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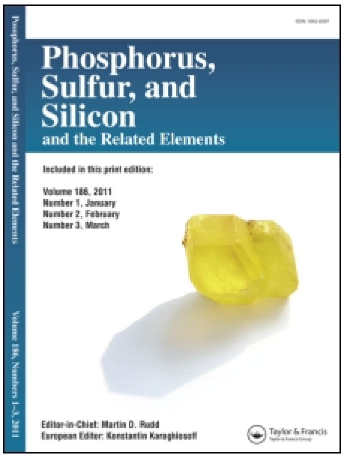

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MASS SPECTRAL FRAGMENTATION STUDIES ON THIOPHENOTROPONE AND THIOPHENOTROPILIDENE DERIVATIVES AND THEIR METAL TRICARBONYL COMPLEXS

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MASS SPECTRAL FRAGMENTATION STUDIES ON THIOPHENOTROPONE AND THIOPHENOTROPILIDENE DERIVATIVES AND THEIR METAL TRICARBONYL COMPLEXES

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The mass spectral fragmentation of thiophenotropone, thiophenotropilidene derivatives and their iron and chromium tricarbonyl complexes are fully reported and discussed. The fragmentation patterns of the complexes are characterised by successive loss of three carbonyl groups. In general, the resulting ions after elimination of the metal behave in the same manner as the organic ligand. The iron complexes behave differently from their corresponding chromium complexes. The thiopheno[b]tropilidene iron tricarbonyl complex and its isomer thiopheno[c]tropilidene iron tricarbonyl complex could not be differentiated by mass spectrometry, such differentiation was achieved by proton magnetic resonance.

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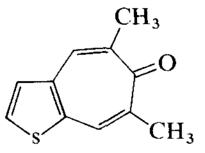
Different method have been applied for the structure elucidation of metal carbonyl complexes, e.g., infrared,[1–3] proton magnetic resonance spectrometry,[4–6] carbon thirteen spectra,[7–9] and X-ray diffraction technique.[10–13] Although the mass spectra of thiophenes[14,15] and alkyl thiophenes[16–18] have been investigated, those of thiophenotropones and thiophenotropilidenes nor of their metal tricarbonyl complexes have not been reported.

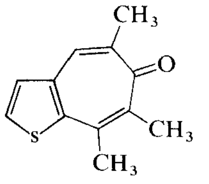
This paper concerns with the mass spectral fragmentation of thiophenotropone, thiophenotropilidene derivatives and their chromium and iron complexes.

A THIOPHENOTROPONE DERIVATIVES

Ia



Ib



The most predominant ions of compounds (Ia, b) are listed in Table I and a representative example of the fragmentation patterns of 5,7,8-trimethylthiopheno-[b]tropone Ib are recorded in Scheme 1 (Figure 1).

The molecular ion did apparently, undergo fragmentation by two major pathways (A and B). Pathway A gives the ion *a* at m/e = 176 by loss of CO, and then loses hydrogen to give the ion *b* at m/e = 175. It has been reported that, the loss of CO as a neutral molecule by the tropone system gives the most intensive ion peak and the resultant ion behaves as an aromatic derivative.[19] Consequently, the thiopheno[b]tropylium cation derivative was characterised by successive elimination of two methylene CH_2 radicals to give fragment ion *c* at m/e = 161 and *d* at m/e = 147, respectively.

Pathway *B* was characterised by loss of HCS radical[14–16] leading to the fragment ion *e* at m/e = 159. The fragment ion *f* at m/e = 131 could be produced from ion *e* by losing a CO molecule or from ion *a* at m/e = 176 by elimination of HCS radical. The fragment ion *f* at m/e = 131 could be produced by hydrogen elimination to the ion *g* at m/e = 130. Finally elimination of two methylene radicals successively gives fragment on ion *h* at m/e = 116 and *i* at m/e = 102, respectively.

