The Fragmentations of Substituted Cinnamic Acids After Electron Impact

Bernd Schaldach and H.-Fr. Grützmacher
Fakultät für Chemie, Universität Bielefeld, D-4800 Bielefeld 1, Universitätsstrasse, West Germany

The fragmentations of a number of cinnamic acids substituted at the phenyl ring have been studied with the aid of 70 eV mass spectra and mass analysed ion kinetic energy spectra. Evidence is presented that the formation of $[C_9H_7O_2]^+$ ions occurs by intramolecular aromatic substitution reactions. A mechanism is proposed for the energetically favourable loss of the substituents from *meta* and *para* positions of the phenyl ring. The analytical use of intramolecular aromatic substitution reactions is briefly discussed.

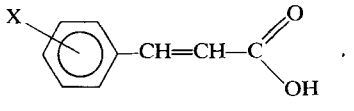
INTRODUCTION

Intramolecular aromatic substitutions of radical cations in the gas phase have been known for some time [1–3] and have been classified as one of the numerous *ortho* effect reactions.[4] Some recent studies[5,6] on this type of reaction revealed not only its analytical value but also elementary details of such substitution reactions.

Cinnamic acid has been reported[7] to lose abundantly a hydrogen atom from the phenyl ring, thus forming 2-hydroxybenzopyrylium ions (*a*, Scheme 1) in a mass spectrometer. The fragmentations of substituted cinnamic acids under electron impact have not yet been reported, with the exception of the 2-fluoro-compound[8] and the three isomeric methoxycinnamic acids.[9] Therefore it was necessary to perform a systematic study of the modes of decay of variously substituted cinnamic acids in order to see (i) whether the substitution reaction occurs with the different substituents chosen as well, (ii) whether the substitution reaction is influenced by competing reactions, and (iii) what changes occur in the mass spectra in relation to the position of the substituent at the phenyl ring.

RESULTS

The cinnamic acids studied are listed below.



X	No.	X	No.
H	**1**	3-Cl	**9**
2-F	**2**	4-Cl	**10**
2-Cl	**3**	3-OH	**11**
2-Br	**4**	4-OH	**12**
2-I	**5**	3-OCH_3	**13**
2-OH	**6**	4-OCH_3	**14**
2-OCH_3	**7**	3-CH_3	**15**
2-CH_3	**8**	4-CH_3	**16**

The 70 eV mass spectra of cinnamic acid (**1**), 2-fluoro- (**2**), 2-chloro- (**3**), 2-bromo- (**4**), 2-iodocinnamic acid (**5**) and 3-chloro- (**9**) and 4-chlorocinnamic acid (**10**) and their modes of fragmentation as suggested by metastable transitions are shown in Fig. 1 and Schemes 1–3, respectively.

Molecular ions of cinnamic acid decompose mainly by two competing pathways (Scheme 1): (i) fragmentation of the sidechain by successive losses of OH, CO, and C_2H_2 (route B)[10] and (ii) loss of a phenylic hydrogen atom following ring closure to give ions *a*.[7]

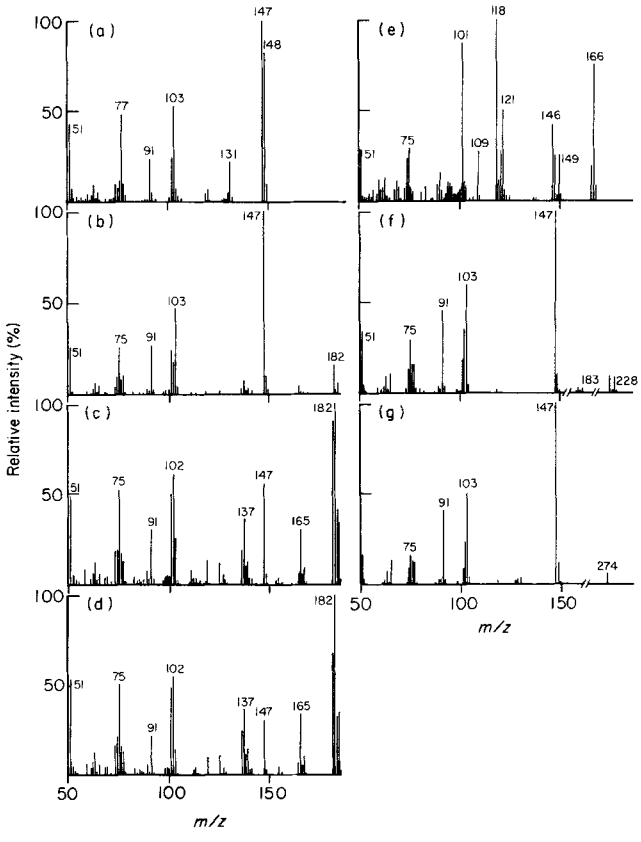


Figure 1. 70 eV mass spectra of cinnamic acid and the halogen substituted derivatives. (a) 2-H; (b) 2-Cl; (c) 3-Cl; (d) 4-Cl; (e) 2-F; (f) 2-Br; (g) 2-I.

