

Reactions of Norcarane and of Norborn-2-ene with Iodine(I) Azide and Iodine(I) Chloride †

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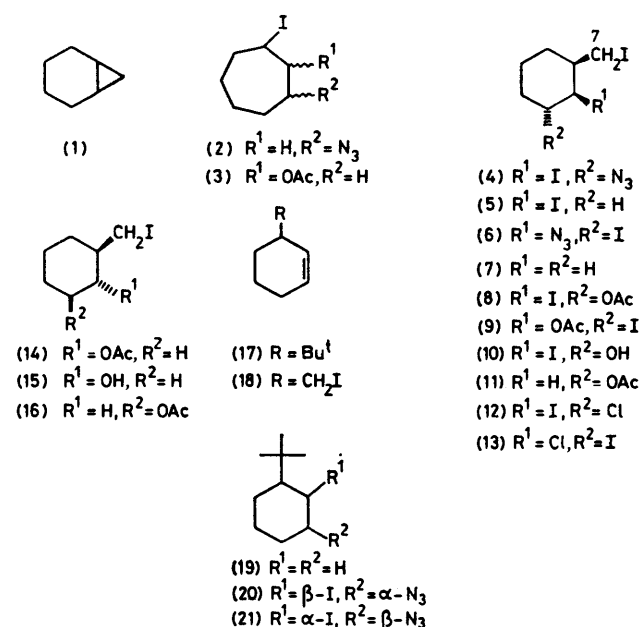
With iodine(I) azide or iodine(I) chloride norcarane gives products of ring opening as well as those of fragmentation followed by addition. Reactions of norborn-2-ene with iodine(I) azide under conditions which favour either an ionic or a radical path have also been examined.

In earlier work¹ we showed that treatment of norcarane (bicyclo[4.1.0]heptane) (1) with iodine(I) acetate afforded products not only of ring opening but also of fragmentation and subsequent addition reactions. We have continued our investigations of the reactions of positive iodine species with the weakly π cyclopropyl system by an examination of those of iodine(I) azide and iodine(I) chloride with norcarane.

Treatment of norcarane (1) with iodine(I) azide (1.1 mol equiv.) in acetonitrile for 75 h gave the iodo-azide (2) (5%) and the di-iodo-azides (4) (24%) and (6) (6%), while reaction in pentane gave the known di-iodide¹ (5) (16%) as well as the di-iodo-azides (4) (30%) and (6) (3%). The i.r. spectrum of the cycloheptyl derivative (2) showed azide absorption (2100 cm^{-1}) while the mass spectrum showed the molecular ion at m/z 265 in agreement with the molecular formula $\text{C}_7\text{H}_{12}\text{IN}_3$, and peaks corresponding to losses of HI and $\cdot\text{N}_3$. The ^1H n.m.r. spectrum included signals at δ 3.50 and 4.20 assigned to methine protons geminal to an iodine atom and to an azido-group, respectively, but no signals corresponding to a side chain substituted on a cyclohexyl or a cyclopentyl ring. Of the structures which are expected to arise from norcarane² and which are consistent with the above data, *viz.* a 1,2- or 1,3-disubstituted cycloheptane, structure (2) is favoured since the ^1H n.m.r. spectrum showed a shoulder on the methylene envelope extending down to δ 2.3 unlike that of 2-iodocycloheptyl acetate (3).¹

The i.r. spectra of the cyclohexyl di-iodo-azides (4) and (6) each showed strong azide absorption while the mass spectra of each showed the molecular ion at m/z 391 supporting the molecular formula $\text{C}_7\text{H}_{11}\text{I}_2\text{N}_3$. Also present in the mass spectra were peaks corresponding to losses of $\cdot\text{N}_3$, $\cdot\text{I}$, and $\text{I}_2 + \cdot\text{N}_3$. The ^1H n.m.r. spectra of compounds (4) and (6) each contained a two-proton signal at δ 3.15 assigned to an iodomethyl group,¹ and signals due to methine protons geminal to an azido-group (δ 4.20 and 4.00, respectively) and to an iodo-group (δ 4.70 and 4.50, respectively). The ^{13}C n.m.r. spectra of these two isomers are reported in Table 1; the signals from the conformationally biased iodo-azide adducts³ of 3-*t*-butylcyclohexene (17) are included for comparison. The high-field chemical shifts of the side-

chain carbon atoms show clearly that compounds (4) and (6) both possess iodomethyl groups,⁴ while the half-height widths of their H-1 and H-2 signals and the chemical shifts of the carbon atoms bearing the azido-function indicate that these substituents are likely to be



axial,³ even although vicinal disubstitution may itself induce an upfield shift of *ca.* 3 p.p.m.⁵

