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STEREOCHEMISTRY OF HYDROGEN BROMIDE ADDITION TO CERTAIN OLEFINS

by

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Dean of Graduate College

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INTRODUCTION

Hydrogen bromide can add to olefins in two well defined ways: by a normal or ionic addition and by an abnormal or free radical addition. Until the past few years, however, the stereochemistry and, by inference, the mechanistic picture of these reactions, received little attention. Recent work with both the normal and abnormal additions have shown that both reactions have a preference for trans addition.

In work on the normal or ionic addition, which was done in these laboratories, hydrogen bromide, when reacted with 1,2-dimethylcyclohexene, was found to give mainly trans-1,2-dimethylcyclohexyl bromide. During the course of this study, however, certain questions presented themselves with regard to the conformations of the bromide products. These questions demanded further study on a different system in order to establish the generality of the results obtained.

Thus, this study of the stereochemistry of the hydrogen bromide addition to 1,2-dimethylcyclopentene was undertaken.

HISTORICAL

Addition of Hydrogen Halides to Olefins

Orientation in olefinic addition reactions has received attention since the early days of organic chemistry. By 1870 enough was known about the direction of the addition of hydrogen halides to unsymmetrical olefins that Markownikoff[1] could formulate his famous rule, later slightly revised[2], for the orientation of the addition of hydrogen halides to olefins. The rule stated that the halogen would go to the least hydrogenated atom, or to the atom already carrying a negative atom. Thus hydrogen chloride would add to isobutylene to produce <u>t</u>-butyl chloride and to ethylene chloride to give 1,1-dichloroethane. That there were, even then, exceptions to the rule is apparent since Markownikoff added that the rule held at low temperatures but that reversed orientation might be observed at higher temperatures.

Much later, Kharasch[3] reviewed the available data on the orientation of hydrogen halide additions to olefins and concluded that, for hydrogen bromide additions, at least, there

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[1] W. Markownikoff, <u>Ann.</u>, <u>153</u>, 256 (1870).

[2] W. Markownikoff, <u>Compt. rend.</u>, <u>81</u>, 670 (1875).

[3] M. S. Kharasch and O. Reinmuth, <u>J. Chem. Ed.</u>, <u>8</u>, 1703 (1931).

must be two types of addition reactions, a "normal" addition in which the orientation would follow Markownikoff's rule and and "abnormal" addition in which the orientation was reversed. Kharasch and Mayo[4] determined that the "abnormal" addition of hydrogen bromide was dependent on peroxides which are nearly always present in olefinic substances that have been exposed to the air. A free radical mechanism is now used to explain this peroxide catalyzed addition[5]. For example, the peroxide could oxidize the hydrogen bromide with liberation of bromine atoms. These atoms start a homolytic chain with the bromine atom adding to the unsaturated molecule to give a free radical which extracts a hydrogen atom from a molecule of hydrogen bromide to leave another bromine atom to start another cycle. The same free radical sequence can also be initiated by photolysis of the hydrogen bromide. Thus it became possible to classify the addition of hydrogen bromide to olefins into two categories: a radical addition catalyzed by peroxides or light and a normal or ionic addition.

Until recently, the stereochemistry of the ionic hydrogen halide addition to multiple bonds was known in only a few cases. Even so, a preference for a <u>trans</u> addition was

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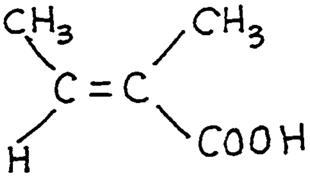
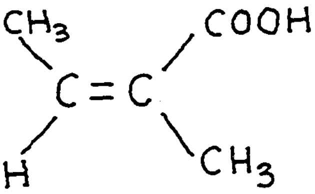
[4] M. S. Kharasch and F. R. Mayo, <u>J. Am. Chem. Soc.</u>, <u>55</u>, 2468 (1933).

[5] F. R. Mayo and C. Walling, <u>Chem. Rev.</u>, <u>27</u>, 351 (1940).

apparent. Thus Friederich[6] showed that the addition of hydrogen chloride to methylpropiolic acid in water yields β-chlorocrotonic acid, the trans olefin. Michael[7] found that the corresponding addition to acetylenedicarboxylic acid gives chlorofumaric acid by trans addition. It was also found that hydrogen iodide added to dimethylacetylenedicarboxylate to give the trans product[8]. In the case of addition to double bonds, Young and his coworkers[9] showed that when hydrogen iodide added to tiglic acid a different product was obtained than in the case of angelic acid. The hydroiodides of angelic and tiglic acid, when treated with sodium carbonate, gave pure cis- and trans-2-butene, respectively. Grovenstein and Lee[10]



tiglic acid



angelic acid

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[6] R. Friederich, Ann., 219, 368 (1883).

[7] A. Michael, J. pract. chem., 52, 289 (1885).

[8] V. G. Ostroverkhov and E. A. Shilov, Ukran. Khim. Zhur., 22, 743 (1956). (Original not examined; abstracted in Chem. Abstr., 51, 7813e (1957).)

[9] W. G. Young, R. T. Dillon and H. J. Lucas, J. Am. Chem. Soc., 51, 2528 (1929).

[10] E. Grovenstein, Jr., and D. E. Lee, ibid., 75, 2639 (1953).

assumed that the decarboxylative elimination to give the 2-butene was a trans elimination, in which case the addition of the hydrogen iodide must have been trans. The addition of hydrogen bromide to bromomaleic acid produced meso-dibromosuccinic acid[11], also by a trans addition, while the reaction between dibenzo-(2,2,2)-bicycloöctatriene-2,3-dicarboxylic acid and hydrogen bromide in glacial acetic acid resulted in trans addition[12].

Each of these examples involve olefinic or acetylinic compounds containing another functional group. The influence of the second group on the course of the addition was not indicated for the examples cited, although participation of neighboring groups in some addition reactions is a significant factor[13]. Thus there may be some question about the overall generality of the trans addition.

Recently, however, Hammond and Nevitt[14] investigated the stereochemistry of the addition of hydrogen bromide to 1,2-dimethylcyclohexene. In acetic acid at room temperature, an

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[11] M. S. Kharasch, J. V. Mansfield and F. R. Mayo, unpublished results in G. W. Wheland, "Advanced Organic Chemistry", Second Edition, John Wiley and Sons, N. Y., p. 302 (1949).

[12] W. R. Vanghan and K. M. Milton, J. Am. Chem. Soc., 74, 5623 (1952).

[13] L. Goodman and S. Winstein, ibid., 79, 4788 (1957).

[14] G. S. Hammond and T. D. Nevitt, ibid., 76, 4121 (1954).

equilibrium mixture of 15% cis-1,2-dimethylcyclohexyl bromide with 85% trans-1,2-dimethylcyclohexyl bromide was obtained for all reactions whose reaction times were more than a few minutes. When the addition in acetic acid was quenched after only 30 seconds the bromide product appeared to be entirely of the trans compound. In pentane at 0°C and at -78°C the product was again solely the trans-bromide, indicating the addition to be entirely stereospecific and completely trans. When the reactants were frozen at -196°C and then warmed to -78°C, however, 20% of the cis bromide was formed.

The ionic addition of hydrogen halides to olefins presents a complicated kinetic picture. Early work by Maass[15-17] on the addition of hydrogen chloride and hydrogen bromide to propylene in sealed tubes in the absence of solvent indicated that a 1:1 mixture reacts in a few days at 20°C, with half the propylene being converted to isopropyl chloride, half to a hexyl chloride with a quarter of the hydrogen chloride or bromide remaining unreacted. With a 2:1 ratio of hydrogen chloride to propylene the reaction was ten to fifteen times as fast, and less hexyl chloride was formed. Hydrogen bromide added about two hundred times as fast as hydrogen chloride,

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[15] O. Maass and C. H. Wright, ibid., 46, 2664 (1924).

[16] O. Maass and C. Sivertt, ibid., 47, 2883 (1925).

[17] B. P. Sutherland and O. Maass, Trans. Roy. Soc. Can., III, 20, 499 (1929).

and the hydrogen bromide addition could also be accelerated by the addition of hydrogen chloride, even though the hydrogen chloride did not react at a significant rate under these conditions. Rates thus depended more on the concentration of hydrogen halide than on the olefin. The additions were also strongly accelerated by relatively small amounts of water. The rate of the hydrogen chloride-propylene reaction increased with temperature up to about 45°C, had a negative temperature coefficient between 45°C and 70°C, and increased very slowly above 70°C with an increase in pressure[18]. Similar observations were made on the addition of hydrogen chloride to the three isomeric butylenes in the liquid phase[19,20]. No evidence of reaction was found in the gas phase.

Kistiakowsky and Stauffer[21] studied the gas phase situation further, at higher temperatures. They determined the activation energy for the addition of hydrogen chloride to isobutylene. The rather high value (29 kcal/mole) obtained explains the very low rate at moderate temperatures. The kinetics did not appear abnormal. Since, however, a dry

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[18] C. H. Holder and O. Maass, Can. J. Res., 16B, 453 (1938).

[19] C. C. Coffin, H. S. Sutherland and O. Maass, ibid., 2, 267 (1930).

[20] C. C. Coffin and O. Maass, ibid., 3, 526 (1930).

[21] G. B. Kistiakowsky and C. H. Stauffer, J. Am. Chem. Soc., 59, 165 (1937).

liquid mixture of isobutylene and hydrogen chloride reacts nearly instantaneously at 0°C and within a minute at -78°C[19], the liquid phase reaction quite probably proceeds by a mechanism different from that of the gas phase.

Hennion and his coworkers[22] qualitatively studied the rate of addition of hydrogen chloride to cyclohexene and 3-hexene in a series of solvents. They concluded that the rates were not of a simple second order but did observe that the reaction was rapid in hydrocarbon solvents such as heptane and xylene but very slow in ether and dioxane, presumably due to a lowering of the effective concentration of the hydrogen chloride through some sort of complex formation. Similar results were obtained with α-pinene[23].

Mayo and his coworkers[24,25] obtained kinetic measurements on the reactions of hydrogen chloride and hydrogen bromide with propylene and isobutylene. In the absence of solvent the reaction of hydrogen bromide with propylene[25] gave, as Maass[15-17] had found, a small amount of a hexyl chloride. In pentane, no hexyl chloride was observed, but the reaction gave

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[22] S. F. O'Connor, L. H. Baldinger, R. R. Vogt and G. F. Hennion, ibid., 61, 1454 (1939).

[23] G. F. Hennion and C. F. Irwin, ibid., 63, 860 (1941).

[24] F. R. Mayo and M. G. Savay, ibid., 69, 1348 (1947).

[25] F. R. Mayo and J. J. Katz, ibid., 69, 1339 (1947).

both the normal and the abnormal addition products. The ionic reaction was apparently fourth order; first order with respect to propylene and third order with respect to hydrogen bromide. When a hydroxylic compound, such as absolute alcohol, was added the reaction became very rapid and gave only the normal product, isopropyl bromide. Dilution of the solution with additional amounts of solvent, however, seemed to accelerate the abnormal reaction until, in sufficiently dilute solution the product was essentially entirely n-propyl bromide even in the presence of inhibitors.

The kinetics of the reaction of hydrogen chloride with isobutylene proved more amenable to study[24]. In n-heptane at 0°C the only product was t-butyl chloride. The uncatalyzed reaction was third order in hydrogen chloride and first order in olefin. With catalysis by water, mercury chlorides or phosphorous pentoxide, the reaction approximated second order. The reaction was greatly accelerated by cooling the reaction vessel to -80°C, then warming rapidly to 0°C. The use of a "reasonable value" for the equilibrium constant for a 1:1 complex of hydrogen chloride and isobutylene simplified the kinetic calculations and made for more reproducible rate constants.

The kinetics for the addition of hydrogen bromide to dimethyl acetylenedicarboxylate from acetic acid solutions containing a bromide salt have recently been shown to be second order; first order in the alkyne and first order in the concentration of the bromide salt[26].

Lack of information on the nature of the stereospecific properties of the addition of hydrogen halides to olefins led the earlier workers to propose that the addition in polar solvents was the microscopic reverse of the unimolecular elimination[27,28]. The addition reaction was thought to involve a carbonium ion intermediate formed by reaction of the olefin and a proton, which then interacted with a hydrogen halide molecule to form the product. Support for the carbonium ion mechanism came from Whitmore[29,30] who observed that in the addition of hydrogen chloride to 3-methyl-1-butene or to 3,3-dimethyl-1-butene, appreciable amounts of rearranged product, the tertiary chloride, was formed. The tertiary chloride was not formed from the secondary chloride and thus must have come from the rearrangement of a carbonium ion intermediate.

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[26] V. G. Ostroverkhov and E. A. Shilov, Ukran. Khim. Zhur., 22, 590 (1956). (Original not examined; abstracted in Chem. Abstr., 51, 6515i (1957).)

[27] C. K. Ingold, Chem. Rev., 15, 225 (1934).

[28] C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N. Y., p. 652 (1953).

[29] F. C. Whitmore and F. Johnstone, J. Am. Chem. Soc., 55, 5020 (1933).

[30] G. C. Ecke, N. C. Cook and F. C. Whitmore, ibid., 72, 1511 (1950).

Ogg[31], believing that the carbonium ion could not account for the observed trans additions, proposed a carbanion mechanism instead, with the addition of a bromide ion as the first step, followed by interaction of the resulting carbanion with hydrogen bromide to give product.

The recent work of Hammond and Nevitt[14] has shown a definite trans stereospecificity for the ionic addition in acetic acid. Moreover, the cis:trans product ratio from the addition of hydrogen bromide to 2,3-dimethylcyclohexene and to 2-methylmethylenecyclohexane are not identical with each other or with that obtained by addition to 1,2-dimethylcyclohexene. This rules out the classical carbonium ion as the only intermediate. Furthermore, since the rate of solvolysis of the cis- and trans-1,2-dimethylcyclohexyl bromides are nearly identical[32], the addition cannot be the reverse of the solvolytic elimination. Hammond and Nevitt proposed that the rate determining step must involve simultaneous formation of the carbon-bromine and carbon-hydrogen bonds with the bromine ion and the hydrogen ion attacking opposite sides of the plane of the olefinic substrate. This may be completely concerted or

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[31] R. A. Ogg, Jr., ibid., 57, 2727 (1935).

[32] T. D. Nevitt and G. S. Hammond, ibid., 76, 4124 (1954).

it may involve the attack of a bromide ion on a proton-olefin complex of the type suggested by Dewar[33] and Taft[34].

In a non-polar solvent, Maass[17,19] proposed that the addition of the hydrogen halide proceeded through the rearrangement of a 1:1 complex of hydrogen halide with the olefin and that the interaction of two of these complexes gave the hexyl chloride observed. Evidence for such 1:1 complexes came from melting point measurements of the halide-olefin mixtures[15]. Complex formation at low temperatures was very rapid and complete before any appreciable amount of addition reaction had occurred. Additional evidence for the 1:1 complex has been obtained in recent studies on the basicity of olefins[35,36].

Complex formation as a prelude to the reaction would help explain the rather strange temperature coefficients observed. Thus the rapid increase in rate observed when the mixture is cooled to -80°C briefly, then warmed rapidly to room temperature is explained as due to the formation, at the lower temperature, of the complex, which, when once formed, readily

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[33] M. J. S. Dewar, J. Chem. Soc., 1946, 406.

[34] R. W. Taft, Jr., J. Am. Chem. Soc., 74, 5372 (1952).

[35] H. C. Brown and J. D. Brady, ibid., 74, 3570 (1952).

[36] E. Terres and T. Assenci, Brennstoff chem., 37, 257 (1956). (Original not examined; abstracted in Chem. Abstr., 51, 695d (1957).)

collapses to product at the higher temperature. Also, the negative temperature coefficient observed for the 45°C to 70°C range may be explained as due to the improbability of complex formation at the higher temperatures.

Mayo[24,25] felt that the observed fourth order kinetics could best be accounted for by the reaction of a 1:1 complex of hydrogen chloride and isobutylene with a dimer of hydrogen chloride or by the reaction of a 2:1 hydrogen chloride-olefin complex with hydrogen chloride. Another possibility, which could not be excluded was the reaction of hydrogen chloride molecule-aggregates with the hydrogen chloride-olefin complex. The lower order of the reaction observed with catalysts present could be explained in terms of the assumption that the catalyst takes the place of some of the excess hydrogen chloride in the reaction.

When the stereochemical nature of the reaction was determined, Hammond and Nevitt[14] proposed that the mechanism of addition in the non-polar solvent was probably similar to that in polar solvents except for a higher molecularity of hydrogen bromide due to the replacement, by hydrogen bromide molecules, of the solvating polar molecules. The cis addition observed at -196°C was thought likely to be a cyclic process involving an even greater number of hydrogen bromide molecules.

In summary, the ionic addition of hydrogen halide to olefins probably goes through a similar mechanism in both polar and non-polar solvents. This mechanism must be consistent with the observed stereochemistry. The molecularity of the hydrogen halide species with regard to the rate of the addition reaction may be greater in the non-polar solvent, as observed, due to a lack of solvating molecules which are capable of assisting in the charge separation.

The π-Complex in Addition Reactions

The acid catalyzed hydration of olefins has received considerable study. Since no acid was used up in the reaction, first order rate constants were obtained when the olefin was hydrated in any given acidic solution[37-42]. These rate constants increased with the acidity of the solution more rapidly than did the hydronium ion concentration. Thus the rate for the hydration of isobutylene was fifteen times as fast in 1 M

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[37] H. J. Lucas and W. F. Eberz, J. Am. Chem. Soc., 56, 460 (1934).

[38] H. J. Lucas and Y. P. Liu, ibid., 56, 2138 (1934).

[39] J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, ibid., 73, 3792 (1951).

[40] R. W. Taft, Jr., J. B. Levy, D. Aaron and L. P. Hammett, ibid., 74, 4735 (1952).

[41] J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, ibid., 75, 3955 (1953).

[42] E. L. Purlee, R. W. Taft, Jr., C. A. DeFazio, ibid., 77, 837 (1955).

nitric acid as in 0.1 M nitric acid[37,39]. Added potassium nitrate had a noticeably smaller effect[39]. The rates for the hydration of trimethylethylene[41,42] and asym-methylethylethylene[41] were nearly identical to that for isobutylene, although the enthalpy and entropy values differed somewhat. 1-Methylcyclopentene[40] hydrated three times as fast with a considerably smaller entropy change.

The hydration of isobutylene in chloroacetic acid solvents exhibited a specific hydronium ion catalysis[43]. With this in mind, Taft and his coworkers[44,45] measured the dependence of the rate of hydration on the acid concentration for several olefins. With each they found a linear dependence between the logarithm of k_p, the rate of hydration of the gaseous olefin at unit pressure, and H_o, the Hammett acidity function. A similar linearity was observed between k_c, the hydration rate at unit concentration, and h_o, the antilog of H_o.

Hammett[46] has presented evidence that for those acid-catalyzed reactions in aqueous solution for which the rates parallel the stoichiometric acid concentration, the transition

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[43] F. G. Ciapetta and M. Kilpatrick, ibid., 70, 639 (1948).

[44] R. W. Taft, Jr., ibid., 74, 5372 (1952).

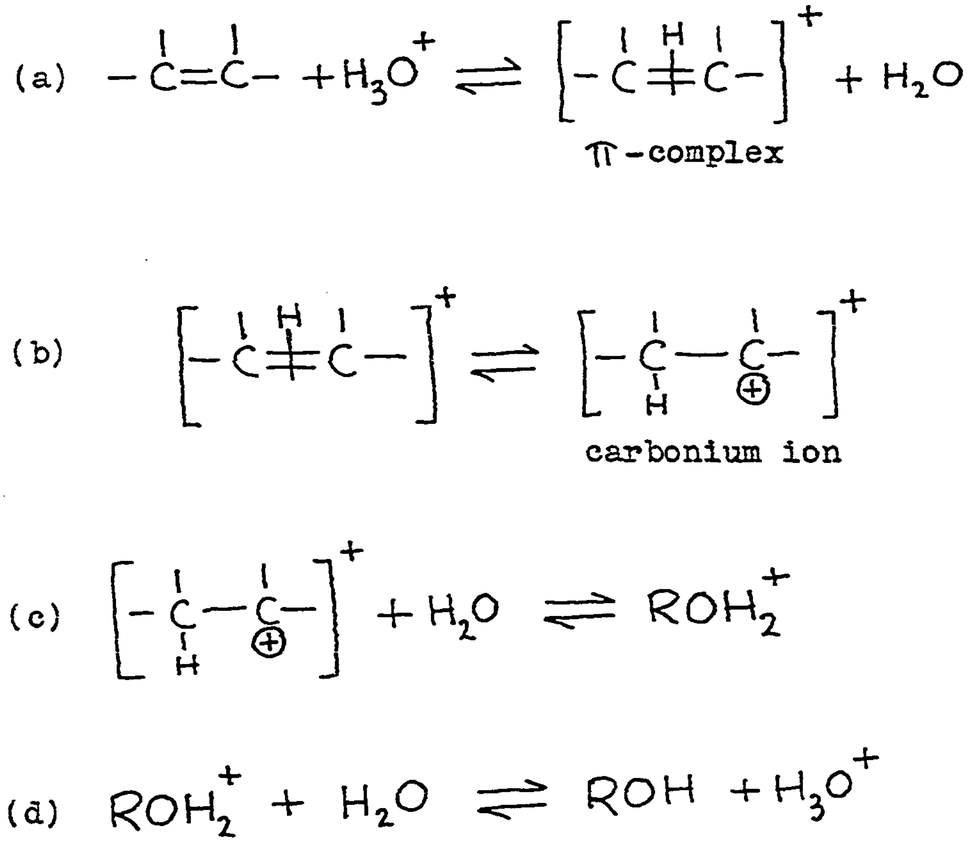
[45] R. W. Taft, Jr., E. L. Purlee, P. Riesz and C. A. DeFazio, ibid., 77, 1584 (1955).

[46] L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., New York, p. 273 (1940).

state of the reaction consists of substrate, a proton and a water molecule, but in those reactions whose rates parallel h_o, the transition state does not contain the added water molecule.

In the light of the acidity data, Taft[42] stated that the mechanism for the acid-catalyzed hydration of olefins could not be a proton transfer from water to olefin with the formation of an unstable carbonium ion intermediate, or the reaction of a carbonium ion (previously formed in a fast reversible step) with water to form the conjugate acid of the resulting alcohol, since both would involve a tightly bound water molecule in the transition state. Neither could it be a concerted process involving an electrophilic attack by hydronium ion at one of the unsaturated carbons and a nucleophilic attack by water at the other, which would involve at least two "bound" water molecules.

It then became apparent that the transition state must involve a "free" cation, that is, simply the olefin and a proton with hydration only by ion-dipole interaction between the ion and a water molecule. A suitable mechanism would involve a rate-controlling unimolecular reaction of a protonated form of the reactant. Taft proposed the following mechanism as being consistent with the known information. Steps (a), (c) and (d) are equilibria with (b) the rate controlling step. The π-complex was of the type suggested



$$(a)\quad -\overset{|}{C}=\overset{|}{C}- + H_3O^+ \rightleftharpoons \left[-\overset{|}{C}\overset{H}{\ddagger}\overset{|}{C}-\right]^+ + H_2O$$

π-complex

$$(b)\quad \left[-\overset{|}{C}\overset{H}{\ddagger}\overset{|}{C}-\right]^+ \rightleftharpoons \left[-\underset{H}{\overset{|}{C}}-\underset{\oplus}{\overset{|}{C}}-\right]^+$$

carbonium ion

$$(c)\quad \left[-\underset{H}{\overset{|}{C}}-\underset{\oplus}{\overset{|}{C}}-\right]^+ + H_2O \rightleftharpoons ROH_2^+$$

$$(d)\quad ROH_2^+ + H_2O \rightleftharpoons ROH + H_3O^+$$

by Dewar[47] in which the proton is embedded in the π-orbitals which extend above and below the plane of the double bond. The stereochemistry is preserved in the fast, reversible step (a). In step (b), the carbonium ion formed has the proton covalently bound to one of the carbon atoms and the stereochemistry probably is not preserved.

Support for this mechanism was given by the fact that in the hydration of two isomeric pentenes, 2-methyl-1-butene and 2-methyl-2-butene, olefin removed after 50% of the original

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[47] M. J. S. Dewar, J. Chem. Soc., 1946, 406.

had reacted, contained none of its isomer[41,48]. These two olefins have a common carbonium ion so this observation precluded a reaction sequence in which a carbonium ion is formed in a preliminary proton transfer.

Further support came as a result of following the rate of hydration of 2-methyl-2-butene and 1-methylcyclopentene in heavy water[49]. A linear relationship was not obtained for a plot of the hydration rate vs. the mole fraction of deuterium in the solvent. Such a relationship would be expected for a rate determining proton transfer step. On the other hand, an exact agreement was had between the observed solvent isotope effect and calculations from Butler's equation, which was based on a proton transfer previous to the rate determining step.

