REACTION OF CHROMYL CHLORIDE WITH SOME OLEFINS

PART I. THE PRODUCTS FROM CYCLOHEXENE, CYCLOPENTENE, 1-HEXENE, AND 2-METHYL-1-PENTENE

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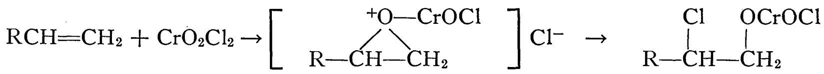
ABSTRACT

Chromyl chloride in carbon tetrachloride solution reacts in the cold with cyclohexene, cyclopentene, and 1-hexene to give the various isomeric chlorohydrins as the major products. The major product from 2-methyl-1-pentene was 2-methylpentanal. Significant amounts of α-chloro carbonyl compounds and some α,β-unsaturated carbonyl compounds were also produced. The significance of these results is discussed.

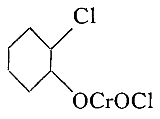
INTRODUCTION

The reaction of chromyl chloride with olefins has received little attention in contrast to the better known Étard reaction, involving the oxidation of an alkyl side chain of an aromatic hydrocarbon. Étard (1), and later Henderson and others (see references quoted in ref. 2), oxidized olefinic terpenes to obtain brown complexes containing about two atoms of chromium per molecule of olefin. On hydrolysis these complexes yield aldehydes, ketones, and chlorinated compounds that were for the most part unidentified. The first significant study of the chromyl chloride – olefin reaction was made by Cristol and Eilar (3). They reported that oxidation of cyclohexene gave *trans*-2-chlorocyclohexanol, and a series of terminal olefins yielded the chlorohydrins corresponding to anti-Markownikoff addition of hypochlorous acid. It was postulated that only 1 mole of chromyl chloride took part in the main reaction. This was later verified by Stairs (4).

From these results it was concluded that the reaction involves electrophilic attack on the double bond by an oxygen of chromyl chloride. A cyclic oxonium ion intermediate would then account for the observed positional isomerism and stereoisomerism.



More recently Sulima and Gragerov (5) have shown by use of O^{18} tracers that in the case of cyclohexene all the oxygen in the 2-chlorocyclohexanol comes from the chromyl chloride. This suggests that the most probable structure of the complex is A (or as is highly likely, a polymer of A containing cyclohexane and chlorochromate residues, possibly linked through oxygen–chromium bridges) and that hydrolysis involves the O—Cr bond of the chlorochromate IV ester.



A

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Reinvestigation of the chromyl chloride – olefin reaction, using gas chromatography to separate the products, has revealed a number that were previously unreported. The nature of these products permit certain speculations regarding the mechanism of the reaction.

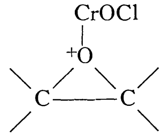
RESULTS AND DISCUSSION

Reaction of chromyl chloride with cyclohexene in carbon tetrachloride solution gave a nearly quantitative yield of a brown precipitate assumed to be $C_6H_{10}\cdot CrO_2Cl_2$. Hydrolysis with aqueous sodium bisulphite followed by distillation gave as the major fraction what was believed to be *trans*-2-chlorocyclohexanol. However, infrared spectral comparison of this product with authentic samples of *cis*- and *trans*-2-chlorocyclohexanol indicated that the product of the oxidation was a mixture of both isomers. This was confirmed by the preparation of both α-naphthylurethan derivatives, and by quantitative analysis with alkali (6). Treatment of the product mixture with α-naphthylisocyanate afforded the derivative of the trans chlorohydrin in a fairly pure state. To obtain the derivative of the cis chlorohydrin, the trans isomer was converted to cyclohexene oxide by treatment with aqueous alkali and removed from the mixture by distillation. Since this treatment was essential, the failure of Cristol and Eilar to detect the cis isomer is easily understood.

The more volatile fractions of the distillate showed infrared absorptions at 1710 and 1680 cm^{-1} which were attributed to a non-conjugated and an α,β-unsaturated ketone. Chromatography on a Bentonite–Celite column of the 2,4-dinitrophenylhydrazone obtained from this fraction resulted in separation of the 2,4-dinitrophenylhydrazones of cyclohexanone and Δ^2-cyclohexenone (7). Quantitative estimation was made of the reaction of 0.167 mole of cyclohexene with 0.160 mole of chromyl chloride. The yields (in parentheses) of the products formed were: *trans*-2-chlorocyclohexanol (21%), *cis*-2-chlorocyclohexanol (14%), cyclohexanone (5.5%), Δ^2-cyclohexenone (17%). In addition 21% of unreacted cyclohexene was recovered, and 21.5% was unidentified high-boiling material. A similar oxidation of cyclopentene yielded *trans*-2-chlorocyclopentanol (6%), *cis*-2-chlorocyclopentanol (18%), and a small amount of 2-chlorocyclopentanone.

