

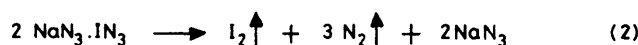
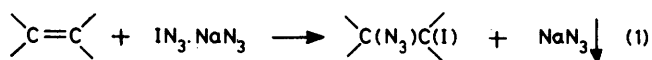
Aspects of the Addition of Iodine(I) Azide to Alkenes

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Iodine(I) azide, formed from sodium azide-iodine(I) chloride, exists in acetonitrile as a complex with sodium azide. Addition of iodine(I) azide to cyclohexene gives a *cis*-iodo-azide as well as the expected *trans*-adduct. The addition of iodine(I) azide to a mixture of (*Z*)- and (*E*)-[β -²H]styrene occurs in a stereospecific manner. In contrast to a literature report, the addition of iodine(I) azide to 1-methylcyclohexene is faster than to cyclohexene. Intermediates in these reactions are discussed.

THE addition of iodine(I) azide to alkenes has been regarded as a highly regioselective and stereoselective method of introducing an azide function into an organic molecule.¹ However, our recent studies^{2,3} have shown that the addition of iodine(I) azide to certain alkenes is more complex than hitherto believed. For example, depending upon the polarity of the solvent, addition to 3-methyl-5 α -androst-2-ene can lead to a *cis*-iodo-azide as the major adduct or to a product of ring contraction.³ We now report further studies on the nature of the reagent and on its mode of addition to alkenes.

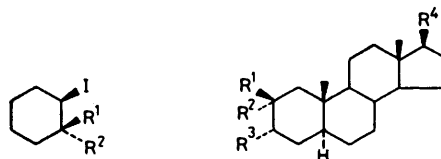
The most widely used method of forming iodo-azides is that of Hassner⁴ in which an alkene is added to a pre-formed solution of iodine(I) azide in acetonitrile. Hassner prepared the reagent from iodine(I) chloride and sodium azide using a mole ratio of 1 : 2.3 but gave no explanation of why such a large excess of sodium azide was required. Our studies indicate that iodine(I) azide is present in this solution as a complex with sodium azide. U.v. measurements showed that a filtered solution of iodine(I) azide formed from a 1 : 1 mixture of iodine(I) chloride and sodium azide in acetonitrile absorbs at 273 nm, while that from a 1 : 2.3 mixture absorbs at 307 nm. Addition of an excess of sodium azide to the former solution caused the absorption band to shift from 273 to 307 nm, suggesting that the latter band was due to a complex. Sodium azide, which is only sparingly soluble in acetonitrile,⁴ showed a weak absorption band at 230 nm while iodine(I) chloride showed a strong absorption band at 230 nm which has been attributed⁵ to the ICl₂⁻ species. The crystalline residues remaining after filtration of the iodine(I) azide solutions were isolated and the amount of sodium azide in each was determined.⁶ These measurements showed that the iodine(I) azide-sodium azide ratio in the complex was *ca.* 1 : 1. The formation of a complex was also shown when a filtered solution of iodine(I) azide prepared from a 1 : 2.3 mixture of reagents in acetonitrile was treated with an alkene whereupon sodium azide was



precipitated [reaction (1)]. Moreover, if the solution was evaporated to dryness, iodine was evolved and sodium

azide was deposited, presumably reflecting the stoichiometry (2). Iodine(I) azide can also be pre-formed in dichloromethane, but repetition of the above experiments provided no evidence that it complexed with sodium azide in this solvent.