Isolation of unreacted olefin after 50% of the reaction had been completed revealed that there was no deuterium in the olefin. Thus the conjugate acid formed in the prior equilibrium lost the same hydrogen ion (deuterium ion) that had added; that is, all the hydrogens were not equivalent. These facts also supported the previously described mechanism.

A comparison of the equilibria between the rates of hydration and dehydration for 1-methylcyclopentene,

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[48] J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, J. Am. Chem. Soc., 75, 1253 (1953).

[49] E. L. Purlee and R. W. Taft, Jr., ibid., 78, 5907 (1956).

1-methylcyclobutene and methylenecyclobutane[50] indicated that the formation of carbinol from olefin was more favorable for the four-membered ring compound than for the five-membered ring by a factor of 10^4. This was in accord with the I-strain hypothesis of Brown[51] that increasing the coordination number of the carbon atom in a four-membered ring from three to four would be favorable because of the release of some ring strain, while it would not be favorable in a five-membered ring due to increased eclipsing of the ring hydrogen atoms.

The rate of hydration, however, had little dependence on structure. A factor of ten favored the hydration of the five-membered olefin over the four-membered counterparts. This indicated that the transition state cannot be like the alcohol for this would have resulted in increasing the coordination number from three to four and should have favored the four-membered ring compounds over the five-membered ring compound. On the other hand, both the equilibrium values and the rates indicated that the dehydration of 1-methylcyclopentanol was more rapid, in accord with the I-strain hypothesis that a decrease of coordination number from four to three would be more favored in a five-membered ring. Thus the water must be lost before the transition state of the dehydration is reached.

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[50] P. Riesz, R. W. Tafts, Jr., and R. H. Boyd, ibid., 79, 3724 (1957).

[51] H. C. Brown, R. S. Fletcher and R. B. Johannesen, ibid., 73, 212 (1951).

Once again the only mechanism consistent with this description was the one previously given involving a π-complex collapse to a carbonium ion in the rate determining step. And, since the rate of hydration of 1-methylcyclopentene was faster than that for the hydration of 1-methylcyclobutene, the transition state of this step must not involve much carbonium ion character for if it did the opposite rates would have been observed, since the coordination number change to four at one of the two carbons in the carbonium ion formation is more favored in the four membered ring. But since the transition state was stabilized by certain structural features which stabilize carbonium ions, Taft concluded that the transition state of the hydration process possessed carbonium ion character with respect to the electronic but not with respect to the molecular structure, the latter more closely resembling a π-complex.

De la Mare[52], comparing the hydration of olefin results with some results he obtained on the hydrogen halide addition to olefins, in which he found retardation by adding halide ion, concluded that the prior equilibrium, rather than a formation of π-complex, was the formation of a free "protonium" ion, which then reacted with the olefin to form the carbonium ion.

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[52] P. B. D. de la Mare, J. Chem. Soc., 1954, 2930.

$$H_3O^+ \rightleftharpoons H_2O + H^+ \quad \text{(equilibrium)}$$

$$H^+ + \text{olefin} \longrightarrow \text{carbonium ion} \quad \text{(slow)}$$

Neither the mechanisms of Taft[44] nor that of de la Mare[52] would be expected to give any stereospecificity. Although the hydration of olefins has not been investigated from the stereochemical standpoint, analogy with the hydrogen halide addition would suggest that some stereospecificity might occur. This could be explained, if it occurred, by a mechanism which required a direct attack on the π-complex[53].

Such a directed attack on the π-complex had been used to explain the stereospecificity of the addition of hydrogen bromide to 1,2-dimethylcyclohexene[54], and of formic acid to 4-t-butylcyclohexene[55].

In a recent paper, Taft[56] distinguished between the two types of π-complexes indicated by Dewar[45]. The "true" π-complex, involving a mainly olefinic structure with a

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[53] J. Hine, "Physical Organic Chemistry", McGraw-Hill Book Co., New York, p. 217, (1956).

[54] G. S. Hammond and T. D. Nevitt, J. Am. Chem. Soc., 76, 4121 (1954).

[55] S. Winstein and N. J. Holness, ibid., 77, 5562 (1955).

[56] L. G. Cannell and R. W. Taft, Jr., ibid., 78, 5812 (1956).

trigonal coplanar arrangement of carbons and the proton imbedded in the π-orbitals, is a weakly bonded state, as observed in the hydration of olefins. On the other hand, a "bridged" proton species with the hydrogen approximately equidistant between the carbons involves a hydrogen firmly bonded by the overlap of its orbital with the tetrahedral sp^3 orbitals of the carbons. The "bridged" proton intermediate was used by Taft to explain the lack of exchange of hydrogen when isobutylamine was diazotized in heavy water[56].

Acetate Pyrolysis

A large variety of methods are available for the preparation of olefins from alcohols. All have certain advantages and disadvantages.

The acid or iodine catalyzed direct dehydrations usually lead to the most stable olefin[57,58], but the method sometimes results in extensive rearrangement of the carbon skeleton[59,60], depending on the structure of the initial alcohol. No

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[57] F. K. Signaigo and P. H. Cramer, ibid., 55, 3326 (1933).

[58] W. A. Mosher, ibid., 62, 552 (1940).

[59] F. C. Whitmore and H. S. Rothrock, ibid., 55, 1106 (1933).

[60] C. S. Marvel and H. L. R. Williams, ibid., 70, 3842 (1948).

structural rearrangements have been observed in the formation of olefins by distillation of the methyl xanthate of the alcohol[59,61,62,63]. However, the formation of the xanthate is quite inconvenient and the method has generally been replaced by the pyrolysis of a carboxylate ester of the alcohol. Passage of the ester through a glass packed tube heated at 400-600°C results in good yields of olefin and is apparently independent of the nature of the acid moiety[57,64-68]. Acetates are the most frequently utilized esters but others include the benzoates, stearates and methyl carbonates. Bailey and his coworkers[67,68] made a thorough study of the esters of various acids and concluded that acetates were the most convenient for olefin syntheses but that the method could

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[61] L. A. Tschugaev, Ber., 32, 3332 (1899).

[62] E. R. Alexander and A. Mudrock, J. Am. Chem. Soc., 72, 1810 (1950).

[63] E. R. Alexander and A. Mudrock, ibid., 72, 3194 (1950).

[64] C. D. Hurd and F. H. Blunck, ibid., 60, 2419 (1938).

[65] G. L. O'Connor and H. R. Nace, ibid., 74, 5454 (1952).

[66] J. P. Wibaut, H. C. Beyerman and H. B. Van Leeuwen, Rec. trav. chim., 71, 1027 (1952).

[67] W. J. Bailey and J. J. Hewitt, J. Org. Chem., 21, 543 (1956).

[68] W. J. Bailey and W. N. Turek, J. Am. Oil Chemists Soc., 33, 317 (1956).

be modified and used to produce good yields of many different acids by the pyrolysis of their ethyl esters.

Some evidence exists that structural rearrangements may occur during acetate pyrolysis. While many workers[62-64,69-77] report only the expected product, a few workers[78,79] have indicated that rearranged products have been isolated. Thus, for example, Wibaut and his coworkers[70,72,73] reported that 2,2-dimethyl-3-pentyl acetate pyrolyzed at 400°C to give

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[69] J. B. Wibaut and A. J. van Pelt, Rec. trav. chim., 57, 1055 (1938).

[70] J. P. Wibaut, H. Hoog, S. L. Langedijk, J. Overhoot, and J. Smittenberg, ibid., 58, 329 (1939).

[71] A. J. van Pelt and J. B. Wibaut, ibid., 60, 55 (1941).

[72] J. P. Wibaut and H. L. P. Gitsels, ibid., 60, 241 (1941).

[73] J. P. Wibaut and J. Smittenberg, ibid., 61, 348 (1942).

[74] M. H. Gold, J. Am. Chem. Soc., 68, 2544 (1946).

[75] C. G. Overberger, A. Fiscman, C. W. Roberts, H. Arnold, and L. Lal, ibid., 73, 540 (1951).

[76] R. Paul and S. Tchelitcheff, Compt. rend., 233, 1116 (1951).

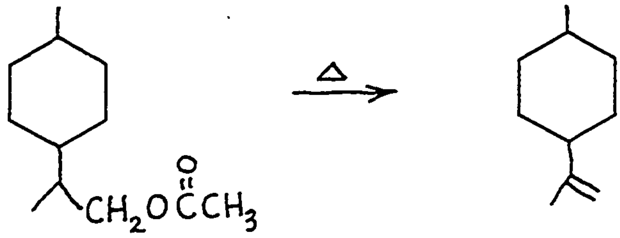
[77] R. J. P. Allan, E. Jones and P. D. Ritchie, J. Chem. Soc., 1957, 524.

[78] P. L. Cramer and M. J. Mulligen, J. Am. Chem. Soc., 58, 373 (1936).

[79] P. L. Cramer and V. A. Miller, ibid., 62, 1452 (1940).

exclusively 4,4-dimethyl-2-pentene, as determined by fractionation and measurement of physical constants. Cramer and Miller[79] indicated that in pyrolysis at the same temperature 93% of the total product is 4,4-dimethyl-2-pentene while rearranged products, including 2,3-dimethyl-2-pentene, made up the other 7%. Wibaut and Smittenberg[73] felt that the rearrangement observed by Cramer and Miller occurred after the pyrolysis but their reasons were not given.

The isomerization of the double bond during the pyrolysis has undergone much consideration. Houtman *et al.*[80] found that n-butyl acetate gave measurable amounts of 2-butene, as well as the expected 1-butene, when longer contact times were involved. On the other hand, Frank and Berry[81] reported that although 8(9)-*p*-menthene readily isomerized with a large variety of catalysts to a mixture of 4(8)-*p*-menthene and 3-*p*-menthene, it could be obtained without isomerization by pyrolyzing *p*-menthanyl-9-acetate.



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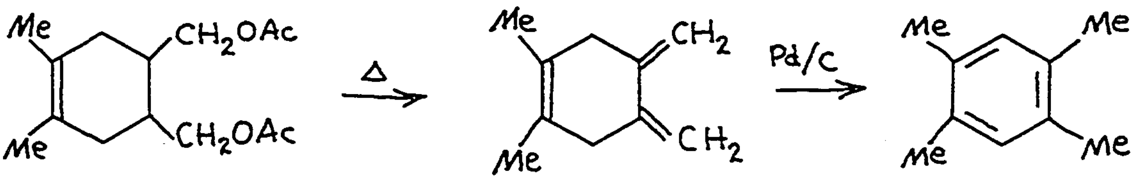
[80] J. P. Houtman, J. VanSteenis and P. M. Heertjis, *Rec. trav. chim.*, *65*, 781 (1946).

[81] R. L. Frank and R. E. Berry, *J. Am. Chem. Soc.*, *72*, 2985 (1950).

Bailey and his coworkers[82-86] undertook an extensive study of isomerization with methylenecyclohexane derivatives. For example, it was found that 4,5-dimethyl-1,2-dimethylene-4-cyclohexene could be obtained without isomerization to durene from a pyrolysis at 500°C[86].



Analysis involved distillation followed by infrared analysis of the distillate. It was observed that the compound readily isomerized by treatment with various catalysts. Small amounts of durene were also obtained under more stringent conditions. Some recent work in Bailey's laboratory[87] indicated that with

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[82] W. J. Bailey and H. R. Golden, <u>ibid.</u>, <u>75</u>, 4780 (1953).

[83] W. J. Bailey, J. Rosenberg and L. J. Young, <u>ibid.</u>, <u>76</u>, 2251 (1954).

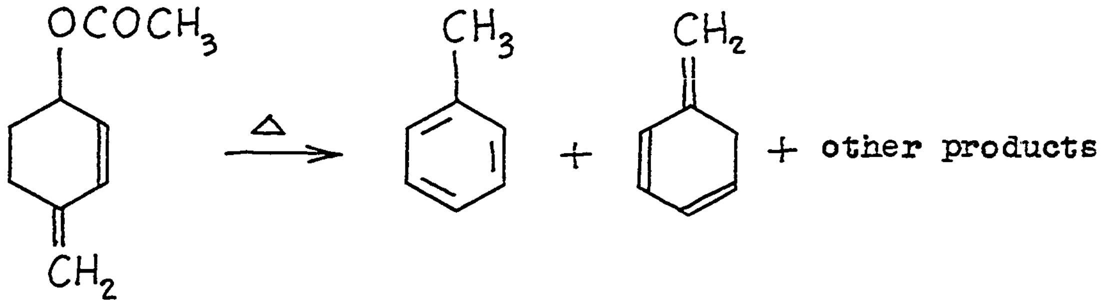
[84] W. J. Bailey and W. R. Arenson, <u>ibid.</u>, <u>76</u>, 5421 (1954).

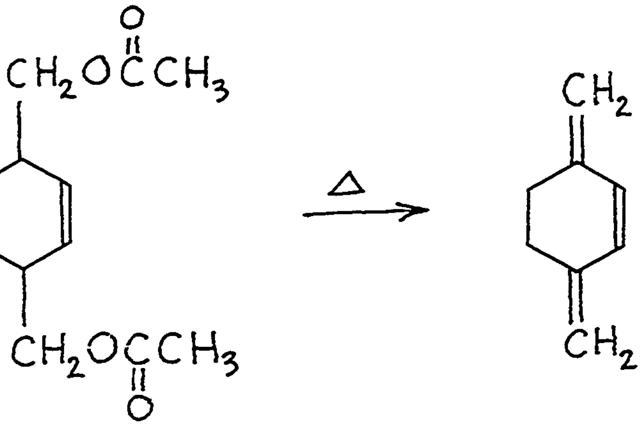
[85] W. J. Bailey and J. Rosenberg, <u>ibid.</u>, <u>77</u>, 73 (1955).

[86] W. J. Bailey, J. Rosenberg and L. J. Young, <u>ibid.</u>, <u>77</u>, 1163 (1955).

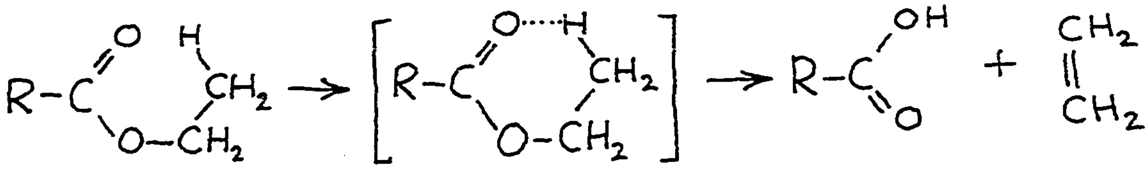
[87] R. Barclay, <u>Diss. Abs.</u>, <u>17</u>, 1460 (1957).

certain compounds isomerization might occur at normal pyrolytic temperatures. Thus the pyrolysis of methylenecyclohex-2-enyl-4-acetate gave measurable amounts of toluene, as indicated by gas chromatography. On the other hand, pyrolysis of 1,4-diacetoxymethyl-1-cyclohexene gave pure 1,4-dimethylene-2-cyclohexene. The latter was also analyzed by gas chromatography.





When it had been determined that acetate pyrolysis was relatively easy with an available β-hydrogen but occurred only at a much higher temperature with the production of different products when a β-hydrogen was not present, Hurd and Blunck[64] proposed that the mechanism for acetate pyrolysis involved a cyclic intermediate formed by a loose association of the carbonyl oxygen with the β-hydrogen.



A study of the stereochemistry of acetate pyrolysis has supported the cyclic mechanism since it has been shown[62,63,88-91] that the pyrolysis has, in common with the Tschugaev xanthate pyrolysis[92,93] and the pyrolyses of halides[94] and of amine oxides[95,96], a definite preference for

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[88] E. R. Alexander and A. Mudrock, J. Am. Chem. Soc., 73, 59 (1951).

[89] R. T. Arnold, G. G. Smith and R. M. Dodson, J. Org. Chem., 15, 1256 (1950).

[90] D. Y. Curtin and D. B. Kellom, J. Am. Chem. Soc., 75, 6011 (1953).

[91] T. D. Nevitt and G. S. Hammond, ibid., 76, 4124 (1954).

[92] W. Hückel, and W. Tappe, Ann., 537, 113 (1939).

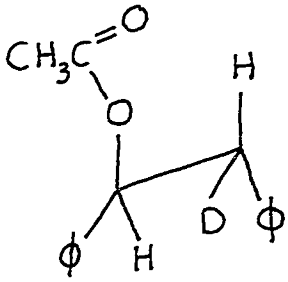
[93] W. Hückel, W. Tappe and G. Legutke, ibid., 543, 191 (1940).

[94] D. H. R. Barton, J. Chem. Soc., 1949, 2174.

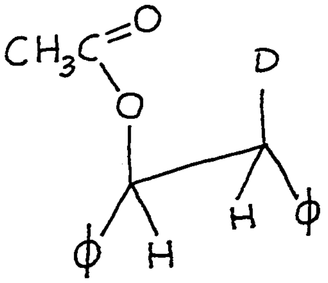
[95] D. J. Cram and J. McCarty, J. Am. Chem. Soc., 76, 5740 (1954).

[96] A. C. Cope and C. L. Bumgardner, ibid., 79, 960 (1957).

cis elimination. That is, the proton and the acetoxy group are both lost from the same side of the plane of the molecule. Thus Alexander and Mudrock[62] found that in the pyrolysis of *cis*-2-phenylcyclohexyl acetate 93-100% of the product was 3-phenylcyclohexene while *trans*-2-phenylcyclohexyl acetate gave 88% 1-phenylcyclohexene with 12% of the 3-phenylcyclohexene. Analysis was by the refractive indices of the products. However, results of Arnold, Smith and Dodson[89] and of Curtin and Kellom[90] indicate that although there is a preference for *cis* elimination it is not completely directional. Thus the former[89] found, using infrared analysis, that *trans*-2-methylcyclohexyl acetate eliminated to give 55% of 1-methylcyclohexene and 45% 3-methylcyclohexene with *cis*-2-methylcyclohexyl acetate giving 75% of the 3-methyl olefin and 25% of the 1-methyl olefin. Since 1-methylcyclohexene cannot be formed from *cis*-2-methylcyclohexyl acetate by a *cis* elimination, another mechanism is indicated. Curtin and Kellom[90] pyrolyzed *dl*-*erythro*- and *dl*-*threo*-2-deutero-1,2-diphenylethyl acetate and found that some *trans* elimination had occurred. Thus *erythro*-2-deutero-1,2-diphenylethyl acetate gave



erythro



threo

trans-α-D-stilbene (1-deutero-1,2-diphenylethylene) with a 90% retention of deuterium while threo-2-deutero-1,2-diphenyl ethyl acetate gave trans-stilbene with a 26% retention of deuterium. The retention must have occurred through a non-stereospecific mechanism. These authors felt that the extra energy required to break the carbon-deuterium bond in the cis-elimination would give the non-stereospecific mechanism a better chance of success.

Although no kinetic work on the acetate pyrolysis has been reported, a recent study by Gordon *et al.*[97] on the pyrolysis of t-butyl formate indicated that this reaction obeyed first order kinetics and involved a molecular elimination of the acid portion since various tests for a free radical mechanism were negative.

Considerable controversy among the users of acetate pyrolysis has arisen with regard to the direction of the elimination. Barton[94] proposed that the direction of the elimination would be toward the most substituted carbon, with a tertiary hydrogen the most readily removed, a secondary hydrogen next and a primary hydrogen the least. Such a directional preference was observed by two groups of workers[66,98], in the pyrolyses of (-) menthyl acetate (with trans

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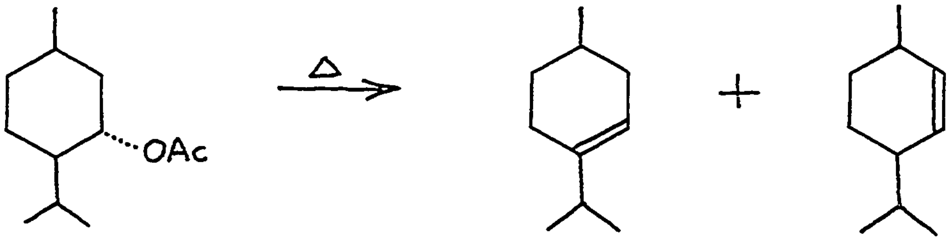
[97] E. Gordon, J. J. Price and A. F. Trotman-Dickenson, *J. Chem. Soc.*, *1957*, 2813.

[98] W. L. McNiven and J. Read, *ibid.*, *1952*, 2067.

acetate and iso-propyl group) which can cis-eliminate to give both (+) p-menthene-3 and (+) trans-p-menthene-2. The relative amounts of products, as determined by the optical activity of the pyrolysis product mixture, was 35% (+) trans-p-menthene-2 and 65% (+) p-menthene-3.



On the other hand Bailey and his coworkers[99-102] observed that in simple aliphatic and cyclic acetates, the elimination proceeded in such a direction as to remove the β-hydrogen from the carbon having the greatest number of hydrogens (Hofmann elimination). His analyses were made by fractional distillation of the pyrolysis product followed by infrared analysis of the fractions. In contrast to the results of

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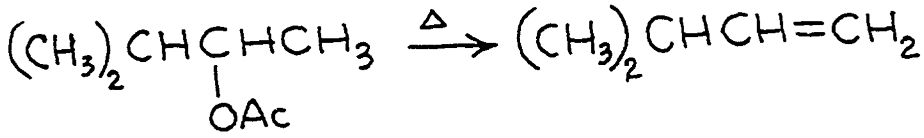
[99] W. J. Bailey and C. King, J. Am. Chem. Soc., 77, 75 (1955).

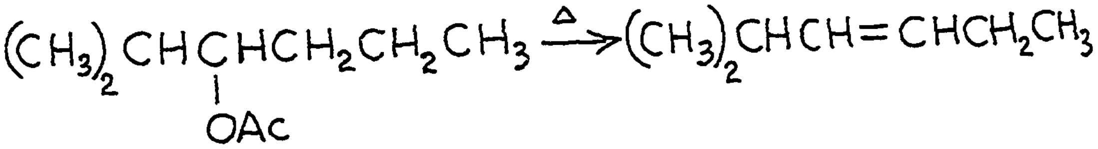
[100] W. J. Bailey, J. J. Hewitt, and C. King, ibid., 77, 357 (1955).

[101] W. J. Bailey and L. Nicholas, J. Org. Chem., 21, 854 (1956).

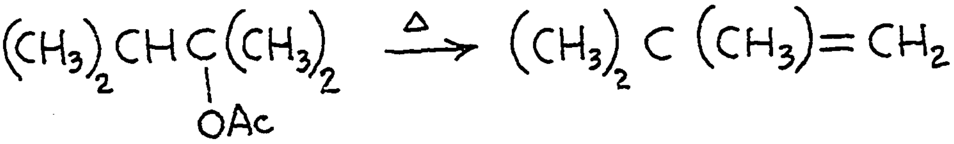
[102] W. J. Bailey, F. E. Naylor and J. J. Hewitt, ibid., 22, 1076 (1957).



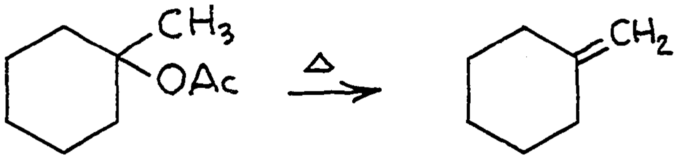
$$(CH_3)_2CH\underset{OAc}{\underset{|}{C}}HCH_3 \xrightarrow{\Delta} (CH_3)_2CHCH{=}CH_2$$



$$(CH_3)_2CH\underset{OAc}{\underset{|}{C}}HCH_2CH_2CH_3 \xrightarrow{\Delta} (CH_3)_2CHCH{=}CHCH_2CH_3$$



$$(CH_3)_2CH\underset{OAc}{\underset{|}{C}}(CH_3)_2 \xrightarrow{\Delta} (CH_3)_2C(CH_3){=}CH_2$$



Arnold, Smith and Dodson[89], Bailey and Nicholas[101] found that both isomers of 2-methylcyclohexyl acetate gave exclusively 3-methylcyclohexene, but that at higher temperatures, when a slight carbonization of the helices occurred during the pyrolysis or when pyrolysis took place on a dirty tube, 10-15% of the 1-methyl isomer was formed. Bailey concluded that the uncatalyzed acetate pyrolysis was a cis elimination toward the least substituted olefin where the steric requirements would be lowest and where the inductive effect due to the largest possible number of hydrogens would be operative.

Whenever some impurity was present Bailey considered another mechanism to be operative and this accounts for the non-Hofmann eliminations observed by the others.

Other workers[103-105] have also reported exclusively Hofmann elimination in acetate pyrolysis. For example, Siegel and Dunkel found that the pyrolysis of 1,2-, 1,3-, and 1,4-dimethylcyclohexyl acetates gave 100% exomethylene compound at all times at normal pyrolysis temperatures. Use of a higher temperature gave mixtures of exo- and endo-cyclic olefins. Previously, Nevitt and Hammond[91] had reported the formation of 90% exomethylene olefin in the pyrolysis of cis- and trans-dimethylcyclohexyl acetates and the related 1-methylcyclohexyl acetate.

