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]

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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).

copper catalyst and at 50° with commercial cuprous chloride. No evidence for the higher boiling *cis* dichloride could be found. The earlier physical data,[4] along with those determined for the pure isomers obtained later in this study, are shown in Table I.

For the preparation of the dichlorides by replacement reactions, the isomeric chlorohydrins had to be prepared. The *trans*-chlorohydrin was obtained in satisfactory purity from the addition of hydrogen chloride to cyclohexene oxide.[5] The melting points reported for the *cis*-chlorohydrin, which was first prepared by Bartlett[5] in admittedly impure form, were −4, 21 and 31.5°.[9] In this work the Meerwein–Ponndorf–Verley reduction of 2-chlorocyclohexanone[9b] gave a mixture of *cis*- and *trans*-2-chlorocyclohexanols in which the latter predominated. With the method of Bartlett[5] for the separation of the two chlorohydrins the *cis* isomer was obtained as a hygroscopic solid, m.p. 36–37°, after repeated crystallization from pentane. Infrared spectra of the chlorohydrins are shown in Fig. 1.

The reaction of both isomeric chlorohydrins with thionyl chloride alone and that of the *cis* chlorohydrin with thionyl chloride–pyridine gave *trans*-1,2-dichlorocyclohexane as the only isolable dichloride (Chart I). These products and a sample of dichloride made by the addition of chlorine to cyclohexene were shown to be identical by mixed melting points. The reaction of the *trans*-chlorohydrin with thionyl chloride–pyridine gave a mixture of dichlorides boiling over a considerable range. Fractional distillation indicated that about one-third of this mixture was the *trans*-dichloride and the remainder the *cis* isomer (Table I and Fig. 1).

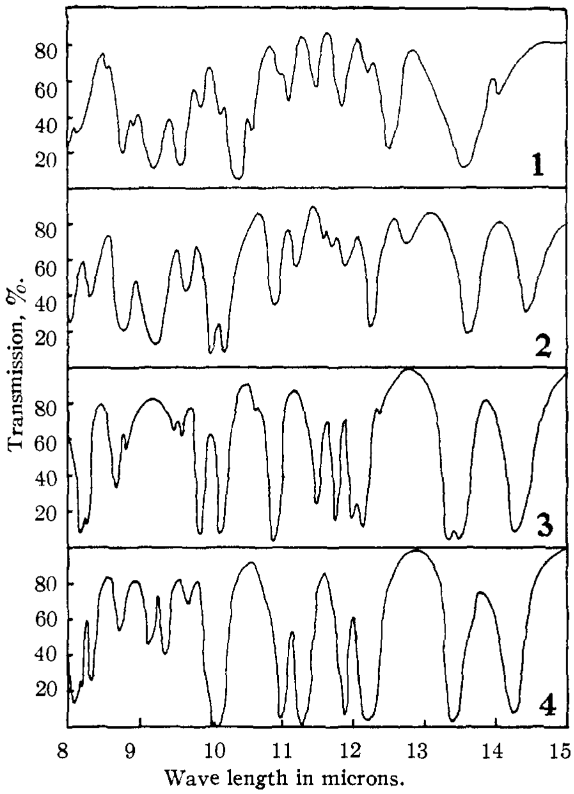

Fig. 1.—Infrared absorption spectra: 1, *trans*-2-chlorocyclohexanol; 2, *cis*-2-chlorocyclohexanol; 3, *trans*-1,2-dichlorocyclohexane; 4, *cis*-1,2-dichlorocyclohexane.

