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Stereochemistry of the reduction of tertiary cyclohexyl halides by chromium (II) complexes

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STEREOCHEMISTRY OF THE REDUCTION OF TERTIARY CYCLOHEXYL HALIDES BY CHROMIUM(II) COMPLEXES

By

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INTRODUCTION AND HISTORICAL

I. Cr(II) Reductions

The first reduction of an organic compound with a chromium(II) salt was reported in 1916.[1] In an inert atmosphere chromium(II) chloride reduced both maleic and fumaric acids to succinic acid, and chromium(II) hydroxide reduced cinnamic acid to β-phenyl propionic acid under similar conditions. Infrequent use of chromium(II) salts in the next forty years revealed that other types of organic compounds, such as aromatic aldehydes, β-unsaturated ketones, and benzal acetophenone were reduced to bimolecular products.[2] Such results suggested a free radical intermediate.

In 1957, Anet and Leblanc[3] presented the first evidence for an intermediate alkyl chromium complex, $[Cr(H_2O)_5CH_2C_6H_5]^{2+}$. The complex was prepared by reaction of benzyl halides with aqueous chromium perchlorate in perchloric acid. A visible spectrum of the yellow to brown-red (the color was concentration dependent) solution revealed a low intensity maximum at 540 mμ and a high intensity maximum at 358 mμ. The intermediate decomposed in 5 days in the absence of oxygen to yield bibenzyl, but decomposed in the presence of oxygen to give benzaldehyde.

Further evidence of a free radical intermediate was demonstrated by Anet[4] in 1959 when he found the order of reduction of chloro-substituted methanes by $Cr(ClO_4)_2$ to be the following:

$$CCl_4 > CHCl_3 > > CH_2Cl_2 \sim CH_3Cl$$

seconds minutes

Anet proposed that the first step in the reduction was a direct transfer of a chlorine atom to chromium to form the free radical:

$$CHCl_3 + Cr^{+2} + 5\ H_2O \longrightarrow [Cr(H_2O)_5Cl]^{2+} + \cdot CHCl_2$$

The fact that CCl_4 was reduced most easily and CH_3Cl least, was consistent with the knowledge that chlorine substitution stabilizes a free radical.[5]

Anet also found spectroscopic evidence of an intermediate alkyl chromium complex. The following mechanism was suggested to account for the complex:

$$CHCl_3 + Cr^{2+} + 5\ H_2O \xrightarrow{1} [Cr(H_2O)_5Cl]^{2+} + \cdot CHCl_2$$

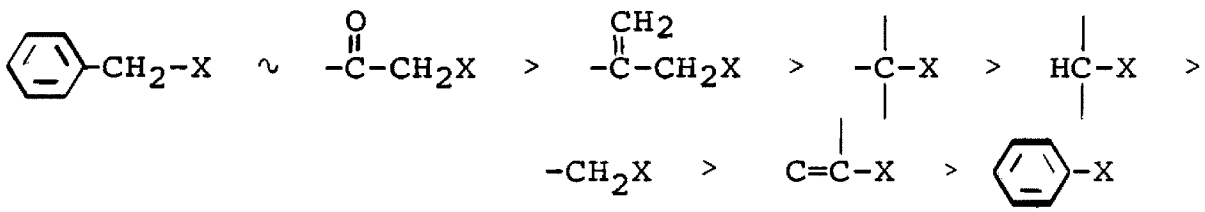
$$\cdot CHCl_2 + Cr^{++} + 5\ H_2O \xrightarrow{2} [Cr(H_2O)_5CHCl_2]^{2+}$$

If the second step is fast, less dimerization will be observed.

Kochi and Rust[6] found in 1961 that chromous sulfate reacted with phenyl-t-butyl hydroperoxide to form an

insoluble benzylchromous ion identical spectroscopically to that found by Anet.[4] Its decomposition products were also the same.

Two years later, Castro and Kray[7] suggested that the rate-determining step in the chromium(II) reductions was the attack of the metal ion on the alkyl halides. They based this suggestion on the order of reactivity of the following halides:



(X = I > Br >> Cl)

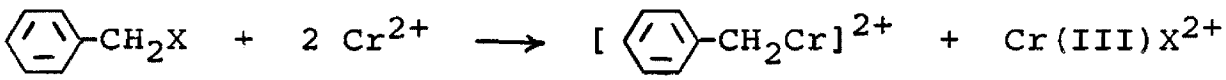
They believed that the course of the chromium(II) reductions of alkyl halides was determined by the stability of the alkyl radical which was characterized by the amount of dimer product.

In 1964, Kochi and Davis[8] proposed that the transformation of benzyl chloride to the chromous complex consisted of two consecutive reactions involving an intermediate benzyl radical:

$$C_6H_5CH_2X + Cr^{2+}(aq) \xrightarrow{slow} C_6H_5CH_2\cdot + CrX^{2+}(aq)$$

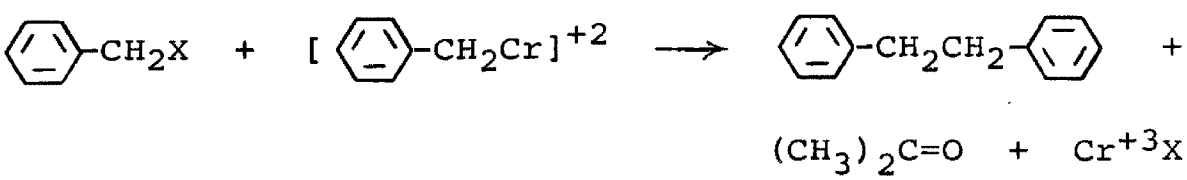
$$C_6H_5CH_2\cdot + Cr^{2+}(aq) \xrightarrow{fast} [C_6H_5CH_2Cr]^{2+}(aq)$$

They believed the above two-step sequence was required since the stoichiometry was found to proceed according to the following equation,

