

COMPARATIVE REACTIVITIES OF AXIAL  
AND EQUATORIAL CARBINOL DERIVATIVES

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## CHAPTER I

### INTRODUCTION

In an earlier work,<sup>1</sup> rates of reaction of iodide ion with cyclopentylmethyl bromide and cyclohexylmethyl bromide in dry acetone were determined. These two compounds reacted at about the same rate, but there were differences in the entropies of activation and in the energies of activation. Cyclopentylmethyl bromide was found to have the lower entropy of activation. This lower value suggests that it is more difficult for the cyclopentylmethyl bromide molecule to assume the transition state. Since the favorable conformation for the bromomethyl group in cyclohexylmethyl bromide is the equatorial one, and since the bromomethyl group of cyclopentylmethyl bromide is similarly oriented, it was decided to study bromides in which the bromomethyl group is rigidly held in the axial or in the equatorial position. Then, by determining rates of reaction of iodide ion with these bromides, the effects of the different conformations would be apparent.

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<sup>1</sup>G. C. Williams, M. S. Thesis, 1957, University of Alabama, University, Alabama.

In a study of aliphatic sulfonyl chlorides,<sup>2</sup> it has been found that the chlorine undergoes bimolecular displacement comparable to the analogous alkyl chloride when the sulfonyl group is viewed as a pseudo-methylene group. Results of the present study should give some indication of differences to be expected for different conformations of the chlorosulfonyl group.

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<sup>2</sup>R. B. Scott, Jr. and R. E. Lutz, J. Org. Chem., 19, 830 (1954).

## CHAPTER II

### HISTORICAL

Probably the simplest form of the displacement reaction takes place between a Lewis base and an alkyl halide. As the base collides with the alkyl halide, the halide ion moves away and a new molecule is produced. If the base is an iodide ion and the alkyl halide is a bromide, the bromide ion moves away and an alkyl iodide is formed. To collide effectively with the alkyl halide molecule, the iodide ion must approach at a point opposite to the position occupied by the bromine atom. When the negative iodide ion approaches the alkyl bromide properly, bonding begins and the bromide ion begins to form and to move away. The originally tetrahedrally disposed elements bonded to the central carbon atom now are  $120^\circ$  apart (sp<sup>2</sup> hybridized) and the iodine and bromine atoms are on a common axis through the central carbon atom. This axis is perpendicular to the plane in which the three groups and carbon atoms are in. The bromine and iodine atoms are attached to a p orbital of the central carbon atom. The transition state is that of a trigonal bipyramid like that in phosphorus pentahalides. The steric configuration of the new alkyl iodide molecule is inverted relative to the original bromide molecule.

The above-described mechanism is said to be S<sub>N</sub>2, which indicates that the reaction is a bimolecular substitution by a

nucleophilic reagent. The rate of reaction is that of the bimolecular step.<sup>1</sup>

The displacement reaction is reversible, but if an alkyl bromide is reacted with potassium iodide in acetone, the potassium bromide precipitates and it has been found that fairly good second-order rate constants<sup>2</sup> are obtained for early stages in the reaction when using the second-order rate equation. By using potassium iodide in dry acetone, the second-order constants hold for about 60% of the reaction supposedly because potassium iodide is fairly soluble in acetone while the produced potassium bromide is not. Thus, the potassium bromide precipitates, and the reaction is not appreciably reversed. When aqueous acetone<sup>3</sup> is used for the reaction, the rate constants indicate that the reverse reaction becomes more prominent than when dry acetone is used.

Hine<sup>4</sup> states that acetone is used as the solvent because of its poor ionizing power, but since primary bromides have a greater tendency to undergo second-order displacement reactions than first-order,<sup>5</sup> it seems that a more significant point is that potassium

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<sup>1</sup>Carl R. Noller, "Chemistry of Organic Compounds," 2nd Ed., W. B. Saunders Company, Philadelphia, 1957, p. 116.

<sup>2</sup>I. Dostrovsky and E. D. Hughes, J. Chem. Soc., 162 (1946).

<sup>3</sup>A. L. Solomon and H. C. Thomas, J. Am. Chem. Soc., 72, 2028 (1950).

<sup>4</sup>Jack Hine, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, 1956, p. 157.

<sup>5</sup>Elliot R. Alexander, "Principles of Ionic Organic Reactions," John Wiley & Sons, Inc., New York, 1950, p. 80.

bromide is essentially insoluble in acetone. However, if secondary or tertiary halides were used, dry acetone or a similar solvent having a low dielectric constant would be essential to maintain a second-order reaction.

The approach of the iodide ion must be at the back of the carbon atom to which the bromine atom is attached and the iodide ion must be in line with the bromine atom. Thus, if methyl bromide is being attacked by iodide ion, the reaction is very fast because there are no bulky groups to obstruct the approach of the iodide ion. Also, the nature of the leaving group must be considered.<sup>6</sup> The leaving group or atom must be relatively weakly bonded to the carbon atom; thus, the attacking nucleophile can push off less basic substituents more easily. If a secondary bromide is considered, the reaction is much slower because of the bulky groups. When a tertiary halide<sup>7</sup> is attacked, the reaction hardly proceeds if a solvent which does not aid ionization of the bromide is used.

When a primary bromide has an isopropyl or tertiary butyl group attached, as in isobutyl and neopentyl bromides, the reaction is found to be very slow relative to ethyl bromide or n-butyl bromide. A comparison of the rates of reaction of ethyl and neopentyl bromides with potassium iodide in acetone has been made.<sup>8</sup> Ethyl bromide was found to react 1800 times faster than neopentyl bromide, and it is

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<sup>6</sup>Edwin S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, Inc., New York, 1959, p. 261.

<sup>7</sup>H. J. McDonald, L. R. Rothstein, and H. E. Robison, J. Am. Chem. Soc., 66, 1984 (1944).

<sup>8</sup>Dostrovsky and Hughes, loc. cit., p. 161.

apparent that the tertiary butyl group has greatly hindered the approach of the attacking iodide ion. Also, Bartlett and Rosen<sup>9</sup> have studied the reaction of neopentyl bromide with potassium iodide in acetone. They made a comparison with n-butyl bromide which was found to react 474 times faster than neopentyl bromide. This study also included 2-methyl-1-butyl bromide which may be considered a homologue of isobutyl bromide. The 2-methyl-1-butyl bromide reacts 29 times faster than neopentyl bromide.

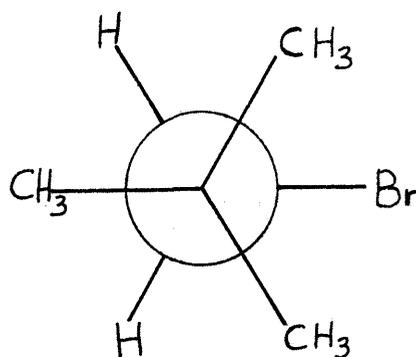


Figure I

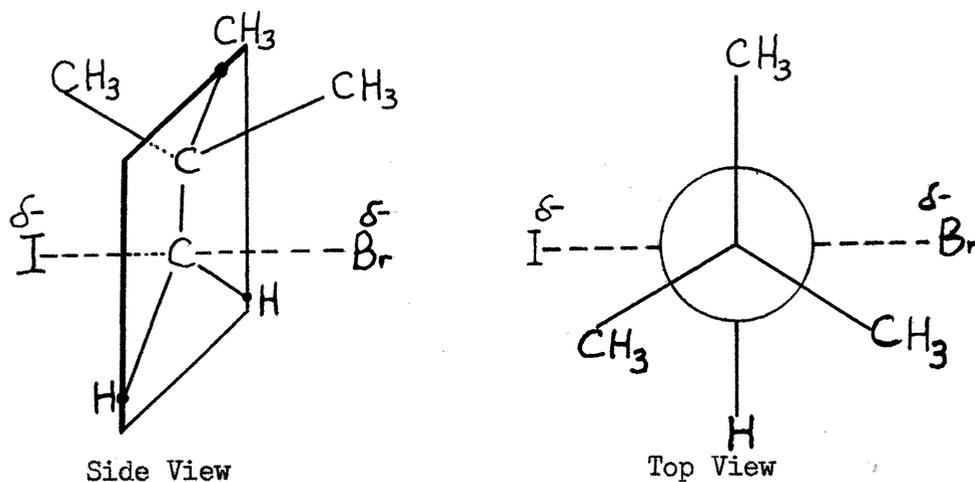


Figure II

<sup>9</sup>P. D. Bartlett and L. J. Rosen, J. Am. Chem. Soc., 64, 543 (1942).