Bailey and his coworkers[106,107] studied the effect of polar groups on the direction of the elimination. They found that methoxy and β-dimethylamino- substituents in the alkyl portion did not change the direction of the elimination but that the introduction of unsaturated, electron withdrawing

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[103] A. Brenner and H. Schinz, Helv. chim. acta, 35, 1333 (1952).

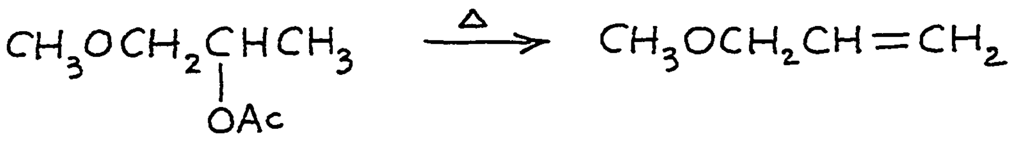
[104] A. Brenner, V. Steiner and H. Schinz, ibid., 35, 1336 (1952).

[105] S. Siegel and M. Dunkel, Abstracts of the 129th Meeting of the American Chemical Society, p. 28N (1956).

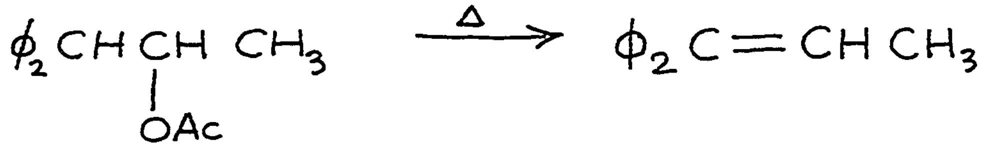
[106] W. J. Bailey and L. Nicholas, J. Org. Chem., 21, 648 (1956).

[107] W. J. Bailey and C. King, ibid., 21, 858 (1956).

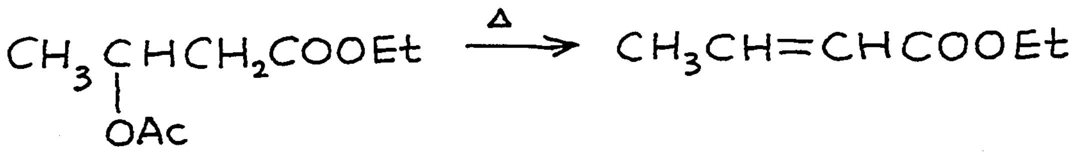
groups in the β position of the alkyl portion did reverse the direction of the elimination.



$$CH_3OCH_2\underset{OAc}{\underset{|}{C}}HCH_3 \xrightarrow{\Delta} CH_3OCH_2CH{=}CH_2$$

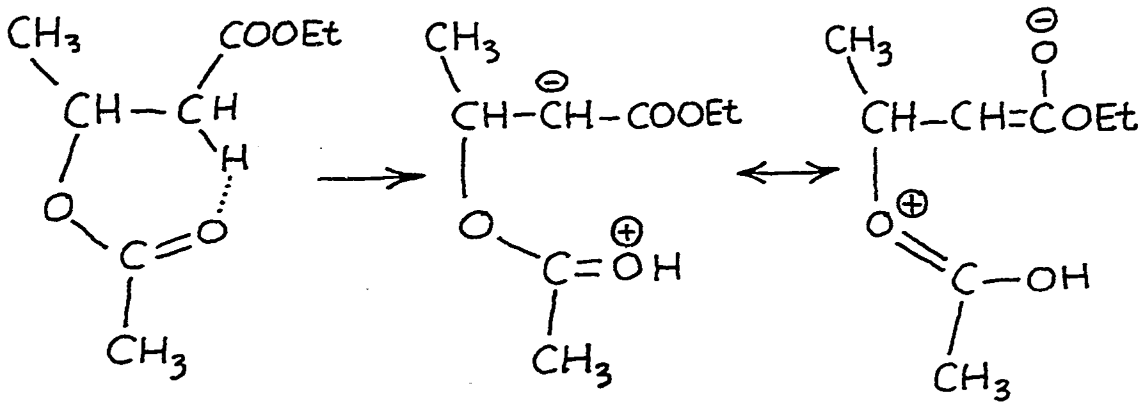


$$\phi_2CH\underset{OAc}{\underset{|}{C}}H\,CH_3 \xrightarrow{\Delta} \phi_2C{=}CH\,CH_3$$



$$CH_3\underset{OAc}{\underset{|}{C}}HCH_2COOEt \xrightarrow{\Delta} CH_3CH{=}CHCOOEt$$

Bailey did not feel that this reversal was due to a conjugation of the new double bond with the other double bond, but was rather due to a new set of resonance hybrids now possible.



DePuy and Leary[108] pyrolyzed the acetates of some substituted 1,3-diphenyl-2-propanols and found that the acidity of the hydrogen was not the determining factor but rather that a mixture of olefins was formed with the predominant olefin being the one which was more stable under acid catalyzed equilibrium conditions. Thus they proposed that the transition state for the pyrolysis closely resembled the products and that when steric factors were not present, the olefin formed was the most stable one.

Very recent results in these laboratories[109], utilizing gas chromatography as the analytic tool, indicate that the direction of the elimination is not necessarily toward the most acidic hydrogen. Rather, in a series of secondary and tertiary aliphatic acetates, a mixture of olefins was obtained which could be accounted for statistically on the basis of the number of available hydrogens. Thus sec-butyl acetate gave a mixture of 57% 1-butene and 43% 2-butene, iso-amyl acetate gave a mixture consisting of 80% 3-methyl-1-butene and 20% 3-methyl-2-butene, t-amyl acetate gave 76% 2-methyl-1-butene and 24% 2-methyl-2-butene and 2-methyl-3-hexyl acetate gave 27% of 2-methyl-2-hexene and 73% of 2-methyl-3-hexene. These values, which contradict those given by Bailey and his coworkers[99,100] on the same compounds may well be the more

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[108] C. H. DePuy and R. E. Leary, J. Am. Chem. Soc., **79**, 3705 (1957).

[109] D. E. Froemsdorf, Unpublished observations, Ames, Iowa (1957).

reliable, due to the greater sensitivity of the analytical method. The acetate pyrolysis results then fall more in line with those observed in amine oxide pyrolyses[110-112], wherein a preferentially cis elimination is considered to be by a cyclic mechanism.

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[110] A. C. Cope, N. A. LeBel, H. H. Lee and W. R. Moore, *J. Am. Chem. Soc.*, *79*, 4720 (1957).

[111] A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *ibid.*, *79*, 4724 (1957).

[112] A. C. Cope and E. M. Acton, *ibid.*, *80*, 355 (1958).

EXPERIMENTAL*

Preparations

Preparation of dimethylcyclopentyl compounds

Ethyl cyclopentanone-2-carboxylate. The literature contains several procedures for the Dieckman condensation of diethyl adipate to ethyl cyclopentanone-2-carboxylate[113-116]. There are minor variations among these but, in general, finely divided sodium metal in benzene or toluene was allowed to react with diethyl adipate at reflux for times varying from four hours to overnight. Hydrolysis with acid, washing the organic layer and removing the solvent preceeded distillation of the desired product, which still contained a small amount of unreacted diethyl adipate, unless special modifications were followed. Reported yields varied from 66 to 86%.

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*All melting points and boiling points in this section are uncorrected. Unless otherwise noted, the reagents used were of reagent grade and were used without further purification.

[113] M. van Rysselberghe, B. Acad. Roy. Belg. Soc., (5) 12, 171 (1926).

[114] G. Chiurdoglu, Bull. Soc. Chim. Belg., 41, 152 (1932).

[115] R. P. Linstead and E. M. Meade, J. Chem. Soc., 1934, 940.

[116] P. S. Pinkey in A. A. Blatt, ed., "Organic Syntheses", Collective Volume 2, John Wiley and Sons, Inc., New York, p. 116 (1943).

The procedure used in the current preparations was essentially the same. Diethyl adipate, containing a few milliliters of absolute alcohol, was added slowly to a slight excess of sodium or sodium hydride in toluene. When addition was completed, the reaction was stirred vigorously at a slow reflux for 10-15 hours. During this period, the mixture became very thick and care was necessary to insure sufficient solvent to permit efficient stirring. When cooled, the mixture was hydrolyzed with dilute acetic acid and the separated toluene layer was washed, dried, and the solvent was removed by distillation under a reduced pressure. In the earlier reactions the ethyl cyclopentanone-2-carboxylate was distilled under reduced pressure. In the later reactions, the crude product was used in the next step without distillation.

The first two condensations were carried out using finely cut sodium metal. The yield from these was quite low so "powdered sodium"[117] was tried. Yields did improve but the inconvenience of its preparation prompted a trial of sodium hydride as the condensing agent. An average 75% yield was obtained with its use (average of five trials).

A typical preparation proceeded as follows: Two liters of toluene and 2.5 moles of sodium hydride (dry powder or in a mineral oil dispersion) were placed in a five-liter three-

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[117] L. Fieser, "Experiments in Organic Chemistry", second edition, D. C. Health and Co., New York, p. 385 (1941).

necked flask equipped with a large paddle stirrer, a condenser and a dropping funnel. One and twenty-five hundredths moles of diethyl adipate, with five milliliters of absolute ethanol, were added dropwise over a period of two hours. A thickening of the solution had begun by the time addition was complete. This thickening continued while the flask was heated to cause a slow reflux. Between one and two liters of toluene were added to maintain fluidity. Heating at reflux continued for 14-16 hours, after which the mixture was cooled and hydrolyzed by pouring into a solution of 200 grams of acetic acid in two liters of distilled water. The toluene was separated and washed once with water, twice with a 5% sodium carbonate solution and once again with water. The organic layer was then placed over anhydrous calcium sulfate overnight and the toluene removed by use of a water aspirator. The crude ethyl cyclopentanone-2-carboxylate was then ready for distillation or a further reaction.

Ethyl 2-methylcyclopentanone-2-carboxylate. Van Rysselberghe[113] prepared this compound by treating ethyl cyclopentanone-2-carboxylate with sodium ethoxide, isolating the solid and treating this with methyl iodide for a forty-eight hour period. Case and Reid[118] used "molecular sodium" in benzene to form the salt and reacted this with methyl

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[118] F. H. Case and E. E. Reid, J. Am. Chem. Soc., 50, 3062 (1928).

iodide at reflux for several hours. Both reported 80% yields. Chiurdoglu[119] used the ethyl cyclopentanone-2-carboxylate salt directly without hydrolysis, but had difficulty with the ethyl alcohol formed in the condensation reaction.

In the current series of preparations of ethyl 2-methylcyclopentanone-2-carboxylate, sodium hydride in benzene or toluene was used to obtain the 2-sodium salt. Methyl iodide was then added and the solution was refluxed for 8-12 hours. The precipitated sodium iodide was filtered off and the solvent was removed by distillation. The crude product was distilled or used directly. The yield in this step was 81% (average of five trials).

In a typical reaction, 1.9 moles of ethyl cyclopentanone-2-carboxylate in a liter of toluene were added to a five-liter flask containing 2.5 moles of sodium hydride in one and a half liters of toluene. Stirring continued until the hydrogen evolution ceased (about 12-15 hours). The mixture was quite thick at this point. Then an excess of methyl iodide (2.8 moles), was added rapidly and the solution was heated to a slow reflux. The heating and stirring continued for 12-14 hours, during which time the cream-white precipitate of sodium iodide appeared, the yellower sodium salt disappearing. When cool, the sodium iodide was filtered off, using "Celite

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[119] G. Chiurdoglu, <u>Bull. Soc. Chem. Belg.</u>, <u>44</u>, 527 (1935).

Filter-Aid", to help "hold" the very fine precipitate. The solvent was removed from the resulting toluene solution under reduced pressure. The crude ethyl 2-methylcyclopentanone-2-carboxylate was then distilled or used in the next step.

2-Methylcyclopentanone. Moderately high yields of this ketone have been obtained by a number of workers[113,114,118,119] by refluxing ethyl 2-methylcyclopentanone-2-carboxylate with a dilute acid solution, the acid being either hydrochloric or sulfuric, followed by separation of the aqueous and organic layers. The organic layer is then distilled to remove the alcohol and water impurities from the desired product.

Physical constants for 2-methylcyclopentanone are reported to be[120]: boiling point 139-140°C (760 mm), refractive index (20/D) 1.435, density (20/4) 0.920, semicarbazone m.p. 171°C. Umland and Jeffrain[121] report a boiling range 133-137°C and a semicarbazone m.p. 175.4-176.2°C.

In the current work, both sulfuric acid and hydrochloric acid were tried. The hydrochloric acid decarboxylation was found to be the better method. The average yield for this step was 65% (average of five trials).

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[120] F. K. Beilstein, "Beilsteins Handbuch der Organische Chemie", Edwards Brothers, Lithographers, Ann Arbor, Michigan, Vol. 7, p. 11, Vol. EI7, p. 8, Vol. EII7, p. 13 (1942).

[121] J. B. Umland and M. I. Jeffrain, J. Am. Chem. Soc., 78, 2788 (1956).

As mentioned in the discussion of the previous steps, after the methods for the individual steps had been adequately worked out, no attempt was made to purify the intermediate ethyl cyclopentanone-2-carboxylate and ethyl 2-methylcyclopentanone-2-carboxylate; rather, the preparation was carried out from the diethyl adipate directly to the 2-methylcyclopentanone. The yield from these reactions, based on the initial diethyl adipate, was 45%. The yield of 2-methylcyclopentanone when each intermediate is isolated and purified was 39%. The difference in the amount of yield was not significant but the method was felt to be far superior because of time saved by its adoption.

A typical preparation involved refluxing approximately 1.5 moles of crude 2-methylcyclopentanone-2-carboxylate with one liter of 1:2 hydrochloric acid-water mixture for 24 hours. The organic and aqueous layers were separated and then the water layer was saturated with solid ammonium sulfate. The organic material that then separated was combined with the first amount. The aqueous layer was then extracted with ether. The ether was washed with a 5% sodium carbonate solution and with water, dried over Drierite and removed, the residue being combined with the organic layers previously obtained. The organic portion was then distilled through an eighteen inch, nichrome "Heli-Pak" filled column. The major fraction was taken between 135.0-139.0°C (n_D^{20} 1.4353). A further fraction was found in each case (b.p. 139.0-142.0°C, n_D^{20} 1.434) which had a nearly identical infrared spectra, the sole difference being that the peak at 7.1μ was a bit shorter than in the spectra of the main fraction. Semicarbazones of both fractions melted at 167-170°C. This higher boiling fraction was used in the succeeding step and gave the desired product.

1,2-Dimethylcyclopentanols. The mixed cis and trans isomers of 1,2-dimethylcyclopentanol have previously been prepared by van Rysselberghe[113] and Chiurdoglu[119]. Both used a Grignard reagent on 2-methylcyclopentanone, letting the mixture react from 12-24 hours. Hydrolysis was carried out with dilute aqueous hydrochloric acid, followed by extraction of the aqueous solution with ether. The ether was then dried and removed, and the mixed alcohols were distilled under reduced pressure.

The isomers were separated by reduced pressure distillations, followed by fractional crystallization in ether. The physical constants for the isomers are listed in Table 1. The assignment of configuration was based on von Auwers' rule, supported by the ease of formic acid dehydration of the trans isomer. In his preparation, Chiurdoglu obtained a cis to trans isomer ratio of approximately 3:2, with a considerable amount of mixed product.

Table 1. Physical constants of the isomeric 1,2-dimethylcyclopentanols

	b.p. °C		f.p. °C		n_D^{20}	
	Cis	Trans	Cis	Trans	Cis	Trans
constants[a]	69.6 (25 mm)	58.4 (25 mm)	28.9	27.3		
constants[b]	59.5-61.0 (17 mm)	50.0-51.2 (16 mm)			1.4541	1.4506

[a] G. Chiurdoglu, Bull. Soc. Chim. Belg., 44, 527 (1935).

[b] This thesis.

In the present work, 2-methylcyclopentanone was added to an excess of freshly prepared methylmagnesium chloride in ether. This mixture was refluxed for 15-20 hours, cooled and the addition product was hydrolyzed with a saturated solution of ammonium chloride. The ether was dried and removed. The alcohol was then fractionated. The total yield of both isomers and the mixed product was 50% (average of six trials).

In a typical preparation, 1.4 moles of 2-methylcyclopentanone was added, with stirring, to 1.8 moles of freshly prepared methylmagnesium chloride in ether (the preparation of this is discussed later) in a five-liter flask with 1½ liters of ether as solvent. Addition was dropwise at a sufficient rate to allow a slow reflux. When addition had been completed, heat was applied to maintain the slow reflux rate for eighteen hours. At the end of this time, the flask was cooled in ice and a saturated solution of ammonium chloride added, cautiously at first, to hydrolyze the solid addition product. Only enough ammonium chloride solution was added to precipitate the magnesium salts, leaving an essentially anhydrous ether layer containing the desired products. The ether was placed over anhydrous calcium sulfate overnight and then removed. The alcohol was then fractionated.

One fractionation of the mixed 1,2-dimethylcyclopenanols was carried out on a concentric tube column with approximately 50 theoretical plates. Another fractionation was performed on an 18" spinning brush column and the others on a 30" spinning brush column. Both spinning brush columns are rated at approximately 20 theoretical plates.

Separations of cis alcohol from the trans alcohol were obtained although there was mixed product. The cis to trans isomer ratio was 7:3. The physical constants of the alcohols are listed in Table 1.

Both the cis alcohol and the trans alcohol had distinguishing infrared absorption bands.

In all except the last preparation, at least some of the fractions showed a carbonyl peak in their infrared spectra. The carbonyl persisted even when the distillation was carried out from a small amount of 2,4-dinitrophenylhydrazine. It was believed to be unreacted 2-methylcyclopentanone. Alcohol containing the carbonyl was used in the subsequent dehydrations.

Gas chromatograms indicated that small amounts of olefins (both 1,2- and 2,3-dimethylcyclopentene) were present in the isomeric alcohols, even those which were free from carbonyl. This may be due to a slow elimination of the elements of water, and was previously observed by Chavanne and deVogel[122].

1,2-Dimethylcyclopentene. Preparation of 1,2-dimethylcyclopentene has been reported by Van Rysselberghe[123], Chavanne[124] and Chiurdoglu[125]. Van Rysselberghe dehydrated 1,2-dimethylcyclopentanol with *p*-toluenesulfonic acid, while the other two used formic acid in their dehydrations. Chiurdoglu reported an 80% crude yield in his preparation. Chavanne and van Rysselberghe indicated that the *cis* and *trans* alcohols dehydrated to give slightly different mixtures of products. Chiurdoglu reported that both alcohols gave the same products. Both Chiurdoglu and Chavanne further fractionated the dehydration product to get 1,2-dimethylcyclopentene and 2,3-dimethylcyclopentene.

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[122] G. Chavanne and L. DeVogel, *Bull. Soc. Chim. Belg.*, *37*, 141 (1928).

[123] M. van Rysselberghe, *ibid.*, *35*, 319 (1926).

[124] G. Chavanne, *ibid.*, *39*, 402 (1930).

[125] G. Chiurdoglu, *ibid.*, *47*, 363 (1938).

The physical constants given by Chiurdoglu and Chavanne for the two isomeric olefins are in Table 2. Included also are the values given in the American Petroleum Institute tables[126].

Table 2. Physical constants of the isomeric dimethylcyclopentenes

	b.p. °C	f.p. °C	d_4^{20}	n_D^{20}
	1,2-dimethylcyclopentene			
constants[a]	105.03	-91.3	0.7950	
constants[b]	105.0-105.3	-90.4	0.7952	
constants[c]	105.8	-90.4	0.7976	1.4448
constants[d]	103.2-104.0			1.4442
	2,3-dimethylcyclopentene			
constants[a]	95.48-95.50	-118.1	0.7805	
constants[b]	96.0-97.0	-124.8	0.7831	
constants[c]	102.	-118.	0.780	1.4331
constants[d]	96.-99.			1.4358

[a] G. Chiurdoglu, Bull. Soc. Chim. Belg., 47, 363 (1938).

[b] G. Chavanne, ibid., 39, 402 (1930).

[c] American Petroleum Institute Project 44, "Selected Values of Properties of Hydrocarbons", American Petroleum Institute, Washington, D. C., Table 18a (October 31, 1952).

[d] This thesis.

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[126] American Petroleum Institute Project 44, "Selected Values of Properties of Hydrocarbons", American Petroleum Institute, Washington, D. C., Table 18a (October 31, 1952).

In the current work, the 1,2-dimethylcyclopentanol was dehydrated in the presence of oxalic acid, since this method had already been successfully used in the preparation of 1-methylcyclopentene, which is discussed later in this thesis. The olefin was dried and distilled from barium oxide. A total yield of 62% was obtained (average of four trials). The major product (90% of the total product as indicated by gas chromatography) was 1,2-dimethylcyclopentene which distilled at 103.2-104.0° C (733 mm). In each distillation there was a small amount of material which distilled over at 96.0-99.0° C (733 mm). The infrared spectrum of this material showed olefin character. There were no fractions showing any exomethylene character in the infrared.

A gas chromatogram of the major fraction indicated only a single component, 1,2-dimethylcyclopentene. In the lower boiling fraction two components were indicated. Most prominent was the lower boiling material, 2,3-dimethylcyclopentene, although this was always contaminated with small amounts of the 1,2-isomer.

Some instability was experienced at room temperature with the olefins. After one month at room temperature both the gas chromatogram and the infrared spectra showed that the major fractions had decomposed considerably. Storage over barium oxide at refrigerator temperature retarded this deterioration, although it did not completely stop it.

In a typical run, 100 grams of 1,2-dimethylcyclopentanol was refluxed with five grams of oxalic acid for twenty hours. The resultant olefin-water mixture was then distilled, giving an azeotrope. The layers were separated and the organic layer was washed with concentrated sodium hydroxide and with water, dried over anhydrous calcium sulfate and then distilled from a small amount of barium oxide on the eighteen inch spinning brush column. The olefin was stored at refrigerator temperature over barium oxide.

Cis- and trans-1,2-dimethylcyclopentyl acetates. The acetates of the *cis*- and *trans*-1,2-dimethylcyclopentanols have not been previously reported. They were prepared by means of the general method suggested by Nevitt and Hammond[127]. This included reacting acetyl chloride with the alcohol dissolved in dimethylaniline while the reaction vessel was cooled in ice. This was followed by heating in a steam bath for several hours then quenching the reaction with dilute hydrochloric acid. The acetate was extracted into pentane. Only fair yields were obtained.

A typical preparation included the mixing of 0.08 mole of the desired alcohol with 50 ml of dimethylaniline and the cooling of the stirred solution in an ice bath while 0.25 moles of acetyl chloride was added. This mixture was allowed

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[127] T. D. Nevitt and G. S. Hammond, *J. Am. Chem. Soc.*, *74*, 4124 (1954).

to stand at room temperature for one hour. It was then heated on a steam bath for three to four hours. The solution was cooled, then poured into a cold 10% hydrochloric acid solution. The acetate was extracted into pentane. The pentane solution was washed with water and a 5% sodium bicarbonate solution, then dried over anhydrous calcium sulfate. The acetates were then distilled under reduced pressure.

Cis-1,2-dimethylcyclopentyl acetate was obtained in 65% yield (average of 3 trials) by this method. Its physical constants were b.p. 70.5-71.0° C (19 mm), n_D^{20} 1.4367.

The yield of trans-1,2-dimethylcyclopentyl acetate was 58% (average of 2 trials). Its physical constants were b.p. 65.5-66.0° C (19 mm), n_D^{20} 1.4329.

Infrared spectra of both acetates showed strong carbonyl bands. The spectra of both acetates contained distinguishing absorption peaks. Both acetates also contained trace amounts of olefin as indicated by the gas chromatograms.

Preparation of the 1-methylcyclopentyl compounds

1-Methylcyclopentanol. This compound has previously been prepared by Zelinsky and Namjetkin[128] and by Chavanne and deVogel[122]. Both utilized a 1:1 mole ratio of cyclopentanone

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[128] N. Zelinsky and S. Namjetkin, Ber., 35, 2683 (1902).

and methylmagnesium iodide. No reports of yield were given.

The 1-methylcyclopentanol is a white, needle-like solid with a melting point of 35-37° C. Its boiling point is reported as[129] 135° C (760 mm), 82° C (100 mm) and 53-54° C (30 mm).

In the present work the general method for the preparation of 1-methylcyclopentanol included reaction of cyclopentanone with freshly prepared Grignard reagent in ether. The addition product was hydrolyzed, the ether washed, dried and removed. The crude product was then distilled. Often, if the crude product was a solid, it would be used in the next step without further purification.

