# Iodo-azide Adducts of Exocyclic Alkenes; Structure and Solvolysis

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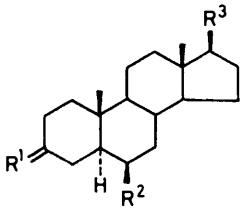
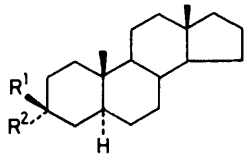
The addition of iodine(I) azide, generated from sodium azide–iodine(I) chloride in acetonitrile, to 3-methylene-5α-androstane (1) and to 1-methylene-4-t-butylcyclohexane (42) in the presence of oxygen is regioselective and gives adducts containing an iodomethyl group, but is not stereoselective. Under a nitrogen atmosphere adducts containing an azidomethyl group are obtained, which arise *via* a radical pathway. Iodomethyl- and azidomethyl-groups are readily identified by $^{13}C$ n.m.r. spectroscopy and this has been used to confirm the structures of the products of addition of iodine(I) azide to camphene (45). Migration of an azide group occurs during solvolysis of the iodo-azide adducts (6) and (7) from 3-methylene-5α-androstane.

DURING an examination of the addition of iodine(I) azide to 3-methyl-$\Delta^2$-steroids [1] we also investigated its addition to 3-methylene-5α-androstane (1). This afforded the adducts (6) and (7), which were assumed to arise *via* attack of an azide ion on a C-3 tertiary carbocation and then compound (8), which we suggested arose from an anti-Markownikov opening of an α-iodonium ion rather than *via* a primary carbocation. Thus, the addition of iodine(I) azide to exocyclic alkenes did not appear to be regioselective or stereoselective, as suggested by Hassner *et al.*[2] However, since the regio- and stereochemistry of the adducts (6), (7), and (8) rested mainly on tentative $^1H$ n.m.r. assignments for azidomethyl- and iodomethyl-groups we have continued our investigation of the iodo-azide adducts of substrates containing exocyclic double bonds.

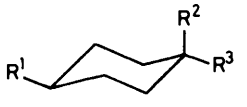
In the earlier work [1] it was assumed that protons geminal to a primary iodide resonated further upfield than those geminal to a primary azide. In the present study, preparation and examination of the $^1H$ n.m.r. spectra of 1-azidomethylcyclohexane (28) [3] and of 1-iodomethylcyclohexane (29) [4] indicated that the protons ($\delta_H$ 3.08)



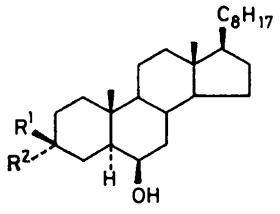
(1) $R^1 = CH_2$, $R^2 = R^3 = H$
(2) $R^1 = CH_2$, $R^2 = OH$, $R^3 = C_8H_{17}$
(3) $R^1 = O$, $R^2 = R^3 = H$
(4) $R^1 = CHN_3$, $R^2 = R^3 = H$
(5) $R^1 = CH_2$, $R^2 = H$, $R^3 = C_8H_{17}$



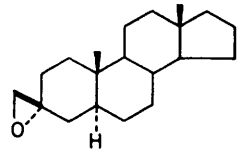
(6) $R^1 = N_3$, $R^2 = CH_2I$
(7) $R^1 = CH_2I$, $R^2 = N_3$
(8) $R^1 = CH_2N_3$, $R^2 = I$
(9) $R^1 = H$, $R^2 = CH_2N_3$
(10) $R^1 = CH_2N_3$, $R^2 = H$
(11) $R^1 = H$, $R^2 = CH_2I$
(12) $R^1 = CH_2I$, $R^2 = H$
(13) $R^1 = H$, $R^2 = CH_2OH$
(14) $R^1 = CH_2OH$, $R^2 = H$
(15) $R^1 = H$, $R^2 = CH_2O$–3,5–DNB
(16) $R^1 = CH_2O$–3,5–DNB, $R^2 = H$
(17) $R^1 = H$, $R^2 = CH_2OTs$
(18) $R^1 = CH_2OTs$, $R^2 = H$
(19) $R^1 = H$, $R^2 = CHO$
(20) $R^1 = CHO$, $R^2 = H$
(21) $R^1 = OH$, $R^2 = CH_2N_3$
(22) $R^1 = CH_2N_3$, $R^2 = OH$
(23) $R^1 = H$, $R^2 = Me$
(24) $R^1 = Me$, $R^2 = H$
(25) $R^1 = I$, $R^2 = CH_2N_3$
(26) $R^1 = OAc$, $R^2 = CH_2N_3$
(27) $R^1 = CH_2N_3$, $R^2 = OAc$