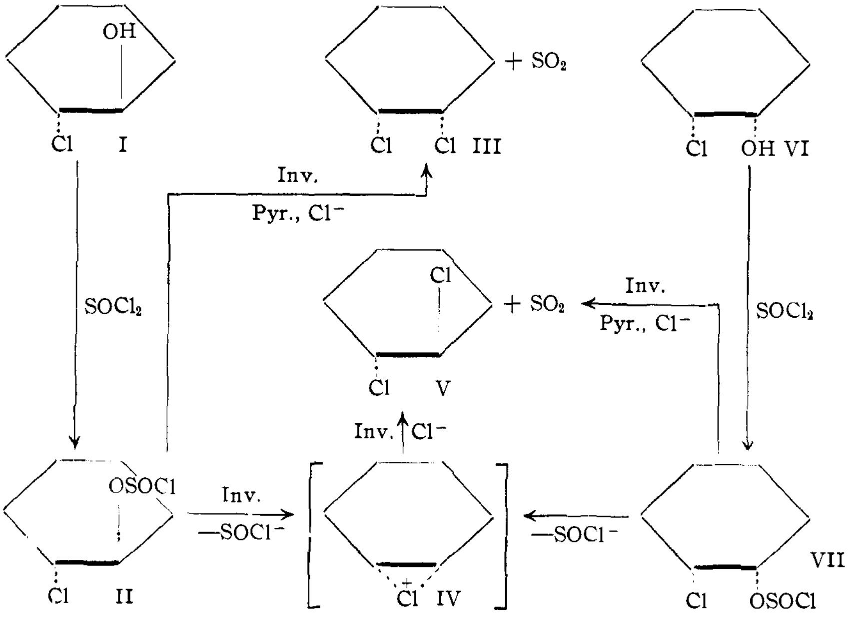

CHART I.

To confirm the structure and configuration of the two dichlorides the products of dehydrochlorination were examined. The *cis*-dichloride when refluxed with quinoline[10a] was rapidly converted to 1-chlorocyclohexene in 77% yield. The *trans*-dichloride under the same conditions reacted slowly to form a mixture of cyclohexadiene-1,3 (47%) and 1-chlorocyclohexene (40%). The identity of the chloroölefins obtained in these two reactions was established by (1) a comparison of physical properties including infrared spectra (Fig. 2) to those of an authentic sample prepared by the reaction of cyclohexanone with phosphorus pentachloride followed by treatment with quinoline,[10b] and (2) oxidation with potassium permanganate to adipic acid. The difference in rates of dehydrochlorination between the *cis*- and *trans*-1,2-dichlorides was further demonstrated by the extent of reaction in refluxing methanolic potassium hydroxide[11]; when 0.86 mole of hydrogen chloride had come from the

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[9] (a) M. Mousseron, R. Granger, F. Winternitz and G. Combes, *Bull. soc. chim. France*, 615 (1946); (b) T. Bergkvist, *Svensk. Kem. Tid.*, **59**, 215 (1947); *C. A.*, **42**, 5431 (1948); (c) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, THIS JOURNAL, **70**, 819 (1948).

[10] (a) This method of structure proof was used by W. Markownikoff, *Ann.*, **302**, 30 (1898), on the dichlorides from the substitutive chlorination of cyclohexane; (b) Markownikoff, *ibid.*, **302**, 11 (1898).

[11] D. H. R. Barton and E. Miller, THIS JOURNAL, **72**, 370 (1950), employed this reaction to characterize the isomeric dichlorides of cholesterol benzoate.

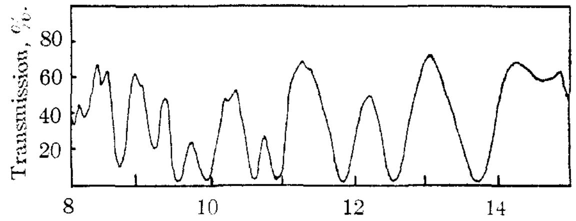

Fig. 2.—Infrared absorption spectrum of 1-chlorocyclohexene.

cis isomer, the *trans* gave only 0.01–0.02 mole. A reversed difference in reactivity was observed in the dechlorination reaction with zinc in acetic acid; cyclohexene was isolated upon prolonged refluxing of the *trans* dichloride while the *cis* isomer appeared entirely inert under identical conditions.

The evidence thus clearly confirmed the assignment of structures and configurations for both isomeric dichlorides. The facile *trans* elimination of hydrogen chloride from the 1,2-carbon atoms of the *cis* dichloride and the slow *cis* elimination from the corresponding atoms of the *trans* isomer were in accord with the findings of Cristol[12] on the rates of dehydrochlorination of the isomers of benzene hexachloride.[13] The difference in reactivity observed in the dechlorination reaction with zinc was also in agreement with accepted theory.[14]

As shown in Chart I, the *trans* chlorohydrin I was assumed to pass through chlorosulfinate II without change in configuration.[6] In the presence of pyridine a displacement of the chlorosulfinate group by chloride ion (from pyridine hydrochloride) accounted for the predominant inversion observed, resulting in the formation of the *cis*-dichloride III. In the absence of pyridine (and to a lesser extent in the presence), the neighboring chlorine atom in II, favorably located for participation, effected the displacement of the chlorosulfinate group with inversion and formation of the cyclic chloronium ion, IV.[6] The backside attack of chloride ion on one of the carbon atoms of IV gave rise to a second inversion, formation of the *trans*-dichloride V, and an over-all retention of configuration.