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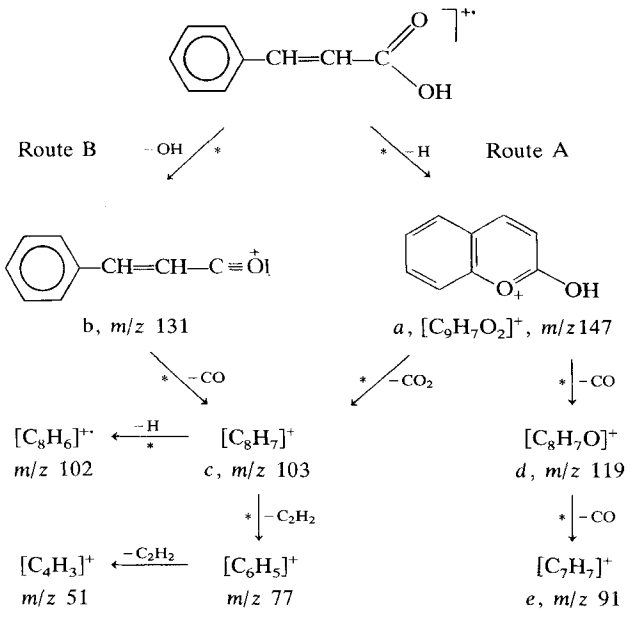


Scheme 1. Fragmentation routes of ionized cinnamic acid.

The introduction of Cl, Br and I, respectively, as *ortho* substituents X drastically changes the fragmentation patterns of the corresponding cinnamic acids **3–5**. Both the losses of H and OH from $[\mathbf{1}]^{+\cdot}$ are almost completely replaced by the loss of the substituent X (Fig. 1). The loss of X from *metastable* ions $[\mathbf{3}]^{+\cdot}$–$[\mathbf{5}]^{+\cdot}$ is the only reaction observed for these ions (Table 1) and gives rise to intense signals in their mass analysed ion kinetic energy (MIKE) spectra. In consequence of the clean reaction to ions *a* the mass spectra of compounds **3–5** do not differ greatly from one another, except in the position of the $[M]^{+\cdot}$ peaks. The 2-fluorocinnamic acid ions $[\mathbf{2}]^{+\cdot}$ lose H, OH and F (Fig. 1). The fluoro substituted analogues of ions *a* and *b* (Scheme 1), cf. *a'* and *b'*, decompose by reactions analogous to those illustrated in Scheme 1, thus yielding the F-containing ions *c'*, *m/z* 121 and *e'*, *m/z* 109. Ions *c'* subsequently eliminate HF and C_2H_2 to give the peaks at *m/z* 101 and *m/z* 75, respectively. All metastable transitions are clearly detectable for these reactions. In addition to these decompositions, $[\mathbf{2}]^{+\cdot}$ ions also eliminate HF. The direct formation of ions *m/z* 146 is indicated by an intense metastable peak, which is the only one observed for metastable $[\mathbf{2}]^{+\cdot}$ ions (Table 1). A thermal fragmentation of **2** gives HF and coumarin.[8] It was suggested therefore that the analogous ionic reaction of $[\mathbf{2}]^{+\cdot}$ results in the formation of coumarin ions *f* (Scheme 2, X = F).[8] This conclusion is corroborated by two successive losses of CO from metastable ions *f* and g (Scheme 2) which are also observed in case of coumarin itself.[11]

Within the series of the *ortho* substituted cinnamic acids **2–5** and including the parent compound **1** the abundance of ions *a* in the 70 eV mass spectra increases with decreasing strength of the bond cleaved (F > H > Cl > Br > I). This effect is accompanied by a decrease of the respective $[M]^{+\cdot}$ ion intensities and by a decrease in reactions competitive with the formation of *a*. The occurrence of abundant metastable transitions for the loss of X=H, Cl, Br, I (Table 1) indicates

