[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Studies in the Terpene Series. XIV.[1] Skeletal Isomerization and Hydrogen Transfer of Cyclic Olefins in the Presence of Alumina–Hydrogen Chloride and Silica–Alumina Catalysts[2]

BY HERMAN PINES, R. C. OLBERG AND V. N. IPATIEFF

RECEIVED APRIL 16, 1952

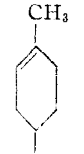
d-Limonene, dihydrolimonene, isopropylcyclohexene and ethylcyclohexene underwent a complex reaction when passed over activated alumina in the presence of hydrogen chloride. An intramolecular rearrangement occurred accompanied by a hydrogen transfer which resulted in the formation of polymethylated alicyclic and aromatic hydrocarbons. A similar reaction occurred when silica–alumina was used as a catalyst. An ionic mechanism is proposed to explain the formation of the various hydrocarbons.

During an investigation into the feasibility of effecting ring cleavage of bicyclic dihydroterpenes by means of hydrogen chloride in the presence of activated alumina at 300°, it was found that pinane (I) was converted to a complex mixture of hydrocarbons.[3] The product consisted of a mixture of hydrocarbons from which 1,2,4,5-tetramethylbenzene (durene), *p*-cymene and their cycloölefinic counterparts were isolated. It was, therefore, concluded that structural evaluation of bicyclic terpenes by ring cleavage with the above method was of little value. However, the complex nature of the reaction, involving intramolecular rearrangement accompanied by hydrogen transfer, warranted further study.

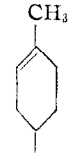
For that reason, the effect of alumina–hydrogen chloride upon monocyclic olefins and diolefins has been investigated; the hydrocarbons studied were limonene (II), dihydrolimonene (III), 4-ethylcyclohexene, 4-isopropylcyclohexene, *p*-menthane (IV) and *p*-cymene (V).

Discussion of Results

I



II



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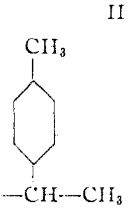

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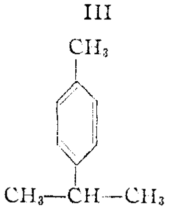

V

***d*-Limonene,** when passed over activated alumina at 300° in the presence of hydrogen chloride, yielded a mixture of hydrocarbons composed of 51% aromatics, 40% monocyclic olefins and 9% higher boiling compounds. The aromatic hydrocarbons contained *p*-cymene and durene. The cycloölefins were composed of six and five membered rings; among the alkylcyclohexenes the presence of only 1-methyl-4-isopropyl-x-cyclohexene which was the major constituent and of 1,2,4,5-tetramethyl-x-cyclohexene could be confirmed.

The skeletal isomerization of limonene occurred prior to its conversion to aromatic hydrocarbons. This was shown by the fact that *p*-cymene, when subjected to the same treatment, remained unchanged. Similarly *p*-menthane did not undergo rearrangement under the above conditions.

Dihydrolimonene (III), containing only one double bond per molecule underwent reaction similar to that of limonene; among the products of reaction *p*-cymene, durene, menthene and alkylcyclopentenes were found. The extent of hydrogen disproportionation was considerably smaller than that with limonene; only 15% of aromatic hydrocarbons and 33% of cycloparaffins were produced.

Since limonene and dihydrolimonene gave rise to a large number of isomerization products, it was deemed desirable to carry out the reaction with simpler alkylcyclohexenes such as ethyl- and isopropylcyclohexene. The number of isomeric products possible from these substances is markedly reduced and their quantitative determination facilitated.

Ethylcyclohexene yielded a product which contained about 15% aromatic hydrocarbons, 20% cycloparaffins and the remainder cycloölefins. The aromatic portion was composed of ethylbenzene, as a major constituent, and *p*-xylene. *o*- and *m*-xylene were presumably present in small proportion, but this was not verified by chemical means. A portion of the product obtained from the reaction was selectively hydrogenated and the aromatic hydrocarbons removed. The composition of the cycloparaffins thus separated is given in Table I.

TABLE I

COMPOSITION OF THE HYDROGENATED NAPHTHENES FROM ETHYLCYCLOHEXENE

	%
Ethylcyclohexane	47
1,2-Dimethylcyclohexane	2
1,3-Dimethylcyclohexane	6
1,4-Dimethylcyclohexane	2
Alkylcyclopentanes	42

The high proportion of ethylcyclohexane indicates that much of the ethylcyclohexene failed to react.

