

## Flash-vacuum Pyrolysis of *N*-Vinylbenzotriazoles: Formation of *N*-Phenylketenimines

Andre Maquestiau,\* Didier Beugnies, and Robert Flammang

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

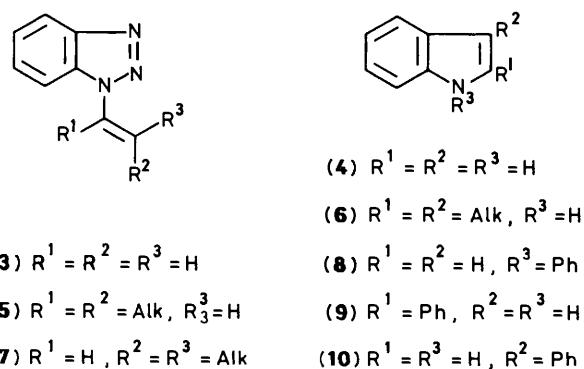
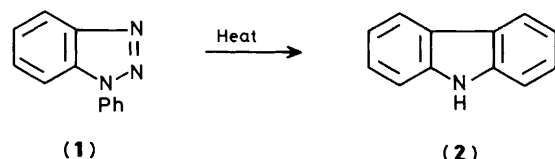
Alan R. Katritzky,\* Mohammed Soleiman, Terry Davis, and Jamshed N. Lam

Department of Chemistry, University of Florida, Gainesville, FL 32611, USA

A real-time analysis of the flash-vacuum pyrolysis products of 1-vinyl-, 1-(2-methylprop-1-enyl)-, and 1-styryl-benzotriazole (**3**), (**16**), and (**18**) has been performed by tandem mass spectrometry. In the 500–700 °C temperature range, these compounds lose nitrogen yielding the *N*-phenylketenimines (**14**), (**17**), and (**19**), respectively. At higher pyrolysis temperatures (**3**) gives indole (**4**) *via* isomerization of (**14**), whereas from (**16**) the secondary products of (**17**) are benzene and methacrylonitrile. In a preparative pyrolysis of (**18**) at 800 °C 2- and 3-phenylindole (**9**) and (**10**) respectively, have also been detected.

The behaviour of benzotriazole derivatives under photolytic or pyrolytic conditions has already received considerable attention.<sup>1</sup> In particular, 1-substituted-1*H*-benzotriazoles pyrolyse to give intermediate 1,3-diradicals which can interact with aromatic or unsaturated substituents to give cyclic and rearranged products.<sup>2</sup> One example of such reactions is the well-known Graebe–Ullmann synthesis<sup>3</sup> of carbazole (**2**) from 1-phenylbenzotriazole (**1**), which can also be performed in the gas phase by flash-vacuum pyrolysis (FVP).<sup>4a</sup> Recently, this synthesis has been extended to 4*aH*-carbazoles.<sup>4b</sup>

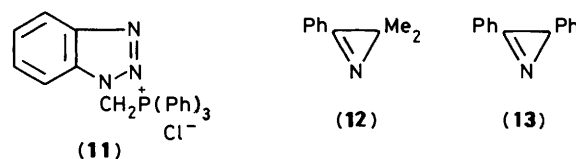
During the course of the present work, Wender and Cooper<sup>5a</sup> found that photolysis of 1-alkenylbenzotriazoles (**5**) provides a practical synthesis for indoles (**6**); some examples had been reported earlier.<sup>5b</sup> It has also been briefly reported that 1-vinylbenzotriazole (**3**) is converted into indole (**4**) under FVP conditions at 700 °C.<sup>6</sup>



Recently, an efficient synthesis of 1-(alk-1-enyl)benzotriazoles of general formula (7) has been developed based on a Wittig condensation of (1-benzotriazolylmethyl)triphenylphosphonium chloride (**11**) with various aldehydes or ketones.<sup>7</sup>

