FORMATION OF 2-METHYLBENZOPYRYLIUM IONS FROM THE MOLECULAR IONS OF BENZALACETONES *

B. SCHALDACH and H. Fr. GRÜTZMACHER

Faculty of Chemistry, University of Bielefeld, Universitätsstrasse, D-4800 Bielefeld 1 (W. Germany)

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ABSTRACT

It can be shown by the method of metastable ion characteristics that different \( \text{C}_{10}\text{H}_9\text{O}^+ \) ions do not rearrange to a common reactive form. The metastable ion characteristics of \( \text{C}_{10}\text{H}_9\text{O}^+ \) ions can therefore be used to determine the structure of the ion. Using these methods, metastable \( \text{C}_{10}\text{H}_9\text{O}^+ \) derived from the molecular ions of substituted benzalacetones 1 are shown to correspond to 2-methyl-benzopyrylium ions 3. This confirms that the loss of a hydrogen atom or a substituent from the phenyl group of the molecular ions of 1 occurs by an intramolecular aromatic substitution reaction. 3 is formed not only from ortho-substituted benzalacetones, but also from the meta- and para-substituted derivatives. In the latter cases a sufficiently long-lived intermediate must be formed, which reacts to produce 3 by hydrogen migrations prior to elimination of the substituent. This reaction model is corroborated by a calculation of the dependence of ion abundances on the electron energy, and of the frequency factors of the gas phase reactions of the three isomeric chlorobenzalacetones.

INTRODUCTION

Molecular ions of benzalacetone, 1a, lose a hydrogen atom to form \( \text{C}_{10}\text{H}_9\text{O}^+ \) ions in a relatively high yield. According to Williams et al. [2], this unexpected reaction is due to an intramolecular aromatic substitution which results in the formation of 2-methylbenzopyrylium ions, 3, possibly via an intermediate, 2 (see Scheme 1, \( R = \text{H or D} \)). Reactions of this type thus seem to resemble the corresponding solution reactions. In a previous paper [3] (dealing with the analogous cyclisation of molecular ions of \( N,N' \)-dimethyl-\( N' \)-phenylformamidines to yield benzimidazolium ions) it was shown that mass-spectrometric methods can give valuable information regarding the nature of the intermediates, the energetics of their formation and their decay in the gas phase.

Unlike the ionized \( N,N' \)-dimethyl-\( N' \)-phenylformamidines [3] and the ionized thioformanilides [4,5], which both lose a D atom or a substituent

* Ref. 1.
specifically from the ortho positions of the N-phenyl ring, all six hydrogen atoms of the benzal moiety of 1a are equally involved in the formation of 3 [2].

We have therefore studied the formation of 3 from the molecular ions of various phenyl-substituted benzalacetones (see Scheme 1) in order to gain more information about the possible intermediate 2 and the energetics of this intramolecular substitution reaction.

\[
\begin{array}{c|c}
\text{R} & \text{R}' \\
\hline
1a & H \\
1b & 2-Cl \\
1c & 2-Br \\
1d & 2-OCH₃ \\
1e & 2-NO₂ \\
1f & 2-CH₃ \\
1g & 2-F \\
\end{array}
\]

Scheme 1. Intramolecular aromatic substitution of substituted benzalacetones.

In this part of our investigation we report attempts to determine the structure of the C₁₀H₁₀O⁺ ions formed by the loss of a substituent (or a hydrogen atom) from ionized 1. We propose a reaction model, which is corroborated by a calculation of the dependence of ion abundances on the electron energy, and an estimate of the frequency factors of the gas phase reactions of the three isomeric chlorobenzalacetones 1b, 1h and 1i.

In a second paper [6], we report on the energetic requirements of this intramolecular substitution reaction, and discuss some properties of the transition states connected with the formation of 3.

RESULTS

The relative abundances of the ions formed directly from the molecular ions of 1a—1n at 70-eV electron energy are given in Table 1.