Abstraction of substituent chemical shift additivity values from the spectra of compound (20) and its parent hydrocarbon⁶ (19), and application of the derived $\Delta\delta$ values to the spectrum of iodomethylcyclohexane⁴ (7) gives a calculated spectrum for (4) in good agreement with that observed. In contrast, use of substituent

TABLE 1

^{13}C N.m.r. spectra of *vic*-iodo-azides and related compounds

Compd.	C-1	C-2	C-3	C-4	C-5	C-6	C-7
(7) ^a	26.1	33.4	40.0	33.4	26.1	25.9	16.1
(4)	63.7	41.6 ^b	38.8 ^b	28.5	20.1	24.5	14.3
(6)	30.9	66.4	38.2	30.1 ^b	21.6 ^b	27.2 ^b	9.1
(19) ^a	27.8	28.2	48.9	28.2	27.8	27.2	32.3
(20)	65.8	36.9	44.7	25.0	21.7	24.3	32.6
(21)	68.8	36.2	53.3	21.7 ^b	25.6 ^b	29.7 ^b	34.4

^a Numbered as for the other compounds for ease of comparison. ^b Tentative assignments.

† *Editor's Note:* IUPAC now recommends the names 'trinnorbornane' and 'trinnorcarane' for the structures previously referred to as 'norbornane' and 'norcarane', respectively. The older names are retained here for clarity.

data derived from the spectra of the stereoisomers (21) and (19) does not give acceptable chemical shift values for (6), indicating that this compound is a regioisomer rather than a stereoisomer of (4). In the spectrum of (6) the signals for the carbon atoms bearing iodine atoms are significantly upfield from those in the spectrum of (4) indicating increased steric interaction⁷ in the former compound.

attached. Consequently, the iodomethyl alkene (18) might be expected to react in electrophilic additions in a manner similar to that of 3-*t*-butylcyclohexene (17).^{3,9} However, whereas 3-*t*-butylcyclohexene gives a *trans*-diaxial adduct and a *trans*-diequatorial adduct as the major products from reactions with a variety of electrophilic reagents, the analogous reactions with 3-iodomethylcyclohexene give two diaxial adducts exclusively,

TABLE 2
Reactions of norcarane with iodine(i) chloride (for *ca.* 75 h)

Reagent	Solvent	Substrate-reagent ratio	Products (% yield)								
			(14)	(15)	(8)	(9)	(10)	(11), (16)	(12)	(13)	
ICl	HOAc	1:1	35	3	7	2			6	4	1
ICl-NaOAc	HOAc	1:1:1	27	7	1	Trace			3	12	3
ICl-NaOAc	HOAc	1:1.5:3	50	13	1	0.5			6	23	5
ICl	CH ₂ Cl ₂	1:2								47	42
ICl-H ₂ O	CHCl ₃ -TS ^a (1:1)	1:2:2		6				9.5		16	3

^a TS = tetramethylene sulphone.

Because iodine(i) chloride is a more reactive source of electropositive iodine than iodine(i) acetate,⁸ the reactions of norcarane with this reagent were also examined. Products are summarized in Table 2. With the exception of the di-iodochlorides (12) and (13) the products have been obtained previously from the reaction of iodine(i) acetate with norcarane.¹ However, no product of the addition of only 1 equiv. of iodine(i) chloride was detected. The structures of the di-iodochlorides (12) and (13) were assigned by comparison of their spectra with those of the corresponding di-iodo-acetates (8) and (9).¹

