Mass spectrometry study of methyl pyridyl ketones and phenyl pyridyl ketones; isolation and mass spectra of tautomeric forms of dibenzoylacetylmethane and 3-phenyl-2,4-pentanedione.

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PART I
MASS SPECTROMETRY STUDY OF METHYL PYRIDYL KETONES
AND PHENYL PYRIDYL KETONES

PART II
ISOLATION AND MASS SPECTRA OF TAUTOMERIC FORMS
OF.
DIBENZOYLACETIMETHANE AND 3-PHENYL-2,4-PENTANEDIONE

by
Pachih Chen

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, Canada

1976
© Pachih Chen Master of Science 1976
To my dear parents
ABSTRACT

Part I

An investigation of the fragmentation pathways of methyl 2-pyridyl ketone, methyl 3-pyridyl ketone, methyl 4-pyridyl ketone, phenyl 2-pyridyl ketone, phenyl 3-pyridyl ketone, and phenyl 4-pyridyl ketone has been done by electron impact mass spectrometry. The mass spectra of the 2-substituted pyridine compounds reported in this study are different from those of their corresponding 3- and 4-isomers. The differences are attributable to the interaction of the side chain in the 2-isomers with the ring nitrogen. This interaction generally results in a substituent transfer to the ring nitrogen and elimination of carbon monoxide. The field ionization and field desorption mass spectrometry of these compounds have also been attempted.

With the aid of deuterated methyl 2-pyridyl ketone, the fragmentation patterns of these compounds are proposed by electron impact. Comparisons of the field ionization mass spectra of methyl pyridyl ketone isomers with those
obtained by Migahed et al. have also been made. Electron impact mass spectrometry has been shown to have potential as an analytical tool in this area.

Part II

The isolation of ketonic and enolic dibenzoylacetethyl-methane has been accomplished. Comparison of the fragmentation behavior of the separated enolic tautomer with that of the corresponding ketonic tautomer by electron impact and field ionization reveals a striking difference. The isolation of the tautomeric forms of 3-phenyl-2,4-pentanediione was also attempted.

The results are not definitive enough to make a proper conclusion. This is because of the poor reproducibility of the separate mass spectra which may be due to the temperature effect of the mass spectrometer on the tautomeric equilibrium. However, one interesting fact is observed under the appropriate conditions; the McLafferty rearrangement can only be occurring from the ketonic tautomer, while the enolic tautomer undergoes predominant simple alpha-cleavage.
ACKNOWLEDGEMENTS

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Also, I would like to thank Dr. Pui-Yan Lau and Mr. B. Charlton for their technical assistance with the mass spectrometer.

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TABLE OF CONTENTS

Page

TITLE PAGE ................................................................. i
DEDICATION ................................................................. iv
ABSTRACT ................................................................. v
ACKNOWLEDGEMENTS ................................................... vii
TABLE OF CONTENTS ..................................................... viii
TABLE OF ABBREVIATIONS ............................................... x
LIST OF FIGURES ........................................................ xi
LIST OF TABLES ............................................................ xiii
LIST OF SCHEMES ........................................................ xv

PART I

Chapter

1 INTRODUCTION .......................................................... 1
2 THE MASS SPECTROMETRY OF SUBSTITUTED PYRIDINES .......... 6
3 RESULTS AND DISCUSSION .......................................... 17

I Electron Impact Mass Spectrometry of
Methyl Pyridyl Ketones

II Mass Spectrometry Of Methyl Pyridyl Ketones

By Field Ionization

viii
III Attempted Field Desorption Mass Spectrometry Of Methyl Pyridyl Ketones

IV Electron Impact Mass Spectrometry Of Phenyl Pyridyl Ketones

V Attempted Field Desorption Mass Spectrometry Of Phenyl Pyridyl Ketones

4 EXPERIMENTAL ............................................. 42
REFERENCES .................................................. 45

PART II

1 INTRODUCTION ............................................. 48

2 RESULTS AND DISCUSSION ............................... 55
   I Dibenzoylacetylmethane
   II 3-Phenyl-2,4-Pentanedione

3 EXPERIMENTAL ............................................. 70
REFERENCES .................................................. 74
VITA AUCTORIS .............................................. 77
**TABLE OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>e.g.</td>
<td>for example</td>
</tr>
<tr>
<td>e.i.</td>
<td>electron impact</td>
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<td>e.i.m.s.</td>
<td>electron impact mass spectrometry</td>
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<td>Et</td>
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<td>eV</td>
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</tr>
<tr>
<td>f.d.</td>
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<tr>
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<tr>
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<td>i.r.</td>
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<td>mA</td>
<td>milli amper</td>
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<td>Me</td>
<td>methyl</td>
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<tr>
<td>m/e</td>
<td>mass to charge ratio</td>
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<td>m/s.</td>
<td>mass spectrometer/spectrometry</td>
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<td>n.m.r.</td>
<td>nuclear magnetic resonance</td>
</tr>
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<td>Ph</td>
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</tr>
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<td>versus</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figures</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Electron Impact Mass Spectrum of Pyridine</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Electron Impact Mass Spectrum of 2-Ethyl Pyridyl Ketone</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>Electron Impact Mass Spectrum of 2-Butyl Pyridyl Ketone</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>Electron Impact Mass Spectrum of 2-Pentyl Pyridyl Ketone</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>Electron Impact Mass Spectrum of Methyl Pyridyl Ketone</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>The Electron Impact Mass Spectrum of Methyl 3-Pyridyl Ketone</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>Electron Impact Mass Spectrum of Methyl 2-Pyridyl Ketone</td>
<td>21</td>
</tr>
<tr>
<td>8</td>
<td>Electron Impact Mass Spectrum of Phenyl 4-Pyridyl Ketone</td>
<td>31</td>
</tr>
<tr>
<td>9</td>
<td>Electron Impact Mass Spectrum of Phenyl 3-Pyridyl Ketone</td>
<td>34</td>
</tr>
<tr>
<td>10</td>
<td>Electron Impact Mass Spectrum of Phenyl 2-Pyridyl Ketone</td>
<td>36</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figures</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>PART II</td>
<td></td>
</tr>
<tr>
<td>1 Effect of Variation of Source Temperature Upon the Spectrum of Acetylacetone</td>
<td>54</td>
</tr>
<tr>
<td>2 Mass Spectrum of Enolic Dibenzoylacetyl-methane by Electron Impact</td>
<td>58</td>
</tr>
<tr>
<td>3 Mass Spectrum of Ketonic Dibenzoylacetyl-methane by Electron Impact</td>
<td>58</td>
</tr>
<tr>
<td>4 Mass Spectrum of the Keto-Enol Tautomers of Dibenzoylacetylmethane by Electron Impact</td>
<td>63</td>
</tr>
<tr>
<td>5 The Mass Spectrum of the Ketonic Dibenzoylacetylmethane by Field Ionization</td>
<td>64</td>
</tr>
<tr>
<td>6 The Mass Spectrum of the Enolic Dibenzoylacetylmethane by Field Ionization</td>
<td>64</td>
</tr>
<tr>
<td>7 The n.m.r. Spectrum of 3-Phenyl-2,4-Pentanedione</td>
<td>66</td>
</tr>
<tr>
<td>8 The Mass Spectrum of 3-Phenyl-2,4-Pentanedione by Electron Impact</td>
<td>67</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Tables</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PART I</strong></td>
<td></td>
</tr>
<tr>
<td>1 Electron Impact Mass Spectral Results of</td>
<td>22</td>
</tr>
<tr>
<td>The Methyl-d$_5$,2-Pyridyl Ketone</td>
<td></td>
</tr>
<tr>
<td>2 Significant Peaks In Electron Impact Mass Spectra Of Methyl Pyridyl</td>
<td>26</td>
</tr>
<tr>
<td>Ketone Isomers</td>
<td></td>
</tr>
<tr>
<td>3 Significant Peaks In Field Ionization Mass Spectra Of Methyl</td>
<td>28</td>
</tr>
<tr>
<td>2-Pyridyl Ketone Under Different Anod Temperatures</td>
<td></td>
</tr>
<tr>
<td>4 Comparison Of Field Ionization Mass Spectra Of Methyl 2-Pyridyl</td>
<td>29</td>
</tr>
<tr>
<td>Ketone Under Different Anod Temperatures</td>
<td></td>
</tr>
<tr>
<td>5 Attempted Field Desorption Mass Spectral Results Of Methyl 2-Pyridyl</td>
<td>30</td>
</tr>
<tr>
<td>Ketone</td>
<td></td>
</tr>
<tr>
<td>6 Significant Peaks In Electron Impact Mass Spectra Of The 2, 3, And</td>
<td>38</td>
</tr>
<tr>
<td>4-Phenyl Pyridyl Ketone Isomers</td>
<td></td>
</tr>
<tr>
<td>7 Attempted Field Desorption Mass Spectral Results Of Phenyl Pyridyl</td>
<td>39</td>
</tr>
<tr>
<td>Ketone Isomers</td>
<td></td>
</tr>
<tr>
<td><strong>PART II</strong></td>
<td></td>
</tr>
<tr>
<td>1 The Enol Content Of Some Carbonyl Compounds</td>
<td>51</td>
</tr>
<tr>
<td>2 Mass Spectrum Of Acetylacetone As A Function Of Inlet Temperature</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>xiii</td>
<td></td>
</tr>
<tr>
<td>Tables</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>PART II (cont'd)</td>
<td></td>
</tr>
<tr>
<td>3 Important Fragments Of The Ketonic And Enolic Tautomers By Electron Impact</td>
<td>59</td>
</tr>
</tbody>
</table>
### LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Schemes</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PART I</strong></td>
<td></td>
</tr>
<tr>
<td>1  The Fragmentation Pathways Of Pyridine</td>
<td>8</td>
</tr>
<tr>
<td>2  Proposed Mechanism Of The Four-Membered Ring</td>
<td></td>
</tr>
<tr>
<td>Formation Of 2-Ethyl And 2-Propyl Pyridines</td>
<td>11</td>
</tr>
<tr>
<td>3  The Major Fragmentation Pathways Of 3- and 4-</td>
<td></td>
</tr>
<tr>
<td>Alkyl Pyridyl Ketones By Electron Impact</td>
<td>12</td>
</tr>
<tr>
<td>4  Proposed Mechanism Of Migration Of Methyl</td>
<td></td>
</tr>
<tr>
<td>Group To The Pyridine Ring</td>
<td>14</td>
</tr>
<tr>
<td>5  The Major Fragmentation Of Methyl 4-Pyridyl Ketone</td>
<td>19</td>
</tr>
<tr>
<td>6  The Proposed Fragmentation Pattern Of Methyl</td>
<td></td>
</tr>
<tr>
<td>2-Pyridyl Ketone</td>
<td>23</td>
</tr>
<tr>
<td>7  Proposed Pathways Of Migration Of Proton Of</td>
<td></td>
</tr>
<tr>
<td>Methyl 2-Pyridyl Ketone</td>
<td>24</td>
</tr>
<tr>
<td>8  The Major Fragmentation Pathways Of Phenyl</td>
<td></td>
</tr>
<tr>
<td>4-Pyridyl Ketone</td>
<td>32</td>
</tr>
<tr>
<td>9  Minor Fragmentation Pathway of Phenyl 3-Pyridyl</td>
<td></td>
</tr>
<tr>
<td>Ketone</td>
<td>34</td>
</tr>
</tbody>
</table>
LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Schemes</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Mechanism Of McLafferty Rearrangement</td>
<td>49</td>
</tr>
<tr>
<td>2 Mechanism Of Hydrogen Loss From The Enolic Dibenzoylacetylmethane Molecule Ion</td>
<td>60</td>
</tr>
<tr>
<td>3 Mechanism Of The Pronounced Fragmentation Of The Ketonic And Enolic Dibenzoylacetylmethane</td>
<td>62</td>
</tr>
</tbody>
</table>
PART I

