

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230146248>

Flash-vacuum pyrolysis of 1-acylbenzotriazole: Direct observation of cyclopenta-2,4- dienylidenemethaneimines by tandem mass spectrometry and low-temperature infrared spectrometry

ARTICLE *in* JOURNAL OF MASS SPECTROMETRY · APRIL 1990

Impact Factor: 2.38 · DOI: 10.1002/oms.1210250404

CITATIONS

8

READS

21

5 AUTHORS, INCLUDING:



Beat Freiermuth

Solvias AG

13 PUBLICATIONS 514 CITATIONS

SEE PROFILE



Curt Wentrup

University of Queensland

576 PUBLICATIONS 6,483 CITATIONS

SEE PROFILE

Flash-vacuum Pyrolysis of 1-Acylbenzotriazole: Direct Observation of Cyclopenta-2,4-dienylidenemethaneimines by Tandem Mass Spectrometry and Low-temperature Infrared Spectrometry

André Maquestiau, Didier Beugnies and Robert Flammang

Organic Chemistry Laboratory, State University of Mons, B-7000 Mons, Belgium

Beat Freiermuth and Curt Wentrup

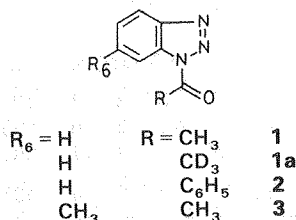
Department of Chemistry, University of Queensland, St. Lucia, Brisbane, Queensland, Australia 4067

A real-time analysis of the flash-vacuum pyrolysis products of 1-acetylbenzotriazole (1) and 1-benzoylbenzotriazole (2) was performed by tandem mass spectrometry. In the temperature range 500–600 °C, these compounds lose nitrogen, yielding *N*-acetyl- and *N*-benzoylcyclopenta-2,4-dienylidenemethaneimines (10 and 17, respectively). At higher pyrolysis temperatures, 1 gives 2-methylbenzoxazole, cyanocyclopentadiene, methylcyanocyclopentadiene(s), benzonitrile and ketene, which were identified by collision-activated dissociation mass spectrometry. Low-temperature infrared experiments confirmed the pyrolytic transformation 1(2) → 10(17) at mediated temperatures.

INTRODUCTION

The behaviour of benzotriazole derivatives on photolytic, pyrolytic or electron impact excitation has already received considerable attention. In particular, 1-substituted-1*H*-benzotriazoles pyrolyse or photolyse to give intermediate 1,3-diradicals which can interact with aromatic or unsaturated substituents to give cyclic and rearranged products. At moderate flash-vacuum pyrolysis (FVP) temperatures, vinylbenzotriazoles have been reported recently to give *N*-phenylketenimines.¹

The conversion of 1-acetylbenzotriazole (1) into 2-methylbenzoxazole (6) has not previously been observed under photolytic² or pyrolytic conditions³ (this process is now reported), but has been proposed for the corresponding molecular ions.⁴ Pyrolysis of 1-benzoylbenzotriazole (2) in a sealed tube at 350–400 °C affords 11% 2-phenylbenzoxazole,⁵ whereas photolysis yields, depending on the conditions, solvent hydrogen abstraction products⁶ or solvent condensation products.⁷ ¹³C-labelling experiments have been interpreted in terms of the formation of ionized 2-phenylbenzoxazole (15) together with ionized 6-phenanthridone (16) for the loss of nitrogen from the molecular ions of 2.⁸ The latter process is ruled out as a result of this study.

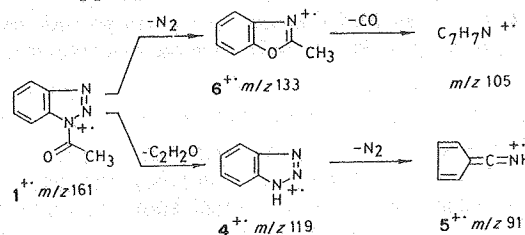


In this paper, we describe the behaviour of the benzotriazoles 1–3 when the pyrolysis is performed under low-pressure conditions (FVP), the structure of the products being monitored by real-time tandem mass spectrometric analysis and low-temperature infrared (IR) spectroscopy.

