

AN ABSTRACT OF THE THESIS OF

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Title ADDITION OF HYDROGEN BROMIDE TO ^{unsymmetrical olefin} ~~3-METHYLCYCLOHEXENE~~.

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In this investigation the addition of hydrogen bromide to 3-methylcyclohexene has been studied in order to see if the theory of hyperconjugation could be extended to include olefins of this type. Since the olefin has an equal number of hydrogens on both carbons carrying the double bond, a mixture of bromides was expected in the addition product. The bromides expected were cis-2- or trans-2-bromomethylcyclohexane or a mixture of the isomers and cis-3- or trans-3-bromomethylcyclohexane or a mixture of those isomers.

An infrared method of analyzing the addition product was used. To use this method it was necessary to make up known mixtures of the compounds expected in the addition product. In order to prepare some of the isomeric bromides, trans-2- and trans-3-methylcyclohexanol were prepared. Then, because no good methods could be found in the literature for the conversion of isomeric alcohols to isomeric bromides, the alcohols were not used. Instead, the known mixtures for the infrared work were prepared from 2-bromo- and 3-bromo-methylcyclohexanes, both containing unknown amounts of the cis-trans isomers.

The 3-methylcyclohexene used in the hydrogen bromide addition was prepared from 3-bromomethylcyclohexene and methylmagnesium iodide. The addition of hydrogen bromide was conducted at 0°C and at room temperature using glacial acetic acid as a solvent. The addition product was obtained in a very low yield and was very difficult to isolate. The product isolated was found to be about 70 per cent 3-bromomethylcyclohexane. Because of the low yield and isolation difficulties, no conclusions could be drawn regarding hyperconjugation.

ADDITION OF HYDROGEN BROMIDE TO
UNSYMMETRICAL OLEFINS

by

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ADDITION OF HYDROGEN BROMIDE TO UNSYMMETRICAL OLEFINS

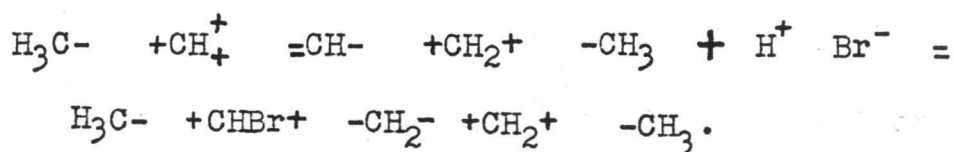
INTRODUCTION

Markownikoff's rule has been found to predict accurately the addition of hydrogen halides to olefins in which the carbon atoms at the double bond carry an unequal number of hydrogens. But this rule cannot be applied to those olefins in which the carbon atoms in the ethylenic linkage carry an equal number of hydrogen atoms. Since 2-pentene is the simplest unsymmetrical olefin of this type, much attention has been directed toward it in the attempt to formulate a supplementary rule to explain its addition reactions.

In 1863 Wurtz (38) reported the preparation of 2-pentene and its reaction with hydrogen bromide, but Wagner and Saytzeff (37, p.325) were the first workers to attempt to formulate a rule to explain the addition. They prepared 2-pentene by dehydrohalogenation of 3-iodopentane and concluded that the product obtained upon addition of hydrogen iodide was 2-iodopentane. In view of these results, they formulated the rule that the halogen attaches itself to the carbon atom bearing the shorter chain.

Later, Cuy (8, p.511), using the work of Wagner and Saytzeff as experimental proof, advanced the theory of

alternately polarized carbon atoms and predicted that the reaction between hydrogen bromide and 2-pentene would yield predominately 2-bromopentane since the reaction would be



Lucas and Jameson (23, p.2476), upon studying Wurtz's work, became convinced that he did not have pure 2-pentene but a mixture of pentenes obtainable from a mixture of iso-amyl and active amyl alcohols.

Since Lewis (21, p.781) had shown, by comparison of the relative ionization constants of organic acids and bases¹, that the effect of the alkyl substituent on the acid or base could be explained on the basis of electronic displacement, and that the effect of the displacement of electrons on one end of the chain could extend throughout the chain, Lucas and Jameson applied this theory to the problem. They found that the addition of hydrogen halides to propylene, to acrylic acid and to dimethyl allene could be explained just as satisfactorily with the theory of

¹K_a acetic acid 1.86×10^{-5} , K_a propionic acid 1.45×10^{-5} ,
K_b methylamine 5.0×10^{-4} , ethylamine 5.6×10^{-4} ,
K_b dimethylamine 7.4×10^{-4} , K_b diethylamine 1.3×10^{-3}

electronic displacement as with the theory of alternately polarized carbon atoms; the addition of hydrogen bromide to diethyl allene and the subsequent rearrangement to 1-bromobutane and 2-bromobutane could be better explained by electronic displacement.

Since the relative ionization constants of organic acids and bases show that methyl exerts a stronger pull on electrons than does ethyl, it would follow that in 2-pentene, where a methyl is attached to one end of a double bond and an ethyl to the other, the electrons of the double bond would be closer to the methyl. Consequently, Lucas predicted that the predominant product in the reaction between hydrogen bromide and 2-pentene would be 3-bromopentane.

The addition reaction would be expected to yield a mixture of 2-bromopentane and 3-bromopentane; this mixture could not be separated by chemical or physical means since the boiling point of the 3-bromo-compound is 118.0-118.5°C and that of the 2-bromo- 117.5-118.5°C. Searching for a method to analyze the mixture, Lucas, Simpson and Carter (26, p.1468) found a slight difference in the refractive indices of the two compounds (2-bromo- 1.4416, 3-bromo- 1.4443) and then showed that the refractive index of a mixture of the two compounds was a linear function of the composition.

Lucas and Moyse (24, pp.1460-1) prepared the olefin by the action of alcoholic potash on 3-bromopentane and carried out the addition of hydrogen bromide using glacial acetic acid as a solvent. The refractive index of the product indicated 78 per cent 3-bromopentane and 22 per cent 2-bromopentane. Lucas considered the theory of electronic displacement confirmed by these results.

Kharasch (19, p.408), having determined the electronegativity of certain organic radicals (but in a different manner than Lewis), agreed with Lucas that the methyl group was more electronegative (or had a stronger pull on electrons) than the ethyl group. He disagreed, however, with Lucas' interpretation of the resultant polarity of the bonds in 2-pentene. Kharasch said that since methyl was more electronegative than ethyl, the carbon atom in the ethylenic linkage carrying the methyl group would be less electronegative than the one carrying the ethyl. Consequently the electron pair should be displaced toward the carbon atom to which the ethyl group is attached and when hydrogen bromide is added, the product should be predominately 2-bromopentane.

As a supplement to his theory of the partial polarity of the double bond, Kharasch (17, pp.589-94) postulated the existence of electronic isomers in the case of ethylenic linkages to which radicals of differing

electronegativity were attached. One electromer would have the extra electron pair displaced toward the carbon atom carrying the methyl group and in the other the electron pair would be displaced toward the carbon atom to which the ethyl group was attached; the latter isomer would be the more stable.

In order to confirm this theory, Kharasch prepared 2-pentene from 3-bromopentane, believing that this would give the less stable electromer, since the carbon atom to which the bromine was attached would have its electronegativity decreased in the dehydrohalogenation. The extra pair of electrons would then be displaced toward the methyl group and the addition of hydrogen bromide would yield 2-bromopentane.

Kharasch obtained results which were identical to those of Lucas when the addition was carried out using glacial acetic acid as a solvent, but addition to the olefin in a non-polar solvent such as carbon tetrachloride or petroleum ether, or in the absence of a solvent yielded a product which was 97-100 per cent 3-bromopentane.

Upon heating 2-pentene with xylene in a sealed tube at 90-100°C for varying lengths of time, to transform the olefin into its electromer, he found that the addition product varied from 63 per cent 3-bromo- and 37 per cent

2-bromopentane to 16 per cent 3-bromo- and 84 per cent 2-bromopentane depending upon the length of time heated. The composition of the addition product was determined from its refractive index.

This work indicated to Kharasch that the two electromers which he believed theoretically possible did exist. He requested Sherrill and her associates (32, 33) to obtain additional information. These investigators prepared 2-pentene from 3-pentanol and 3-bromopentane. Realizing the possible existence of cis-trans isomers in the pentene, they endeavored to separate them. Using a previously published technique (35, p.211), they fractionated an azeotropic mixture of the pentene with methanol and obtained what appeared to be a reasonably pure isomer.