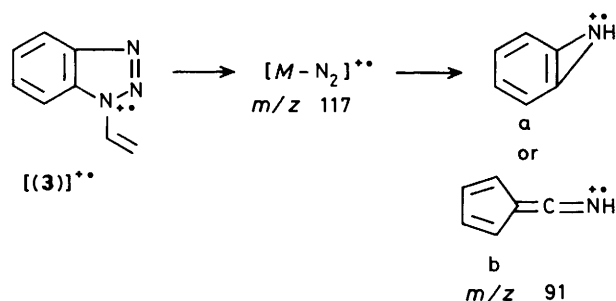
In this paper, we describe the unexpected behaviour of these benzotriazoles (**7**) when the pyrolysis is performed under very low pressure conditions (FVP), the structure of the products

being monitored by real-time tandem mass spectrometry<sup>8</sup> analysis.



### Results and Discussion

Our 70 eV electron impact mass spectrum of 1-vinylbenzotriazole (**3**) agrees well with that described in the literature,<sup>5</sup> displaying the molecular ion at  $m/z$  145 and intense fragment ion peaks at  $m/z$  117 (loss of nitrogen),  $m/z$  91 (consecutive losses of  $N_2$  and  $C_2H_2$ ),  $m/z$  90 (losses of  $N_2$  and HCN), and  $m/z$  89 (losses of  $N_2$ , HCN, and  $H^{\bullet}$  in sequence). Collisional activation (c.a.) of the ion of  $m/z$  91 shows that its structure is identical with the  $[M - N_2]^{++}$  ion derived from the parent benzotriazole for which a benzazirene structure (a) or (more likely) an *N*-cyclopenta-2,4-dienemethylenimine structure (b) have been proposed previously (Scheme 1).<sup>9</sup>



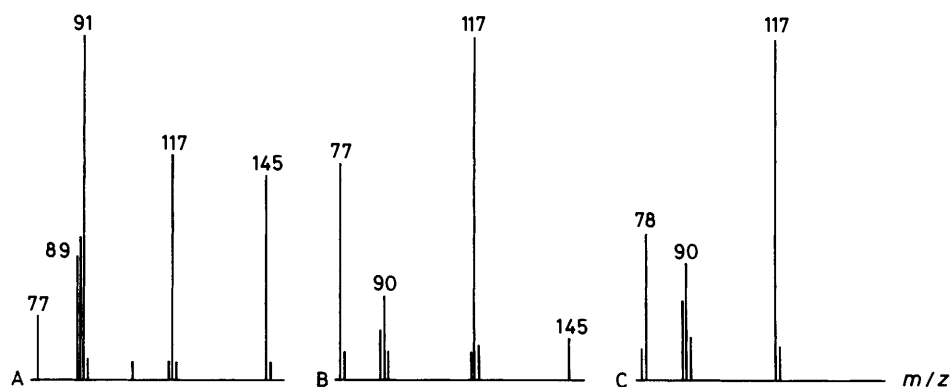
Scheme 1.

The FVP pyrolysis of (**3**) was monitored by conventional mass spectrometry (Figure 1). At 600 °C transformation of (**3**) is almost complete and the intensities of the  $m/z$  145 and 91 peaks are considerably reduced with respect to the  $m/z$  117 and 77 signals. At higher temperatures (1 000 °C), the major changes are the decreased intensity of  $m/z$  77 and the appearance of a new signal at  $m/z$  78.

That different  $[C_8H_7N]^{++}$  ions are formed at different temperatures is clearly established by the c.a. spectra reported in

**Table 1.** Collisional activation spectra of  $[\text{C}_8\text{H}_7\text{N}]^{++}$  ions ( $m/z$  117) produced from 1-vinylbenzotriazole (3), indole (4), and  $\alpha$ -azidostyrene (15). Abundances relative to the base peak except  $m/z$  90 (unimolecular fragmentation). The losses of hydrogens are not included (E/B/E mass spectrometer)

