Formation of Indoles, Isoquinolines, and Other Fused Pyridines from Azidoacrylates

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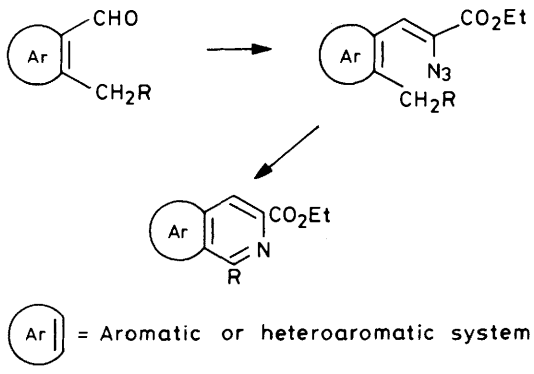
Mild thermal decomposition in boiling toluene or xylene of the azidocinnamates (**1**)—(**6**), readily prepared from the corresponding aldehyde and ethyl azidoacetate, gives indoles in good yield when there is an unsubstituted *ortho* position, and dihydroisoquinolines, and hence isoquinolines, when there is an *o*-methyl or methylene group. In the presence of iodine, which seems to favour a radical type process, the yield of isoquinoline is increased, and isoquinoline formation can compete with the indole-forming cyclisation to a free *ortho*-position. Iodine also catalyses primary enamine formation by a hydrogen abstraction process. The thiophene (**7**) and pyrazole (**8**) are formed and decomposed similarly to give the corresponding *c*-fused pyridines (**28**) and (**29**). The 2,6-dichloro compound (**9**) thermolyses to the stable 2*H*-azirine (**32**) which isomerises to the nitrile (**33**) on stronger heating. Yields in these azide decompositions are sometimes high, though they can be variable and the reactions, though easily carried out, can be complex.

The generation and subsequent intramolecular reactions of nitrenes can give rise to a range of heterocyclic products.[1] Whilst many of these reactions are only of mechanistic interest, some are synthetically useful. In this respect we have been interested in developing a simple, general procedure for pyrido-annelation under completely neutral conditions, and we now report our results in detail.[2,3]

The method, which involves formation of the 1–2 bond as the ring closure step, is based on readily available vinyl azides which decompose thermally to give, after oxidation of the intermediate dihydro species, fused pyridines (Scheme 1). Other groups have also reported the synthesis of fused pyridines from vinyl nitrene precursors.[4,5]

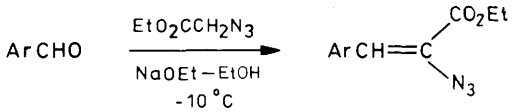


Scheme 1.

Results and Discussion

Synthesis of Vinyl Azides.—The vinyl azides (**1**)—(**9**) were readily prepared by the condensation of the aromatic or heteroaromatic aldehyde with ethyl azidoacetate in ethanolic sodium ethoxide.[6,7] Yields were not optimised, but in general it was found that better yields were obtained when an excess of ethyl azidoacetate (4 equiv.) was used, and the condensation was carried out between −10 and −15 °C (Table). The azides (**1**), (**5**), (**7**),[8] and (**9**),[6] have been prepared previously. The stereochemistry about the double bond is not known but is assumed to be *Z*, the more thermodynamically stable isomer. However, from the point of view of product formation, the geometry about the double bond does not matter, since vinyl azides decompose *via* 2*H*-azirines which are in thermal equilibrium with the corresponding vinyl nitrenes,[9,10] and hence stereochemistry is lost.

Table. Synthesis of vinyl azides from aromatic and heteroaromatic aldehydes



Azide	Ar	Yield (%)
(**1**)	2,4,6-$Me_3C_6H_2$	77
(**2**)	2-$PhCH_2C_6H_4$	56—64
(**3**)	2-$PhCH_2OC_6H_4$	34
(**4**)	Fluoren-1-yl	80
(**5**)	2-MeC_6H_4	54—74
(**6**)	2-$Pr^iC_6H_4$	63
(**7**)	3-Methyl-2-thienyl	52
(**8**)	1,3,5-Trimethylpyrazol-4-yl	69
(**9**)	2,6-$Cl_2C_6H_3$	39

Various other bases were examined for the condensation reaction, but were all unsatisfactory. Thus the use of sodium carbonate, potassium hydroxide, and sodium hydroxide in a two-phase system in the presence of triethylbenzylammonium chloride, 1,8-diazabicyclo[5.4.0]undec-7-ene, and piperidinium acetate [8] failed to give any of the required vinyl azide. A titanium tetrachloride-mediated condensation reaction [11] was also unsuccessful. Attempts were made to replace the ester with other electron-withdrawing groups. However, both azidoacetonitrile and azidonitromethane failed to give any condensation products.

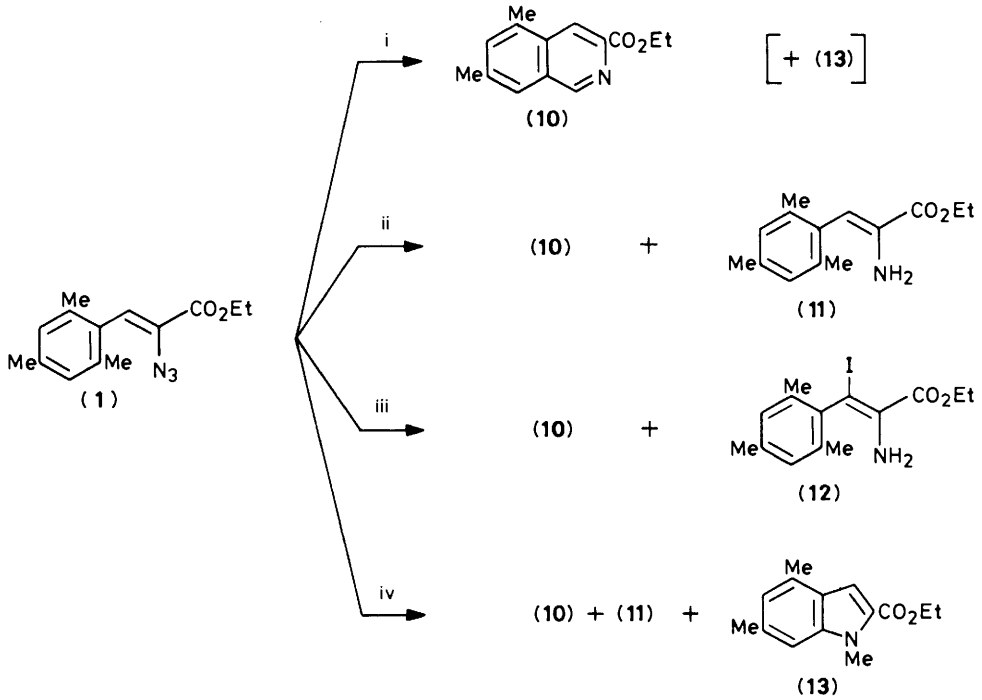
Thermal Decomposition of Vinyl Azides.—The azide (**1**) was decomposed in boiling toluene, with the reflux condenser open to the atmosphere to give, after chromatography, ethyl 5,7-dimethylisoquinoline-3-carboxylate (**10**) (32%), together with some mesitaldehyde (5%) (but see below). The formation of the isoquinoline is rationalised by loss of nitrogen from the azide to give the corresponding azirine, in equilibrium with the vinyl nitrene. Formal insertion of the nitrene into the *ortho*-methyl group then leads to the 1,2-dihydroisoquinoline which is aromatised, presumably by aerial oxidation.