The reaction between this pentene and hydrogen bromide in a non-polar solvent gave 98-99 per cent 3-bromopentane; addition in glacial acetic acid produced a product which was 78 per cent 3-bromopentane and 22 per cent 2-bromopentane. Irradiating the 2-pentene with sunlight or ultraviolet light produced an olefin which they believed to be an electromer because the addition product was 15 per cent 3-bromopentane and 85 per cent 2-bromopentane (no solvent).

2-pentene was also made from 2-bromopentane and 2-pentanol. Fractionation of constant-boiling mixtures

of the olefin with alcohol permitted an almost complete separation of 1-pentene in the lower boiling fractions. The 2-pentene produced by this method possessed slightly different physical properties than the pentene derived from 3-bromopentane and 3-pentanol, and added hydrogen bromide in the absence of a solvent to form a bromide which was 93-95 per cent 2-bromopentane. In glacial acetic acid the product was 85 per cent 2-bromopentane. It was also observed that the action of ultraviolet light on the 2-pentene from 3-bromopentane was to alter its physical properties in the direction of those of the olefin derived from 2-bromopentane. This latter olefin was unaffected by ultraviolet light.

While the differences in physical properties of the pentenes derived from different sources were such as might be expected in the case of cis-trans isomers, it was concluded that the isomers were electronic instead of geometrical because the expected product was obtained in each case. The fact that the 2-pentene from 3-bromopentane was transformed into a more stable form was also in accord with the theory. In addition, it was concluded from spectroscopic studies (7), that the isomers were electronic instead of geometrical.

Noting that previous investigators had made use of the small difference in the refractive indices of 3-bromo-

and 2-bromopentane to determine the composition of the addition product, and realizing the limitations of such a method since a small amount of an unsuspected substance could lead to very erroneous conclusions, Lauer and Stodola (22) deemed it advisable to reinvestigate the problem using a different analytical method. They devised a method based upon the fact that the bromides could be converted into solid anilides by treating them with magnesium and phenyl isocyanate.

A melting point-composition curve was constructed by mixing the pure anilides. The mixture of bromides obtained in the addition was converted into an anilide mixture, the melting point of which gave the composition of the mixture.

The olefin was prepared from 3-bromopentane in order to duplicate the work of Sherrill and was also prepared from the stable form of α -ethylcrotonic acid. The latter source being used because it differed from those used in preparing the electromeric pentenes, and would allow a demonstration of the fact that the addition products were the same regardless of the source of the pentene as long as it was pure 2-pentene. This method of preparation also was one which would yield a trans isomer or cis-trans mixture very rich in the trans isomer.

Addition of hydrogen bromide to both pentenes in

glacial acetic acid and in no solvent produced identical products. The melting points of the anilide mixtures indicated near equivalent amounts of 3-bromopentene and 2-bromopentane. Consequently Lauer and Stodola considered Kharasch's theory of electronic isomerism refuted.

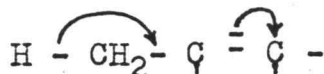
Lucas and Prater (25) synthesized the cis- and trans-2-pentenes from cis- and trans- α -methyl- β -ethylacrylic acids and found the two isomers had slightly different refractive indices; the trans isomer checked very closely with that prepared by Lauer and Stodola. By refractive indices Lucas and Prater found that the two isomers did not add hydrogen bromide to give products of identical composition. An assertion was also made that the 2-pentene prepared by previous workers from 2-bromopentane was contaminated with 1-pentene.

Kharasch, Walling and Mayo (20), being unsatisfied with the proof that Lucas and Prater had offered that the cis and trans isomers gave different products, decided to study the problem using both the melting point method and the refractive index method to analyze the addition product. In their comprehensive investigation, they prepared a trans-pentene, whose properties agreed with that prepared by other workers (22, p.1216), from 2-bromo- and 3-bromopentane. The cis isomer was prepared by partial hydrogenation of 2-pentyne. The addition to both isomers

was carried out in glacial acetic acid, in the absence of solvent and in the presence of peroxides. The melting point analysis indicated that the composition of the product was the same in each case. The results checked those of Lauer and Stodola. The refractive indices of the products indicated the proportion of 3-bromopentane to be too high by 2-28 per cent.

Similar results were obtained with the addition of hydrogen chloride. Consequently Kharasch agreed that his theory of electromers could be set aside.

In 1935 Baker and Nathan (4, p.1845) advanced the theory of hyperconjugation (9) in order to explain the abnormal behavior of certain series of alkyl substituted compounds. They postulated that the electron pair forming the carbonhydrogen bond of an alkyl group which is attached to the carbon atom of an unsaturated linkage, or to an electronically deficient atom, is less localized than in a similar carbon-carbon bond. Consequently electron release could take place by a mechanism very similar to a tautomeric effect.

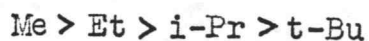


The effect operates in the same direction and in addition to the inductive effect. The order of increase of the two effects is the reverse, however. The inductive

effect increases in the order



while if only hydrogens alpha to the ethylenic linkage contribute to the hyperconjugative effect, the order would be:

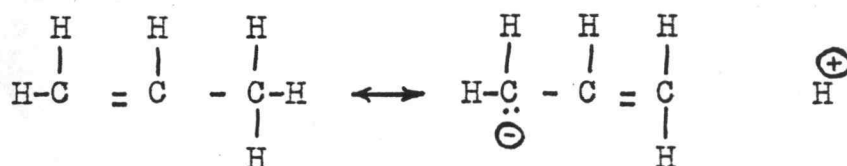


Evidence for the existence of hyperconjugation has been obtained through physical and organic chemical approaches to the problem. The fact that electron diffraction studies (29, pp.1230-1;30) indicate that the carbon-carbon single bonds in methyl and dimethyl acetylenes are shorter than normal bonds and that there is a large increase in the dipole moment of methyl chloroform as compared with chloroform (14, p.2833; 15, p.96) constitute two of the many examples of physical chemical proof.

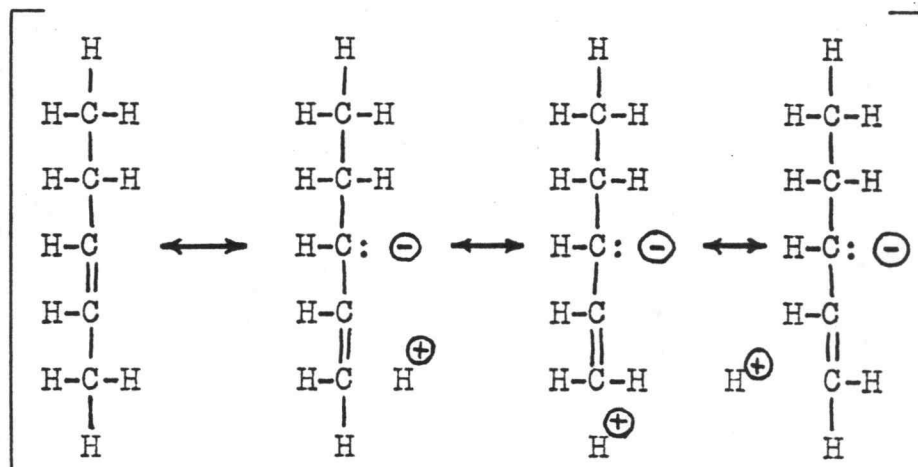
One example of organic chemical proof may be found in the relative rates of bromination of monoalkylbenzenes (10, p.288). The rate of bromination varies with the number of hydrogen atoms on the carbon atom alpha to the benzene ring; hence toluene which has three α -hydrogens brominates faster than ethylbenzene which has only two. Ethylbenzene in turn reacts more rapidly than isopropylbenzene which has only one α -hydrogen and t-butylbenzene

possessing no α -hydrogens is less reactive than the latter compound.

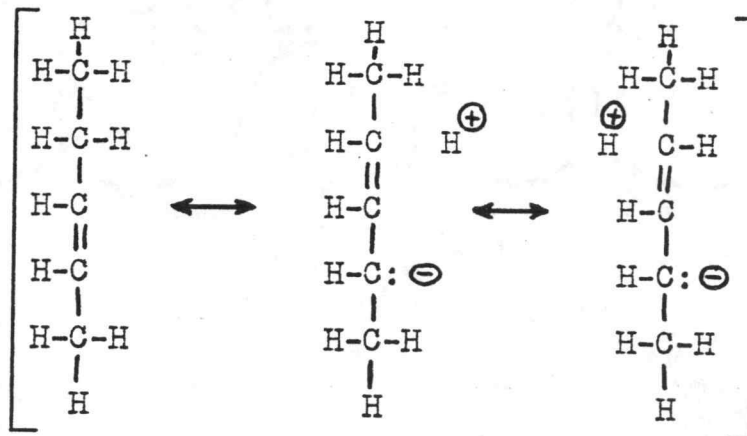
Applying the principle to olefins, Alexander (2, p.32) shows how hyperconjugation gives new meaning to Markownikoff's rule when the resonance forms of propylene are considered.