$T(^{\circ}\text{C})$	Relative abundances of the fragment ions															
	$m/z$ 103	102	91	[90]	89	77	76	75	63	51	50	41	39	38	27	
(3)	200	<1	1	83	271	24	100	5	3	7	9	6	1	2	2	1
	650	10	3		98	75	100	14	6	16	19	10	1	5	3	1
	1 000	1	2		292	100	4	4	4	19	8	7	1	6	3	2
(4)	200	1	1		227	100	4	5	5	19	9	8	1	7	3	2
	200	8	2		106	64	100	12	5	16	20	10	1	6	3	1
	650	6	1		214	74	100	6	5	16	16	9	2	5	3	1
(15)	650	6	1		214	74	100	6	5	16	16	9	2	5	3	1
	1 000	2	1		372	100	9	5	4	19	9	7	1	6	3	1



**Figure 1.** Mass spectra (region  $m/z$  75–150) of 1-vinylbenzotriazole (3) at 200 °C (A) and after low-pressure pyrolysis at 600 °C (B) and 1 000 °C (C) (E/B/E mass spectrometer)

Table 1. The most significant modifications of the c.a. spectra going from 200–650 °C are:

- (i) the appearance of a loss of 14 daltons characteristic of ions containing a terminal methylene group;
- (ii) the complete disappearance of the peak at  $m/z$  91;
- (iii) the reduced intensity of the peak at  $m/z$  90 which corresponds to fragment ions already observed without the collision gas (unimolecular fragmentation).

Increasing the furnace temperature up to 1 000 °C completely changes the c.a. spectrum which is now completely superimposable on the c.a. spectrum of the molecule ion of indole (4).

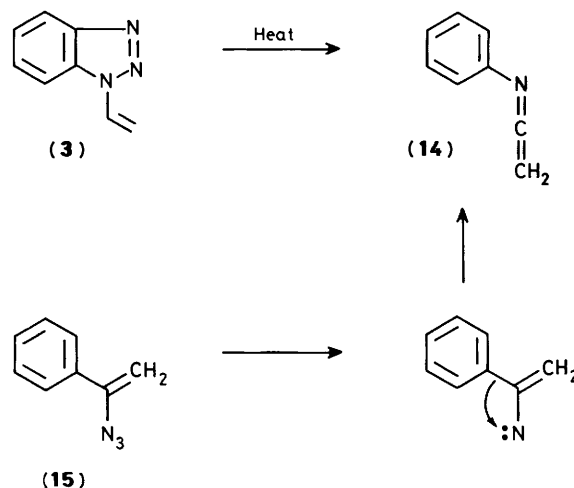
The presence of an intense peak at  $m/z$  77 ( $\text{C}_6\text{H}_5^+$ ) in the spectrum recorded at 650 °C and the characteristic loss of  $\text{CH}_2$  suggest that the first compound formed in the pyrolysis of (3) is *N*-phenylketenimine (14) which, under more drastic conditions, is isomerized into the indole (4). This sequence of events is supported by the following observations:

- (i) ionized  $\alpha$ -azidostyrene (15) shows a very strong peak at  $m/z$  117 in its mass spectrum; the c.a. spectra of these ions with or without pyrolysis is quite comparable to the spectra of the analogous ions of (3) after pyrolysis at 650 °C. The thermal conversion of vinyl azides into ketenimines has been previously reported;<sup>10,11</sup> the nitrene is formed from the azide function *via* a 1,2-shift with the elimination of nitrogen (*cf.* Scheme 2). The spectral analogy between  $[(3) - \text{N}_2]^{++}$  and  $[(15) - \text{N}_2]^{++}$  thus supports the formation of the ketenimine (14) at moderate pyrolysis temperatures.

- (ii) Formation of indole (4) from (14) at high temperatures is also evident from the c.a. data and thus suggests that its appearance during the pyrolysis of (3) is the result of a consecutive (not competitive) reaction.