Much difficulty was experienced in perfecting a technique for obtaining a reasonable yield of the alcohol. Two preparations were tried in which cyclopentanone was added to an equimolecular amount of methylmagnesium iodide. The addition product was then hydrolyzed with dilute acetic acid. The crude yield was 20% (average of two trials). One trial was an "invert Grignard" reaction, adding methylmagnesium iodide in ether to cyclopentanone. Again a 20% crude yield was obtained. The invert reaction of methyllithium and cyclopentanone was tried. Only a 10% crude yield (average of two trials)

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[129] F. K. Beilstein, "Beilsteins Handbuch der Organische Chemie", Edwards Brothers, Lithographers, Ann Arbor, Michigan, Vol. 6, p. 8, Vol. EI6, p. 7, Vol. EII6, p. 14 (1942).

of 1-methylcyclopentanol was obtained. Other invert reactions between methylmagnesium chloride and cyclopentanone were tried, with 15% crude yields (average of two trials).

The large amount of "byproduct" obtained in these unsuccessful reactions was fractionated. Infrared spectra of the several fractions indicated some products with hydroxyl and carbonyl groups and one with an α,β-unsaturated carbonyl group. Two fractions were positively identified: 1-cyclopentylidene-2-cyclopentanone with boiling range 103-118° C (13 mm), oxime m.p. 122° C (literature values are[130] b.p. 117° C (12 mm), oxime m.p. 122° C); and 2,5-dimethylcyclopentylidenecyclopentanone, a yellow solid melting at 66-68° C (literature value[131] is 72° C). The 1-cyclopentylidene-2-cyclopentanone had previously been observed whenever cyclopentanone was allowed to stand with base[130] and was also found as a "prominent byproduct" in the reaction of isopropylmagnesium iodide with cyclopentanone[132].

Finally, addition of cyclopentanone to methylmagnesium chloride was tried. This reaction gave a 62% yield (average of four trials) with very little "byproduct".

A typical preparation by this scheme involved, first, preparation of the methylmagnesium chloride by bubbling methyl

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[130] F. K. Beilstein, ibid., Vol. 7, p. 159, Vol. EI7, p. 103, Vol. EII7, p. 131.

[131] F. K. Beilstein, ibid., Vol. 7, p. 380.

[132] H. Meerwein, Ann., 405, 155 (1914).

chloride gas (purified by bubbling through concentrated sulfuric acid and then sodium hydroxide pellets) into an ether solution containing 100 grams of magnesium metal. A one-liter flask, flamed out and flushed with nitrogen, was used and equipped with a dry ice condenser, stirrer and gas bubbler. The reaction time was 10-12 hours. An aliquot was then titrated to give an accurate measure of the amount of methylmagnesium chloride[133], and the entire solution was filtered under nitrogen into a previously flamed out five-liter flask. Two liters of ether were added, then cyclopentanone was added dropwise at a rate to allow a slow reflux. The refluxing was continued for twenty hours, then the solution was cooled and hydrolyzed with dilute acetic acid or a saturated solution of ammonium chloride. The ether layer was washed with a five per cent solution of sodium hydrogen sulfite, then a five per cent solution of sodium bicarbonate and finally with water, then dried over anhydrous calcium sulfate. The drying was carried out very carefully since small amounts of water cause the product to liquefy. The ether was then removed and the alcohol was distilled at 45-46° C (15 mm). Whenever the crude product was a solid, it was used directly.

1-Methylcyclopentene. Chavanne and deVogel[122] obtained 1-methylcyclopentene by distilling the water-olefin azeotrope

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[133] L. Fieser, "Experiments in Organic Chemistry", second edition, D. C. Heath and Co., New York, p. 407 (1941).

from p-toluene sulfonic acid. Other cyclic tertiary alcohols have been dehydrated using a variety of catalysts including sulfuric acid[134], formic acid[125], oxalic acid[135] and iodine[136,137]. Yields from all these methods are reported as good.

Physical constants for 1-methylcyclopentene are given[138] as: b.p. 75.1° C (760 mm); density (20/4) 0.7780; and refractive index (15/D) 1.4347.

In the current preparations, both the iodine and oxalic acid methods were tried. The oxalic acid dehydration was the more successful. The 1-methylcyclopentene was distilled at 74.8° C (730 mm) and had a refractive index (20/D) of 1.4340. The infrared spectrum of this fraction showed good olefinic bands. Neither this fraction nor those obtained before or after showed any exomethylene character in their infrared spectra.

In a typical reaction, 1.5 moles of 1-methylcyclopentanol were refluxed with oxalic acid for six to eight hours. The

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[134] G. Chiurdoglu, Bull. Soc. Chim. Belg., 44, 527 (1935).

[135] W. N. Haworth, J. Chem. Soc., 103, 1246 (1913).

[136] F. K. Signaigo and P. H. Cramer, J. Am. Chem. Soc., 55, 3326 (1933).

[137] G. S. Hammond and T. D. Nevitt, ibid., 76, 4121 (1954).

[138] G. Egloff, "Physical Constants of Hydrocarbons", Vol. 2, Reinhold Publishing Corp., New York, p. 306 (1940).

water-olefin azeotrope was distilled and the organic layer was washed with a concentrated sodium hydroxide solution and with water. This was then dried over anhydrous calcium sulfate and distilled on a twenty-four inch nichrome "Heli-Pak" filled column or a thirty inch spinning brush column to obtain the 1-methylcyclopentene in a 70% yield (average of six trials).

Upon standing at room temperature, the 1-methylcyclopentene deteriorated slowly, which made necessary a further distillation before use. This deterioration was retarded by storing the samples over barium oxide at refrigerator temperature.

1-Methylcyclopentyl acetate. 1-Methylcyclopentyl acetate has not been reported in the literature. The preparation of this compound from 1-methylcyclopentanol was performed in a manner similar to that of the dimethyl-acetates. A 56% yield (average of 2 trials) of 1-methylcyclopentyl acetate distilling at 55.5-57.0° C (19 mm), with a refractive index (20/D) of 1.4306 was obtained.

Preparation of dimethylcyclohexyl compounds

2-Methylcyclohexanone. 2-Methylcyclohexanone has been prepared[136,139] by the aqueous chromic acid oxidation of

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[139] T. D. Nevitt, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa, p. 34 (1953).

2-methylcyclohexanol. The crude ketone thus obtained was separated from the oxidizing solution and was distilled at 164.8-165.0° C. This product contained a small amount of unreacted 2-methylcyclohexanol (b.p. 165-166° C) which, in several instances, was removed by precipitating the 2-methylcyclohexanone with sodium bisulfite. This was regenerated by means of a treatment with a solution of sodium carbonate.

In the current preparations, the method followed that of Nevitt[139]. The 2-methylcyclohexanone, obtained in 54% yield, was distilled at 162.0° C (738 mm) and had a refractive index (20/D) of 1.4481.

In one preparation, it was desired to remove all of the contaminating 2-methylcyclohexanol, so the sodium bisulfite addition product was washed with copious amounts of ether. The 2-methylcyclohexanone was recovered by treatment of the addition product with a 5% sodium carbonate solution. The aqueous solution was extracted into benzene. The benzene solution was dried and distilled. The ketone was then further purified by distillation. The yield from the precipitation and recovery operation was less than 40%. The infrared spectrum of the product indicated that all of the alcohol had been removed.

For these preparations two moles of 2-methylcyclohexanol (practical grade) were mixed in a beaker with 500 cc of water which contained 0.05 mole of sodium dichromate. Slowly and with efficient stirring, a solution of 0.5 mole of sodium dichromate and 4 moles of concentrated sulfuric acid in 600 cc of water was added at a rate sufficiently slow that a temperature of 70-80° C was maintained. An organic layer separated and this was combined with crude product obtained by extracting the aqueous layer several times with chloroform. The chloroform solution was then dried and the chloroform was removed. The ketone was then distilled or further treated with sodium sulfite solution.

1,2-Dimethylcyclohexanols. The isomeric alcohols have been prepared by Chiurdoglu[140] and by Nevitt and Hammond[139,141]. Both workers refluxed a mixture of methylmagnesium bromide and 2-methylcyclohexanone overnight. Chiurdoglu hydrolyzed the addition product with acetic acid, while Nevitt used a saturated ammonium chloride solution. Both fractionated the alcohols. The reported constants are listed in Table 3.

In the present work, one preparation was made by condensing 2-methylcyclohexanone with freshly prepared methylmagnesium chloride. The procedure was similar to that used for the preparation of the dimethylcyclopentanols. The crude yield was better than 98%. A second preparation involved the

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[140] G. Chiurdoglu, Bull. Soc. Chim. Belg., 47, 241 (1938).

[141] T. D. Nevitt and G. S. Hammond, J. Am. Chem. Soc., 76, 4124 (1954).

Table 3. Physical constants of the isomeric 1,2-dimethylcyclohexanols

	b.p. °C		n_D^{25}	
	Cis	Trans	Cis	Trans
constants[a]	82.8 (25 mm)	74.0 (25 mm)	1.4613	1.4648
constants[b]	95.7 (53 mm)	86.8 (52 mm)	1.4588	1.4628
constants[c]	78.9-79.6 (25 mm)	72.4-72.9 (25 mm)		

[a] G. Chuirdoglu, Bull. Soc. Chim. Belg., 47, 249 (1938); 50, 20 (1941).

[b] T. D. Nevitt and G. S. Hammond, J. Am. Chem. Soc., 76, 4124 (1954).

[c] This thesis.

use of 2-methylcyclohexanone with methylmagnesium iodide, followed by ammonium chloride hydrolysis. After the ether had been removed, distillation from 2,4-dinitrophenylhydrazine on an 18" spinning bush column produced the ketone-free isomeric alcohols, with a very small amount of mixed product. The constants are listed in Table 3.

1,2-Dimethylcyclohexene. Hammond and Nevitt[137] and Signaigo and Cramer[136], among others, have prepared 1,2-dimethylcyclohexene. Although many different means of preparation of the olefin have been used, the above authors used catalytic amounts of iodine to dehydrate 1,2-dimethylcyclohexanol. Signaigo and Cramer reported that a single product was obtained: 1,2-dimethylcyclohexene. Hammond and Nevitt report a product consisting of about 85% 1,2-dimethylcyclohexene, 14% 2,3-dimethylcyclohexene, and a trace of 2-methylmethylenecyclohexane. The constants reported for these compounds are listed in Table 4.

In the current work, a single dehydration of the mixed isomers of 1,2-dimethylcyclohexanol by means of distillation from a gram of iodine gave, after separation from the aqueous layer, washing, and crude distillation, a product which contained 68% 1,2-dimethylcyclohexene, 29% of the 2,3- isomer and 3% of 2-methylmethylenecyclohexane as indicated by gas chromatographic analysis. Fractionation was attempted on a 30" spinning brush column. Several fractions were obtained. The constants for the major fractions are listed in Table 4. No fraction was completely free from the other isomers, as indicated by gas chromatograms. For example, the best sample of 1,2-dimethylcyclohexene, distilling sharply at 136.0-136.1° C (735 mm) contained approximately 15% of the 2,3-isomer. The 2,3-isomer, distilling at 131.1-131.4° C contained both the 1,2-isomer and some exomethylene compound. This contamination of one product by another was not indicated by the infrared spectra of the compounds. The spectra

Table 4. Physical constants of some isomeric dimethylcyclohexenes

	b.p. °C	n_D^{25}	n_D^{20}	d_{20}^{20}	d_4^{20}
		1,2-dimethylcyclohexene			
constants[a]	136.2	1.4587			
constants[b]	135.4-135.9	1.4590			0.8232
constants[c]	135.4-135.9		1.4630	0.826	
constants[d]	136.0-136.1		1.4611		
		2,3-dimethylcyclohexane			
constants[a]	130.3-130.7	1.4537			
constants[d]	131.1-131.4		1.4572		
		2-methylmethylenecyclohexene			
constants[a]	124.5-124.8	1.4514			
constants[b]	122-125		1.4516	0.808	

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[a] G. S. Hammond and T. D. Nevitt, J. Am. Chem. Soc., 76, 4121 (1954).

[b] G. Egloff, "Physical Constants of Hydrocarbons", Vol. 2, Reinhold Publishing Corp., New York, pp. 162, 330 (1940).

[c] F. K. Signaigo and P. H. Cramer, J. Am. Chem. Soc., 55, 3326 (1933).

[d] This thesis.

of 1,2- and 2,3-dimethylcyclohexene are identical to those of Nevitt[142].

Cis- and trans-1,2-dimethylcyclohexyl acetate. Nevitt and Hammond[141] prepared the two 1,2-dimethylcyclohexyl acetates by reacting the appropriate alcohol with acetyl chloride in dimethyl aniline. Nearly quantitative yields were reported. The physical constants are listed in Table 5.

Table 5. Physical constants of the isomeric 1,2-dimethylcyclohexyl acetates

	b.p. °C		n_D^{20}	
	Cis	Trans	Cis	Trans
constants[a]	84 (18 mm)	78 (20 mm)	1.4460	1.4421
constants[b]	80-82 (22 mm)	77-78 (21 mm)	1.4465	1.4423

[a] T. D. Nevitt and G. S. Hammond, J. Am. Chem. Soc., 76, 4124 (1954).

[b] This thesis.

A single sample of each acetate was prepared in the present work using the same method that was employed in the

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[142] T. D. Nevitt, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa, p. 84 (1953).

preparation of the 1,2-dimethylcyclopentyl acetates. The constants are given in Table 5.

Preparation of methylcyclohexyl compounds

1-Methylcyclohexanol. Nevitt and Hammond[141] prepared this compound by the reaction of methylmagnesium bromide with cyclohexanone. The crude product was fractionated through a center rod column, with a yield of 90%. The physical constants reported by these authors are b.p. 68° C (24 mm) and n_D^{25} 1.4582.

Mosher[143] obtained a 60% yield of 1-methylcyclohexanol by a similar method. His constants were b.p. 70° C (25 mm) and n_D^{20} 1.4546.

1-Methylcyclohexanol was prepared for the present work by the reaction of methylmagnesium iodide with cyclohexanone. The work-up was similar to that for the dimethylcyclohexanols. Distillation on the 18" spinning brush column from 2,4-dinitrophenylhydrazine produced ketone-free alcohol, b.p. 65.5° C (20 mm), in 74% yield.

1-Methylcyclohexene. Mosher[143] prepared this olefin by dehydrating 1-methylcyclohexanol with iodine. He reported a 98% yield of olefin which he identified as only 1-methyl-

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[143] W. A. Mosher, J. Am. Chem. Soc., 62, 552 (1940).

cyclohexene. The identification was based on the fact that no formaldehyde was found upon ozonolysis of the olefin.

Egloff[144] lists the physical constants as b.p. 109° C d_4^{20} 0.8117, n_D^{20} 1.4505.

For this work, distillation of the alcohol from iodine, as was previously discussed for the preparation of 1,2-dimethyl cyclohexene, produced an 83% yield of olefin which distilled at 103° C (728 mm) and had an index of refraction (20/D) of 1.4572. The infrared spectrum of this product was identical to that given by Nevitt[145]. A gas chromatogram indicated that the sample was 97% 1-methylcyclohexene and 3% methylenecyclohexane.

<u>1-Methylcyclohexyl acetate.</u> 1-Methylcyclohexyl acetate has been prepared by Nevitt and Hammond[141] and by Bailey, Hewitt and King[146]. The former used acetyl chloride in dimethyl aniline as the acetylating agent while the latter used acetic anhydride in glacial acetic acid. The constants reported are listed in Table 6.

The current preparations used the procedure outlined for the preparation of 1,2-dimethylcyclopentyl acetate. In one

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[144] G. Egloff, "Physical Constants of Hydrocarbons", Vol. 2, Reinhold Publishing Corp., New York, p. 326 (1940).

[145] T. D. Nevitt, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa, p. 86 (1953).

[146] W. J. Bailey, J. J. Hewitt and C. King, J. Am. Chem. Soc., 77, 357 (1955).

Table 6. Physical constants for 1-methylcyclohexyl acetate

	b.p. °C	n_D^{25}	n_D^{20}	d_{25}^{25}
constants[a]	74 (20 mm)	1.4435		
constants[b]	177-178 (740 mm)	1.4355		0.9545
constants[c]	70.5-71 (21 mm)		1.4403	

[a] T. D. Nevitt and G. S. Hammond, J. Am. Chem. Soc., 76, 4124 (1954).

[b] W. J. Bailey, J. J. Hewitt and C. King, ibid., 77, 357 (1955).

[c] This thesis.

sequence the amounts of the reactants were increased six fold without loss in yield (75%, average of three trials). The physical constants are given in Table 6.

2-Methylcyclohexyl acetate. The acetates of cis and trans 2-methylcyclohexanol, have been prepared by Arnold, Smith, and Dodson[147] and by Bailey and Nicholas[148]. The former used acetyl chloride in anhydrous chloroform-pyridine solvent for their acetylation, removing the precipitated pyridine hydrochloride and distilling the acetates. He

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[147] R. T. Arnold, G. G. Smith and R. M. Dodson, J. Org. Chem., 15, 1256 (1950).

[148] W. J. Bailey and L. Nicholas, ibid., 21, 854 (1956).

obtained an 84% yield of each isomer by this method. Bailey and Nicholas used acetic anhydride as both acetylating agent and solvent, quenching the reaction in a sodium bicarbonate solution and extracting the acetates with ether. The physical constants reported for the acetate isomers are given in Table 7.

The preparation of 2-methylcyclohexyl acetate for the present work was carried out by the general procedure used for the tertiary acetates. Since the 2-methylcyclohexanol used was of the mixed cis and trans isomers, the product acetates were also the mixed isomers. The isomer ratio was not determined. The constants for the product obtained are given in Table 7.

Preparation of ethylcyclohexyl compounds

1-Ethylcyclohexanol. This compound has been prepared in 40% yield by Mosher[143] who reacted ethylmagnesium bromide with cyclohexanone. He reports the b.p. as 78° C (20 mm), n_D^{20} 1.4642. Other constants reported are[149] b.p. 76° C (20 mm), 166° C (760 mm) and n_D 1.4638.

For the current preparation of 1-ethylcyclohexanol, ethylmagnesium bromide was condensed with cyclohexanone,

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[149] P. Sabatier and A. Mailhe, Compt. Rend., 138, 1321 (1904).

Table 7. Physical constants of the 2-methylcyclohexyl acetates

	b.p. °C			n_D^{25}			n_D^{20}
	Cis	Trans	Mixed	Cis	Trans	Mixed	Mixed
constants[a]	68.5-69.5 (16 mm)	63-64 (11.5 mm)		1.4376	1.4353		
constants[b]		54 (5 mm)	52 (3.5 mm)*		1.4353	1.4363	
constants[c]			76.0-76.5 (19 mm)				1.4393

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[a] R. T. Arnold, G. G. Smith and R. M. Dodson, J. Org. Chem., 15, 1256 (1950).

[b] W. J. Bailey and L. Nichols, ibid., 21, 854 (1956).

*Reported to be 68% trans.

[c] This thesis.

followed by refluxing for nine hours. Hydrolysis was brought about by treatment with aqueous ammonium chloride. After removal of the ether, distillation gave an alcohol with a b.p. of 77-78° C (21 mm) in 63% yield.

1-Ethylcyclohexene. Mosher[143] dehydrated 1-ethylcyclohexanol by distillation from iodine, obtaining a product which he analyzed by the method of ozonolysis and found 99% 1-ethylcyclohexene and 1% ethylenecyclohexane. Signaigo and Cramer[136] also used iodine dehydration to obtain olefin product reported to be entirely 1-ethylcyclohexene with a b.p. of 135.7-136.6° C, d_{20}^{20} 0.828, and n_D^{20} 1.4583. Bergmann and Bergmann[150] dehydrated the same alcohol with oxalic acid and obtained an olefin which distilled at 49° C (30 mm). They reported no indication of ethylenecyclohexane. Values given by other workers[151] for the physical constants include b.p. of 135.8-136.8° C (768 mm), n_D^{20} 1.4576, and $d^{19.4}$ 0.8238.

1-Ethylcyclohexene was prepared in the current work by distillation of 1-ethylcyclohexanol from several grams of oxalic acid. After washing the olefin layer with aqueous sodium hydroxide, the olefin was distilled through a short

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[150] E. Bergmann and F. Bergmann, J. Am. Chem. Soc., 59, 1443 (1937).

[151] G. Egloff, "Physical Constants of Hydrocarbons", Vol. 2, Reinhold Publishing Corp., New York, p. 326 (1940).

column at 95-100° C (747 mm). The refractive index (20/D) was 1.4574.

An infrared spectrum of the product showed olefinic character. A gas chromatogram of the material indicated only a single component.

1-Ethylcyclohexyl acetate. This compound has been prepared by Sabatier and Mailhe[149] by acetylating 1-ethylcyclohexanol with acetic anhydride. The acetate is a liquid which boils at 190° C (760 mm) and having a refractive index (12/D) of 1.448.

For this work the same acetylating procedure as previously mentioned, involving the treatment of the alcohol with acetyl chloride in dimethylaniline, was employed. A 56% yield of acetate distilling at 86-88° C (21 mm) and having a refractive index (20/D) 1.4458, was obtained.

Analysis Apparatus

Infrared spectrophotometer

The infrared spectra mentioned in this thesis were obtained on a Baird Associated, Inc. Model B Infrared Recording Spectrophotometer operated by the Institute for Atomic Research of Iowa State College. Capillary cells were used in all cases.

Nuclear magnetic resonance spectrometer

Nuclear magnetic resonance spectra of several of the compounds used in this work were obtained on a Varian Associates NMR Spectrometer with a high resolution proton probe. They were obtained through the courtesy of Dr. Keith McCallum of the Rohm and Haas Redstone Arsenal Research Center.

Gas chromatograph

The gas chromatograms were run on a gas chromatograph constructed by Donald H. Froemsdorf of the Iowa State College Chemistry Department. The detection cell, a Gow-Mac thermal conductivity cell, and the chromatography column were thermostated to ± 2^{o} C in a constant temperature oven. The carrier gas was helium. Chromatograms were recorded on a 20 mv recording potentiometer. Samples were injected through a serum cap into the heated sample chamber by means of a hypodermic syringe.

Both 40-60 mesh firebrick and 30-60 mesh Celite were used as supports in the columns. Liquid phases included dibutyl phthalate, dioctyl phthalate, and silicone oil 702, all in a 40 to 100 weight ratio on firebrick. Apiezon L grease was another liquid phase and was used in a 10-30 weight ratio on firebrick. Another liquid phase, tricresyl phosphate (tri-m-tolyl phosphate), was used in a 40-100 weight ratio on Celite.

The percent composition of mixtures run in the gas chromatograph were calculated from the peak areas of the chromatograms, as approximated by triangulation. The sum of the areas was considered to be the reference total and the individual percentage of a given component was taken to be the percentage of the total area represented by the area of its peak. Such calculations are somewhat inaccurate for peaks in which an abnormal "tailing" occurs and for peaks which have breadth-to-height ratios of the order of one or more. Enough sample was usually injected to minimize the latter problem. Duplicate calculations on the same peak have been reproducible to ± 0.5%. Duplicate chromatograms, run on the same sample, are generally reproducible to ± 1.0%. Occasionally, however, such chromatograms are significantly different. The reasons for this are unclear.

Pyrolysis of Acetates

Apparatus

The pyrolysis tube was a vertical pyrex tube, ten inches long with a 10 mm, o.d., standard taper joints and several indentations near the bottom for support of the column packing. The packed tube was heated with a Fisher Microcombustion Furnace. The temperature was measured by means of a Chromel-Alumel thermocouple. The temperature variation during a typical pyrolysis run was ± 5° C or less. A dropping funnel equipped with a three-way stopcock on a nitrogen inlet (to maintain constant pressure in both funnel and pyrolysis tube) was used for the addition of sample at the top of the tube. The lower end of the tube extended into a trap which was cooled in dry ice. The trap had a nitrogen outlet protected by a drying tube filled with calcium chloride. During each pyrolysis, nitrogen gas, purified and dried, was passed through the entire apparatus.

In most of the pyrolyses the column packing was either 1/8" or 1/16" pyrex helices. These were prepared by a cleaning treatment with hot concentrated sulfuric acid, rinsing with ammonia, distilled water and acetone, and then an air drying. Occasionally, after one pyrolysis, the helices on the column were washed with acetone, dried and reused. In some cases coated helices were used. These were prepared by soaking the helices in the desired solution, draining and air drying. Four hundred and twenty micron diameter glass beads were prepared similarly. Granular silica packings were either used directly (the silica was obtained from the G. F. Smith Chemical Co. and was suspected of having a perchloric acid coated surface, since water rinsings were acidic) or it was rinsed with ammonia and then dried in a 100° C oven.