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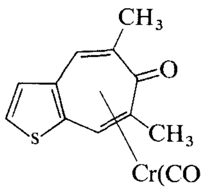
TABLE I

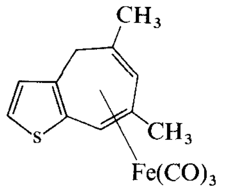
Mass spectral data of thiopheno[b]tropones and their chromium tricarbonyl complexes

Ia:	m/e	190	188	163	162	161	160	159	148
	I(%)	90.40	8.78	12.69	84.53	58.80	11.44	10.03	10.81
		147	145	118	117	102			
		100.00	14.09	9.09	9.72	12.69			
Ib:	m/e	204	177	176	175	163	162	161	160
	I(%)	49.62	12.55	87.62	26.42	8.65	18.35	100.00	11.37
		159	147	131	130	116	102		
		6.81	10.87	11.90	26.30	5.04	33.38		
IIa:	m/e	326	270	243	242	240	190	162	161
	I(%)	5.92	7.44	17.35	75.45	22.15	43.83	59.07	40.90
		148	147	145	134	121	117	116	115
		11.56	100.00	6.43	14.37	21.72	52.40	47.40	22.35
		108	102	52					
		23.62	7.83	14.20					
IIb:	m/e	340	284	257	256	254	204	176	175
	I(%)	3.77	9.88	24.38	80.14	27.25	10.93	50.44	21.73
		162	161	160	159	147	134	131	130
		12.36	100.00	9.54	5.86	13.69	17.20	17.90	12.04
		116	103	102	52				
		33.39	8.05	7.63	52.13				

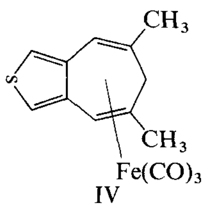
B METAL CARBONYL COMPLEXES OF THIOPHENOTROPONES AND THIOPHENOTROPILIDENES



IIa: R=H
IIb: R=CH$_3$



III: R$_1$R$_2$=H
IIIb: R$_1$=CH$_3$, R$_2$=H
IIIc: R$_1$=H, R$_2$=CH$_3$



IV

The mass spectral data of compounds (IIIa–c) and (IV) are recorded in Table II and a representative example of the fragmentation patterns of 5,7,8-trimethylthiopheno[b]tropone chromium tricarbonyl complex (IIb) and 5,7,8-trimethylthiopheno[b]tropilidene iron tricarbonyl complex (IIIb) are shown in Scheme 2 and 3 respectively.

It is noteworthy that, the mass spectral fragmentation patterns of thiopheno[b]tropone chromium tricarbonyl complex (IIa–b), thiopheno[b]tropilidene iron tricarbonyl complexes (IIIa–c) and thiopheno[c]tropilidene iron tricarbonyl complex (IV) have unique pathway of fragmentation by losing the three carbonyl groups successively giving fragment ions of different intensities at (M^{+}—CO•), (M^{+}—2CO•) and (M^{+}—3CO•),[20] In general the peak ion intensity increases with further elimination of carbonyl groups (Table II).

A different situation was observed by comparing the spectra of both chromium and iron complexes.[20–22] This is illustrated by typical representative examples of the fragmentation of compound IIb Scheme 2 (Figure 2) and compound IIIb Scheme 3 (Figure 3).

The behavioiur of thiopheno[b]tropone chromium tricarbonyl complexes (IIa, b) cannot be observed in the fragmentation patterns of both thiopheno[b]tropilidene iron tricarbonyl complexes (IIIa–c) and thiopheno[c]tropilidene iron tricarbonyl complex (IV). The situation here is more complicated, after successive elimination of the three carbonyl groups from the molecular ion, the produced intense ion at m/e = (M^{+}—3CO•) undergo fragmentation by four pathways.