- (iii) Finally, in the case of the homologous 1-(2-methylprop-1-enyl)benzotriazole (16), direct comparison with an authentic sample of dimethyl *N*-phenylketenimine (17) proves the

formation of the iminocumulenes by pyrolytic nitrogen elimination from benzotriazoles (*vide infra*).



**Scheme 2.**

The mass spectrum of (3) and the c.a. spectrum of the  $m/z$  117 ions (at 200 °C) are noteworthy in that the sequence  $m/z$  117–91 (loss of  $\text{C}_2\text{H}_2$ ) is observed only in this particular case. We tentatively propose that the molecular ion of (3) undergoes nitrogen elimination to give the *N*-cyclohexadienyldienevinylamine cation (c) which (just as for its neutral counterpart<sup>12</sup>) undergoes a Wolff-type ring contraction into ion (d) (Scheme 3). This type of reaction has already been proposed for ionized  $\alpha$ -iminocarbenes.<sup>13</sup> The unusually high  $m/z$  77:51 ratio (100:9) may indicate that the  $\text{C}_6\text{H}_5^+$  ions are isomers of the phenyl ions.

**Table 2.** Collisional activation spectra of  $[C_{10}H_{11}N]^{++}$  ions ( $m/z$  145) produced from 1-(2-methylprop-1-enyl)benzotriazole (16), dimethyl *N*-phenylketenimine (17), and 2,2-dimethyl-3-phenyl-2*H*-azirene (12)

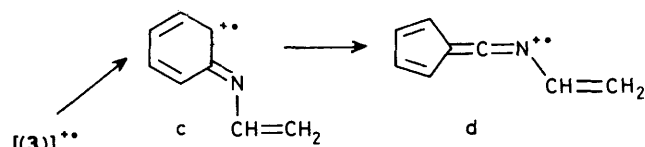
	$T(^{\circ}C)$	Relative abundances of the fragment ions*											
		$m/z$ 130	115/7	104	91	89	77	68	63	51	41	39	27
(12)	260	16	18	[1 160]		29	$\frac{100}{100}$	8	28	36	91	46	16
(16)	265	[465]	14	55	15		$\frac{100}{100}$	3	7	27	15	8	3
	570	[102]	7	40	7		$\frac{100}{100}$	2	5	21	9	6	3
(17)	270	86	4	34	5		$\frac{100}{100}$	2	5	18	7	4	2

\* Abundances relative to the base peaks except those (within brackets) associated with unimolecular fragmentations (B/E mass spectrometer).

**Table 3.** Collisional activation spectra of  $[C_{14}H_{11}N]^{++}$  ions ( $m/z$  193) produced from 1-styrylbenzotriazole (18), 1,3-diphenylketenimine (19), phenylindoles (8), (9), (10), and 2,3-diphenyl-2*H*-azirene (13). Abundances relative to the base peak except  $m/z$  166 (unimolecular fragmentations)

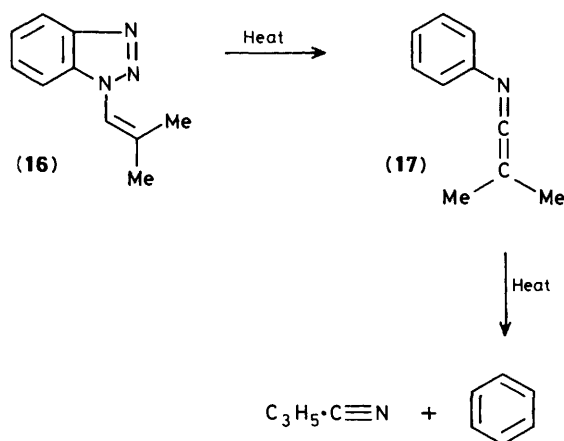
	$T(^{\circ}C)$	Relative abundances of the fragment ions											
		$m/z$ * 177	[166]	151	125	116	101	89	77	63	51	39	CS
(8)	200	28	305	27	19	43	16	100	60	30	33	10	77
(9)	200	39	567	49	44	62	28	100	60	30	33	10	77
(10)	200	27	338	28	21	30	16	100	45	27	24	8	61
(18)	250	36	113	25	20	47	17	100	64	26	27	7	49
	510	15	189	14	9	64	16	100	83	22	31	5	25
	750	20	225	14	10	67	18	100	80	22	28	6	23
(19)	260	11	133	9	5	70	15	100	88	18	27	5	12
	510	11	136	10	6	74	18	100	91	18	26	5	11
(13)	250	16	260	18	12	22	10	100	29	23	18	5	51