In efforts to improve the yield of the isoquinoline (**10**), the thermolysis was repeated in the presence of oxidants. Thus thermolysis in the presence of iodine (0.05 mol equiv.) gave a similar yield (31%) of (**10**), but also gave the enamine (**11**) (17%). Thermolysis in the presence of larger amounts (2 mol equiv.) of iodine and potassium acetate (as HI scavenger) gave a reduced yield of (**10**) (14%), the major product being the iodinated enamine (**12**) (29%). This is in contrast to our earlier report in which the yield of isoquinoline (**10**) was claimed to be much increased in the presence of 2 mol equiv. of iodine.[2] Unfortunately, we have been unable to reproduce this result. Thermolysis in the presence of chloranil (1 equiv.) gave the isoquinoline (**10**) (27%), the enamine (**11**) (24%), and a third product, assigned as the *N*-methylindole (**13**) (15%) (Scheme 2). The structure of (**13**) was confirmed by an independent synthesis from 2,4-dimethylbenzaldehyde *via* ethyl 2-azido-3-(2,4-dimethylphenyl)propenoate (see Experimental section). With authentic indole (**13**) in hand, a careful re-examination of the thermolysis of the azide (**1**) in toluene, revealed that the indole (**13**) is also formed (15%) in the absence of chloranil.

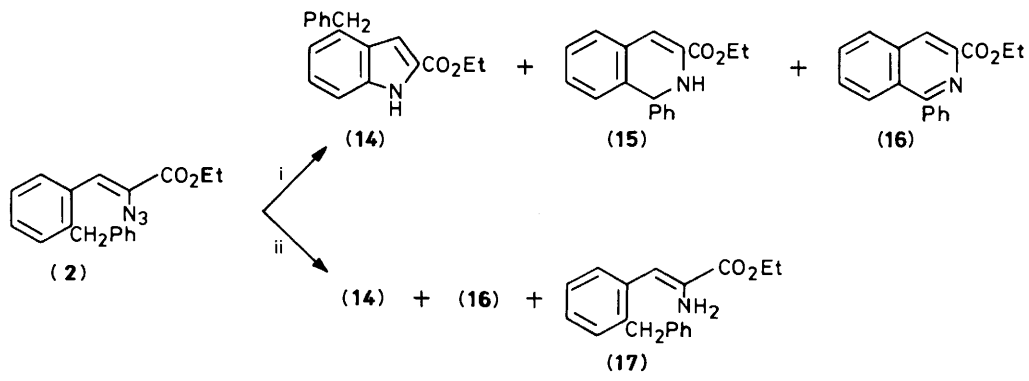
The isolation of the indole (**13**) is interesting since it is presumably formed by closure of the nitrene to the blocked *ortho*-position, followed by a shift of the methyl group to nitrogen. This process, although always formally possible, has not been observed in these types of system previously.

In the case of azide (**1**), and in other examples of fused pyridine formation,[4] formal insertion into an alkyl group only occurs when cyclisation directly onto the aromatic ring is blocked or disfavoured, formation of products such as the indole (**13**) being very unusual. In the case of azides prepared from benzaldehydes, 4-substituted indoles are usually formed if one *ortho*-position is free.[1,2] This is a serious limitation from the point of view of isoquinoline synthesis, since starting from symmetrical 2,6-disubstituted benzaldehydes necessarily gives isoquinolines with a 5-substituent. Therefore an investigation of vinyl azides containing only one *ortho*-substituent was undertaken to see which, if any, substituents would lead to isoquinoline formation.

Decomposition of the azide (**2**) in boiling toluene under nitrogen gave three products: the 4-benzylindole (**14**) (42%), the 1,2-dihydroisoquinoline (**15**) (26%), and the isoquinoline (**16**) in trace amounts (*ca.* 2%) (Scheme 3).



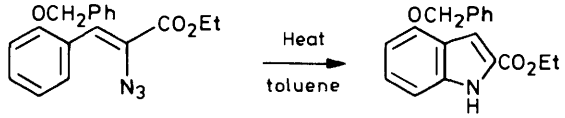
Scheme 2. i, Heat, toluene; ii, heat, toluene, I_2; iii, heat, toluene, KOAc, I_2; iv, heat, toluene, chloranil



Scheme 3. i, Heat, toluene; ii, heat, toluene, I_2

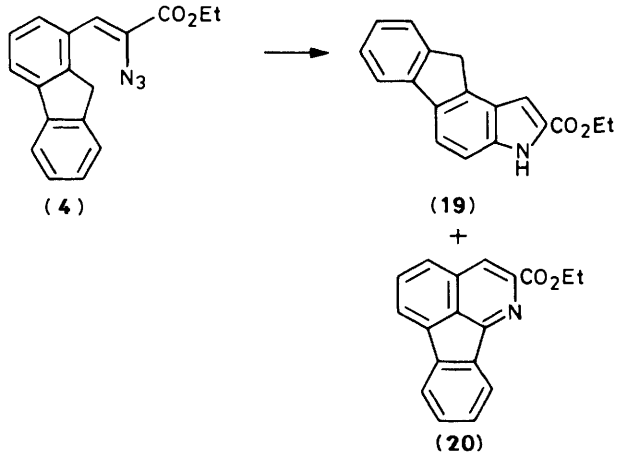
When the decomposition of the azide (**2**) was carried out in the presence of iodine (0.1 mol equiv.), the ratio of products was markedly changed. The isoquinoline (**16**) was the major product (40%) with the yield of indole (**14**) much reduced. No 1,2-dihydroisoquinoline (**15**) was formed, although the enamine (**17**) was isolated, and characterised as its *N*-acetyl derivative, readily prepared by treatment with acetic anhydride in pyridine.[13] It seemed likely that the enamine (**17**) was being formed from an intermediate nitrene by hydrogen abstraction from the 1,2-dihydroisoquinoline. Therefore, despite the disappointing results obtained in the decomposition of (**1**), an attempt was made to suppress enamine formation and to increase the yield of isoquinoline (**16**) by performing the decomposition in the presence of more iodine (1 mol equiv.) as oxidant, and potassium acetate. Enamine formation was totally suppressed under these conditions, though the yield of (**16**) was increased only to 52%, indole (**14**) being the other isolated product. The dihydroisoquinoline (**15**) was recovered unchanged after being heated in toluene (2 h), but was rapidly dehydrogenated by iodine at room temperature.

In contrast to the *ortho*-benzyl azide (**2**), where some 'insertion' into the benzyl group does occur, the benzoyloxy substituted azide (**3**) gave only the corresponding indole (**18**) (88%) when heated. No products resulting from insertion into the benzylic CH_2 were isolated.