Figure I probably represents the lowest energy conformation of the neopentyl bromide molecule. The transition state of neopentyl bromide<sup>10</sup> undergoing an  $S_N2$  attack can be seen in Figure II which best represents the lowest energy transition state conformation because the beta-methyl groups are so spaced that there is a minimum of steric interaction between these groups and both the iodine and bromine atoms. Thus, the attack is repelled by the two beta-methyl groups and possibly two of the three gamma-hydrogen atoms on the third methyl group; consequently, neopentyl bromide reacts more slowly than 2-methyl-1-butyl bromide.

In a previous work,<sup>11</sup> it was shown that cyclohexylmethyl bromide and cyclopentylmethyl bromide react about one-half as fast as 2-methyl-1-butyl bromide and fifteen times as fast as neopentyl bromide. It was suggested in this work that the bromomethyl group attached to the cyclohexane ring must be equatorial to the ring. Otherwise, if the equatorial conformation for the bromomethyl group were not favored, one would expect this compound to be very unreactive. In order to test the validity of this suggestion, it was proposed that cis- and trans-4-tert-butylcyclohexylmethyl bromides be considered in order to have compounds in which the bromomethyl group is actually held in the axial and equatorial positions depending on whether it is

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<sup>10</sup>I. Dostrovsky, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 173 (1946).

<sup>11</sup>Williams, loc. cit.

the cis or trans isomer. It has been shown<sup>12</sup> that if a tert-butyl group is attached to a cyclohexane ring and if the other group attached to the ring is not too bulky, the tert-butyl group is equatorial to the ring; and if the tert-butyl group is in the 4-position relative to the other group, the tert-butyl group does not interfere with the functional group. It can be seen from Figure III that the bromomethyl group is axial in the cis isomer and equatorial in the trans. Thus, it would appear from this figure that rear attack by an iodide ion on the cis isomer would be greatly hindered.

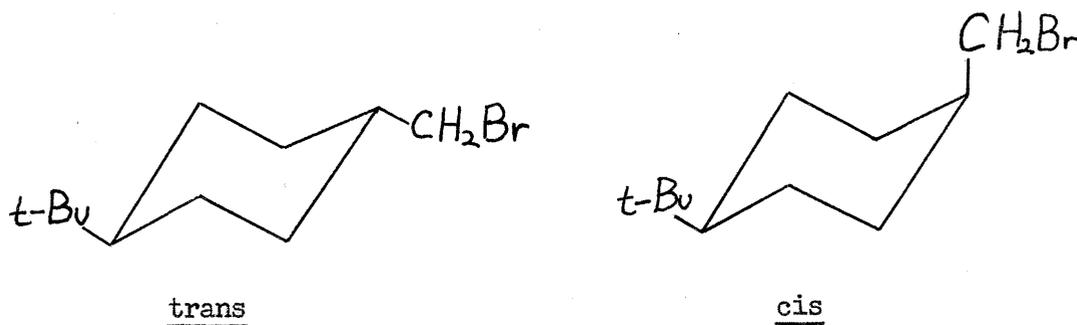


Figure III

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<sup>12</sup>S. Winstein and N. J. Holness, J. Am. Chem. Soc., 77, 5562 (1955).

## CHAPTER III

### EXPERIMENTAL

#### Preparation of cis-4-tert-Butylcyclohexanecarboxylic Acid

A solution prepared by dissolving 9 g (0.22 mole) of sodium hydroxide (Reagent, A. C. S., pellets) and 36 g (0.20 mole) of p-tert-butylbenzoic acid (Eastman Kodak, P 6965) in 150 ml of water was added directly to a Parr hydrogenation bomb cylinder. Then, 10 g of Raney nickel (W-2 catalyst)<sup>1</sup> was added. After the bomb had been purged with hydrogen several times, hydrogen pressure was applied at 2000 psi at room temperature. The bomb was heated and rocked at 150° C for about twelve hours. After hydrogenation, the resulting alkaline solution was filtered with suction to remove the catalyst. Then, the solution was acidified with concentrated hydrochloric acid to a pH of 1. The mixture of cis and trans acids was filtered with suction, washed several times with water, and dried.<sup>2</sup>

The mixture of cis- and trans-4-tert-butylcyclohexanecarboxylic acids was separated by passing a solution consisting of 12 g of the acid mixture dissolved in low boiling petroleum ether through a

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<sup>1</sup>E. C. Horning, "Organic Syntheses," Collective Volume III, Revised Edition, John Wiley and Sons, Inc., New York, 1955, p. 181.

<sup>2</sup>R. C. Morris and V. W. Buls, U. S. Patent 2,771,487, Nov. 20, 1956; C. A., 51, 2857 (1957).

19 X 700-mm column filled with 100 g of adsorption alumina (Fisher, 80-200 mesh). More petroleum ether was added as long as elution of cis acid took place. The cis acid then was crystallized from alcohol-water solution. After two crystallizations, it melted at 117-118° C.<sup>3</sup> About 2.4 g of pure cis acid was recovered from each 12-g portion of the mixture put through the column.

#### Preparation of trans-4-tert-Butylcyclohexanecarboxylic Acid

The trans isomer was prepared by hydrogenation of an alkaline solution of p-tert-butylbenzoic acid in the same manner as the cis isomer except that the temperature was kept at 200° C. At the higher temperature, the trans isomer was formed in good yield, possibly as high as 90%.<sup>4</sup> After several recrystallizations from alcohol-water solution, this compound melted at 176-177° C.<sup>5</sup>

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<sup>3</sup>The melting point reported by K. Alder, K. Heimbarck, and E. Kühle, Chem. Ber., 86, 1364 (1953) is 111° C. No analysis was reported and there was no distinction made regarding geometric isomers. The melting point reported by Morris and Buls, loc. cit., for the cis isomer is 89.5-90.5° C. An analysis was reported, but the experimental value for carbon was 1% too high. The melting point reported by R. D. Stolow, J. Am. Chem. Soc., 81, 5811 (1959) is 117-118° C. The ultimate analysis and infrared spectrum show this compound to be pure.

<sup>4</sup>Morris and Buls, loc. cit.

<sup>5</sup>The melting point reported by Morris and Buls, loc. cit., is 174.5-175.5° C. The melting point reported by Stolow, loc. cit., p. 5810, is 176-177° C. The ultimate analysis and infrared spectrum show this compound to be pure.

Preparation of cis-4-tert-Butylcyclohexylmethanol and Derivatives

cis-4-tert-Butylcyclohexylmethanol.<sup>6</sup> About 450 ml of an approximately 1 M ether solution of lithium aluminum hydride was added to a two-liter, three-neck, round-bottom flask, equipped with a dropping funnel, a glass half-moon stirrer, and a reflux condenser vented through a tube of calcium chloride. A solution of 48 g of cis acid (m.p. 117-118° C) in 500 ml of ether, which had been previously dried with calcium hydride, was allowed to drop into the flask at such a rate that gentle boiling ensued. After the addition of acid solution, the reaction mixture was heated about an hour. Then, the flask was cooled by an ice bath and ice water was dropped into the ether solution very slowly. When such an amount of water had been added that the solution no longer boiled, a cold, dilute sulfuric acid solution, prepared from 100 ml of concentrated acid, was added until no precipitate remained. The ether layer was separated, and the water layer was extracted once with a 100-ml portion of ether. The ether extract was added to the ethereal solution and this was washed with a dilute solution of sulfuric acid, then once with water and twice with 5% aqueous sodium bicarbonate, then again with water. The washed solution was dried with magnesium sulfate, and the ether was removed by evaporation. The residue was sublimed to yield 40 g (0.24 mole, 91% conversion) of cis-4-tert-butylcyclohexylmethanol, m.p. 60-61° C.

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<sup>6</sup>Norman G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, 1956, p. 322.

Anal.<sup>7</sup> Calculated for  $C_{11}H_{22}O$ : C 77.58%; H 13.02%.

Found: C 77.65%; H 12.83%.

cis-4-tert-Butylcyclohexylmethyl-N-1-naphthylcarbamate.<sup>8</sup> About

2 ml of 1-naphthyl isocyanate (Eastman Kodak, 1816) was added to approximately 2 ml of cis-4-tert-butylcyclohexylmethanol (m.p. 60-61° C) in a specially dried test tube. The reaction mixture was heated a few minutes in a water bath, and crystals of the derivative soon formed. The derivative was dissolved in hot petroleum ether and the solution was filtered. Upon cooling the filtrate, the derivative crystallized as needles. It was recrystallized several times from petroleum ether, finally melting at 118-119° C.

Anal.<sup>9</sup> Calculated for  $C_{22}H_{29}O_2N$ : C 77.82%; H 8.61%.

