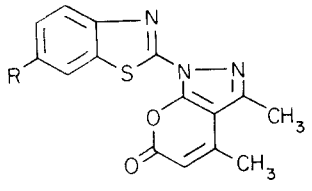
New Mass Spectra

Electron Impact Induced Fragmentation of 1-(6′-Substituted-2′-benzothiazolyl)-3,4-dimethyl-pyrano[2,3-*c*]pyrazol-6-(1*H*)ones

A survey of the literature reveals that a lot of work has been carried out on the mass spectral fragmentation of pyrazoles.[1] Surprisingly there is no report on the electron-impact induced fragmentation of pyranopyrazoles, although this nucleus has been known for some time.[2] In continuation of our work on the mass spectral behaviour of heterocyclic compounds,[3–5] it was thought of interest to study the mass spectra of pyranopyrazoles (Compounds **1–5**).



1: R = H
2: R = CH_3
3: R = OCH_3
4: R = Cl
5: R = F

Synthesis of the title compounds was undertaken to evaluate them for anti-inflammatory activity, as a large number of benzothiazolylpyrazoles have been found to display significant anti-inflammatory activity.[6,7] Many of the title compounds have indeed displayed a moderate level of anti-inflammatory property.[8]

Table 1. Significant mass spectral data showing the principal ions in compounds (1–5)† (*m/z*; % intensity)

Ion	1	2	3	4	5
$[M]^{+\cdot}$	297 (100)	311 (100)	327 (100)	331/333 (100)	315 (100)
d	282 (42)	296 (33)	312 (28)	316/318 (22)	300 (16)
e	269 (35)	283 (18)	299 (19)	303/305 (29)	287 (26)
i	268 (19)	282 (14)	298 (16)	302/304 (21)	286 (19)
f	254 (27)	268 (20)	284 (23)	288/290 (21)	272 (26)
j	241 (33)	255 (18)	271 (18)	275/277 (16)	259 (17)
k	240 (29)	254 (16)	270 (16)	274/276 (14)	258 (18)
g	227 (22)	241 (20)	257 (10)	261/263 (12)	245 (10)
h	226 (13)	240 (12)	256 (9)	260/262 (10)	244 (8)
m	214 (27)	228 (10)	244 (8)	248/250 (16)	232 (9)
l	199 (16)	213 (12)	229 (10)	233/235 (9)	217 (8)
n	175 (17)	175 (10)	175 (8)	175 (8)	175 (10)
b	163 (21)	163 (20)	163 (12)	163 (8)	163 (18)
c	150 (27)	164 (18)	180 (10)	184/186 (13)	168 (8)
	135 (60)	135 (18)	135 (20)	135 (19)	135 (22)
a	134 (35)	148 (19)	164 (21)	168/170 (21)	152 (23)
	108 (25)	122 (18)	138 (8)	142/144 (18)	126 (18)

† Isotopic peaks have been omitted to describe the lower mass limit and lower intensity limit.

Table 1 and Fig. 1 shows that the molecular ion is the base peak. The molecular ion also results in the generation of an ion *m/z* 108 by the characteristic cleavage of benzothiazole ring[9] (Process A), besides undergoing the homolytic fission of C—N bond thereby separating the two heterocyclic moieties to give ions *a* and *b* (Process B). Accurate mass measurement technique shows that the molecular ion undergoes an extensive rearrangement to give rise to ion *c*. The parent ion loses a methyl radical and carbon monoxide respectively to generate ions *d* and *e*. The ion *f* may be generated from either ion *d* or ion *e* by the loss of carbon monoxide from the former ion and a methyl radical from the latter ion. Ions *g* and *h* are derived from ion *f* by the loss of hydrogen cyanide and carbon monoxide respectively. The ion *e* loses a hydrogen atom to generate ion *i* which may have either of the structures shown in Scheme 1, it undergoes the loss of hydrogen cyanide and carbon monoxide thus resulting in the formation of ions *j* and *k*. High resolution mass

