Molecular Rearrangements. V.[1] Studies of the Rearrangements of 1-Chloro-*cis*- and -*trans*-4-methylcyclohexene Oxide. Stereospecific Chlorine Migration

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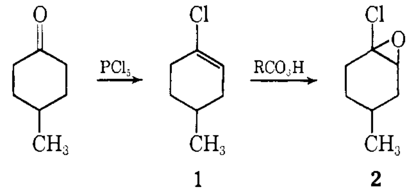
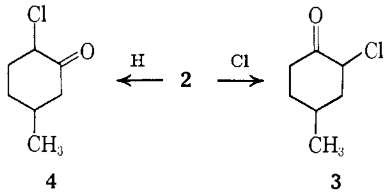
Abstract: A mixture of 1-chloro-*cis*- (**2a**) and -*trans*-4-methylcyclohexene oxide (**2b**) is obtained in the peracid epoxidation of 1-chloro-4-methylcyclohexene. Neat thermal rearrangements of this mixture give exclusively *trans*-2-chloro-4-methylcyclohexanone (**3a**) through about the first 35% of rearrangement. Essentially no rearrangement rate difference is observed for **2a** and **2b**. The results are interpreted in terms of a common α-ketocarbonium ion–chloride ion-pair intermediate. Zinc chloride catalyzed rearrangements give rise to a mixture of **3a** and the *cis* isomer (**3b**).

Our previous reports of α-chloro epoxide rearrangements with preferential chlorine migration in the peracid oxidation of α-chlorostilbenes[3] and the Darzens condensation of benzaldehyde and methyl dichloroacetate[1b] were based on product studies and assumed the intermediacy of α-chloro epoxides. In the hope of gaining information about the mechanism of this novel chlorine migration, the synthesis of stable α-chloro epoxides became an obvious necessity. Of particular interest in this regard were the reports by Mousseron and his co-workers[4] on alicyclic α-chloro epoxides and their relative stability allowing for purification by distillation under reduced pressure. Under the influence of heat or acid catalysts, these α-chloro epoxides readily rearranged to ketones. 1-Chloro-5-methylcyclohexene oxide was reported to rearrange to 2-chloro-5-methylcyclohexanone on exposure to air or in contact with palladium black in acetic acid.[4d] No yield data were given and no discussions advanced of chlorine as the migrating group in the rearrangement.

The vinyl chloride chosen for our studies was 1-chloro-4-methylcyclohexene (**1**). 4-Methylcyclohexanone was treated with phosphorus pentachloride to give good yields of **1**.[5] Epoxidation of **1** using either perbenzoic acid or *m*-chloroperbenzoic acid gave 1-chloro-4-methylcyclohexene oxide (**2**) in *ca.* 65% yield. The α-chloro epoxide **2** could readily be distilled at reduced pressure and could be stored under Dry Ice for relatively long periods of time with little or no rearrangement. However, when allowed to remain at room temperature and atmospheric pressure, the epoxide soon began to undergo rearrangement as was evidenced by development of a strong carbonyl absorption in its infrared spectrum. Decomposition and/or polymerization were also indicated by development of a deep red color and evolution of hydrogen chloride fumes.



The products considered possible from the rearrangement of α-chloro epoxide **2** were 2-chloro-4-methylcyclohexanone (**3**), formed by chlorine migration, and 2-chloro-5-methylcyclohexanone (**4**), formed by hydrogen migration. These α-chloro ketones have been prepared by chlorination of 4-methylcyclohexanone and 3-methylcyclohexanone, respectively.



Two isomers of 2-chloro-4-methylcyclohexanone (**3**) have been reported previously in the literature,[6-8] but have been described[6] only as a "low-boiling isomer" and a "high-boiling isomer." A mixture of these two isomers was prepared by chlorination of 4-methylcyclohexanone using either sulfuryl chloride or aqueous chlorine.[6] Quite pure samples of each isomer could be obtained by distillation of the mixture through a semimicro spinning band column. The "low-boiling isomer" exhibited bp 74.0–74.7° (10 mm) and the "high-boiling isomer" had bp 107–108° (10 mm).

In a study of the carbonyl absorption in the infrared spectra of solutions of various α-chlorocyclohexanones, Corey and Burke[9] observed that carbonyl absorption is displaced from that of the parent ketone, +26 to +31 cm^{-1} for equatorial chlorine and +10 to +18 cm^{-1} for axial chlorine substitution. In the present study the carbonyl absorption frequencies of

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[1] (a) A portion of this work was communicated in *Chem. Commun.*, 655 (1966). (b) For paper III in this series, see R. N. McDonald and P. A. Schwab, *J. Org. Chem.*, **29**, 2459 (1964).

[2] NDEA Fellow, 1962–1965. This represents a portion of a dissertation presented by T. E. Tabor to the Graduate School of Kansas State University in partial fulfillment of the requirements for the Ph.D. degree.

[3] R. N. McDonald and P. A. Schwab, *J. Am. Chem. Soc.*, **85**, 4004 (1963).

[4] (a) M. Mousseron and R. Jacquier, *Bull. Soc. Chim. France*, 698 (1950); (b) M. Mousseron, F. Winternitz, and R. Jacquier, *ibid.*, **81**, (1947); (c) M. Mousseron, F. Winternitz, and R. Jacquier, *ibid.*, 260 (1948); (d) M. Mousseron, F. Winternitz, and R. Jacquier, *Compt. Rend.*, **223**, 1014 (1946).