The reaction of 1-hexene with an equimolar amount of chromyl chloride gave a liquid which was separated by preparative gas chromatography into five chromatographically pure products. These were found to be 2-chloro-1-hexanol (32.6%), 1-chloro-2-hexanol (9.3%), 2-chlorohexanal (1.7%), 1-chloro-2-hexanone (4.6%), and a 1.8% yield of a substance having an ultraviolet absorption maximum at 217 mμ in ethanol, which could be either 2-hexenal or 1-hexene-3-one. Oxidation of 2-methyl-1-pentene gave mainly 2-methylpentanal. The chlorohydrins, if they were formed at all, represented less than 10% of the major product.

The formation of cis as well as trans chlorohydrins from both cyclohexene and cyclopentene indicates that a cyclic oxonium ion intermediate, B, cannot represent the only reaction route. On the other hand, an intermediate such as C would be expected to yield entirely cis chlorohydrin. Finally, an intermediate such as D would lead to both



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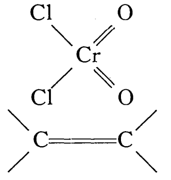

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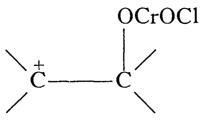

D

cis and trans chlorohydrins with proportions of the isomers thermodynamically controlled. Unfortunately, the thermodynamic information is not available. The situation is complicated by the possibility of selective overoxidation of one of the isomeric chlorohydrins, either during the first step as the chlorochromate IV ester or during the hydrolysis. This is probably the origin of the α-chloro carbonyl compounds.

A further source of complication lies in the possible elimination of hydrogen chloride from both the α-chloro carbonyl compounds and from the chlorohydrins. The conjugated unsaturated compounds found among the products from cyclohexene and 1-hexene may arise in this way, and not, as we first supposed, by an Étard reaction on the allylic carbon of the olefin. That this elimination does not appear to happen with 2-chlorocyclopentanone may be due to steric difficulty in the flat cyclopentane ring. The configuration of 2-chlorocyclohexanone, on the other hand, with an axial chlorine atom (8) is very favorable for trans elimination. Elimination of hydrogen chloride from 2-methyl-2-chloropropanol has been shown to occur readily (9). If it is assumed that 2-methylpentanal, the main product from 2-methyl-1-pentene, arose in this manner, the ratio of 2-chloro-1-ol to 1-chloro-2-ol is 10:1 or greater for the 2,2-dialkylethylene, as compared to about 3:1 for the monoalkyl, i.e. 1-hexene. This is reasonable for a weak Markownikoff effect, with chlorine acting as the negative, and CrO_2Cl as the positive, part of the addend. Depending on whether the ratio is kinetically or thermodynamically controlled, this corresponds to a $\Delta(\Delta G^*)$ or $\Delta(\Delta G)$ of about 0.7 kcal/mole for 1-hexene and >1.5 kcal/mole for 2 methyl-1-pentene. This is compatible with any of the intermediates B, C, or D, though the small size of the effect favors C.

It is clearly not possible to favor any single route or particular combination of routes for the reaction on the basis of the products reported here. A kinetic study would be simpler if there were fewer products and higher yields, but it is clearly needed before the mechanism can be further discussed. Such a study is now in progress.

EXPERIMENTAL

Melting points were determined by the capillary tube method and are uncorrected. Gas chromatograms were obtained using a Burrell Model K-3 for qualitative work and a Burrell Model K-2 for preparative separations and analysis. Nuclear magnetic resonance spectra were obtained on the Varian A60 spectrometer with tetramethylsilane as external standard, this being set at 10.0 τ on the Tiers scale.

Reagents

Chromyl chloride (Allied Chemical) was purified by bubbling dry nitrogen through the liquid to remove traces of hydrogen chloride and was then distilled through a 30-cm Vigreaux column. The fraction boiling at 114–115° was retained. The reagent was protected from light during the distillation and storage and was repurified when any turbidity was noticeable. The olefins were dried and distilled before use and the purity was shown to be greater than 99% by gas chromatography using a silver nitrate-ethylene glycol column. This column efficiently separated a mixture of 1-hexene and 2-hexene prepared by the dehydration of 2-hexanol.

