Reactions of Iodine(I) Azide with αβ-Unsaturated Carbonyl Compounds

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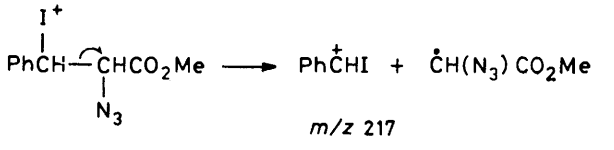
The addition of iodine(I) azide to some αβ-unsaturated esters and ketones has been examined. Addition to the esters under nitrogen gives products consistent with a radical pathway. Preliminary kinetic results indicate that addition of iodine(I) azide to αβ-unsaturated ketones in the presence of air involves a slow electrophilic attack. Reaction with methyl *trans*-cinnamate under these conditions does not go to completion.

THE addition of iodine(I) azide to some αβ-unsaturated esters and ketones has been examined by Hassner *et al.*,[1] who proposed a mechanism analogous to that for the addition to alkenes [2] in order to account for the regio- and stereo-selectivity of the reactions. Although addition of sodium azide–iodine(I) chloride in acetonitrile to methyl (*E*)-3-phenylpropenoate (methyl *trans*-cinnamate) (1) was reported [1] to give a moderate yield (43%) of the *erythro*-adduct (10), in our hands the reaction afforded a crude yield of 79% and an isolated yield of 42%.[3] † Treatment of methyl *trans*-cinnamate with thallium(I) azide–iodine in dichloromethane gave a mixture of azide-containing products which did not include the expected adduct (10). In recent work we have shown [4] that when the addition of iodine(I) azide to disubstituted exocyclic alkenes is carried out under nitrogen, products arising from a radical pathway are obtained. As a consequence we have examined the reaction of iodine(I) azide with some αβ-unsaturated esters [5] and ketones both under nitrogen and in the presence of air.

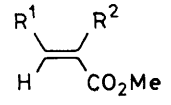
Treatment of methyl *trans*-cinnamate (1) with 1.1 or 2.2 mol. equiv. of sodium azide–iodine(I) chloride in acetonitrile in the presence of air confirmed the earlier result.[3] However, under nitrogen the reaction gave an iodo-azide (21%) and the vinyl azide methyl (*Z*)-2-azido-3-phenylpropenoate (2) (16%) which was identified from a comparison of its ^{1}H n.m.r. spectrum with that recorded.[3] The iodo-azide was distinct from compound (10) and was identified as its regioisomer methyl *erythro*-2-azido-3-iodo-3-phenylpropanoate (11) by elemental analysis and from its spectral parameters. Thus, the i.r. spectrum showed azide absorption (2 100 cm^{-1}), the ^{1}H n.m.r. spectrum showed a doublet of doublets (H-2,3) with a *vicinal* coupling constant (*J* 10 Hz) indicative of an



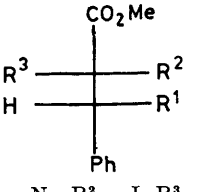
SCHEME 1

erythro-adduct,[6] while the mass spectrum showed low intensity peaks at *m/z* 331 ($M^{+\cdot}$), 289 ($M^{+\cdot} - N_3^{\cdot}$), and 204 ($M^{+\cdot} - I^{\cdot}$). The latter spectrum also contained a peak at *m/z* 217, which provides support for the regiochemical assignment (Scheme 1), and which contrasted with one at *m/z* 200 in the spectrum of the isomer (10). The latter ion, which was shown by metastable refocusing to be formed directly from the molecular ion, could arise as in Scheme 2.

Addition of iodine(I) azide to the ester (1) in the absence of oxygen is probably initiated by attack of an azido radical (Scheme 3). Although the generation of a radical site adjacent to the methoxycarbonyl group can be a favoured process,[7,8] the adduct from this pathway was not detected. The vinyl azide (2) did not arise from the iodo-azide (11) since the latter was recovered quantitatively after treatment with iodine(I) azide in acetonitrile under nitrogen. However, compound (2) may have arisen from the iodo-azide (10) *via* an intermediate diazide (*cf.* ref. 9) since treatment of the adduct (10) with sodium azide in anhydrous dimethylformamide [5,10] gave a 1 : 1 mixture of the (*Z*)- (2) and the (*E*)-vinyl azide (15). Compound (2) may also have arisen *via* a *cis*-adduct (*cf.* refs. 4 and 11) by stereoselective *trans*-elimination of hydrogen iodide, but a more probable route involves loss of a hydrogen radical from the benzylic radical (a). Formation of the iodo-azide (11) and of the vinyl azide



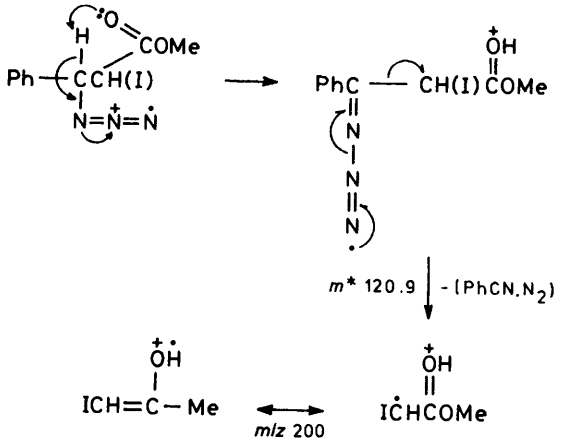
(1) R^1 = Ph, R^2 = H
(2) R^1 = Ph, R^2 = N_3
(3) R^1 = H, R^2 = Me
(4) R^1 = N_3, R^2 = Me
(5) R^1 = Me, R^2 = H
(6) R^1 = R^2 = H
(7) R^1 = N_3, R^2 = H
(8) R^1 = H, R^2 = N_3
(9) R^1 = *p*-MeOC$_6$H$_4$, R^2 = H



(10) R^1 = N_3, R^2 = I, R^3 = H
(11) R^1 = I, R^2 = N_3, R^3 = H
(12) R^1 = OAc, R^2 = N_3, R^3 = H
(13) R^1 = OAc, R^2 = H, R^3 = N_3
(14) R^1 = Cl, R^2 = I, R^3 = H

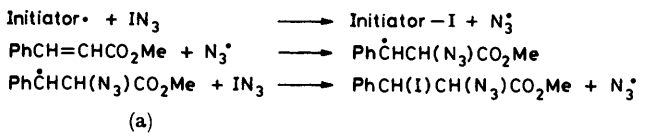
† Structures (19) and (22) in ref. 3 should be interchanged.