[5] The general procedure is that described by M. S. Newman, G. Fraenkel, and W. N. Kirn, *J. Org. Chem.*, **28**, 1851 (1963).

[6] E. Campaigne and R. D. Lake, *ibid.*, **24**, 478 (1959).

[7] M. Godchot and P. Bedos, *Compt. Rend.*, **180**, 295 (1925).

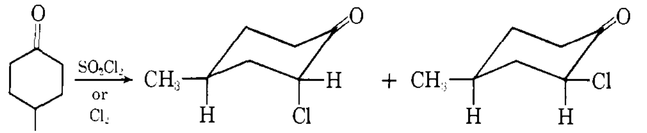
[8] M. S. Newman and W. T. Booth, *J. Org. Chem.*, **12**, 737 (1947).

[9] E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **77**, 5418 (1955).

the two isomers of **3** appeared at 1727 cm^{-1} in the "low-boiling isomer" and 1736 cm^{-1} in the "high-boiling isomer," compared to 1718 cm^{-1} for the parent 4-methylcyclohexanone. This suggested that the chlorine substituent was axial in the "low-boiling isomer" ($\Delta\nu_{C=O}$ +9 cm^{-1}) and equatorial in the "high-boiling isomer" ($\Delta\nu_{C=O}$ +18 cm^{-1}).[10]

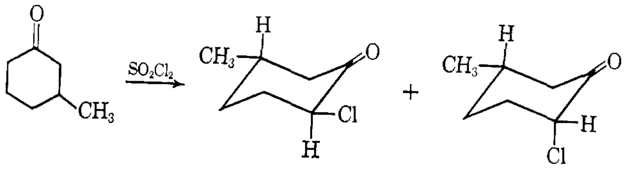
The neat nuclear magnetic resonance (nmr) spectra of the two isomers of **3** confirmed the conclusions obtained from the infrared spectra. In the nmr spectrum of the "low-boiling isomer," the proton on the carbon bearing the chlorine substituent appeared as a triplet centered at τ 5.44, with an over-all spacing of 7.6 cps and with each peak further split into a doublet, showing this proton to be equatorially oriented (axial chlorine). In the nmr spectrum of the "high-boiling isomer," this proton appeared as a four-line multiplet centered at τ 4.88, with an over-all spacing of 18.4 cps, showing this proton to be axially oriented (equatorial chlorine). These results are in excellent agreement with the report of Garbisch[11] for the conformationally homogeneous *cis* and *trans* isomers of 2-bromo-4-phenylcyclohexanone and 2-bromo-4-*t*-butylcyclohexanone. Also, Wellman and Bordwell[12] have discussed the shielding of α protons in cyclohexanones and have shown that, in contrast to cyclohexanes, the absorption for an axial proton α to the carbonyl group in cyclohexanones appears downfield with respect to its equatorial counterpart.

Assuming the methyl group to be equatorial in the two isomers of **3** allows a configurational assignment of *trans*-2-chloro-4-methylcyclohexanone (**3a**) to the "low-boiling isomer" and *cis*-2-chloro-4-methylcyclohexanone (**3b**) to the "high-boiling isomer."[13]



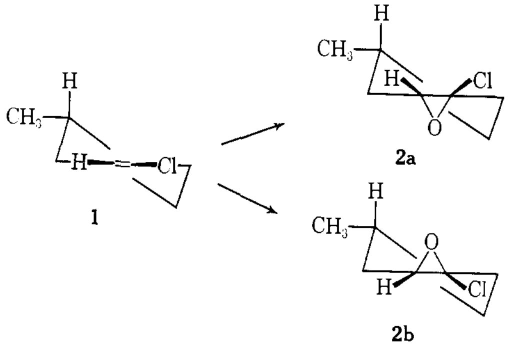
3a **3b**

Chlorination of 3-methylcyclohexanone with chlorine gave rise to two isomers of 2-chloro-5-methycyclohexanone (**4**), one being a liquid, bp 90° (6 mm), and the other a solid, mp 55–56°.[14] In the present study the chlorination procedure was executed using sulfuryl chloride, and gc analysis of the reaction mixture showed two major products. The solid isomer **4** readily separated from this mixture upon cooling and after recrystallization showed mp 56.5–57.0°. The infrared spectrum showed the carbonyl absorption displaced +18 cm^{-1} from that of 3-methylcyclohexanone. In the nmr spectrum of this solid isomer of **4** in carbon tetrachloride solution, the proton on the carbon bearing the chlorine substituent appeared as a four-line multiplet centered at τ 5.54, with an over-all spacing of 16.8 cps. Again assuming the methyl group to be equatorial, the results show that this solid isomer is *trans*-2-chloro-5-methylcyclohexanone (**4a**). No further attempts were made to isolate the liquid isomer, which is now indicated to be *cis*-2-chloro-5-methylcyclohexanone (**4b**).



4a **4b**

In the epoxidation of 1-chloro-4-methylcyclohexene (**1**), the peracid can approach the double bond from either side and thus should give rise to two isomeric α-chloro epoxides in which the methyl group is either *cis* (**2a**) or *trans* (**2b**) to the epoxide ring.[15] The nmr spectrum of the epoxidation product confirms this by showing a pair of methyl doublets at τ 9.11 and 9.15. The chemical shift difference for the methyl groups of the isomers is believed to be due to a long-range shielding effect of the α-chloro epoxide ring on the methyl group. However, it is not known whether the methyl group *cis* or *trans* to the epoxide ring is the most shielded. The multiplicity of the epoxide ring proton was also approximately that expected for a mixture of **2a** and **2b**.