Loss of the terminal methyl group from ionised 1a, its meta- and para-substituted derivatives 1h—1n and from ortho-fluorobenzalacetone 1g gives rise to the base peaks in the mass spectra. Methyl loss is also a significant reaction for the ortho-substituted derivatives 1b—1f. This (apparently) simple bond cleavage competes with the expulsion of a hydrogen atom and the substituent R from the phenyl ring. The latter reactions produce the C₁₀H₉O⁺ ions considered here, and which predominate for the ortho-substituted compounds 1b—1f. This is shown for the ortho-methylbenzalacetone 1f in the mass spectrum of compound 4 (see Table 2), where the peaks for the loss of the terminal CD₃ group and the CH₃ substituent are separated by three mass units. Not only the ortho-substituted benzalacetones but also the
TABLE 1

Relative abundances (% base peak) of the indicated ions from the compounds 1a–1n and 4 at 70 eV

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>M⁺⁺</th>
<th>M⁺⁺ – H</th>
<th>M⁺⁺ – R</th>
<th>M⁺⁺ – CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>H</td>
<td>69</td>
<td>44</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1b</td>
<td>2-Cl</td>
<td>13</td>
<td>1</td>
<td>100</td>
<td>36</td>
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<tr>
<td>1c</td>
<td>2-Br</td>
<td>10</td>
<td>1</td>
<td>100</td>
<td>24</td>
</tr>
<tr>
<td>1d</td>
<td>2-OCH₃</td>
<td>7</td>
<td>3</td>
<td>100</td>
<td>38</td>
</tr>
<tr>
<td>1e</td>
<td>2-NO₂</td>
<td>0.5</td>
<td>0.1</td>
<td>25</td>
<td>2.5</td>
</tr>
<tr>
<td>1f</td>
<td>2-CH₃</td>
<td>14</td>
<td>8</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1g</td>
<td>2-F</td>
<td>50</td>
<td>17</td>
<td>7</td>
<td>100</td>
</tr>
<tr>
<td>1h</td>
<td>3-Cl</td>
<td>59</td>
<td>19</td>
<td>30</td>
<td>100</td>
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<tr>
<td>1i</td>
<td>4-Cl</td>
<td>51</td>
<td>17</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>1j</td>
<td>3-OCH₃</td>
<td>76</td>
<td>38</td>
<td>53</td>
<td>100</td>
</tr>
<tr>
<td>1k</td>
<td>4-OCH₃</td>
<td>54</td>
<td>14</td>
<td>9</td>
<td>100</td>
</tr>
<tr>
<td>1l</td>
<td>3-NO₂</td>
<td>42</td>
<td>5</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>1m</td>
<td>4-NO₂</td>
<td>38</td>
<td>5</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>1n</td>
<td>4-CH₃</td>
<td>18</td>
<td>12</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>2-CH₃</td>
<td>29</td>
<td>14</td>
<td>100</td>
<td>87c</td>
</tr>
</tbody>
</table>

a Intensities refer to the sum of the isotope-peaks.
b m/z 43 = base peak.
c M⁺⁺ — CD₃.

Meta- and para-substituted derivatives lose their substituents with considerable ease, in contrast to the meta- and para-substituted N,N-dimethyl-N’-phenylformamidines [3].

Comparing the relative proportion of (M — R)⁺ ions to (M — CH₃)⁺ ions within the series of ortho-substituted benzalacetones 1a—1g and 4, formation of C₁₀H₉O⁺ ions is shown to be favoured by decreasing strength of the phenyl—substituent bond. The fact that the (M — H)⁺ peak is more intense than the (M — F)⁺ peak in the mass spectrum of 1g is also in accord with this effect. The formation of C₁₀H₉O⁺ ions depends not only on the nature of the substituent to be lost but also on the position of the substituent on the phenyl ring, decreasing in the series ortho > meta > para.

To gain further insight into the mechanism of formation of C₁₀H₉O⁺ from the benzalacetones studied, we wished to determine whether or not these ions have the cyclic structure of 2-methylbenzopyryllium ions 3. Therefore ions 3 were independently generated from molecular ions of 2,2-dimethylchromene, 5, (see Fig. 1) and their metastable ion characteristics [7] compared with those of the C₁₀H₉O⁺ ions derived from the benzalacetones. The C₁₀H₉O⁺ ions, m/z = 145, form the predominant peak in the 70-eV mass spectrum of 5 and carry about 60% of the total ion current. Apart from the molecular ions (relative abundance: 18% of the base peak) only ions with m/z = 115 have an abundance greater than 5% of the base peak. Furthermore the activation energy, ε⁺, needed to form C₁₀H₉O⁺ ions from ionised 5 is
small ($\epsilon^+ = A \cdot (C_{10}H_9O^+) - I(5) = 1.0$ eV), indicating the formation of a thermodynamically stable fragment ion which does not decompose significantly any further. These facts can only be explained if the $C_{10}H_9O^+$ ions arising from compound 5 assume structure 3, which is also a priori the most probable structure.