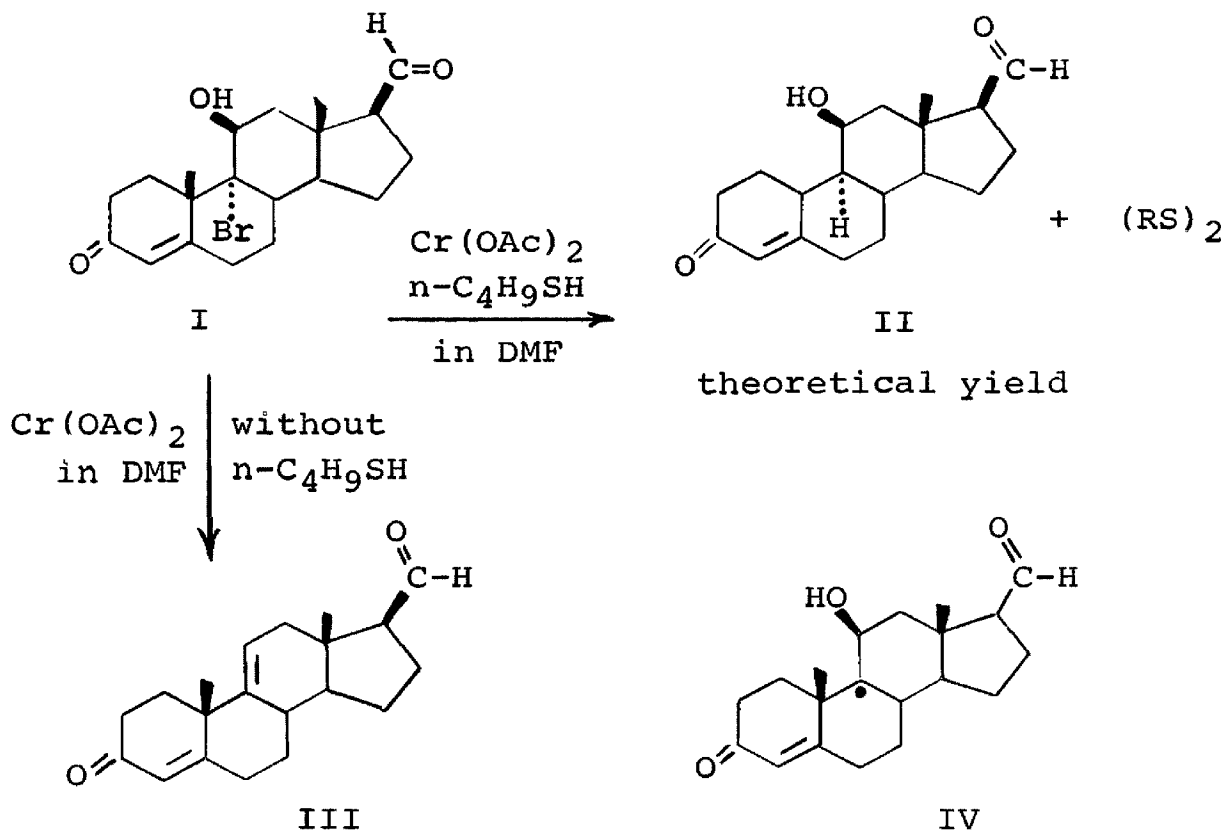


and the rate of formation of $[C_6H_5CH_2Cr]^{2+}$ was found to be first order in both organic halide and chromous ion.

At this time, further attempts to firmly establish the existence of a free radical intermediate were reported. Slaugh and Raley[9] found for diphenylmethyl chloride, that the free radical, if formed, must have a short half-life, since the addition of a good hydrogen transfer agent, such as ethyl thioglycolate, did not appreciably increase the yield of diphenylmethane. Kochi and Davis[8] attempted to trap the benzyl free radical with butadiene and acrylonitrile, but found that these reagents reacted with the benzyl-chromous complex. A year later Kochi and Buchanan[10] found dimeric products to be formed from the reaction of unconsumed benzyl halide with the organochromium intermediate:



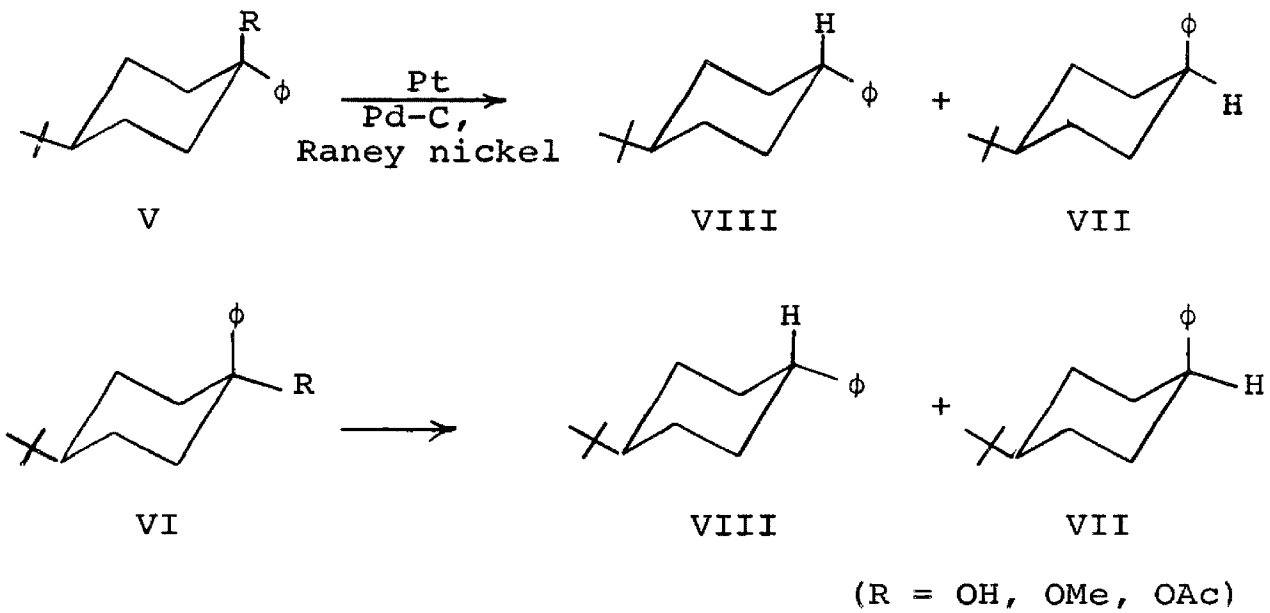
Barton, et al.,[11] demonstrated in 1966, what they thought to be conclusive evidence for the existence of a radical intermediate in the conversion of progesterone bromohydrin to 11-β-hydroxy progesterone by n-butyl mercaptan and chromous acetate in dimethyl formamide.



Other hydrogen donors such as 1,4-cyclohexadiene and cyclopentadiene, which were not regarded as capable of protonolyzing a carbon-chromium bond were investigated. In all cases, compound II was the major product. These results were regarded as direct evidence for free radical intermediate IV.

II. Stereochemistry of Reductions of 4-t-Butylcyclohexyl Ring Systems

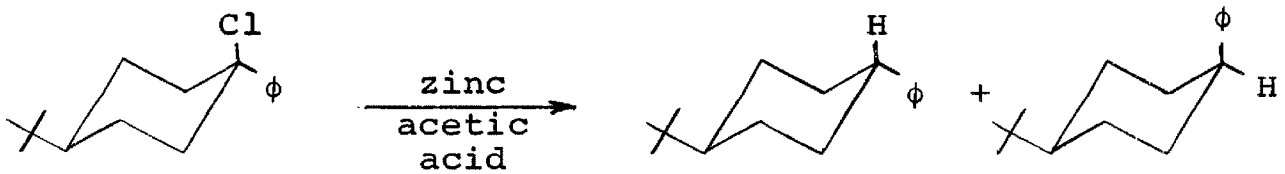
Other workers have investigated the stereochemistry of reductions involving 4-t-butylcyclohexyl ring systems. Garbisch, Schreader, and Frankel[12] studied the hydrogenolysis of compounds (V) and (VI):



