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CONVERSION OF TRIAZOLIDES INTO OXAZOLES BY FLASH-VACUUM PYROLYSIS.

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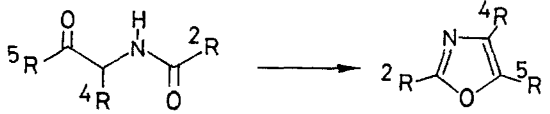
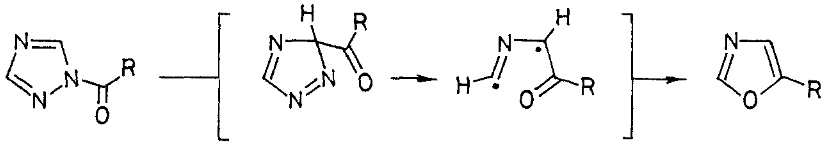
Flash-vacuum pyrolysis of azolides of 1,2,4-triazole affords 5-monosubstituted oxazoles.

One of the most general methods for the preparation of various oxazole derivatives is the dehydration reaction of α-acylamino carbonyl compounds[1]. Surprisingly, the introduction of a single alkyl or aryl substituent on the carbon 5 of the oxazole ring appears to be quite time consuming. For instance, the synthesis of 5-phenyloxazole (2) requires four steps from α-aminoacetophenone and ethyloxalylchloride[2]. Also, the simple 5-methyloxazole (6) has been synthetised only very recently through another four steps sequence from the methylester of formylglycine[3]. In this communication, we report on a new efficient and rapid method for obtaining these 5-monosubstituted oxazoles which is based on a flash-vacuum pyrolysis (FVP)[4] reaction of the readily available azolides[5] of 1,2,4-triazole (scheme 1).



For instance, on pyrolysis at 800°C/10^{-2} Torr through a 25 cm x 1 cm i.d. quartz tube, 1-benzoyltriazole (1) gives 5-phenyloxazole (2), the structure of which followed from consideration of PMR (table 1) and mass ($M^{+\cdot}$ at m/z 145) spectra. The yield after chromatography on neutral alumina comes up to 90 % (m.p.(ligroin) = 39-40°, litt.[2] 40-42°). The new 5-(p-tolyl) oxazole (4) was similarly obtained with a very high yield (> 90 %) by pyrolysis of 3 at 800°/10^{-2} Torr = m.p. (pentane) 65-66°, MW 159 (M.S.), PMR (table 1).



R = - C_6H_5 1 — 2
- $C_6H_4CH_3$(p) 3 — 4
- CH_3 5 — 6

Scheme 1.

When 1-acetyltriazole (5) was submitted to the pyrolysis, a white crystalline deposit was observed in the exit tube preceeding the liquid nitrogen cooling trap = it appeared to be the parent 1,2,4-triazole (7) as identified by PMR (δ(60 MHz, $CDCl_3$) 8,25 (s, CH) 9,12 (broad s, NH)), MS ($M^{+\cdot}$ at m/z 69) and m.p. 120° (yield 26 %). This compound originates from a decay process (loss of ketene) which is well documented for the azolides of pyrazole[6]. On warming up, the white oil collected in the trap turns to a yellow, then reddish liquid in which 5-methyloxazole (6) is readily identified by PMR (table 1). Intensive degradation of this reaction mixture was however observed. We found that stable solutions of 6 are obtained if the pyrolysis products are trapped within methanol = the yield of 6 is about 25 %, together with 52 % of the starting material. At higher temperatures, the conversion efficiency was improved, but secondary unidentified substances were then observed.

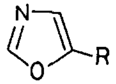
			Chemical shifts (δ, ppm)			
R = 		Solvent	H_2	H_4	$H_{arom.}$	CH_3
C_6H_5-	2	$CDCl_3$	7.87	7.33	7.50 (m)	-
		CD_3OD	8.13	7.40	7.46 (m)	-
p-$CH_3C_6H_4$-	4	$CDCl_3$	7.82	7.25	7.51(AA'),7.32(BB')	2.32
		CD_3OD	8.10	7.32	7.47(AA'),7.21(BB')	2.27
CH_3	6	CD_3Cl_3	7.75	6.77		2.28
		CD_3OD	7.95	6.73		2.22

TABLE 1. PMR spectra of oxazoles 2, 4, 6 recorded on a Varian (EM 360L, 60 MHz) spectrometer.

The following spectral data were obtained with samples purified by preparative GC. The allylic coupling constant, J_{CH_3/H_4} = 1.2 Hz, identical to the coupling observed for 2,5-dimethyloxazole and the small downfield shift of the H_2 proton with more polar solvents are characteristic PMR features of the oxazole ring system[7]. The mass spectrum displays intense peaks at m/z 83 (47 %), 68 (24), 55 (16), 54 (24), 43 (100), 41 (40) and 40 (27) confirming the mass (m/z 83) and the presence of a methyl group (m/z 68) on carbon five of the ring (m/z 43 = $CH_3\overset{+}{C}=O$).

A mechanism for this ring transformation process is proposed in scheme 1. A [1,5] sigmatropic shift of the carbonyl substituent from nitrogen to carbon is followed by nitrogen loss and cyclisation of the diradical intermediate. It is notewhorthy that oxazoles are also formed by the photochemical cleavage of the C-C bond of 3-carbonylsubstituted azirines[8].

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