

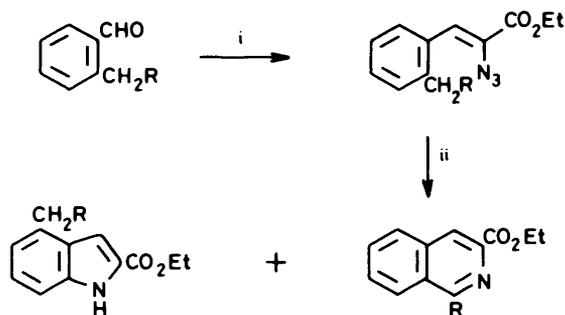
## Vinyl Azides in Heterocyclic Synthesis. Part 2.<sup>1</sup> Selectivity in the Decomposition of Azidocinnamates with Olefinic *ortho*-Substituents<sup>2</sup>

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Thermolysis of azidocinnamates with an olefinic *o*-substituent gives products (isoquinolines, azepines, aziridines) formed by selective interaction of the azide, and the derived nitrene, with the olefinic substituent, cyclisation onto the unsubstituted aromatic *ortho* position now being a minor reaction. However when this interaction is removed by epoxidation of the alkene, cyclisation occurs exclusively to the aromatic ring to give 4-substituted indoles in high yield. Thus *o*-vinyl azidocinnamate (**1a**) gives isoquinoline (**5a**), and (**1b**) gives isoquinoline (**5b**) together with the 3-benzazepine (**7**); *o*-allyl azidocinnamate (**2a**) gives indole (**12**), the 3-benzazepine (**13**), and the tricyclic aziridines (**14**) and (**15**), and (**2b**) gives an analogous mixture of products from which only the indole (**19**) was isolated. A mechanism is proposed (Scheme 2) in which the azide partitions itself between intramolecular cycloaddition to the double bond and loss of nitrogen to give the azirine-nitrene equilibrium. This rationalises the formation of the 4 temperature-dependent products from azidocinnamate (**2a**), the aziridine (**15**) involving an intramolecular ene reaction of the imine bond. Thermolysis of the epoxy-azidocinnamates (**3**) and (**4**) gives indoles (**20**) and (**21**) respectively in high yield; treatment of (**3**) with triethyl phosphite gives the aziridine (**8**), presumably by formation of an iminophosphorane and intramolecular nucleophilic attack by this on the epoxide, the counterpart of a known intermolecular reaction.

In a previous paper<sup>1</sup> we have described the thermal decomposition of a range of azidocinnamates bearing *ortho*-alkyl substituents. The vinylnitrenes derived from these azides, easily prepared from the corresponding benzaldehydes, either cyclise onto the free *ortho*-position to give 4-substituted indoles, or give isoquinolines by interaction with the alkyl substituent (Scheme 1), the presence of iodine increasing the preference for the latter reaction.

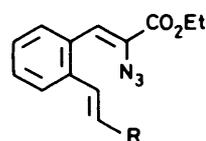


Scheme 1. Reagents: i,  $\text{EtO}_2\text{CCH}_2\text{N}_3\text{-NaOEt-EtOH}$ ,  $-10^\circ\text{C}$ ; ii, Heat

Since nitrenes (and azides) react readily with olefinic double bonds, we investigated the thermal decomposition of azidocinnamates bearing an olefinic *ortho*-substituent in the expectation that the major products might arise from interaction of the nitrene (or azide) with the double bond in preference to the aromatic ring,<sup>2</sup> and we now report our results in detail.

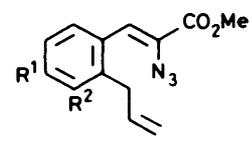
### Results and Discussion

The azidocinnamates (**1**) and (**2**) were prepared from the corresponding known benzaldehydes by condensation with ethyl azidoacetate under basic conditions. The epoxides (**3**) and (**4**) were obtained by treatment of the azides (**1b**) and (**2a**) with 3-chloroperbenzoic acid in dichloromethane.



