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The Ozonolysis of Organomercurials

by

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B.A., St. Cloud State College, 1968

Presented in partial fulfillment of the requirements
for the degree of

Master of Science

UNIVERSITY OF MONTANA

1970

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ACKNOWLEDGEMENTS

I wish to express my appreciation to my advisor, Dr. W. L. Waters, for guidance and helpful suggestions in this research.

I wish to thank Dr. R. E. Erickson for his many helpful suggestions.

I also wish to thank my wife, Emily, for her inspiration and assistance in writing this thesis, as well as my children, Paula and Damian, for their patience and understanding.

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CHAPTER I

INTRODUCTION

Objective of the Research

The primary objective of this research was to determine if ozone would cleave a carbon-mercury bond. If cleavage occurred, the products of this reaction were to be identified and yields found for various organomercurials.

The overall objective of this research was to provide a starting point for the long term project of developing the synthetic utility of ozonation coupled with mercuriation reactions.

Literature Background

Electrophilic Attack of Carbon-Mercury Bond. Since mercuric ions are easily able to bear positive charges, organomercurials would be expected to be especially susceptible to electrophilic substitution at carbon.

1. Halogen. The carbon-mercury bond is attacked electrophilically by halogens. An example of this is the electrophilic attack of bromine on the carbon-mercury bond as shown by Jensen and Gale.¹

Dialkyl mercury compounds react rapidly with halogen to give an alkyl halide and an alkyl-mercuric halide. Alkyl-mercuric halides react more slowly with halogen to give an

alkyl halide and a mercuric halide.

2. Protic Acids. The carbon-mercury bond cleavage by protic acids is also electrophilic as described in Electrophilic Substitution of Organomercurials.² Here it is shown that cleavage is much more rapid for dialkyl mercury compounds than for the alkyl mercuric salts. This infers that the reactions are electrophilic cleavages since electron-negative elements attached to mercury would lower the electron density at the reaction site.

3. Mercuric Salts. It has also been shown that the carbon-mercury bond undergoes electrophilic attack by mercuric salts.³

where ${}^*Hg = Hg^{203}$

Diethyl mercury reacts 125 times slower than diphenyl mercury which supports the supposition that electrophilic substitution takes place more slowly at a saturated carbon than at an aryl carbon.

As stated by Jensen and Rickborn⁴ the relative rates of electrophilic substitution will depend on small structural as well as electronic changes in the molecule. The carbon-mercury bond in the structure C-Hg-C has about 8% ionic character whereas the carbon-mercury bond in the structure C-Hg-Cl has less than 8% ionic character due to the electronegative halogen atom. Therefore one would expect the relative rate of electrophilic attack to be C-Hg-C > C-Hg-I > C-Hg-Br > C-Hg-Cl > C-Hg-F.

Ozonolysis of Carbon-Metal Bonds

1. Carbon-Tin. Ozone was reacted with tetraethyl tin in a 1:1 ratio in nonane at an unspecified temperature⁵ and gave acetaldehyde, diethyl tin oxide, and an unidentified organotin compound which was a peroxide.

2. Carbon-Lead. Aleksandrov and Sheyanov⁶ reported that in the reaction of ozone with tetraethyl lead the reaction mixture turned brown at 20°C and formed triethyl lead hydroxide, diethyl lead oxide, triethyl-ethoxy lead, acetaldehyde and ethanol.

The yields of this reaction were little affected by temperature.

In another reference lead was ozonized for the purpose of removing the former from the air.⁷

3. Carbon-Silicon. There has been much work on the reaction of ozone with the carbon silicon bond.

When tetraethyl silane was treated with ozone⁸ the products were acetic acid, hydrogen peroxide, triethylsilyl hydroperoxide and hexaethyl disiloxane.

Spailter and Austin⁹ found that when they ozonized hexaethyl disiloxane at room temperature they got a mixture of silicon compounds. The ethyl groups which were cleaved were subsequently identified in the product mixture as acetic acid. They also found that the cleavage of the ethyl-silicon bond was not complete even after a reaction time of forty hours.

4. Carbon-Selenium. G. Ayrey and workers¹⁰ found that when dialkyl monoselenides were reacted with ozone the products were selenoxides. These selenoxides then slowly decomposed to the aldehyde and the alkyl selenide.

5. Carbon-Mercury. The only reference found on ozonation of organomercurials was by Bockemuller and Pfeuffer.¹¹ Three sentences in the experimental section of their paper entitled "Induced Peroxide Formation in the Bromination of Olefins" stated that ozonolysis of diisopropyl mercury yielded acetone, which was identified by its 2,4-dinitrophenylhydrozone derivative.

CHAPTER II

EXPERIMENTAL

Instrumentation

All nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian Associates Model HA-60 Analytical NMR Spectrometer. Probe temperatures for all spectra were between 33-37°C. Solutions were generally 20% in deuteriochloroform using a small amount of CHCl_3 for a lock signal.

All melting points were taken using a Meltemp melting point apparatus. The melting points were not corrected.

All vapor-phase chromatography (v.p.c.) was performed on a Beckman GC-2A Gas Chromatograph employing a thermal conductivity detector. The columns used were a 6' x $\frac{1}{4}$ ", 30% Carbowax 20 M on Chromasorb W and a 6' x $\frac{1}{4}$ ", 20% SE-30 on Chromasorb W. Hereafter in this thesis they will be referred to as the "Carbowax" or the "SE-30" column. All internal standards were reagent grade and were used without further purification. All products which were identified by vapor-phase chromatography were identified by retention times of known compounds under identical conditions. Those yields found by vapor-phase chromatography were of the raw reaction mixture with internal standard added unless stated otherwise.

X-ray powder diffraction patterns were taken with a Nurelco Analytical X-ray Diffractometer. The diffraction analysis specifications were as follows: scale factor 16, multiplier 0.8, time constant 1 at 30 kilovolts and 20 milliamperes, scan time -1° per minute using the span 50° to 18° . The X-ray powder diagrams were made using a copper tube and a nickel filter.

Experimental Apparatus

The ozone was produced by a Welsbach T-408 electric discharge ozonator. Ozone was produced at the rate of 18-26 millimoles per hour. The flow rate of ozone was determined by the standard iodide-thiosulfate method. To obtain the flow rate, the ozone was allowed to flow through a KI solution for a few minutes. This solution was then made acidic and titrated with a 0.1 molar solution of sodium thiosulfate.

The equation used to find the flow rate is:

$$(\text{Liters}) (\text{Molarity}) \left(\frac{1}{2}\right) \left(\frac{1}{\text{time}}\right) = \frac{\text{moles O}_3}{\text{min.}}$$

Liters = liters of $\text{Na}_2\text{S}_2\text{O}_3$ used.

Molarity = molarity of $\text{Na}_2\text{S}_2\text{O}_3$ used.

time = number of minutes O_3 was passed through KI solution.

Oxygen was used as the carrier gas in all experiments unless specifically stated otherwise. The ozonation temperatures were maintained by the following methods: -76°C was

O Z O N A T I O N A P P A R A T U S

maintained by using a dry ice acetone bath, 0°C was obtained with an ice water mixture, and 10°C was obtained by carrying out the reaction in a large Dewar vacuum flask, with addition of crushed ice periodically to maintain the desired temperature.