Figure 1 shows the MIKE spectrum of the $C_{10}H_9O^+$ ions obtained from compound 5; it consists of two signals of approximately equal heights but different shapes. Signal $b$, for CO-loss, is broad and trapezoidal in shape, indicating the release of a large amount of kinetic energy, whereas signal $a$ for $H_2O$-loss is narrow and Gaussian in shape. The ratio of the peak areas $A_b/A_a$ and the kinetic energy data from the half-widths $T_{50}$ of signals $a$ and $b$ constitute the metastable ion characteristics of 3 and are used as structural parameters.

Table 2 contains the metastable ion characteristics of the $C_{10}H_9O^+$ ions derived from benzalacetone, 1a, and its ortho-substituted analogues 1b—1g and 4. The data of Table 2 agree within experimental error with that of the ions 3 obtained from compound 5, with two exceptions ($C_{10}H_9O^+$ ions from 1f and $C_{10}H_8DO^+$ ions from 4, vide infra). The identical reactivity of the metastable $C_{10}H_9O^+$ ions listed in Table 2 suggests that they are most probably formed with an identical ion structure (or a similar mixture of structures) and a similar energy distribution.

The losses of $H_2O$ and CO observed from metastable $C_{10}H_9O^+$ ions are eliminations of thermodynamically stable, neutral molecules, which often are not structurally specific for slowly reacting ions. In order to determine
TABLE 2

Area ratio $A_b/A_a$ and kinetic energy release, $T_{50}$, of the reactions a and b (Fig. 1) of metastable $C_{10}H_9O^+$ ions from ortho-substituted benzalacetones and 2,2-dimethylchromene, 5

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>$A_b/A_a$</th>
<th>$T_{50}$ (a) $^a$</th>
<th>$T_{50}$ (b) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>H</td>
<td>4.8</td>
<td>52 ± 3</td>
<td>595 ± 40</td>
</tr>
<tr>
<td>1b</td>
<td>2-Cl</td>
<td>5.5</td>
<td>53 ± 3</td>
<td>605 ± 25</td>
</tr>
<tr>
<td>1c</td>
<td>2-Br</td>
<td>5.5</td>
<td>53 ± 6</td>
<td>610 ± 12</td>
</tr>
<tr>
<td>1d</td>
<td>2-OCH$_3$</td>
<td>6.1</td>
<td>55 ± 4</td>
<td>634 ± 16</td>
</tr>
<tr>
<td>1e</td>
<td>2-NO$_2$</td>
<td>5.2</td>
<td>52 ± 3</td>
<td>602 ± 16</td>
</tr>
<tr>
<td>1f</td>
<td>2-CH$_3$</td>
<td>7.1</td>
<td>35 ± 4</td>
<td>177 ± 23</td>
</tr>
<tr>
<td>1g $^b$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4 $^c$</td>
<td>2-CH$_3$</td>
<td>6.9</td>
<td>35 ± 4</td>
<td>189 ± 14</td>
</tr>
<tr>
<td>4 $^d$</td>
<td>2-CH$_3$</td>
<td>4.8 $^e$</td>
<td>- $^e$</td>
<td>594 ± 48</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>4.8</td>
<td>56 ± 3</td>
<td>650 ± 25</td>
</tr>
</tbody>
</table>

$^a$ meV.

$^b$ These $C_{10}H_9O^+$ ions do not decompose further.

$^c$ (4$^+$ — CD$_3$) ions.

$^d$ (4$^+$ — CH$_3$) ions.

$^e$ The $C_{10}H_5D_4O^+$ ions lose H$_2$O and HDO, the respective peaks not being resolved in the MIKE-spectrum; $T_{50}$ could therefore not be determined, and $A_a$ is the sum of the peak areas.

whether the reactivity data obtained for metastable $C_{10}H_9O^+$ ions are characteristic only of ions 3, or of isomeric $C_{10}H_9O^+$ ions in general, a number of isomeric $C_{10}H_9O^+$ ions was generated from the precursors 6—15 shown in Table 3.