\* The masses indicated are only indicative due to low resolution of the c.a. spectra (B/E mass spectrometer).



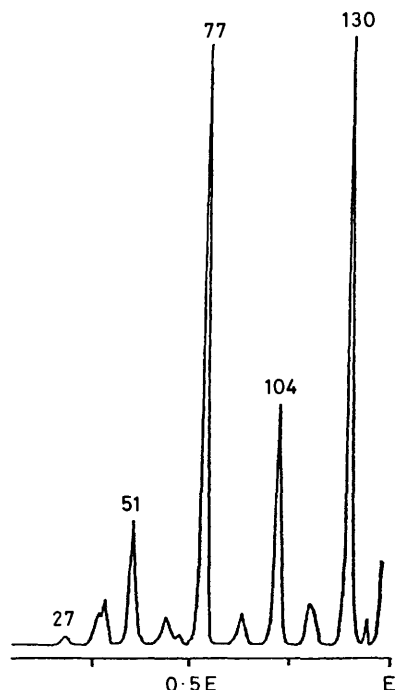
Scheme 3.

1-(2-Methylprop-1-enyl)benzotriazole (16) is also cleanly pyrolysed at 570 °C into nitrogen and dimethyl *N*-phenylketenimine (17) (Scheme 4) as exemplified in the c.a. spectrum (Figure 2) by the  $m/z$  145 peak which again shows a very prominent fragment signal for  $C_6H_5^+$  ions ( $m/z$  77) incompatible with the formation of an indole structure. More-



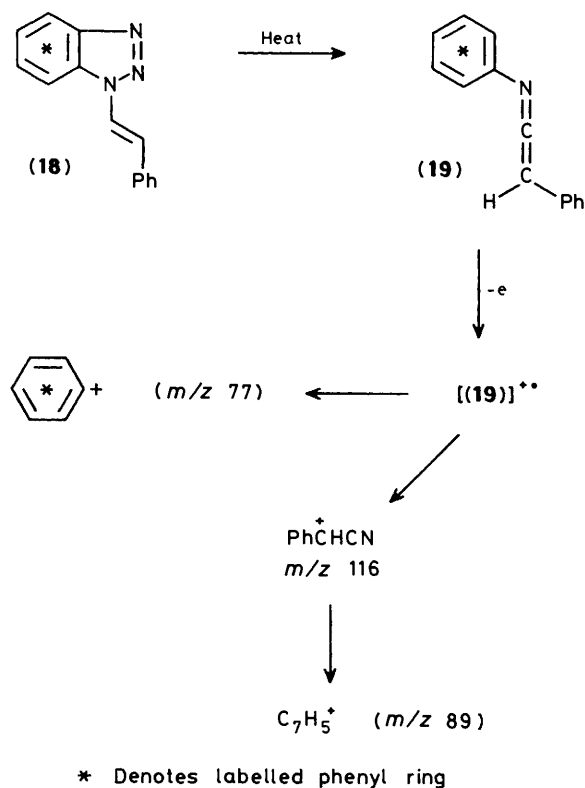
Scheme 4.

over, a superimposable spectrum is obtained with an authentic sample of the ketenimine (17) synthesized following Bestmann's procedure<sup>14</sup> (Table 2).

