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Summary

It has been proposed that naturally occurring naphthenic acids may be degradation products of sterols.

Irradiation of a naphthenic acid by alpha particles and deuterons has led to its transformation into a naphthenic constituent of crude oils.

It has been demonstrated that cyclohexane rings, and presumably the more stable cyclopentane rings, are not opened as a result of alpha or deuteron bombardment.

The mechanism by which cyclohexanecarboxylic acid was transformed into cyclohexane and cyclohexene is as yet unknown. The transformation may have taken place through any one of a number of processes as (1) simultaneous decarboxylation and dehydrogenation to cyclohexene, with subsequent hydrogenation of part of this compound to form the saturated hydrocarbon; (2) decarboxylation to cyclohexane followed by partial dehydrogenation to cyclohexene; (3) preliminary bimolecular reduction to intermediate dicyclohexyl ketone with subsequent conversion of this compound into hydrocarbons.

Work now in progress on the bombardment of benzoic acid and proposed for the bombardment of oleic acid may clarify the question of reaction mechanism depending upon whether or not hydrogenation of double bonds can be shown to take place.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Isomerization of Alkanes. III.¹ The Water-Aluminum Halide Reaction and Isomerization of *n*-Butane with the Reaction Product

BY R. C. WACKHER AND HERMAN PINES

In preceding papers of this series^{1,2} it was shown that the isomerization of alkanes in the presence of aluminum bromide or aluminum chloride can be greatly influenced by "impurities" which might be present in the reagents as such or introduced through an improper experimental technique. Thus, it was found that under certain conditions, aluminum bromide-hydrogen bromide or aluminum chloride-hydrogen chloride does not cause the isomerization of *n*-butane to isobutane unless traces of olefins are present. Similarly, it was found that aluminum bromide or aluminum chloride can catalyze isomerization of *n*-butane even in the absence of olefins and hydrogen bromide if the reaction is carried out in the presence of traces of oxygen; the amount of oxygen in the form of air necessary to promote the isomerization being less than one mole per ten thousand moles of hydrocarbon present.

The present paper reports results on the effect of a third possible impurity, water, on the isomerization of *n*-butane, using aluminum chloride and aluminum bromide. We have found, in this investigation, some evidence of a new series of compounds formed by the reaction of aluminum chloride or aluminum bromide and water, and have produced in this reaction an isomerization catalyst for *n*-butane which does not require added hydrogen halide promoter and which pro-

duces only very small amounts of hydrogen halide during the isomerization reaction.

In order to investigate the role of water upon isomerization, it was necessary first to determine the effect of water upon the aluminum halides and then to investigate the effect of the compounds resulting from such an action upon the isomerization of *n*-butane.

The effect of water upon the isomerization of *n*-butane, using aluminum bromide or aluminum chloride catalyst, was studied by two methods. 1. Aluminum bromide or aluminum chloride was treated with various amounts of water, the mixture was heated, and any liberated hydrogen chloride or hydrogen bromide was pumped off. The resulting product, freed of non-combined hydrogen halide, was then used as a catalyst for isomerization of *n*-butane. 2. Aluminum halide, *n*-butane and water were mixed.

Aluminum Bromide-Water.—Preliminary exploratory experiments gave indications that possibly the aluminum bromide-water reaction, under certain conditions at least, was not the simple production of aluminum hydroxide and hydrogen bromide generally indicated. For example, when water was added to aluminum bromide at liquid nitrogen temperature and warmed slowly to room temperature, very little hydrogen bromide was generated. Upon further heating in a water-bath, the evolution of hydrogen bromide was still slow up to 75°, at which point the reaction was very rapid, with melting of the aluminum

(1) For Paper II of this series see H. Pines and R. C. Wackher, *THIS JOURNAL*, **68**, 595 (1946).

(2) H. Pines and R. C. Wackher, *ibid.*, **68**, 599 (1946).