MASS SPECTROMETRY STUDY OF METHYL PYRIDYL KETONES
AND PHENYL PYRIDYL KETONES
Part I

MASS SPECTROMETRY STUDY OF METHYL PYRIDYL KETONES

AND PHENYL PYRIDYL KETONES

Chapter 1

INTRODUCTION

During the last ten years, mass spectrometry has been widely used by organic chemists in structural elucidation and in the identification of organic compounds. Many workers have devoted their efforts to the development of this technique. This rapid growth has been accompanied by the development of relatively simple theories for the rationalization of the observed fragmentations (1-4).

Although mass spectra of alkyl phenyl ketones and alkyl substituted pyridines have been studied (4), very little attention has been directed toward the comparison of the unimolecular decomposition of alkyl pyridyl ketones by electron impact, field ionization, and field desorption. Mass spectral studies of some isomeric monosubstituted pyridine derivatives (5-8) have pointed out the differences in fragmentation patterns. For example, differences
between the 2-isomer and 3-, 4-isomers have been attributed to interactions between the substituent group and the ring nitrogen; that is the ring position of the alkyl substituent greatly influences the decomposition pathway of the molecular ion. The differences can be explained as a result of ortho effects (9) or peri effects (10).

A paper published (11) after the present work was completed indicated that the mass spectra of the 2-isomers of the methyl and ethyl esters of isomeric pyridinecarboxylic acids, pyridyl acetic acids, and pyridyl acrylic acids differed from their corresponding 3- and 4-isomers. The participation of the ring nitrogen in the fragmentation of the 2-isomers was involved to explain this difference. It was also suggested that this participation of the ring nitrogen may be useful for identification purposes in differentiating the 2-isomer from the 3- and 4-isomers.

The most significant fragmentation peak of 2-isomer was the $M^+ - 28$ peak which arose from the expulsion of a CO fragment. This can be understood by assuming a rearrangement process followed by an elimination of a CO fragment.
In contrast to the 2-isomer, a simple alpha cleavage to the carbonyl group of the 3- and 4-isomers was observed, which showed a negligible influence by the ring nitrogen in these isomers.

However, up till now, the investigation of these isomers by field ionization mass spectrometry (i.e. removal of an electron by the action of a strong electrostatic
field) has only been attempted by Migahed and his co-workers (12). With an electron impact ion source, fragmentation of the investigated molecules occurs only if the ionizing electrons have an energy in excess of the ionization potential of the molecules. The resulting mass spectra are generally complicated. This, however, is not the case with field ionization. If a very high electric field of the order of about \(10^7\) to \(10^8\) V/cm acts on a molecule, the potential energy of the molecule is changed in such a way that an electron in the ground state of the molecule is removed. This can be explained by the quantum mechanical tunnel effect (13). During this type of ionization process, generally, the molecules do not acquire sufficient energy to lead to extensive fragmentation. Therefore the field ionization mass spectrum often consists of only one intense mass line (the parent peak of the molecule), the intensities of other lines are small. Hence, the field ionization mass spectra are simpler than the electron impact spectra. Advances are being made in the application of field ionization mass spectrometry to
structural investigation (14, 15, 16).

Migahed et al. have investigated the fragmentation of isomeric methyl pyridyl ketones by means of field ionization under a very high field anode temperature (400°C). Their results led to the conclusion that the specific fragment at m/e 93 for methyl 2-pyridyl ketone is due to a rearrangement process followed by the elimination of a CO fragment. In contrast, there is no such fragmentation occurs in the spectra of 3- and 4-isomers.

It was decided to investigate the fragmentation of isomeric methyl pyridyl ketones and isomeric phenyl pyridyl ketones by means of electron impact, field ionization and field desorption. It was recognized that this work may have significant applications in distinguishing the ring position of substituted pyridyl ketones and may serve as proof of the structures.
Chapter 2

THE MASS SPECTROMETRY OF SUBSTITUTED PYRIDINES

The mass spectrum of pyridine (17) (Fig. 1) is simple and reflects the great stability of the aromatic ring. The base peak corresponds to the molecular ion and the loss of hydrogen cyanide ($M^+ - 27$) furnishes the only abundant fragment ions (Scheme 1). Such a mode of fragmentation is typical for unsubstituted aromatic nitrogen heterocycles. A minor process, loss of HCN from the $M^+ - 1$ ion, leads to the peak at m/e 51. A study of 2,6-d$_2$-pyridine and 2-d-pyridine had shown that statistical involvement of the alpha, beta, and gamma-hydrogen atoms occurs in the loss of HCN from the molecular ion (18).

The mechanism of the loss of HCN is, so far, uncertain. For benzene, the intervention of prismane and benzvalene structures has been suggested (19, 20) as one possibility and for pyridine the aza-analogue of those structures could be involved, as:

![Chemical Diagram]
As for benzene, yet another possibility is that the pyridine molecular ion may be represented by an open chain structure.