Chemicals

The diethyl ether used to prepare the Grignard reagents was anhydrous Baker Analytical Reagent and without further purification was stored over sodium wire. The dichloromethane used as a solvent for ozonations was Eastman Spectra grade. The magnesium used to prepare the Grignard reagents was J. T. Baker purified magnesium chips which were stored in a desiccator with P_2O_5 . The mercuric bromide and mercuric chloride were Mallinckrodt Analytical Reagents and were used without further purification.

Preparation and Ozonation of Organomercurials

All organomercuric halides except 1-chloromercuri-2-methoxycyclohexane were prepared using the Grignard method as outlined by C. S. Marvel, C. G. Gauerke and E. L. Hill¹² and references cited therein.

The dialkyl mercurials were prepared using the Grignard method as outlined by Gilman and Brown¹³ and references cited therein.

1-Bromomercurihexane. Aldrich white label 1-bromohexane was purified following the procedure outlined in Purification

of Laboratory Chemicals.¹⁴ The 1-bromohexane was shaken with sulphuric acid. It was then washed three times with distilled water and dried with K_2CO_3 . On fractional distillation the center portion (87-88°C at 90 mm.) was saved for use (lit.¹⁵ b.p. 155 at 743 mm.).

The corresponding Grignard reagent was prepared by slowly adding with vigorous stirring 130 g. (0.78 mole) of 1-bromohexane, diluted to 250 ml. with diethyl ether, to 200 ml. diethyl ether containing 24.3 g. (1.0 mole) magnesium chips. The addition took 3 hours. The solution of the Grignard reagent was then filtered through glass wool. This was done to remove any unreacted magnesium since metallic magnesium will reduce mercuric salts to mercurous salts¹⁶ and thereby lower the yield of organomercurials. The solution of the Grignard reagent was then diluted to 1000 ml. with diethyl ether and cooled in an ice bath. To this solution 180 g. (0.5 mole) of finely ground mercuric bromide in 5 g. portions was added through an efficient condenser at 5 minute intervals. The reaction mixture was stirred vigorously at all times to prevent caking. When the addition of mercuric bromide was complete, the condenser was rinsed with diethyl ether. The reaction was then refluxed for 2 hours.

The reaction mixture was again cooled in an ice bath, after which 300 ml. of ice water was added very slowly through the condenser to destroy any unreacted Grignard

reagent as well as to dissolve the inorganic salts.

After separation of the water and diethyl ether layers, the water portion was washed twice with 100 ml. portions of chloroform. The diethyl ether and chloroform portions were combined. The product was isolated by removing the chloroform and diethyl ether with a Rinco rotary evaporator, giving a yield of 165 g. (90%) of white crystals (m.p. 118.5-120°C). These were recrystallized from diethyl ether to yield 156 g. (85%) of 1-bromomercurihexane m.p. 121.5-2°C (lit.¹⁷ m.p. 127.5°C, lit.¹⁸ m.p. 118.5°C).

The nmr spectrum of the product shows a triplet at 2.5 δ , a multiplet from 1.20-1.6 δ and a triplet at 0.9 δ with an area ratio of approximately 2 to 8 to 3, respectively.

About the downfield triplet there was a set of mercury satellite peaks with a $J_{\text{Hg}^{199}\text{-H}^1} = 193.1$ c.p.s. signifying α -coupling.¹⁹ These satellite peaks were formed because mercury -199 has a nuclear spin number of $\frac{1}{2}$, a negligible quadrupole moment and sufficient natural abundance (17%). Therefore Hg^{199} can spin couple with hydrogen nuclei on nearby carbon atoms. For the alkylmercuric halides J. V. Hatton and others¹⁹ found that the mercury-proton coupling constant ($J_{\text{Hg}^{199}\text{-H}^1}$) for the protons on the carbon α to mercury was between 180 and 220 c.p.s. and for protons on the carbon β to mercury the coupling constant ($J_{\text{Hg}^{199}\text{-H}^1}$) was about 300 c.p.s. Kiefer and Waters²⁰ found that the mercury-

proton coupling constant ($J_{\text{Hg}}^{199}\text{-H}^1$) for the protons on the carbon γ to mercury was between 0 and 48 c.p.s. The dialkylmercurials appear to have greatly reduced proton-mercury coupling constants compared to those of the alkyl mercuric halides.³⁹

1-Bromomercurihexane (3.657 g., 0.01 mole) was dissolved in dichloromethane in a 200 ml. reaction vessel (see page 8). The reaction was then cooled to 10°C. Ozone was then flushed through the system as shown on page 8 using oxygen as the carrier gas at a rate of 24 millimoles per hour for 4 hours. Within three minutes after the introduction of ozone into the reaction vessel a reaction of ozone with the potassium iodide in the trap appeared, indicating a fairly slow uptake of ozone in the reaction vessel. In the latter a white solid began to precipitate shortly after the ozone was first introduced. After ozonizing for 4 hours, this precipitate was filtered away from the reaction mixture. A sample of the resultant clear reaction solution was analyzed by v.p.c. using the SE-30 column at 160°C with a helium flow rate of 150 ml. per minute. By comparison of the v.p.c. spectrum with spectra of known compounds, the products were identified as 30% hexanoic acid, 40% pentanoic acid, 10% butanoic acid, 10% propanoic acid and 5% acetic acid. These percentages represent ratios only, since the complexity of the reaction did not allow for yield calculations.

The same procedure was followed in the ozonation of 1-bromomercurihexane at 0°C. The products and product ratios were determined in the same manner as before and were identical in all respects to those described in the previous reaction. This reaction did not go to completion in 4 hours.

At -76°C the reaction was so slow that not enough starting material had reacted to be able to determine the product ratios.

The 1-bromomercurihexane was then ozonized at 10°C using nitrogen as the carrier gas.²¹ This was done by placing 100-150 g. of 6-12 mesh silica gel in a 200 ml. side arm trap (identical to cold trap on page 8) and cooling to -76°C. The ozone was introduced into this trap using oxygen as the carrier gas. After the desired amount of ozone had been absorbed on the silica gel, the trap was then flushed with nitrogen for a few seconds to remove all the oxygen. The silica gel was then allowed to warm very slowly while nitrogen continued through the trap, thereby carrying ozone to the reaction solution. A violent explosion occurred when the silica gel was allowed to warm too rapidly. After filtration the products and product ratios determined in the same manner as before and were identical in all respects to those described in the previous reaction.

1-Bromomercuripropene. The 1-bromopropene used was J. T. Baker reagent grade and was purified by the method used

to purify 1-bromohexane.¹⁴ The 1-bromopropane boiling point was 66.5°C at 682 mm. (lit.²² b.p. 71°C at 760 mm.).

Following the procedure outlined for 1-bromomercuri-hexane, 26 g. (0.211 mole) of 1-bromopropane, 7.3 g (0.3 mole) of magnesium chips and 65 g. (0.18 mole) of powdered mercuric bromide were reacted to yield 51.23 g. of white crystals, m.p. 134-5°C. After recrystallization from methanol the product yield was 49.2 g. (84%) 1-bromomercuripropene m.p. 137-8°C (lit.²³ m.p. 138°C).

The n.m.r. spectrum of the product showed a triplet at 1.08 δ , a multiplet from 1.56 δ to 2.1 δ and a triplet at 2.17 δ with an area ratio of 3 for the upfield triplet to 4 for the region 1.56-2.20 δ . About the triplet at 2.17 δ there appeared a set of mercury satellites with $J_{\text{Hg}^{199}\text{-H}^1} = 195$ c.p.s. signifying α coupling. About the multiplet there was a set of mercury satellites with $J_{\text{Hg}^{199}\text{-H}^1} = 282.1$ c.p.s. signifying β coupling.

