

Dehalogenation Reactions in Chemical Ionization Mass Spectrometry†

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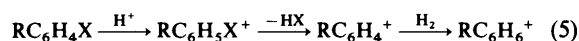
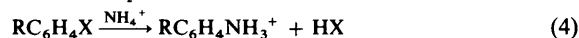
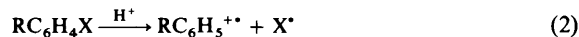
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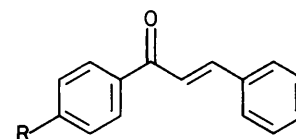
The dehalogenation reactions occurring in certain halogenated chalcones and α -phenylcinnamionitriles under chemical ionization conditions have been studied. Reductive dehalogenation in halogenated chalcones leads to the formation of the MH^+ ion of the parent unsubstituted chalcone, while a similar reaction in halogenated α -phenyl cinnamionitriles leads to a radical-induced cyclization product, 3-phenylquinoline, in the 2'-chloro and 2'-bromo derivatives and mostly to the parent nitrile in the case of 3'- and 4'-chloro derivatives. The abundance of the dehalogenation ion increases in the order $F < Cl < Br$. The operation of a radical mechanism for this process is confirmed by experiments with radical traps such as tetracyanoquinodimethane.

Under chemical ionization (CI) conditions halogenated aromatic molecules are known to undergo dehalogenation reactions by a number of pathways.¹ These are: (a) loss of hydrogen halide [Scheme 1, reaction (1)], (b) elimination of a halogen radical [reaction (2)], (c) reductive dehalogenation involving replacement of a halogen atom by a hydrogen [reaction (3)], and (d) substitution of a halogen atom by the reagent, especially when NH_3 is used [reaction (4)].

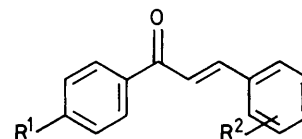


Scheme 1.

Upon CI, protonation of the halogen atom normally results in the loss of hydrogen halide, while the loss of a halogen radical from MH^+ depends on the relative stabilities of the respective hydrogen halide and the halogen radical. Thus losses of Br^{\cdot} and I^{\cdot} are favoured over the losses of HBr and HI , while fluoro derivatives do not lose F^{\cdot} . Both Cl^{\cdot} and HCl losses are observed in chloroaromatics. Harrison and co-workers^{1e} have shown that the reductive dehalogenation occurs by a multi-step process in halobenzenes under CI conditions [reaction (5)]. Dehalogenation processes involving the successive replacement of Cl by H were also observed in the electron-capture negative-ion spectra of polycyclic chlorinated pesticides,² and in fluoranil and chloranil.³ The mechanisms proposed include hydrogen radical addition followed by fragmentation and successive repeated electron capture and neutralization by ion-ion recombination steps.²⁻⁴ A radical-induced cyclization reaction was postulated and confirmed in the CI spectra of chlorine-substituted nitriles.⁵ A recent review describes the various reactions, including dehalogenation, that occur between substrate molecules and CI reagents.⁶ There have also been reports of such dehalogenation reactions under fast atom bombardment (FAB)⁷ and plasma desorption conditions.⁸ When NH_3 or CH_3NH_2 is used as the reagent, haloaromatics are known to give rise to ions resulting from substitution of a halogen by the reagent.^{1f} We have recently studied the dehalogenation reactions in certain



- (1) $R = H$
 (2) $R = 4'-F$
 (3) $R = 4'-Cl$



- (4) $R^1 = H, R^2 = 2'-F$
 (5) $R^1 = H, R^2 = 2'-Cl$
 (6) $R^1 = H, R^2 = 3'-Cl$
 (7) $R^1 = H, R^2 = 4'-Cl$
 (8) $R^1 = H, R^2 = 2'-Br$
 (9) $R^1 = 4'-F, R^2 = 4'-Cl$
 (10) $R^1 = 4'-Cl, R^2 = 2'-Cl$
 (11) $R^1 = H, R^2 = 3'-Cl, 4'-Cl$
 (12) $R^1 = 4'-Cl, R^2 = 3'-Cl, 4'-Cl$

halogenated chalcones and α -phenyl cinnamionitriles under CI conditions and the results are presented here.

