

FLASH-VACUUM PYROLYSIS OF 1,2,4-TRIAZOLIDES : A NEW  
 SYNTHESIS OF FUNCTIONALIZED OXAZOLES

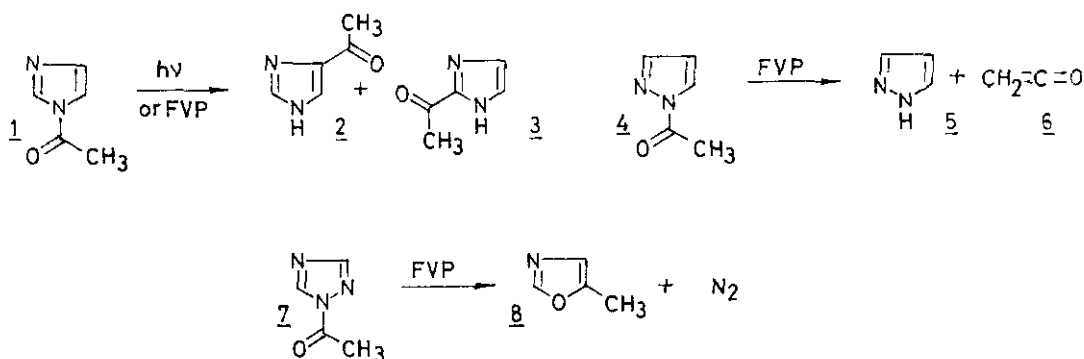
 André Maquestiau, Robert Flammang, and Fouad-Bachir Ben Abdelouahab.  
 Organic Chemistry Laboratory

State University of Mons - B-7000 Mons - Belgium.

**Abstract** — Tandem mass spectrometry (MS/MS) has been applied to investigate the behaviour of 1,2,4-triazolides upon flash-vacuum pyrolysis (FVP) conditions. Monosubstituted (position 5) oxazoles (loss of nitrogen) and in some cases oxygenated cumulenes (loss of 1,2,4-triazole) are the most important pyrolysis products. Pyrolysis at a preparative scale indicates moreover the interest of the technique as the synthesized oxazoles were usually unknown or very difficult to prepare owing the conventional procedures.

## INTRODUCTION

N-Acylated derivatives of azoles, also called azolides, constitute a special class of heterocyclic compounds. Their synthetic interest has been reviewed by Staab<sup>1</sup> and peculiar behaviour relative to the infrared<sup>2</sup>, proton magnetic resonance<sup>3,4</sup> and mass<sup>5,6</sup> spectra has also been reported. Among all the azolides, 1-acetylimidazole [**1**] has received much attention as it can be used as a specific acetylating reagent in biochemistry<sup>7</sup>.



Scheme 1.

The structural modification of azolides upon pyrolytic and photolytic conditions has also been studied in some details. Iwasaki<sup>8</sup> has shown that the irradiation of **1** induces isomerization into its C-acetylated isomers **2** and **3** with moderate yields. A similar result has been obtained by flash-vacuum pyrolysis (FVP)<sup>9</sup> at short contact times, real-time identification of the products being performed by tandem mass spectrometry (MS/MS)<sup>10</sup>. Such migrations of carbonylated substituents from nitrogen to carbon have also been observed photochemically and thermally for pyrrole derivatives<sup>11-14</sup>. Acylated derivatives of pyrazole, like **4**, besides a small amount of isomerization<sup>15</sup>, mainly undergo fragmentation into pyrazole [**5**] and ketene [**6**]<sup>16-18</sup>. Photolysis of 1-acetyl-1,2,4-triazole [**7**] does not yield any identifiable product<sup>19</sup>; on the contrary, upon FVP conditions, ring transformation into

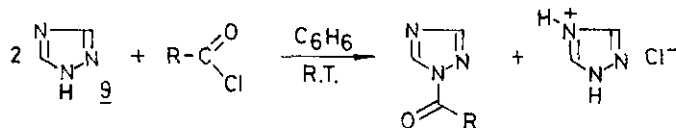
5-methyloxazole [8] has been described by our laboratory<sup>20</sup>. For aryl substituents which preclude the formation of ketenes, the yields were quite high and the method proved to be one of the best entries into the 5-substituted oxazole series. Examples of this kind of compounds are indeed scarcely found in the literature and the synthesis, when described, is often complex or fastidious<sup>21,22</sup>.