![Pyridine molecule diagram](image)

**Fig. 1** Electron impact mass spectrum of pyridine  
*relative intensity with reference to the largest peak as 100%.

Similar behavior is observed with 2-, 3-, and 4-methyl pyridines (21). It seems very likely that, to a large extent, the loss of hydrogen is (instaneously, at least) from the methyl groups. It is of some significance that the mass spectrum (22) of 2,6-dimethyl pyridine exhibits the elimination of a hydrogen atom as well as a methyl radical.
and also shows the expulsion of methyl cyanide instead of hydrogen cyanide.

\[
\begin{align*}
\text{Scheme 1} & \quad \text{The fragmentation pathways of pyridine} \\
& \quad \text{It is interesting that the fragmentation of pyridines substituted with higher alkyl groups shows that their cleavage processes depend on the relative position of the substituent and heteroatom (2). These principle fragmentation patterns may be divided into four categories.}
\end{align*}
\]
Nomenclature for bond cleavage is standard, i.e., for the propyl pyridine:

\[ \text{Py} \xrightarrow{\alpha} \text{CH}_2 \xrightarrow{\beta} \text{CH}_2 \xrightarrow{\gamma} \text{CH}_2 \xrightarrow{\delta} \text{H} \quad \text{where Py=pyridyl} \]

i) **alpha-cleavage with hydrogen rearrangement**

According to Spiteller (23), this cleavage process is especially favored by pyridines having a C2-chain in position 2. Thus 2-ethyl pyridine eliminates ethylene; 2-vinyl pyridine, acetylene; 2-acetyl pyridine, ketene; etc. These seem possible as a result of a four-center hydrogen-transfer reaction, i.e.

\[ \text{Py} \xrightarrow{-\text{C}_2\text{H}_4} \]

ii) **beta-cleavage**

Examination of the mass spectra (24) of the three ethyl pyridine isomers shows that M\(^+\)-\text{CH}_3 is the base peak of the spectrum of 3-ethyl pyridine but is con-
siderably weaker in those of 2- and 4-ethyl pyridines. This behavior can be understood (25) when it is realized that, in pyridine, the electron density is relatively larger at the 3-position but lower at the 2- and 4-positions. In each case, the fragments formed by beta-fission undergo further elimination of hydrogen cyanide.

iii) \textbf{gamma-cleavage}

Spiteller (23) has called attention to the fact that such bond fission is especially favored in 2-substituted pyridines. This interpretation is supported by the mass spectrum of 2-ethyl pyridine (24), where the $M^+ - 1$ peak greatly exceeds the molecular ion peak in intensity, in contrast to the situation encountered with its 3- and 4-isomers. It is also confirmed by the observation that 2-n-propyl pyridine shows a very intense $M^+ - \text{CH}_3$ ion whereas in its 3- and 4-isomers such methyl loss is only a minor process (17,25).

It seems likely that (23) gamma-fission is involved in stabilization of the resultant fragment by the four-membered ring formation as shown in Scheme 2. But the point has not been explicitly demonstrated.
Scheme 2  Proposed mechanism of the four-membered ring formation of 2-ethyl and 2-propyl pyridines

iv) McLafferty rearrangement

This type of fragmentation can take place if side chains of at least three carbon atoms are attached to the pyridine nucleus. Again, this mode of cleavage is most important for pyridines substituted in position 2. Thus, in 2-n-propyl pyridine (1), loss of ethylene by a McLafferty rearrangement yields the base peak, while the fragment arising from simple beta-cleavage is hardly discernible. However, this is not always true (17,25). It seems that the extent of McLafferty rearrangement is dependent on the nature of the substituent (26).
It is somewhat surprising in view of so much work on the fragmentation pattern of monosubstituted pyridines that so little information on the electron impact mass spectra of the three isomeric substituted pyridyl ketones has appeared (6,27,28). In those reports, the fragmentation behavior of 3- and 4-isomers show the major fragmentation pathway being simple cleavage alpha to the carbonyl group. This is shown in Scheme 3.

Scheme 3  The major fragmentation pathways of 3- and 4-alkyl pyridyl ketones by electron impact
Furthermore, the high resolution mass measurements of 3- and 4-propyl pyridyl ketone (29) and 3- and 4-cyclopropyl pyridyl ketone (5) indicate no significant contribution from the loss of a CO fragment rather a simple alpha cleavage fragmentation. This suggests that, for 3- and 4-substituted pyridyl ketones, the loss of a CO fragment accompanied by substituent migration can be neglected.

On the other hand, placement of the substituent group on the 2-position of the pyridine ring causes fragmentation patterns different from those of the 3- and 4-isomers. It was observed that the most abundant ions in 3- and 4-isomers fall into obscurity in 2-isomer. The peak arising from the expulsion of a CO fragment by means of rearrangement of the substituent is now enhanced. This is owing to the increased influence of the pyridine nitrogen on the fragmentation.

Two mechanisms can be drawn for this rearrangement involving either substituent group migration to nitrogen or extrusion of a CO fragment with bonding between the 2-position and the alkyl moiety (Scheme 4).
Scheme 4  Proposed mechanism of migration of methyl group to the pyridine ring

The mass spectra of 2-ethyl pyridyl ketone, 2-butyl pyridyl ketone, and 2-pentyl pyridyl ketone are shown in Fig. 2, 3, and 4. The peaks corresponding to the loss of a CO fragment (mass unit = 28) are also observed. From the occurrence of this fragmentation in these compounds, it may be concluded that chain length is not a significant factor in the rearrangement.
Fig 2  Electron impact mass spectrum of 2-ethyl pyridyl ketone (23)

Fig 3  Electron impact mass spectrum of 2-butyl pyridyl ketone (23)
Fig. 4  Electron impact mass spectrum of 2-pentyl pyridyl ketone (23)
Chapter 3
RESULTS AND DISCUSSION

The mass spectra of the isomeric methyl pyridyl ketones and phenyl pyridyl ketones were obtained by electron impact, field ionization, and field desorption techniques in order to compare the strength of the nitrogen influence. Specifically, ions due to loss of the CO fragment are particularly noticeable in the spectra of 2-isomers but make little or no contribution to the spectra of 3- and 4-isomers. Not all fragmentation processes will be discussed since many are predictable from a given molecular ion. Only those that are unique or offer an interesting comparison will be mentioned.

I Electron Impact Mass Spectrometry Of Methyl Pyridyl Ketones

(A) Methyl 4-Pyridyl Ketone

The mass spectrum of methyl 4-pyridyl ketone is shown in Fig. 5. The major fragmentation pathways are illustrated in Scheme 5. The behavior of this compound under electron impact is predictable, with simple cleavage alpha to the carbonyl and the subsequent fragmentation. Its major fragmentation pathways are
quite similar to that of substituted pyridyl ketones producing ions at m/e 106, 78, 51, and 43. The mass measurements showed that the expulsion of the CO fragment from the molecular ion producing m/e 93 occurs to the extent of only 0.27% of m/e 106 (base peak). A hydrogen rearrangement of the proton alpha to the carbonyl group was also noted in the formation of the m/e 79 fragment.

![Diagram of mass spectrum](image)

**Fig. 5** Electron impact mass spectrum of methyl 4-pyridyl ketone

*only the relative intensities larger than 2% are plotted in the EI mass spectra within this thesis*
Scheme 5  The major fragmentation of methyl 4-pyridyl ketone

(B) Methyl 3-Pyridyl Ketone

The mass spectrum of methyl 3-pyridyl ketone is shown in Fig. 6. A comparison of Fig. 5 and 6 shows that the mass spectra are almost the same. Even the behavior of the deuterium-labeled analogs shows only a minor difference (6). Therefore, the major fragmentation pathways are the same as those for the methyl 4-pyridyl ketone. The expulsion of the CO fragment from
the molecular ion occurs only to the extent of 0.3% of the base peak (m/e 106). As previously mentioned (5, 6, 27, 29), it can be concluded that the loss of the CO fragment from these 3- and 4-isomers can be neglected.

Fig. 6 The electron impact mass spectrum of methyl 3-pyridyl ketone

(C) Methyl 2-Pyridyl Ketone

Placement of the substituent group in the 2-position of the pyridine ring causes striking changes in the mass spectrum (Fig 7) compared to the spectra
(Fig 5 and 6) of the 3- and 4-isomers. The most abundant peak in the 3- and 4-isomers, m/e 106, falls into obscurity in 2-methyl pyridyl ketone, being only 6.14% of the base peak (m/e 79).

![Mass Spectrogram](image)

**Fig. 7** Electron impact mass spectrum of methyl 2-pyridyl ketone

The mass spectrum of methyl 2-pyridyl ketone has an intense peak at m/e 93 corresponding to the loss of 28 mass units (CO fragment). This expulsion of
the CO fragment was also observed from phenyl 2-
pyridyl ketone but not from 3- and 4-isomers. This
behavior may correspond to the interaction between
the substituted group and ring nitrogen. This will
be discussed further in this thesis.

