N,N-dimethylhomopiperonylamine hydrochloride, which separated was recrystallized twice from an alcohol–ether mixture, m. p. 203–204°.

Anal. Calcd. for $C_{11}H_{16}ClNO_2$: C, 57.52; H, 7.02; N, 6.10. Found: C, 57.88; H, 7.31; N, 5.96.

B. A solution of 1 g. of the methiodide in 80 ml. of water was refluxed for one hour with 15 g. of sodium hydroxide. The cooled reaction mixture was extracted with ether and the ether extracted with *N* hydrochloric acid. The acid extracts were made alkaline with dilute sodium hydroxide and extracted with ether. After drying, the ether was treated with alcoholic hydrogen chloride and the crystalline solid which separated was recrystallized from an alcohol–acetone–ether mixture. The N,N-dimethyl-3-methoxybenzylamine hydrochloride melted at 173–174° (lit.[17] m. p. 173°).

Degradation of N-(3-Methoxybenzyl)-N-methyl-3,4-methylenedioxy-5-methoxyphenethylamine Methiodide.—A solution of 0.7 g. of the methiodide in 56 ml. of water was refluxed one hour with 12.6 g. of sodium hydroxide. The product, N,N-dimethyl-3-methoxybenzylamine hydrochloride, melted at 176–177°, cor., and was identical with the product obtained from the corresponding homopiperonylamine methiodide described above.

Summary

The preparation of myristicin aldehyde by a series of reactions starting with pyrogallol 1-monomethyl ether is reported.

N-(3-Methoxybenzyl)-N-methyl-3-methoxy-4,5-methylenedioxyphenethylamine has been synthesized and found to be different from α-fagarine.

The synthesis of N-(3-methoxybenzyl)-N-methyl-3,4-methylenedioxyphenethylamine is also reported.

RENSSELAER, N. Y. RECEIVED APRIL 7, 1948

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

The Isomerization of Cyclohexane and Methylcyclopentane in the Presence of Aluminum Halides. I. The Nature of the Catalyst

BY D. P. STEVENSON AND O. BEECK

Introduction

In the recent past a number of papers dealing with the aluminum halide catalyzed isomerization of hydrocarbons, particularly the alkanes, have appeared.[1] Leighton and Heldman[1a] and Powell and Reid[1b] interpreted the results of their investigations of the isomerization of the butanes as providing substantiation for the theory that the catalytic isomerizing activity of the aluminum halides resides in the hypothetical, strong acids, $HAlX_4$.[2] The more recent work of Pines and Wackher[1c,1d] has shown that substances other than hydrogen halide must be present in order that the aluminum halides may have isomerizing activity for the butanes and pentanes.

A general investigation of the nature of aluminum halide catalyzed reactions of hydrocarbons has been under way in these laboratories for several years. In this and the following paper some of the results obtained in a study of the isomerization of cyclohexane and methylcyclopentane are reported. This paper deals with the nature of the catalyst. It is shown that, as Pines and Wackher[1c,1d] found for alkane isomerization, hydrogen halide by itself is not a promoter of isomerizing activity of the aluminum halides for cyclohexane and methylcyclopentane, and thus that the simple hydro-aluminum halide complex, $HAlX_4$, is not the catalytically active species.[3] The second paper presents new data on the equilibrium composition of liquid mixtures of cyclohexane and methylcyclopentane and the side reactions which accompany the isomerization reaction.

The interconversion of cyclohexane and methylcyclopentane has been the subject of several previous investigations.[4] These authors agree that pure, anhydrous aluminum chloride is without catalytic activity toward the isomers, cyclohexane and methylcyclopentane. They have shown that in the presence of small quantities of water, aluminum chloride becomes a very active isomerization catalyst and that the reaction is reasonably free from side reactions.

The results of these investigations indicated that the rate of isomerization of cyclohexane and methylcyclopentane should be measurable in an easily accessible temperature range, 25–70°. The ready availability of the pure isomers combined with their physical properties, which results in ease of handling and analysis, suggested that this isomerization should be particularly suitable for studying the nature of the catalysis. Thus this reaction was selected for intensive investigation.

