Vinyl Azides in Heterocyclic Synthesis. Part 5.[1] Thermal and Photochemical Decomposition of Azidocinnamates Containing *ortho*-Cycloalkylidene Substituents

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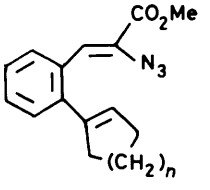
Heating the *ortho*-cycloalkylidene azidocinnamates (**2b**—**e**) in boiling toluene gives the indeno[1,2-*b*]tetrahydroazirines (**8**), derived by intramolecular ene reaction involving the C=N bond of the intermediate 2*H*-azirines (**11**), as the major product. The intramolecular ene reaction is a highly favourable process, and also occurs at *ca.* 40 °C when the azirines (**11**) are formed by irradiation of the azides (**2**), although photochemical ring opening of the azirines does compete. Only when the possibility for such an intramolecular ene reaction is removed, by epoxidation of the cycloalkylidene double bond, are vinylnitrene derived products formed to any extent, the epoxy azides (**7**) giving the 4-substituted indoles (**14**) in high yield.

In the previous paper,[1] we reported that thermal decomposition of the *o*-cycloalkenylazidocinnamates (**1**; n = 1—3) led to a variety of products depending on the ring size of the cyclic alkene substituent. Two reaction pathways were observed, although the major products were derived by intramolecular cycloaddition of the vinyl azide to the double bond, rather than from the corresponding vinylnitrene. In order to gain further insight into the exact mechanism of decomposition of azidocinnamates containing *ortho*-unsaturated substituents, and in particular to establish the role of vinylnitrene and/or 2*H*-azirine intermediates, we have now investigated the thermal and photochemical decomposition of the azidocinnamates (**2**; n = 2—5), which contain an *ortho*-cycloalkylidene substituent.



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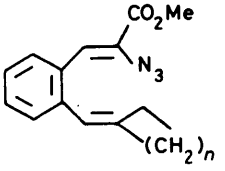

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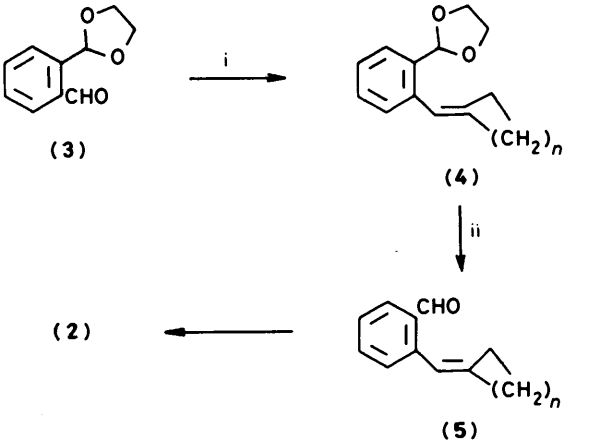
Results and Discussion

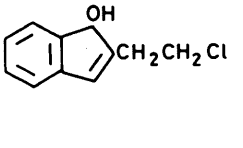
The azidocinnamates (**2**) were prepared from the mono ethylene acetal of phthaldehyde (**3**) *via* the benzaldehydes (**5**) as shown in Scheme 1. Thus the aldehyde (**3**), prepared from 2-bromobenzaldehyde by a modification of a literature procedure,[2] underwent Wittig reaction with the ylides derived from the corresponding cycloalkylphosphonium bromides to give the acetals (**4**). Acid hydrolysis of the acetals (**4**) to the benzaldehydes (**5**) was uneventful except in the case of the cyclopropyl derivative (**4a**), where the normal conditions (dilute hydrochloric acid) gave a crystalline solid which was clearly not the required aldehyde. This compound was assigned the chloroethylindenol structure (**6**), and is presumably formed by attack of chloride on the cyclopropane ring followed by acid-mediated ring closure. The aldehyde (**5a**) could be obtained in a crude state by hydrolysis of the acetal (**4a**) using 'wet' silica gel in dichloromethane,[3] although no attempt was made to use the small amount of material so obtained in subsequent reactions. Finally the aldehydes (**5b**—**e**) were condensed with methyl azidoacetate under the usual conditions[1] to give the required azidocinnamates (**2b**—**e**).



a, n = 1; **b**, n = 2; **c**, n = 3; **d**, n = 4; **e**, n = 5

Scheme 1. *Reagents:* i, $\overline{CH_2-(CH_2)_n-CH}\overset{+}{P}Ph_3\bar{B}r$, base; ii, H_3O^+; iii, $MeO_2CCH_2N_3$, NaOMe, MeOH

The cycloalkylidene azides (**2**) were epoxidised by treatment with 3-chloroperbenzoic acid to give the epoxides (**7**) in high yield. As in previous related studies,[1,4] no epoxidation of the azidocinnamate side chain was observed.



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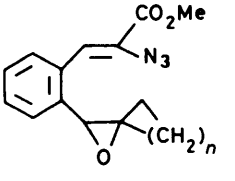


(7)

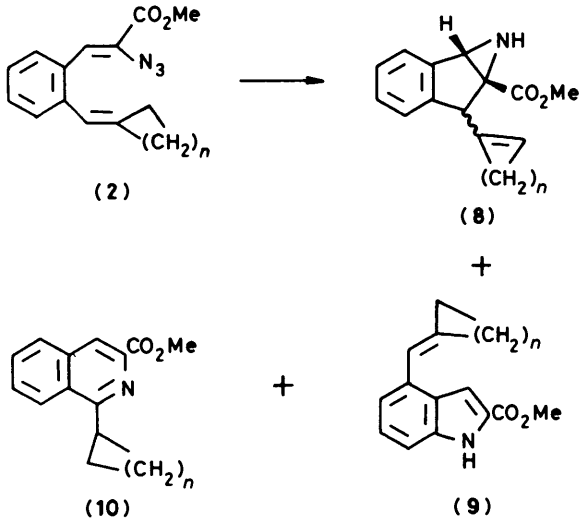
The azidocinnamates (**2b**—**e**) were stable at room temperature, solutions in deuteriochloroform showing no change by n.m.r. spectroscopy after several days, but decomposed rapidly on heating in boiling toluene to give one major and two minor products. The major product in each case was assigned the 1-cycloalkenylindeno[1,2-*b*]aziridine structure (**8**), formed as a mixture of diastereoisomers, on the basis of its ^{1}H n.m.r. spectrum (see Experimental section). The minor products were

Table 1. Thermolysis of the *o*-cycloalkylideneazidocinnamates (**2**) in toluene

Azide	*n*	Isolated yields (n.m.r. yields)[a] (%) (**8**)	(**9**)	(**10**)
(**2b**)	2	44 (70)	4 (5)	6 (8)
(**2c**)	3	74 (91)	3 (5)	2 (3)
(**2d**)	4	85 (92)	4 (5)	[b](1)
(**2e**)	5	72 (94)	3 (4)	0 (0)

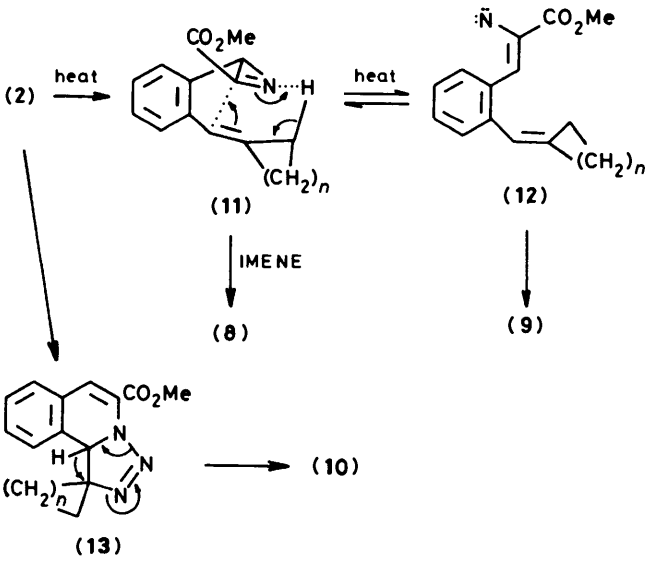
[a] Yield based on ^{1}H n.m.r. spectra of mixture directly after the thermolysis. [b] Not isolated.

the 4-substituted indole-2-carboxylate (**9**) and the 1-cycloalkylisoquinoline-3-carboxylate (**10**), although in the case of the cyclobutylidene azide (**2b**), two other unidentified minor products were formed, the amounts of which increased if the thermolysis was carried out at higher temperature. In contrast, the ratio of products (**8**), (**9**), and (**10**) obtained from the azides (**2c**—**e**) was independent of the thermolysis temperature. The results are summarised in Table 1.