Found: C 77.72%; H 8.75%.

cis-4-tert-Butylcyclohexylmethyl-N-phenylcarbamate.<sup>10</sup> About

2 ml of phenyl isocyanate (Matheson) was added to approximately 2 ml of melted cis-4-tert-butylcyclohexylmethanol (m.p. 60-61° C) in a specially dried test tube. The reaction mixture was heated a few minutes in a water bath, then allowed to cool and solidify. The derivative was recrystallized several times from petroleum ether. It melted at 90-90.5° C.

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<sup>7</sup>E. Thommen, Basel, Switzerland.

<sup>8</sup>Nicholas D. Cheronis and John B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Company, New York, 1947, p. 224.

<sup>9</sup>Thommen, loc. cit.

<sup>10</sup>Cheronis and Entrikin, loc. cit., p. 224.

Anal.<sup>11</sup> Calculated for  $C_{18}H_{27}O_2N$ : C 74.71%; H 9.41%.  
 Found: C 74.52%; H 9.46%.

Preparation of trans-4-tert-Butylcyclohexylmethanol and Derivatives

trans-4-tert-Butylcyclohexylmethanol.<sup>12</sup> The same procedure employed for the preparation of the cis alcohol was used for the preparation of the trans isomer. An ether solution consisting of 55 g of trans acid (m.p. 176-177° C) was added to 450 ml of 1 M lithium aluminum hydride in ether. About 41 g (0.24 mole, 86% conversion) of trans-4-tert-butylcyclohexylmethanol was obtained. This alcohol was distilled twice through a Podbielniak Whirling Helix-Band Mini-Cal column. A fraction boiling at 97° C/3 mm was collected ( $n_D^{30}$  1.4659,  $d_4^{30}$  0.8975,  $M_D$  observed 52.55, calculated 52.23).

Anal.<sup>13</sup> Calculated for  $C_{11}H_{22}O$ : C 77.58%; H 13.02%.  
 Found: C 77.33%; H 12.85%.

trans-4-tert-Butylcyclohexylmethyl hydrogen phthalate.<sup>14</sup>

Approximately 1 g (0.006 mole) of trans-4-tert-butylcyclohexylmethanol (b.p. 97° C/3 mm), 0.74 g (0.005 mole) of phthalic anhydride (prepared by heating phthalic acid with acetic anhydride), and 0.47 g (0.006 mole) of pyridine (dried over sodium hydroxide) were put into a test

<sup>11</sup>Thommen, loc. cit.

<sup>12</sup>Gaylord, loc. cit., p. 322.

<sup>13</sup>Clark Microanalytical Laboratory, Urbana, Illinois.

<sup>14</sup>G. A. Haggis and L. N. Owen, J. Chem. Soc., 389 (1953).

tube. This mixture was heated three hours in an oven at 120° C. After several recrystallizations from "isooctane" the derivative melted at 145.5-146.5° C.

Anal.<sup>15</sup> Calculated for C<sub>19</sub>H<sub>26</sub>O<sub>4</sub>: C 71.67%; H 8.23%.

Found: C 71.71%; H 8.31%.

trans-4-tert-Butylcyclohexylmethyl-N-1-naphthylcarbamate.<sup>16</sup>

The urethane of the trans alcohol was prepared in a manner analogous to that described for the cis isomer. After several recrystallizations, this derivative melted at 97-97.5° C.

Anal.<sup>17</sup> Calculated for C<sub>22</sub>H<sub>29</sub>O<sub>2</sub>N: C 77.82%; H 8.61%.

Found: C 78.04%; H 8.72%.

Preparation of the Isomeric Bromides of the  
4-tert-Butylcyclohexylmethanols

cis-4-tert-Butylcyclohexylmethyl Bromide.<sup>18</sup> About 41 g (0.24 mole) of cis-4-tert-butylcyclohexylmethanol (m.p. 60-61° C) was added to a 50-ml distilling flask in an oil bath. The temperature of the oil bath was kept between 115-128° C for about twelve hours during which time gaseous hydrogen bromide (Matheson, anhydrous) was bubbled into the alcohol. After addition of the hydrogen bromide, ether was added to the reaction mixture, the solution was washed once with water, several times with sodium bicarbonate solution, and finally

<sup>15</sup>Thommen, loc. cit.

<sup>16</sup>Cheronis and Entrikin, loc. cit., p. 224.

<sup>17</sup>Thommen, loc. cit.

<sup>18</sup>W. Marchwald, Ber., 37, 1038 (1904).

with water. The ether solution of the bromide was dried with anhydrous calcium chloride, and the ether was removed by evaporation. The residual bromide was washed several times with concentrated sulfuric acid, followed by water, dilute sodium bicarbonate solution, water again, and finally was dried with calcium chloride. The bromide was fractionally distilled under reduced pressure through a 1.6 X 36-cm Vigreux column, the fraction boiling at  $81.5^{\circ}$  C/3 mm being collected ( $n_D^{20}$  1.4920,  $d_4^{20}$  1.166,  $M_D$  observed 58.27, calculated 58.56).

Anal.<sup>19</sup> Calculated for  $C_{11}H_{21}Br$ : C 56.65%; H 9.08%.

Found: C 57.87%; H 9.17%.

The percentage of carbon is too high in this sample. No better analysis was obtained for a sample from a subsequent preparation,  $n_D^{30}$  1.4876, which is just slightly lower than the previous sample.

Anal.<sup>20</sup> Calculated for  $C_{11}H_{21}Br$ : C 56.65%; H 9.08%; Br 34.27%.

Found: C 55.76%; H 9.06%; Br 34.05%.

In this case, the percentage of carbon is low. A gas chromatogram<sup>21</sup> for the compound represented by the first analysis shows the presence of traces of two impurities assumed to be olefins from pyrolysis of

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<sup>19</sup>Clark, loc. cit.

<sup>20</sup>Clark, loc. cit.

<sup>21</sup>The chromatographic analysis was carried out on a Perkin-Elmer Model 154 vapor Fractometer using a packing of Apiezon L on fluebrick at  $190^{\circ}$  C. Helium was the elutant gas for a 0.005-ml sample under a column pressure of 10 psi. The flowmeter was set at a reading of 5.2, and the detector voltage was at 8.0. The analysis was carried out with the kind assistance of Mr. O. L. Gumprecht, Research Laboratory, Reichhold Chemicals, Inc., Tuscaloosa, Alabama.

the bromide. The infrared spectrum<sup>22</sup> of this bromide does not show the presence of olefinic impurities. The C-Br absorption band is at  $680\text{ cm}^{-1}$ . Consequently, these impurities may have been brought about by the action of the gas chromatographic column. However, if they were actually present in the bromide, the concentration was such that it would not be significant in a kinetic determination.

trans-4-tert-Butylcyclohexylmethyl Bromide.<sup>23</sup> About 40 g (0.24 mole) of trans-4-tert-butylcyclohexylmethanol ( $n_D^{30}$  1.4659) was added to a three-neck flask equipped with a thermometer, an addition funnel, and a glass half-moon stirrer. The alcohol was cooled to about  $10^\circ\text{ C}$  by means of an ice bath. To this, 56 g of phosphorus tribromide (Eastman Kodak, 1354) was added at such a rate that the solution was kept at about  $10^\circ\text{ C}$ . After addition of the phosphorus tribromide, the solution was stirred overnight at room temperature, then was heated at about  $80\text{-}120^\circ$  for several hours. A yellow, oily layer separated on standing. The bromide was extracted from the cooled reaction mixture with petroleum ether. The extract was washed first with water, then with aqueous sodium bicarbonate solution. When the latter was added to the petroleum ether solution of the bromide, a white solid formed. This is believed to have been the mono ester of

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<sup>22</sup>The infrared analysis was carried out on a Beckman IR-7 Infrared Spectrophotometer at a speed of  $80\text{ cm}^{-1}/\text{min}$ , gain of 2%, period 2, and slit select. The light path was 0.02 mm and the reference beam was passed through a wedge cell. No solvent was necessary. The analysis was carried out with the kind assistance of Mr. Lamar Payne and Mr. James Franklin.

<sup>23</sup>G. S. Hiers and R. Adams, J. Am. Chem. Soc., 48, 2385 (1926).

phosphorous acid and the alcohol. The bromide was extracted from this solid with petroleum ether. The extract was washed with water, then was dried with anhydrous calcium chloride. The petroleum ether was removed under reduced pressure, and the bromide was distilled under reduced pressure from a small Claisen flask. The distillate was fractionally distilled through a Podbielniak Whirling Heli-Band Mini-Cal column. A fraction boiling at 78° C/1.8 mm pressure was collected ( $n_D^{20}$  1.4884,  $d_4^{20}$  1.151,  $M_D$  observed 58.37, calculated 58.27).

Anal.<sup>24</sup> Calculated for  $C_{11}H_{21}Br$ : C 56.65%; H 9.08%; Br 34.27%.