Experimental Methods

The isomerization of cyclohexane and methylcyclopentane was investigated in the presence of three catalysts. These catalysts were: (a) an atmospheric moisture dampened aluminum chloride, (b) anhydrous aluminum chloride and (c) anhydrous aluminum bromide. The "moist aluminum chloride," (a), was taken from a five-pound bottle of J. T. Baker C. P. anhydrous aluminum chloride powder which had been originally opened one year before

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[1] (a) Leighton and Heldman, THIS JOURNAL, **65**, 2276 (1943); (b) Powell and Reid, *ibid.*, **67**, 1020 (1945); (c) Wackher and Pines, *ibid.*, **68**, 1642 (1946); (d) Pines and Wackher, *ibid.*, **68**, 2518 (1946).

[2] (a) Egloff, Wilson, Hulla and Van Ardsell, *Chem. Rev.*, **20**, 345 (1937); (b) Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Pub. Corp., New York, N. Y., 1941, Chapter 4, pp. 57–76; (c) II, THIS JOURNAL, **70**, 2773 (1948).

[3] Some of the results described in the present paper were discussed by one of the authors (O. B.) at Gibson Island, June, 1944, AAAS Conference on Catalysis.

[4] (a) Nenitzescu and Cantunari, *Ber.*, **66**, 1097 (1933); (b) Glasebrook and Lovell, THIS JOURNAL, **61**, 1717 (1939); (c) Mizusima, Morino and Hugisiro, *Sci. Papers Inst., Phys. Chem. Res.* (*Tokyo*), **38**, No. 1034, 401 (1941); (d) Pines, Abraham and Ipatieff, Atlantic City meeting, American Chemical Society, April, 1947, Div. of Phys. Inorg. Chem.

the present work was started. A number of analyses of this material showed it to have a composition represented by the empirical formula, $Al_2Cl_{5.5}(OH)_{0.5}$. In the experiments with this catalyst (a), only casual precautions against further exposure to atmospheric moisture were observed. This catalyst was weighed into constricted test-tubes with standard taper female joints. Five ml. of hydrocarbon was then added from a pipet, and the test-tube was affixed to a vacuum system. The tube and contents were chilled with liquid oxygen and evacuated. When a hard vacuum, as indicated by a "leak tester," had been attained, the manifold was cut off from the diffusion pump and the hydrocarbon was permitted to melt so that adsorbed and dissolved air was released. The tube and contents were again chilled and pumped for an additional five minutes.[5] A suitable quantity of water or hydrogen chloride was then measured manometrically and frozen into the test-tube. The tube was sealed off at the constriction while evacuated. Typical examples of experiments such as those just described are given in Table II, entries 1 through 7.

TABLE I

PROPERTIES OF THE CYCLOHEXANE AND METHYLCYCLOPENTANE AFTER PURIFICATION

		MCP	CH
Distillation	Theoretical plates	45	60
	Reflux ratio	50:1	50:1
	Boiling range, 760 mm.	72.3 ± 0.1 (71.8)[a]	80.7 ± 0.1 (80.74)[a]
$n^{20}D$ (Pulfrich)		1.4094 (1.4097)[a]	1.4260(0) (1.4262)[a]
Aromatic (benzene)		<0.0001%[b]	<0.0001%[b]
Diolefin (cyclohexadiene)		<0.0001%[b]	<0.0001%[b]
Hexane (normal)		0.1%[c]	<0.01%[c]
Methylcyclopentane		>99.7%[d]	<0.2%[d]
Cyclohexane		<0.3%[d]	>99.8%[d]

[a] From the Tables of Physical Properties of Hydrocarbons issued under the auspices of API Project 44. [b] From ultraviolet absorption λλ 2400–2800 Å. [c] From mass spectrometric analysis. [d] From comparison of infrared absorption (liquid) with that of certified samples from the National Bureau of Standards.