Reaction of Chromyl Chloride with Cyclohexene

A solution of 20.09 g (0.24 mole) of cyclohexene in carbon tetrachloride (500 ml) was treated with 38 g (0.24 mole) chromyl chloride in carbon tetrachloride (200 ml) during a 1-hour period. The temperature was maintained at 0–5°. Precipitation of the brown complex began on the addition of the first few drops of the chromyl chloride solution. The complex was hydrolyzed *in situ* by the addition of a mixture of water (200 ml), ice (100 g), and sodium metabisulphite (15 g). The mixture was stirred for 15 minutes and the organic layer was then separated, washed with saturated sodium chloride solution, dried over sodium sulphate, and the solvent removed. A gas chromatogram (115°, Apiezon T on Embacel, H_2, 55 ml/min) of crude product showed peaks with retention times of 40 seconds (solvent), 125 seconds (small), 145 seconds (medium), and 290 seconds (large). Distillation under reduced pressure through a 15-cm Vigreaux column gave the following fractions: (1) 0.30 g, b.p. 36° at 150 mm; (2) 0.66 g, b.p. 68–84° at 90 mm; (3) 1.18 g, b.p. 84–85° at 80 mm; (4) 2.26 g, b.p. 104–109° at 60 mm; (5) 2.18 g, b.p. 96–98° at 40 mm; (6) 3.15 g, b.p. 98–100° at

36 mm; (7) 2.24 g, b.p. 92–97° at 20 mm; (8) 1.69 g, b.p. 90–92° at 20 mm; (9) 0.70 g, b.p. 92–97° at 20 mm. The following compounds were identified in the distillate.

(a) Cyclohexanone and Δ^2-Cyclohexenone

Gas chromatography of fraction 3 from the distillation showed two major peaks (125 and 145 seconds). The infrared spectrum of this fraction in carbon tetrachloride had absorption maxima attributed to the carbonyl absorption frequencies at 1710 and 1680 cm^{-1}. Treatment of fraction 3 with 2,4-dinitrophenylhydrazine gave a precipitate from which cyclohexanone-2,4-dinitrophenylhydrazone and Δ^2-cyclohexenone 2,4-dinitrophenylhydrazone were obtained after chromatography on a Bentonite–Celite column (7). The first eluted, a yellow band, when crystallized from ethanol, had m.p. 160–161°. The mixed melting point and infrared spectrum were identical with those of cyclohexanone 2,4-dinitrophenylhydrazone as was the retention time on gas chromatography of the original ketone. The second band on elution chromatography was a deep red-orange which when crystallized from ethanol had m.p. 162–163°. Lit. m.p. 163° (10). The infrared spectrum and mixed melting point were identical with those of an authentic sample of Δ^2-cyclohexenone 2,4-dinitrophenylhydrazone (11). Anal. Calc. for $C_{12}H_{12}N_4O_4$: C, 52.19; H, 4.38; N, 20.27. Found: C, 51.91; H, 4.25; N, 20.27.

(b) cis and trans-2-Chlorocyclohexanols

Fractions 5 to 9 showed strong infrared absorption at 3600 cm^{-1} assigned to the hydroxyl group. The spectra differed from that of authentic *trans*-2-chlorocyclohexanol prepared by the addition of hypochlorous acid to cyclohexene (12), and that of *cis*-2-chlorocyclohexanol prepared by the aluminum isopropoxide reduction of 2-chlorocyclohexanone (13), and appeared to be a composite of these. Known mixtures of these isomers were not resolved by gas chromatography under the conditions used. Treatment of the oxidation product mixture with α-naphthylisocyanate on the steam bath for 30 minutes gave *trans*-2-chlorocyclohexanol α-naphthylurethan which when recrystallized twice from hexane had m.p. and mixed m.p. 164–165°. Lit. m.p. 164° (6). Anal. Calc. for $C_{17}H_{18}NO_2Cl$: C, 67.19; H, 6.32; Cl, 11.68. Found: C, 66.70; H, 5.92; Cl, 11.40. Separation of the cis isomer from the mixture by the method of Bartlett (6) followed by treatment with α-naphthylisocyanate on the steam bath for 2 hours afforded *cis*-2-chlorocyclohexanol α-naphthylurethan, m.p. and mixed m.p. 93–94°. Lit. 93° (6). Calc. for $C_{17}H_{18}NO_2Cl$: C, 67.19; H, 6.32; Cl, 11.68. Found: C, 66.92; H, 6.34; Cl, 11.46.