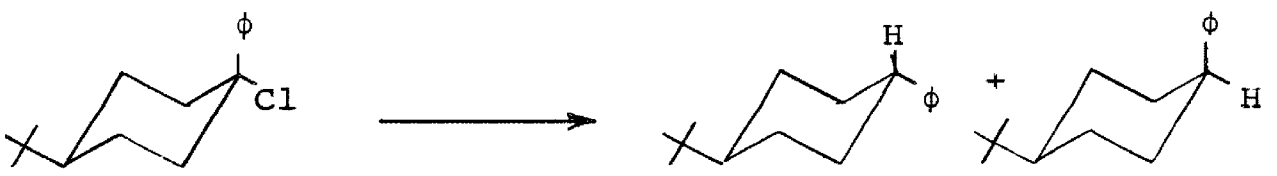
with platinum, paladium on carbon, and Raney nickel. They found stereoconvergent hydrogenolysis of (V) and (VI) led to 83 ± 7% cis isomer (VII). They suggested that hydrogenolysis could proceed either through a) a common intermediate or b) (V) and (VI) proceed with about 83% retention or inversion, respectively. Alternative (b) was disproved by deuterogenolysis of (V) and (VI), (R=OH) with DOAc over Pd-C.

They believed that a free radical equilibrium favored the cis-monoadsorbed substrate where the catalyst surface would be bonded equatorially. But the results directed them to the conclusion that the hydrogenolysis must occur by some direct substitution process.

Chadha[13] has found that the reduction of IX and X with zinc in acetic acid gave the same ratio of isomers XI and XXII.



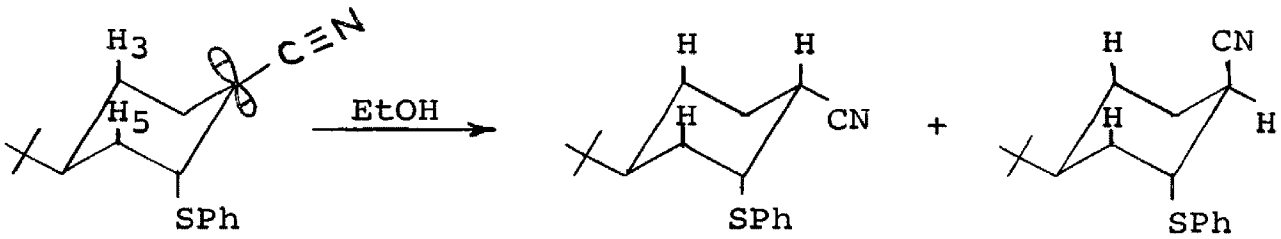
IX XI, 30% XII, 70%



X XI, 30% XII, 70%

Chadha proposed an anion as a reasonable intermediate to account for the reduction products, where protonation has taken place from the least hindered[14] equatorial side.

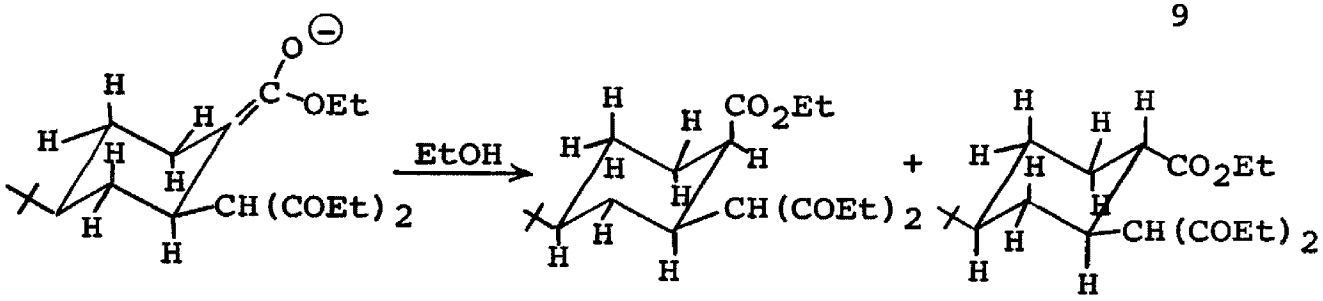
Abramoritch, et al.,[15] have investigated the protonation of 2-substituted cyclohexyl anions. They found that the addition of thiophenoxide ion to 4-t-butyl-1-cyanocyclohexene in ethanol gave a mixture of products, XIV and XV, in which the thiophenoxy group was axial.



XIII XIV XV

Under conditions of kinetic control (16 hours), adducts were formed in the ratio XIV:XV = 52.5:1. Under conditions of thermodynamic control (90 hours) the equilibrium mixture contained XIV and XV in the ratio 1.97:1. XIV Was the main product in both cases, which indicates that protonation took place from the axial side. This is understandable in terms of the greater steric hindrance by the axial thiophenoxy group to approach of a proton donor from the equatorial side, than by the 3 and 5 protons to its approach from the axial side.

To support this explanation, they next added diethyl sodiomalonate to ethyl 4-t-butylcyclohexene-1-carboxylate in alcohol solution to give enolate anion XVI.



XVI XVII XVIII

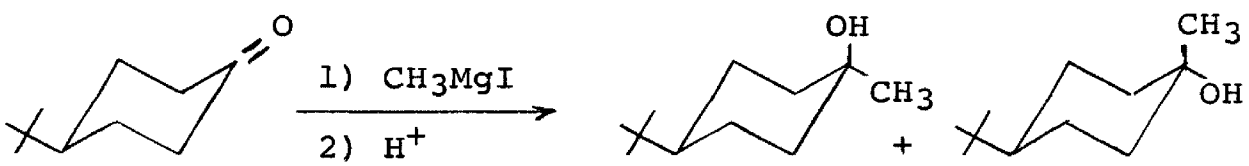
Under conditions of kinetic control, XVII was the main product, but under thermodynamic control conditions XVIII was the main product, as expected. They concluded that equatorial approach was least hindered for small proton donors, despite the presence of the bulky equatorial substituent.

The mechanism of alkyl halide reductions by chromium(II) salts and the stereochemistry of the protonolysis of cyclohexyl radicals and anions remains inconclusive.

The purpose of this research was to synthesize tertiary cyclohexyl halides, study their reduction by a chromous perchlorate--ethylene diamine complex, and to determine the stereochemistry of the reaction.