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(1) For paper XIII of this series, see Ipatieff and Pines, *J. Org. Chem.*, **17**, 485 (1952).

(2) This work was made possible through the financial assistance of Universal Oil Products Company, Chicago, Illinois.

(3) H. Pines and V. N. Ipatieff, U. S. Patent 2,419,690 (April 29, 1947).

4-Isopropylcyclohexene yielded on reaction with alumina and hydrogen chloride a mixture of hydrocarbons consisting of 21% aromatics, 38% cycloparaffins and 41% cycloölefins. The composition of the aromatic hydrocarbons present in the reaction product is given in Table II.

TABLE II

COMPOSITION OF AROMATIC HYDROCARBONS PRODUCED FROM 4-ISOPROPYLCYCLOHEXENE

	%
Isopropylbenzene	3
1,2,3-Trimethylbenzene	14
1,2,4-Trimethylbenzene	39
1,3,5-Trimethylbenzene	23
m-Ethyltoluene	20

The cycloparaffins were not separated from the cycloölefins, but the total after conversion to cycloparaffins was analyzed.

The composition of the total alkylcyclohexanes is given in Table III and it is based on the dehydrogenation and determination by means of infrared spectral analysis, of the composition of the aromatic hydrocarbons thus formed. The product which did not undergo dehydrogenation was assumed to be composed of alkylcyclopentanes, since the latter did not undergo dehydrogenation under the experimental conditions used for the dehydrogenation of alkylcyclohexanes or even geminal alkylcyclohexanes. The cycloparaffins fraction obtained from selective hydrogenation was composed of 60% alkylcyclohexanes and 40% alkylcyclopentanes.

TABLE III

COMPOSITION OF THE PRODUCT OBTAINED FROM THE DEHYDROGENATION OF THE HYDROGENATED NAPHTHENES OBTAINED FROM ISOPROPYLCYCLOHEXENE

	%		%
o-, *m*- and *p*-xylene	4	*p*-Ethyltoluene	10
Isopropylbenzene	27	1,2,3-Trimethylbenzene	3
o-Ethyltoluene	13	1,2,4-Trimethylbenzene	21
m-Ethyltoluene	15	1,3,5-Trimethylbenzene	7

According to the analytical results obtained, only about 12% of the original isopropylcyclohexene failed to undergo a skeletal isomerization.

It was of interest to determine whether each of the components, of the alumina–hydrogen chloride catalyst, alone would also effect the skeletal isomerization and hydrogen transfer reaction.

Limonene–Alumina.—When limonene was passed over alumina alone, very little hydrogen disproportionation occurred. The major portion of the product recovered appeared to be unchanged limonene, though products resulting from the migration of the double bonds might have been formed.

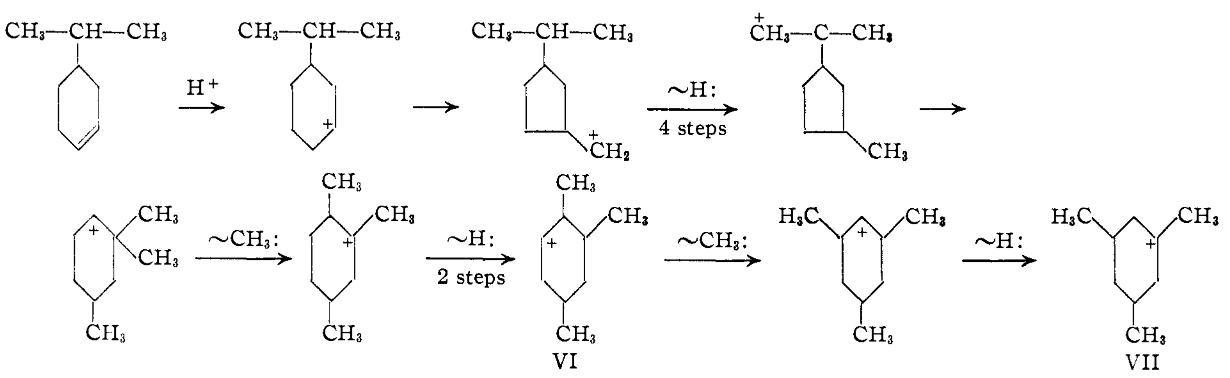
Limonene–hydrogen chloride was passed over pumice. Pumice, which *per se* has no catalytic effect, was used in order to reproduce the experimental conditions existing when alumina–hydrogen chloride was used as a catalyst. It was found that in the presence of hydrogen chloride only hydrogen disproportionation reaction occurred; *p*-cymene and 1-methyl-4-isopropyl-x-cyclohexene were found in the reaction product. The results obtained with hydrogen chloride were similar to those reported previously.[4]