The aim of the present work is to demonstrate that the FVP induced ring transformation of readily accessible triazolides allows the introduction of functional groups into position 5 of oxazole. This functionalization step may be of importance given the increasing interest of oxazoles in synthetic organic chemistry, not only as precursors of furans or pyridines via Diels-Alder reactions with alkynes or alkenes<sup>23</sup>, but also as potential carbonyl masked groups<sup>24</sup>.

This paper summarizes not only the results of preparative pyrolysis experiments, but also the results of real-time analysis of the products in the gas phase by a direct combination of FVP with tandem mass spectrometry. The advantage of this last (analytical) technique resides on the eventual identification of reactive molecules in the gaseous pyrolysate<sup>25</sup>.

## RESULTS AND DISCUSSION

Various 1-substituted 1,2,4-triazole derivatives have been synthesized by action of acid chlorides on two equivalents of triazole 9 in benzene at room temperature (Scheme 2). The nmr spectra of these compounds (Table 1) show two signals corresponding to the heterocyclic protons at ca 8 and 9 ppm respectively. The most deshielded signal is attributed to H<sub>5</sub> and thus confirm the position of the substituents. Electron impact ionization induces two common fragmentation routes for all the compounds, namely  $\alpha$ -cleavage giving rise to acylium ions R-C=O<sup>+</sup> and decarbonylation of the molecular ions. This last process appears to be quite general for azolides<sup>26</sup> whatever the nature of the carbonylated substituent.



Scheme 2.

In our experimental conditions, position 4 of the triazole ring appears to be unreactive. Previous works<sup>27-29</sup> have shown that the regioselectivity of the nitrogen substitution depends mainly on the nature of the reagent and solvent.

### A. Analytical results : FVP/MS/MS

The 70 eV mass spectrum of 1-acryloyl-1,2,4-triazole [11] presents a base peak at  $m/z$  66 corresponding to vinylacylium ions H<sub>2</sub>C=CH-C=O<sup>+</sup> (Figure 1). Consecutive decarbonylation of these ions yields vinyl ions at  $m/z$  27. Loss of CO from the molecular ions (measured mass : 95.0485) is also a prominent process not only within the ion source, but also within the field-free regions (FFR). The actual structure of these fragment ions (vinyltriazole *viz* carbene/triazole complex) is presently under study<sup>30</sup>. Pyrolysis of 11 before ionization produces major changes in the mass spectrum (Figure 1). Compared to the base peak at  $m/z$  55, there is a strong increase of the peaks at  $m/z$  95, 69-67, 42-38 and 28-26.

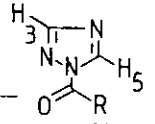
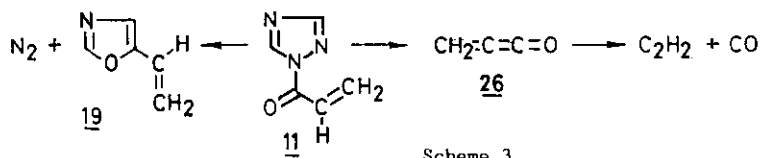
	Pmr $\delta$ (CDCl <sub>3</sub> )			Ms, $m/z$ (Ab.Rel.)			
	H <sub>3</sub>	H <sub>5</sub>	Others	M <sup>+</sup>	[M-CO] <sup>+</sup>	R-C=O	
R = C <sub>6</sub> H <sub>5</sub> <sup>20</sup>	<u>10</u>	8.10	9.10	Arom. 7.80 (m)	173 (26 %)	154 (4)	105 (100)
- CH <sub>a</sub> =C <sub>b</sub>   H <sub>c</sub>	<u>11</u>	8.02	8.96	H <sub>a</sub> :7.40(q) ; H <sub>b</sub> :6.76(q) ; H <sub>c</sub> :6.18(q)	123 (2 %)	95 (32)	55 (100)
- CH <sub>a</sub> =CH <sub>b</sub> -CH <sub>3</sub>	<u>12</u>	8.02	8.96	H <sub>a</sub> :7.46(q) ; H <sub>b</sub> :7.33(q) ; CH <sub>3</sub> :2.02(d)	137 (5 %)	109 (24)	69 (100)
- C(CH <sub>3</sub> ) <sub>2</sub> =C <sub>b</sub>   H <sub>a</sub>	<u>13</u>	8.07	9.00	H <sub>a</sub> :6.44(s) ; H <sub>b</sub> :6.05(q) ; CH <sub>3</sub> :2.15(q)	137 (3 %)	109 (49)	69 (100)
- CH-CH <sub>2</sub> CH <sub>2</sub>	<u>14</u>	8.09	8.97	C <sub>3</sub> H <sub>5</sub> : 1.27 (m)	-	109 (8)	69 (100)
- CH <sub>3</sub> <sup>20</sup>	<u>15</u>	7.83	8.73	CH <sub>3</sub> : 2.53 (s)	111 (13 %)	83 (13)	43 (100)
- COOCH <sub>3</sub>	<u>16</u>	8.13	9.26	CH <sub>3</sub> : 3.92 (s)	-	127 (23)	-
- CH <sub>2</sub> -CH=C <sub>b</sub>   H <sub>c</sub>	<u>17</u>	8.09	9.00	H <sub>a</sub> :6.10(m) ; H <sub>b</sub> :5.32(m) ; H <sub>c</sub> :3.90(m)			See text.