(2) indicates that reaction of iodine(I) azide with methyl *trans*-cinnamate *via* a radical pathway is highly regioselective. The isolation of only the *trans*-adduct (11) suggests that the addition is also stereoselective. The ionic addition [3] to methyl *trans*-cinnamate is also both regio- and stereo-selective.



SCHEME 2

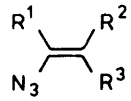
Solvolysis of the *erythro*-iodo-azide (11) with silver(I) acetate in acetic acid gave a mixture (3.2 : 1) of the *erythro*- and *threo*-azido-acetates (12) and (13). Although these isomers could not be separated by p.l.c. the stereochemistry of each was deduced readily from the *vicinal* [H(2)—H(3)] coupling constant (J 4 and 8 Hz, respectively) in the ^{1}H n.m.r. spectrum of the mixture. The solvolysis may proceed by S_N2 and/or S_N1 mechanisms but could also involve some neighbouring group participation by the azido group (*cf.* ref. 4).



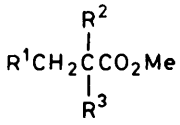
SCHEME 3

Treatment of methyl 2-methylpropenoate (3) with iodine(I) azide in acetonitrile in the presence of air gave a mixture (4.6 : 1) of methyl 3-azido-2-iodo-2-methylpropanoate (18) and methyl 2-azido-3-iodo-2-methylpropanoate (19), which were separated by p.l.c. The regiochemistry of the adducts followed from an examination of their ^{1}H and ^{13}C n.m.r. spectral parameters (Experimental), and in the case of the major isomer (18) was confirmed by elimination of hydrogen iodide to give the (*Z*)-vinyl azide (16). The stereochemistry of the latter followed from the *vicinal* ^{13}C—^{1}H coupling constant (^3J 5.9 Hz) for the C-3 proton and the carbon atom of the C-2 methyl group in the ^{13}C single-resonance spectrum, which was consistent [11] with a *Z*-configuration but inconsistent with the alternative structure (4).

Addition of iodine(I) azide to methyl 2-methylpropenoate (3) under nitrogen also gave the adduct (18), but afforded only a trace of the regioisomer (19). Thus, in contrast to the addition under conditions which favour initial attack by electrophilic iodine, the latter reaction was highly regioselective. However, a different ratio (1.3 : 1) of the products (18) and (19) was obtained when the reaction was carried out under oxygen. The increase in the amount of the adduct (19) relative to (18) in the presence of oxygen or air is consistent with the operation of an ionic pathway since the C-2 methyl group would lead to a stabilization of an intermediate with the developing positive charge on C-2.



(15) R^1 = Ph, R^2 = CO_2Me, R^3 = H
(16) R^1 = H, R^2 = Me, R^3 = CO_2Me
(17) R^1 = Me, R^2 = CO_2Me, R^3 = H



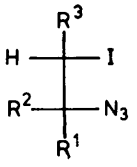
(18) R^1 = N_3, R^2 = I, R^3 = Me
(19) R^1 = I, R^2 = N_3, R^3 = Me
(20) R^1 = N_3, R^2 = I, R^3 = H
(21) R^1 = I, R^2 = N_3, R^3 = H

Addition of iodine(I) azide to methyl (*E*)-but-2-enoate (5) in the presence of air or under nitrogen gave only the *erythro*-adduct (22) (*cf.* the regio- and stereo-selective addition to the corresponding ethyl ester [12]) which was converted into the elimination product (17) [12] and the triphenylphosphoranylideneamino-derivative (28).

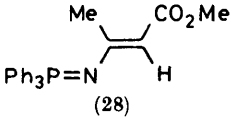
The addition of iodine(I) azide to methyl propenoate (6) was deduced by Hassner and Fowler [12] to have given the adducts (20) and (21), since treatment of the crude product with 1,4-diazabicyclo[2.2.2]octane (DABCO) afforded a mixture (1 : 7.4) of the vinyl azides (7) and (8). In the present work addition of iodine(I) azide to methyl propenoate (6) in the presence of air followed by elimination of hydrogen iodide, gave a mixture (*ca.* 1 : 2.6) of the vinyl azides (7) and (8). A slight increase in the relative amount of the compound (8) was observed when the addition was carried out under nitrogen.

The products from addition to the double bond of an unsubstituted αβ-unsaturated carbonyl system may be expected to be regioisomeric when a species (*e.g.* electrophilic iodine) which acts as the electrophile in an ionic process (i), behaves also as the radical addend (*e.g.* an iodine atom) in a competitive homolytic pathway (ii) (Scheme 4). If, however, the alkyl radical is formed (iii) by delivery of a radical species corresponding to the nucleophilic partner in the ionic process, then the product from either route will be the same. In the case of a radical process, the incorporation of an aryl or alkyl substituent on the β-carbon atom of the enone system may result in alteration of the site of attack of an azido radical to the other possible position (iv) (Scheme 5).

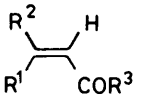
Methyl cinnamate (1) and methyl 2-methylpropenoate (3) are analogous in that the expected sites of both radical



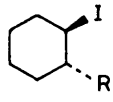
(22) R^1 = Me, R^2 = H, R^3 = CO_2Me
(23) R^1 = Ph, R^2 = H, R^3 = COPh
(24) R^1 = R^2 = Me, R^3 = COMe
(25) R^1 = *p*-$MeOC_6H_4$, R^2 = H, R^3 = COMe
(26) R^1 = Ph, R^2 = H, R^3 = COMe
(27) R^1 = *p*-$MeOC_6H_4$, R^2 = H, R^3 = CO_2Me



(28)



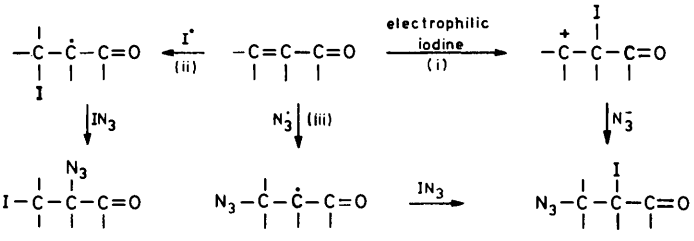
(29) R^1 = H, R^2 = R^3 = Ph
(30) R^1 = R^2 = R^3 = Me
(31) R^1 = H, R^2 = *p*-$MeOC_6H_4$, R^3 = Me
(32) R^1 = H, R^2 = Ph, R^3 = Me