RESULTS AND DISCUSSION

The two isomers of 4-t-butyl-1-methylcyclohexanol (XX and XXI) were prepared from 4-t-butylcyclohexanone (XIX) and methylmagnesium iodide by a Grignard reaction:

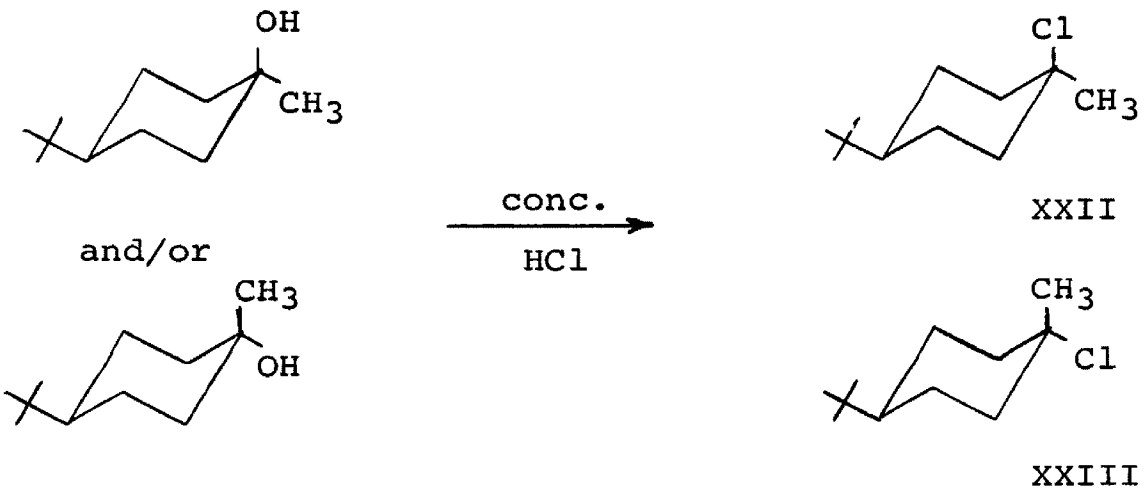


XIX XX XXI

This method yielded a 50:50 mixture of alcohol isomers. Chadha[13] had successfully converted cis- and trans-4-t-butyl-1-phenylcyclohexanols to chlorides with retained configuration by passing dry hydrogen chloride gas through a cis or trans alcohol, which was dissolved in pentane and kept in an acetone-dry ice bath.

To attempt this method, the cis XXI and trans XX alcohols were separated by column chromatography according to the method of Allinger and Liang.[17] The separation was successful, but the fractions obtained were from different eluant mixtures than reported. We found that the alcohols were not soluble in pentane or methylene chloride at -70°. At 0° the alcohols were soluble, but no chlorides were found using this method.

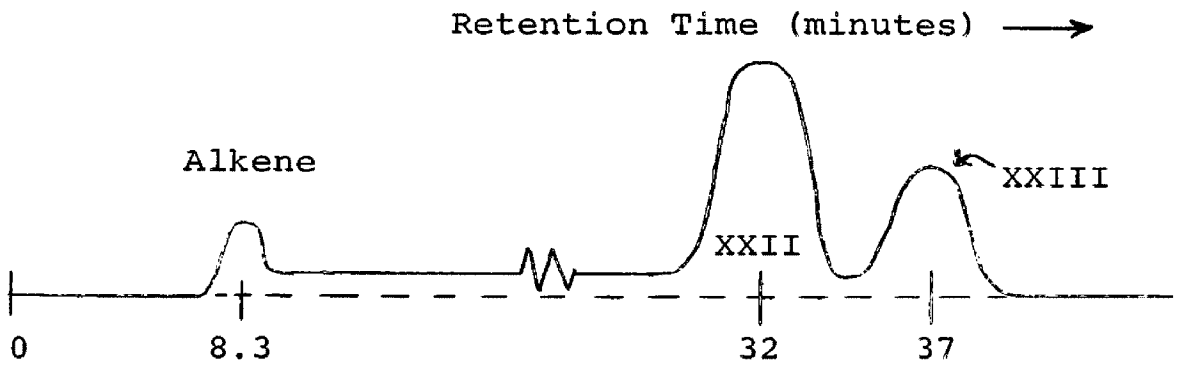
Brown, Fletcher, and Johannesen[28] had successfully prepared tertiary chlorides by adding a tertiary alcohol to a five-fold excess of concentrated hydrochloric acid in a separatory funnel. We found this method to be successful. Whether the starting alcohol was pure cis XXI, pure trans XX, or a mixture of the two, the isomer ratio of the chlorides formed was always XXII:XXIII = 3.83:1.



Allinger and Liang[17] were able to separate XXII and XXIII by gas chromatography. We attempted this method and several problems became apparent. Separation of the cis XXIII, and trans XXII chloride was accomplished by preparative gas chromatography, but from the 4-t-butyl-1-methylcyclohexene content found in both isomer collections, it was clear that an elimination reaction was occurring both on the wall of the column and on the detector

surface. The alkene peak, which had a much shorter retention time than either chloride peak (8.3 min vs. 32 min) would not return to the baseline of the recorder chart paper. On the other hand, after both chloride peaks had been recorded, the recorder pen returned to the original baseline (See Diagram I.)

DIAGRAM I



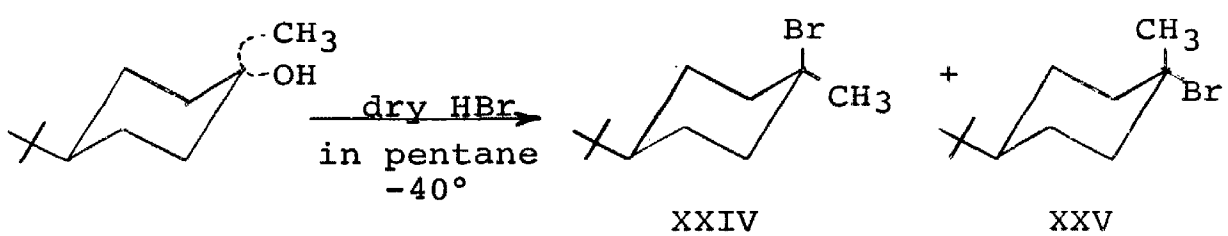
Certainly, the continual elimination of hydrogen chloride from the chlorides on the column walls would explain this phenomenon. This circumstance also made isomer ratio analysis impossible with a Disc integrator and it was necessary to cut out and weigh the recorded peaks to compare isomer ratios.

Allinger and Liang[17] found that the trans chloride XXII was the major product in the chlorination of the corresponding alcohols and had a shorter retention time than the cis XXIII chloride. The infrared spectra gave confirmatory evidence for the chloride structures.

assigned. They found the carbon-chlorine stretching frequency of an equatorial chlorine atom to be higher than the axial carbon-chlorine stretching frequency. Although the potassium bromide optics necessary to examine the region of the axial-chlorine bond (ν555 cm^{-1}) were not available, the band found at 668 cm^{-1} for the peak collected at 37 min was in close agreement to the 670 cm^{-1} band found by Allinger and Liang for a tertiary carbon-chlorine bond in an equatorial position. We felt this evidence was conclusive for the structure assignments.

The nuclear magnetic resonance spectra of the two halides (XXII, XXIII) were consistent with the structures assigned. The suspected chemical shift difference between the axial (XXIII) and equatorial (XXII) methyl groups was not found, and the spectra of the isomers were essentially identical.

The cis- and trans-4-t-butyl-1-methylcyclohexyl bromides (XXIV and XXV) were prepared from the corresponding alcohols by the method of Chadha,[13] using dry hydrogen bromide gas.