1-Bromomercuripropene (3.236 g., 0.01 mole) was ozonated for 4 hours at 10°C and 0°C with the flow rate of ozone being 20 millimoles per hour. The same procedure and apparatus were used as mentioned previously. The analysis was done by v.p.c. using the SE-30 column, temperature of 130°C and a helium flow rate of 150 ml. per minute. Cyclohexanone was added as a standard after ozonation in order to get mole percent yields. The products were 44% propanoic acid and 54% acetic acid for

the ozonation at 10°C. At 0°C the products were 48% propanoic acid and 50% acetic acid.

The ozonation at -76°C was again too slow to get an appreciable yield of any products after 4 hours.

While 1-bromomercuripropene was being ozonated at 10°C, a trap containing aqueous barium hydroxide was placed just ahead of the KI trap to see if carbon dioxide was one of the products of ozonation of primary organomercurials. A white precipitate formed in a short time indicating the evolution of CO₂.

Ozone was then passed through pure dichloromethane at 0°C. The aqueous barium hydroxide trap showed a white precipitate in about the same time as when 1-bromomercuripropene was present. (See page 26 for more data on CO₂ solution.)

1-Chloromercuri-2,2-dimethylpropane. Chemical Samples Co. 1-chloro-2,2-dimethylpropane was used without further purification.

The corresponding Grignard reagent was prepared as described previously for 1-bromomercurihexane with the exception that it was prepared in a very concentrated solution²⁴ in order to insure the completion of the reaction. 1-Chloro-2,2-dimethylpropane (13 g., 0.123 mole) was added to 5 g. (0.206 mole) of magnesium in 25 ml. of diethyl ether. The Grignard reaction was very difficult to start.

After all other attempts had failed, 4 drops of 1,2-dibromoethane was added to the reaction. This initiated the Grignard reaction quickly. After the addition of the alkyl chloride was complete, the mixture was refluxed for 48 hours in a nitrogen atmosphere. The same procedure was followed as outlined previously to remove excess magnesium and to add 27.1 g. (0.10 mole) of mercuric chloride. The workup was the same as for 1-bromomercurihexane and yielded 26 g. (84%) of white crystals, m.p. 102-6°C. The raw product was then recrystallized from diethyl ether to yield 19.2 g. (63%) of 1-chloromercuri-2,2-dimethylpropane m.p. 116-118°C (lit.²⁵ m.p. 117-118°C).

The n.m.r. spectrum of the product showed two singlets at 1.87 and 2.19 δ with an area of 9 to 2, respectively. About the low field peak there was a set of mercury satellite peaks with $J_{\text{Hg}^{199}\text{-H}^1} = 190$ c.p.s. indicating α coupling. About the upfield peak there was also a set of mercury satellite peaks with $J_{\text{Hg}^{199}\text{-H}^1} = 13.5$ c.p.s. indicating γ coupling.

1-Chloro-2,2-dimethylpropane (3.072 g., 0.01 mole) was ozonated at 10°C for 4 hours with an ozone flow rate of 22 millimoles per hour in the same manner described previously. The dispersion tube plugged in two hours and had to be replaced. The raw products were checked by v.p.c. using the carbowax column at 70°C with a helium flow rate of 150 ml.

per minute. The products were also checked on the SE-30 column at 220°C with a helium flow rate of 273 ml. per minute. The products identified were 2-propanone, 2-methyl-2-propanol and a slight amount of 2,2-dimethyl propanoic acid.

This reaction was very slow as shown by n.m.r. Only a slight amount had reacted after 4 hours, therefore no yields of the various products could be determined.

1-Bromomercuric-3-methylbutane. This compound was prepared by Mr. P. G. Marsh.

Aldrich 1-bromo-3-methylbutane was purified following the procedure used for 1-bromomercurihexane. The boiling point of the purified 1-bromo-3-methylbutane was 117.1°C at 682 mm. (lit.²⁶ b.p. 119.2 at 737 mm.).

Following the usual procedure, 30 g. (0.198 mole) of 1-bromo-3-methylbutane, 4.82 g. (0.198 mole) of magnesium chips and 71.5 g. (0.198 mole) of mercuric bromide yielded 32.5 g. (46%) of 1-bromomercuri-2-methylbutane m.p. 79-81°C (lit.²⁷ m.p. 80°C).

The n.m.r. spectrum of the product showed a doublet at .95 δ , a multiplet at 1.66 δ and a triplet at 2.13 δ with the relative intensities of about 6 to 3 to 2, respectively. About the downfield triplet was a set of mercury satellite peaks with $J_{\text{Hg}^{199}\text{-H}^1} = 198$ c.p.s. indicating α coupling. About the multiplet at 1.66 δ there was a set of mercury satellites with $J_{\text{Hg}^{199}\text{-H}^1} = 259$ c.p.s. indicating β coupling.

1-Bromomercuri-3-methylbutane (1.39 g., 0.004 mole) was ozonated at 10°C, 0°C and -76°C for 3 hours with ozone flow rate of 18 millimoles per hour. All other procedures followed were the same as for ozonating 1-bromomercurihexane. After the reaction, the dichloromethane was very slowly distilled.

An n.m.r. spectrum of the raw product revealed a complex mixture which represented not only the expected acids but also tertiary hydrogen cleavage products.

1-Bromomercuricyclohexane. Aldrich 95% 1-bromocyclohexane was purified in the same manner as 1-bromohexane. The boiling point of the purified 1-bromocyclohexane was 61-2°C at 20 mm. (lit.²⁸ b.p. 163-5 at 76 mm.).

Following the usual procedure, 32.61 g. (0.2 mole) of bromocyclohexane, 10 g. (0.411 mole) of magnesium chips and 63.1 g. (0.17 mole) of mercuric bromide reacted to yield 51.5 g. of white crystals m.p. 148-152°C. This raw product was recrystallized from benzene to yield 50 g. (80%) of 1-bromomercuricyclohexane m.p. 152-3°C (lit.²⁹ m.p. 153°C).

The n.m.r. spectrum of the product showed a broad singlet at 1.58 δ , a broad doublet at 2.08 δ and a quintuplet at 3.2 δ with a relative ratio of 6 to 4 to 1, respectively.

1-Bromomercuricyclohexane (3.637 g., 0.01 mole) was ozonated at 10°C with an ozone flow rate of 26 millimoles per hour for 4 hours. When the ozonation was complete, 50 ml.

of tetrahydrofuran was added to the reaction mixture, since adipic acid is more soluble in tetrahydrofuran than in dichloromethane. The solution was then concentrated to 50 ml. by distillation with 0.346 g. (0.002 mole) of 4-bromophenol added as an internal standard for the expected adipic acid. Cyclopentanone (0.421 g., 0.005 mole) was added as an internal standard for the expected cyclohexanone. The SE-30 column at a temperature of 220°C with a helium flow rate of 273 ml. per minute was used to analyze the solution for adipic acid and the SE-30 column at 100°C with a helium flow rate of 150 ml. per minute was used to analyze the solution for cyclohexanone. The mole percent yields of the products were 60% cyclohexanone and 38% adipic acid.