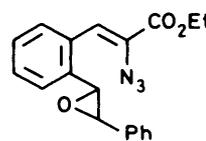
(1)

a; R = H  
b; R = Ph

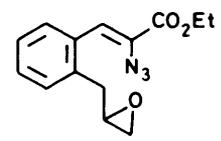


(2)

a; R<sup>1</sup> = R<sup>2</sup> = H  
b; R<sup>1</sup> = MeO, R<sup>2</sup> = HO



(3)

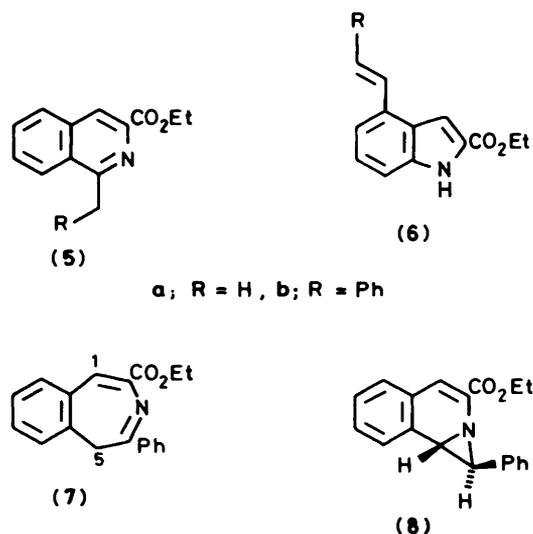


(4)

The azide (**1a**) is an unstable oil, decomposing slowly on standing at  $5^\circ\text{C}$  to ethyl 1-methylisoquinoline-3-carboxylate (**5a**) (ca. 50% conversion after 21 days). A similar conversion into the isoquinoline was achieved by heating in refluxing ether (19 h) or in deuteriochloroform at  $35^\circ\text{C}$  (21 h). When the latter reaction was followed by  $^1\text{H}$  n.m.r. spectroscopy, no intermediates could be detected. Heating the azide (**1a**) in refluxing toluene caused rapid decomposition, and the isoquinoline (**5a**) was isolated in 75% yield, together with a small amount (7%) of the 4-vinylindole (**6a**). The *ortho*-styrylazidocinnamate (**1b**) is stable at room temperature but on heating in boiling toluene decomposed to give the 1-benzylisoquinoline (**5b**) (36%) and the indole (**6b**) (9%). The major product, however, was the 3-benzazepine (**7**) (37%), or the 5*H*-tautomer,<sup>†</sup> the yield increasing slightly when the thermolysis was carried out at a higher temperature in boiling xylene. Again, no intermediates in

<sup>†</sup> It was not possible, on the basis of i.r. or n.m.r. spectroscopy, to assign unambiguously the position of the tautomeric hydrogen atom.

the formation of the isoquinoline (**5b**) and the benzazepine (**7**) were observed, but when the tricyclic aziridine (**8**) was isolated (from a reaction described later), it was cleanly converted into the benzazepine (**7**) when heated in toluene, suggesting that it may be an intermediate in the thermolysis of the azide.