TABLE II

THE ISOMERIZATION OF CYCLOHEXANE AND METHYLCYCLOPENTANE BY ALUMINUM CHLORIDE AT 60°

No.	Al_2Cl_6[a]	HCl[a]	H_2O[a]	C_6H_{12}[a]	Contact time[b]	Mole % MCP $t = 0$	Mole % MCP $t = t$	Naphthene treatment	Catalysts
1	0.37	0.00	0.00[e]	46	24	0.0	5.0 ± 0.1[d]	None	$Al_2Cl_{5.5}(OH)_{0.5}$[c]
2	0.37	.00	.00	45	24	100	85.3 ± 0.2	None	$Al_2Cl_{5.5}(OH)_{0.5}$
3	1.65	.00	.00	46	24	0.0	15.0 ± 0.5	None	$Al_2Cl_{5.5}(OH)_{0.5}$
4	0.17	.00	.00	46	48	.0	10.0 ± 1.0	None	$Al_2Cl_{5.5}(OH)_{0.5}$
5	.19	.27	.00	46	48	.0	3.2 ± 0.4	None	$Al_2Cl_{5.5}(OH)_{0.5}$
6	.20	.00	.27	46	16	.0	3.7 ± 0.3	None	$Al_2Cl_{5.5}(OH)_{0.5}$
7	.87	.00	8.7	46	16	.0	6.1 ± 0.2	None	$Al_2Cl_{5.5}(OH)_{0.5}$
8	.46	.35	0.00	35	17.2	100	>99.5 ± 0.1	SiO_2	Anhy. Al_2Cl_6
9	.52	.00	.068	46	21.3	0.0	21.1 ± 0.8	SiO_2	Anhy. Al_2Cl_6
10	.11	.00	.00	33	17.2	100	>99.5	SiO_2	Anhy. Al_2Cl_6
11	.011	.46	.00	46	23	0.0	< 0.5	SiO_2	Anhy. Al_2Cl_6

[a] Units, millimoles. [b] Units, hours. [c] The empirical formula of the "moist aluminum chloride" established by analysis. [d] The uncertainties here given indicate the mean deviation of a pair of duplicate experiments. [e] In these tables, this column gives the quantity of water deliberately added but does not include accidental water.

The anhydrous aluminum chloride (b), aluminum bromide (c), were freed of water by multiple distillation in an all-glass vacuum system. A number of tubes with break-off seals were sealed to a manifold by means of constricted side arms. The manifold was connected to the vacuum system through a reëntrant trap. Several distilling flasks were sealed to the manifold with the crude, anhydrous aluminum halide in the last one. The manifold and side arms were wrapped with asbestos paper, nichrome wire, and a second layer of asbestos. After a hard vacuum had been attained, the manifold was heated to *ca.* 250° and special 100-watt furnaces about the break-off tubes were brought to *ca.* 250°. After several hours of pumping at the elevated temperature a small quantity of aluminum halide was distilled through the system and collected in the reëntrant trap (liquid nitrogen cooled). The manifold was then sealed off (between manifold and reëntrant trap) and a flask to flask distillation of the aluminum halide performed, the last 25% being discarded in each distillation step. The distillations were performed with the manifold and break-off tubes heated. When the first 75% of the aluminum chloride had distilled from one flask to the next, the residue flask was sealed off. When the last distillation of this type was finished (usually the third), the 100-watt furnaces were removed from the break-off tubes. The aluminum halide was distributed between the tubes by manipulation of a flame. The tubes were then sealed off for storage.[6]

The reaction tubes were similar to the aluminum halide storage tubes with the addition of a constriction in the body of the tube below the side arm. The aluminum halide was introduced into these vessels in the same manner that the storage vessels were filled. Glass encased pieces of drill rod (3/8") were used to break the break-off tips after the evacuation and baking of the manifold and reaction tubes was completed.

The crude, anhydrous aluminum chloride was taken from a freshly opened bottle of J. T. Baker C. P. anhydrous, granular aluminum chloride. Aluminum bromide was synthesized from the elements and subjected to two atmospheric pressure distillations from aluminum prior to final purification as described above.

In order to introduce the hydrocarbon into the reaction tubes containing the anhydrous aluminum halides, the reaction tubes were sealed to the manifold used in the experiments with the moist aluminum chloride powder. The manifold was thoroughly evacuated and flamed before breaking the tip by means of the glass-encased steel rod. In experiments 11 and 12 of Table III the naphthene was vacuum distilled from a vessel containing anhydrous calcium bromide powder fixed to the vacuum

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[5] In order to obtain reproducible results these precautions to remove air were necessary. This may be taken as evidence that oxygen influences the activity of the catalyst for cyclane isomerization as has been found to be the case for alkane isomerization by Pines and Wackher, THIS JOURNAL, **68**, 599 (1946).