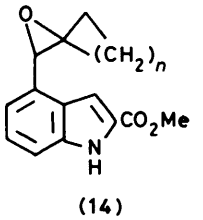
The formation of the major product from the thermolysis, the indenoaziridine (**8**), is best explained by an intramolecular ene (IMENE) reaction of the 2*H*-azirine (**11**). Although ene reactions involving the C=N bond of 2*H*-azirines are known, the only intramolecular examples are those reported in previous papers in this series.[1,4] The azirine (**11**) is presumably in thermal equilibrium with the vinylnitrene (**12**), from which the 4-substituted indole (**9**) is derived, but the fact that the indole (**9**) is only a minor product indicates that the IMENE reaction of the azirine (**11**) must be particularly favourable. The isoquinoline (**10**) is envisaged as arising from intramolecular addition of the azide to the cycloalkylidene double bond to give the triazoline (**13**), followed by loss of nitrogen and 1,2-rearrangement as shown (Scheme 2). In contrast to the thermolysis of *o*-cycloalkenylazidocinnamates where cycloaddition of the azide as a 1,3-dipole was a major reaction,[1] the corresponding reaction in the cycloalkylidene derivatives is disfavoured, possibly on steric grounds, the α,α′-methylene groups of the cycloalkyl ring preventing approach of the azide to the double bond.

Thus in the decomposition of the azides (**2**), summarised in Scheme 2, the key intermediate responsible for the formation of

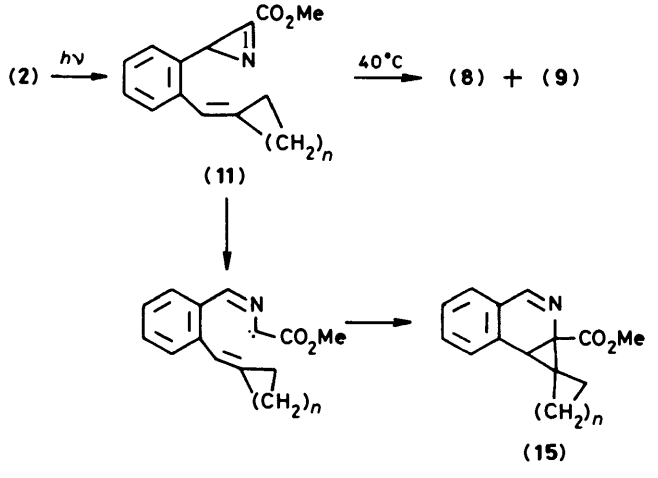


Scheme 2.

the major product is the 2*H*-azirine (**11**), which is efficiently intercepted in an IMENE reaction by the neighbouring double bond before significant amounts of the vinylnitrene (**12**), and hence indole (**9**) can be formed. When the double bond of the azides (**2**) is 'protected' by epoxidation, the resulting epoxy azides (**7**) gave only one product on thermolysis in toluene, the indoles (**14**) in high yield (79—85%).



Since vinyl azides also give 2*H*-azirines on irradiation, the photolysis of the azides (**2b**—**e**) was investigated. However under photochemical conditions azirines readily ring open by irreversible C–C bond cleavage to give nitrile ylides, which act as 1,3-dipoles or as iminocarbenes in both inter- and intramolecular addition reactions.[5] Therefore in the present case it was not clear whether the azirine (**11**) would be intercepted by



Scheme 3.

Table 2. Photolysis of the azidocinnamates (**2**) in light petroleum at 300 nm

Azide	*n*	Isolated yields (n.m.r. yields)[a] (%) (**8**)	(**15**)	(**9**)
(**2b**)	2	[b](3)	82 (96)	[b](1)
(**2c**)	3	41 (74)	14 (24)	2 (2)
(**2d**)	4	57 (83)	13 (15)	2 (2)
(**2e**)	5	88 (91)	5 (7)	2 (2)

[a] Yield based on ^{1}H n.m.r. spectrum of mixture directly after the photolysis. [b] Not isolated.

the double bond *before* ring opening, or whether the major product would result from intramolecular interception of the iminocarbene as in our previous work.[1,5] In the event both types of product were observed, the tetrahydroazirine (**8**) and the spirocyclopropane (**15**), in addition to small amounts of the indole (**9**), although the results were dependent on the ring size of the cycloalkylidene substituent (Table 2).

The formation of the three products is rationalised as shown in Scheme 3. The 2*H*-azirine (**11**) is the initial photoproduct from the vinyl azide (**2**), and as before undergoes IMENE reaction to give the tetrahydroindenoazirine (**8**). The indole (**9**) presumably arises by further thermal reaction of the azirine (**11**), to give a vinylnitrene, due to warming of the solution during the irradiation, whilst the spirocyclopropane (**15**) derives from photochemical ring opening of the azirine to an iminocarbene which is intercepted intramolecularly. These results emphasise the ease with which the IMENE reaction of the azirine (**11**) occurs, since the temperature of the solution during irradiation is only *ca.* 40 °C, and only in the case of the cyclobutylidene derivative is the reaction sufficiently slow at this temperature to allow the normal photochemical ring opening to compete effectively.

An overall picture thus emerges in which the products from the thermal decomposition of azidocinnamates containing an alkenic *ortho*-substituent are derived by selective interaction with the substituent in preference to the free *ortho*-position of the aromatic ring. The exact form of the reaction depends on the nature of the alkene substituent, and can involve intramolecular cycloaddition of the azide, before decomposition, to the double bond as with simple alkene[4] or cycloalkene[1] substituents, or IMENE reaction of 2*H*-azirine intermediates as in the present work. Only when the possibility for such interactions is removed by epoxidation, is cyclisation to the aromatic ring, with the formation of 4-substituted indoles, observed. The photochemical decomposition of the same azides again involves 2*H*-azirine formation, although depending on the alkene substituent, the azirine may undergo IMENE reaction, or ring open to iminocarbene intermediates, which can be trapped intramolecularly by the neighbouring double bond.

Experimental

For general points see ref. 1.

o-(1,3-*Dioxolan*-2-*yl*)*benzylidenecyclopropane* (**4a**).—A solution of phenyl-lithium [prepared from lithium wire (0.82 g, 118 mmol) and bromobenzene (9.0 g, 57.3 mmol)] in ether (30 ml) was added to a suspension of cyclopropyltriphenylphosphonium bromide (Aldrich; 21.5 g, 56.1 mmol) in anhydrous THF (200 ml) under nitrogen. The resulting dark red solution was stirred for 0.75 h at room temperature, then phthalaldehyde monoethylene acetal[2] (**3**) (10.0 g, 56.1 mmol) was added dropwise over 0.5 h at room temperature. The mixture was stirred at room temperature overnight and concentrated under reduced pressure. The residue was triturated with hexane (100 ml) and filtered to remove triphenylphosphine oxide. The filtrate was concentrated under reduced pressure to leave a brown oil which was distilled at 95 °C and 0.1 mmHg (Kugelrohr) to afford the dioxolane (**4a**) (4.0 g, 35%) as a pale yellow oil, $\nu_{max.}$(neat) 2 973, 1 601, 1 392, 1 223, 1 080, 945, and 757 cm^{-1}; δ($CDCl_3$) 1.15—1.25 (2 H, m, cyclopropyl H), 1.35—1.59 (2 H, m, cyclopropyl H), 3.8—4.2 [4 H, m, $O(CH_2)_2O$], 6.15 (1 H, s, CH–O), and 7.1—7.9 (5 H, m, ArH + ArC*H*=C).

o-(1,3-*Dioxolan*-2-*yl*)*benzylidenecyclobutane* (**4b**).—A solution of phenyl-lithium (2.0M in cyclohexane–ether; 16 ml, 32 mmol) was added to a stirred suspension of cyclobutyltriphenylphosphonium bromide[6] (1.50 g, 29.54 mmol) in anhydrous ether (125 ml) under nitrogen at room temperature. The salt dissolved to give a deep red solution of the ylide. A solution of phthalaldehyde mono ethylene acetal (**3**) (5.1 g, 28.6 mmol) in anhydrous ether (20 ml) was added dropwise over 5 min. The reaction mixture was stirred at room temperature overnight, diluted with hexane (100 ml) and filtered to remove triphenylphosphine oxide. The organic phase was concentrated under reduced pressure to leave a pale yellow oil which was distilled at 106 °C and 0.1 mmHg to afford the *dioxolane* (**4b**) (3.51 g, 57%) as a colourless oil (Found: C, 77.6; H, 7.5. $C_{14}H_{16}O_2$ requires C, 77.7; H, 7.5%); $\nu_{max.}$(neat) 2 950, 1 668, 1 601, 1 482, 1 390, 1 223, 1 085, 944, and 756 cm^{-1}; δ($CDCl_3$) 2.06 (2 H, quintet, *J* 8 Hz, $CH_2CH_2CH_2$), 2.80—3.03 (4 H, m, $CH_2CH_2CH_2$), 3.92—4.20 [4 H, m, $O(CH_2)_2O$], 6.01 (1 H, s, OCHO), 6.44 (1 H, quintet, *J* 2 Hz, CH=C), 7.0—7.3 (3 H, m, ArH), and 7.52—7.62 (1 H, m, ArH).