(**3**) (**18**)

The vinyl azide (**4**) behaved similarly to (**2**) on thermolysis. Refluxing the azide (**4**) in xylene (1 h) gave the indole (**19**) (90%) and the azafluoranthene (**20**) (4%) (Scheme 4). When the azide



(**4**) (**19**) + (**20**)

Scheme 4.

was thermolysed in the presence of iodine (0.1 mol equiv.) the yield of (**20**) was increased to 10%. Increasing the amount of iodine to 1.0 mol equiv. raised the yield of (**20**) to 24%, but the reaction was much less clean. Although, at this stage, the yields of (**20**) are not synthetically useful, the decomposition of vinyl azides derived from fluorene-1-carbaldehydes represents a novel route to azafluoranthenes, a ring system found in alkaloids such as rufescine and imeluteine.[14]

Iodine had a similar effect on the decomposition of the azide (**5**) with only an *ortho*-methyl group. Whereas thermolysis in boiling toluene gave exclusively ethyl 4-methylindole-2-carboxylate (**21**) (>95%) as previously reported,[12] thermolysis in the presence of iodine (0.1 mol equiv.) reduced the yield of (**21**) to 28% and gave ethyl isoquinoline-3-carboxylate (**22**) (20%) and the enamine (**23**) (13%) (Scheme 5). Increasing the amount of iodine to 1.0 mol equiv. suppressed enamine formation, and increased the yield of the isoquinoline to 32%. Although the yield of ethyl isoquinoline-3-carboxylate is low, the effect of iodine is well illustrated by this example. In the absence of iodine only the indole (**21**) is formed.

Thermolysis of the *o*-isopropyl azide (**6**) followed a similar pattern in that heating in xylene gave the indole (**24**) (65%) as the major product, together with the dihydroisoquinoline (**25**) (3%) and the enamine (**26**) (16%). The yield of the enamine (**26**) was low, owing to decomposition on chromatography. In the presence of iodine (0.1 mol equiv.) the yield of indole (**24**) was reduced to 30%, the yield of enamine (**26**) reduced to trace amounts (<5%), the yield of isoquinoline (**25**) increased to 14%, and a new compound was formed (Scheme 6). This was identified as the naphthalene (**27**) (17%), possibly formed by electrocyclic ring closure of the enamine (**26**), followed by loss of ammonia.

Therefore although isoquinolines can be obtained from the mono-*ortho*-substituted azides (**2**), (**4**), (**5**), and (**6**), the yields can be disappointing and the reactions complex. However, iodine has a marked and unexpected effect on the amount of isoquinoline formed from these azides, and therefore a series of experiments was undertaken to try to elucidate the mechanism of the reactions involving iodine.

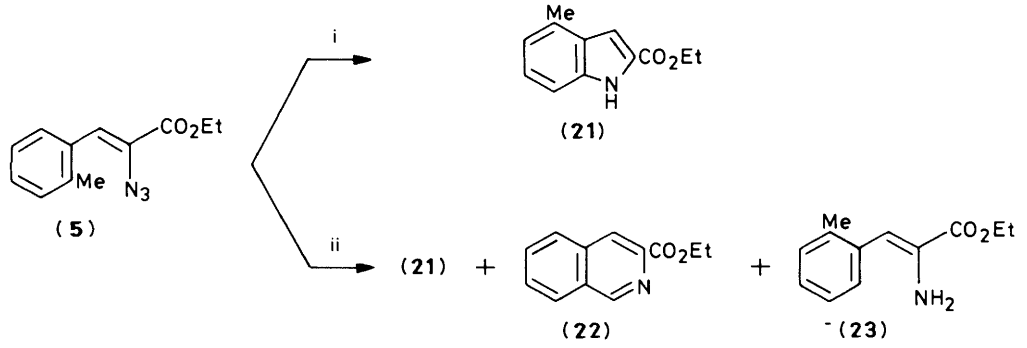
It seems likely that in the absence of iodine, the azides decompose to give singlet vinyl nitrenes *via* 2*H*-azirines, and that these nitrenes are responsible for the formation of indoles by electrocyclic ring closure, and of 1,2-dihydroisoquinolines by the mechanism recently proposed by Taniguchi and co-workers.[4a] This mechanism also accounts for the formation of enamine (**26**) from azide (**6**).

In the presence of iodine (0.1 mol equiv.), typical triplet nitrene or radical processes supervene; *i.e.* hydrogen abstraction to give enamines (**11**), (**17**), and (**23**). Indeed in the presence of iodine (0.1 mol equiv.) and the good hydrogen donor hydroquinone (1.0 mol equiv.), the azide (**5**) decomposed to give an increased amount of the enamine (**23**) (39%), together with the indole (**21**) (58%) and only a trace of the isoquinoline (**22**). There is no hydrogen abstraction from hydroquinone in the absence of iodine.

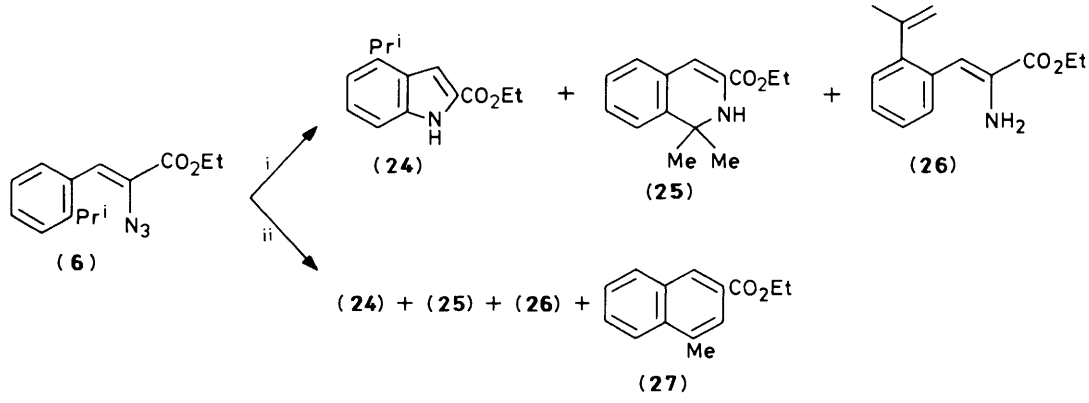
Hydrogen iodide and potassium iodide had little or no effect on the decomposition of the azide (**5**), the only product being the indole (**21**). Similarly, the indole (**21**) was the sole product when the decomposition was carried out in 1-iodopropane (b.p. 102 °C) or bromobenzene (b.p. 156 °C), indicating that iodine was not simply acting as a heavy atom, facilitating singlet to triplet intersystem crossing of the nitrene. The presence of free radical initiators such as di-t-butyl peroxide and dibenzoyl peroxide in the thermolysis had no effect as did diphenyl disulphide and diphenyl diselenide.

Thus it appears that the effect of iodine is unique and cannot be mimicked by radical initiators, heavy atom solvents, or iodine containing organic or inorganic compounds. No definite conclusions can be reached about the mechanism of the iodine effect, and triplet nitrenes or aminyl radicals, possibly formed *via* *N*-iodo compounds, remain the most likely intermediates.