This indicates that in the normal addition of hydrogen bromide, the product will be 2-bromopropane. He extends the application of the theory to predict the addition of hydrogen chloride to 2-pentene. Hyperconjugation would predict a predominance of 2-chloropentane since it is possible to write three hyperconjugative structures involving the three α -hydrogens in the methyl group but only two forms



involving the two α -hydrogens in the ethyl radical.



EXPERIMENTAL

The review of earlier work reported in the introduction shows that experimental evidence does not indicate that 2-chloropentane is the predominant product when hydrogen chloride is added to 2-pentene nor is 3-bromopentane the predominant product when hydrogen bromide is added to the olefin. But, because there is considerable experimental evidence for hyperconjugation in other types of compounds, it appeared advisable to study the addition of hydrogen bromide to some other unsymmetrical olefin to see whether or not the principle can be applied to this type of compound.

In 2-pentene, the hyperconjugative effect of a methyl group was compared with that of an ethyl group. Another interesting comparison would be that of an

isopropyl group with an ethyl group, i.e., 2-methyl-hexene-3 or 3-methylcyclohexene. Use of the former compound would necessitate the preparation of pure cis and trans isomers.

Consequently, it was decided to carry out the study using 3-methylcyclohexene because this compound has no cis-trans isomers. A serious complication arises, however, when hydrogen bromide is added to 3-methylcyclohexene because there are four possible products, i.e., cis-2-bromo-, trans-2-bromo-, cis-3-bromo- and trans-3-bromomethylcyclohexane. The methods used by previous workers to determine the composition of the addition product would be of very little use because of the complexity of the reaction product.

After surveying existing methods, it was concluded that an infrared spectroscopic method of analysis would be the most useful. Using this method, it was proposed to obtain the spectrum of each compound that was likely to be formed in the addition. Characteristic absorption bands would be selected from each compound and known mixtures of the compounds prepared. It would then be possible to correlate the height of the characteristic absorption bands of each compound with the concentration of that compound in the mixture. With this information, it should be possible to establish the identity and

concentration of each compound in the addition product from the spectrum of the addition product.

Because of the limits of resolution of the infrared spectrophotometer, it was not known whether the spectrum of cis-trans-2-bromomethylcyclohexane would differ from that of cis-2-bromo- or trans-2-bromomethylcyclohexane (similarly for the cis-trans-3-bromo- and cis-3-bromo- or trans-3-bromomethylcyclohexane). The best approach to the problem appeared to be to make one isomeric bromide of the 2- and the 3-bromo-compound and to compare the spectrum of that isomer with the spectrum of each cis-trans mixture.

The most convenient starting materials for preparation of these isomeric bromides are the isomeric alcohols of 2-methylcyclohexanol and 3-methylcyclohexanol.

Preparation of trans-3-methylcyclohexanol

Gough, Hunter and Kenyon (12, p.2062) have reported the preparation of trans-3-methylcyclohexanol by fractional crystallization of the p-nitrobenzoate of 3-methylcyclohexanol from methanol. They obtained a trans ester which melted at 65°C and a cis ester melting at 58°C. An attempt was made to repeat this work.

Eastman, practical grade, 3-methylcyclohexanol was carefully fractionated on a packed column. The fraction

boiling 61-63 °C at 8 mm. was collected.

$$n_D^{23} \quad 1.4852$$

p-Nitrobenzoate of 3-methylcyclohexanol: 11.4 grams (0.1 moles) of 3-methylcyclohexanol were added to a solution of 18.5 grams (0.1 moles) of p-nitrobenzoyl chloride in dry benzene. Contrary to the report of Gough, Hunter and Kenyon, no visible reaction occurred. After standing overnight the benzene solution was successively washed with water, dilute hydrochloric acid, sodium carbonate solution, and then water. The benzene was steam distilled and a brown solid was left behind in the pot. This material had a melting point of 240°C (melting point p-nitrobenzoic acid 242°C).

When this procedure was repeated using a benzene solution of 77 grams (0.415 moles) p-nitrobenzoyl chloride and 47.5 grams (0.417 moles) 3-methylcyclohexanol in the presence of 39.5 grams (0.50 moles) of anhydrous pyridine, a vigorous reaction occurred. After the reaction mixture had set overnight, the white precipitate (pyridine hydrochloride) was filtered off. Steam distillation of the benzene left a yellow, viscous oil. The oil was dissolved in warm methanol and the solution cooled. Tiny globules of oil precipitated. Finally all of the dissolved material precipitated as an oil. The oil was put into

solution in excess methanol and the solution allowed to evaporate very slowly in the cold; an oil precipitated again.

The oil was distilled under reduced pressure (150-156 C° at approximately 1 mm.) to remove any unreacted 3-methylcyclohexanol. The previously described techniques were repeated on the distillate in an attempt to obtain crystalline material. Scratching the side of a beaker containing a saturated solution of the ester or cooling a saturated solution in a dessicator (to prevent evaporation) also did not produce a crystalline material. Petroleum ether was tried as a solvent but the results in each case were the same; an oil precipitated.

More encouraging results were obtained when the work of Skita and Faust (34, p.2890) was repeated. These workers fractionally crystallized the 3,5-dinitrobenzoate of 3-methylcyclohexanol from methanol.

3,5-Dinitrobenzoate of 3-methylcyclohexanol: The ester was prepared in a manner identical to that used for preparation of the p-nitrobenzoate. The heavy oil remaining in the pot after steam distillation readily crystallized from methanol. 46 grams (0.2 moles) of 3,5-dinitrobenzoyl chloride and 22.8 grams (0.2 moles) of 3-methylcyclohexanol yielded 49 grams of ester which melted at

80-85°C.

Theory 61.6 grams. Percentage yield 79%.

Using methanol as a solvent, the ester was fractionally crystallized. Recrystallization was continued until two successive fractions of crystals melted simultaneously when placed side by side on a melting point block. From the fractional crystallization scheme, involving about sixty separate recrystallizations, 4.8 grams of the trans ester was obtained.

Melting point 99.0-100.0°C.

Literature (34,p.2889) 97-98°C.

Because this procedure was such a tedious one, it did not seem to be a practical one to use in obtaining further quantities of the ester.

Skita and Faust (34, p.2889) found that a 3-methylcyclohexanol enriched in the trans form was obtained by the reduction of a very pure 3-methylcyclohexanone with sodium in moist ether.

3-Methylcyclohexanone: As no 3-methylcyclohexanone was available, it was prepared by the oxidation of 3-methylcyclohexanol (1, p.185).

82 grams (0.28 moles) potassium dichromate were dissolved in 400 ml. of water and 38 ml. of concentrated

sulfuric acid added. The solution was cooled to 30°C and poured into a flask containing 45.6 grams (0.40 moles) 3-methylcyclohexanol. The flask was shaken and cooled to keep the temperature between 55-60°C. When the temperature no longer rose above 60°C, cooling was discontinued and the flask left setting for an hour. Then the ketone was steam distilled and the steam distillate extracted with ether. The ether extract was dried over magnesium sulfate. The ketone was distilled under atmospheric pressure after the ether was removed.

Boiling point 170°C (Literature 169.6°C).

n_D^{23} 1.4440

Yield 30.5 grams. Theory 45.2 grams.

Percentage yield 67.5.

The ketone was purified through its sodium bisulfite addition product.

Sodium bisulfite addition product of 3-methylcyclohexanone: A saturated solution of sodium bisulfite was prepared by dissolving 50 grams of sodium bisulfite in 80 ml. of water. Seventy per cent of this volume of alcohol was added and then a small amount of water to dissolve the precipitate formed when the alcohol was added. 30.5 grams (0.27 moles) of 3-methylcyclohexanone were stirred into the solution. After several minutes

the solution solidified. The solid material was filtered off under suction with the aid of a rubber dam. The solid was washed several times with cold absolute ethanol and then with ether.

