Cyclisation of Azidoformates, Formation of Aziridines

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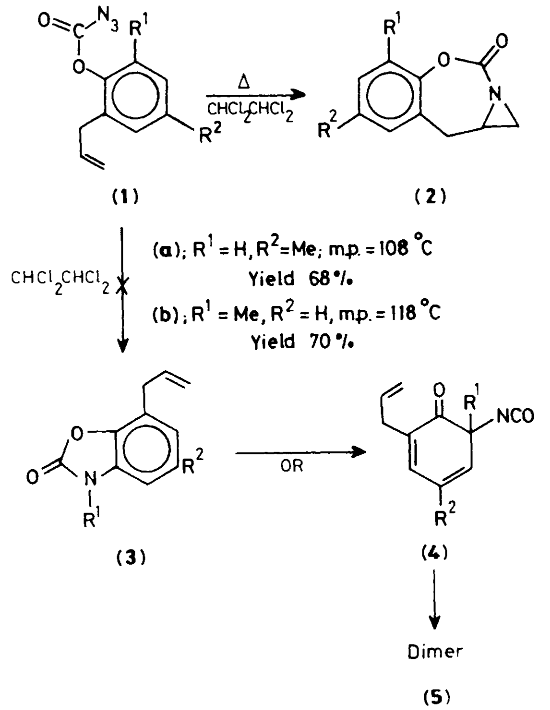
Thermolysis of azidoformate (**1**) in refluxing 1,1,2,2-tetrachloroethane gave aziridine (**2**), while the same azide decomposed in toluene gave the phenoxy carbonyl azepine (**6**).

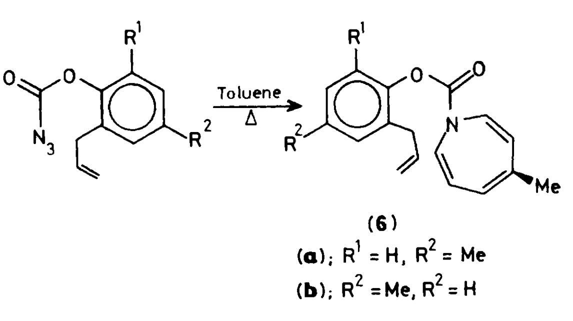
Phenyl and benzyl azidoformates decompose in the vapour phase to yield a wide variety of heterocycles.[1,2] Meth-Cohn *et al.*[3] reported that the decomposition of 2,6-disubstituted phenyl azidoformate, both on spray pyrolysis[3] and on refluxing in tetrachloroethane, gave a number of products including isocyanatocyclohexadienones and their dimers and benzoxazolones. The course of the reaction was dependent on the position and the nature of the substituents.

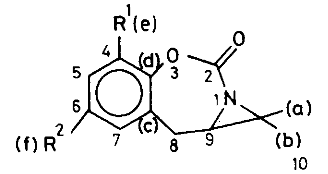
If an allyl substituent is present, addition to its double bond might compete with insertion into the benzene ring. Here we

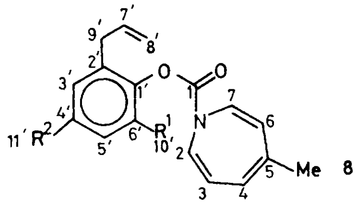
Table 1. Chemical shifts ($^1H/^{13}C$ n.m.r.) of the aziridine [(**2a**) and (**2b**)]. Solvent: $CDCl_3$.