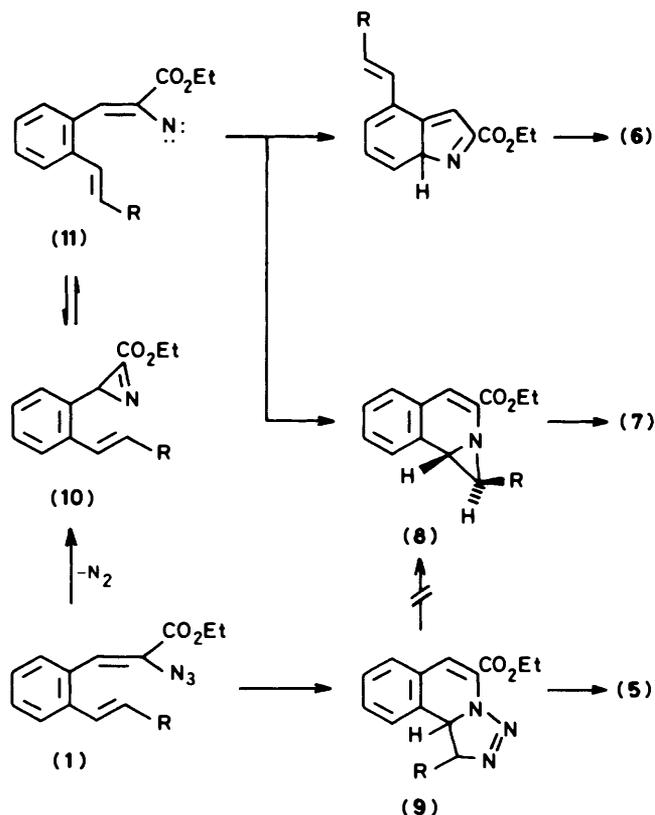


A possible pathway for the decomposition of the azides (**1**) is shown in Scheme 2, in which the azide initially partitions itself between intramolecular cycloaddition to the double bond to give the triazoline (**9**), and decomposition to the azirine (**10**), which will be in thermal equilibrium with the vinylnitrene (**11**).<sup>3</sup> The indoles (**6**) are almost certainly formed by electrocyclicisation of the vinylnitrene (**11**) followed by an aromatising [1,5]-hydrogen shift, and since in the case of the azide (**1a**), isoquinoline formation occurs at 5 °C, conditions under which nitrene formation is very unlikely, the isoquinoline is probably formed from the triazoline (**9**) by loss of nitrogen accompanied by a [1,2]-hydrogen shift. The tricyclic aziridine (**8**), and hence the benzazepine (**7**), can arise by loss of nitrogen from the triazoline, or by intramolecular addition of the nitrene (**11**) to the double bond. Evidence in favour of the latter pathway was obtained when a sample of the azirine (**10b**), prepared by low intensity irradiation of the azide (**1b**) gave, on heating in benzene, the indole (**6b**) and the benzazepine (**7**) in the ratio 1:4, and no isoquinoline (**5b**).

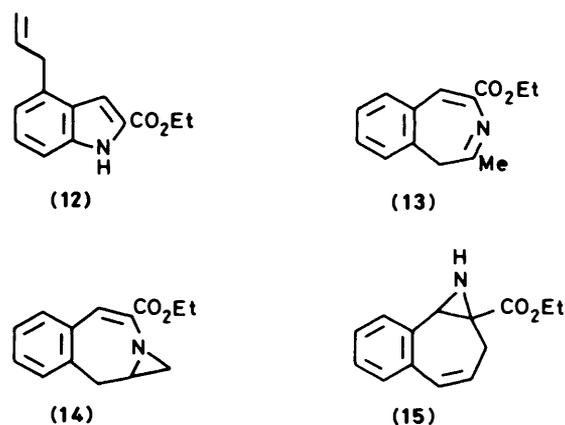
The difference in product ratio from the azides (**1a**) and (**1b**) presumably reflects the ease with which intramolecular addition of the azide to the double bond occurs, and finds precedent in the fact that in intermolecular 1,3-dipolar cycloadditions, styrenes react more readily than stilbenes.<sup>4</sup>

Further evidence that the decomposition of azidocinnamates bearing *ortho*-olefinic substituents follows the general pattern proposed in Scheme 2 was obtained with the *ortho*-allyl azide (**2a**). Decomposition of the azide (**2a**) in a range of solvents at reflux gave 4 products identified as the indole (**12**), the 3-benzazepine (**13**) (or the 1*H*-tautomer), and the tricyclic aziridines (**14**) and (**15**). No ethyl 1-vinylisoquinoline-3-carboxylate was observed. The relative yields of products, which were temperature dependent, are shown in the Table, and since the aziridines (**14**) and (**15**) were unstable to chromatography the yields based on n.m.r. spectra of the product mixture obtained immediately after the thermolysis are shown for comparison.

The formation of all of these products can be explained by a temperature dependent competition between cycloaddition and decomposition of the vinyl azide (Scheme 3). Intramolecular