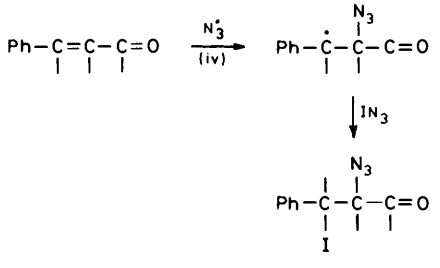
(33) R = N_3
(34) R = Cl

and ionic attack are coincident in each case, albeit at C-2 in the former substrate owing to resonance stabilisation of the radical centre by the adjacent phenyl group, and at C-3 in the latter substrate owing to the electronic effect of the C-2 methyl group. Although it was possible experimentally to make the radical pathway dominant when the addition of iodine(I) azide was carried out under nitrogen, we were unable to suppress completely the radical process when the reaction of (3) was carried out in the presence of air, under which conditions we would expect regioisomer (19) to be the major product. However, as indicated earlier, the proportion of product resulting from ionic attack was increased when an oxygen atmosphere was used instead of air. The possibility that adduct (18) may be formed by a residual ionic pathway is discounted by analogy with the results obtained under nitrogen with methyl cinnamate, where a complete reversal of product regiochemistry was established.

In contrast to the above examples, attack of electrophilic iodine or of an azido radical on methyl(*E*)-but-2-enoate (5) is expected to occur at different sites, C-2 and C-3, respectively. Either route leads to the same regioisomer (22), in accord with the observed result. Methyl propenoate (6) presents a similar case in that, although the site of attack of an azido radical or of electrophilic iodine would be expected to be different, the same iodo-azide (20) should be formed,[7,8] notwithstanding the difficulty in evaluating competitive attack by different species at different sites. The results obtained in the present work from the reaction of iodine(I) azide with methyl propenoate are not, however, in accord with this expectation. A possible explanation is that a different initiation step operates to produce an iodo radical, and that formation of adduct (21) then occurs unexceptionally *via* attack at C-3. It is noteworthy that methyl propenoate is expected not only to react more slowly than its homologues,[18] but also to form a primary iodide at C-3 more readily than methyl(*E*)-but-2-enoate would form the analogous C-3 secondary iodide. An alternative rationale which we cannot discount is that regioisomer (21) is generated *via* conjugate addition of iodide ion, and electron transfer from the resulting carbanion affording a β-iodoalkyl radical which completes adduct formation by a chain termination step (Scheme 6).



SCHEME 4

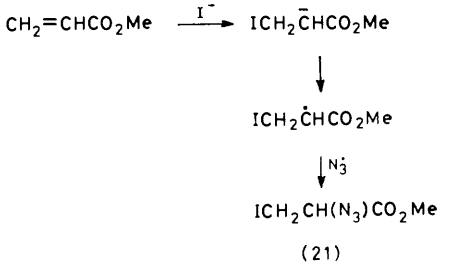


SCHEME 5

As indicated above, addition of iodine(I) azide to methyl *trans*-cinnamate (1) in the presence of air consistently gave an approximately 25% return of starting material even with 2.2 mol equiv. of the reagent.* In contrast, addition of iodine(I) azide to (*E*)-1,3-diphenyl-

* The iodo-azide (10) was not stable in the presence of iodine(I) azide: treatment with 1.0 mol equiv. of reagent resulted in formation of a mixture (*ca.* 6 : 1) of the adduct (10) and the (*E*)-vinyl azide (15). The possibility thus existed that the 75% yield of iodo-azide (10) reflected consumption of reagent by a secondary reaction. However, this should have been overcome when the ester (1) was treated with 2.2 mol equiv. of reagent.

propenone (chalcone) (29) and to 4-methylpent-3-en-2-one (mesityl oxide) (30) under the same conditions gave the respective adducts (23) and (24) in nearly quantitative yields; isolated yields were 76% (*cf.* 100% in ref. 1) and



SCHEME 6

78%, respectively. Biffin *et al.*,[14] have suggested that the addition of iodine(I) azide to αβ-unsaturated carbonyl compounds occurs *via* an Ad_N mechanism rather than by an Ad_E mechanism as suggested by Hassner *et al.*[1] From studies of the addition of iodine(I) isocyanate [15] and of iodine(I) azide [13,16] to alkenes, it was concluded [14] that the former reagent is the stronger electrophile and since only iodine(I) azide will add to αβ-unsaturated carbonyl compounds this is not consistent with an Ad_E mechanism. Moreover, the greater nucleophilicity of an azide ion compared with that of an isocyanate ion would also favour an Ad_N mechanism.

In order to provide mechanistic information, the rates of addition of iodine(I) azide to the *p*-methoxy-derivatives (9) and (31) were compared with those of addition to methyl (*E*)-3-phenylpropenoate (1) and (*E*)-4-phenylbut-3-en-2-one (32), respectively, since the mesomeric effect of a *p*-methoxy-substituent should result in a decrease in rate for an Ad_N mechanism. However, the results (see Figure) show that the rates of reaction with the *p*-methoxy-derivatives are greater than those for the parent compounds and thus, as in the addition to simple alkenes,[3] are consistent with an electrophilic mechanism and inconsistent with rate-determining attack of azide ion.

Addition to the αβ-unsaturated ketones (31) and (32) in the presence of air gave the adducts (25) and (26) respectively in nearly quantitative yields. In contrast, addition to the methyl cinnamates (1) and (9) to form the adducts (10) and (27) appeared to stop after 6—8 h, suggesting that an equilibrium is established during the ionic addition of iodine(I) azide to αβ-unsaturated esters. That the adduct can regenerate methyl *trans*-cinnamate was shown when treatment of this ester with 1.1 mol. equiv. of iodine(I) azide gave a mixture (1.2 : 1) of starting material and the adduct (10); addition of a slight excess of cyclohexene followed by work-up afforded the iodo-azide (33) [1] and a different mixture (2.7 : 1) of the unsaturated ester (1) and the iodo-azide (10).

