Vinyl Azides in Heterocyclic Synthesis. Part 4.[1] Thermal and Photochemical Decomposition of Azidocinnamates Containing *ortho*-Cycloalkenyl Substituents

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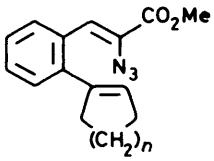
Thermolysis of azidocinnamates containing *ortho*-cycloalkenyl substituents leads to isoquinolines and benzazepines formed by interception of the azide, or derived vinylnitrene, by the neighbouring double bond, the stability of the azide varying with the ring size of the cyclic alkene substituent. The cycloheptenyl (**1a**) and cyclopentenyl (**1c**) azides decompose at room temperature by intramolecular cycloaddition of the azide to the double bond to give products derived from the corresponding triazoline intermediates (**9**) and (**22**). Some n.m.r. spectroscopic evidence for the triazoline (**9**) is obtained. The cyclohexenyl azide (**1b**) is more stable, and hence requires the decomposition to be carried out at higher temperatures, where the azirine–vinylnitrene products, indole (**15**) and aziridine (**14**), are formed in competition with the isoquinoline (**12**) and the benzazepine (**13**). Photochemical decomposition of the azides (**1b,c**) gives tetracyclic cyclopropanes (**26**) formed by intramolecular cycloaddition of the cyclic alkene to iminocarbene intermediates.

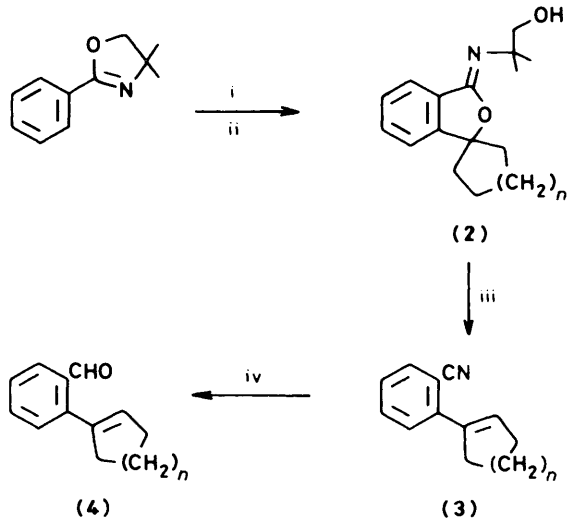
In the previous papers[1,2] we have reported that the thermal and photochemical decomposition of azidocinnamates containing *ortho*-vinyl, -styryl and -allyl substituents leads to products formed by interception of the reactive intermediates derived from the azide by the neighbouring olefinic substituent, in preference to cyclisation onto the unsubstituted aromatic *ortho*-position. As an extension to this work, we have also investigated the decomposition of azidocinnamates (**1**) bearing cycloalkenyl *ortho*-substituents. We now report our results which show that the ring size of the cyclic alkene has a considerable effect on the stability of, and the products derived from, the azidocinnamates (**1**).



(**1**)
a; *n* = 3
b; *n* = 2
c; *n* = 1

Results and Discussion

The starting materials for the investigation were the *ortho*-cycloalkenylbenzaldehydes (**4**), and these were prepared from 4,4-dimethyl-2-phenyl-4,5-dihydro-oxazole[3] by the route shown in Scheme 1. *ortho*-Lithiation of the dihydro-oxazole followed by addition of the appropriate cycloalkanone gave the spirobenzoisofuran derivatives (**2**), rather than the expected dihydro-oxazole tertiary alcohols reported by other workers.[3,4] After this phase of the work was completed, these results were confirmed by a recent report from Mellor and co-workers.[5] In a very thorough study, these workers also showed that the alcohols (**2a,b**) could be converted into *ortho*-cycloalkenylbenzonitriles (**3a,b**) by treatment with phosphorus oxychloride and pyridine,[6] and we have used the same conditions for the cyclopentenyl derivative (**3c**). The benzonitriles (**3**) have also been prepared previously by a different route.[7] Reduction of the nitriles to give the required benzaldehydes (**4**) was readily achieved by the use of di-isobutylaluminium hydride or lithium (triethoxy)aluminium hydride.



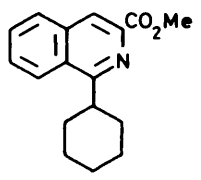
a; *n* = 3; **b**; *n* = 2; **c**; *n* = 1

Scheme 1. *Reagents:* i, BuLi–THF, −70 °C; ii, cycloalkanone; iii, $POCl_3$–pyridine, 80 °C; iv, $^iBu_2AlH$ or $LiAlH(OEt)_3$

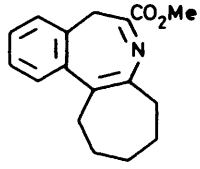
Condensation of the benzaldehydes (**4**) with methyl azidoacetate under basic conditions gave the required azidocinnamates (**1**).