As indicated above, *cis*-addition played a major part in the addition of iodine(I) azide to cholest- and androst-2-ene derivatives. That iodine(I) azide also gives *cis*-addition with simpler alkenes has now been established. Reinvestigation of the addition of iodine(I) azide, formed from sodium azide-iodine in acetonitrile, to cyclohexene showed that a hitherto unidentified minor product² from this reaction was the *cis*-iodo-azide (1).⁷ The compound was distinct from the *trans*-isomer (2), its ¹H n.m.r. spectrum showing the presence



- (1) R¹ = N₃, R² = H
 (2) R¹ = H, R² = N₃
 (3) R¹ = H, R² = OH
 (4) R¹ = H, R² = Cl

- (5) R¹ = N₃, R² = R⁴ = H, R³ = I
 (6) R¹ = I, R² = R⁴ = H, R³ = N₃
 (7) R¹ = R⁴ = H, R² = I, R³ = N₃
 (8) R² = N₃, R¹ = R⁴ = H, R³ = I
 (9) R¹ = N₃, R² = R⁴ = H, R³ = OAc
 (10) R¹ = OAc, R² = R⁴ = H, R³ = N₃
 (11) R¹ = N₃, R² = H, R³ = I, R⁴ = C₈H₁₇
 (12) R¹ = I, R² = H, R³ = N₃, R⁴ = C₈H₁₇
 (13) R¹ = N₃, R² = H, R³ = OAc, R⁴ = C₈H₁₇
 (14) R¹ = OAc, R² = H, R³ = N₃, R⁴ = C₈H₁₇

of both equatorial and axial proton multiplets at δ 3.25 and 4.55 [*cf.* δ 3.50 and 3.98 for (2)^{7a}]. Each isomer was stable (t.l.c. analysis) when individually re-subjected to the reaction conditions indicating that they were the products of kinetic control. Hassner¹ has suggested that addition of iodine(I) azide to alkenes generally proceeds by an ionic mechanism *via* a three-membered iodonium ion, thereby accounting for the usual preponderance of *anti*- over *syn*-addition. He has pointed out that orbital symmetry considerations forbid a concerted non-photochemical *syn*-addition and has suggested that once a cyclic iodonium ion has formed, it will open preferentially by *anti*-addition, unless 'equilibration' to a free carbocation occurs. In the cases where

both *cis*- and *trans*-iodo-azides are formed, a simple interpretation is that a cyclic iodonium ion gives the *trans*-product and an open ion may give both the *cis*- and *trans*-products. However, there is little evidence to indicate whether or not these ions are formed simultaneously, sequentially, or are in equilibrium.

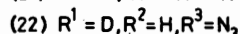
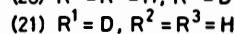
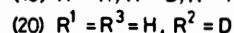
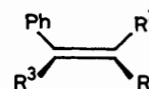
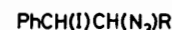
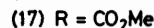
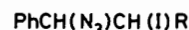
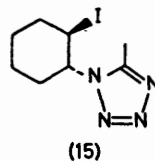
No reaction occurred when cyclohexene was treated with sodium azide-iodine in chloroform but with the addition of 18-crown-6 the *trans*-iodo-azide (2) was formed as the sole product in quantitative yield. The crown ether may facilitate the reaction by solubilizing the sodium azide.*

Treatment of 5 α -androst-2-ene with sodium azide-iodine in the presence of 18-crown-6 also enhanced the formation of adducts (*cf.* ref. 2) resulting in the formation of a 3.4 : 1 mixture (68%) of 2 β -azido-3 α -iodo- (5) and 3 α -azido-2 β -iodo-5 α -androstane (6) and the *cis*-derivatives, 3 α -azido-2 α -iodo- (7) (10%), and 2 α -azido-3 α -iodo-5 α -androstane (8) (trace). Solvolysis of a pure sample of the iodo-azide (5) with silver(I) acetate in acetic acid gave the azido-acetate (9) (81%) while similar solvolysis of the compound (6) gave the azido-acetate (10) (86%). Solvolysis of the mixture of *trans*-adducts (11) and (12) obtained previously² from 5 α -cholest-2-ene gave a mixture of the azido-acetates (13) and (14).

A further examination of the reaction of cyclohexene with sodium azide-iodine in chloroform-water^{7a} showed that while the relative molar ratio of the *cis*-iodo-azide (1) remained constant that of the *trans*-iodo-azide (2) increased with the addition of the phase-transfer catalyst Adogen 464 or of Adogen 464 plus more sodium azide. The relative molar amounts of the *trans*-iodohydrin (3)⁸ but not of the *trans*-iodo-chloride (4),⁹ decreased with these changes. A simple interpretation of these results is that both iodo-azides arise from bridged ion intermediates which are not in equilibrium and that the *cis*-iodo-azide is formed from a bridged ion which contains azide whereas the *trans*-iodo-azide is formed from a cyclic iodonium ion.