The neighboring chlorine atom in the chlorosulfinate VII, derived from the *cis*-chlorohydrin VI, was unfavorably located for participation in view of the restricted rotation about the carbon-to-carbon bonds in cyclohexane. The *trans*-dichloride V was obtained in the presence and absence of pyridine. A direct displacement with Walden inversion again appeared to be the probable mechanism at high chloride concentrations due to the presence of pyridine. However, two courses were possible to account for the result in the absence of pyridine. First, the same bimolecular displacement could have occurred as in the presence of pyridine, though at possibly lower rates. Secondly, a unimolecular dissociation of the chlorosulfinate group of VII, unaided by the neighboring chlorine atom, could have led to the cyclic intermediate IV without inversion. The ring opening attack of chlorine ion would then account for the single inversion observed. Since the latter course involves a racemized intermediate, IV, an experiment with an optically active *cis*-chlorohydrin might elucidate the mechanism in question.

Acknowledgment.—The authors wish to thank the Columbia-Southern Chemical Corporation, in whose laboratory this work was done, for making possible this investigation by a major grant to one of us (H. C. S.).

Experimental

The Addition of Chlorine to Cyclohexene in the Presence of Cuprous Chloride.—The following experiments were attempts to duplicate the work of Komatsu and Kawamoto.[1] Cupric nitrate was heated in an open beaker until completely decomposed into black copper oxide. Hydrogenation at 200° gave a finely divided copper powder. Forty grams (0.63 atom) was suspended in chloroform (400 g., b.p. 60.1–60.3°) and treated with chlorine (22.0 g., 0.31 mole) to make cuprous chloride. Cyclohexene (120 g., 1.43 moles, b.p. 82.5–82.9°, $n^{20}\text{D}$ 1.4467) was added and chlorine (100 g., 1.41 moles, 0.23 g./min.) bubbled in at 50 ± 2° with efficient agitation. A preliminary distillation at 7 mm. gave a chlorocyclohexene fraction (39–50°, 29.9 g., $n^{20}\text{D}$ 1.4860, yield 18%), a dichloride fraction (50–90°, 129 g., $n^{20}\text{D}$ 1.4909, yield 60%), and a polychlorocyclohexane residue (17.0 g., $n^{20}\text{D}$ 1.5225; yield as $C_6H_9Cl_3$, 13%). The dichloride was fractionated at 30 mm. through a 2.0 × 60 cm. Fenske column packed with 1/4" helices. Almost 90% of the material distilled at 89–90°, $n^{20}\text{D}$ 1.4903–1.4904; the residue weighed 3.0 g., $n^{20}\text{D}$ 1.4912. A second run at 6° with this catalyst and a third at 50° with Merck cuprous chloride gave similar results. The properties of the dichloride fractions are summarized in Table II.

TABLE II

PHYSICAL PROPERTIES OF *trans*-1,2-DICHLOROCYCLOHEXANE[a]

Source of material	B.p., °C. at 30 mm.	$n^{20}\text{D}$	M.p., °C.[b]
C_6H_{10} + Cl_2 (Cu), 50°	88–89	1.4903	−6
C_6H_{10} + Cl_2 (Cu), 6°	87–89	1.4903	−6.5
C_6H_{10} + Cl_2, Cu_2Cl_2, 50°	87–89	1.4896	−7
trans-Chlorohydrin + $SOCl_2$	64–65[c]	1.4904	−6.5
cis-Chlorohydrin + $SOCl_2$	64–65[c]	1.4900	−6.5
trans-Chlorohydrin + $SOCl_2$ + Pyr.	88–89	1.4902	−7
cis-Chlorohydrin + $SOCl_2$ + Pyr.	88–89	1.4904	−7

[a] Carroll, *et al.*,[3] give b.p. 78.1° (20 mm.), 99.0° (50 mm.); $n^{20}\text{D}$ 1.4902; m.p. 6.3°. [b] The method of Winstein (ref. 8) was used. Melting ranges were 0.5–1.5°. Mixed m.p. determinations on various pairs showed no depression. [c] At 9 mm. pressure.

***trans*-2-Chlorocyclohexanol (I).**—This was prepared by the addition of hydrochloric acid to an ether solution of cyclohexene oxide.[5] Material boiling 88–89° (20 mm.), m.p. 27.5–28.0°, $n^{20}\text{D}$ 1.4899 (by supercooling), was used in this work.