The azide (**1a**) was found to be quite unstable at room temperature and slow decomposition was even observed at 4 °C. Heating the azide (**1a**) in benzene for 0.75 h gave 3 products assigned as the 1-cyclohexylisoquinoline (**5**) (16%), and the cycloheptabenzazepines (**6**) (12%) and (**7**) (22%), although examination of the crude thermolysis mixture by n.m.r. spectroscopy showed that the yields of compounds (**5**) and (**6**) were higher (*ca.* 36% each). For comparison, the azide (**1a**) was also decomposed at higher temperatures in toluene and xylene. However, analysis of the product mixture by n.m.r. spectroscopy showed that the same three products were formed

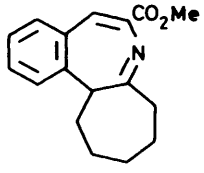
in approximately the same ratio, indicating that there is no significant temperature effect on the reaction. Surprisingly, no methyl 4-cyclohept-1-enylindole-2-carboxylate (**8**) was isolated from the reactions.



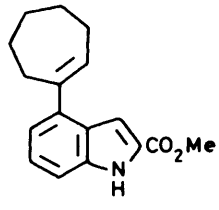
(**5**)



(**6**)



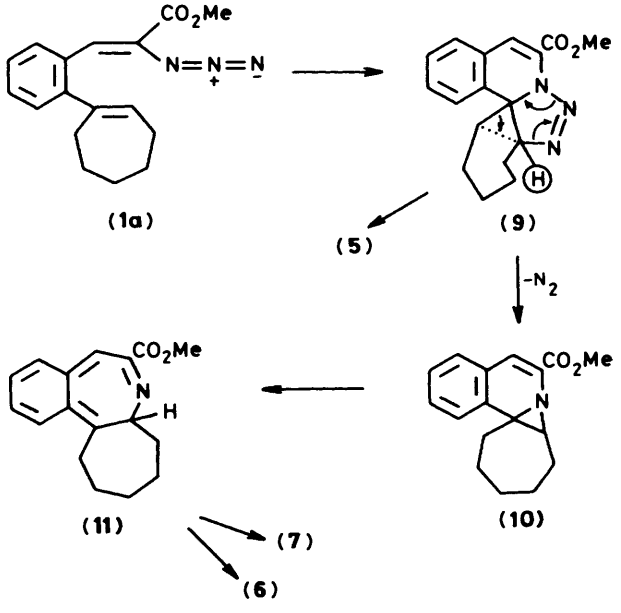
(**7**)



(**8**)

The decomposition of the azide (**1a**) in deuteriochloroform at room temperature could be monitored by ^{1}H n.m.r. spectroscopy, the ester OMe signals being particularly valuable. By expanding and integrating this region of the spectrum it was possible to follow the disappearance of the azide (**1a**) (δ 3.91), and the appearance of the products (**5**) (δ 4.03), (**6**) (δ 3.83), and (**7**) (δ 3.94) with time. However, an additional signal (δ 3.96) together with a double doublet at δ 5.00 (*J* 3, 7 Hz) also appeared after 29 h, and then slowly decreased in intensity. It is thus likely that the material responsible for these unassigned n.m.r. signals is an intermediate in the formation of products.

The fact that the azide (**1a**) decomposes to products at room temperature, well below the expected decomposition temperature of the vinyl azide to give a vinylnitrene, suggests an alternative mechanism involving 1,3-dipolar cycloaddition of the azide to the cycloheptene double bond. The absence of the indole (**8**), a nitrene derived product, supports the cycloaddition



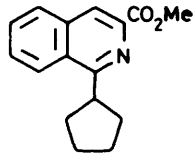
Scheme 2.

Table. Products from the thermolysis of azide (**1b**)

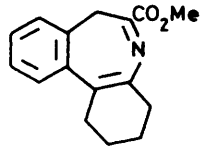
Thermolysis solvent	Temp. (°C)	Time (h)	Isolated yield (N.m.r. yield) (**12**)	(**13**)	(**14**)	(**15**)
Benzene	80	5.75	23(37)	26(49)	6(10)	2(4)
Toluene	110	1.5	−(24)	−(52)	−(12)	−(12)
Xylene	140	0.75	12(17)	27(58)	9(12)	9(14)

mechanism. The result of such an intramolecular cycloaddition would be the dihydrotriazole (**9**), which may be the intermediate observed by n.m.r. spectroscopy, the proton indicated being responsible for the double doublet at δ 5.00. The triazoline (**9**) can then lead to the isoquinoline (**5**) by loss of nitrogen accompanied by a [1,2]-alkyl shift (arrows), or to the aziridine (**10**) by loss of nitrogen (Scheme 2). The benzazepines (**6**) and (**7**) presumably arise from the aziridine (**10**) by ring opening to (**11**) followed by the appropriate hydrogen shifts. Such a mechanistic scheme is in line with our previous results on the decomposition of *ortho*-vinyl and -styryl azidocinnamates.[2]

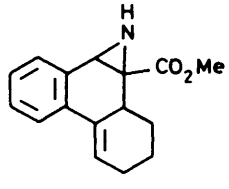
In contrast to the cycloheptenyl azide (**1a**), the cyclohexenyl derivative (**1b**) was stable at room temperature, and no decomposition was observed even after refluxing in ether for 2 days. Heating the azide (**1b**) at higher temperatures in solution resulted in complete decomposition and the formation of 4 products identified as the isoquinoline (**12**), the benzazepine (**13**), the aziridine (**14**), and the indole (**15**). The relative yields of products, which were temperature dependent, are shown in the Table, together with the yields based on n.m.r. spectra of the product mixture obtained immediately after the thermolysis.