In an identical reaction an aqueous extraction as well as a base extraction was attempted in order to extract the expected adipic acid; neither extraction was successful due to the presence of inorganic mercury salts.

2-Chloromercuripropene. 2-Chloromercuripropene was prepared by Mr. P. G. Marsh.

Eastman 2-bromopropene was purified following the procedure used to purify 1-bromohexane. The boiling point of the purified 2-bromopropene was 55.5°C at 682 mm. (lit.³⁰ b.p. 59.4°C at 760 mm.).

Following the procedure outlined for 1-bromomercurihexane, 61.5 g. (0.5 mole) of 2-bromopropene, 12.15 g.

(0.5 mole) of magnesium chips and 135.75 g. (0.50 mole) of mercuric chloride were reacted to yield 76.1 g. (51%) of a mixture of 2-bromomercuripropene and 2-chloromercuripropene m.p. 78-83°C, lit.³¹ m.p. 77-82°C.

Since a pure compound was needed for ozonation, the procedure outlined by Robson and Wright³² was followed. This consisted of dissolving the mixture in methanol, and with stirring, adding a 10% molar excess of silver nitrate. The reaction mixture was then filtered to remove the insoluble silver halide. Excess reagent grade sodium chloride was then added to the methanol solution which, after heating to reflux temperature, was then filtered. Upon cooling, the pure chloride product precipitated to yield an 80% conversion (from the chloride-bromide mixture) of 2-chloromercuripropene m.p. 94-95°C (lit.³³ m.p. 94.5-95.5).

The n.m.r. spectrum of the product showed a doublet at 1.51 δ and a multiplet at 2.53 δ with an area ratio of 6 to 1, respectively. About the low field peaks there was a set of mercury satellites with $J_{\text{Hg}^{199}\text{-H}^1} = 185$ c.p.s. indicating α coupling. About the upfield doublet there was a set of mercury satellite peaks with $J_{\text{Hg}^{199}\text{-H}^1} = 288.5$ c.p.s. indicating β coupling.

2-Chloromercuripropene (5.583 g., 0.02 mole) was ozonated at 10°C for 4 hours with the flow rate of ozone

being 28 millimoles per hour. No ozone reached the KI trap for 10-15 minutes. When the ozonation was discontinued the liquid trap and reaction vessel were combined. To these 0.741 g. (.01 mole) of 2-methyl-2-propanol was added as an internal standard for 2-propanone and 0.76 g. (0.002 mole) of butanoic acid was added as an internal standard for acetic acid. The carbowax column at 70°C with a helium flow rate of 150 ml. per minute was used to analyze the reaction solution for 2-propanone and the SE-30 column at 130°C with a helium flow rate of 150 ml. per minute was used to analyze the reaction solution for acetic acid. The product yields were 79% 2-propanone and 19.7% acetic acid. After product analyses were complete, the reaction mixture was filtered. The weight of the dried white precipitate was 4.397 g. The solvent was then distilled away from the filtrate. There was a white solid remaining which weighed 1.087 g. The dispersion tube had a net weight difference of 0.213 g. after cleaning. Therefore the total weight of solids for the reaction was 5.697 g.

This precipitate was analyzed by powder X-ray diffraction. It proved to be approximately 77% mercuric chloride and 23% mercurous chloride. A slight trace of mercuric oxide was also observed. The percentages were found by comparing the X-ray diffraction pattern of the product with the X-ray diffraction pattern of known mixtures of mercuric chloride, mercurous chloride and mercuric oxide.

2-Chloromercuri-2-methylpropane. The t-butyl chloride was prepared by the method described in "Experiments in Organic Chemistry."³⁴ To 50 ml. of Mallinckrodt t-butanol, 100 ml. of concentrated HCl was added, this was stirred vigorously for 2 hours, then distilled until a temperature of 50°C was reached. The distillate was then washed with 40 ml. of concentrated H₂SO₄, followed by two washings with 5% aqueous NaHCO₃, and dried over anhydrous CaCl₂. It was then fractionally distilled and the center portion boiling at 47-48°C (684 mm.) was used (lit.³⁵ b.p. 50.7 at 760 mm.).

With the exception that the Grignard reagent was prepared in a much more concentrated form to insure completion of the reaction, the procedure was the same as usual. t-Butyl chloride (37 g., 0.5 mole), 12 g. (0.5 mole) of magnesium chips in 100 ml. of diethyl ether, and 81.3 g. (0.3 mole) of powdered mercuric chloride were used to yield 42 g. white crystals which decomposed without melting. After recrystallization from methanol 39 g. (44%) of white crystals were obtained which decomposed without melting (lit.³⁶ 2-chloromercuri-2-methylpropane decomposed without melting).

The n.m.r. spectrum of the product showed a singlet at 1.5δ. About this peak was a set of mercury satellite peaks with $J_{\text{Hg}^{199}\text{-H}^1} = 262.5$ c.p.s. indicating β coupling.

1-Chloromercuri-2-methylpropane (5.252 g., 0.018 mole) was ozonated as a suspension at 10°C for 3 hours with an ozone flow rate of 22 millimoles per hour. After ozonation, 0.730 g. (14%) of starting material was left unreacted. The KI trap was titrated with $\text{Na}_2\text{S}_2\text{O}_3$ to determine the amount of ozone which had not reacted. The ratio of reacted ozone to reacted 2-chloromercuri-2-methylpropane was about 1.2 moles to 1 mole, respectively.

The products were identified by combining the reaction vessel and the -76°C liquid trap. V.p.c. was again used, this time employing the carbowax column at a temperature of 70°C with a helium flow rate of 150 ml. per minute. The only products were 50% 2-methyl-2-propanol, 22% 2-propanone and 28% formic acid.

In order to check the stability of the tertiary alcohol towards ozone, 1.48 g. (0.02 mole) of 2-methyl-2-propanol was ozonized for 4 hours at 10°C with an ozone flow rate of 24 millimoles per hour. The v.p.c. analysis was done under identical conditions as above and showed that less than 2% of the 2-methyl-2-propanol was attacked by ozone to produce 2-propanone and formic acid.

Di-n-propyl Mercury. The 1-bromopropane used was the same as that used earlier to prepare 1-bromomercuripropene.

The procedure followed to prepare di-n-propyl mercury was that as outlined by Gilman and Brown.³⁷ The Grignard

reagent was prepared using 120 g. (0.98 mole) of 1-bromopropane and 26 g. (1.07 mole) of magnesium chips in 700 ml. anhydrous diethyl ether. After reflux, the Grignard reagent was filtered through glass wool into a 2 liter, three neck distilling flask and diluted to 1500 ml. with diethyl ether.

A Soxhlet extractor was used to add 104 g. (0.38 mole) of mercuric chloride while the Grignard reagent was being stirred rapidly. After the addition was complete, the Soxhlet extractor was removed and 2 condensers were put on the reaction flask. The reaction was then refluxed for 56 hours.

The reaction mixture was then cooled and 300 ml. of water was slowly added through the condenser. The diethyl ether layer was separated from the water layer, and the latter was washed twice with diethyl ether. The combined diethyl ether solution was dried with anhydrous calcium chloride and the ether was removed by distillation at atmospheric pressure. From the remaining solution, 94 g. of di-n-propyl mercury was distilled at 33-34°C at 1 mm. (lit.³⁸ b.p. 81-84°C at 19 mm.). After a second distillation through a 6 inch Vigreux column at 33-34°C at 1 mm., 91.4 g. (83%) of di-n-propyl mercury was obtained.