***cis*-2-Chlorocyclohexanol (VI).**—The method of Bergkvist[9b] was modified. A solution of 2-chlorocyclohexanone[15] (199 g., 1.5 moles) in 1 l. of anhydrous isopropyl alcohol was heated with commercial aluminum isopropoxide (193 g., 0.94 mole) in an ordinary distillation apparatus. About 60 g. of distillate at 60–65° was collected in the course of six hours. After removal of the alcohol at reduced pressure the

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(12) S. J. Cristol, THIS JOURNAL, **69**, 338 (1947).

(13) It appears significant that the yields of cyclohexadiene-1,3 and 1-chlorocyclohexene from the quinoline dehydrochlorination of the *trans*-dichloride were approximately equal. This may be due to a similarity in the rates of (a) *cis* elimination initiated at the hydrogen atom of a chlorine-holding carbon atom, this hydrogen having an acidic character due to the inductive effect of the chlorine, and (b) *trans* elimination involving the *trans* hydrogen atoms of the methylene groups adjacent to the substituted carbon atoms.

(14) S. Winstein, D. Pressman and W. G. Young, THIS JOURNAL, **61**, 1645 (1939).

(15) P. D. Bartlett and R. H. Rosenwald, *ibid.*, **56**, 1992 (1934).

residue was hydrolyzed with 1 l. of 6 *N* sulfuric acid. Distillation of the organic layer gave 163 g. of chlorohydrin mixture, b.p. 79–83° (13 mm.), $n^{20}D$ 1.4889. The separation of the isomeric chlorohydrins was done by stirring this distillate with 2 l. of 0.5 *N* sodium hydroxide at 10–15° for one hour. Ether extraction and subsequent distillation of the extract gave 49.0 g. of wet cyclohexene oxide, b.p. 40–50° (32 mm.), $n^{20}D$ 1.4503, and 52.1 g. of crude VI, b.p. 76–82° (13 mm.), which partially solidified in the receiver. After repeated crystallization from pentane (pract.) VI was obtained as a hygroscopic solid, m.p. 36–37°.

Anal. Calcd. for $C_6H_{11}OCl$: Cl, 26.3. Found: Cl, 26.3.

The α-naphthylurethan melted at 93° (cor.) after three recrystallizations from *n*-hexane; lit. 94°.[5]

Reaction of Chlorohydrins I and VI with Thionyl Chloride.—The chlorohydrin was refluxed with 100% excess thionyl chloride (colorless, b.p. 74.8–75.0° (632 mm.)) for seven hours. The products were isolated by direct distillation of the reaction mixture. The *trans*-chlorohydrin I in a 0.3-mole preparation gave a chlorocyclohexene boiling 33° (8 mm.), 5.4 g., $n^{20}D$ 1.4889, yield 16%; and *trans*-1,2-dichlorocyclohexane, 22.7 g., yield 49%. Its physical properties are shown in Table II.

Anal. Calcd. for C_6H_9Cl: Cl, 30.4. Found: Cl, 30.2. Calcd. for $C_6H_{10}Cl_2$: Cl, 46.3. Found: Cl, 46.1.

The *cis*-chlorohydrin VI in a similar experiment gave 18% of chlorocyclohexene (b.p. 33–34° (9 mm.)) and 21% of *trans*-1,2-dichlorocyclohexane (Table II).

Reaction of I and VI with Thionyl Chloride–Pyridine.—A solution of chlorohydrin (40.4 g., 0.3 mole) and dry pyridine (7.9 g., 0.1 mole) was added dropwise to thionyl chloride (71.4 g., 0.6 mole) followed by three hours of refluxing. The mixture was hydrolyzed with ice and the oil phase, diluted with methylene chloride, was washed with water. Distillation of the product from the *trans*-chlorohydrin I gave a mixed dichloride fraction boiling over a wide range: 20.9 g. at 60–73° (7 mm.), $n^{20}D$ 1.4954; Cl, 46.1; yield 46%. By fractionation in a 1.0 × 40 cm. Fenske column packed with $^1/_8$″ helices this was separated into the *trans*-dichloride (V), b.p. 88–89° (30 mm.) (Table II), and the *cis*-dichloride (III), b.p. 103° (30 mm.) (Table I). The *cis*/*trans* ratio was approximately 3/1.

The *cis*-chlorohydrin (VI) under identical conditions gave 14.7 g. (32%) of *trans*-dichloride (V) as the only isolable dichloride (Table II).