All of the metastable $C_{10}H_9O^+$ ions examined (Table 3) eliminate H$_2$O and CO, except those produced by compounds 8 and 14, where the $C_{10}H_9O^+$ ions do not lose water. In the cases of compounds 7, 9, 12 and 15 additional signals are also present. A comparison of the intensity ratio $A_b/A_a$ and the $T_{50}$-data obtained for CO- and H$_2$O-loss within the series of the methyl-substituted cinnamoyl compounds 6—11 reveals that the position of the methyl group has an influence on the ease of H$_2$O-elimination and on the amount of kinetic energy released on loss of CO. In this connection the two exceptions mentioned earlier (see Table 2) can be explained; loss of the terminal CD$_3$ group from 4 forms ortho-methylcinnamoyl ions $C_{10}H_9DO^+$, whose metastable ion characteristics fit the data obtained for the corresponding ions derived from 6 and 7. The $C_{10}H_9O^+$ ions produced by 1f are a mixture of isomeric ions and obviously only the o-methylcinnamoyl component can be detected in the MIKE spectrum. The metastable ion characteristics of the $C_{10}H_9O^+$ ions derived from 1f therefore deviate from those of 3, but fit those of 6 and 7.

The characteristics of the metastable $C_{15}H_9O^+$ ions generated from compounds 12—15 differ from each other and also from those produced by com-
TABLE 3
Area ratio $A_b/A_a$ and kinetic energy release, $T_{50}$ (meV), for the loss of $\text{H}_2\text{O}$ (a) and $\text{CO}$ (b) from metastable $\text{C}_{10}\text{H}_9\text{O}^+$ ions generated as indicated from the compounds shown

<table>
<thead>
<tr>
<th>Compound</th>
<th>$A_b/A_a$</th>
<th>$T_{50}$ (a)</th>
<th>$T_{50}$ (b)</th>
<th>$A_b/A_c$</th>
<th>$T_{50}$ (c)</th>
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<tbody>
<tr>
<td>6</td>
<td>4.1</td>
<td>$35 \pm 3$</td>
<td>238 $\pm 21$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>8.8</td>
<td>$35 \pm 2$</td>
<td>185 $\pm 13$</td>
<td>30</td>
<td>36 $\pm 4$</td>
</tr>
<tr>
<td>11</td>
<td>7.1</td>
<td>$35 \pm 4$</td>
<td>177 $\pm 23$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>6.9</td>
<td>$35 \pm 4$</td>
<td>189 $\pm 14$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>—</td>
<td>145 $\pm 15$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>56</td>
<td>$35 \pm 4$</td>
<td>132 $\pm 12$</td>
<td>15</td>
<td>195 $\pm 12$</td>
</tr>
<tr>
<td>1n</td>
<td>63</td>
<td>$35 \pm 4$</td>
<td>146 $\pm 8$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10</td>
<td>19</td>
<td>$35 \pm 4$</td>
<td>99 $\pm 10$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>19</td>
<td>$35 \pm 4$</td>
<td>99 $\pm 10$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>12</td>
<td>4.8</td>
<td>27 $\pm 2$</td>
<td>240 $\pm 14$</td>
<td>13</td>
<td>92 $\pm 9$</td>
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<td></td>
<td>—</td>
<td>30 $\pm 2$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>15</td>
<td>2.4</td>
<td>$35 \pm 3$</td>
<td>333 $\pm 30$</td>
<td>5.0</td>
<td>23 $\pm 3$</td>
</tr>
</tbody>
</table>

*CH$_3$-loss.

*Loss of m/z = 41.*
pounds 6–11. Although the metastable ion data are not sufficient to specify
the structures of the C_{10}H_{9}O^{+} ions generated from compounds 12–15, it is
clearly shown that these C_{10}H_{9}O^{+} ions and those obtained from compounds
6–11 do not isomerise to a common reactive structure (or mixture of struc-
tures). Furthermore, the characteristics of all the metastable C_{10}H_{9}O^{+} ions
derived from compounds 6–15 are quite different from the data obtained
for the C_{10}H_{9}O^{+} ions generated from ortho-substituted benzalacetones 1a—
1e, 4 and 2,2-dimethylchromene. There is therefore considerable evidence
that all the product ions of reaction 1 (see Scheme 1, R in ortho-position)
have the same structure. Comparison with the product ions obtained from
reaction 2 (see Fig. 1) suggests that this structure is that of the 2-methylben-
zopyrylium ion, 3.