1 **2a** **2b**

Thermal rearrangement of **2** was first attempted with samples sealed in ampoules under vacuum and placed in a thermostated bath. However, this method caused considerable decomposition and/or polymerization of the samples. During vacuum distillation of the epoxide it was observed that partial rearrangement would occur with apparently little or no decomposition. Thus, it was found that thermal rearrangements could be carried out with essentially no decomposition by allowing the epoxide to reflux at reduced pressure (*ca.* 10 mm). Zinc chloride catalyzed rearrangements were carried out in the same manner. Gas chromatographic (gc) analysis of these rearrangement mixtures showed that apparently the only α-chloro ketone products were the isomers of 2-chloro-4-methylcyclohexanone, **3a** and **3b**, the products of chlorine migration.

When known mixtures of 2-chloro-4-methylcyclohexanone (isomers **3a** and **3b**) and 2-chloro-5-methylcyclohexanone (isomers **4a** and **4b**) were subjected to gc analysis under the conditions used for analysis of the

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[10] The difference in the magnitudes of the shifts compared with those in ref 9 is that the present spectra were determined on neat liquid samples.

[11] E. W. Garbisch, *J. Am. Chem. Soc.*, 86, 1780 (1964).

[12] K. M. Wellman and F. G. Bordwell, *Tetrahedron Letters*, 1703 (1963).

[13] Calculations of the conformer populations of 3a and 3b were carried out using Garbisch's[11] coupling values of 18.2 and 5.7 cps for the axial and equatorial protons, respectively. Thus, in the neat liquid, the *trans* isomer 3a was shown to be 85% in the conformation depicted and 15% in the other conformation in which the methyl group is axial and the chlorine equatorial. In the neat liquid the *cis* isomer 3b was shown to be 100% in the conformation shown.

[14] M. Godchot and P. Bedos, *Compt. Rend.*, 178, 1374 (1924).

[15] B. Rickborn and S.-Y. Lwo, *J. Org. Chem.*, 30, 2212 (1965), have reported that epoxidation of 4-methylcyclohexene yields a 46.4:53.6 mixture of the *cis*- and *trans*-epoxides.

rearrangement mixtures, no clear-cut separation of all four components was observed. Therefore, an additional method had to be employed to show the absence of any 2-chloro-5-methylcyclohexanone isomers in these rearrangement mixtures. To do this, the thermal and catalyzed rearrangement mixtures were reduced with zinc dust and acetic acid. By this procedure the isomers of **3** would be converted to 4-methylcyclohexanone, whereas if any of the isomers of **4** were present they would give rise to 3-methylcyclohexanone.

The yield of the dechlorinated ketone by this reduction was 86% for the thermal rearrangement mixture and 11–15% lower for the catalyzed rearrangement mixtures. In all cases the infrared spectrum of the ketonic reduction product was identical with that of 4-methylcyclohexanone, showing that very little, if any, of the isomers of **2** were formed in these rearrangements. Quantitative infrared studies on known mixtures of 3- and 4-methylcyclohexanone showed that the presence of 5.6% of 3-methylcyclohexanone could readily have been detected, but that 2.4% or less would have been nearly impossible to detect. Control experiments using pure **3** and pure **4** in the zinc–acetic acid reductions gave average yields of 84.9% of 4-methylcyclohexanone and 81.8% of 3-methylcyclohexanone, respectively.

When aliquots of neat thermal rearrangements were analyzed by gc, it was found that only epoxide **2** and α-chloro ketone **3a** were present through about the first 35% of rearrangement. Only after this point did measurable amounts of **3b** begin to appear. We believe these data to be most significant since it is known that in equilibrations of **3a** and **3b**, the latter isomer predominates.[16]

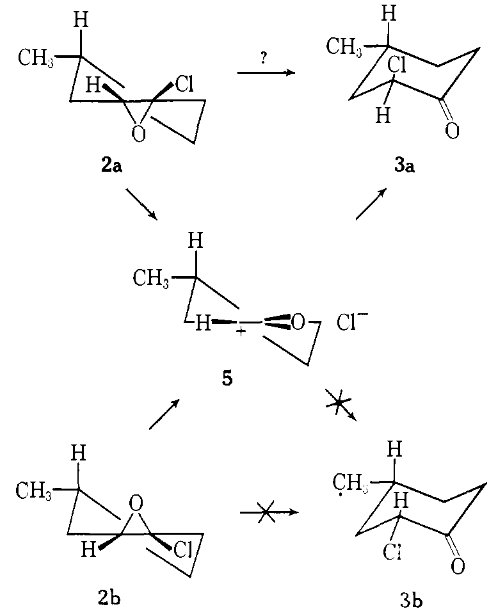
Two possible explanations were considered to explain these observations: (1) epoxide isomer **2a** was rearranging much faster to chloro ketone **3a** than epoxide isomer **2b** rearranged to chloro ketone **3b** (in terms of a chloronium ion process) or (2) both isomers of the epoxide were rearranging *via* a common intermediate which gives rise specifically to the chloro ketone **3a**.

To demonstrate that there is no significant difference in the rates of rearrangement of the epoxide isomers, nmr spectra were taken of successive fractions of the epoxide mixture during a very slow distillation in which partial rearrangement occurred. These spectra showed essentially no change in the composition of the epoxide mixture, therefore, no significant rearrangement rate difference. The pot residue showed only the presence of **3a** in addition to some epoxide.