Dehydrochlorination of the Dichlorides (V) and (III) with Quinoline.—A mixture of 12.6 g. (0.082 mole) dichloride and 30 g. (0.23 mole) or quinoline was heated in an ordinary distillation apparatus. The *trans*-dichloride (V) allowed a slow distillation (b.p. 80–142°) in the course of three hours. Redistillation gave cyclohexadiene-1,3, 3.1 g. (47%), b.p. 80–85°, $n^{20}D$ 1.4742; maleic anhydride adduct, m.p. 146–147° (cor.)[16a,b]; and 1-chlorocyclohexene, 3.8 g. (40%), b.p. 140–142°, $n^{20}D$ 1.4810.

Anal. Calcd. for C_6H_9Cl: Cl, 30.4. Found: Cl, 30.4.

The *cis*-dichloride (III) under the same conditions dehydrochlorinated in 0.5 hour to give a 77% yield of 1-chlorocyclohexene, b.p. 140–141.5°, $n^{20}D$ 1.4809, d^{20}_4 1.0371; Cl, 30.5.

Oxidation of 1-Chlorocyclohexene.—To a solution of 0.45 g. of 1-chlorocyclohexene from III in 30 ml. of acetone was added dropwise with stirring a solution containing 1.23 g. of potassium permanganate and 0.5 g. of sodium carbonate in 50 ml. of water. The temperature rose to 35° during the one hour reaction time. The mixture was filtered, evaporated to about one half its volume, and acidified with hydrochloric acid. Further evaporation and cooling gave 0.15 g. of adipic acid, m.p. 152–153° (cor.) after two recrystallizations from hot water. The melting point on mixing with an authentic sample was not depressed.

1-Chlorocyclohexene from Cyclohexanone.—The procedure of Markownikoff[10b] was modified: to 20 g. (0.20 mole) of cyclohexanone was added in portions, with cooling in ice-water, 60 g. (0.29 mole) of phosphorus pentachloride. The decanted liquid was hydrolyzed with ice, the oil layer dissolved in methylene chloride and washed with sodium bisulfite solution and water. After removal of the solvent, the residue was heated with 50 g. of quinoline as before. Redistillation of the product gave 6.5 g. of 1-chlorocyclohexene, b.p. 140–141.5°, $n^{20}D$ 1.4810, d^{20}_4 1.0367; Cl, 30.4.

The infrared absorption spectrum for 1-chlorocyclohexene thus prepared is shown in Fig. 2. The products from the reaction of III and V with quinoline gave spectra indistinguishable from this.

The Reactivity of Dichlorides (III) and (V) toward Methanolic Potassium Hydroxide.—Weighed samples (0.05–0.10 g.) of dichloride were refluxed for one hour with 25 ml. of 1 *N* methanolic potassium hydroxide. The amount of potassium chloride formed was determined by Volhard titration. The *cis*-dichloride (III) showed 86% reaction while the *trans*-dichloride (V) reacted only to the extent of 1–2%. These results are expressed on the basis of the elimination of one equivalent of hydrogen chloride.

The Reaction of Dichlorides (V) and (III) with Zinc.—A solution of *trans*-dichloride (V) (30.6 g., 0.20 mole) in 100 ml. of glacial acetic acid was heated with powdered zinc (20.7 g., 0.32 atom) in a packed distillation apparatus with variable take-off. A two phase distillate, b.p. 80–85°, was collected in the course of six hours. The product was neutralized to phenolphthalein and steam distilled. The oil layer of the distillate was separated and dried. Distillation gave 4.9 g. of cyclohexene, b.p. 81–82°, $n^{20}D$ 1.4478. About one-half of the starting material (V) was recovered unchanged from the still residue.

When *cis*-dichloride (III) was subjected to identical conditions the vapor temperature remained above 110° throughout the heating period. About 80% of III was recovered unchanged as shown by the following properties: $n^{20}D$ 1.4965; Cl, 46.2.

Infrared Spectra.—A Beckman IR2 infrared spectrophotometer with sodium chloride optics was used. The compounds in Fig. 1 were run in carbon disulfide solution (10 g./l.), those in Fig. 2 without a solvent.

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[16] (a) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, THIS JOURNAL, **58**, 146 (1936), report for cyclohexadiene-1,3, b.p. 80.3°, $n^{20}D$ 1.4740; (b) O. Diels and K. Alder, *Ann.*, **460**, 115 (1928), give the melting point of the maleic anhydride adduct as 147°.