In earlier work we showed that treatment of cyclohexene with thallium(I) azide-iodine in acetonitrile gave the *trans*-iodotetrazole (15)² as the major product, the compound probably arising by attack of azide ion on a Ritter-type intermediate followed by cyclization.^{2,10} When the solvent was changed to dichloromethane this reaction gave the *trans*-iodo-azide (2).² In the present study, treatment of styrene with thallium(I) azide-iodine in dichloromethane gave (1-azido-2-iodoethyl)-benzene (16) in 30% yield, but no trace of the regioisomer (18) which was formed as a minor product when styrene was treated with sodium azide-iodine(I) chloride in dichloromethane. Hassner reports the isolation of only the compound (16) when the latter reaction is carried out in acetonitrile.^{4,11} Treatment of methyl *trans*-cinnamate with thallium(I) azide-iodine in dichloromethane gave starting material and a mixture of azide-containing products but none of the expected iodo-azide (17). The

latter was isolated in 43% yield by Hassner when methyl cinnamate was treated with sodium azide-iodine(I) chloride in acetonitrile.⁴ In our hands, repetition of this reaction afforded a crude yield of 79% of (17) but only a



42% yield was obtained after work up. Compound (17) was recovered unchanged from attempted solvolysis with silver(I) acetate.

Hassner found that iodine(I) azide in acetonitrile added to (*Z*)-[β -²H]styrene to give a product (isolated in 83% yield) of *anti*-addition which on elimination of hydriodic acid gave the alkene (19) in 96% yield.¹² Adduct formation occurs either by a process not involving a carbocationic intermediate or if *via* a carbocation by one with a lifetime or structure such that no rotation is possible before capture by an azide ion to give a *trans*-product.† However, in view of our results it is still possible that the 17% of unaccounted material in Hassner's experiment could reflect a reaction *via* an open carbocation. In an attempt to gain further insight into the mode of addition of iodine(I) azide we have examined the reaction of sodium azide-iodine(I) chloride in acetonitrile with a 50% molar excess of a 4 : 1 mixture of (*Z*)- and (*E*)-[β -²H]styrenes as substrate. These conditions were designed to ensure complete consumption of the reagent. Whereas Hassner¹² reports iodo-azide formation in 83% yield, the conversion obtained in the present work amounted to 97% after allowance is made for recovery of excess of styrene. Integration of the ¹H n.m.r. spectrum of the crude recovered material confirmed that the ratio of iodo-azides to labelled styrene was 2 : 1 as required. In accord with Hassner's report for styrene the addition to each diastereoisomeric labelled alkene was regiospecific and stereospecifically *anti* as shown by the fact that the *Z* : *E* ratio in the derived vinyl azides (19) and (22) was the same as that, 4 : 1, in the starting alkenes. However, the *Z* : *E* ratio in the recovered labelled styrenes was found to have changed to 3 : 1. Thus the addition of iodine(I) azide to the alkene mixture is faster than isomerization of the alkenes. The

* A referee has suggested that the crown ether may polarise the iodine molecule rather than solubilize the sodium azide.

† We suggest that these intermediates be described as 'closed,' in order to signify their difference from bridged intermediates which still allow *cis*-adduct formation.

precise mode of isomerization of the styrene is uncertain¹³ but can be attributed to traces of iodine formed by decomposition of the iodine(I) azide despite attempts to ensure this did not occur. In an independent experiment a catalytic amount of iodine in diethyl ether was found to scramble the label. Another possibility is that traces of acid (*e.g.* HI or HCl) could be responsible for catalysing the alkene isomerization. Traces of hydrochloric acid could be formed by iodine(I) chloride reacting initially with acetonitrile. Although hydriodic acid could be generated as a result of the adducts decomposing to the vinyl azides, the ¹H n.m.r. spectrum of the total product showed no detectable evidence of such decomposition. The above results indicate that the rate of iodo-azide formation from styrene is faster than the rate of attack by iodine or protic acids and therefore formation of the adduct does not occur *via* a carbocation derived from either iodine or acidic impurities. For this substrate, formation of the iodo-azide occurs *via* one or more closed intermediates, one of which may be a cyclic iodonium ion.

