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THE INTRAMOLECULAR CHEMISTRY OF BENZYL AND PHENETHYL AZIDOFORMATES

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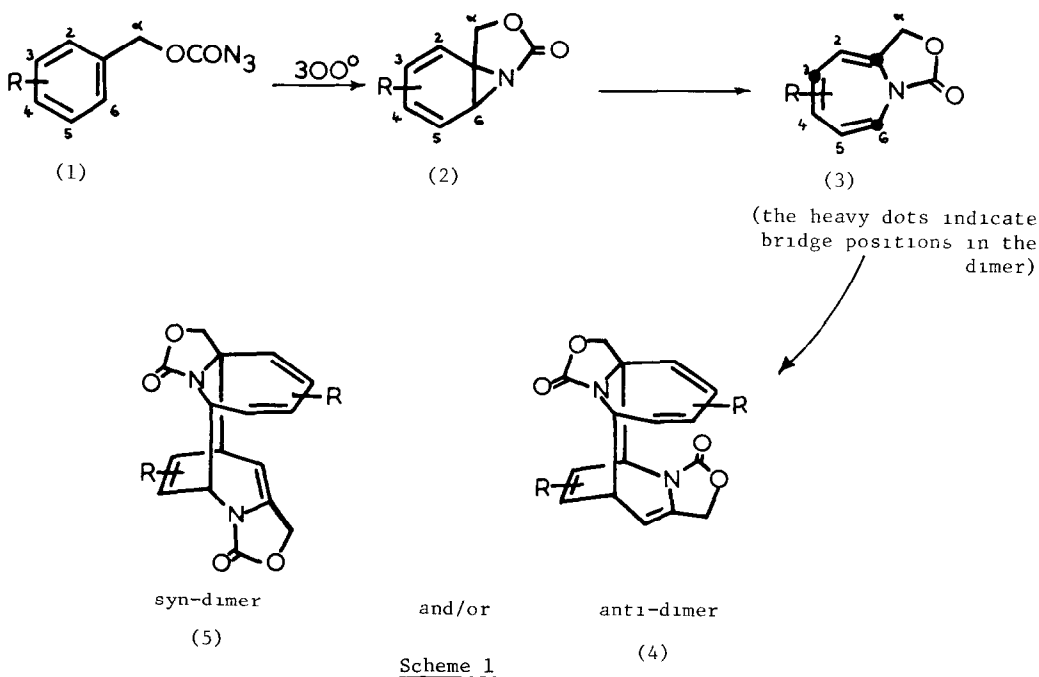
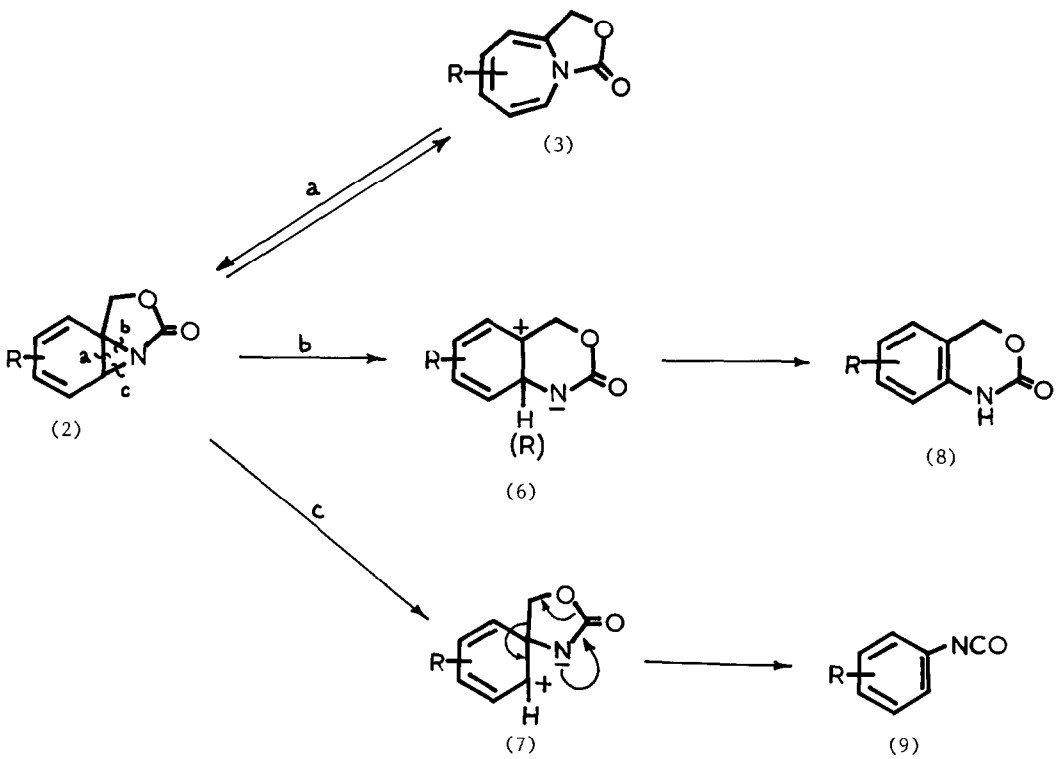
Summary *Benzyl azidoformates yield one of a variety of products on spray pyrolysis dependent upon substitution, including oxazoloazepines, their syn or anti [6 + 4] dimers, their [6 + 6] dimers, a benzoxazinone or an aryl isocyanate, the phenethyl analogues give stable oxazinoazepines.*