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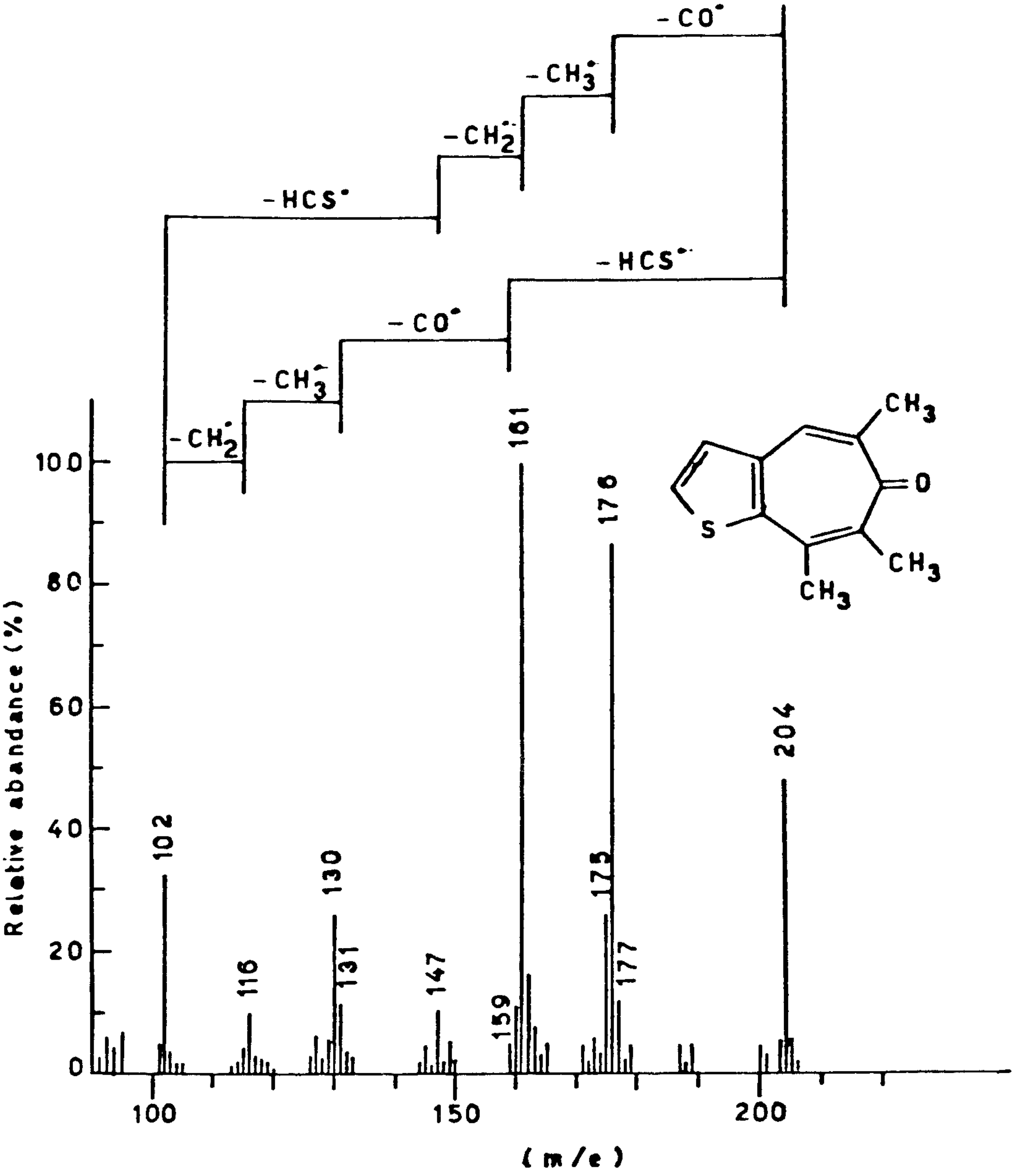

FIGURE 1 Mass spectrum of 5,7,8-trimethylthiopheno[b]tropone (Ib).