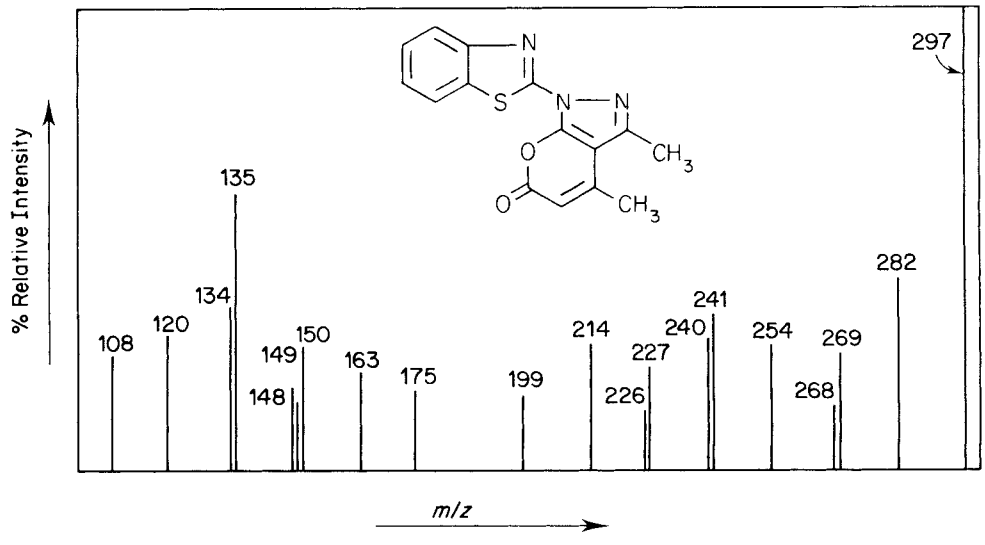


Figure 1. Mass spectrum of 1-(2′-benzothiazolyl)-3,4-dimethyl-pyrano[2,3-*c*]pyrazol-6(1H)-one. Isotopic peaks have been omitted to describe the lower mass limit and lower intensity limit.

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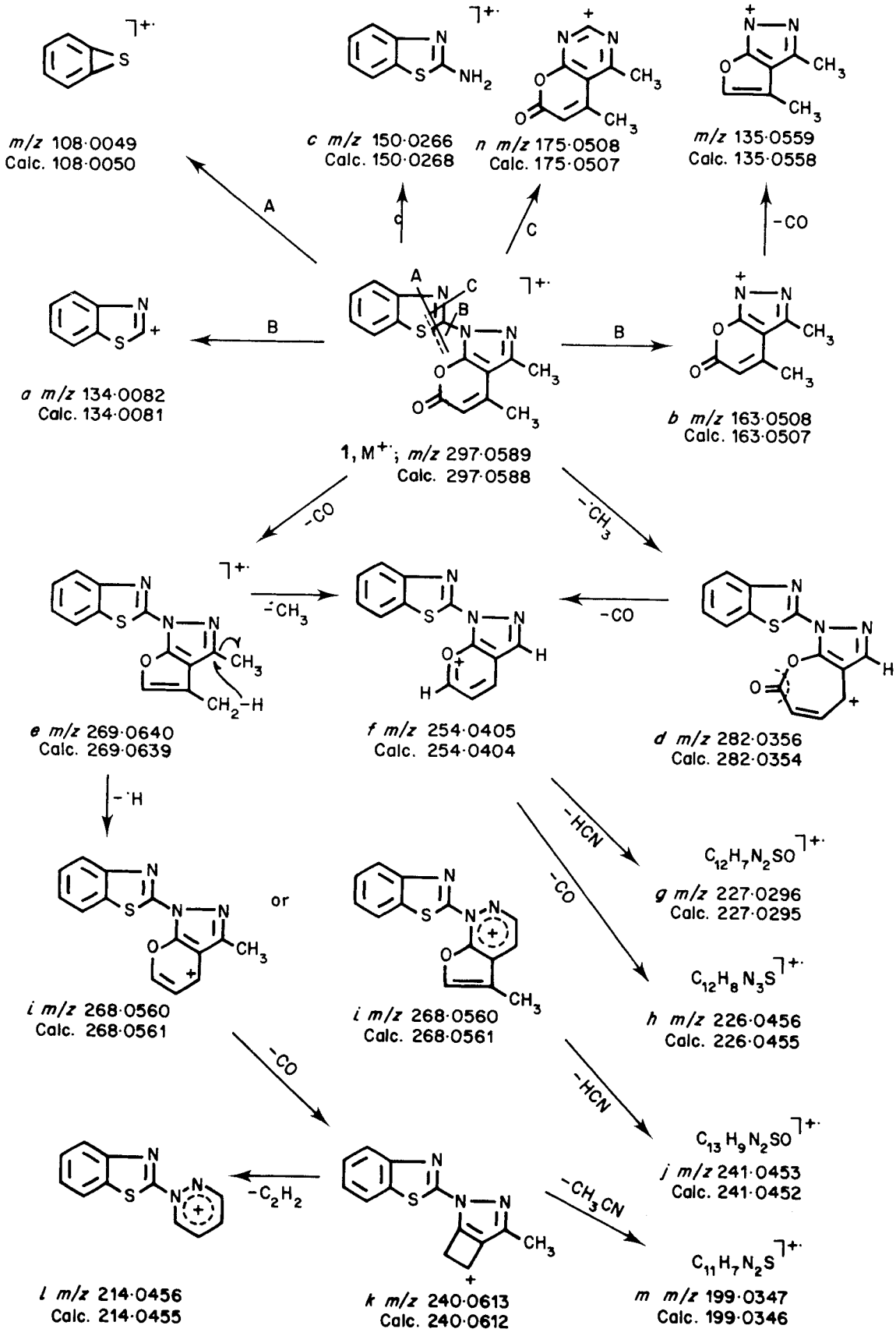
m/z 108·0049
Calc. 108·0050
c m/z 150·0266
Calc. 150·0268
n m/z 175·0508
Calc. 175·0507
m/z 135·0559
Calc. 135·0558
A
a
C
-CO
B
B
a m/z 134·0082
Calc. 134·0081
b m/z 163·0508
Calc. 163·0507
1, M+·; m/z 297·0589
Calc. 297·0588
-CO
-·CH3
-·CH3
-CO
e m/z 269·0640
Calc. 269·0639
f m/z 254·0405
Calc. 254·0404
d m/z 282·0356
Calc. 282·0354
-·H
-HCN
C12H7N2SO+·
g m/z 227·0296
Calc. 227·0295
-CO
C12H8N3S+·
h m/z 226·0456
Calc. 226·0455
or
i m/z 268·0560
Calc. 268·0561
i m/z 268·0560
Calc. 268·0561
-CO
-HCN
C13H9N2SO+·
j m/z 241·0453
Calc. 241·0452
-C2H2
-CH3CN
C11H7N2S+·
l m/z 214·0456
Calc. 214·0455
k m/z 240·0613
Calc. 240·0612
m m/z 199·0347
Calc. 199·0346

