Addition of Iodine(I) Azide to 3-t-Butylcyclohexene and 3-Methoxycyclohexene

By **Richard C. Cambie,** * **Peter S. Rutledge, Truis Smith-Palmer,** and **Paul D. Woodgate,** Department of Chemistry, University of Auckland, Auckland, New Zealand

Iodo-azides have been prepared from 3-t-butylcyclohexene and 3-methoxycyclohexene. In each case the major product can be rationalised as that arising by antiparallel opening of a *cis*-iodonium ion to give a *trans*-diaxial adduct, and the minor product as that arising by parallel opening of a *trans*-iodonium ion to give a *trans*-diequatorial adduct. However, the major product from 3-methoxycyclohexene undergoes a conformational inversion to give a *trans*-diequatorial adduct. The ratio of products derived from *cis*- and *trans*-iodonium ions varies with the iodo-azide producing system and is larger for 3-methoxycyclohexene, especially when dichloromethane is the solvent. Solvolysis of the products has been investigated.

THE stereoselectivity of electrophilic addition to substituted cyclohexenes is determined largely by the steric and electronic effects of the substituent. Thus, in the addition of bromine(I) chloride [1] or bromine(I) acetate [2] to 3-t-butylcyclohexene (1) the steric hindrance of the t-butyl group to *syn*-attack [3] by the electrophile leads to products which indicate that a 21 : 79 ratio of *cis*- † to *trans*-bromonium ions is formed in the initial step. However, the electrophilic addition of several addends such as N-bromosuccinimide and water,[2] iodine(I) azide,[5] and iodine(I) acetate,[5] has been reported to occur stereoselectively *syn* to the t-butyl group. Bellucci and his co-workers [2] have suggested that in such cases both the stereo- and regio-selectivity is determined mainly by substituent effects in the nucleophilic step. The addi-

tion of iodine(I) azide to 3-t-butylcyclohexene was examined by Freppel and Richer [5] who converted the adducts into the corresponding *cis*- and *trans*-aziridines because they considered the adducts would be too unstable for isolation. G.l.c. analysis of the aziridines indicated that the ratio of electrophilic attack *syn* and *anti* to the t-butyl group was 85 : 15. While analysis of the iodo-azide mixture as the aziridines would enable minor products to be taken into account, the method suffers from the disadvantages that elimination usually accompanies aziridine formation and that aziridines may be unstable to g.l.c. analysis.[6] Moreover, the relative ease of aziridine formation from *trans*-diaxial and *trans*-diequatorial isomers would be expected to differ. Accordingly, in a continuation of our study of

† Relative to the t-butyl group. The terms *cis, trans, syn,* and *anti* are used in the same sense as by Hassner (footnote 4 of ref. 4).

[1] G. Bellucci, G. Ingrosso, F. Marioni, E. Mastrorilli, and I. Morelli, *J. Org. Chem.,* 1974, **39**, 2562.

[2] G. Bellucci, M. Ferretti, G. Ingrosso, F. Marioni, A. Marsili, and I. Morelli, *Tetrahedron Letters,* 1972, 3527.

[3] J-C. Richer and C. Freppel, *Canad. J. Chem.,* 1968, **46**, 3709; D. J. Pasto and F. M. Klein, *J. Org. Chem.,* 1968, **33**, 1468.

[4] A. Hassner, F. P. Boerwinkle, and A. B. Levy, *J. Amer. Chem. Soc.,* 1970, **92**, 4879.

[5] C. Freppel and J-C. Richer, *Tetrahedron Letters,* 1972, 2321.

[6] A. Hassner, G. J. Matthews, and F. W. Fowler, *J. Amer. Chem. Soc.,* 1969, **91**, 5046.

the addition of iodine(I) azide to alkenes,[7,8] and in view of our re-examination [9] of the iodoacetoxylation of 3-t-butylcyclohexene [5] which showed that the ratio of *syn* to *anti* attack was *ca.* 3 : 1 rather than 53 : 47, we have re-investigated the action of iodine(I) azide on this substrate.
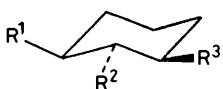
Treatment of 3-t-butylcyclohexene with iodine(I) azide under various conditions (Table 1) followed by p.l.c.
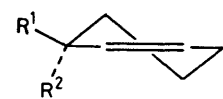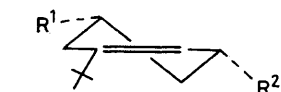