RESULTS AND DISCUSSION

Electron impact mass spectrum of 1-acetylbenzotriazole (1)

The 70 eV mass spectrum of 1 (Fig. 1) displays an intense fragment ion peak at *m/z* 43 [CH₃CO]⁺ and characteristic peaks at *m/z* 161 [M]⁺, *m/z* 133 [M – N₂]⁺, *m/z* 119 [M – C₂H₂O]⁺ and *m/z* 91 [M – C₂H₂O – N₂]⁺. Two competitive processes are thus occurring: a nitrogen loss yielding *m/z* 133 ions which decarbonylate into *m/z* 105 and a ketene loss giving the ionized parent benzotriazole [4]⁺. This last reaction is usually observed for ionized azolides.⁹ The sequence proposed in Scheme 1 is also supported by the mass spectrum of the labelled compound 1a where the appropriate shifts are observed.



Scheme 1

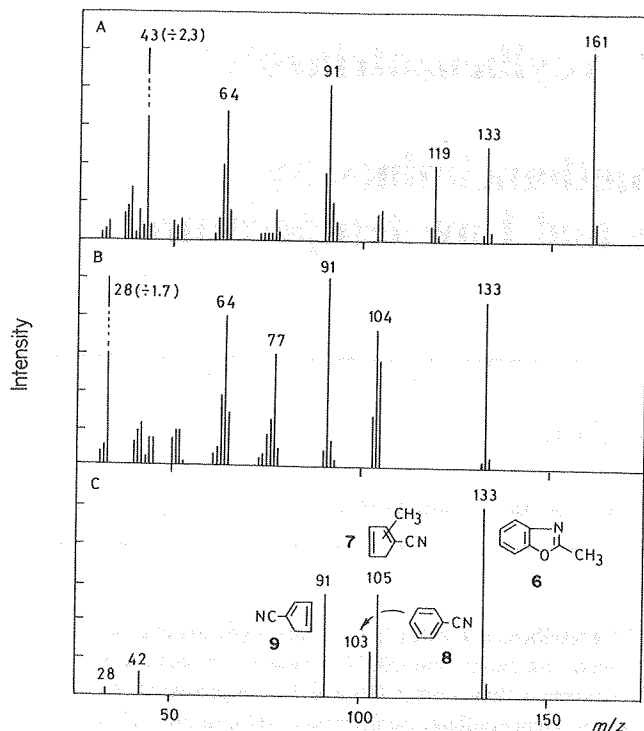


Figure 1. (A, B) Mass spectra (70 eV) of 1-acetylbenzotriazole (1) at 200 and 750 °C. (C) Mass spectrum (at 750 °C) recorded at 15 eV.

Metastable molecular ions of 1 behave similarly, losing competitively N_2 and $CH_2=C=O$; these two processes are characterized by very different kinetic energy releases, 512 meV ($T_{N_2}^{50}$) and 21 meV ($T_{C_2H_2O}^{50}$), respectively.

On the basis of a comparison with appropriate reference ions,¹⁰ the collision-activated dissociation (CAD) mass spectra indicate that the m/z 119 ions correspond to ionized benzotriazole $[4]^+$ ions which fragment to cyclopenta-2,4-dienylidenemethanimine ions $[5]^+$. Loss of nitrogen yields ionized 2-methylbenzoxazole $[6]^+$, in agreement with previous conclusions of Ohashi *et al.*⁴ which were based on an external reference method. Some minor differences, as the different m/z 78 to m/z 63 ratio (Table 1) or the smaller kinetic energy release (KER) during the decarbonylation indicate the probable coexistence of an isomeric, undefined structure. At a 10^4 resolving power, a significant loss of CO from the molecular ions, sometimes observed for ionized azolides,¹¹ is not detected; formation of isobaric ions is thus ruled out.

Flash-vacuum pyrolysis of 1-acetylbenzotriazole (1)

The pyrolysis starts at ~ 500 °C and appears to be complete at temperatures higher than 650 °C, as evidenced by the disappearance of the m/z 161 molecular ion peak (Fig. 1). At these temperatures, the CAD and Mass-analysed ion kinetic energy (MIKE) data (Table 1) indicate that the m/z 133 ions correspond to the molecular ions of 2-methylbenzoxazole (6). The complexity of the mass spectrum points, however, to the presence of other components in the pyrolysate which are easily localized at m/z 105, 103, 91, 42 and 28 by decreasing the ionizing electron energy to 15 eV. The CAD spectra of these ions readily permit their identification as methylcyanocyclopentadiene(s) (7), benzonitrile (8), cyanocyclopentadiene (9), together with ketene and nitrogen. In particular, the structural modification of the $C_6H_5N^{++}$ (m/z 91) ions is noticeable. The high-temperature spectrum matches exactly the CAD spectrum of the molecular ions of cyanocyclopentadiene (9), whereas at low temperature, the very different abundance ratios and an intense charge stripping (CS) peak indicate the formation of cyclopenta-2,4-dienyl idene-methanimine ions.¹² Compounds 7–9 are not the result of a consecutive pyrolysis of 6, as an authentic sample of 6 appears to be perfectly stable in this high temperature range.