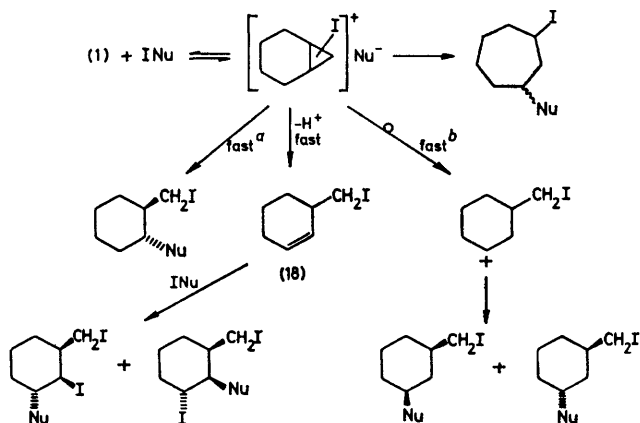
As in the case of reaction of iodine(i) acetate with norcarane, the formation of the products of addition of iodine(i) azide and of iodine(i) chloride can be rationalized if opening of the cyclopropane ring is concerted with nucleophilic attack (Scheme 1).

viz. (4) and (6). In the latter case antiparallel opening of the iodonium ion by attack of the nucleophile at C-2 to give the diaxial adduct (6) is possible because rotation about the C(3)-CH₂I bond can position the iodine atom away from the nucleophile. This process contrasts with that proposed for 3-*t*-butylcyclohexene,³ where twisting of the cyclohexane ring leads to a diequatorial adduct.

Reaction of phenylcyclopropane (22) with iodine(i) azide in acetonitrile gave unidentified products in less than 5% conversion, whereas in pentane 62% conversion occurred to afford only 1-azido-3-iodo-1-phenylpropane (23). The structure of the latter followed from an examination of its spectra; in particular the azido-group could be placed in a benzylic position since the mass spectrum showed a peak attributable to C₇H₈N₃⁺ but none to C₇H₈I⁺. The ¹H n.m.r. spectrum included a two-proton multiplet at δ 2.25 assigned to methylene protons vicinal to three non-equivalent protons, two overlapping one-proton triplets at δ 3.19 and 3.23 assigned to the diastereotopic protons of an iodomethyl group, and a one-proton triplet at δ 4.67 assigned to a benzylic proton geminal to an azido-group. Double irradiation experiments confirmed that the protons giving rise to the signals at δ 2.25 and 4.67 were coupled.

Earlier¹⁰ we showed that the products of iodoacetoxyl-ation of norborn-2-ene (bicyclo[2.2.1]hept-2-ene) (24) included up to 90% of the tricyclic iodide (25), which arose presumably *via* abstraction of a proton from an intermediate cation (26). The similarity of the process to that giving rise to the iodoalkene (18) encouraged us to examine the reaction of iodine(i) azide with norborn-2-ene (Table 3).

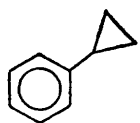
The iodide (28) was identified from its spectra¹⁰ while the structures of the vicinal adducts (32)—(34) were assigned from elemental analyses and their respective ¹H n.m.r., ¹³C n.m.r., and mass spectra (see Experimental section). The structure of the 2-*exo*-7-*syn*-adduct (27) was assigned similarly but since the signals due to the protons on C-2 and C-7 overlapped, a more detailed



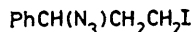
SCHEME 1

^a For Nu = -OAc and -OH only. ^b For Nu = -OAc only.

The ¹H n.m.r. spectra of the adducts isolated from norcarane suggest that the iodomethyl group is able to lock conformationally the cyclohexyl ring to which it is



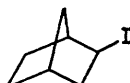
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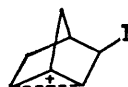
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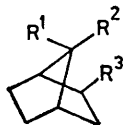
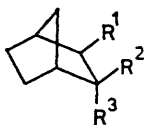
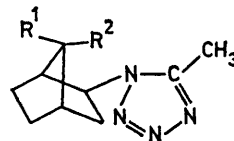
(24)



(25)



(26)