The n.m.r. spectrum of the product showed a triplet at 1.07 δ , a triplet at 1.14 δ and a quartet at 2.01 δ with an area ratio of 5 for the upfield triplets to 2 for the quartet. About the low field quartet there was a set of mercury

satellites with a $J_{\text{Hg}^{199}\text{-H}^1} = 107.2$ c.p.s. indicating β coupling. About the triplet at 1.14 δ there was a set of mercury satellites with $J_{\text{Hg}^{199}\text{-H}^1} = 94.8$ c.p.s. indicating α coupling. These values of $J_{\text{Hg}^{199}\text{-H}^1}$ were very near those reported by Dessy and others.³⁹

Di-n-propyl mercury (2.868 g., 0.01 mole) was ozonated at 10°C for 4 hours, with an ozone flow rate of 21 millimoles per hour. The ozone did not reach the KI solution for about 15 minutes. The dispersion tubes plugged after 2 hours and were replaced. After the ozonation was completed, the reaction solution was slowly concentrated to 50 ml. by distillation through a 6 inch Vigreux column. To this solution was added 0.981 g. (0.01 mole) of cyclohexanone as an internal standard. The v.p.c. analysis was done at 130°C on the SE-30 column with a helium flow rate of 150 ml. per minute. The products were 67% propanoic acid, 20% acetic acid and 15% formic acid.

The precipitate from the ozonation reaction was analyzed by X-ray powder diffraction in the same way as described for 2-chloromercuripropene. The precipitate was composed of about 45% mercuric chloride, 35% mercurous chloride and 20% mercuric oxide.

Di-n-propyl mercury was also ozonated at 0°C, under the same conditions as above. The analysis of organic products was done by v.p.c. as outlined above. The products were 67% propanoic acid, 19% acetic acid and 14% formic acid.

At -76°C , the dialkyl mercurial produced 72% propanoic acid, 16% acetic acid and 12% formic acid although the reaction was considerably slower at this temperature.

Since dichloromethane produced CO_2 slowly during ozonation, another solvent which was inert to ozone must be used to determine if CO_2 was one of the products from the ozonation of primary organomercurials. When freon 114 (1,1-dichloro-1,2,2,2-tetrafluoroethane) was ozonized at -76°C no CO_2 was given off, as shown by a lack of precipitate in a $\text{Ba}(\text{OH})_2$ solution. When di-n-propyl mercury was added to freon 114 and this mixture was ozonated at -76°C it was found that CO_2 was given off slowly after about 15 minutes. When formic acid in freon 114 was ozonized at -76°C CO_2 was given off slowly after 10 to 15 minutes.

Di-n-hexyl Mercury. The 1-bromohexane used was part of that purified for the synthesis of 1-bromomercurihexane.

The Grignard reagent was prepared using 36.3 g. (0.22 moel) of 1-bromohexane and 8.92 g. (0.367 mole) of magnesium chips in 300 ml. anhydrous diethyl ether. When the Grignard reagent formation was complete, the solution was filtered through glass wool and diluted by 500 ml. of diethyl ether. To the ethereal solution, 36.5 g. (0.1 mole) of finely ground 1-bromomercurihexane was added slowly through the condenser. The reaction mixture was then refluxed for 24 hours, and the product was isolated in the usual manner.

Twenty-six grams of raw product were vacuum distilled at a temperature of 110-113°C at 1.0-0.9 mm. and then re-distilled through a 6 inch Vigreux column at 110-113°C at 1.0-0.9 mm. to yield 23.15 g. (62%) of di-n-hexyl mercury (lit.⁴⁰ b.p. 110-112°C at 0.5 mm.).

The n.m.r. spectrum of the product showed a triplet at 0.91 δ , a triplet at 1.08 δ , a broad methylene peak at 1.33 δ and a broad triplet at 1.89 δ . The area ratio was 11 for peaks from .8 δ to 1.65 δ to 2 for the downfield triplet. About the broad triplet at 1.89 δ there was a set of mercury satellites with $J_{\text{Hg}^{199}\text{-H}^1} = 104.6$ c.p.s. indicating β coupling. About the triplet at 1.08 δ there was a set of mercury satellites with $J_{\text{Hg}^{199}\text{-H}^1} = 97.4$ c.p.s. indicating α coupling.

Di-n-hexyl mercury (3.709 g., 0.01 mole) was ozonated for 4 hours at 10°C with an ozone flow rate of 30 millimoles per hour. No ozone reacted with KI for about 15 minutes. When the ozonation was complete, the usual white inorganic precipitate was filtered. The clear reaction solution was analyzed by v.p.c. using the SE-30 column at 160°C and a helium flow rate of 150 ml. per minute. The products identified were 50% hexanoic acid, 25% pentanoic acid, 10% butanoic acid, 10% propanoic acid, 5% acetic acid and 5% formic acid. These percentages represent ratios only however, since the complexity of the reaction did not allow

for yield calculations. Besides those products identified, slight amounts of what were presumably isomers appeared in the gas chromatographic trace. Of these, isovaleric acid was identified as a minor component.

Di-n-hexyl mercury was also ozonated at 0°C, producing 70% hexanoic acid, 10% pentanoic acid, and less than 5% of smaller acids. Again, these percentages represent only ratios.

At -76°C the dialkylmercurial yielded 80% hexanoic acid, 5% pentanoic acid and less than 5% of smaller acids.

As a check to determine if acids could be degraded by ozone to acids having a shorter carbon chain, 2.04 g. (0.02 mole) of pentanoic acid with a small amount of mercuric chloride and mercurous chloride was ozonated at 10°C for 4 hours with an ozone flow rate of 28 millimoles per hour. The v.p.c. analysis on the SE-30 column at 160°C and a helium flow rate of 150 ml. per minute indicated no acids other than pentanoic acid.

Di-isopropyl Mercury. Di-isopropyl mercury was prepared by Mr. J. G. Rivera.

The procedure followed was the same as that used to prepare di-n-propyl mercury. 2-Bromopropane (123 g., 1.0 mole) which was purified as before, 28 g. (1.15 mole) of magnesium and 95 g. (0.35 mole) of mercuric chloride were used to yield 80.3 g. of product with a b.p. of 37-39°C at

2 mm. The raw product was redistilled through a 6 inch Vigreux column at 37-39°C and 2 mm. to yield 74.5 g. (74%) of di-isopropyl mercury, lit.⁴¹ b.p. 119-121°C at 125 mm.

The n.m.r. spectrum of the product showed a singlet at 1.33 δ . The α mercury satellites could not be distinguished from the noise in the spectrum but about the singlet there are two sets of mercury satellites with $J_{\text{Hg}^{199}\text{-H}^1} = 115$ c.p.s. indicating β coupling.

Di-isopropyl mercury (5.735 g., 0.02 mole) was ozonated at 10°C for 3.5 hours with an ozone flow rate of 27 millimoles per hour. No ozone reached the KI trap for the first 65 minutes. Since the dispersion tubes did not plug during this reaction, it was felt that the titration of the KI trap after reaction was a fairly accurate indication of the uptake of ozone. It was found that approximately 3.5 moles of ozone reacted for each mole of di-isopropyl mercury. After ozonation, 2.224 g. (0.03 mole) of 2-methyl-2-propanol was added as an internal v.p.c. standard for 2-propanone. Using the carbowax column at 70°C with a flow rate of 150 ml. per minute, the yield of 2-propanone was calculated to be 89%. The reaction solution was then concentrated to 25 ml. by distillation of dichloromethane. To this was added 0.353 g. (0.004 mole) of butanoic acid as an internal v.p.c. standard for the acetic acid. Using the SE-30 column at 130°C

and a helium flow rate of 150 ml. per minute, the yield of acetic acid was calculated to be 10%.