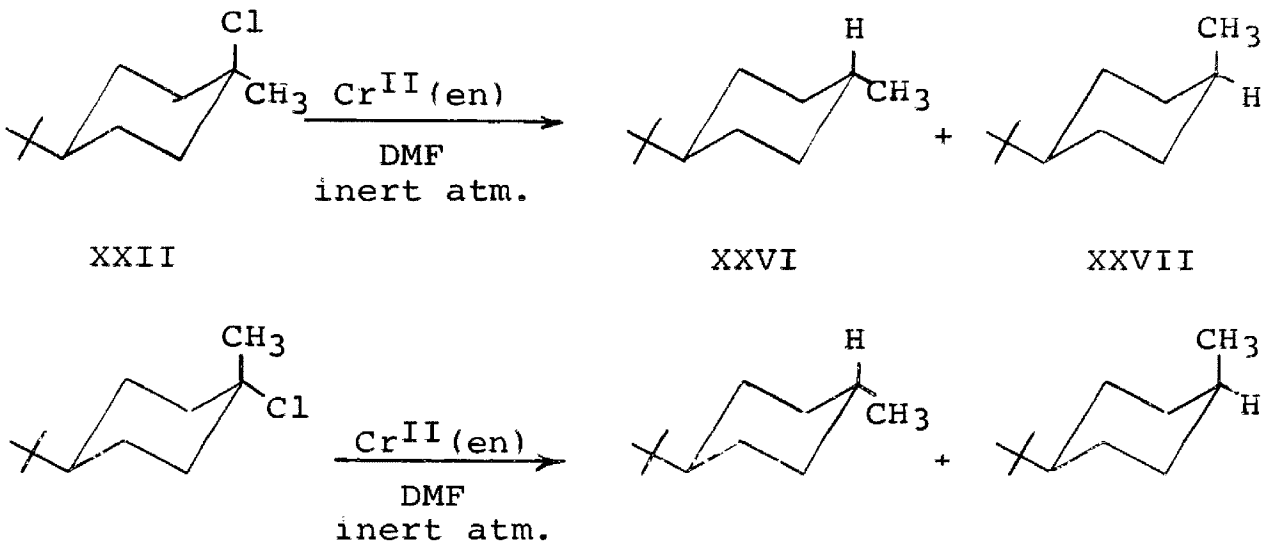
XXIV XXV

Although the alcohols were not soluble in pentane at -78°, they were soluble at -40°, and the reaction was partially successful with an 80% yield of bromide isomers. However, the reaction was not stereospecific under these conditions, for both the cis and trans alcohols gave 87% XXIV and 13% XXV.

Infrared data from the literature regarding cyclohexyl tertiary bromides is nil, and the only basis of structure assignment is that the cis-trans conformational energy difference of bromine is less than for methyl (0.4 compared to 1.8 kcal/mole).[29] Therefore we would expect the methyl group to be predominantly equatorial. We would expect the trans bromide to have a shorter retention time than the cis bromide, in correlation with chromatographic results found for the trans and cis chlorides.

The reduction of the 4-t-butyl-1-methylcyclohexyl chlorides was accomplished by Cr(II)-(en) in dimethyl formamide (DMF) at room temperature under a nitrogen atmosphere.

The ratio of the reduction products XXIV and XXVII was determined by gas chromatography. Retention times were comparable to synthesized cis- and trans-4-t-butyl-1-methylcyclohexanes (see Experimental).



Results are summarized in Table II.

TABLE II

Stereochemistry of Cr(II)-(en) Reductions

Red. No	4-t-Butyl-1-methyl cyclohexyl halide	% XXVI (trans)	% XXVII (cis)	% Yield
1	98% trans chloride (XXII)	41.0	59.0	82
2	81.3% trans chloride (XXII)	46.0	54.0	40.4
3	81.3% trans chloride (XXII)	41.9	58.1	17.8
4	[a]98.0% trans chloride (XXII)	47.8	52.2	100.0
5	84.7% cis chloride (XXIII)	35.5	64.5	36.0
6	87.0% trans bromide (XXIV)	38.5	61.5	22.5

[a]Internal standard was added to reaction mixture before the products were extracted with hexane.

The experiments of Barton, et al.[11] that demonstrated evidence of a radical intermediate utilized

hydrogen donor reagents such as 1,4-cyclohexadiene, cyclopentadiene, and n-butyl mercaptan to trap the radical. Since our results were not indicative of a free radical intermediate, an experiment was executed to demonstrate or disprove existence of a free radical. n-Butyl mercaptan was added in excess to the solution of DMF, ethylene diamine, and $Cr(ClO_4)_2$; compound XXII was then added to this mixture. Results are listed below in Table III.

TABLE III

4-t-Butyl-1-methyl-cyclohexyl chloride	% XXVI trans	% XXVII cis	Yield
98% trans (XXII)	92.0	8.0	90%
92% cis (XXIII)	90.0	10.0	96%

Early reductions of alkyl halides with chromous salts were restricted to rather reactive halides such as allylic, benzylic, α-halocarbonyl and α-halocyano compounds. Kochi and Mocadlo[30] discovered that complexing Cr(II) ion with ligands such as ethylene diamine (en) greatly enhanced the ability of the chromous salt to reduce even primary alkyl chlorides to alkanes. They found, for example, that n-butyl chloride is reduced to n-butane by Cr^{II}(en) complex in 20-30 minutes at room temperature

in aqueous DMF or DMSO solutions. The reaction required more than 12 hours without the complexed ligand. Since we were using a chloride, the least reactive organic halide, we complexed the chromous salt with ethylene diamine in all our reductions.