(1) $R^1 = Bu^t$, $R^2 = H$
(2) $R^1 = Bu^t$, $R^2 = N_3$
(3) $R^1 = OMe$, $R^2 = H$
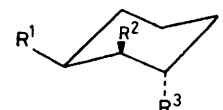
(4) $R^1 = Bu^t$, $R^2 = I$, $R^3 = N_3$
(5) $R^1 = Bu^t$, $R^2 = I$, $R^3 = OAc$
(6) $R^1 = Bu^t$, $R^2 = N_3$, $R^3 = I$
(7) $R^1 = Bu^t$, $R^2 = R^3 = H$
(8) $R^1 = Bu^t$, $R^2 = N_3$, $R^3 = OAc$
(9) $R^1 = OMe$, $R^2 = N_3$, $R^3 = I$
(10) $R^1 = OMe$, $R^2 = p\text{-}NO_2 \cdot C_6H_4CO_2$, $R^3 = Cl$
(11) $R^1 = OMe$, $R^2 = I$, $R^3 = N_3$

(12) $R^1 = Bu^t$, $R^2 = I$, $R^3 = N_3$
(13) $R^1 = Bu^t$, $R^2 = I$, $R^3 = OAc$
(14) $R^1 = H$, $R^2 = I$, $R^3 = N_3$
(15) $R^1 = Bu^t$, $R^2 = N_3$, $R^3 = I$
(16) $R^1 = OMe$, $R^2 = I$, $R^3 = N_3$
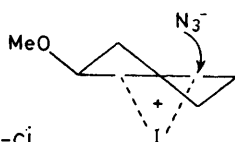

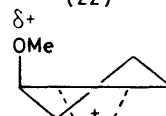(17) $R^1 = H$, $R^2 = N_3$
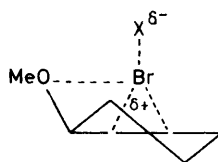(18) $R^1 = N_3$, $R^2 = H$

(20)
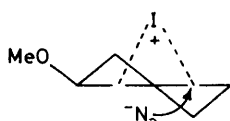
(21)

(22)

(23) R = Br
(24) R = I

(19)

signal and its similarity with the corresponding signal in the spectrum of the *trans*-iodo-acetate (5),[9] indicated that the azido-group was not vicinal to the t-butyl group thereby ruling out the alternative structure (6). The

TABLE 1

Products of iodine(I) azide addition (% yield)

From 3-t-butylcyclohexene (1)

Reagent	Solvent	(4)	(12)	(2)
NaN$_3$–ICl	MeCN	35	15	Trace
NaN$_3$–ICl	CH$_2$Cl$_2$	34	15	
TlN$_3$–I$_2$	CH$_2$Cl$_2$	26	10	Trace

From 3-methoxycyclohexene (3)

Reagent	Solvent	(20)	(16)	(9)
NaN$_3$–ICl	MeCN	30	7	1
NaN$_3$–ICl	CH$_2$Cl$_2$	34	4	
NaN$_3$–I$_2$–18-Crown-6	CHCl$_3$	43	8	7

^{1}H n.m.r. spectrum of compound (12) showed a broad two-proton multiplet (δ 4.00) for which $W_{\frac{1}{2}}$ values could not be determined with accuracy because of the overlap. However, the chemical shift (δ 1.09) of the t-butyl group indicated that the iodo-group was equatorial and vicinal to the t-butyl group [*cf.* δ 1.07 for

TABLE 2

^{1}H N.m.r. chemical shifts: δ values [$W_{\frac{1}{2}}$/Hz]

Compd.	1-H	2-H	3- or 4-H	CMe$_3$	OMe
(4)	4.18 [6]	4.53 [6]		0.97	
(12)	4.00 (m)	4.00 (m)		1.09	
(2)	5.53 [8]	5.53 [8]		0.95	
(17)	3.84 [14]		5.48 [8]	1.08	
(18)	3.58 [18]	5.50 [8]		1.03	
(8)	5.05 [8]	3.86 [8]		0.96	2.06 (OAc)
(9)	4.40 [6]	4.40 [6]	3.08 [15]		3.40
(20)	3.95 [18]	4.26 (dd, $J_{obs.}$ 8 and 3 Hz)	3.33 [6]		3.38
(16)	3.30 [18]	3.80 (m)	3.80 (m)		3.44