(27) $\text{R}^1 = \text{H}, \text{R}^2 = \text{I}, \text{R}^3 = \text{N}_3$ (28) $\text{R}^1 = \text{R}^2 = \text{H}, \text{R}^3 = \text{I}$ (29) $\text{R}^1 = \text{H}, \text{R}^2 = \text{I}, \text{R}^3 = \text{OAc}$ (30) $\text{R}^1 = \text{I}, \text{R}^2 = \text{H}, \text{R}^3 = \text{OAc}$ (31) $\text{R}^1 = \text{H}, \text{R}^2 = \text{I}, \text{R}^3 = \text{Cl}$ (32) $\text{R}^1 = \text{I}, \text{R}^2 = \text{H}, \text{R}^3 = \text{N}_3$ (33) $\text{R}^1 = \text{N}_3, \text{R}^2 = \text{H}, \text{R}^3 = \text{I}$ (34) $\text{R}^1 = \text{I}, \text{R}^2 = \text{N}_3, \text{R}^3 = \text{H}$ (35) $\text{R}^1 = \text{I}, \text{R}^2 = \text{H}, \text{R}^3 = \text{Cl}$ (36) $\text{R}^1 = \text{H}, \text{R}^2 = \text{I}$ (37) $\text{R}^1 = \text{I}, \text{R}^2 = \text{H}$

examination of its ^1H n.m.r. spectrum was undertaken. Although use of $\text{Eu}(\text{fod})_3$ failed to induce any shift of the signals, change of the solvent to either $[\text{2H}_5]$ pyridine or $[\text{2H}_4]$ acetic acid resulted in sufficient resolution to allow

TABLE 3

Reactions of iodine(I) azide ^a with norbornene (24)

Solvent	Products (% yields)					
	(27)	(32)	(33)	(34)	(28)	Tetrazoles
CH_2Cl_2	33	44		4		
$\text{CH}_3\text{CN}(\text{O}_2)$	49	8			5	13 ^b
$\text{CH}_3\text{CN}(\text{N}_2)$	26	2	15	33	3	11 ^c

^a Prepared from $\text{ICl}-\text{NaN}_3$ (ca. 1 : 10) at -10°C to -15°C .

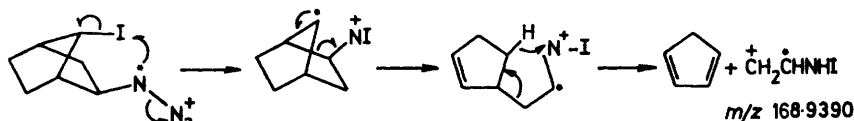
^b An inseparable mixture of compounds. ^c A mixture (1 : 1) of (36) and (37).

identification of half of the expected eight-line pattern ¹⁰ for the 2-*endo*-proton. Two couplings of 4.5 and ca. 1.1 Hz could be attributed to vicinal *endo-exo* coupling [cf. 4.4 Hz for (29) and 3.5 Hz for (30) ¹⁰] and to long-range H-2-*endo*, H-7-*anti* coupling, respectively.

A significant ion of m/z 168.9390 corresponding to a fragment $\text{C}_2\text{H}_4\text{IN}^{++}$ appeared in a high resolution mass

(37) showed the required molecular ion at m/z 304; their ^1H n.m.r. spectra each showed a three-proton singlet at δ ca. 2.58 attributable to a methyl group on a tetrazole ring. ^{11,12} Each spectrum also showed signals consistent with 2-*exo*,7-disubstitution and the stereochemistries at C-7 were assigned on the basis of the presence of long-range coupling (ca. 1 Hz) in the signal due to the 2-*endo*-proton of (36) but absence of similar coupling in the corresponding proton signal of (37).

Products from the reaction of norbornene with iodine (I) azide, carried out in acetonitrile under an atmosphere of oxygen to inhibit any radical reactions, ⁴ can be assumed to arise according to the routes commonly accepted for electrophilic additions to this alkene ^{10,13} (Scheme 3). The fact that the yield of the rearranged iodo-azide (27) is higher than that of the 2,3-adduct (32) suggests that a stabilizing influence, presumably solvation, operates on the intermediate cation since such a species must be sufficiently long-lived to allow rearrangement. Solvation of a developed or developing cation ^{11,12,14} may be responsible for formation of the tetrazoles (36) and (37) but the possibility of



SCHEME 2

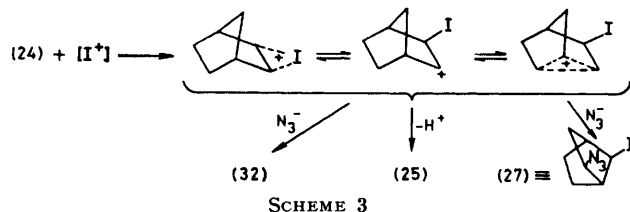
spectrum of (27) but not in those of compounds (32)—(34). This and a four-fold increase in the relative abundance of the $M^{++} - \text{N}_2$ ion (m/z 235) with respect to those in the spectra of (32)—(34) support the stereochemistry assigned to compound (29) and can be explained by invoking an 'ortho' effect between the 2-*exo*-azido- and 7-*syn*-iodo-functions (Scheme 2).