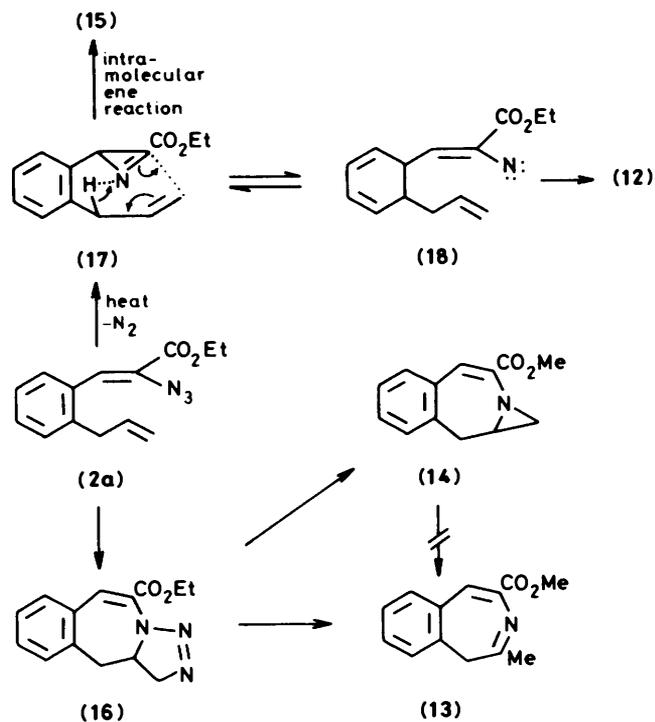
Scheme 2. a, R = H; b, R = Ph



cycloaddition to the allyl double bond gives the triazoline (**16**), whilst decomposition with loss of nitrogen leads to the azirine (**17**)-vinylnitrene (**18**) equilibrium. The latter pathway is the minor one at lower temperatures but is favoured with increasing reaction temperature, and the products which increase at higher temperature, the indole (**12**) and the aziridine (**15**), are thus azirine-vinylnitrene derived. The indole (**12**) is almost certainly formed by cyclisation of the nitrene (**18**) followed by a [1,5]-hydrogen shift, and the formation of the aziridine (**15**) is rationalised by an intramolecular ene reaction involving the C=N bond of the azirine (**17**). Ene reactions involving carbon-nitrogen double bonds are relatively rare,<sup>5</sup> and although two examples involving azirines have been reported,<sup>6</sup> this appears to be the first intramolecular example. However, since our preliminary account of this work appeared,<sup>2</sup> further examples of the intramolecular ene reactions of C=N bonds have been reported.<sup>7</sup>

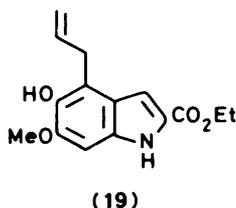
**Table.** Products from the thermolysis of the azide (2a)

Thermolysis solvent	Temp. (°C)	Time (h)	Isolated yield (N.m.r. yield)			
			(12)	(13)	(14)	(15)
Benzene	80	4.5	—(5)	—(28)	—(44)	—(23)
Toluene	110	1.5	8(9)	21(22)	12(37)	31(34)
Xylene	140	0.75	11(11)	16(17)	20(33)	29(37)
Decalin	190	0.1	20(20)	6(7)	13(13)	20(44)

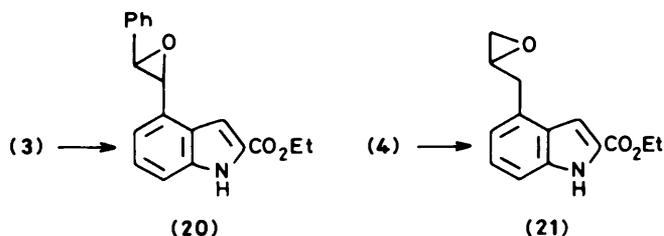


The aziridine (14) could arise by intramolecular addition of the nitrene (18) to the allyl double bond, or from the triazoline (16). However, since both the aziridine (14) and the azepine (13) are favoured at lower temperatures, it is likely that both arise from the triazoline (16). Furthermore, when the aziridine (14) is heated in toluene it is not converted into the azepine (13).

Thermolysis of the more highly substituted *ortho*-allyl azido-cinnamate (2b) gave a mixture of products, and although n.m.r. spectroscopy indicated that they were analogous to those obtained from the simpler azide (2a), the only product which we were able to characterise was the indole (19) (28%).



When the double bond of the *ortho*-substituent was 'protected' by epoxidation, as in the azides (3) and (4), indoles were the major products of thermolysis. Thus heating the azide (3) in toluene gave the 4-substituted indole (20) in good yield



(79%). Similarly, the azide (4) gave the indole (21) in quantitative yield.\*

Decomposition of the epoxy azide (3) in tetrahydrofuran in the presence of triethyl phosphite at room temperature took a different course, and the aziridine (8) was isolated as the major (40%) product. The aziridine (8), which was assigned the *trans* stereochemistry on the basis of the coupling constant (3 Hz) for the three-membered ring protons, is presumably formed by attack of the phosphite on the azide to give an iminophosphorane, which then undergoes intramolecular nucleophilic attack on the epoxide. Iminophosphoranes are known to react intermolecularly with epoxides to give aziridines.<sup>8</sup>

A general picture thus emerges in which the products from the thermolysis of azidocinnamates containing an olefinic *ortho*-substituent are derived by selective interaction with the substituent in preference to the free *ortho*-position of the aromatic ring. However, when the possibility for such interaction is removed by epoxidation, cyclisation onto the aromatic ring with formation of indoles is the exclusive reaction.

### Experimental

For general points see ref. 1.

**2-Vinylbenzaldehyde.**—Prepared from 2-phenylethylamine by the literature procedure and had b.p. 88–92 °C at 7 mmHg (lit.,<sup>9</sup> 113–115 °C at 18 mmHg).