o-(1,3-*Dioxolan*-2-*yl*)*benzylidenecyclopentane* (**4c**).—Anhydrous cyclopentyltriphenylphosphonium bromide[7] (34.5 g, 83.88 mmol) suspended in anhydrous ether (200 ml) was treated with butyl-lithium (1.6M solution in hexane; 52.5 ml, 84 mmol) at *ca.* 10 °C under nitrogen. The salt gradually dissolved to give a deep red solution of the ylide. The mixture was stirred for a further 2 h after which a solution of phthalaldehyde monoethylene acetal (**3**) (15.0 g, 84.18 mmol) in anhydrous ether (50 ml) was added dropwise at *ca.* 0 °C, the mixture was then stirred overnight at room temperature. Work-up as above gave a pale yellow oil which was distilled at 108 °C and 0.1 mmHg to afford the *dioxolane* (**4c**) (11.86 g, 61%) as a colourless oil (Found: C, 78.1; H, 7.7. $C_{15}H_{18}O_2$ requires C, 78.2; H, 7.9%); $\nu_{max.}$(neat) 3 060w, 2 952, 1 602w, 1 390, 1 225, 1 108, 1 071, and 756 cm^{-1}; δ($CDCl_3$) 1.5—1.7 [4 H, m, $CH_2(CH_2)_2CH_2$], 2.2—2.45 (4 H, m, CH_2CCH_2), 3.95—4.20 [4 H, m, $O(CH_2)_2O$], 5.99 (1 H, s, OCHO), 6.59 (1 H, quintet, *J* 2 Hz, CH=C), 7.15—7.25 (1 H, m, ArH), 7.27—7.35 (2 H, m, ArH), and 7.52—7.60 (1 H, m, ArH).

o-(1,3-*Dioxolan*-2-*yl*)*benzylidenecyclohexane* (**4d**).—Cyclohexyltriphenylphosphonium bromide[8] (35.7 g, 83.88 mmol) suspended in anhydrous ether (200 ml) was treated with butyl-lithium (1.55M solution in hexane; 55 ml, 85.2 mmol) at *ca.* 10 °C under nitrogen. The salt gradually dissolved to give a blood red solution of the ylide. The mixture was stirred for a further 1.5 h after which a solution of phthalaldehyde monoethylene acetal (**3**) (15.0 g, 84.18 mmol) in anhydrous ether (15 ml) was added over 5 min; the mixture was then stirred overnight at room temperature. Work-up as above gave a brown syrup which was distilled at 110 °C and 0.1 mmHg (Kugelrohr) to afford the *dioxolane* (**4d**) (18.08 g, 88%) as a pale yellow oil (Found: C, 78.2; H, 8.05. $C_{16}H_{20}O_2$ requires C, 78.65; H, 8.25%); $\nu_{max.}$(neat) 2 926, 1 648, 1 602, 1 445, 1 391, 1 112, 1 072, 945, and 757 cm^{-1}; δ($CDCl_3$) 1.4—1.75 [6 H, m, $CH_2(CH_2)_3CH_2$], 2.14 (2 H, t, *J* 6

Hz, cyclohexyl H), 2.27 (2 H, t, *J* 6 Hz, cyclohexyl H), 3.92—4.20 [4 H, m, $O(CH_2)_2O$], 5.93 (1 H, s, OCHO), 6.34 (1 H, s, CH=C), 7.07—7.15 (1 H, m, ArH), 7.21—7.35 (2 H, m, ArH), and 7.52—7.60 (1 H, m, ArH).

o-(1,3-*Dioxolan*-2-*yl*)*benzylidenecycloheptane* (**4e**).—Cycloheptyltriphenylphosphonium bromide[9] (30.0 g, 68.28 mmol) suspended in anhydrous ether (250 ml) was treated with butyl lithium (1.55M solution in hexane; 45 ml, 70 mmol) at *ca.* 10 °C under nitrogen. The salt gradually dissolved to afford a blood red solution of the ylide. The mixture was stirred at *ca.* 10 °C for 1.75 h after which a solution of phthalaldehyde monoethylene acetal (**3**) (12.1 g, 67.93 mmol) in anhydrous ether (10 ml) was added over 5 min; the mixture was then stirred overnight at room temperature. Work-up as above gave a dark brown syrup which was distilled at 110 °C and 0.1 mmHg (Kugelrohr) to afford the *dioxolane* (**4e**) (14.64 g, 84%) as a pale yellow oil (Found: C, 78.6; H, 8.8. $C_{17}H_{22}O_2$ requires C, 79.0; H, 8.6%); $\nu_{max.}$(neat) 3 060w, 2 921, 1 639, 1 602, 1 451, 1 390, 1 112, 1 071, and 758 cm^{-1}; $\delta(CDCl_3)$ 1.4—1.8 [8 H, m, CH_2 $(CH_2)_4CH_2$], 2.2—2.35 (2 H, m, cycloheptyl H), 2.35—2.5 (2 H, t, *J* 6 Hz, cycloheptyl H), 3.90—4.20 [4 H, m, $O(CH_2)_2O$], 5.93 (1 H, s, OCHO), 6.41 (1 H, s, CH=C), 7.10—7.17 (1 H, m, ArH), 7.22—7.35 (2 H, m, ArH), and 7.52—7.60 (1 H, m, ArH).

Attempted Hydrolysis of o-(1,3-*Dioxolan*-2-*yl*)*benzylidenecyclopropane* (**4a**) *with Dilute Hydrochloric Acid.*—A solution of the dioxolane (**4a**) (0.59 g, 2.47 mmol) in ether (10 ml) was stirred overnight with hydrochloric acid (2M; 10 ml). The organic phase was separated, dried (Na_2SO_4), and concentrated under reduced pressure to leave a colourless oil which crystallised with standing. Recrystallisation from hexane gave 2-(2-*chloroethyl*)*inden*-1-*ol* (**6**) (0.41 g, 85%) as colourless needles, m.p. 77—77.5 °C (Found: C, 68.0; H, 5.5. $C_{11}H_{11}ClO$ requires C, 67.9; H, 5.7%); $\nu_{max.}$(Nujol) 3 270, 3 178, 1 604, 1 461, 1 377, 1 050, 899, 754, and 736 cm^{-1}; $\delta_H(CDCl_3)$ 1.57 (1 H, d, *J* 10 Hz, CHO*H*), 2.94 (2 H, ~t*, *J* 7 Hz, CH_2CH_2Cl), 3.81 (2 H, ~td*, *J* 7, 1.5 Hz, CH_2CH_2Cl) 5.03 (1 H, d, *J* 10 Hz, C*H*OH), 6.50 (1 H, ~s*, CH=C), 7.1—7.3 (3 H, m, ArH), and 7.49 (1 H, ~d, ArH) (* indicates long range coupling also present); $\delta_C(CDCl_3)$ 31.60 (t, *J* 129 Hz), 42.98 (t, *J* 152 Hz), 78.02 (d, *J* 142 Hz), 120.81 (d), 123.38 (d), 125.59 (d), 128.59 (d), 128.70 (d), 142.24 (s), 145.01 (s), 147.94 (s); *m/z* 194 (M^+, 16%), 145 (100), 131 (12), 117 (14), and 115 (20).

o-*Formylbenzylidenecyclopropane* (**5a**).—Water (0.3 ml) was added with stirring to a suspension of silica gel (silica gel 60, Merck, 70—230 mesh; 3.0 g) in dichloromethane (4 ml) and stirring continued for *ca.* 5 min. A solution of *o*-(1,3-dioxolan-2-yl)benzylidenecyclopropane (**4a**) (1.00 g, 4.94 mmol) in dichloromethane (0.5 ml) was added and stirring continued for 48 h at room temperature. The mixture was then filtered and the silica residue washed with dichloromethane (2 × 5 ml). The combined filtrate and washings were evaporated to leave a yellow oil which was distilled at 95 °C and 0.1 mmHg (Kugelrohr) to afford the benzaldehyde (**5a**) (0.64 g, 82%) as a pale yellow oil, $\nu_{max.}$(neat) 2 730, 1 683, 1 596, 1 478, 1 401, 1 203, 800, and 745 cm^{-1}; δ (60 MHz; $CDCl_3$) 1.1—1.6 (4 H, m, cyclopropyl H), 7.0—8.0 (5 H, m, ArH + ArCH=C), and 10.30 (1 H, s, ArCHO).

o-*Formylbenzylidenecyclobutane* (**5b**).—*o*-(1,3-Dioxolan-2-yl)benzylidenecyclobutane (**4b**) (3.0 g, 13.87 mmol) was stirred overnight at room temperature in a mixture of hydrochloric acid (2M; 50 ml) and ether (50 ml). The organic phase was separated, washed with saturated aqueous sodium hydrogencarbonate (25 ml), and then with brine (10 ml). The ether layer was dried (Na_2SO_4) and concentrated under reduced pressure to give a colourless oil which was distilled at 82 °C and 0.12 mmHg to afford the *benzaldehyde* (**5b**) (1.72 g, 72%) (Found: C, 83.8; H, 7.0. $C_{12}H_{12}O$ requires C, 83.7; H, 7.0%); $\nu_{max.}$(neat) 2 951, 1 692, 1 595, 1 563, 1 479, 1 210, 1 187, and 764 cm^{-1}; $\delta(CDCl_3)$ 2.09 (2 H, quintet, *J* 8 Hz, $CH_2CH_2CH_2$), 2.82—3.00 (4 H, m, $CH_2CH_2CH_2$), 6.87 (1 H, quintet, *J* 2 Hz, CH=C), 7.25—7.38 (2 H, m, ArH), 7.45—7.56 (1 H, m, ArH), 7.78—7.87 (1 H, m, ArH), and 10.27 (1 H, s, CHO).