If either a concerted epoxide ring opening with 1,2-chlorine transfer[17] or epoxide ring opening followed by 1,2-chlorine shift *via* a chloronium ion was operative in the rearrangement of the mixture of α-chloro epoxide isomers **2a** and **2b**, then a mixture of the chloro ketones **3a** and **3b** would be expected (Scheme I). By either of these mechanisms the *cis*-epoxide **2a** would yield the *trans*-chloro ketone **3a**, and the *trans*-epoxide **2b** would give the *cis*-chloro ketone **3b**. The results suggest then that a chloronium ion process is *not* occurring and that the two epoxides are rearranging through a common intermediate which gives rise specifically to the chloro ketone **3a**.

In considering the nature of such an intermediate we must, of course, account for (1) chlorine as the migrating group, (2) Lewis acid catalysis, and (3) the specificity of axial carbon-chlorine bond formation. We also bear a certain prejudice from previous work in the general epoxide–carbonyl rearrangement involving heterolysis of a carbon–oxygen bond leading to some degree of carbonium ion character. Carbon–chlorine bond heterolysis could occur in a concerted manner with the cleavage of the carbon–oxygen bond or as a discrete step from a dipolar species yielding an α-ketocarbonium ion–chloride ion pair, structure **5**. Axial carbon–chlorine bond formation would be favored stereoelectronically, just as the protonation of the enol of cyclohexanone occurs preferentially, but not exclusively, by axial bond formation.[18] Also, bromination of various ketosteroids often gives rise to predominantly axial α-bromo ketones, provided that the process is kinetically controlled, even in instances where the equatorial α-bromine substituent is the more stable.[18]

Scheme I



The analogies drawn above deal with reactions of enols or enolate ions. We propose that the α-ketocarbonium ion **5** has the same orbital arrangement as these electron-rich systems and that back-donation by the carbonyl stabilizes the carbonium ion center. This proposal may explain why with protonic acids α-chloro epoxides tend to ring open more in the opposite direction to give acid addition products[19,20] and further rearrangement products of the α-ketocarbonium ion.[20] Protonation of the carbonyl would be expected to remove much, if not all, of the back-donating stabilization of the carbonyl group.

Acceptance of this proposal of parallel arrangement of the p–π orbitals in **5** raises another question. That

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(16) See the present work and ref 7. This equilibration probably occurs *via* acid-catalyzed enolization.

(17) This path has already been pointed out as being unreasonable.[3]

(18) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 241, 242, and references therein.

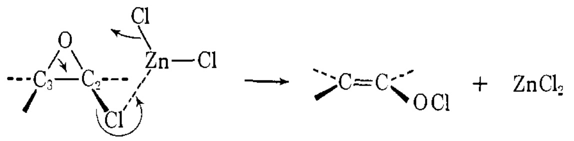
(19) A. Kirrmann, P. Duhamel, and R. Nouri-Bimorghi, *Ann.*, **691**, 33 (1966); *Bull. Soc. Chim. France*, 3264 (1964); R. Nouri-Bimorghi, *Compt. Rend.*, **C262**, 759 (1966).

(20) T. E. Tabor, unpublished results.[2]

is, why do we find exclusive initial formation of the axial carbon–chlorine bond to give **3a** when in the protonation of the enol of cyclohexanone axial carbon–hydrogen bond formation is preferred but not exclusive?

The steric factor should be far more important with the approaching group a large chloride ion (in **5**) than a proton (ketonization). Approach of chloride ion from the side of **5** would have as its major steric repulsive interaction the C_3 pseudo-equatorial hydrogen while approach from the under side has the C_3 pseudo-axial hydrogen interaction.[21] This will cause an increase in the energy separation of the transition states for C–X axial and equatorial bond formation processes when X = Cl relative to X = H. An increased specificity for axial bond formation, assuming the formation of product from **5** is kinetically controlled, is then expected. For such kinetic control to operate the α-ketocarbonium ion–chloride ion pair must be stabilized, according to the Hammond postulate.[22,23]

An alternate possibility to the direct formation of the α-ketocarbonium ion–chloride ion pair would be the formation of an enol hypochlorite by a 1,2-shift of chlorine. Zinc chloride catalysis could be accommodated by coordination at chlorine rather than oxygen. This would account for the fact that with protonic acid C_2–O epoxide ring fission is observed,[19,20] while in the present work, catalysis by zinc chloride gives predominately C_3–O bond fission, the same as found in neat thermal rearrangement.



The chlorination step (by decomposition of the enol hypochlorite) could be considered to proceed by either an enolate anion–chloronium ion pair or an α-ketocarbonium ion–chloride ion pair.[24] The latter process is definitely favored from considerations of the ionization potentials and electron affinities of the respective species[25] by about 5 ev. It appears to us that solvation energies in α-chloro epoxide as solvent would not be sufficiently different to invert these energetics. The enol hypochlorite might also be an intermediate in moving chloride ion from below the plane defined by C_1, C_2, C_3, C_6 in **5** to above this plane by simple rotation of the C–O bond for the α-ketocarbonium ion–chloride ion pair.

The proposed mechanisms deal with this rearrangement as an intramolecular process. Presently this is argued by analogy with the similar rearrangement of enol ester epoxides[26–28] which has been shown to be intramolecular.[27] An ion-pair mechanism would also appear most reasonable to explain the cyano group[29] and fluorine[30] as migrating groups in rearrangements of their respective α-substituted epoxides.

