ORGANIC MASS SPECTROMETRY, VOL. 21, 77–79 (1986)

Mass Spectra of Some 2-(4′-Butyl-3′,5′-dimethylpyrazol-1′-yl)-6-substituted Benzothiazoles

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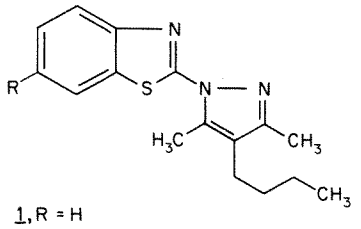
The fragmentation of the title compounds on electron impact has been studied and the major processes interpreted. The base peak invariably appears at $[M-43]^+$ whose origin from the butyl chain has been traced with the help of metastable ion studies and accurate mass measurements. Loss of methyl cyanide, involving the decomposition of the pyrazole moiety, is observed only from the fragment ions.

INTRODUCTION

Mass spectral fragmentation of pyrazole derivatives is greatly influenced by the presence of substituents in the molecule.[1] The initial fragmentation may involve only the substituents, and fission of pyrazole ring may proceed as a subsequent step or the ring itself may undergo initial cleavage.[2] Fission of the pyrazole ring may also take place in two ways. It may either result in the loss of $N_2R^{\cdot}$ radical or alternatively in the expulsion of RCN from the molecular ion.[3] In view of these divergent modes of fragmentation, it was considered of interest to study the mass spectra of pyrazole derivatives (compounds **1–3**) having a butyl chain attached to position 4.



1, R = H
2, R = CH_3
3, R = Cℓ

These compounds were synthesized bearing in mind the importance of the butyl chain in the well-known anti-inflammatory drug, phenylbutazone.[4] Many of the title compounds have indeed displayed remarkable anti-inflammatory drug, phenylbutazone.[4] Many of the synthesis consists of the condensation of 6-substituted (or unsubstituted) 2-hydrazinobenzothiazoles with 3-butylpentane-2,4-dione. The compounds were characterized by elemental analysis and PMR spectra (see Experimental section).

RESULTS AND DISCUSSION

An inspection of the mass spectrum of compound **1** reveals that the molecular ion, although abundant, does not constitute the base peak (Fig. 1). The base peak invariably appears at $[M-43]^+$ (ion *a*). Accurate mass measurement of the fragment ion has established that this peak arises by the loss of the elements of C_3H_7 from the molecular ion. Loss of this moiety obviously involves the butyl chain located at position 4 of the pyrazole nucleus. Linked scan data obtained on **3** (Fig. 2) have suggested two modes for the formation of *a*: (i) loss of methyl radical followed by ethylene from the resultant ion, and (ii) loss of propene from the molecular ion followed by a hydrogen from the fragment ion.

Whereas process (i) may be visualized as proceeding through simple carbon–carbon bond fissions, process (ii) requires a McLafferty-type rearrangement in the molecular ion as depicted in Scheme 1. The linked scan data (Fig. 2) further suggest that ion *a* undergoes extensive rearrangement yielding an ion corresponding to an ionized 2-aminobenzothiazole (ion *f*). It is significant that there is no loss of CH_3CN directly from the molecular ion, rather this molecule is expelled from the fragment ions $[M-C_2H_5]^+$ and *c*. Since loss of CH_3CN has been found to be a significant process in the mass spectra of several 3,5-dimethylpyrazole derivatives,[3] it can be inferred that the presence of a butyl chain provides an alternative low-energy pathway which completely prevents fission of the pyrazole moiety in the molecular ion of these compounds.

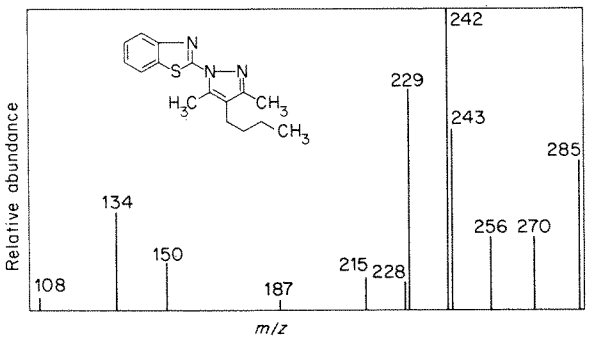


Figure 1. Mass spectrum of 2-(4′-butyl-3′,5′-dimethylpyrazol-1′-yl)-benzothiazole (**1**).

