g. isobutylene
0.5	.244	.333 g. 2-butene
0.5	.182	.081 g. 2-butene

The Action of Sulfuric Acid and of Ethanesulfonic Acid on Several Hydrocarbons.—Results with these acids are given in Table II. In the last column, $q = a/b + 1$, where a is the number of gram atoms of hydrogen in the quantity of hydrocarbon employed and b equals that in the acid; and X_{alkane} represents the fraction of the hydrogen atoms in the hydrocarbon replaced by deuterium. Recoveries were within a few per cent. of quantitative save with the dodecane where the technique prevented an accurate estimation.

TABLE II

THE ACTION OF SULFURIC ACID AND OF ETHANESULFONIC ACID ON SEVERAL HYDROCARBONS

Acid	Temp., °C.	Time, hr.	Loss in rotation, $\Delta a/a_0$	X_{alkane}	$\frac{\log(1-qX)}{q\log\alpha/\alpha_0}$
		(+)3-Methylhexane			
95.3% H_2SO_4	60	25.0	0.737	....	..
95.0% D_2SO_4	60	5.0	.230	0.180	0.95
	60	6.0	.220	.170	.92
	60	50[b]	.994	.847	..
D_2SO_4–H_2SO_4[a]	55	5.5	.254	....	..
	44.5	5.0	.149	.129	.99
	66	1.8	.168	....	..
		(+)3-Methylhendecane			
D_2SO_4–H_2SO_4[a]	60	14.0	.014	.0175	1.2
	60	17.5	.023	.0272	1.2
		2-Methylpentane			
D_2SO_4–H_2SO_4[a]	55	13.5	...	.357[c]	..
	55	5.0[e]	...	.352[d]	..
	44.5	5.6	...	.251[e]	..
		2,2-Dimethylhexane			
D_2SO_4–H_2SO_4[a]	60	24	..	.0004	..
		n-Octane			
95.6% D_2SO_4	60	27.5	..	.0027	..
		(+)3-Methylheptane			
$C_2H_5SO_3H$	60	5.5	<.001	....	..
	106	15	.053	....	..
$C_2H_5SO_3D$	106	50	.080	.0572	.87
	102	25	.045	.0404	1.01

[a] 20.2 mole % of water in this acid, H:D is 3:1. The value of X_{alkane} was corrected to the value which would have obtained for pure D_2SO_4. 20.2 mole % D_2O in D_2SO_4 would correspond to 95.2% acid. [b] Acid replaced four times during the run. [c,d,e] % of equilibrium exchange 96, 89 and 68% computed on the assumption that the equilibrium constant for the exchange is unity.

Infrared absorption spectroscopy of the product of the first listed run with (+)3-methylhexane was consistent with the presence of 25 to 30% of 2-methylhexane and negligible quantities of other isomerization products. The spectra of 2- and 3-methylhexanes are much better suited to this analysis than the corresponding pair, 2- and 3-methylheptane.[2] The product of the second listed run with 2-methylpentane seemed to contain 20 to 30% of 3-methylpentane. On the other hand, examination of 2,2-dimethylhexane which had been treated with 95.0% sulfuric acid for forty hours showed no detectable isomerization.

In runs with ethanesulfonic acid at the higher temperatures, only a slow and probably not very uniform stirring was possible.

The action of 4.2 cc. of the H_2SO_4–D_2SO_4 mixture on 2.7 cc. of *n*-octane containing 5.5% of (+)3-methylheptane for a contact time of twenty-four hours at 60° resulted in a 10% drop in rotation and 0.0084 mole fraction of deuterium in the hydrogens of the hydrocarbon after correction to pure D_2SO_4.

The Action of Chlorosulfonic Acid on Several Hydrocarbons.—With 3-methylheptane at 60°, reaction was violent and no volatile hydrocarbon was recovered; at 0° the acid layer was slightly discolored, considerable sulfur dioxide was evolved but there was no larger loss of hydrocarbon. At −78° the reaction mixture could be stirred only rather slowly because of its viscosity. Results are given in Table III.