Zinc chloride catalyzed rearrangements of the α-chloro epoxide **2** were conducted at 80 and 25° with no observation of a preferential formation of **3a**. This is reasonable because the zinc chloride would be expected to equilibrate the α-chloro ketone isomers at a rate competitive with that of rearrangement. In addition to the α-chloro ketone isomers, **3a** and **3b**, another product was observed to the extent of *ca.* 20% of the total products in both catalyzed rearrangements. Also, seven minor products were observed in these reactions. This other major product was indicated by its infrared spectrum to be a nonketonic alcohol, but has remained unidentified. This compound may be coming from zinc chloride coordination at oxygen causing ring opening to occur in the opposite direction as is observed with protonic acids[19,20] which would indicate that its structure probably is 2,2-dichloro-5-methylcyclohexanol by analogy.

The catalyzed rearrangements appeared to proceed very rapidly and, in contrast to the controlled thermal rearrangements, were characterized by a rapid development of a deep red color. Distillation of these catalyzed rearrangement mixtures gave clear, colorless distillates, which soon turned pink upon standing, and extremely viscous, dark red pot residues.

Experimental Section[31]

1-Chloro-4-methylcyclohexene. To a well-stirred, refluxing mixture of 163.2 g (0.784 mole) of phosphorus pentachloride and 300 ml of methylene chloride was added dropwise a solution of 80.0 g (0.713 mole) of 4-methylcyclohexanone (Eastman, redistilled) in 150 ml of methylene chloride. Heating and stirring were continued for 8 hr. After cooling the reaction mixture was added dropwise with stirring to ice water. The organic layer was separated and the aqueous layer extracted twice with a mixture of 200 ml of benzene and 200 ml of ether. The combined organic layer and extracts were washed well with 10% sodium carbonate solution, water, and saturated sodium chloride solution, and dried. The solvents were removed by distillation (Hopkin's head) at atmospheric pressure and the liquid residue was vacuum distilled (30-cm Vigreux column). The material of bp 102–105° (150 mm), $n^{20}\text{D}$ 1.4722, was collected, giving 67.0 g (72%) of 1-chloro-4-methylcyclohexene. Redistillation (semimicro spinning band column) gave an analytical sample: bp 91.0–91.3° (99 mm); $n^{20}\text{D}$ 1.4727. The infrared spectrum was

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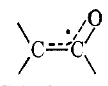
[21] Models indicate that these repulsions should be far greater than the more remote effects of the C_6 C–H bonds. The axial hydrogens at C_4 and C_5 will be approximately equal in their effect of approach from both sides.

[22] G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955).

[23] Charge-transfer complexes have not been dealt with in the present discussion but cannot be ruled out of consideration.

[24] A free-radical decomposition would not be expected to give the required stereospecificity.

[25] The estimates of EA and IP of



are that EA is the same as $C_6H_5O\cdot$ or $\cdot CH_3$ and the IP is that of $\cdot CH_3$.

[26] R. N. McDonald and T. E. Tabor, unpublished results. Preliminary studies with a mixture of 1-acetoxy-*cis*- and -*trans*-4-methylcyclohexene oxide[27] gave the following ratios of *cis*- and *trans*-2-acetoxy-4-methylcyclohexanone: rearrangement on a gc column, 2:1; pyrolysis on a glass bead column at 300°, 3:4; a neat rearrangement of 100°, 1:4. These preliminary results fit the idea that as the polarity of the medium increases a change occurs from an undissociated bridged mechanism of a 1,2-acetoxy migration to one involving greater stereospecificity, namely, ion pairs. In the gc rearrangement, equilibration may account for the inverted order.

[27] A. L. Draper, W. J. Heilman, W. E. Schaefer, H. J. Shine, and J. N. Shoolery, *J. Org. Chem.*, 27, 2727 (1962).

[28] N. S. Leeds, D.K. Fukushima, and T. F. Gallagher, *J. Am. Chem. Soc.*, 76, 2943 (1954).

[29] M. Mousseron and J. Jullien, *Compt. Rend.*, 231, 410 (1950); M. Mousseron, J. Jullien, and Y. Jolchine, *Bull. Soc. Chim. France*, 1209 (1950).

[30] P. M. Barna, *Chem. Ind.* (London), 2054 (1966).

[31] All melting points were taken on a Kofler hot stage and are corrected. Boiling points are uncorrected. Infrared absorption spectra were determined on a Perkin-Elmer Model 137 double beam recording spectrophotometer. Nmr spectra were determined on a Varian A-60 recording spectrometer. The gc analysis were performed using an F & M Model 500 programmed temperature gas chromatograph. Microanalysis were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

consistent with the structure assigned (6.01 μ, C=C), as was the nmr spectrum (neat, external TMS) which exhibited absorptions at τ 3.95 (multiplet, 1, vinyl), 7.1–8.5 (multiplet, 7, ring), and 8.65 (doublet (J = 5.3 cps), 3, methyl).

Anal. Calcd for $C_7H_{11}Cl$: C, 64.36; H, 8.50. Found: C, 64.41; H, 8.68.