TABLE 1. Proton magnetic resonance spectra and major common ions in the 70 eV mass spectra of the triazolides 10 to 17.

Precursors	T(°C)	$m/z$ [67]	Relative abundances of fragment ions											
			55	53	52	51	50	41	40	39	29	28	27	26
[ <u>11</u> ]	650	[578]	86	14	31	20	18	55	98	<u>100</u>	17	25	45	16
[ <u>19</u> ]	200	[586]	91	17	25	21	18	55	95	<u>100</u>	20	26	42	16

TABLE 2. CA spectra of  $m/z$  95 ions originating from the pyrolysis of 1-acryloyltriazoled [11] at 650° followed by 70 eV EI ionization and from ionized 5-vinylloxazole [19].

The MIKE spectrum of the ions at  $m/z$  95 shows an intense peak corresponding to the loss of CO. Moreover the collisional activated decompositions (Table 2) clearly indicate that, first, these ions are different from the isobaric ions recorded at low temperature and, second, they have the structure of ionized 5-vinyloxazole [19]. FVP of 11 thus induces a nitrogen loss with subsequent cyclisation into an oxazole ring system (Scheme 3).



Taking into account the complete mass spectrum of an authentic sample of 19, it is also clear that other compounds are formed during the pyrolysis of 11 [see fig. 1B vs 1C]. CID spectra\* unambiguously indicate that the  $m/z$  69 ions are molecular ions of 1,2,4-triazole [9] resulting from an elimination reaction of ketene. Ionized propadienone [26] at  $m/z$  54 is however not observed; probably [26] cannot survive our pyrolysis conditions and decomposes into vinylidene (which isomerises into ethyne) and CO. The chemistry of methyleneketenes has been reviewed<sup>16</sup> and it appears that quite mild FVP conditions are required in order to allow their observation even with real-time analysis techniques.

Finally, ions at  $m/z$  67 must also constitute (at least partly) molecular ions. They remain present in a 12 eV mass spectrum and show prominent peaks at  $m/z$  41-39 in their CID spectrum which are also found in the spectra of most  $[C_4H_5N]^+$  isomers<sup>31</sup>. They probably result from a consecutive decarbonylation of vinyloxazole at elevated temperatures. Moreover, CID indicates that they have a nitrile structure, most probably allylcyanide; pyrrole formation can be excluded, but the distinction between the various  $NC-C_3H_5$  isomers appears to be difficult on the lone MS/MS data.

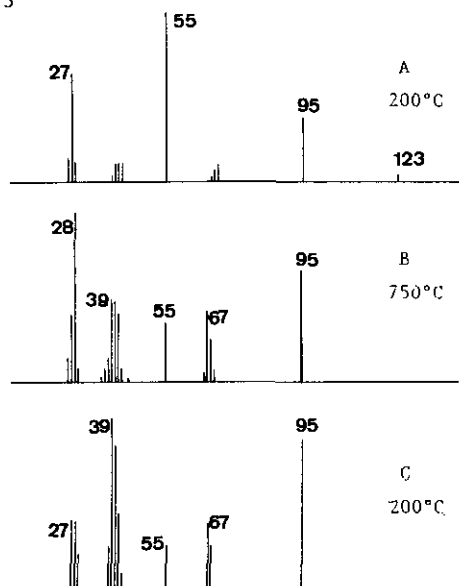


Figure 1. Mass spectra of 1-acryloyl-1,2,4-triazole [11] at various pyrolysis temperatures (A,B) and mass spectrum of 5-vinyloxazole [19] (C).