Limonene–Silica–Alumina.—This catalyst caused both skeletal isomerization and hydrogen disproportionation of the hydrocarbons. The reaction product was composed of 65% aromatics, 34% cycloparaffins and 1% cycloölefins. In the aromatic portion, *p*-cymene and durene were identified.

Mechanism

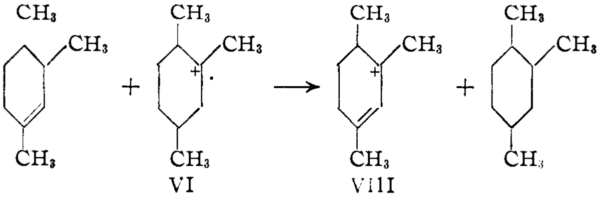
The application of the carbonium ion mechanism seems to explain adequately the formation of the various products. For the purpose of illustration the steps leading to the formation of the various types of hydrocarbons obtained from the isomerization of isopropylcyclohexene are given.

The presence of polymethyl-cyclohexenes, -cyclohexanes and -benzenes can be explained by assuming the formation of cyclopentane derivatives as intermediary steps as indicated by the equations



The trimethylcyclohexenes can be obtained from (VI) or (VII) by loss of a proton.

The trimethylbenzenes and trimethylcyclohexanes are probably formed by a hydride transfer reaction involving the allylic carbon atom of a cycloölefin and a carbonium ion; this can be illustrated as



Carbonium ion (VIII) through a loss of a proton

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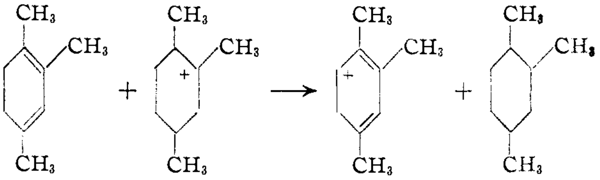
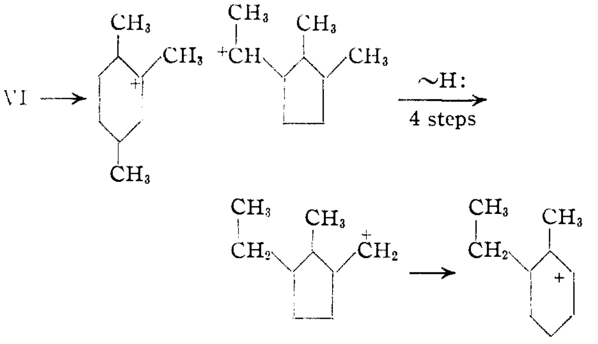
(4) V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **67**, 694 (1945).

can form a conjugated cyclohexadiene (IX), which in turn can again react with a carbonium ion to undergo a hydride shift followed by a loss of a proton to yield a trimethylbenzene



IX

1-Methyl-x-ethylcyclohexene or the corresponding saturated or aromatic hydrocarbons are most probably produced from isopropylcyclohexene through an intermediary formation of a cyclopentyl ring



X

The mechanism of the ring contraction and expansion has been described previously.[5,6]

Compound (X) can form a cycloölefin through a loss of proton, or a cycloparaffin through a capture of a hydride ion. Ethyltoluene can be produced from (X) by a hydride transfer reaction according to the steps described above for the production of trimethylbenzene.

Analytical Procedure.—The procedure used for the determination of the various hydrocarbons is given in Table IV.

The monomeric fractions were separated from the high boiling product by means of distillation which was made on a column of 7 to 10 theoretical plates. The fractional distillation of aromatic hydrocarbons obtained from the chromatographic separation was made on a column of 15–25 theoretical plates.