In order to explore the synthesis of other fused pyridines, the decomposition of the azides (**7**) and (**8**) was investigated. Thermolysis of (**7**) in boiling xylene gave the known[5] ethyl thieno[3,2-*c*]pyridine-6-carboxylate (**28**) (27%) as the only identifiable product. When the reaction was repeated in the presence of iodine (1 mol equiv.), analysis of the thermolysis mixture by ^{1}H n.m.r. spectroscopy showed that no (**28**) was

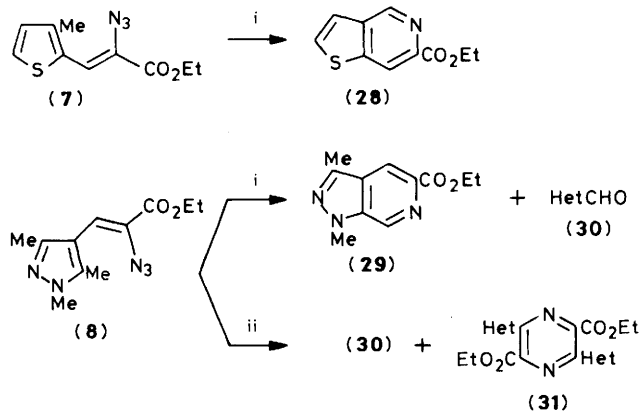


Scheme 5. i, Heat, toluene; ii, heat, toluene, I_2



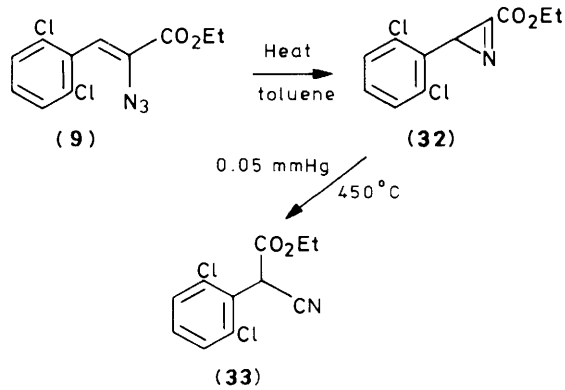
Scheme 6. i, Heat, xylene; ii, heat, xylene, I_2

present. It is interesting to note that previous attempts to thermolyse the azide (**7**) resulted only in the formation of intractable tars.[8] Decomposition of the azide (**8**) in boiling xylene gave the fused pyridine (**29**) (22%) together with a significant amount of 1,3,5-trimethylpyrazole-4-carbaldehyde (**38**) (16%). Thermolysis in xylene in the presence of iodine gave (**29**) (16%) and the aldehyde (**30**) (22%). However, thermolysis in toluene in the presence of iodine gave the aldehyde (**30**) (17%) and a new product, tentatively assigned as the pyrazine (**31**) (11%), formally a dimer of the intermediate nitrene/azirine. Unfortunately, the yields of the required fused pyridines (**28**) and (**29**) that are reproducibly attainable are somewhat lower than reported earlier.[2]



Het = 1,3,5-trimethylpyrazol-4-yl. i, Heat, xylene; ii, heat, toluene, I_2

When both *ortho*-positions of the azide are blocked with chlorine substituents, then the intermediate 2*H*-azirine can be isolated from the pyrolysis of the azide. Thus heating the azide (**9**) in boiling toluene for 2.5 h gave the azirine (**32**) (97%). On stronger heating under flash vacuum pyrolysis conditions at 450 °C/0.05 mmHg, the azirine (**32**) isomerised to the nitrile (**33**) (55%), m.p. 68 °C,* probably by a mechanism similar to that proposed for the rearrangement of analogous azido ketones.[15]



Conclusions. The ready synthesis and decomposition of vinyl azides provides a route to fused pyridines from *ortho*-alkylated aromatic and heteroaromatic aldehydes. Although the yields are only moderate in most cases, the procedure is extremely

* We regret that the nitrile (**33**) was initially reported[2] to have m.p. 245—247 °C; this is the melting point of a very minor product of unknown structure.

simple and easy to carry out, and the addition of iodine has an unexpected beneficial effect in some cases. The heterocyclic ring is formed under relatively mild, neutral conditions, and further applications of vinyl azides derived from aromatic aldehydes to the synthesis of heterocyclic compounds are under investigation.

Experimental

I.r. spectra were recorded in the range 600—4 000 cm $^{-1}$ using Perkin-Elmer 257, or 298 spectrophotometers and were calibrated against polystyrene. U.v. spectra were recorded using a Pye Unicam SP800 spectrophotometer and were calibrated against holmium glass. ^{1}H N.m.r. spectra were obtained at 60, 90, and 250 MHz using Varian EM360, Perkin-Elmer R32, and Bruker WM250 instruments respectively using tetramethylsilane as internal reference. ^{13}C N.m.r. spectra were recorded at 62.9 MHz on the Bruker instrument, and were broad band decoupled. Mass spectra were recorded on a VG Micromass 7070B instrument at 70 eV using a direct insertion probe. Column chromatography was carried out on silica H, type 60, or silica gel (0.063—0.2 mm) (Merck). Solvents were dried by standard procedures, light petroleum refers to the fraction of b.p. 40—60 °C, and ether refers to diethyl ether.

Preparation of Azides.—General procedure. Sodium (1.84 g, 0.08 g atom) was dissolved in ethanol (55 ml), and the solution was cooled to −22 °C. A mixture of the aldehyde (0.02 mol) and ethyl azidoacetate (10.32 g, 0.08 mol) was added dropwise with stirring at a rate which maintained the temperature below −10 °C. (If the aldehyde was insoluble in ethyl azidoacetate, sufficient ethanol or tetrahydrofuran was added to achieve complete dissolution). The reaction mixture was stirred at *ca.* −10 °C until t.l.c. indicated that all the aldehyde had been consumed (1—5 h), and then allowed to warm to room temperature. The mixture was poured into ice–water and extracted with ether (3 × 100 ml). The combined ether extracts were washed with water, dried, and evaporated to give the crude azide, which was purified by chromatography, and recrystallisation if solid. The following azides were prepared.

Ethyl 2-azido-3-(2,4,6-trimethylphenyl)propenoate (**1**), 77% from mesitaldehyde, oil (lit.,[6] m.p. 9—11 °C).

Ethyl 2-azido-3-(2-benzylphenyl)propenoate (**2**), 56—64% from 2-benzylbenzaldehyde,[16] m.p. 61—62 °C (Found: C, 70.4; H, 5.6; N, 13.7. $C_{18}H_{17}N_3O_2$ requires C, 70.3; H, 5.6; N, 13.7%); $\nu_{max.}$(Nujol) 2 130 and 1 725 cm^{-1}; $\lambda_{max.}$(EtOH) 225 and 306 nm; δ (90 MHz; $CDCl_3$) 1.33 (3 H, t), 4.03 (2 H, br s), 4.30 (2 H, q), 7.0—7.4 (9 H, m), and 7.9—8.05 (1 H, m); *m/z* 307 (M^+), 279 (base), 233, 202, and 179.

Ethyl 2-azido-3-(2-benzyloxyphenyl)propenoate (**3**), 34% from 2-benzyloxybenzaldehyde, m.p. 97.5—98.5 °C (from ether–light petroleum); $\nu_{max.}$(Nujol) 2 120 and 1 697 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.30 (3 H, t), 4.29 (2 H, q), 5.05 (2 H, s), 6.8—7.5 (8 H, m), 7.56 (1 H, s), and 8.15—8.32 (1 H, m); *m/z* 295 (M^+ − 28).

Ethyl 2-azido-3-fluoren-1-ylpropenoate (**4**), 80% from fluorene-1-carbaldehyde,[17] m.p. 110—112 °C (from dichloromethane–light petroleum) (Found: C, 71.0; H, 5.0; N, 13.4. $C_{18}H_{15}N_3O_2$ requires C, 70.8; H, 4.95; N, 13.8%); $\nu_{max.}$(Nujol) 2 110 and 1 703 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.35 (3 H, t), 3.68 (2 H, br s), 4.35 (2 H, q), 6.95 (1 H, s), 7.15—7.80 (6 H, m), and 8.05 (1 H, m); *m/z* 305 (M^+), 277, 203, 194, and 165 (base).