\* Experimental data not included in this paper are available upon request.

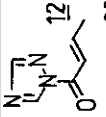
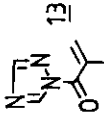
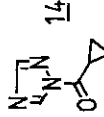
Compounds	Relative Abundances																											
	m/z	137	122	109	95	86	82	81	80	70	69	68	55	54	53	52	51	50	43	42	41	40	39	38	37	29	28	27
 <chem>C=CC(=O)N1C=NC=N1</chem>	[200°	5	10	24					8	<u>100</u>	8	2							4	6	58	8	33	13			13	5
	[700°			20		6	6	7	11	4	87	79	3	11	11	4	4	4	3	52	28	43	<u>100</u>	22	14	6	58	27
 <chem>C=CC(=O)N1C=NC(C)=N1</chem>	[200°	3		49	3	3			22	61	25	5	5	4	17	13	12	5	12	<u>100</u>	22	45	10	6		15	11	5
	[650°			93	7	6	16	37	4	20	24	7	46	30	37	35	31	9	13	63	34	94	20	13	8	<u>100</u>	28	11
 <chem>C=CC(=O)N1C=NC(C1)C2CC2</chem>	[200°										6	20	4	38	21	5	6	5	6	28	20	52	6		5	20	16	4
	[700°			8	4		4		8	<u>100</u>	32	6							2	6	64	8	26	5		11	8	
				45		22	20	14	4	34	38	24	36	25	11	10	7	5	18	44	37	64	13	8	7	<u>100</u>	48	16

TABLE 3. Modifications of the 70 eV mass spectra of triazolides 12 - 14 as a function of pyrolysis temperature.

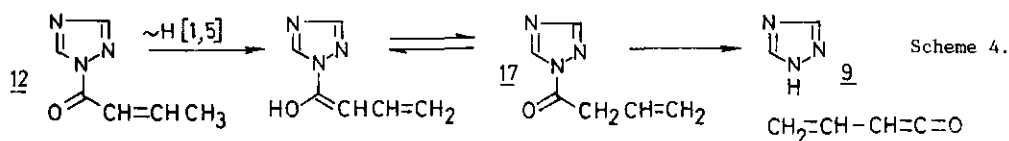
The behaviour of the homologous 1-crotonyl- [12], 1-methacryloyl- [13] and cyclopropanecarbonyl- [14] 1,2,4-triazoles upon electron impact parallels those of [11] : low intensity (if at all) of the molecular ion peaks and prominent  $\alpha$ -cleavage giving rise to isomeric acylium ions ( $m/z$  69) (easily identified by their CA spectra<sup>32</sup>) which decarbonylate into  $C_3H_5^+$  ( $m/z$  41) ions. Other common features are peaks at  $m/z$  109 (decarbonylation of the molecular ions ; major peaks in the MIKE spectra) and  $m/z$  68 (ketene ions, due to the loss of triazole). For 12, loss of  $CH_3^{\cdot}$  is also observed and probably is due to a concerted intramolecular cyclisation (Table 3).

As expected, pyrolysis of 1-methacryloyltriazole [13] produces 5-(2-propenyl)oxazole [21] as evidenced by the CA spectra of the  $m/z$  109 ions which show intense peaks for the loss of CO ( $m/z$  81) and  $HCO^{\cdot}$  ( $m/z$  80) (Table 4). The peak at  $m/z$  68 remains present in the mass spectrum but corresponds at high temperature to  $C_3H_2NO^+$  ions originating from a loss of the propenyl radical. Loss of substituents at position 5 of oxazole is an already known reaction<sup>6</sup> which is preceded by a ring opening process<sup>33</sup>.

Precursors	T°	Relative Abundances																		
		$m/z$	94	82	81	80	70	69	68	55	54	53	52	43	42	41	40	39	29	28
[13] <sup>+</sup>	200°	-	10	6	-	100	8	-	4	4	-	-	-	-	-	6	8	-	6	-
	700°	10	-	89	100	-	9	17	4	26	25	4	-	-	-	19	17	7	8	10
[21] <sup>+</sup>	200°	6	-	87	100	-	4	14	4	18	17	6	-	-	-	12	16	3	4	7
[12] <sup>+</sup>	200°	4	44	5	-	100	6	-	28	18	-	-	1	3	4	6	9	-	7	-
	700°	5	100	28	-	4	8	15	-	10	10	-	-	-	7	-	8	1	3	4
[20] <sup>+</sup>	200°	4	100	29	-	7	12	14	-	13	12	-	-	-	8	-	9	2	3	4
[14] <sup>+</sup>	200°	1	100	36	-	18	85	24	23	20	-	-	-	4	6	4	2	-	6	-
	700°	4	100	28	36	-	29	13	-	8	9	-	-	-	6	4	6	1	1	2

TABLE 4. CA spectra of  $m/z$  109 ions from triazolides 12 - 14 at low and high temperature and from the oxazoles 20 and 21.