The CAD spectrum of the molecular ions $[1]^{++}$ was also monitored during the pyrolysis; it remains completely unchanged, indicating the absence of ring opening to an iminodiazocompound, a process which has recently been described during the photolysis of benzotriazole in a matrix of alcoholic glass at 77 K.¹³

In a relatively narrow range of temperatures around 550 °C, it appears that the MIKE and CAD spectra of the m/z 133 ions are modified and present an intense peak at m/z 118 (loss of CH_3) (Fig. 2). Other characteristic signals are also seen at m/z 90 (loss of 43 daltons) and m/z 43 ($[CH_3C=O]^+$). Moderate temperature FVP of 1 thus induces a loss of nitrogen with the formation of an intermediate bearing an acetyl group. Single metastable ion monitoring¹⁴ allows an accurate determination of the optimum temperature for the observation of this new intermediate. Thus, the intensity of the metastable peak for the m/z 133 \rightarrow m/z 118 fragmentation within the third field-free region of an E/B/E spectrometer shows a maximum at a pyrolysis temperature of ~ 575 °C; a similar behaviour is noted for the m/z 90 fragment ion.

All these experimental data support the mechanism depicted in Scheme 2: nitrogen loss produces an imin-

Table 1. CAD and MIKE spectra (values in parentheses) of the m/z 133 ions from 1 and 6 and kinetic energy releases (meV) associated with the major unimolecular fragmentation

Compound	<i>T</i> (°C)	<i>m/z</i> :	Collision-induced (unimolecular) fragmentations											Kinetic energy releases				
			118	105	93	92	91	90	78	64	63	51	43	41	39	<i>T</i> _{CO}	<i>T</i> _{C₂H₂N}	<i>T</i> _{C₂H₂}
1	200		<1 (—)	100 (100)	29 (22)	18	15 (10)	—	14	16	13	6	3	2	4	397	29	52
	575		89 (14)	100 (100)	28 (21)	21	25 (15)	21	17	24	22	7	11	2	5	389	34	42
	650		1 (4)	100 (100)	27 (22)	20	19 (10)	—	17	25	22	6	4	2	5	380	38	45
6	200		<1 (—)	100 (100)	25 (26)	21	18 (9)	—	16	23	22	7	3	2	4	381	29	47

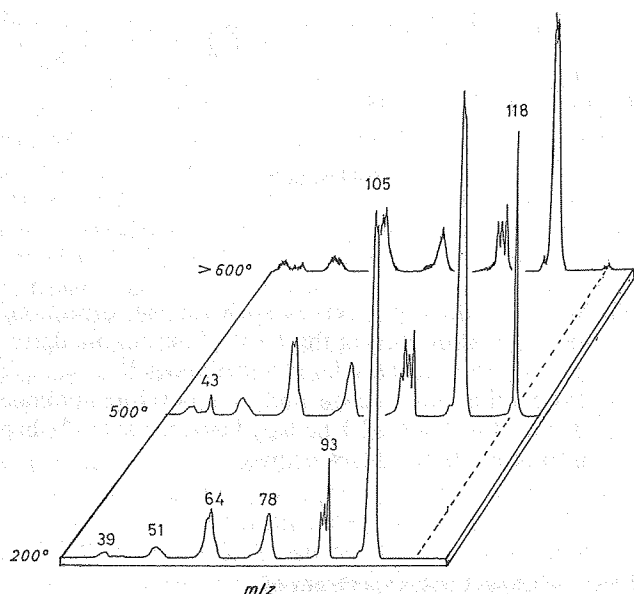
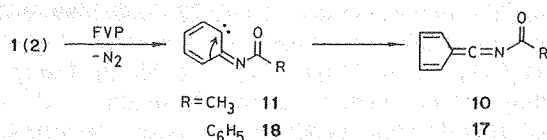


Figure 2. Evolution of the CAD spectrum of m/z 133 ions observed in the mass spectrum of **1** during FVP.



Scheme 2

ocarbene intermediate which undergoes a Wolff-type ring contraction into *N*-acetylcyclopenta-2,4-dien-1-imine (**10**). After ionization, $[\mathbf{10}]^{++}$ undergoes a methyl loss, producing m/z 118 ions. The MIKE (and also CAD) spectrum of these fragment ions is largely dominated by one intense fragmentation consisting, as expected, in a CO loss (m/z 90).