0030–493X/86/020077–03$05.00

Received 10 June 1985
Accepted 12 August 1985

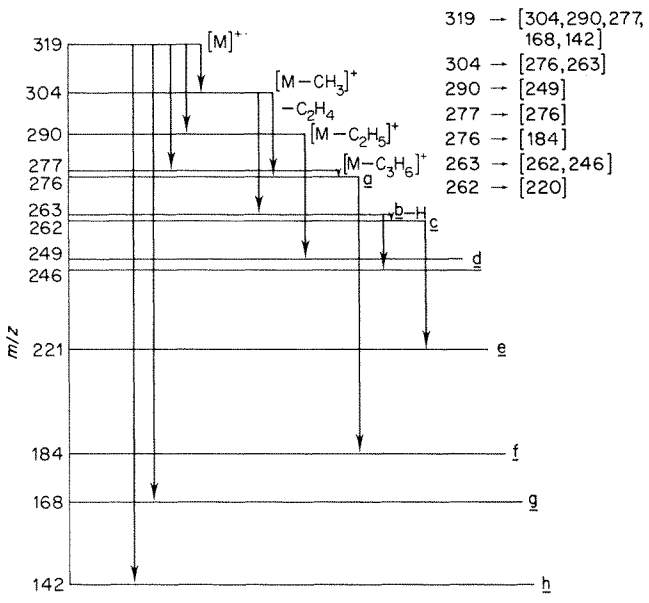
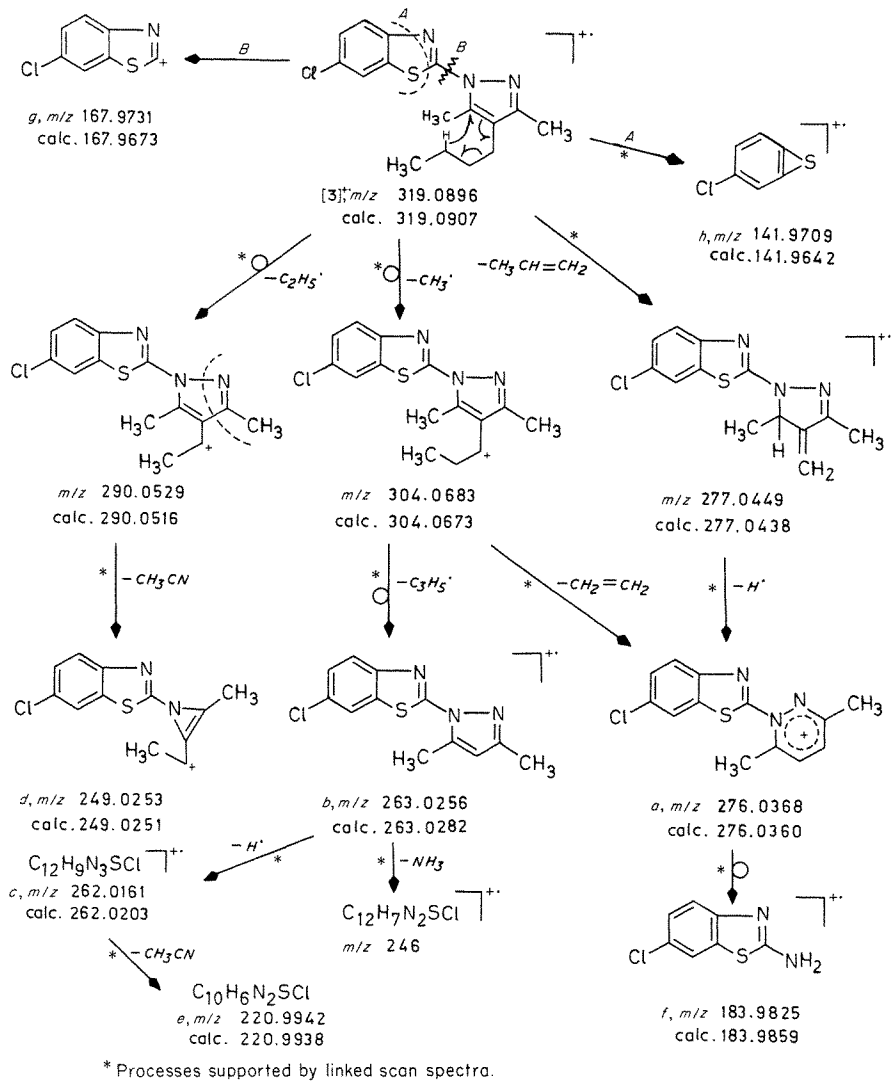


Figure 2. Linked scan spectra of **3**.