Results and Discussion

Halogenated Chalcones.—The ion abundances ($\% \Sigma$) in the CI (NH_3) spectra of the halogenated chalcones (2)–(12) are given in Table 1. As the basicities of chalcones⁹ are comparable to that of NH_3 , the most abundant ion in the CI (NH_3) spectra of the chalcones (2)–(12) corresponds to MH^+ . Apart from varying amounts of MNH_4^+ , the other ions observed are $M^{+ \cdot}$, $[M - X]^+$, $[M - X + 2H]^+$, and $[M - X + 2H + NH_3]^+$, where $X = \text{halide}$. Only the fluoro compounds give small amounts of $M^{+ \cdot}$ ions formed by charge exchange. No shift was observed for the $[M - X]^+$ ion in the CI (ND_3) spectrum of the bromochalcone (8). The $[M - X]$ ions are significant only in the spectra of the 2'-chloro (5), 2'-bromo (8), and 2',4'-dichloro

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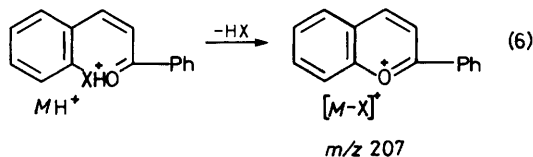
Table 1. CI (NH₃) spectral data of halogenated chalcones (2)–(12).^a

Compd.	MNH ₄ ⁺	MH ⁺	[M - X + 2H] ⁺	[M - X] ⁺	Others
(2)	244 (5.0)	227 (94.0)	209 (0.1)	—	226 (0.8) ^b
(3)	260 (7.3)	243 (92.0)	209 (1.0)	—	—
(4)	244 (13.1)	227 (83.0)	209 (0.4)	—	226 (1.4) ^b
(5)	260 (15.7)	243 (79.6)	209 (2.7)	207 (2.0)	—
(6)	260 (12.0)	243 (86.8)	209 (1.0)	207 (0.4)	—
(7)	260 (5.6)	243 (88.5)	209 (5.6)	—	—
(8)	304 (16.9)	287 (46.0)	209 (29.0)	207 (4.0)	226 (4.0) ^c
(9)	278 (7.3)	261 (91.3)	227 (0.8)	225 (0.5)	—
(10)	294 (18.1)	277 (70.7)	243 (8.0)	241 (3.1)	—
(11)	294 (12.3)	277 (83.8)	243 (3.8)	—	—
(12)	328 (12.0)	311 (80.0)	277 (8.0)	—	—

^a In Tables 1–4 the ion abundances are expressed as percentages of total ion current. ^b M⁺. ^c [M - X + 2 + NH₃]⁺.

Table 2. Effect of emission current on the abundance of [M - X + 2H]⁺ in (2)–(12). Abundance of [M - X + 2H]⁺ at different emission currents (μA).

Compound	600	300	100	50
(2)	0.1	0.1	—	—
(3)	1.0	0.7	0.4	—
(4)	0.4	0.2	0.1	0.1
(5)	2.7	1.7	0.5	0.2
(6)	0.9	0.6	—	—
(7)	5.8	4.8	3.8	3.1
(8)	27.0	17.0	6.1	2.4
(9)	0.8	0.4	—	—
(10)	7.1	3.9	1.7	—
(11)	3.8	2.2	1.1	—
(12)	8.0	5.4	3.0	—



(10) derivatives. This shows that the [M - X]⁺ ion might have a cyclized structure and might correspond to the benzopyrylium ion¹⁰ [reaction (6)]. The [M - X + 2H]⁺ ion cannot be formed directly from MH⁺ or MNH₄⁺ as such loss would correspond to (X - 1) or [NH₃ + (X - 1)], respectively. A B²/E scan of [M - X + 2H]⁺ ion at m/z 209 in the bromo chalcone (8) showed that the ion at m/z 226 corresponding to [M - X + 2H + NH₃]⁺ is the only parent for this ion. The [M - X + 2H]⁺ ion should, therefore, arise by substitution of a halogen by a hydrogen atom. In the CI spectrum of compound (8), recorded using ND₃ as the reagent gas, the ion at m/z 209 was found to be shifted to m/z 210 and 211 in the ratio 2:3 suggesting thereby that the added hydrogen species arises from both the background and the reagent, resulting in the ions [M - Br + H + D]⁺ and [M - Br + 2D]⁺. It is already known that moisture present in the ion source also leads to side reactions.⁶ In view of the fact that the plasma generated in a CI source contains radical species⁴ (as well as ions and neutral molecules), that the radical population in a CI source can be as high or many times higher than the ion concentration,¹¹ and that radical reactions prior to ionization in a CI source have earlier been demonstrated in many systems,^{4,5,11,12} it appears that the reductive dehalogenation in these chalcones also takes