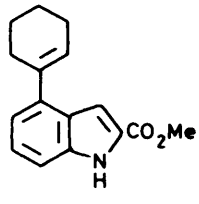
(**12**)



(**13**)



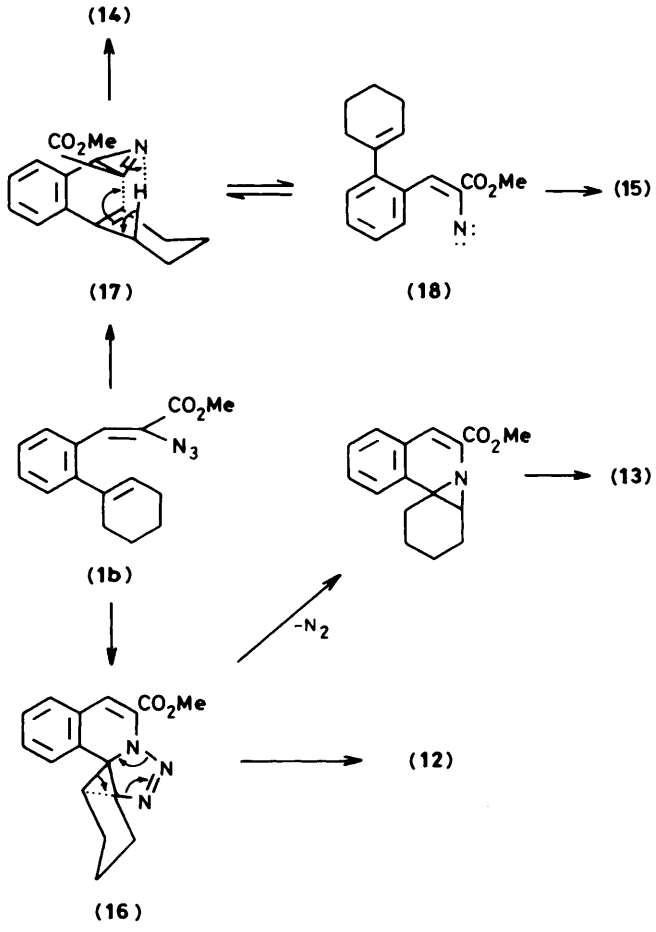
(**14**)



(**15**)

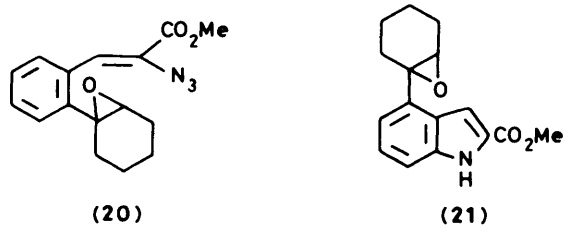
The fact that the product distribution is temperature dependent, in contrast to the azide (**1a**), suggests that in this case there is competition between cycloaddition and decomposition of the vinyl azide. Intramolecular cycloaddition to the cyclohexenyl double bond gives the dihydrotriazole (**16**), whilst decomposition with loss of nitrogen leads to the azirine (**17**) –vinylnitrene (**18**) equilibrium. The latter pathway increases with increasing temperature, and thus the amount of the indole (**15**), derived from electrocyclisation of the nitrene (**18**), and the aziridine (**14**), derived from an intramolecular ene reaction of the azirine (**17**),[2] also increase with temperature. The isoquinoline (**12**) presumably derives from the dihydrotriazole (**16**) by loss of nitrogen accompanied by a [1,2]-alkyl shift (arrows) (Scheme 3), and the benzazepine (**13**) from the aziridine (**19**) formed by loss of nitrogen from the dihydro-

triazole (**16**). The mechanism (Scheme 3) for the decomposition of the azide (**1b**) is consistent with, and supports, that proposed for the decomposition of similar azidocinnamates.[2]

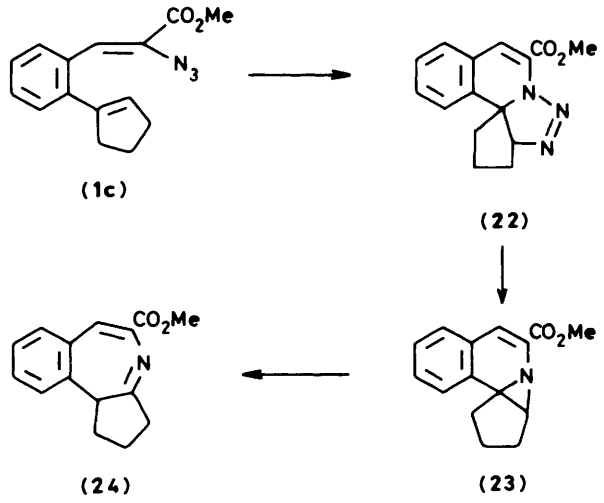


Scheme 3.