TABLE III

THE ACTION OF CHLOROSULFONIC ACID ON (+)3-METHYLHEPTANE

Acid, cc.	Alkane, cc.	Temp., °C.	Time, hr.	Loss in rotation	X_{alkane}	$\frac{\log(1-qX)}{q\log\alpha/\alpha_0}$
2.1[a]	6.0	0	0.33	1.000	.....	....
2.1[a]	6.0	−20	.17	1.000	.....	....
2.1[a]	6.0	−78	.25	.039	.....	....
2.1[b]	3.0	0	.08	1.000	0.0895[c]	
2.1[b]	3.0	−78	1.0	.541	.0115	0.0192
2.1[b]	4.0	−78	1.5	.430	.0099	.0156
2.1[b]	4.0	−50	0.17	.112	.0038	.031

[a] HSO_3Cl. [b] DSO_3Cl. [c] 99% of equilibrium exchange assuming constant for this equal unity.

A sample of (+)3-methylheptane which had been 41.2% racemized in 1.75 hours at −78° exhibited an infrared absorption identical with the starting material. The sample which had been completely racemized at 0° appeared to have been isomerized to the 2-isomer to an extent of about 50%.

At 0° the action of chlorosulfonic acid on *n*-octane and on 2,2-dimethylhexane was slight. In twenty minutes at 30° with *n*-octane, much sulfur dioxide was evolved, the acid layer became black and about 40% of the hydrocarbon layer disappeared. In all cases the infrared absorption spectra of the recovered hydrocarbons were unchanged.

Mixtures of Chlorosulfonic and Sulfuric Acids.—Two experiments on mixtures of chlorosulfonic acid and sulfuric acid were run with 4.2 cc. acid mixture, 4.0 cc. (+)3-methylheptane, a temperature of 1°, and fifteen minutes reaction time. With a mixture containing 32% chlorosulfonic acid and 68% sulfuric acid, a loss in rotation of 0.101 was found. With a solution of 50% of each, in which 17.6% of the total acidic hydrogen was deuterium, the loss in rotation was 0.401, the fraction of the hydrocarbon hydrogen atoms exchanged after correcting to 100% deuterium, X_{alkane} was 0.124 and correspondingly $\log(1 - qX)/q \log \alpha/\alpha_0$ was 0.381. The infrared absorption spectrum of this product in the region 8.5 to 14 μ indicated 15–20% isomerization to 2-methylheptane.

Discussion

Relative Rate of Exchange and Racemization of Various Hydrocarbons.—From the data of this and the preceding paper[2] one can estimate the relative rates of exchange of seven hydrocarbons. Results are given in Table IV. Owing to the variations inherent in heterogeneous reactions and to slight variations in experimental conditions, not too much emphasis should be given to the precise figures entered.

TABLE IV

RELATIVE RATES OF EXCHANGE OF SEVERAL HYDROCARBONS WITH 95% SULFURIC ACID-d_2

Hydrocarbon	Relative rate
2-Methylpentane	4200
3-Methylhexane	2100
2-Methylheptane	1200
3-Methylheptane	800
3-Methylhendecane	50
n-Octane	7
2,2-Dimethylhexane	1

The 2,2-dimethylhexane contained 0.4% impurity. The *n*-octane exhibited the proper boiling point and infrared spectrum but this would still permit a few per cent. of impurity. Thus the exchange actually exhibited by these two hydrocarbons may in part be due to impurity and the listed rates are to be taken as upper limits only and even their order might be wrong. The contrast between the behavior of these and the other hydrocarbons is, however, considerable. Further, with these two hydrocarbons, the acid layer remained colorless and no sulfur dioxide was evolved.

With the singly branched chain hydrocarbons, the rates of exchange decrease with chain length and strikingly between C_8 and C_{12}. Contrariwise, the degree of coloring of the acid layer increases with chain length, being unobservable with 2-methylpentane, slight with 3-methylhexane, stronger with 3-methylheptane, and very strong with 3-methylhendecane. Sulfur dioxide formation is also less with the lowest molecular weight hydrocarbon.

Ingold, Raisin and Wilson[6] shook heavy sulfuric acid (77 mole per cent. acid or about the same strength as the acid used in this research) with several hydrocarbons for about two weeks at room temperature. They reported the following number of hydrogen atoms exchanged: *n*-hexane, 1.82; *n*-heptane, 0.06; cyclohexane, 0.02; and methylcyclohexane, 5.43. Considering their result with *n*-heptane and the present result with *n*-octane, one must suspect that the *n*-hexane was a petroleum fraction containing easily exchangeable impurities.

