Thermal decomposition of some aromatic diazonium hexafluoroarsenate salts; The thermal decomposition of some methyl ethers of trans-1-phenyl-2-methylcyclohexanol and para-substituted derivatives.

Richard S. Steevensz

University of Windsor

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PART I

THERMAL DECOMPOSITION

OF SOME AROMATIC DIAZONIUM HEXAFLUOROARSENATE SALTS

PART II

THE THERMAL DECOMPOSITION OF SOME METHYL ETHERS OF TRANS-1-PHENYL-
2-METHYLCYCLOHEXANOL AND PARA-SUBSTITUTED DERIVATIVES

BY

RICHARD S. STEEVENSZ

A THESIS

Submitted to the Faculty of Graduate Studies through the
Department of Chemistry in Partial Fulfillment
of the Requirements for the Degree of
Master of Science at the
University of Windsor

Windsor, Ontario
1973
ABSTRACT

PART I

Attempts at the preparation of four (4) fluoroaromatic hydrocarbons from o-, p-, m- nitroaniline and p-aminotoluene via decomposition of the intermediate diazonium hexafluoroarsenates are reported. A comparison is made with the modified and normal Schiemann Reaction which involves decomposition of hexafluorophosphate and tetrafluoroborate salts respectively.

The investigation showed the hexafluoroarsenate method to be inferior to previous procedures in the cases studied.

PART II

The thermal decomposition of some trans-1,1'-methoxy (p-Xphenyl)-2-methylcyclohexanes was investigated in diphenyl ether at various temperatures and the results are reported. The pyrolysis products indicate a predominance of the "Hofmann type" olefins, 1-(p-Xphenyl)-2-methylcyclohex-1-enes (by nmr and glc analyses).

From the estimated rate constants, the thermodynamic quantities calculated for ΔH* and ΔS* would indicate that in the case of most of the ethers studied that some ionic character is evident in the transition state of decomposition. When X = CH$_3$O, CH$_3$, H and Cl the Hammett plot supports this conclusion ($ρ$ = -19.6). Such was not the case however when X = Br and NO$_2$. It is concluded that another mechanism may be operative for the pyrolytic decomposition of these compounds.
ACKNOWLEDGEMENTS

The author would like to acknowledge his sincere appreciation to Dr. K.G. Rutherford for his understanding, patience and guidance during the course of these studies.

The author is indebted to Dr. L.K. Lam for the many helpful suggestions and discussions, as well as for his assistance with the computer programme.

The author thanks Mr. D. Hill for his technical assistance with the nmr and ir spectrometers.

He further wishes to thank many of his colleagues who have rendered any assistance in this research programme and Miss S. Steevensz for her assistance in the production of this thesis.
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PART I

THERMAL DECOMPOSITION

OF SOME AROMATIC DIAZONIUM HEXAFLUOROARSENATE SALTS

CHAPTER I

INTRODUCTION

A study on the replacement of the aromatic amino group by fluorine has been done by only a few investigators since the late 1940's. The most common and classical procedure of incorporating a fluorine atom into an aromatic nucleus is known as the Schiemann reaction. This particular reaction involves the use of fluoroatomic acid (HBF₄) for the conversion of aromatic amines to aromatic fluorides as shown by Figure 1.

$$\text{ArNH}_2 + \text{NaNO}_2, \text{HCl} \xrightarrow{0 \text{ to } -10^\circ} [\text{ArN}_2]^+\text{Cl}^- \xrightarrow{\text{HBF}_4} [\text{ArN}_2]^+\text{BF}_4^- \xrightarrow{\Delta} \text{ArF} + \text{N}_2 + \text{BF}_3$$

I \hspace{1cm} II \hspace{1cm} III \hspace{1cm} IV

Figure 1 - Schiemann Reaction - Conversion of Aromatic Amines to Aromatic Fluorides

The above general reaction scheme involves a simple diazotization of the aromatic amine I, producing an unstable diazonium salt intermediate II (stable at $-10^\circ$ or lower). However upon the addition of the fluoroatomic ion, a relatively insoluble crystalline salt III is obtained which can be easily washed with cold water and in certain cases can be recrystallized from aqueous solution. The dry diazonium fluoroatomicate is then converted by heat to the aromatic fluoride IV, nitrogen and boron trifluoride. This
latter step in the Schiemann reaction is the most important step, since trace amounts of impurities will lower the yield of the aromatic fluoride. It has been known and reported of cases whereby aromatic chlorides have been found as an extraneous product. The incorporation of a chlorine atom into the aromatic nucleus has been attributed to the coprecipitation of sodium chloride with the fluoroborate salt. The sodium chloride probably originates from the diazotization step which involves the use of sodium nitrite and hydrochloric acid to generate the required nitrous acid.

The mechanism of the pyrolytic decomposition of the aryldiazonium fluoroborates has been studied by several investigators such as Makarova and co-workers and by Olah. No definite conclusions have been drawn. As early as 1949, Roë proposed several mechanisms (Figure 2) for the decomposition of aryldiazonium fluoroborates, but evidence for any one of these proposals as being operative in any or all cases studied is still lacking. Indeed it is possible that one or more routes could contribute to the formation of the aromatic fluoride.

\[
[\text{ArN}_2]^+[\text{FBF}_3]^- \xrightarrow{\Delta} \]

a) Carbyonum Ion Mechanism
\[
\text{Ar}^+ + [\text{FBF}_3]^- + \text{N}_2
\]
\[
\text{Ar}^+ + [\text{FBF}_3]^- \rightarrow \text{ArF} + \text{BF}_3
\]

b) Free Radical Mechanism
\[
\text{Ar}^\cdot + \text{N}_2 + \text{BF}_3 + \cdot\text{F}
\]
\[
\text{Ar}^\cdot + \cdot\text{F} \rightarrow \text{ArF}
\]
c) Concerted Displacement Mechanism

\[ \text{Ar-N=N} \xrightarrow{\text{ArF + N}_2 + BF}_3 \text{F-BF}_3 \]

**Figure 2 - Proposed Mechanisms for the Pyrolytic Decomposition of Aryldiazonium Fluoroborates**

As previously mentioned, the success of the Schiemann reaction is highly dependent on the purity of the intermediate salt. Thus, side reactions in the pyrolysis step can be caused by the presence of impurities such as sodium chloride. Subsequently other workers have attempted to improve the existing Schiemann reaction. In 1930 Lange and Mueller used diazonium hexafluorophosphate salts instead of the corresponding fluoroborates to prepare 4,4'-difluorodiphenyl and fluorobenzene. It was not until 30 years later that in 1960, Newman and Galt reported a slight increase in yield in the synthesis of 6-bromo-2-naphthylfluoride and 1-bromo-3-naphthylfluoride using hexafluorophosphoric acid instead of fluoroboric acid. This prompted Rutherford and co-workers to reinvestigate the Schiemann reaction by the hexafluorophosphoric method, since it was felt that the intermediate aryldiazonium hexafluorophosphate salts (ArN_2PF_6) should be even less soluble than the corresponding fluoroborates. Thus overall yields of aromatic fluorides may be realized. Table I shows that indeed that the hexafluorophosphoric method indicates a decided improvement in the Schiemann reaction.

It was decided to investigate the decomposition of diazonium hexafluoroarsenate salts as a further modification in the Schiemann reaction since it may be possible to obtain higher yields of arsenates over
the corresponding fluorophosphates, perhaps due to greater insolubility because of a molecular weight factor. Again if these salts decomposed smoothly to obtain the corresponding fluorides in greater yields, then the overall Schiemann reaction would be again improved (perhaps even better than that of the hexafluorophosphate modification).
### TABLE I

**HPF₆ vs. HBF₆ in the SCHIEMANN REACTION**

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<thead>
<tr>
<th>Aromatic Amine</th>
<th>Yield of ArN₂BF₄, %</th>
<th>Decomp. temp.</th>
<th>Yield of ArF, %</th>
<th>Yield of ArN₂PF₆, %</th>
<th>Decomp. temp.</th>
<th>Yield of ArF, %</th>
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<td>o-Aminobenzoic acid</td>
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<td>19</td>
<td>79</td>
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<td>Failed</td>
<td>77</td>
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<td>o-Bromoaniline</td>
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CHAPTER II
RESULTS AND DISCUSSION

Synthetic Study of Some Substituted Methyl and Nitrobenzene Fluorides by the Thermal Decomposition from their Corresponding Hexafluoroarsenate Salts

As previously mentioned in the Introduction, the Schiemann reaction generally gives low yields due to the relatively high solubility of the fluoroborate salts. This reaction was greatly improved by the use of hexafluorophosphoric acid instead of tetrafluoroboric acid. Thus the synthesis of fluoroaromatic compounds was chosen by this route since diazonium hexafluorophosphates perhaps, because of their larger molecular size were less soluble in aqueous solution than the corresponding fluoroborates.

Furthermore, increased yield of the intermediate salts resulted in an increased yield of the desired aromatic fluoride upon thermal decomposition. Since the hexafluorophosphates proved to be a convenient method of preparing the desired arylfluorides, it was decided that a further investigation be made using potassium hexafluoroarsenate (KAsF₆) as the fluorinating agent. KAsF₆ should produce a salt of higher molecular weight which presumably could further increase the overall yield of arylfluorides.

Unlike hexafluorophosphoric acid (HF₆), potassium hexafluoroarsenate is a white powdery solid. On the otherhand, HF₆ is liquid which has a tendency to fume (slowly decompose) at room temperature, releasing gaseous hydrogen fluoride (HF) and phosphorous pentafluoride (PF₅). Since hydrogen fluoride has a tendency to etch glass-ware it would appear more advantageous to use a more milder reagent such as KAsF₆ which is safer and easier to handle.
As a consequence, the investigation in using KAsF₆ as a possibility in synthesizing arylfluorides was undertaken. The following reaction sequence is shown in Figure 3.

\[
\text{C}_{6}H_{5}-\text{NH}_{2} \xrightarrow{\text{NaNO}_{2}, \text{HCl}\text{, 0 to -10}} \left[\text{C}_{6}H_{5}\text{N}^{\text{+}}\text{N}\right]^{\text{Cl}^{-}} \xrightarrow{\text{KAsF}_{6}} \left[\text{C}_{6}H_{4}\text{N}^{\text{+}}\text{N}\right]^{\text{AsF}_{6}^{-}}
\]

\[
\left[\text{C}_{6}H_{5}\text{N}^{\text{+}}\text{N}\right]^{\text{AsF}_{6}^{-}} \xrightarrow{\Delta} \text{C}_{6}H_{4}\text{F} + \text{N}_{2} + \text{PF}_{5}
\]

**Figure 3 - Proposed Alternative Synthesis of Arylfluorides using Potassium Hexafluoroarsenate (KAsF₆)**

The preparation in the synthesis of four aryldiazonium hexafluoroarsenate salts chosen, proceeded in a facile manner. The yields of these salts are indicated in Table II. In comparison with the yields of the hexafluorophosphate method (Table I) it is quite apparent that the yields for the hexafluoroarsenate salts are comparable to that of the hexafluorophosphates. These hexafluoroarsenates are as expected, more insoluble in aqueous solution.

All the diazotized arsenate salts are white powders with decomposition temperatures not too different from the corresponding phosphate salts. Identification of the arsenate salts was realized by comparison with nmr and ir spectral analysis of the analogous phosphate salts and each corresponding salt showed similar, if not, identical characteristic peaks.