Similarly treatment of the unsaturated ester (1) with 1.0 mol equiv. of iodine(I) chloride afforded the adduct (14) in 75% yield (^{1}H n.m.r. analysis) but the product was isolated in only 37% yield after work-up. Addition of a slight excess of cyclohexene to the reaction mixture followed by work-up afforded a mixture (*ca.* 1 : 1) of the unsaturated ester (1) and *trans*-1-chloro-2-iodocyclohexane (34). Either of the adducts (10) or (14) can therefore regenerate the starting ester. This does not, however, mean that the reactions of iodine(I) azide with the methyl *trans*-cinnamates (1) and (9) are equilibrium processes. This view finds support in the fact that where-

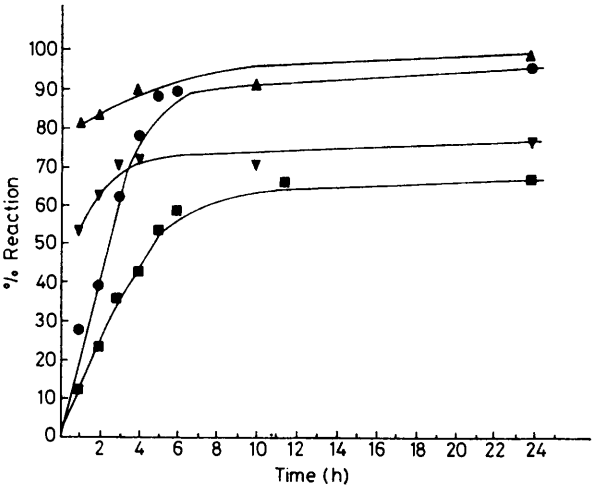


FIGURE Rates of addition of iodine(I) azide to (■) Methyl (*E*)-3-phenylpropenoate (1), (●) (*E*)-4-phenylbut-3-en-2-one (32), (▼) methyl (*E*)-3-(4-methoxyphenyl)propenoate (9), and (▲) (*E*)-4-(4-methoxyphenyl)but-3-en-2-one (31)

$$I\cdot + PhCH(N_3)\dot{C}HCO_2Me \xrightarrow{fast} PhCH{=}CHCO_2Me + IN_3$$

SCHEME 7

as these esters afford the adducts in only *ca.* 65% yield, reactions using the thermodynamically more stable αβ-unsaturated ketones (31) and (32) proceed nearly quantitatively.

The reason for the apparent reversibility of adduct formation from methyl cinnamate may be due to the operation of an alternative pathway reflecting the decreased energy of the C–I bond when compared with the corresponding adducts from the phenylbutenones. Bond homolysis in the methyl cinnamate adduct gives a radical stabilised by the adjacent methoxycarbonyl group and this process may thus be facilitated relative to that in the less oxygenated system. The reversion step would thus be that in Scheme 7. This reversion process regenerates both reagents which might therefore be expected to react to form the alternative regioisomer. Since, however, an azido radical is not produced during the reversion process, the alternative isomer cannot be formed.

It is clear that the mechanism of iodine(I) azide addition to double bonds is more complex than hitherto believed and requires further study.

EXPERIMENTAL

General experimental details and methods (a)—(f) for the preparation of iodo-azides are given in ref. 4. All azides showed iir. absorption at $\nu_{max.}$ *ca.* 2 100 cm^{-1} (N_3).

Methyl erythro-3-*Azido*-2-*iodo*-3-*phenylpropanoate* (10).—Methyl (*E*)-3- phenylpropenoate (1) (1.62 g, 10.0 mmol) was treated with iodine(I) azide (11.0 mmol) in acetonitrile (22 ml) for 45 h using procedure (a). Work-up gave a mixture (1 : 3) of starting material and the adduct (10) as a brown oil (2.18 g) which afforded methyl *erythro*-3-azido-2-iodo-3-phenylpropanoate (1.38 g, 42%), needles (from aqueous methanol), m.p. 52—54° (lit.,[3] 49.5—50.5°), $\nu_{max.}$ 1 720 cm^{-1} (CO), δ_H (incorrect in ref. 3) 3.83 (s, CO_2CH_3), 4.50 (d, *J* 10 Hz, 2-H), 5.00 (d, *J* 10 Hz, 3-H), and 7.27 (m, ArH), δ_C 22.5 (C-2), 53.2 (CH_3), 68.1 (C-3), 127.8 (*o*-C), 128.8 (*m*-C), 129.4 (*p*-C), 136.1 (*ipso*-C), and 170.1 (C=O), *m/z* 331 ($M^{+\cdot}$), 300 ($M^{+\cdot}$ — $\dot{O}CH_3$), 289 ($M^{+\cdot}$ — $\dot{N}_3$), 200 ($M^{+\cdot}$ — N_2 — C_6H_5-CN), 176 ($M^{+\cdot}$ — $\dot{I}N_2$), and 162 ($M^{+\cdot}$ — IN_3).

Repetition of the experiment with iodine(I) azide (22.0 mmol) gave (10) in 77% yield (^{1}H n.m.r. analysis) but in only 49% yield after crystallisation.

Methyl erythro-2-*Azido*-3-*iodo*-3-*phenylpropanoate* (11).—Methyl (*E*)-3-phenylpropenoate (1) (0.81 g, 5.0 mmol) was treated with iodine(I) azide (5.0 mmol) in acetonitrile (11 ml) as in procedure (f). Work-up yielded a brown oil (1.02 g) which on p.l.c. (hexane–ether, 9 : 1) gave (i) starting material (0.13 g, 16%); (ii) *methyl* erythro-2-*azido*-3-*iodo*-3-*phenylpropanoate* (0.34 g, 21%), rods (from hexane–dichloromethane), m.p. 45—47° (Found: C, 36.0; H, 3.3; I, 37.8; N, 12.5. $C_{10}H_{10}IN_3O_2$ requires C, 36.3; H, 3.1; I, 38.3; N, 12.7%), $\nu_{max.}$ 1 720 cm^{-1} (CO), δ_H 3.88 (s, CO_2CH_3), 4.52 (d, *J* 10 Hz, 3-H), 5.38 (d, *J* 10 Hz, 2-H), and 7.43 (m, ArH), δ_C 25.8 (C-2), 53.0 (CH_3), 68.1 (C-3), 128.1 (*o*-C), 129.0 (*m*, *p*-C), 138.6 (*ipso*-C), and 168.1 (C=O), *m/z* 331 ($M^{+\cdot}$), 289 ($M^{+\cdot}$ — $\dot{N}_3$), 217($M^{+\cdot}$ — $\dot{C}_3H_4N_3O_2$), 204 ($M^{+\cdot}$ — I·), and 162 ($M^{+\cdot}$ — IN_3); and (iii) methyl (*Z*)-2-azido-3-phenylpropenoate (2) [5] (0.16 g, 16%), as an oil, $\nu_{max.}$ 1 705 (CO), and 1 610 cm^{-1} (C=C), δ 3.90 (s, CO_2CH_3), 6.96 (s, C=CH), 7.40 and 7.67 (m, ArH), *m/z* 203 ($M^{+\cdot}$), 175 ($M^{+\cdot}$ — N_2), and 144 ($M^{+\cdot}$ — $\dot{C}O_2CH_3$).