Found: C 56.14%; H 9.46%; Br 34.39%.

The results of the analysis show that the calculated value for the percentage of bromine agrees well with the value found, but the carbon and hydrogen percentages are too far off. Neither the gas chromatogram<sup>25</sup> nor the infrared spectrum<sup>26</sup> for this compound shows an impurity. The C-Br absorption band is at 655  $cm^{-1}$ .

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<sup>24</sup>Clark, loc. cit.

<sup>25</sup>The chromatographic analysis was carried out on a Perkin-Elmer Model 154 vapor Fractometer using a packing of Apiezon L on fluebrick at 190° C. Helium was the elutant gas for a 0.005-ml sample under a column pressure of 10 psi. The flowmeter was set at a reading of 5.2, and the detector voltage was at 8.0. The analysis was carried out with the kind assistance of Mr. O. L. Gumprecht, Research Laboratory, Reichhold Chemicals, Inc., Tuscaloosa, Alabama.

<sup>26</sup>The infrared analysis was carried out on a Beckman IR-7 Infrared Spectrophotometer at a speed of 80  $cm^{-1}/min$ , gain of 2%, period 2, and slit select. The light path was 0.02 mm and the reference beam was passed through a wedge cell. No solvent was necessary. The analysis was carried out with the kind assistance of Mr. Lamar Payne and Mr. James Franklin.

## Kinetic Studies

The acetone used in these kinetic studies was purified according to the method of Conant and Kirner.<sup>27</sup> Acetone (Baker and Adamson, Reagent, A. C. S.) was refluxed with solid sodium hydroxide and potassium permanganate for several hours. It was filtered, then distilled through a 1.5 X 115-cm column packed with glass helices. The column was vented through a tube of calcium chloride. The fraction boiling at 56.5-57° C was collected.

Potassium iodide (Baker and Adamson, Reagent, A. C. S.) was dried in an oven at 110° C for several hours. It was kept in a desiccator.

Weighed quantities of the cis- and trans-4-tert-butylcyclohexylmethyl bromides were added to 100-ml volumetric flasks and acetone was added to dilute the solutions to 100 ml. For each kinetic study, 5 ml of 0.04000 M potassium iodide solution was pipetted into a 25-ml round-bottom flask fitted with a standard taper joint, and 5 ml of the 0.04000 M alkyl bromide solution was added directly to make the total volume 10 ml. The flask was stoppered and immediately was put into the constant temperature bath. Because the reactions were relatively slow, the time of mixing was taken as zero time. The results are shown in Tables 1 through 5 and Figures 1 through 5.

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<sup>27</sup>J. B. Conant and W. R. Kirner, J. Am. Chem. Soc., 46, 232 (1924).

TABLE 1

Bimolecular Nucleophilic Attack of Iodide Ion on trans-4-tert-Butylcyclohexylmethyl Bromide at 250 C

Time hrs	KIO <sub>3</sub> , ml <sup>a</sup> 0.004351 N	Concentration of Reactants mole/liter		K <sub>2</sub> X 10 <sup>5</sup> liter/mole-sec
		KI <sup>b</sup>	RBr <sup>c</sup>	
0	45.97	0.02000	0.02000	
22.72	40.80	0.01775	0.01775	7.75
35.40	38.42	0.01672	0.01672	7.70
48.00	36.36	0.01582	0.01582	7.65
76.32	33.11	0.01441	0.01441	7.06
100.62	30.62	0.01332	0.01332	6.92
Average				7.42

<sup>a</sup>This solution was prepared by weighing 0.9310 g of potassium iodate (Mallinckrodt Analytical Reagent), which had been previously dried for several hours at 110° C and kept in a desiccator, and diluting to 2 liters in a volumetric flask.

<sup>b</sup>The initial concentration of potassium iodide was obtained by weighing 3.3202 g of potassium iodide and diluting to 500 ml with acetone in a volumetric flask. A 5-ml aliquot was taken. The molarity was checked by titrating with the standard potassium iodate solution.

<sup>c</sup>The initial concentration of trans-4-tert-butylcyclohexylmethyl bromide was obtained by weighing 0.9328 g of trans-4-tert-butylcyclohexylmethyl bromide and diluting to 100 ml with acetone in a volumetric flask. A 5-ml aliquot was taken.

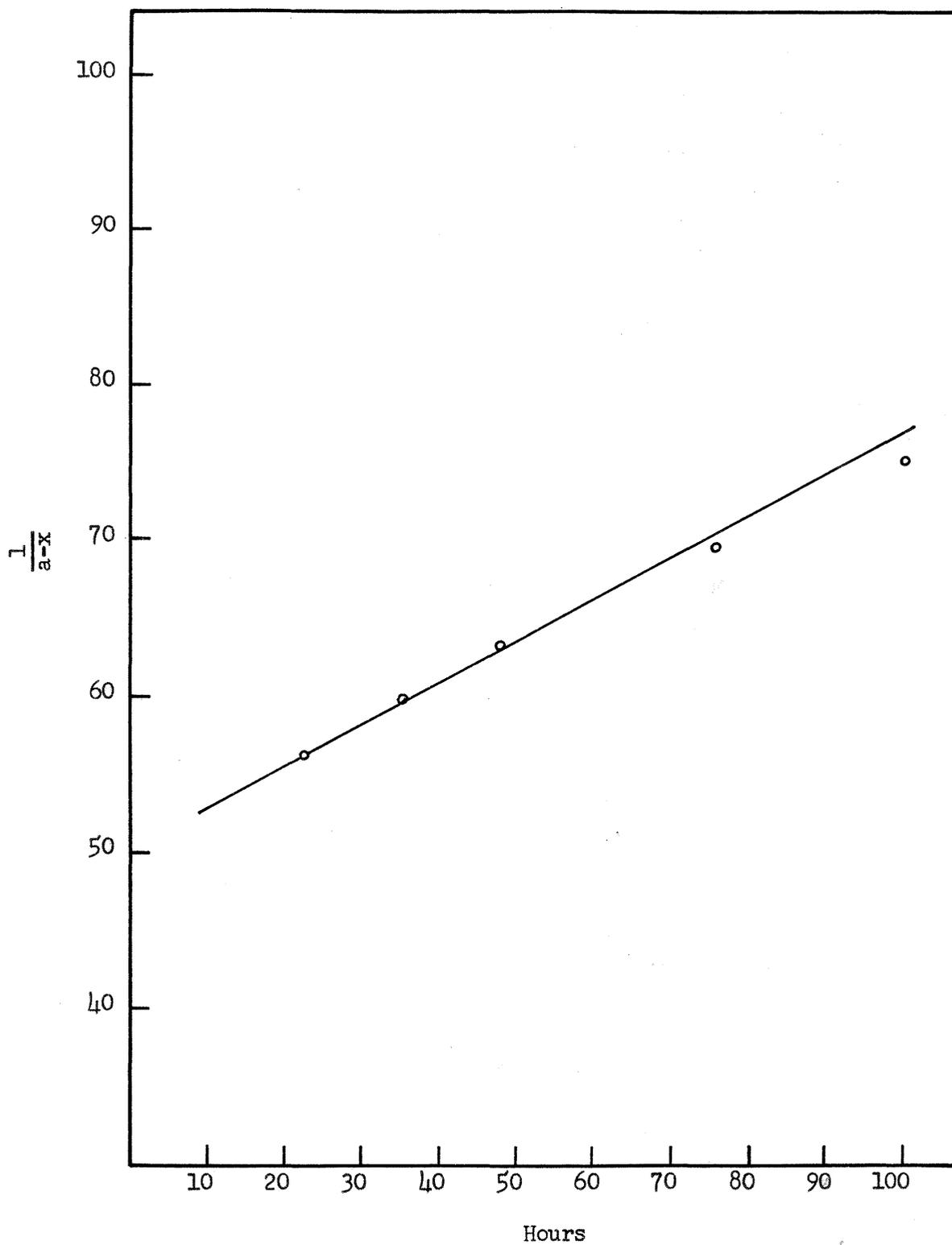


Figure 1. S<sub>2</sub> attack of iodide ion on trans-4-tert-  
butylcyclohexylmethyl bromide at 25° C.

TABLE 2

Bimolecular Nucleophilic Attack of Iodide Ion on trans-4-tert-Butylcyclohexylmethyl Bromide at 35° C

Time hrs	KIO <sub>3</sub> , ml <sup>a</sup> 0.004351 N	Concentration of Reactants mole/liter		K, X 10 <sup>4</sup> liter <sup>2</sup> /mole-sec
		KI <sup>b</sup>	RBr <sup>c</sup>	
0	45.97	0.02000	0.02000	
12.20	39.35	0.01712	0.01712	1.92
15.11	37.50	0.01632	0.01632	2.07
24.00	33.70	0.01467	0.01467	2.10
29.50	31.85	0.01386	0.01386	2.09
42.40	28.35	0.01231	0.01231	2.09
Average				2.05

<sup>a</sup>This solution was prepared by weighing 0.9310 g of potassium iodate (Mallinckrodt Analytical Reagent), which had been previously dried for several hours at 110° C and kept in a desiccator, and diluting to 2 liters in a volumetric flask.