1-Chloro-4-methylcyclohexene Oxide. 1. Using Perbenzoic Acid. To a solution of 11.6 g (0.087 mole) of 1-chloro-4-methylcyclohexene in 50 ml of chloroform cooled in an ice bath was added dropwise with stirring 220 ml of a cold 0.49 *M* chloroform solution (0.108 mole) of perbenzoic acid.[32] The reaction mixture was then allowed to come to room temperature and after 12 hr was washed well with 5% sodium carbonate solution and water and dried. The solvent was removed using a rotary evaporator and the yellow liquid residue distilled (30-cm Vigreux column). The material, bp 48.0–53.0° (6 mm), 10.35 g (68%), was collected. Redistillation (semimicro spinning band column) gave a center cut with bp 51.5–52.0° (5.7 mm), n^{19}_{D} 1.4630. The infrared spectrum shows epoxide ring absorption at 11.66 μ (s), while the nmr spectrum (CCl_4, internal TMS) exhibits absorptions at τ 6.99 (multiplet, epoxide ring), 7.2–9.0 (complex multiplet, ring), 9.11 (doublet, methyl), and 9.15 (doublet, methyl).

Anal. Calcd for $C_7H_{11}ClO$: C, 57.34; H, 7.56. Found: C, 57.11; H, 7.71.

2. Using *m*-Chloroperbenzoic Acid. A cold solution of 50.0 g of 85% minimum purity *m*-chloroperbenzoic acid (FMC Corp.) (*ca.* 42.5 g, 0.246 mole of peracid) in 675 ml of methylene chloride was added dropwise with stirring to an ice-cold solution of 29.2 g (0.224 mole) of 1-chloro-4-methylcyclohexene in 25 ml of methylene chloride. After stirring for 2 hr the precipitated *m*-chlorobenzoic acid was filtered from the cold reaction mixture and the filtrate washed with two 200-ml portions of saturated sodium bicarbonate solution and dried. The solution was then concentrated leaving a light yellow liquid residue which was distilled through a short path column giving 24.8 g of a colorless liquid distillate (Dry Ice cooled receiver) and leaving a yellow-brown solid pot residue. The crude epoxide was redistilled (semimicro spinning band column), giving a main fraction with bp 65.3–66.0° (9 mm), 20.6 g (62%), whose infrared and nmr spectra were identical with the product obtained using perbenzoic acid.

2-Chloro-4-methylcyclohexanone. 1. 4-Methylcyclohexanone with Chlorine. The method of Campaigne and Lake[6] was employed, giving rise to a mixture of the two isomers of 2-chloro-4-methylcyclohexanone. From 30.0 g (0.27 mole) of 4-methylcyclohexanone there was obtained 26.0 g (66%) of product, bp 55–98° (10 mm), n^{20}_{D} 1.4764. This material was redistilled and after 0.96 g of forerun, there was obtained 1.62 g of the "low-boiling isomer": bp 75.6–79.0° (10 mm), n^{21}_{D} 1.4707 (lit.[6] bp 76–77° (10 mm), n^{18}_{D} 1.4720). Following an intermediate fraction (5.52 g, bp 79.9–109.0° (10 mm), n^{21}_{D} 1.4742), two fractions of the "high-boiling isomer" were collected: a, 5.62 g, bp 109.0–111.0° (10 mm), n^{21}_{D} 1.4791; and b, 8.08 g, bp 111.0–111.5° (10 mm), n^{21}_{D} 1.4798 (lit.[6] bp 109–110° (10 mm), n^{18}_{D} (1.4798).

The nmr spectrum (neat, external TMS) of the "low-boiling isomer" exhibited absorptions at τ 5.44 [triplet (J = 3.8 cps, each peak further split into doublets, J = 1.3 cps, over-all spacing of 7.6 cps); 1, C_2-H (equatorial)], 6.4–8.5 (complex absorption, 7, ring), and 8.65 [doublet (J = 6.0 cps), 3, methyl]. The nmr spectrum (neat, external TMS) of the "high-boiling" isomer exhibited absorptions at τ 4.88 [four-line multiplet (over-all spacing of 18.4 cps), 1, C_2-H (axial)], 7.9–8.5 (complex absorption, 7, ring), and 8.55 [doublet (J = 5.8 cps), 3, methyl].

As previously reported by Godchot and Bedos,[7] the two isomers were found to equilibrate upon heating or upon standing in the refrigerator over periods of several weeks, with the "high-boiling isomer" predominating in the equilibrated mixtures. For example, in the present study it was found that a sample of pure "low-boiling isomer," after storage in the refrigerator for *ca.* 7 months, consisted of a mixture of the "low-" and "high-boiling isomers" in a ratio of 31.1:68.9, respectively.[33]

2. 4-Methylcyclohexanone with Sulfuryl Chloride. To a solution of 30.0 g (0.268 mole) of 4-methylcyclohexanone in 200 ml of carbon tetrachloride maintained at 45° was added dropwise with stirring a solution of 36.5 g (0.27 mole) of sulfuryl chloride in 100 ml of carbon tetrachloride. Heating and stirring were continued for an additional 18 hr. After cooling, the reaction mixture was washed with water until free of chloride ion and dried. The solvent was removed under reduced pressure and the yellow liquid residue distilled (30-cm Vigreux column) giving 28.8 g (73%) of the mixture of isomers **3a** and **3b** very similar to that from the aqueous chlorination above.