We have proposed[2] that the racemization–exchange reaction of (+)3-methylheptane in the presence of sulfuric acid occurs by the following sequence: (1) oxidation of the hydrocarbon at the chain branch to form an olefin or its equivalent; (2) exchange between the hydrogen atoms of the olefin and those of the sulfuric acid; and (3) hydrogen transfer between the olefin and an unreacted hydrocarbon molecule. The chain then continues with a chain length of 10 to 20.

The results of this investigation on the similar reaction with (+)3-methylhexane and (+)3-methylhendecane are consistent with this mechanism. The values of the function $\log (1 - qX)/q \log \alpha/\alpha_0$ are consistent with the view that nearly all of the hydrogen atoms of each molecule racemized are exchanged. The rate of racemization falls with increasing molecular weight to the same degree as that of exchange. Owing to the small extent of the observed reactions with (+)3-methylhendecane, the precision in the value of the function $\log (1 - qX)/q \log \alpha/\alpha_0$ is low.

The chain ending processes for the proposed mechanism would be polymerization and possibly alkylation. The much lower rates of reaction of 3-methylhendecane may be occasioned by intermolecular alkylation in the chain carrier. It would also appear probable that the slower rate of reaction of the higher molecular weight hydrocarbons is connected with the greater degree of acid coloring and sulfur dioxide formation.

The low rates of reaction of *n*-octane and 2,2-dimethylhexane[7] are also consistent with the proposed mechanism since the initial oxidation of these molecules is much more difficult. Furthermore, the reaction of an isoparaffin does not sensitize that of *n*-octane. This follows from the experiment in which the action of heavy sulfuric acid on a solution containing 5.5% (+)3-methylheptane in *n*-octane resulted in a 10% loss in rotation. Had all the hydrogens in the racemized molecules been exchanged, the fraction of all hydrocarbon hydrogens exchanged would be 0.0055. The observed fraction was 0.0084. The difference between the two, 0.003, is just about the frac-

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(6) Ingold, Raisin and Wilson, *J. Chem. Soc.*, 1643 (1936).

(7) Caesar and Francis, *Ind. Eng. Chem.*, **33**, 1426 (1941), report that in two and one-half hours of agitation with 97% sulfuric acid at 20°, 2,2-dimethylbutane is 50% decomposed. Birch and Dunstan, *Trans. Faraday Soc.*, **35**, 1013 (1939), report that concentrated sulfuric acid is without effect. It is hard to understand the result of Caesar and Francis save on the basis that the reaction is enormously sensitive to the concentration of the sulfuric acid.

tion exchange of *n*-octane alone under the same conditions. These results, although necessarily of low precision, are consistent with the view that a large fraction of the hydrogen atoms of each molecule racemized are exchanged.

Effect of Added Olefin on the Rate of Racemization.—Since an olefin or its equivalent is assumed to be the chain carrier, it appeared necessary to study the effect of addition of foreign olefin. As the results of Table I demonstrate, the addition of either 2-butene or of isobutylene definitely augments the rate of the racemization reaction and to a greater extent than could be accounted for by mere dilution of the reaction product by butylene polymer. The results are, thus, consistent with the proposed reaction sequence.

Morton and Richards,[8] finding the effect of 1-butanol on the action of 98.5% sulfuric acid on 2,2,4- and 2,2,3-trimethylpentane at 10° to be slight, concluded that olefins played no part in the reaction. They mixed 1-butanol and 100% sulfuric acid and presumed the product to be 98.5% acid and *n*-butene, but there was no evidence that this procedure resulted in the presence of olefin in the acid layer at the time of reaction. 1-Butanol and *n*-butyl hydrogen sulfate are much more stable *in re* dehydration than their secondary equivalents.