(13),[9] δ 0.95 for (5),[9] and δ 0.97 for (4) (this work)]. Assuming that the iodo-azide (12) is a product of *trans*-addition, the azido-group would be in an equatorial C-3 position. The structural assignments for (4) and (12) were supported by comparison of their ^{13}C n.m.r. spectra with those of related compounds (Table 3). As ex-

TABLE 3

^{13}C N.m.r. chemical shifts

Compd.	C-1	C-2	C-3	C-4	C-5	C-6	CMe$_3$	Me$_3$
(4)	65.8	36.9	44.7	21.7 *	25.0	24.3 *	32.6	27.7
(12)	68.8	36.2	53.3	25.7 *	21.7 *	29.7 *	34.4	28.9
(14)	66.9	33.5 *	38.2	26.9 *	23.7 *	31.8 *		
(7)[10] †	27.8	28.2	48.9	28.2	27.8	27.2	32.3	27.9
(1)[10]	129.3	127.9	46.0	24.5	22.9	25.3	32.7	27.3

* Tentative assignments. † Numbered to correspond with the other compounds.

gave compounds (4), (12), and (2), the structures of which were assigned on the basis of microanalytical, mass spectral, i.r., ^{1}H n.m.r., and ^{13}C n.m.r. data. A greater multiplicity of the CHN$_3$ signal (δ 4.18) in the ^{1}H n.m.r. spectrum of (4) (Table 2) relative to that of the CHI

pected,[11] signals in the spectrum of (12) were generally at lower field than those in the spectrum of (4).

The iodo-azides (4) and (12) were isolated in a ratio of 2.3 : 1 whereas ^{1}H n.m.r. analysis of the crude product showed the ratio to be closer to 2 : 1. Neither of the

[7] R. C. Cambie, R. C. Hayward, P. S. Rutledge, T. Smith-Palmer, and P. D. Woodgate, *J.C.S. Perkin I*, 1976, 840.
[8] R. C. Cambie, P. S. Rutledge, T. Smith-Palmer, and P. D. Woodgate, *J.C.S. Perkin I*, 1977, 2250.
[9] R. C. Cambie, D. M. Gash, P. S. Rutledge, and P. D. Woodgate, *J.C.S. Perkin I*, 1977, 1157.
[10] J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, 1970, **92**, 1338.

[11] D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, 1967, **89**, 5315; D. K. Dalling and D. M. Grant, *ibid.*, 1967, **89**, 6612; A. S. Perlin and H. J. Koch, *Canad. J. Chem.*, 1970, **48**, 2639; J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972, pp. 63 and 163.

other possible isomers (6) and (15) were isolated but by analogy with the iodoacetoxylation of 3-t-butylcyclohexene,[9] they may have been present in less than 5% yield and hence remained undetected by ¹H n.m.r. analysis. The 2 : 1 ratio differs from that obtained by Freppel and Richer indicating that, as anticipated, analysis of the iodo-azide mixture as the aziridines does not give a true measure of the iodo-azide ratio.

Scheme 1, involving reversible formation of asymmetric iodonium ions followed by preferential attack of the nucleophile at C-1 in a manner similar to that suggested [9] for iodoacetoxylation of 3-t-butylcyclohexene, would account for formation of compounds (4) and (12). The nucleophile would be expected to react more
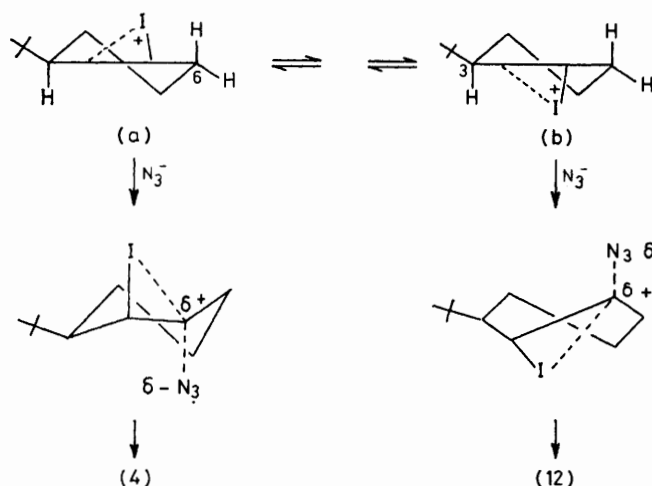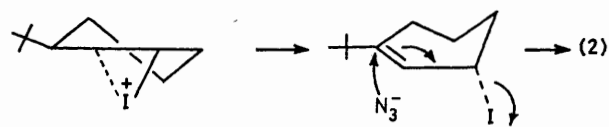
SCHEME 1