**2-(E)-Styrylbenzaldehyde.**—Prepared from (*E*)-stilbene-2-carboxylic acid<sup>10</sup> by reduction with lithium aluminium hydride (100%) followed by oxidation with Jones' reagent (85%),  $\nu_{\max}$  (neat) 2 740, 1 685, and 1 595  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 6.99 (1 H, d, *J* 16 Hz), 7.20–7.83 (9 H, m), 8.00 (1 H, d, *J* 16 Hz), and 10.21 (1 H, s). The literature<sup>11</sup> quotes this compound as having m.p. 83 °C; the present material did not solidify.

**2-Allylbenzaldehyde.**—2-Allylchlorobenzene was prepared from 2-bromochlorobenzene in 62% yield, b.p. 62–68 °C at 5 mmHg (lit.,<sup>12</sup> 60–70 °C at 5 mmHg). 2-Allylchlorobenzene (11.60 g, 0.08 mol) in THF (20 ml) was added to a suspension of active magnesium<sup>13</sup> (ca. 0.14 mol) in THF (250 ml) at room temperature. The mixture was stirred at room temperature for 3 h, before being quenched with excess of dimethylformamide. The reaction was stirred overnight prior to being poured into a mixture of water (50 ml) and hydrochloric acid (3M; 50 ml). Extraction with ether and chromatography gave the title compound<sup>14</sup> (2.30 g, 21%),  $\delta$  (90 MHz;  $\text{CCl}_4$ ) 3.76 (2 H, m), 4.78–5.17 (2 H, m), 5.72–6.25 (1 H, m), 7.10–7.85 (4 H, m), and 10.14 (1 H, s).

**2-Allyl-3-hydroxy-4-methoxybenzaldehyde.**—Prepared from isovanillin by the literature procedure and had m.p. 57–58 °C (lit.,<sup>15</sup> 58–59 °C).

\* Although n.m.r. spectroscopy of the product after thermolysis indicated that the indole (21) had been formed in quantitative yield, we were not able to determine a 'true' isolated yield owing to the instability of the product, and the small scale nature of the experiment.

*Preparation of Azides.*—The general procedure described previously<sup>1</sup> was used to prepare the following azides.

*Ethyl 2-azido-3-(2-vinylphenyl)propenoate (1a).* Yield 28%, unstable pale yellow oil,  $v_{\max}$ (neat) 2 120, 1 710, and 1 617  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ )\* 1.32 (3 H, t), 4.33 (2 H, q), 5.37 (1 H, dd,  $J$  1.5, 11 Hz), 5.60 (1 H, dd,  $J$  1.5, 17 Hz), 6.95 (1 H, dd,  $J$  11, 17 Hz), and 7.15–7.95 (5 H, m);  $m/z$  215 ( $M^+$  – 28, base).

*Ethyl 2-azido-3-[2-(E)-styrylphenyl]propenoate (1b).* Yield 63%, pale yellow needles, m.p. 69–70 °C (from ether–light petroleum) (Found: C, 71.4; H, 5.3; N, 13.0.  $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2$  requires C, 71.5; H, 5.4; N, 13.2%);  $v_{\max}$ (Nujol) 2 120 and 1 705  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.36 (3 H, t), 4.40 (2 H, q), 6.98 (1 H, d,  $J$  15 Hz), and 7.30–8.05 (11 H, m);  $m/z$  291 ( $M^+$  – 28, base).

*Ethyl 2-azido-3-(2-allylphenyl)propenoate (2a).* Yield 54%, pale yellow oil,  $v_{\max}$ (neat) 2 125 and 1 713  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.39 (3 H, t), 3.43 (2 H, m), 4.37 (2 H, q), 4.37–5.20 (2 H, m), 5.72–6.20 (1 H, m), and 7.10–8.09 (5 H, m);  $m/z$  257 ( $M^+$ ), 229, 220, and 156 (base).

*Ethyl 2-azido-3-(2-allyl-3-hydroxy-4-methoxyphenyl)propenoate (2b).* Yield 40%, pale yellow needles, m.p. 97–99 °C (from ether–light petroleum) (Found: C, 59.1; H, 5.6; N, 13.6.  $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_4$  requires C, 59.4; H, 5.65; N, 13.85%);  $v_{\max}$ (Nujol) 3 510, 2 120, 1 710, and 1 610  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.37 (3 H, t), 3.40–3.60 (2 H, m), 3.92 (3 H, s), 4.36 (2 H, q), 4.80–5.12 (2 H, m), 5.65 (1 H, s), 5.62–6.10 (1 H, m), 6.75 (1 H, d,  $J$  8 Hz), 7.13 (1 H, s), and 7.65 (1 H, d,  $J$  8 Hz);  $m/z$  303 ( $M^+$ ) and 275 (base).