Consecutive pyrolysis with two separate furnaces seems to indicate that this fulvene **10** decomposes at temperatures $>600^\circ\text{C}$ into cyclopentadiene, but ketene could not be unambiguously detected in the mass spectrum. Indeed, if the temperature of the first oven is fixed at 575°C , an increase in the temperature of the second oven from 200 to 800°C modifies the abundance ratio m/z 133/91/42 from 85:100:4 to 58:100:4. Radical formation therefore appears to be the preferred decomposition pathway (see below). Moreover, combined with the previous observations of Wiersum,³ these results seem to indicate that benzoxazole cyclization does not compete with the ring contraction reaction at mediated temperatures.

Low-temperature infrared spectroscopy of **1**

The pyrolysis of **1** at 550 – 620°C with isolation of the products on a KBr window at 77 K gives rise to new species with absorptions at 2253, 2217 and 2088 cm^{-1} . At a pyrolysis temperature of 700°C a further strong band at 2128 cm^{-1} is observed. The absorption in the 2080 cm^{-1} region decreases in intensity and shifts its

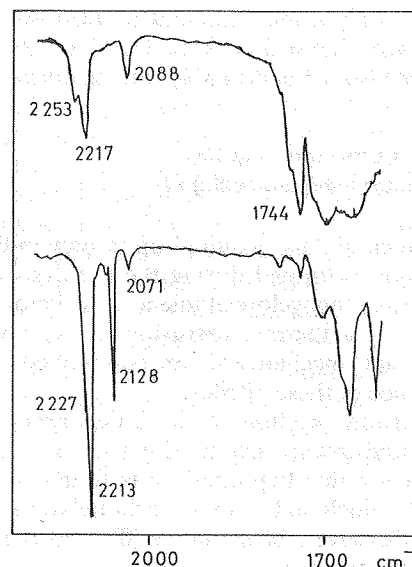


Figure 3. Low-temperature IR spectra recorded at -196°C after pyrolysis of **1** at 560 – 620°C (top) and 700°C (bottom).

maximum to 2071 cm^{-1} . The 2253 cm^{-1} band disappears completely (Fig. 3). On warming, absorptions at 2071 and 2128 cm^{-1} disappear at -40 to -30°C . Assuming that the band in the 2080 cm^{-1} region belongs to a species such as **10** and the 2217 cm^{-1} to cyanocyclopentadiene (**9**) and methylcyanocyclopentadienes (**7**), the IR data support the observations from MIKE and CAD spectra. The 2128 cm^{-1} band is attributed to ketene and the shoulder at 2227 cm^{-1} to benzonitrile.

Ketene was also identified by isolation in an argon matrix at 14 K. ν_{CH} was observed at 3063 cm^{-1} and ν_{CCO} at 2142 cm^{-1} , in agreement with literature values.¹⁵ Compounds **6**, **9** and **10** were identified by gas chromatography (GC), GC/mass spectrometry (GC/MS) and ^1H NMR spectroscopy of the products of preparative pyrolyses (see below).

Preparative pyrolysis of **1**

1-Acetylbenzotriazole (**1**) was pyrolysed at 700°C and the products were first condensed on a liquid nitrogen cold finger and then dissolved in chloroform. The GC analysis of the solution showed only five major products; their yield was measured by their flame-ionization detector signal integral: cyanocyclopentadiene (**9**) (21%), three isomers of methylcyanocyclopentadiene (**7**) (43%), 2-methylbenzoxazole (**6**) (24%) and starting material **1** (12%). Compounds **6**, **7**, **8** and **9** were identified by comparison with authentic samples using GC/MS and ^1H NMR spectroscopy. At 620°C , where most of the starting material passed through the oven unreacted, only **6** was detected. However, at pyrolysis temperatures of 800 and 700°C the ratios of the products were similar, with the exception of benzonitrile, which was produced in 5% yield at 800°C but only in a trace amount at 700°C . These results agree well with those obtained by mass and IR spectroscopy, but conflict with the observations of Wiersum,³ who did not report any of the compounds that we found.

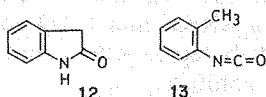
At 700 °C, only a small amount of unsubstituted benzotriazole was obtained (1–2%). This indicates that the loss of ketene from **1** is probably not significant.