Selective Hydrogenation.—The degree of unsaturation was determined by hydrogenating a weighed portion of the hydrocarbons dissolved in an equal volume of pentane in the presence of 10–15% by weight of nickel–Kieselguhr catalyst.[7] The hydrogenation was made in a 125-ml. capacity rotating autoclave at 40° and in the presence of 60 atmospheres of initial pressure of hydrogen. The degree of unsaturation was calculated from the drop of pressure

Chromatographic Separation.—The aromatic hydrocarbons were separated from the cycloparaffins chromatographically by means of silica gel according to the method of Mair and Forziati.[8] The aromatic and cycloparaffinic portions were each distilled and analyzed.

Dehydrogenation.—The alkylcyclohexanes present in the cycloparaffinic portion were dehydrogenated at 200° to the corresponding aromatic hydrocarbons using platinized alumina as a catalyst.[9] The aromatic hydrocarbons thus produced were separated chromatographically. The unreacted naphthenes were passed over the catalyst three times until the dehydrogenation was completed. The aromatic hydrocarbons were combined, distilled and the various fractions were submitted to an infrared spectral analysis. The alkylaromatic hydrocarbons produced were also identified by means of solid derivatives. Alkylcyclopentanes are stable toward dehydrogenation even at a temperature of 330°.[10,11]

The saturated product which remained from the dehydrogenation consisted of alkylcyclopentanes; this was all confirmed by elementary analysis.

Test for Diolefins.—One ml. of hydrocarbons was dissolved in two ml. of benzene and to the solution was added 0.5 ml. of 96% sulfuric acid. In the presence of cyclic diolefins, the acid becomes dark brown; while in the presence of monoölefins the acid layer is colored yellow.[12]

Infrared Spectral Analysis.—The analytical procedure used was the same as described by Gallaway.[13]

Materials.—**Pinane** was prepared by hydrogenating pinene according to the procedure described previously[9]: b.p. 165°, $n^{20}\mathrm{D}$ 1.4605.

d-Limonene obtained from Eastman Kodak Company was purified by distillation; b.p. 176° (750 mm.), $n^{20}\mathrm{D}$ 1.4733.

Dihydrolimonene (1-methyl-4-isopropylcyclohexene) was prepared according to the method reported previously[14]; b.p. 170°, $n^{20}\mathrm{D}$ 1.4540.

Ethylcyclohexene and **isopropylcyclohexene** were prepared from the corresponding 4-ethyl and 4-isopropylcyclohexanol by means of dehydration. These compounds were passed over Harshaw alumina at 450° and a liquid hourly space velocity of 0.75. The yield of the alkylcyclohexenes was over 90%; ethylcyclohexene, b.p. 132° (750 mm.), $n^{20}\mathrm{D}$ 1.4499; isopropylcyclohexene, b.p. 150–152° (750 mm.), $n^{20}\mathrm{D}$ 1.4560.

p-Cymene was obtained from Eastman Kodak Company. It was washed twice at 5° with 10% by volume of 96% sulfuric acid, followed by water, alkali and water wash. It was dried over calcium chloride and distilled over sodium; b.p. 176°, $n^{20}\mathrm{D}$ 1.4895.

p-Menthane was obtained by hydrogenating *p*-cymene under pressure at 135° in the presence of a nickel–kieselguhr catalyst; b.p. 167°, $n^{20}\mathrm{D}$ 1.4398.

Alumina (activated) in the form of $^1/_8 \times {}^1/_8''$ pills was obtained from Harshaw Chemical Company. It was calcined at 700°.

Silica–alumina in the form of cylinders $^1/_8 \times {}^1/_{16}''$ was obtained from the Universal Oil Products Company. The catalyst contained about 90% by weight of silica and about 10% by weight of alumina.

Apparatus and Procedure.—The apparatus consisted of a Pyrex reaction tube of 21-mm. outside diameter heated by a thermostatically controlled vertical furnace. The hydrocarbons were fed into the reaction tube, containing about 80 cc. of the appropriate catalyst, by means of a liquid feed pump and were preheated before reaching the catalyst bed. The catalyst consisted of cylinders having a height and a diameter of 3.5 mm.; pilled catalysts were used with the exception of pumice, in which case particles of 8–12 mesh size were used. The reaction tube contained an inlet through which hydrogen chloride could be introduced. The lower end of the tube was connected to a liquid receiver, which in turn was attached through an ice and Dry Ice–acetone cooled trap, and through a soda-lime scrubber into a gas sampling bottle.

In the experiments where hydrogen chloride was used, the catalyst prior to the reaction while at the temperature of the reaction was saturated with hydrogen chloride. This was done in order to maintain the concentration of hydrogen chloride uniform throughout the bed of the catalyst. The

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(5) H. Pines, B. S. Abraham and V. N. Ipatieff, THIS JOURNAL, **70**, 1742 (1948).