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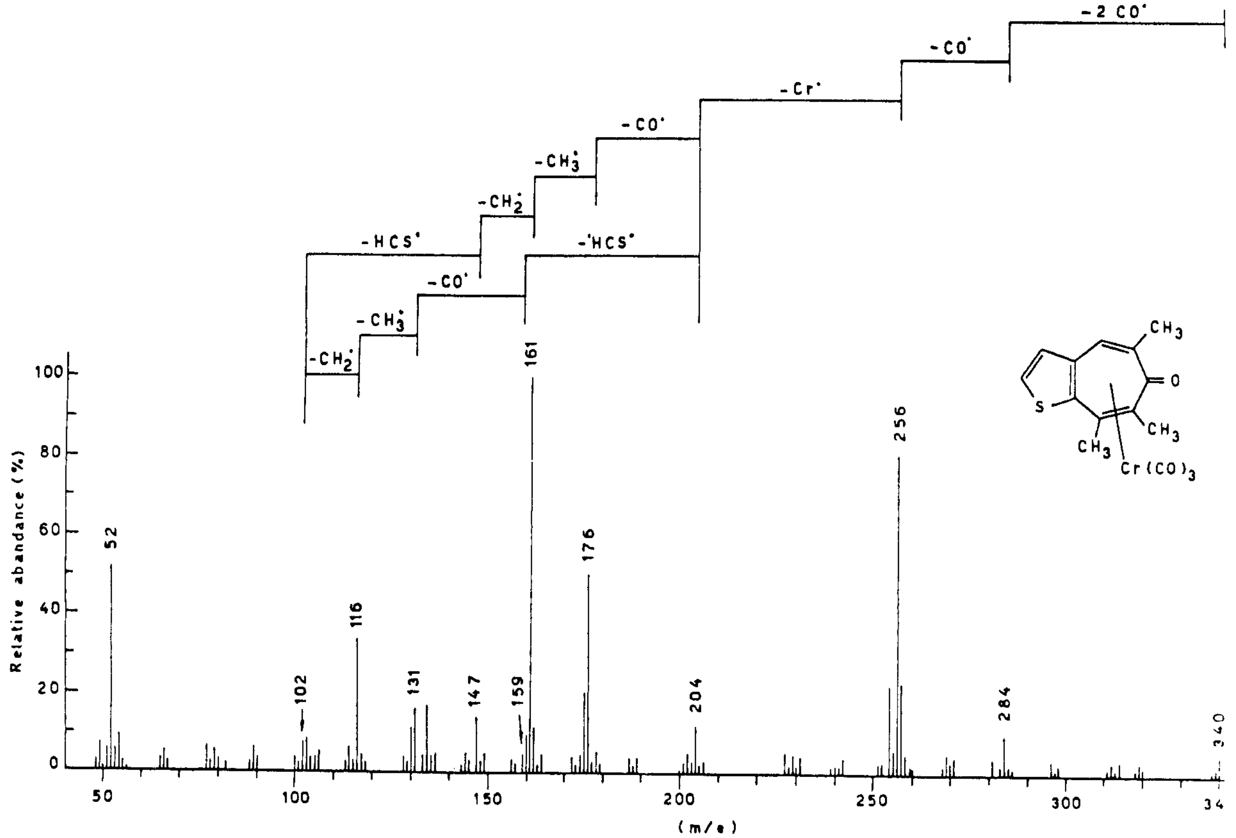


FIGURE 2 Mass spectrum of 5,7-8-trimethyl-thiopheno[b]tropone chromium tricarbonyl complex (IIb).