Ethyl 2-azido-3-(2-methylphenyl)propenoate (**5**), 54—74% from 2-tolualdehyde, m.p. 53—54 °C (lit.,[6] 55—56 °C).

Ethyl 2-azido-3-(2-isopropylphenyl)propenoate (**6**), 63% from 2-isopropylbenzaldehyde (prepared from commercially available 2-isopropylaniline by a standard procedure[18]), oil (Found: C, 65.3 H, 6.8; N, 16.2. $C_{14}H_{17}N_3O_2$ requires C, 64.85; H, 6.6; N, 16.2%); $\nu_{max.}$(film) 2 130 and 1 715 cm^{-1}; δ (90 MHz; CCl_4) 1.25 (6 H, d, *J* 7 Hz), 1.48 (3 H, t), 3.19 (1 H, heptet, *J* 7 Hz), 4.37 (2 H, q), 7.05—7.35 (3 H, m), and 7.8 (2 H, m); *m/z* 259 (M^+), 231, 216, 189, 172, 158, and 144 (base).

Ethyl 2-azido-3-(3-methyl-2-thienyl)propenoate (**7**), 52% from 3-methylthiophene-2-carbaldehyde, m.p. 64 °C (lit.,[8] 68 °C).

Ethyl 2-azido-3-(1,3,5-trimethylpyrazol-4-yl)propenoate (**8**), 69% from 1,3,5-trimethylpyrazole-4-carbaldehyde,[19] oil, $\nu_{max.}$ (thin film) 2 120 and 1 710 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.38 (3 H, t), 2.25 (3 H, s), 2.28 (3 H, s), 3.71 (3 H, s), 4.35 (2 H, q), and 6.79 (1 H, s); *m/z* 249 (M^+), 221, 148 (base), and 137.

Ethyl 2-azido-3-(2,6-dichlorophenyl)propenoate (**9**), 39% from 2,6-dichlorobenzaldehyde, oil (lit.,[6] yield 27%).

Thermolysis of Ethyl 2-Azido-3-(2,4,6-trimethylphenyl)-propenoate (**1**).—(a) *In toluene.* A solution of the azide (**1**) (790 mg) in toluene (30 ml) was refluxed for 3 h. The solvent was evaporated, and the residue chromatographed to give mesitaldehyde (5%), and *ethyl 5,7-dimethylisoquinoline-3-carboxylate* (**10**) (226 mg, 32%), m.p. 89—90 °C (from light petroleum) (Found: C, 73.2; H, 6.6; N, 6.1. $C_{14}H_{15}NO_2$ requires C, 73.3; H, 6.6; N, 6.1%); $\nu_{max.}$(KBr) 1 710 and 1 620 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.52 (3 H, t), 2.56 (3 H, s), 2.74 (3 H, s), 4.57 (2 H, q), 7.47 (1 H, m), 7.68 (1 H, m), 8.70 (1 H, m), and 9.24 (1 H, m).

(b) *In toluene with iodine* (0.05 mol equiv.). A solution of the azide (**1**) (832 mg, 3.21 mmol) and iodine (38 mg, 0.15 mmol) in toluene (30 ml) was heated under reflux for 1.5 h. The solvent was evaporated, and the residue chromatographed to give (i) *ethyl 2-amino-3-(2,4,6-trimethylphenyl)propenoate* (**11**) (123 mg, 17%) as a colourless oil, b.p. 95—105 °C/0.35 mmHg (Kugelrohr) (Found: C, 72.3; H, 8.4. $C_{14}H_{19}NO_2$ requires C, 72.1; H, 8.2%); $\nu_{max.}$(neat) 3 480, 3 380, and 1 710 cm^{-1}; δ (60 MHz; $CDCl_3$) 1.36 (3 H, t), 2.20 (6 H, s), 2.25 (3 H, s), 3.50 (2 H, br), 4.26 (2 H, q), 6.35 (1 H, m), and 6.83 (2 H, m); *N*-acetyl derivative, m.p. 153—154 °C (from ether); and (ii) ethyl 5,7-dimethylisoquinoline-3-carboxylate (**10**) (231 mg, 31%).

(c) *In toluene with iodine* (2 mol equiv.) *and potassium acetate* (2 mol equiv.). A mixture of the azide (**1**) (274 mg, 1.06 mmol), iodine (545 mg, 2.15 mmol), and potassium acetate (210 mg, 2.15 mmol) was heated under reflux in toluene (25 ml) for 3 h. The solvent was evaporated, the residue dissolved in dichloromethane and the solution washed with brine, dried over $MgSO_4$ and evaporated to an oil. Chromatography gave (i) *ethyl 2-amino-3-iodo-3-(2,4,6-trimethylphenyl)propenoate* (**12**) (110 mg, 29%), m.p. 67 °C (from light petroleum) (Found: C, 47.0; H, 5.0; N, 3.9. $C_{14}H_{18}INO_2$ requires C, 46.8; H, 5.05; N, 3.9%); $\nu_{max.}$(KBr) 3 450, 3 360, and 1 715 cm^{-1}; δ (90 MHz; $CDCl_3$) 0.78 (3 H, t), 2.12 (6 H, s), 2.25 (3 H, s), 3.88 (2 H, q), 4.31 (2 H, br), and 6.76 (2 H, m); *m/z* 359 (M^+), 232, 158 (base), 144, 131, and 127; and (ii) ethyl 5,7-dimethylisoquinoline-3-carboxylate (**10**) (35 mg, 14%).

(d) *In toluene with chloranil.* The azide (**1**) (274 mg, 1.06 mmol) and chloranil (300 mg, 1.22 mmol) in toluene (25 ml) were heated under reflux for 1.5 h. The solvent was evaporated, and the residue triturated with dichloromethane. Chloranil (183 mg) was filtered off, and the filtrate was concentrated and chromatographed to give (i) *ethyl 1,4,6-trimethylindole-2-carboxylate* (**13**) (38 mg, 15%), identical (t.l.c. and n.m.r.) with an independently prepared specimen (see below); (ii) ethyl 2-amino-3-(2,4,6-trimethylphenyl)propenoate (**11**) (60 mg, 24%); and (iii) ethyl 5,7-dimethylisoquinoline-3-carboxylate (**10**) (64 mg, 27%).

(e) *In toluene.* The azide (**1**) (200 mg) was heated under reflux in toluene for 3 h. After evaporation of the solvent, the residue was chromatographed to give the indole (**13**) (27 mg, 15%), identical with the authentic specimen, and the isoquinoline (**10**) (*ca.* 50 mg, 28%).

Independent Synthesis of Ethyl 1,4,6-*Trimethylindole*-2-*carboxylate* (**13**).—2,4-Dimethylbenzaldehyde (2.68 g, 20 mmol) was condensed with ethyl azidoacetate in ethanolic sodium ethoxide under the conditions described previously. Work-up and chromatography gave *ethyl* 2-*azido*-3-(2,4-*dimethylphenyl*)*propenoate* (2.96 g, 60%), m.p. 71—72 °C (from ether) (*Found*: C, 63.8; H, 6.1; N, 16.9. $C_{13}H_{15}N_3O_2$ requires C, 63.7; H, 6.2; N, 17.1%); $\nu_{max.}$(KBr) 2 130 and 1 705 cm^{-1}; δ (60 MHz; $CDCl_3$) 1.39 (3 H, t), 2.32 (6 H, s), 4.34 (2 H, q), and 6.9—7.15 and 7.8—8.0 (4 H, m). A solution of the above azide (484 mg) in xylene (50 ml) was heated under reflux for 0.3 h. The solvent was evaporated to give *ethyl* 4,6-*dimethylindole*-2-*carboxylate* (350 mg, 82%) as colourless crystals, m.p. 118—119 °C (from light petroleum) (Found: C, 71.8; H, 6.9; N, 6.45. $C_{13}H_{15}NO_2$ requires C, 71.9; H, 7.0; N, 6.45%).