Ethanesulfonic Acid.—In its action on (+)3-methylheptane, ethanesulfonic acid-*d* resembles sulfuric acid, in general. However, temperatures 70 to 80° higher than those with sulfuric acid would apparently be required for the attainment of similar rates of racemization and exchange. The value of $\log (1 - qX)/q \log \alpha/\alpha_0$ is close to unity and accordingly substantially every hydrogen atom is exchanged on each molecule racemized. This similarity to the behavior of sulfuric acid would suggest that a rather similar mechanism was involved in both cases. At above 100°, sulfur dioxide is formed in very small but finite quantities, in any case at a rate far below that with sulfuric acid. This greatly reduced rate of oxidation by ethanesulfonic acid may in part account for its reduced reactivity as compared with sulfuric acid, but other steps in the proposed reaction sequence might also proceed more slowly since Proell and Adams[9] report that alkanesulfonic acids are active in polymerizing olefins only at temperatures above 60° and that below that temperature, stable esters are formed by the addition of the acid to the olefin.

Chlorosulfonic Acid.—The reaction between chlorosulfonic acid and (+)3-methylheptane is a most unusual one since it constitutes a specific reaction of an aliphatic hydrocarbon proceeding rather rapidly at −78°, an apparently unprecedentedly low temperature for a specific reaction of a paraffin. At 0°, the hydrocarbon is completely racemized in less than five minutes.

The ratio of racemization to exchange presents a striking contrast to that observed in using sulfuric acid. At −78°, the value of $\log (1 - qX)/q \log \alpha/\alpha_0$ is less than 0.02 and about three molecules are racemized for every single hydrogen atom exchanged.

That violent attack on 3-methylheptane occurs at 60° should, perhaps, have been expected since chlorosulfonic acid has been shown to remove branched chain hydrocarbons from straight chain ones.[10] At 0°, chlorosulfonic acid does not attack *n*-octane at any but a very slow rate. At 30°, however, considerable reaction occurs but all oxidation products are absorbed into the acid layer (and from which dilution releases them in the form of an oil).[11] Recovered *n*-octane is unchanged. Lower molecular weight normal hydrocarbons must be attacked more slowly since Grün and Limpächer,[12] for example, purified petroleum ether by warming it with chlorosulfonic acid for protracted periods.

2,2-Dimethylhexane is likewise unaffected by the action of chlorosulfonic acid at 0°. Thus treatment with chlorosulfonic acid should constitute an effective way of removing many isomers from neoalkanes.

In view of the high ratio of rate of racemization to rate of exchange in the action of chlorosulfonic acid on (+)3-methylheptane at low temperatures, it is difficult to see how the reaction can proceed save by a chain reaction initiated by chlorosulfonic acid (and involving exchange at initiation or termination) but propagated in the hydrocarbon layer without interposition of the acid. For example, a tertiary carbonium ion might be formed by oxidation at the acid–hydrocarbon interface and propagate in the hydrocarbon layer by abstraction of a hydrogen atom from the tertiary position of another hydrocarbon. The hydrogen transfer step in the proposed reaction sequence for sulfuric acid probably also occurs by a similar "hydride ion" transfer between isoparaffin and carbonium ion. Such a hydrogen transfer reaction has been proposed by Bartlett, Condon and Schneider[13] as a step in the reaction between a tertiary halide, an isoalkane and aluminum bromide. This reaction, incidentally, proceeds so fast at room temperatures, that it is probably of about the same order of rapidity as the racemization by chlorosulfonic acid reported in the present paper.

The unusual features of the chlorosulfonic acid–hydrocarbon reaction suggest that the catalytic activity of chlorosulfonic acid ought to be

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(8) Morton and Richards, *J. Inst. Petroleum*, **34**, 133 (1948).

(9) Proell and Adams, Meeting of the American Chemical Society, Chicago, Ill., April 22, 1948.

(10) Shepard, Henne and Midgely, THIS JOURNAL, **53**, 1948 (1931).

(11) Whitely (U. S. Patent 2,344,890) reports, however, that chlorosulfonic acid plus boron trifluoride will catalyze the isomerization of straight chain hydrocarbons at 75-200°F.

(12) Grün and Limpächer, *Ber.*, **60B**, 260 (1927).

(13) Bartlett, Condon and Schneider, THIS JOURNAL, **66**, 1531 (1944).

thoroughly studied particularly in its possible behavior as a general Friedel–Crafts catalyst.