The significant processes occurring during the electron impact induced fragmentation of these compounds may be typified as in Scheme 1. Apart from the cleavage of the benzothiazole nucleus in a characteristic manner[6] (process A) and fission of the

Table 1. Significant mass spectral data showing the principal ions in compounds 1–3

	m/z (% intensity)		
Ion	1	2	3
$[M]^{+\cdot}$	285 (50)	299 (91)	319/321 (20)
$[M-CH_3]^+$	270 (25)	284 (20)	304/306 (10)
$[M-C_2H_5]^+$	256 (25)	270 (8)	290/292 (18)
$[M-C_3H_6]^+$	243 (60)	257 (24)	277/279 (50)
a	242 (100)	256 (100)	276/278 (100)
b	229 (75)	243 (7)	263/265 (8)
c	228 (10)	242 (5)	262/264 (3)
d	215 (11)	229 (8)	249/251 (7)
e	187 (3)	201 (2)	221/223 (3)
f	150 (16)	164 (10)	184/186 (5)
g	134 (32)	148 (7)	168/170 (3)
h	108 (3)	122 (4)	142/144 (3)



Scheme 1

two heterocyclic moieties (process B) generating ions *h* and *g*, respectively, the intense molecular ion undergoes losses of methyl radical, ethyl radical and propene. The $[M - C_3H_6]^+$ ion loses a hydrogen yielding the base peak (*a*). The ion *a* also arises by the loss of ethylene from the $[M - CH_3]^+$ ion. There is loss of CH_3CN from the $[M—C_2H_5]^+$ ion generating ion *d*. The $[M—CH_3]^+$ ion also loses a moiety of 41 units (ion *b*). The elemental composition of this ion indicates that it arises by the loss of $C_3H_5^{\cdot}$ radical not CH_3CN.

All these processes are supported by an inspection of the mass spectra of other compounds which show analogous ions. These ions are arranged in Table 1 in such a way as to display the corespondence of the fragment ions.

EXPERIMENTAL

Compounds **1–3** were synthesized in about 60% yield by treating 6-substituted (or unsubstituted) 2-hydrazinobenzothiazoles,[7] with 3-butylpentane-2,4-dione[8] in refluxing ethanol containing a few drops of acetic acid. The compounds were crystallized from ethanol.

Compound 1. M.p. 89 °C Found: N, 14.40; $C_{16}H_{19}N_3S$ requires N, 14.73%. PMR ($CDCl_3$): 0.7–1.7 (m, 7H, $—CH_2CH_2CH_2CH_3$), 2.3 (s, 3H, pyrazol-3-CH_3), 2.45 (t, 2H, $—CH_2CH_2CH_2CH_3$), 2.75 (s, 3H, pyrazol-5-CH_3), 7.2–7.9 (m, 4H, aromatic protons).

Compound 2. M.p. 110 °C. Found: N, 13.98; $C_{17}H_{21}N_3S$ requires N, 14.04%. PMR ($CDCl_3$): 0.7–1.7 (m, 7H, $—CH_2CH_2CH_2CH_3$), 2.3 (s, 3H, pyrazol-3-CH_3), 2.40 (t, 2H, $—CH_2CH_2CH_2CH_3$), 2.50 (s, 3H, CH_3), 2.70 (s, 3H, pyrazol-5-CH_3), 7.3–7.9 (m, 3H, aromatic protons).

Compound 3. M.p.115 °C. Found: N, 12.85; $C_{16}H_{18}N_3SCl$ requires N, 13.16%. PMR ($CDCl_3$): 0.7–1.7 (m, 7H, $—CH_2CH_2CH_2CH_3$), 2.25 (s, 3H, pyrazol-3-CH_3), 2.45 (t, 2H, $—CH_2CH_2CH_2CH_3$), 2.75 (s, 3H, pyrazol-5-CH_3), 7.12–7.7 (m, 3H, aromatic protons).

Low-resolution mass spectra were obtained at 70 eV on a MS-12 mass spectrometer fitted with a direct inlet system (source temperature being kept at about 165° C). High-resolution measurements and linked scan data were recorded on a JEOL JMS-DX 300 mass spectrometer linked to a JEOL, JMA-3100 data system at 70 eV, ionizing current 300 μA, accelerating voltage 3.0 kV and ion source temperature 150 °C.

Acknowledgements

We are grateful to the UGC, New Delhi, India for providing financial assistance; the Chairman, Chemistry Department, Kurukshetra University, Kurukshetra for providing facilities and Dr. T. Marunaka, Taiho Pharmaceutical Co. Ltd, Japan for providing high-resolution and linked scan data.

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