TABLE I

REACTION OF ALUMINUM BROMIDE WITH WATER, AND ISOMERIZATION OF *n*-BUTANE IN THE PRESENCE OF THE RESULTING REACTION PRODUCT

Part A								
Experiment no.	1	2	3	4	5	6	7	
Reaction time	Hours at 25°	70	18	24	45	20	112	47
	Hours at 100°	0.75	1.25	1.50	1.25	1.50	0.50	0.50
Charge	AlBr ₃ , moles	0.00349	0.01026	0.01027	0.0133	0.0121	0.01170	0.01177
	H ₂ O, moles	0.00856	0.02060	0.03073	0.0532	0.0727	0.04672	0.07040
	Moles H ₂ O:mole AlBr ₃	1.01	2.01	2.99	4.01	6.00	3.99	6.00
HBr generated	Moles	0.00932	0.01009	0.00877	0.00914	0.0002	0.00780	0.0002
	Moles/mole AlBr ₃ reacted	1.25	1.06	0.85	0.69	0.017	0.67	0.017
Unreacted AlBr ₃ , moles	0.00103	0.00071	0	0	0	0	0	
Unreacted H ₂ O, moles	0	0	0	0	0.00078	0	0.00061	
Part B								
Isomerization of <i>n</i> -Butane in the Presence of the Catalyst Described in Part A								
Reaction time, hours	20					15	12	
Reaction temp., °C.	25.0					80	80	
<i>n</i> -Butane charged, moles	0.0935	0.1108	0.1105	0.1428	0.1308	0.1256	0.1266	
HBr generated, moles	0.000066	0.00035	0.00037	0.00013	0.000013	0.00275	0.000012	
HBr generated, moles/mole AlBr ₃ reacted in Part A	0.01	0.03	0.04	0.01	0	0.23	0	
Analysis of hydrocarbon product, mole %	Isobutane	18.7	30.9	16.6	2.7	0.0	62.8	0
	<i>n</i> -Butane	81.3	69.0	82.6	96.0	99.9	35.4	100
	Pentanes and higher	0	0.1	0.8	1.3	0.1	1.8	0

bromide to a glassy substance, very viscous at 100°, and solid at room temperature. Additional heating in a boiling water-bath resulted in only a very slow evolution of hydrogen bromide.

It was found that the amount of hydrogen bromide liberated from the action of water upon aluminum bromide depended upon the molal ratio of water to aluminum bromide^{2a} used. With the increase of the ratio of the water to aluminum bromide, the amount of hydrogen bromide liberated decreased. The maximum, 1.25 moles of hydrogen bromide produced per mole of aluminum bromide reacted, was formed when the molal ratio of aluminum bromide to water was one. When the water-aluminum bromide ratio was two, three and four, the respective amounts of hydrogen bromide produced were 1.1, 0.8, and 0.7 (Table I, Part A). By using six moles of water per mole of aluminum bromide, aluminum bromide hexahydrate is formed and therefore no hydrogen bromide evolved.

The complex, resulting from the action of water on aluminum bromide and freed from any non-combined hydrogen bromide, was used as a catalyst for the isomerization of *n*-butane. The experimental data are given in Table I, Part B. It was found that by making contact between *n*-butane at 25° for twenty hours and the catalysts obtained from the action of water on aluminum bromide, isomerization of *n*-butane occurred when the molal ratio of water-aluminum bromide was one, two or three. When the ratio was four,

slight isomerization occurred at 25° but appreciably more occurred at 80°, while with a ratio of six, *n*-butane did not isomerize at all. The most active catalyst was the one prepared from the action of two moles of water on one mole of aluminum bromide. In none of the isomerization reactions was there any appreciable evolution of hydrogen bromide noticed. The results obtained demonstrate that the isomerizing catalyst formed by the action of water on aluminum bromide is not equivalent to an aluminum bromide-hydrogen bromide catalyst.

The activity of the isomerization catalyst prepared by the action of one mole of water on one mole of aluminum bromide does not deteriorate with use. This is substantiated by the results summarized in Table II. The increase in activity of the catalyst, as shown by 23.2% of isobutane produced in Run 1 and 35.6% in Run 2, might be attributed to a more intimate contact of the reactants since the catalyst becomes more finely divided through use.