Bradley[14] has reported that chlorosulfonic acid will catalyze the alkylation of olefins by isoparaffins at temperatures below −20°. In view of the high reactivity of the chlorosulfonic acid–isoparaffin system, the mechanism of this alkylation reaction could differ, at least in part, from that catalyzed by sulfuric acid.[2]

Mixtures of sulfuric and chlorosulfonic acid exhibit reactivity and ratio of rates of racemization and exchange intermediate between those of the two components. This suggests that the reaction sequences with sulfuric acid and with chlorosulfonic acid may not be completely antithetical; that there may be steps common to both sequences; and that the changing relative rate of exchange may involve changes in the degree of certain intermediate steps only.

Slotterbeck[15] has reported the use of mixtures containing small amounts (1–10%) of chlorosulfonic acid in sulfuric acid as catalysts for the alkylation of olefins by isoparaffins. From the data given, there is apparently no great increase in rate of reaction over that with sulfuric acid alone. Better yields are claimed, however.

Isomerization.—Sulfuric acid seems to be a specific catalyst for the shifting of a methyl group among the secondary positions of a hydrocarbon chain. The ratio of rates of isomerization and exchange seems to be about the same for 2-methylpentane, 3-methylhexane and 3-methylheptane. In the case of the latter two, the rate of racemization is two to three times greater than that of isomerization. No sensitive method for the detection of more highly branched isomers was available but it would seem that the rate of formation of such compounds was at least an order of magnitude less than that of a simple methyl shift.

At 0°, treatment with chlorosulfonic acid for twenty minutes results in near equilibrium with respect to the methyl shift and no detectable production of more highly branched isomers. No estimate could be made as to the ratio of the rate of this to that of racemization. At −78°, however, the rate of racemization is at least an order of magnitude faster, save for the unlikely contingency that at that temperature the position of equilibrium be strongly in favor of the 3-isomer.

Mixtures of sulfuric acid and chlorosulfonic acid at 0° result in about the same ratio of racemization to isomerization as observed with sulfuric acid alone at 60°.

Aluminum Halides.—It is of interest to compare the exchange reactions of this paper with those occurring between hydrocarbons and the deuterium bromide–aluminum bromide catalyst reported by Pines and Wackher.[16] At room temperatures in the total absence of olefins, exchange with both *n*-butane and isobutane is very slow, of the same order as that of our results with sulfuric acid and 2,2-dimethylhexane. In the presence of catalytic traces of butylenes, exchange is rapid and is accompanied by isomerization. The data cannot be analyzed by the methods employed in the first paper of this series[2] because the value of q would be 100 which would too seriously impair sensitivity. However, it can be concluded that at least several atoms of hydrogen must be exchanged for each molecule isomerized. It is difficult to interpret the results of Pines and Wackher[16] with $DOAlBr_2$ since this material is a solid and the low exchange–isomerization ratio could have resulted from the inability of any but the skin of these particles to exchange.

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Summary

Sulfuric acid-d_2 acting on (+)3-methylhexane causes exchange and racemization. The behavior of (+)3-methylhendecane is similar but the rates are much slower. In both cases, substantially all hydrogen atoms are exchanged for each molecule racemized.

The relative rates of exchange with sulfuric acid-d_2 of 2-methylpentane, 3-methylhexane, 2-methylheptane, 3-methylheptane, 3-methylhendecane, *n*-octane and 2,2-dimethylhexane decrease in that order with an over-all range of about 4000 to 1. The last two are particularly inert.

Isomerization involving a methyl shift along the chain occurs with 2-methylpentane, 3-methylhexane and 3-methylheptane to about the same relative extent and at a rate much less than that of exchange.

Ethanesulfonic acid acts very much like sulfuric acid but a temperature about 75° higher is necessary to attain similar rates.

Chlorosulfonic acid racemizes (+)3-methylheptane at −78° with very little isomerization and with about one hydrogen atom exchanged for every three molecules racemized. At 0°, its action on *n*-octane and 2,2-dimethylhexane is very slight.

Mixtures of chlorosulfonic acid and sulfuric acid behave in an intermediate fashion.

Possible reaction sequences are considered.

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[14] Bradley, U. S. Patent 2,255,610; see also Vesterdal, U. S. Patent 2,282,505.

[15] Slotterbeck, U. S. Patent 2,425,472.

[16] Pines and Wackher, THIS JOURNAL, **68**, 2518 (1946), corrected, *ibid.*, **69**, 3153 (1947). Dr. Pines has kindly informed me that the entries, "Atom %D in H_2O of combustion," in Tables I and II should also be divided by 2.