Upon thermal decomposition of the aryldiazonium hexafluoroarsenates, disappointingly low yields were obtained. Yields could not be bettered
## TABLE II

**Experimental Data Obtained Using Potassium Hexafluoroarsenate in the Schiemann Reaction**

<table>
<thead>
<tr>
<th>Aromatic Amine</th>
<th>% Yield ArN$_2$AsF$_6$</th>
<th>Decomposition temperature</th>
<th>% Yield ArF Neat</th>
<th>Mineral Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Nitroaniline</td>
<td>80</td>
<td>146-150</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>m-Nitroaniline</td>
<td>87</td>
<td>144-146</td>
<td>23</td>
<td>11</td>
</tr>
<tr>
<td>p-Nitroaniline</td>
<td>88</td>
<td>143-145</td>
<td>tar</td>
<td>20</td>
</tr>
<tr>
<td>p-Aminotoluene</td>
<td>74</td>
<td>122-125</td>
<td>tar</td>
<td>15</td>
</tr>
</tbody>
</table>
than 25% under optimum conditions. Pyrolysis was undertaken both at low (100°) and high (210°-220°) temperatures. Under mild decomposition temperatures (100°) no aromatic fluorides were detected, while under more severe conditions (210°-220°) an increased yield of 10 to 20% was observed. Similarly, increased yield was also accomplished if the thermal decomposition of the hexafluoroarsenate salts was performed in the presence of an appropriate diluent such as mineral oil (Nujol) or silicon oil rather than in the neat. The observation in pyrolyzing the diazonium arsenate salts in the neat was that thick intractable tars were obtained which were accompanied with only a low detectable amount of the fluorinated aromatic compounds.

The modification with the KAsF₆ salts resulted in only partial success in the synthesis of the four aromatic fluorides. Although relatively high yields were obtained for the hexafluoroarsenates, very poor yields were obtained for the desired aromatic fluorides in the decomposition step. The lack of success in this final step is difficult to explain. Since the As-F bond energy of the hexafluoroarsenate anion is 6 kcal/mole less than that of the corresponding fluorophosphate (111 kcal/mole versus 117 kcal/mole) one might expect higher yields in the case of the arsenate decomposition. Thus, if a carbonium ion or radical mechanism is operative, there should be less competition for capture of fluoride by either the Ar⁺ or Ar⁻ species. If the concerted mechanism is operative however, then the greater molecular size of AsF₆⁻ versus PF₆⁻ would adversely affect the reaction. It is indeed possible then, that the mechanism of the Schiemann reaction involves a concerted breakdown of the aryldiazenium species.

In view that the synthetic objective was not accomplished for reasons not readily explainable, further investigation of this modification of the
Schiemann reaction was discontinued. If this particular project had been successful, then further investigation into the study of other amines would have been undertaken; especially in the case of the aminopyridines which give only modest yields of corresponding fluorides using the hexafluorophosphate procedure. Again, the next obvious undertaking would involve a study of the corresponding hexafluoroantimonates as a further modification of the Schiemann reaction.
CHAPTER III
EXPERIMENTAL

Identification of the organic compounds was accomplished using infrared (IR) spectra which were obtained using both Beckman IR-10 and/or IR-10 spectrophotometers equipped with potassium bromide cells. Identification of the functional groups are reported from the observed specific absorptions (cm⁻¹) and their intensities are expressed using the following code system: w = weak (100-75 percent transmission), m = medium (70-40 percent transmission) and s = strong (39-0 percent transmission). The solutions to be analyzed were prepared on the basis of weight percent in the stipulated solvents. The melting and decomposition points were determined on a Fisher-Johns apparatus and are uncorrected. Further analyses were also performed on a JEOL C-6HL nuclear magnetic resonance (NMR) spectrometer. The internal standard used was tetramethylsilane (TMS) and the chemical shifts are reported in τ units downfield from the internal standard. The splitting pattern of each resonance is reported using the following code system: s = singlet, d = doublet, t = triplet, m = multiplet and bm = broad multiplet. The compounds analyzed were prepared by weight-volume percent in the specified solvent.

m-Nitrobenzenediazonium Hexafluoroarsenate

To a 125 ml erlenmeyer flask containing 10 ml of distilled water, was added (2 g, 0.015 moles) m-nitroaniline after which concentrated 35 ml (37%) hydrochloric acid was added. The reaction was cooled to ca -15°C in a dry-ice methanol bath whereupon formation of white crystalline m-nitro-
aniline hydrochloride occurred. Diazotization was effectively accomplished when sodium nitrite (1.5 g, 0.028 moles) dissolved in 10 ml of distilled water was added at such a rate that the temperature did not rise above -5°. The blue coloration on KI-starch paper indicated excess nitrous acid upon completion of the addition. After a further cooling to -20°, potassium hexafluoroarsenate (6 g, 0.026 moles) dissolved in 50 ml of distilled water was added to the reaction flask whereupon white solids precipitated from the aqueous phase. After filtration the white precipitate was washed several times with copious amounts of cold distilled water. This was followed by washing with ether. The vacuum dried product yielded 4.3 g (87%) of m-nitrobenzenediazonium hexafluoroarsenate as white powdery solid: mp 144-146° d.; ir (KBr pellet, 12) 3140 (s, CN and NO₂), 700 (s, meta-monomosubstitution); nmr (CD₃SOCD₃, 8%) 0.38, 1.00 and 1.8 (s, bm and t, C₆H₄). Further analysis by comparing the nmr and ir spectra of the m-nitrodiazonium hexafluorophosphate salt proved to be in accord with the correct identification.

**o-Nitrobenzenediazonium Hexafluoroarsenate**

This salt was prepared in a similar manner as the above m-nitrobenzenediazonium hexafluoroarsenate salt, yielding 3.9 g (80%) white powdery crystals of o-nitrobenzenediazonium hexafluoroarsenate: mp 146-150° d.; ir (KBr pellet, 0.5%) 3110 (m, C₆H₄), 2300 (w, N₂), 1800-2100 (w, C₆H₄), 1560 and 1610 (m, C₆H₄), 1350 (s, C-N and NO₂), 840 (s, ortho-disubstituted); nmr (CD₃SOCD₃, 9%) 1.40 (bm, C₆H₄).

**p-Nitrobenzenediazonium Hexafluoroarsenate**

This salt was prepared in a similar manner as the m-nitrobenzenediazon-
ium hexafluoroarsenates yielding 4.3 g (88%) white crystalline powder
of p-nitrobenzenediazonium hexafluoroarseniate: mp 143-145° d.; ir (KBr
pellet, 1%) 3110 (m, C₆H₄), 2950 (m, CH₃, CH₂ and CH), 2280 (s, N₂), 1700-
2000 (w, C₆H₄), 1600 (s, C₆H₄), 1100 (s, NO₂), 1075 (s, C-N), 850 (s, para-
disubstituted); nmr (CD₂SOCD₃, 10%) 1.0 and 1.3 (d, J = 6.0 Hz, C₆H₄).

m-Fluoronitrobenzene

A dropping powder bulb, containing m-nitrobenzenediazonium hexafluoro-
arsenate (2 g, 0.006 moles) was attached to a 1 litre, round-bottomed, three-
necked flask equipped with a condenser, containing 300 ml of mineral oil
(Nujol). The entire flask was placed in a hot silicon oil bath (200°) of
which the temperature was ca 50° above the decomposition point of the ar-
senate. The decomposition was carried out at a rate sufficient to evolve
arsenious pentafluoride rapidly yet without explosiveness. After all the
powdered reactant was added, the flask was cooled to room temperature and
an aqueous solution of 5% sodium carbonate (20 ml) was introduced through
the top of the condenser in order to wash down any condensed fluoromatic
and neutralize the acidic reaction mixture. The desired m-nitrofluoro-
benzene was separated by steam distillation, extracted from the aqueous
layer with chloroform and dried over anhydrous sodium sulfate. The concen-
trated organic layer yielded 0.25 g (11.4%) of m-nitrofluorobenzene: ir
(CS₂, 5%) 3100 (w, C₆H₄), 2910 (w, CH₂ and CH), 2000-1700 (w, C₆H₄), 1350
(s, NO₂ and C-N), 810 (s, para-disubstituted); nmr (CS₂, 5%) 2.4 (bm, C₆H₄).

o-Fluoronitrobenzene

Synthesis of this aromatic fluoride was done in the similar manner as
for the m-nitrofluorobenzene resulting in a yield of 0.48 g (24%): ir
- (CS₂, 5%) 3050 (w, C₆H₄), 2900 (w, CH₂ and CH), 2000-1700 (w, C₆H₄), 1615 (s, C₆H₄), 1350 (s, NO₂ and C-N), 750 (s, ortho-disubstituted); nmr (CS₂, 5%) 2.5 (bm, C₆H₄).

**p-Fluoronitrobenzene**

The synthetic procedure was followed in the same manner as in the case of m-fluoronitrobenzene resulting in the yield of 0.39 g, (20%) of p-fluoronitrobenzene: IR (CS₂, 10%) 3100 (w, C₆H₄), 2915 (w, CH₂ and CH), 2000-1700 (w, C₆H₄), 1350 and 1365 (s, C-N and NO₂), 850 (s, para-disubstituted); nmr (CS₂, 14%) 1.85 and 2.90 (bm, C₆H₄).

**p-Fluorotoluene**

This aromatic fluoride was prepared using the same procedure as in the synthesis of the m-fluoronitrobenzene yielding 0.25 g, (15%) of product: IR (CHCl₃, 10%) 3040 (w, C₆H₄), 2915 (w, CH₂ and CH), 1500 and 1600 (s, C₆H₄), 835 (s, para-disubstituted); nmr (CS₂, 14%) 2.30 (bm, C₆H₄).
REFERENCES

PART II

THE THERMAL DECOMPOSITION OF SOME METHYL ETHERS OF TRANS-1-PHENYL-

2-METHYLCYCLOHEXANOL AND PARA-SUBSTITUTED DERIVATIVES

CHAPTER I

INTRODUCTION

It is generally known that ethers, under normal conditions, are thermally stable compounds. As regards the geometry and experimental bond energy data of simple aliphatic ethers, it is found that the C-O-C bond angle is ca 112°, the C-O bond length ca 1.41 Å and the bond energy ca 83-85 kcal/mole which is comparable to that of the usual C-C bond energy of 83 kcal/mole. From the bond energies alone, one can readily see why studies on thermal decomposition of organic ethers have been largely confined to gas phase type pyrolysis.

Although much work has been recorded on the thermal decomposition of ethers, it was not until the early 1950's that kineicicists have elucidated the mechanisms involved in gas phase pyrolysis. For example it is well known that the thermal decomposition of dimethyl and diethyl ether prior to 1950 was given only cursory treatment as regards to mechanism of breakdown. Since, workers such as Benson, Laidler, and Long have studied the kinetics on the thermal decomposition of these compounds in great detail. These ethers undergo pyrolysis in the temperature range of 500° to 600° with an applied pressure in the region of 400 to 1600 mm. The main pyrolytic products obtained for dimethyl and diethyl ether may be respec-
tively presented in the following equations (Figure 1).

\[
\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_4 + \text{CH}_2\text{O} \quad \text{CO} + \text{H}_2
\]
\[
\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{C}_2\text{H}_4
\]
\[
\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow \text{CH}_3\text{CHO} + \text{C}_2\text{H}_6
\]

**Figure 1 - Pyrolysis of Dimethyl and Diethyl Ether**

More complex organic ethers have also been extensively investigated. In 1961, De Puy and co-workers studied the decomposition of vinyl ethers such as s-butyl vinyl ether and found that it underwent a pyrolytic cis elimination at a temperature of 450°. The products obtained were as follows: 47 percent 1-butene, 37 percent trans-2-butene and 16 percent cis-2-butene. The reaction mechanism postulated (from a product study only) was that which involves a cyclic non-chain path. The percent olefinic mixture is undoubtedly obtained from a thermodynamically controlled process at this high temperature.

**Figure 2 - The Pyrolysis of s-Butyl Vinyl Ether**

The above postulated mechanism (Figure 2) is similar to that proposed by
Molera for the pyrolytic rearrangement of vinyl allyl ether. This was further elucidated by the $^{14}$C labelling technique of Pocker (Figure 3).