The electron impact mass spectrum of the methyl-
d$_2$,2-pyridyl ketone was also examined. The results
are shown in Table 1.

Table 1

<table>
<thead>
<tr>
<th>m/e</th>
<th>process</th>
<th>relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>124</td>
<td>M$^+$</td>
<td>80</td>
</tr>
<tr>
<td>121</td>
<td>M$^+$(undeuterated)</td>
<td>1.8</td>
</tr>
<tr>
<td>106</td>
<td>M$^+-18$</td>
<td>4.1</td>
</tr>
<tr>
<td>96</td>
<td>M$^+-28$</td>
<td>30</td>
</tr>
<tr>
<td>80</td>
<td>M$^+-44$</td>
<td>100</td>
</tr>
<tr>
<td>78</td>
<td>M$^+-46$</td>
<td>56</td>
</tr>
<tr>
<td>53</td>
<td>M$^+-71$</td>
<td>28</td>
</tr>
<tr>
<td>51</td>
<td>M$^+-73$</td>
<td>27</td>
</tr>
<tr>
<td>46</td>
<td>M$^+-78$</td>
<td>31</td>
</tr>
</tbody>
</table>

*only the relative intensities larger than 2% are listed
in the tables within this thesis
With the aid of this deuterium labeling, the fragmentation patterns are proposed as shown in Scheme 6.

Scheme 6  The proposed fragmentation pattern of methyl 2-pyridyl ketone
It can be seen that the methyl group first migrates to the ring nitrogen or ring carbon followed by a loss of the CO fragment to form the C₆H₇N⁺ fragment (m/e 95) which was further decomposed by the loss of the CH₃ radical and then HCN. The fragmentation patterns of 2-methyl pyridine are similar to that of methyl 2-pyridyl ketone and on this basis the mechanism in Scheme 6 is assigned to this reaction.

On examining the mass spectrum of the methyl 2-pyridyl ketone (Fig. 7), it was found that the peak at m/e 79 is the base peak. The deuterium labeling results show that expulsion of CH₂CO fragment occurs with the proton transfer from the methyl group. On this basis, the fragment at m/e 79 is proposed in Scheme 7.

Scheme 7 Proposed pathways of migration of proton of methyl 2-pyridyl ketone
Although the mass spectrum of deuterated cyclopropyl 2-picoly1 ketone* (5) indicated that the hydrogen may migrate to the pyridine nitrogen, there is no direct evidence to prove whether this hydrogen is migrated to the ring nitrogen or the ring carbon.

Comparing the mass spectrometrical results of these three isomers (Table 2) by the electron impact, it can be seen that the methyl 2-pyridyl ketone exhibits a strikingly different fragmentation patterns from those of the 3- and 4-isomers. These differences are considered to be attributable to an interaction

*Deuterium exchange of the cyclopropyl proton alpha to the carboxyl shows that the rearrangement to form the m/e 93 ion is due exclusively to the transfer of the alpha hydrogen. The fact that the peak at m/e 66, resulting from the loss of HCN, remains at m/e 66 whereas the m/e 93 moves to mass 94 may indicate hydrogen transfer to the pyridyl nitrogen. However, it is still an unsolved problem.
between the substituent and ring nitrogen. In the case of the methyl pyridyl ketones, the ease of cleavage of \( \text{CH}_2\text{CO} \) radical (i.e. migration of proton) to form the fragment at m/e 79 is also dependent on the position of the substituent.

Table 2

Significant peaks in electron impact mass spectra of methyl pyridyl ketone isomers

<table>
<thead>
<tr>
<th>m/e</th>
<th>process</th>
<th>relative intensities %</th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2-isomer</td>
<td>3-isomer</td>
<td>4-isomer</td>
<td></td>
</tr>
<tr>
<td>121</td>
<td>M⁺</td>
<td>76</td>
<td>57</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>106</td>
<td>M⁺⁻15</td>
<td>6.4</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>93</td>
<td>M⁺⁻28</td>
<td>.34</td>
<td>0.3</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>M⁺⁻42</td>
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<td>14</td>
<td>29</td>
<td></td>
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<tr>
<td>78</td>
<td>M⁺⁻43</td>
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<td>83</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>M⁺⁻69</td>
<td>32</td>
<td>8.8</td>
<td>12</td>
<td></td>
</tr>
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<td>51</td>
<td>M⁺⁻68</td>
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<td>30</td>
<td>41</td>
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</table>
II Mass Spectrometry Of Methyl Pyridyl Ketones By Field Ionization

The field ionization mass spectra the three isomers were studied at different emitter currents. The results are shown in Table 3. In these spectra, the peak due to loss of a CO fragment (m/e 93) did not appear. In the field ionization mass spectra of these methyl pyridyl ketone isomers, there is no evidence of the acetyl substituent being influenced by the ring nitrogen during the decomposition of the molecular ion. However, several significant differences are apparent. The differing peak intensities of the three isomers at m/e 43, 78, 122, and 242 seem significant, although we can not interpret them at this time.

Migahed (12) using the field ionization mass spectra with anode current of 30mA observed a fragment of methyl 2-pyridyl ketone at m/e 93 which was formed by a rearrangement process followed by the elimination of the CO fragment. However, as is shown in Table 4, we were unable to observe this fragmentation under different anode currents from 0mA, 5mA 10mA, ... to 40mA. The failure to
Table 3

Significant peaks in field ionization mass spectra of methyl pyridyl ketone isomers

<table>
<thead>
<tr>
<th>m/e</th>
<th>Process</th>
<th>relative intensities %</th>
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<th>3-isomer</th>
<th>4-isomer</th>
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<tr>
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<td>9.8</td>
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<tr>
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<td>M⁺+189</td>
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<td>2.6</td>
<td></td>
</tr>
<tr>
<td>242</td>
<td>2M⁺</td>
<td>0.8</td>
<td>4.5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>123</td>
<td>M⁺+2</td>
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<td>1.3</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>122</td>
<td>M⁺+1</td>
<td>11</td>
<td>18</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>121</td>
<td>M⁺</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>M⁺-43</td>
<td>1.3</td>
<td>9.1</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>M⁺⁻78</td>
<td>1.6</td>
<td>10</td>
<td>11</td>
<td></td>
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<tr>
<td>28</td>
<td>M⁺⁻93</td>
<td>0.6</td>
<td>-</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

*only absolute intensity larger than 10 (arbitrary units which represent within a factor of 2, the number of ions) is shown in the Table.
to reproduce the published results may be due to one of three reasons: (a) thermal rearrangement may have occurred; (b) different instrumentation (double focusing vs single focusing; focusing at different region from the emitter etc.); (c) different ion source temperature.

Table 4
Comparison of field ionization mass spectra of methyl 2-pyridyl ketone under different anode temperatures

<table>
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<th>m/e</th>
<th>process</th>
<th>present work</th>
<th>published report</th>
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<tr>
<td></td>
<td></td>
<td>0mA</td>
<td>15mA</td>
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<tr>
<td>242</td>
<td>2M+</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>123</td>
<td>M+2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>122</td>
<td>M+1</td>
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<td>-</td>
<td>0.4</td>
</tr>
<tr>
<td>28</td>
<td>M+93</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
III Attempted Field Desorption Mass Spectrometry of Methyl Pyridyl Ketones

The mass spectral results of methyl 2-pyridyl ketone using the field desorption technique are shown in Table 5. Unfortunately, these three isomers are quite volatile, that is, most of the samples have been vaporized prior to the field desorption. As a result, the mass spectrum obtained could be a combination of both field ionization and field desorption. No significant fragmentation occurred.

Table 5

<table>
<thead>
<tr>
<th>m/e</th>
<th>process</th>
<th>relative intensity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>122</td>
<td>M⁺⁺1</td>
<td>10</td>
</tr>
<tr>
<td>121</td>
<td>M⁺</td>
<td>100</td>
</tr>
<tr>
<td>51</td>
<td>M⁺⁻70</td>
<td>0.1</td>
</tr>
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</table>
IV Electron Impact Mass Spectrometry of Phenyl Pyridyl Ketones

(A) Phenyl 4-Pyridyl Ketone

The electron impact mass spectrum of phenyl 4-pyridyl ketone is shown in Fig. 8. Its behavior is quite similar to the mass spectra of substituted benzophenones; the formation of the benzoyl ion, the C₆H₅⁺ ion and their substituted counterparts are the most important processes for the decomposition of the singly charged molecular ion (30). It is possible to propose the fragmentation pathways shown in Scheme 8.