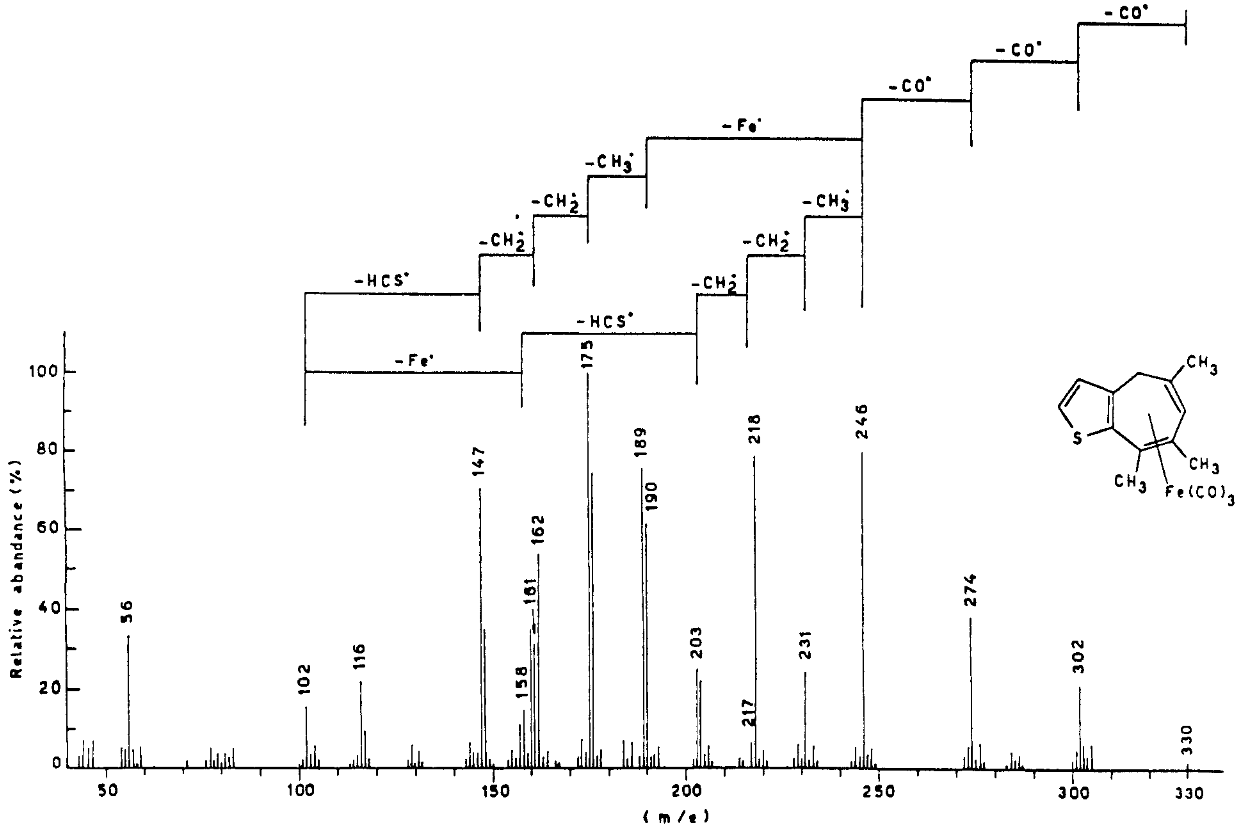
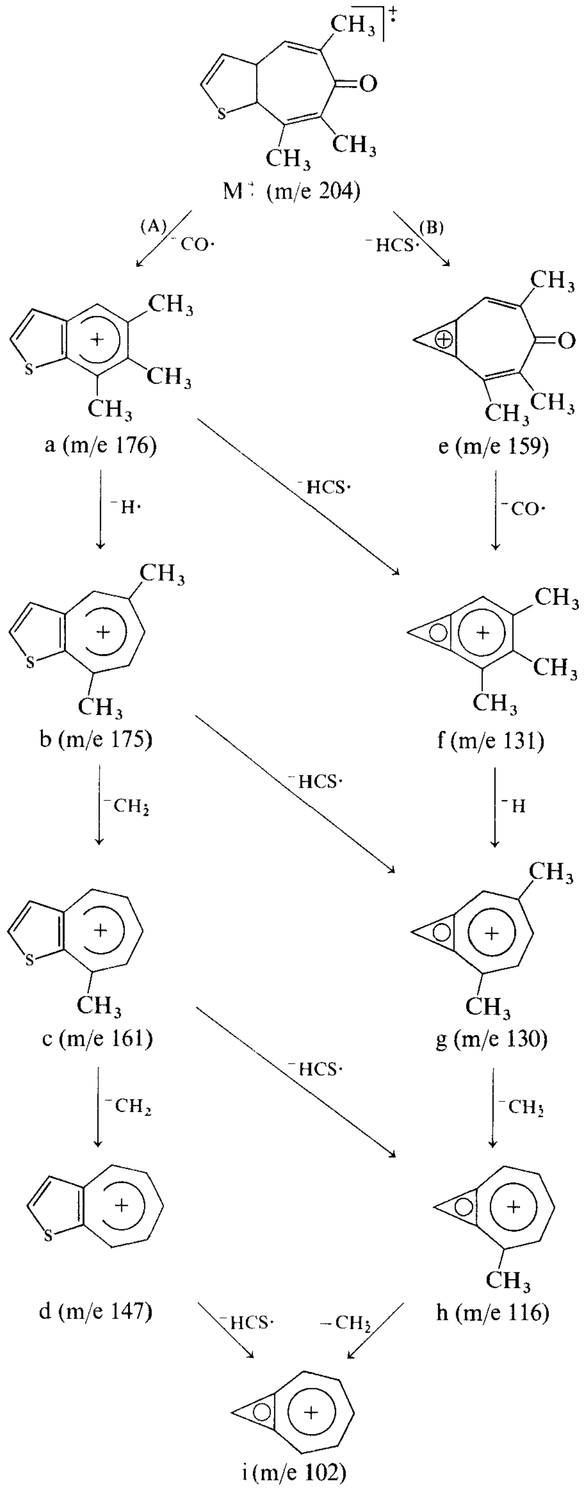


FIGURE 3 Mass spectrum of 5,7,8-trimethyl-thiopheno[b]tropilidene iron tricarbonyl complex (IIIb).



SCHEME I

Mass spectral fragmentation of 5,7,8-trimethylthiopheno[b]tropone (1b).