The addition product was decomposed with 200 ml. of 10 per cent sodium hydroxide and the liberated ketone steam distilled. The ketone was extracted with ether and dried over sodium sulfate.

Boiling point 170°C .

n_D^{23} 1.4442

Yield 21.8 grams. Theory 30.5 grams.

Percentage yield 71.5.

Reduction of 3-methylcyclohexanone: In a 3-necked flask, equipped with a condenser, a dropping funnel and a stirrer, were placed 25 grams of metallic sodium, 21.8 grams (0.195 moles) of 3-methylcyclohexanone and 250 ml. of ether. While stirring gently, water was added dropwise through the dropping funnel until all the sodium had reacted. The ether and alcohol were steam distilled and the distillate extracted with ether. After drying over sodium sulfate, 15.1 grams of alcohol was obtained.

Theory 22.2 grams. Percentage yield 68.

This alcohol gave no ketone test when treated with semi-

carbazine hydrochloride.

3,5-Dinitrobenzoate of 3-methylcyclohexanol: The ester was prepared as before.

Melting point 94.1-95.5°C.

Yield 31.5 grams. Theory 40.8 grams.

Percentage yield 77.4.

Twenty recrystallizations yielded 14.0 grams of the ester whose melting point could not be changed by further recrystallization.

Melting point 99.0-100.0°C.

Hydrolysis of 3,5-Dinitrobenzoate of trans-3-methylcyclohexanol: Skita and Faust (34, p.2889) hydrolyzed the ester in a sodium hydroxide-methanol medium and obtained a 62 per cent yield of the alcohol. Using some of the crude ester, their procedure was repeated.

15.4 grams (0.05 moles) of the ester were dissolved in 125 ml. of methanol. 75 ml. of water containing 4 grams (0.1 moles) of sodium hydroxide were added and the solution refluxed for two hours. The alcohol was steam distilled and the distillate extracted with ether.

Yield 3.16 grams. Theory 5.7 grams.

Percentage yield 55.5.

Because of the difficulty in obtaining the trans ester, it was desirable to obtain a higher yield of alcohol in the hydrolysis. Since the actual hydrolysis of the ester had probably been complete, the loss undoubtedly occurred in the isolation steps.

To check the efficiency of the steam distillation, a quantity of 3-methylcyclohexanol was placed in water and steam distilled. Using super heated steam, 92 per cent of the alcohol was recovered. It was found that this loss did not occur in the steam distillation but in the extraction of the steam distillate with ether. The efficiency of the extraction decreased when the 3-methylcyclohexanol was steam distilled from a aqueous methanol solution comparable to that used in the hydrolysis. Better results were obtained when the methanol was almost completely removed on a fractionating column before the steam distillation was carried out.

Using the most efficient procedure found, 18.8 grams (0.061 moles) of the trans ester were dissolved in 150 ml. of warm methanol. 4.9 grams (1.22 moles) of sodium hydroxide in 50 ml. of water were added and the solution refluxed for two hours. 140 ml. of methanol were removed on a packed column before carrying out the steam distillation. The product was worked up as before.

Boiling point 77-78°C at 22 mm.

n_D^{25} 1.4544

Literature (34, p.2889) n_D^{20}

Yield 4.78 grams. Theory 6.97 grams.

Percentage yield 68.5.

Phenylurethane of trans-3-methylcyclohexanol: To check the purity of the trans alcohol a small quantity was converted to the phenylurethane.

0.5 grams of trans-3-methylcyclohexanol and 0.6 grams of phenylisocyanate were placed in a dry test tube and left in the ice box overnight. The precipitate was treated with warm petroleum ether and the insoluble diphenylurea filtered off. The solution was cooled and the phenylurethane precipitated.

Melting point 93-94°C.

Literature (34, p.2889; 3, p.365) 93-94°C.

Preparation of trans-2-methylcyclohexanol

Trans-2-methylcyclohexanol was obtained by fractional crystallization of the phthalic acid ester. The ester was prepared according to Gough, Hunter and Kenyon (12, p.2061).

Phthalic ester of 2-methylcyclohexanol: Eastman

"yellow label" 2-methylcyclohexanol was fractionally distilled on a packed column (boiling point $77-78^{\circ}\text{C}$ at 20 mm.). 114 grams (1.0 moles) of the alcohol and 173 grams (1.1 moles) of phthalic anhydride were placed in 250 ml. of freshly distilled toluene and solution refluxed for 12 hours. The toluene was removed by distillation and the molten ester poured into a solution containing excess sodium carbonate. This solution was diluted with a large volume of water and then extracted 10 times with benzene. Air was bubbled through the aqueous solution for 3 hours to remove the last traces of benzene. The ester, precipitated by adding hydrochloric acid, was filtered off and dissolved in chloroform to free it from phthalic anhydride. The phthalic anhydride was filtered off and the chloroform removed by distillation. The solid ester was slightly colored and melted at $94-95^{\circ}\text{C}$ (Literature $95-96^{\circ}\text{C}$).

To obtain a purer product, the ester was dissolved in sodium carbonate and the above procedure repeated. The white ester melted at $95-96^{\circ}\text{C}$.

Yield 155 grams. Theory 262 grams.

Percentage yield 59.2

The ester was fractionally crystallized from glacial acetic acid. After twenty systematic

recrystallizations, 44 grams of ester were obtained whose melting point could not be altered by continued recrystallization.

Melting point 126.5-127.5°C.

Literature (12, p.2061) 124-5°C.

Hydrolysis of phthalic acid ester of trans-2-methylcyclohexanol: Following Gough, Hunter and Kenyon's method, 44 grams (0.168 moles) of the ester were dissolved in a solution of 14.8 grams (0.336 moles) of sodium hydroxide and 200 ml. of water. After the ester dissolved, the solution was steam distilled. The major portion of the alcohol was collected in the first 50 ml. of distillate but the distillation was continued until 250 ml. of the distillate were collected. The distillate was extracted 6 times with ether and the ether extract dried over sodium sulfate. The ether was removed and the alcohol distilled under vacuum.

Yield 16.88 grams. Theory 19.15 grams.

Percentage yield 88.

Boiling point 77-78°C at 20 mm.

n_D^{25} 1.4605

Literature (34, p.2881) n_D^{20} 1.4611

Phenylurethane of trans-2-methylcyclohexanol: The phenylurethane was prepared and treated in a manner similar to that used in preparing the phenylurethane of trans-3-methylcyclohexanol.

Melting point 105.5-106.5°C.

Literature (12, p.2066) 105-106°C.

Preparation of 3-methylcyclohexene

3-methylcyclohexene was prepared by coupling 3-bromocyclohexene with methylmagnesium iodide. The 3-bromocyclohexene was formed by treating cyclohexene with N-bromosuccinimide. The reactions leading to 3-methylcyclohexene were run several times and the range of the yields obtained is cited in each preparation.

Succinimide: (6, p.562) 1 kilogram (8.46 moles) of succinic acid was placed in a 3-liter distilling flask. 1150 ml. (16.92 moles) of 28 per cent aqueous ammonia were slowly added while cooling and shaking the flask. The side arm of the flask was attached to a water-cooled receiver which in turn was provided with a tube leading to an ammonia trap. The flask was heated gently with a free flame; all of the undissolved acid went into solution. As heating was increased, some uncombined ammonia came over. After about a liter of water had distilled, the ammonium succinate began to decompose with

the evolution of ammonia. An intermediate fraction of distillate boiling 102-275°C was collected. The receiver was removed and an air condenser fitted to the flask. The succinimide distilled over the range 275-289°C with a portion of it solidifying in the condenser. Distillation was stopped when yellow fumes were evolved. Redistillation of the intermediate fraction yielded 20-25 grams of the solid imide. The crude succinimide was recrystallized from cold alcohol.

Yield 630-664 grams.

Percentage yield 75-79.

N-Bromosuccinimide: N-Bromosuccinimide was prepared according to Ziegler (39, p.109).

198 grams (2.0 moles) of succinimide were placed in a solution containing 84 grams (2.1 moles) sodium hydroxide and 500 ml. of water. 375 grams of chopped ice were added and the mixture placed in an ice bath. As soon as the imide dissolved, 106 ml. (4.18 moles) of bromine were added at once and the mixture stirred violently. The reaction was complete almost at once as evidenced by the formation of a pale yellow flocculent precipitate. This precipitate was filtered and washed repeatedly with ice water to remove the excess bromine, (if the stirring was not extremely violent when the

bromine was added, it was found that the washing process took much longer). The precipitate was rapidly recrystallized from hot water and dried in a vacuum desiccator over concentrated sulfuric acid.