*Ethyl 2-Azido-3-[2-(3-phenyloxiran-2-yl)phenyl]propenoate (3).* A solution of 3-chloroperbenzoic acid (80%; 0.833 g, 3.8 mmol) in dichloromethane (10 ml) was added dropwise to a stirred solution of the azide (1b) (1.12 g, 3.5 mmol) in dichloromethane (5 ml), and the mixture stirred overnight at room temperature. Standard work-up and chromatography on alumina gave the title compound (3) (0.662 g, 56%) as colourless needles, m.p. 86–88 °C (Found: C, 68.3; H, 5.1; N, 12.5.  $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_3$  requires C, 68.05; H, 5.1; N, 12.5%);  $v_{\max}$ (Nujol) 2 115 and 1 700  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.12 (3 H, t), 3.78 (1 H, d,  $J$  2 Hz), 4.02 (1 H, d,  $J$  2 Hz), 4.23 (2 H, q), 7.14 (1 H, s), and 7.25–8.05 (9 H, m).

*Ethyl 2-Azido-3-(oxiran-2-ylmethylphenyl)propenoate (4).* The azide (2a) (285 mg) was epoxidised with 3-chloroperbenzoic acid exactly as described above to give, after chromatography, the title compound (4) (7 mg, 2%) as an unstable colourless oil,  $v_{\max}$ ( $\text{CCl}_4$ ) 2 120, 1 715, 1 620, and 1 240  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.39 (3 H, t), 2.45–2.62 (1 H, m), 2.70–2.85 (1 H, m), 2.87–3.22 (3 H, m), 4.41 (2 H, q), 7.22 (1 H, s), and 7.20–8.05 (4 H, m);  $m/z$  273 ( $M^+$ ), 245 (base), and 199.

*Thermolysis of the Azide (1a).*—A solution of the azide (1a) (168 mg) in toluene (38 ml) was heated under reflux for 1.5 h. Evaporation of the solvent and chromatography gave (i) ethyl 4-vinylindole-2-carboxylate (6a) (10 mg, 7%),  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.40 (3 H, t), 4.44 (2 H, q), 5.46 (1 H, dd,  $J$  1.5, 11 Hz), 5.95 (1 H, dd,  $J$  1.5, 17 Hz), 7.14 (1 H, dd,  $J$  11, 17 Hz), 7.20–7.52 (4 H, m), and 8.90 (1 H, br s); and (ii) ethyl 1-methylisoquinoline-3-carboxylate (5a) (112 mg, 75%), m.p. 104 °C (Found: C, 72.8; H, 6.1; N, 6.5.  $\text{C}_{13}\text{H}_{13}\text{NO}_2$  requires C, 72.5; H, 6.1; N, 6.5%);  $v_{\max}$ (Nujol) 1 727  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.46 (3 H, t), 3.00 (3 H, s), 4.53 (2 H, q), 7.55–8.20 (4 H, m), and 8.37 (1 H, s);  $m/z$  215 ( $M^+$ ), 171, 170, and 143 (base).

*Thermolysis of the Azide (1b).*—A solution of the azide (1b) (254 mg) in toluene (40 ml) was heated under reflux for 2.25 h. The solvent was evaporated and the residue chromatographed

to give (i) ethyl 1-benzylisoquinoline-3-carboxylate (5b) (84 mg, 36%), m.p. 94 °C (Found: C, 78.2; H, 5.9; N, 4.8.  $\text{C}_{15}\text{H}_{17}\text{NO}_2$  requires C, 78.3; H, 5.9; N, 4.8%);  $v_{\max}$ (Nujol) 1 725  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.45 (3 H, t), 4.54 (2 H, q), 4.79 (2 H, s), 7.10–8.25 (9 H, m), and 8.47 (1 H, s);  $m/z$  291 ( $M^+$ ), 262, 245, 217, and 216 (base); (ii) ethyl 4-phenyl-1H-3-benzazepine-2-carboxylate (7) (86 mg, 37%), b.p. 160 °C at 0.3 mmHg (Kugelrohr) (Found: C, 77.95; H, 5.9; N, 4.8.  $\text{C}_{19}\text{H}_{17}\text{NO}_2$  requires C, 78.3; H, 5.9; N, 4.8%);  $v_{\max}$ ( $\text{CCl}_4$ ) 1 722 and 1 634  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.32 (3 H, t), 3.30–3.90 (2 H, br s), 4.32 (2 H, q), 7.28 (1 H, s), 7.30–7.65 (7 H, m), and 7.85–8.03 (2 H, m);  $m/z$  291 ( $M^+$ ), 219, and 102 (base); and (iii) ethyl 4-(E)-styrylindole-2-carboxylate (6b) (20 mg, 9%), m.p. 173–174 °C (Found: C, 78.6; H, 5.9; N, 4.8.  $\text{C}_{19}\text{H}_{17}\text{NO}_2$  requires C, 78.3; H, 5.9; N, 4.8%);  $v_{\max}$ (Nujol) 3 350, 1 690, and 1 672  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.43 (3 H, t), 4.48 (2 H, q), 6.97–7.80 (11 H, m), and 9.05 (1 H, br s);  $m/z$  291 ( $M^+$ , base).