[6] In a few experiments the aluminum chloride was synthesized in the reaction tube from pure aluminum and chlorine. Elementary iodine was used as a catalyst for the reaction of chlorine and aluminum. The iodine and excess chlorine were removed by evacuation after the reaction. The results obtained with catalyst prepared in this manner differ in nowise from those carried out with the multiply distilled aluminum chloride and thus are not reported further.

system by a standard taper joint. For all other experiments with anhydrous aluminum bromide and all experiments with anhydrous aluminum chloride the hydrocarbon was distilled from the anhydrous calcium bromide into a tube containing 28–200 mesh Davco Silica Gel and then distilled from the silica gel into the reaction vessel. This silica gel was activated by baking at 375° for six hours at a pressure below 10^{-5} mm. The hydrogen halide or water was added as described above.

Table III

The Isomerization of Cyclohexane and Methylcyclopentane by Aluminum Bromide at 60°

25–46 Millimoles C_6H_{12}

No.	Al_2Br_6[a]	HBr[a]	H_2O[a]	Time[b]	Mole % MCP $t = 0$	$t = t$	Naphthene treatment
12	0.0070	0.0000	0.0000[c]	42	100	58.2	$CaBr_2$
13	.0082	.0043	.0000	42	100	50.6	$CaBr_2$
14	.0018	.0000	.0000	49	100	> 99.8	SiO_2
15	.0013	.0000	.0013	20	100	59.8	SiO_2
16	.0185	.0000	.0000	15.3	0.0	< 0.2	SiO_2
17	.0043	.0098	.0000	21	.0	< 0.2	SiO_2
18	.0067	.0000	.00067	15.9	.0	4.2	SiO_2
19	.0083	.0000	.0170	15.3	.0	12.1	SiO_2

[a] Units, mole fraction. [b] Units, hours. [c] See "*e*" of Table II.

After the loaded reaction tubes were sealed off, they were quickly warmed to room temperature and then placed in an air thermostat (60 ± 1°) on a rotating disk to facilitate attainment of thermal equilibrium. After a suitable time at 60° the reaction tubes were taken out and the reaction quenched by cooling in a Dry Ice–isopropyl alcohol slush. The vessels were stored in this cold bath until opened.

Prior to opening, the tubes were warmed quickly to room temperature and weighed. The contents were then frozen (liquid oxygen) and opened by means of a file scratch and the application of a hot glass rod. An excess of 6 *N* sodium hydroxide solution was then added and the tube and contents permitted to warm to 0° by immersion in an ice–water mixture. The hydrocarbon was siphoned off and dried with potassium hydroxide pellets.

The alkaline solution of the aluminum halide was washed into a volumetric flask (250 ml.) and diluted to the mark. The aluminum and halogen were then determined volumetrically on aliquot portions. The cleaned and dried glass tube was weighed, which datum when combined with the previously obtained weight and the weight of the catalyst provided enough data to calculate the weight of hydrocarbon used in the experiment.

The hydrocarbon product was analyzed by an infrared spectrophotometric method for liquid samples. Methylcyclopentane and cyclohexane certified by the National Bureau of Standards were used to calibrate the spectrophotometer. As estimated from the reproducibility and the accuracy with which mixtures (prepared by weight) could be analyzed, the accuracy of the method was ±0.5% on the total sample. The methylcyclopentane content of the products shown in Tables II and III are the average of independent determinations of the methylcyclopentane and cyclohexane content of the sample.

The extent of side reactions and the effect of the products on the accuracy of the analysis is discussed in the second paper.

The refractive index of the product of each run was measured with an Abbe refractometer. The composition, determined from a smooth refraction–composition curve prepared from measurements of synthetic mixtures of the pure compounds, agreed with that determined by the infrared method to within the rather large uncertainty of the refraction analysis (±1.2%).

Phillips Petroleum Company Research Grade methylcyclopentane and Eastman Kodak Company White Label cyclohexane were subjected to the following purification treatment. The hydrocarbons were shaken with successive portions of 96% sulfuric acid until the acid layer remained colorless after three minutes of shaking at room temperature. They were then washed with water and dried with anhydrous calcium chloride. The drying treatment was followed by percolation through tightly packed 28–200 mesh Davco Silica Gel, about 100 g. of gel being used per liter of hydrocarbon. The ultraviolet absorption after this treatment showed the aromatic (as benzene) and diolefin (as cyclohexadiene) content of the naphthenes to be less than 0.0001%. The naphthenes were then subjected to careful fractional distillation through glass bubble-plate columns. The distillation data and final properties of the materials used are shown in Table I.