Yield 167-242 grams.

Percentage yield 47-68.

Melting point 173.5-174.5°C.

Reported 175°C.

3-Bromocyclohexene: N-Bromosuccinimide is a brominating agent which brominates specifically in the allyl position. If a large excess of cyclohexene (an excess is used so that a dibromo compound will not be formed) is treated with N-bromosuccinimide, 3-bromocyclohexene (39, p.110) is formed.

178 grams (1.0 moles) of N-bromosuccinimide were mixed with a solution containing 515 ml. (5 moles) of cyclohexene and 750 ml. of carbon tetrachloride. The solution was placed in a 2-liter round bottom flask and the flask fitted with a good condenser. The mixture was heated to initiate the reaction. Once the reaction started it became very vigorous and cooling was necessary to keep the reactants within the flask and condenser. When the reaction subsided, heating was continued for about an hour. Succinimide floated on top of the

solvent when the solution was cooled. A few drops of the solvent were placed in an acidified potassium iodide solution. If a brown color appeared, heating was continued.

The succinimide was filtered from the solution and the excess cyclohexene and carbon tetrachloride removed by distillation. The bromo compound was then distilled under vacuum.

Boiling point 57-61°C at 10 mm.

n_D^{24} 1.5330.

Yield 90-140 grams.

Percentage yield 56-87.

Methylmagnesium iodide: 24 grams (1.0 moles) of magnesium turnings and 400 ml. of dry ether were placed in a 3-necked flask equipped with a condenser, a dropping funnel and a mercury seal stirrer. 142 grams (1.0 moles) of methyl iodide were added drop-wise at a rate which kept the ether boiling briskly. The solution was refluxed for 15 minutes after the addition of the halide was completed.

Using a stream of dry nitrogen and a glass tube with a loose plug of glass wool in one end, the Grignard was transferred into another flask to remove it from the unreacted magnesium.

3-Methylcyclohexene: Following a general method given by Berlande (5, p.438), the flask containing the Grignard was cooled to -10°C in an ice-salt bath. 161 grams (1.0 moles) of 3-bromocyclohexene in 200 ml. of dry ether were added over a period of 6 hours, being careful to keep the temperature below 0°C . The flask was then cooled and kept at room temperature for one-half hour. 300 ml. of dilute hydrochloric acid were added and the solution became a dark red.

The olefin and ether were steam distilled and the olefin separated from the water layer of the distillate. The olefin was refluxed for several hours with metallic sodium to remove any unreacted 3-bromocyclohexene. After filtering off the sodium, the product was steam distilled, separated from the distillate, dried over calcium chloride and distilled at atmospheric pressure.

Boiling point $104-105^{\circ}\text{C}$.

Reported 104°C (5, p.438), $106-106.5^{\circ}\text{C}$
(31, p.1848).

n_{D}^{20} 1.4425

Reported n_{D}^{20} 1.4426 (5, p.438), 1.4423
(31, p.1848).

Yield 48.9-61.4 grams.

Percentage yield 51-64.

A survey of the literature revealed no known methods of converting trans alcohols to pure isomeric bromides. Mousseron and Granger (27, p.1487) have reported the preparation of a pure cis-bromide from active trans-3-methylcyclohexanol with hydrogen bromide and a trans-bromide from the same alcohol using phosphorous pentabromide. These workers do not give sufficient evidence to indicate whether they are justified in designating the bromides as the pure isomers.

Kenyon, Phillips and Taylor (16, p.174), in their studies with the phenylmethylecarbinols, found that the reaction of the p-toluenesulfonate of the D-carbinol with acetate ion yielded an L-acetate. Assuming that chloride ion would react similarly, displacement of the p-toluenesulfonoxo anion by chloride should yield an L-chloride. Accordingly, the chloride obtained by the action of lithium chloride in acetic anhydride on the sulfonate was designated as belonging to the L series.

A number of workers (12, pp.2066-8; 13, p.2894; 36, p.649) have obtained the acetate of cis-2-methylcyclohexanol by the reaction of the p-toluenesulfonate of trans-2-methylcyclohexanol with acetate ion. In view of this, and the work of Kenyon et al., it appeared that if the p-toluenesulfonate of trans-2- or trans-3-methylcyclohexanol were treated with lithium bromide

in the presence of acetic anhydride, the cis-bromides should be formed. In order to check the method the reactions were tried on 3-methylcyclohexanol.

3-Bromocyclohexane

p-Toluenesulfonate of 3-methylcyclohexanol: The method of Vavon, Perlin and Horeau (36, p.649) was followed. These workers found that the tendency of the alcohol to dehydrate was lessened if the reaction was conducted in chloroform.

20 grams (0.175 moles) of 3-methylcyclohexanol and 40 grams (0.21 moles) of p-toluenesulfonyl chloride were dissolved in 250 ml. of chloroform. 75 grams (0.95 moles) of dry pyridine were added and the mixture shaken. A vigorous reaction resulted. After the solution was stirred for several hours, it was washed successively with water, dilute sodium carbonate solution, dilute hydrochloric acid and water. Distillation of the chloroform left a viscous yellow oil which could not be crystallized by cooling or from petroleum ether. The oil was then dried in a vacuum desiccator over phosphorous pentoxide.

Reaction of p-toluenesulfonate of 3-methylcyclohexanol with lithium bromide: 10 grams (0.053 moles) of the sulfonate were dissolved in 50 ml. of acetic anhydride. 10 grams (0.155 moles) of lithium bromide were added and

the solution allowed to stand for 8 hours with intermittent shaking. After refluxing for 4 hours, the solution was poured into a dilute sodium carbonate solution and extracted with ether. Evaporation of the ether left a black solid. Consequently this method could not be used to prepare the isomeric bromides.

It was now realized that an extensive study would be necessary in order to develop a method to obtain the pure isomeric bromides. As an alternative, it was decided to compare the spectra of 3-bromo- and 2-bromomethylcyclohexane in order to see what information could be obtained disregarding the cis-trans isomerism. The bromides were prepared according to the general procedure given in Organic Synthesis (6, p.358).

3-Bromomethylcyclohexane

22.8 grams (0.2 moles) of 3-methylcyclohexanol were placed in a 3-necked flask equipped with a stirrer, a dropping funnel and a thermometer. The alcohol was stirred and cooled to -10°C in an ice-salt bath and 19.8 grams (0.073 moles) of phosphorous tribromide slowly added so that the temperature did not rise above 0°C . After the phosphorous tribromide had been added, stirring was continued until the reaction mixture came to room temperature and then was left overnight. The crude

bromide was distilled under vacuum, cooled and washed with three 15-ml. portions of cold concentrated sulfuric acid, and shaken with several grams of anhydrous potassium carbonate until no more hydrogen bromide was evolved. The compound distilled at 64°C (19 mm).

Literature (27, p.1487) 58°C at 10 mm.

n_D^{25} 1.4868

Literature (27, p.1487) n_D^{25} 1.4867

Yield 23.0 grams. Theory 35.4 grams

Percentage yield 65.

2-Bromomethylcyclohexane

2-Bromomethylcyclohexane was prepared in the same manner as the 3-bromo- compound and an identical yield was obtained. The refractive index of the compound changed when the compound was allowed to stand for several days, i.e., n_D^{25} 1.4871 to n_D^{25} 1.4865. Murat (28, p.111) observed that the compound had a tendency to split out hydrogen bromide.

The splitting of hydrogen bromide from this compound would form 1-methylcyclohexene. If the hydrogen bromide added to the olefin, the addition would follow Markownikoff's rule and the product would be 1-bromo-methylcyclohexane.

It was advisable therefore to prepare 1-bromo-1-methylcyclohexane in order to compare its spectrum with the 2-bromo-compound. The bromide was prepared from 1-methylcyclohexanol.

1-Bromo-1-methylcyclohexane

1-Methylcyclohexanol: 5 grams (0.208 moles) of magnesium turnings and 150 ml. of dry ether were placed in a 3-necked flask fitted with a stirrer, a condenser and a dropping funnel. 28.4 grams (0.20 moles) of methyl iodide were added at a rate which kept the ether boiling. After the addition was complete, the solution was refluxed for 15 minutes.