The 70-eV mass spectra of meta- and para-substituted benzalacetones,
1k–1m, show (Table 1) that these derivatives also form C_{10}H_{9}O^{+} ions, in
some cases with quite considerable abundance. The MIKE spectra of these
C_{10}H_{9}O^{+} ions are very similar to those of the ions generated from ortho-sub-
stituted benzalacetones as regards the loss of H_{2}O and CO. However, the
MIKE spectra of all the m- and p-substituted benzalacetones studied show
additional signals due to the elimination of C_{2}H fragments; the methoxy-
derivatives 1j and 1k also eliminate C_{2}H_{2}. The observation of additional frag-
mentations means either that metastable C_{10}H_{9}O^{+} ions from m- and p-substi-
tuted benzalacetones contain more internal energy, thus opening more reac-
tion channels than are available to ions from the ortho-isomers, or that an
additional C_{10}H_{9}O^{+} isomer is formed, capable of eliminating C_{2}H and C_{2}H_{2},
respectively. Were an additional isomeric ion being formed in a high energy
process, (e.g. direct cleavage of the phenyl—substituent bond), a distinct
dependence of the relative intensities of the signals in the MIKE spectra on
the electron energy should be observed. If the C_{10}H_{9}O^{+} ions were identical
in structure or comprised a mixture of structurally equilibrating ions, the
electron energy should exert only a slight influence on the intensity distribu-
tion down to the vicinity of the appearance energies of the product ions,
because competing metastable fragmentations must have similar activation
energies [8,9].

In contrast, if one is dealing with a mixture of non-equilibrating C_{10}H_{9}O^{+}
ions with different appearance energies, the composition of the mixture will
vary with electron energy, decreasing electron energy discriminating against
the higher energy processes. A significant decrease in the relative abundance
should therefore be observed for these fragmentation reactions some eV
above the appearance energies, e.g. below 20 eV. The results of a correspon-
ding experiment with p-chlorobenzalacetone, 1i, are shown in Table 4.

It appears that the intensity ratio of the signals for H_{2}O- and CO-elimina-
tion remains constant over the 70–18-eV region of nominal electron ener-
gies, whereas the relative intensity of the signal for the loss of C_{2}H decreases
rapidly from 25 eV downwards. Consequently the additional fragmentations
observed in the cases of meta- and para-substituted benzalacetones (loss of
TABLE 4
Relative intensities \( I \), for the loss of \( \text{H}_2\text{O} \) (a), \( \text{CO} \) (b) and \( \text{C}_2\text{H} \) (c) from metastable \( \text{C}_{10}\text{H}_9\text{O}^+ \) ions generated from \( p \)-chlorobenzalacetone at different electron energies

<table>
<thead>
<tr>
<th>( E ) (eV)</th>
<th>( I ) (a)</th>
<th>( I ) (b)</th>
<th>( I ) (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.8</td>
<td>1</td>
<td>1.6</td>
</tr>
<tr>
<td>34</td>
<td>0.9</td>
<td>1</td>
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<td>25</td>
<td>1</td>
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<td>1.4</td>
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<td>1.1</td>
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<tr>
<td>18</td>
<td>1</td>
<td>1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\( a \) \( I \) was determined as a peak-height with an Ortec ion-counting device.
\( b \) Nominal.

\( \text{C}_2\text{H} \) and \( \text{C}_2\text{H}_2 \) are attributed to \( \text{C}_{10}\text{H}_9\text{O}^+ \) of a different kind (i) not formed by the \textit{ortho}-substituted compounds, (ii) being formed with a high appearance energy, and (iii) not interconverting with the other \( \text{C}_{10}\text{H}_9\text{O}^+ \) ions prior to fragmentation. The characteristics of the remaining metastable \( \text{C}_{10}\text{H}_9\text{O}^+ \) ions are in good agreement with those of ions 3 (see Tables 5 and 2).

Only in the case of the nitrobenzalacetones \( 11 \) and \( 1\text{m} \) does the intensity ratio \( A_b/A_a \) obviously deviate to higher values.