(6) H. Pines, F. J. Pavlik and V. N. Ipatieff, *ibid.*, **73**, 5738 (1951).

(7) V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

(8) B. J. Mair and A. F. Forziati, *J. Research Natl. Bureau Standards*, **32**, 151, 165 (1944).

(9) H. Pines, R. C. Olberg and V. N. Ipatieff, THIS JOURNAL, **70**, 533 (1948).

(10) V. N. Ipatieff, H. Pines and R. C. Olberg, *ibid.*, **68**, 1709 (1946).

(11) V. N. Ipatieff, H. Pines and M. Savoy, *ibid.*, **69**, 1948 (1947).

(12) V. N. Ipatieff, H. Pines, V. Dvorkovitz, R. C. Olberg and M. Savoy, *J. Org. Chem.*, **12**, 37 (1947).

(13) References 10 and 11.

(14) V. N. Ipatieff, H. R. Appell and H. Pines, THIS JOURNAL, **72**, 4260 (1950).

TABLE IV

OUTLINE OF THE ANALYTICAL PROCEDURE

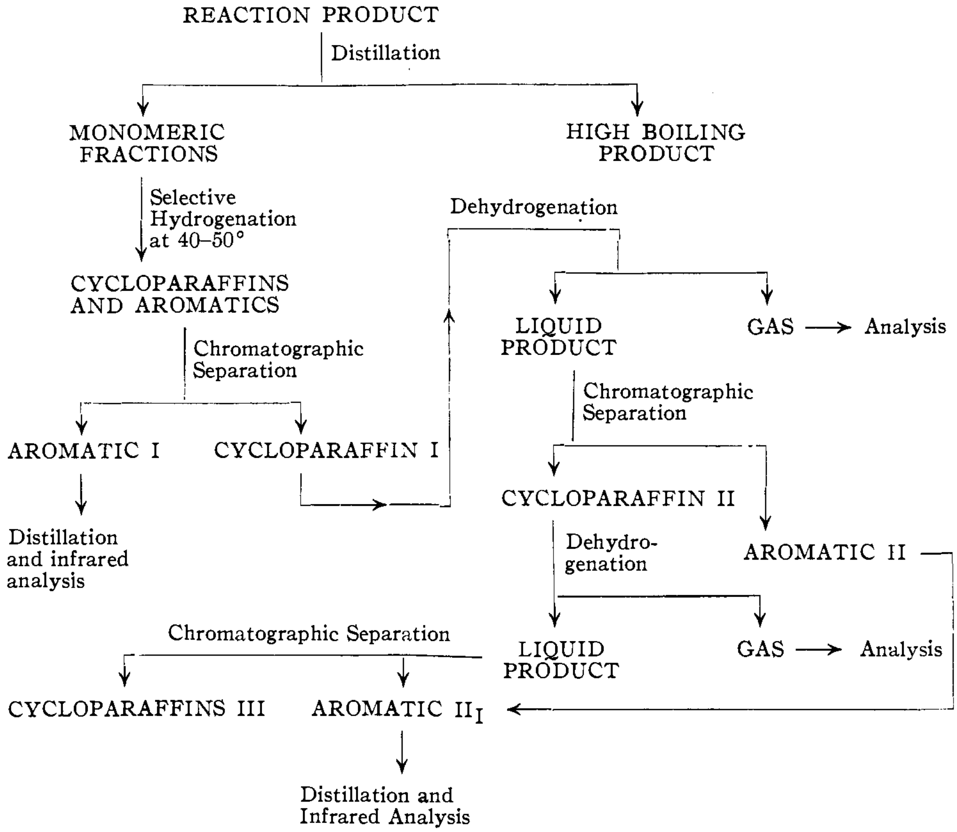

TABLE V

SUMMARY OF THE EXPERIMENTAL RESULTS OBTAINED FROM THE TREATMENT OF HYDROCARBONS WITH CATALYSTS

Catalyst used: 87–90 g.; the experiments were made at 300°.