19.6 grams (0.2 moles) of cyclohexanone were added drop-wise, then the solution refluxed for 15 minutes. The Grignard was decomposed by pouring it into a solution of cold sulfuric acid and silver sulfate. The precipitated silver iodide was filtered off, and the ether layer separated and steam distilled. The ether extract of the distillate was dried over potassium carbonate and the ether evaporated.

The crude alcohol was cooled and saturated with dry hydrogen bromide (11, p.3591). The red solution which resulted was poured into water and the bromide separated from the water layer. It was then washed three

times with cold concentrated sulfuric acid. After drying over anhydrous potassium carbonate, the bromide was distilled.

n_D^{23} 1.4879

Literature (11, p.3591) n_D^{25} 1.4868

Boiling point 70°C at 30 mm.

Literature (11, p.3591) 66°C at 22 mm.

Overall yield 13.4 grams. Theory 35.4 grams.

Percentage yield 37.8.

The infrared analytical method

Qualitative: The instrument used was a Perkin-Elmer model 12-C spectrophotometer equipped with a Brown recording potentiometer. The recorder produces a permanent record of the intensity of the light striking the thermocouple as a function of wavelength.

The potassium bromide region of the spectrum was selected for the analytical studies because it is in this region that absorptions involving a carbon-bromine bond occur. Therefore the greatest differences in the spectra of the compounds studied could be expected in this region.

Survey spectra of 2-bromo- and 3-bromomethylcyclohexane were obtained in the region of 3 to 13 microns. For operation in this region, the spectrophotometer was equipped with a sodium chloride prism and the sample was

placed between two sodium chloride windows. The spectra were obtained by the double beam method.

To obtain the spectrum of each compound in the region 13 to 22 microns, a potassium bromide prism and the single beam method of operation were employed. The sample in this case was injected into a fixed-type cell by means of a syringe. The cell which had potassium bromide windows and was 0.05 mm. long, was used for all spectra in this region.

The spectra over the region 3 to 22 microns are shown in Figures 1 and 2. Absorption bands were found at the following wavelengths.

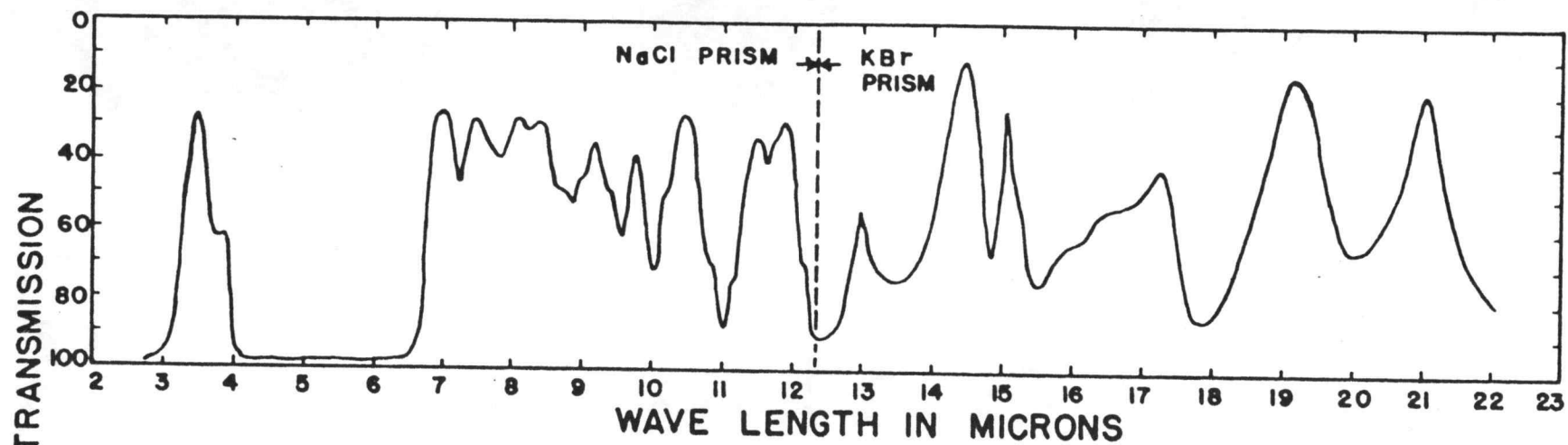


FIGURE 1. INFRARED SPECTRUM OF 3-BROMOMETHYLCYCLOHEXANE (LIQUID AT ROOM TEMPERATURE).

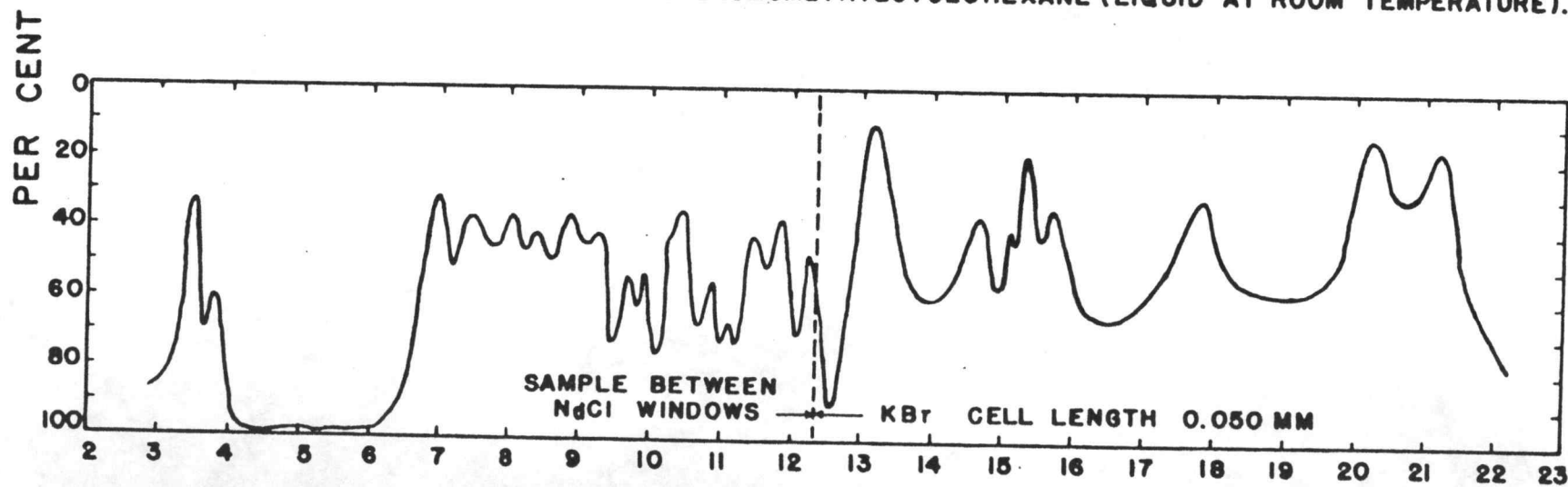


FIGURE 2. INFRARED SPECTRUM OF 2-BROMOMETHYLCYCLOHEXANE (LIQUID AT ROOM TEMPERATURE).

TABLE I
ABSORPTION BANDS IN NaCl-KBr RANGE

2-Bromomethylcyclohexane
(Wavelength in microns)

3.47
3.75
6.95
7.39
8.01
8.39
8.84
9.22
9.68
9.88
10.44
10.87
11.07
11.43
11.81
12.24
13.10
14.62
15.30
15.61
17.79
20.16
21.11

3-Bromomethylcyclohexane
(Wavelength in microns)

3.47
3.76
6.99
7.42
8.11
8.43
9.13
9.76
10.44
11.45
11.84
13.00
14.47
15.07
17.20
19.02
21.02

The spectrum of 1-bromo-1-methylcyclohexane in the potassium bromide region was obtained (Figure 3) so that it could be compared with the spectrum of 2-bromomethylcyclohexane. Absorption bands were found at the following wavelengths.