Ethyl 2,4-dimethylindole-2-carboxylate (obtained from pyrolysis of the azide) (300 mg) was dissolved in *N,N*-dimethylformamide (DMF) (2 ml), and added to a stirred slurry of sodium hydride (37.5 g, 1.56 mmol) in DMF (2 ml). Iodomethane (182 mg, 1.28 mol) was then added, and the solution stirred at room temperature overnight. Work-up gave a yellow oil which crystallised from light petroleum to give *ethyl* 1,4,6-*trimethylindole*-2-*carboxylate* (**13**) (217 mg, 77% from the azide), m.p. 58—59 °C (Found: C, 72.6; H, 7.4; N, 6.0. $C_{14}H_{17}NO_2$ requires C, 72.7; H, 7.4; N, 6.05%); $\nu_{max.}$(KBr) 1 705 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.41 (3 H, t), 2.46 (3 H, s), 2.51 (3 H, s), 4.02 (3 H, s), 4.36 (2 H, q), 6.78 (1 H, m), 6.98 (1 H, m), and 7.27 (1 H, d); *m/z* 231 (M^+, base), 217, 203, 186, 158, and 117.

Thermolysis of Ethyl 2-*Azido*-3-(2-*benzylphenyl*)*propenoate* (**2**).—(a) *In toluene*. A solution of the azide (**2**) (92 mg) in toluene (25 ml) was refluxed for 2.75 h. Evaporation of the solvent and chromatography of the residue gave (i) *ethyl* 4-*benzylindole*-2-*carboxylate* (**14**) (35 mg, 42%), m.p. 164—165 °C (from chloroform–light petroleum) (Found: C, 77.5; H, 6.15; N, 5.0. $C_{18}H_{17}NO_2$ requires C, 77.4; H, 6.1; N, 5.0%); $\nu_{max.}$(Nujol) 3 315 and 1 682 cm^{-1}; $\lambda_{max.}$(EtOH) 207, 232, and 296 nm; δ (90 MHz; $CDCl_3$) 1.39 (3 H, t), 4.29 (2 H, s), 4.44 (2 H, q), 6.95 (1 H, m), 7.14—7.60 (8 H, m), and 9.28 (1 H, br); *m/z* 279 (M^+ base), 233, 204, and 178; (ii) ethyl 1,2-dihydro-1-phenylisoquinoline-3-carboxylate (**15**) (22 mg, 26%), m.p. 69—74 °C (from light petroleum); $\nu_{max.}$(Nujol) 3 390 and 1 677 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.35 (3 H, t), 4.30 (2 H, q), 4.73—4.92 (1 H, br s), 5.66 (1 H, s), 6.47 (1 H, s), 6.72—6.78 (1 H, m), 7.05—7.30 (3 H, m), and 7.27—7.42 (5 H, m); *m/z* 279 (M^+), 202 (base), 156, and 128; and (iii) *ethyl* 1-*phenylisoquinoline*-3-*carboxylate* (**16**) (*ca.* 2 mg, *ca.* 2%), data given later.

(b) *In toluene with iodine* (0.1 mol equiv.). A solution of the azide (**2**) (121 mg, 0.39 mmol) and iodine (11 mg, 0.04 mmol) in toluene (40 ml) was refluxed under nitrogen for 2.5 h. The solvent was evaporated, and the residue chromatographed to give (i) the indole (**14**) (14 mg, 13%); (ii) *ethyl* 1-*phenylisoquinoline*-3-*carboxylate* (**16**) (45.5 mg, 42%), m.p. 100—101 °C (Found: C, 77.7; H, 5.6; N, 4.9. $C_{18}H_{15}NO_2$ requires C, 78.0; H, 5.45; N, 5.05%); $\nu_{max.}$(Nujol) 1 740 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.47 (3 H, t), 4.52 (2 H, q), 7.45—8.30 (9 H, m), and 8.59 (1 H, s); *m/z* 277 (M^+), 233, 205 (base), 176, and 102; and (iii) ethyl 2-amino-3-(2-benzylphenyl)propenoate (**17**) (23 mg, 20%), oil, $\nu_{max.}$(film) 3 485, 3 390, 1 710, and 1 633 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.33 (3 H, t), 3.96 (4 H, br), 4.25 (2 H, q), 6.37 (1 H, s), 6.97—7.30 (8 H, m), and 7.48 (1 H, m); *m/z* 279 (M^+); N-*acetyl derivative*, m.p. 143—145 °C (from dichloromethane–light petroleum) (Found: C, 73.9; H, 6.5; N, 4.3. $C_{20}H_{21}NO_3$ requires C, 74.3; H, 6.55; N, 4.3%).

(c) *In toluene with iodine* (1.0 mol equiv.) *and potassium acetate*. Potassium acetate (38 mg, 0.30 mol) was added to a solution of the azide (**2**) (119 mg, 0.39 mmol) and iodine (98.5 mg, 0.39 mmol) in toluene (20 ml), and the mixture was heated under reflux under nitrogen for 2.75 h. The cooled reaction mixture was diluted with ether and washed with saturated aqueous sodium thiosulphate (20 ml) and aqueous sodium chloride (10 ml), dried, and evaporated. Chromatography of the residue gave the indole (**14**) (8 mg, 7%) and the isoquinoline (**16**) (56 mg, 52%).

Thermolysis of Ethyl 2-*Azido*-3-(2-*benzyloxyphenyl*)-*propenoate* (**3**).—A solution of the azide (**3**) (141.7 mg) in toluene (20 ml) was refluxed for 3.75 h. Evaporation of the solvent gave a solid which was recrystallised from dichloromethane and light petroleum to give *ethyl* 4-*benzyloxyindole*-2-*carboxylate* (**18**)[20] (77 mg, 60%). A further quantity was obtained from the filtrate, and the combined yield of (**18**) was 113 mg (88%), m.p. 169—171 °C (Found: C, 73.0; H, 5.8; N, 4.75. $C_{18}H_{17}NO_3$ requires C, 73.2; H, 5.8; N, 4.75%); $\nu_{max.}$(Nujol) 3 325 and 1 685 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.37 (3 H, t), 4.41 (2 H, q), 5.21 (2 H, s), 6.45—6.70 (1 H, m), 6.9—7.6 (8 H, m), and 9.25 (1 H, br); *m/z* 295 (M^+), 222, 204, 99, 85, and 83 (base).

Thermolysis of Ethyl 2-*Azido*-3-*fluoren*-1-*ylpropenoate* (**4**).—(a) *In toluene*. A solution of the azide (**4**) (151 mg) in toluene (30 ml) was refluxed under nitrogen for 24 h. The solvent was evaporated and the residue chromatographed to give *ethyl indeno*[2,1-e]*indole*-2-*carboxylate* (**19**) (125 mg, 90%), m.p. 210—211.5 °C (Found: C, 78.1; H, 5.4; N, 5.1. $C_{18}H_{15}NO_2$ requires C, 77.95; H, 5.45; N, 5.05%); $\nu_{max.}$(Nujol) 3 330, 1 724, and 1 635 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.40 (3 H, t), 4.03 (2 H, br s), 4.46 (2 H, q), 7.1—7.9 (7 H, m), and 9.1 (1 H, br); *m/z* 277 (M^+), 204, 194, and 165 (base); and *ethyl* 1-*azafluoranthene*-2-*carboxylate* (**20**) (5 mg, 4%), data given later.