Experiment number	1	2	3	4	5	6	7	8	9
Charged:									
Catalyst, kind	Al_2O_3–HCl						Al_2O_3	Pumice–HCl	SiO_2–Al_2O_3
Hydrocarbon, kind	Limonene	Dihydrolinonene	*p*-Men.	*p*-Cymene	4-Ethylcyclohexene	Isopropylcyclohexene	Limonene		
Experimental conditions,									
amount, g.	196	96	67	113	94	70	148	130	98
Liquid space velocity	1.2	1.1	1.0	1.3	1.1	1.0	1.4	1.0	0.7
Duration, hr.	2	1.1	0.8	1.0	1.0	0.8	1.3	1.2	1.4
Composition of liquid product, wt., %									
Cycloparaffins	0[a]	33[d]	100[e]		20[f]	38[h]	0	82[j]	34
Cycloölefins	40[b]	44		100[e]	64[f]	42[h]	100[j]		1
Aromatics	51[c]	15			16[g]	21[i]	0	18[k]	65[l]
Higher boiling products	9	8							

[a] Gaseous products were formed which were composed of: (1) non-condensable gas, 1300 ml., consisting of 23% hydrogen, 17% paraffins and 57% olefins; (2) condensable gas, 2 g., containing 68% olefins and 31% paraffins having on the average 3.3 carbon atoms. [b] According to the sulfuric acid–benzene color test diolefins were absent. The liquid product was selectively hydrogenated and the cycloparaffins were separated chromatographically from the aromatics. The cycloparaffins consisted of 34% of alkylcyclohexanes and 66% of alkylcyclopentanes. The alkylcyclohexanes contained 1,2,4,5-tetramethylcyclohexane and *p*-menthane which were identified through the conversion to corresponding aromatic hydrocarbons. [c] Durene (1,2,4,5-tetramethylbenzene), m.p. 78–79°, was separated. It showed no depression in melting point when mixed with an authentic sample. The dibromide melted at 200–201.5°. [d] Contained about 58% alkylcyclohexanes and 42% of alkylcyclopentanes. [e] Reaction did not occur. [f] The composition of the cycloparaffins and of the cycloölefins after hydrogenation is given in Table I. [g] The composition of the alkylcyclohexanes and of the alkylcyclohexenes was determined from the composition of the alkylaromatics obtained from the dehydrogenation. The analysis was made by means of ultraviolet absorption spectra. The aromatic hydrocarbons consisted of: *o*-xylene 3%, *m*-xylene 10%, *p*-xylene 4% and ethylbenzene 80%. The presence of *m*-xylene in the dehydrogenated product was also confirmed by the solid nitro derivative which was identified as 3,4,6-trinitro-*m*-xylene melting at 181–182°; it did not depress the melting point of an authentic sample. [h] The alkylcycloparaffins and alkylcycloölefins after hydrogenation were composed of 60% alkylcyclohexanes and 40% alkylcyclopentanes. The composition of alkylcyclohexanes was determined from the infrared absorption spectra of the various narrow boiling fractions of the alkylbenzenes obtained on dehydrogenation (Table III). [i] The composition of the aromatics

formed which is given in Table II was based on the infrared absorption spectra. [j] Skeletal isomerization did not occur. [k] Consisted of *p*-cymene. [l] 1,2,4,5-Tetramethylbenzene was present.

molar ratio of hydrocarbons to hydrogen chloride which was passed over the catalyst was 1.00 to 0.75.

The liquid product recovered from the reaction was washed with dilute aqueous sodium hydroxide and dried. In the case any organic chlorides were admixed with the hydrocarbons, the total liquid product was repassed at 240–300° through a tube containing soda-lime; this effected the complete removal of the halogen. The halogen-free product was distilled and analyzed.

The experimental results are summarized in Table V.

Acknowledgment.—The authors are indebted to the Physics Laboratory of the Universal Oil Products Company for the infrared spectral analysis. This analytical work was supervised by Dr. W. S. Gallaway, presently at Beckman Instruments Incorporated, South Pasadena, California.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Stereochemistry of the Reactions of *cis*- and *trans*-2-Chlorocyclohexanol with Thionyl Chloride[1]

BY HENRY C. STEVENS[2] AND OLIVER GRUMMITT

RECEIVED APRIL 15, 1952

The reactions of the *cis*- and *trans*-chlorohydrins of cyclohexene with thionyl chloride have been studied to determine the configuration of the 1,2-dichlorides obtained. The reaction of both isomers with thionyl chloride alone, and that of the *cis* with thionyl chloride–pyridine, gave *trans*-1,2-dichlorocyclohexane. The *trans*-chlorohydrin with thionyl chloride–pyridine gave a $^1/_3$ mixture of *trans*- and *cis*-dichlorides from which the pure *cis* was obtained by distillation. The *cis* dichloride was more readily dehydrochlorinated by quinoline or by potassium hydroxide and less readily dechlorinated by zinc. The mechanism of the replacement is discussed in the light of steric considerations influencing neighboring group participation.