rapidly with the *cis*-iodonium ion (a) than with the *trans*-iodonium ion (b) to give the *trans*-diaxial iodo-azide (4) as the major product by antiparallel (to the C-6 pseudo-axial H) opening.[12] Since antiparallel (to the C-3 pseudo-axial H) opening of the *trans*-iodonium ion (b) would be impeded by the t-butyl group it would be expected to react more slowly with the nucleophile by parallel (to the C-6 pseudo-axial H) opening *via* a twist-boat conformation. Formation of the diequatorial iodo-azide (12) in preference to the presumably more stable [2] *trans*-diaxial product (6) indicates that like iodoacetoxylation,[9] the second stage of the reaction is kinetically controlled. An increase in the ratio of diequatorial to diaxial products when iodine(I) azide rather than iodine(I) acetate is the addend reflects the greater nucleophilicity of the azide ion.

The product (2) obtained in trace amount from the addition of iodine(I) azide to (1) probably arises as shown in Scheme 2.
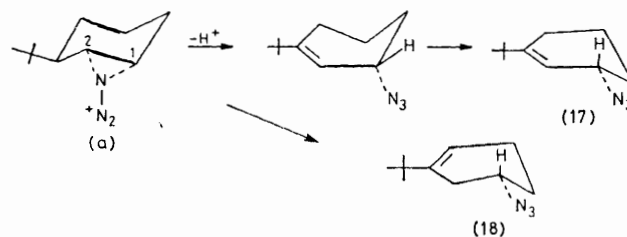
Solvolysis of the iodo-azide (4) with silver acetate in acetic acid gave a 3 : 2 mixture of two unsaturated azides but only a trace of a compound containing an acetate group. Attempts to separate the unsaturated azides were unsuccessful. However, the major product was

[12] D. N. Kirk and M. P. Hartshorn, ' Steroid Reaction Mechanisms,' Elsevier, Amsterdam, 1968, p. 96.

identified as 3α-azido-1-t-butylcyclohexene (17) from the ¹H n.m.r. spectrum of an enriched fraction which showed signals (Table 2) assigned to a pseudo-axial proton geminal to an azido-group and to an olefinic proton. It may arise *via* the *trans*-diazonioaziridine ion (a) (Scheme
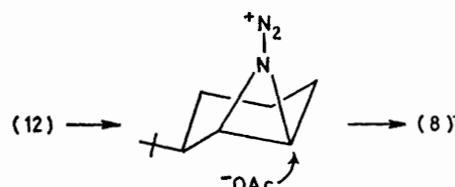
SCHEME 2

3) followed by a conformational inversion to the more stable half-chair form (17) in which the azido-group is pseudo-equatorial. The minor compound was tentatively identified as 4-azido-2-t-butylcyclohexene (18) from the ¹H n.m.r. spectrum (Table 2) of an enriched fraction. Its precise mode of formation is not clear. Formation of unsaturated azides (Scheme 3) rather than azido-acetates is attributed to steric hindrance by the t-butyl group to *syn*-approach of an acetate ion at the C-2

SCHEME 3

position. Attack at C-1 would be less hindered but would necessitate parallel opening of the *trans*-diazonioaziridine ion and thus is not favoured.

In contrast to compound (4), solvolysis of the iodo-azide (12) gave the azido-acetate (8) as the major product. Its ¹H n.m.r. spectrum showed low field multiplets (Table 2) which indicated that the protons geminal to the azido and acetate groups were each equatorial. The shape of the latter multiplet was identical with that of the multiplet at δ 4.18 in the spectrum of the *trans*-iodo-azide (4) and thus the acetate group was in the axial C-1 position and the azido-group was in the C-2 position. The azido-acetate could arise (Scheme 4) by attack of

SCHEME 4

acetate ion on a *cis*-diazonioaziridine ion at C-1 by antiparallel opening. Attack at C-2 would be unfavourable since this would necessitate parallel opening *via* a twist-boat form.