Reactions of Methyl erythro-3-*Azido*-2-*iodo*-3-*phenylpropanoate*.—(a) *With sodium azide in dimethylformamide*. The iodo-azide (10) (0.30 g, 0.91 mmol) was treated with sodium azide (0.19 g, 2.92 mmol) in anhydrous dimethylformamide (5 ml) at 20 °C for 22 h. The mixture was poured into water and extracted with ether, and the extract was worked up to give a mixture (1 : 1) of methyl (*Z*)-2-azido-3-phenylpropenoate (2) and methyl (*E*)-3-azido-3-phenylpropenoate (15) [5] (^{1}H n.m.r. analysis) as an oil (0.20 g).

(b) *With iodine*(I) *azide*. The iodo-azide (10) (0.20 g, 0.60 mmol) was added to a solution of iodine(I) azide (0.60 mmol) in acetonitrile, prepared in as procedure (a). Work-up after 24 h gave an oil (0.16 g) containing starting material (85%) and methyl (*E*)-3-phenylpropenoate (1) (15%) (^{1}H n.m.r. and t.l.c. analysis).

The iodo-azide was recovered after treatment with sodium azide in acetonitrile at 20 °C for 24 h.

Solvolysis of Methyl erythro-2-*Azido*-3-*iodo*-3-*phenylpropanoate*.—The iodo-azide (11) (0.41 g, 1.24 mmol) was treated with silver(I) acetate (0.22 g, 1.31 mmol) in glacial acetic acid (10 ml) at 80 °C for 1 h. Precipitated silver iodide was filtered off, water was added to the filtrate, and the solution was extracted with ether. The extract was washed with water and saturated sodium hydrogen carbonate solution until neutral. Solvent was evaporated from the dried solution to yield an oil (0.30 g) which on p.l.c. (hexane–ether, 19 : 1) gave (i) a mixture (3.2 : 1) of *methyl* erythro-3-*acetoxy*-2-*azido*-3-*phenylpropanoate* (12), and *methyl* threo-3-acetoxy-2-azido-3-phenylpropanoate (13) as an oil (0.15 g), b.p. 170° (Kugelrohr) at 0.1 mmHg (Found: C, 54.9; H, 5.1; N, 16.1. $C_{12}H_{13}N_3O_4$ requires C, 54.9; H, 5.0; N, 15.9%), $\nu_{max.}$ 1 750 cm^{-1} (CO), $\delta(CCl_4)$, 2.12 (s, $OCOCH_3$), 3.73 (s, CO_2CH_3), 3.87 [d, *J* 4 Hz, 2-H of (12)], 4.20 [d, *J* 8 Hz, 2-H of (13)], 5.36 [d, *J* 4 Hz, 3-H of (12)], 7.68 (d, *J* 8 Hz, 3-H), and 7.30 (s, ArH); (ii) methyl *erythro*-3-azido-2-iodo-3-phenylpropanoate (32 mg); and (iii) methyl (*Z*)-2-azido-3-phenylpropenoate (2) (40 mg) (^{1}H n.m.r. and i.r. spectra).

Treatment of Methyl 2-*Methylpropenoate with Iodine*(I) *Azide*.—(a) *Using procedure* (*a*). Freshly distilled methyl 2-methylpropenoate (3) (0.50 g, 5.0 mmol) was added to a solution of iodine(I) azide (5.5 mmol) in acetonitrile (11 ml), prepared as in procedure (a). Work-up after 24 h gave an oil (0.90 g) which on p.l.c. (hexane–ether, 19 : 1) gave (i) *methyl* 3-*azido*-2-*iodo*-2-*methylpropanoate* (18) (0.71 g, 53%), as an oil, b.p. 72° (Kugelrohr) at 0.1 mmHg (Found: C, 22.5; H, 2.9; I, 46.9; N, 15.5. $C_5H_8IN_3O_2$ requires C, 22.3; H, 3.0; I, 47.2; N, 15.6%), $\nu_{max.}$ 1 730 cm^{-1} (CO), δ_H 2.10 (s, CH_3), 3.83 (s, CO_2CH_3), and 3.93 (dd, *J* 10 Hz, CH_2N_3), δ_C 28.1 (2-CH_3), 34.6 (C-2), 53.5 (OCH_3), 61.8 (C-3), and 171.7 (C-1), *m/z* 269 ($M^{+\cdot}$), 238 ($M^{+\cdot}$ — $\dot{O}CH_3$), 154 ($M^{+\cdot}$ — $\dot{C}H_2N_3$ — $\dot{C}O_2CH_3$), 142 ($M^{+\cdot}$ — I), 141 ($M^{+\cdot}$ — HI), 114 ($M^{+\cdot}$ — $\dot{I}N_2$), and 100 ($M^{+\cdot}$ — IN_3); and (ii) *methyl* 2-*azido*-3-*iodo*-2-*methylpropanoate* (19) (80 mg, 6%), as an oil, b.p. 90° (Kugelrohr) at 0.1 mmHg (Found: C, 22.3; H, 2.9; I, 47.2; N, 15.5. $C_5H_8IN_3O_2$ requires C, 22.3; H, 3.0; I, 47.2; N, 15.6%), $\nu_{max.}$ 1 740 cm^{-1} (CO), δ_H 1.73 (s, CH_3), 3.47 (s, CH_2I), and 3.90 (s, CO_2CH_3), δ_C 10.0 (C-3), 23.1 (2-CH_3), 53.2 (OCH_3), 65.5 (C-2), and 169.8 (C-1), *m/z* 269 ($M^{+\cdot}$), 241 ($M^{+\cdot}$ — N_2), 227 ($M^{+\cdot}$ — $\dot{N}_3$), 226 ($M^{+\cdot}$ — HN_3), 210 ($M^{+\cdot}$ — $\dot{C}O_2CH_3$), 142 ($M^{+\cdot}$ — $\dot{I}$), 141 ($M^{+\cdot}$ — HI), 128 ($M^{+\cdot}$ — $\dot{C}H_2I$), 114 ($M^{+\cdot}$ — $\dot{I}N_2$), and 100 ($M^{+\cdot}$ — IN_3).