Although the relative rates of reaction of cyclohexene and styrene with iodine(I) azide are not known, values for bromination in methanol show that cyclohexene reacts faster than styrene.¹⁴ The isolation of both *cis*- and *trans*-iodo-azides from cyclohexene compared with the formation of only the Markownikov adduct (16) from styrene in acetonitrile accords with the greater likelihood of the intermediacy of an open carbocation in the former case. This is because the increased electron accession reduces the necessity for bridging in the rate-limiting transition state and increases the lifetime of a carbocationic intermediate.

Hassner has reported that iodine(I) azide reacts faster with cyclohexene than with 1-methylcyclohexene and has attributed this to a lesser steric inhibition to the approach of electrophilic iodine in the case of cyclohexene.⁴ The competition experiment has now been modified with the comparative rates of reaction determined by ¹H n.m.r. analysis of the products rather than by a method which involves correction for losses of volatile alkene prior to analysis by g.l.c. The ¹H n.m.r. analysis showed that 1-methylcyclohexene and cyclohexene had reacted in the ratio 4.5 : 1 rather than in the 1 : 2.5 ratio reported by Hassner. Kinetic experiments in acetonitrile-water (2 : 1) as solvent showed that the rate of addition of iodine(I) azide to 1-methylcyclohexene at 50% reaction was approximately five times that for the reaction with cyclohexene under the same conditions. The similarity of this result to that from the competitive experiment is consistent with a common ionic mechanism in the presence or absence of water. The water was necessary in the kinetic experiments in order to dissolve the sodium azide and thus keep the reactions homogeneous. Although Hassner⁴ and Dehnicke¹⁵ have reported that iodine(I) azide is water sensitive, iodine(I) azide solutions in the present work were found to be stable to water during kinetic runs. Control experiments showed that addition of water to ace-

tonitrile increased the rate of addition of iodine(I) azide to cyclohexene. This effect of water and the increase in rate observed with replacement of a hydrogen atom by a methyl group on an olefinic carbon are clear indications that we are dealing with an electrophilic reaction proceeding *via* carbocationic intermediates. Furthermore, preliminary kinetic results indicate, but do not prove, that second-order kinetics are being followed.

de la Mare¹⁶ has suggested recently that iodo-azides may be formed from alkenes by a termolecular mechanism between the substrate, iodine or iodine azide, and azide ion, pointing out that such a hypothesis is supported by the fact that solvent incorporation occurs less frequently in reactions involving iodine(I) azide than in those involving other molecular iodinating agents. On this basis the formation of the *trans*-iodotetrazole (15) as the major product from the reaction of cyclohexene with thallium(I) azide-iodine in acetonitrile suggests that a termolecular mechanism is not operative in this case. We have found also that addition of azide ions to the reaction of cyclohexene with sodium azide-iodine(I) chloride in acetonitrile-water represses the rate of reaction. This argues against a termolecular reaction in which one species is an azide ion.

EXPERIMENTAL

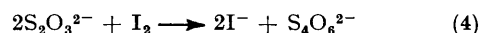
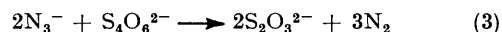
General experimental details are given in ref. 17.

Preparation of Iodine(I) Azide Solutions.—(a) Iodine(I) chloride (0.30 g, 1.9 mmol) in acetonitrile (6 ml) was added dropwise to a stirred suspension of sodium azide (0.28 g, 4.3 mmol) in acetonitrile (6 ml) in a methanol-ice bath. Iodine(I) azide formation was indicated by the colour change reported by Hassner *et al.*⁴ The mixture was stirred for 10 min, filtered through Celite, and diluted to 25 ml with acetonitrile, λ_{\max} 307 nm.