Quantitative Analysis of the Cyclohexene – Chromyl Chloride Reaction

(a) Unreacted Cyclohexene

The reaction was carried out as previously outlined and the brown complex was then collected by filtration, washed with carbon tetrachloride, and dried under vacuum. Escaping vapor from both the filter flask and the vacuum desiccator were trapped in a dry ice – acetone trap and returned to the main filtrate. This filtrate was then diluted to 1000 ml with carbon tetrachloride and aliquots were titrated for cyclohexene with a standard solution of bromine according to the method of Siggia (14). The analysis was found to be accurate to within 2% when samples of known concentration were titrated.

(b) cis and trans-2-Chlorocyclohexanols

The reaction was carried out as previously described. The organic layer was extracted several times with saturated sodium chloride solution to remove any hydrochloric acid formed during the hydrolysis. The carbon tetrachloride was distilled off and the residue made up to volume with ethanol. Suitable aliquots were titrated with standard sodium hydroxide by Bartlett's method (6) for both chlorohydrins.

(c) Δ^2-Cyclohexenone and Cyclohexanone

These products were determined from their retention volumes on gas chromatography after calibration with known volumes of the pure liquids.

Reaction of Chromyl Chloride and 1-Hexene

1-Hexene (20 g, 0.24 mole) and chromyl chloride (20 ml, 0.24 mole) were reacted as described for cyclohexene. A gas chromatogram of the crude product, after removal of the solvent (125°, neopentylglycol sebacate on Embacel, He, 40 ml/min), showed five major peaks with retention times 420 seconds (small), 595 seconds (small), 730 seconds (medium), 1030 seconds (medium), 1235 seconds (large). These components were gas chromatographically separated and the various fractions condensed and collected. About 20 injections of 100 μl each were required to obtain a workable sample for the identification of the components.

(a) 2-Chlorohexanal

The infrared spectrum showed absorption maxima at 1730 and 2720 cm^{-1} assigned to carbonyl and aldehyde carbon–hydrogen absorption frequencies respectively. This fraction gave positive Schiff's and Fehling's tests, and contained chlorine (Beilstein's test). Treatment with 2,4-dinitrophenylhydrazine gave yellow needles, m.p. 106–107°. An authentic sample of 2-chlorohexanal prepared by the α-chlorination of hexanal with sulphuryl chloride (15) was identical with the chromyl chloride oxidation product in every way (retention time on gas chromatography, infrared spectrum, m.p. and mixed m.p. of the 2,4-dinitrophenylhydrazone).

(b) Unsaturated Carbonyl Compound

The component with retention time 595 seconds could not be obtained in sufficient quantity for complete characterization because of failure to condense in the fraction collector. However, sufficient sample was obtained for an ultraviolet spectrum, which showed a single maximum at $\lambda_{\max}$ 217 mμ. A value for the extinction coefficient was not obtained.

(*c*) *1-Chloro-2-hexanone*

The infrared spectrum of this oxidation product showed a carbonyl absorption at 1720 cm^{-1}. This compound failed to react with 2,4-dinitrophenylhydrazine. Analysis of the liquid for chlorine by the Schoeniger combustion method gave: Cl, 25.2. Calc. for $C_6H_{11}OCl$, 26.4. The n.m.r. signals were as follows: distorted triplet centered at 8.62 τ (terminal methyl, area = 3 H), large number of lines centered at 8.11 τ (β- and γ-methylenes area = 4 H), triplet centered at 6.08 τ (α-methylene, area = 2 H), and singlet at 5.64 τ (α-chloromethyl, area = 2 H).

(*d*) *1-Chloro-2-hexanol*

This component showed strong hydroxyl absorption in the infrared and gave a positive Beilstein's test for chlorine. Upon admixture of this product with an authentic sample prepared by the hypochlorous acid addition to 1-hexene, and gas chromatography of the mixture, a single peak was obtained. Treatment with an equivalent of α-naphthylisocyanate for 3 hours at 100° C gave the α-naphthylurethan, m.p. and mixed m.p. 86–87°. (The authentic 1-chloro-2-hexanol had to be gas chromatographically purified to remove about 10% 2-chloro-1-hexanol before a good α-naphthylurethan could be obtained.) Anal. Calc for $C_{17}H_{20}NO_2Cl$: C, 66.80; H, 6.58; Cl, 11.60. Found: C, 66.85; H, 6.65; Cl, 11.33.