Mechanism of formation of the methylcyanocyclopentadiene(s) (7)

The experimental data acquired up to now indicate that the m/z 105 ions formed during the pyrolysis of **1** have the methylcyanocyclopentadiene structure, thus resulting from a thermal extrusion of $N_2 + CO$. Two 'intramolecular' mechanisms can be invoked to explain the occurrence of these nitriles:

- (i) An insertion reaction of the iminocarbene **11** into the methyl group, giving rise to the oxindole **12**; support for this hypothesis was found in the literature,¹⁶ which indicates decarbonylation of **12** on FVP. Moreover, benzonitrile (**8**) is also formed at elevated temperatures.
- (ii) Methyl migration from the acetyl group to the benzene ring, forming o-tolyl isocyanate (**13**); consecutive decarbonylation should produce a tolyl nitrene, potential precursor¹⁷ of methyl cyanocyclopentadiene(s).

It appears, however, that authentic samples of **12** and **13** remain completely unchanged when submitted to FVP at temperatures appropriate to pyrolyse **1**. An 'intermolecular' mechanism therefore seems more likely and is supported by the following experimental data:



- (i) The 15 eV mass spectrum of the labelled triazole **1a** pyrolysed at 650 °C (Fig. 4) shows the expected peaks at m/z 136, 108, 92, but also an intense signal at m/z 91 corresponding (CAD spectrum) to unlabelled cyanocyclopentadiene. This can be explained by the participation of a homolytic cleavage of **10a** (Scheme 3) giving cyanocyclopentadienyl radicals (**14**) which recombine with hydrogen atoms by collision with the reactor walls. Decarbonylation of the associated acetyl radicals produces $\cdot CD_3$ which also recombines with **14** to produce methyl- d_3 -cyanocyclopentadiene(s).
- (ii) The co-pyrolysis of a mixture of two differently labelled compounds **1a** and **3** confirms this conclusion. The increased intensity of the m/z 105 peak combined with the appearance of a new peak at m/z 122 support the radical mechanism (Fig. 4).

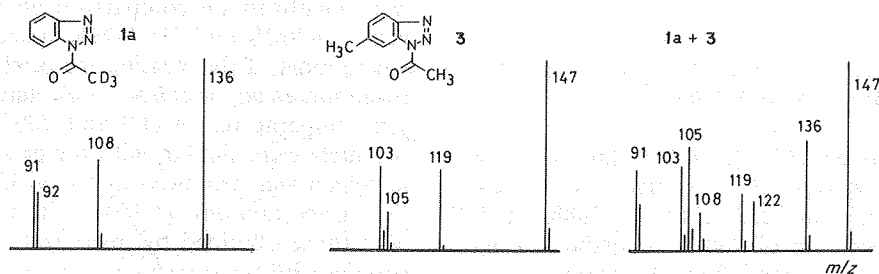
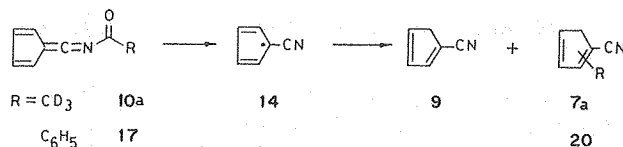


Figure 4. Mass spectra (15 eV) recorded at an oven temperature of 650 °C of **1a**, **3** and a mixture of **1a** and **3**.



Scheme 3

- (iii) We have already observed such radical formation/recombination during the FVP of oxazolone derivatives into *N*-carbonylated ketenimines.¹⁸
- (iv) Production of benzene and cyanocyclopentadiene during the FVP of 1-benzoylbenzotriazole (**2**) has also been observed (see below).

Electron impact mass spectrum of 1-benzoylbenzotriazole (**2**)

Our 70 eV EI mass spectrum of 1-benzoylbenzotriazole (**2**) agrees well with that described in the literature,⁸ displaying the molecular ion at m/z 223 and intense fragment ion peaks at m/z 195 (loss of N_2), 105 ($[C_6H_5CO]^+$) and 77 ($[C_6H_5]^+$) (Table 2). Using ^{13}C labelling at the carbonyl group, Yamada *et al.*⁸ concluded that N_2 loss produces a mixture of ionized 2-phenylbenzoxazole (**15**) and phenanthridone (**16**). We therefore compared the MIKE and CAD spectra of these various $[C_{13}H_9NO]^{++}$ ions (Table 2). The CAD spectrum of the $[M - N_2]^{++}$ ions of **2** is similar to that of the molecular ions of 2-phenylbenzoxazole (**15**) except for the peaks due to unimolecular fragmentation, which are of lower abundance when the ions are generated by direct ionization. The phenanthridone molecular ions display a very different CAD spectrum with a base peak at m/z 139; moreover, the KER for the CO loss is significantly lower (420 meV). These features thus exclude the possibility of the formation of phenanthridone ions by dissociative ionization of **2**; the occurrence of a mixture of $[15]^{++}$ and $[16]^{++}$ would indeed produce an intermediate T_{CO} value. It therefore seems more likely that $[2]^{++}$ loses N_2 to give mainly $[15]^{++}$ and a small amount of isomeric ions capable of losing CO with a comparable large KER value. A possible candidate in *N*-benzoylcyclopenta-2,4-dienylidene-methanimine ions $[17]^{++}$, as suggested by the slight intensity increase of the m/z 118 peak compared with $[2]^{++}$.