When the cyclohexenyl double bond of the azide (**1b**) was epoxidised by treatment with 3-chloroperbenzoic acid, the resulting azide (**20**) gave only one product on thermolysis in toluene, the indole (**21**) (50%). Thus when the possibility for participation of the double bond is removed, the nitrene intermediate cyclises onto the unsubstituted *ortho*-position as expected.[2]



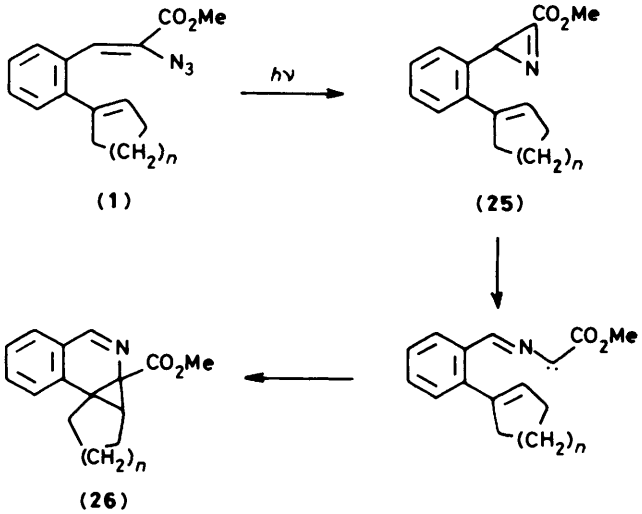
The cyclopentenyl azide (**1c**) again proved to be relatively unstable at room temperature, and on heating in benzene was converted into one major component (76%) assigned as the benzazepine (**24**). This product is presumably formed *via* the dihydrotriazole (**22**) and the aziridine (**23**) (Scheme 4). No 1-cyclobutylisoquinoline analogous to (**5**) and (**12**) was observed, and this presumably reflects the increased strain present in the cyclopentenyl series.



Scheme 4.

Thus in the thermal decomposition of the azides (**1**) an effect of ring size is observed. Both the cycloheptenyl and cyclopentenyl derivatives contain double bonds which are sufficiently reactive to undergo intramolecular cycloaddition to the azide 1,3-dipole at room temperature, and hence the major reaction pathway is *via* the corresponding dihydrotriazoles for these two systems. The greater stability of the cyclohexenyl derivative requires the decomposition to be carried out at higher temperatures, where azirine–vinylnitrene derived products are formed in competition with the dihydrotriazoline derived products.

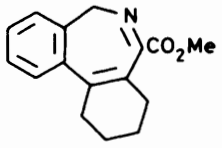
The photochemical decomposition of the azides (**1b**) and (**1c**) was also investigated, and as expected on the basis of our previous results[1] involved the intramolecular interception of the iminocarbene, derived from photochemical ring-opening of the azirine (**25**), by the cycloalkenyl double bond as the major pathway (Scheme 5).



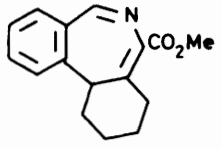
Scheme 5. **b**; $n = 2$, **c**; $n = 1$

Thus the cyclopentenyl azide (**1c**) gave the unstable cyclopropane (**26c**) as the sole product (*ca.* 95%) on being irradiated in hexane. Similarly, the cyclohexenyl azide (**1b**) gave the unstable cyclopropane (**26b**) (67%) on photolysis, although the indole (**15**) was formed in trace amounts together with two compounds assigned as the benzazepines (**27**) and (**28**). The

indole (**15**) arises by thermal decomposition of the azide (**1b**) due to the heating of the solution during the irradiation, and the benzazepines (**27**) and (**28**) are probably formed by further thermal decomposition of the cyclopropane (**26b**). Some evidence for this was obtained when a sample of the cyclopropane (**26b**) was found to decompose when allowed to stand at room temperature over several weeks. From the resulting complex mixture, the benzazepine (**27**) was isolated in *ca.* 35% yield.



(**27**)



(**28**)

Experimental

I.r. spectra were recorded in the range 400—4 000 cm^{-1} on a Perkin-Elmer 983G spectrometer and are calibrated against polystyrene. ^1H N.m.r. spectra were obtained at 60 and 200 MHz on Varian EM360 and Bruker WP200 instruments respectively using tetramethylsilane as the internal standard. ^{13}C N.m.r. spectra were recorded at 50.3 MHz on the Bruker instrument and are broad band decoupled. Mass spectra were obtained at 70 eV on a A.E.I. MS 3074 instrument at the University of York. Light petroleum refers to the fraction with b.p. 40—60 °C, and ether refers to diethyl ether. Chromatography was carried out on Kieselgel 60 (0.063—0.2 mm) unless otherwise stated, and radial t.l.c. was carried out using a Chromatotron 7924 instrument. Photochemical reactions were carried out in quartz vessels in a Rayonet Photochemical Reactor.