(b) Iodine(I) chloride (0.30 g, 1.9 mmol) and sodium azide (0.12 g, 1.9 mmol) were reacted as above in acetonitrile, λ_{\max} 273 nm.

(c) Iodine(I) chloride and sodium azide were reacted as in (a) but with dichloromethane as solvent, λ_{\max} 245 and 337 nm.

Determination of Sodium Azide.—Sodium azide was dissolved in water, iodine solution (0.08M) was added in portions (10 ml) until no more reacted with the azide, and the solution was titrated with sodium thiosulphate solution (0.1M) until all the iodine colour had disappeared. Further iodine solution (10 ml) was added and the solution was again titrated with sodium thiosulphate, the procedure being repeated until the quantity of thiosulphate solution required to react with 10 ml of iodine solution was constant. The number of moles of iodine used minus half the number of moles of sodium thiosulphate used, could then be equated to half of the number of moles of sodium azide present. This follows from the fact that 2 moles of azide regenerates 2 moles of thiosulphate which can then react with 1 mole of iodine [reactions (3) and (4)].



Reactions of Cyclohexene with Iodine(I) Azide.—(a) A solution of iodine (0.32 g, 1.25 mmol) in acetonitrile (20 ml)

was added dropwise to a stirred suspension of sodium azide (0.165 g, 2.5 mmol) in cyclohexene (82 mg, 1.0 mmol) and acetonitrile (10 ml). The mixture was stirred at 20 °C for 18 h, poured into water, and extracted with ether. Work-up and p.l.c. (hexane-ether, 9:1) gave *trans*-(2) ^{2,4} (70 mg, 28%), and *cis*-1-azido-2-iodocyclohexane (1) ⁷ (20 mg, 8%) as an oil, ν_{\max} 2 100 cm⁻¹ (N₃), δ 3.25 (m, 1-H) and 4.55 (m, 2-H), *m/e* 251 (M⁺), 96 (M⁺ - I⁻ - N₂), and 81 (M⁺ - HI - N₃⁺).

(b) A suspension of sodium azide (0.39 mg, 6.0 mmol) in a solution of 18-crown-6 (0.32 g, 1.2 mmol) and chloroform (15 ml) was stirred at 20 °C for 10 min and then treated with iodine (0.61 g, 2.4 mmol). Cyclohexene (82 mg, 1.0 mmol) was added and the mixture stirred overnight. Water was added and the mixture extracted with dichloromethane. The extract was washed with aqueous sodium disulphite, dried, and passed through a column of silica gel to remove the crown ether. Removal of solvent gave *trans*-1-azido-2-iodocyclohexane (100%).

(c) (With H. H. LEE) The reactions in the Table were carried out by adding a solution of sodium azide (0.41 g, 6.25 mmol) in water (1.5 ml) to iodine (0.76 g, 3.0 mmol) in chloroform (10 ml). Cyclohexene (0.10 g, 1.25 mmol) was added and the mixture stirred at 20 °C for 24 h. Work-up gave an oil which was analysed by ¹H n.m.r. spectroscopy.

Conditions	Total % conversion	(1)	(2)	(3)	(4)
CHCl ₃ -H ₂ O	53	12	29	12	
CHCl ₃ -H ₂ O-Adogen 464	74	11	52	7	4
CHCl ₃ -H ₂ O-Adogen 464 (with doubled NaN ₃)	68	11	54	Trace	3

(d) A suspension of thallium(I) azide ¹⁸ (1.48 g, 6.0 mmol) in a solution of 18-crown-6 (0.32 g, 1.2 mmol) in dichloromethane (15 ml) was stirred for 10 min and then treated with iodine (0.61 g, 2.4 mmol). Cyclohexene was added and the mixture was stirred overnight. The precipitate was filtered off and dichloromethane was added to the filtrate. Work-up of the solution as in (b) and purification by p.l.c. gave *trans*-1-azido-2-iodocyclohexane (70 mg, 28%).