Experimental Results

In Tables II and III, selected, representative examples chosen from several hundred experiments which were performed are described in detail. The uncertainties indicated in the methylcyclopentane content of the reaction product gives a direct measure of the reproducibility of duplicate experiments.

Discussion

Essentially two series of experiments were carried out. In the first of these (typical examples, 1–7 of Table II) moist aluminum chloride was used. The results of experiments 1 and 2 prove the activity of the catalyst as an isomerization catalyst for both cyclohexane and methylcyclopentane at 60°. Comparison of the conversion achieved in experiments 1 and 3 indicates that the rate of isomerization is dependent on the relative quantity of catalyst present. The results of experiments 6 and 7 show the isomerization activity of this catalyst is not impaired by the addition of water, even when the quantity of added water exceeds the quantity of catalyst by a factor of ten (molal ratio). Comparison of experiments 4 and 5 proves the addition of hydrogen chloride decreases the activity of the catalyst.

The second series of experiments was carried out with anhydrous aluminum halide (typical examples, 8–11 of Table II and 12–19 of Table III). The results of experiments 8 and 11 of Table II confirm the lack of promotional activity of hydrogen chloride for isomerization activity of aluminum chloride toward the cyclanes.

At the time these experiments were performed (1943), the absence of promotional activity of hydrogen chloride was quite unexpected and new. Since that time, the work of Pines and Wackher[1c] on the isomerization of butane has shown this to be the case for alkane isomerization, and thus it is not unexpected that the same should obtain for cyclane isomerization.

The solubility of aluminum chloride in cyclohexane and methylcyclopentane is extremely small at 60°. Even in experiment 11 there was no observable diminution in the quantity of solid aluminum chloride after twenty-three hours of shaking at 60°. Thus the solubility is considerably less than 0.6 g. per liter. The apparent increase in the isomerization rate with relative quantity of aluminum chloride (compare 1 and 3 of Table II) can be taken as evidence that at 60° at least a portion of the isomerization reaction is heterogeneous.[7]

It was thought that perhaps the necessary presence of water for isomerization activity of the aluminum chloride arose through the heterogeneous nature of the catalysis. However, the results of the experiments with aluminum bromide prove this not to be the case. In none of the experiments described in Table III was any evidence of a solid phase observed. The results of experiments 14 through 19 of Table III show that the aluminum bromide catalysis is directly comparable with the aluminum chloride catalysis in all respects but the heterogeneity of the latter.

The data on experiments 12 and 13 (Table III) are given only to show the sensitivity of the aluminum bromide to water. Anhydrous calcium bromide is ordinarily considered one of the better drying agents, but it is clearly inadequate for such purposes as the present investigation.

It has been suggested by Wackher and Pines[1c] that the isomerizing activity of the system derived from aluminum halide and water resides in a hydroxyaluminum halide, $HOAlX_2$, for instance. From observations of the reaction between various quantities of water with both aluminum bromide and chloride they adduce evidence for the existence of such compounds. The homogeneity of the reacting system of experiment 19 of Table III provides confirmatory evidence for the existence of intermediate compounds in the aluminum bromide–water system.

The moist aluminum chloride catalyst used in experiments 1–7 of Table II had a reasonably definite composition, represented by the formula $Al_2Cl_{5.5}(OH)_{0.5}$. This could be an intimate mixture of Al_2Cl_6 with $Al_2Cl_5(OH)$ or $AlCl_3$[3] with $HOAlCl_2$(1) or a solid solution of the hydroxyaluminum chloride in the aluminum chloride. That an equilibrium of the type

$$Al_2Cl_6 + H_2O \rightleftarrows Al_2Cl_5(OH) + HCl$$

exists is strongly suggested by the quite evident lesser isomerization activity in experiment 5 of Table II as compared with experiment 4.

An effort to obtain independent evidence for the existence of the hydroxyaluminum halides was made by comparing X-ray powder photographs of anhydrous aluminum chloride, aluminum chloride hexahydrate, and the catalytically active $Al_2Cl_{5.5}(OH)_{0.5}$.[8]

The interplanar distances, d_{hkl}, and the visual (uncorrected) intensities are shown in Table IV. The results of Ketalaar[9] on anhydrous aluminum chloride are included in the table for comparison.