The mass spectrum of each of the tetrazoles (36) and

1,3-dipolar cycloaddition of norbornyl azide to acetonitrile has not been ruled out.

Formation of the stereoisomeric adducts (33) and (34) from the reaction carried out in acetonitrile under nitrogen can be explained by initial *exo*-attack by an azido-radical on the alkene followed in the case of (34) by *syn-exo* delivery of an iodine atom. Although the 2-norbornyl radical is non-planar ¹⁵ and thus attack at the *exo* face of

C-2 would be favoured, the stereoelectronic requirements of the azido-group and of the incoming iodine species are apparently sufficient to allow some *endo*-attack¹⁶ to give the *trans*-adduct (33) whose stereochemistry is the reverse of that expected for addition *via* an ionic mechanism. However, the occurrence of a radical reaction does not preclude a competing ionic mechanism and indeed,



the product distribution (Table 3) suggests that the latter is still operating in this case. The large increase in the amount of adduct (32) relative to (27) when the reaction was carried out in dichloromethane is attributed to the decreased solvation of ionic species in this less polar solvent. Thus, the cation formed by attack of the electrophilic iodine species will be more reactive to azide ion and will compete successfully with the non-classical intermediate (26). The formation of a small amount of the adduct (34) in dichloromethane probably reflects the incomplete quenching of radical pathways by adventitious oxygen since in this reaction no attempt was made to purge the system of air.

Treatment of norbornene (24) with iodine(I) chloride in dichloromethane gave the compounds (31) (21%) and (35) (56%), analogous to the compounds (27) and (32) formed with iodine(I) azide in the same solvent.

EXPERIMENTAL

General experimental details are given in ref. 17.

Reaction of Norcarane (1) with Iodine(I) Azide.—(a) *In acetonitrile.* A cooled solution of norcarane (0.25 g, 2.60 mmol) in acetonitrile (10 ml) was added to a stirred mixture of sodium azide (0.43 g, 6.61 mmol) and iodine(I) chloride (0.47 g, 2.89 mmol) in acetonitrile (15 ml) and the mixture was warmed to room temperature and stirred in the dark for 75 h. Work-up and p.l.c. of the resulting oil (0.25 g) gave (i) 1-azido-2-iodo-3-iodomethylcyclohexane (4) (24%); ν_{\max} 2 100 cm^{-1} (N_3); δ 0.6–2.3 (m, CH_2), 3.15 (m, CH_2I), 4.20 (m, $W_{\frac{1}{2}}$ 8.6 Hz, CHN_3), and 4.70 (m, $W_{\frac{1}{2}}$ 7 Hz, CHI); m/z 391 (M^{++}), 349 ($M^{++} - \cdot\text{N}_3$), 264 ($M^{++} - \cdot\text{I}$), 222 ($M^{++} - \cdot\text{I} - \cdot\text{N}_3$), 221 ($M^{++} - \text{HI} - \cdot\text{N}_3$), and 95 ($M^{++} - 2\text{I} - \cdot\text{N}_3$); (ii) 2-azido-1-iodo-3-iodomethylcyclohexane (6) (6%); ν_{\max} 2 100 cm^{-1} (N_3); δ 0.6–2.4 (m, CH_2), 3.15 (m, CH_2I), 4.00 (m, $W_{\frac{1}{2}}$ 8 Hz, CHN_3), and 4.50 (m, $W_{\frac{1}{2}}$ 9 Hz, CHI); m/z as for (4); (iii) 1-azido-3-iodocycloheptane (2) (5%); ν_{\max} 2 100 cm^{-1} (N_3); δ 0.8–2.3 (m, CH_2), 3.50 (m, $W_{\frac{1}{2}}$ 6 Hz, CHI), and 4.20 (m, CHN_3); m/z 265 (M^{++}), 223 ($M^{++} - \cdot\text{N}_3$), and 137 ($M^{++} - \text{HI}$); and (iv) two unidentified compounds (trace).