(b) *In xylene with iodine* (0.1 mol equiv.). A solution of the azide (**4**) (100 mg, 0.33 mmol) and iodine (8.7 mg, 0.034 mmol) in xylene (20 ml) was refluxed under nitrogen for 1 h. Evaporation of the solvent and chromatography of the residue gave the indole (**19**) (45 mg, 49%), and the azafluoranthene (**20**) (10 mg, 10%).

(c) *In xylene with iodine* (1.0 mol equiv.). A solution of the azide (**4**) (141 mg, 0.46 mmol) and iodine (117 mg, 0.46 mmol) in xylene (30 ml) was refluxed for 0.5 h. The solution was cooled, washed with aqueous sodium thiosulphate (10%; 2 × 15 ml) and water (10 ml), dried, and evaporated. Chromatography gave the indole (**19**) (6 mg, 5%) and *ethyl* 1-*azafluoranthene*-2-*carboxylate* (**20**) (30 mg, 24%), m.p. 124.5—126.5 °C (Found: M^+ 275.0942. $C_{18}H_{13}NO_2$ requires M^+ 275.0946); $\nu_{max.}$(Nujol) 1 744 and 1 635 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.53 (3 H, t), 4.56 (2 H, q), 7.35—7.95 (6 H, m), 8.25 (1 H, m), and 8.52 (1 H, s); *m/z* 275 (M^+) and 203 (base).

When this experiment was repeated in refluxing toluene in the presence of iodine (1 mol equiv.), the yield of (**20**) was 18%.

Thermolysis of Ethyl 2-*Azido*-3-(2-*methylphenyl*)*propenoate* (**5**). (a) *In toluene*. A solution of the azide (**5**) in toluene was refluxed for 2.75 h. The solvent was evaporated to give a solid which was shown to be ethyl 4-methylindole-2-carboxylate (**21**) m.p. 139—140 °C (lit.,[12] 140.5 °C).

(b) *In toluene with iodine* (0.1 mol equiv.). A solution of the azide (**5**) (241 mg, 1.04 mmol) and iodine (25 mg, 0.10 mmol) in toluene (40 ml) was refluxed for 3 h. Evaporation of the solvent and chromatography of the residue gave ethyl 4-methylindole-2-carboxylate (**21**) (59 mg, 28%), ethyl isoquinoline-3-carboxylate (**22**) (42 mg, 20%), picrate m.p. 156—158 °C (lit.,[21] 154—155 °C), and ethyl 2-amino-3-(2-methylphenyl)propenoate (**23**) (28 mg, 13%), n.m.r. data given later.

(c) *In toluene with iodine* (1.0 mol equiv.) *and potassium acetate*. A mixture of potassium acetate (62 mg, 0.66 mmol), iodine (169 mg, 0.66 mmol), and the azide (**5**) (154 mg, 0.66

mmol) was heated under reflux in toluene (33 ml) for 2.75 h. The cooled mixture was diluted with ether (10 ml), and washed with aqueous sodium thiosulphate (10%; 2 × 10 ml) and water (10 ml), dried, and evaporated. Chromatography of the residue gave ethyl isoquinoline-3-carboxylate (**22**) (42.4 mg, 32%).

(d) *In toluene with iodine* (0.1 mol equiv.) *and hydroquinone*. A solution of the azide (**5**) (87.4 mg, 0.378 mmol), hydroquinone (41.6 mg, 0.378 mmol), and iodine (9.6 mg, 0.038 mmol) in toluene (20 ml) was refluxed for 3.25 h. The cooled reaction mixture was diluted with ether, and washed with saturated aqueous sodium thiosulphate (10 ml), aqueous sodium hydroxide (1M; 3 × 10 ml), and saturated aqueous sodium chloride (10 ml), dried, and evaporated. Analysis of the residue by n.m.r. spectroscopy suggested that it was composed of the indole (**21**) (*ca.* 58%), the isoquinoline (**22**) (*ca.* 2%), and the enamine (**23**) (*ca.* 39%). Chromatography gave the indole (**21**) (39 mg, 51%) and the enamine (**23**) (20 mg, 26%), δ (90 MHz; $CDCl_3$) 1.37 (3 H, t), 2.30 (3 H, s), 4.0 (2 H, br, exchangeable D_2O), 4.32 (2 H, q), 6.37 (1 H, s), and 7.05—7.55 (4 H, m).

(e) *In toluene with hydrogen iodide*. A toluene solution of hydrogen iodide (0.06M; 1.6 ml, 0.1 mmol) was added to a solution of the azide (**5**) (231 mg, 1 mmol) in toluene (30 ml). The solution was heated under reflux for 2.75 h, and evaporated to give a solid which was shown by n.m.r. spectroscopy to consist only of the indole (**21**).

(f) *In toluene with potassium iodide*. Potassium iodide (199 mg, 1.2 mmol) was added to a solution of the azide (**5**) (138 mg, 0.6 mmol) in toluene (30 ml). The mixture was refluxed for 2.75 h, filtered, and evaporated to give a solid which was shown by n.m.r. spectroscopy to consist only of the indole (**21**).

(g) *In toluene with dibenzoyl peroxide*. A solution of the azide (**5**) (57 mg, 0.258 mmol) and dibenzoyl peroxide (6 mg, 0.026 mmol) in toluene (16 ml) was refluxed for 3 h. The indole (**21**) was the only product.

(h) *In toluene with diphenyl disulphide*. A mixture of the azide (**5**) (231 mg, 1 mmol) and diphenyl disulphide (218 mg, 1 mmol) was heated in boiling toluene (50 ml) for 2.75 h. Evaporation of the solvent left a residue which was shown by n.m.r. spectroscopy and t.l.c. to consist only of the indole (**21**) and diphenyl disulphide.

(i) *In toluene with diphenyl diselenide*. Carried out exactly as described in (h). The only products were the indole (**21**) and unchanged diphenyl diselenide.

(j) *In bromobenzene*. The azide (**5**) (60 mg) was heated in bromobenzene (17 ml) at 110 °C for 3 h. Evaporation of the solvent gave the indole (**21**) as the sole product.

(k) *In 1-iodopropane*. The azide (**5**) (60 mg) was heated in refluxing 1-iodopropane for 6 h. Evaporation of the solvent gave the indole (**21**) as the sole product.