![Diagram of Phenyl 4-Pyridyl Ketone Mass Spectrum]

**Fig. 8** Electron impact mass spectrum of phenyl 4-pyridyl ketone
The spectrum of phenyl 4-pyridyl ketone showed that the expulsion of the CO fragment from the molecular ion yields an ion with relative intensity of 0.8%. From the relative abundance of the peaks at m/e 106, it is readily seen that the formation of the C₆H₄NO⁺ (m/e 106) ion is heavily disfavored over that of C₇H₅O⁺ (m/e 105) ion. This is easily explained as

Scheme 8  The major fragmentation pathways of phenyl 4-pyridyl ketone
the $\text{C}_6\text{H}_4\text{NO}^+$ ion is expected to be destabilized as compared to $\text{C}_7\text{H}_5\text{O}^+$ ion due to the electron withdrawal of nitrogen atom in the para-position.

(B) Phenyl 3-Pyridyl Ketone

The mass spectrum of phenyl 3-pyridyl ketone is shown in Fig. 9. The major fragmentation pathways followed by the 3-isomer are as shown in Scheme 8. The formation of $\text{C}_7\text{H}_6\text{O}^+$ ion is still favored over that of $\text{C}_6\text{H}_4\text{NO}^+$ ion, but not by as large a margin as for the 4-isomer. The ratio of the ratio of the relative abundance of $\text{C}_6\text{H}_4\text{NO}^+: \text{C}_7\text{H}_5\text{O}^+$ is 0.21 for the 3-isomer and 0.02 for the 4-isomer. This is expected as in the 3-isomer the ring nitrogen, being meta to the 3-carbon, can withdraw electrons from the reaction site by the inductive effect while in the 4-isomer the ring nitrogen can do so by a stronger resonance effect.

Close examination of the mass spectrum indicates that another fragmentation pathway, though relatively minor, also exists. This is shown in Scheme 9.
Fig. 9  Electron impact mass spectrum of phenyl 3-
pyridyl ketone

This fragment which arises from the expulsion of the
CO fragment from the molecular ion is found with a
yield of 2.9% (relative intensity). Similar skeletal
rearrangements have been reported in the mass spectra
of many aromatic ketones (29).

\[
\begin{align*}
C_{12}H_{9}NO & \xrightarrow{-\text{CO}} C_{11}H_{9}N^+ \\
\text{m/e 183, } M^+ & \quad \text{m/e 155 (3%)}
\end{align*}
\]

Scheme 9  Minor fragmentation pathway of phenyl
3-pyridyl ketone
(C) Phenyl 2-Pyridyl Ketone

The mass spectrum of phenyl 2-pyridyl ketone is shown in Fig. 10. The fragmentation pathway followed by the 3- and 4-isomers (Scheme 8) is also followed by the 2-isomer. The forming of \( \text{C}_7\text{H}_5\text{O}^+ \) (m/e 105) ion is highly favored over that of \( \text{C}_6\text{H}_4\text{NO}^+ \) (m/e 106) ion. The ratio (0.017) of relative abundance \( \text{C}_6\text{H}_4\text{NO}^+ : \text{C}_7\text{H}_5\text{O}^+ \) of 2-isomer is somewhat smaller than that obtained from the 4-isomer. The abundance sequence for the four ions is:

\[ \text{C}_6\text{H}_5\text{CO}^+ > 3-\text{C}_5\text{H}_4\text{NCO}^+ > 4-\text{C}_5\text{H}_4\text{NCO}^+ > 2-\text{C}_5\text{H}_4\text{NCO}^+ \]

This is expected as the nitrogen atom in the ortho position to the reaction site can withdraw electrons by both resonance and inductive effects. Another important feature of the spectrum is a loss of a hydrogen atom by the molecular ion.

The most striking difference between the mass spectra of the 2-isomer and the 3-, or 4-isomers, however, is that the most abundant peak is not formed
Fig. 10. Electron impact mass spectrum of the phenyl 2-pyridyl ketone

by the alpha cleavage to the carbonyl group but by the loss of a neutral fragment of mass units 28 (the CO fragment) which occurred after the rearrangement of molecular ion (Scheme 4) as is mentioned earlier. The presence of such an abundant ion giving rise to the base peak can only be explained if the neutral fragment lost is a stable molecule like carbon monoxide. An excellent article (30) has surveyed the mass spectra of bis-aryl compounds and indicated this tendency to lose a small stable molecule.
Although the loss of carbon monoxide from the molecular ion of aromatic ketones has been reported (30), the resulting rearrangement ions do not give rise to major peaks in the spectra. The only case of an abundant peak resulting from such a loss of carbon monoxide is found in the spectrum of anthraquinone (31) where o-diphenylene is formed. It should be noted that this type of rearrangement is quite important in all of the 2-pyridyl ketones examined (5,6,28,32) but is relatively unimportant in the 3- and 4-isomers. The comparison of the mass spectra of 2-, 3-, and 4-isomers (Table 6) allows easy differentiation of the structures.
Table 6

Significant peaks in electron impact mass spectra of the 2-, 3-, and 4-phenyl pyridyl ketone isomers

<table>
<thead>
<tr>
<th>m/e</th>
<th>process</th>
<th>2-isomer</th>
<th>3-isomer</th>
<th>4-isomer</th>
</tr>
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<tbody>
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<td>183</td>
<td>M⁺</td>
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<td>100</td>
<td>58</td>
</tr>
<tr>
<td>182</td>
<td>M⁺-1</td>
<td>60</td>
<td>28</td>
<td>2.4</td>
</tr>
<tr>
<td>155</td>
<td>M⁺-28</td>
<td>100</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td>154</td>
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<tr>
<td>105</td>
<td>M⁺-78</td>
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<td>75</td>
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<td>78</td>
<td>M⁺-105</td>
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<tr>
<td>77</td>
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</tr>
<tr>
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<td>M⁺-132</td>
<td>44</td>
<td>34</td>
<td>27</td>
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</table>
Attempted Field Desorption Mass Spectrometry of Phenyl Pyridyl Ketones

The field desorption mass spectral results of these three isomers are shown in Table 7. Again, unfortunately, these compounds, like the methyl pyridyl ketones, are too volatile for field desorption runs. Hence, these spectra are obtained via the field desorption technique but observing a combination of field ionization and field desorption spectra.

Table 7

Attempted field desorption mass spectral results of phenyl pyridyl ketone isomers

<table>
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<tr>
<th>m/e</th>
<th>process</th>
<th>relative intensity %</th>
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<tbody>
<tr>
<td></td>
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<td>185</td>
<td>$M^+ + 2$</td>
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<td>184</td>
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<td>13</td>
</tr>
<tr>
<td>183</td>
<td>$M^+$</td>
<td>100</td>
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<tr>
<td>91</td>
<td>$M^+ - 92$</td>
<td>1.2</td>
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<tr>
<td>46</td>
<td>$M^+ - 137$</td>
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<tr>
<td>19</td>
<td>$M^+ - 164$</td>
<td>1</td>
</tr>
<tr>
<td>18</td>
<td>$M^+ - 165$</td>
<td>1.3</td>
</tr>
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</table>
From examination of these spectra (Table 7), it is evident that no rearrangement occurred for 2-, 3-, and 4-isomers. In fact, no significant fragmentation occurred. Distinguishing these three isomers by field ionization spectra is not feasible. In conclusion, the fragmentation pattern of 2-substituted pyridyl ketones by electron impact is simple but strikingly different from those of 3- and 4-substituted isomers. This characteristic behavior of the 2-isomer can be explained by assuming that the pyridine nitrogen atom near the substituent in position 2 induces the rearrangement process, whereas in the 3- and 4-isomers it has little effects. In other words, the rearrangements observed for particular compounds are markedly dependent upon the type(s) of pyridyl group(s) initially present in that compound; therefore, they are of potential diagnostic use in problems involving structural elucidation. Specifically, with the monoketones, ions due to loss of the CO fragment are particularly noticeable in the spectrum of 2-pyridyl derivatives. Hence, as already reported for several series of related compounds, the variation in
abundance in the mass spectra by electron impact may provide a better means for distinguishing isomers and may serve as proof of the structure. However, a similar distinction of 2-isomer from 3- and 4-isomers by field ionization and field desorption has not been found to be possible.
Chapter 4

EXPERIMENTAL

The n.m.r. spectra were measured by means of a JEOL C60 HL Spectrometer or Varian EM 360 60MHZ Spectrometer using T.M.S. as internal reference.