**Figure 2.** Collisional activation spectrum of the  $m/z$  145 ions of 1-(2-methylprop-1-enyl)benzotriazole (16) after pyrolysis at 570 °C (B/E mass spectrometer)

Another improbable<sup>15,16</sup> candidate containing an 'intact' phenyl ring, 2,2-dimethyl-3-phenyl-2*H*-azirene (12) can be excluded by collisional activation, as no significant loss of  $CH_3\cdot$  is noticed in the c.a. spectrum. An increase of the furnace temperature up to 950 °C in this case induces decay of the ketenimine (17) into benzene and methacrylonitrile as evidenced by tandem mass spectrometry.

1-Styrylbenzotriazole (**18**), in which the *N*-1 double bond of the alkenylbenzotriazole bears an aromatic substituent, shows similar behaviour upon pyrolysis. Table 3 summarizes the c.a. data for the  $m/z$  193 ions formed by dissociative ionization, or pyrolysis followed by ionization of (**18**), the direct ionization of 1,3-diphenylketenimine (**19**), 2,3-diphenyl-2*H*-azirene (**13**), and the isomeric 1-, 2-, and 3-phenylindole (**8**), (**9**), and (**10**). Although the spectra all show qualitative similarities, the data indicate that (**18**) is pyrolysed at 510 °C into nitrogen and diphenylketenimine (**19**). This explains convincingly the occurrence, after ionization, of the major collision-induced fragments at  $m/z$  116, 89, and 77 (Scheme 5). This fragmentation scheme is



Scheme 5.

supported by the fact that these peaks undergo the expected displacements when the phenyl ring is specifically labelled (with a methyl group for instance).

The diphenylketenimine (**19**) appears to be stable up to 750 °C. In a preliminary preparative pyrolysis experiment on (**18**) (800 °C), however, 2- and 3-phenylindole (**9**) and (**10**) have been detected by thin-layer chromatography as secondary pyrolysis products. It is noteworthy that the ketenimine (**19**) and phenylindoles have also been detected during the FVP of isomeric diphenyl-1,2,3-triazoles.<sup>17,18</sup>

### Conclusions

Flash-vacuum pyrolysis of  $\beta$ -substituted derivatives of 1-vinylbenzotriazole at 500–700 °C affords *N*-phenylketenimines. Comparisons with the c.a. spectra of authentic samples suggests that these reactions are almost quantitative. At higher temperatures, indoles are formed (probably in a consecutive reaction) except in the case of 1-(2-methylprop-1-enyl)benzotriazole (**16**) for which benzene and methacrylonitrile are detected as the secondary pyrolysis products. Work is now in progress to define the usefulness of the method at a preparative scale and to clarify the reaction mechanism.

### Experimental

Mass spectra were recorded on two instruments, depending on the volatility of the samples, (i) a triple sector (E/B/E) modified AEI MS 902 instrument<sup>19</sup> (accelerating voltage of 8 kV, trap current of 100–500  $\mu$ A, 70 eV ionizing energy) using He as the collision gas for obtaining the c.a. spectra,<sup>20</sup> and (ii) a Varian MAT 311 A (B/E) instrument (3 kV, 1 mA, 70 eV) using air as the collision gas.<sup>21</sup>

Samples were pyrolysed (E/B/E instrument) using an external furnace, consisting of a 25 cm (1 cm i.d.) quartz tube, electrically heated connected to the ion source *via* the all-glass heated inlet system. An internal furnace (*ca.* 10 cm quartz tube, 1 cm i.d.) situated within 2 cm of the electron gun was used on the B/E instrument. In this last case, the temperature limit is approximately 750 °C.