Reaction of 5 α -Androst-2-ene with Iodine(I) Azide and Crown Ether.—A mixture of sodium azide (98 mg, 1.5 mmol) and 18-crown-6 (79 mg, 0.3 mmol) in chloroform was stirred at 20 °C for 10 min and then treated with iodine (0.15 g, 0.6 mmol). 5 α -Androst-2-ene (65 mg, 0.25 mmol) in chloroform (0.5 ml) was added and the mixture was stirred at 20 °C for 53 h. Work-up gave a solid (0.11 g, 97%) which was separated by p.l.c. (hexane) into (i) a mixture (73 mg, 68%) of 2 β -azido-3 α -iodo- (5) ² and 3 α -azido-2 β -iodo-5 α -androstane (6) ² in the ratio 3.4:1; and (ii) 3 α -azido-2 α -iodo- (7) ³ (11 mg, 10%) containing a trace of 2 α -azido-3 α -iodo-5 α -androstane (8), δ [for (8)] 0.67 (s, 18-H₃), 0.90 (s, 19-H₃), 4.00* (m, *W*_{1/2} 8 Hz, CHN), and 4.50 (m, *W*_{1/2} 22 Hz, CHI).

Solvolysis of 2 β -Azido-3 α -iodo-5 α -androstane.—A solution of the iodo-azide (5) (0.19 g, 0.45 mmol), in dry acetic acid (10 ml) was stirred with silver(I) acetate (82 mg, 0.49 mmol) overnight at 20 °C and the mixture was warmed on a water-bath for 30 min. Silver iodide was filtered off, the product was extracted into ether, and the extract was washed with water and saturated sodium hydrogencarbonate solution. Solvent was removed from the dried solution to give a solid (0.16 g) which after purification by p.l.c. (hexane-ether, 9:1) afforded 2 β -azido-5 α -androstane-3 α -yl acetate (9) (0.13 g,

* The corresponding peak in the spectrum of (7) should read δ 4.05 not δ 4.50 as recorded.²

81%), needles (from methanol-ether), m.p. 129–132.5° (Found: C, 70.3; H, 9.3; N, 11.45. C₂₁H₃₃N₃O₂ requires C, 70.2; H, 9.25; N, 11.7%), ν_{\max} 2 100 (N₃) and 1 720 cm⁻¹ (OAc), δ 0.71 (s, 18-H₃), 1.01 (s, 19-H₃), 2.08 (s, OAc), 3.84 (m, *W*_{1/2} 9 Hz, 2-H), and 4.87 (m, *W*_{1/2} 7 Hz, 3-H).

Solvolysis of 3 α -Azido-2 β -iodo-5 α -androstane.—The iodo-azide (6) (0.12 g, 0.28 mmol) was treated with silver(I) acetate (52 mg, 0.31 mmol) in acetic acid (6 ml) as above. Work-up gave crystals (0.10 g) which were purified by p.l.c. to give 3 α -azido-5 α -androstane-2 β -yl acetate (10) (87 mg, 86%), needles (from methanol-ether), m.p. 115–116° (Found: C, 70.2; H, 9.2; N, 11.6. C₂₁H₃₃N₃O₂ requires C, 70.2; H, 9.25; N, 11.7%), ν_{\max} 2 100 (N₃) and 1 735 cm⁻¹ (OAc), δ 0.71 (s, 18-H₃), 0.97 (s, 19-H₃), 2.07 (s, OAc), 3.78 (m, *W*_{1/2} 6 Hz, 3-H), and 4.89 (m, *W*_{1/2} 7 Hz, 2-H).