In an earlier publication[1] we noted that using our new technique of 'Spray Pyrolysis'[2], benzyl azidoformates (1) were transformed into the dimers (4 and 5) of the oxazoloazepines (3) The reaction was explained by involvement of the tricyclic aziridine (2) (Scheme 1), an intermediate type commonly invoked in nitrene pathways



Scheme 1

We now report that dependent upon the substituent(s) R, this intermediate (2) has several novel courses open to it (Scheme 2) and that the planar, antiaromatic azepines (3) have other modes of subsequent reaction



Scheme 2

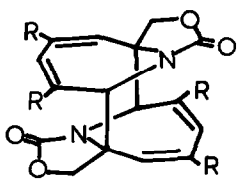
If one considers cleavage of each of the three aziridine bonds of (2) in turn, then the ability of the substituent(s) R to stabilise the putative ionic intermediates (6 and 7) may be seen as the driving force behind these alternative pathways [3]

The dimers (4) were obtained from the azides (1) with R = H, 2-Cl, α-alkyl, α-aryl and α-OPh Similarly, with R = 4 - CMe_3, 2,4-Cl_2 or 4-Br the isomers (5) were obtained while in one case (R = 4-Cl) a mixture of both dimers (4 and 5) in a 3 2 ratio was noted However, the azide (1, R = 2,6-Cl_2) gave a stable, orange azepine (85%) which on further heating (4h, 130°) gave the benzoxazinone (8, R = 2,5-Cl_2) in 64% yield which we explain by way of the equilibrium revealed in Scheme 2, and a 1,2-chlorine shift of intermediate (6, Cl in place of 6-H, R = 2-Cl) [4]

From the azide (1, R = 4-t-butyl) an orange azepine (3, R = 4-t-butyl) was again isolated, dimerisation of which gave the syn isomer (5) only slowly on heating (130°, 4h) due to steric problems However, the mesityl and durenyl azidoformates (1, R = 2,4,6-Me_3 and R = 2,3,5,6-Me_4 respectively) both yielded unstable azepine monomers (3) which readily and almost

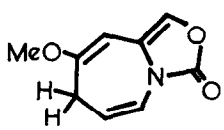
quantitatively were converted into the isocyanates (8 and 9) on brief heating in xylene or merely on standing overnight at ambient temperature In both of these cases the methyl groups stabilised the positive charge on the ring in the intermediate (7)

In none of the cases in which azepine dimers (4 and 5) were formed, were substituents present at the bridgehead positions (marked by heavy dots in (3)) If such substituents are present, either the dimers are not formed (as with the 2,6-Cl_2, 2,4,6-Me_3 and 2,3,5,6-Me_4 substituted azepines (3) discussed above) or else the dimerisation takes a different course than the [6 + 4] mode Thus the 3,5-dichlorophenyl- and 3,5-dimethylphenyl azidoformates (1) gave only the symmetrical [6 + 6] dimers (10) on spray pyrolysis Unlike our [6 + 4] dimers,