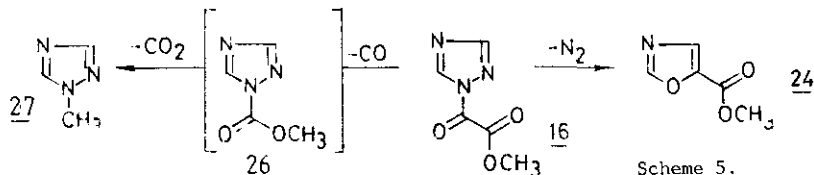
The major difference between the pyrolyzed isomers 13 and 12 is the relative high intensity of the peak at  $m/z$  109 for 13 and the relative high intensity of the peaks at  $m/z$  69 and 68 for 12. These last peaks can be ascribed to a competitive elimination pathway forming triazole 9 and a ketene identified, by collisional activation, as vinylketene 27. Such a ketene has been described for a pyrazole analogue of 13<sup>18</sup> as resulting from the tautomerization of the initially formed ethylideneketene ( $CH_3CH=C=C=O$ ) 28. In the case of [12] however, it appears that formation of vinylketene [27] originates in another reaction mechanism starting with a [1,5]-hydrogen shift (Scheme 4). This proposal is supported by the fact that, during a preparative pyrolysis experiment (vide infra), 2-(3-butenyl)triazole [17] has been detected in the pyrolysate as a secondary product. This observation also implies that the ions at  $m/z$  109 result from the ionization of at least two isomeric oxazole compounds.



Compound 13 cannot give rise to the formation of a ketene and this explains the high intensity of the  $m/z$  109 peak.

Competitive losses of  $C_2H_3$  and  $^1CHO$  are observed in the CA spectrum of the  $m/z$  109 ions issued from the pyrolysis/ionization processes of 1-cyclopropylcarbonyltriazone [14]. This is due to the formation of a mixture of isomeric oxazoles as shown in a preparative pyrolysis experiment (see part B).

Condensation of methyloxalyl chloride with triazole 9 affords methyloxalyltriazone 16 with a 70 % yield. The electron ionization of this compound gives rise to very unstable molecular ions at  $m/z$  155 (1 %) which mainly decompose to  $m/z$  127 (23 %) ions by decarbonylation,  $m/z$  69 ions (60 %) triazole formation and  $m/z$  59 (88 %) carbonyl-induced  $\alpha$ -cleavage. The base peak which appears at  $m/z$  56 corresponds to  $C_2O_2^{+}$  ions as evidenced by the CA spectrum characterized by one intense peak at  $m/z$  28 ( $CO^{+}$ ). Relative to this  $m/z$  56 peak, pyrolysis induces an intensity enhancement of the peaks at  $m/z$  127, 83, 68, 44, 40 and 28 (Table 5).



The comparison with an authentic sample of 5-methoxycarbonyloxazole [24] and the CA spectra of the  $m/z$  127 ions (Table 6) indicate that pyrolysis has competitively induced the formation of 24 [responsible of the sequence  $m/z$  127 ( $M^{+}$ ),  $m/z$  68 ( $M-CO_2CH_3$ ) $^{+}$  and  $m/z$  40 ( $M-CO_2CH_3-CO$ ) $^{+}$ ] and of 1-methyltriazone 27 ( $m/z$  83). This last compound probably originates in a decarbonylation reaction into 1-methoxycarbonyltriazone 26 which decarboxylates readily into 27 and  $CO_2$ . A similar fast decarboxylation reaction has been described for 1-methoxycarbonylpyrazole<sup>34</sup>.