Mass spectra were obtained on a Varian MAT CH-5 mass Spectrometer equipped with a combined field ionization, field desorption, and electron impact source. All of the spectra were obtained with data acquisition and mass scanning under the control of an INCOS Model 2000 computer interfaced with the mass spectrometer. In all cases, the samples for field desorption were applied to the anode by the dipping technique (33). Acetone and toluene were injected through batch inlet system as internal mass markers. The pressure of the ion source was 5x10⁻⁶ torr and a potential difference of 10KV (+5KV for anode and -5KV for extraction plate) was applied across the electrodes. The ion source temperature was between 50°C and 100°C for field desorption; about 70°C and 250°C for field ionization and electron impact respectively. The field ionization and field desorption spectra have been obtained under different emitter
current from 0mA to 40mA and from 0mA to 20mA respectively.

Isomeric methyl pyridyl ketones and isomeric phenyl pyridyl ketones were purchased from Aldrich Chemical Company, Inc. All compounds' purity were checked by vapor phase chromatography which was conducted on an HP 720 instrument using 8'x375'OD aluminum columns packed with 10% Deksil with He as carried gas. The deuterated compound was determined by comparison of its n.m.r. spectrum with that of an authentic nondeuterated sample. The purity of the deuterated compound was confirmed by the mass spectrometer.

Methyl-\textsubscript{d}\textsubscript{5},2-pyridyl ketone was prepared (6) from methyl 2-pyridyl ketone. To 10ml of 1.0M NaOMe/MeOD under \textsubscript{N}2, with the exclusion of moisture, was added 121 mg of methyl 2-pyridyl ketone. The solution was heated under reflux for 24 hours and the methanol removed to give an oil. This product was taken up in 10ml of CH\textsubscript{2}Cl\textsubscript{2} which was then washed with D\textsubscript{2}O (3x2ml) followed by repeated washing with D\textsubscript{2}O (1x3ml) over a 2 hour period. After separation of the D\textsubscript{2}O, the combined CH\textsubscript{2}Cl\textsubscript{2} layer, were dried by Na\textsubscript{2}SO\textsubscript{4}. The solvent was removed to yield 78 mg of crude product.
The ketone was then purified through column chromatography over Alumina, (Neutral) using CH₂Cl₂ as eluting solvent.
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PART II

ISOLATION AND MASS SPECTRA OF TAUTOMERIC FORMS

OF

DIBENZOYLACETYLMETHANE AND 3-PHENYL-2,4-PENTANEDIONE
Part II

ISOLATION AND MASS SPECTRA OF TAUTOMERIC FORMS
OF
DIBENZOYLACETYLIMETHANE AND 3-PHENYL-2,4-PENTANEDIONE

Chapter 1

INTRODUCTION

The keto-enol equilibrium in beta-diketones has been the subject of numerous studies. There have been few publications, however, on the investigation of keto-enol tautomerism by means of mass spectrometry. The mass spectra of several beta-diketones have been studied (1,2) and by comparing different substituted compounds, it has been found that the fragmentation is influenced by tautomeric composition of the compounds. In the comparison of differently substituted beta-diketones, it has been tentatively assumed that peaks which represent the keto form or enol form arise exclusively from the keto or the enol form. However, it is very difficult to assign fragment ions to particular tautomeric forms of diketone compounds. Lamir et al. (3) assigned the peaks arising from the cleavage of the diketone to simple alpha-cleavage of the enol form of the molecular ion and to McLafferty rearrangement of the keto form.
In an effort to examine the two tautomeric forms, the enol methyl ether of acetylacetone was prepared (4). Its mass spectrum shows $M^+\cdot CO$ and $M^+\cdot CH_2CO$ (via McLafferty rearrangement) probably arising exclusively from keto form as well as concomitant formation of $M^+\cdot CH_3$ (via alpha-cleavage) probably due to both keto and enol forms, although the latter may well be predominant (5). There is still no strong evidence that the enol form will not undergo McLafferty rearrangement.

The McLafferty rearrangement is defined as the transfer of a gamma hydrogen to a double-bonded atom through a six-membered transition state, with beta bond cleavage (6). This may be present in carbonyl compounds as shown in Scheme 1.

![Scheme 1](image)

**Scheme 1** Mechanism of McLafferty rearrangement

The evidence leading to this formulation of the reaction has been ample (7). In principle the McLafferty rearrangement could proceed either in a concerted manner, with simultaneous
hydrogen transfer and beta-cleavage, or in stepwise fashion with initial hydrogen transfer being followed by beta-cleavage. There is now a convincing body of evidence to indicate that the reaction occurs via a stepwise pathway (8,9).

Although simple carbonyl compounds show hardly detectable amount of enol, the introduction of a second unsaturated group into a simple aldehyde or ketone changes the situation, sometimes dramatically. For example, beta-diketones may contain a large amount of enolic forms compared to the beta-keto esters but have less enolic content compared to beta-ketoaldehydes.

In general, enolization is increased by the presence of the unsaturated group attached to the alpha-carbon atom that is in the beta-position to the carbonyl group. The same unsaturation at other positions in the molecule has minor effect. The trend is illustrated in Table 1 (10). The possibility of intramolecular hydrogen-bonding also stabilized the enol form (11).

Although many compounds can be shown to be equilibrium mixtures of ketonic and enolic forms, only a very few of them have been separated into their respective pure tautomers. Also, no attention has been directed toward the comparison of the fragmentation pathways of the separated keto-enol tautomers using mass spectrometry.
Table 1

The enol content of some carbonyl compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Enol content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylaldehyde</td>
<td>no enol found</td>
</tr>
<tr>
<td>CH₃COOEt</td>
<td>no enol found</td>
</tr>
<tr>
<td>CH₂COEt</td>
<td>1.2 x 10⁻¹</td>
</tr>
<tr>
<td>CH₂COCH₂COCH₃</td>
<td>76.4</td>
</tr>
<tr>
<td>CH₂COCH₂COOEt</td>
<td>8.0</td>
</tr>
<tr>
<td>PhCOCH₂COCH₃</td>
<td>89.2</td>
</tr>
<tr>
<td>EtOOCCH₂COOEt</td>
<td>7.7 x 10⁻³</td>
</tr>
</tbody>
</table>

It has been indicated (12,13) that attempts to understand unimolecular gas-phase reactions induced by electron impact have previously been hampered by a relatively long reaction interval (10⁻⁶ sec). Such techniques can fail to distinguish among competing and consecutive reactions. On the other hand, field ionization mass spectrometry permits the observation of the competing and consecutive unimolecular gas-phase reactions (induced by ionization of a molecule) over a time range from 10⁻¹² to 10⁻⁹ sec. Beckey et al. have pointed out that field ionization fragments may be very helpful in structural investigations of
organic molecules, especially if compared to electron impact induced fragmentation. Field ionization unlike electron impact gives rise almost exclusively to simple bond splitting. Thus, comparison of electron impact and field ionization spectra may indicate whether or not intense electron impact produced fragments reflect directly the structure of the parent molecules or are due to complicated rearrangements (14).

Cooks et al. (4) have investigated the effects of the heated inlet system temperature and source temperature of the mass spectrometer on the keto-enol tautomeration in beta-diketones. They concluded that the position of tautomeric equilibrium has only been slightly affected by the changes of the inlet system temperature (Table 2). Conversely, small changes in the source temperature of the mass spectrometer cause appreciable changes in the tautomeric compositions (Fig 1). Hence, it is the source temperature which determines the position of tautomeric equilibrium.

Consequently, the isolation of the keto-enol isomers of dibenzoylacetyl methane and 3-phenyl-2,4-pentanedione was attempted, and a comparison of the mass spectra of the pure tautomers upon electron impact and field ionization was examined to determine their characteristic fragmentation processes.
### Table 2 (4)

**Mass spectrum of acetylacetone as a function of inlet temperature**

<table>
<thead>
<tr>
<th>ion</th>
<th>temperature range</th>
<th>abundance %</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M^+ )</td>
<td>27 - 207</td>
<td>69 - 62</td>
</tr>
<tr>
<td>( M^+ - CH_3 )</td>
<td>27 - 207</td>
<td>82 - 75</td>
</tr>
<tr>
<td>( M^+ - CO )</td>
<td>67 - 207</td>
<td>1.4 - 2.3</td>
</tr>
<tr>
<td>( M^+ - CH_2CO )</td>
<td>67 - 207</td>
<td>1.6 - 5.3</td>
</tr>
<tr>
<td>( CH_3CO^+ )</td>
<td>67 - 207</td>
<td>100 - 100</td>
</tr>
</tbody>
</table>

Ion abundances relative to base peak, m/e 43. All temperature in °C. Source temperature was 65°C.
Fig. 1: Effect of variation of source temperature upon the spectrum of acetylacetonate (inlet system 30°C)