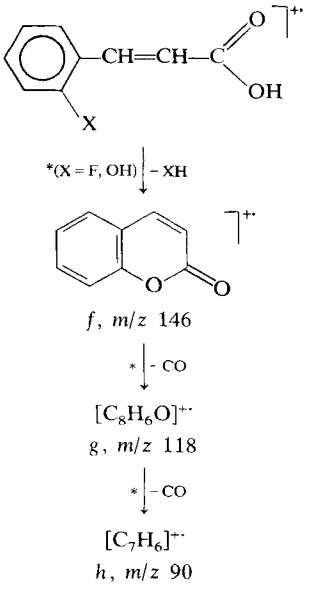
Table 1. Abundances of $[M-H]^+$ and $[M-X]^+$ ions generated from metastable $[M]^{+\cdot}$ ions of substituted cinnamic acids relative to the stable $[M]^{+\cdot}$ ions

X	$\frac{[M-H]^{+a}}{[M]^{+\cdot}}$	$\frac{[M-x]^{+a}}{[M]^{+\cdot}}$
H	5.1	5.1
2-F	0.18	0.47[b]
2-Cl	—	1.6
3-Cl	5.3	0.97
4-Cl	4.8	0.68
2-Br	—	1.3
2-I	—	3.0
2-OH	—	2.6[b]
3-OH	5.4	1.3
4-OH	3.3	0.94
2-OCH_3	—	2.2
3-OCH_3	4.6	1.0
4-OCH_3	3.6	0.25
2-CH_3	—	6.2[b]
3-CH_3	1.4	2.6
4-CH_3	1.1	1.3

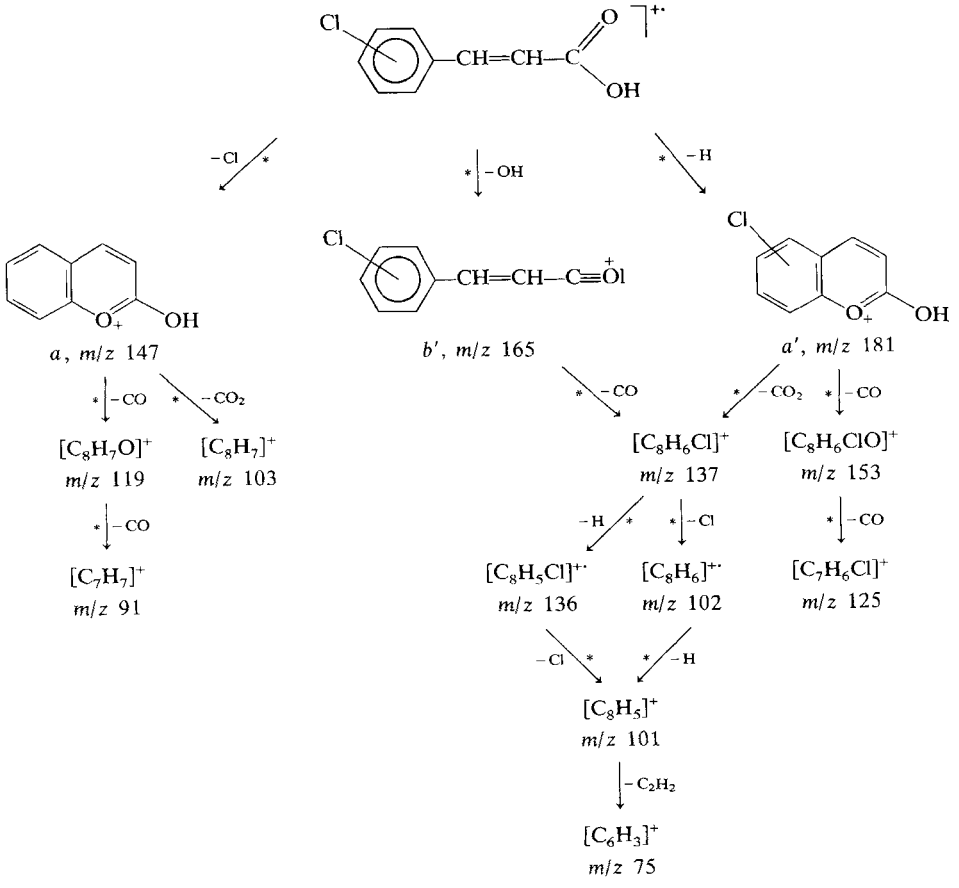
[a] $\times 10^3$. [b] Loss of HX.

that the formation of ions *a* is energetically most favourable in these cases. With X = F, however, formation of ions *f* is energetically more favourable than that of ions *a*, thus supporting the trend mentioned above.