<sup>b</sup>The initial concentration of potassium iodide was obtained by weighing 3.3202 g of potassium iodide and diluting to 500 ml with acetone in a volumetric flask. A 5-ml aliquot was taken. The molarity was checked by titrating with the standard potassium iodate solution.

<sup>c</sup>The initial concentration of trans-4-tert-butylcyclohexylmethyl bromide was obtained by weighing 0.9328 g of trans-4-tert-butylcyclohexylmethyl bromide and diluting to 100 ml with acetone in a volumetric flask. A 5-ml aliquot was taken.

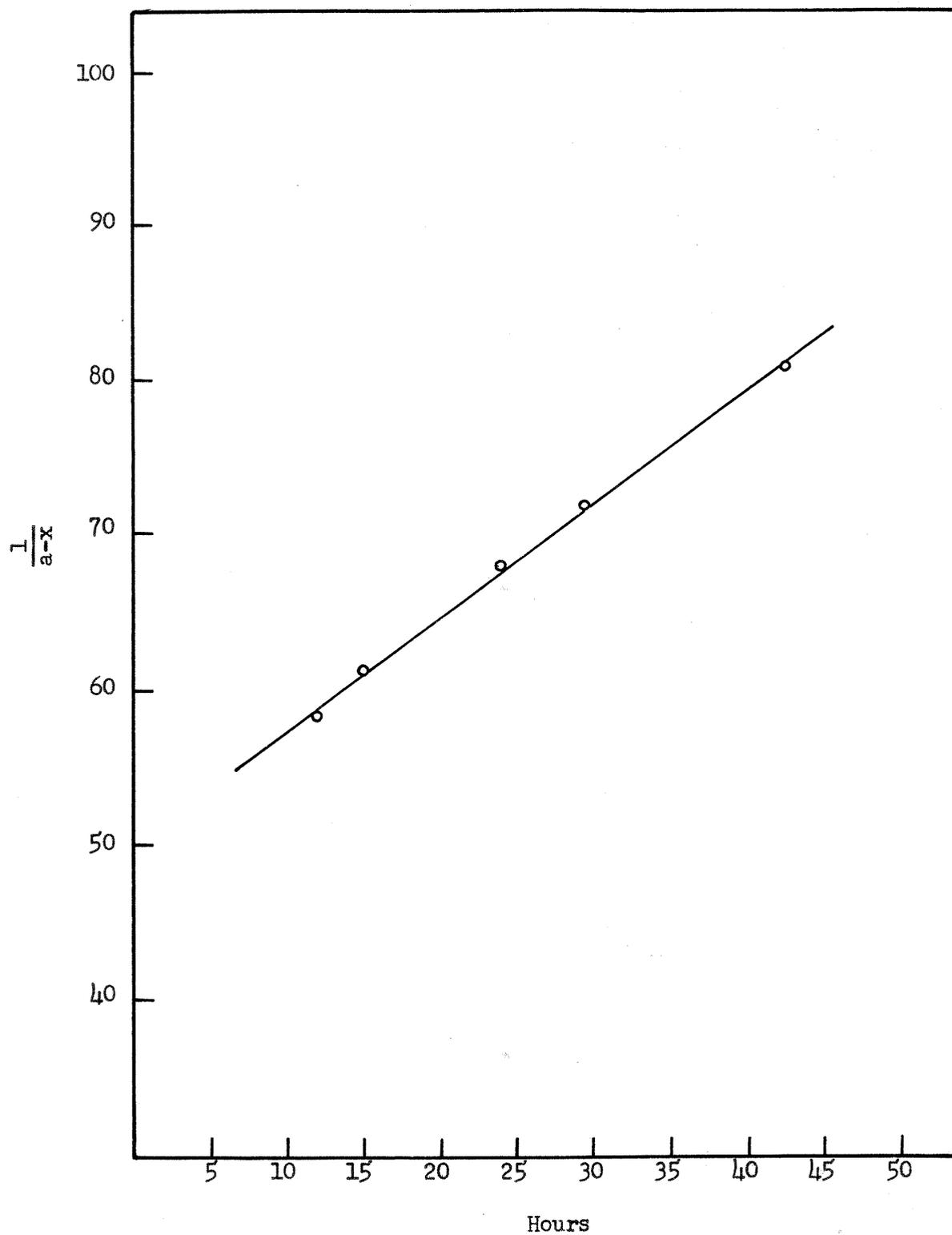


Figure 2. S<sub>2</sub> attack of iodide ion on trans-4-tert-butylcyclohexylmethyl bromide at 35° C.

TABLE 3

Bimolecular Nucleophilic Attack of Iodide Ion on trans-4-tert-Butylcyclohexylmethyl Bromide at 50° C

Time hrs	KIO <sub>3</sub> , ml <sup>a</sup> 0.004351 N	Concentration of Reactants mole/liter		K <sub>2</sub> X 10 <sup>4</sup> liter/mole-sec
		KI <sup>b</sup>	RBr <sup>c</sup>	
0	45.97	0.02000	0.02000	
6.00	33.21	0.01445	0.01445	8.89
9.27	28.12	0.01224	0.01224	9.51
11.18	26.10	0.01136	0.01136	9.45
19.92	21.35	0.00929	0.00929	8.23
Average				9.02

<sup>a</sup>This solution was prepared by weighing 0.9310 g of potassium iodate (Mallinckrodt Analytical Reagent), which had been previously dried for several hours at 110° C and kept in a desiccator, and diluting to 2 liters in a volumetric flask.

<sup>b</sup>The initial concentration of potassium iodide was obtained by weighing 3.3202 g of potassium iodide and diluting to 500 ml with acetone in a volumetric flask. A 5-ml aliquot was taken. The molarity was checked by titrating with the standard potassium iodate solution.

<sup>c</sup>The initial concentration of trans-4-tert-butylcyclohexylmethyl bromide was obtained by weighing 0.9328 g of trans-4-tert-butylcyclohexylmethyl bromide and diluting to 100 ml with acetone in a volumetric flask. A 5-ml aliquot was taken.