(b) *Using procedure* (*f*). Freshly distilled methyl 2-methylpropenoate (1.00 g, 10.0 mmol) was treated with a solution of iodine(I) azide (5.5 mmol) in acetonitrile (11 ml), prepared using procedure (f), for 24 h. Work-up yielded an oil (1.27 g) consisting almost entirely of one product (t.l.c. and ^{1}H n.m.r. analysis). Distillation (Kugelrohr) gave methyl 3-azido-2-iodo-2-methylpropanoate (18) (1.11 g, 41%).

Repetition of the experiment in an atmosphere of oxygen gave a mixture (1.3 : 1) (^{1}H n.m.r. analysis) of methyl 3-azido-2-iodo-2-methylpropanoate (18) and methyl 2-azido-3-iodo-2-methylpropanoate (19) in 67% yield.

Methyl (Z)-3-*Azido*-2-*methylpropenoate* (16).—The iodo-azide (18) (1.11 g, 4.13 mmol) was treated with 1,4-diazabicyclo[2.2.2]octane (0.55 g, 4.90 mmol) in anhydrous acetone (20 ml) at 20 °C for 24 h. Work-up gave *methyl* (*Z*)-3-*azido*-2-*methylpropenoate* (0.53 g, 91%), as plates (from pentane), m.p. 58—62° (Found: C, 42.7; H, 4.9; N, 29.6. $C_5H_7N_3O_2$ requires C, 42.6; H, 5.0; N, 29.8%), $\nu_{max.}$ 1 705 (CO), and 1 640 cm^{-1} (C=C), δ_H 1.80 (s, CH_3), 3.78 (s, CO_2CH_3), and 7.47 (s, $W_{\frac{1}{2}}$ 4.5 Hz, CHN_3), δ_C 11.1 (2-CH_3), 51.8 (OCH_3), 117.5 (C-2), 137.8 (C-3), and 167.3 (C-1), *m/z* 141 ($M^{+\cdot}$), 110 ($M^{+\cdot}$ — $\dot{O}CH_3$), 85 ($M^{+\cdot}$ — $\dot{C}H_2N_3$), 82 ($M^{+\cdot}$ — $\dot{C}O_2CH_3$), and 68 ($M^{+\cdot}$ — $\dot{O}CH_3$ — $\dot{N}_3$).

Methyl erythro-3-*Azido*-2-*iodobutanoate* (22).—Methyl (*E*)-but-2-enoate (5) (0.30 g, 3.0 mmol) was treated with iodine(I) azide (3.5 mmol) in acetonitrile (10 ml) as in pro-

cedure (a) for 24 h. Work-up gave methyl *erythro*-3-azido-2-iodobutanoate (0.36 g, 45%), as an oil, b.p. 110° (Kugelrohr) at 1.0 mmHg, $\nu_{max.}$ 1 740 cm^{-1} (CO), δ_H (CCl_4) 1.52 (d, *J* 6 Hz, CH_3), 3.78 (s, CO_2CH_3), and 4.05 (m, 2,3-H), δ_C 19.1 (C-4), 23.9 (C-2), 53.0 (OCH_3), 59.2 (C-3), and 170.0 (C-1), *m/z* 269 ($M^{+\cdot}$), 238 ($M^{+\cdot} - \dot{O}CH_3$), 227 ($M^{+\cdot} - \dot{N}_3$), 200 ($M^{+\cdot} - C_2H_3N_3$), 168 ($M^{+\cdot} - \dot{N}_3 - \dot{C}O_2CH_3$), 141 ($M^{+\cdot}$ — HI), 114 ($M^{+\cdot} - \dot{I}N_2$), 100 ($M^{+\cdot} - IN_3$).

The iodo-azide (22) (0.18 g, 0.67 mmol) was treated with 1,4-diazabicyclo[2.2.2]octane (90 mg, 0.80 mmol) in anhydrous acetone (5 ml) at 20 °C for 24 h. Work-up gave methyl (*E*)-3-azidobut-2-enoate (17) (90 mg, 96%), as a volatile oil, $\nu_{max.}$ 1 705 cm^{-1} (CO), and 1 630 cm^{-1} (C=C), δ 2.40 (s, CH_3), 3.77 (s, CO_2CH_3), and 5.58 (s, $W_{\frac{1}{2}}$ 2 Hz, C=CH).

Methyl (E)-3-(*Triphenylphosphoranylideneamino*)*but*-2-*enoate* (28).—Methyl (*E*)-3-azidobut-2-enoate (17) (90 mg, 0.64 mmol) was treated with triphenylphosphine (0.17 g, 0.65 mmol) in anhydrous dichloromethane (5 ml) at 20 °C for 1 h. Pentane was added until turbidity occurred and the cooled (0 °C) suspension was filtered to yield a pale yellow powder (0.10 g, 42%). Crystallisation from dichloromethane–pentane gave *methyl* (E)-3-(*triphenylphosphoranylideneamino*)*but*-2-*enoate*, m.p. 146—149° (Found: $M^{+\cdot}$, 375.1409. $C_{23}H_{22}NO_2P$ requires *M*, 375.1389), $\nu_{max.}$ 1 680 (CO), and 1 530 cm^{-1} (C=C), δ 2.52 (d, *J* 2 Hz, CH_3), 3.53 (s, CO_2CH_3), 4.75 (m, $W_{\frac{1}{2}}$ 2.0 Hz, C=CH), and 7.60 (m, ArH), *m/z* 360.1145 ($M^{+\cdot} - \dot{C}H_3$), 344.1150 ($M^{+\cdot} - \dot{O}CH_3$), and 316.1196 ($M^{+\cdot} - \dot{C}O_2CH_3$).