o-*Formylbenzylidenecyclopentane* (**5c**).—*o*-(1,3-Dioxolan-2-yl)benzylidenecyclopentane (**4c**) (11.6 g, 50.37 mmol) was dissolved in acetone (50 ml) and concentrated hydrochloric acid (2 drops) added. The mixture was warmed on a steam-bath for 10 min and then evaporated under reduced pressure. ^1H N.m.r. indicated the presence of *ca.* 20% starting material so the material was redissolved in acetone (50 ml) and more concentrated hydrochloric acid (4 drops) added. The mixture was warmed for 10 min on a steam-bath and then evaporated under reduced pressure. The residue was dissolved in ether (50 ml), and the solution was washed with aqueous sodium hydrogencarbonate (10 ml) followed by brine (10 ml). The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure to leave a pale yellow oil which was distilled at 92 °C and 0.1 mmHg (Kugelrohr) to afford the *benzaldehyde* (**5c**) (8.60 g, 92%) as a colourless oil (Found: C, 83.7; H, 7.2. $C_{13}H_{14}O$ requires C, 83.8; H, 7.6%); $\nu_{max.}$(neat) 3 061w, 2 739, 1 692, 1 595, 1 563, 1 477, 1 214, 1 190, and 751 cm^{-1}; $\delta(CDCl_3)$ 1.6—1.8 [4 H, m, $CH_2(CH_2)_2CH_2$] 2.2—2.35 (2 H, m, cyclopentyl H), 2.4—2.6 (2 H, m, cyclopentyl H), 6.85 (1 H, m, ArCH=C), 7.25—7.4 (2 H, m, 3,5-ArH), 7.50 (1 H, dt, *J* 7 Hz, 1.5 Hz, 4-ArH), 7.84 (1 H, dd, *J* 7 Hz, 1 Hz, 6-ArH), and 10.26 (1 H, s, ArCHO).

o-*Formylbenzylidenecyclohexane* (**5d**).—*o*-(1,3-Dioxolan-2-yl)benzylidenecyclohexane (**4d**) (16.88 g, 69.09 mmol) was dissolved in acetone (150 ml) containing toluene-*p*-sulphonic acid monohydrate (1.0 g) and the mixture allowed to stand at room temperature overnight. ^1H N.m.r. indicated the presence of 25% starting material. The reaction was driven to completion by repeatedly adding acetone and concentrating the mixture under reduced pressure until ^1H n.m.r. indicated that no starting material remained. The yellow-brown residue was partitioned between ether (200 ml) and saturated aqueous sodium hydrogencarbonate (100 ml). The organic phase was separated, washed with brine (25 ml), dried (Na_2SO_4), and concentrated under reduced pressure to afford a yellow oil (10.8 g). Distillation afforded the *benzaldehyde* (**5d**) (9.43 g, 68%), b.p. 110 °C at 0.15 mmHg (Kugelrohr) as a colourless oil (Found: C, 83.7; H, 7.9. $C_{14}H_{16}O$ requires C, 84.0; H, 8.05%); $\nu_{max.}$(neat) 3 061, 2 927, 1 692, 1 647, 1 595, 1 446, 1 209, 829, and 752 cm^{-1}; $\delta(CDCl_3)$ 1.4—1.8 [6 H, m, $CH_2(CH_2)_3CH_2$], 2.10 (2 H, t, *J* 6 Hz, cyclohexyl H), 2.33 (2 H, t, *J* 6 Hz, cyclohexyl H), 6.51 (1 H, s, CH=C), 7.21 (1 H, dm, *J* 7.5 Hz, 3-ArH), 7.33 (1 H, tm, *J* 7.5 Hz, 5-ArH), 7.52 (1 H, dt, *J* 7.5 Hz, 1 Hz, 4-ArH), 7.88 (1 H, dd, *J* 7.5 Hz, 1 Hz, 6-ArH), and 10.26 (1 H, d, *J* 0.8 Hz, ArCHO).

o-*Formylbenzylidenecycloheptane* (**5e**).—*o*-(1,3-Dioxolan-2-yl)benzylidenecycloheptane (**4e**) (14.47 g, 56.00 mmol) was dissolved in acetone (150 ml) containing toluene-*p*-sulphonic acid monohydrate (1.0 g) and the mixture allowed to stand at room temperature overnight. ^1H N.m.r. indicated the presence of *ca.* 30% starting material. The reaction was driven to completion by repeatedly adding acetone and concentrating the mixture under reduced pressure until ^1H n.m.r. indicated the absence of starting material. The brown residue was partitioned between ether (200 ml) and saturated aqueous sodium hydrogencarbonate (100 ml). The organic phase was separated, washed with brine (25 ml), and dried (Na_2SO_4). Concentration

under reduced pressure afforded an orange-brown syrup (11.0 g) which was distilled at 110 °C and 0.1 mmHg (Kugelrohr) to afford the *benzaldehyde* (**5e**) (8.64 g, 72%) as a pale yellow oil (Found: C, 83.5; H, 8.85. $C_{15}H_{18}O$ requires C, 84.1; H, 8.5%); $\nu_{max.}$(neat) 3 060w, 2 923, 1 692, 1 637, 1 595, 1 448, 1 214, and 758 cm^{-1}; $\delta(CDCl_3)$ 1.4—1.8 [8 H, m, $CH_2(CH_2)_4CH_2$], 2.1—2.3 (2 H, m, cycloheptyl H), 2.4—2.6 (2 H, m, cycloheptyl H), 6.59 (1 H, s, CH=C), 7.21 (1 H, dm, *J* 8 Hz, 3-ArH), 7.33 (1 H, tm, *J* 8 Hz, 5-ArH), 7.52 (1 H, dt, *J* 8 Hz, 1 Hz, 4-ArH), 7.87 (1 H, dd, *J* 8 Hz, 1 Hz, 6-ArH), and 10.28 (1 H, s, ArCHO).

Methyl 2-*Azido*-3-(o-*cyclobutylidenephenyl*)*propenoate* (**2b**).—A sodium methoxide solution was prepared by the addition of sodium (0.73 g, 31.6 mmol) to methanol (25 ml). The solution was cooled to −15 °C and a mixture of *o*-formylbenzylidenecyclobutane (**5b**) (1.363 g, 7.91 mmol) and methyl azidoacetate (3.64 g, 31.6 mmol) in methanol (5 ml) was added below 10 °C over 0.1 h under nitrogen. The reaction mixture was allowed to warm to room temperature over 3 h and then poured into water (50 ml). The mixture was extracted with ether (3 × 25 ml) and the combined extracts were washed with brine (15 ml), dried (Na_2SO_4), and concentrated under reduced pressure to leave a yellow oil. The residue was purified by chromatography (SiO_2:chloroform) to afford the *azide* (**2b**) (1.19 g, 56%) as a viscous pale yellow oil (Found: C, 67.0; H, 5.9; N, 15.2. $C_{15}H_{15}N_3O_2$ requires C, 66.9; H, 5.6; N, 15.6%); $\nu_{max.}$(neat) 2 951, 2 125, 1 714, 1 612, 1 592, 1 254, 1 084, and 763 cm^{-1}; $\delta(CDCl_3)$ 1.98 (2 H, quintet, *J* 8 Hz, $CH_2CH_2CH_2$), 2.80 (4 H, dt, *J* 8 Hz, 2 Hz, $CH_2CH_2CH_2$), 3.83 (3 H, s, CO_2Me), 6.15 (1 H, quintet, *J* 2 Hz, CH=C), 7.05—7.22 [3 H, +1 H, m + s (δ 7.09), ArH + CH=C(CO_2Me)], and 7.78—7.86 (1 H, m, ArH *ortho* to vinyl azide).

Methyl 2-*Azido*-3-(o-*cyclopentylidenephenyl*)*propenoate* (**2c**).—A sodium methoxide solution was prepared by the addition of sodium (3.2 g, 0.139 mol) to methanol (100 ml). The solution was cooled to −15 °C (ice–salt bath) and a mixture of *o*-formylbenzylidenecyclopentane (**5c**) (6.50 g, 34.90 mmol) and methyl azidoacetate (16.0 g, 0.139 mol) in methanol (10 ml) was added below 10 °C over 0.5 h under nitrogen. The reaction mixture was stirred at this temperature for a further 1 h after which it was stored at 4 °C overnight, and then poured into water (200 ml). Work-up as above gave the *azide* (**2c**) (6.31 g, 64%) as a viscous pale yellow oil (Found: C, 68.1; H, 6.25; N, 14.6. $C_{16}H_{17}N_3O_2$ requires C, 67.8; H, 6.05; N, 14.8%); $\nu_{max.}$(neat) 3 059, 2 953, 2 121, 1 714, 1 612, 1 252, 1 097, 1 074, and 767 cm^{-1}; $\delta(CDCl_3)$ 1.6—1.8 [4 H, m, $CH_2(CH_2)_2CH_2$], 2.2—2.4 (2 H, m, cyclopentyl H), 2.4—2.6 (2 H, m, cyclopentyl H), 3.91 (3 H, s, CO_2Me), 6.40 [1 H, quintet, *J* 2 Hz, $(CH_2)_2C{=}CH$], 7.16 (1 H, s, CH=C–N_3), 7.17—7.33 (3 H, m, ArH), and 7.98 (1 H, dd, *J* 6 Hz, 1 Hz, 6-ArH).