![Chemical Reaction](image)

**Figure 3 - Rearrangement of Vinyl Allyl Ether with Labelled $^{14}$C**

The above reaction has been commonly referred to as an extension of the Claisen rearrangement. Again, Cookson and Wallis in 1963 pyrolyzed eleven different allyl ethers where, in each case, the products obtained were those expected from a 6-membered ring molecular rearrangement. This type of pyrolysis is somewhat analogous to the classic pyrolyses of acetates (Figure 4) although in this case, elimination of an organic acid is obtained via the cyclic 6-membered ring process to yield olefinic products.

![Ester Pyrolysis](image)

**Figure 4 - Ester Pyrolysis**

In order for the C-O bond to be broken between the oxygen atom and the smaller alkyl group in the case of ethers, it is necessary to supply much energy. However the addition of a catalyst may facilitate the cleavage of the ether linkage. The chemical properties of the ether linkage is highly dependent on the non-bonded electrons of oxygen. Thus the addition of a proton would effectively withdraw electrons from the oxygen atom and in turn
from the adjacent carbon atom, thus tending to weaken the C-O bond due to partial carbonium ion character.

In 1967 Olah and O'Brien studied protonated [FSO$_3$H-SbF$_3$] n-alkyl ethers such as n-butyl methyl ether by nmr at a low temperature of 40°. With the protonated s-butyl methyl ether and t-butyl methyl ether, pyrolysis could be followed even at lower temperatures of -30° and -70° respectively. From their experimental data, it was indicated that the rate determining step is the formation of the n-alkyl carbonium ion, followed by a rapid rearrangement to the more stable trimethyl carbonium ion as shown in the following equation (Figure 5).

\[
\begin{align*}
\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 & \xrightarrow{k_1} \text{CH}_3\text{OH}_2 + \text{CH}_3\text{CH}_2\text{CHCH}_3 \xrightarrow{k_2} (\text{CH}_3)_3\text{C}^+ \\
& \text{H}^+ \quad \text{H}^+ \\
& \text{CH}_3 \\
\end{align*}
\]

\(k_1 \ll k_2\)

**Figure 5 - Pyrolysis of s-Butyl Methyl Ether in the Presence of a Proton Catalyst**

Not all catalytic pyrolyses occur in such a facile manner. Recently in 1972 Daly and Steele investigated the pyrolysis of t-butyl isopropyl ether catalyzed by hydrogen chloride at 319-420°. It should be noted that for a non-catalytic reaction of this ether, the pyrolysis is of necessity investigated at higher temperatures (550-600°). The catalytic reaction afforded first order kinetics and the major products obtained were isobutene and isopropyl alcohol with trace amounts of propene and t-butyl alcohol (Figure 6).

\[
\begin{align*}
(\text{CH}_3)_3\text{C}^-\text{O}^-\text{CH} & \xrightarrow{\text{HCl}} \text{C}^-\text{CH}_2^- + \text{C}^-\text{OH} + \text{HCl} \\
\text{CH}_3 \quad \text{CH}_3 \\
\end{align*}
\]

**Figure 6 - Catalytic Pyrolysis of t-Butyl Isopropyl Ether**
The effect of introducing various substituents to an organic ether compound can also alter the rates of reaction in pyrolyses. This is caused by different changes in the free energies of the initial and transition or final states. This has been shown in the thermal decomposition of aryl allylethers as in the ortho Claisen Rearrangement. Goering and Jacobson, in their pyrolysis of para and meta substituted ethers indicated that the p-ethoxy and p-methoxy allyl phenyl ethers had kinetic rates about six times more rapid than that of the p-nitro substituent. On the other hand the m-methoxy derivative exhibits a slightly greater rate than the p-methoxy substituent as shown in Table I'.

\[
\begin{array}{cccc}
X & p-$\text{EtO}$ & p-$\text{MeO}$ & m-$\text{MeO}$ & p-$\text{NO}_2$ \\
\hline
k_1/k_4 & 3.15 & 3.01 & 3.24 & 0.59 \\
\end{array}
\]

**Table I'**

Rate Constant for the Substituted Allyl Phenyl Ethers
From the observed data, the facility of the methoxy group to generate the rearranged products was explained by White and co-workers as a homolytic splitting of the C-O bonds to produce two radicals (Figure 7).

![Chemical structures](image)

Figure 7 - Radical Type Mechanism Involved in the Pyrolysis of the p-Methoxy and p-Nitro Substituted Allyl Phenyl Ether

It can be argued that the p-methoxy substituent in the allyl phenyl ether as shown in Figure 7, facilitates (as indicated by C-O·) the initial bond-fission but in the p-nitro allyl phenyl ether case there exist a retardation of electron release (C-O·) towards the reaction centre and therefore a much lower reaction rate is realised. It was argued that the m-methoxy substituent has a slightly more accelerating effect than the p-methoxy substituent because its electron release is in the para position with respect to product formation as shown in the following structures (Figure 8).

![Chemical structures](image)

Figure 8 - Postulated Product Formation for the Pyrolysis of p-Methoxy and m-Methoxy Substituted Allyl Phenyl Ether
In general, experiments can be performed to correlate structure with reactivity by the information obtained on the effect of substituents on kinetically controlled reaction rates. The relationship between the rate (or equilibrium) constant of a substituted constituent \( k_x \), and that of its unsubstituted parent compound \( k_n \), can usually be presented in the form of the Hammett equation as follows:

\[
\log \frac{k_x}{k_n} = \sigma \rho
\]  

[1]

The character of the substituent is represented by \( \sigma \) notation, and this parameter measures the ability of the substituent to change the density of electrons at the reaction centre and is also independent of the reaction involved. The characteristic of the reaction series is represented by the \( \rho \) notation and this parameter measures the sensitivity of the reaction series to change in the electron density at the reaction centre. However there exist certain limits to the Hammett equation. The equation generally does not apply to the reactions of aliphatic compounds since the bending and twisting of the aliphatic chain may produce an appreciable amount of steric interaction. It should also be noted that in most cases the equation is valid only for substituents in the meta and para positions but not in the ortho position of the benzene ring. Ortho-substituted benzene derivatives lie close to the reaction site which may influence the reaction by steric as well as electron attracting and releasing interactions. The Hammett equation may also be written in the following form:

\[
\log k_x = \sigma \rho + \log k_n
\]  

[2]

or in the thermodynamic terms of Gibbs Free-Energy of Activation changes
\( \Delta F^* \) for kinetic studies:

\[-\Delta F^* = (RT)\sigma - \Delta F_0^* \]

where \( R \) is the ideal gas constant and \( T \) temperature in °K units

The above equation [3] can be compared to the mathematical form of \( y = mx + b \) which would indicate that the Hammett equation is a linear function with respect to a given series of \( \sigma \) values. Reactions have been followed by the kinetic studies on ionization, pH, hydrolysis, reduction, halogenation, pyrolysis, etc. In most cases cited, the Hammett treatment produced a linear relationship with a slope value of \( \rho \). However, recently (1971) Schreck indicated that although there exist a vast number of reactions which give a linear relationship, there exist in his review a small number of non-linear Hammett plots. These he attributed to changes in reaction mechanism in the presence of certain substituents or a composite quantity of rate constants of several reaction steps.

The reaction constant \( \rho \) can be quite important when determining the type of mechanism presently occurring in a reaction process. The \( \rho \) value is not only a measure of electron demand at the reaction centre but also on the structure of the system which governs the efficiency of the transmission to the reaction centre of electron displacements initiated by the substituents. Thus many reactions can be roughly interpreted by the \( \rho \)-values alone. Radical type reactions have \( \rho \)-values usually less than 1.6 while other type of reactions such as those which involve ionic type transition states have values far smaller (0 to -50).

As previously mentioned, most ether pyrolyses are performed in vapor phase systems at high temperatures whereby the transition state encompasses
a radical-or concerted type mechanism rather than that of the ionic or pseudo-ionic type (ion pair). In 1971, Spangler and Hennis\textsuperscript{20} pyrolysed ethyl methyldicyclohexenyl ethers by vapor phase passage over alumina at temperatures of 250–300° to produce ethanol and olefinic products.

\[
\begin{align*}
\text{OEt} & \quad \text{OEt} \\
\text{R} & \quad \text{R} \\
\text{(73\%)} & \quad \text{(69\%)} \\
\text{(24\%)} & \quad \text{(41\%)}
\end{align*}
\]

Figure 9 - Pyrolysis of Ethyl Methyldicyclohexenyl Ethers

Their supposition to the above reaction mechanism is that each ether proceeds through an allylic carbonium ion intermediate from which the diene products are then formed. However, no evidence for this mechanism was given other than that based on product distribution.

It can be readily seen that there has been little work accomplished on the pyrolysis of ethers which might decompose via an ionic type mechanism although this type of mechanism has been well documented in solvolysis reactions. Thus Winstead and his colleagues proposed from their kinetic, stereochemical and rearrangement studies along with common ion and special salt effects, a scheme involving intimate and solvent-separated ion pairs.
and as well as dissociated ions (Figure 10).

\[
\begin{align*}
RX & \leftrightarrow R^+X^- \quad \text{intimate ion-pair} \quad \Pi \\
& \leftrightarrow R^+||X^- \quad \text{solvent-separated ion-pair} \\
& \rightarrow R^+ + X^- \quad \text{dissociated ions} \\
& \rightarrow \text{Products}
\end{align*}
\]

**Figure 10 - Ion-Pair Mechanism Proposed by Weinstein in Solvoysis Reactions**

In our previous discussion on the pyrolysis of substituted allyl phenyl ethers (Figure 7 and 8) the radical type of mechanism can probably be ignored as a possibility. White and his co-workers did however suggest the possibility of ion-pairs intervening between the allyl arylether and the dienone intermediate. For an ion-pair mechanism, it would be a requisite that the allyl group ionize as an anion and the aromatic moiety as a cation (Figure 11).

**Figure 11 - Proposed Ion-Pair Intermediate in the Pyrolysis of Allyl Phenyl Ethers**

Work in our laboratory on low temperature pyrolysis began in 1960 when it was found that the hydrogen phthalate ester of 2-phenyl-2-butanol decomposed at 111° to yield an olefinic mixture and phthalic acid. Indeed, it was found that hydrogen phthalate esters of several tertiary alcohols decom-
posed at temperatures of ca 150° and lower, and a further exhaustive study by several workers (10-15) indicated that the normal C-O-C bond breaking process involved the following factors: ease of carbonium ion formation and acid catalysis which is inherent in the hydrogen phthalate system. From these studies, a generalized reaction scheme (Figure 12) was proposed for both neat and solution pyrolysis.

![Diagram](image)

**Figure 12 - Proposed Reaction Paths for Neat and Solution Pyrolyses**

As can be seen, the above reaction paths encompass both neat and solvent ionic type pyrolyses reactions. The next obvious approach was to make a study of the thermal decomposition of some tertiary ethers to see the effect of structure on the decomposition temperature and study the mechanism(s) involved.

Since exhaustive work on the pyrolysis of the hydrogen phthalates of 1-phenyl-2-methylcyclohexanol system was already accomplished, it was decided to study the pyrolysis of the methyl ethers of trans-1-aryl-2-methyl-cyclohexanols to obtain information as regards to the above mentioned structure-mechanistic relationships. This choice of structure is ideal since the stereochemistry of the Grignard reaction of the phenyl magnesium bromide (23,24) with 1-methylcyclohexanone was previously shown in our laboratory. Thus good yields of trans-1-aryl-2-methylcyclohexanols can be obtained from
this reaction.