Procedure

The pyrolyses were carried out by dropping 1-2 grams of the desired acetate onto the preheated, packed pyrolysis tube. The rate of addition of sample was varied from very slow to moderately fast. The rate of nitrogen flow was also varied. A single pass through the tube was used. The pyrolysis products were condensed into a trap cooled in dry ice acetone. When the pyrolysis was complete, the trap was removed, and the pyrolysis products were melted and dissolved in pentane. The pentane was extracted with water and with standardized dilute sodium hydroxide. The pentane was then dried and removed by distillation at 36° C. The olefinic products remained. These were analyzed by gas chromatography and by infrared spectrophotometry. In some cases the gas chromatograms were run only on the crude pyrolysis product mixture. These chromatograms were not very accurate for analytical purposes as there was some contamination due to the acetic acid which was present. The amount of acetate pyrolyzed was determined by titrating the combined aqueous solutions from the extraction and from the washing of the pyrolysis tube with standardized base.

The percent conversion was calculated from the apparent number of moles of acetic acid present.

The removal of the pentane from the olefins before samples were run in the gas chromatograph made it much easier to obtain good chromatograms due to the absence of large amounts of diluent. To show that this distillation has little effect on the composition of the olefin sample, a pentane solution containing olefin was run before distillation and the results compared with those obtained after distillation. These results are shown in Table 8.

A slight amount of carbonization was observed in a few of the pyrolyses, especially with a slow addition rate and slow nitrogen flow. It did not appear to affect the results. The helices, when once carbonized, were cleaned before being used again.

Table 8. The effect of pentane removal on olefinic composition

	% Olefin in sample	
	1,2-dimethylcyclopentene	2,3-dimethylcyclopentene
before distillation	75.1	24.9
after distillation	76.8	23.2

Results

The results (as indicated by gas chromatography) of the pyrolyses of the acetates of *cis*- and *trans*-1,2-dimethylcyclopentanol and of 1-methylcyclopentanol are given in Tables 9 and 10.

Assignment of the configuration of the olefins to the various peaks was done by mixing an olefin of known composition with some of the pyrolysis product. The peak areas corresponding to the known compound would increase while the areas of the other olefins present would decrease. Pure 1,2-dimethylcyclopentene was used to identify this peak. An olefin sample containing known amounts of 1,2- and 2,3-dimethylcyclopentene was used to identify the peak of the latter. 2-Methylmethylenecyclopentane was the compound assigned to the third peak. That the exomethylene olefin was present was confirmed by the identification of formaldehyde (by reaction with chromotropic acid) in the products of a periodate-permanganate oxidation[152,153] of the acetate pyrolysis products. Pure 1-methylcyclopentene was used to

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[152] R. A. Lemieux and E. von Rudloff, *Can. J. Chem.*, *33*, 1701 (1955).

[153] R. A. Lemieux and E. von Rudloff, *ibid.*, *33*, 1710 (1955).

Table 9. Olefin composition from pyrolyses of isomeric 1,2-dimethylcyclopentyl acetates

No.	Acetate	Add. rate mole/min	Temp. °C	Support	% Pyrolysis	Carbon	% 2,3-Olefin[a]	% 1,2-Olefin[b]	% Exo-olefin[c]
1	<u>cis</u>	0.015	450	1/8" helices	73	none	25	40	35
2	<u>cis</u>	0.014	450	1/8" helices	70	none	21	47	32
3	<u>cis</u>	0.0003	450	1/16" helices	84	slight[d]	25	46	29
4	<u>cis</u>	0.0016	450	1/16" helices	77	slight[d]	30	50	20
5	<u>cis</u>	0.0014	450	1/16" helices	75	slight[d]	30[e]	50[e]	20[e]
6	<u>trans</u>	0.010	450	1/8" helices	78	none	89	10	1
7	<u>trans</u>	0.0002	450	1/16" helices	84	slight[d]	92	5	3
8	<u>trans</u>	0.0009	450	1/16" helices	44	none	71[e]	18[e]	12[e]

[a] 2,3-Dimethylcyclopentene.

[b] 1,2-Dimethylcyclopentene.

[c] 2-Methylmethylenecyclopentane.

[d] A small amount of carbonization appears at the top of the pyrolysis tube.

[e] Analysis is by a gas chromatogram on crude product.

Table 10. Olefin composition from pyrolyses of 1-methylcyclopentyl acetate

No.	Add. rate mole/min	Temp. °C	Support	% Pyrolysis	Carbon	% Endo-olefin[a]	% Exo-olefin[b]
9	0.015	450	1/8" helices	72	none	100	0
10	0.0004	450	1/16" helices	73	slight[c]	100	0
11	0.092	450	1/16" helices	38	none	100	0

[a] 1-Methylcyclopentene.

[b] Methylenecyclopentane.

[c] A small amount of carbonization appears at the top of the pyrolysis tube.

confirm the assignment of the structure of the pyrolysis product from the 1-methylcyclopentyl acetate.

Pyrolyses 4 and 5 were done with a sample of *cis*-1,2-dimethylcyclopentyl acetate which had been thoroughly washed with sodium bicarbonate to remove all traces of acid while prior to the other pyrolyses on *cis* acetate this very careful washing procedure was not followed. Similarly, pyrolyses 7 and 8 were done on acid-free *trans*-1,2-dimethylcyclopentyl acetate and pyrolyses 10 and 11 on acid-free samples of 1-methylcyclopentyl acetate. When the gas chromatograms were run only on the crude pyrolysis product, this fact is noted, since the acetic acid in the mixture may cause some overlapping of the peaks.

Infrared spectra of the extracted pyrolysis products all showed the presence of some remaining acetate. Absorption bands 6.1μ and 10.95μ were characteristic of the 1,2- and 2,3-dimethyl olefins. The absorption band at 11.35μ, characteristic of exomethylene ($=CH_2$), was present in the spectra of the pyrolysis products of both *cis* and *trans* acetates. Unfortunately, the spectra were not consistently of such a resolution as to permit quantitative estimation of composition. The 11.35μ band was absent from spectra of the 1-methylcyclopentyl acetate pyrolysis products.

Pyrolyses were also done on several alkyl cyclohexyl acetates, repeating and extending previous work[154-157] with the newer analytical technique. Results of the pyrolysis of 1-methylcyclohexyl acetate are given in Tables 11 and 12. Confirmation of the assignment of olefin structure to the proper peaks was done with a 1-methylcyclohexene sample. All samples except those for pyrolyses 12, 13, and 14 were run on completely acid-free samples. In the pyrolyses over 1/8" or 1/16" pyrex helices at 450° C an average value of 24% methylenecyclohexane was found.

Two nuclear magnetic resonance spectra were run by Dr. McCallum on the products of pyrolysis 15. The amounts of methylenecyclohexane indicated were 25% and 27% (average 26%). Calculations by Dr. McCallum from high resolution infrared spectra of this sample and authentic samples of the two olefins indicated the presence of 29% of the exomethylene compound.

Since the earlier workers had reported much higher concentrations of methylenecyclohexane from the pyrolysis of

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[154] T. D. Nevitt and G. S. Hammond, J. Am. Chem. Soc., 76, 4124 (1954).

[155] W. J. Bailey, J. J. Hewitt and C. King, ibid., 77, 357 (1955).

[156] R. J. Arnold, G. G. Smith, and R. M. Dodson, J. Org. Chem., 15, 1256 (1950).

[157] W. J. Bailey and L. Nicholas, ibid., 21, 854 (1956).

Table 11. Olefin composition from pyrolyses of 1-methylcyclohexyl acetate

No.	Add. rate mole/min	Temp. °C	Support	% Pyrolysis	Carbon	% Endo-olefin[a]	% Exo-olefin[b]
12	0.041	450	1/8" helices	29	none	76	24
13	0.0003	450	1/8" helices	77	slight[c]	74	26
14	0.0002	450	1/16" helices	78	slight[c]	76	24
15	0.06	450	1/16" helices	94	slight[c]	78	23
16	0.0006	350	1/16" helices	19	none	82	18
17	0.0002	350	1/16" helices	62	none	77	23
18	0.0002	350	420μ beads	71	slight[c]	77	23

[a] 1-Methylcyclohexene.

[b] Methylenecyclohexane.

[c] A small amount of carbonization appears at the top of the pyrolysis tube.

Table 12. Olefin composition from pyrolyses of 1-methylcyclohexyl acetate on coated supports

No.	Add. rate mole/min	Temp. °C	Support	% Pyrolysis	Carbon	% Endo-olefin[a]	% Exo-olefin[b]
19	0.0003	350	1/16" helices treated with "Desicote"	66	slight[c]	74	26
20	0.0003	350	1/16" helices treated with "Desicote"	71	slight[c]	75	25
21	0.001	450	1/16" helices treated with conc. NaOH	55	complete[d]	82	19

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[a] 1-Methylcyclohexene.

[b] Methylenecyclohexane.

[c] A small amount of carbonization appears at the top of the pyrolysis tube.

[d] Helices completely covered with carbon.

Table 12. (Continued)

No.	Add. rate mole/min	Temp. °C	Support	% Pyrolysis	Carbon	% Endo-olefin[a]	% Exo-olefin[b]
22	0.001	450	1/16" helices treated with conc. HCl	73	slight[c]	89	11
23	0.0008	450	1/16" helices treated with conc. HNO_3	81	slight[c]	84	16
24	0.0003	450	1/16" helices treated with conc. H_2SO_4	40	complete[d]	99	1
25	0.0001	350	acid treated silica	74	slight[c]	99	1
26	0.0002	350	NH_3 treated silica	55	slight[c]	89	11
27	0.0001	300	NH_3 treated silica	66	slight[c]	96	4

1-methylcyclohexyl acetate, using comparisons of infrared spectra for the analysis, this acetate was pyrolyzed under a variety of conditions in an attempt to duplicate the previous results.

Variation of the temperature and the type of support appeared to make no significant change in the composition of the olefinic products. Coating 1/16" pyrex helices with Desicote (Beckman Instruments, Inc.) caused no change. The helices were still "desicoted" after the pyrolysis as indicated by the fact that they still repelled water. Sodium hydroxide coated helices caused a slight decrease in the exomethylene content of the pyrolysis products, while coating the helices with various acids caused a significant decrease in the percent of methylenecyclohexane formed. Pyrolyses over acid coated and base treated silica also gave lowered exomethylene production.

One sample (pyrolysis 12), which still contained considerable acetate after the acid had been extracted, was sent through the pyrolysis tube a second time. The amount of methylenecyclohexane found was 26%. This sample was again passed through the heated tube after a drop of glacial acetic acid had been added to the sample. The exomethylene content of the mixture collected was 21%.

Pyrolysis 15 was carried out on a ten gram sample of 1-methylcyclohexyl acetate. The amount of methylenecyclohexane obtained for this run was 23%. In other work in these laboratories[158], a 100 g. sample of 1-methylcyclohexyl acetate was pyrolyzed. The exomethylene content of the products, before the acetic acid extraction, was found to be 27%.

Infrared spectra were run on the olefinic products after the acetic acid had been removed by extraction. These spectra, as well as one on 1-methylcyclohexene, compared closely to those given by Nevitt[159] with strong 10.40, 10.95, and 11.35 absorption bands and weak absorption bands at 5.98 and 6.08 . From a cursory examination of the spectra, a higher concentration of methylenecyclohexane could be estimated.

Results from the gas chromatography analyses of pyrolysis products of other alkylcyclohexyl acetates are given in Tables 13, 14, and 15. Structural assignments of the various peaks were done with samples of 1,2-dimethylcyclohexene, 2,3-dimethylcyclohexene, 1-methylcyclohexene, and 1-ethylcyclohexene. The other peaks were assigned by the process of elimination. The samples for all the pyrolyses were acid-free acetates.

Infrared spectra of the pyrolysis products of the *cis-* and *trans*-dimethylcyclohexyl acetates showed an appreciable content of 2-methylmethylenecyclohexane, as indicated by the

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[158] D. H. Froemsdorf, Unpublished observations, Ames, Iowa (1957).

[159] T. D. Nevitt, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa, p. 86 (1953).

Table 13. Olefin composition from pyrolyses of isomeric 1,2-dimethylcyclohexyl acetates

No.	Acetate	Add. rate mole/min	Temp. °C	Support	% Pyrolysis	Carbon	% 1,2-Olefin[a]	% 2,3-Olefin[b]	% Exo-olefin[c]
28	*cis*	0.0002	450	1/16" helices	77	none	30	25	45
29	*cis*	0.0002	450	1/16" helices	80	none	27	27	46
30	*trans*	0.0002	450	1/16" helices	80	none	0	46	54
31	*trans*	0.0003	450	1/16" helices	70	none	0	44	56

[a] 1,2-Dimethylcyclohexene.

[b] 2,3-Dimethylcyclohexene.

[c] 2-Methylmethylenecyclohexane.

Table 14. Olefin composition from pyrolyses of 2-methylcyclohexyl acetate

No.	Add. rate mole/min	Temp. °C	Support	% Pyrolysis	Carbon	% 1-Methylolefin[a]	% 3-Methylolefin[b]
32	0.0005	450	1/16" helices	13	none	39	61
33	0.0007	450	1/16" helices	27	none	40	60

[a] 1-Methylcyclohexene.

[b] 3-Methylcyclohexene.

Table 15. Olefin composition from pyrolyses of 1-ethylcyclohexyl acetate

No.	Add. rate mole/min	Temp. °C	Support	% Pyrolysis	Carbon	% Endo-olefin[a]	% Exo-olefin[b]
34	0.0001	450	1/16" helices	79	none	100	0
35	0.0002	450	1/16" helices	80	none	100	0

[a] 1-Ethylcyclohexene.

[b] Ethylenecyclohexane.

6.12 and 11.28 bands. A spectrum of authentic 2-methylmethylenecyclohexane is given by Nevitt[160].

The pyrolysis products of 2-methylcyclohexyl acetate gave infrared spectra with bands at 6.08, 6.12, 10.15, 10.70 and 11.05μ. Notably absent were the absorption bands at 10.40 and 10.95μ which are characteristic of 1-methylcyclohexene.

The infrared spectra of the products of the pyrolyses of 1-ethylcyclohexyl acetate were neither of adequate resolution nor of adequate reproducibility to be useful.

Reactions with Hydrogen Bromide

Reagents

Hydrogen bromide. Anhydrous hydrogen bromide (Matheson, 99.9%) was condensed in the vacuum line and distilled once before use.

Hydrobromic acid. Eastman White Label, 48% hydrobromic acid was added to glacial acetic acid to give a 30% solution.

Normal pentane. Phillips Pure Grade, 99 mole percent minimum n-pentane was dried over sodium before use.

Acetic acid. Mallinckrodt analytical reagent grade acetic acid was used without further purification.

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[160] T. D. Nevitt, *ibid.*, p. 84.

Cis- and trans-1,2-dimethylcyclopentanol. These were prepared as described above.

1,2-Dimethylcyclopentene and 1-methylcyclopentene. These were prepared as described above.

Cis-1,2-dimethylcyclohexanol and 1,2-dimethylcyclohexene. These were prepared as described above.

Vacuum line

The vacuum line used for the reaction of hydrogen bromide with the alcohols and olefins was identical to that of Nevitt[161]. A Welch DuoSeal Vacuum Pump and a mercury diffusion pump were used to obtain a pressure of five microns. Before being used the vacuum line was evacuated at this pressure for ten hours or longer.

At the start of a reaction, hydrogen bromide was introduced into the system in the following manner. The stopcocks leading to the storage bulb, reaction flasks and vacuum gauge were closed. A tank of hydrogen bromide was attached to an inlet with a short piece of tygon tubing. The inlet and tubing were evacuated. The stopcock to the traps and pumps was closed and the hydrogen bromide gas allowed to flow into the system, using the manometer to insure that the pressure

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[161] T. D. Nevitt, ibid., pp. 50, 51.

did not exceed atmospheric. The gas was condensed in the hydrogen bromide condensation flasks by immersing the flasks in a liquid nitrogen bath. When sufficient hydrogen bromide had been condensed, the tank and the inlet stopcock were closed and the system was evacuated briefly by opening the stopcock to the traps and pumps, keeping the hydrogen bromide frozen with liquid nitrogen. Any excess hydrogen bromide was condensed in a removable trap cooled in a liquid nitrogen bath. The stopcocks on the hydrogen bromide condensation flasks were then closed and the bulbs kept immersed in liquid nitrogen. As hydrogen bromide was needed for reactions, it was distilled from one of the condensation flasks to the 2.2 liter storage bulb by opening the proper stopcocks (those to the traps and the pumps were closed) and removing the liquid nitrogen bath until the pressure in the storage bulb, as indicated by the manometer, was about 760 mm. The stopcock to the condensation flask was then closed and the flask reimmersed in a liquid nitrogen bath.

Procedures

Reactions in pentane on the vacuum line. Addition of hydrogen bromide to the olefins previously described and substitution reactions with hydrogen bromide on several of the alcohols were run on the vacuum line using n-pentane as the solvent. The temperatures used for these reactions included about 25° C (room temperature), about 0° C (achieved by the use of an ice-water bath), and about -78° C (achieved by means of a dry ice-acetone bath). For several reactions, the initial temperature was -196° C (achieved by means of a liquid nitrogen bath). Then, after 5 minutes reaction time, the liquid nitrogen bath was replaced by a dry ice-acetone bath and the reaction mixture was allowed to warm to -78° C during the remainder of the reaction time.

The reaction time was varied from five to sixty minutes. The reaction was quenched by pouring the pentane solution (containing the bromide) into water. The pentane solution was then dried before further steps were taken. In several of the later runs the reaction was quenched by pouring the solution directly into the next reaction medium.

The initial pressure of hydrogen bromide was near 760 mm. Even though a number of different substrates were used, the uptake of hydrogen bromide by the various substrates was about the same at a given temperature, as indicated by the drop in the hydrogen bromide pressure from its initial value. For the reaction in pentane at 0° C, the average amount of hydrogen bromide taken up by the solution was 12 mm per millimole of substrate. Assuming a volume of 2.2 liters for the hydrogen bromide in the vacuum line, this means about 1.5 millimoles of hydrogen bromide were absorbed for each millimole of substrate. At -78° C, the uptake of hydrogen bromide was 26 mm per millimole or 4.6 millimoles of hydrogen bromide for each mole of substrate. When the reaction flask was initially cooled in a liquid nitrogen bath, the amount of hydrogen bromide taken into the reaction flask was 40 mm (6.6 millimoles) for each millimole of substrate.

A few reactions were tried with a lower initial pressure of hydrogen bromide. In these cases the relative pressure drop was considerably reduced with much less than 1 millimole of hydrogen bromide per millimole of substrate being absorbed. In other ways, also, the reaction did not appear to be normal.

Although the contact times were varied over a considerable range, the amount of hydrogen bromide absorbed was about the same. This is due to the rapid absorption of the hydrogen bromide. After only five minutes of reaction time, 90% of the hydrogen bromide to be absorbed was already taken up. After ten minutes, 96% was absorbed and at the twenty minute mark over 99% was taken up.

In a typical run, one to two grams of, for example, 1,2-dimethylcyclopentene, were dissolved in twenty five milliliters of pentane. The reaction flask was then placed on the vacuum line and cooled in a liquid nitrogen bath. When the solution had become frozen, the flask was evacuated briefly by opening the stopcock on the reaction flask to the vacuum line. This stopcock was then closed and the liquid nitrogen bath removed. While the pentane solution was melting, hydrogen bromide was distilled into the 2.2 liter storage bulb until the pressure was near 760 mm. The reaction flask was kept in a bath of the desired reaction temperature and stirred by means of a magnetic stirrer. The stopcock on the reaction flask was then opened to the storage bulb. An immediate drop in the hydrogen bromide pressure was observed, followed by a slower decrease throughout the remainder of the reaction time. At the end of this time, the pentane solution was poured into a separatory funnel containing 25 ml of water, and the hydrogen bromide removed by thorough washing. Further 25 ml portions of water and a 5% sodium bicarbonate solution were used for washings. The pentane was dried over anhydrous calcium sulfate before proceeding with the next step.

On some occasions the pentane was removed by vacuum distillation, either on the vacuum line or by means of a small distillation apparatus. On other occasions the pentane solution of the bromide itself was used in the next step.

Reactions with 1-methylcyclopentene, 1,2-dimethylcyclopentene, both cis- and trans-1,2-dimethylcyclopentanol, 1,2-dimethylcyclohexene and cis-1,2-dimethylcyclohexanol were carried out by the above procedure. Some specific observations on the individual reactions follow.

In the addition of hydrogen bromide to both 1-methyl- and 1,2-dimethylcyclopentene at 0° C the pentane solution rapidly became deep yellow in color. Soon, within the first five minutes, a few dark brown or black deposits would appear on the sides of the reaction flask. These dark deposits were of a material quite soluble in water although apparently insoluble in the pentane. In the reactions carried out at -78° C, a white solid formed immediately upon opening the reaction flask to the hydrogen bromide. This solid became yellow in color as the reaction proceeded, although none of the dark colored material appeared. When the solid had melted, the pentane solution was yellow to yellow-orange in color. In the addition of hydrogen bromide to 1,2-dimethylcyclopentene, carried out at 25° C, the pentane solution rapidly became quite green in color with a larger than normal amount of dark black material forming on the walls.

The reaction of hydrogen bromide with the isomeric 1,2-dimethylcyclopentanols showed similar color effects. Here, however, the pentane-insoluble deposits were more of a yellow-brown in color. The pentane solution was yellow.

In the reactions with the cyclohexyl compounds, the solutions remained colorless. At -78° C a white solid product formed immediately upon contact with hydrogen bromide. When this melted the solution was colorless.

Reactions in pentane at atmospheric pressure. Two reactions were carried out in an open flask by bubbling the hydrogen bromide gas into the stirred pentane solution. The hydrogen bromide addition was followed by stirring for an additional hour. The reaction was then quenched in water and worked up in the usual manner. In the reaction of 1,2-dimethylcyclohexene a brown-colored lower layer, several milliliters in volume, formed and the pentane solution became yellow. With 1,2-dimethylcyclopentene, the lower layer was dark black and quite viscous, the pentane solution was dark green. The green color did not become less intense during the washing process.

Reactions in acetic acid on the vacuum line. Hydrogen bromide was reacted with 1-methylcyclopentene, 1,2-dimethylcyclopentene, and the isomeric 1,2-dimethylcyclopentanols on the vacuum line, with glacial acetic acid as the solvent. These reactions were run at about 25° C. In some cases the hydrogen bromide was initially frozen onto the frozen acetic acid solution by means of a liquid nitrogen bath. The solution then warmed to room temperature during the course of the reaction. The reaction time was 60 minutes. The initial hydrogen bromide pressure was near 760 mm. Over 90% of the total absorbable hydrogen bromide was absorbed in the first five minutes, with over 99% absorbed in twenty five minutes. For all of the substrates used, the average amount of hydrogen bromide absorbed during a reaction was 25 mm for each millimole of substrate, or about 3.0 millimoles of hydrogen bromide per millimole of substrate.

The reaction procedure involved was similar to that of the vacuum line reactions with pentane as solvent. The reactions were quenched in water and the bromides formed were extracted into pentane. The pentane was washed and dried before beginning the next step.

During the course of the reaction of hydrogen bromide with either of the olefins, the solution became dark purple. Upon quenching the reaction, the dark color remained in the aqueous layer. The pentane solution resulting from the extraction was usually yellow. In the reactions with the isomeric alcohols, the acetic acid solution became yellow. A yellow color appeared also in the extracting pentane.

Reaction with acetic acid at atmospheric pressure. In some of the reactions, 30% hydrobromic acid was added in excess to the solution of the olefin in twenty five milliliters of glacial acetic acid. The immediate formation of a dark green-black color was characteristic. Quenching and extraction were the same as previously described. The resulting pentane solution was usually orange or orange brown.

Analyses on the Bromides

Physical methods of analysis

Following the removal of pentane from samples of 1-methylcyclopentyl bromide and 1,2-dimethylcyclopentyl bromide several physical methods of analysis were tried on undistilled bromide. Much difficulty accompanies these attempts since the bromides appeared to decompose rapidly at room temperature. Fumes, identified as a halide with a silver nitrate moistened paper, were observed. The color of the bromide, initially a light yellow, readily became an intense green, and, in a short while, a dark solid deposited on the walls of the container. Treatment of a small portion of the green-colored solution with a crystal of sodium thiosulfate caused a fading of the color. Carbon tetrachloride became brown when added. This decomposition was not retarded by storage in an ice bath but was appreciably slowed by freezing the bromide in a dry ice-acetone bath. A discussion of the physical methods follows.

Fractional distillation. After the dried pentane solvent was removed from 1,2-dimethylcyclopentyl bromide (prepared from the corresponding olefin in pentane at atmospheric pressure) a reduced pressure distillation was attempted. No fractionation of products occurred. All the bromide distilled at or below 24° C (room temperature) at a pressure of 3 mm, although it was necessary to heat the distilling flask slightly (by means of a 45° C bath) before this distillation started. The refractive index, (20/D) was 1.4829. The distillate showed the same tendency toward rapid decomposition at room temperature as did undistilled samples of the bromide.