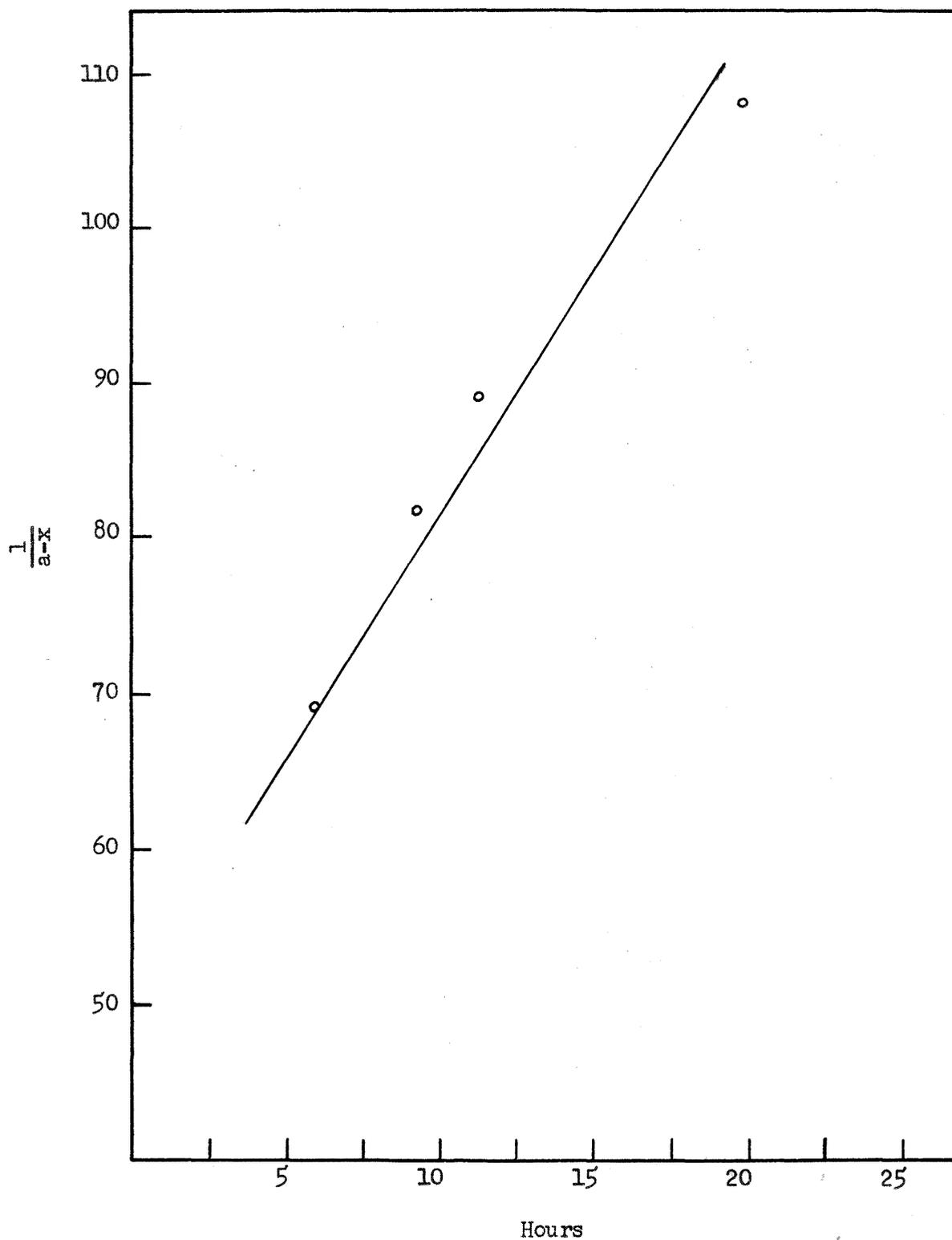


Figure 3.  $S_N2$  attack of iodide ion on trans-4-tert-butylcyclohexylmethyl bromide at  $50^\circ\text{C}$ .

TABLE 4

Bimolecular Nucleophilic Attack of Iodide Ion on *cis*-  
4-tert-Butylcyclohexylmethyl Bromide at 45° C

Time hrs	KIO <sub>3</sub> , ml <sup>a</sup> 0.004351 N	Concentration of Reactants mole/liter		K <sub>2</sub> X 10 <sup>5</sup> liter/mole-sec
		KI <sup>b</sup>	RBr <sup>c</sup>	
0	45.97	0.02000	0.02000	
42.17	43.23	0.01881	0.01881	2.08
49.50	43.00	0.01871	0.01871	1.94
138.42	38.30	0.01666	0.01666	2.01
167.60	37.85	0.01647	0.01647	1.78
224.32	35.31	0.01536	0.01536	1.87
Average				1.94

<sup>a</sup>This solution was prepared by weighing 0.9310 g of potassium iodate (Mallinckrodt Analytical Reagent), which had been previously dried for several hours at 110° C and kept in a desiccator, and diluting to 2 liters in a volumetric flask.

<sup>b</sup>The initial concentration of potassium iodide was obtained by weighing 3.3202 g of potassium iodide and diluting to 500 ml with acetone in a volumetric flask. A 5-ml aliquot was taken. The molarity was checked by titrating with the standard potassium iodate solution.

<sup>c</sup>The initial concentration of *cis*-4-tert-butylcyclohexylmethyl bromide was obtained by weighing 0.9328 g of *cis*-4-tert-butylcyclohexylmethyl bromide and diluting to 100 ml with acetone in a volumetric flask. A 5-ml aliquot was taken.

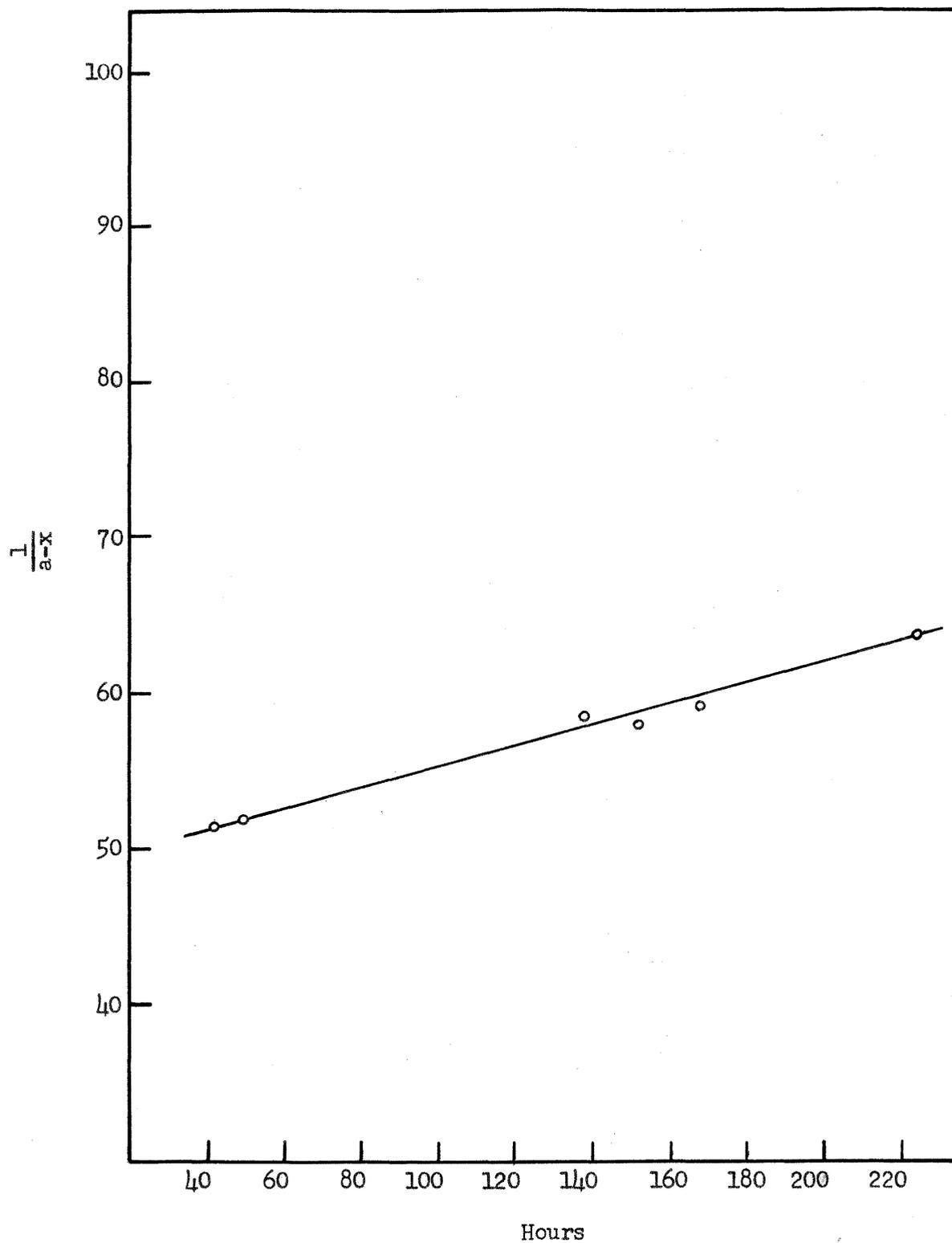


Figure 4. S<sub>2</sub> attack of iodide ion on cis-4-tert-butyl-  
cyclohexylmethyl bromide at 45° C.

TABLE 5

Bimolecular Nucleophilic Attack of Iodide Ion on *cis*-4-tert-Butylcyclohexylmethyl Bromide at 50° C

Time hrs	KIO <sub>3</sub> , ml <sup>a</sup> 0.064351 N	Concentration of Reactants mole/liter		K X 10 <sup>5</sup> liter <sup>2</sup> /mole-sec
		KI <sup>b</sup>	RBr <sup>c</sup>	
0	45.97	0.02000	0.02000	
38.33	42.80	0.01862	0.01862	2.69
42.02	42.24	0.01838	0.01838	2.91
49.33	41.35	0.01799	0.01799	3.15
75.93	38.54	0.01677	0.01677	3.44
103.27	36.35	0.01581	0.01581	3.56
139.03	35.10	0.01527	0.01527	3.09
225.25	30.50	0.01327	0.01327	3.13
Average				3.14

<sup>a</sup>This solution was prepared by weighing 0.9310 g of potassium iodate (Mallinckrodt Analytical Reagent), which had been previously dried for several hours at 110° C and kept in a desiccator, and diluting to 2 liters in a volumetric flask.

<sup>b</sup>The initial concentration of potassium iodide was obtained by weighing 3.3202 g of potassium iodide and diluting to 500 ml with acetone in a volumetric flask. A 5-ml aliquot was taken. The molarity was checked by titrating with the standard potassium iodate solution.