Although the methoxy-group of 3-methoxycyclohexene (3) exerts a steric effect in promoting conform-

ational rigidity of the molecule and in directing addition reactions, it is more important for its inductive effect which directs nucleophilic attack to the more distant carbon atom once a halogenonium ion has been formed.[13] The ratio of nucleophilic attack at C-1 to that at C-2 usually exceeds 9 : 1 for both *cis*- and *trans*-ions, and this regioselectivity is independent of the reaction conditions.[13] A variety of addition reactions to 3-methoxycyclohexene initiated by electrophilic bromine or chlorine species have been reported, but little is recorded on the addition of electrophilic iodine. Bellucci and his co-workers [13] have shown that for some reactions involving electrophilic bromine the stereoselectivity of the electrophilic step changes considerably according to the reagent used, *e.g.* the ratio of products formed from *cis*- and *trans*-bromonium ions increases from 4 : 6 for bromine(I) acetate, through 7 : 3 for bromine(I) chloride, to 9 : 1 for molecular bromine. Bellucci suggested that in aprotic solvents of low polarity, bromine and bromine(I) chloride are activated by co-ordination with the methoxy-group as in (19), the electrophile then being transferred intramolecularly to the double bond.[13,14] The slight preference for *anti*-attack by electrophilic bromine in the addition of bromine(I) acetate was taken to show that co-ordination by the methoxy-group was not important for this reagent. However, since a greater proportion of the reaction of bromine(I) acetate with 3-methoxycyclohexene proceeds *via* the *cis*-bromonium ion than in the reaction of bromine(I) acetate with 3-t-butylcyclohexene, some co-ordination must still occur.

Treatment of 3-methoxycyclohexene with iodine(I) azide under various conditions (Table 1) gave compounds (20), (16), and (9) as oils which were identified from their spectral parameters and, in the case of (20), by comparison with the spectrum of the compound (10).[15] A higher proportion of products from *cis*- to *trans*-iodonium ions compared with those from 3-t-butylcyclohexene, suggests that complexing between iodine azide and the methoxy-group may be important even in a polar solvent such as acetonitrile. As expected, complexing appeared to be even more pronounced in the less polar solvent dichloromethane. Compound (20) is presumably formed from the *trans*-diaxial iodo-azide (11) by a conformational inversion to the more stable chair form in which the iodo- and azido-substituents are equatorial and the methoxy-group is axial. In the ^{1}H n.m.r. spectrum of the adduct (16) two downfield signals assigned to protons geminal to the azido- and iodo-groups were superimposed on the methoxy-signal but their overall shape was almost identical with that of the low field signal of the corresponding adduct (12) from 3-t-butylcyclohexene. A one-proton signal at δ 3.08 in the ^{1}H n.m.r. spectrum of the minor product (9)

was assigned to the axial proton geminal to the methoxy-group, while a two-proton signal centred at δ 4.40 was assigned to equatorial protons geminal to iodo- and azido-substituents. Compounds similar to (9) have been isolated from the addition of reagents containing electrophilic bromine or chlorine to 3-methoxycyclohexene.[13,16]

As in the case of 3-t-butylcyclohexene, it is suggested that initial formation of iodonium ions from 3-methoxycyclohexene is reversible. However, equilibrium must be displaced more towards the *cis*-iodonium ion than in the case of 3-t-butylcyclohexene because of the assistance given to its formation by the methoxy-group. In the reaction of the *cis*-iodonium ion (21), attack of azide ion at C-1 would be favoured by both the polar effect of the methoxy-group and the unhindered approach of the azide ion (*cf.* ref. 17) yielding a chair conformation on diaxial opening and thus the iodo-azide (11) and subsequently its more stable conformer (20) as the major product. Attack at C-2 would be unfavourable on both electronic and steric grounds, thereby accounting for the absence of product from this mode of attack. In the reaction of the *trans*-iodonium ion (22), opening at C-1 would be favoured both electronically and sterically but such a mode of attack is unfavourable since it would lead to a less stable ' boat ' intermediate. Even so, this form of attack still led to the second most abundant product (6). Attack by azide ion at C-2 of the *trans*-iodonium ion (22) with *trans*-diaxial opening *via* a chair intermediate would lead to the minor product (9).