TABLE IV

X-RAY POWDER PATTERNS OF SOME ALUMINUM CHLORIDES

Legend: f = faint, m. = medium, s = strong, v = very.

Anhy. Al_2Cl_6[a]		Anhy. Al_2Cl_6[b]		$Al_2Cl_{5.5}(OH)_{0.5}$		$AlCl_3 \cdot 6H_2O$	
d_{hkl}	I	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I
				5.96	m. f.	5.93	m.
5.80	s.	5.84	s.	5.77	m.		
				5.04	v. v. f.	5.16	m.
				3.90	v. v. f.	3.88	m. s.
						3.69	m. s.
				Several very		3.39	m. s.
				faint diffuse		3.28	v. s.
				lines visible		3.21	s.
				3.07	v. v. f.		
2.912	v. s.	2.932	s.	2.905	s.	2.93	v. f.
2.81	f.	2.812	m.	2.791	s.		
						2.74	f.
						2.55	s.
2.45	m. f.	2.459	v. s.	2.45	v. s.		
						2.295	s.
						2.18	m. s.
						2.05	s.
						2.02	v. f.
						1.94	m. s.
		1.915	f.	1.905	v. f.	1.902	v. f.
1.759	v. f.	1.759	m.	1.754	m.	1.752	v. s.
1.706	m.	1.707	s.	1.703	s.		
						1.678	v. v. f
						1.665	f.
		1.639	f.	1.634	v. v. f.	1.641	m.
		1.531	f. f.			1.54	v. v. f.
		1.505	m. f.	1.506	v. v. f.	1.51	m.
				1.472	m. f.	1.475	m. f.
1.457	m.	1.460	m.	1.457	m. f.	1.462	f.
1.405	v. f.	1.40	m.	1.399	m.	1.405	m. f.
						1.375	m.
						1.354	m.
						1.312	v. f.
		1.272	v. f.				
		1.222	m. f.	1.223	m. f.	1.222	m.
1.170	v. f.	1.167	f.				
1.111	m. f.	1.107	m. s.	1.107	m.		
1.056	v. f.	1.097	m. s.	1.082	m.	1.067	v. v. f.

[a] This research. [b] Ketalaar.

In addition to a number of lines not present in the spectrum of the anhydrous aluminum chloride, the spectrum of the "moist" aluminum chloride powder, $Al_2(Cl)_{5.5}(OH)_{0.5}$ shows lines coincident with those of the spectrum of the anhydrous chloride but of different intensity. Some of the

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(7) The rate of formation of methylcyclopentane from cyclohexane at 27° was found to be represented by the equation, $dp/dt = \alpha h - \beta p$, where h and p are the mole fractions of cyclohexane and methylcyclopentane, respectively, and α and β were restricted by the condition that $\alpha/\beta = k_e = p_e/h_e$. The rate constants were proportional to the ratio of catalyst (the moist aluminum chloride powder) to naphthene over a forty-fold range of this ratio. At 60° the rate of isomerization showed much less dependence on the catalyst–hydrocarbon ratio, the rate constants being of the form, $\alpha = \alpha_0 + \alpha_1 r$, where r is the ratio of catalyst to hydrocarbon. These results may be taken as indication that at 27° the reaction is predominantly heterogenous, while at 60° both homogeneous and heterogeneous reactions take place.

(8) Anhydrous aluminum chloride was distilled into side arms on a manifold as in charging reaction tubes (see experimental section). The side arms had suitable capillaries drawn on their lower end and were of special potassium-calcium free glass. The side arms were sealed off from the manifold after a suitable quantity of aluminum chloride had been collected. The tube and capillary were suspended in an air bath and heated to about 210°. The molten aluminum chloride flowed into the capillary. Upon slow cooling in air a tightly packed, polycrystalline mass of aluminum chloride was formed in the capillary. The photographs were taken with a General Electric Company unit. The camera radius was *ca.* 7.2 inches, and nickel filtered copper radiation was employed.