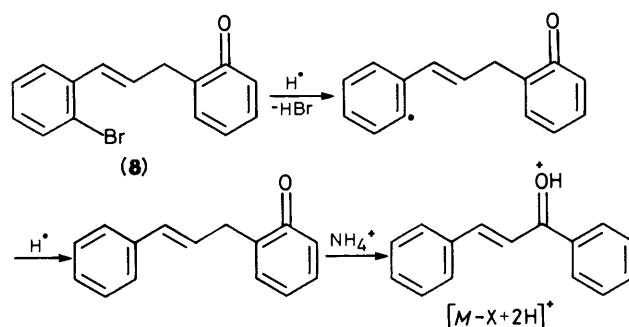
place *via* a radical mechanism. This is supported by the following observations:

(a) The abundance of the dehalogenation ion increases with increase in emission current as shown in Table 2. The sum of the abundances of the [M - X + 2H]⁺ and [M - X + 2H + NH₃]⁺ ions also increases with increase in the pressure of NH₃. For example, the value of the abundance in the spectrum of compound (8) increases from 8.3% at a source housing pressure of 6 × 10⁻⁶ Torr* to 19.7% at 3 × 10⁻⁵ Torr.

(b) When the spectrum of the bromochalcone (8) was recorded in the presence of a radical trap such as tetracyanoquinodimethane (TCNQ), the sum of the abundances of the dehalogenation ions [M - X + 2H]⁺ and [M - X + 2H + NH₃]⁺ was reduced from 22% without TCNQ to 6.3% with TCNQ. This shows that TCNQ and the bromochalcone compete with each other in consuming the hydrogen radicals present in the CI plasma.

(c) The relative abundance of the dehalogenated ion in the fluoro (4), chloro (5), and bromo (8) derivatives increases in that order. The carbon-halogen bond strength increases in the reverse order, *i.e.*, Br < Cl < F.

The above results clearly indicate the operation of a radical mechanism for the substitution of a halogen by a hydrogen atom in these chalcones under CI conditions (Scheme 2). It is

**Scheme 2.**

also possible that these reactions are metal-catalysed surface reactions.⁶ The structure of the dehalogenated ion could be confirmed by a comparison of the CA spectra of the MH⁺ ion of the unsubstituted parent chalcone (1) at m/z 209 and the same ion produced from the bromochalcone (8) shown in the Figure. The two CA spectra are superimposable thus showing that the [M - X + 2H]⁺ ion from (8) has a structure identical with that of the MH⁺ ion of (1).