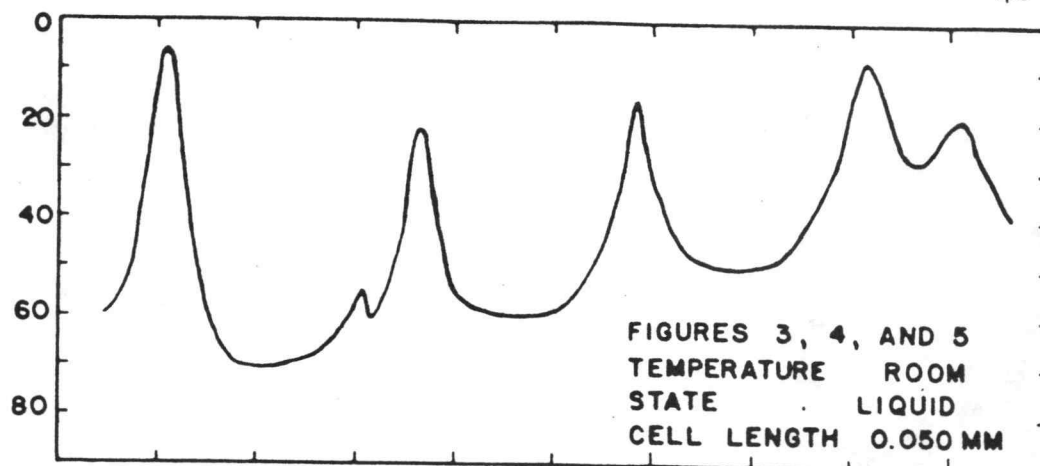


FIGURE 3. INFRARED SPECTRUM OF
1-BROMO-1-METHYLCYCLOHEXANE.

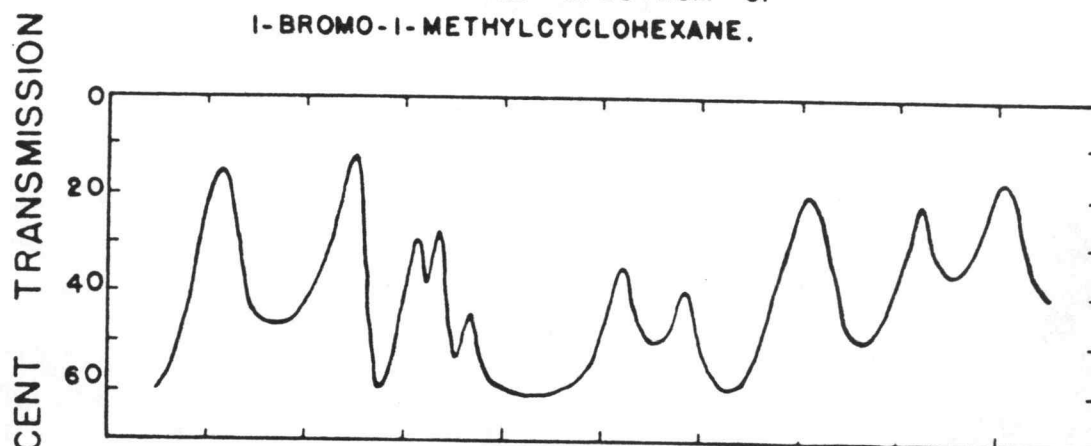


FIGURE 4. INFRARED SPECTRUM OF A 50-50
MIXTURE OF 2-BROMOMETHYLCYCLOHEXANE
AND 3-BROMOMETHYLCYCLOHEXANE.

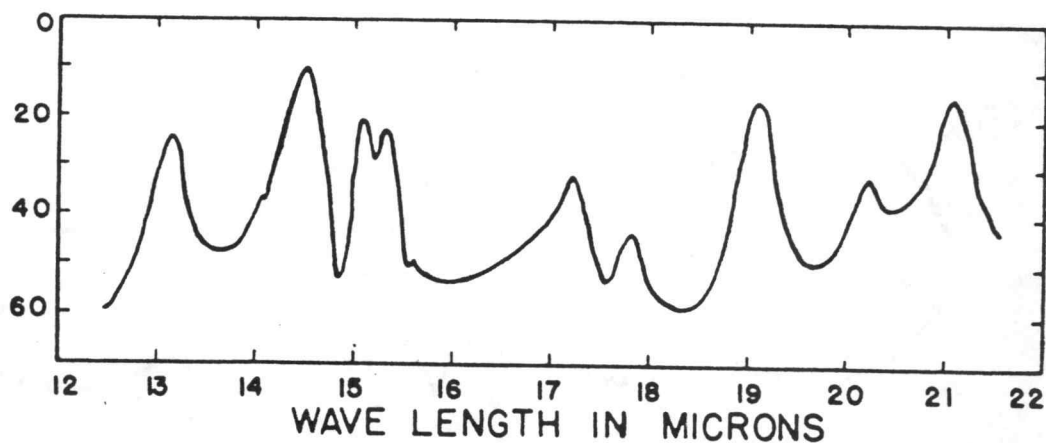


FIGURE 5. INFRARED SPECTRUM OF THE ADDITION
PRODUCT OF HBr AND 3-METHYLCYCLOHEXENE IN
GLACIAL ACETIC ACID AT 0° CENTIGRADE.

TABLE II
ABSORPTION BANDS IN KBr RANGE

1-Bromo-1-methylcyclohexane
(Wavelength in microns)

13.10
15.61
17.79
20.16
21.11

Comparison of these bands with those found in the potassium bromide region of the 2-bromo- compound indicates that all of the bands present in the 1-bromo- are also in the 2-bromo-. These bands may be characteristic for each of the pure compounds and therefore it is not possible to ascertain whether the 2-bromomethylcyclohexane is free of the 1-bromo- compound. Because of this, freshly prepared 2-bromomethylcyclohexane was always used.

In order to determine which bands could be used for the quantitative studies, the spectrum of a 50-50 mixture of 2-bromo- and 3-bromomethylcyclohexane was obtained. It would seem from Figure 4 that the absorption bands in the 2-bromo- compound at 15.30 and 20.16 microns could be used to indicate the concentration of that compound in a mixture, since the absorption appears to vary markedly with the concentration. Likewise, it appears that the 15.07 and 19.02 micron bands

could be used for the 3-bromo- compound.

A close inspection reveals considerable overlapping of the 15.07 and 15.30 micron bands. Also a 15.07 micron band appears in the 1-bromo- compound. The 20.16 micron band occurring in the 2-bromo compound also occurs in the 1-bromo- and this band overlaps the 21.02 and 21.11 micron bands in the 3- and 1-bromo- compounds. Consequently, the band which would give the best quantitative results appears to be the 19.07 micron band of the 3-bromomethylcyclohexane. This will give the amount of the 3-bromo- compound in the mixture and the remainder of the mixture must be 2-bromo- and 1-bromo-, if it is assumed that some of the latter compound is present.

Comparison of the spectrum of the addition compound (Figure 5) with that of the 50-50 mixture indicates that all of bands in the 50-50 mixture are also in the addition compound. If the 2-bromo- and 3-bromo- compounds used in making up the mixture are assumed to be a mixture of cis- and trans- bromides, then the addition must give a mixture of cis- and trans- bromides, or the instrument does not possess sufficient resolving power to indicate the difference between a cis-trans mixture and a pure isomeric bromide.

Quantitative: In order to correlate the transmittancy of a given absorption band with the concentration of the 2- and the 3- bromo- compound, known mixtures of 2- and 3-bromomethylcyclohexane were prepared. Spectra of these mixtures from 18.5 to 22 microns were obtained using a constant slit width. Values corresponding to 100 per cent transmission (I_0) and the percentage transmission of the sample (I) at a given wavelength were obtained from the recorder chart, and the transmittancy (I/ I_0) correlated with concentration.

The percentage transmission at a given wavelength cannot be read directly from the recorder chart. The value recorded is the result of the total amount of radiation falling upon the thermocouple of the spectrophotometer. This radiation is derived from two sources; the light in the potassium bromide region transmitted by the sample and a certain amount of stray light. Most of this stray or false light is of fairly high frequency, and it may be assumed that all of it will be transmitted by a lithium fluoride plate. Since light transmitted in the potassium bromide region will not be transmitted by this plate, it is possible to determine the amount of stray light reaching the thermocouple so that the percentage recorded on the chart may be corrected.

The 100 per cent transmission line on the chart

was determined with a sample in the cell. Two regions where no absorption took place were selected on both sides of the absorption band. A curve, with the slope of the black body radiation curve, was drawn through these regions. Intersection of this curve with the wavelength of the absorption band gave, when corrected for stray light, the value for 100 per cent transmission (I_0). The height of the absorption peak was corrected for stray light to obtain the percentage transmission of the compound (I).

Figure 6 was obtained by plotting the logarithm of the transmittancy (I/I_0), of the 19.02 micron band, as a function of the concentration of 3-bromomethylcyclohexane in a mixture with 2-bromomethylcyclohexane.

Addition of hydrogen bromide to 3-methylcyclohexane

The conditions for the additions were essentially the same as those used by Kharasch (20, p.1562) so that a comparison of the results obtained could be made with his results.