Infrared analysis. Infrared spectra were run on both distilled and undistilled bromide samples. Several characteristic bands could be discerned but there was little consistency from spectrum to spectrum between two samples prepared by identical procedure or even between duplicate spectra of the same sample. It was noted that the sample, small though it was, turned quite green during the process of taking the infrared spectrum, and also that the sodium chloride capillary cell became badly etched during the run. It was felt that the infrared spectra, although interesting, could not be used in the development of a quantitative technique.

Gas chromatography. Samples of the crude bromide were run on the gas chromatograph at 110° C using the Apiezon L column. Each of the chromatograms run in this manner showed considerable amounts of olefin. Samples of 1-methylcyclopentyl bromide gave chromatograms indicating the presence of large amounts of 1-methylcyclopentene and one other lower boiling (near 100° C) compound as well as smaller amounts of two higher boiling compounds. With 1,2-dimethylcyclopentyl bromide, prepared both from the olefin and the alcohol, on the Apeizon L column, three olefins were identified. Four higher boiling substances also gave small peaks. Calculations from the peak areas indicated that 89-90% of the olefin was 1,2-dimethylcyclopentene, 8-9% was 2,3-dimethylcyclopentene while 1-2% was 2-methylmethylenecyclopentane.

With the tricresyl phosphate column, at 100° C, the amount of observed olefin was reduced, in fact nearly eliminated in some cases, the higher boiling peaks becoming more prominent. Difficulty was had in obtaining a reproducible chromatogram since the amount of olefin varied with each sample and between duplicate runs of the same sample. It was decided that the spontaneous elimination of hydrogen bromide by the bromide, to give olefin, made this direct method too unreliable for purposes of analysis.

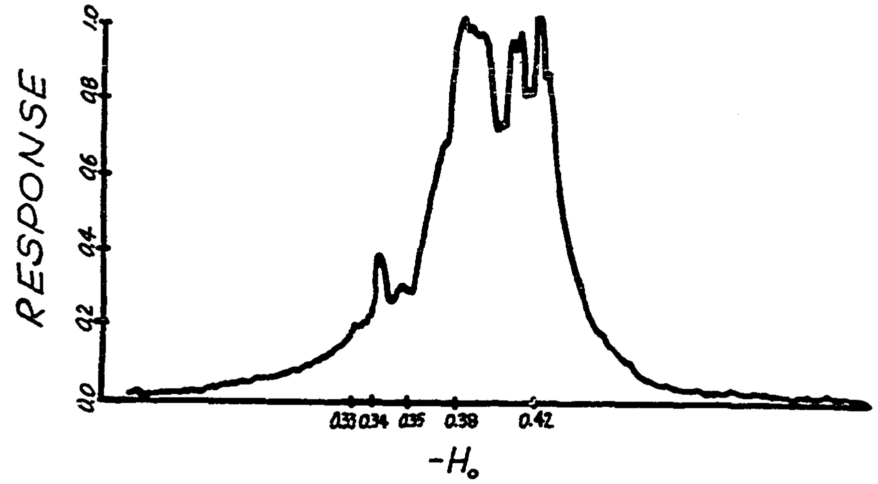
Nuclear magnetic resonance analysis. Samples of 1,2-dimethylcyclopentyl bromide, prepared in pentane from 1,2-dimethylcyclopentene and from both *cis*- and *trans*-1,2-dimethylcyclopentanol, were sent in sealed ampules for nuclear magnetic resonance analysis. The spectra obtained from the bromides which were prepared from *cis*- and *trans*-1,2-dimethylcyclopentanol were essentially identical (Plates 1 and 2). The spectrum of the bromide product from 1,2-dimethylcyclopentene was nearly identical to those of the products from the alcohols (Plate 3). The bromide sample of the latter had undergone considerable decomposition before the nuclear magnetic resonance spectrum was run, however.

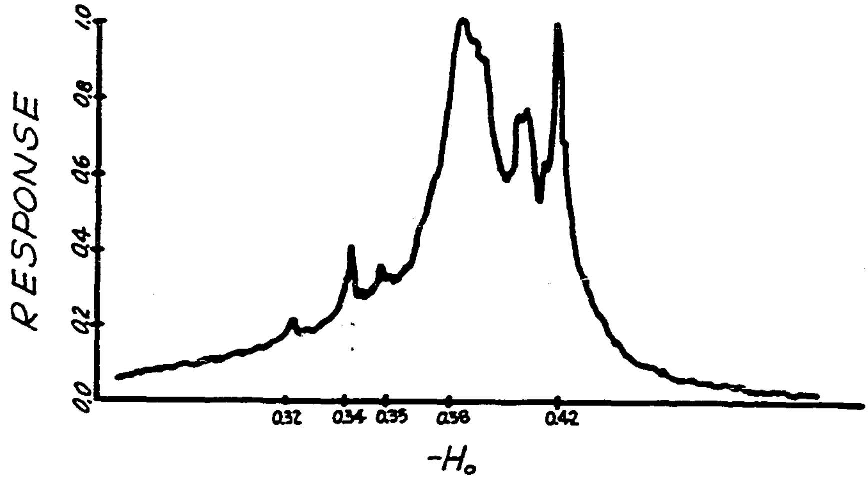
The nuclear magnetic resonance spectra of *cis*- and *trans*-1,2-dimethylcyclopentanol show some significant differences (Plates 4 and 5). The hydroxyl proton peak occurs at a higher magnetic field in the spectrum of the *trans*-alcohol

Plate 1. Nuclear magnetic resonance spectrum of 1,2-dimethylcyclopentyl bromide prepared from _trans_-1,2-dimethylcyclopentanol and hydrogen bromide in pentane

Plate 2. Nuclear magnetic resonance spectrum of 1,2-dimethylcyclopentyl bromide prepared from _cis_-1,2-dimethylcyclopentanol and hydrogen bromide in pentane

Plate 3. Nuclear magnetic resonance spectrum of 1,2-dimethylcyclopentyl bromide prepared from 1,2-dimethylcyclopentene and hydrogen bromide in pentane


RESPONSE
0.0
0.2
0.4
0.6
0.8
1.0
0.33
0.34
0.35
0.38
0.42
$-H_o$


RESPONSE
0.0
0.2
0.4
0.6
0.8
1.0
0.32
0.34
0.35
0.36
0.42
$-H_o$

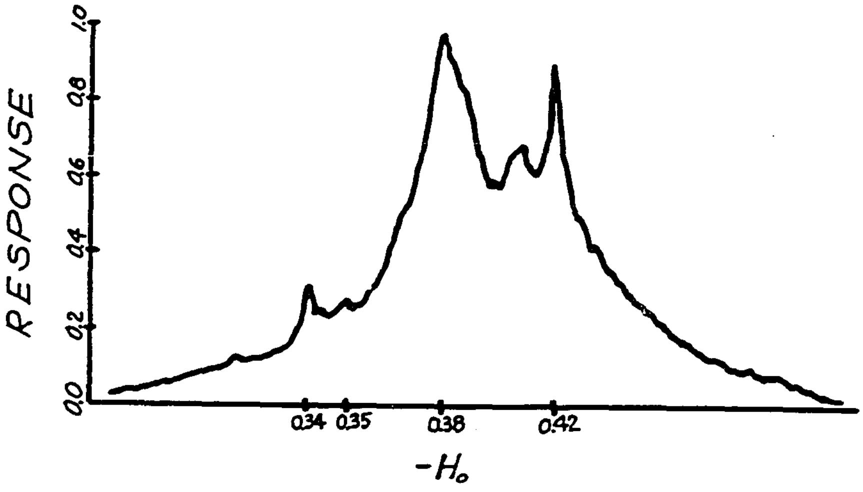
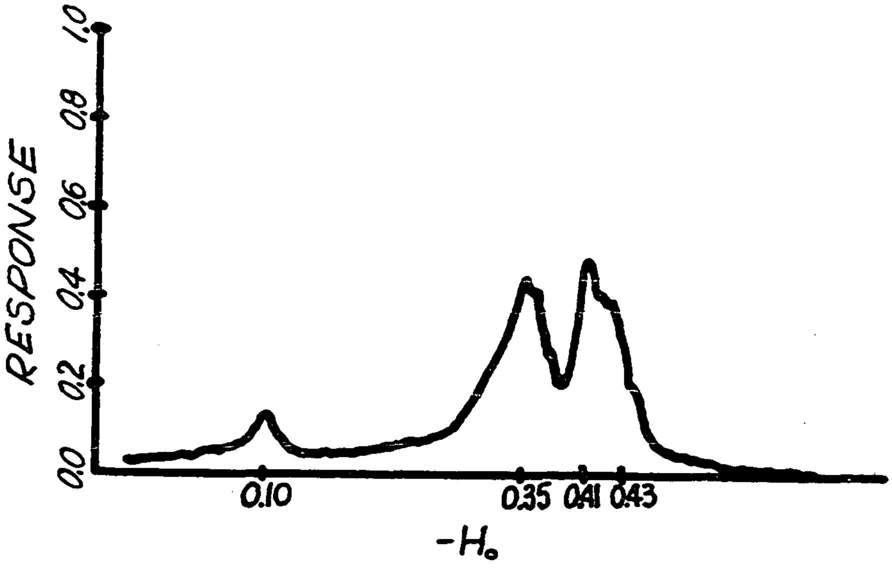

RESPONSE
0.0
0.2
0.4
0.6
0.8
1.0
0.34
0.35
0.38
0.42
$-H_o$

Plate 4. Nuclear magnetic resonance spectrum of
cis-1,2-dimethylcyclopentanol

Plate 5. Nuclear magnetic resonance spectrum of
trans-1,2-dimethylcyclopentanol


RESPONSE
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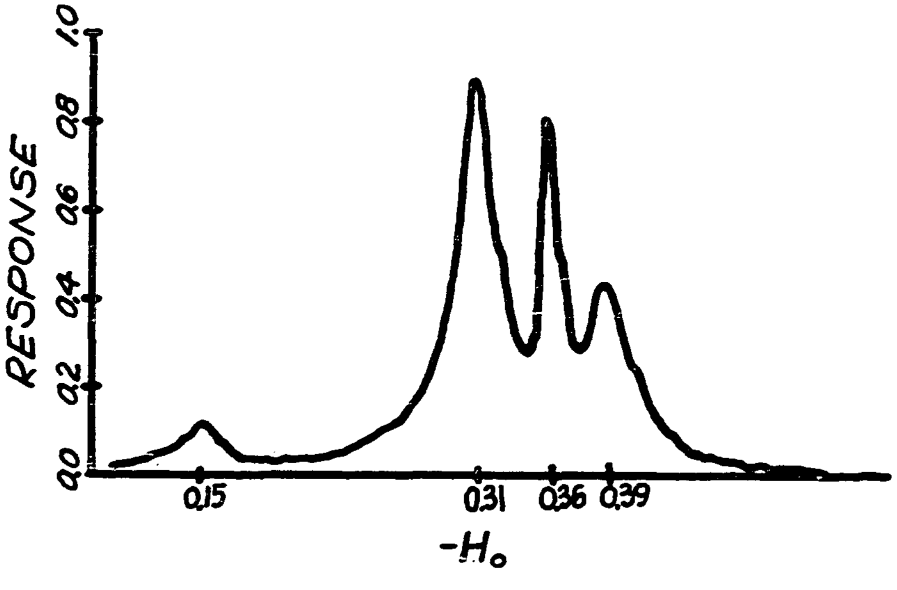
0.4
0.6
0.8
1.0
0.10
0.35
0.41
0.43
$-H_o$


RESPONSE
0.0
0.2
0.4
0.6
0.8
1.0
0.15
0.31
0.36
0.39
$-H_o$

(-0.15 Gutowsky units compared to -0.10 for the *cis* compound). Methyl groups are split somewhat further apart in the spectrum of the *trans* compound than in that of the *cis* (at -0.36 and -0.39 Gutowsky units, compared to -0.41 and -0.43).

It thus appears that the pure *cis* and *trans* compounds give distinguishing nuclear magnetic resonance spectra.

Elimination reactions

Since the bromide seemed to spontaneously eliminate under certain conditions, an analysis of the products of these eliminations was made. This was compared with the products of solvolytic (unimolecular) elimination and of base catalyzed (bimolecular) eliminations. Bimolecular eliminations with several bases were tried as described below.

Reagents.

Ethanol. Reagent grade ethanol was distilled from sodium hydroxide after refluxing at atmospheric pressure over the sodium hydroxide for about twenty hours. Water was added to some of the ethanol to prepare a ninety eight weight percent ethanol solution.

Mesitylene. Eastman reagent grade mesitylene was used without further purification.

Sodium hydroxide. This was prepared by dissolving enough freshly cut sodium in ninety-eight weight percent ethanol to make up a 2 normal solution. This was made up fresh before use.

Sodium ethoxide. Two normal sodium ethoxide was prepared by dissolving freshly cut sodium in absolute ethanol.

Sodium sec-butoxide. This was prepared by dissolving equimolecular amounts of freshly cut sodium and sec-butyl alcohol in mesitylene. A reflux period of 12-14 hours was necessary for complete reaction of the sodium with the alcohol. The resulting solution was about one normal. Sodium sec-butoxide of this concentration is not soluble in cold mesitylene but can be transferred easily when the solvent is hot.

1-Methylcyclopentyl bromide, 1,2-dimethylcyclopentyl bromide and 1,2-dimethylcyclohexyl bromide. These were prepared as previously described.

Procedures. Both the sodium hydroxide and sodium ethoxide eliminations were carried out by placing a 15 ml sample of a pentane solution, which contained the bromide, in a flask containing 50 ml of the basic solution. Within an hour some sodium bromide precipitate had formed. The solution was allowed to stand at room temperature for a day or two and was then poured into a separatory funnel containing 25 ml of water and 20 ml of pentane. The pentane solution was extracted twice more with water, then dried over anhydrous calcium sulfate before the pentane was removed by distillation. The mixed olefins remaining were placed in vials and maintained at refrigerator temperature until they could be analyzed by gas chromatography. The analysis was the same as that described for the olefin samples which resulted from the acetate pyrolysis.

In the case of the eliminations with sodium sec-butoxide in mesitylene, a 25 ml sample of pentane containing bromide was placed in a small flask containing 50 ml of the warm mesitylene solution. An immediate formation of sodium bromide was noted. The solution was refluxed slowly for three hours and then allowed to stand overnight before being poured into a separatory funnel containing 30 ml of water. The pentane-mesitylene solution was washed twice more, and then dried over anhydrous calcium sulfate. The pentane was removed by distillation and the gas chromatogram of the resulting mesitylene solution of the olefinic products was obtained.

In some of the eliminations involving sodium sec-butoxide in mesitylene, the pentane which contained the bromide was poured directly into the mesitylene solution without washing or drying. Fumes due to hydrogen bromide were observed briefly when the pentane solution first contacted the warm mesitylene solution. The remainder of the treatment was the same as that mentioned above.

Since the treatment with sodium sec-butoxide in mesitylene was quite harsh, a sample of olefin of known composition was refluxed for four hours in 50 ml of the sodium sec-butoxide solution to determine whether any isomerization occurs. The results are listed in Table 16.

Solvolysis reactions

Reagents.

Ethanol. The ethanol has been described above.

Lithium perchlorate. An approximately 0.1 N solution was prepared by dissolving in ethanol the required amount of the anhydrous powder (obtained from Dr. Fabian T. Fang).

Triethylamine. A redistilled fraction of triethyl amine, with a boiling point of 86.8° C (726 mm) (also obtained from Dr. Fang) was diluted with ethanol to give an approximately

Table 16. Composition of olefin sample before and after treatment with sodium sec-butoxide in mesitylene

	Olefin composition (%)	
	1,2-Dimethylcyclopentene	2,3-Dimethylcyclopentene
before	36.8	63.3
after[a]	39.0	61.1

[a] After treatment with base and removal of pentane.

1.0 N solution. This solution was standardized before each run against a 1.000 N solution of potassium acid phthalate.

Bromphenol blue. Harleco reagent bromphenol blue was dissolved in ethanol to give a 0.2% solution.

1-Methylcyclopentyl bromide and 1,2-dimethylcyclopentyl bromide. These have been described previously.

Apparatus. The solvolysis rates were determined by the rapid intermittent titration method[162,163]. The main apparatus consisted of a sixteen inch diameter thermostated water bath, 25.00 ± 0.02° C. A reaction cell assembly was mounted on the support rods of the bath. This consisted of a water jacketed five milliliter microburet with attached reservoir for titrant storage, a stirring motor and a glass reaction cell, all rigidly mounted on a common support so that the entire assembly could be raised or lowered easily. The reaction cell was of the type described by Reeder[164], with three side arms. Since the end-point was determined visually, the two side arms for the electrodes of the pH meter were not used, except for sample addition.

Procedure. The general procedure of the intermittent titration method is to follow the course of the solvolysis of

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[162] J. K. Kochi and G. S. Hammond, J. Am. Chem. Soc., 75, 3445 (1953).

[163] C. E. Reeder, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa, p. 34 (1955).

[164] C. E. Reeder, ibid., p. 36.

the bromide by the titration of liberated acid directly in the reaction cell as it is formed. This method is applicable to irreversible reactions which are neither acid nor base catalyzed.

For these titrations, the procedure consisted of placing in the reaction cell 75 ml of the 0.1 N lithium perchlorate solution with three drops of bromphenol blue indicator. The cell and solutions were allowed to equilibrate at the bath temperature. Previously standardized triethylamine was placed in the buret. A 10 ml sample of pentane containing the bromide was pipetted into the stirred solution. The 10 ml sample was removed from a 25 ml volumetric flask filled to the mark with the pentane solution, so that an estimate of the initial bromide concentration could be made. Zero time was defined as that time when half of the pentane solution had been added. As soon as was possible, some triethylamine was added and a first reading taken. The end-point each time was judged to be the instant the indicator color became yellow (acid) from the blue (basic) color. Additions of base occurred at intervals of 1-2 minutes for about 45 minutes. Several additional points were taken during the succeeding 30 minutes. At the end of this time the solvolysis was more than 90% complete. A final measurement was taken the next day.

In three of the titrations, the pentane solution containing the bromide was introduced to the reaction cell directly after removal from the vacuum line, without removing the excess hydrogen bromide with the water and bicarbonate washings. In these cases, zero time measurements were not made until the excess hydrogen bromide had been titrated with the triethylamine solution. After this point, the solvolysis proceeded in the usual manner. In one of these runs, that on a sample of 1,2-dimethylcyclopentyl bromide which was prepared by the addition of hydrogen bromide to the olefin, some difficulty was had in determining the final titration end-point, as the solution had become rather brown in color overnight. This brown color somewhat masked the yellow color of the indicator. An estimate of the end-point was made, however.

Calculations. The unimolecular rate constants were calculated from the integrated rate equation

$$K = \frac{1}{(t_2 - t_1)} \ln \frac{a - x_1}{a - x_2}$$

where a is the initial amount of the bromide, x_1 is the amount of hydrogen bromide liberated at time t_1 and x_2 is the amount of the hydrogen bromide liberated at time t_2. For these calculations x was taken as the titer, in milliliters of titrant added, at time t.

Product analysis. Since it was of interest to determine the composition of the olefinic products resulting from the solvolysis reaction, when the final titer had been taken, the solution was poured into a separatory funnel containing 50 ml of water and 30 ml of pentane. The olefins were extracted into the pentane and the pentane solution was washed with water several times before being dried over anhydrous calcium sulfate. The pentane was removed by distillation and the olefin composition determined by gas chromatography.

Results

The reaction of hydrogen bromide with cis- and trans-1,2-dimethylcyclopentanol was essentially complete, as indicated by the final titer in the solvolysis titration of a sample of bromide was prepared from the alcohols. However, the apparent yield of 1,2-dimethylcyclopentyl bromide from 1,2-dimethylcyclopentene, as indicated by the solvolysis experiments, was only 84%. This is probably due to some decomposition of the bromide having taken place during the washing of the pentane or perhaps even before the reaction flask was removed from the vacuum line.

The products from the base-catalyzed elimination experiments with the bromides, prepared from the various dimethylcyclopentyl substrates, are reported in Tables 17-19. All reactions were carried out on the vacuum line. The lack of 2-methylmethylenecyclopentane and methylenecyclopentane, as indicated by the gas chromatograms, may be due to the

Table 17. Olefin composition from eliminations on 1,2-dimethylcyclopentyl bromides with sodium hydroxide in ethanol

Rxn. no.	Initial substrate	Medium	Temp. °C	Time min.	% 1,2-Olefin[a]	% 2,3-Olefin[b]	% Exo-olefin[c]
1	1,2-olefin[a]	pentane	0	60	90	11	0
2	1,2-olefin[a]	pentane	0	60	93	7	0
3	1,2-olefin[a]	pentane	0	60	92	8	0
4	1,2-olefin[a]	pentane	0	60	91	9	0
5	1,2-olefin[a,d]	pentane	0	60	93	7	0
6	*cis*-alcohol[e]	pentane	0	60	91	8	0
7	*cis*-alcohol[e]	pentane	0	60	92	8	0
8	*trans*-alcohol[f]	pentane	0	60	90	10	0
9	*trans*-alcohol[f]	pentane	0	60	90	10	0

[a] 1,2-Dimethylcyclopentene.

[b] 2,3-Dimethylcyclopentene.

[c] 2-Methylmethylenecyclopentane.

[d] Two drops of water added to olefin before reaction.

[e] *Cis*-1,2-dimethylcyclopentanol.

[f] *Trans*-1,2-dimethylcyclopentanol.

Table 18. Olefin composition from eliminations on 1,2-dimethylcyclopentyl bromides with sodium ethoxide in ethanol

Rxn. no.	Initial substrate	Medium	Temp. °C	Time min.	% 1,2-Olefin[a]	% 2,3-Olefin[b]	% Exo-olefin[c]
5[d]	1,2-olefin[a]	pentane	0	60	91	10	0
10	1,2-olefin[a]	pentane	0	60	91	10	0
7[d]	*cis*-alcohol[e]	pentane	0	60	93	7	0
11	*cis*-alcohol[e]	pentane	0	60	93	8	0
9[d]	*trans*-alcohol[f]	pentane	0	60	92	8	0
12	*trans*-alcohol[f]	pentane	0	60	90	10	0
13	1,2-olefin[a]	acetic acid	25	60	93	7	0
14	*cis*-alcohol[e]	acetic acid	25	60	82	19	0

[a] 1,2-Dimethylcyclopentene.

[b] 2,3-Dimethylcyclopentene.

[c] 2-Methylmethylenecyclopentane.

[d] Elimination run 16 days after preparation of the bromide.

[e] *Cis*-1,2-dimethylcyclopentanol.

[f] *Trans*-1,2-dimethylcyclopentanol.

Table 19. Olefin composition from eliminations on 1,2-dimethylcyclopentyl bromides with sodium <u>sec</u>-butoxide in mesitylene

Rxn. no.	Initial substrate	Medium	Temp. °C	Time min.	% 1,2-Olefin[a]	% 2,3-Olefin[b]	% Exo-olefin[c]
15	1,2-olefin[a]	pentane	0	60	73	27	0
16[d]	1,2-olefin[a]	pentane	0	60	67	33	0
17[d]	1,2-olefin[a]	pentane	0	30	89	11	0
18[d]	1,2-olefin[a]	pentane	0	15	83	17	0
19[d]	1,2-olefin[a]	pentane	0	5	78	22	0
20[d]	1,2-olefin[a]	pentane	25	60	84	16	0
21[d]	1,2-olefin[a]	pentane	-78	60	82	19	0
22[d]	1,2-olefin[a]	pentane	-78[e]	60	92	8	0

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[a] 1,2-Dimethylcyclopentene.

[b] 2,3-Dimethylcyclopentene.

[c] 2-Methylmethylenecyclopentane.

[d] Bromide eliminated without previously washing the pentane.

[e] Sample plus hydrogen bromide frozen in liquid nitrogen for five minutes.

Table 19. (Continued)

Rxn. no.	Initial substrate	Medium	Temp. °C	Time min.	% 1,2-Olefin[a]	% 2,3-Olefin[b]	% Exo-olefin[c]
23	*cis*-alcohol[f]	pentane	0	60	70	30	0
24[d]	*cis*-alcohol[f]	pentane	0	60	68	32	0
25[d]	*cis*-alcohol[f]	pentane	0	5	79	21	0
26[d]	*cis*-alcohol[f]	pentane	-78	60	77	23	0
27[d]	*cis*-alcohol[f]	pentane	-78[e]	60	78	22	0
28	*trans*-alcohol[g]	pentane	0	60	72	28	0
29[d]	*trans*-alcohol[g]	pentane	0	60	69	31	0
30[d]	*trans*-alcohol[g]	pentane	0	5	84	16	0
31[d]	*trans*-alcohol[g]	pentane	-78	60	82	18	0
32[d]	*trans*-alcohol[g]	pentane	-78[e]	60	80	20	0
33[d]	1,2-olefin[a]	acetic acid	25	60	60	40	0
34	*trans*-alcohol[g]	acetic acid	25	60	55	45	0
35[h]	*cis*-alcohol[f]	acetic acid	25	60	75	25	0

[f] *Cis*-1,2-dimethylcyclopentanol.