The inorganic salts (5.624 g.) were recovered from the reaction and were analyzed by powder X-ray diffraction in the same manner as described before. The white precipitate was made up of approximately 55% mercuric chloride, 35% mercurous chloride and 10% mercuric oxide.

trans-1-Chloromercuri-2-methoxycyclohexane. This compound was prepared by Dr. W. L. Waters.

To prepare trans-1-chloromercuri-2-methoxycyclohexane, 31.8 g. (0.1 mole) of mercuric acetate was placed in 250 ml. methanol. To this rapidly stirred solution 8.21 g. (0.1 mole) of cyclohexene was added. This reaction mixture was then stirred for an additional 5 minutes. Two drops of the solution was then added to a small amount of sodium carbonate on a watch glass. The sodium carbonate remained clear, indicating the reaction was complete. Sodium carbonate (5.83 g., 0.055 mole) was added and the reaction was stirred for another 5 minutes. The reaction mixture was then filtered and the methanol was carefully removed on a rotary evaporator with the bath temperature not exceeding 50°C. Benzene (200 ml.) was added to the reaction mixture and it was shaken. Solid sodium acetate was then removed by filtration. The benzene was removed and 250 ml. of distilled water was added. Potassium chloride (22.4 g,

0.3 mole) was added to the water solution and the mixture was shaken vigorously. The white precipitate which formed was filtered and recrystallized from an ethanol-water solution to yield 30.7 g. (88%) of trans-1-chloromercuri-2-methoxycyclohexane m.p. 116-117°C (lit.⁴² m.p. 115.5°C).

The n.m.r. of the product showed a singlet at 3.38 δ (area 3), a multiplet from 3.1 to 3.4 δ (area 1), a multiplet from 2.4 δ to 2.8 δ (area 1), and a multiplet from 0.85 δ to 2.4 δ (area 8). No mercury satellites were found.

trans-1-Chloromercuri-2-methoxycyclohexane (2.01 g., 0.006 mole) was ozonated for 2 hours at 0°C with an ozone flow rate of 19 millimoles per hour. After ozonation, the reaction was filtered and the dichloromethane was removed using a rotary evaporator. An n.m.r. of the remaining oil was taken. The methoxy singlet appeared at 3.67 δ representing a 17 c.p.s. downfield shift compared to the starting material. This was good indication that the mercury function had been replaced by the more deshielding carbonyl oxygen. The 2,4-dinitrophenyl hydrazone derivative of the product had a melting point of 218-221°C (lit.⁴³ m.p. 218-219°C, lit.⁴⁴ m.p. 220-221°C) for the 2,4-dinitrophenylhydrazone of 2-methoxycyclohexanone. Since there was no indication of other products under the conditions used to study the reaction, it was assumed that 2-methoxycyclohexanone was the sole product.

Ozonation of Bromocyclohexylmagnesium

The cyclohexyl Grignard reagent was prepared using 4.26 g. (0.026 mole) of 1-bromocyclohexane and 1.27 g. (0.052 mole) of magnesium chips in 200 ml. anhydrous diethyl ether. After reaction, diethyl ether was distilled until a volume of about 15 ml. remained. Anhydrous Eastman reagent grade n-heptane (25 ml.) was then added, and the reaction mixture was heated to 75°C to remove all of the remaining diethyl ether.

The Grignard reagent was then ozonated at -76°C in heptane using oxygen as the carrier gas for 4 hours with an ozone flow rate of 24 millimoles per hour. When the ozonation was complete, the reaction mixture was filtered at -76°C, and the precipitate was added to wet diethyl ether. When it was added to the wet solvent a gas was produced but not identified. The diethyl ether solution was checked by v.p.c. using the carbowax column at a temperature of 160°C and a helium flow rate of 150 ml. per minute. The products were 50% cyclohexanone and 50% cyclohexanol. The cyclohexyl Grignard reagent was also ozonated under the same conditions but using nitrogen as the carrier gas, as described for 1-bromomercurihexane. The products were analyzed under the same conditions and were 50% cyclohexanone and 50% cyclohexanol.

CHAPTER III

RESULTS

Products from Ozonation of Organomercurials

Eleven organomercurials and one Grignard reagent were ozonized at 10°, 0° and -76°C.

The ozonolysis products of n-alkylmercuric halides were CO₂ and a mixture of acids which had a carbon chain equal to or shorter than the alkyl group of the parent organomercurial. Thus the ozonolysis of the carbon-mercury bond of primary organomercurials was accompanied by considerable carbon-carbon cleavage along the parent carbon chain. This carbon-carbon cleavage was most prominent for the n-alkylmercuric halides when ozonated at 10°C (see reactions 1 and 4, Table I). The carbon-carbon cleavage was less prominent for the di-n-alkyl mercurials when ozonated at 10°C (see reactions 11 and 14, Table I) and was reduced to the lowest level for primary organomercurials when the di-n-alkyl were ozonated at -76°C, as shown by reactions 13 and 16, Table I.

As a check on the reaction pathway for the formation of the shorter acids, pentanoic acid was ozonized for 4 hours at 10°C in dichloromethane which contained small amounts of

mercuric chloride and mercurous chloride. No acids of shorter length were detected by v.p.c. analysis of this reaction.

As was shown for di-n-propyl mercury, neither the ratio of products nor the products themselves were altered noticeably if the ozonation was discontinued before all the organomercurial had reacted, indicating the rate determining step was the attack of the carbon-mercury bond.

The ozonolysis of the secondary carbon-mercury bond resulted in some carbon-carbon cleavage, although it was usually less than for the reaction of primary organomercurials.

Contrary to the results reported by Bockemuller and Pfeuffer⁴⁵ that ozonation of diisopropyl mercury yielded only 2-propanone, reaction 17, Table I shows that the products from the ozonation of diisopropyl mercury were acetic acid and 2-propanone.

The ozonolysis of the tertiary carbon-mercury bond produced considerable amounts of the corresponding alcohol as well as some carbon-carbon cleavage products as shown in reaction 10, Table I.

The qualitatively attained relative rates observed for organomercuric halides were tertiary < primary < secondary although it was found that 1-chloro-2,2-dimethylpropane was very inert to ozone.

The inorganic mercury salts which were produced during the ozonation of organomercurials were identified by X-ray powder diffraction. The inorganic salts produced during the ozonation of 2-chloromercuripropene were 77% mercuric chloride and 23% mercurous chloride, as shown in reaction 9, Table I.

When the dialkyl mercurials were ozonated in dichloromethane, the inorganic salts were 45% mercuric chloride, 35% mercurous chloride and 20% mercuric oxide for di-n-propyl mercury and 55% mercuric chloride, 35% mercurous chloride and 10% mercuric oxide for diisopropyl mercury as shown in reactions 11 and 17 in Table I, respectively.

As a test to see if part of the mercurous chloride produced during the ozonation of organomercurials was oxidized to mercuric chloride, known mercurous chloride was ozonated in dichloromethane for 4 hours at 10°C. No mercuric chloride could be detected from this reaction. Therefore 23 to 35% of the mercury was being reduced during the ozonation of organomercurials.