3-(2-*Hydroxy*-1,1-*dimethylethylimino*)-1,3-*dihydroisobenzofuran*-1-*spirocycloalkanes* (**2**).—These were prepared from 4,4-dimethyl-2-phenyl-4,5-dihydro-oxazole[3] and the appropriate cycloalkanone using a method essentially identical to that described by Mellor and co-workers[5] for a range of similar compounds. The following compounds were prepared:

3-(2-Hydroxy-1,1-dimethylethylimino)-1,3-dihydroisobenzofuran-1-spirocycloheptane (**2a**), 35%, m.p. 107—110 °C (lit.,[5] 105—107 °C).

3-(2-Hydroxy-1,1-dimethylethylimino)-1,3-dihydroisobenzofuran-1-spirocyclohexane (**2b**), 60%, m.p. 125—125.5 °C (lit.,[5] 122—124 °C).

3-(2-*Hydroxy*-1,1-*dimethylethylimino*)-1,3-*dihydroisobenzofuran*-1-*spirocyclopentane* (**2c**), 16%, m.p. 99—101 °C (Found: C, 73.9; H, 8.3; N, 5.2. $C_{16}H_{21}NO_2$ requires C, 74.1; H, 8.2; N, 5.4%); $\nu_{max.}$(Nujol) 3 140 and 1 670 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.35 (6 H, s), 1.8—2.2 (8 H, m), 3.20 (1 H, br, exch. D_2O), 3.40 (2 H, s, sharpens on addition of D_2O), and 7.24—7.75 (4 H, m).

2-*Cycloalken*-1-*ylbenzonitriles* (**3**).—These were prepared from the benzofurans (**2**) by treatment with phosphorus oxychloride and pyridine using the method of Mellor and co-workers.[6] The following compounds were prepared:

2-Cyclohept-1-enylbenzonitrile (**3a**), 29%, b.p. 90 °C at 0.03 mmHg (Kugelrohr) (lit.,[6] not given; lit.,[7] 85—95 °C at 0.2 mmHg).

2-Cyclohex-1-enylbenzonitrile (**3b**), 57%, b.p. 100 °C at 0.1 mmHg (Kugelrohr) (lit.,[6] not given; lit.,[7] 92—94 °C at 0.05 mmHg).

2-Cyclopent-1-enylbenzonitrile (**3c**), 57%, b.p. 100 °C at 0.1 mmHg (Kugelrohr) (lit.,[7] 106—107 °C at 0.7 mmHg), $\nu_{max.}$ (neat) 2 215 and 1 588 cm^{-1}.

2-*Cyclohept*-1-*enylbenzaldehyde* (**4a**).—Ethyl acetate (3.55 g, 38 mmol) was added over 1 h to an ice-cooled solution of lithium aluminium hydride in ether (1.0M; 26 ml, 26 mmol) under nitrogen. The mixture was stirred for a further 1 h at 0 °C, and then the benzonitrile (**3a**) (5.0 g, 25 mmol) was added over 5 min maintaining the temperature below 10 °C. Stirring was continued for 1 h at 0 °C, and then the mixture was hydrolysed by the careful addition of aqueous sulphuric acid (2.5M; 10 ml), and extracted with ether (4 × 25 ml). The combined organic phases were washed with water, dried and evaporated. The residue was purified by chromatography to give 2-*cyclohept*-1-*enylbenzaldehyde* (**4a**) (3.0 g, 59%) as a pale yellow oil, b.p. 110 °C at 0.1 mmHg (Kugelrohr) (Found: C, 83.7; H, 8.0. $C_{14}H_{16}O$ requires C, 84.0; H, 8.0%); $\nu_{max.}$(neat) 2 742, 1 690, and 1 595 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.33—2.00 (6 H, m), 2.29 (2 H, m), 2.58 (2 H, m), 5.77 (1 H, t), 7.24—7.55 (3 H, m), 7.87 (1 H, dd, *J* 1, 8 Hz), and 10.16 (1 H, d, *J* 1 Hz).

2-*Cyclohex*-1-*enylbenzaldehyde* (**4b**).—Prepared in 89% yield by the method described above as a pale yellow oil, b.p. 100 °C at 0.1 mmHg (Kugelrohr) (lit.,[7] not given) (Found: C, 83.9; H, 7.75. $C_{13}H_{14}O$ requires C, 83.8; H, 7.6%); $\nu_{max.}$(neat) 2 740, 1 690, and 1 595 cm^{-1}; δ (60 MHz; $CDCl_3$) 1.2—2.7 (8 H, m), 5.40 (1 H, m), 6.8—7.5 (3 H, m), 7.65 (1 H, m), and 9.93 (1 H, s).