	(**2a**); $R^1 = H, R^2 = Me$			(**2b**); $R^1 = Me, R^2 = H$		
Proton	$^1H/\delta$	J	$^{13}C/\delta$	$^1H/\delta$	J	$^{13}C/\delta$
4	7.2 d	7.5	129.83	2.25 s		127.95
5	7.02 d	7.5	119.99	7.01 dd	7.5, 3	124.58
6	2.32 s		127.86	7.01 dd	7.5, 7.5	126.73
7	7.03 d	3	129.62	7.0 dd	7.5, 3	130.81
8	2.40 d	7	32.09	2.4 dd	7	31.97
9	2.95 h	3	44.33	2.90 h	3	44.19
10(a)	2.60 dd	14	34.68	2.60	14	34.56
10(b)	3.20 dd	14		3.20	14	
2			159.00			158.49
4(e)						16.34
6(f)			20.76			
7(c)			134.77			129.17
7(d)			149.26			149.57









report the first examples of an intramolecular addition of the azidoformate nitrene to an alkenic double bond, giving rise to a very stable substituted aziridine. The reaction is remarkable and possibly unique, in that it gives a 7-membered product rather than the preferred 5-membered (or occasionally 6-membered) easily achieved alternative.

When phenyl azidoformates (**1a**) and (**1b**) were thermolysed in refluxing tetrachloroethane, white crystalline aziridines were formed, which recrystallised from ethyl acetate–light petroleum to give 68% and 70% of (**2a**) and (**2b**) respectively.

It is obvious that the nitrene prefers addition into the alkenic double bond rather than insertion into the aromatic ring, because no sign of benzoxazolone (**3**), cyclohexadienone monomer (**4**) or dimer (**5**) were observed. This led us to investigate the competiton between this intramolecular insertion by the nitrene and intermolecular insertion into a solvent having a benzene ring. When the azides were thermolysed in boiling toluene the sole products were the aryloxycarbonylazepines (**6**).

The aziridines [(**2a**) and (**2b**)] showed characteristic carbonyl absorption frequencies (1715 cm^{-1}) in their i.r. absorption spectra, and also gave analyses (C,H,N) consistent with the formula ($C_{11}H_{11}NO_2$). However, their ^1H n.m.r. and ^{13}C n.m.r. spectra allowed unambiguous assignment of their structures. The ^1H n.m.r. and ^{13}C n.m.r. spectral data are summarised in the Table 1.

Whereas the azepines [(**6a**) and (**6b**)] showed carbonyl absorption frequencies (1710 cm^{-1}) in their i.r. absorption spectra, they gave analyses (C,H,N) consistent with the fomula ($C_{17}H_{19}NO_2$) and showed appropriate molecular ions in their mass spectra. ^1H N.m.r. and ^{13}C n.m.r. spectra obtained were similar to the reported results[4] of their analogues, and are summarised in Table 2.

We would like to thank Professor Pete and Professor Chuche in Reims, France, for their help and for allowing Mr.

Table 2. Chemical shifts (^1H/^{13}C n.m.r.) of the azepines [(**6a**) and (**6b**)]. Solvent: $CDCl_3$.

	(**6a**); $R^1 = H, R^2 = Me$			(**6b**); $R^1 = Me, R^2 = H$		
Proton	$^1H/\delta$	*J*	$^{13}C/\delta$	$^1H/\delta$	*J*	$^{13}C/\delta$
1			151.21			151.04
2	5.55—5.70m		136.33	5.50—5.60m		136.19
3	5.95—6.20m		129.62	5.92—6.15m		129.02
4	5.95—6.20m		125.90	5.92—6.15m		126.03
5			122.37			123.18
6	5.95—6.20m		124.84	5.92—6.15m		125.06
7	5.55—5.70m		134.08	5.50—5.65m		133.08
8	1.80s		19.75	1.80s		21.31
1′			140.60			139.58
2′			132.62			132.65
3′	7.15dd	3	127.79	7.05m		129.75
4′			129.24	7.05m		127.87
5′	7.02dd	3,7	128.76	7.05m		128.08
6′	6.95d	7	130.84			130.97
7′	5.84m		120.25	5.80m		119.77
8′	5.02m		116.15			116.02
9′	3.25d	2	35.41	3.30d	2	34.69
10′				2.30s		16.37
11′	2.29s		19.02			

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