It was of interest to determine the effect of water upon the isomerization of *n*-butane that contains aluminum bromide. These experiments are not comparable with those given in Table I, as the hydrogen bromide formed was not removed from the reaction zone. It was found that the aluminum bromide promoted by water, in spite of the free hydrogen bromide present, is a less active catalyst (Table III) than the corresponding catalyst described in Table I. In this case, it was again shown that the addition of six moles of water per mole of aluminum bromide has no

(2a) Within the scope of the paper, a mole of aluminum bromide or aluminum chloride is represented as AlX₃.

TABLE II

REPEATED ISOMERIZATION OF *n*-BUTANE IN THE PRESENCE OF A CATALYST PREPARED FROM THE REACTION OF ALUMINUM BROMIDE WITH WATER

Part A			
Experiment no.			8
Reaction time	Hours at 25°		0
	Hours at 100°		1.25
Charge	AlBr ₃ , moles	0.01294	
	H ₂ O, moles	0.01294	
	Moles H ₂ O:AlBr ₃	1.00	
HBr generated	Moles	0.01495	
	Moles/mole AlBr ₃ reacted	1.20	
Unreacted AlBr ₃ , moles		0.00046	
Unreacted H ₂ O, moles		0	

Part B

Isomerization of <i>n</i> -Butane in the Presence of the Catalyst Described in Part A			
	(1)	(2)	(3)
Reaction time, hrs.	...	20	...
Reaction temp., °C.	...	25.0	...
<i>n</i> -Butane charged, moles	0.1386	0.1389	0.1389
HBr generated, moles	0.00014	0.00014	0.00016
HBr generated, moles/mole AlBr ₃ reacted	0.01	0.01	0.01
Analysis of hydrocarbon product, mole %			
Isobutane	23.2	33.6	35.6
<i>n</i> -Butane	76.7	66.2	64.0
Pentanes and higher	0.1	0.2	0.4

catalytic activity upon the isomerization of *n*-butane.

TABLE III

ISOMERIZATION OF *n*-BUTANE IN THE PRESENCE OF ALUMINUM BROMIDE AND WATER

Experiment no.	9	10	11
Reaction time, hours	...	20	...
Reaction temp., °C.	...	25.0	...
Charge			
AlBr ₃ , moles	0.00940	0.00968	0.01069
H ₂ O, moles	0.00942	0.02906	0.06417
<i>n</i> -Butane, moles	0.1012	0.1040	0.1147
Moles H ₂ O: mole AlBr ₃	1.00	3.00	6.00
HBr generated			
Moles	0.00460	0.00465	0.00027
Moles/mole AlBr ₃	0.49	0.48	0.025
Analysis of hydrocarbon product, mole %			
<i>i</i> -Butane	13.2	11.8	1.0
<i>n</i> -Butane	86.6	87.1	98.0
Pentanes and higher	0.2	1.1	1.0

Aluminum Chloride-Water.—The catalysts produced from the action of water on aluminum chloride are less active than those obtained from aluminum bromide. The isomerization experiments using aluminum chloride type catalyst were carried out at 80–100° in sealed reaction tubes placed in a stationary autoclave submerged in an oil-bath. Since no agitation was used, minor variations in catalyst aggregation would have a great effect on the results. These results

are probably less comparable than those obtained with aluminum bromide.

The reaction of aluminum chloride with water is to some extent similar to the one of aluminum bromide, namely, the larger the amount of water added, the smaller is the amount of hydrogen chloride liberated. With a one molal ratio of water to aluminum chloride used, 0.71 mole of hydrogen chloride was formed; when the water-aluminum chloride ratio is increased to two, only 0.29 mole of hydrogen chloride was generated per mole of aluminum chloride reacted (Table IV). This reaction product, free of non-combined hydrogen chloride, caused the isomerization of *n*-butane. Similarly to aluminum bromide, the catalytic activity of the product formed by the action of two moles of water on one mole of aluminum chloride is greater than that obtained from the action of one mole of water.