Flash-vacuum pyrolysis of 1-benzoylbenzotriazole (2)

Loss of nitrogen is also the predominant pyrolysis process of 2, as shown by the decrease of the m/z 223 peak and the increase in m/z 195 (Table 2). The CAD spectrum is not substantially modified during the temperature increase but one notes the persistence of peaks at m/z 105 ($[\text{C}_6\text{H}_5\text{CO}]^+$), 118 (loss of C_6H_5^+) and 90 (loss of $\text{C}_6\text{H}_5\text{CO}^+$) (Table 3), indicating the presence of the benzoyl group in the new m/z 195 ions. By analogy with the preceding case, we therefore propose (Scheme 2) the formation of *N*-benzoylcyclopenta-2,4-dienylidenemethanimine (17) by a Wolff-type ring contraction of the initially formed iminocarbene 18. Although the pyrolysis device used in this experiment has a limited temperature range, it has been possible to confirm the formation of 2-phenylbenzoxazole (15) at higher temperatures through the evolution of the CAD and KER data (Table 3). Moreover, in a separate preparative pyrolysis experiment at 750°C (50 cm \times 1 cm i.d. quartz tube, 0.2 Torr (1 Torr = 133.3 Pa)), 15 has been isolated with a 32% yield, thus confirming previous observations of Wiersum.³

The new peaks observed at m/z 91 and 78 in the mass spectrum are also noteworthy. Their CAD spectra indicate the cyanocyclopentadiene (9) and benzene struc-

tures, respectively. This confirms the homolytic fragmentation of 17 into radicals 14 and benzoyl radicals which decarbonylate readily (Scheme 3) (biphenyl was identified as a product of the preparative pyrolysis of 2). Recombination reactions followed by ionization then gives rise to the m/z 78, 91 and perhaps partly the 167 ions. Table 4 compares the CAD spectra of these m/z 167 ions with the $[\text{M} - \text{CO}]^{++}$ ions of 15 and the $[\text{M} - 2\text{CO}]^{++}$ generated by dissociative ionization of 5-phenylisatin (19). This last compound has been shown to be the precursor of phenylcyanocyclopentadiene(s) (10) on FVP;¹⁹ unfortunately, our pyrolysis conditions are too mild to pyrolyse this compound. The data seem to indicate that dissociation of $[\text{19}]^{++}$ produces a cyclopentadienylidenemethanimine structure, but more detailed experiments are required to elucidate the actual structures.

Low-temperature infrared spectroscopy of 2

With 1-benzoylbenzotriazole (2), the formation of pyrolysis products sets in at $\sim 500^\circ\text{C}$. At this temperature, weak product absorptions at 2052 and 2216 cm^{-1} have about the same intensity. On increasing the temperature, the 2216 cm^{-1} signal grows and the band at

Table 2 Mass spectra (70 eV) of *N*-benzoylbenzotriazole (2) and 2-phenylbenzoxazole (15)

Compound	<i>T</i> (°C)	<i>m/z</i> :	Relative abundance																
			224	223	196	195	167	105	92	91	90	78	77	64	63	51	50	40	28
2	200		10	42	12	58	10	100	10	0	6	8	80	12	10	31	13	11	9
	750		1	9	12	100	17	57	13	31	11	53	55	27	18	43	7	13	186
15	200		0	0	3	100	13	10	0	7	0	0	6	5	6	4	0	12	13

Table 3. Collisional activation spectra of $[\text{C}_{13}\text{H}_9\text{NO}]^{++}$ ions (m/z 195) produced from *N*-benzoylbenzotriazole (2), 2-phenylbenzoxazole (15) and 6-phenanthridone (16)

Precursor	T ($^\circ\text{C}$)	m/z :	Relative abundances of the fragments											T_{CO}^a (meV)
			167	154	140/139	128	118	105/103	92	90	77	63	51	
2	200		387	6	100	11	19	48	73	21	62	54	0	593
	500		358	6	100	12	21	40	68	22	66	61	10	609
	700		358	10	100	12	22	22	43	18	43	34	6	538
	800		355	5	100	13	22	31	54	19	56	50	8	598
15	200		345	6	100	13	22	28	66	22	69	62	9	594
16	200		262	17	100	15	21	10	10	13	14	13	3	419

^a The KER values, for the unimolecular loss of CO, were measured by HV scan (BE mass spectrometer with air collision gas).