It is therefore not certain whether these \( \text{C}_{10}\text{H}_9\text{O}^+ \) ions actually possess the 2-methylbenzopyrylum structure 3, or not. The deviations found with \( p \)-methylbenzalacetone, \( 1\text{n} \), may be explained in a manner analogous to that used for \( o \)-methylbenzalacetone, \( 1\text{f} \) (vide supra). The values obtained for compound \( 1\text{n} \) are therefore in good accord with the characteristics of metastable \( p \)-methylcinnamoylum ions (see Table 3).

The data of Table 5 and the additional experiment with \( p \)-chlorobenzalacetone described above show clearly that the \textit{meta} and \textit{para} chloro- and

TABLE 5
Area ratio \( A_b/A_a \) and kinetic energy release, \( T_{50} \) (meV) for reactions a and b (Fig. 1) of metastable \( \text{C}_{10}\text{H}_9\text{O}^+ \) ions derived from \textit{meta}- and \textit{para}-substituted benzalacetones

<table>
<thead>
<tr>
<th>Compound</th>
<th>( R )</th>
<th>( A_b/A_a )</th>
<th>( T_{50} ) (a)</th>
<th>( T_{50} ) (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1\text{h} )</td>
<td>3-Cl</td>
<td>5.2</td>
<td>51 ( \pm ) 3</td>
<td>593 ( \pm ) 28</td>
</tr>
<tr>
<td>( 1\text{i} )</td>
<td>4-Cl</td>
<td>5.1</td>
<td>54 ( \pm ) 4</td>
<td>610 ( \pm ) 64</td>
</tr>
<tr>
<td>( 1\text{j} )</td>
<td>3-OCH\text{( 3 )}</td>
<td>5.8</td>
<td>57 ( \pm ) 6</td>
<td>687 ( \pm ) 123</td>
</tr>
<tr>
<td>( 1\text{k} )</td>
<td>4-OCH\text{( 3 )}</td>
<td>7.9</td>
<td>54 ( \pm ) 6</td>
<td>628 ( \pm ) 25</td>
</tr>
<tr>
<td>( 1\text{l} )</td>
<td>3-NO\text{( 2 )}</td>
<td>16.5</td>
<td>51 ( \pm ) 6</td>
<td>601 ( \pm ) 41</td>
</tr>
<tr>
<td>( 1\text{m} )</td>
<td>4-NO\text{( 2 )}</td>
<td>14.2</td>
<td>54 ( \pm ) 6</td>
<td>634 ( \pm ) 41</td>
</tr>
<tr>
<td>( 1\text{n} )</td>
<td>4-CH\text{( 3 )}</td>
<td>63</td>
<td>35 ( \pm ) 4</td>
<td>146 ( \pm ) 8</td>
</tr>
</tbody>
</table>
methoxy-derivatives 1h—1k are capable of forming 2-methylbenzopyrylum ions, 3, in the same way as the ortho-substituted isomers.

DISCUSSION

From the large variety of metastable ion characteristics observed for C_{10}H_{9}O^{+} ions it follows that there exists a large number of structurally stable, isomeric C_{10}H_{9}O^{+} ions, their structures depending on the nature of the precursor compound. Isomerization of these metastable ions does not occur before fragmentation (a property of even-electron hydrocarbon ions [10]). In this respect the C_{10}H_{9}O^{+} ions behave like many other ions containing heteroatoms [11,12,13] i.e. structurally stable up to the excitation energies necessary for the decomposition of metastable ions. The majority of the C_{10}H_{9}O^{+} ions studied eliminate the thermodynamically stable molecules H_{2}O and CO, giving rise to clearly detectable signals in the MIKE spectra. However, the intensity ratio of these signals alone is not always sufficient to distinguish between different C_{10}H_{9}O^{+} ions. It is often necessary to include the peak shapes, using the kinetic energy release, T_{50}, as a valuable parameter for detecting small differences in peak shapes [14]. In the case of the C_{10}H_{9}O^{+} ions, the most significant differences in kinetic energy release are observed during CO-elimination which, together with the intensity ratio of the MIKE signals, are the most reliable structural parameters for these ions.