(9) Ketalaar, *Z. Kryst.*, **A90**, 237 (1935).

extra lines in the spectrum of $Al_2(Cl)_{5.5}(OH)_{0.5}$ correspond to interplanar distances of aluminum chloride hexahydrate. However, the intensities of most of these lines are not in accord with the expected upper limit to the concentration of hexahydrate set by the composition of the catalytically active material. The extra lines in the spectrum of $Al_2(Cl)_{5.5}(OH)_{0.5}$ do not correspond to lines in the spectra of any of the alumina hydrates which have been studied in these laboratories or in the published spectra.[10]

Although the X-ray data are not definitive, they do provide corroborating evidence for the existence of one or more hydroxyaluminum chlorides.

It is apparent that a comparison of the catalytic activity of aluminum chloride and bromide as isomerization catalysts for naphthenes must be made with extreme care. It is likely that several aluminum hydroxy halides exist and that each has its own specific activity as a catalyst. If, as is suggested by certain experiments (as noted above), the equilibria between the various molecular species are affected by the quantity of hydrogen halide present, it becomes virtually impossible to determine hydroxyl halides, let alone to compare the activities of particular chlorides and bromides. Furthermore, the evidence that at 60° (and below) the aluminum chloride catalysis is heterogeneous in part, while the aluminum bromide catalysis is homogeneous, results in the lack of really common ground for a comparison of activities.

Acknowledgments.—The authors wish to acknowledge the assistance of Mr. Donald Mayers and Mrs. Jane H. Morgan in carrying out the many experiments, of which those reported herein form but a small fraction. The X-ray photographs were made under the direction of Mr. A. E. Smith. The infrared spectrophotometric analytical method for cyclohexane and methylcyclopentane was developed under the direction of Dr. F. S. Mortimer.

Summary

The results of a study of the isomerization of cyclohexane and methylcyclopentane in the presence of aluminum chloride and bromide are presented. The experiments confirm the lack of catalytic activity on the part of aluminum halides in the absence of a promoter.

It is shown that at 60° for the isomerization of cyclohexane and methylcyclopentane: (1) Hydrogen halides have no promotional affect on the isomerizing activity of aluminum halides. (2) Water is a promoter of isomerization activity in aluminum halides. (3) The catalysis by the aluminum bromide–water complex is homogeneous. (4) The catalysis by the aluminum chloride–water complex is partially homogeneous and partially heterogeneous.

New evidence for the existence of an intermediate compound (or compounds) of the form $Al_2X_{6-n}(OH)_n$ $(1 \leq n \leq 5)$ is presented, and it is suggested that any or all of the intermediates have catalytic activity.

EMERYVILLE, CALIFORNIA RECEIVED MARCH 3, 1948

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[10] Hanewalt, A. S. T. M. X-Ray Diffraction Data Cards.

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Synthetic Estrogens. Tetraalkyl Substituted Analogs of Dienestrol and Hexestrol[1,2]

BY JOSEPH B. NIEDERL AND PHILIP WEISS[3]

In continuation of studies in the introduction of alkyl[5,6] and aryl[4] groups into the benzene nuclei of dienestrol and hexestrol, it was decided to synthesize tetra alkyl substituted analogs of dienestrol and hexestrol. The phenols used were *p*-xylenol, thymol and carvacrol.

The following method of synthesis[7] was used in preparing the substituted dienestrols and hexestrols. The phenols were esterified with propionyl chloride, and the resulting esters were subjected to the Fries rearrangement to give the cor-

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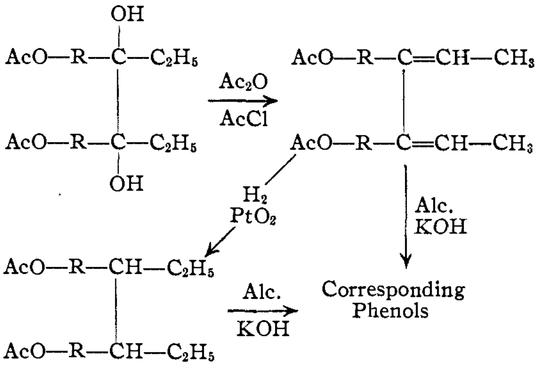

R = 2,5-dimethylphenyl, 2-methyl-5-isopropylphenyl, 2-isopropyl-5-methylphenyl

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[1] Abstracted from a dissertation submitted by Philip Weiss to the Faculty of the Graduate School of New York University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Presented before the Medicinal Chemistry Division of the American Chemical Society at New York, N. Y., September, 1947.

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