The 70 eV mass spectra of *m*-and *p*-chlorocinnamic acid, **9** and **10**, are very similar to each other but differ drastically from the spectrum of the *ortho* isomer **3** (Fig. 1). The stabilities of $[\mathbf{9}]^{+\cdot}$ and $[\mathbf{10}]^{+\cdot}$ ions are greatly enhanced with respect to ions $[\mathbf{3}]^{+\cdot}$. However, in spite of their obvious stability, $[\mathbf{9}]^{+\cdot}$ and $[\mathbf{10}]^{+\cdot}$ not only lose the Cl substituent with considerable abundance, but also H and OH (Scheme 3). Metastable $[\mathbf{9}]^{+\cdot}$ and $[\mathbf{10}]^{+\cdot}$ most abundantly lose a H atom, as expected. Surprisingly, an intense peak for Cl loss is also observed (Table 1), whereas the signal for OH



Scheme 2. Formation and decomposition of coumarin ions *f* (X=F, OH, OCH_3).



Scheme 3. Fragmentation routes of ionized *m*-and *p*-chlorocinnamic acids.

loss is only weak. Thus, the formation of $[M-Cl]^+$ ions from *meta* and *para* substituted cinnamic acids must remain an energetically favourable reaction. It is proposed therefore that these ions also possess structure *a* (*vide infra*).

Summarizing, ionized cinnamic acid and its halogen substituted derivatives form $[C_9H_7O_2]^+$ ions *a*. The relative abundances of ions *a* depend on the position of the substituent at the phenyl ring and on the respective bond strength. Cinnamic acids with weakly bonded *ortho* substituents (X = Cl, Br, I) form ions *a* abundantly without any significant side reaction. The formation of $[C_9H_7O_2]^+$ ions from *m*-and *p*-chlorocinnamic acids remains an energetically favourable reaction. However, this fragmentation reaction is obviously kinetically hampered. Thus, other reaction paths are in competition with the formation of ions *a*. This explanation appears to be valid, too, in case of cinnamic acids with more firmly bound *ortho* substituents (X = H, F).

Hydroxy and methoxy substituted cinnamic acids

The 70 eV mass spectra of 2-hydroxy- (**6**) and 2-methoxycinnamic acid (**7**) and 3-hydroxy- (**11**), 4-hydroxy- (**12**), 3-methoxy- (**13**) and 4-methoxycinnamic acid (**14**) are shown in Fig. 2. Obviously the *o*-hydroxy isomer $[\mathbf{6}]^{+\cdot}$ does not lose the OH radical either from the carboxyl group or from the phenyl ring to any significant extent. However, a molecule of H_2O is eliminated. This reaction is also the only one observed for metastable $[\mathbf{6}]^{+\cdot}$. The ions *f* thus formed (Scheme 2) further decompose by two successive CO eliminations. In contrast, the *m*- and *p*-hydroxy analogues undergo this reaction sequence only to a negligible extent. A similar *ortho* effect has been reported by Seibl and co-workers[11] who observed the formation of ions *f* from ionized methyl *o*-hydroxycinnamate by the loss of CH_3OH.

The loss of OH radicals from the molecular ions of *m*-and *p*-hydroxycinnamic acid **11** and **12** is due mainly to the α-cleavage in the carboxyl group. The $[M-OH]^+$ ions successively eliminate two molecules of CO thus giving rise to the peaks at *m/z* 119 and *m/z* 91, respectively.

The *o*-methoxy compound **7** predominantly loses the OCH_3 group after ionization. The appropriate metastable transition is the only significant one observed (Table 1). The surprisingly facile displacement of the *o*-methoxy group from the phenyl ring does not reflect the high strength of the (C_{ar}—O) bond in $[\mathbf{7}]^{+\cdot}$. This is an exception to the generally observed trend that the leaving ability of a substituent alters inversely with the strength of the bond to be cleaved. An analogous exception has been reported previously in the case of *o*-methoxybenzalacetone.[6] Thus, the abundant loss of an *o*-methoxy group in compounds disposed to undergo intramolecular aromatic substitution might be taken as evidence of the presence of an isomeric compound with the OCH_3 group at a different position. This effect can be demonstrated by the

closely similar mass spectra of methyl (3- or 4-hydroxy)cinnamate[11] and 2-methoxycinnamic acid **7** (Fig. 2).

The mass spectrum of **7** contains a minor peak at *m/z* 146. The corresponding ions decompose by two successive CO losses, thus giving rise to the peaks at *m/z* 118 and *m/z* 90. These peaks are negligible in the mass spectrum of the isomeric compounds **13** and **14**. Thus it is reasonable to accept the formation of ions *f* (Scheme 2). However, there is no evidence from metastable $[\mathbf{7}]^{+\cdot}$ that *f* is formed directly by the loss of CH_3OH. Thus, contrary to the *o*-fluoro- and *o*-hydroxycinnamic acids, the formation of ions *f* from $[\mathbf{7}]^{+\cdot}$ is energetically less favourable than the formation of ions *a*. It is interesting to note that a simple trend, cf. increasing ease of formation of ions *f* with increasing heat of formation of the eliminated neutral molecule ($HF > H_2O > CH_3OH$) is not observed. This is in contrast to what might have been suspected from previous work on *ortho* effects.[12] Rather, there is a maximum for the formation of ions *f* in the case of the *o*-hydroxycinnamic acid.