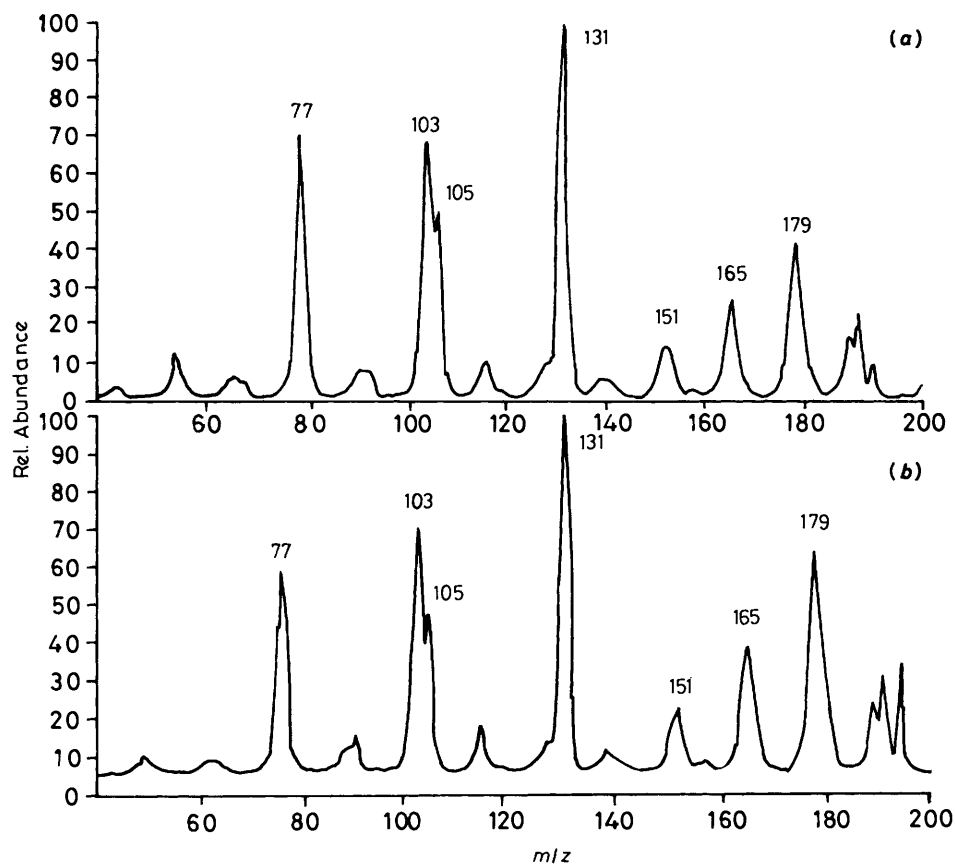
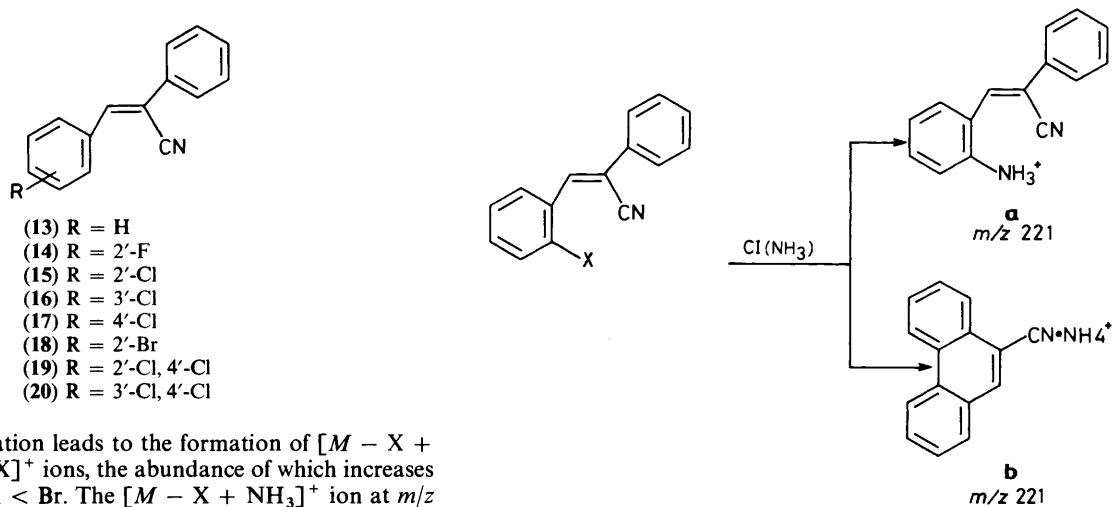
In the case of the di- and tri-substituted compounds (9)–(12) only one of the halogens is replaced. In compound (9), which contains both F and Cl, the dehalogenation occurs only by the replacement of Cl. The greater ease of replacement of 2'- or 4'-halogen can be explained on the basis of the extended conjugation possible in these cases. This also explains why the loss of 4'-Cl is less favoured compared to 4'-Cl.

Halogenated α -Phenyl Cinnamionitriles.—The CI (NH₃) spectral data of the halogenated α -phenyl cinnamionitriles (14)–(20) are given in Table 3. Being less basic than NH₃, these molecules give MNH₄⁺ as the most abundant ion. Practically no protonation occurs in these molecules under CI (NH₃) conditions. The dehalogenated ions observed in their spectra are [M - X + NH₃]⁺, [M + X + 2H + NH₃]⁺, and [M - X + 4H]⁺ in addition to [M - X]⁺ and [M - X + 2H]⁺ observed in the spectra of the halogenated chalcones.

* 1 Torr \approx 133.322 Pa.

Table 3. CI (NH_3) spectral data of α -phenyl cinnamitriles (14)–(20).