<sup>c</sup>The initial concentration of *cis*-4-tert-butylcyclohexylmethyl bromide was obtained by weighing 0.9328 g of *cis*-4-tert-butylcyclohexylmethyl bromide and diluting to 100 ml with acetone in a volumetric flask. A 5-ml aliquot was taken.

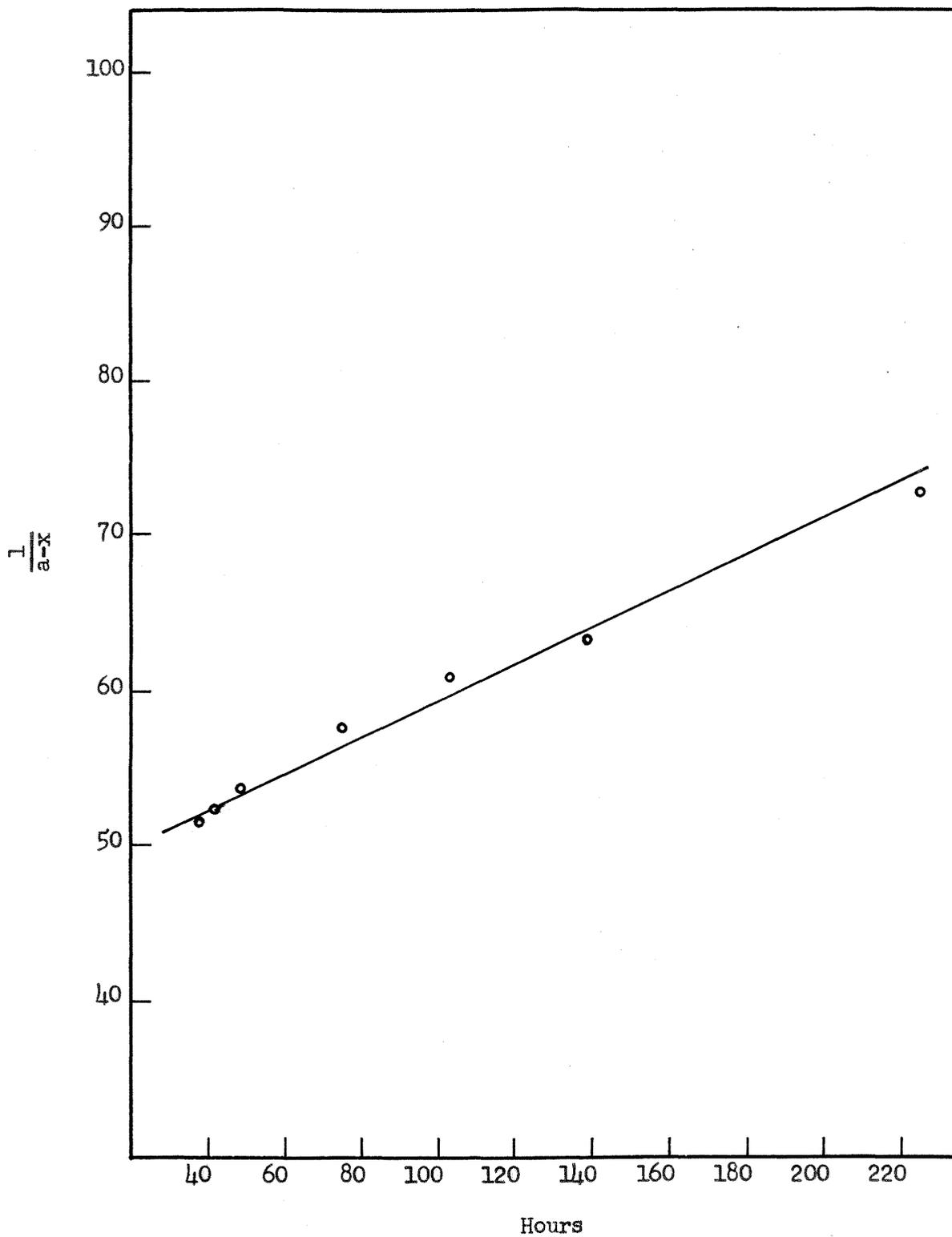


Figure 5. S<sub>N</sub>2 attack of iodide ion on cis-4-tert-butyl-cyclohexylmethyl bromide at 50° C.

All solutions of potassium iodide in acetone and the organic bromides in acetone were kept in a dark place, and the volumetric flasks were made opaque by wrapping with aluminum foil.<sup>28</sup> The reaction vessels in all experiments also were wrapped with aluminum foil. At a specific time the reaction was stopped by quenching with a mixture of crushed ice and water,<sup>29</sup> and 20 ml of a solution of sulfuric and hydrochloric acids (12 N in sulfuric and 3 N in hydrochloric) was added to acidify the solution. Then 5 ml of a 15% aqueous solution of potassium cyanide and about 0.4 ml of freshly prepared starch solution were added, and the solution was titrated with standard potassium iodate to the disappearance of the blue color.<sup>30</sup>

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<sup>28</sup>Jack Hine, Cyrus H. Thomas, Stanton J. Ehrenson, J. Am. Chem. Soc., 77, 3886 (1955).

<sup>29</sup>I. Dostrovsky and E. D. Hughes, loc. cit., p. 164.

<sup>30</sup>R. Lang, Z. Anorg. Allgem. Chem., 144, 75 (1925); C. A., 19, 2316 (1925).

## CHAPTER IV

### INTERPRETATION OF EXPERIMENTAL RESULTS

The rate constants for  $S_N2$  attack of iodide ion in dry acetone on n-butyl bromide, cyclopentylmethyl bromide, and cyclohexylmethyl bromide were determined previously.<sup>1</sup> At that time the rate constant for n-butyl bromide also was determined in order to make a comparison with the constants reported by Bartlett and Rosen<sup>2</sup> for n-butyl bromide, 2-methyl-1-butyl bromide, and neopentyl bromide. In the present study, the rate constant for n-butyl bromide again was determined in order to compare the constants already reported with those in this study. It was found again that the value for n-butyl bromide is in agreement with that determined earlier so that a comparison can be made. The relative and absolute rates are shown in Table 6. There it can be seen that cyclohexylmethyl bromide and trans-4-tert-butylcyclohexylmethyl bromide react at about the same rate and much faster than neopentyl bromide, but cis-4-tert-butylcyclohexylmethyl bromide reacts about half as fast as neopentyl bromide.

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<sup>1</sup>G. C. Williams, loc. cit.

<sup>2</sup>Bartlett and Rosen, loc. cit., p. 543.

TABLE 6

Comparative Rates of Bimolecular Displacement on Alkyl Bromides  
by Iodide Ion in Acetone Solution at 25° C

Alkyl Bromide	Absolute Rate Liter/mole-sec	Relative Rate
<u>n</u> -Butyl	$1.7 \times 10^{-3}$	474
2-Methyl-1-Butyl	$1.1 \times 10^{-4}$	29
Cyclohexylmethyl	$6.4 \times 10^{-5}$	18
Cyclopentylmethyl	$5.7 \times 10^{-5}$	15
Neopentyl	$3.8 \times 10^{-6}$	1
<u>trans</u> -4- <u>tert</u> -Butylcyclohexylmethyl	$7.4 \times 10^{-5}$	19
<u>cis</u> -4- <u>tert</u> -Butylcyclohexylmethyl <sup>a</sup>	$1.8 \times 10^{-6}$	0.47

<sup>a</sup> Calculated rate.

The molar energies of activation for the reaction of potassium iodide in acetone with cyclopentylmethyl bromide, cyclohexylmethyl bromide, trans-4-tert-butylcyclohexylmethyl bromide, and cis-4-tert-butylcyclohexylmethyl bromide are respectively 20.2, 20.6, 19.0, and 22.0 kcal. The corresponding values for cyclopentylmethyl bromide and cyclohexylmethyl bromide were determined previously<sup>3</sup> from the rates of reaction at three temperatures and then according to the Arrhenius equation by plotting log k versus 1/T. The activation energy for trans-4-tert-butylcyclohexylmethyl bromide was determined by averaging the values determined by using the integrated form of the Arrhenius equation. For the calculation of the activation energy of cis-4-tert-butylcyclohexylmethyl bromide, the integrated form of the Arrhenius equation was used.

The entropies of activation were calculated at 25° C according to the equation<sup>4</sup>

$$k_2 = \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

in which

$k_2$  is the rate constant,

$k$  is Boltzman's constant,

$h$  is Planck's constant,

$\Delta S^*$  is the entropy of activation,

$T$  is the absolute temperature,

<sup>3</sup>Williams, loc. cit.

<sup>4</sup>Keith J. Laidler, "Chemical Kinetics," McGraw-Hill Book Company, Inc., New York, 1950, p. 75.