*Thermal Rearrangement of the Aziridine (8).*—A sample of the aziridine (8) (prepared as described later) was heated in toluene under reflux for 2 h. The solvent was evaporated, and the residue was shown by t.l.c. and n.m.r. spectroscopy to consist only of the benzazepine (7).

*Thermolysis of the Azide (2a).*—(a) *In toluene.* A solution of the azide (2a) (107 mg) in toluene (20 ml) was heated under reflux for 1.5 h. Evaporation of the solvent, and chromatography of the residue gave (i) ethyl 4-allylindole-2-carboxylate (12), (8 mg, 8%), m.p. 89–91 °C,  $v_{\max}$ (Nujol) 3 310 and 1 695  $\text{cm}^{-1}$ ,  $\delta$  (250 MHz;  $\text{CDCl}_3$ ) 1.44 (3 H, t), 3.68 (2 H, br d), 4.41 (2 H, q), 5.06–5.22 (2 H, m), 6.00–6.17 (1 H, m), 6.92–7.40 (4 H, m), and 8.91 (1 H, br s);  $m/z$  229 ( $M^+$ ), 189, 183, 156, 143, 119 (base), 116, and 105; (ii) ethyl 9,9a-dihydro-1H-azirino[1,2-b]-[3]benzazepine-3-carboxylate (14) (12 mg, 12%), colourless oil,  $v_{\max}$ ( $\text{CCl}_4$ ) 1 715  $\text{cm}^{-1}$ ;  $\delta$  (250 MHz;  $\text{CDCl}_3$ ) 1.40 (3 H, t), 1.57 (1 H, br d,  $J$  5.5 Hz), 2.23 (1 H, br d,  $J$  7 Hz), 2.35 (1 H, dd,  $J$  15, 21.5 Hz), 3.00 (1 H, dddd,  $J$  5.5, 6.7, 15 Hz), 3.30 (1 H, dd,  $J$  6, 21.5 Hz), 4.34 (2 H, q), 6.95 (1 H, s), and 7.15–7.32 (4 H, m);  $m/z$  229 ( $M^+$ ), 200, 155, 115, 85, and 83 (base); (iii) ethyl 1,1a,2,8b-tetrahydrobenzocyclohepta[5,6-b]azirine-1a-carboxylate (15) (30 mg, 31%), colourless oil,  $v_{\max}$ ( $\text{CCl}_4$ ) 3 300 and 1 720  $\text{cm}^{-1}$ ;  $\delta$  (250 MHz;  $\text{CDCl}_3$ ) 1.34 (3 H, t), 2.11 (1 H, br s, exch.  $\text{D}_2\text{O}$ ), 2.50 (1 H, dd,  $J$  8, 15 Hz), 2.91 (1 H, dd,  $J$  5.7, 15 Hz), 3.23 (1 H, br s), 4.31 (2 H, qq), 6.05 (1 H, ddd,  $J$  5.7, 8, 11.5 Hz), 6.59 (1 H, d,  $J$  11.5 Hz), and 7.05–7.65 (4 H, m);  $m/z$  229 ( $M^+$ ), 200, 183, 156, 119 (base), and 117; and (iv) ethyl 4-methyl-1H-3-benzazepine-2-carboxylate (13) (20 mg, 21%), colourless oil,  $v_{\max}$ ( $\text{CCl}_4$ ) 1 710 and 1 635  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.41 (3 H, t), 2.28 (3 H, s), 3.15 (2 H, br s), 4.39 (2 H, q), 7.25–7.50 (4 H, m), and 7.82 (1 H, s);  $m/z$  229 ( $M^+$ ), 200 (base), 143, 129, and 115.

(b) *In benzene.* The azide (2a) was heated in benzene under reflux for 4.5 h. The products were not separated but n.m.r. analysis indicated that the crude yields were as shown in the Table.