Methyl 2-*Azido*-3-(o-*cyclohexylidenephenyl*)*propenoate* (**2d**).—A sodium methoxide solution was prepared by the addition of sodium (4.13 g, 0.180 mmol) to methanol (120 ml). The solution was cooled to −15 °C and a mixture of *o*-formylbenzylidenecyclohexane (**5d**) (9.0 g, 44.94 mmol) and methyl azidoacetate (20.7 g, 0.180 mol) in methanol (10 ml) was added below 10 °C over 0.75 h under nitrogen. The reaction mixture was stirred at this temperature for a further 2.5 h and then stored at 4 °C overnight. Work-up as above gave the *azide* (**2d**) (8.05 g, 60%) as a pale yellow viscous oil. Low-temperature recrystallisation from hexane at −78 °C afforded the *azide* (**2d**) (7.95 g, 60%) as pale yellow needles, m.p. 27—28 °C (Found: C, 68.3; H, 6.6; N, 13.8. $C_{17}H_{19}N_3O_2$ requires C, 68.7; H, 6.4; N, 14.1%); $\nu_{max.}$(Nujol) 2 215, 1 718, 1 648, 1 612, 1 593, 1 247, 1 074, and 767 cm^{-1}; $\delta_H(CDCl_3)$ 1.4—1.8 [6 H, m, $CH_2(CH_2)_3CH_2$], 2.04 (2 H, t, *J* 6 Hz, cyclohexyl H), 2.30 (2 H, t, *J* 6 Hz, cyclohexyl H), 3.90 (3 H, s, CO_2Me), 6.20 [1 H, s, $CH{=}C(CH_2)$], 7.1—7.2 [1 H, +1 H, m + s (δ 7.16), ArH + $CH{=}CN_3$], 7.2—7.3 (2 H, m, ArH), and 8.05—8.15 (1 H, m, ArH *ortho* to vinyl N_3).

Methyl 2-*Azido*-3-(o-*cycloheptylidenephenyl*)*propenoate* (**2e**).—A sodium methoxide solution was prepared by the addition of sodium (2.5 g, 108.7 mmol) to methanol (100 ml). The solution was cooled to −15 °C and a mixture of *o*-formylbenzylidenecycloheptane (**5e**) (8.00 g, 37.3 mmol) and methyl azidoacetate (12.9 g, 0.112 mol) in methanol (10 ml) was added below 10 °C over 0.25 h under nitrogen. The reaction mixture was allowed to stir at this temperature for a further 1 h then allowed to warm to 5 °C over 2 h. Work up as above gave the *azide* (**2e**) (7.88 g, 69%) as a pale yellow viscous oil (Found: C, 69.7; H, 6.9; N, 13.2. $C_{18}H_{21}N_3O_2$ requires C, 69.4; H, 6.8; N, 13.5%); $\nu_{max.}$(neat) 2 923, 2 122, 1 715, 1 612, 1 304, 1 250, 1 074, and 678 cm^{-1}; $\delta(CDCl_3)$ 1.4—1.9 [8 H, m, $CH_2(CH_2)_4CH_2$], 2.0—2.3 (2 H, br s, cycloheptyl H), 2.3—2.5 (2 H, t, *J* 6 Hz, cycloheptyl H), 3.90 (3 H, s, CO_2Me), 6.28 (1 H, s, $CH{=}CCH_2$), 7.1—7.4 [3 H + 1 H, m + s (δ 7.18), ArH + $CH{=}CN_3$], and 8.1—8.2 (1 H, m, ArH *ortho* to vinyl N_3).

Methyl 2-*Azido*-3-[o-(1-*oxaspiro*[2.3]*hexyl*)*phenyl*]-*propenoate* (**7b**).—A solution of MCPBA (200 mg, 1.16 mmol) in dichloromethane (5 ml) was added dropwise to a solution of the azide (**2b**) (280 mg, 1.04 mmol) in dichloromethane (10 ml) and the resulting solution stirred at room temperature for 18 h. The reaction mixture was washed with 10% aqueous sodium sulphite (2 × 5 ml), saturated aqueous sodium hydrogen carbonate (10 ml), and then brine (5 ml). The organic phase was then dried (Na_2SO_4) and concentrated under reduced pressure to leave a yellow viscous oil which was purified by chromatography (SiO_2:dichloromethane) to afford the *epoxide* (**7b**) (191 mg, 90%) as a pale yellow viscous oil (Found: C, 63.15; H, 5.5; N, 14.4. $C_{15}H_{15}N_3O_3$ requires C, 63.1; H, 5.3; N, 14.7%); $\nu_{max.}$(neat) 2 953, 2 125, 1 720, 1 618, 1 434, 1 257, 1 077, and 770 cm^{-1}; $\delta(CDCl_3)$ 1.65—2.00 (3 H, m, cyclobutyl H), 2.25—2.55 (2 H, m, cyclobutyl H), 2.60—2.80 (1 H, m, cyclobutyl H), 3.95 (3 H + 1 H, s + s, CO_2Me + ArCH–O), 7.15—7.38 (3 H + 1 H, ArH + ArCH=C), and 7.90—8.00 (1 H, m, ArH *ortho* to vinyl azide).

Methyl 2-*Azido*-3-[o-(1-*oxaspiro*[2.4]*heptyl*)*phenyl*]-*propenoate* (**7c**).—A solution of MCPBA (1.5 g, *ca.* 8.7 mmol) in dichloromethane (20 ml) was added dropwise to a solution of the azide (**2c**) (2.00 g, 7.06 mmol) in dichloromethane (20 ml) and the resulting solution stirred at room temperature for 21 h. Chloroform (10 ml) was added to dissolve the white precipitate which had formed. Work-up as above gave the *epoxide* (**7c**) (2.11 g, 100%) as a pale yellow syrup which slowly crystallised with time to form pale yellow needles, m.p. 155—157 °C (change of crystal form at *ca.* 130 °C) (from hexane) (Found: C, 64.1; H, 5.75; N, 14.0. $C_{16}H_{17}N_3O_3$ requires C, 64.2; H, 5.7; N, 14.0%); $\nu_{max.}$(neat) 2 956, 2 127, 1 721, 1 617, 1 435, 1 307, 1 253, and 769 cm^{-1}; $\delta(CDCl_3)$ 1.1—2.1 [8 H, m, $(CH_2)_4$], 3.85 (3 H, s, CO_2Me), 3.98 (1 H, s, OCH), 7.01 (1 H, s, ArCH), 7.2—7.4 (3 H, m, ArH), and 7.9—8.1 (1 H, m, ArH).

Methyl 2-*Azido*-3-[o-(1-*oxaspiro*[2.5]*octyl*)*phenyl*]-*propenoate* (**7d**).—A solution of MCPBA (1.5 g, *ca.* 8.7 mmol) in dichloromethane (75 ml) was added dropwise to a solution of the azide (**2d**) (2.00 g, 6.73 mmol) in dichloromethane (50 ml) and the resulting solution stirred at room temperature for 17 h. Work-up as above gave a pale yellow syrup (2.2 g, *ca.* 100%) which crystallised with time. Recrystallisation from hexane afforded the *epoxide* (**7d**) (1.68 g, 80%) as small pale yellow needles, m.p. 85—87 °C (Found: C, 65.5; H, 6.3; N, 13.6.

$C_{17}H_{19}N_3O_3$ requires C, 65.15; H, 6.1; N, 13.4%); $\nu_{max.}$(Nujol) 2 135, 1 711, 1 611, 1 250, 1 101, 920, 817, and 770 cm^{-1}; $\delta(CDCl_3)$ 1.1—2.0 [10 H, m, $(CH_2)_5$], 3.88 (1 H, s, OCH), 3.93 (3 H, s, CO_2Me), 7.22 (1 H, s, ArCH=C), 7.27—7.43 (3 H, m, ArH), and 8.06—8.18 (1 H, m, ArH *ortho* to vinyl azide).