Treatment of Methyl Propenoate with Iodine(I) *Azide*.—(a) *Using procedure* (*a*). Freshly distilled methyl propenoate (6) (0.43 g, 5.0 mmol) was added to a solution of iodine(I) azide (5.5 mmol) in acetonitrile (11 ml), prepared as in procedure (a). Work-up after 24 h gave a mixture of iodo-azides (20) and (21) as an oil (0.86 g, 67%), b.p. 100° (Kugelrohr) at 0.7 mmHg, $\nu_{max.}$ 1 740 cm^{-1} (CO), δ_C 14.8, 53.2, 54.7, and 170.0, *m/z* 255 ($M^{+\cdot}$).

The crude adducts (0.89 g, 3.49 mmol) were treated with 1,4-diazabicyclo[2.2.2]octane (0.41 g, 3.66 mmol) in anhydrous acetone (10 ml) at 0 °C for 24 h.[12] Work-up gave a mixture (2.6 : 1) of methyl 2-azidopropenoate (8) [12] and methyl (*E*)-3-azidopropenoate (7) [12] as a yellow oil (0.31 g, 70%).

(b) *Using procedure* (*f*). Methyl propenoate (6) (0.43 g, 5.0 mmol) was treated with iodine(I) azide (5.5 mmol) in acetonitrile (11 ml) for 24 h using procedure (f). Work-up gave a mixture of iodo-azides (20) and (21) as an oil (1.24 g, 97%), which was treated with 1,4-diazabicyclo[2.2.2]octane (0.72 g, 6.4 mmol) in anhydrous acetone (15 ml) as in (a). Work-up gave a mixture (3.3 : 1) (^{1}H n.m.r. analysis) of methyl 2-azidopropenoate (8) and methyl (*E*)-3-azidopropenoate (7) (0.45 g, 73%).

Repetition of the experiment, replacing the nitrogen with oxygen, gave a 78% yield of the crude iodo-azide adducts which were converted into a mixture (2.5 : 1) of the vinyl azides (8) and (7).

erythro-3-*Azido*-1,3-*diphenyl*-2-*iodopropan*-1-*one* (23).—(*E*)-1,3-Diphenylpropenone (29) was treated with iodine(I) azide using procedure (a). Work-up gave *erythro*-3-azido-1,3-diphenyl-2-iodopropan-1-one (76%), as needles (from ethanol), m.p. 105—107° (lit.,[1] 104—105°), $\nu_{max.}$ 1 680 cm^{-1} (CO), δ_H 5.32 (d, *J* 10 Hz, 2-H), 5.52 (d, *J* 10 Hz, 3-H), 7.47 and 8.07 (m, ArH), δ_C 27.3 (C-2), 67.2 (C-3), 127.9 (*o*-C of 3-Ph), 128.8 (*o*-C of 1-Ph, *m*-C), 129.2 (*p*-C of 3-Ph), 133.8 (*p*-C of 1-Ph), 134.1 (*ipso*-C of 1-Ph), 137.2 (*ipso*-C of 3-Ph), and 193.1 (C-1), *m/z* 377 ($M^{+\cdot}$), 246 ($M^{+\cdot} - C_7H_5N_2$), 222 ($M^{+\cdot} - IN_2$), and 208 ($M^{+\cdot} - IN_3$).

4-*Azido*-3-*iodo*-4-*methylpentan*-2-*one* (24).—4-Methylpent-3-en-2-one (30) (0.5 g, 5.1 mmol) was treated with iodine(I) azide (5.61 mmol) in acetonitrile (5.5 ml) using procedure (a). Work-up gave 4-*azido*-3-*iodo*-4-*methylpentan*-2-*one* (1.06 g, 78%), b.p. 117° (Kugelrohr) at 0.5 mmHg (Found: C, 27.1; H, 3.8; N, 16.3. $C_6H_{10}IN_3O$ requires C, 26.9; H, 3.8; N, 15.7%), $\nu_{max.}$ 1 705 cm^{-1} (CO), δ_H (CCl_4) 1.58 (s, 4-CH_3), 2.42 (s, $COCH_3$), and 4.57 (s, CHI), δ_C 24.3 (C-5), 25.2 (4-CH_3), 28.1 (C-1), 41.8 (C-3), 61.6 (C-4), and 200.9 (C-2), *m/z* 267 ($M^{+\cdot}$), 225 ($M^{+\cdot} - \dot{N}_3$), and 98 ($M^{+\cdot} - IN_3$).

erythro-4-*Azido*-3-*iodo*-4-*phenylbutan*-2-*one* (26).—This was prepared from (*E*)-4-phenylbut-3-en-2-one (32) in 60% yield using procedure (a). It had m.p. 80—82° (from aqueous methanol) (lit.,[17] 86—87°), $\nu_{max.}$ 1 715 cm^{-1} (CO), δ 2.50 (s, $COCH_3$), 4.58 (d, *J* 11 Hz, 3-H), 4.98 (d, *J* 11 Hz, 2-H), and 7.25 (m, ArH), *m/z* 315 ($M^{+\cdot}$), 272 ($M^{+\cdot} - HN_3$), 184 ($M^{+\cdot} - N_2 - C_6H_5CN$), 160 ($M^{+\cdot} - \dot{I}N_2$), 146 ($M^{+\cdot} - IN_3$), and 145 ($M^{+\cdot} - I - HN_3$).

erythro-4-*Azido*-3-*iodo*-4-(4-*methoxyphenyl*)*butan*-2-*one* (25).—(*E*)-4-(4-Methoxyphenyl)but-3-en-2-one (31) (0.44 g, 2.5 mmol) was treated with iodine(I) azide (2.5 mmol) in acetonitrile (5.5 ml) using procedure (a). Work-up gave a yellow oil (0.75 g) which solidified. Crystallisation from aqueous methanol gave erythro-4-*azido*-3-*iodo*-4-(4-*methoxyphenyl*)*butan*-2-*one* (0.56 g, 65%) as needles, m.p. 87—88° (Found: C, 38.4; H, 3.5; I, 36.4; N, 12.5. $C_{11}H_{12}IN_3O_2$ requires C, 38.3; H, 3.5; I, 36.8; N, 12.2%), $\nu_{max.}$ 1 720 cm^{-1} (CO), δ_H 2.45 (s, $COCH_3$), 3.97 (s, OCH_3), 4.55 (d, *J* 10 Hz, 3-H), 4.92 (d, *J* 10 Hz, 2-H), 6.80 and 7.15 (2d, *J* 8 Hz, ArH), δ_C 26.7 (C-2), 34.0 (C-4), 55.3 (OCH_3), 66.6 (C-4), 114.2 (*m*-C), 128.5 (*ipso*-C), 129.0 (*o*-C), 160.1 (*p*-C), and 200.4 (C-2), *m/z* 345 ($M^{+\cdot}$), 303 ($M^{+\cdot} - \dot{N}_3$), 190 ($M^{+\cdot} - \dot{I}N_2$), and 176 ($M^{+\cdot} - IN_3$).