[g] *Trans*-1,2-dimethylcyclopentanol.

[h] Reaction started at low initial hydrogen bromide pressure.

experimental limits of the method employed. It is possible that 1-2% of the exo-olefin could be present without being detected with the size sample that it was possible to use in the present equipment.

The results of the product analysis from the solvolyses on the cyclopentyl bromides are reported in Table 20. All of these reactions took place on the vacuum line.

Similar conditions appear to give similar results, with little or no distinction between the bromides on the basis of their starting material.

A distinct difference in the olefin composition is noted when the solvolysis was carried out directly, with no washing of the pentane solution to rid it of excess hydrogen bromide.

Some higher boiling substances, probably ethers, were also formed during the solvolysis. Two distinct peaks were observed. The ethers made up less than 25% of the total solvolysis product.

An interesting result which can be compared with the solvolysis results is that, in a single experiment, a pentane solution of the bromide, after washing, was allowed to stand for two days. The solution became deep green and a dark material was deposited on the walls of the flask. The pentane solution was washed with water at the end of this time, then dried. After the pentane had been removed, the olefin composition, indicated by gas chromatography, was 79% of

Table 20. Olefin composition from the solvolytic elimination of 1,2-dimethylcyclopentyl bromide

Rxn. no.	Initial substrate	Medium	Temp. °C	Time min.	% 1,2-Olefin[a]	% 2,3-Olefin[b]	% Exo-olefin[c]
36	1,2-olefin[a]	pentane	0	60	79	21	0
10	1,2-olefin[a]	pentane	0	60	78	22	0
16[d]	1,2-olefin[a]	pentane	0	60	87	13	0
11	*cis*-alcohol[e]	pentane	0	60	75	25	0
24[d]	*cis*-alcohol[e]	pentane	0	60	80	20	0
12	*trans*-alcohol[f]	pentane	0	60	77	23	0
29[d]	*trans*-alcohol[f]	pentane	0	60	87	13	0

[a] 1,2-Dimethylcyclopentene.

[b] 2,3-Dimethylcyclopentene.

[c] 2-Methylmethylenecyclopentane.

[d] Bromide titrated without previously washing the pentane.

[e] *Cis*-1,2-dimethylcyclopentanol.

[f] *Trans*-1,2-dimethylcyclopentanol.

1,2-dimethylcyclopentene, 22% of 2,3-dimethylcyclopentene. These values are seen to be quite similar to the solvolytic results.

Results of the elimination experiments on the bromide, prepared on the vacuum line from 1-methylcyclopentene, are given in Table 21. The results obtained from elimination reactions on some 1,2-dimethylcyclohexyl bromides are given in Table 22. In a reaction sequence similar to experiments 44 and 45, Nevitt[165] reported that the product was 100% _trans_-1,2-dimethylcyclohexyl bromide, which eliminated in a 98% ethanol solution of sodium hydroxide to give 100% 1,2-dimethylcyclohexene.

The reported product of a reaction sequence similar to experiment 46 was a bromide mixture containing about 30% of the _cis_ bromide, while the product from the reaction of _cis_-1,2-dimethylcyclohexanol with hydrogen bromide at -78°C contained about 55% of the _cis_ bromide. The elimination product from a sample containing 22% _cis_ bromide was reported as 87% of the 1,2-olefin, 13% of the exomethylene olefin. A sample containing 63% of _cis_ bromide eliminated to give 50% 1,2-dimethylcyclohexene and 50% 2-methylmethylenecyclohexane. None of the 2,3-isomer was reported. The present results indicate that the 2,3-olefin is formed by both _cis_- and _trans_-1,2-

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[165] T. D. Nevitt, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa, pp. 55, 75, 79 (1953).

Table 21. Olefin composition from eliminations on 1-methylcyclopentyl bromide

Rxn. no.	Medium	Temp. °C	Time min.	Eliminating agent	% Endo-olefin[a]	% Exo-olefin[b]
37	pentane	0	60	sodium hydroxide in ethanol	100	0
38	pentane	0	60	sodium ethoxide in ethanol	100	0
39	pentane	0	60	solvolysis in 100% ethanol[c]	100	0
40	pentane	0	60	solvolysis in 100% ethanol[c]	100	0
41	pentane	0	60	elimination in pentane	100	0

[a] 1-Methylcyclopentene.

[b] Methylenecyclopentane.

[c] About 50% of the total product is olefin.

Table 22. Olefin composition from eliminations on 1,2-dimethylcyclohexyl bromides

Rxn. no.	Initial substrate	Medium	Temp. °C	Time min.	Eliminating agent	% 1,2-Olefin[a]	% 2,3-Olefin[b]	% Exo-olefin[c]
42	1,2-olefin[a]	pentane	-78	45	sodium hydroxide in ethanol	89	11	0
43	1,2-olefin[a]	pentane	0	30	sodium ethoxide in ethanol	89	11	0
44	*cis*-alcohol[d]	pentane	0	60	sodium hydroxide in ethanol	69	27	4
45	*cis*-alcohol[d]	pentane	-78	60	sodium ethoxide in ethanol	74	25	2

[a] 1,2-Dimethylcyclohexene.

[b] 2,3-Dimethylcyclohexene.

[c] 2-Methylmethylenecyclohexane.

[d] *Cis*-1,2-dimethylcyclohexanol.

dimethylcyclohexyl bromide under the conditions of base catalyzed elimination.

The rate constants observed in the solvolysis reactions are given in Tables 23 and 24. In all cases except those specifically noted, the first order rate constant was decreasing rapidly near the end of the solvolysis. Certain very low values thus obtained were omitted from the calculation of the average value for the rate constant. The three cases in which the rate constant did not fall off rapidly were those in which there was no washing of the pentane before the start of the solvolysis.

Table 23. First order rate constants from the solvolysis of 1,2-dimethylcyclopentyl bromides[a]

Rxn. no.	Initial substrate	% Reaction followed		$k_1 \times 10^2$
4	1,2-olefin[b]	99		6.01
36	1,2-olefin[b]	85		5.36
10	1,2-olefin[b]	86		4.85
16[c]	1,2-olefin[b]	93		5.75[d]
			average	5.49
11	*cis*-alcohol[e]	98		6.26
24[c]	*cis*-alcohol[e]	92		5.74[f]
			average	6.00
12	*trans*-alcohol[g]	90		6.69
29[c]	*trans*-alcohol[g]	89		5.06[f]
			average	5.88

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[a] All the bromides were prepared in pentane at 0° C, with a 60 minute reaction time.

[b] 1,2-Dimethylcyclopentene.

[c] Solvolysis started with out previously washing the pentane.

[d] No decrease in k_1 is noted to 90%.

[e] *Cis*-1,2-dimethylcyclopentanol.

[f] A very slight decrease in k_1 is noted at 90%.

[g] *Trans*-1,2-dimethylcyclopentanol.

Table 24. First order rate constants from the solvolysis of 1-methylcyclopentyl bromide[a]

Rxn. no.	% Reaction followed		$k_1 \times 10^2$
37	99		3.75
40	97		3.15
39	94		3.04
		average	3.31

[a] All samples were prepared from 1-methylcyclopentene in pentane at 0° C, with a 60 minute reaction time.

DISCUSSION

Acetate Pyrolysis

Since in acetate pyrolysis a preference for _cis_ elimination has been well established[166,167], the pyrolysis of isomeric alicyclic acetates should allow assignment of structural configuration on the basis of the products obtained. Previously, this method was used to distinguish between _cis_- and _trans_-1,2-dimethylcyclohexanol[168]. Thus, since it was necessary in the present work to confirm the earlier structural assignments[169] of the isomeric 1,2-dimethylcyclopentanols, an analysis of the products obtained by pyrolysis of their acetates was made. If _cis_ elimination were rigidly followed, the products from _cis_-1,2-dimethylcyclopentanol would be expected to include all three of the isomeric olefins; 1,2-dimethylcyclopentene, 2,3-dimethylcyclopentene and 2-methylmethylenecyclopentane. The _trans_ isomer, however, could not give 1,2-dimethylcyclopentene by _cis_ elimination.

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[166] E. R. Alexander and A. Mudrock, _J. Am. Chem. Soc._, _72_, 1810 (1950).

[167] E. R. Alexander and A. Mudrock, _ibid._, _72_, 3194 (1950).

[168] T. D. Nevitt and G. S. Hammond, _ibid._, _76_, 4124 (1954).

[169] G. Chiurdoglu, _Bull. Soc. Chim. Belg._, _44_, 527 (1935).

The results of the pyrolyses are given in Table 9, page 75. The acetate of the cis-alcohol is seen to produce all three olefins, with some 45% of the olefin produced being 1,2-dimethylcyclopentene. The acetate of the trans-alcohol also pyrolyzed to give all three isomers, but the amount of the symmetrical olefin was quite small. On the basis of these results, it appears that the original assignment of configuration[169], with the cis-alcohol the higher boiling of the two, was correct.

Several explanations may be advanced to account for the approximately 10% of 1,2-dimethylcyclopentene obtained from the trans-acetate. The trans-alcohol may have been contaminated with some cis-alcohol. This is not very probable, however, since each of the two alcohols have distinct and well separated physical constants and give infrared spectra containing some mutually exclusive absorption bands. Somewhat more plausible is the possibility that some isomerization of the acetates occurred during their preparation, although previous workers[168] reported this did not occur with their compounds. Others of the 1,2-dimethylcyclopentyl compounds were found to be unstable, and this may be true, to some extent, of the alcohols and acetates although gas chromatograms run on the trans-alcohol and trans-acetate indicated only a single high boiling compound, contaminated with a very small amount of olefin. (A mixture of cis- and trans-alcohols had two peaks.) This contaminating olefin mixture consisting of both 1,2- and 2,3-dimethylcyclopentene, contained much too small an amount of the symmetric olefin to entirely account for its appearance in the pyrolysis product.

A third explanation of the observed occurrence of 1,2-dimethylcyclopentene in the pyrolysis products from the <u>trans</u>-acetate concerns the possibility that the olefins themselves may isomerize. It was noted in two cases that gas chromatographic analyses obtained four weeks after an original had been run indicated somewhat less of the exomethylene olefin and more of the endocyclic olefins than appeared in the original chromatograms. No determination was made of how rapid this isomerization was, but it may be possible that the values obtained for the composition of the products may depend on the length of time occurring between the running of the pyrolysis and the analysis of products. It is likewise possible that a small amount of product may have been formed in a <u>trans</u> manner, as was observed in the pyrolysis of <u>erythro</u>- and <u>threo</u>-2-deutero-1,2-diphenylethyl acetate[170]. In this case, the <u>threo</u>-acetate, with acetoxy and deuterium eclipsed in the most stable <u>cis</u> orientation, pyrolyzed to give a product which had retained 26% of its deuterium content. The extra energy required to break the C-D bond was the reason advanced by

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[170] D. Y. Curtin and D. B. Kellom, <u>J. Am. Chem. Soc.</u>, <u>75</u>, 6011 (1953).

these authors for the large amount of non-*cis* elimination. However, *erythro*-2-deutero-1,2-diphenylethyl acetate, with the acetoxy and the hydrogen adjacent in the most stable eclipsed conformation lost 10% of its deuterium in the pyrolysis. In the present case, the presence of the methyl group on the carbon atom adjacent to the one carrying the acetoxy group and on the same side of the plane of the 1,2-dimethylcyclopentyl acetate molecule may contribute enough steric interference to initiate a small amount of a *trans*-type elimination.

It is not possible on the basis of the information available to determine which of the last two possible explanations is the more probable. Further work on the rapidity of the olefin isomerization is necessary to check this point.

While the work on the 1,2-dimethylcyclopentyl acetates was in progress, the results of Froemsdorf[171] on some acyclic acetates, became known. Since these results were at variance with the results on similar compounds reported by Bailey and his coworkers[172,173], an investigation on some alicyclic acetates was begun in order to check on the results previously reported[168,173] for these compounds. The results of the

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[171] D. H. Froemsdorf, Unpublished observations, Ames, Iowa (1957).

[172] W. J. Bailey and C. King, *J. Am. Chem. Soc.*, *77*, 75 (1955).

[173] W. J. Bailey, J. J. Hewitt and C. King, *ibid.*, *77*, 357 (1955).

present investigations are given in Tables 11 and 13, pages 79 and 84. These results, obtained by the use of gas chromatography and, in the case of the 1-methylcyclohexyl acetate, checked by nuclear magnetic resonance analysis and quantitative infrared analysis, do not agree with those obtained by earlier workers. For example, previous workers have reported 87%[168] and 100%[173] of methylenecyclohexane were formed upon pyrolysis of 1-methylcyclohexyl acetate. The present work shows that only 24% of the exo-olefin is formed. Similar disagreement with the earlier results was obtained on <u>cis</u>- and <u>trans</u>-1,2-dimethylcyclohexyl acetate[168], although the newer results in no way invalidate the structural assignments made as a result of the previous work, since in both sets of results the <u>trans</u>-1,2-dimethylcyclohexyl acetate gives no 1,2-dimethylcyclohexene upon pyrolysis.

To ascertain that perhaps some experimental variable previously unnoticed was not the cause for the difference between the present results and those reported earlier, several pyrolyses of 1-methylcyclohexyl acetate were run on columns of beads and helices which had several different surface treatments. These results are given in Table 12, page 80. In no case did more than 25% of the product consist of methylenecyclohexane. Pyrolysis over "Desicote", a water repellent coating, gave identical results to those obtained over uncoated helices. Similar results were obtained in pyrolysis over 420μ beads, indicating that surface area effects are not prominent and the pyrolysis probably does occur essentially in the vapor phase. The same thing is indicated by the lack of any effect due to carbonization on the helices. Use of helices coated with sodium hydroxide slightly lowered the amount of methylenecyclohexane obtained, while treating the helices with various acids caused a variable but considerable decrease in the amount of exocyclic olefin obtained. Whether this last effect is due to a new, acid catalyzed pyrolysis mechanism or whether it is due to isomerization of the olefinic products to the more stable olefin cannot be determined at present. It can be concluded, however, that the results obtained in the recent work were not caused by spurious effects but were indications of the actual products of a vapor phase acetate pyrolysis.

As some of the earlier work had been performed in these laboratories[168], the infrared spectra used for analyses were available for study. Comparisons between these spectra and those run on the pyrolysis products of the present work showed great similarities, especially in the relative sizes of the absorption bands characteristic of the various olefins. In fact, examination of these spectra alone would lead one to estimate that considerably more of the exocyclic olefin had been produced than was indicated by the gas chromatograms. For this reason, nuclear magnetic resonance spectra were run on the pyrolysis products from 1-methylcyclohexyl acetate.

The nuclear magnetic resonance analysis results were nearly identical with the gas chromatography results. It is apparent, then, that either the infrared is not resolving the characteristic olefin peaks or that the particular absorption bands chosen for the analysis do not follow Beer's Law. The inaccuracy of the earlier results of pyrolyses of these alicyclic acetates, and perhaps also of the acyclic acetates, is probably due to the use of this less sensitive analytical technique.

The pyrolyses of 2-methylcyclohexyl acetate, reported in Table 14, page 85, indicate that earlier work of Bailey and Nicholas[174], which indicated that only the least substituted olefin was obtained is in error. The present work was done on a sample of acetate containing an unknown amount of *cis*-2-methylcyclohexyl acetate, so no quantitative results on the direction of the elimination are possible, but the presence of 40% of 1-methylcyclohexene in the products suggests that at least 40% of the mixed isomers was *trans*.

The results reported here lead to an interesting interpretation of the mechanism of the acetate pyrolysis. The degree of *cis*-character of the elimination led to an early acceptance of some cyclic intermediate or transition state in

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[174] W. J. Bailey and L. Nicholas, *J. Org. Chem.*, *21*, 854 (1956).

the pyrolytic elimination[175]. Such a cyclic transition state was presumed to require that all the atoms involved assume a rigid coplanar structure. This has been cited as a reason for the predominance of methylene cyclohexane in the product of the pyrolysis of 1-methylcyclohexyl acetate since a shift of the cyclohexane ring from the chair to the less stable boat form would be necessary for the exact eclipsing of the acetoxy and adjacent hydrogen in the formation of 1-methylcyclohexene. According to the earlier workers[173] the reluctance of the cyclohexane to do this led to the predominance of the exocyclic olefin. However, these earlier results were in error, and consequently the earlier explanation must be revised.

The newer results indicate that although a _cis_ preference is maintained (_trans_-1,2-dimethylcyclohexene gives only 2,3-dimethylcyclohexene and 2-methylenecyclohexane, both obtainable by _cis_ elimination) the coplanarity of the cyclic transition state is by no means as important as previously assumed. The size of this transition state ring, consisting of six atoms, may allow for considerable variation, thus permitting the endocyclic six membered olefin to form without necessitating a severe conformational change on the part of the cyclohexane molecule. In addition, the ring hydrogen may be more "available" for removal than are the hydrogen atoms on the

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[175] C. D. Hurd and F. H. Blunck, _J. Am. Chem. Soc._, _60_, 2419 (1938).

methyl substituent, since the latter may undergo free rotation while the former is more rigidly fixed.

Support for this interpretation is obtained in a comparison of the results of the amine oxide pyrolysis of similar ring compounds[176], also thought to occur by a cyclic mechanism. Both 1-methylcyclopentyl acetate and N,N-dimethyl-1-methylcyclopentylamine oxide give predominantly 1-methylcyclopentene (100% and 98%, respectively). However, while 1-methylcyclohexyl acetate pyrolyzes to give 75% 1-methylcyclohexene and 25% methylenecyclohexane, the corresponding amine oxide gives 97% of the exo-olefin and only 3% of the endo-olefin. This may be accounted for by a consideration of the size of the proposed cyclic transition state. The transition state for acetate pyrolysis is a six membered ring while that for the amine oxide pyrolysis is a five membered ring, which would require a greater degree of coplanarity from the atoms comprising it. Thus, in the cyclopentyl cases, where there is no steric resistance to the formation of an eclipsed cyclic transition state with acetate or amine oxide, the results are nearly identical. In the cyclohexyl compounds, however, the amine oxide, with a greater requirement for coplanarity in its transition state than is required in the acetate transition state, should form more of the exo-olefin,

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[176] A. C. Cope, C. L. Bumgardner and E. E. Schweizer, ibid., 79, 4729 (1957).

as is observed, since this may be formed without requiring any conformational change by the cyclohexane ring.

A cyclic transition state for the pyrolytic elimination of the acetic acid also permits an explanation of the results obtained in the pyrolysis of the cyclopentyl acetates. 1-Methylcyclopentyl acetate gives entirely endocyclic olefin which is possible since the acetoxy and hydrogen in the parent molecule are already eclipsed. The presence of an adjacent methyl, on the same side of the plane, as in the case of the trans-1,2-dimethylcyclopentyl acetate, causes a small amount of the exo-cyclic olefin to form. Placing the two methyl groups cis to one another, however, contorts the cyclopentane ring so that the acetoxy and hydrogen are no longer nearly eclipsed and the formation of more exo-olefin is encouraged as the coplanarity for the endocyclic olefin in no longer already attained.

Steric factors also explain the results obtained in the pyrolysis of 1-ethylcyclohexyl acetate. The additional methylene unit, besides removing one of the available hydrogens, also may interfere with facile formation of the transition state for the exo-olefin. There are no steric interferences with the formation of the endocyclic transition state. Thus 100% of the endo isomer, 1-ethylcyclohexene, is formed.

In summary, it has been shown that certain results reported by earlier workers on acetate pyrolysis were in error.

This has been attributed to an inadequacy in the infrared analytical technique employed by these workers. The mechanism of the pyrolysis has been reviewed and is considered to involve a cyclic transition state or intermediate, which, due to its size, does not require an exact eclipsing of the elements to be lost before the pyrolysis occurs. The preference shown by acetate pyrolysis for the *cis* elimination of the acetic acid has been used to confirm the previous assignment of configuration of the isomeric *cis*- and *trans*-1,2-dimethylcyclopentanols.

Reactions with Hydrogen Bromide

The stereochemistry of hydrogen bromide addition to olefins has been studied using 1,2-dimethylcyclohexene as substrate[177]. The study of this cyclic olefin, in which *cis-trans* isomerism is not possible, gave rise to the first demonstration of a *trans* stereospecificity for the ionic addition of hydrogen bromide under conditions where the possibility of neighboring group effects were remote. The predominant product in all cases was *trans*-1,2-dimethylcyclohexyl bromide. A series of reactions of 1,2-dimethylcyclohexene and its isomers, 2,3-dimethylcyclohexene and

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[177] G. S. Hammond and T. D. Nevitt, *J. Am. Chem. Soc.*, *76*, 4121 (1954).

2-methylmethylenecyclohexane, with hydrogen bromide in acetic acid gave different percentages of the *cis* bromide, indicating that a common cation was not formed in each case. The carbonium ions which would have formed from these olefins would have been identical, and consequently the resultant products would have been identical. Additional support for the argument that a carbonium ion is not involved in the rate determining step is that the isomeric *cis*- and *trans*-bromides solvolyzed at nearly identical rates while in the second order elimination, the *trans*-bromide reacted a hundred times as fast as did the *cis*-bromide. Since the solvolytic intermediate is probably a carbonium ion[178] while the E2 process does not involve such a species[179], it follows that the addition of hydrogen bromide to olefins is not the microscopic reverse of the first order elimination and if ionic intermediates are involved in the addition of hydrogen bromide to the three isomeric olefins, they are not identical to each other and are not the common carbonium ion.

The ionic addition of hydrogen bromide to 1,2-dimethylcyclohexene produced a product which was unambiguously shown to be *trans*-1,2-dimethylcyclohexyl bromide, indicating that the addition was entirely stereospecific and completely *trans*.

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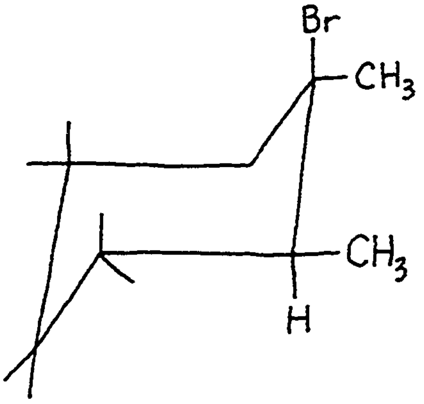
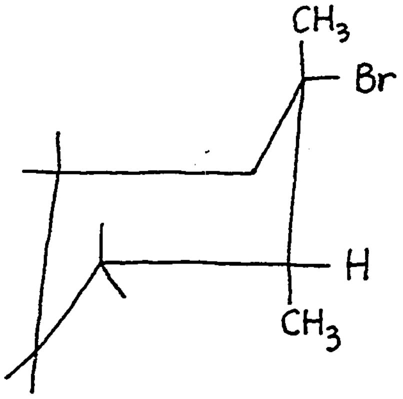
[178] E. D. Hughes, *Trans. Faraday Soc.*, *37*, 603 (1941).

[179] S. J. Cristol, *J. Am. Chem. Soc.*, *69*, 338 (1947).

Unfortunately, the lack of rigidity of the cyclohexyl system presents somewhat of a problem in the determination of the exact mode of the addition. The conformation assigned to the trans-bromide has the bromine atom in an axial position, the two trans-methyl groups in equatorial positions in the chair form of the cyclohexane ring (I). This conformation has been estimated[177] to be several kilocalories per mole more stable than the alternative trans conformation (chair form) in which the bromine is equatorial and the two methyl groups are axial (II). Although both are trans-1,2-dimethylcyclohexyl bromide an inspection of II shows that the equatorial hydrogen and bromine atoms are oriented in an eclipsed configuration. Thus it is possible that trans-1,2-dimethylcyclohexyl bromide could be formed by what is formally equivalent to a cis addition in a more planar compound. This less stable bromide could then revert spontaneously to the more stable conformation.



I



II

1,2-Dimethylcyclopentene has all, save one, of the advantages claimed for the 1,2-dimethylcyclohexyl olefin. It is cyclic and symmetrical so only two diasteromeric products can be formed unless skeletal rearrangements occur. It has no neighboring groups with unshared electron pairs, rendering the possibility of neighboring group reactions remote. It is tetrasubstituted, so will undergo rapid ionic addition and hence will obviate the difficulties arising from competitive free radical processes.

The major drawback to the use of 1,2-dimethylcyclopentene as a substrate was the lack of ready availability of the olefin. It had been prepared previously in low yields by a five step reaction sequence[180,181]. These reactions were modified in the current work to obtain a somewhat better overall yield, but nevertheless, the necessity for obtaining reasonable quantities of the olefin and its parent alcohol meant that the preparative work was quite time consuming.

Once the olefins had been prepared, the addition of hydrogen bromide could be accomplished and an analytic tool for the determination of the stereochemistry of the addition could be worked out. The experimental section of this thesis contains a description of the analytical methods attempted.

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[180] G. Chiurdoglu, Bull. Soc. Chim. Belg., 47, 363 (1938).

[181] G. Chavanne, ibid., 39, 402 (1930).