(b) *In n-pentane.* Norcarane (0.25 g) was treated with iodine(I) azide in n-pentane as in (a). Work-up and p.l.c. gave (i) 1-iodo-2-iodomethylcyclohexane¹ (5) (16%) as a yellow oil (correct ¹H n.m.r. spectrum); m/z 350 (M^{++}), 223 ($M^{++} - \cdot\text{I}$), 95 ($M^{++} - \text{I} - \text{HI}$), 67 ($M^{++} - \text{I} - \cdot\text{CH}_2\text{I}$),

142.2 (m^* , 350 \rightarrow 223), 47.4 (m^* , 95 \rightarrow 67), and 40.6 (m^* , 223 \rightarrow 95); (ii) 1-azido-2-iodo-2-iodomethylcyclohexane (4) (22%); (iii) 2-azido-1-iodo-3-iodomethylcyclohexane (6) (3%); and (iv) an unidentified compound (trace).

Compound (5) was identical with the product obtained by treatment of norcarane with iodine (1 equiv.) in n-pentane.

Reaction of Norcarane (1) with Iodine(I) Chloride.—(a) *In acetic acid.* A solution of norcarane (0.20 g, 2.08 mmol) in acetic acid (10 ml) was added to a stirred solution of iodine(I) chloride (0.34 g, 2.09 mmol) in acetic acid and the stirring was continued at room temperature for 75 h. The mixture was diluted with water and extracted with ether, and the extracts were washed with water and saturated aqueous sodium hydrogen carbonate. Work-up gave (i) *trans*-2-iodomethylcyclohexyl acetate¹ (14) (35%); (ii) *trans*-2-iodomethylcyclohexanol¹ (15) (3%); (iii) 3-iodomethylcyclohexyl acetates¹ (11) and (16) (6%); (iv) *trans*-2-iodo-*trans*-3-iodomethylcyclohexyl acetate¹ (8) (7%); (v) *trans*-2-iodo-*cis*-6-iodomethylcyclohexyl acetate¹ (9) (2%); (vi) *r*-1-chloro-*t*-2-iodo-*t*-2-iodomethylcyclohexane (12) (4%), b.p. 110–115° at 1.5 mmHg (Found: C, 21.5; H, 2.8; Cl, 9.0; I, 65.1. $\text{C}_7\text{H}_{11}\text{ClI}_2$ requires C, 21.8; H, 2.9; Cl, 9.2; I, 66.0%); δ (CCl_4) 3.05 (m, CH_2I), 4.65 (q, J_{obs} 3 Hz, CHI), and 4.85 (br, s, CHCl); m/z 384/386 (M^{++}), 258/256 ($M^{++} - \text{HI}$), 221 ($M^{++} - \text{HI} - \cdot\text{Cl}$), 131/129 ($M^{++} - \text{HI} - \cdot\text{I}$), 190.8 (m^* , 256 \rightarrow 221), 189.3 (m^* , 258 \rightarrow 221), 172.4 (m^* , 386 \rightarrow 258), 66.5 (m^* , 258 \rightarrow 131), 65.0 (m^* , 256 \rightarrow 129), and 40.0 (m^* , 221 \rightarrow 94); and (vii) *r*-1-chloro-*t*-2-iodo-*c*-6-iodomethylcyclohexane (13) (1%); δ 4.5–4.9 (m, CHI and CHCl).

(b) *In acetic acid with sodium acetate.* Reaction (a) was repeated with the addition of sodium acetate (1 equiv.) (Table 2) and again with a substrate- $\text{ICl}-\text{NaOAc}$ ratio of 1 : 1.5 : 3.

(c) *With iodine(I) chloride, tetramethylene sulphone, and water.* Norcarane (0.20 g) was added to a stirred solution of iodine(I) chloride (0.67 g, 4.12 mmol) and water (0.10 g, 5.56 mmol) in tetramethylene sulphone (5 ml) and chloroform (5 ml), and the mixture was stirred at room temperature for 75 h. Work-up gave compounds (15) (6%), (10) (9.5%), (12) (16%), and (13) (3%), and several minor unidentified products.

(d) *In dichloromethane.* Norcarane (0.10 g, 1.04 mmol) was added to a stirred solution of iodine(I) chloride (0.33 g, 2.03 mmol) in dried dichloromethane (20 ml) and the mixture was stirred at room temperature for 75 h. Work-up and p.l.c. gave compounds (12) (47%) and (13) (42%).