Hence pyrolyses was undertaken of tertiary substituted ethers, 1,1'-methoxy(p-Xphenyl)-2-methylcyclohexane, in inert solvent at low temperatures (230° to 295°) and under non-catalytic conditions. With such mild solvent pyrolytic conditions, the rate of thermal decomposition of each ether derivative to its alcohol and olefinic products can then be followed. By applying the Hammett equation, a proposed mechanism may demonstrate an ion-pair intermediate as suggested in the solvent pyrolyses of the hydrogen pthalates.
CHAPTER II
RESULTS AND DISCUSSION

General Synthetic Procedure and the Elucidation of the Olefinic Products

The elucidation of the structure of the final olefinic products obtained on pyrolysis of the ethers was accomplished by nmr spectral analysis. The olefins (both Hofmann and Saytzeff products) were obtained conveniently by the dehydration (using acid conditions) of the corresponding alcohols to yield an isomeric mixture. This isomeric mixture was easily separated by gas-liquid chromatography (glc). For example an isomeric mixture of 1-(p-methoxyphenyl)-2-methylcyclohexanol yielded a mixture of 1-(p-methoxyphenyl)-2-methylcyclohex-1-ene (Saytzeff product) and 1-(p-methoxyphenyl)-2-methylcyclohex-6-ene (Hofmann product) in the ratio of 6:1 respectively. The ratio 6:1 is to be expected because under these conditions the Saytzeff product should be more stable than the corresponding Hofmann isomer from thermodynamic considerations. The synthesis of the intermediate trans-alcohols was accomplished by the reaction of 2-methylcyclohexanone and the desired aryl magnesium grignard reagent. This reaction had been previously shown in our laboratory to yield predominantly the trans-1-aryl-2-methylcyclohexanol (in greater than 90% yield). The cyclohexanols were converted directly to the desired methyl ethers via the Williamson reaction and the final products were purified by recrystallization. Figure 13 shows the ethers prepared for kinetic studies.

![Figure 13](image)

Figure 13 - trans-p-Substituted-1-Aryl-2-methylcyclohexyl Methyl Ethers

X = H, CH₃O, CH₃, Cl, Br, NO₂.
As can be seen from Figure 13, a reasonably broad spectrum of substituents (X) were chosen to study the electron donating and withdrawing effects on the pyrolyses of the ethers. Pyrolyses studies were carried out in high boiling, inert, diphenyl ether.

*Kinetic Studies on the Pyrolyses of trans-1,1'-Methoxy (p-Xphenyl)-2-methylcyclohexane in Diphenyl Ether*

The kinetic experiments on the substituted ether derivatives were performed mainly at two temperatures 255° and 295°, except for the 1,1'-methoxy (p-methoxyphenyl)-2-methylcyclohexane which was performed at temperatures of 255° and 230°. To avoid any temperature fluctuation as well as air oxidation of the wood metal bath, maximum allowed temperature of 255° (±3.0°) was maintained while a sand-bath was used for the more elevated temperature of 295° (±3.0°).

After each interval of pyrolysis at the desired temperature, the pyrolysis tube was immediately analysed by nmr. Each spectrum was integrated at least three times and an average peak area of the methoxy peak of the starting material was recorded (Figure 14).

The observed experimental rate constants for each substituted ether are given in Table I. These constants indicate first order kinetics which would suggest unimolecular decomposition. The reactivity of the compounds may be shown in decreasing order of OCH₃ > CH₃ > R > Cl, which indicates that the effects of the substituent groups are quite comparable by inductive and/or resonance effects through the aromatic ring. This order of reactivity is to be expected; that is the methoxy group greatly accelerates the pyrolysis since resonance of this group (-I, +R group) in the para position of the benzene
**TABLE I**

Summary on the Experimental Rate Constants \( (k, \text{sec}^{-1}) \) Obtained on the Pyrolysis of 1,1'-methoxy (p-Xphenyl)-2-methylcyclohexanes

<table>
<thead>
<tr>
<th>Substituents ((X)) on Parent Compound</th>
<th>Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>255(^\circ)</td>
</tr>
<tr>
<td>bromo ((-\text{Br}))</td>
<td>(1.221 \times 10^{-5})</td>
</tr>
<tr>
<td>chloro ((-\text{Cl}))</td>
<td>(1.407 \times 10^{-7})</td>
</tr>
<tr>
<td>methoxy ((-\text{OCH}_3))</td>
<td>(2.303 \times 10^{-4})</td>
</tr>
<tr>
<td>methyl ((-\text{CH}_3))</td>
<td>(1.059 \times 10^{-5})</td>
</tr>
<tr>
<td>nitro ((-\text{NO}_2))</td>
<td>(3.366 \times 10^{-6})</td>
</tr>
<tr>
<td>unsubstituted ((-\text{H}))</td>
<td>(5.112 \times 10^{-7})</td>
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</tbody>
</table>

\(\text{(a)}\) Pyrolysis temperature at 230\(^\circ\).

\(\text{(b)}\) Theoretically calculated on computer programme.
Figure 14 - Systematic Time Interval Pyrolysis of 1,1'-Methoxy (p-methyl phenyl)-2-methylcyclohexane Observed by Nuclear Magnetic Resonance (nmr)
ring increases the electron density at the 1 position of the cyclohexane ring, thus enhancing the bond breaking of the ether linkage (Figure 15).

![Figure 15 - Resonance Structure of 1,1'-Methoxy (p-methoxylphenyl)-2-methylcyclohexane Carbonium Ion](image)

At the other end of the reactivity scale, the chlorine atom (-I, +R group), unlike the electron-donating character of the methoxy substituent, tends to withdraw electrons from the reactive site and therefore retards the C-O bond cleavage drastically (Figure 16).

![Figure 16 - Inductive Effect of 1,1'-Methoxy (p-chlorophenyl)-2-methylcyclohexane](image)
It should be noted indeed that experimentally, the inductive effect for the chlorine atom supersedes the resonance effect. Comparing both substituents one should also point out that the chlorine atom is more electronegative (3.0) than the methoxy group (1.0). Under such conditions it is not too surprising to observe that the rate for the methoxy substituent is $5 \times 10^9$ (at 100°) faster than the chloro substituent. Similarly, the same analogy of inductive and resonance effect can be applied to the methyl and proton substituents. The methyl group (+I, +R group) will tend to donate electrons to another group due to the carbon atom having slightly greater electronegativity value than the hydrogen atom (2.5 and 2.15 respectively) (Figure 17).

\[ \begin{align*}
\Delta H_\delta \\
\delta H + C \rightarrow \\
\delta H
\end{align*} \]

**Figure 17 - Electron-donating (Pushing) Effect of the Methyl Group**

However due to the more readily available non-bonded electrons on the methoxy substituent, a lesser rate is observed for the methyl group. Again, the methyl substituted compound shows a faster rate than the hydrogen and chlorine substituted ethers. This phenomena could be attributed to the resonance conjugation involving "non-bonded" resonance forms of hydrogen, often termed as hyperconjugation (Figure 18).

\[ \begin{align*}
\text{CH}_3\text{OCH}_3\text{CH}_3
\end{align*} \]

**Figure 18 - Hyperconjugative Effect of the p-Methyl Group in the Case of 1,1'-Methoxy (p-methylphenyl)-2-methylcyclohexane**
This type of resonance indicates that there exists some electron density at the 1 position of the cyclohexane ring enhancing the rate of olefin production by $2.2 \times 10^{-6}$ (at 100°) greater in the case of the chloro substituent. The unsubstituted ether has neither as strong an electron donating character comparable to the methyl substituent nor as strong an electron-withdrawing character comparable to the chloro substituent. The hydrogen atom has an electronegativity value (2.15) less than the carbon atom (3.5) and an even a smaller value than the chlorine atom (3.0). Furthermore, the electronegativity of the methyl group would be negated by a much smaller value due to the attached protons as explained above. It is therefore not too surprising to observe the rate constant of the unsubstituted ether to exist in between the rate constants of the chloro and methyl substituted ethers ($\text{CH}_3\text{O} > \text{CH}_3 > \text{H} > \text{Cl}$).

As previously suggested, the ether pyrolysis seems to demonstrate a preference to an overall Hofmann product. From the stereochemical point of view, this could be accounted for by the fact that there could exist a cis effect between the substituted benzene ring and the methyl group inhibiting the formation of the Saytzeff olefin (Figure 19).

**Figure 19** - Sterically Inhibited Formation of the Saytzeff Olefin due to a trans-Ether Configuration
Furthermore there can also exist a definite anion proximity effect which may operate through an ion-pair intermediate. If this is the case, then the anion would preferentially remove a proton at position 6 (closer proximity to the Hydrogen atom on C-6) leading to the Hofmann product rather than the more thermodynamically stable Saytzeff olefinic product. Such a proposed common intermediate can very well explain the observed rate constants and the predominance of the 1-(p-Xphenyl)-2-methylcyclohex-6-ene olefin product.

From the thermodynamic data (Table II), the ether compound containing the p-methoxy substituent appears to have a rate determining step to be that of a solvent separated ion-pair intermediate since the experimental entropy of activation ($\Delta S^+ = -31.99$ eu) indicates a more ordered arrangement with less thermal energy required ($\Delta H^+ = 23.41$ kcal/mole). If this postulate holds to be true, then the solvent separated ion-pair is probably formed after formation of an intimate ion-pair. The least reactive ether of this system, is the chloro substituted ether ($\Delta H^* = 61.12$ kcal/mole) and it indicates from the experimental data to undergo a transition state of a more molecular random configuration ($\Delta S^* = +24.70$ eu), perhaps that of an intimate ion-pair formation. The methyl substituted ether and the unsubstituted ether seem to produce a combination effect of either the intimate or the solvent separated ion-pair ($\Delta S^* = -16.48$ eu and $-16.0$ eu respectively); that is the possible existence of reversibly formed intimate and solvent separated ion-pairs in which product formation may occur from either of these two steps. The reversibility of the intimate and solvent separated ion-pair has already been determined by Weinstein and his co-
TABLE II

Experimental Values Obtained on the Thermodynamic Parameters

$\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ from the Pyrolysis of 1,1'-Methoxy (p-Xphenyl)-2-methyl-cyclohexanes in Diphenyl Ether at 100°

<table>
<thead>
<tr>
<th>Substituent (X) on Parent Compound</th>
<th>$\Delta H^\circ$ (kcal/mole)</th>
<th>$\Delta S^\circ$ (eu)</th>
<th>$\Delta G^\circ$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bromo (-Br)</td>
<td>26.24</td>
<td>-32.46</td>
<td>38.35</td>
</tr>
<tr>
<td>chloro (-Cl)</td>
<td>61.12</td>
<td>+24.70</td>
<td>51.91</td>
</tr>
<tr>
<td>methoxy (-OCH₃)</td>
<td>23.41</td>
<td>-31.99</td>
<td>35.34</td>
</tr>
<tr>
<td>methyl (-CH₃)</td>
<td>34.83</td>
<td>-16.48</td>
<td>40.98</td>
</tr>
<tr>
<td>nitro (-NO₂)</td>
<td>29.14</td>
<td>-29.54</td>
<td>40.16</td>
</tr>
<tr>
<td>unsubstituted (-H)</td>
<td>38.26</td>
<td>-16.01</td>
<td>44.23</td>
</tr>
</tbody>
</table>
workers in their dual ion-pair hypothesis and special salt effect. Recently, Rutherford and co-workers studied the pyrolysis of labelled 18 hydrogen phthalates and concluded an involvement of intimate and solvent separated ion-pairs during thermal decomposition. The kinetic rates as already discussed, can also be explained by the Gibbs free energy parameter ($\Delta G^\circ$). It indicates that the reaction for the methoxy substituent is more spontaneous ($\Delta G^\circ = 35.34$ kcal/mole) than the chloro substituent in which a slower reaction is noted ($\Delta G^\circ = 51.91$ kcal/mole).

The Hammett $\sigma$-$\rho$ Relationship on the Solvent Pyrolysis of Tertiary Ethers.