7.6 grams (0.094 moles) of dry hydrogen bromide from a tank were dissolved in 10.4 grams (0.173 moles) of glacial acetic acid contained in a dry glass-stoppered flask. In the case of the additions at 0°C , the solution was cooled to 0°C , 5 grams (0.052 moles) of the olefin

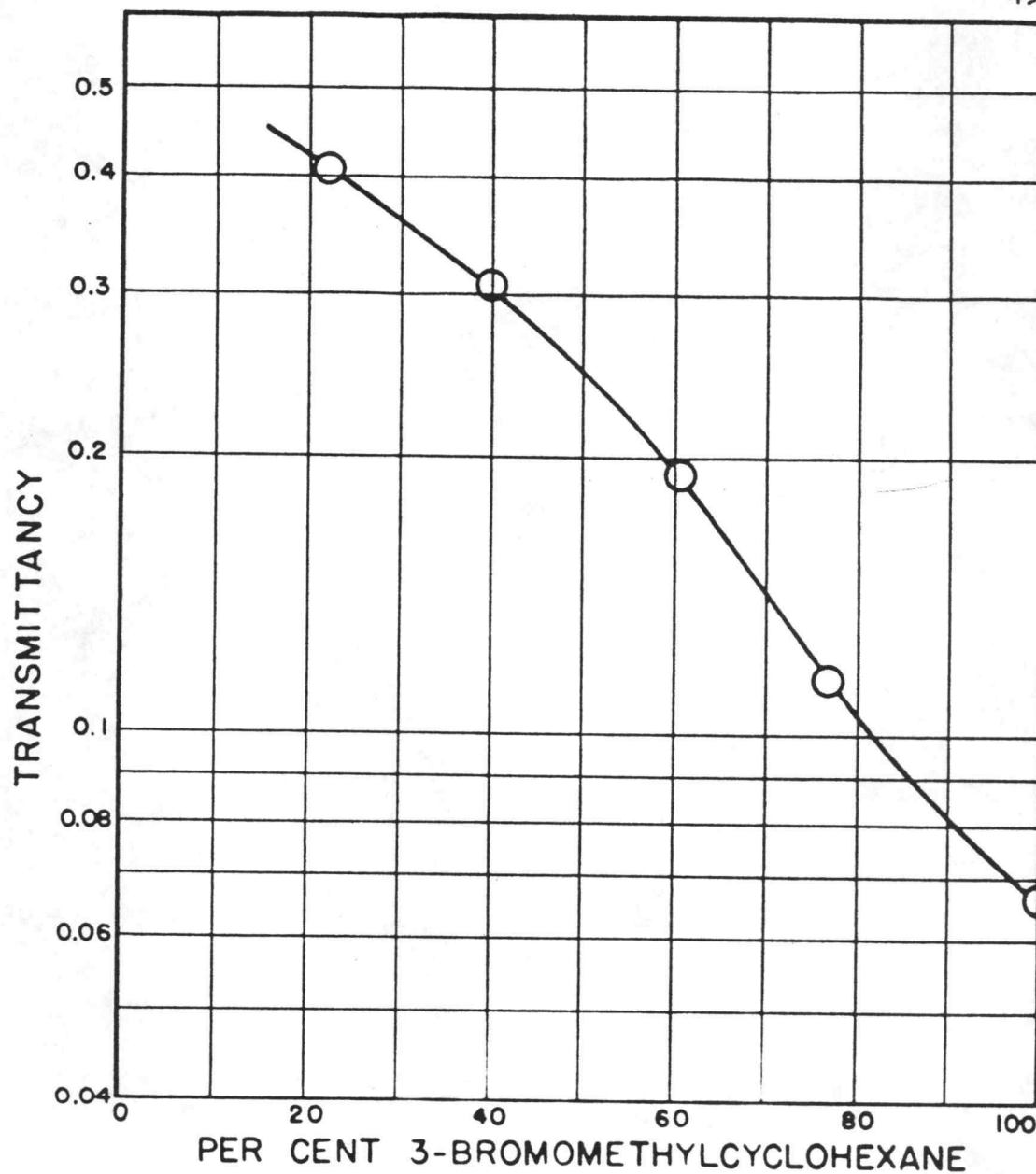


FIGURE 6. SEMI-LOGARITHMIC PLOT OF THE TRANSMITTANCY (AT 19.02 MICRONS) AS A FUNCTION OF THE CONCENTRATION OF 3-BROMOMETHYLCYCLOHEXANE IN 2-BROMOMETHYLCYCLOHEXANE AT ROOM TEMPERATURE.

added and the flask left in the ice box for two hours. When the reaction was carried out at room temperature, the olefin was added without cooling and the solution left for 45 minutes.

The addition product always contained some black tarry material and this complicated the isolation problem. To improve the isolation procedure, two different methods of isolation were used. Method 1 consisted of successively washing the reaction product with cold concentrated sulfuric acid, water, dilute sodium carbonate solution and water, then drying over potassium carbonate and distilling.

Using this method, the black material in the addition product was not completely eliminated by the acid wash. The color also made it impossible to tell whether or not the concentrated sulfuric acid was decomposing the addition product.

Another method was tried in order to eliminate the black material and to check whether the concentrated acid was decomposing some of the addition compound. In Method 2 the reaction mixture was diluted with water and the addition product extracted with ether. The dark colored ether extract was decolorized with Norite, and washed with dilute sodium carbonate solution to remove the hydrogen bromide. The ether was evaporated and the slightly

colored product washed with cold sirupy phosphoric acid, then water, sodium carbonate solution and water again. The product was dried over magnesium sulfate and distilled. This method simplified the isolation procedure somewhat. The product obtained had the same composition as that isolated by Method 1.

The percentage yield in the additions was very low, 25-30. In fact the yield was so low in some runs that it was impossible to recover a workable amount of the addition product. This was the case in two runs conducted in the presence of benzoyl peroxide. The refractive indices of all the addition compounds were approximately 1.4900 (25°C). This is a good indication that no olefin was present in the addition compound.

The spectrum of each addition compound was obtained over the same range with the same slit width used for the known mixtures. I and I_0 were obtained in the same manner as before, and the percentage 3-bromomethylcyclohexane in the product determined from Figure 6.

TABLE III
COMPOSITION OF ADDITION PRODUCT

From 19.02 micron band of
3-bromomethylcyclohexane

Run No.	Temperature (°C)	Time (Hrs.)	Method of Isolation	I/I ₀	Percentage 3-Bromo- methylcyclo- hexane
1	0	2	1	0.218	57
2	0	2	1	0.143	71
3	0	2	1	0.153	70
4	0	2	2	0.161	68
5	Room	0.75	1	0.155	69
6	Room	0.75	1	0.185	63
7	Room	0.75	1	0.163	68

Although, as stated before, the results obtained with the 19.02 micron band of the 3-bromomethylcyclohexane should be the most accurate, the concentration of 2-bromomethylcyclohexane was also calculated in each run.

TABLE IV
COMPOSITION OF ADDITION PRODUCT

From 20.16 micron band of
2-bromomethylcyclohexane

<u>Run No.</u>	<u>I/I₀</u>	<u>Percentage 2-bromo- methylcyclo- hexane</u>	<u>Percentage 3-bromo- methylcyclo- hexane</u>	<u>Total Percentage Composition</u>
1	0.270	32	57	89
2	0.573	15	71	86
3	0.308	29	70	99
4	0.458	20	68	88
5	0.446	19	69	88
6	0.365	24	63	87
7	0.325	27	68	94

The values obtained for the percentage composition of the 2-bromo-methylcyclohexane do not agree too closely. The total percentage concentration is fairly consistent, however.

DISCUSSION OF RESULTS

The results obtained indicate a greater percentage of 3-bromomethylcyclohexane in the product isolated. Because of the abnormally low yields in the addition, and the lack of knowledge regarding the stability of the 2-bromomethylcyclohexane, no conclusions regarding hyperconjugation can be drawn. Hence, a more extensive study of the stability of the 2-bromo- compound under the reaction conditions, and in the method of isolation, must be carried out so that some conclusion can be reached.

The average deviation in determining the amount of 3-bromomethylcyclohexane, excluding run number 1, was ± 1.8 per cent. Using the concentration range of 40 to 80 per cent and taking into account the maximum and minimum noise levels, the limits of the accuracy of the results obtained are at the best ± 2 per cent and at the worst ± 10 per cent.

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