Reaction of Phenylcyclopropane (22) with Iodine(I) Azide.—A solution of phenylcyclopropane (0.31 g, 2.63 mmol) in pentane (5 ml) was added to a stirred and cooled mixture of sodium azide (0.42 g, 6.46 mmol) and iodine(I) chloride (0.46 g, 2.83 mmol) in n-pentane (25 ml) and the mixture was stirred at room temperature for 75 h. Work-up gave a yellow oil (0.40 g) containing (¹H n.m.r. analysis) starting material (38%) and 1-azido-3-iodo-1-phenylpropane (23) (62%). P.l.c. gave (23) as a pale yellow oil, b.p. 120–122° at 0.2 mmHg; ν_{\max} 2 100 cm^{-1} (N_3); δ 2.25 (m, CH_2), 3.15 (t, CH_2I), 4.67 (t, J 6.2 Hz, CHN_3), and 7.38 (s, ArH); m/z 287 (M^{++}), 245 ($M^{++} - \cdot\text{N}_3$), 155 ($\text{C}_2\text{H}_4\text{I}^+$), 132 ($M^{++} - \cdot\text{C}_2\text{H}_4\text{I}$), 117 ($M^{++} - \cdot\text{N}_3 - \text{HI}$), 104 ($M^{++} - \cdot\text{N}_3 - \cdot\text{CH}_2\text{I}$), and 77 (C_6H_5^+).

Reaction of Norbornene (24) with Iodine(I) Azide.—*In dichloromethane.* Norbornene (1.06 g, 11.28 mmol) was added to a stirred and cooled mixture of sodium azide (6.1 g, 93.8 mmol) and iodine(I) chloride (2.18 g, 13.42 mmol) in di-

chloromethane (110 ml) and the mixture was stirred at room temperature for 20 h. Work-up and p.l.c. gave (i) 2-exo-azido-7-syn-iodobicyclo[2.2.1]heptane (27) (32.5%) as a mobile liquid, b.p. 89–92° at 0.3 mmHg (Found: C, 32.5; H, 4.1; I, 46.5; N, 17.0. $C_7H_{10}IN_3$ requires C, 32.0; H, 3.8; I, 48.2; N, 16.0%); ν_{\max} 2100 cm^{-1} (N_3); δ_H 3.6–4.0 (m, 2-H and 7-H); δ_C 25.5 (C-5), 26.6 (C-6), 27.3 (C-7), 37.2 (C-3), 44.3 (C-4), 47.3 (C-1), and 63.4 (C-2); m/z 263 (M^{+}), 234.9838 ($C_7H_{10}IN$ requires 234.9858), 221 ($M^{+} - N_3$), 208 ($M^{+} - CHN_3$ and $M^{+} - C_2H_3N_2$), 168.9403 ($C_2H_4 - IN^{+}$ requires 168.9390), 166.9364 ($C_3H_4I^{+}$ requires 166.9360), and 127 (I^{+}); (ii) 2-endo-azido-3-exo-iodobicyclo[2.2.1]heptane (32) (44%) as a mobile liquid, b.p. 80–82° at 0.2 mmHg (Found: C, 32.1; H, 4.0; I, 48.3; N, 16.2. $C_7H_{10}IN_3$ requires C, 32.0; H, 3.8; I, 48.2; N, 16.0%); ν_{\max} 2100 cm^{-1} (N_3); δ_H 3.40 (t, J_{obs} , 3, $J_{3,4}$ 3 Hz, 3-H) and 4.40 (t, J_{obs} , 4, $J_{1,2}$ 4.4 Hz, 2-H); δ_C 20.3 (C-6), 29.4 (C-5), 31.3 (C-3), 36.0 (C-7), 42.9 (C-1), 48.6 (C-4), and 75.5 (C-2); m/z 263 (M^{+}), 167 ($C_3H_4I^{+}$), 136 ($M^{+} - I$), and 81 ($M^{+} - CHIN_3$); and (iii) 2-exo-azido-3-exo-iodobicyclo[2.2.1]heptane (34) (3.5%) as a mobile liquid, b.p. 116–118° at 0.25 mmHg (Found: C, 31.9; H, 3.8; I, 47.7; N, 15.9. $C_7H_{10}IN_3$ requires C, 32.0; H, 3.8; I, 48.2; N, 16.0%); ν_{\max} 2100 cm^{-1} (N_3); δ_H 3.30 (d, $J_{2,3}$ 6.5 Hz, 2-H), and 4.15 (dd, $J_{2,3}$ 6.5, $J_{3,4}$ 2 Hz, 3-H); δ_C 25.7 (C-6), 28.8 (C-5), 33.7 (C-7), 37.7 (C-3), 43.1 (C-4), 43.6 (C-1), and 66.7 (C-2); m/z 263 (M^{+}), 167 ($C_3H_4I^{+}$), and 127 (I^{+}).