The loss of the methoxy group from *m*-methoxycinnamic acid ions $[\mathbf{13}]^{+\cdot}$ is drastically reduced with respect to the *ortho* isomer and is negligible in case of the molecular ions of the *para* isomer $[\mathbf{14}]^{+\cdot}$. Correspondingly, the respective mass spectra are poor in intense fragment ion peaks (Fig. 2). This demonstrates again the high stability of molecular ions of *meta* and *para* substituted cinnamic acids. However, in spite of the enormous decrease of the $[M-OCH_3]^+$ ion abundance, metastable $[\mathbf{13}]^{+\cdot}$ still gives rise to an intense peak for the loss of OCH_3 (Table 1). This indicates that OCH_3 loss from $[\mathbf{13}]^{+\cdot}$ remains an energetically favourable reaction too. Metastable $[\mathbf{13}]^{+\cdot}$ also abundantly loses a H atom and an OH group. These remain the most prominent reactions in case of metastable $[\mathbf{14}]^{+\cdot}$, OCH_3 loss being only of minor importance.

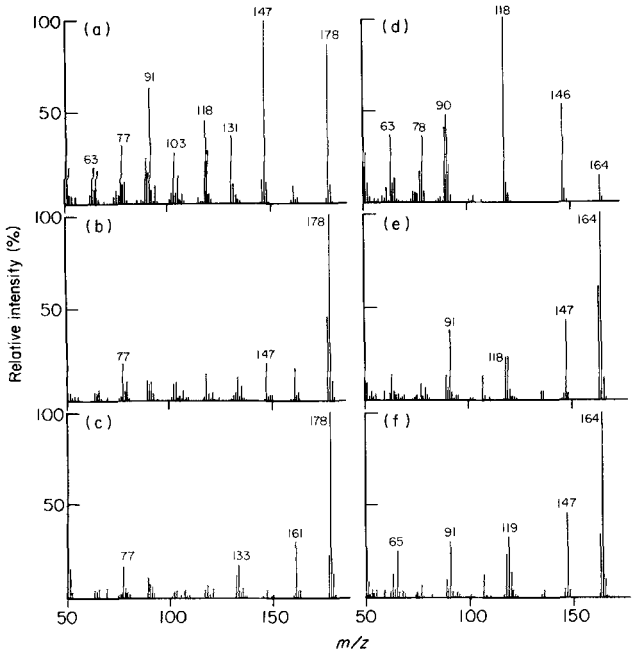


Figure 2. 70 eV mass spectra of methoxy and hydroxy substituted cinnamic acids. (a) 2-OCH_3; (b) 3-OCH_3; (c) 4-OCH_3; (d) 2-OH; (e) 3-OH; (f) 4-OH.

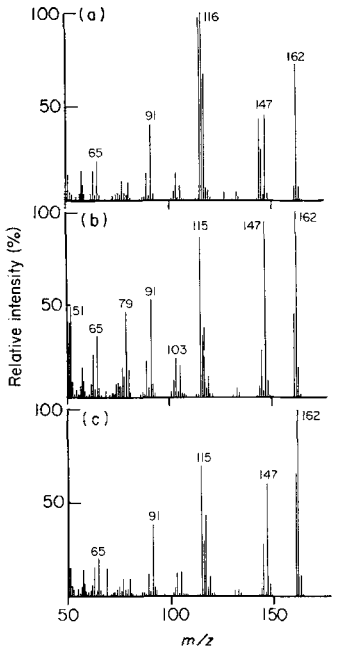


Figure 3. 70 eV mass spectra of methyl substituted cinnamic acids. (a) 2-CH_3; (b) 3-CH_3; (c) 4-CH_3.