1,1'-Methoxy (p-Xylenyl)-2-methylcyclohexanes

In order to further examine the mechanistic properties of this particular series of tertiary ethers, the data obtained was subjected to the Hammett $\sigma$-$\rho$ relationship. The preliminary graph (Figure 20), showing the log $k$ (rate) versus the respective Hammett $\sigma$ values, resulted in a linear curve for this series of ethers (chloro, hydrogen, methyl and methoxy para-substituents) indicating significantly the trend of the electron density at the reaction site; that is, the experimental Hammett $\sigma$ value is directly proportional to the electron attracting or electron withdrawing power of the substituent. A further application of the $\sigma$ values were plotted against the logarithmic ratios of the rate constant of the substituted and the unsubstituted compound, and another linear function was obtained (Figure 21). The estimated $\rho$ parameter has a very low value of $-19.6$, highly indicative of a substituent sensitive reaction. The negative value of $\rho$ would primarily indicate that the facility of the reaction is enhanced when electron donor substituents are present. In general, the results would appear to indicate the
### TABLE III

Experimental Data Obtained from the Pyrolyses of trans-1,1'-Methoxy (X-Phenyl)-2-methylcyclohexanes in Diphenyl Ether at 100°(a), Subjected to the Hammett \( \sigma \) values

<table>
<thead>
<tr>
<th>Substituent (X) on Parent Compound</th>
<th>( \sigma )</th>
<th>log. ( k )</th>
<th>( k_x/k_H )</th>
<th>log. ( k_x/k_H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>bromo( (-Br) )</td>
<td>+0.23</td>
<td>-9.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>chloro( (-Cl) )</td>
<td>+0.23</td>
<td>-17.51</td>
<td>( 3.23 \times 10^{-5} )</td>
<td>-4.50</td>
</tr>
<tr>
<td>methoxy( (-OCH_3) )</td>
<td>-0.27</td>
<td>-7.81</td>
<td>( 1.61 \times 10^{-5} )</td>
<td>+5.20</td>
</tr>
<tr>
<td>methyl( (-CH_3) )</td>
<td>-0.17</td>
<td>-11.11</td>
<td>( 8.05 \times 10^{-10} )</td>
<td>+1.91</td>
</tr>
<tr>
<td>nitro( (-NO_2) )</td>
<td>+0.78</td>
<td>-10.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>unsubstituted( (-H) )</td>
<td>0.0</td>
<td>-13.02</td>
<td>1.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

(a) Theoretically calculated on computer programme.
Figure 20 - Plot of Hammett σ Values Versus Logarithmic k (Rate Constant) on the Pyrolyses of trans-1,1'-Methoxy (X-Phenyl)-2-methylcyclohexanes in Diphenyl Ether at 100° (Table III)
Figure 21 - Application of the Hammett $\rho$ Equation to the Pyrolyses of 1,1'-Methoxy (X-Phenyl)-2-methylcyclohexanes in Diphenyl Ether at 100°C (Table IID) with an Estimated $\rho$ value of -19.6
presence of carbonium ion character which is drastically affected by the presence of substituents attached to the aromatic ring. The chloro substituent, although weak electron donating (resonance effect) is strong electron attracting (inductive effect) which would decrease the stability of an intimate ion-pair species (\(\Delta S^+\)) and cause an increase in the required thermal energy (\(\Delta H^+ = 61.32\) kcal/mole). On the other hand the methoxy group is a weak electron withdrawer (inductive effect) but a strong electron donator (resonance effect) which would increase the stability of a solvated carbonium ion (\(-\Delta S^+\)) and cause a decrease in the required energy (\(\Delta H^+ = 23.41\) kcal/mole).

Most ion-pairs that presumably exist in the solvent phase have negative \(\rho\) values in the range of 0 to -11.35. However gas phase studies have produced \(\rho\) values as low as -19.1. This particular gas phase study was studied by Harrison and co-workers whereby ionization potentials of substituted benzyl radicals were determined by electron impact resulting in the stabilization of ions in the gas phase where solvation played no role (Figure 22).

\[ \begin{array}{c}
\text{X-CH}_2^- \\
\text{electro}\text{n impact} \\
\text{X-CH}_2^+ \\
\end{array} \]

**Figure 22 - Substituted Benzyl Radicals Studied in the Gas Phase**

His \(\rho\) value was derived from Brown's \(\sigma^+\) constant rather than from Hammett's \(\sigma\) constant and it was concluded that the \(\rho\) value obtained, was a measure of
the energy susceptibility for ion-pair formation in the gas phase. Other investigators such as Taft and his colleagues have done similar gas phase work and obtained even lower \( \rho \) values (based on \( \sigma^+ \)) of about -45.0 using substituted methyl radicals to produce the methyl cation (Figure 23).

\[
\text{CH}_3X \rightarrow + \text{CH}_2X + 2e^{-} + \text{H}
\]

**Figure 23 - Gas Phase Studies of Substituted Methane Derivatives**

It should be noted that the bromo and nitro groups were excluded in our series as regards to comparative discussion, since the substituents did not conform to the Hammett \( \rho \sigma \) plot. The observed experimental rate constants for the bromo and nitro group were close to the average of the methoxy and methyl substituents. The nmr spectrum of the bromo substituted ether did not correlate to the spectrum of the corresponding chloro substituted ether, although one would expect a similarity. The peaks as well as the integration of both compounds (bromo and nitro) on the nmr spectrum proved to be the correct desired ether derivatives; however elemental analysis indicated possible inseparable impurities. One would otherwise presume that the nitro substituent, being strong in both inductive and resonance effect would considerably decrease the stability of the carbonium ion and therefore would have a much lower rate constant than the observed experimental rate constant.

**Summary and Conclusions**

In view of the experimental results obtained, it would appear from the entropy and enthalpy of activation as well as from the \( \rho \) values, that the pyrolysis is consistent (in the case of the four compounds earlier mentioned)
with the rate-determining formation of an ion-pair mechanism either solvated or unsolvated (Figure 24).

![Chemical structure](image)

Figure 24 - Proposed Ion-pair Mechanism for the Pyrolysis of 1,1'-Methoxy (p-Xphenyl)-2-methylcyclohexanes

From the present data obtained one can only speculate on the detail of the actual ion-pair mechanism. A general ion-pair scheme for solution pyrolysis may involve any or all four (a, b, c and d) reaction pathway(s) as shown in the following diagram (Figure 25).

![Diagram](image)

Figure 25 - Proposed Ion-Pair Scheme for Solvent Pyrolysis

The pathway would be reflected by the thermodynamic quantities calculated for $\Delta S^*$ and $\Delta H^*$ as well as from the $\rho$ values obtained. In the case of the anomalous p-bromo and p-nitrophenyl ethers, the thermodynamic data and $\rho$ values might possibly be accounted for by a radical or concerted breakdown of the ethers. Apart from such deviations, the proposed scheme (Figure 25) would be appropriate for solvent pyrolysis since the experimental data indicated as follows:
(i) a unimolecular reaction (1st order kinetics).
(ii) reversibility of intimate and solvent separated ion-pair
(extrme high and low values of $\Delta S^*$).
(iii) the existence of ion-pair formation in the ether series ($\rho = -19.6$, carbonium ion character).
CHAPTER III

EXPERIMENTAL

Melting and decomposition points were determined on a Fisher-Johns apparatus and are uncorrected. The infrared (ir) spectra were obtained using Beckman IR-10 and Beckman IR-12 spectrophotometers equipped with potassium bromide cells. The specific absorptions are reported \( \text{cm}^{-1} \) and their intensities are expressed using the following code system: \( w = \text{weak} \) (100-75 percent transmission), \( m = \text{medium} \) (74-40 percent transmission) and \( s = \text{strong} \) (39-0 percent transmission). The solutions were prepared by weight-weight percent in the solvent stipulated. Microanalysis were determined by Microanalysis Laboratories Limited, Toronto, Ontario. Nuclear magnetic resonance (nmr) spectra were recorded on a JEOL C-60HL nmr spectrometer. The chemical shifts are expressed in \( \tau \) units downfield from the internal standard, tetramethylsilane (TMS). The splitting pattern of each resonance is reported using the following code system: \( s = \text{singlet} \), \( d = \text{doublet} \), \( t = \text{triplet} \), \( m = \text{multiplet} \) and \( bm = \text{broad multiplet} \). The solutions were prepared by weight-volume percent in the solvent specified. Gas liquid chromatography (glc) studies were conducted on a Hewlett Packard 720 and 5750 instruments equipped with a disc integrator. Analytical analyses were done with the following columns: 6ft x 0.25in aluminum column packed with 10 percent LAC-728 on Chromosorb W A/W DMCS, 80-100 mesh, 6ft x 0.25in aluminum column packed with 10 percent Carbonwax 20 M on Chromosorb W NAW, 60 mesh and 10 percent UCW-998 on Chromosorb W HP 80/100 mesh. Preparative analyses were done on 8ft x 0.5in 10 percent Carbonwax 20 M or 10 percent LAC-728 on Chromosorb W A/W DMCS, 60-80 mesh.
1-(p-Methoxyphenyl)-2-methylcyclohexene

This preparative method of dehydration was followed according to the procedure of Garbisch. The isomeric alcohol mixture, 1-(p-methoxyphenyl)-2-methylcyclohexanol (5.0 g, 22.7 mmole), was dehydrated in a solution of 2.5 ml 16 N concentrated sulfuric acid in 12.5 ml acetic acid. The solution was stirred for 4 hours at 25° after which it was poured into 125 ml 2:3 hexane-water solution. The organic layer was separated, neutralized with 5% sodium bicarbonate, washed with water, dried over anhydrous magnesium sulfate, concentrated and distilled yielding the 1-(p-methoxyphenyl)-2-methylcyclohexene (4.0 g, 87%) as a viscous clear colorless liquid; bp 80° (0.02 mm):

ir (CCl₄, 10%) 3040 (m, C₆H₄), 2930 and 2850 (s, CH₃, CH₂ and CH), 2815 (s, OCH₃), 1610 and 1505 (s, C₆H₄), 1440 and 1460 (s, CH₃ and CH₂), 1250 (s, C-O-C), 835 (s, para, dissubstitution); nmr (CDCl₃, 8%), 3.08 and 3.33 (d, J = 8.5 Hz, C₆H₄), 6.28 (s, OCH₃), 7.67-8.70 (bm, (CH₂)₄), 9.12 (d, J = 7 Hz, CH₃). The isomers were separated by preparative glc (10% carbowax, 190°), the shorter retention time being 1-(p-methoxyphenyl)-2-methylcyclohex-1-ene, which was 100% pure by nmr and glc analysis (10% UCW-998, 100° to 250°, 6°/min): ir (CCl₄, 10%) 3038 (m, C₆H₄), 2930 and 2850 (s, CH₃, CH₂ and CH), 2815 (s, OCH₃), 2100-1850 (w, C₆H₄), 1610 and 1515 (s, C₆H₄), 1440 and 1465 (s, CH₃ and CH₂), 1250 (s, C-O-C); nmr (CCl₄, 8%) 3.07 and 3.33 (d, J = 9.0 Hz, C₆H₄), 6.25 (s, OCH₃), 7.63-8.70 (bm, (CH₂)₄), 8.47 (s, CH₃). Analysis on the 1-(p-methoxyphenyl)-2-methylcyclohex-6-ene was similarly verified by nmr, ir and glc analysis (10% UCW-998, 100° to 250°, 6°/min): ir (CDCl₃, 10%) 3040 (m, C₆H₄), 2960, 2935 and 2865 (s, CH₃, CH₂ and CH), 2815 (s, OCH₃), 1610 and 1518 (s, C₆H₄), 1465 (s, CH₃ and CH₂), 1250 (s, C-O-C); nmr (CDCl₃,
10% 2.78 and 3.20 (d, J = 9.0 Hz, C₆H₄), 4.20 (m, H), 6.22 (s, OCH₃), 7.00–
8.70 (bm, (CH₂)₃, (CH)₂), 9.08 (d, J = 7 Hz, CH₃).