The following were prepared by the literature methods quoted: 1-vinylbenzotriazole (**3**),<sup>5b</sup> an oil,  $\delta$ (CDCl<sub>3</sub>) 5.28 and 5.99 (CH=CH,  $J_{cis}$  9.3 and  $J_{gem}$  1.5 and  $J_{trans}$  16 and  $J_{gem}$  1.5 Hz) and 7.8 (ArH); 1-phenylindole (**8**), b.p. 115–117 °C/0.5 mmHg (lit.,<sup>22</sup> b.p. 189–191 °C/20 mmHg); 3-phenylindole (**10**), m.p. 87–89 °C (lit.,<sup>23</sup> m.p. 87–88 °C); (1-benzotriazolylmethyl)-triphenylphosphonium chloride (**11**),<sup>7</sup> m.p. 286–288 °C (lit.,<sup>24</sup> m.p. 274–275 °C); 2,2-dimethyl-3-phenyl-2*H*-azirene (**12**), b.p. 119 °C/20 mmHg (lit.,<sup>25</sup> b.p. 96 °C/17 mmHg); 2,3-diphenyl-2*H*-azirene (**13**), m.p. 60–62 °C (lit.,<sup>26</sup> m.p. 60–62 °C);  $\alpha$ -azidostyrene (**15**),<sup>27</sup>  $\delta$ (CDCl<sub>3</sub>) 4.32 and 5.32 (CH<sub>2</sub>,  $J_{gem}$  2.4 Hz) and 7.3 (ArH); 1-(2-methylprop-1-enyl)benzotriazole (**16**), m.p. 69–71 °C (lit.,<sup>5b</sup> m.p. 70–71 °C); dimethyl-*N*-phenylketenimine (**17**), b.p. 96–99 °C (lit.,<sup>14</sup> b.p. 99–100 °C); 1-styrylbenzotriazole (**18**),<sup>7</sup> m.p. 115–117 °C (lit.,<sup>24</sup> m.p. 115–116 °C); 1,3-diphenylketenimine (**19**),<sup>14</sup>  $\delta$ (CDCl<sub>3</sub>) 5.3 (PhCH) and 7.35 (ArH).

Indole (**4**) and 2-phenylindole (**9**) were commercial samples (Janssen).

### Acknowledgements

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.). The contribution of Professor C. Wentrup (University of Queensland, Australia) to the construction of our pyrolysis units is gratefully acknowledged.

### References

- See for example: (a) M. S. Gibson, *J. Chem. Soc.*, 1956, 1076; (b) B. W. Ashton and H. Suschitzky, *ibid.*, 1957, 4559; (c) F. B. Mallory and C. S. Wood, *Tetrahedron Lett.*, 1965, 2643; (d) E. M. Burgess, R. Carithers, and L. McCullagh, *J. Am. Chem. Soc.*, 1968, **90**, 1923; (e) A. J. Hubert, *J. Chem. Soc. C*, 1969, 1334; (f) N. J. Leonard and K. Golankiewicz, *J. Org. Chem.*, 1969, **34**, 359; (g) M. Ohashi, K. Tsujimoto, and T. Yonezawa, *J. Chem. Soc., Chem. Commun.*, 1970, 1089; (h) M. Ohashi, K. Tsujimoto, A. Yoshino, and T. Yonezawa, *Org. Mass Spectrom.*, 1970, **4**, 203; (i) H. Meier and I. Menzel, *Justus Liebigs Ann. Chem.*, 1970, 739, 56; (j) A. J. Hubert and H. Reimlinger, *Chem. Ber.*, 1970, **103**, 2828; (k) K. Tsujimoto, M. Ohashi, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 515; (l) M. A. Ratcliff, Jr., and J. K. Kochi, *Tetrahedron*, 1972, **28**, 4467; (m) K. Tsujimoto, M. Ohashi, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3605; (n) M. P. Servé and H. M. Rosenberg, *J. Heterocycl. Chem.*, 1973, **10**, 245; (o) M. P. Servé, *ibid.*, 1974, **11**, 245; (p) M. P. Servé, *J. Org. Chem.*, 1974, **39**, 3788; (q) J. de Mendoza and J. Elguero, *Bull. Soc. Chim. Fr.*, 1974, **12**, 2987; (r) D. C. K. Lin and D. C. DeJongh, *J. Org. Chem.*, 1974, **39**, 1780; (s) F. Razmara, B. Behjati, N. Aftandilians, and Th. Bluhm, *J. Heterocycl. Chem.*, 1979, **16**, 1641; (t) H. Murai, M. Torres, and O. P. Strausz, *J. Am. Chem. Soc.*, 1980, **102**, 1421.
- R. F. C. Brown, 'Pyrolytic Methods in Organic Chemistry,' Academic Press, New York, 1980.
- C. Graebe and F. Ullmann, *Justus Liebigs Ann. Chem.*, 1896, **291**, 16.