Solvolysis of the Mixture of 2 β -Azido-3 α -iodo- and 3 α -Azido-2 β -iodo-5 α -cholestane.—The iodo-azides (11) and (12) ² (0.17 g, 0.32 mmol) were treated with silver(I) acetate (58 mg, 0.35 mmol) in acetic acid (10 ml) as above. Work-up gave an oil (0.15 g) which was purified by p.l.c. to give a mixture (0.10 g, 67%) of 2 β -azido-5 α -cholestan-3 α -yl acetate (13) and 3 α -azido-5 α -cholestan-2 β -yl acetate (14) as an oil (Found: C, 74.0; H, 10.5; N, 8.4. Calc. for C₂₉H₄₉O₂N₃: C, 73.8; H, 10.5; N, 8.9%), ν_{\max} 2 100 (N₃) and 1 730 cm⁻¹ (OAc), δ 0.65 (s, 2 × 18-H₃), 0.82–1.00 (8 × Me), 2.04 (s, OAc), 2.07 (s, OAc), 3.80 (m, 2 × CHN), and 4.91 (m, *W*_{1/2} 7 Hz, 2 × CHOAc).

Reaction of Methyl trans-Cinnamate with Sodium Azide-Iodine(I) Chloride.—A solution of methyl *trans*-cinnamate (0.16 g, 1.0 mmol) in acetonitrile (20 ml) was treated with sodium azide (0.16 g, 2.5 mmol) and iodine(I) chloride (0.16 g, 0.11 mmol) by Hassner's method.⁴ The mixture was stirred overnight and worked up to give an oil. P.l.c. (benzene-hexane, 1:1) gave methyl 3-azido-2-iodo-3-phenylpropionate (17) (0.14 g, 42%) (Found: C, 55.4; H, 5.1. C₁₂H₁₃N₃O₄ requires C, 54.8; H, 5.0%), ν_{\max} 2 100 cm⁻¹ (N₃), δ 3.55 (d, *J* 10 Hz, 2-H), 3.83 (s, OMe), 5.30 (d, *J* 10 Hz, 3-H), and 7.27 (m, ArH).

The iodo-azide (17) was recovered after attempted solvolysis with silver(I) acetate in glacial acetic acid under reflux for 1 h.

Reaction of Methyl trans-Cinnamate with Thallium(I) Azide-Iodine.—A solution of iodine (0.32 g, 1.25 mmol) in dichloromethane (20 ml) was added dropwise to a stirred suspension of thallium(I) azide (0.62 g, 2.5 mmol) in a solution of methyl *trans*-cinnamate (0.81 g, 5.0 mmol) in dichloromethane (10 ml). The mixture was stirred for 24 h, filtered, and the filtrate was worked up as above to give an orange oil which contained ca. 30% of starting material. P.l.c. (hexane-ether, 9:1) gave a number of azide-containing products but no methyl 3-azido-2-iodo-3-phenylpropionate.

Reaction of Styrene with Thallium(I) Azide-Iodine.—Styrene (0.52 g, 5.0 mmol) was treated with iodine and thallium(I) azide in dichloromethane as in the previous experiment. Work-up gave a yellow oil (1.38 g) which contained no starting material. P.l.c. gave (1-azido-2-iodoethyl)benzene (16) (30%); the ¹H n.m.r. spectrum was identical with that of an authentic sample.⁴ Minor products were not identified.

(*Z*)- and (*E*)-[β -³H]Styrenes (20) and (21).—This material was prepared by the method of Hassner *et al.*¹² via phenyldeuterioacetylene. ¹H n.m.r. analysis showed that the product contained β -deuterioethylbenzene (21%), (*E*)-[β -³H]styrene (16%), δ 5.64 (d, *J* 18 Hz, β -H), and (*Z*)-[β -³H]styrene (63%), δ 5.20 (d, *J* 11 Hz, β -H).

Addition of Iodine(I) Azide to (Z)- and (E)-[β - 2 H]Styrenes.—The 4 : 1 mixture of (*Z*)- and (*E*)-[β - 2 H]styrene (0.16 g, 1.5 mmol) in acetonitrile was treated with iodine(I) azide, prepared from sodium azide (0.16 g, 2.5 mmol) and iodine(I) chloride (0.16 g, 1.0 mmol). Work-up gave an oil (0.30 g) in which unchanged material was analysed from the 1 H n.m.r. spectrum. P.l.c. gave the iodo-azides (0.18 g, 66%) which were treated with potassium *t*-butoxide by Hassner's method.⁴ Work-up gave an oil (72 mg) which contained (1 H n.m.r. analysis) the *cis*-(19)¹² and *trans*-(22) vinyl azides in the ratio 4 : 1.