2-Chloro-5-methylcyclohexanone. A solution of 13.5 g (0.10 mole) of sulfuryl chloride in 50 ml of carbon tetrachloride was added dropwise with stirring to a solution of 10.0 g (0.089 mole) of 3-methylcyclohexanone in 200 ml of carbon tetrachloride maintained at 45°. After heating and stirring for an additional 17 hr, the reaction mixture was cooled, washed with water until free of chloride ion, and dried. Removal of the solvent under reduced pressure gave a yellow liquid residue which was vacuum distilled (30-cm Vigreux column). The following three fractions were collected: fraction 1, 3.65 g, bp 72.5–73.5° (8 mm), n^{23}_{D} 1.4697; fraction 2, 1.97 g, bp 79.6–94.0° (8 mm), n^{23}_{D} 1.4739; fraction 3, 1.78 g, bp 94.0–94.3° (8 mm), n^{23}_{D} 1.4774. Gc analysis under the conditions employed for the 2-chloro-4-methylcyclohexanone isomers showed the presence of two major components in all three fractions with retention times of 1.63 and 2.95 min. The component with the 2.95-min retention time was predominant in all three fractions, although there were greater quantities of the 1.63-min component in the lower boiling fractions. Upon standing in the refrigerator, white needles separated from fraction 1. These were filtered off and recrystallized from Skelly B, mp 56.5–57.0° (lit.[14] mp 55–56°).

Anal. Calcd for $C_7H_{11}ClO$: C, 57.34; H, 7.56. Found: C, 57.23; H, 7.38.

The neat infrared spectrum showed carbonyl absorption at 5.78 μ (1730 cm^{-1}), whereas the carbonyl absorption of 3-methylcyclohexanone (neat) appears at 5.84 μ (1772 cm^{-1}). The nmr spectrum (CCl_4, internal TMS) exhibited absorptions at τ 5.54 [four-line multiplet (over-all spacing of 16.8 cps), 1, C_2-H, axial], 7.2–8.85 (complex absorption, 7, ring), and 8.96 [doublet (J = 4.4 cps), 3, methyl]. These spectra show this solid isomer to be *trans*-2-chloro-5-methylcyclohexanone (**4a**).

Rearrangements of 1-Chloro-4-methylcyclohexene Oxide. 1. Neat Thermal Rearrangements. A 3.77-g sample of 1-chloro-4-methylcyclohexene oxide was placed in a 10-ml distillation flask connected to a semimicro platinum spinning band column, and with a bath temperature of 80° was brought to a reflux at reduced pressure, bp 63° (9.75 mm). After heating at these conditions for 20 hr the material ceased to reflux. The flask was cooled in an ice bath and a 1-μl sample removed for gc analysis, using a 0.25-in. × 2 ft 10% diisodecyl phthalate on 60–80 Chromosorb W column at 100°. Three components were observed with retention times of 3.95, 6.59, and 24.70 min. These were found to be unrearranged epoxide, *trans*-2-chloro-4-methylcyclohexanone (**3a**), and *cis*-2-chloro-4-methylcyclohexanone (**3b**), respectively, by comparison of retention times with known samples. Relative areas indicated considerable epoxide had not yet rearranged.

Gc analysis after continued heating at reduced pressure for another 22 hr still showed considerable epoxide remaining, so then the bath temperature was increased to 100°. After heating at these conditions for an additional 25 hr, analysis by gc again showed only the same three components, now in the ratio 4.4:40.4:55.2. Although the integration showed *ca.* 4.4% of the epoxide remaining, no further attempt was made to drive the rearrangement to completion. At this point the sample weight was 3.35 g. Thus, there was a loss of 0.42 g owing to column holdup and any vaporization loss.

After redistillation of a sample of the epoxide, gc analysis showed that the pot residue consisted of only *trans*-2-chloro-4-methylcyclohexanone in addition to a small amount of epoxide and a trace of *cis*-2-chloro-4-methylcyclohexanone. In order to recheck this observation, rearrangements were carried out as before, allowing the epoxide to reflux at reduced pressure (10 mm) with a bath temperature of 80°. Aliquots were removed periodically and analyzed as before by gc. After heating for 86.3 hr, the analysis showed only epoxide and *trans*-2-chloro-4-methylcyclohexanone in the ratio of 66.6:33.4. Only a trace of a peak was observed at the retention time for the *cis* isomer of the chloro ketone. After 104.1 hr, the ratio was 56.1:39.7:4.2 for epoxide, **3a**, and **3b**, respectively, and at the end of 112.6 hr the ratio was 48.6:44.0:7.4.

2. Zinc Chloride Catalyzed Rearrangement at 80°. A 5.03-g sample of the epoxide and several small crystals of freshly fused zinc chloride were placed in a 25-ml distillation flask connected to a 30-cm Vigreux column. The system was evacuated to a pressure of 10 mm and then heated with a wax bath maintained at 80°. The

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[32] G. Brown, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 431.

[33] Gc analyses were carried out using a 0.25 × 2 in. silicone gum rubber on Chromosorb P column at 100°.

sample immediately began to turn pink, and when refluxing first started the temperature, bp 70.3° (9.8 mm), was about 7° above the boiling point of the epoxide at this pressure, bp 63° (10 mm), indicating that rearrangement was proceeding very rapidly. After refluxing for about 10 min, the sample had turned dark red. Heating was continued at these conditions for 9 hr, during which time refluxing had stopped. The sample was cooled with an ice bath and then analyzed by gc using conditions similar to those described above. A series of six minor components with poor separation appeared in a retention time range of 1.2–2.5 min (4.5% by integration). Other peaks appeared at 4.67 (30.5%), 7.02 (0.9%), 9.92 (17.1%), and 17.11 min (47.0%). The components with retention times of 4.67 and 17.11 min were identified as *trans*- and *cis*-2-chloro-4-methylcyclohexanone, respectively, by comparison with known samples.