TABLE IV

REACTION OF ALUMINUM CHLORIDE WITH WATER AND ISOMERIZATION OF *n*-BUTANE IN THE PRESENCE OF THE RESULTING REACTION PRODUCTS

Part A			
Experiment no.	12	13	14
Reaction time	Hours at 25°	460	117
	Hours at 100°	1	4.50
Charge			
AlCl ₃ , moles	0.0116	0.0113	0.0115
H ₂ O, moles	0.0116	0.0113	0.0230
Moles H ₂ O: Mole AlCl ₃	1.00	1.00	2.00
HCl generated			
Moles	0.0082	0.0084	0.0033
Moles/mole AlCl ₃	0.71	0.74	0.29
Unreacted AlCl ₃ , moles	0	0	0
Unreacted H ₂ O, moles	0	0	0

Part B

Isomerization of *n*-Butane in the Presence of the Catalysts Described in Part A

	12	13	14
Reaction time, hours	12	12	12
Reaction temp., °C.	80	100	80
<i>n</i> -Butane charged, moles	0.125	0.124	0.124
HCl generated, moles/mole of AlCl ₃ used in Part A			
	0.24	0.03	0.46
Analysis of hydrocarbon product, mole %			
<i>i</i> -Butane	9.0	42.3	14.7
<i>n</i> -Butane	89.7	56.0	84.5
Pentanes and higher	1.3	1.7	0.8

Isomerization of *n*-butane in the presence of aluminum chloride and water was studied. The hydrocarbon and the water were added to the aluminum chloride and the reagents were heated for twelve hours at 100°. The experimental results, which are summarized in Table V, show that the amount of hydrogen chloride formed and the degree of butane isomerization decrease with the increase of the molal ratio of water to aluminum chloride used. These experiments confirm also the observation made previously that aluminum

chloride to which six moles of water was added, shows no catalytic activity toward isomerization.

TABLE V
ISOMERIZATION OF *n*-BUTANE IN THE PRESENCE OF
ALUMINUM CHLORIDE AND WATER

Experiment no.	15	16	17	18
Reaction time, hours	—————12—————			
Reaction temp., °C.	—————100—————			
Charge				
AlCl ₃	0.0112	0.0113	0.0113	0.0112
H ₂ O	0.0112	0.0339	0.0452	0.0672
<i>n</i> -Butane	0.124	0.124	0.124	0.124
Moles H ₂ O: mole AlCl ₃	1.00	3.00	4.00	6.00
HCl generated				
Moles	0.0057	0.0051	0.0025	0.0014
Moles/mole AlCl ₃	0.51	0.46	0.22	0.12
Unreacted AlCl ₃ , moles	0	0	0	0
Unreacted H ₂ O, moles	0	0	0	0.0008
Analysis of hydrocarbon product, mole %				
<i>i</i> -Butane	35.1	16.8	11.3	0
<i>n</i> -Butane	63.6	81.9	87.8	100
Pentanes and higher	1.3	1.3	0.9	...

Mechanism of Isomerization.—The isomerization catalysts prepared by the action of water on aluminum halide probably consist of complexes which include aluminum halide, hydroxyaluminum halides, hydrogen halide, water, etc. For the sake of simplicity, it is assumed that hydroxyaluminum dihalide, which was formed according to equation 1, is probably one of the isomerization catalysts.



It was of interest to determine whether the halogen or the hydrogen of the hydroxyaluminum dihalide was the active part of the catalyst. If the hydroxy group was responsible for the catalytic activity, then by replacing the hydrogen by deuterium one might reasonably expect an exchange to take place between the hydrogen of the butanes and the deuterium.