Carrier Gas Effects on Products

Organomercurials. When the carrier gas was changed from oxygen to nitrogen as shown in reactions 1 and 3, Table I, no differences in product ratios were detected.

Grignard Reagents. No differences were detected when the carrier gas used for ozonation of Grignard reagents was

changed from oxygen to nitrogen as shown in reactions 19 and 20, Table I.

Temperature Effects on Products and Rates

The rate of the reaction appeared to be slowed considerably by lowering the reaction temperature. The reaction of the primary organomercuric halides was negligible at -76°C as indicated by the lack of enough products after 4 hours to get a ratio of products as shown on page 12.

The ozonolysis of di-n-alkyl mercurials exhibited less carbon-carbon cleavage as the reaction temperature was lowered as shown by reactions 14, 15 and 16, Table I.

Ligand Effects on Products and Rates

Changing the ligand from a halide to another alkyl group increased the reaction rate considerably. This is shown by comparing the reaction of 1-bromomercurihexane at -76°C and the reaction of di-n-hexyl mercury at -76°C . The product ratios could not be detected even after 4 hours of reaction in the case of 1-bromomercurihexane. For di-n-hexyl mercury the product ratios were easily found as the reaction was approximately 50% complete after 4 hours. Also, by changing the ligand from a halide to another alkyl group the carbon-carbon cleavage was reduced by an appreciable amount. This can be shown by comparing reactions 9 and 17, 2 and 15, or 5 and 12 of Table I.

The general relative rates observed for different ligands on alkyl mercurials were alkyl $\gg$ Br $>$ Cl.

Stoichiometry of Ozone Uptake

During most of the reactions, the sintered glass on the dispersion tube (figure 1, page 8) plugged slowly with the inorganic mercury salts during ozonation of the organo-mercurials, making it impossible to keep the flow rate of ozone exactly constant. This in turn made the calculation of the ozone uptake only a rough estimation. Moreover, it has been shown (page 15) that the ozone reacts slowly with dichloromethane, which of course was used as the solvent for the ozonolysis. This fact also probably upset the exact stoichiometry of ozone uptake.

The ozonolysis of the primary carbon-mercury bond took up as much as five moles of ozone to one mole of organo-mercurial as indicated in the case of 1-bromomercurihexane. The ozonolysis of di-n-alkyl mercurials took up five to six moles of ozone for each mole of mercurial.

The ozonolysis of the secondary carbon-mercury bond was shown to take up as much as three equivalents of ozone in the case of 1-bromomercuricyclohexane, and as little as two equivalents of ozone in the case of 2-chloromercuripropene. During the ozonation of di-isopropyl mercury three and one half moles of ozone reacted for each mole of di-isopropyl mercury.

The ozonation of the tertiary carbon-mercury bond was shown to take up between one and one and three tenths mole of ozone for each mole of organomercurial as illustrated by 2-chloromercuri-2-methylpropane.

Thus, in general, ozonolysis of the tertiary carbon-mercury bond required approximately one equivalent of ozone, the secondary carbon-mercury bond 1.5 to 3 equivalents of ozone, and the primary carbon-mercury bond 3 to 5 equivalents of ozone.

TABLE I

	Organomercurials	Carrier Gas	Reaction Temp.	Inorganic Products	Organic Products
1.	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{HgBr}$	O_2	10°C	----	30% $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ 40% $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ 10% $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ 10% $\text{CH}_3\text{CH}_2\text{COOH}$ 5% CH_3COOH
2.	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{HgBr}$	O_2	0°C	----	30% $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ 40% $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ 10% $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ 10% $\text{CH}_3\text{CH}_2\text{COOH}$ 5% CH_3COOH
3.	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{HgBr}$	N_2	10°C	---	30% $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ 40% $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ 10% $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ 10% $\text{CH}_3\text{CH}_2\text{COOH}$ 5% CH_3COOH
4.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{HgBr}$	O_2	10°C	----	44% $\text{CH}_3\text{CH}_2\text{COOH}$ 54% CH_3COOH
5.	$\text{CH}_3\text{CH}_2\text{CH}_2\text{HgBr}$	O_2	0°C	----	48% $\text{CH}_3\text{CH}_2\text{COOH}$ 50% CH_3COOH
6.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2\text{HgCl} \\ \\ \text{CH}_3 \end{array}$	O_2	10°C	----	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{OH} \\ \\ \text{CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{COOH} \\ \\ \text{CH}_3 \end{array}$

Table I (Continued)

Organomercurials	Carrier Gas	Reaction Temp.	Inorganic Products	Organic Products
7. $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2\text{CH}_2\text{HgBr} \\ \\ \text{H} \end{array}$	O_2	10°C	----	Complex Mixture
8.	O_2	10°C	----	60% 38% $\text{HOOC}(\text{CH}_2)_4\text{COOH}$
9. $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{HC}-\text{HgCl} \\ \diagup \\ \text{CH}_3 \end{array}$	O_2	10°C	77% HgCl_2 23% Hg_2Cl_2	79% $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$ 19% CH_3COOH
10. $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{HgCl} \\ \\ \text{CH}_3 \end{array}$	O_2	10°C	----	50% $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$ 22% $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$ 28% HCOOH
11. $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Hg}$	O_2	10°C	45% HgCl_2 35% Hg_2Cl_2 20% HgO	64% $\text{CH}_3\text{CH}_2\text{COOH}$ 20% CH_3COOH 15% HCOOH
12. $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Hg}$	O_2	0°C	----	67% $\text{CH}_3\text{CH}_2\text{COOH}$ 19% CH_3COOH 14% HCOOH
13. $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{Hg}$	O_2	-76°C	----	72% $\text{CH}_3\text{CH}_2\text{COOH}$ 16% CH_3COOH 12% HCOOH

Table I (Continued)

Organomercurials	Carrier Gas	Reaction Temp.	Inorganic Products	Organic Products
14. $[\text{CH}_3(\text{CH}_2)_5]_2\text{Hg}$	O_2	10°C	----	50% $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ 25% $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ 10% $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ 10% $\text{CH}_3\text{CH}_2\text{COOH}$ 5% CH_3COOH
15. $[\text{CH}_3(\text{CH}_2)_5]_2\text{Hg}$	O_2	0°C	----	70% $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ 10% $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ 5% $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ <5% $\text{CH}_3\text{CH}_2\text{COOH}$ <5% CH_3COOH
16. $[\text{CH}_3(\text{CH}_2)_5]_2\text{Hg}$	O_2	-76°C	----	80% $\text{CH}_3(\text{CH}_2)_4\text{COOH}$ 5% $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ <5% $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ <5% $\text{CH}_3\text{CH}_2\text{COOH}$ <5% CH_3COOH
17. $\left[\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{H}-\text{C} \\ \diagup \\ \text{CH}_3 \end{array} \right]_2 \text{Hg}$	O_2	10°C	55% HgCl_2 35% Hg_2Cl_2 10% HgO	89% $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$ 10% CH_3COOH
18.	O_2	0°C	----
19.	O_2	-76°C	----	50% 50%
20.	N_2	-76°C	----	50% 50%

CHAPTER IV

DISCUSSION

Products from Ozonation of Organomercurials

The ozonation of organomercurials yielded acids, ketones, and alcohols.