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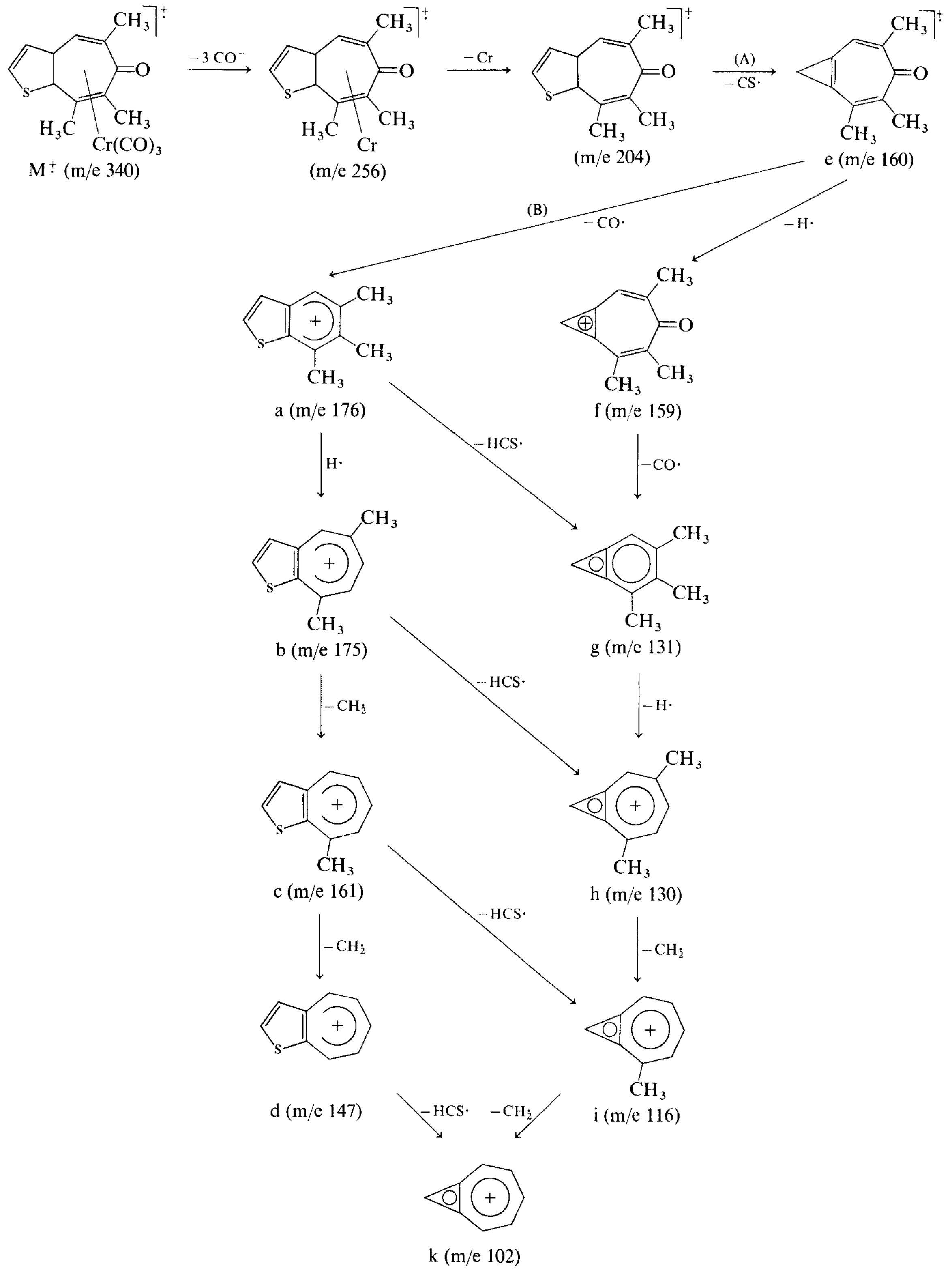

SCHEME 2

Mass spectral fragmentation of 5,7,8-trimethylthiopheno[b]tropone chromium tricarbonyl complex (IIb).