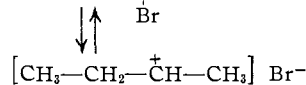
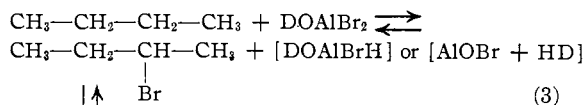
The deuterioaluminum dibromide was produced by the action of deuterium oxide on aluminum bromide.³



It was found that by carrying out the isomerization in the presence of the deuterioaluminum dibromide and under essentially the same experimental conditions as for Expt. 1, Table I, 5.4% of deuterium underwent an exchange reaction although 21% of isomerization of *n*-butane to isobutane occurred.³ The degree of hydrogen-deuterium exchange reaction is not proportional to isomerization; virtually the same percentage of an exchange was noticed in a reaction in which the degree of isomerization of *n*-butane to isobutane was only 3.7%.³ It is fair to conclude

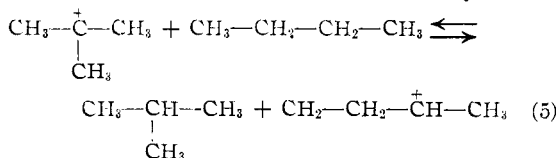
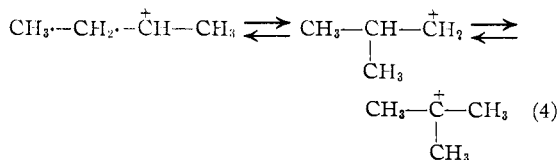
(3) A detailed description of this reaction will be in a subsequent paper of this series.

therefore that the isomerization of *n*-butane by means of hydroxyaluminum dibromide involves the bromine atoms. We believe that the isomerization proceeds through a chain mechanism as postulated in a previous paper.⁴ The chain is probably initiated by an exchange reaction as expressed in equation 3.



This hypothesis will be checked when the analytical tools, which can detect traces of HD, are at our disposal.

The bromide which serves as a source of carbonium ion acts in the presence of the catalyst as a chain starter and needs to be present in small quantity only.



The steps expressed in equations 4 and 5 are the same as described previously.⁴

Experimental

Apparatus.—A complete description of the high-vacuum equipment with reaction vessel and thermostats will be found in previous publications of this series.^{1,2}

Materials.—The sources and methods of purification of the aluminum halides, hydrogen halide and *n*-butane have been previously described by us.^{1,2}

Distilled water used in these experiments.

The only other purification steps used were those of degassing and single distillation stages commonly encountered in high-vacuum work.

Procedure.—The general procedure on the addition of the reagents has been described in previous publications.^{1,2}

In the water-aluminum halide reactions, the water was slowly condensed on the aluminum halide at liquid nitrogen temperature by gradually raising the liquid nitrogen level from near the bottom to the top of the aluminum halide deposited during the condensation. Then with the stock valve closed the tube was allowed to warm slowly to room temperature. After the reaction period at room temperature, all material was recondensed in the tube with liquid nitrogen and then with the tube in Dry Ice and generated hydrogen halide was pumped off, condensed in liquid nitrogen and measured volumetrically. The reaction tube was then sealed off, immersed in cool water and the water then heated slowly to boiling for the reaction period, after which the tube was resealed to the vacuum line and pumped out while being heated with boiling water. Any unreacted aluminum halide sublimed under these

(4) H. S. Bloch, H. Pines and L. Schmerling, *THIS JOURNAL*, **68**, 153 (1946).

conditions and deposited on the cool walls of the outlet tube which was later cut off and weighed. Any unreacted water was condensed along with the generated hydrogen halide in a trap of the fractionating line at liquid nitrogen temperatures and, after separation from the hydrogen halide at Dry Ice temperature, was weighed. *n*-Butane was then added to the reaction tube and the run was made in the usual manner.¹

In those experiments in which *n*-butane was isomerized in the presence of aluminum halide and water, all the reagents were added and the vessel was then slowly warmed to reaction temperature without the intermediate step of reacting the aluminum halide and water and pumping off the generated hydrogen halide.

The apparatus and procedure used in preparing deuterio-aluminum bromide and in determining the deuterium content of the water of combustion of the product in the deuterium transfer experiments will be described in a subsequent paper.³

Summary

The effect of water upon aluminum bromide and

aluminum chloride, employing high-vacuum technique, has been studied.