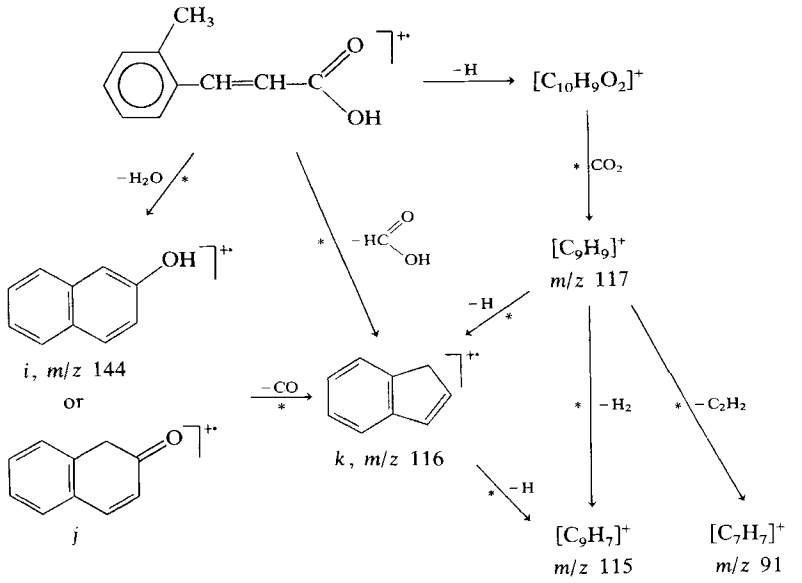
Methyl substituted cinnamic acids

The 70 eV mass spectra of 2-methyl- (**8**), 3-methyl- (**15**) and 4-methylcinnamic acid (**16**) are shown in Fig. 3.

Again considerable differences are noted between the mass spectra of the *ortho* substituted isomer **8** and the *meta* and *para* substituted analogues **15** and **16**, respectively. However, contrary to the three chloro and methoxy substituted cinnamic acids, the loss of CH_3 from $[\mathbf{15}]^{+\cdot}$ and $[\mathbf{16}]^{+\cdot}$ gives rise to *more* intense peaks at *m/z* 147 than does the displacement of the *ortho* CH_3 group. From its mass spectrum it is noted that $[\mathbf{8}]^{+\cdot}$ also loses H, OH and H_2O. Metastable $[\mathbf{8}]^{+\cdot}$ ions predominantly eliminate H_2O and to a minor extent also a fragment CH_2O_2, probably formic acid. Thus, there are two rearrangement reactions in addition to the formation of ions *a* which are energetically more favourable than the loss of CH_3. The elimination of H_2O probably leads to the β-naphthol ion *i* or its keto tautomer *j*, *m/z* 144 (Scheme 4).

Ions *i* and *j* further eliminate CO to yield the base peak at *m/z* 116 in the mass spectrum of **8**. Ions at *m/z* 116 are also formed directly from $[\mathbf{8}]^{+\cdot}$ by elimination of formic acid. There exists a third and a fourth pathway to ions at *m/z* 116, via successive losses from $[\mathbf{8}]^{+\cdot}$ of OH, CO and H and of H, CO_2 and H, respectively (cf. routes B and A, Scheme 1). Therefore it is not certain whether the ions with *m/z* 116 consist of a single species, e.g. indenylium ions *k*, as suggested in Scheme 4.

The mass spectra of **15** and **16** arise by fragmentations analogous to Scheme 4 with two main exceptions. First, the elimination of H_2O is negligible for



Scheme 4. Fragmentation of ionized *o*-methylcinnamic acid. The route analogous to route B (Scheme 1) has been omitted.

unstable and metastable $[\mathbf{15}]^{+\cdot}$ and $[\mathbf{16}]^{+\cdot}$. Second, the elimination of formic acid is absent at least in the cases of *metastable* $[\mathbf{15}]^{+\cdot}$ and $[\mathbf{16}]^{+\cdot}$. Therefore, the peak at *m/z* 116 is only of moderate size, due to the lack of two out of four ways of formation for ions *k*. Furthermore, the absence of the two energetically favourable *ortho* effect reactions renders the formation of ions *a* the easiest reaction of $[\mathbf{15}]^{+\cdot}$ and $[\mathbf{16}]^{+\cdot}$. This is not only evident from the unexpected increase in intensity of the peaks at *m/z* 147 as compared with the *ortho* compound, but is also shown by a very intense peak for the loss of CH_3 from metastable $[\mathbf{15}]^{+\cdot}$ and $[\mathbf{16}]^{+\cdot}$. The corresponding peak is not observed in the case of metastable $[\mathbf{8}]^{+\cdot}$. In addition, the absence of the eliminations of H_2O and CH_2O_2 from $[\mathbf{15}]^{+\cdot}$ and $[\mathbf{16}]^{+\cdot}$ indicates that the CH_3 group does not move to the *ortho* position within the range of energies necessary for the decomposition of $[\mathbf{15}]^{+\cdot}$ and $[\mathbf{16}]^{+\cdot}$.