**trans-1-(p-Chlorophenyl)-2-methylcyclohexanol**

The Grignard reagent, p-chlorophenylmagnesium chloride was prepared
from magnesium turnings (8.0 g, 0.33 mole) and p-dichlorobenzene (37.0 g,
0.25 mole) in 200 ml of freshly distilled THF (refluxed in lithium aluminum
hydride for 1 hour before distilling) under nitrogen at reflux temperature.
After the addition period of 1.5 hours was completed, the reaction flask
was allowed to reflux an additional 18 hours. 2-Methylcyclohexanone (28.0 g,
0.25 mole) dissolved in 150 ml of freshly distilled THF was slowly added at
room temperature and refluxed for a period of 18 hours. The addition of
300 ml of saturated ammonium chloride produced two layers of which the THF
layer was separated and concentrated after drying over anhydrous sodium sul-
fate. The distillation yielded 1-(p-chlorophenyl)-2-methylcyclohexanol
(38.2 g, 68%) as a thick colourless liquid: bp 104-105°, R₂ 1.5515; ir
(CCl₄, 10%) 3610 (m, free OH), 3450 (w, associated OH), 3060 and 3020 (w,
C₆H₄), 2940 and 2850 (s, CH₃, CH₂ and CH), 1900 to 1655 (w, C₆H₄), 1480 (s,
C₆H₄), 1450 (s, CH₃ and CH₂); nmr (CCl₄, 10%) 2.62 (d, J = 2.0 Hz, C₆H₄),
8.33 (bs, (CH₂)₃ and CH), 8.40 (s, OH), 9.40 (d, J = 7.8 Hz, CH₃).

**trans-1-(p-Methoxyphenyl)-2-methylcyclohexanol**

The Grignard reagent, p-methoxyphenyl magnesium bromide was prepared
from magnesium turnings (8.0 g, 0.33 mole) and p-bromoanisole (54.0 g,
0.29 mole) in 200 ml of anhydrous ether under atmospheric nitrogen at 0°.
After refluxing for 1/2 hour, 2-methylcyclohexanone (30.0 g, 0.27 mole) dis-
solved in 100ml of anhydrous ether was slowly added and further refluxed for a period of 2 hours. The addition of 200 ml of saturated ammonium chloride produced two layers, of which the etheral layer was filtered and dried over anhydrous sodium sulfate. The distillation yielded the 1-(p-methoxyphenyl)-2-methylcyclohexanol (40.0 g, 68%) as a colourless viscous oil: bp 100-103° (0.02 mm) \( n_D^{25} 1.5409 \); ir (CHCl₃, 10%) 3610 (m, free OH), 3565 (w, associated OH), 3020 (m, C₆H₅), 2930 and 2850 (s, CH₃, CH₂ and CH), 2815 (s, OCH₃), 2100-1850 (w, C₆H₅), 1615 and 1515 (s, C₆H₅), 1460 (m, CH₃ and CH₂), 1255 (s, C-O-C), 830 (s, para dissubstitution); nmr (CCl₄, 10%) 2.78 and 3.32 (d, \( J = 12.0 \) Hz, C₆H₅), 6.28 (s, OCH₃), 8.00-8.80 (m, (CH₂)₄ and CH), 8.60 (s, OH), 9.43 (d, \( J = 7.0 \) Hz, CH₃).

**trans-1-(p-Methylphenyl)-2-methylcyclohexanol**

This alcohol was prepared in exactly the same manner as the p-methoxyalcohol above, yielding (38.0 g, 74.5%) as a clear, colourless viscous oil: bp 130-133° (0.01 mm); \( n_D^{25} 1.5368 \); ir (CCl₄, 10%) 3615 (m, free OH), 3445 (w, associated OH), 3015 (m, C₆H₅), 2868 (s, CH₃, CH₂ and CH), 2825 (s, OCH₃), 1910-1620 (w, C₆H₅), 1510 (s, C₆H₅), 1450 (m, CH₃ and CH₂); nmr (CCl₄, 10%) 2.82 and 3.10 (d, \( J = 12.0 \) Hz, C₆H₅), 7.73 (s, CH₃), 8.00-8.80 (m, (CH₂)₄ and CH), 8.58 (s, OH), 9.43 (d, \( J = 7.8 \) Hz, CH₃).

**trans-1-Phenyl-2-methylcyclohexanol**

This alcohol was prepared in exactly the same manner as the above p-methoxyalcohol, yielding (35.5 g, 74.8%) as a colourless oil: bp 90°-92° (0.02 mm); \( n_D^{21} 1.5368 \); ir (CCl₄, 10%) 3609 (m, free OH), 3450 (w, associated OH), 3070 and 3018 (m, C₆H₅), 2935 and 2848 (s, CH₃, CH₂ and CH), 1600
and 1700 (w, C₆H₅), 1445 (s, CH₃ and CH₂); nmr (CCl₄, 10%) 2.77 (br, C₆H₅), 7.75 and 8.85 (br, \((\text{CH}_2)\text{H}_4\) and \(\text{CH}\)), 8.58 (s, OH), 9.43 (d, \(\text{J} = 7.8 \text{ Hz, CH}_3\)).

The data obtained are in accord with the literature data of K.G. Rutherford and J.F. Brien.

**trans-1-((p-Bromophenyl)-2-methylcyclohexanol**

The preparation of this alcohol was followed in the same manner as the above mentioned p-methoxyalcohol: yielding (53.8 g, 80%) as a clear colourless thick liquid; bp 108-110° (0.01 mm). This crystallized as a white solid: mp 37-38°; ir (CCl₄, 10%) 3608 (m, free OH), 3450 (w, associated OH), 3060 and 3018 (w, C₆H₄), 2938 and 2855 (s, CH₃, CH₂ and CH), 1905 to 1650 (w, C₆H₄), 1480 (s, C₆H₄), 1445 (s, CH₃ and CH₂); nmr (CCl₄, 10%) 2.75 (d, \(\text{J} = 2.0 \text{ Hz, C₆H₄}\)), 8.38 (br, \((\text{CH}_2)\text{H}_4\) and \(\text{CH}\)), 8.53 (s, OH), 9.42 (d, \(\text{J} = 7.8 \text{ Hz, CH}_3\)).

The data obtained verified with the literature data of K.G. Rutherford and S. Wassenaar.

**trans-1,1'-Methoxy(p-chlorophenyl)-2-methylcyclohexane**

The trans-1-((p-chlorophenyl)-2-methylcyclohexanol (2.0 g, 8.9 mmole), dissolved in 10 ml of freshly distilled tetrahydrofuran (THF) was quenched in 7.0 ml of n-butyllithium (15.13 g/100 g hexane) dissolved in 10 ml of THF for 1/2 hour at 25°. An additional neat sample of 7.0 ml methyl iodide (0.05 mole) was introduced into the solution and refluxed for 17 hours. An equal volume of distilled water was added to the reaction flask and the organic layer was separated, concentrated and 4 to 5 solvent extractions were made with hexane. Concentration of the hexane layers and cooling below -10° in dry-ice methanol bath, induced yellow lumps of solid. The crude product
was purified by crystallization from a minimum amount of cold (-10°C) methanol or ethanol (absolute). Crystallization may be effected rapidly by addition of distilled water, yielding fine white, flat-shaped crystals of trans-1,1′-methoxy (p-chlorophenyl)-2-methylcyclohexane (1.07 g, 45%): mp 42-43°C; ir (CCl₄, 10%) 3040 (m, C=H₄), 2850 and 2940 (s, CH₃, CH₂ and CH), 2815 (s, OCH₃), 2200 to 1700 and 1600 (w, C₆H₄), 1515 (s, C₆H₄), 1445 and 1460 (s, CH₃ and CH₂), 1255 (s, C=O-C), 835 (s, para disubstituted); nmr (CCl₄, 10%) 2.81 (s, C₆H₄), 3.88 (s, OCH₃), 7.80-8.90 (bm, (CH₂)₃, CH), 9.40 (bd, J = 7.0 Hz, CH₃).

Anal. Calcd for C₁₄H₁₉ClO: C, 70.42; H, 8.04; Cl, 14.85. Found: C, 70.51; H, 7.97; Cl, 14.86.

trans-1,1′-Methoxy (p-methoxyphenyl)-2-methylcyclohexane

This ether was prepared in exactly the same manner as the above p-chloroether yielding (0.52 g, 24.8%): mp 55-57°C; ir (CCl₄, 10%) 3042 (w, C₆H₄), 1615 and 1515 (s, C₆H₄), 1440 and 1460 (s, CH₃ and CH₂), 1255 (s, C=O-C); nmr (CCl₄, 7%) 2.93 and 3.33 (d, J = 12.0 Hz, C₆H₄), 6.28 (s, OCH₃), 6.93 (s, OCH₃), 7.80 and 9.00 (bm, (CH₂)₃ and CH), 9.40 (bd, J = 7.0 Hz, CH₃).


trans-1,1′-Methoxy (p-methylphenyl)-2-methylcyclohexane

Preparation of this ether was followed in the same manner as the above mentioned p-chlorophenyl ether, yielding (0.79 g, 41.9%): mp 40-41°C; ir (CCl₄, 10%) 3030 (w, C₆H₄), 2855, 2875 and 2940 (s, CH₃, CH₂ and CH), 2820 (m, OCH₃), 2100 to 1700 (w, C₆H₄), 1440 and 1450 (s, CH₃ and CH₂), 1208 and
\[ 1.175 \text{ (s, C-O-C); nmr (CCl}_4, 10\% \text{) 3.00 (s, C}_6\text{H}_4, 6.92 (s, OCH}_3, 7.72 (s, CH}_3, 7.80 \text{ to 9.00 (brm, (CH}_2)_3 \text{ and CH), 9.42 (bd, J = 7.5 Hz, CH}_3).} \]


**trans-1,1'-Methoxy (phenyl)-2-methylcyclohexane**

The same preparation was followed as in the p-chloroether compound, yielding (0.8 g, 40\%): mp 47-48°; ir (CCl\(_4\), 10\%) 3040, 1442 and 1460 (s, CH\(_3\) and CH\(_2\)), 1208 and 1173 (s, C-O-C); nmr (CCl\(_4\), 10\%) 2.85 (s, C\(_6\)H\(_5\)), 6.92 (s, OCH\(_3\)), 7.80 to 8.95 (brm, (CH\(_2\))\(_3\) and CH), 9.40 (bd, J = 7.0 Hz, CH\(_3\)).


**trans-1,1'-Methoxy (p-bromophenyl)-2-methylcyclohexane**

This ether was prepared in exactly the same manner as the above synthesis of p-chloroether yielding (0.75 g, 37.5\%): mp 41-43°; ir (CCl\(_4\), 10\%) 3040 (m, C\(_6\)H\(_4\)), 2858 and 2942 (s, CH\(_3\), CH\(_2\) and CH), 2815 (m, OCH\(_3\)), 2200 to 1800 and 1600 (v, C\(_6\)H\(_5\)), 1445 and 1455 (s, CH\(_3\) and CH\(_2\)), 1210 and 1075 (s, C-O-C); nmr (CCl\(_4\), 10\%) 2.65 and 2.97 (d, J = 12.0 Hz, C\(_6\)H\(_4\)), 6.92 (s, OCH\(_3\)), 7.80 and 9.00 (brm, (CH\(_2\))\(_3\) and CH), 9.43 (bd, J = 7.00 Hz, CH\(_3\)).

Anal. Calcd for C\(_{14}\)H\(_{19}\)BrO: C, 59.38; H, 6.76; Br, 28.25. Found: C, 60.51; H, 6.87; Br, 26.05.