#### B. Preparative pyrolysis experiments.

In order to evaluate the efficiency of the method at a preparative scale, larger amounts of the azolides (up to  $\sim$  4-5 g) have been pyrolyzed at about  $800^{\circ}/10^{-2}$  torr using an electrically heated quartz tube, the pyrolysis products being collected in a liquid nitrogen cooling trap containing methanol. In all cases, oxazoles represent the major constituents of the pyrolyzate and, after conventional isolation by column or gas chromatography, they were identified by their pmr and mass spectra (Table 7). The  $H_2$  protons appear in the range 7.7-8.0 ppm while  $H_4$  protons are found in the range 6.7-7.3 ppm (for oxazole itself, these figures are respectively 7.95 and 7.09 ppm<sup>35</sup>). Unlike the parent azolides, the molecular ions of the oxazoles are quite stable and one of the common fragmentations consists in a loss of the substituent giving  $m/z$  68 ions.

Two particular cases merit some more comments : i) when 1-cyclopropylcarbonyltriazone [14] pyrolyzed, the mass spectrum indicates that the major constituent(s) of the pyrolyzate has the mass  $m/z$  109 in agreement with structure 5-cyclopropyloxazole [22]. Gc analysis however indicates the coexistence of several compounds in comparable amounts which is confirmed by pmr pointing to the formation of all the 5- $C_3H_5$ -oxazole isomers 20-22 and 25. It thus appears that the cyclopropane ring does not survive the used temperature conditions due probably to chemical activation<sup>36</sup>. Similar ring opening of gaseous cyclopropanes have already been described<sup>37</sup>. Among all the isomers formed in this experiment, we were only able to separate by gc a pure sample of 25. ii) when 1-crotonyltriazone [12] was submitted to pyrolysis, a white crystalline deposit was observed in the exist tube preceeding the liquid nitrogen trap : it appeared to be 1-(3-butenyl)triazone [17] whose possible origin is proposed in Scheme 4. The enolic form of 17



Compounds	T°	Relative Abundances																									
		m/z	155	127	118	100	99	97	96	83	71	70	69	68	59	56	55	47	45	44	43	42	41	40	39	29	28
 $\text{16}$	200°	1	23	-	-	-	9	14	11	-	7	60	-	88	<u>100</u>	-	-	-	19	11	16	13	8	-	11	44	8
	700°	-	8	<1	2	2	2	7	18	6	-	17	24	13	21	3	-	-	76	2	12	8	18	6	14	<u>100</u>	30
 $\text{24}$	200°	-	60	-	6	6	11	37	-	39	-	8	<u>100</u>	13	-	6	14	11	6	20	7	15	87	13	21	22	8

TABLE 5. Modification of the 70 eV mass spectra of triazolide 16 as a function of pyrolysis temperature and mass spectrum of 5-methoxycarbonyloxazole (24).

Precursors	T°	Relative Abundances																	
		m/z	100	99	98	97	96	82	83	77	71	70	69	68	59	56	44	49	
<u>16</u>	200°		2	6	-	<u>100</u>	-	-	3	2	-	11	4	-	7	31	-	1	
	700°		<u>100</u>	10	18	62	32	4	-	-	12	-	-	38	5	17	2	5	
<u>24</u>	200°		<u>100</u>	6	18	18	27	4	-	-	12	-	-	31	3	3	2	5	

TABLE 6. CA spectra of m/z 127 ions from triazolide 16 at low and high temperature and from the oxazole 24.