Methyl 2-Azido-3-[o-(1-oxaspiro[2.6]nonyl)phenyl]-propenoate (**7e**).—A solution of MCPBA (1.5 g, *ca.* 8.7 mmol) in dichloromethane (20 ml) was added dropwise to a solution of the azide (**2e**) (2.00 g, 6.42 mmol) in dichloromethane (20 ml) and the resulting solution stirred at room temperature for 18 h. Work-up as above gave the *epoxide* (**7e**) (2.10 g, 100%) as a viscous pale yellow oil (Found: C, 65.85; H, 6.6; N, 12.5. $C_{18}H_{21}N_3O_3$ requires C, 66.0; H, 6.5; N, 12.8%); $\nu_{max.}$(neat) 2 927, 2 127, 1 720, 1 611, 1 433, 1 254, and 771 cm^{-1}; $\delta(CDCl_3)$ 1.2—2.0 (12 H, m, cycloheptyl H), 3.88 (1 H, s, OCH), 3.93 (3 H, s, CO_2Me), 7.16 (1 H, s, CH=C), 7.3—7.4 (3 H, m, ArH), and 8.05—8.15 (1 H, m, ArH *ortho* to vinyl azide).

Thermolysis of the Azide (**2b**).—A solution of the azidocinnamate (**2b**) (53 mg) was heated to reflux in toluene (5 ml) for 1 h under nitrogen. Evaporation of the solvent and chromatography of the residue using radial t.l.c. (SiO_2 : hexane–ether) afforded (i) *methyl* 1,1a,2,6b-*tetrahydro*-2-*cyclobut*-1-*enylindeno*[1,2-b]*azirine*-1a-*carboxylate* (**8b**) (21 mg, 44%), a pale yellow oil (Found: $M^+ - CO_2Me$, 182.0972. $C_{15}H_{15}NO_2 - CO_2Me$ requires 182.0970); $\nu_{max.}$(neat) 3 265, 1 722, 1 627, 1 438, 1 222, 1 165, and 747 cm^{-1}; n.m.r. indicated a 60:40 mixture of diastereoisomers (A:B); $\delta(CDCl_3)$ 1.6 (1 H, br s, NH, isomer A + B), 2.2—2.8 [4 H, m, $(CH_2)_2$ isomer A + B], 3.67 (1 H, br s, HC≡CC*H*, isomer A + B), 3.84 (3 H, s, CO_2Me, isomer A + B), 4.63 (1 H, br s, C*H*NH, isomer A + B), 5.86 (1 H, br s, C=CH, isomer A + B), and 7.00—7.57 (4 H, m, ArH, isomer A + B); $\delta(CDCl_3 + D_2O)$, 2.2—2.8 [4 H, m, $(CH_2)_2$], 3.78 (1 H, br s, HC≡CC*H*, isomer B), 3.825 (3 H, s, CO_2Me, isomer A), 3.835 (3 H, s, CO_2Me, isomer B), 4.54 (1 H, br s, C*H*NH, isomer B), 4.63 (1 H, br s, C*H*NH, isomer A), 5.84 (1 H, br s, C=CH, isomer A), 5.92 (1 H, br s, C=CH, isomer B), and 7.00—7.57 (4 H, m, ArH, isomer A + B); *m/z* 241 (M^+), 210, and 182 (base); (ii) *methyl* 4-*cyclobutylidenemethylindole*-2-*carboxylate* (**9b**) (2 mg, 4%) colourless prisms, m.p. 184—186 °C (from ether–light petroleum) (Found: C, 74.4; H, 6.25; N, 5.6. $C_{15}H_{15}NO_2$ requires C, 74.7; H, 6.3; N, 5.8%); $\nu_{max.}$(KBr) 3 317, 1 686, 1 339, 1 259, 1 207, and 761 cm^{-1}; $\delta(CDCl_3)$ 2.0—2.3 (2 H, m, cyclobutyl H), 2.90—3.15 (1 H, m, cyclobutyl H), 3.94 (3 H, s, CO_2Me), 6.52 [1 H, m, C*H*=C$(CH_2)_2$], 7.00—7.08 (1 H, m, ArH), 7.18—7.38 (3 H, m, ArH's), and 8.86 (1 H, br s, NH); and (iii) *methyl* 1-*cyclobutylisoquinoline*-3-*carboxylate* (**10b**) (3 mg, 6%) colourless needles, m.p. 74—77 °C (from ether–light petroleum) (Found: C, 74.6; H, 6.3; N, 5.9. $C_{15}H_{15}NO_2$ requires C, 74.7; H, 6.3; N, 5.8%); $\nu_{max.}$(Nujol) 1 731, 1 278, 1 245, 1 152, 904, 804, 790, and 764 cm^{-1}; $\delta_H(CDCl_3)$ 1.9—2.35 (2 H, m, cyclobutyl H), 2.45—1.85 (4 H, m, cyclobutyl H), 4.04 (3 H, s, CO_2Me), 4.39 (1 H, quintet, *J* 9 Hz, CH_2CHCH_2), 7.63—7.80 (2 H, m, ArH), 7.90—8.00 (1 H, m, ArH), 8.05—8.15 (1 H, m, ArH), and 8.43 (1 H, s, ArCH).

The n.m.r. spectrum of the crude reaction mixture indicated that the yield of each component was (**8b**) 70%, (**9b**) 5%, and (**10b**) 8%. The n.m.r. also indicated the presence of two other (unidentified) components at 13% and 4%.

Thermolysis of the Azide (**2c**).—A solution of the azidocinnamate (**2c**) (147 mg) was heated to reflux in toluene (10 ml) for 2.5 h under nitrogen. Evaporation of the solvent and chromatography of the residue using radial t.l.c. (SiO_2 : hexane–ether) gave: (i) *methyl* 1,1a,2,6b-*tetrahydro*-2-*cyclopent*-1-*enylindeno*[1,2-b]*azirine*-1a-*carboxylate* (**8c**) (98 mg, 74%), a pale yellow oil (Found: M^+, 255.1204. $C_{16}H_{17}NO_2$ requires *M*, 255.1259); $\nu_{max.}$(neat) 3 263, 1 723, 1 231, 1 166, and 767 cm^{-1}; n.m.r. indicated at 60:40 mixture of diastereoisomers (A:B); $\delta_H(CDCl_3)$ 0.80 (1 H, br d, *J* 6 Hz, NH, exchanges D_2O, isomer A + B), 1.8—2.05 (2 H, m, $CH_2CH_2CH_2$, isomer A + B), 2.05—2.60 (4 H, m, $CH_2CH_2CH_2$, isomer A + B), 3.59 (1 H, d, *J* 6 Hz, C*H*NH, isomer A), 3.75 (1 H, d, *J* 8 Hz, C*H*NH, isomer B), 3.82 (3 H, s, CO_2Me, isomer A + B), 4.70 (1 H, br s, ArC*H*C=C, isomer B), 4.82 (1 H, br s, ArCHC=C, isomer A), 5.39 (1 H, br s, C=CH, isomer A), 5.64 (1 H, br s, C=CH, isomer B), 7.1—7.3 (3 H, m, ArH, isomer A + B), and 7.3—7.45 (1 H, m, isomer A + B). Addition of D_2O resulted in the disappearance of the signal at δ 0.80 (NH) and the doublets at δ 3.59 and 3.75 became singlets. Also the CO_2Me signal at δ 3.82 resolved into two singlets at δ 3.82 (isomer A) and δ 3.84 (isomer B); *m/z* 255 (M^+, 4%), 210 (39), 196 (100), 194 (39), 188 (70, 167 (20), 156 (71), and 128 (95); (ii) *methyl* 4-*cyclopentylidenemethylindole*-2-*carboxylate* (**9c**) (4 mg, 3%), colourless needles, m.p. 165—168 °C (from light petroleum) (Found: C, 75.4; H, 6.5; N, 5.45. $C_{16}H_{17}NO_2$ requires C, 75.3; H, 6.7; N, 5.5%); $\nu_{max.}$(Nujol) 3 338, 1 679, 1 605, 1 243, 1 207, 998, and 767 cm^{-1}; $\delta(CDCl_3)$ 1.6—1.9 [4 H, m, $CH_2(CH_2)_2CH_2$], 2.5—2.7 [4 H, m, $(CH_2)_2CH_2$], 3.94 (3 H, s, CO_2Me), 6.77 (1 H, m, CH=C), 7.14—7.40 (4 H, m, ArH), and 8.90 (1 H, br s, NH); (iii) methyl 1-cyclopentylisoquinoline-3-carboxylate (**10c**) (3 mg, 2%), colourless needles, m.p. 71—73 °C (lit.,[1] 71.5—73 °C).

The n.m.r. spectrum of the crude reaction mixture indicated that the yield of each component was (**8c**) 91%, (**9c**) 5%, and (**10c**) 3%.