Table 4. Collisional activation spectra of $[\text{C}_{12}\text{H}_9\text{N}]^{++}$ ions (m/z 167) produced from *N*-benzoylbenzotriazole (2), 2-phenylbenzoxazole (15) and 5-phenylisatin (19)

Precursor	T (°C)	m/z :	Relative abundances of the fragments							T_{HCN} (meV)	
			140	126	115	103	89	77	63		50
2	200		213	16	29	29	22	100	76	14	122
	500		282	21	36	34	25	100	74	12	128
	600		325	23	43	34	30	100	78	13	129
	700		367	24	47	33	30	100	76	13	133
	800		355	23	46	34	29	100	76	14	125
15	200		175	12	21	31	19	100	68	10	126
19	200		875	36	96	53	53	100	82	20	70

2052 cm^{-1} is no longer visible at 640°C when almost all starting material is pyrolysed.

On warming, the absorption band at 2052 cm^{-1} disappears between -50 and -40°C and the band at 2216 cm^{-1} shifts to 2212 cm^{-1} at room temperature. Rinsing the cold trap with chloroform gives a solution with absorption band at 2214 cm^{-1} . This observed IR frequency corresponds well with the value of 2215 cm^{-1} in CCl_4 previously found for cyanocyclopentadiene (9).²⁰

CONCLUSION

FVP of *N*-carbonylated benzotriazoles proceeds by two competitive reaction pathways initiated by a common nitrogen loss: a Wolff-type ring contraction reaction producing *N*-carbonylated cyclopentadienylidenemethanimines and a cyclization reaction giving 2-substituted benzoxazoles. The degree of competition between these two channels depends strongly on the temperature conditions indicating a lower activation energy and/or a lower frequency factor for the first process. Evidence is also presented for the occurrence of homolytic consecutive dissociations of the cyclopentadienylidenemethanimines. These results were inferred from a tandem mass spectrometric real-time analysis of the FVP products and from a low-temperature IR study.

Dissociative ionization of these benzotriazoles mainly produces the molecular ions of the corresponding benzoxazoles. The previously proposed formation of ionized phenanthridone for $[\text{M} - \text{N}_2]^+$ ions of 2 is ruled out on the basis of KER measurements and CAD spectra.

EXPERIMENTAL

The mass spectra were recorded on two instruments, depending on the volatility of the samples: (i) a triple sector E/B/E spectrometer, a modified AEI MS 902²¹ (8 kV accelerating voltage, 100–500 μA trap current, 70 eV electron energy) using helium as the collision gas in the third field-free region for the CAD spectra and (ii) a reversed geometry B/E Varian-MAT 311 A spectrom-

eter (3 kV, 1 mA, 70 eV) using air as the collision gas in the second field-free region.

Samples were pyrolysed within an external furnace consisting of a 25 cm \times 1 cm i.d. quartz tube connecting the ion source to an all-glass heated inlet system (E/B/E spectrometer). An 'internal' furnace (10 cm \times 1 cm i.d. quartz tube) located near the electron gun on the ion source (\sim 2 cm) was used on the B/E spectrometer.

Pyrolyses for IR observation were carried out in a quartz tube of i.d. 1 cm, hot zone length 10 cm, pumped at 5×10^{-4} Torr and the products were collected on a liquid nitrogen-cooled KBr disk. The spectra were recorded with a Perkin-Elmer 1720-X spectrometer.

The preparative pyrolysis was done under similar conditions, in a 25 \times 2 cm i.d. quartz tube pumped at $\sim 10^{-3}$ Torr. The products were trapped on a liquid nitrogen cold finger and collected by rinsing with chloroform when the finger was still at low temperature. The reaction mixture was analysed by GC/MS. Cyanocyclopentadiene,²⁰ benzonitrile and 2-methylbenzoxazole were identified by comparison with authentic samples. The three isomers of methylcyanocyclopentadiene could be easily detected by their characteristic ^1H NMR spectra²⁰ and by virtually identical mass spectrometric fragmentation patterns for three consecutive peaks in the GC/MS run.