The amount of hydrogen halide produced by the action of water upon aluminum halide depends upon the molal ratio of water to aluminum halide used.

The isomerization of *n*-butane in the presence of catalysts, produced by the action of water on aluminum halide and freed of non-combined hydrogen halide, has been studied.

The isomerization of *n*-butane in the presence of aluminum bromide or aluminum chloride and water has been investigated.

A mechanism of isomerization of alkanes using a catalyst produced by the action of water on aluminum halide is suggested.

CHICAGO, ILLINOIS

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[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY¹]

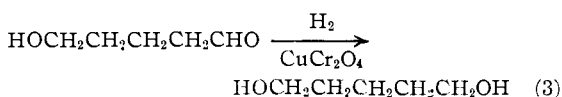
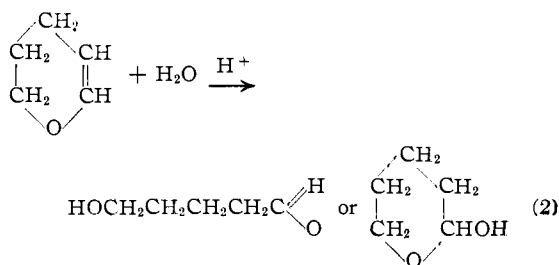
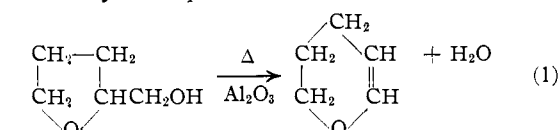
Preparation of Dihydropyran, δ -Hydroxyvaleraldehyde and 1,5-Pentanediol from Tetrahydrofurfuryl Alcohol

BY L. E. SCHNIOPP AND H. H. GELLER

Furfural and its hydrogenation derivatives present many interesting possibilities as starting materials for the preparation of four-, five-, six- and seven-carbon difunctional compounds. Investigations of these possibilities have resulted in the development of an improved method for the synthesis of 1,5-pentanediol. This method, previously investigated by Paul,^{2,3} consists in catalytically converting tetrahydrofurfuryl alcohol to dihydropyran, hydrolysis of the latter to δ -hydroxyvaleraldehyde, and hydrogenation of the aldehyde to the diol. This procedure has an advantage over the hydrogenolysis method of Connor and Adkins,⁴ which produces a mixture of the 1,2- and 1,5-pentanediols, in that the 1,5-diol is the sole product.

Substantial improvements in the yields of dihydropyran and δ -hydroxyvaleraldehyde over those previously reported^{3,5,6} have been accomplished by thorough investigation of the reaction conditions. The catalytic conversion of tetrahydrofurfuryl alcohol over activated alumina has been increased from 65 to 70%^{3,4} up to 85 to 90% and the hydrolysis of dihydropyran to δ -hydroxyvaleraldehyde from 38³ to 78%. The hydrogenation of δ -hydroxyvaleraldehyde to 1,5-pentanediol proceeds almost quantitatively over copper

chromite. By a combination of the best conditions for this three-step process, a 70% yield of 1,5-pentanediol from tetrahydrofurfuryl alcohol has been obtained. These reaction may be illustrated by the equations



A study of the catalytic conversion of tetrahydrofurfuryl alcohol to dihydropyran showed that the main factor in limiting yields and production rates was the highly exothermic reaction which occurred when the alcohol vapors came in contact with the alumina catalyst at temperatures above 300°. The extent of this heat rise was dependent upon the size of the catalyst bed and the feed rate. For example, a feed rate of 5 g./min. to a tube containing 500 cc. of catalyst heated to

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) R. Paul, *Bull. soc. chim.*, [4] **53**, 1489-1495 (1933).

(3) R. Paul, *ibid.*, [5] **1**, 971-980 (1934).

(4) Connor and Adkins, *THIS JOURNAL*, **53**, 1091 (1931).

(5) C. H. Kline and J. Turkevich, *ibid.*, **67**, 498 (1945).

(6) R. L. Sawyer and D. W. Andrus, "Organic Syntheses," **23**, 25 (1943).