DISCUSSION

The main object of this work was to ascertain whether the substituents are displaced in an intramolecular aromatic substitution reaction of the molecular ions of substituted cinnamic acids. It turns out that the formation of $[C_9H_7O_2]^+$ ions *m/z* 147 via loss of the substituents from the $[M]^{+\cdot}$ ions is one of the most favourable reactions of these ions. There are, however, in some cases favourable *ortho* effect reactions which can compete effectively with the displacement of the substituent. Thus, in the case of *o*-hydroxycinnamic acid no loss of the OH group is observed, probably because of the formation of coumarin ions *f* (Scheme 3). In all other cases peaks at *m/z* 147 are observed with varying intensities. The direct formation of these $[C_9H_7O_2]^+$ ions from the respective $[M]^{+\cdot}$ ions is confirmed by the appropriate intense metastable peaks in most cases, irrespective of the position of the substituent at the phenyl ring. Only the eliminations of HF from 2-fluorocinnamic acid ions $[\mathbf{2}]^{+\cdot}$ and of H_2O from 2-methylcinnamic acid ions $[\mathbf{8}]^{+\cdot}$ prevent the direct observation of the loss of the substituent.

The intensities of the peaks at *m/z* 147 in the 70 eV mass spectra depend on the type and on the position of the substituents at the phenyl ring. If side reactions of the $[M]^{+\cdot}$ ions are negligible a drastic decrease in abundance of $[C_9H_7O_2]^+$ ions in the series *ortho* ≫ *meta* > *para* substitution (X = Cl, OCH_3) is observed. Parallel with this decrease the intensities of the $[M]^{+\cdot}$ peaks increase. A decrease in abundance of $[C_9H_7O_2]^+$ ions and a parallel increase in the $[M]^{+\cdot}$ peak intensities is also observed with increasing strength of the (C_{ar}—X) bonds (I < Br < Cl < H < CH_3 < OCH_3 < F) in $[M]^{+\cdot}$ of the *ortho* substituted derivatives.

The generally observed sharp decrease of the (M − X) peak intensities in the mass spectra of the *meta* and *para* substituted derivatives compared with those of the *ortho* isomers provides a basis for the use of aromatic substitution reactions analytically.[4] However, in contrast to other types of *ortho* effect reactions, the intensities of the diagnostically important (M − X) peaks are sometimes of considerable size in the case of the *meta* and *para* isomers too. This becomes especially notable in the case of the methyl substituted cinnamic acids, where the $[M-CH_3]^{+\cdot}$ peak is even smaller in the *ortho* isomer than in the *meta* or *para* isomers. The *ortho* compound **8** can easily be distinguished from its isomers by using the $[M-H_2O]^{+\cdot}$ or $[M-CH_2O_2]^{+\cdot}$ reaction, however. With the aid of the $[M-CH_3]^{+\cdot}$ reaction alone, a misinterpretation seems to be unavoidable. Attention should also be paid to the use of metastable transitions which generally are intense too in the case of substituent losses from the *meta* or *para* positions (Table 1).

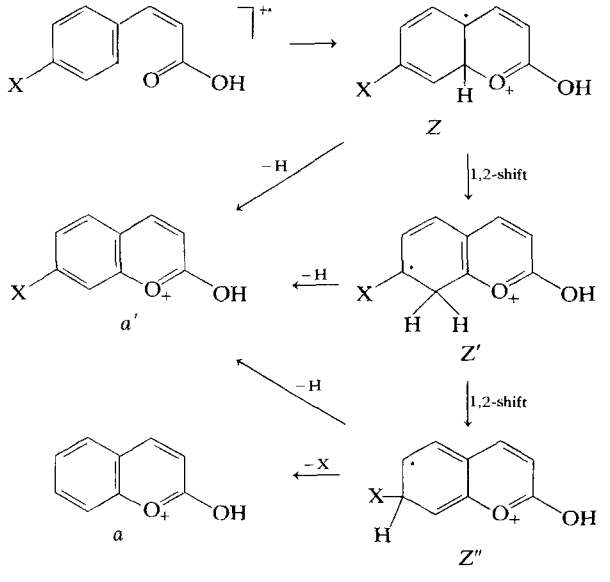
The fact that intense metastable transitions are observed in most cases for the formation of $[C_9H_7O_2]^+$ ions indicates that loss of the substituent is energetically more favourable than other reactions of the $[M]^{+\cdot}$ ions. It is unlikely therefore that the substituents are

lost by a simple bond cleavage. This reaction should have a high activation energy (e.g. *c.* 3 eV for the loss of Cl from ionized chlorobenzene[13]), with the consequence that the formation of cinnamoylium ions (*b*, Scheme 1 and substituted analogues) would probably be energetically more favourable in that case. As this is not observed a new bond must be formed within the $[C_9H_7O_2]^+$ ions during the course of their formation. Furthermore, the high intensities of the peaks at *m/z* 147 in the 70 eV mass spectra of the *ortho* substituted compounds suggest that the formation of a new bond cannot be accompanied by an extensive rearrangement of the molecular ions. Finally, the large intensities also indicate that the corresponding ions are quite stable towards further decompositions.