(*e*) *2-Chloro-1-hexanol*

This component showed strong hydroxyl absorption in the infrared and contained chlorine. The α-naphthylurethan had m.p. 93–94°. Anal. Calc for $C_{17}H_{20}NO_2Cl$: C, 66.8; H, 6.80; Cl, 11.60. Found: C, 66.21; H, 6.90; Cl, 11.21.

(*f*) *Yields*

1-Hexene (5.0 g, 0.0591 mole) and chromyl chloride (4.8 ml, 0.059 mole) were reacted in the usual way. The carbon tetrachloride was distilled off until a volume of 30 ml was obtained as a residue. This residue was then transferred to a 50-ml volumetric flask and made up to volume with the rinse from the distilling flask. The yields of the various components were determined from the retention volumes on gas chromatography. The instrument was calibrated by obtaining retention volume versus volume injected for each of the gas chromatographically pure components.

Reaction of Chromyl Chloride with Cyclopentene

Cyclopentene (8.0 g, 0.12 mole) was oxidized with chromyl chloride (9.0 ml, 0.11 mole) in the previously described manner. A gas chromatogram (125°, neopentylglycol sebacate on Embacel, He, 40 ml/min) of the crude product showed three major peaks and one minor peak with retention times 310 seconds (small), 700 seconds (large), 950 seconds (medium), 1170 seconds (medium). These products were separated in pure fractions by the same method as applied with 1-hexene and then identified.

(*a*) *trans-2-Chlorocyclopentanol*

This fraction showed a strong infrared absorption at 3470 cm^{-1} (pure liquid) assigned to the hydroxyl group, and gave a positive Beilstein's test for chlorine. The α-naphthylurethan had m.p. 106–107°. Lit. m.p. 105° (16). Anal. Calc for $C_{16}H_{16}NO_2Cl$: C, 66.40; H, 5.57; Cl, 12.24. Found: C, 66.22; H, 5.72; Cl, 11.79. The oxidation product was found to be identical in every way (retention time on gas chromatography, infrared spectrum, m.p. and mixed m.p. of the α-naphthylurethan) with an authentic sample of *trans*-2-chlorocyclohexanol prepared by the addition of hypochlorous acid to cyclopentene.

(*b*) *cis-2-Chlorocyclopentanol*

The infrared spectrum of this component showed a strong absorption attributed to the hydroxyl group. The α-naphthylurethan had m.p. 100–101°. Anal. Calc for $C_{16}H_{16}NO_2Cl$: C, 66.40; H, 5.57; Cl, 12.24. Found: C, 66.56; H, 5.77; Cl, 11.96. This compound was identical in the infrared spectrum, in retention time on gas chromatography, and in m.p. and mixed m.p. of the α-naphthylurethan derivative with authentic *cis*-2-chlorocyclopentanol, prepared by the aluminum isopropoxide reduction of 2-chlorocyclopentanone and purification through gas chromatography.

(*c*) *2-Chlorocyclopentanone*

This product showed an infrared absorption at 1750 cm^{-1} assigned to carbonyl stretching, and it was found to contain chlorine. Authentic 2-chlorocyclopentanone, prepared by the chlorination of cyclopentanone (17), had an infrared spectrum and retention time on gas chromatography identical with those of this product.

(*d*) *Yields*

The products of the reaction of chromyl chloride with cyclopentene were determined quantitatively by the same method used for 1-hexene.

Reaction of Chromyl Chloride and 2-Methyl-1-pentene

2-Methyl-1-pentene (10 g, 0.12 mole) and chromyl chloride (9.7 ml, 0.12 mole) were reacted in the usual fashion. A gas chromatogram of the crude product showed one major product along with four very minor products. The infrared spectrum of the crude product showed absorption maxima at 2720 and 1720 cm^{-1} attributed to aldehyde carbon–hydrogen and carbonyl absorption respectively. Distillation of the product gave a fraction weighing 3 g, b.p. 55° at 22–26 cm, and leaving a large pot residue. The fraction distilled was identified as consisting mainly of 2-methylpentanal by a positive Fehling's test, and a 2,4-dinitrophenylhydrazone melting point of 104–105°. Lit. m.p. 102–104° (18). Anal. Calc. for $C_{12}H_{16}N_4O_4$: N, 20.0. Found: 19.8. The distilled fraction on gas chromatography had the same retention time as that of the major peak of the crude product.

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