Bannard [17] has suggested that in the addition of electrophilic bromine to 3-methoxycyclohexene, *cis*- and *trans*-bromonium ions might form in which the methoxy-group is axial. Of these the *trans*-ion (23) is the more stable. If a similar iodonium ion (24) was formed during the addition of iodine azide then it would be expected to react faster than its conformer (22).[17] Diaxial opening at C-1 of the ion (24) to yield a chair form would be facilitated by the inductive effect of the methoxy-group although approach of the azide ion to C-1 would be slightly impeded by a 1,3-diaxial interaction with the methoxy-group. Thus, reaction of any ion (24) would lead to formation of the *trans*-diequatorial product (16).

Neither of the diequatorial iodo-azides (20) and (16) yielded the corresponding azido-acetates on attempted solvolysis with silver acetate in acetic acid. Presumably, this lack of reaction reflects the reluctance for the equatorial conformers to adopt a diaxial form, since in the latter case solvolysis would be expected to occur readily as a result of neighbouring-group participation.[8]

EXPERIMENTAL

General experimental details are given in ref. 18. ^{13}C N.m.r. spectra were measured for solutions in $CDCl_3$ with

[13] G. Bellucci, G. Berti, R. Bianchini, G. Ingrosso, and E. Mastrorilli, *Gazzetta*, 1976, **106**, 955.
[14] P. L. Barili, G. Bellucci, G. Berti, M. Golfarini, F. Marioni, and V. Scartoni, *Gazzetta*, 1974, **104**, 107.
[15] E. J. Langstaff, E. Hamanaka, G. A. Neville, and R. Y. Moir, *Canad. J. Chem.*, 1967, **45**, 1907.

[16] J. G. Buchanan and H. Z. Sable, ' Selective Organic Transformations,' Wiley–Interscience, New York, vol. 2, 1972, p. 73.
[17] R. A. B. Bannard, A. A. Casselman, and L. R. Hawkins, *Canad. J. Chem.*, 1965, **43**, 2398.
[18] R. C. Cambie, G. J. Potter, P. S. Rutledge, and P. D. Woodgate, *J.C.S. Perkin I*, 1977, 530.

a JEOL JNM-FX60 Fourier transform spectrometer. General methods for the preparation and solvolysis of iodo-azides are given in refs. 7 and 8. All products showed i.r. absorption at ν_{max} 2 100 cm^{-1} (N$_3$).

Reaction of 3-t-Butylcyclohexene with Sodium Azide and Iodine(I) Chloride.—3-t-Butylcyclohexene (0.69 g, 5.0 mmol), prepared by Richer and Freppel's method [3] and purified immediately prior to use by passage in n-pentane through alumina, was treated with iodine(I) azide in acetonitrile. Work-up gave a yellow oil which was separated by p.l.c. (hexane–ether, 9 : 1) into (i) r-1-*azido*-t-2-*iodo*-t-3-*t-butylcyclohexane* (4) (0.48 g) (Found: C, 39.3; H, 5.9; N, 13.5. C$_{10}$H$_{18}$IN$_3$ requires C, 39.1; H, 5.9; N, 13.7%), *m/e* 307 (*M$^{+\cdot}$*), 265 (*M$^{+\cdot}$* — N$_3$), 249 (*M$^{+\cdot}$* — CHMe$_3$), 180 (*M$^{+\cdot}$* — I), and 152 (*M$^{+\cdot}$* — IN$_2$), and (ii) r-1-*azido*-t-2-*iodo*-c-3-*t-butylcyclohexane* (12) (0.20 g) (Found: C, 40.0; H, 6.0; N, 14.0. C$_{10}$H$_{18}$IN$_3$ requires C, 39.1; H, 5.9; N, 13.7%), *m/e* 152 (*M$^{+\cdot}$* — IN$_2$). An initial contaminant of the latter fraction was 3-azido-3-t-butylcyclohexene (2).

Repetition of the reaction in dichloromethane gave (4) and (12) in a ratio of 2.3 : 1.

Reaction of 3-t-Butylcyclohexene with Thallium(I) Azide and Iodine.—3-t-Butylcyclohexene (0.35 g, 2.5 mmol) in dichloromethane was treated with thallium(I) azide–iodine for 24 h. Work-up gave an oil (0.59 g) which was separated by p.l.c. into the iodo-azides (40) (0.20 g) and (12) (81 mg), and the azido-alkene (2) (trace).