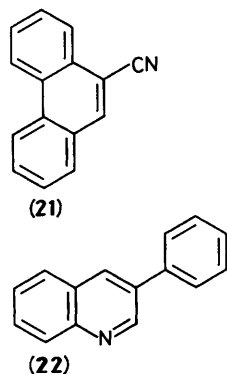
Compound	MNH_4^+	M^{++}	$[M - X + 2H + \text{NH}_3]^+$	$[M - X + \text{NH}_3]^+$	$[M - X + 4H]^+$	$[M - X + 2H]^+$	$[M - X]^+$	Others
(14)	241 (79.7)	223 (16.0)	—	221 (1.1)	—	—	—	203 (1.0)
(15)	257 (76.8)	239 (8.1)	223 (0.5)	221 (2.6)	208 (5.5)	206 (3.8)	204 (1.4)	203 (1.9)
(16)	257 (78.9)	239 (7.1)	223 (1.1)	221 (1.0)	—	206 (0.2)	204 (1.0)	203 (1.0)
(17)	257 (81.5)	239 (11.2)	223 (2.2)	221 (2.0)	—	206 (0.3)	204 (1.2)	203 (1.4)
(18)	301 (53.4)	283 (6.4)	—	221 (3.1)	208 (7.2)	206 (13.5)	204 (1.6)	205 (1.6)
(19)	291 (31.0)	273 (7.3)	257 (2.4)	255 (3.3)	242 (33.0)	240 (17.7)	—	221 (2.1)
(20)	291 (74.2)	273 (9.0)	257 (9.0)	—	—	240 (1.0)	—	—

**Figure.** CA spectra of (a) the MH^+ (m/z 209) of (1) and (b) the $[M - X + 2H]^+$ (m/z 209) of (8).

Dehydrohalogenation leads to the formation of $[M - X + \text{NH}_3]^+$ and $[M - X]^+$ ions, the abundance of which increases in the order $\text{F} < \text{Cl} < \text{Br}$. The $[M - X + \text{NH}_3]^+$ ion at m/z 221 could correspond to a substitution ion a (Scheme 3). In the

CD (ND₃) spectrum of the 2'-chloro derivative (15) the $[M - X + ND_3]^+$ ion appeared at m/z 225. If the substitution ion had been present this peak would have appeared at m/z 224. It therefore appears that the substitution reaction does not occur in this case. α -Phenyl cinnamitriles are known to undergo cyclization under photolytic conditions giving rise to 9-cyanophenanthrene.¹³ In order to confirm the operation of a similar process under CI conditions, the CA spectrum of the $[M - X + NH_3]^+$ ion of (15) was compared with that of the MNH_4^+ ion of 9-cyanophenanthrene (21). The two spectra given in Table 4 are superimposable showing the formation of 9-cyanophenanthrene from 2'-chloro- α -phenylcinnamitrile under CI conditions. No metastable ion could be observed for the loss of HX from MNH_4^+ . The abundance of the $[M - X + NH_3]^+$ ion was found to depend on ion-source parameters, e.g. the $[M - X + NH_3]^+$ ion abundance increased from 0.3% at 50 μ A to 2.6% at 600 μ A emission current and from 0.8% at 6×10^{-6} Torr (source housing pressure) to 2.6% at 2×10^{-5} Torr. Similar results were also observed in the case of 2'-bromo- α -phenylcinnamitrile (18).

As in the case of the chalcones, the $[M - X + 2H]^+$ and



$[M - X + 2H + NH_3]^+$ ions, corresponding to MH^+ and MNH_4^+ of the dehalogenated compounds, cannot arise directly from MH^+ and MNH_4^+ of the halogenated nitrile. It has

previously been shown that the $[M - X + 2H]^+$ ion of the 2'-chloro derivative (15) and MH^+ of 3-phenylquinoline (22) in their CI (CH₄) spectra gave similar CA spectra and that (22) is formed from (15) under CI conditions via a radical-induced cyclization process.^{5b} Among the monochloro compounds (15)–(17), the $[M - X + 2H]^+$ ion is more abundant in the 2'-chloro compound, while the $[M - X + 2H + NH_3]^+$ ion is more abundant in the 3'- and 4'-chloro compounds. The 2'-bromo derivative (18) gives rise to the most abundant $[M - X + 2H]^+$ ion among the monohalogenated nitriles, while $[M - X + 2H + NH_3]^+$ is absent in this compound. This is a clear indication of the fact that 2'-chloro and 2'-bromo derivatives give rise to a dehalogenated species which is different from those produced from 3'- and 4'-chloro compounds. The above results also show that the dehalogenation product from 2'-chloro and 2'-bromonitriles is more basic than that from either 3'- or 4'-chloro derivatives. This is to be expected if the 2'-chloro and 2'-bromo derivatives give rise to 3-phenylquinoline and the 3'- and 4'-chloro derivatives give rise to the parent nitrile, (13) (Scheme 4).