Scheme 1

Table 2. Physical data of compounds 1–5

Compound	m.p. °C	IR data in cm^{-1} (Nujol)	PMR data in TFA (δ)
1	274	1740 (C=O stretch.)	2.72 (*s*, 3H, CH_3), 2.78 (*s*, 3H, CH_3), 6.45 (*s*, 1H, pyran-5-H), 7.42–7.9 (*m*, 4H, aromatic protons).
2	260	1740 (C=O stretch.)	2.72 (*s*, 3H, CH_3), 2.76 (*s*, 3H, CH_3), 2.78 (*s*, 3H, CH_3), 6.45 (*s*, 1H, pyran-5-H), 7.4–7.8 (*m*, 3H, aromatic protons).
3	284	1740 (C=O stretch.)	2.72 (*s*, 3H, CH_3), 2.78 (*s*, 3H, CH_3), 4.1 (*s*, 3H, OCH_3), 6.45 (*s*, 1H, pyran-5-H), 7.1–7.5 (*m*, 3H, aromatic protons).
4	289	1740 (C=O stretch.)	2.73 (*s*, 3H, CH_3), 2.78 (*s*, 3H, CH_3), 6.45 (*s*, 1H, pyran-5-H), 7.4–7.95 (*m*, 3H, aromatic protons).
5	295	1740 (C=O stretch.)	2.73 (*s*, 3H, CH_3), 2.78 (*s*, 3H, CH_3), 6.45 (*s*, 1H, pyran-5-H), 7.5–8.1 (*m*, 3H, aromatic protons).

spectrometry indicates that the latter ion loses two neutral moieties, ethylene and methyl cyanide leading to the formation of ions *l* and *m* respectively. It is also confirmed by accurate mass measurements that the molecular ion also undergoes the formation of ion *n* by the insertion of the carbon atom of benzothiazole nucleus (Process C). Ion *b* generates an ion at *m/z* 135 by the loss of carbon monoxide which in turn loses a methyl radical to give an ion at *m/z* 120.

All these processes are supported by inspection of the mass spectra of other compounds which show analogous ions. These ions are arranged in Table 1 in such a manner as to display the correspondance of fragment ions. The composition of all the fragment ions shown in Scheme 1 were confirmed by high resolution mass spectrometry.

Compounds **1–5** were synthesized at about 60 % yield by treating 6-substituted or unsubstituted-2-hydrazinobenzothiazoles,[6,10] with ethylacetoacetate at 160°C. The compounds were crystallized from *N,N*-dimethylformamide. The physical data of compounds **1–5** are listed in Table 2.

Low resolution mass spectra were obtained at 70 eV on MS-12 mass spectrometer fitted with a direct inlet system (source temperature kept about 165°C). High resolution measurements were obtained on a Kratos MS-50S instrument equipped with 23 K gauss magnet. Running conditions were source temperature 200°C, electron energy 50 eV, resolution 8500, scan speed 30 s/decade. The sample was calibrated against PFK and data were collected on a LOGOS II/Sigma 7 data system.

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