(b) *In acetonitrile under oxygen.* Norbornene was treated with sodium azide and iodine(i) chloride as in (a) but using acetonitrile as solvent under an atmosphere of oxygen. Work-up and p.l.c. gave compounds (27) (49%), (32) (8%), and (28) (5%), and an inseparable mixture of three tetrazoles (13%), δ 2.57, 2.60, and 2.65 (3 s, tetrazole CH_3).

(c) *In acetonitrile under nitrogen.* Norbornene was treated with sodium azide and iodine(i) chloride as in (b) but under an atmosphere of nitrogen. Work-up and p.l.c. gave (i) 2-exo-azido-7-syn-iodobicyclo[2.2.1]heptane (29) (26%); (ii) 2-endo-azido-3-exo-iodobicyclo[2.2.1]heptane (32) (2%); (iii) 2-exo-azido-3-endo-iodobicyclo[2.2.1]heptane (33) (15%) as a mobile liquid, b.p. 75–77° at 0.27 mmHg (Found: C, 32.1; H, 3.8; I, 47.8; N, 16.0. $C_7H_{10}IN_3$ requires C, 32.0; H, 3.8; I, 48.2; N, 16.0%); ν_{\max} 2100 cm^{-1} (N_3); δ_H 3.60 (t, J_{obs} , 3.0 Hz, 2-H) and 3.95 (t, J_{obs} , 3.5 Hz, 3-H); δ_C 25.8 (C-6), 27.2 (C-5), 33.4 (C-7), 34.9 (C-3), 42.0 (C-1), 44.3 (C-4), and 74.9 (C-2); m/z 263 (M^{+}), 221 ($M^{+} - N_3$), 167 ($C_3H_4I^{+}$), and 136 ($M^{+} - I$); (iv) 2-exo-azido-3-exo-iodobicyclo[2.2.1]heptane (34) (33%); (v) 1-(7'-syn-iodobicyclo[2.2.1]heptan-2'-exo-yl)-5-methyltetrazole (36) (5.5%) as needles, m.p. 109–110.5°; δ 2.55 (s, tetrazole

CH_3), 4.20 (dd, J_{obs} , 5, 8 Hz, 2-H), and 4.60 (br, s, 7'-H); m/z 304 (M^{+}), 177 ($M^{+} - I$), and 93 (C_7H_9); and (vi) 1-(7'-anti-iodobicyclo[2.2.1]heptan-2'-exo-yl)-5-methyltetrazole (37) (5.5%), δ 2.58 (s, tetrazole CH_3), 3.85 (br, s, 7'-H), and 4.20 (dd, J_{obs} , 6, 8 Hz, 2'-H); m/z 304 (M^{+}), 177 ($M^{+} - I$), 149, and 93 (C_7H_9).

Reactions of Norbornene (24) with Iodine(i) Chloride.—Norbornene was treated with iodine(i) chloride (1.1 equiv.) in dried dichloromethane as for norcarane. Work-up and p.l.c. gave 2-endo-chloro-3-exo-iodobicyclo[2.2.1]heptane (35)¹⁸ (56%) and 2-exo-chloro-7-syn-iodobicyclo[2.2.1]heptane (31) (21%) (Found: C, 32.7; H, 3.9; Cl, 14.1; I, 48.2. $C_7H_{10}ClI$ requires C, 32.8; H, 3.9; Cl, 13.8; I, 49.5%).

Reaction of either (31) or (35) with an excess of sodium azide or iodine(i) azide, performed as above, gave quantitative recoveries of starting materials.

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