Thermolysis of Ethyl 2-Azido-3-(2-isopropylphenyl)-propenoate (**6**).—(a) *In xylene*. A solution of the azide (**6**) (212 mg, 0.82 mmol) in xylene (40 ml) was refluxed for 0.75 h. The solvent was evaporated and the residue chromatographed to give *ethyl 4-isopropylindole-2-carboxylate* (**24**) (122.5 mg, 65%), m.p. 105—108 °C (Found: C, 72.5; H, 7.4; N, 6.1. $C_{14}H_{17}NO_2$ requires C, 72.7; H, 7.4; N, 6.1%); $\nu_{max.}$(Nujol) 3 345 and 1 686 cm^{-1}; δ (90 MHz; CCl_4) 1.37 (6 H, d, *J* 7 Hz), 1.41 (3 H, t), 2.25 (1 H, heptet, *J* 7 Hz), 4.44 (2 H, q), 6.92 (1 H, m), 7.20 (3 H, m), and 10.10 (1 H, br); *m/z* 231 (M^+ base), 216, 185, and 170; ethyl 2-amino-3-(2-propen-2-ylphenyl)prop-2-enoate (**26**) (30 mg, 16%), oil, $\nu_{max.}$(film) 3 460, 3 370, 1 705, and 1 630 cm^{-1}; δ (90 MHz; CCl_4) 1.36 (3 H, t), 2.05 (3 H, m), 4.05 (2 H, br, exchangeable D_2O), 4.31 (2 H, q), 4.95 (1 H, m), 5.23 (1 H, m), 6.41 (1 H, s), 7.05—7.37 (3 H, m), and 7.50—7.66 (1 H, m); *m/z* 231 (M^+), 216, 170, 140, and 115; N-*acetyl derivative*, m.p. 145—146 °C; and *ethyl 1,2-dihydro-1,1-dimethylisoquinoline-3-carboxylate* (**25**) (6 mg, 3%), data given later.

(b) *In xylene with iodine* (0.1 mol equiv.). A solution of the azide (**6**) (184 mg, 0.71 mmol) and iodine (18 mg, 0.07 mmol) in xylene (35 ml) was heated under reflux for 0.75 h. Evaporation of the solvent, and chromatography of the residue gave the indole (**24**) (49 mg, 30%); *ethyl 1,2-dihydro-1,1-dimethylisoquinoline-3-carboxylate* (**25**) (22 mg, 14%), pale yellow prisms from dichloromethane–light petroleum, m.p. 89—91 °C (Found: M^+ 231.1254. $C_{14}H_{17}NO_2$ requires M^+ 231.1259); $\nu_{max.}$(Nujol) 3 365, 1 690, and 1 620 cm^{-1}; δ (90 MHz; CCl_4) 1.30 (3 H, t), 1.48 (6 H, s), 3.52 (1 H, br, exchangeable D_2O), 4.29 (2 H, q), 6.32 (1 H, s), and 6.97—7.20 (4 H, m); *m/z* 231 (M^+), 216, 170, 142, and 115; and *ethyl 1-methylnaphthalene-3-carboxylate* (**27**) (20 mg, 17%), oil, $\nu_{max.}$(film) 1 713 cm^{-1}; δ (90 MHz; CCl_4), 1.45 (3 H, t), 2.75 (3 H, s), 4.41 (2 H, q), 7.45—7.70 (2 H, m), 7.82—8.05 (3 H, m), and 8.41 (1 H, br s); *m/z* 241 (M^+ base), 199, 186, 169, 141, and 115. Only a trace (<5%) of the enamine (**26**) was observed.

Thermolysis of Ethyl 2-Azido-3-(3-methyl-2-thienyl)-propenoate (**7**).—A solution of the azide (**7**) (300 mg) in xylene (30 ml) was heated under reflux for 1 h. The solvent was evaporated, and the residue chromatographed to give ethyl thieno[3,2-*c*]pyridine-6-carboxylate (**28**) (71 mg, 27%), m.p. 65 °C (from light petroleum) (lit.,[5] m.p. 65 °C).

Thermolysis of Ethyl 2-Azido-3-(1,3,5-trimethylpyrazol-4-yl)-propenoate (**8**).—(a) *In xylene*. A solution of the azide (**8**) (430 mg) in xylene (30 ml) was heated under reflux for 20 min. The mixture was concentrated and the residue chromatographed to give 1,3,5-trimethylpyrazole-4-carbaldehyde (**30**) (45 mg, 16%), and *ethyl 1,3-dimethylpyrazolo[3,4-c]pyridine-5-carboxylate* (**29**) (100 mg, 22%), m.p. 176—178 °C (Found: C, 60.45; H, 6.1; N, 19.4. $C_{11}H_{13}N_3O_3$ requires C, 60.3; H, 6.0; N, 19.15%); $\nu_{max.}$(KBr) 1 710 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.47 (3 H, t), 2.63 (3 H, s), 4.15 (3 H, s), 4.52 (2 H, q), 8.45 (1 H, d, *J* 1 Hz), and 8.89 (1 H, d, *J* 1 Hz).

(b) *In xylene with iodine* (0.04 mol equiv.). A solution of the azide (**8**) (509 mg, 2.04 mmol) and iodine (20 mg, 0.08 mmol) in xylene (30 ml) was heated under reflux for 30 min. The mixture was concentrated, and the residue chromatographed to give the aldehyde (**30**) (63 mg, 22%), and the pyrazolopyridine (**29**) (72 mg, 16%).

(c) *In toluene with iodine* (0.09 mol equiv.). A solution of the azide (**8**) (475 mg, 1.90 mmol) and iodine (42 mg, 0.17 mmol) in toluene (25 ml) was heated under reflux for 30 min. The solvent was evaporated, and the residue chromatographed to give the aldehyde (**30**) (45 mg, 17%) and *diethyl 3,6-bis(1,3,5-trimethylpyrazol-4-yl)pyrazine-2,5-dicarboxylate* (**31**) (45 mg, 11%), m.p. 187—188 °C (from dichloromethane–ether) (Found: C, 59.9; H, 6.45; N, 18.6. $C_{22}H_{28}N_6O_4$ requires C, 60.0; H, 6.4; N, 19.1%); $\nu_{max.}$(KBr) 1 710 and 1 645 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.26 (6 H, t), 2.18 (6 H, s), 2.27 (6 H, s), 3.75 (6 H, s), and 4.31 (4 H, q); *m/z* 440 (M^+, base), 395, 367, 321, 293, and 228.

Thermolysis of Ethyl 2-Azido-3-(2,6-dichlorophenyl)-propenoate (**9**).—A solution of the azide (**9**) (560 mg) in toluene (25 ml) was heated under reflux for 2.5 h. Evaporation of the solvent gave a colourless oil which crystallised on standing to give *ethyl 2-(2,6-dichlorophenyl)-2H-azirine-3-carboxylate* (**32**) (492 mg, 97%), m.p. 94 °C (from ether–light petroleum) (Found: C, 50.7; H, 3.6; N, 5.1. $C_{11}H_9Cl_2NO_2$ requires C, 51.2; H, 3.5; N, 5.4%); $\nu_{max.}$(KBr) 1 750 and 1 720 cm^{-1}; δ (60 MHz; $CDCl_3$) 1.42 (3 H, t), 3.61 (1 H, s), 4.53 (2 H, q), and 7.1—7.5 (3 H, m).

Ethyl 2-Cyano-2-(2,6-dichlorophenyl)acetate (**33**). The azirine (**32**) (96 mg) was sublimed through a tube heated to 450 °C at 0.05 mmHg. The crude pyrolysate was chromatographed to give

the *title compound* (**33**) (53 mg, 55%), m.p. 68 °C (from light petroleum) (Found: C, 51.3; H, 3.5; N, 5.3. $C_{11}H_9Cl_2NO_2$ requires C, 51.2; H, 3.5; N, 5.4%); $\nu_{max.}$(KBr) 1 745 cm^{-1}; δ (60 MHz; $CDCl_3$) 1.31 (3 H, t), 4.28 (2 H, q), 5.49 (1 H, s), and 7.15—7.40 (3 H, m); δ_C($CDCl_3$) 13.9, 39.4, 63.6; 113.4, 128.0, 128.9, 130.9, 135.9, and 163.4.

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