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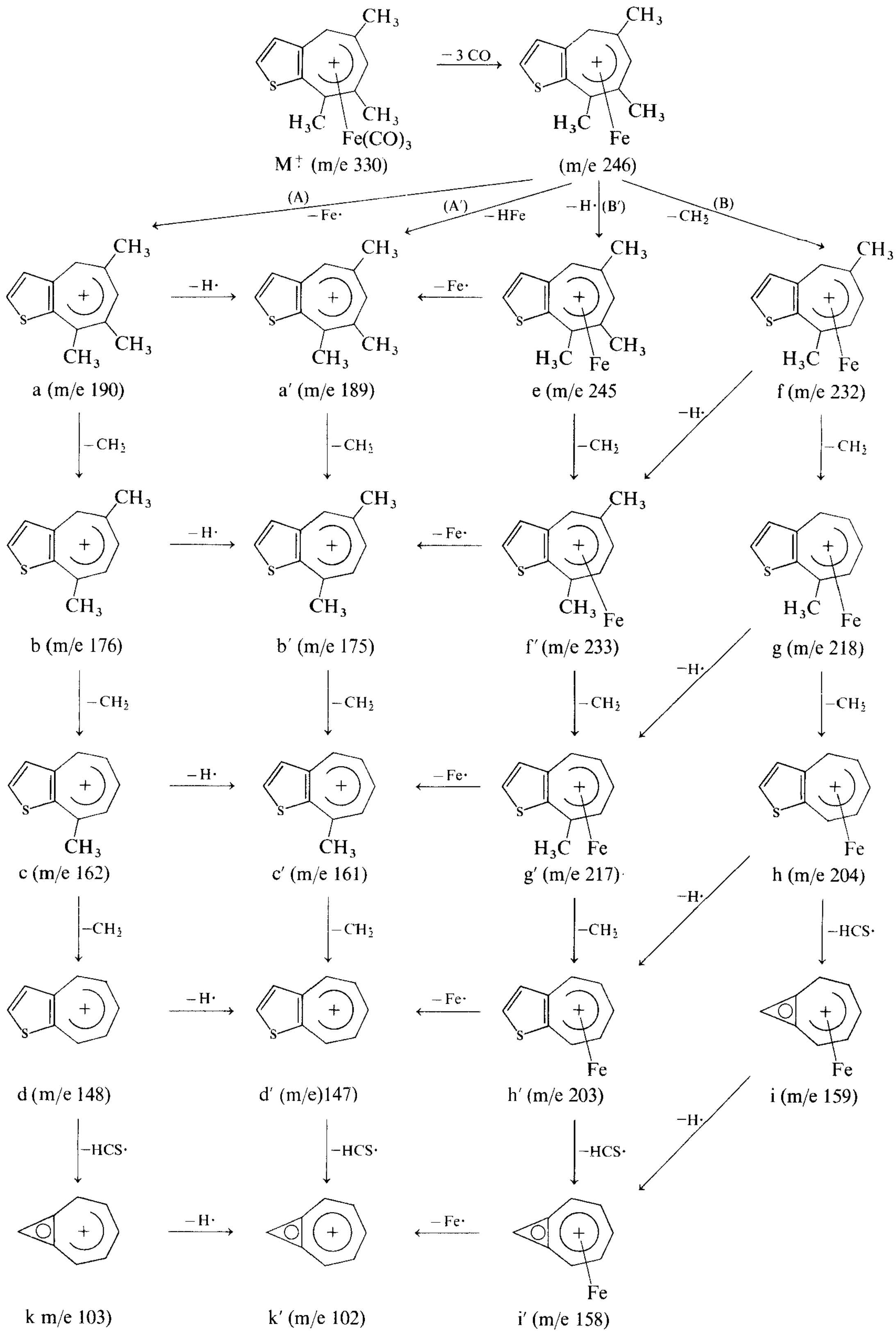

SCHEME 3

Mass spectral fragmentation of 5,7,8-trimethylthiopheno[b]tropilidene iron tricarbonyl complex (IIIb).