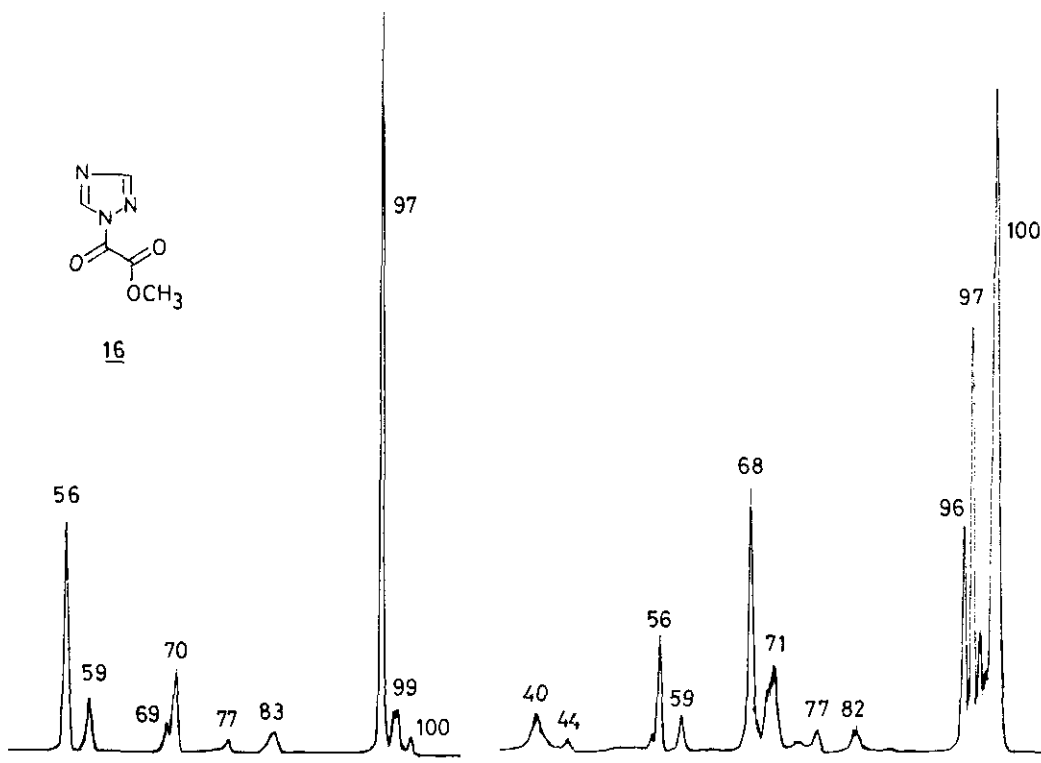


Figure 2. CID spectra of the m/z 127 ions observed in the mass spectra of 16 without pyrolysis (left) or with pyrolysis at 700° (right).



R =	Pmr $\delta$ (CDCl <sub>3</sub> )		Ms, m/z (Rel.Ab.)	Yield
	H <sub>2</sub>	H <sub>4</sub>		
- C <sub>6</sub> H <sub>5</sub>	7.87	7.33	145 (100)	90 % <sup>20</sup>
- CH <sub>a</sub> =C(H <sub>b</sub> )(H <sub>c</sub> )	7.76	6.90	95 (88)	68 (25)
- CH <sub>a</sub> =C(H <sub>b</sub> )(CH <sub>3</sub> )	7.70	6.80	109 (100)	68 (43)
- C(CH <sub>3</sub> )=C(H <sub>a</sub> )(H <sub>b</sub> )	7.80	7.00	109 (100)	68 (10)
- CH-CH <sub>2</sub> -CH <sub>2</sub>	7.71	6.73	-	-
- CH <sub>3</sub>	7.75	6.77	83 (47)	68 (24)
- CO <sub>2</sub> CH <sub>3</sub>	8.05	7.11	127 (60)	68 (100)
- CH <sub>2</sub> -CH=C(H <sub>a</sub> )(H <sub>b</sub> )(H <sub>c</sub> )	7.78	6.84	109 (100)	68 (59)

TABLE 7. Proton magnetic resonance and major common ions in the 70 eV mass spectra of the oxazoles 18 - 25.

resulting from a [1,5] hydrogen sigmatropic shift is probably more resistant to pyrolysis than 12 as a lower migratory aptitude of the hydroxylated substituent can be anticipated<sup>38</sup>; condensation is then followed by ketonization into 17.

## CONCLUSIONS

Real-time analysis of the FVP products of some azolides has been performed by direct coupling to tandem mass spectrometry. Monosubstituted oxazoles (position 5) usually unknown or difficult to prepare by conventional procedures are readily obtained by flash-vacuum pyrolysis of triazoles. The method thus constitutes a novel procedure for the synthesis of 5-substituted oxazoles. When the starting compound contains an hydrogen in the appropriate position, loss of ketene becomes an important competitive pathway. However, under the temperature conditions used, alkylideneketenes suffer decarbonylation. Ring opening of the cyclopropyl derivative 22 is also observed.

## EXPERIMENTAL

The mass spectra of all the samples, as well as the MIKE and CA spectra, were recorded on a triple sector (E/B/E) modified AEI MS 902 instrument<sup>39</sup> (accelerating voltage 8 kV, trap current 100-500  $\mu$ A, 70 eV ionizing energy) using helium as the collision gas.

The vapour pressure of all the samples was high enough to allow their vaporization within an all-glass heated ( $\sim 150^\circ$ ) inlet system (AGHIS). Part of the pyrex line connecting this AGHIS to the ion source was modified by inserting a 25 cm (1 cm, i.d.) quartz tube, electrically heated (up to  $1200^\circ$ ); the distance between the middle of the pyrolysis zone and the ionization chamber was  $\sim 30$  cm.