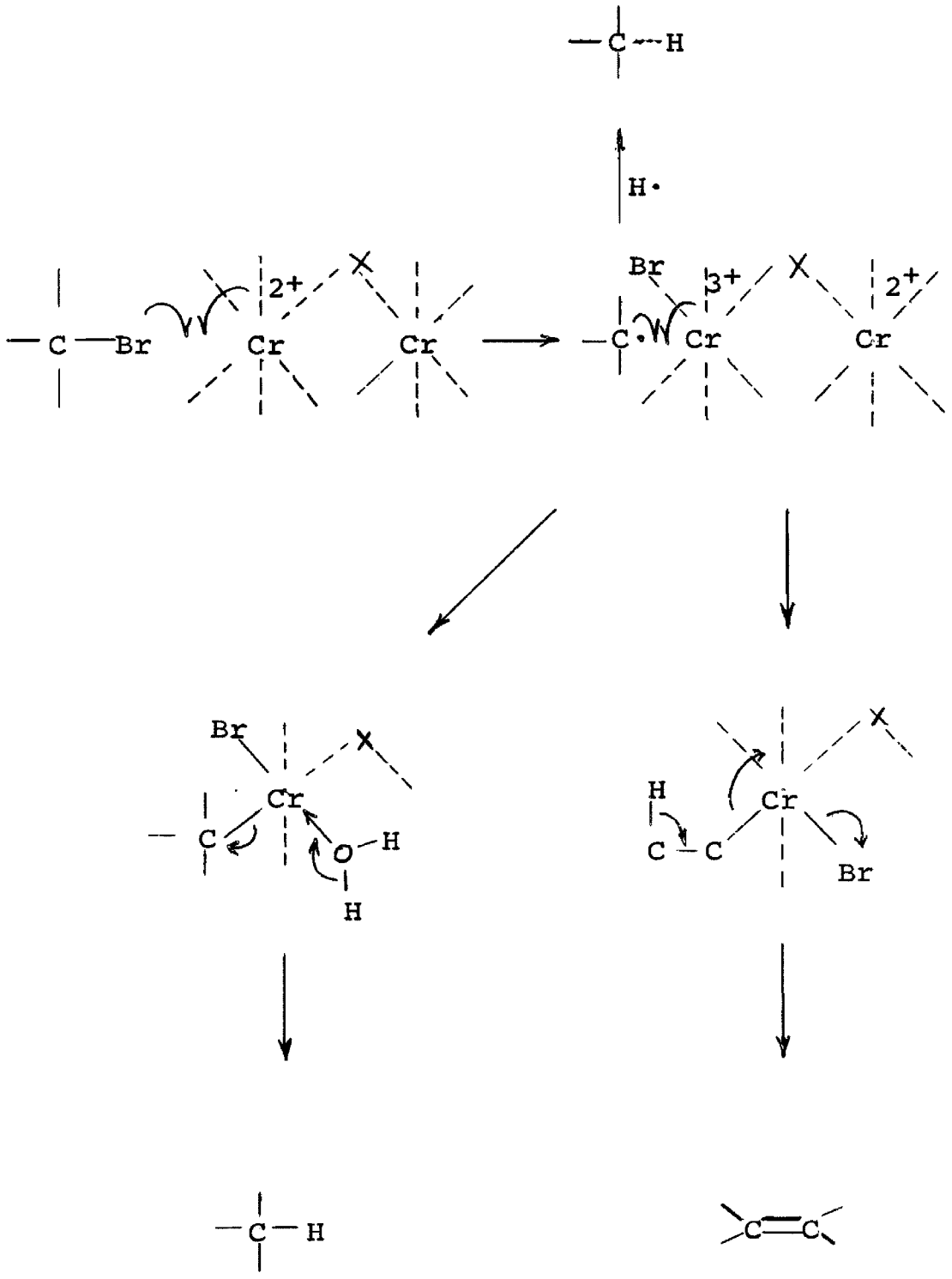
We found our results to be consistent with the proposed free radical mechanism[31] in Scheme I.

This mechanism shows the first step in the reduction of an alkyl halide as the attack of the chromium(II) ion on the halogen atom. The second stage involves a migration of the alkyl residue to form a new carbon-chromium bond. This process is accompanied by a one-electron transfer from a second chromium(II) ion through a bridging anion. Decomposition of this intermediate by elimination, protonolysis, or attack on unchanged organic halide can account for the majority of products.

Our results indicate that the reduction occurs with some stereospecificity. The trans chloride XXII was reduced to a 59:41 cis:trans product ratio and the cis chloride XXIII was reduced to a 65:35 cis:trans product ratio.

Such results denote some stereospecific retention for the reductions. Either a) the intermediate radical formed by the first one-electron transfer is not entirely free of the Cr^{II}(en) complex or b) formation of the carbon-chromium bond occurs with partial stereospecificity.

SCHEME I



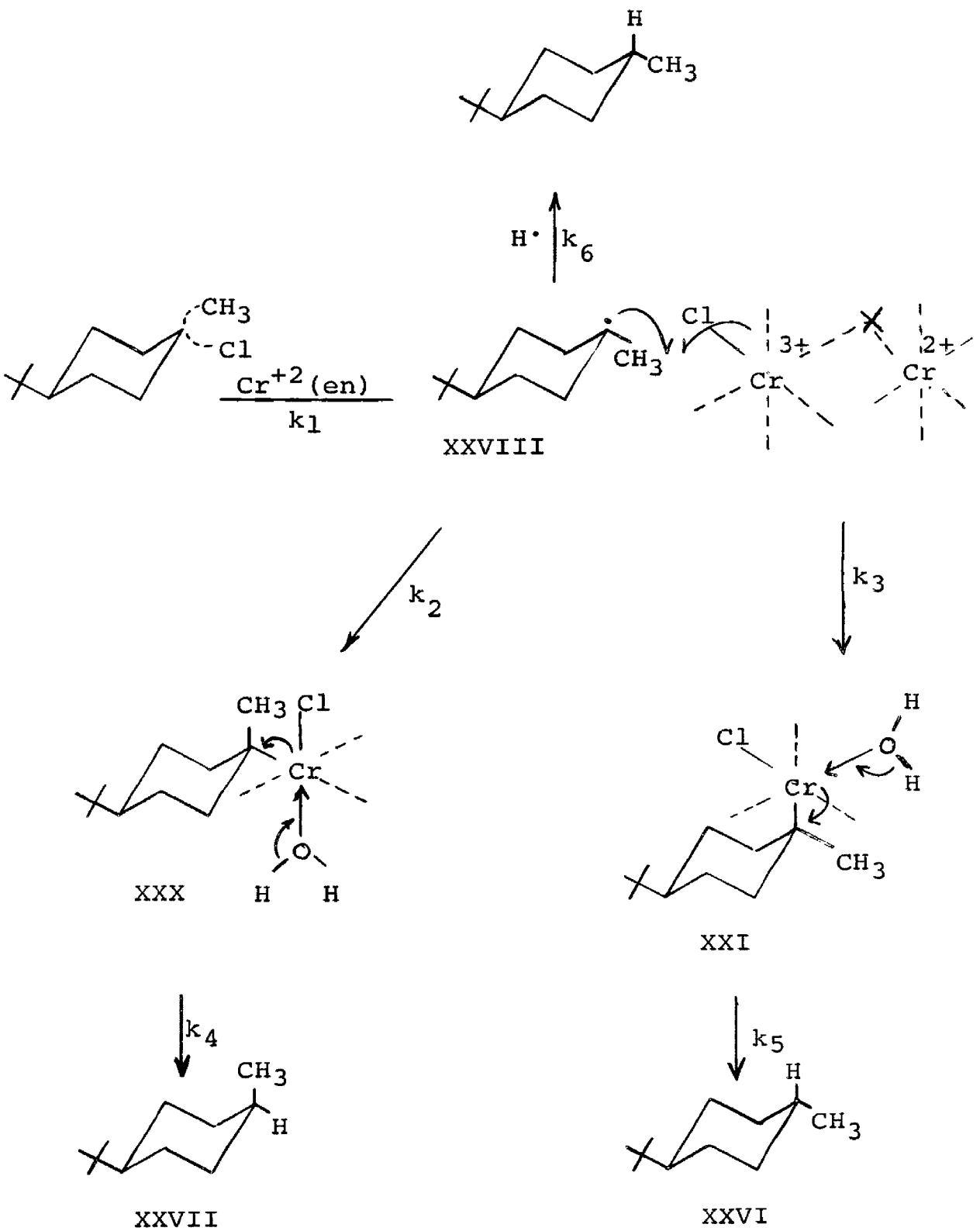
n-Butyl mercaptan, a well-known free radical trapping reagent, was added to the reduction reaction mixture. If the radical were truly free, we should expect protonolysis of the free radical by mercaptan to be completely non-stereospecific. We found instead that the reduction of trans chloride XXII with n-butyl mercaptan present occurred with retention of configuration, but that reduction of cis chloride XXIII with n-butyl mercaptan present occurred with inversion of configuration to give trans product XXVI. (See Table III.)