The Vigreux column was rinsed with ether to recover the column holdup and after removal of the ether the total sample weight was 4.96 g. A short-path distillation under vacuum, collecting the distillate in a Dry Ice cooled receiver, gave 3.79 g (75.4%) of a clear, colorless distillate and 1.14 g (22.6%) of a dark red, extremely viscous pot residue. After standing for several hours, the distillate developed a light pink color. Gc analysis of the distillate gave results very similar to those obtained before distillation. Integration now showed that *trans*- and *cis*-2-chloro-4-methylcyclohexanone comprised 29.8 and 40.3%, respectively, of the total mixture.

The component with the retention time of 9.92 min now integrated as 19.7% of the mixture. Since this component was not observed in the thermal rearrangements, a small quantity was collected from the gc as a colorless liquid. The infrared spectrum showed strong hydroxyl absorption at 2.94 μ, but only weak carbonyl absorption at 5.81 μ. The nmr spectrum (CCl_4, internal TMS), taken in a microtube, showed the following absorptions: τ 5.98 (singlet), 6.68 (singlet), complex absorption from τ 7.0 to 8.8 with peaks centered at τ 7.63 and 8.03, and 9.10 (doublet). The integration suggested the presence of a total of 12 protons, based on the methyl doublet at τ 9.10 (3 H) and the two singlets at τ 5.98 (1 H) and 6.68 (1 H).

3. Zinc Chloride Catalyzed Rearrangement at 25°. This rearrangement was carried out as in part 2 except at room temperature (*ca.* 25°) and 10 mm pressure. A 5.72-g sample had turned dark red. Gc analysis after 51 hr showed a reaction mixture with the same components as observed in the rearrangement at 80°. *trans*- and *cis*-2-chloro-4-methylcyclohexanone integrated as 39.2 and 28.6%, respectively, and the unidentified alcoholic product integrated as 22.6%. A short-path distillation under vacuum gave 3.85 g (67.3%) of a clear, colorless distillate and 1.59 g (27.8%) of a dark red, viscous pot residue. As before, the distillate developed a light pink color upon standing. Gc analysis of the distillate again gave results very similar to that of the crude rearrangement mixture. *trans* and *cis*-2-chloro-4-methylcyclohexanone now integrated as 43.2 and 23.6%, respectively, and the unidentified alcoholic product integrated as 22.1%.

Zinc–Acetic Acid Reductions of 1-Chloro-4-methylcyclohexene Oxide Rearrangement Products. The reduction procedure was similar to that described by Whalley.[34] In each reduction a 2.0-g sample of the rearrangement mixture (distilled in the case of the catalyzed rearrangements) was dissolved in 5 ml of glacial acetic acid. While stirring, 1.8 g (0.0275 g-atom) of zinc dust was added in portions, cooling the reaction mixture periodically with an ice-water bath. The reaction was then allowed to stir at room temperature for several hours. The mixture was filtered, the acetic acid neutralized with saturated sodium bicarbonate solution, and the resulting mixture extracted continuously with ether overnight. The ether extract was dried and concentrated by distillation at atmospheric pressure. The light yellow liquid residue was then analyzed by gc using a 0.25 in. × 6 ft 10% diisodecyl phthalate on 60–80 Chromosorb W column at 150°. In each case the analysis showed the presence of two major components whose retention times were identical with those of ether and 4-methylcyclohexanone. Traces of several other minor components were observed; one was indicated to be acetic acid by its retention time. The per cent yield of ketone by reduction was then obtained by gc integration of these ether solutions of the product, corrections being made for weight per cent *vs.* integrated per cent by integration of known weighed mixtures of ether and 4-methylcyclohexanone. The results for the thermal and the two zinc chloride catalyzed rearrangements are shown in Table I.

Table I

Catalyst	Approx reaction temp, °C	Reaction time, hr	Yield of ketone by reduction, %
1. None	80–100	67	86
2. $ZnCl_2$	80	9	75
3. $ZnCl_2$	25	51	71

The lower yields of reduction product for the catalyzed rearrangements compared to the thermal rearrangements are most likely due to the presence of the unidentified products formed in the presence of zinc chloride. However, if calculations are made on the basis of only the amount of 2-chloro-4-methylcyclohexanone isomers present in these catalyzed rearrangement mixtures, the yields of ketone by reduction are in excess of 100%. This would seem to indicate that at least a portion of these unidentified products are also giving rise to the same ketone reduction product.

Since 3- and 4-methylcyclohexanone have the same retention times under these conditions, gc collections were made of the ketonic reduction product for spectral analysis. The infrared spectrum of the collected material was identical with that of 4-methylcyclohexanone.

Zinc–Acetic Acid Reduction of 2-Chloro-4-methylcyclohexanone. Reduction of 2-chloro-4-methylcyclohexanone was carried out in the same manner as described above for the reduction of the rearrangement products. Pure *trans* isomer was used for the reduction, but this would be expected to isomerize under the reaction conditions. The yield of 4-methylcyclohexanone varied from 81.5 to 87.8%, with an average yield of 84.9% for four runs.

Zinc–Acetic Acid Reduction of 2-Chloro-5-methylcyclohexanone. Reduction of 2-chloro-5-methylcyclohexanone was conducted in the same manner as described above. The purified solid *trans* isomer of the chloro ketone was used. The yields of 3-methylcyclohexanone from two runs were 80.3 and 82.8% (average 81.6%).

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[34] W. B. Whalley, *J. Chem. Soc.*, 3229 (1951).