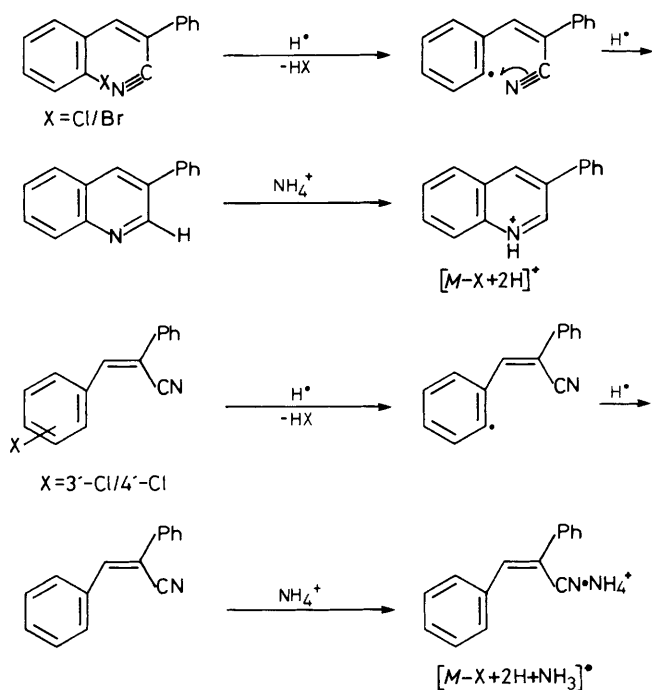
This could be confirmed by comparing the CA spectra of the $[M - X + 2H]^+$ ion at m/z 206 from compounds (15)–(18) with those of the MH^+ ions of 3-phenylquinoline (22) and the parent nitrile (13). Table 4 also gives the CA spectral data of these compounds. As the abundance of the $[M - X + 2H]^+$ ion is low under CI (NH₃) conditions in the spectra of (13), (16), and (17), the CA spectra of their $[M - X + 2H]^+$ ions were recorded under CI (CH₄) conditions. The ion abundances in the CA spectra of the $[M - X + 2H]^+$ ion from 2'-chloro (15) and 2'-bromo (18) compounds are similar to that of the MH^+ ion of 3-phenylquinoline, while the ion abundances in the CA spectra of the $[M - X + 2H]^+$ ions from compounds (16) and (17) are similar to that of the MH^+ ion of (13). Moreover, the CA spectrum of the $[M - X + NH_3]^+$ ion of (17) is found to be superimposable onto that of the MNH_4^+ of the parent nitrile (13), as shown in Table 4.

In the CI (NH₃) spectra of the 2'-, 4'- and 3',4'-dichloro derivatives (19) and (20), as expected, the abundance of the $[M - X + 2H]^+$ ion is more in the 2',4'-dichloro compound (17.7%) than in the 3',4'-dichloro compound (0.9%). However, the $[M - X + 2H + NH_3]^+$ ion is more abundant in (20)

Table 4. Ion abundances in the CA spectra of the ions at m/z 221, 206, 223, and 240.