○ = M⁺ –CH₂/M⁺ –CH₂CO
● = M⁺ –CH₂/M⁺ –CO

Reference: (4)
Chapter 2
RESULTS AND DISCUSSION

I Dibenzoylethylmethane

The synthesis of dibenzoylethylmethane (15) was carried out as indicated below:

\[
\begin{align*}
\text{benzylacetone} & \quad \text{PhCOCl} \\
\text{NaOEt} & \quad \text{NaOEt}
\end{align*}
\]

In the preparation of this compound, we obtained a solid in a yield of about 69%. It was of moderate acid strength, gave an instantaneous coloured ferric ion complex and formed a water soluble sodium salt. This compound has been identified by infrared and nuclear magnetic resonance spectra. In the infrared spectrum, the strong band at about 1625 cm\(^{-1}\) is due to the C=O stretching vibration in the enol tautomer which is modified by hydrogen bonding and resonance in the ring. The hydroxyl band is also characteristic of the enol form since it is very broad and has shifted.
from its usual region to around 3100 cm⁻¹, where it overlaps with the C–H (phenyl) stretching bands. In the nuclear magnetic resonance spectrum, there is no carbon-bonded proton situated between three carbonyl groups (in case of ketonic tautomer) but a single peak at δ = 17.36, which is considered to be that of the hydroxyl proton. Consequently, the nuclear magnetic resonance spectrum and infrared spectrum showed it to be relatively pure enolic tautomer.

As mentioned earlier, the effect of electron-withdrawing groups will shift the keto–enol tautomeric equilibrium towards the enol form. Hence in the case of dibenzoyl-acetylmethane, sufficient stability is conferred on the enol form to shift the equilibrium completely to that form, under the condition of its formation (see Experimental).

In 1911, Meyer (16) found that more polar solvents favored the ketonic tautomer of beta-diketones and beta-ketoesters. The isolation and identification of tautomers depended on the temperature and the methods of sample handling. This was demonstrated when we successfully converted the enolic tautomer to the ketonic tautomer by treatment with hot aqueous alcohol solution.

Followed the procedure reported by Claisen (15), we
have successfully converted the enolic dibenzoylacetyl-
methane to its ketonic tautomer.

The existence of the ketonic tautomer is supported
by its nuclear magnetic resonance spectrum and infrared
spectrum. In the nuclear magnetic resonance spectrum,
a new peak at $\delta = 7.26$ appeared and the peak at $\delta = 17.36$
had disappeared to an undetectable level. This new peak is
considered to be the single alpha-proton of the keto form
(alpha position to the carbonyl groups). The assignment
of this proton was confirmed by deuterium exchange* in
order to distinguish it from the phenyl proton. In the in-
frared spectrum, the band at 1725 cm$^{-1}$ and 1680 cm$^{-1}$ asso-
cioted with the C=O stretching vibration (CH$_2$C=O and PhC=O
respectively) are characteristic of the unconjugated and
unchelated ketone. This solid gave a coloured ferric
complex slowly and is not soluble in sodium bicarbonate.

*It was done by adding the deuterated water to the same
n.m.r. tube dropwise. The peak at $\delta = 7.26$ was decreased
gradually until it was undetectable. Since the quite
strong electron withdrawing carbonyl groups exist, the
bond between alpha proton and central carbon is relatively
weak.
The electron impact mass spectra of the ketonic and enolic tautomers are shown in Fig. 2 and 3. Important fragments from the spectra are compiled in Table 3.

**Fig 2** Mass spectrum of enolic dibenzoylacetylmethane by electron impact

**Fig 3** Mass spectrum of ketonic dibenzoylacetylmethane by electron impact
Table 3

Important fragments of the ketonic and enolic tautomers upon electron impact

<table>
<thead>
<tr>
<th>m/e</th>
<th>process</th>
<th>relative intensities %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>keto</td>
</tr>
<tr>
<td>266</td>
<td>M⁺</td>
<td>22.</td>
</tr>
<tr>
<td>265</td>
<td>M⁺⁻1</td>
<td>11</td>
</tr>
<tr>
<td>251</td>
<td>M⁺⁻15</td>
<td>0.9</td>
</tr>
<tr>
<td>237</td>
<td>M⁺⁻19</td>
<td>1.5</td>
</tr>
<tr>
<td>224</td>
<td>M⁺⁻42</td>
<td>12</td>
</tr>
<tr>
<td>223</td>
<td>M⁺⁻43</td>
<td>14</td>
</tr>
<tr>
<td>105</td>
<td>M⁺⁻161</td>
<td>100</td>
</tr>
<tr>
<td>77</td>
<td>M⁺⁻189</td>
<td>31</td>
</tr>
</tbody>
</table>

Most of the ions listed in Table 2 can be ascribed to the fragmentations reported earlier (2). Both of the ketonic and enolic tautomers contain the benzyl ion at m/e 105 as the base peak and M⁺⁻189 (m/e 77) as the second dominant peak. One of the fragments of interest is the M⁺⁻1 peak (m/e 265) which may be derived from the loss of a hydrogen atom. In studies involving deuterium labeling
of methylene groups of beta-diketones, Bowic et al. demonstrated that the hydrogen loss originated from the aromatic ring, not from the active methylene group (2). A reasonable mechanism (17) leading to $M^+ - 1$ peak is shown in Scheme 2. for the enolic tautomer.

Scheme 2  Mechanism of hydrogen loss from the enolic dibenzoylacetylmethane molecule ion

Also observed was the fragment with m/e 223 which was formed simply by the loss of CH$_3$CO (m/e 43) radical.

It is here that emphasis and attention should be concentrated upon the differences of the spectra in the high mass unit area. The pronounced fragmentation, which produces a peak at m/e 224, due to beta-cleavage from the molecular
ion via the McLafferty rearrangement is present only in the ketonic form. In sharp contrast, m/e 224 peak is barely discernible (less than 1%) in the spectrum of the enolic form where the major fragmentation is a simple alpha-cleavage, losing the methyl radical and producing the m/e 251 peak. On the other hand, only negligible alpha-cleavage occurred (less than 1%) from the molecular ion of the ketonic tautomer. These two different fragmentation pathways are shown in Scheme 3.

Unfortunately, these strikingly different spectra of the tautomers could not be reproduced again. The irreproducibility could be due to the enolization occurring, as mentioned earlier, before electron impact ionization (18) and the keto-enol equilibrium might be re-established caused by the effect of source temperature of the mass spectrometer (4). The effect of the inlet system temperature (5) may also be a cause of this problem. Since, there are many factors which effect the equilibrium of keto-enol tautomers, it is difficult to reproduce the spectra for a separate and complete distinction of ketonic and enolic tautomers. Consequently, a spectrum of the mixture of dibenzoylacetyl methane tautomers was obtained which is shown in Fig. 4.
Ketonic tautomer

\[ \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \]

\[ \text{M}^+ \quad m/e \ 266 \]

\[ \rightarrow \]

\[ \text{OH} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{OH} \quad \text{Ph} \quad \text{Ph} \]

\[ m/e \ 224 \]

Enolic tautomer

\[ \text{Enolic tautomer} \]

\[ \text{Ph} \quad \text{OH} \quad \text{CH}_3 \quad \text{Ph} \quad \text{Ph} \quad \text{OH} \quad \text{Ph} \quad \text{Ph} \]

\[ \text{M}^+ \quad m/e \ 266 \]

\[ \rightarrow \]

\[ \text{OH} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{OH} \quad \text{Ph} \quad \text{Ph} \]

\[ m/e \ 251 \]

Scheme 3  Mechanism of the pronounced fragmentation of the ketonic and enolic dibenzoylacetylmethane
Fig. 4 Mass spectrum of the keto-enol tautomers of dibenzoylacetylmethane by electron impact

The mass spectra of these tautomers obtained by field ionization are shown in Fig. 5 and 6. The only significant fragmentation peak (m/e 224) is shown in the mass spectrum of the ketonic tautomer. This fragment is considered to be a betacleavage via McLafferty rearrangement. However, as with those electron impact mass spectra of ketonic and enolic dibenzoylacetylmethane, these field ionization mass spectra are not reproducible. The irreproducibility may be due to the temperature effects as mentioned earlier.
Fig. 5 The mass spectrum of the ketonic dibenzoylacetyl-methane by field ionization

Fig. 6 The mass spectrum of the enolic dibenzoylacetyl-methane by field-ionization
It is difficult to determine whether a peak is 'pure', that is such a peak may either be derived from the enolic or ketonic molecule alone or from both. However, under the appropriate conditions, it may be suggested that the keto-tautomer will undergo beta-cleavage via McLafferty rearrangement while the enolic tautomer will undergo alpha-cleavage through loss of a terminal radical, which is only a minor contribution from the other form. Because we cannot repeat these original conditions, the data was not observed again. Hence, it may be necessary to find the optimal conditions for the mass spectrometer (especially the temperature) effect in order to get the desired spectra.