R is the gas constant, and

$\Delta H^*$  is the energy of activation.

Cis-4-tert-butylcyclohexylmethyl bromide has a  $\Delta S^*$  value of -11.1 cal/mole-deg and trans-4-tert-butylcyclohexylmethyl bromide has a  $\Delta S^*$  value of -13.6 cal/mole-deg. Previously, cyclopentylmethyl bromide had been found to have a  $\Delta S^*$  value of -10.1 cal/mole-deg and cyclohexylmethyl bromide a value of -8.6 cal/mole-deg. Because Bartlett and Rosen made rate determinations at only one temperature, it is not possible to estimate activation energies and entropies for comparison with these values.

Since it was found earlier that cyclopentylmethyl bromide has a lower activation entropy than cyclohexylmethyl bromide, it was concluded that the cyclohexylmethyl bromide molecule is more favorably oriented for assuming the transition state. Examination of the Stuart model of the cyclohexylmethyl bromide molecule indicates that the lowest energy conformation of cyclohexylmethyl bromide is the one in which the bromomethyl group is equatorial to the ring. Examination of the Stuart model of the trans-4-tert-butylcyclohexylmethyl bromide molecule shows that (assuming the tert-butyl group is equatorial) the only conformation of the bromomethyl group is that in which the bromomethyl group is equatorial. But the entropy of activation of trans-4-tert-butylcyclohexylmethyl bromide is lower than that of cyclohexylmethyl bromide and this lower value probably indicates that there is less probability that the molecule will assume the transition state. Thus, because the tert-butyl group restricts the conformation of the bromomethyl group, the bromomethyl group is not as free to assume the transition state as the equatorial bromomethyl group which does not have this restriction.

Examination of the Stuart model of the cis-4-tert-butylcyclohexylmethyl bromide molecule indicates that a rear attack on the carbon atom to which the bromine atom is attached is greatly hindered, and the rate constant, which is about one-half that of neopentyl bromide, confirms this; however, the entropy of activation value of the cis compound is slightly more positive than that of the trans. One must conclude that although attack of iodide ion is difficult, the molecule must be favorably oriented for assuming the transition state.

Because the molecular conformation favorable for reaction is the most ordered conformation, energy must be supplied to a molecule to effect the ordered transition conformation. When the reaction conformation is realized, the transition state can begin to be formed. The probability that a molecule is in the favorable conformation for reaction is shown by the magnitude of the entropy of activation; thus, the more positive the entropy of activation, the greater the probability of assuming the transition state. The model shows that in the cis-4-tert-butylcyclohexylmethyl bromide molecule, the bromomethyl group is turned such that the rear of the carbon is toward the tert-butyl group. However, attack of the iodide ion from that direction is greatly hindered because of the presence of the tert-butyl group and the gamma hydrogen atoms. Thus, the favorable conformation for rear attack on the carbon to which the bromine atom is attached is that represented in Figure 1, wherein the bromomethyl group is turned such that the large iodide ion can approach at an angle of about  $45^\circ$ . In this conformation the bromine atom is trans to either of the beta methylene groups of the cyclohexane ring. Another possible conformation is that in which the bromine atom is oriented toward the tert-butyl

group. In this conformation, rear attack is not hindered, but since the path of the leaving group must be considered, it would seem almost impossible for the bromine atom to leave in the direction of the tert-butyl group. In other words, there is steric hindrance to departure of the bromine.

The transition state of trans-4-tert-butylcyclohexylmethyl bromide is shown in Figure 2. In this transition conformation, which must be the most ordered one, the bromine atom is cis to the tert-butyl group. This transition conformation seems most likely because the approach of the iodide ion is unhindered, although the leaving bromine atom does encounter some repulsion by the gamma hydrogen atoms.

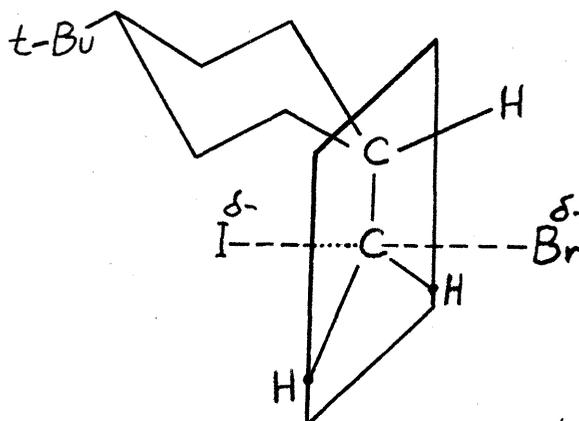


Figure 1

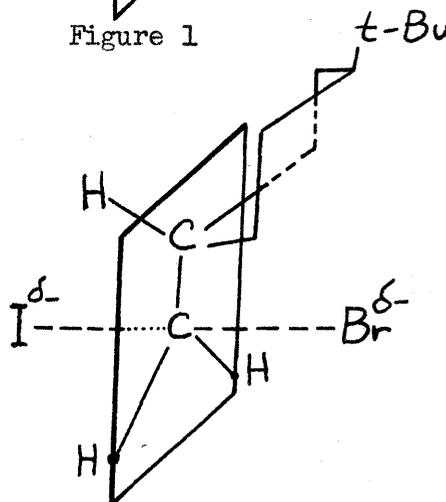


Figure 2

## CHAPTER V

### SUMMARY

The rates of  $S_N2$  attack of iodide ion in acetone on trans-4-tert-butylcyclohexylmethyl bromide were determined at 25°, 35°, and 50° C, and on cis-4-tert-butylcyclohexylmethyl bromide at 45° and 50° C, and were found to be  $3.1 \times 10^{-5}$  liter/mole-sec for the cis bromide and  $9.0 \times 10^{-4}$  liter/mole-sec for the trans bromide. These reaction rates are compared with those previously determined for cyclopentylmethyl bromide, cyclohexylmethyl bromide, and neopentyl bromide. The trans bromide reacts at about the same rate as these cyclic bromides and much faster than neopentyl bromide, while the cis bromide reacts much more slowly, about one-half as fast as neopentyl bromide.

The molar energies of activation for the cis and trans bromides are respectively 22.0 and 19.0 kcal. The entropies of activation for the cis and trans bromides are respectively -11.1 and -13.6 cal/mole-deg. Although the cis isomer reacts more slowly than the trans, the activation entropy of the cis isomer is lower than that of the trans. The lower activation entropy of the trans isomer probably indicates that this isomer does not assume the transition state as easily as the cis isomer.

New compounds which were prepared are cis-4-tert-butylcyclohexylmethanol, cis-4-tert-butylcyclohexylmethyl-N-1-naphthylcarbamate, cis-4-tert-butylcyclohexylmethyl-N-phenylcarbamate, cis-4-tert-butylcyclohexylmethyl bromide, trans-4-tert-butylcyclohexylmethanol, trans-4-tert-butylcyclohexylmethyl hydrogen phthalate, trans-4-tert-butylcyclohexylmethyl-N-1-naphthylcarbamate, and trans-4-tert-butylcyclohexylmethyl bromide.

APPENDIX

## APPENDIX

### METHODS OF CALCULATIONS

Molar Refraction:

$$M_D = \frac{(n^2 - 1)}{(n^2 + 2)} \cdot \frac{M}{d}$$

$M_D$  = Molar Refraction from Sodium-D light.  
 $n$  = Index of Refraction at  $t^\circ$  C.  
 $M$  = Molecular Weight.  
 $d$  = Density at  $t^\circ$  C.

Rate Constants:

$$k_2 = \frac{x}{at(a-x)}$$

$a$  = Initial Concentration of the Organic Bromide.

$a$  = Initial Concentration of Potassium Iodide.

$a-x$  = Concentration of Potassium Iodide at time  $t$ .

$a-(a-x) = x$  or Concentration of the Organic Iodide at time  $t$ .

Activation Energy:

$$\log \frac{k_2}{k_1} = \frac{\Delta E (T_2 - T_1)}{2.303R(T_1 T_2)}$$

$k_2$  = the Rate Constant at  $T_2$ , the temperature at which the rate was determined.

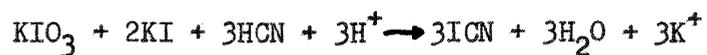
$k_1$  = the Rate Constant at  $T_1$ , the temperature at which the rate was determined.

$\Delta H^* = \Delta E =$  Activation Energy.

$R = 1.986$  cal/deg-mole.

Method of Determination of Potassium Iodide:

The potassium iodide was determined according to the following equation:



In this study the equivalent weight of the potassium iodate is one-half of the molecular weight; however, by definition the equivalent weight of the potassium iodate is one-fourth of the molecular weight, and the equivalent weight of the potassium iodide is one-half the molecular weight.

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