2-*Cyclopent*-1-*enylbenzaldehyde* (**4c**).—A solution of diisobutylaluminium hydride in toluene (25%; 29 ml, 51 mmol) was added dropwise over 1.25 h to a stirred solution of the benzonitrile (**3c**) (8.6 g, 51 mmol) in toluene (50 ml), and the mixture was stirred overnight at room temperature. Standard aqueous work-up and distillation gave 2-*cyclopent*-1-*enylbenzaldehyde* (**4c**) (4.9 g, 56%) as a pale yellow oil, b.p. 95 °C at 0.1 mmHg (Kugelrohr) (Found: C, 84.0; H, 7.0. $C_{12}H_{12}O$ requires C, 83.7; H, 7.0%); $\nu_{max.}$(neat) 2 840, 1 680, and 1 594 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.98—2.18 (2 H, m), 2.58 (2 H, m), 2.75 (2 H, m), 5.72 (1 H, m), 7.28—7.60 (3 H, m), 7.53 (1 H, m), and 10.20 (1 H, s).

Methyl 2-*Azido*-3-(2-*cyclohept*-1-*enylphenyl*)*propenoate* (**1a**).—A solution of the aldehyde (**4a**) (2.0 g, 10 mmol) and methyl azidoacetate (4.60 g, 40 mmol) in methanol (25 ml) was added dropwise over 45 min to a stirred solution of sodium methoxide [from sodium (0.92 g, 40 mmol)] in methanol (50 ml) at −10 °C. The reaction mixture was warmed to 0 °C over 2 h, stored at 4 °C overnight, and finally stirred at room temperature for 3 h. Aqueous work-up and chromatography gave the *title azide* (**1a**) (0.78 g, 26%) as unstable pale yellow *needles*, m.p. 31—36 °C (Found: C, 68.8; H, 6.7; N, 14.05. $C_{17}H_{19}N_3O_2$ requires C, 68.7; H, 6.4; N, 14.1%); $\nu_{max.}$(Nujol) 2 123, 1 713, and 1 613 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.50—1.93 (6 H, m), 2.27 (2 H, m), 2.48 (2 H, m), 3.91 (3 H, s) 5.76 (1 H, t), 7.10—7.32 (4 H, m), and 8.07 (1 H, m).

Methyl 2-*Azido*-3(2-*cyclohex*-1-*enylphenyl*)*propenoate* (**1b**).—Prepared from the aldehyde (**4b**) exactly as described above in 49% yield as pale yellow *needles*, m.p. 31—34 °C (Found: C, 67.9; H, 6.2; N, 14.85. $C_{16}H_{17}N_3O_2$ requires C, 67.8; H, 6.05; N, 14.8%); $\nu_{max.}$(Nujol) 2 123, 1 720, and 1 613 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.60—1.87 (4 H, m), 2.07—2.30 (4 H, m), 3.90 (3 H, s), 5.56 (1 H, m), 7.12 (1 H, s), 7.13—7.33 (3 H, m), and 8.08 (1 H, m).

Methyl 2-*Azido*-3-(2-*cyclopent*-1-*enylphenyl*)*propenoate* (**1c**).—Prepared from the aldehyde (**4c**) exactly as described above in 77% yield as unstable pale yellow *needles*, m.p. 42—45 °C (Found: C, 66.9; H, 5.5; N, 15.4. $C_{15}H_{15}N_3O_2$ requires C, 66.9; H, 5.6; N, 15.6%), $\nu_{max.}$(Nujol) 2 120, 1 715, and 1 612 cm^{-1};

δ (200 MHz; $CDCl_3$) 2.0 (2 H, m), 2.56 (2 H, m), 2.68 (2 H, m), 3.90 (3 H, s), 5.74 (1 H, m), 7.19 (1 H, s), and 7.20—7.42 (3 H, m) and 7.97 (1 H, m).

Methyl 2-Azido-3-[2-(7-oxabicyclo[4.1.0]heptan-1-yl)-phenyl]propenoate (**20**).—A solution of 3-chloroperbenzoic acid (0.60 g) in dichloromethane (10 ml) was added dropwise to a stirred ice-cold solution of the azide (**1b**) (0.85 g, 3 mmol) in dichloromethane (25 ml). The resulting mixture was stirred at room temperature overnight, filtered, and the filtrate washed successively with aqueous sodium sulphite (10%; 20 ml), saturated aqueous sodium hydrogen carbonate (20 ml), and water (20 ml). The organic layer was dried (Na_2SO_4), evaporated, and the residue purified by chromatography on basic alumina to give the *title compound* (**20**) (0.82 g, 91%) as a pale yellow syrup (Found: C, 64.6; H, 5.75; N, 13.9. $C_{16}H_{17}N_3O_3$ requires C, 64.2; H, 5.7; N, 14.0%); $\nu_{max.}$(neat) 2 121, 1 720, and 1 617 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.3—2.2 (8 H, m), 3.14 (1 H, m), 3.93 (3 H, s), 7.24 (1 H, s), 7.25—7.49 (3 H, m), and 8.12 (1 H, m).