The large amount of carbon-carbon cleavage observed from the ozonolysis of primary organomercurials as shown in reaction 1 through 5 and 11 through 6, Table I was somewhat puzzling since it was assumed the reaction was a simple electrophilic substitution reaction. One possibility considered was that the original acid formed during the ozonolysis of the primary carbon-mercury bond was being slowly degraded to smaller acids. This possibility was discarded when pentanoic acid with ozone produced no acids of a shorter chain, as shown on page 28.

Since no difference was detected in the products when the ozonolysis was discontinued before the starting material had completely reacted, and no intermediates could be identified, it was assumed that the slow step in the ozonolysis of organomercurials was the attack of the carbon-mercury bond by ozone.

It was therefore apparent that the intermediate from the ozone insertion into the carbon-mercury bond must decompose to another intermediate which has the ability to migrate as an active site along the carbon chain. This active site can then be attacked by ozone to give the acids of shorter length. This active intermediate was given support by the detection of an isomer of pentanoic acid as described on page 28. The formation of the pentanoic isomer could have arisen from this active entity rearranging before being further attacked by ozone. This active site could be a radical, carbonium ion or a carbanion.

The CO_2 produced during ozonation of primary organomercurials (page 26) was one aspect which should be studied in more detail in the future. It was not determined if the CO_2 was formed immediately or if it was formed through the ozonation of formic acid. Moreover, the CO_2 formed was a complicating factor in determining the stoichiometry of ozone uptake during ozonation of primary organomercurials.

The ozonation of the secondary carbon-mercury bond exhibited considerably less carbon-carbon cleavage than the ozonation of the primary carbon-mercury bond. This can be seen by comparing reactions 1 and 9, Table I. The product yields in reaction 8 do not reflect this point, although this is not too surprising since cyclohexanone can be oxidized to adipic acid by other reagents.⁴⁶

When a tertiary organomercurial was ozonized (see reaction 10, Table I) the corresponding alcohol was obtained in fairly high yield. This would make it possible to study the stereospecificity of the reaction of ozone with an optically active organomercurial. The starting material for this study must be a tertiary organomercurial, as a secondary organomercurial would result in a ketone. Also there must be no tertiary hydrogen since hydrogen bonds such as these will result in a competing reaction and produce a complex mixture of products (see reaction 7, Table I).

When the carrier gas was changed from O_2 to N_2 , no significant change in product ratios was detected. If oxygen was taking part in the reaction, one would expect significant change in products as well as product ratios. However, these results do not necessarily preclude oxygen taking part in the reaction with organomercurials. Oxygen might still be taking part in the reaction in some insignificant non-product determining step.

The inorganic salts produced during the ozonolysis of the carbon-mercury bond as shown on page 30 are evidence that the ozonolysis of the carbon-mercury bond takes place by more than one mechanism.

If the intermediate from ozone insertion into carbon-mercury bond breaks down homolytically, mercurous salts can be formed.

If this intermediate breaks in a heterolytic manner then mercuric salts could be formed.

Rates of Ozonation of Organomercurials

From the experiments which were run a general qualitative order of relative rates can be found.

The order of rates observed by changing the alkyl groups were neopentyl << t-butyl < n-hexyl < n-propyl $\approx$ cyclohexyl < isopropyl. It appeared that the alkylmercuric chlorides

reacted more slowly than the alkylmercuric bromides which reacted much slower than the dialkyl mercurials when all of the alkyl groups were identical. These relative rates agree generally with the rates expected for electrophilic cleavage of the carbon-mercury bond as shown by March⁴⁷ as well as Jensen and Rickborn.⁴⁸

As mentioned by Jensen and Rickborn,⁴⁸ the electrophilic scission of a bond is more rapid as the bond becomes more polarized. This is a direct reflection of the electronegativity of the atoms attached to mercury.

As can be seen, the dialkyl mercurials should be attacked much more rapidly than alkyl mercuric chlorides or bromides. This was shown by the much more rapid consumption of ozone by the dialkyl mercurials than by the organomercuric halides. This greater reactivity is also apparent from the ozonolysis of the primary carbon-mercury bond at -76°C as shown by comparing the reaction of 1-bromomercurihexane with ozone at -76°C (page 13) with the reaction of di-n-hexyl mercury

with ozone at -76°C (page 28), since it was assumed that the more starting material which remained the slower it reacted with ozone.

Mechanism of Ozonation of Organomercurials

The mechanism for the ozonation of organomercurials was not fully elucidated by the reactions and other studies which were done. However, due to the electrophilicity of ozone as shown by Belew and Augustine⁴⁹ and the tendency for the organomercurials which were ozonized to follow the accepted reactivity sequence for electrophilic substitution, it was assumed that the ozonolysis of organomercurials was an electrophilic substitution reaction.

In view of the above evidence and the proposed mechanism for electrophilic cleavage of carbon-mercury bonds as shown by Jensen and Rickborn,⁵⁰ the first step of the transition state might appear as below.

This transition state could then lead to the intermediate shown below.

The breakdown of this high energy intermediate could then take place through a homolytic or heterolytic pathway as shown on page 45.

A similar mechanism has been proposed by Ouellette and Marks⁵¹ for ozonation of silicon compounds.

Synthetic Utility of Ozonation of Organometallics

Organomercurials. The reaction which has shown promise of synthetic utility is reaction 18, Table I. This appears to be a good method of preparing α methoxy ketones from the products of oxymercuration of double bonds.

Another reaction sequence which may be synthetically useful is the preparation of α diketones through the ozonolysis of hydroxymercuration products.

The preparation of acids or α -keto acids by ozonolysis of the primary carbon-mercury bond appears to be of little synthetic value since there is much carbon-carbon cleavage in this type of reaction and a mixture of products would be obtained.

Grignard Reagents. When the cyclohexyl Grignard reagent was ozonated at -76°C under O_2 or N_2 , only a solid was obtained. This solid yielded a mixture of cyclohexanol and cyclohexanone when decomposed in aqueous diethyl ether, as shown in reaction 19 and 20, Table I.

Since only a mixture of products was obtained, the synthetic utility of this reaction is probably negligible, as the alcohol can be obtained from the alkyl halide directly or by the reaction of excess Grignard reagent with oxygen and decomposition with acid as shown by Walling and Buckler.⁵²

CHAPTER V

SUMMARY

Eleven different organomercurials were ozonated in methylene chloride to yield acids, ketones and alcohols. The carbon-mercury bond is readily cleaved by ozone and the reaction appears to proceed by electrophilic attack of ozone.

The products from the ozonolysis of primary carbon-mercury bonds are a mixture of acids containing both the parent carbon chain as well as the shorter analogs. The products from the ozonolysis of secondary carbon-mercury bonds are primarily ketones with lesser yields of acids which result from carbonyl- α -carbon cleavage. The products from the ozonolysis of tertiary carbon-mercury bonds are the corresponding alcohols as well as some carbon-carbon cleavage products.

The inorganic by-products from the ozonation of organomercurials are both mercuric and mercurous halides, thus suggesting more than one reaction pathway for breakdown of the primary ozonation intermediate.

Although a mechanism for the reaction cannot be unambiguously assigned from the experimental work contained

within, it appears that the alkyl intermediate may be a radical or carbanion.

The synthetic utility of this reaction appears promising. The preparation of α -methoxy ketones and α -diketones via mercuriation (of alkenes) followed by ozonation should prove useful to the synthetic organic chemist.

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