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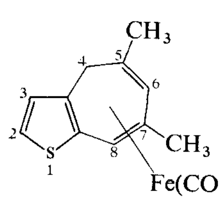
TABLE II

Mass spectral data of thiophenotropilidene iron tricarbonyl complexes (IIIa–c) and (IV)

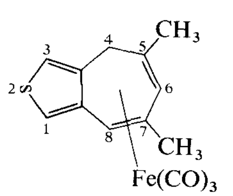
m/e	IIIa I(%)	IIIb I(%)	IIIc I(%)	IV I(%)
$M^{+\cdot} = 330$	—	0.23	0.07	—
$M^{+\cdot} = 316$	0.36	—	—	0.72
$M^{+\cdot} - CO$	28.40	21.35	9.29	72.69
$M^{+\cdot} - 2CO$	38.29	39.82	16.31	37.37
$M^{+\cdot} - 3CO$	100.00	79.23	48.84	100.00
245	—	9.98	2.92	—
232	($M^{+\cdot}$ − 3CO)100.00	3.67	3.40	($M^{+\cdot}$ − 3CO)100.00
231	6.11	25.03	22.18	7.05
218	19.00	79.72	34.21	—
217	29.90	7.88	10.70	14.04
204	64.46	22.39	8.27	5.53
203	9.86	25.50	5.40	10.50
190	14.68	61.87	15.01	7.39
189	—	76.54	17.85	—
176	22.66	38.64	20.21	27.10
175	67.11	100.00	100.00	30.40
162	14.18	54.27	18.44	11.10
161	22.16	30.33	17.04	14.85
160	83.94	34.19	10.52	78.78
159	11.19	16.54	19.08	9.41
158	7.75	12.21	19.10	10.80
148	22.90	35.02	13.57	32.60
147	30.30	71.90	31.32	27.71
117	11.31	10.79	14.26	14.04
116	19.78	22.17	11.33	21.90
103	10.36	16.74	9.10	13.16
102	15.66	17.72	8.11	16.06
56	13.05	33.25	4.69	11.13

All peaks greater than (2%) of the base peak (arbitrarily taken as 100%) are recorded, except in cases of special significance.

Pathways (A and A′) were characterised by the elimination of iron and the resulting ions behave in the same manner as the organic ligand, while pathways (B and B′) were characterised by keeping the metal to yield fragment ions as shown in Scheme 3. It is worthy to note that, fragment ions of pathway B′ could eliminate iron to produce fragment ions of pathway A′. It is not possible to distinguish between thiopheno[b]tropilidene iron tricarbonyl complexes (IIIa–c) and thiopheno[c]tropilidene iron tricarbonyl complex (IV). The mass spectral fragmentation patterns of these complexes are very similar (apart from small differences in the relative abundances of ions). However, the fragment ion peaks of compound IIIa are more intense in comparison with the spectrum of compound IV (cf. Table II), especially the step of HCS· elimination to give the same fragment ion at m/e = 102 as shown in Table II. The nmr spectra have been found useful for such differentiation, the chemical shift values for hydrogens in the thiopheno[b]tropilidene iron tricarbonyl complex (IIIa) and thiopheno[c]tropilidene iron tricarbonyl complex (IV):



IIIa



IV

(IIIa) 6.75 (1H, d, $H_{(2)}$); 6.50 (1H, d, $H_{(3)}$; 5.17 (1H, m, $H_{(6)}$); 3.55 (1H, m, $H_{(8)}$); 2.91 (2H, q, $H_{(4)}$); 2.15) (3H, s, $CH_{3(7)}$); 1.80 (3H, s, $CH_{3(5)}$).

(IV) 6.92 (1H, d, $H_{(1)}$); 6.77 (1H, m, $H_{(3)}$); 5.26 (1H, m, $H_{(6)}$); 3.76 (1H, m, $H_{(8)}$); 3.10 (2H, q, $H_{(4)}$); 2.17 (3H, s, $CH_{3(7)}$); 1.75 (3H, s, $CH_{3(5)}$).

Chemical shift values were detrmined as in ppm.

s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Generally, the protons of compound (IIIa) resonate at lower magnetic field than those of the corresponding protons of compound (IV). This suggests that the density of electrons on the thiopheno[b]tropilidene system might be higher and consequently the diamagnetic ring current could be more effective than on the thiopheno[c]tropilidene system.

EXPERIMENTAL

Samples used in this investigation were prepared according to the procedures described by EL-Borai *et al*,[23] the purity of compounds were established by TLC using silica G Merk (7731) and colone chromatography using silica G 60 Merk (7734). The nmr spectra were measured on a JEOL–60 MHZ), in $CDCl_3$(40 mg/0.4 ml) and TMS as internal reference. The mass spectra were determined with a Finnigan 3300 mass Spectrometer by use of a direct inlet (source temperature 90 to 300°C, and beam energy of 70 eV.

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