Thermolysis of the Azide (**1a**).—A solution of the azide (**1a**) (43 mg) in benzene (10 ml) was heated under reflux for 45 min. Evaporation and chromatography of the residue using radial t.l.c. gave (i) *methyl 1-cyclohexylisoquinoline-3-carboxylate* (**5**) (6.3 mg, 16%), colourless needles, m.p. 135—136.5 °C (Found: C, 75.7; H, 7.05; N, 5.45. $C_{17}H_{19}NO_2$ requires C, 75.8; H, 7.1; N, 5.2%); $\nu_{max.}$($CHCl_3$) 1 728 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.3—2.1 (10 H, m), 3.57 (1 H, m), 4.03 (3 H, s), 7.64—8.33 (4 H, m), and 8.39 (1 H, s); *m/z* 269 (M^+), 240, 214 (base), 201, 182, and 154; (ii) *methyl 1,2,3,4,5,8-hexahydrocyclohepta*[a][3]*benzazepine-7-carboxylate* (**6**) (4.7 mg, 12%), pale yellow oil (Found: M^+, 269.1417. $C_{17}H_{19}NO_2$ requires 269.1416); $\nu_{max.}$($CHCl_3$) 1 718 and 1 602 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.69—2.10 (6 H, m), 2.26 (1 H, d, *J* 11.4 Hz), 2.69—3.00 (4 H, m), 3.83 (3 H, s), 4.51 (1 H, d, *J* 11.4 Hz), and 7.24—7.58 (4 H, m); *m/z* 269 (M^+, base), 254, 237, 210, 184, and 155; and (iii) *methyl 1,2,3,4,5,12b-hexahydrocyclohepta*[a][3]*benzazepine-7-carboxylate* (**7**) (8.4 mg, 22%), colourless oil (Found: M^+, 269.1417); $\nu_{max.}$($CHCl_3$) 1 715 and 1 597 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.20—1.73 (4 H, m), 1.96—2.47 (6 H, m), 2.56 (1 H, m), 3.94 (3 H, s), 7.33—7.64 (4 H, m), and 7.86 (1 H, s); *m/z* 269 (M^+), 254, 211, 180, 156 (base), and 128.

Thermolysis of the Azide (**1b**).—A solution of the azide (**1b**) (250 mg) in xylene (5 ml) was heated under reflux for 0.75 h. Evaporation of the solvent and chromatography of the residue using radial t.l.c. gave (i) *methyl 1-cyclopentylisoquinoline-3-carboxylate* (**12**) (28 mg, 12%), colourless needles, m.p. 71.5—73 °C (Found: C, 75.3; H, 6.9; N, 5.55. $C_{16}H_{17}NO_2$ requires C, 75.2; H, 6.7; N, 5.5%); $\nu_{max.}$(Nujol) 1 724 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.67—2.33 (8 H, m), 4.02 (3 H + 1 H, s + m), 7.65—8.35 (4 H, m), and 8.41 (1 H, s); *m/z* 255 (M^+), 226, 214 (base), 194, 182, 167, and 154; (ii) *methyl 1,2,3,4-tetrahydrocyclohexa*[a][3]*benzazepine-6-carboxylate* (**13**) (60 mg, 27%), colourless oil (Found: M^+, 255.1256. $C_{16}H_{17}NO_2$ requires 255.1259); $\nu_{max.}$(Nujol) 1 716, 1 620, and 1 598 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.60—2.60 (7 H, m, including δ 2.43, d, *J* 12 Hz), 2.88 (1 H, m), 3.12 (1 H, m), 3.83 (3 H, s), 4.48 (1 H, d, *J* 12 Hz), and 7.10—7.58 (4 H, m); *m/z* 255 (M^+, base), 240, 223, 197, 182, and 155; (iii) *methyl* 1a,1b, 2,3,4,9b-*hexahydro-1H-phenanthro*[9,10-b]*aziridine-1a-carboxylate* (**14**) (21 mg, 9%), an unstable solid which could not be completely purified, $\nu_{max.}$(Nujol) 3 279 and 1 728 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.4—2.4 (7 H, m), 3.08 (2 H, br, 1 H, exch. D_2O), 3.83 (3 H, s), 6.20 (1 H, m), and 7.1—7.45 (4 H, m); and (iv) *methyl 4-(cyclohex-1-enyl)indole-2-carboxylate* (**15**) (21 mg, 9%), colourless *needles*, m.p. 123—125 °C (Found: M^+, 255.1253); $\nu_{max.}$(Nujol) 3 321, 1 693, and 1 604 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.6—1.9 (4 H, m), 2.2—2.6 (4 H, m), 4.00 (3 H, s), 6.1 (1 H, m), 7.02—7.38 (4 H, m), and 8.9 (1 H, br); *m/z* 255 (M^+, base), 223, 196, 167, and 154.

Thermolysis of the Azide (**20**).—A solution of the azide (**20**) (79 mg) in toluene (7 ml) was heated under reflux for 16 h. Evaporation of the solvent and crystallisation of the residue from chloroform–hexane gave *methyl 4-(7-oxabicyclo*[4.1.0]*heptan-1-yl)indole-2-carboxylate* (**21**) (36 mg, 50%), colourless needles, m.p. 170—175 °C (Found: C, 70.9; H, 6.4; N, 5.45. $C_{16}H_{17}NO_3$ requires C, 70.8; H, 6.3; N, 5.2%); $\nu_{max.}$(Nujol) 3 336 and 1 703 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.4—1.8 (4 H, m), 2.0—2.4 (4 H, m), 3.21 (1 H, m), 3.98 (3 H, s), 7.1—7.4 (4 H, m), and 9.00 (1 H, br); *m/z* 271 (M^+, base), 242, 212, 188, 154, and 127.