Solvolysis of r-1-*Azido*-t-2-*iodo*-t-3-*t-butylcyclohexane.*— The iodo-azide (4) (0.24 g, 0.78 mmol) was treated with silver acetate (0.14 g, 0.85 mmol) in dry acetic acid (3 ml) at 20 °C for 1 h and the mixture was then warmed on a water-bath for 30 min. Work-up gave an oil (0.14 g) which was separated by p.l.c. into fractions enriched in 3-azido-1-t-butylcyclohexene (17) and 4-azido-2-t-butylcyclohexene (18).

Solvolysis of r-1-*Azido*-t-2-*iodo*-c-3-*t-butylcyclohexane.*— The iodo-azide (12) (0.17 g, 0.55 mmol) was treated with silver acetate (0.10 g, 0.60 mmol) in dry acetic acid (3 ml) as above. The crude product (0.12 g) was purified by p.l.c. to give t-2-*azido*-t-3-*t-butylcyclohexyl acetate* (8) as an oil (Found: C, 60.2; H, 8.9; N, 17.5. C$_{12}$H$_{21}$N$_3$O$_2$ requires C, 60.2; H, 8.85; N, 17.6%), ν_{max} 1 720 cm^{-1} (OAc).

Reaction of 3-Methoxycyclohexene with Sodium Azide and Iodine(I) Chloride.—3-Methoxycyclohexene, b.p. 138—139 °C, n_D^{20} 1.458 8 (lit.,[19] 138—139 °C, 1.453 0) (0.22 g, 2 mmol) was treated with iodine(I) azide in acetonitrile. Work-up gave an oil (0.42 g) which was separated by p.l.c. into (i) r-2-azido-t-1-iodo-c-3-methoxycyclohexane (9) (8 mg), *m/e* 281 (*M$^{+\cdot}$*), and 110 (*M$^{+\cdot}$* — HI — HN$_3$); (ii) r-1-*azido*-t-2-*iodo*-t-3-*methoxycyclohexane* (20) (0.17 g) (Found: C, 30.2; H, 4.3; I, 44.6; N, 15.3. C$_7$H$_{10}$IN$_3$O requires C, 30.0; H, 4.0; I, 45.3; N, 15.0%), *m/e* 281 (*M$^{+\cdot}$*), 154 (*M$^{+\cdot}$* — I), 127 (I$^+$), 128 (HI$^{+\cdot}$), and 111 (*M$^{+\cdot}$* — I — HN$_3$); and (iii) r-1-*azido*-t-2-*iodo*-c-3-*methoxycyclohexane* (16) (40 mg) (Found: C, 30.6; H, 4.5; N, 14.6. C$_7$H$_{10}$IN$_3$O requires C, 30.0; H, 4.0; N, 15.0%), *m/e* 281 (*M$^{+\cdot}$*), 153 (*M$^{+\cdot}$* — HI), and 110 (*M$^{+\cdot}$* — HI — HN$_3$).

Repetition of the reaction in dichloromethane gave the iodo-azide (20) (0.19 g) and the iodo-azide (16) (22 mg).

Reaction of 3-methoxycyclohexene with thallium(I) azide–iodine in dichloromethane gave only a trace of iodo-azides.

Reaction of 3-Methoxycyclohexene with Sodium Azide–Iodine and Crown Ether.—A suspension of sodium azide (0.78 g, 12.0 mmol) in a solution of 18-crown-6 (0.64 g, 2.4 mmol) and chloroform (30 ml) was stirred for 10 min and then treated with iodine (1.21 g, 4.8 mmol). 3-Methoxy-cyclohexene (0 22 g, 2 mmol) was added and the mixture was stirred overnight. Work-up gave an oil (0.46 g) which was separated by p.l.c. into the iodo-azides (9) (42 mg), (20) (0.24 g), and (16) (44 mg).

Attempted Solvolyses of Iodo-azides (20) *and* (16).—The iodo-azide (20) (0.16 g, 0.58 mmol) was treated with silver acetate (0.11 g, 0.64 mmol) in acetic acid (10 ml) as above. Work-up gave an oil (85 mg) which was mainly starting material. Refluxing for longer periods decreased the amount of recovered starting material. No reaction occurred in the absence of heat.

Treatment of the iodo-azide (16) (0.12 g, 0.43 mmol) with silver acetate (78 mg, 0.47 mmol) in acetic acid (10 ml) gave an oil (67 mg) which was mainly starting material.

[19] R. A. B. Bannard and L. R. Hawkins, *Canad. J. Chem.*, 1958, **36**, 1241.