Most of the samples were commercially available (4, 6, 8, 12, 13) or prepared following literature procedures: 1-acetylbenzotriazole (1),²² 1-benzoylbenzotriazole (2),²² 6-phenanthridone (16),²³ 5-phenylisatin (19).²⁴ 2-Phenylbenzoxazole (15) was prepared by FVP of 2: 3 g of 2 were sublimed through an electrically heated (750°C) quartz tube (40 cm \times 1 cm i.d.) and connected to a liquid nitrogen cooling trap. The pyrolysate, purified by alumina column chromatography (elution with benzene), affords 15, m.p. 104–105°C (lit.²⁴ m.p. 101°C) with a 32% yield. Acetylation of 5-methylbenzotriazole (21) yields a mixture (by NMR) of 5- and 6-methyl-1-acetylbenzotriazoles (22 and 3). Fractional crystallization (benzene/light petroleum) allows the isolation of pure 6-methyl-1-acetylbenzotriazole (3), m.p. 91°C; NMR, $\text{H}_4 = 7.95$ ppm ($J_{4,5} = 9$ Hz); $\text{H}_5 = 7.15$ ppm ($J_{4,5} = 9$ Hz; $J_{5,7} = 2$ Hz); $\text{H}_7 = 7.7$ ppm.

Acknowledgement

We thank the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture for the award of a fellowship (to D.B.), and the Australian Research Council for support.

REFERENCES

1. A. Maquestiau, D. Beugnies, R. Flammang, A. R. Katritzky, M. Soleiman, T. Davis and J. N. Lam, *J. Chem. Soc., Perkin Trans. 2*, 1071 (1988), and references cited therein.
2. H. Meier and I. Menzel, *Justus Liebigs Ann. Chem.* **739**, 56 (1970).
3. U. E. Wiersum, *Recl. Trav. Chim. Pays-Bas* **101**, 365 (1982).
4. M. Ohashi, K. Tsujimoto, A. Yoshino and T. Yonezawa, *Org. Mass Spectrom.* **4**, 203 (1970).
5. J. Druliner, *J. Am. Chem. Soc.* **90**, 6879 (1968).
6. K. Tsujimoto, M. Ohashi and T. Yonezawa, *Bull. Chem. Soc. Jpn.* **45**, 515 (1972).
7. M. Ohashi, K. Tsujimoto and T. Yonezawa, *J. Chem. Soc., Chem. Commun.* 1089 (1970).
8. S. Yamada, Y. Kamiyama and M. Ohashi, *Org. Mass Spectrom.* **15**, 1 (1980).
9. A. Maquestiau, Y. Van Haverbeke, R. Flammang, R. M. Claramunt and J. Elguero, *Bull. Soc. Chim. Fr.* 2693 (1975).
10. A. Maquestiau, Y. Van Haverbeke, R. Flammang, A. Menu and C. Wentrup, *Org. Mass Spectrom.* **13**, 518 (1978).
11. A. Maquestiau, A. Tommasetti, C. Pedregal-Freire, J. Elguero and R. Flammang, *Bull. Soc. Chim. Belg.* **93**, 1057 (1984).

12. A. Maquestiau, Y. Van Haverbeke, R. Flammang, A. Menu and C. Wentrup, *Org. Mass Spectrom.* **13**, 518 (1978).
13. H. Shizuka, H. Hiratsuka, M. Jinguji and H. Hiraoka, *J. Phys. Chem.* **91**, 1793 (1987).
14. R. W. Kondrat, G. A. McLuckey and R. G. Cooks, *Anal. Chem.* **50**, 2017 (1978).
15. C. B. Moore and B. C. Pimentel, *J. Chem. Phys.* **38**, 2816 (1963).
16. R. F. C. Brown and M. Butcher, *Aust. J. Chem.* **25**, 149 (1970).
17. R. F. C. Brown (Ed.), *Pyrolytic Methods in Organic Chemistry*, Chap. 5. Academic, New York (1980).
18. C. Wentrup and W. Reichen, *Helv. Chim. Acta* **50**, 2615 (1976).
19. C. Wentrup, in R. A. Abramovitch (Ed.), *Reactive Intermediates* Vol. 1, p. 303. Plenum, New York (1980).
20. C. Wentrup and W. D. Crown, *Tetrahedron* **26**, 3965 (1970); **26**, 4375 (1970); **27**, 880 (1971).
21. A. Maquestiau, Y. Van Haverbeke, R. Flammang, M. Abrassart and D. Finet, *Bull. Soc. Chim. Belg.* **87**, 765 (1978).
22. H. A. Staab, *Chem. Ber.* **90**, 1320 (1957).
23. H. Meyer and A. Hofman, *Monatsh. Chem.* **37**, 681 (1916).
24. L. C. Galatis, *J. Am. Chem. Soc.* **70**, 1967 (1948).