Thermolysis of the Azide (**1c**).—A solution of the azide (**1c**) (150 mg) in benzene (5 ml) was heated under reflux for 1.5 h. Evaporation of the solvent and chromatography of the residue gave *methyl 1,2,3,10b-tetrahydrocyclopenta*[1,2-a][3]*benzazepine-5-carboxylate* (**24**) (102 mg, 76%) as a colourless oil which could not be completely purified (Found: C, 74.2; H, 6.5; N, 5.5. $C_{15}H_{15}NO_2$ requires C, 74.7; H, 6.3; N, 5.8%); $\nu_{max.}$($CHCl_3$) 1 712 and 1 599 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.92—2.40 (3 H, m), 2.50—2.91 (4 H, m), 3.92 (3 H, s), 7.28—7.60 (4 H, m), and 7.85 (1 H, s).

Photolysis of the Azide (**1c**).—A solution of the azide (**1c**) (217 mg) in hexane (180 ml) was irradiated at 300 nm for 1 h under a stream of nitrogen. Evaporation of the solvent gave one major component (*ca.* 95%) contaminated with another unidentified component (*ca.* 5%). The major component was identified as *methyl 2,3,3a,3b-tetrahydro-1H-cyclopenta*[2,3]*cyclopropa*[1,2-c]*isoquinoline-3b-carboxylate* (**26c**), a pale brown glass unstable to recrystallisation, $\nu_{max.}$(KBr) 2 930, 1 721, and 1 620 cm^{-1}; δ (200 MHz; $CDCl_3$) 0.64 (1 H, d, *J* 5 Hz), 1.15—1.45 (1 H, m), 1.8—2.3 (3 H, m), 2.48 (1 H, ddd, *J* 13, 9, 1 Hz), 2.87 (1 H, dt, *J* 13, 9 Hz), 3.83 (3 H, s), 7.2—7.7 (4 H, m), and 8.23 (1 H, s); *m/z* 241 (M^+), 182, 168, 153, 128, and 115.

Photolysis of the Azide (**1b**).—A solution of the azide (**1b**) (217 mg) in light petroleum (200 ml) was irradiated for 1 h under a stream of nitrogen. Evaporation of the solvent and chromatography of the residue using radial t.l.c. gave (i) methyl 4-(cyclohex-1-enyl)indole-2-carboxylate (**15**) (3 mg, 2%); (ii) *methyl 1,2,3,4,4a,4b-hexahydrocyclohexa*[2,3]*cyclopropa*-[1,2-c]*isoquinoline-4b-carboxylate* (**26b**) (130 mg, 67%), as a pale brown glass unstable to recrystallisation (Found: M^+, 255.1249. $C_{16}H_{17}NO_2$ requires 255.1259); $\nu_{max.}$(KBr) 1 710 and 1 618 cm^{-1}; δ (200 MHz; $CDCl_3$) 0.57 (1 H, dd, *J* 8, 2 Hz), 1.3—2.0 (6 H, m), 2.3—2.7 (2 H, m), 3.83 (3 H, s), 7.2—7.7 (4 H, m), and 8.15 (1 H, s); *m/z* 255 (M^+), 196, 182, 168, 128, and 115; (iii) *methyl 1,2,3,4-tetrahydro-7H-cyclohexa*[d][2]*benzazepine-5-carboxylate* (**27**) (3 mg, 2%), colourless oil (Found: M^+, 255.1252); $\nu_{max.}$(neat) 1 725, 1 618, and 1 592 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.6—2.0 (4 H, m), 2.15—2.55 (2 H, m), 2.70 (1 H, m), 3.05 (1 H, m), 3.79 (3 H, s), 3.83 (1 H, d, *J* 9.5 Hz), 4.85 (1 H, d, *J* 9.5 Hz), and 7.25—7.52 (4 H, m); *m/z* 255 (M^+, base), 240, 195, 182, 167, 154, 141, and 115; and (iv) *methyl 1,2,3,4-tetrahydro-11bH-cyclohexa*[d][2]*benzazepine-5-carboxylate* (**28**) (18 mg, 9%), pale yellow oil (Found: C, 75.0; H, 7.0; N, 5.5. $C_{16}H_{17}NO_2$ requires C, 75.2; H, 6.7; N, 5.5%); $\nu_{max.}$(neat) 1 721 and 1 625 cm^{-1}; δ (200 MHz; $CDCl_3$) 1.6—2.5 (5 H, m), 2.75—2.90 (1 H, m), 3.73 (1 H, m), 3.83 (3 H, s), 7.25—7.62 (4 H, m), and 8.95 (1 H, s).

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