(c) *In xylene.* The azide (2a) was heated in refluxing xylene for 0.75 h. The results are summarised in the Table.

(d) *In decalin.* The azide (2a) was heated in refluxing decalin for 0.1 h. The results are summarised in the Table.

*Thermolysis of the Azide (2b).*—A solution of the azide (2b) (207 mg) in toluene (30 ml) was heated under reflux for 0.75 h. Evaporation of the solvent gave a mixture of 4 products (t.l.c., n.m.r.) from which was isolated ethyl 4-allyl-5-hydroxy-6-methoxyindole-2-carboxylate (19) (53 mg, 28%), m.p. 179–180 °C (from chloroform–light petroleum) (Found: C, 65.3; H, 6.3; N, 5.1.  $\text{C}_{15}\text{H}_{17}\text{NO}_4$  requires C, 65.4; H, 6.2; N, 5.1%);  $v_{\max}$ (Nujol) 3 548, 3 465, 1 687, and 1 637  $\text{cm}^{-1}$ ;  $\delta$  (90 MHz;  $\text{CDCl}_3$ ) 1.40 (3 H, t), 3.69 (2 H, m), 3.95 (3 H, s), 4.43 (2 H, q),

\* Where the signals for the ethyl groups are quoted as t and q the corresponding coupling constants are normal ( $J$  7 Hz).

4.96—5.30 (2 H, m), 5.63 (1 H, s), 5.85—6.30 (1 H, m), 6.77 (1 H, s), 7.22 (1 H, s), and 8.89 (1 H, br s);  $m/z$  275 ( $M^+$ , base).

**Thermolysis of the Azide (3).**—A solution of the azide (3) (59 mg) in toluene (5 ml) was heated under reflux for 5.5 h. Evaporation of the solvent and chromatography of the residue on alumina gave ethyl 4-(3-phenyloxiran-2-yl)indole-2-carboxylate (20) (43 mg, 79%), m.p. 153.5—155 °C (Found: C, 74.2; H, 5.55; N, 4.6.  $C_{19}H_{17}NO_3$  requires C, 74.25; H, 5.6; N, 4.6%);  $\nu_{\max}$  (Nujol) 3 300 and 1 700  $cm^{-1}$ ;  $\delta$  (90 MHz;  $CDCl_3$ ) 1.38 (2 H, t), 4.10 (1 H, d,  $J$  2 Hz), 4.23 (1 H, d,  $J$  2 Hz), 4.43 (2 H, q), 7.05—7.60 (9 H, m), and 9.48 (1 H, br s);  $m/z$  307 ( $M^+$ ) and 278 (base).

**Decomposition of the Azide (3) in the Presence of Triethyl Phosphite.**—A solution of the azide (3) (95 mg, 0.28 mmol) in THF (5 ml) was stirred with triethyl phosphite (52 mg, 0.31 mmol) at room temperature for 12 h. Evaporation of the solvent and chromatography of the residue on alumina gave ethyl 1-phenyl-1,8b-dihydroazirino[2,1-a]isoquinoline-2-carboxylate (8) (33 mg, 40%) as a colourless oil,  $\nu_{\max}$  ( $CCl_4$ ) 1 710 and 1 625  $cm^{-1}$ ;  $\delta$  (90 MHz;  $CDCl_3$ ) 1.30 (3 H, t), 2.84 (1 H, d,  $J$  3 Hz), 3.46 (1 H, d,  $J$  3 Hz), 4.30 (2 H, q), 7.10 (1 H, s), and 7.15—7.55 (9 H, m);  $m/z$  291 ( $M^+$ , base).

**Thermolysis of the Azide (4).**—A solution of the azide (4) (6 mg) in toluene (5 ml) was heated under reflux for 1.75 h. The solvent was evaporated to give a colourless oil, pure by n.m.r., identified as ethyl 4-(oxiran-2-ylmethyl)indole-2-carboxylate (21) (ca. 100%) (Found:  $M^+$  245.1052.  $C_{14}H_{15}NO_3$  requires 245.1052);  $\nu_{\max}$  ( $CCl_4$ ) 3 475 and 1 715  $cm^{-1}$ ;  $\delta$  (250 MHz;  $CDCl_3$ ) 1.44 (3 H, t), 2.55—2.60 (1 H, m), 2.77—2.83 (1 H, m),

3.05—3.30 (3 H, m), 4.42 (2 H, q), 7.00—7.40 (4 H, m), and 9.90 (1 H, br s);  $m/z$  245 ( $M^+$ , base), 199, and 156. This material decomposes on standing.

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