Preparative pyrolysis conditions were similar to the FVP/MS conditions (quartz tube, 25 cm length, 1 cm i.d.) except higher working pressure ( $10^{-2}$  torr going up to 1 torr when nitrogen evolved). The products were collected in a liquid nitrogen cooling trap containing methanol. All pyrolysis were performed on  $\sim 4$  g quantities of starting materials.

The pmr spectra have been recorded on a Varian EM 360-L spectrometer (60 MHz) using 10 %  $\text{CDCl}_3$  solution. Preparative gc has been performed with a GIRA 1700 chromatograph.

The triazolides have been prepared following the procedure described previously<sup>8</sup>. They proved to be unstable on standing and were thus prepared just before the pyrolysis step. Pmr data are given in Table 1.

1-acryloyl-1,2,4-triazole [11] : mp :  $52-54^\circ$  (hexane), yield : 60 %.

Ms.  $m/z$  123 (5 %), 95(38), 70(11), 69(7), 68(3), 55(100), 42(11), 41(10), 40(11), 39(4), 28(12), 27(65), 26(14).

1-crotonyl-1,2,4-triazole [12] : mp :  $62-65^\circ$  (hexane), yield : 80 %.

Ms.  $m/z$  137 (5 %), 122(10), 109(24), 70(8), 69(100), 68(8), 43(4), 42(6), 41(58), 40(8), 39(33), 38(13), 28(13), 27(5).

1-methacryloyl-1,2,4-triazole [13] : oil, yield : 80 %.

Ms.  $m/z$  137 (3 %), 109(49), 86(3), 82(3), 70(22), 69(61), 68(25), 55(5), 54(5), 52(17), 51(3), 50(12), 43(5), 42(12), 41(100), 40(22), 39(45), 38(10), 37(6), 28(15), 27(11), 26(5).

1-cyclopropylcarbonyl-1,2,4-triazole [14] : mp :  $45-47^\circ$  (hexane), yield : 70 %.

Ms.  $m/z$  109 (8 %), 95(4), 82(4), 70(8), 69(100), 68(32), 55(6), 42(6), 41(64), 40(8), 39(26), 28(11), 27(8).

1-methyloxalyl-1,2,4-triazole [16] : oil, yield : 70 %.

Ms.  $m/z$  127 (24 %), 97(8), 96(14), 83(11), 69(51), 59(89), 56(100), 44(19), 43(11), 42(16), 41(14), 40(8), 29(11), 28(46), 27(8).

5-vinyloxazole [19] : oil, yield : 25 %.

Ms.  $m/z$  95 (88), 68(25), 67(38), 55(25), 42(9), 41(44), 40(84), 39(100), 38(24), 29(20), 28(39), 27(40).

5-(1-propenyl)oxazole [20] : oil, yield : 30 %.

Ms.  $m/z$  109(100 %), 82 (24), 81 (28), 70 (41), 69 (21), 68 (43), 55 (15), 54 (63), 53 (53), 52 (29), 51 (18), 41 (90), 40 (45), 39 (72), 28 (54), 27 (39), 26 (21).

5-(2-propenyl)oxazole [21] : oil, yield : 80 %.

Ms.  $m/z$  109(100 %), 82 (7), 81 (12), 80 (31), 69 (6), 68 (20), 55 (4), 54 (38), 53 (21), 52 (5), 51 (6), 50 (5), 42 (6), 41 (28), 40 (20), 39 (52), 38 (6), 29 (5), 28 (20), 27 (16), 26 (4).

5-methylcarbonyloxazole [24] : mp : 44-46°, yield : 60 %.

Ms.  $m/z$  127 (42 %), 100 (5), 97 (4), 96 (25), 83 (31), 71 (32), 68(100), 59 (38), 56 (18), 40 (67), 28 (92), 15 (58).

5-allyloxazole [25] : oil, yield : 10 %.

Ms.  $m/z$  109(100 %), 82 (31), 81 (32), 80 (51), 69 (38), 68 (59), 55 (8), 54 (60), 53 (45), 52 (13), 51 (11), 50 (9), 42 (7), 41 (56), 50 (26), 39 (62), 38 (9), 29 (12), 28 (24), 27 (25), 26 (7).

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