Attempts at fractional distillation, infrared analysis and gas chromatography on the bromide products proved dishearteningly unsuccessful, as it appeared that the bromides decomposed quite rapidly at 0° C or above. Fumes of hydrogen bromide were identified and olefinic products were determined in the undistilled pentane solution after a sample of the bromide in pentane had been allowed to stand for several days. Thus, since it appeared that the bromide eliminated spontaneously but relatively slowly, it was decided to circumvent this difficulty by promoting a rapid base-catalyzed elimination of the products from the addition reaction. The stereospecific preference for <u>trans</u> elimination in a base catalyzed bimolecular elimination has been previously demonstrated[179,182-187]. Thus, a difference should be observed in case the 1,2-dimethylcyclopentyl bromides prepared in the different ways contained different amounts of <u>cis</u> and <u>trans</u> bromide. <u>Trans</u>-1,2-

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[182] S. J. Cristol, N. L. Hause and J. S. Meek, <u>J. Am. Chem. Soc.</u>, <u>73</u>, 674 (1951).

[183] S. J. Cristol and A. Begoon, <u>ibid.</u>, <u>74</u>, 5025 (1952).

[184] S. J. Cristol and W. P. Norris, <u>ibid.</u>, <u>76</u>, 3005 (1954).

[185] S. J. Cristol, A. Begoon, W. P. Norris and P. S. Ramey, <u>ibid.</u>, <u>76</u>, 4558 (1954).

[186] M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. D. Woolf, <u>J. Chem. Soc.</u>, <u>1948</u>, 2117.

[187] E. D. Hughes, C. K. Ingold and R. Pasternack, <u>ibid.</u>, <u>1953</u>, 3832.

dimethylcyclopentyl bromide could eliminate to give all three possible olefins--1,2-dimethylcyclopentene, 2,3-dimethylcyclopentene and 2-methylmethylenecyclopentane--while the cis isomer could not eliminate in a trans manner to give 1,2-dimethylcyclopentene. The amount of this olefin, then, as a product of the bimolecular elimination of the bromides, would serve as a tool to indicate the probable amount of trans-1,2-dimethylcyclopentyl bromide found in the addition reaction. A complicating factor is that the product of the uncatalyzed unimolecular elimination from both cis and trans-1,2-dimethylcyclopentyl bromide is predicted by the Saytzeff rule[188] to be the symmetrical olefin, 1,2-dimethylcyclopentene. The extent of unimolecular reaction, then, must be sufficiently small that the symmetric olefin formed will be a measure of the amount of trans bromide undergoing the bimolecular elimination.

Tables 17 and 18, pages 111 and 112, give the product analysis for the base-catalyzed eliminations which were carried out in 98% and 100% ethanol. The olefin compositions obtained from eliminations on bromides prepared from 1,2-dimethylcyclopentene were nearly identical in both solvents and contained very high amounts of the symmetric olefin. The

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[188] C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N. Y., p. 427 (1953).

solvolysis rate of the bromide product in absolute ethanol was determined and the solvolysis was found to be very rapid, the half time for the reaction being about thirteen minutes. This indicates that a considerable portion of the elimination in the ethanol solvents is probably solvolytic, giving rise to the most stable olefin by a unimolecular mechanism involving a carbonium ion, rather than by the base-catalyzed stereospecific *trans* type of elimination. Solvolysis should not be a problem with a mesitylene solution of sodium sec-butoxide, since there is no hydroxylic type compound to solvolyze the carbonium ion. The results of the eliminations in mesitylene, reported in Table 19, page 113, should reflect the stereospecific requirement of the bimolecular elimination. The amount of 1,2-dimethylcyclopentene formed is less than that observed in the eliminations in the ethanolic solutions.

Since the 1,2-dimethylcyclopentene can be formed by *trans* elimination only from *trans*-1,2-dimethylcyclopentyl bromide, at least 70% of the product from the reaction of 1,2-dimethylcyclopentene with hydrogen bromide at 0° C in pentane was the *trans*-bromide. At 25° C, about 84% of the product was *trans*-bromide, and at -78° C at least 82% of the product was the *trans*-bromide. Freezing an excess of hydrogen bromide onto the pentane solution with liquid nitrogen, then rapidly warming the flask to -78° C, produced 92% of the *trans*-bromide. In acetic acid at 25° C, a product containing of about 60% of the trans-bromide was indicated. The contact time for all of these reactions was one hour. When the contact time was shortened, at 0° C in pentane, different amounts of the trans-bromide were formed. Eighty-nine percent of the trans-bromide is indicated in the thirty minute reaction, 83% in the fifteen minute reaction and 78% in the five minute reaction.

If the amount of trans-1,2-dimethylcyclopentyl bromide found is accurately indicated by the base catalyzed elimination, several tentative conclusions may be made. First the addition of hydrogen bromide to 1,2-dimethylcyclopentene shows a trans spereospecificity but this stereospecificity is not as complete as the addition of hydrogen bromide to 1,2-dimethylcyclohexene was reported to be[177]. Second, the amount of trans-1,2-dimethylcyclopentyl bromide formed in the addition reaction increases as the temperature decreases, that is, the stereospecificity appears to increase with a decrease in temperature. Lastly, varying the contact time changes the amount of trans-bromide produced but this effect does not appear to follow a regular sequence. Rather a maximum amount of trans-bromide appeared to be formed during a thirty minute contact time, with lesser amounts of trans-bromide indicated for times both longer and shorter than thirty minutes.

There exists the possibility, however, that the elimination products observed are not a true indication of the actual reaction products. The *trans* preference of the elimination itself is not questioned. However, consideration of the products formed from the reaction of *cis*- and *trans*-1,2-dimethylcyclopentanol with hydrogen bromide, as indicated by olefin produced in the elimination, does cause considerable doubt about whether the bromides present in pentane solution, when it is placed in the base for the elimination reaction, are actually those initially formed by the addition and not the products of some post-addition isomerization. Comparison of the results of eliminations on bromides prepared from three different substrates, 1,2-dimethylcyclopentene, and both *cis*- and *trans*-1,2-dimethylcyclopentanol, is given in Table 25. The bromide products from all three substrates, when prepared in pentane at 0° C during a contact time of one hour, all eliminate to give nearly identical percentages of olefins. Additional confirmation of this observation may be had by examining the nuclear magnetic resonance spectra of the bromides produced by the reaction of hydrogen bromide with each of the three substrates (Plates 1, 2 and 3). The nuclear magnetic resonance spectra for the bromide products are essentially identical while those of the isomeric alcohols (Plates 4 and 5) do show differences. If the bromides had different composition, this difference should have been reflected in the nuclear magnetic resonance spectra. Since no

Table 25. Olefin composition from eliminations on 1,2-dimethylcyclopentyl bromides

Initial substrate	Medium	Temp. °C	Time min.	Eliminating agent	% 1,2-Olefin[a]	% 2,3-Olefin[b]	% Exo-olefin[c]
1,2-olefin[a]	pentane	0	60	sodium hydroxide in ethanol	91	9	0
cis-alcohol[d]	pentane	0	60	sodium hydroxide in ethanol	92	8	0
trans-alcohol[e]	pentane	0	60	sodium hydroxide in ethanol	90	10	0
1,2-olefin	pentane	0	60	sodium sec-butoxide in mesitylene	70	30	0
cis-alcohol	pentane	0	60	sodium sec-butoxide in mesitylene	69	31	0
trans-alcohol	pentane	0	60	sodium sec-butoxide in mesitylene	71	29	0

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[a] 1,2-Dimethylcyclopentene.

[b] 2,3-Dimethylcyclopentene.

[c] 2-Methylmethylenecyclopentane.

[d] *Cis*-1,2-dimethylcyclopentanol.

[e] *Trans*-1,2-dimethylcyclopentanol.

Table 25. (Continued)

Initial substrate	Medium	Temp. °C	Time min.	Eliminating agent	% 1,2-Olefin[a]	% 2,3-Olefin[b]	% Exo-olefin[c]
1,2-olefin	pentane	-78	60	sodium sec-butoxide in mesitylene	82	19	0
cis-alcohol	pentane	-78	60	sodium sec-butoxide in mesitylene	77	23	0
trans-alcohol	pentane	-78	60	sodium sec-butoxide in mesitylene	82	18	0
1,2-olefin	pentane	-78[f]	60	sodium sec-butoxide in mesitylene	92	8	0
cis-alcohol	pentane	-78[f]	60	sodium sec-butoxide in mesitylene	78	22	0
trans-alcohol	pentane	-78[f]	60	sodium sec-butoxide in mesitylene	80	20	0
1,2-olefin	pentane	0	5	sodium sec-butoxide in mesitylene	78	22	0
cis-alcohol	pentane	0	5	sodium sec-butoxide in mesitylene	79	21	0
trans-alcohol	pentane	0	5	sodium sec-butoxide in mesitylene	84	16	0

[f] Sample plus hydrogen bromide frozen in liquid nitrogen for several minutes, then warmed to -78° C.

differences are observed, the bromides were quite probably identical.

A little variation is observed in the reaction carried out at -78° C and a somewhat greater variation is seen when the initial hydrogen bromide concentration was in great excess, as is the case when liquid nitrogen was used to freeze the hydrogen bromide onto the pentane solution before the reaction was carried out at -78° C. Shortening the reaction time to five minutes also produced a slight variation.

This near identity of the olefinic products, even in pentane solution, leads to the conclusion that some sort of an equilibration may have been taking place after the bromide products were initially formed. To demonstrate that this may be so, it is necessary to consider the substitution reaction in which the bromide was formed from the alcohol. In polar solvents, the formation of an intermediate carbonium ion is favored. This destroys the assymmetry of the original alcohol and results in a product demonstrating extensive racemization[178]. In non-polar solvents the reaction usually occurring is one in which the configuration of the original alcohol has been inverted[178]. Several instances wherein a retension of configuration has been observed when hydrogen bromide was reacted with an alcohol have been reported[189-193]. In most of these cases the possibility of neighboring group interactions was considered sufficient to explain the lack of inversion. Of particular interest to the present case, however, are the results of Nevitt and Hammond[189,190]. In reactions of both cis- and trans-1,2-dimethylcyclohexanols with hydrogen bromide in acetic acid a small but detectable amount of retention of configuration was observed. In pentane, considerably more retention of configuration was observed. For example, the reaction of cis-1,2-dimethylcyclohexanol with hydrogen bromide in pentane at -78° C gave a product containing nearly 70% cis-bromide. At 0° C in the same medium, 30% of the product had preserved the configuration. Thus in a system not too different from the present case, very different ratios of the bromide products were obtained by reactions of the isomeric alcohols.

If this retention were observed also with the 1,2-dimethylcyclopentyl compounds, then cis-1,2-dimethylcyclo-

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[189] T. D. Nevitt and G. S. Hammond, J. Am. Chem. Soc., 76, 4124 (1954).

[190] T. D. Nevitt, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa, p. 104 (1953).

[191] S. Winstein and H. J. Lucas, J. Am. Chem. Soc., 61, 1576 (1939).

[192] D. Y. Curtin and D. B. Kellom, ibid., 75, 6011 (1953).

[193] P. A. Levine and A. Rothen, J. Biol. Chem., 127, 237 (1939).

pentanol should produce a compound relatively richer in cis-bromide than would be produced by the trans-alcohol. The elimination analyses do not indicate any such differences, instead indicating that the composition of the bromides produced from the two isomeric alcohols was nearly identical at the time of their analysis. The olefinic addition product is also of this composition.

The readiness with which the bromides decompose into hydrogen bromide and an olefin when allowed to stand after the reaction has been terminated by the removal of the excess hydrogen bromide from the reaction medium (pentane) may indicate that a similar deterioration may be occurring even during the one hour contact time. Thus, if most of the product were formed early in the allowed contact time, a secondary isomerization process, perhaps involving different olefins, for example 2,3-dimethylcyclopentene, or even the formation of a carbonium ion would allow apparent equilibration of products to take place even in the non-polar medium.

Such an occurrence could invalidate some of the conclusions previously drawn. Thus, the observation of a trans specificity to the addition reaction, as indicated by the formation of about 70% of the trans-1,2-dimethylcyclopentyl bromide from the reaction of 1,2-dimethylcyclopentene with hydrogen bromide in pentane at 0° C, may be only a delusion, with the actual composition of the addition product showing far less stereospecificity. The observed increase in *trans*-bromide formation in the reactions at -78° C, with the sixty minute reaction time, and at 0° C with a five minute reaction time, may indicate, however, more *trans*-bromide, rather than less, is present in the initial product of the reaction. The fact that in the five minute reaction the amount of *trans*-bromide prepared from *trans*-1,2-dimethylcyclopentanol is greater than that prepared from either *cis*-alcohol or from the olefin supports the proposal that less of this post-addition isomerization can have taken place in the shorter contact time. Thus, although it is conceivable that all the *trans*-bromide observed was the result of some sort of isomerization, it is not too likely, and a preference for *trans* addition is probably indicated.

The greater amounts of *trans*-bromide which formed at -78° C, both with and without an excess of hydrogen bromide, are probably due to the fact that at the lower temperature, the rate of the isomerization has been considerably diminished. Thus, if the initial product were mainly *trans*, the product composition after the sixty minute contact time should contain a greater amount of *trans*-bromide than is observed for the reaction at 0° C. The maximum in the content of *trans*-bromide which was observed at the thirty minute contact time cannot be readily explained in the light of the present data. Further work on this point is indicated.

The solvolytic work on the 1,2-dimethylcyclohexyl bromides showed that both the *cis*- and *trans*-bromides had essentially the same solvolysis rate constant, 4.5×10^{4} min^{-1}, in 98% ethanol. The 1-methylcyclohexyl compound solvolyzed very slightly slower. Since Brown *et al.*[194] have predicted that the rates of the solvolysis of cyclopentyl compounds would be considerably faster than the rates of the corresponding cyclohexyl compounds, a fact fairly well verified in other work[195-197], it was of interest to compare the solvolysis rates of the dimethylcycloalkyl bromides. Although experimental limitations may be a cause for considerable lack of precision in the solvolysis of the 1,2-dimethylcyclopentyl bromides, it was observed that the 1,2-dimethylcyclopentyl bromide solvolyzed at a considerably faster rate than did the corresponding dimethylcyclohexyl bromides. The average rate constant for all the 1,2-dimethylcyclopentyl bromide solvolyses in 100% ethanol is 5.7×10^{-2} min^{-1}. The values for the dimethylcyclohexyl bromides are given for 98% ethanol. Using the quantitative correlation of solvolysis rates of Grunwald

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[194] H. C. Brown, R. S. Fletcher and R. B. Johannsen, *J. Am. Chem. Soc.*, *73*, 212 (1951).

[195] H. C. Brown and M. Borkowski, *ibid.*, *74*, 1894 (1952).

[196] H. C. Brown and G. Ham, *ibid.*, *78*, 2735 (1956).

[197] M. Mousseron, J. Julien and H. Bodot, *Compt. rend.*, *244*, 87 (1957).

and Winstein[198] an estimate of 2.5×10^{-4} min^{-1} for the solvolysis of the 1,2-dimethylcyclohexyl bromides in 100% ethanol can be made. The dimethylcyclopentyl bromides then, solvolyze at a rate two hundred times faster than do the cyclohexyl bromides. This value is in reasonable agreement with the value observed for the relative rates of solvolyses of 1-methylcycloalkyl chlorides[194], and fits well into the Brown interpretation of I-strain effects in cycloalkyl compounds. However, the difference between the solvolysis rate constants for 1-methylcyclopentyl bromide (3.3×10^{-2}) and for 1,2-dimethylcyclopentyl bromide (5.7×10^{-2}) is much smaller than would be predicted solely on the basis of Brown's hypothesis. In this hypothesis, the relative rapidity of solvolysis for cyclopentyl compounds is based on the probability that the cyclopentyl compound will release ring strain by forming a carbonium ion while the cyclohexyl compound will increase its ring strain in so doing. The strain in the cyclopentane ring results from the eclipsed configurations of all the ring hydrogens. The carbonium ion transition state has relieved two of these H-H eclipsings. Replacing a hydrogen with a methyl group should, therefore, increase considerably the strain due to eclipsing and thus contribute to a manifold increase in the solvolysis rate, since the carbonium ion would

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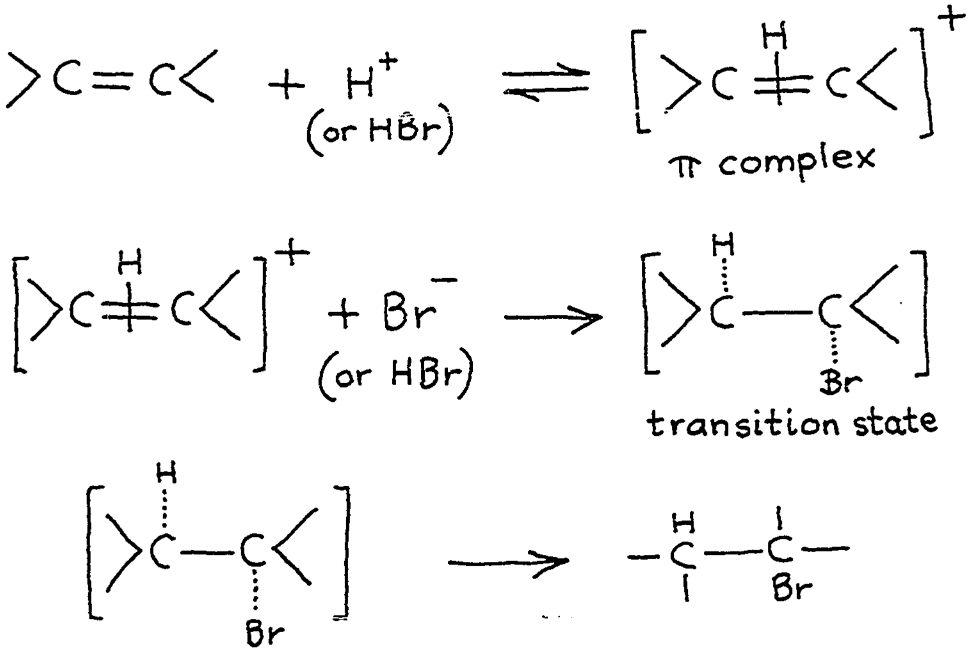
[198] E. Grunwald and S. Winstein, _J. Am. Chem. Soc._, _70_, 846 (1948).

relieve this increased strain. Such a marked increase in rate is not observed. Thus, it may be that steric factors such as eclipsing are but part of the reason for the preference of the five-membered ring for an unsaturated situation, as compared to the six-membered ring.

The solvolysis rate constants obtained for 1,2-dimethylcyclopentyl bromides prepared from the different substrates showed some small but persistent differences which may indicate the presence of something in addition to the two diasteriomeric bromides. For instance, the average rate constant for bromide prepared from 1,2-dimethylcyclopentene was smaller than constants for bromide prepared from either cis- or trans-1,2-dimethylcyclopentanol. Such differences were not observed with the dimethylcyclohexyl bromides. Further indication that something else may have been in the pentane solution was the observation that the rate constants for the 1,2-dimethylcyclopentyl bromides decreased markedly as the solvolysis neared completion. However, the three solvolyses which were run on samples of the bromide in pentane which had not been extracted prior to the solvolysis shower significantly less decrease than did the others.

Since the conclusions drawn from this work are, at best, somewhat speculative, no substantial contribution can be made toward the elucidation of the mechanism of the addition reaction. The results are not contrary to the mechanism of

Hammond and Nevitt[177], which is illustrated below. This mechanism was proposed by these authors to account for the



trans stereospecificity observed in the addition of hydrogen bromide to 1,2-dimethylcyclohexene. Since the molecularity of the hydrogen bromide in a non-polar solvent is not specified by this mechanism, it can easily be adapted to account for the fourth order kinetics observed by Mayo and his co-workers[199,200] by assuming a chain of hydrogen bromide as either the protonating species or as providing the bromide. Since this mechanism was proposed, the use of a π-complex,

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[199] F. R. Mayo and J. J. Katz, *J. Am. Chem. Soc.*, *69*, 1339 (1947).

[200] F. R. Mayo and M. G. Savoy, *ibid.*, *69*, 1348 (1947).

such as the one indicated here, has been more widespread. A discussion of some of its newer applications appears earlier in this thesis. It is generally felt[201,202] that if the π-complex has not yet been completely transformed into a carbonium ion, the stereospecificity for the reaction will be preserved.

Since the olefinic product distributions resulting from the base catalyzed eliminations on the isomeric 1,2-dimethylcyclohexyl bromides were estimated on the basis of an infrared analytic technique which was shown, in the discussion of the acetate pyrolysis work, to be in question, several preparations of the 1,2-dimethylcyclohexyl bromide were made and the eliminations carried out. The results are given in Table 22, page 119. Nevitt[203] reported that reactions with 1,2-dimethylcyclohexene at 0° C and at -78° C gave pure trans bromide which eliminated to give pure 1,2-dimethylcyclohexene while reactions with cis-1,2-dimethylcyclohexanol at 0° C and at -78° C contained 22% and 60% of cis-bromide respectively, which eliminated to give, in the first case, 87% of the 1,2-olefin and 13% of the exocyclic olefin, and in the second case, 50%

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[201] S. Winstein and N. J. Holness, ibid., 77, 5562 (1955).

[202] J. Hine, "Physical Organic Chemistry", McGraw Hill Book Co., N. Y., p. 217 (1956).

[203] T. D. Nevitt, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa, pp. 55, 75, 79 (1953).

of each of these olefins. Although no estimate was made of the bromide concentration in the reaction products in the present work, it is presumed that they could not be far different from those observed by Nevitt. The olefinic composition of the elimination products, then, is seen to be at variance with the results reported by Nevitt. Gas chromatographic analysis showed that 2,3-dimethylcyclohexene was present in all of the elimination products and yet this had gone unnoticed in the infrared analysis. The amount of 2-methylmethylenecyclohexane present is much smaller than had previously been estimated. These results give further support to the idea that the infrared spectral method for determining proportions of olefinic product is not completely reliable for these compounds.

In summary, it may be said that the high reactivity of the tertiary 1,2-dimethylcyclopentyl bromides makes impossible a rigorous assertion that the addition of hydrogen bromide to 1,2-dimethylcyclopentene occurred by a stereospecific <u>trans</u> addition, although there are indications that this is the case.

Suggestions for Future Work

Since the addition of hydrogen bromide to 1,2-dimethylcyclopentene did not unambiguously answer the query posed by the alternate conformations of trans-1,2-dimethylcyclohexyl bromide, some additional work on the stereochemistry of hydrogen halide additions is necessary.

To help clarify the present problem, a more extensive investigation of the time and temperature dependence of the composition of the 1,2-dimethylcyclopentyl bromides should be made. Also, the possibility of the post-addition isomerization could be investigated by the addition of hydrogen bromide to either 2,3-dimethylcyclopentene or 2-methylmethylenecyclopentane, since the bromide product, except for its cis-trans isomer ratio, should be identical with that of the symmetrical olefin. Post-addition isomerization should result in the same products as obtained in the present work, while if such isomerization did not occur, it could reasonably be expected that a different ratio might be obtained.

The high reactivity of the tertiary bromides made work with them quite difficult. It is possible that the corresponding chlorides would be more stable and thus more amenable to direct product analysis. Thus, a study of the addition of hydrogen chloride to both 1,2-dimethylcyclopentene and 1,2-dimethylcyclohexene might elucidate further the stereospecificity and mechanism of the reaction.

SUMMARY

The structures assigned to the isomeric cis- and trans-1,2-dimethylcyclopentanols were confirmed by the pyrolysis of their acetates. Further acetate pyrolyses were carried out which indicated errors, probably due to the lack of an adequate analytical tool, in the acetate pyrolysis results previously reported in these and other laboratories. The observed preference for the formation of endocyclic olefins with both five- and six-membered methyl-substituted alicyclic acetates was interpreted on the basis of a cyclic, six-membered transition state for the pyrolysis in which there was considerable latitude in the degree of coplanarity required of the transition state.

Addition of hydrogen bromide to 1,2-dimethylcyclopentene and 1-methylcyclopentene and the reaction of hydrogen bromide with the isomeric cis- and trans-1,2-dimethylcyclopentanols produced bromides which were quite unstable. The compositions of the bromides were estimated on the basis of the olefins formed in base catalyzed elimination reactions. Some sort of equilibration mechanism is probably operating even during the course of the addition reaction itself since a near identity of the product bromides from the three substrates was found. Thus, it is impossible to rigorously establish the stereospecificity of the addition reaction, although it is probable

that it was of a trans nature. Some support was given the mechanism for the addition that had previously been proposed.

In line with the I-strain hypothesis, the solvolysis rates for the mixed 1,2-dimethylcyclopentyl bromides were found to be approximately two hundred times greater than the rates for the solvolysis of the corresponding dimethylcyclohexyl compounds. The increase in rate for the solvolyses of 1,2-dimethylcyclopentyl bromide over the 1-methylcyclopentyl bromide was not as great as was expected, however.

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