Competitive Reaction of Cyclohexene and 1-Methylcyclohexene with Iodine(I) Azide.—Cyclohexene (0.82 g, 1.0 mmol) and 1-methylcyclohexene (0.96 g, 1.0 mmol) in acetonitrile were treated with iodine(I) azide (1.0 mmol), prepared from sodium azide and iodine(I) chloride as above. The mixture was stirred at 20 °C for 4.3 h and worked up to give a yellow oil (0.26 g). 1 H N.m.r. analysis showed that it contained *trans*-1-azido-2-iodo-1-methylcyclohexane and *trans*-1-azido-2-iodocyclohexane in the ratio 4.5 : 1.

[7/2250 Received, 22nd December, 1977]

REFERENCES

- ¹ A. Hassner, *Accounts Chem. Res.*, 1971, **4**, 9.
- ² R. C. Cambie, R. C. Hayward, P. S. Rutledge, T. Smith-Palmer, and P. D. Woodgate, *J.C.S. Perkin I*, 1976, 840.
- ³ R. C. Cambie, P. S. Rutledge, T. Smith-Palmer, and P. D. Woodgate, *J.C.S. Perkin I*, 1977, 2250.
- ⁴ W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, 1967, **89**, 2077.
- ⁵ R. E. Buckles and J. F. Mills, *J. Amer. Chem. Soc.*, 1954, **76**, 4845.
- ⁶ (a) S. Suzuki, *Kogyo Kagaku Zasshi*, 1962, **65**, 898 (*Chem. Abs.*, 1963, **58**, 10,732); (b) A. Wtorkowska-Zaremba, *Chem. Analyt. (Warsaw)*, 1969, **14**, 847 (*Chem. Abs.*, 1970, **72**, 8996).
- ⁷ (a) P. D. Woodgate, H. H. Lee, P. S. Rutledge, and R. C. Cambie, *Synthesis*, 1977, 462; (b) H. Loibner and E. Zbiral, *Helv. Chim. Acta*, 1976, **59**, 2100.
- ⁸ R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, *J.C.S. Perkin I*, 1974, 1858.
- ⁹ R. C. Cambie, W. I. Noall, G. J. Potter, P. S. Rutledge, and P. D. Woodgate, *J.C.S. Perkin I*, 1977, 222.
- ¹⁰ A. Hassner, L. A. Levy, and R. Gault, *Tetrahedron Letters*, 1966, 3119.
- ¹¹ A. Hassner and F. Boerwinkle, *Tetrahedron Letters*, 1969, 3309.
- ¹² A. Hassner, F. P. Boerwinkle, and A. B. Levy, *J. Amer. Chem. Soc.*, 1970, **92**, 4879.
- ¹³ H.-O. Kalinowski and H. Kessler in 'Topics in Stereochemistry,' eds. E. L. Eliel and N. L. Allinger, Interscience, New York, 1975, vol. 7, p. 305.
- ¹⁴ J. E. Dubois and A. Schwarcz, *Tetrahedron Letters*, 1964, 2167; J. E. Dubois and G. Barbier, *ibid.*, 1965, 1217.
- ¹⁵ K. Dehnicke, *Angew. Chem. Internat. Edn.*, 1976, **15**, 553.
- ¹⁶ P. B. D. de la Mare, 'Electrophilic Halogenation,' Cambridge University Press, Cambridge, 1976, p. 174.
- ¹⁷ R. C. Cambie, G. J. Potter, P. S. Rutledge, and P. D. Woodgate, *J.C.S. Perkin I*, 1977, 530.
- ¹⁸ W. S. McEwan and M. M. Williams, *J. Amer. Chem. Soc.*, 1954, **76**, 2182.