Methyl erythro-3-*Azido*-2-*iodo*-3-(4-*methoxyphenyl*)*propanoate* (27).—Methyl (*E*)-3-(4-methoxyphenyl)propenoate (9) (0.48 g, 2.50 mmol) was treated with iodine(I) azide (2.5 mmol) in acetonitrile (5.5 ml) using procedure (a). Work-up followed by p.l.c. (hexane–ether, 19 : 1) gave starting material (80 mg, 17%) and *methyl* erythro-3-*azido*-2-*iodo*-3-(4-*methoxyphenyl*)*propanoate* (0.64 g, 71%), needles (from methanol), m.p. 47—49° (Found: C, 36.4; H, 3.4; N, 11.5. $C_{11}H_{12}IN_3O_3$ requires C, 36.6; H, 3.4; N, 11.6%), $\nu_{max.}$ 1 740 cm^{-1} (CO), δ_H 3.70 (s, OCH_3), 3.73 (s, CO_2CH_3), 4.45 (d, *J* 10 Hz, 2-H), 4.95 (d, *J* 10 Hz, 3-H), 6.92 and 7.25 (2d, *J* 10 Hz, ArH), δ_C 23.3 (C-2), 47.7 (C-3), 53.2 (OCH_3), 55.3 (*p*-C), 114.2 (*o*-C), 128.1 (C-4), 129.0 (*ipso*-C), 160.3 (*m*-C), and 170.1 (C-1), *m/z* 361 ($M^{+\cdot}$), 333 ($M^{+\cdot} - N_2$), 319 ($M^{+\cdot} - \dot{N}_3$), 289 ($M^{+\cdot} - \dot{N}_3 - CH_2O$), 258 ($M^{+\cdot} - \dot{N}_3 - CH_2O - \dot{O}CH_3$), and 192 ($M^{+\cdot} - IN_3$).

Treatment of Methyl (E)-3-*Phenylpropenoate with Iodine*(I) *Azide and then Cyclohexene*.—The unsaturated ester (1) (0.41 g, 2.5 mmol) was added to a solution of iodine(I) azide (2.53 mmol) in acetonitrile (5.5 ml) prepared as in procedure (a). Analysis (^{1}H n.m.r.) after 7 h at 20 °C indicated that the mixture contained starting material and the iodo-azide adduct (10) in the ratio 55 : 45. Addition of cyclohexene (0.25 g, 3.0 mmol) as in procedure (a) and work-up after 24 h at 20 °C gave an oil (0.87 g). P.l.c. (hexane–ether, 9 : 1) gave (i) a mixture (^{1}H n.m.r.) (0.42 g) of starting material (1) and the iodo-azide adduct (10) in the ratio 73 : 27, and (ii) *trans*-1-azido-2-iodocyclohexane (33) (0.25 g) (i.r. and ^{1}H n.m.r. spectra).

Reactions of Methyl (E)-3-*Phenylpropenoate with Iodine*(I)

Chloride.—(a) *In acetonitrile*. Methyl (*E*)-3-phenylpropenoate (1) (0.60 g, 3.70 mmol) was added to a solution of iodine(I) chloride (0.72 g, 4.43 mmol) in acetonitrile (15 ml) and the mixture was stirred at 20 °C for 3 h. The mixture was poured into 10% aqueous sodium thiosulphate and extracted with ether, and the extract was dried and concentrated to yield an oil (1.02 g). Crystallisation from aqueous methanol gave methyl *erythro*-3-chloro-2-iodo-3-phenylpropanoate (14) (0.44 g, 37%), as needles, m.p. 101—105° (decomp.), $\nu_{max.}$ 1 710 cm^{-1}, δ 3.87 (s, CO_2CH_3), 4.83 (d, *J* 10 Hz, 2-H), 5.35 (d, *J* 10 Hz, 3-H), and 7.35 (m, ArH), *m/z* 326, 324 ($M^{+\cdot}$), 295, 293 ($M^{+\cdot}$ — $\dot{O}CH_3$), 288 ($M^{+\cdot}$ — HCl), 199, 197 ($M^{+\cdot}$ — $\dot{I}$), and 162 ($M^{+\cdot}$ — ICl).

(b) *With addition of cyclohexene*. Iodine(I) chloride (0.41 g, 2.52 mmol) was added to a solution of the unsaturated ester (1) (0.41 g, 2.53 mmol) in acetonitrile (5.5 ml) and the mixture was stirred at 20 °C for 2 h. Analysis (^1H n.m.r.) of the mixture indicated the presence of starting material (25%) and the iodo-chloride adduct (14) (75%). Cyclohexene (0.25 g, 3.0 mmol) was added to the mixture which was stirred at 20 °C for 24 h. Work-up as in part (a) gave an oil (0.86 g) containing approximately equal amounts of methyl (*E*)-3-phenylpropenoate (1) and *trans*-1-chloro-2-iodo-cyclohexane [18] (^1H n.m.r. spectrum).

Kinetics of Iodine(I) *Azide Addition to α,β-Unsaturated Carbonyl Compounds*.—A 0.455 mol l^{-1} solution of iodine(I) azide in acetonitrile was prepared by reaction of sodium azide with iodine(I) chloride as described in procedure (a). A known mass of the unsaturated substrate was added to the solution to give a mixture which was also 0.455 mol l^{-1} in unsaturated substrate. The heterogeneous mixture was stirred at 19—20 °C and at intervals samples of the supernatant solution were removed by pipette and analysed by ^1H n.m.r. The relative integral heights of the upfield doublet of the *vicinal* protons of the unsaturated substrate and one half of the *vicinal* protons of the corresponding iodo-azide adduct were used to determine the percentage of reaction. No significant difference in the ratio of unsaturated substrate to iodo-azide adduct was observed before work-up (as above) or after work-up as described in general procedure (a).

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