2,2-dimethylchromene, 5, and the benzalacetones 1a—1m form identical C_{10}H_{9}O^{+} ions; the experimental results suggest the structure of 2-methylbenzopyrylum ions, 3, for the product-ions of reaction 1 (see Scheme 1). This is an obvious result for the ortho-substituted benzalacetones, although it is still unclear whether the cyclisation takes place via an intermediate, e.g. 2. Direct cleavage of the substituent bond would require a high activation energy, since approximately 3.5 eV is required to form C_{4}H_{3}^{+} ions from ionized chlorobenzene [15]. The small activation energy (0.5—0.8 eV) for the formation of ions 3 from the isomeric chlorobenzalacetones 1b, 1h and 1i (see Table 6) indicates that some of the energy gained from the newly formed (C—O) bond compensates in part for the energy needed to dissociate the substituent bond. Hence the new (C—O) bond is formed either prior to, or during, the cleavage of the substituent bond, the ortho-substituent being displaced by intramolecular substitution of the attacking CO group.

The C_{10}H_{9}O^{+} ions formed from the meta- and para-substituted benzalacetones 1h—1m constitute a mixture of ions containing at least one more component than in the case of the corresponding ortho-substituted derivatives. The dependence of the MIKE spectra on the electron energy shows that these are energy-rich C_{10}H_{9}O^{+} ions which disappear if the fragmentation is induced by low-energy electrons. The remaining C_{10}H_{9}O^{+} ions are identical with those generated from compounds 1a—1e and 5, i.e. cyclic 2-methylbenzopyrylum ions, 3. This result is quite surprising and can be explained only by assuming a cyclic intermediate 2 with a lifetime sufficiently long for iso-
merization to take place. In this case the isomeric intermediates 2a and 2b can be formed by 1,2-hydrogen shifts around the phenyl ring, followed by loss of the substituent and formation of the ions 3 (see Fig. 2).

The hydrogen shifts in the intermediate 2 obviously cannot require any large additional excitation energy in the molecular ions since the activation energy for the formation of 3 from the three isomeric chlorobenzalacetones is similar in each case (see Table 6). The activation energy for the hydrogen shifts is obviously supplied by the exoergicity of the formation of intermediate 2.

According to this reaction model, the generation of ions 3 from the molecular ions of meta- and para-substituted benzalacetones is preceded by one or two rearrangement steps to 2a or 2b, respectively. Therefore ions 3

![Diagram](image)

**Fig. 2.** Formation of 2-methylbenzopyrylum ions, 3, from ionized m- and p-substituted benzalacetones via a cyclic intermediate, 2, and subsequent 1,2-H-shifts prior to the loss of R.
should be formed more slowly in these cases than in the *ortho*-substituted compounds, where ions 3 can be formed from intermediate 2 directly. This can be corroborated qualitatively by the sharply decreasing intensities of the *ortho-meta-para* series in the 70-eV mass spectra of the chlorobenzalacetones (see Table 1), despite the fact that they have similar activation energies. Within the framework of the quasi-equilibrium theory (QET) [16] this should correspond quantitatively to a decrease in the frequency factor $\nu$. It therefore seems of interest to test this model by a calculation of the ion abundances at different electron energies and compare the calculated to the experimental values. This should provide some insight into the magnitude and variation of the frequency factors. For this purpose a calculation was carried out on the basis of the model proposed by Heller et al. [17], using the experimental energy data of Table 6 and adjusting for the frequency factors. The results are summarized in Fig. 3 and Table 6.

The best agreement between experimental and calculated curves is found using the frequency factors given in Table 6. In most cases the calculated fragment-ion intensities are too high in the vicinity of the appearance energies, but fit the experimental values quite well from approximately 14 eV upwards. The characteristic shapes of the curves, e.g. monotonous increase in cases of direct bond cleavage and a maximum for rearrangement cases, are always reproduced.

The frequency factors for the loss of the terminal methyl group have values between $3 \times 10^{13}$ s$^{-1}$ and $5 \times 10^{13}$ s$^{-1}$, in accord with a direct cleavage of the C–C bond. A frequency factor of $10^9$ s$^{-1}$ is found for the elimination of the Cl-atom from the *ortho*-chloro-derivative 1b, a value typical for rearrangement reactions [18]. The frequency factors for the formation of ions 3 from *meta*- and *para*-chloro-benzalacetones are lower by one order of magnitude than that for the *ortho* isomer. This result is consistent with the reaction model proposed for *m*- and *p*-substituted benzalacetones assuming (i) the formation of an intermediate 2 and (ii) the isomerization of 2 by hydrogen migration prior to losing the substituent. The higher frequency factors obtained for the *ortho*-substituted benzalacetones do not enable us to determine whether or not an intermediate is formed. Any intermediate produced has no need to rearrange and thus may have a shorter lifetime than the intermediates of *meta*- and *para*-substituted benzalacetones.