- 4 (a) C. Wentrup, *Helv. Chim. Acta*, 1972, **55**, 1613; (b) J. J. Kulagowski, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2725.
- 5 (a) P. A. Wender and C. B. Cooper, *Tetrahedron*, 1986, **42**, 2985; (b) M. Märky, H. Schmid, and H.-J. Hansen, *Helv. Chim. Acta*, 1979, **62**, 2129.
- 6 R. Lawrence and E. S. Waight, *Org. Mass Spectrom.*, 1970, **3**, 367.
- 7 A. R. Katritzky and M. Soleiman, unpublished work.
- 8 K. Levsen, 'Tandem Mass Spectrometry,' ed. F. W. McLafferty, J. Wiley, Chichester, 1983.
- 9 A. Maquestiau, Y. Van Haverbeke, R. Flammang, A. Menu, and C. Wentrup, *Org. Mass Spectrom.*, 1978, **13**, 518.
- 10 (a) G. R. Krow, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 435; (b) G. L'abbi, *ibid.*, 1975, **14**, 775.
- 11 H. Bock, R. Dammel, and S. Aygen, *J. Am. Chem. Soc.*, 1983, **105**, 7681.
- 12 W. D. Crow and C. Wentrup *Chem. Commun.*, 1968, 1026.
- 13 A. Maquestiau, R. Flammang, P. Meyrant, M. Regitz, B. Arnold, and H. Schubert, *Bull. Soc. Chim. Belg.*, 1983, **92**, 121.
- 14 H. J. Bestman, J. Lienert, and L. Mott, *Justus Leibigs Ann. Chem.*, 1968, **718**, 24.
- 15 L. A. Wendling and R. G. Bergman, *J. Am. Chem. Soc.*, 1974, **96**, 308.
- 16 A. Padwa and Per H. J. Carlsen in 'Reactive Intermediates,' ed. R. A. Abramovitch, Plenum Press, New York, 1982, vol. 2.
- 17 T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1.
- 18 T. L. Gilchrist, C. W. Rees, and C. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1975, 8.
- 19 A. Maquestiau, Y. Van Haverbeke, R. Flammang, M. Abrassart, and D. Finet, *Bull. Soc. Chim. Belg.*, 1978, **87**, 765.
- 20 K. Levsen and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 509.
- 21 A. Maquestiau, Y. Van Haverbeke, C. De Meyer, R. Flammang, and J. Perlaux, *Bull. Soc. Chim. Belg.*, 1976, **85**, 69.
- 22 A. F. Pozharskii, B. K. Martsozha, and A. M. Simonov, *J. Gen. Chem. USSR (Engl. Transl.)*, 1963, **33**, 994.
- 23 J. M. Bruce, *J. Chem. Soc.*, 1959, 2366.
- 24 A. R. Katritzky, S. Rachwal, K. C. Caster, F. Mahni, K. W. Law, and O. Rubio, *J. Chem. Soc., Perkin Trans. 1*, 1987, 781.
- 25 R. F. Parcell, *Chem. Ind. (London)*, 1963, 1396.
- 26 F. W. Fowler, A. Hassner, and L. A. Levey, *J. Am. Chem. Soc.*, 1967, **89**, 2077.
- 27 G. Smolinsky, *J. Org. Chem.*, 1962, **27**, 3557.
- 28 A. R. Katritzky, W. Kuzmierkiewicz, B. Rachwal, S. Rachwal, and J. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 1987, 811.

Received 29th May 1987; Paper 7/948