Thermolysis of the Azide (**2d**).—A solution of the azidocinnamate (**2d**) (500 mg) was heated to reflux in toluene (10 ml) for 2 h under nitrogen. Evaporation of the solvent and chromatography of the residue using radial t.l.c. (SiO_2 : hexane–ether) afforded (i) *methyl* 1,1a,2,6b-*tetrahydro*-2-*cyclohex*-1-*enylindeno*[1,2-b]*azirine*-1a-*carboxylate* (**8d**) (385 mg, 85%), a pale yellow oil (Found: M^+, 269.1316. $C_{16}H_{19}NO_2$ requires *M*, 269.1416); $\nu_{max.}$(neat) 3 263, 1 721, 1 229, 1 169, and 751 cm^{-1}; n.m.r. indicated a 60:40 mixture of diastereoisomers (A:B); $\delta(CDCl_3)$ 0.94 (1 H, br d, *J* 5 Hz, NH, isomer A + B), 1.4—2.4 (8 H, m, cyclohexyl H, isomer A + B), 3.54 (1 H, br d, *J* 6 Hz, C*H*–NH, isomer A), 3.64 (1 H, br d, *J* 7 Hz, C*H*–NH, isomer B), 3.82 (3 H, br s, CO_2Me, isomer A + B), 4.48 (1 H, br s, ArCHC=C, isomer B), 4.63 (1 H, br s, ArCHC=C, isomer A), 5.26 (1 H, br s, C=CH, isomer A), 5.69 (1 H, br s, C=CH, isomer B), and 7.1—7.4 (4 H, m, ArH, isomer A + B); *m/z* 269 (M^+, 1%), 252 (2), 224 (14), 188 (100), 156 (59), and 128 (68); (ii) *methyl* 4-*cyclohexylidenemethylindole*-2-*carboxylate* (**9d**) (18 mg, 4%), colourless needles, m.p. 156—160 °C (Found: M^+, 269.1506. $C_{17}H_{19}NO_2$ requires *M*, 269.1416); $\nu_{max.}$(KBr) 3 333, 1 687, 1 605, 1 520, 1 347, 1 243, 1 210, and 771 cm^{-1}; $\delta(CDCl_3)$ 1.3—1.9 [6 H, m, $CH_2(CH_2)_3CH_2$], 2.25—2.48 (4 H, m, CH_2CCH_2), 3.94 (3 H, s, CO_2Me), 6.47 (1 H, br d, *J* <1 Hz, olefinic H), 6.95—7.04 (1 H, m, ArH), 7.2—7.3 (3 H, m, indole H), and 8.85 (1 H, br s, NH); *m/z* 269 (M^+, 100%), 237 (22), 210 (56), 188 (21), 168 (11), and 156 (14).

The n.m.r. spectrum of the crude reaction mixture indicated that the yield of each component was (**8d**) 92%, (**9d**) 5%, and (**10d**) 1%.

Thermolysis of the Azide (**2e**).—A solution of the azidocinnamate (**2e**) (100 mg) was heated to reflux in toluene (5 ml) for 2.5 h under nitrogen. Evaporation of the solvent and chromatography of the residue using radial t.l.c. (SiO_2 : hexane–ether) gave (i) *methyl* 1,1a,2,6b-*tetrahydro*-2-*cyclohept*-1-*enylindeno*[1,2-b]*azirine*-1a-*carboxylate* (**8e**) (66 mg, 72%), a pale yellow oil (Found: C, 76.7; H, 7.45; N, 4.8. $C_{18}H_{21}NO_2$ requires C, 76.3; H, 7.5; N, 4.9%); $\nu_{max.}$(neat) 3 417, 1 721, 1 438, 1 382, 1 231, 1 166, and 750 cm^{-1}; n.m.r. indicated a 60:40 mixture of

diastereoisomers (A:B); δ($CDCl_3$) 1.0 (1 H, br s, NH, isomer A + B), 1.2—2.6 (10 H, m, cycloheptyl H, isomer A + B), 3.56 (1 H, br s, C*H*NH, isomer A), 3.63 (1 H, br s, C*H*NH, isomer B), 3.82 (3 H, s, CO_2Me, isomer A + B), 4.56 (1 H, br s, ArCHC=C, isomer B), 4.74 (1 H, br s, ArCHC=C, isomer A), 5.34 (1 H, br s, C=CH, isomer A), 5.90 (1 H, br s, C=CH, isomer B), and 7.1—7.4 (4 H, m, ArH, isomer A + B); addition of D_2O resulted in the disappearance of the signal at δ 1.10 (NH), the signals at δ 3.56, 3.63, 4.56, and 4.74 became sharp singlets whilst the signals at δ 5.34 and 5.90 became triplets (*J* 7 Hz). Also, the CO_2Me signal at δ 3.82 resolved into two singlets at δ 3.81 (isomer A) and δ 3.83 (isomer B); (ii) *methyl cycloheptylidenemethylindole-2-carboxylate* (**9e**) (3 mg, 3%) colourless needles, m.p. 151—154 °C (from light petroleum) (Found: C, 75.9; H, 7.45; N, 5.15. $C_{18}H_{21}NO_2$ requires C, 76.3; H, 7.5; N, 4.9%); $\nu_{max.}$(KBr) 3 325, 1 692, 1 606, 1 573, 1 257, 1 209, 997, 767, and 758 cm^{-1}; δ($CDCl_3$) 1.4—1.8 (8 H, m, cycloheptyl H), 2.4—2.6 (4 H, m, cycloheptyl H), 3.94 (3 H, s, CO_2Me), 6.58 [1 H, br s, C*H*=C(CH_2)$_2$], 7.05 (1 H, m, indole H), 7.23—7.35 (3 H, m, indole H), and 8.85 (1 H, br s, NH).

The n.m.r. spectrum of the crude reaction mixture indicated that the yield of each component was (**8e**) 94% and (**9e**) 4%.

Thermolysis of the Azide (**7b**).—A solution of the epoxide (**7b**) (49 mg, 0.2 mmol) was heated to reflux in toluene (5 ml) for 1.5 h under nitrogen. The reaction mixture was concentrated under reduced pressure and the residue recrystallised from ether to afford *methyl* 4-(1-*oxaspiro*[2.3]*hexyl*)*indole*-2-*carboxylate* (**14b**) (36 mg, 82%) as colourless prisms, m.p. 150—153 °C (Found: C, 70.0; H, 6.2; N, 5.4. $C_{15}H_{15}NO_3$ requires C, 70.0; H, 5.9; N, 5.45%); $\nu_{max.}$(Nujol) 3 376, 1 709, 1 528, 1 258, 792, and 767 cm^{-1}; δ($CDCl_3$) 1.6—2.0 (3 H, m, cyclobutyl H), 2.4—2.8 (3 H, m, cyclobutyl H), 3.96 (3 H, s, CO_2Me), 4.24 (1 H, s, ArCHO), 6.88—6.95 (1 H, m, 7-ArH), 7.28—7.42 (3 H, m, 3-, 5-, and 6-ArH), and 8.93 (1 H, br s, NH, exchanges D_2O).

Thermolysis of the Azide (**7c**).—A solution of the epoxide (**7c**) (400 mg, 1.34 mmol) was heated to reflux in toluene (5 ml) for 2 h under nitrogen. The reaction mixture was concentrated under reduced pressure and the residue recrystallised from ether to afford *methyl* 4-(1-*oxaspiro*[2.4]*heptyl*)*indole*-2-*carboxylate* (**14c**) (297 mg, 82%) as colourless needles, m.p. 157—159 °C (Found: C, 70.85; H, 6.7; N, 4.95. $C_{16}H_{17}NO_3$ requires C, 70.8; H, 6.3; N, 5.2%); $\nu_{max.}$(Nujol) 3 343, 1 709, 1 612, 1 527, 1 256, 933, and 768 cm^{-1}; δ($CDCl_3$) 1.3—2.25 [8 H, m, (CH_2)$_4$], 3.97 (3 H, s, CO_2Me), 4.37 (1 H, s, CH–O), 7.0—7.1 (1 H, m, 7-ArH), 7.3—7.4 (3 H, m, 3-, 5-, and 6-ArH), and 9.08 (1 H, br s, NH, exchanges D_2O).

Thermolysis of the Azide (**7d**).—A solution of the epoxide (**7d**) (50 mg, 0.17 mmol) was heated to reflux in toluene (5 ml) for 2 h under nitrogen. The reaction mixture was concentrated under reduced pressure and the residue recrystallised from ether to afford *methyl* 4-(1-*oxaspiro*[2.5]*octyl*)*indole*-2-*carboxylate* (**4d**) (36 mg, 79%) as colourless needles, m.p. 160—163 °C (change in crystal form at *ca.* 135 °C) (Found: C, 71.9; H, 6.7; N, 4.5. $C_{17}H_{19}NO_3$ requires C, 71.55; H, 6.7; N, 4.9%); $\nu_{max.}$(Nujol) 3 338, 1 711, 1 526, 1 257, 1 240, and 769 cm^{-1}; δ($CDCl_3$) 1.1—1.6 [6 H, m, CH_2(C*H*$_2$)$_3$$CH_2$], 1.6—2.0 [4 H, m, C*H*$_2$($CH_2$)$_3$C*H*$_2$], 3.97 (3 H, s, CO_2Me), 4.17 (1 H, s, OCH), 7.05—7.12 (1 H, m, 7-ArH), 7.25—7.40 (3 H, m, 3-, 5-, and 6-ArH), and 9.13 (1 H, br s, NH, exchanges D_2O).