The same arguments against the simple bond cleavage of the *ortho* substituents also apply to the *meta* and *para* substituted acids. However, the lower intensities of the peaks at *m/z* 147 in comparison with the *ortho* isomers (X = Cl, OCH_3) requires some comment. A decrease of the $[M-Cl]^+$ peak intensities similar to the one observed for the three chlorocinnamic acids **3**, **9** and **10** has been thoroughly studied previously in case of the analogously substituted chlorobenzalacetones.[14] It turned out that the decrease in intensity is *not* due to an increase in the activation energy which remains nearly constant, but is due to a decrease in the frequency factor for the Cl loss. This kinetic hindrance for the substituent loss from the *meta* and *para* positions has led to the postulation of a reaction mechanism which can also explain the observations in the case of the cinnamic acids (Scheme 5).

(i) The decrease of the intensities of the $[M-X]^+$ peaks in the 70 eV mass spectra in the series *ortho*, *meta*, *para* substituted derivatives (X = Cl, OCH_3) is directly evident. A weakly bonded substituent at the *ortho* position (e.g. X = Cl) can be displaced either directly or via a short-lived intermediate. In order to cleave the substituent from the *meta* or *para* positions one or two additional rearrangement steps within *Z* are necessary. This leads to an increase of the $[M]^{+\cdot}$ ion abundances and to a decrease of the $[M-X]^+$ peak intensities. Thus, a considerable fraction of the $[M]^{+\cdot}$ ions probably exist as non-decomposing intermediates *Z* and *Z'*. The reversed order of the $[M-CH_3]^+$peak intensities in case of the methyl substituted cinnamic acids **8**, **15** and **16** can be explained if one takes into account the two favourable *ortho* effect reactions specific for the *ortho* isomer (Scheme 4). (ii) The increase of the $[M]^{+\cdot}$ ion of *ortho* substituted cinnamic acids relative to the $[M-X]^+$ peak intensities with increasing strength of the (C_{ar}—X) bond can be explained with an increase in lifetime of the intermediate *Z*. In this case too an increasing fraction of the molecular ion peaks is due to non-decomposing intermediates *Z*. Furthermore, the attack at the unsubstituted *ortho* position becomes more and more probable. (iii) Strong metastable transitions are observed for the losses of the substituents from all *meta* and *para* substituted cinnamic acids studied. This indicates the presence of a relatively large number of long-lived molecular ions. All these metastable molecular ions also eject a hydrogen atom abundantly. The corresponding reaction in case of *ortho* substituted cinnamic acids is not observed (Table 1). The competition between the loss of the substituent and of a H atom can easily be understood if one accepts the formation of an intermediate *Z*. The ions *a* of *a'* (Scheme 5) are formed by losing either a H atom from *Z* or *Z'* or the substituent from *Z''*, respectively.

(iv) An intermediate analogous to *Z* has also been discussed by Williams *et al.*[7] in order to explain the complete hydrogen randomization in the styryl ring of ionized benzalacetophenone.



Scheme 5. Mechanism for the formation of 2-hydroxybenzopyrylium ions *a* from *meta* and *para* substituted cinnamic acids, exemplified with a *para* substituted derivative.

EXPERIMENTAL

Materials

Compounds **1**, **3**, **6**, **7**, **9–12** and coumarin were commercial samples (Aldrich Europe). Compounds **2**, **4**, **5**, **8** and **13–16** were synthesized by Knoevenagel-Doebner-Condensation.[15]

Instrumental

The 70 eV mass spectra and the MIKE spectra were recorded on a 311 A mass spectrometer (Varian MAT). The samples were introduced via the direct inlet system. The probe was heated gently until a pressure in the ion source of *c.* 10^{-6} Torr was indicated. No thermal decomposition due to decarboxylation of the cinnamic acids could be detected (source temperature: *c.* 150 °C; filament current: 0.2 mA).

The $[M-H]^+$ peaks in the MIKE spectra of metastable $[\mathbf{9}]^{+\cdot}$ and $[\mathbf{10}]^{+\cdot}$ were recorded after tuning in the $[M]^{+\cdot}$ peaks corresponding to the molecular ions with the heavier isotope. This is necessary due to interference peaks inherent with the MIKES technique.[16,17]

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