Compound	m/z 211		m/z 206					m/z 223		m/z 240			
	(15)	(21)	(15)	(18)	(22)	(16) ^a	(17) ^a	(13) ^a	(17)	(13)	(15) ^a	(17) ^a	(19) ^a
m/z													
213	—	—	—	—	—	—	—	—	—	—	32	34	19
206	—	—	—	—	—	—	—	—	35	36	—	—	—
205	—	—	—	—	—	—	—	—	27	28	15	14	19
204	38	37	—	—	—	—	—	—	—	—	13	15	18
203	34	34	—	—	—	—	—	—	—	—	—	—	—
191	—	—	10	9	8	5	6	4	3	3	—	—	—
189	2	3	—	—	—	—	—	—	—	—	2	2	4
179	—	—	28	27	28	37	37	39	13	11	—	—	—
178	—	—	19	19	18	32	31	32	16	14	—	—	—
177	10	9	—	—	—	—	—	—	—	—	17	13	12
176	10	11	—	—	—	—	—	—	—	—	11	13	10
165	—	—	10	9	8	6	5	4	2	2	—	—	—
163	2	2	—	—	—	—	—	—	—	—	3	2	6
151	3	3	10	9	10	7	7	6	2	2	4	5	6
139	0.4	0.4	3	4	5	3	4	2	1	1	0.7	1	3
128	0.4	0.4	12	11	12	4	3	3	1	0.4	2	1	3
103	—	—	4	6	5	3	6	7	—	—	—	—	—
77	—	—	4	5	6	3	1	3	—	0.4	—	—	—

^a From CI (CH₄) spectra.



(5.7%) than in (19) (2.4%) showing thereby that the major product of dehalogenation could be the corresponding 3-phenylquinoline in (19), and the monochloro- α -phenyl cinnamionitrile in (20). The CA spectral data of the $[M - X + 2H]^+$ ion from (19) and the MH^+ ion of (15) and (17) recorded under CI (CH_4) conditions are also given in Table 4, from which it is clear that the $[M - X + 2H]^+$ ion from (19) has a CA spectrum different from that of either (15) or (17). The loss of HCN is less prominent in the CA spectrum of the $[M - X + 2H]^+$ ion of (19), while the loss of HCN corresponds to the most abundant ion in the CA spectra of the MH^+ ions of (15) and (17). It, therefore, appears that the reductive dehalogenation in the 2'-4'-dichloro derivative (19) involves mainly cyclization resulting in the formation of the MH^+ of, most probably, 3-phenyl-7-chloroquinoline.

As observed in the case of the halogenated chalcones, the abundances of the dehalogenated ions in these nitriles also increase with increase in emission current and NH_3 pressure. When the bromochalcone (8) was introduced from a gas chromatograph (GC) into the CI source during a CI (NH_3) experiment with the bromo nitrile (18) it was found that the abundances of the $[M - X + 2H]^+$ and $[M - X + NH_3]^+$ ions of the nitrile decreased as compound (8) eluted from the column, reached a minimum at the top of the GC peak, and then increased as the elution was completed. These observations indicate that a radical mechanism operates for the dehalogenation processes in these nitriles also under CI conditions. This is also supported by the observation that the abundances of the $[M - X + 2H]^+$ and $[M - X + NH_3]^+$ ions increase in the order $F < Cl < Br$.

The origin of the $[M - X + 4H]^+$ ion has not yet been ascertained. The abundance of this ion also showed a dependence on the ion-source parameters similar to that observed in the case of the $[M - X + 2H]^+$ and $[M - X + NH_3]^+$ ions. It therefore appears that the $[M - X + 4H]^+$ ion is also produced as a result of further radical reactions in the ion source.

In conclusion, the present study indicates that the H^+ radicals

present in the CI plasma are responsible for the dehalogenation reactions that take place in these halogenated chalcones and phenyl cinnamionitriles under CI conditions.

Experimental

The chalcones and α -phenyl cinnamionitriles were prepared by reported procedures.^{14,15} 9-Cyanophenanthrene (21) was prepared from 9-bromophenanthrene.¹⁶ Decarboxylation of 3-phenylquinoline-2,4-dicarboxylic acid prepared from phenyl pyruvic acid and isatin* furnished 3-phenylquinoline (22).¹⁷ The purities of these compounds were checked by t.l.c. and by spectral data. The CI (NH_3) spectra were recorded on a JEOL D-300 mass spectrometer. The source conditions were: electron energy, 200 eV; emission current, 600 μA , and temperature, 180 °C. The pressure of NH_3 was adjusted so that the source housing pressure was 2×10^{-5} Torr unless stated otherwise. Tetracyanoquinodimethane (TCNQ) was obtained from Jansen Pharma, Belgium. For the radical-trap experiments the sample was mixed with TCNQ before being introduced into the ion source. The CA spectra were recorded on a VG-ZAB-HF instrument operating at 8 kV (accelerating voltage), 50 eV (electron energy), 200 μA (emission current) and 150 °C. The collision gas used was helium.

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