These results, obtained with the aid of metastable ion characteristics, indicate that substituted benzalacetones can lose substituents from the phenyl ring to form 2-methylbenzopyrylium ions in a mass spectrometer, irrespective of the position of the substituent. In the case of the *meta*- and *para*-substituted derivatives the ion passes through an intermediate form having a sufficiently long lifetime and enough excitation energy to isomerize by hydrogen migration. The question of whether *ortho*-substituents are displaced directly or via an intermediate is dealt with in the following paper. This is an investigation of the influence of the bond-strengths of *ortho*-substituents on the intramolecular aromatic substitution of benzalacetones.
Fig. 3. Experimental (filled symbol) and calculated (empty symbol) variation of the relative intensities of the indicated ions with the electron energy for (a) ortho-chloro- (b) meta-chloro- (c) para-chlorobenzalacetone. Fragment ions formed by initial CH₃-loss from the molecular ions and by subsequent decompositions are summarized as $\Sigma M - CH_3^+$. 
EXPERIMENTAL

The mass spectra and MIKE spectra [19,20,21] were recorded on a Varian MAT 311 A instrument (reverse Nier—Johnson geometry), at an ionization energy of 70 eV, an emission current of 3 mA, an ion source temperature of 150°C and an ion source pressure of $1 \times 10^{-6} - 2 \times 10^{-6}$ torr. Kinetic energy release data were obtained after correction for the instrumental broadening of metastable peaks [22].

Ionization efficiency curves were obtained using a modified Vacuum Generators MM 12 B single-focussing instrument. The modifications allow preselection of up to 8 peaks of a mass spectrum which are accessible by cyclic magnet scans. After each cycle the electron energy is automatically lowered by preselected steps of 1 eV or less to 0.01 eV. Cycle times can be varied in the range 1—10 s, being fixed at 10 s during the present measurements. This device allows the ion intensities of interest to be measured together with a calibrant (benzene or methyl iodide) under identical conditions in a relatively short time (typically 15 min for one run). Ionization and appearance energies were derived from the ionization efficiency curves by application of the semilogarithmic plot method [23].

The calculation of ion intensities was performed on a Siemens TR 440 computer at the Rechenzentrum der Universität Bielefeld.

The compounds 1a, 1n, 10—12 and 15 were commercially available; the substituted benzalacetones 1h—1m are all known and were prepared from the appropriate benzaldehyde and acetone by the aldol condensation in a manner analogous to the procedure described for compound 4. Compounds 5, 6, 8, 9 and 13 are also known substances which are prepared according to standard procedures [24]. 2-Methylcinnamic amide, 7, (C\textsubscript{10}H\textsubscript{11}NO; mol. weight 161.2; elementary analysis (theoretical values in brackets) C 75.07 [74.51]; H 7.11 [6.88]; N 8.63 [8.69]; m.p. 156°C), has not been described previously and was synthesized as usual from the acid 6 using thionylchloride and aqueous NH\textsubscript{3} solution.

1,1,1-D\textsubscript{3}-3-D\textsubscript{1}-4-(2-methylphenyl)-but-3-ene-2-one, 4

5 g of ortho-tolylaldehyde (0.042 mole) together with 11.3 g acetone-d\textsubscript{6} (0.18 mole) and 50 ml D\textsubscript{2}O were mixed with 5 ml of a 10% NaOD solution in D\textsubscript{2}O and mechanically shaken. After ca. 4 h no aldehyde could be detected in the reaction mixture (TLC on Merck aluminium foil with fluorescent indicator; mobile phase: CHCl\textsubscript{3}). After neutralization with dilute D\textsubscript{2}SO\textsubscript{4} the brown oil was dissolved in dry ether, washed with D\textsubscript{2}O and dried with Na\textsubscript{2}SO\textsubscript{4}. After evaporation of the ether (yield of raw material: 6 g) fractional vacuum distillation yielded 4.3 g ~ 63% of pure 4 at 104—105°C and 0.4 torr. Deuterium content (by mass spectrometry): D\textsubscript{4} : 93%; D\textsubscript{3} : 6%; D\textsubscript{2} : 1%; D\textsubscript{1}, D\textsubscript{0} : 0%.
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REFERENCES