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FLASH VACUUM THERMOLYSIS OF OXAZOLIDINES : A NEW WAY TO REACTIVE AZOMETHINE YLIDES. RING CLOSURE TO AZIRIDINES.

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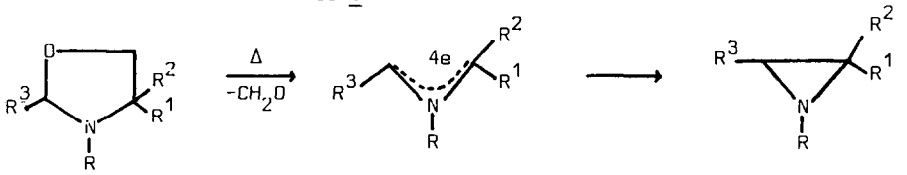
SUMMARY : Flash vacuum thermolysis of oxazolidines leads to azomethine ylides which undergo ring closure to aziridines.

General methods for aziridines synthesis are well documented. However formation of aziridines from ring closure of azomethine ylides has received few applications in the literature[1].

We have shown that the thermal retrocycloaddition of oxazolidines leads to azomethine ylides[2]. We report here the ring closure of such generated 1,3 dipoles to aziridines.

Under flash vacuum thermolysis (FVT) oxazolidines 1[3] underwent 1,3-dipolar cycloreversion giving rise to formaldehyde and azomethine ylides 2. In the gas phase ring closure occured and aziridines 3 were obtained (Scheme 1).



1 2 3

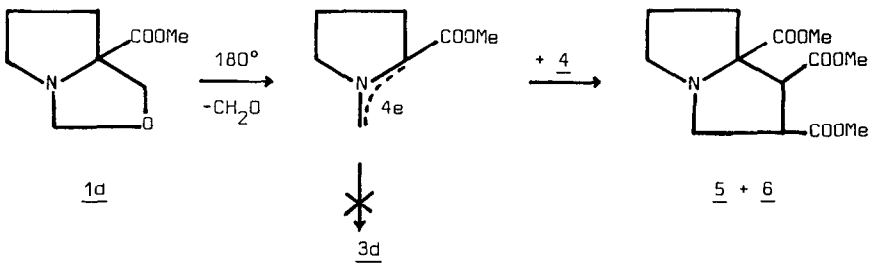
	R	R^1	R^2	R^3	1 (%)[a]	3 (%)[a]
a	CH_2Ph	H	COOMe	H	83	53
b	$(CH_2)_2COOMe$	H	COOMe	H	61	23
c	Ph	H	COOMe	H	55	80
d	$(CH_2)_3$		COOMe	H	45	77
e	Me	H	H	Ph	92	41

a : Yields are given for distillated compounds.

Scheme 1

Cycloreversion of oxazolidines can occur also in solution as it is demonstrated by the following experiments.

Oxazolidine 1d and methyl fumarate 4 heated up to 180° (toluene, sealed tube) gave rise to pyrrolidines 5 and 6 as a mixture of stereoisomers (Scheme 2). In the same conditions oxazolidines 1 alone were recovered unchanged.



Scheme 2

These results show clearly that in the liquid phase cycloreversion occured and azomethine ylides were formed. The only pathway in solution was the intermolecular cycloaddition with the best dipolarophile present in the reaction mixture. Methyl fumarate 4 reacted preferentially leading to pyrrolidines 5 and 6. In the absence of 4 formaldehyde reacted with azomethine ylides and oxazolidines 1 were recovered unchanged.

Retrocycloaddition of oxazolidines opens a new entry to azomethine ylide chemistry. Application directed to aziridines synthesis is under active investigation.

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REFERENCES AND NOTES

1. For a review see : J.A. Deyrup in "Small Ring Heterocycles" Part I, pp 1-82 ; A. Hassner Ed., 1983, John Wiley and Sons.
2. M. Joucla and J. Mortier, preceeding communication.
3. a) Oxazolidines 1a-d have been obtained from the condensation of formaldehyde with α-aminoesters through 1,3-dipolar cycloaddition of azomethine ylide with formaldehyde Oxazolidine 1e was prepared from benzaldehyde and N-méthylaminoéthanol.
b) FVT was performed at 500-600° under vacuum (3.10^{-3} mBar).

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