(10) a, R=Me (87%)

b, R=Cl (64%)



(11)

Paquette and his co-workers[5] noted that the [6 + 4] dimer of N-ethoxycarbonyl azepine (formed at 130°) rearranged at over 200° to the symmetrical [6 + 6] isomer Finally, 3-methoxyphenyl azidoformate (1, R = 3-MeO) gave an unseparated mixture of two dimers together with the rearranged azepine (11) These results are all in accord with the known tendency for dimerisations to proceed at the least substituted available sites[6]

The phenethyl azidoformates (12) behave quite differently on spray pyrolysis In every case a stable yellow crystalline azepine (13) was isolated which showed no tendency to dimerise or otherwise rearrange thermally, thus underlining the particular instability of the 7/5 fused analogue In each case the corresponding 4-aryl oxazolidinone (14) was also formed, in amount dependent upon the substituent R, electron releasing groups favouring the azepines[7]

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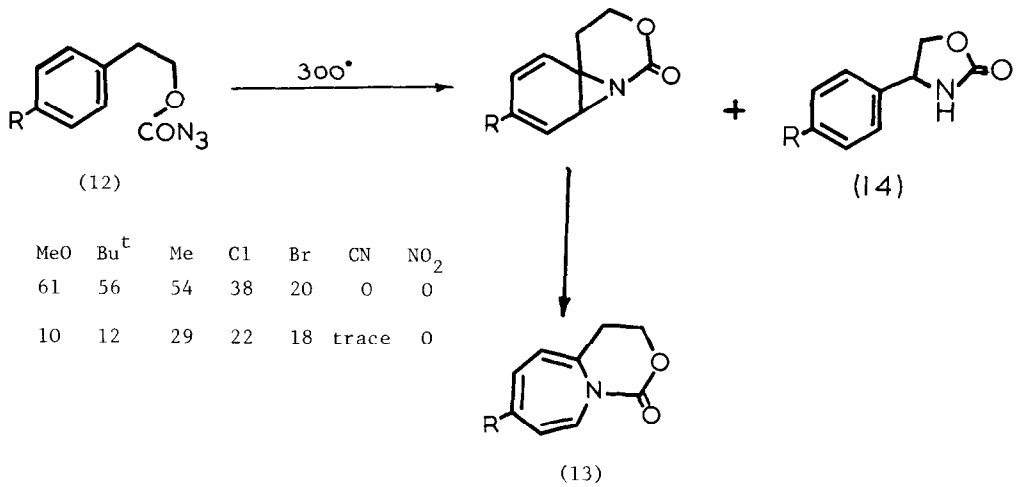

R	MeO	Bu^t	Me	Cl	Br	CN	NO_2
(13)%	61	56	54	38	20	0	0
(14)%	10	12	29	22	18	trace	0

Scheme 2

References and Notes

†All new compounds gave satisfactory analytical and spectroscopic data

1 O Meth-Cohn and S Rhouati, *J C.S Chem Comm*, 1980, 1162.

2 for details of the method see M. Clancy, D.G Hawkins, M.M Hesabi, O Meth-Cohn, and S Rhouati, *J Chem Research (S)*, 1982, 78.

3 It is possible that the 'intermediates' (6 and 7) may be a crude representation of a transition state of a concerted process or even that homolytic analogues could be involved (cf. ref. 6)

4 As revealed below, azepines with substituents at bridgehead positions of the potential dimers do not dimerise under our conditions.

5 L A Paquette, J.H Barrett and D E Kuhla, *J Amer Chem Soc*, 1969, *91*, 3616

6 L.A. Paquette, D E Kuhla and J H. Barrett, *J Org Chem*, 1969, 34, 2879

7. R A Abramovitch, S B Hendi and A O. Kress independently noted the same products in similar yields on flash vacuum pyrolysis of (12, R = H) at 650°. *J C S Chem Comm*, 1981, 1087.

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