Thermolysis of the Azide (**7e**).—A solution of the epoxide (**7e**) (300 mg, 0.9 mmol) was heated to reflux in toluene (10 ml) for 2 h under nitrogen. The reaction mixture was concentrated under reduced pressure and the residue recrystallised from ether to afford *methyl* 4-(1-*oxaspiro*[2.6]*nonyl*)*indole*-2-*carboxylate* (**14e**) (233 mg, 85%) as colourless needles, m.p. 148—152 °C (Found: C, 72.2; H, 7.1; N, 4.6. $C_{18}H_{21}NO_3$ requires C, 72.2; H, 7.1; N, 4.7%); $\nu_{max.}$(Nujol) 3 189, 1 708, 1 528, 1 268, 1 217, 931, and 775 cm^{-1}; δ($CDCl_3$) 1.1—2.1 [12 H, m, (CH_2)$_6$], 3.97 (3 H, s, CO_2Me), 4.17 (1 H, s, ArCHO), 7.06 (1 H, br d, *J* 6 Hz, 7-ArH), 7.24—7.45 (3 H, m, 3-, 5-, and 6-ArH), and 9.18 (1 H, br s, NH, exchanges D_2O).

Photolysis of the Azide (**2b**).—A solution of the azidocinnamate (**2b**) (120 mg) in light petroleum (200 ml) was irradiated for 0.5 h under a stream of nitrogen. Evaporation of the solvent and chromatography of the residue using radial t.l.c. (SiO_2:ether) gave *methyl spiro*(*cyclobutane*-1,1′-3,4-*dihydro*-[1H]*cycloprop*[c]*isoquinoline*)-1a-*carboxylate* (**15b**) (88 mg, 82%), colourless oil (Found: C, 74.6; H, 6.45; N, 5.8. $C_{15}H_{15}NO_2$ requires C, 74.7; H, 6.3; N, 5.8%); $\nu_{max.}$(neat) 1 718, 1 617, 1 435, 1 291, 1 155, 1 047, and 767 cm^{-1}; δ($CDCl_3$) 0.88—1.07 (1 H, m, cyclobutyl H), 1.55—1.95 (3 H, m, cyclobutyl H), 2.42—2.68 (2 H, m, cyclobutyl H), 3.26 (1 H, s, cyclopropyl H), 3.87 (3 H, s, CO_2Me), 7.27—7.53 (4 H, m, ArH), and 8.27 (1 H, s, ArCH=N).

The n.m.r. spectrum of the crude reaction mixture indicated that the yield of (**15b**) was 96% and may contain 3% of (**8b**) though this was not isolated.

Photolysis of the Azide (**2c**).—A solution of the azidocinnamate (**2c**) (304 mg) in light petroleum (200 ml) was irradiated for 0.5 h under a stream of nitrogen. Evaporation of the solvent and chromatography of the residue using radial t.l.c. (SiO_2:ether) gave (i) methyl 2,3-dihydro-1-cyclopent-1-enylindeno[1,2-*b*]-aziridine-2-carboxylate (**8c**) (112 mg, 41%) colourless oil, spectral data given previously; (ii) methyl 4-cyclopentylidenemethylindole-2-carboxylate (**9c**) (5 mg, 2%) colourless needles, m.p. 165—168 °C, spectral data given previously; and (iii) *methyl spiro*(*cyclopentane*-1,1′,3,4-*dihydro*-[1H]*cycloprop*[c]-*isoquinoline*)-1a-*carboxylate* (**15c**) (38 mg, 14%) colourless oil (Found: C, 75.3; H, 6.9; N, 5.5. $C_{16}H_{11}NO_2$ requires C, 75.3; H, 6.7; N, 5.5); $\nu_{max.}$(neat) 1 725, 1 619, 1 297, 1 124, 779, and 754 cm^{-1}; δ_H($CDCl_3$) 0.62 (1 H, dt, *J* 12 Hz, 9 Hz, cyclopentyl H), 1.12—1.28 (1 H, m, cyclopentyl H), 1.43—1.62 (2 H, m, cyclopentyl H), 1.62—1.85 (2 H, m, cyclopentyl H), 1.98—2.10 (2 H, m, cyclopentyl H), 3.25 (1 H, s, cyclopropyl H), 3.86 (3 H, s, CO_2Me), 7.27—7.50 (4 H, m, ArH), and 8.33 (1 H, s, ArCH=N); δ_C($CDCl_3$) 24.8 (t), 25.8 (t), 27.3 (t), 34.1 (t), 34.5 (s), 37.3 (d), 52.5 (q), 57.6 (s), 125.0 (s), 16.8 (d), 128.4 (d), 129.0 (d), 131.8 (d), 133.5 (s), 155.8 (d), and 171.3 (s).

The n.m.r. spectrum of the crude reaction mixture indicated that the yield of each component was (**8c**) 74%, (**15c**) 24%, and (**9c**) 2%.

Photolysis of the Azide (**2d**).—A solution of the azidocinnamate (**2d**) (200 mg) in light petroleum (200 ml) was irradiated for 0.5 h under a stream of nitrogen. Evaporation of the solvent and chromatography of the residue using radial t.l.c. (SiO_2:ether) gave (i) methyl 1,1a,2,6b-tetrahydro-2-cyclohex-1-enylindeno[1,2-b]azirine-1a-carboxylate (**8d**) (113 mg, 57%), pale yellow oil, spectral data already given; (ii) methyl 4-cyclohexylidenemethylindole-2-carboxylate (**9d**) (4 mg, 2%) colourless needles, m.p. 155—160 °C data previously given; and (iii) *methyl spiro*(*cyclohexane*-1,1′-3,4-*dihydro*-[1H]-*cycloprop*-[c]*isoquinoline*)-1a-*carboxylate* (**15d**) (26 mg, 13%) colourless oil (Found: M^+, 269.1410. $C_{17}H_{19}NO_2$ requires M^+, 269,1416); $\nu_{max.}$(neat) 1 722, 1 620, 1 443, 1 293, 1 230, and 754 cm^{-1}; δ_H($CDCl_3$) 0.75—1.90 (10 H, m, cyclohexyl H), 3.00 (1 H, s, cyclopropyl H), 3.86 (3 H, s, CO_2Me), 7.27—7.50 (4 H, m, ArH), and 8.31 (1 H, s, ArCH=N); δ_C($CDCl_3$) 23.1 (t), 24.5 (t), 25.4 (t), 26.2 (t), 26.2 (s), 30.9 (t), 34.9 (d), 52.6 (q), 58.0 (s), 125.5 (s), 126.8 (d), 238.5 (d), 128.7 (d), 131.7 (d), 132.5 (s), 156.3 (d), and 171.2

(s); *m/z* 269 (M^+, 5%), 236 (4), 210 (27), 188 (100), 156 (29), 141 (13), 129 (21), and 128 (22).

The n.m.r. spectrum of the crude reaction mixture indicated that the yield of each component was (**8d**) 83%, (**15d**) 15%, and (**9d**) 2%.

Photolysis of the Azide (**2e**).—A solution of the azidocinnamate (**2e**) (337 mg) in light petroleum (200 ml) was irradiated for 0.5 h under a stream of nitrogen. Evaporation of the solvent and chromatography of the residue using radial t.l.c. (SiO_2:light petroleum–ether) gave (i) methyl 1,1a,2,6b-tetrahydro-2-cyclohept-1-enylindeno[1,2-*b*]azirine-1a-carboxylate (**8e**) (269 mg, 88%), pale yellow oil, spectral data previously given; (iii) methyl 4-cycloheptylidenemethylindole-2-carboxylate (**9e**) (6 mg, 2%), colourless flakes, m.p. 150—153 °C, data previously given; (ii) *methyl spiro(cycloheptane*-1,1′,3,4-*dihydro*-[1H]-*cycloprop*[c]*isoquinoline*)-1a-*carboxylate* (**15e**) (15 mg, 5%), colourless oil (Found: C, 76.25; H, 7.7; N, 5.0. $C_{18}H_{21}NO_2$ requires C, 76.3; H, 7.5; N, 4.9%); $\nu_{max.}$(neat) 1 724, 1 620, 1 565, 1 296, 1 237, 1 126, and 757 cm^{-1}; $\delta_H(CDCl_3)$ 0.8—1.8 (10 H, m, cycloheptyl H), 1.9—2.0 (2 H, m, cycloheptyl H), 3.03 (1 H, s, cyclopropyl H), 3.86 (3 H, s, CO_2Me), 7.30—7.50 (4 H, m, ArH), and 8.34 (1 H, s, ArCH=N); $\delta_C(CDCl_3)$ 24.7 (t), 25.2 (t), 26.5 (t), 27.94 (t), 27.99 (t), 28.09 (t), 33.7 (s), 36.2 (d), 52.7 (q), 59.0 (s), 125.6 (s), 126.9 (d), 128.6 (d), 128.8 (d), 131.8 (d), 132.9 (s), 156.6 (d), and 171.6 (s).

The n.m.r. spectrum of the crude reaction mixture indicated that the yield of each component was (**8e**) 91%, (**15e**) 7, and (**9e**) 2%.

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