It could be argued that mercaptans are capable of protonolyzing the organochromium intermediate through the phenomenon of nucleophilic assistance. However, Barton, et al.[11] showed this did not occur under reaction conditions similar to ours. Indeed, if nucleophilic assistance by mercaptan were taking place, we should expect an increase in product yield, but little difference in product isomer ratios.

Alternative b) would predict that reduction of either cis or trans chloride should result in predominant formation of the cis hydrocarbon product XXVII.

A general reaction pathway is hypothesized in Scheme II. Scheme II augments Scheme I by showing the stereochemistry of the mechanism. Initial formation of the free radical is supported by the reactions where n-butyl mercaptan was added before reduction by Cr(II)

SCHEME II



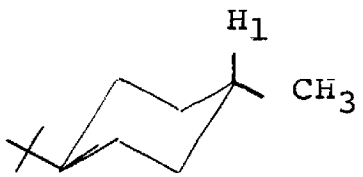
occurred. Both cis and trans chlorides gave a large excess of the trans product XXVI (91 ± 1%). To explain these results, one must suggest that the free radical intermediate is not planar, but favors the equatorially situated methyl group and that the hydrogen transfer from the mercaptan takes place axially. Indeed, Jacobus and Pensak[34] have given evidence that confirms a cyclopropyl radical existing at least transiently as a non-planar entity capable of being trapped.

In the absence of the hydrogen donor reagent, a one-electron transfer occurs from a second chromium(II) ion through a bridging anion. This step can account for the stereospecificity involved in the reductions, if we compare the conformational energies of the methyl group and the chromous complex. The conformational energy of the methyl group is 1.8 kcal/mole,[29] but the conformational energy of the chromous ion, complexed with at least six ethylene diamine ligands and bridged with another chromous complex, should be considerably greater. Thus, we should expect k_2, where the chromium-carbon bond forms at the least hindered equatorial position, to be greater than k_3. However, the exclusive formation of an equatorial carbon-chromium bond would not be expected. The carbon-chromium bond length would be long enough that the steric hindrance by H_3 and H_5 of an axial carbon-chromium bond should not be as important as the steric hindrance by H_3 and H_5 of

a t-butyl group which is a smaller substituent, but forms a shorter carbon-carbon bond.

It was noticed that allowing the reaction mixture to stand for different lengths of time resulted in different product ratios. From Table II, for example, reduction 1 of the trans chloride (XXII) gave a different product isomer ratio than reduction 4 of the same chloride. Reduction 4 was stopped much sooner than reduction 1 (5 hr vs. 12 hr). This would indicate a) that some isomerization of hydrocarbon is occurring in solution or b) that alkene is being reduced by the Cr^{II}-(en) complex.

Alternative a would not seem reasonable for our compound since H_1 is not an acidic hydrogen and our reaction conditions are not basic.



It is possible to reduce olefins to saturated compounds[31] by using chromous salts complexes with ligands, but the only olefins reduced were conjugated to a carbonyl or an aromatic ring. It therefore seems highly unreasonable that the olefin is being reduced, but nonetheless a future experiment is planned to confirm this possibility.

In conclusion, this study has shown that the free radical mechanism proposed by Barton[11] can account for the results of the Cr^{II}-(en) reductions. The stereochemical studies reported here enlarge the scope of the mechanism, and show that the Cr^{II}-(en) reductions occur with some stereospecificity. Different product ratios were obtained by adding n-butyl mercaptan to the reaction mixture.

EXPERIMENTAL

Materials. Electrolytic grade chromium metal (99.996%) was supplied by the Varlacoid Chem. Co. The dimethyl formamide was used as received from Baker. Baker also supplied the ethylene diamine which was distilled at 116°/580 mm (lit.[18] 116.1°C). Iodomethane and 4-t-butylcyclohexanone were obtained from Eastman Organic Chemicals and Dow Chemical Co., and were used without further purification.

Instrumental Data. All infrared spectra were obtained in a Nujol mull or neat on a Beckman Model IR-5A or on a Beckman Model IR-7 recording spectrophotometer. For gas chromatographic analyses, a Varian Aerograph Model A-700 chromatograph and Sargent Model SR recorder containing a Disc Integrator assembly were used with four standard columns. Column A was a 5' x 1/4" ss, 50/80 Poropak Q used at 100° and 150 ml/min flow; column B was a 20' x 3/8" ss, 30% DEGS on 45/60 Chrom W used at 110° and 200 ml/min flow; column C was a 10' x 1/4" ss, 5% QF-1 on 60/80 Chrom G used at 67° and 50 ml/min flow; column D was a 10' x 1/4" ss, 5% DEGS on 60/80 Chrom G used at 88° and 120 ml/min flow.

Nuclear magnetic resonance spectra were obtained with a Varian HA-60 instrument.

cis- and trans-4-t-Butyl-1-methylcyclohexanol (XX and XXI).--The crude alcohol mixture was prepared from the reaction of 4-t-butylcyclohexanone with methylmagnesium iodide as described before.[17] The yield was 89%. The crude alcohol mixture, XX and XXI, was analyzed on column A and the cis:trans isomer ratio found to be 1:1.21. The trans isomer peak occurred at 7.25 minutes and the cis isomer peak at 10.25 minutes.

Separation of XX and XXI was accomplished by dissolving 12.8 g of the alcohol mixture in hexane and chromatographing on 200 g of Alcoa F-20 chromatographic grade alumina. Hexane:benzene mixtures (50:50) eluted alcohol I (4.46 g), m.p. 66-67° (lit.[19] 70-71°). Ether-acetone mixtures (80:20) eluted alcohol II (3.62 g), m.p. 96-97° (lit.[19] 98-99°).

Further evidence for the alcohol structures was provided by n.m.r. The spectrum of the hydroxy hydrogens of the alcohol mixture in DMSO-d_6 was compared to that reported in DMSO.[20] The spectrum of the trans alcohol was also taken under the same conditions. Results are shown in Table I.