**trans-1,1'-Methoxy (p-nitrophenyl)-2-methylcyclohexane**

Nitration of 1,1'-methoxy (phenyl)-2-methylcyclohexane

A 25 ml solution of anhydrous acetic acid, nitric acid and trifluoro-
acetic acid in the ratio of 8:12:1 respectively was slowly added for 30 minutes at room temperature to 1,1'-methoxy (phenyl)-2-methylcyclohexane (1.0 g, 0.005 mole) dissolved in 10 ml acetic anhydride. This was allowed to stir at room temperature for a further 24 hours, after which it was neutralized with aqueous saturated sodium carbonate. After several extractions of the yellow aqueous layer with hexane, the organic layer was concentrated and the 1,1'-methoxy (p-nitrophenyl)-2-methylcyclohexane was crystallized from cold methanol yielding 0.85 g (85%): mp 94-97°; ir (CDCl₃, 10%) 3040 (m, C₆H₅), 1600 and 1525 (s, C₆H₅), 1460 (s, CH₃ and CH₂), 1355 (s, NO₂), 1210 and 1075 (s, C-O-C), 860 (s, para disubstituted; nmr (CCl₄, 10%) 1.90 and 2.61 (d, J = 1200 Hz, C₆H₅), 6.84 (s, OCH₃), 7.70 to 8.90 (m, (CH₂)₃ and CH), 9.45 (bd, J = 7.00 Hz, C₆H₅).


Nuclear Magnetic Resonance (nmr) Kinetic Study on the Pyrolysis of trans-1,1'-Methoxy (p-Xphenyl)-2-methylcyclohexanes in Diphenyl Ether

Pyrolyses of the trans-1,1'-methoxy (p-Xphenyl)-2-methylcyclohexanes were conducted in purified diphenyl ether and dibenzyl ether (internal standard) so that comparison of the rate constants of each derivative could be made.

The inert solvent, diphenyl ether (bp 296° and mp 26.0-27.0°) was re-crystallized several times from cold pentane. The flat diamond shaped crystals were heated to ca 150° for approximately 1 hour under constant stirring to boil off any excess pentane or traces of water. After cooling to room temperature, the solvent ether would solidify (mp 27-28°) and was then
used in the pyrolyses studies.

The standard, dibenzyl ether (spectrograde 99+% pure) was redistilled (bp 131.5-132.0°, 25 mm) to insure purity of the compound.

Three different heating apparatuses were used for pyrolysis. The first was a silicon oil bath which has its limitation of low temperature polymerization. At a temperature of 210° the silicon oil would decompose within 70 hours to a thick sticky substance. The second heating apparatus used was a Woods metal bath (mp 73-75°). It also has a disadvantage in temperature control as well as air oxidation at elevated temperatures of 350° and higher within 10 to 24 hours. Retardation of the metal oxidation was effectively accomplished by spreading a layer of carbon on the hot metal surface of the bath. The apparatus itself consisted of a cylindrical copper cup (3.0 in depth x 2.5 in diameter) wound by electrical wiring and insulated with asbestos powder in a heat resistant container. The third type of bath used consisted of sand. Its disadvantage is that it has low thermal conductivity, but can be used for long periods of pyrolysis at elevated temperatures.

It should be noted that the ether compounds are very sensitive to trace amounts of acids upon pyrolysis. In order to overcome this problem, all glass-ware including the pyrolysis tubes and syringes used, were washed several times in concentrated ammonium hydroxide, thoroughly rinsed with water and oven dried for at least 24 hours. Failing to do so, will cause inconsistent data for the rate constants obtained at the desired temperatures.

For each ether substituent, the following procedure was employed in the
same manner for the kinetic pyrolysis. An accurately weighed sample (96.0 mg, 0.40 mmole) of trans-1,1'-methoxy (p-chlorophenyl)-2-methylcyclohexane was dissolved in 150 to 200 µl of diphenyl ether. The dibenzyl ether which was accurately weighed (62.0 mg, 0.31 mmole) was added to the sample as an internal standard. The volume was then accurately measured to a total of 500 µl by the addition of diphenyl ether. In order to prevent continuous solidification of the solvent, the mixing of the samples was done under an infrared heating lamp. To insure that no acidic protons were present, a small drop of pyridine (dried over potassium hydroxide pellets) was added to the clear colorless sample, of which an aliquot of 100 to 150 µl was placed in either one of the following two pyrolytic nmr tubes:

a. a sealed thick walled (0.5 cm od and 0.25 cm id) 14 to 23 cm long nmr tube containing a thin solid glass rod, the length sufficiently close to that of the pyrolysis tube.

b. a 6 to 7 cm sealed glass tubing contained in a precision fit thin walled (0.5 cm od and 0.40 cm id) nmr tube.

Neither tube a or b produced any difference to the observed rate constants. Tube b was used since it allows pyrolysis at a sufficiently high temperature without causing the sample to rise above the metal or sand-bath. The trans-1,1'-methoxy (p-chlorophenyl)-2-methylcyclohexane sample was pyrolyzed both at a lower temperature of 255° and at an elevated temperature of 295°. The rate of pyrolysis was followed by the decrease of the methoxy singlet peak (6.80-6.90 τ) on a JEOL 0-60 HL nmr spectrometer. The integrated peak areas were measured and the following sample calculation was incorporated after each time interval of pyrolysis:
Temperature 255°; Time Interval = 24.0 hours

Standard (Internal) Peak Height = 4.4 cm (4 protons - MW 198.27)
Methoxy (Ether) Peak Height = 4.6 cm (3 protons)

Concentration of the standard benzyl ether in 1000 μl is

\[ \frac{62.0}{198.27} \times 2 \]

Concentration of the standard benzyl ether peak (area)

\[ \frac{62.0}{198.27} \times 2 \times \frac{4}{3} = 0.8339 \text{ mmolar} \]

Concentration of the methoxy peak (area)

\[ \frac{4.60}{4.40} \times 0.8339 = 0.8718 \text{ mmolar} \]

The concentration of the ether derivative at time interval 24 hours was then incorporated in determining the rate constants.

The rate constant for each ether pyrolysis was determined by using the first-order rate equation.

\[ \ln E_{t} = -kt + \ln E_{0} \quad [4] \]

where: \( E_{t} \) = concentration of ether derivative left at any time \( t \).
\( E_{0} \) = concentration of ether derivative left at time 0.
\( k \) = rate constant (sec \(^{-1}\))
\( t \) = time (sec)

From each temperature of 255° and 295°, a rate constant \( k_{255°} \) and \( k_{295°} \) was obtained and the thermodynamic parameters, enthalpy of activation \( (\Delta H^\ddagger) \) and entropy of activation \( (\Delta S^\ddagger) \) were obtained from a print out computer programme as shown in the appendix.
The compiled rate constants of each ether derivative were treated according to the Hammett φ plot from which an interpretative conclusion was drawn.
PYROLYSIS OF TRANS-1,1'-METHOXY (p-BROMOPHENYL)-2-METHYL CYCLOHEXANE IN DI-
PHENYL ETHER

Concentration of Ether = 0.8 Molar
Weight of Dibenzyl Ether = 50.1 mg

**TABLE IVa**

<table>
<thead>
<tr>
<th>Time</th>
<th>Peak Areas</th>
<th>Log Concentration of Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; O</td>
<td>R-&lt;sub&gt;OC&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>0</td>
<td>3.40</td>
<td>4.90</td>
</tr>
<tr>
<td>3 hours</td>
<td>3.80</td>
<td>5.15</td>
</tr>
<tr>
<td>9 hours</td>
<td>3.90</td>
<td>3.80</td>
</tr>
<tr>
<td>25 hours</td>
<td>3.40</td>
<td>1.50</td>
</tr>
</tbody>
</table>

**TABLE IVb**

<table>
<thead>
<tr>
<th>Time</th>
<th>Peak Areas</th>
<th>Log Concentration of Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; O</td>
<td>R-&lt;sub&gt;OC&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>0</td>
<td>3.90</td>
<td>5.50</td>
</tr>
<tr>
<td>60 min</td>
<td>4.20</td>
<td>4.45</td>
</tr>
<tr>
<td>120 min</td>
<td>3.20</td>
<td>2.70</td>
</tr>
<tr>
<td>180 min</td>
<td>3.80</td>
<td>2.30</td>
</tr>
</tbody>
</table>
**Figure 26a** - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy (p-bromophenyl)-2-methylcyclohexane in Diphenyl Ether at 255° (Table IVa) with an Obtained Estimated Kinetic Rate Constant of $1.22 \times 10^{-5}$ sec$^{-1}$
Figure 26b - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy (p-bromophenyl)-2-methylocyclohexane in Diphenyl Ether at 295° (Table IVb) with an Obtained Estimated Kinetic Rate Constant of 7.64 x 10⁻⁵ sec
PYROLYSIS OF TRANS-1,1'-METHOXY (P-CHLOROPHENYL)-2-METHYLCYCLOHEXANE IN DI-
PHENYL ETHER

Concentration of Ether = 0.8 Molar
Weight of Dibenzyl Ether = 31.0 mg

TABLE Va

<table>
<thead>
<tr>
<th>Time</th>
<th>$(\phi-\text{CH}_2)_2\text{O}$</th>
<th>R-OC$_3$</th>
<th>Log Concentration of Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.20</td>
<td>3.40</td>
<td>-0.05</td>
</tr>
<tr>
<td>24 hours</td>
<td>4.40</td>
<td>4.60</td>
<td>-0.06</td>
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<tr>
<td>114 hours</td>
<td>3.80</td>
<td>3.81</td>
<td>-0.08</td>
</tr>
</tbody>
</table>

TABLE Vb

<table>
<thead>
<tr>
<th>Time</th>
<th>$(\phi-\text{CH}_2)_2\text{O}$</th>
<th>R-OC$_3$</th>
<th>Log Concentration of Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.10</td>
<td>4.60</td>
<td>-0.03</td>
</tr>
<tr>
<td>4 hours</td>
<td>3.40</td>
<td>3.45</td>
<td>-0.07</td>
</tr>
<tr>
<td>16 hours</td>
<td>2.95</td>
<td>1.60</td>
<td>-0.27</td>
</tr>
</tbody>
</table>
Figure 27a - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy (p-chlorophenyl)-2-methylcyclohexane in Diphenyl Ether at 255° (Table Va) with an Obtained Estimated Kinetic Rate Constant of $1.41 \times 10^{-4}$ sec
Figure 27b - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy (p-chlorophenyl)-2-methylcyclohexane in Diphenyl Ether at 295° (Table Vb) with an Obtained Estimated Kinetic Rate Constant of $9.14 \times 10^{-4}$ sec}
PYROLYSIS OF TRANS-1,1'-METHOXY (P-METHOXYPHENYL)-2-METHYLCYCLOHEXANE IN DI-PHENYL ETHER

Concentration of Ether \(- 0.8\) Molar
Weight of Dibenzyl Ether \(- 36.9\) mg

### TABLE VIa

Temperature 230°

<table>
<thead>
<tr>
<th>Time</th>
<th>((\phi-\text{CH}_2)_2\text{O})</th>
<th>R-\text{OCH}_3</th>
<th>Log Concentration of Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 min</td>
<td>3.70</td>
<td>3.30</td>
<td>-0.37</td>
</tr>
<tr>
<td>90 min</td>
<td>3.40</td>
<td>2.65</td>
<td>-0.41</td>
</tr>
<tr>
<td>140 min</td>
<td>3.00</td>
<td>1.85</td>
<td>-0.51</td>
</tr>
</tbody>
</table>

### TABLE VIb

Temperature 255°

<table>
<thead>
<tr>
<th>Time</th>
<th>((\phi-\text{CH}_2)_2\text{O})</th>
<th>R-\text{OCH}_3</th>
<th>Log Concentration of Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.60</td>
<td>5.60</td>
<td>-0.11</td>
</tr>
<tr>
<td>20 min</td>
<td>2.85</td>
<td>3.00</td>
<td>-0.28</td>
</tr>
<tr>
<td>40 min</td>
<td>3.80</td>
<td>3.90</td>
<td>-0.29</td>
</tr>
<tr>
<td>60 min</td>
<td>3.70</td>
<td>2.30</td>
<td>-0.51</td>
</tr>
<tr>
<td>100 min</td>
<td>3.75</td>
<td>1.40</td>
<td>-0.73</td>
</tr>
<tr>
<td>130 min</td>
<td>2.50</td>
<td>1.70</td>
<td>-0.86</td>
</tr>
</tbody>
</table>
Figure 28a - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy (p-methoxyphenyl)-
2-methylcyclohexane in Diphenyl Ether at 255° (Table VIa) with an Obtained
Estimated Kinetic Rate Constant of 2.30 x 10^{-1} sec
Figure 28b - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy (p-methoxyphenyl)-2-methylcyclohexane in Diphenyl Ether at 230° (Table VIIb) with an Obtained Estimated Kinetic Rate Constant of $7.24 \times 10^{-5}$ sec.
PYROLYSIS OF TRANS-1,1'-METHOXY (P-METHYLPHENYL)-2-METHYLCYCLOHEXANE IN DI-