II 3-Phenyl-2,4-pentanedione

The white solid of 3-phenyl-2,4-pentanedione was prepared (19) from phenyl acetone and acetic anhydride in a yield of 41%. The n.m.r. spectrum (Fig. 7) and i.r. spectrum of this compound show the product to exist almost completely as an enolic tautomer. It has been indicated in the previous discussion that enolization is measured by the presence of the unsaturated groups attached to the
single alpha-proton, that is in the alpha position to the carbonyl group. Hence, the enolic tautomer of 3-phenyl-2,4-pentanedione is stabilized by the benzene ring through the resonance effect. As part of this research, we attempted to convert the enolic tautomer to its ketonic isomer, but we were unsuccessful.

Fig. 7 The n.m.r. spectrum of 3-phenyl-2,4-pentanedione

The mass spectrum of 3-phenyl-2,4-pentanedione by electron impact is shown in Fig. 8. Most of the fragmenta-
tion is similar to that described for a mono-functional ketone (20). However, the mass spectrum is noteworthy for the presence of an m/e 134 ion with relative intensity 40%. This fragment is best represented as the enol rather than as the keto form (7). Upon reviewing several experimental observations from the literature (21, 22, 23, 24, 25, 26, 27, 28, 29), strong evidence can be found that such an enol fragment is formed by proton transfer to the oxygen in the diketonic form. This fragmentation is known as McLafferty rearrangement as shown in Scheme 1.

![Diagram of molecular structure and mass spectrum with labels: 176(M⁺), 134, 133, 115, 91, 77, 55, 43, relative intensity scale from 0 to 100%.]

Fig. 8 The mass spectrum of 3-phenyl-2,4-pentanedione by electron impact
Evidence is available to support the three aspects of the mechanism:

(a) that the product ion retains the elements of the original XCOCH₂ group (21, 22, 23, 24);

(b) that the product ion is formed in the enolic configuration (25, 26, 27);

(c) that the migration hydrogen atom originates on the gamma carbon (28, 29).

Hence, the fragment at mass unit 134 formed through McLafferty rearrangement (arising from the ketonic tautomer) and then loss of ketene is more plausible.

Consequently, from the above argument, it may be concluded that the ketonic form is in co-existence with the enolic tautomer during the fragmentation, even though the original synthesis product is 'pure' enolic 3-phenyl-2,4-pentanedione. This, as in the tautomeric dibenzoylacetylmethane, may be due to the effect of either the ion source temperature of the mass spectrometer (4) or the other causes (3, 30).

In conclusion, the isolation of the tautomeric dibenzoylacetylmethane was possible. The mass spectra of isolated ketonic and enolic tautomers did show characteristic
different fragmentation pathways. However, these spectra were obtained only in a single case. The isolation of the 3-phenyl-2,4-pentanedione was also attempted. It should be noted, regarding the foregoing discussion, that our results on the mechanism by which isolated tautomers decomposed in the mass spectrometer is based on evidence which is at best fragmentary. The biggest handicap in making a proper conclusion on the mass spectra of these tautomers is that reproduction these separate spectra was impossible due to the temperature effects in the mass spectrometer. However, an important advantage of this approach is the fact that some insight into the mechanism (molecularity) of the tautomerization process can be obtained. It is suggested to check the effects of temperature of the mass spectrometer on the equilibrium between the keto and enol tautomers. Both of these compounds (i.e. triketone and diketone) should be further investigated under different mass spectrometer conditions. Finally, it should be noted that in the work reported here, emphasis has been placed more on exploring and testing the potentialities of the method rather than solving actual problems.
Chapter 3

EXPERIMENTAL

Proton n.m.r. spectra were measured by means of a JEOL C60 HL Spectrometer or Varian EM360 60 MHz Spectrometer using T.M.S. as internal reference. The infrared spectra were obtained using Beckman IR-10 and Beckman IR-12 Spectro-photometers equipped with potassium bromide cells. Melting points were determined on a Fisher-Johns apparatus and are uncorrected.

All the mass spectra shown in part two were obtained by the methods and conditions mentioned in the experimental section of Part one of this thesis except that they were obtained without the INCOS Model 2000 computer. Identification of all compounds was accomplished using infrared spectra and n.m.r. spectra.

Benzoylacetone and phenylacetone were purchased from Aldrich Chemical Company. Benzoyl chloride and p-toluene-sulfonic acid were purchased from Anachemia Chemical LTD. Acetic anhydride was purchased from Fisher Scientific Company.

The specific i.r. absorption are reported in cm⁻¹ and their intensities are expressed using the following code system: w = weak (100-75 percent transmission), m = medium (74-40 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 n.m.r. chemical shifts are reported in § units downfield from the internal standard. The splitting pattern of each resonance is reported using the following code system: \( s = \) singlet, \( d = \) doublet, \( m = \) multiplet and \( bm = \) broad multiplet. The compounds analyzed were prepared by weight-volume percent in the specified solvent.

**Preparation (10) of dibenzoylacetylmethane (enolic form)**

To a 50ml of 0.2N EtOH/EtONa solution was added 16.2 g. of benzoylacetone and 7 g. of benzoylchloride with ice-cooling. After stirring three hours at \( 0^\circ C \) and three hours at room temperature, the solution was cooled to \( 0^\circ C \) again. Another 25ml of EtOH/EtONa solution was added followed by the addition of 3.5 g. of benzoyl chloride. The solution was stirred for two and half hours at \( 0^\circ C \) and then two and half hours at room temperature. This sequence was repeated one more time. The yellow mixture was allowed to stand for at least 24 hours. There was a heavy precipitate of dibenzoylacetylmethane salt. Water was added to dissolve all the salts, and the benzylether was removed by ether extraction. The aqueous phase was cooled in ice.
bath and then acidified with acetic acid. The solid was filtered, washed with water, and dried in vacumm. Yield 59%, slightly yellow crystals. (ref. mp: 101-103°C) mp 78°C-82°C; ir (CHCl₃, 5%), 3020-3040 (m, C₆H₅), 1655 (s, C=O), 1600-1550 (s, C₆H₅), 1449 and 1415 (m, CH₃), 785 (s, monosubstituted); n.m.r. (CDCl₃, 10%), 17.36 (s, CH₃), 7.28 (m, C₆H₅), 2.16 (s, CH₃).

**Preparation (10) of dibenzoylacetylmethane (ketonic form)**

The enolic dibenzoylacetylmethane was dissolved in hot ethanol. Water was added to make it cloudy and after crystallizing overnight, the solid was filtered. The vacuum-dried product yield 54% of ketonic dibenzoylacetylmethane as white needle crystals. (ref. mp: 117-118°C) mp 98°C-101°C; ir (CHCl₃, 5%), 3050 and 3200 (m, C₆H₅), 2900 (w, CH₃), 1725 and 1680 (m, C=O), 1600 and 1580 (m, C₆H₅), 1448 and 1420 (m, CH₃); n.m.r. (CDCl₃, 10%), 7.50 (m, C₆H₅), 6.28 (s, CH), 2.30 (s, CH₃).

**Preparation (31) of 3-phenyl-2,4-pentanedione**

A mixture of 5.36 g. (0.04 mole) of phenylacetone, 8.16 g. (0.08 mole) of acetic anhydride, and 2.28 g. (0.012 mole) of p-toluensulfonic acid was stirred for five minutes and then saturated at 0°C-10°C with boron trifluoride during three to four hours. The temperature was kept below 10°C. After saturation with the boron trifluoride, the reaction mixture
was allowed to come to room temperature over a three hour period. The reaction mixture was decomposed by refluxing for one hour with 22.0 g. (0.15 mole) of sodium acetate trihydrate in 500 ml of water, then cooled to room temperature and extracted several times with ligroin (bp 60°C-90°C). The extracts were washed with saturated sodium bicarbonate solution, dried by calcium sulfate, and the solvent distilled. The product, after recrystallization from ligroin at -78°C, had 2.89 g. (41%). (ref. mp 58-59°C), mp 58-61°C. ir: (CHCl₃, 5%), 3005 and 3020 (m, C₆H₅), 2900(w, CH₃), 1655 and 1650 (s, C=O), 1595-1560 (s, C₆H₅), 1448-1395 (m, CH₃), 785 (s, mono-substituted); n.m.r. (CDCl₃, 10%), 7.70 (s, OEt), 7.20 (bm, C₆H₅), 1.88 (s, CH₃).
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