TABLE I

	τ (-OH)[a]	reported τ (-OH)
Alcohol mixture	6.30, 5.92	6.24 (axial), 5.87 (equat.)
trans-alcohol	6.30	6.24

[a] τ values of ca. 0.1 molar solution in $(CD_3)_2SO$

4-t-Butyl-1-methylcyclohexene.--To the crude alcohol mixture, XX and XXI, (13.75 g, 0.081 moles) was added 1.5 g of p-toluenesulfonic acid in 50 ml of dry benzene. After refluxing 18 hours, the reaction mixture was washed successively with water, 5% sodium bicarbonate, water, and then dried over anhydrous magnesium sulfate. Distillation of the product mixture, in vacuo, gave the olefin (6.25 g), b.p. 43-45°/8 mm (lit.[21] 74-75°/11 mm). An infrared spectrum of the olefin showed peaks at 800, 910, and 1050 cm^{-1}.[22] An n.m.r. spectrum (carbon tetrachloride solvent) showed a multiplet at 5.20 δ, singlets at 1.53 δ ($-CH_3$) and at 0.80 δ (t-butyl) and multiplets in the 1.0-2.0 δ ($-CH_2-$) region.[23] A good integration was not possible due to overlapping of the methyl and t-butyl singlets by the methylene multiplet(s).

cis- and trans-4-t-Butyl-1-methyl cyclohexane (XXVII and XXVI).--4-t-Butyl-1-methylcyclohexene (2.95 g, 0.0194 moles) in 20 ml of 95% ethanol was hydrogenated with hydrogen gas using 0.35 g of 5% Pd-carbon catalyst. Hydrogenation was continued until a stoichiometric amount of hydrogen gas was used. The saturated hydrocarbon 2.54 g (0.0165 moles) was obtained by filtering the mixture, washing the filtrate in water and n-hexane, and evaporating the n-hexane with a flash evaporator. The yield was 85%. An infrared spectrum showed strong bands at 1367

and 1395 (t-butyl and CH_3-) and at 1455 cm^{-1} ($-CH_2-$).

The trans:cis isomer ratio was determined by gas chromatography on column C and found to be 3.89 in agreement with earlier results.[24] The trans isomer (XVI) peak occurred at 12.2 minutes and the cis isomer (XVII) peak at 13.9 minutes.

cis- and trans-4-t-Butyl-1-methylcyclohexyl chloride (XXIII and XXII).--Trans-4-t-butyl-1-methylcyclohexanol XX (1.54 g, 0.00905 moles) was added to 40 ml of concentrated hydrochloric acid. The mixture was shaken for one hour in a 60 ml separatory funnel. The acid layer was withdrawn and discarded, and a fresh portion of concentrated HCl was added. After the mixture was shaken for another hour, the organic layer was extracted with pentane, washed with water, and dried over anhydrous magnesium sulfate. Distillation gave a chloride mixture (1.80 g, 0.00573 moles), b.p. 83-85°/15 mm Hg. The mixture was analyzed by gas chromatography on column D and the trans:cis isomer ratio was found to be 3.81:1.

Separation of the cis and trans chlorides was successful on column B. The peak at 32 minutes was collected. Its infrared spectrum showed predominant peaks at 784, 841, 977, 1120, 1133, 1185, and 1315 cm^{-1}. Earlier work[17] showed a peak at 555 cm^{-1} for the axial

C-Cl stretching frequency, but optics necessary to observe infrared in this region were not available. An n.m.r. spectrum showed a singlet at 0.85 δ (9H), a singlet at 1.53 δ (3H), and a multiplet between 1.0-1.9 δ (9H).

The 37 minute peak was collected and an infrared spectrum showed peaks at 668, 792, 964, and 1090 cm^{-1}. Earlier workers[17] have reported a peak at 670 cm^{-1} for the equatorial C-Cl stretching frequency of XXIII. An n.m.r. spectrum showed a singlet at 0.82 δ (9H), a singlet and multiplet at 1.52 δ, and a multiplet at 1.88 (12H total). The gas chromatography peak at 8 minutes was collected and shown to be a mixture of 4-t-butyl-1-methylcyclohexene and 4-t-butyl-1-methylenecyclohexane.[25]

cis- and trans-4-t-Butyl-1-methylcyclohexyl bromide (XXV and XXIV).--Dry hydrogen bromide was bubbled for one hour through a solution of trans-4-t-butyl-1-methylcyclohexanol (1.0 g, 0.00588 moles) and pentane (25 ml) kept at -40° in an acetone-dry ice bath. The reaction mixture was then flushed with nitrogen for one hour at -40°, and for one-half hour at room temperature. The reaction mixture was extracted with pentane. The pentane layer was washed with water and dried over anhydrous magnesium sulfate. The pentane was evaporated

and a colorless liquid (1.04 g) was collected and analyzed by gas chromatography on column D at 67° and 70 ml/min flow. Peaks at 19.1 minutes and 25.7 minutes occurred in a ratio of 6.71:1. These were assigned to the trans bromide (XXIV) and the cis bromide (XXV), respectively. A small peak at 2.8 minutes was found to be 4-t-butyl-1-methylcyclohexene.

An infrared spectrum of the isomer mixture showed peaks at 780s, 840m, 978s, 1087m, 1114s, 1188s, 1310m, 1370s, 1445s cm^{-1}. An n.m.r. spectrum showed a singlet at 0.85 δ (9H), a 3H singlet at 1.77 δ[26], and unresolved peaks from 1.2-2.3 δ.

Preparation of Chromous Perchlorate Solutions.--

All chromous perchlorate solutions were prepared from chromium metal (99.996%) and perchloric acid,[27] and were 0.9-1.3 M in strength. The desired concentration was accomplished by adding 2.0 g of chromium metal to 25 ml of 20% perchloric acid (deoxygenated with nitrogen thirty minutes prior to addition of the chromium). Not all the chromium metal reacts, but the unreacted metal facilitates keeping the oxidation state of chromium at +2 rather than +3.

Procedure for Chromium(II)-(en) Reductions.--
All reactions were carried out in a round bottom reaction flask having cylindrical sides and capped by a three-neck flask cover. Fitted to the reaction flask was a stirrer assembly that permitted the introduction of nitrogen gas into the system through a hollow shaft. The second neck of the cover was stoppered and the third neck capped with a rubber septum.

A solution of 40 ml DMF and 0.5 ml ethylene diamine (en) in the reaction flask was flushed with N_2 for 30 minutes. Using a hypodermic syringe, 5.0 ml of 0.9-1.3 M chromous perchlorate was added to the deoxygenated reaction vessel. A homogeneous deep blue-purple solution resulted. When one ml of approximately 0.5 M tertiary halide in DMF was added, the solution color changed to a deep green in five minutes at room temperature.

The mixture was stirred for twelve hours and the dark green solution turned deep maroon. The reaction mixture was quenched with 10% perchloric acid and the products extracted with hexane. Extracts were dried with anhydrous $MgSO_4$ and analyzed by gas chromatography on column C using n-propyl acetate as an internal standard.

Chloride XXII (4.65×10^{-4} moles) was added to a deoxygenated solution containing DMF (40 ml), ethylene

diamine (0.5 ml), $Cr(ClO_4)_2$ (5.75×10^{-3} moles) and n-butyl mercaptan (1.49×10^{-2} moles). Addition of the chloride was not accompanied by the color change from blue to green as noted before. After 15 hours, the reaction mixture was analyzed by gas chromatography and found to contain XXVI and XXVII in 90% yield. Product isomer ratio was XXVI:XXVII = 92.0:8.0.

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