PHENYL ETHER

Concentration of Ether - 0.8 Molar
Weight of Dibenzyl Ether - 43.4 mg

TABLE VIIa

<table>
<thead>
<tr>
<th>Time</th>
<th>Peak Areas</th>
<th>Log Concentration of Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((\cdot)CH(_2))(_2)O</td>
<td>R-CH(_3)</td>
</tr>
<tr>
<td>0</td>
<td>3.40</td>
<td>4.90</td>
</tr>
<tr>
<td>3 hours</td>
<td>3.80</td>
<td>5.15</td>
</tr>
<tr>
<td>9 hours</td>
<td>3.90</td>
<td>3.80</td>
</tr>
<tr>
<td>25 hours</td>
<td>3.40</td>
<td>1.50</td>
</tr>
</tbody>
</table>

TABLE VIIb

<table>
<thead>
<tr>
<th>Time</th>
<th>Peak Areas</th>
<th>Log Concentration of Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((\cdot)CH(_2))(_2)O</td>
<td>R-CH(_3)</td>
</tr>
<tr>
<td>0</td>
<td>3.35</td>
<td>4.45</td>
</tr>
<tr>
<td>20 min</td>
<td>2.50</td>
<td>2.85</td>
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<tr>
<td>80 min</td>
<td>4.30</td>
<td>3.40</td>
</tr>
<tr>
<td>140 min</td>
<td>3.80</td>
<td>1.75</td>
</tr>
</tbody>
</table>
Figure 29a - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy (p-methylphenyl)-2-methylcyclohexane in Diphenyl Ether at 255° (Table VIIa) with an Obtained Estimated Kinetic Rate Constant of $1.06 \times 10^{-5}$ sec$^{-1}$. 
Figure 29b - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy (p-methylphenyl)-
2-methylcyclohexane in Diphenyl Ether at 295° (Table VIIb) with an Obtained
Estimated Kinetic Rate Constant of $1.18 \times 10^{-1}$ sec$^{-1}$
PYROLYSIS OF TRANS-1,1' METHOXY (P-NITROPHENYL)-2-METHYLCYCLOHEXANE IN DI-

PHENYL ETHER

Concentration of Ether = 0.8 Molar
Weight of Dibenzyl Ether = 39.6 mg

<table>
<thead>
<tr>
<th>TABLE VIIIa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature 255°</td>
</tr>
<tr>
<td>Peak Areas</td>
</tr>
<tr>
<td>Time</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>3 hours</td>
</tr>
<tr>
<td>9 hours</td>
</tr>
<tr>
<td>25 hours</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE VIIIb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature 295°</td>
</tr>
<tr>
<td>Peak Areas</td>
</tr>
<tr>
<td>Time</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>.60 min</td>
</tr>
<tr>
<td>120 min</td>
</tr>
<tr>
<td>180 min</td>
</tr>
</tbody>
</table>
Figure 30a - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy (p-nitrophenyl)-
2-methylcyclohexane in Diphenyl Ether at 255° (Table VIIIa) with an Obtained
Estimated Kinetic Rate Constant of $3.37 \times 10^{-6}$ sec$^{-1}$
Figure 30b - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy (p-nitrophenyl)-2-methylenecyclohexane in Diphenyl Ether at 295° (Table VIIIb) with an Obtained Estimated Kinetic Rate Constant of $2.56 \times 10^{-5}$ sec$^{-1}$. 
PYROLYSIS OF TRANS-1,1'-METHOXY (PHENYL)-2-METHYLCYCLOHEXANE IN DIPHENYL ETHER

Concentration of Ether = 0.8 Molar
Weight of Eibenzyl Ether = 50.5 mg

### TABLE IXa

<table>
<thead>
<tr>
<th>Time</th>
<th>$(\phi-\text{CH}_2)_2\text{O}$</th>
<th>$\text{R-0CH}_3$</th>
<th>Log Concentration of Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.10</td>
<td>4.85</td>
<td>-0.07</td>
</tr>
<tr>
<td>68 hours</td>
<td>4.70</td>
<td>5.10</td>
<td>-0.13</td>
</tr>
<tr>
<td>140 hours</td>
<td>2.65</td>
<td>2.65</td>
<td>-0.17</td>
</tr>
<tr>
<td>284 hours</td>
<td>4.00</td>
<td>3.30</td>
<td>-0.29</td>
</tr>
</tbody>
</table>

### TABLE IXb

<table>
<thead>
<tr>
<th>Time</th>
<th>$(\phi-\text{CH}_2)_2\text{O}$</th>
<th>$\text{R-0CH}_3$</th>
<th>Log Concentration of Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.20</td>
<td>4.00</td>
<td>-0.07</td>
</tr>
<tr>
<td>1 hour</td>
<td>4.40</td>
<td>5.35</td>
<td>-0.08</td>
</tr>
<tr>
<td>10.5 hours</td>
<td>3.30</td>
<td>3.40</td>
<td>-0.18</td>
</tr>
</tbody>
</table>
Figure 31a - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy-(phenyl)-2-methylcyclohexane in Diphenyl Ether at 255° (Table IXa) with an Obtained Estimated Kinetic Rate Constant of $5.11 \times 10^{-4}$ sec$^{-1}$
Figure 31b - Pyrolysis of 0.8 Molar trans-1,1'-Methoxy (phenyl)-2-methylcyclohexane in Diphenyl Ether at 295° (Table IXb) with an Obtained Estimated Kinetic Rate Constant of $7.16 \times 10^{-5}$ sec
APPENDIX

The Gibbs-Helmholtz equation may be presented as:

\[ \Delta G^* = \Delta H^* - T \Delta S^* \]  \[5\]

The Gibbs Free Energy may also be represented as:

\[ -\Delta G^* = kT \ln k \] \[6\]

where \( k \) is the temperature dependent rate constant.

The Gibbs-Helmholtz equation can be written in the alternative form of:

\[ \left[ \frac{\delta (\Delta G^*)}{\delta T} \right]_T = \frac{-\Delta H^*}{T} \] \[7\]

Combining equations [6] and [7]

\[ \left[ \frac{\delta (TR \ln k)}{\delta T} \right]_T = \frac{-\Delta H^*}{T^2} \] \[8\]

\[ \frac{d \ln k}{dT} = \frac{\Delta H^*}{RT^2} \] \[9\]

or \[ \frac{d \ln k}{d(1/T)} = \frac{-\Delta H^*}{R} \] \[10\]

Given the rate constants at two different given temperatures \( T_1 \) and \( T_2 \), then \( \Delta H^* \) can be measured from equation [9] or [10].

\[ \int_{T_1}^{T_2} \frac{d \ln k}{d(1/T)} \frac{dT}{TR} = \int_{T_1}^{T_2} \frac{\Delta H^*}{RT^2} \frac{dT}{T} \] \[11\]

\[ \ln \left( \frac{k_{T_2}}{k_{T_1}} \right) = \frac{-\Delta H^*}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \] \[12\]

Based on equation [12], a computer programme print out was written in FORTRAN IV and was used on an IBM 360-50 computer.
$JOB
WATFIV RL21073481

IMPLICIT REAL*8 (A-H,O-Z) C2*00020

DIMENSION (25),T(25),X(25),Y(25) C2*00030

REAL L

READ(5,20) C2*00040

WRITE(6,20) C2*00050

READ(5#21)N C2*00060

READ(5,22) (R(I),I=1,N) C2*00070

READ(5,22) (T(I),I=1,N) C2*00080

SUMX=0.000 C2*00090

SUMY=0.000 C2*00100

SUMP=0.000 C2*00110

SQY=0.000 C2*00120

SQX=0.000 C2*00130

EN=N C2*00140

WRITE(6,26) C2*00150

WRITE(6,27) C2*00160

WRITE(6,28) C2*00170

DO12I=1,N C2*00180

WRITE(6,25)T(I),R(I),DLOG10(R(I)) C2*00190

*EXTENSION*
OTHER COMPILERS MAY NOT ALLOW EXPRESSIONS IN OUTPUT LISTS

B=T(I)+273.16 C2*00200

X(I)=-1.00/B C2*00210

Y(I)=DLOG(R(I)/B) C2*00220

SUMX=SUMX+X(I) C2*00230

SUMY=SUMY+Y(I) C2*00240

SUMP=SUMP+(X(I)Y(I)) C2*00250

SQY=SQY+(Y(I)**2) C2*00260

SQX=SQX+(X(I)**2) C2*00270

CONTINUE

SLOPE=(SUM-EN*SUMP)/(SUMX**2-EN*SQX) C2*00290

SINT=(SUM-SUMX*SLOPE)/EN C2*00300

COR=(SUM/EN-PSUM/(EN**2))/DSQRT((SQX/EN-(SUMX/EN)**2)* C2*00310

1 (SQY/EN-(SUMY/EN)**2)) C2*00320

AVD=0.000 C2*00330

GO13J=1,N C2*00340

Z=SLOPE-(Y(J)-SINT/X(J)) C2*00350

AVD=AVD+DABS(Z) C2*00360

CONTINUE C2*00370

AVD=AVD/EN C2*00380

AVC=0.000 C2*00390

GO14J=1,N C2*00400

Z=SINT-(X(J)-X(J)*SLOPE) C2*00410

AVC=AVC+DABS(Z) C2*00420

CONTINUE C2*00430

AVO=AVC/EN C2*00440

DH=0.0019869*SLOPE C2*00450

DS=1.9869*(SINT-23.7642) C2*00460

C2*00470
CH=0.0019869*AVD
CS=1.9869*AVC
WRITE(6,28)
WRITE(6,23)DH,CH,DS,CS,COR
WRITE(6,24)
WRITE(6,27)
B = 273.16
C=SINT/SLOPE/B
W=B*DEXP(C)
L=DLOG10 (W)
G = 0.
WRITE(6,25)G,W,L
B= 298.16
IF(574.16-B)I7,16,16.
C=SINT/SLOPE/B
W=B*DEXP(C)
L = DLOG10 (W)
G=B-273.16
WRITE(6,25)G,W,L
B=B+.00
GOTO15
GOTO11
FORMAT(1H1,71H)
FORMAT(12)
FORMAT(7E10.4)
FORMAT(26HOENTHALPY OF ACTIVATION = F6.2,4H +/- F5.2,12H
KCAL/M C2*00720
190.25HOENTROPY OF ACTIVATION = F7.2,4H +/- F5.2,5H E.U.
/31HOTH C2*00730
2E CORRELATION COEFFICIENT = F7.4 /1H )
FORMAT(26HOCALCULATED RATE CONSTANTS)
FORMAT(F17.2,IPD21.3,IF29.4)
FORMAT(1H0INPUT DATA)
FORMAT(79HO TEMPERATURE RATE CONSTANT
1 LOGARITHM(10) /1H )
FORMAT(1H )
END
REFERENCES

VITA AUCTORIS

Born:

January 8, 1948; Amboina, Dutch East Indies.
Son of Mrs. Ch.J. Steevensz and the late Mr. J.L. Steevensz.

Education:


Graduate Studies leading to M.Sc. Degree.

University of Windsor, Windsor, Ontario. 1973-
Continuing Graduate Studies leading to Ph.D. Degree.

Professional Societies:

The Chemical Institute of Canada.

Marital Status:

Single.