In conjunction with a study of the stereochemistry of chlorine addition to cyclohexene it became necessary to prepare *cis*- and *trans*-1,2-dichlorocyclohexane in pure form and to determine their properties. When this investigation was undertaken and in progress,[3] the literature showed poor agreement in the physical properties of the *trans*-dichloride and contained only one reference to the *cis*-dichloride.[4]

A careful examination of the published data, along with the results of several experiments on the addition of chlorine to cyclohexene in the presence of cuprous chloride as described by Komatsu and Kawamoto,[4] led to the conclusion that their *cis*-1,2-dichlorocyclohexane was largely impure *trans*-1,2-dichlorocyclohexane. We therefore turned to the possibility of preparing the *cis*-dichloride by replacement reactions with the well established isomeric cyclohexene chlorohydrins.[5] Thionyl chloride appeared to be the most promising reagent in view of the work of Lucas and Gould[6] on *threo*- and *erythro*-2-chlorobutanol-3. With thionyl chloride alone these authors observed retention of configuration in the formation of the corresponding dichlorides, while there was inversion of configuration with thionyl chloride in the presence of pyridine. However, all reported attempts to prepare both isomeric 1,2-dihalides from *cyclic* 1,2-halohydrins have invariably led to dihalides, now known to be *trans*, which were identical with the products of halogen addition to the corresponding olefins. This general behavior was first recognized by Suter and Lutz[7] as part of a study of the dichlorides of indene. An interpretation of these results in terms of neighboring group interaction was advanced by Winstein in the case of cyclohexene dibromide made by a variety of methods.[8] Since the stereochemical result of thionyl chloride–pyridine with cyclic chlorohydrins was not known, it was decided to subject the *cis*- and *trans*-chlorohydrins of cyclohexene to reaction with thionyl chloride in the presence and absence of pyridine.

Attempts to isolate two isomers of 1,2-dichlorocyclohexane from the addition of chlorine to cyclohexene in the presence of cuprous chloride or reduced copper failed. The conditions described[4] were duplicated as closely as possible, but only *trans*-1,2-dichlorocyclohexane could be isolated. Chlorinations were carried out at 6 and 50° with a

TABLE I

PHYSICAL PROPERTIES OF *cis*- AND *trans*-1,2-DICHLOROCYCLOHEXANES

	Komatsu and Kawamoto[4]		This study	
	cis	*trans*	*cis*	*trans*
B.p., °C. (30 mm.)	92–94	87–89	103	88–89
M.p., °C.	.....	.....	−5 to −6	−6 to −7
n_D	1.4902 (25°)	1.4891 (25°)	1.4968 (20°)	1.4904 (20°)
d_4	1.1186 (25°)	1.1172 (25°)	1.2042 (20°)	1.1842 (20°)
M_D (calcd. 37.44)	39.56[a]	39.53[a]	37.18[a]	37.39[a]
% Cl (calcd. 46.3)	44.7[b]	44.3[b]	46.1	46.2

[a] Calculated from data shown. [b] Low chlorine content indicates impure compounds.

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(1) Presented before the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

(2) Columbia-Southern Chemical Corporation, Barberton, Ohio.

(3) After the presentation of this work at the New York meeting a paper on the properties of the isomeric 1,2-dichlorocyclohexanes was published by B. Carroll, D. G. Kubler, H. W. Davis and A. M. Whaley, THIS JOURNAL, **73**, 5382 (1951). In the preparation of the new *cis*-dichloride the same method was used as employed in this study. The physical properties of the *cis*- and *trans*-dichlorides determined by these authors and by us are in excellent agreement.

(4) S. Komatsu and T. Kawamoto, *J. Chem. Soc. Japan*, **52**, 685 (1931); *C. A.*, **26**, 5080 (1932).

(5) P. D. Bartlett, THIS JOURNAL, **57**, 224 (1935).

(6) H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).

(7) C. M. Suter and G. A. Lutz, *ibid.*, **60**, 1360 (1938).

(8) S. Winstein, *ibid.*, **64**, 2792 (1942).