(28) $R^1 = R^2 = H$, $R^3 = CH_2N_3$
(29) $R^1 = R^2 = H$, $R^3 = CH_2I$
(30) $R^1 = Bu^t$, $R^2 = CH_2OH$, $R^3 = H$
(31) $R^1 = Bu^t$, $R^2 = H$, $R^3 = CH_2OH$
(32) $R^1 = Bu^t$, $R^2 = CH_2I$, $R^3 = N_3$
(33) $R^1 = Bu^t$, $R^2 = N_3$, $R^3 = CH_2I$
(34) $R^1 = Bu^t$, $R^2 = I$, $R^3 = CH_2N_3$



(35) $R^1 = H$, $R^2 = CH_2OH$
(36) $R^1 = CH_2OH$, $R^2 = H$



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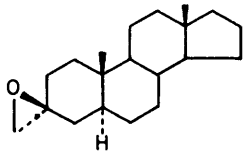
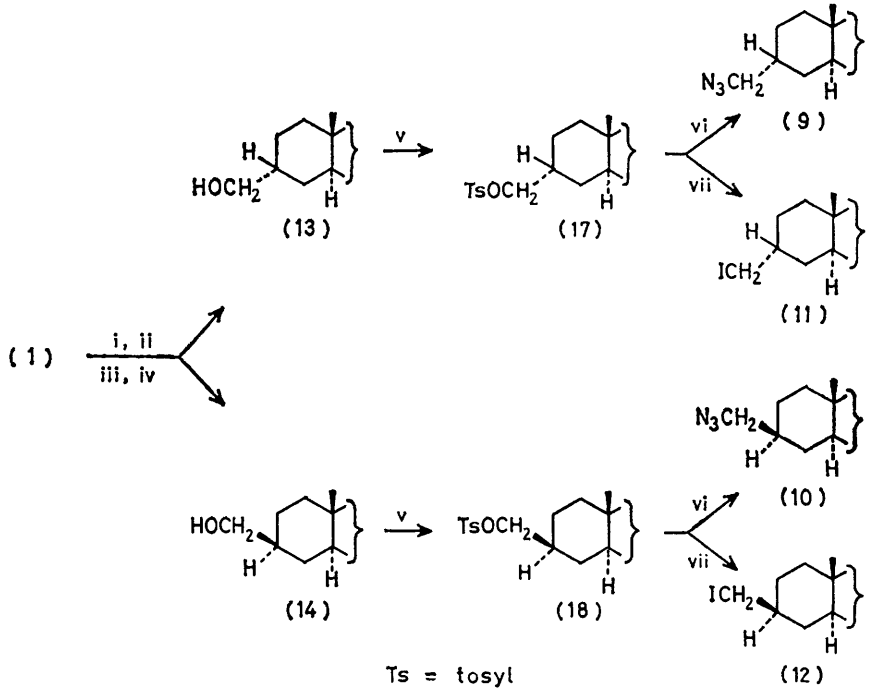


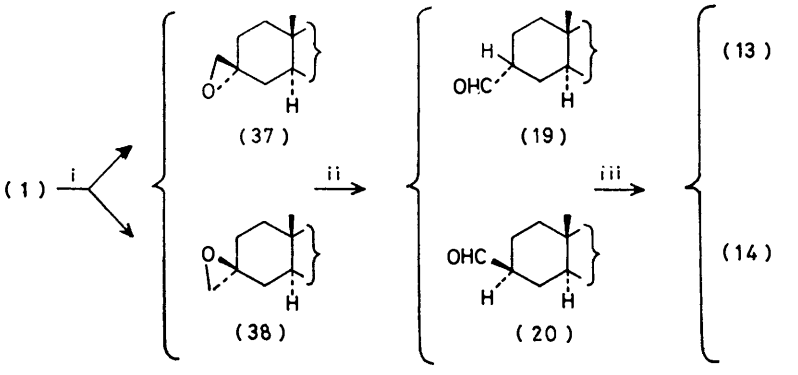
(38)

DNB = dinitrobenzoyl; Ts = tosyl

geminal to the primary iodide in compound (29) did, in fact, resonate slightly upfield from those ($\delta_H$ 3.11) geminal to the primary azide in compound (28), but the chemical-shift difference was insufficient to distinguish clearly between a primary azide or iodide on the basis of these data alone. In contrast, the large difference between the $^{13}C$ n.m.r. signals of the carbon atoms bearing the azide- ($\delta_C$ 58.1 p.p.m.) or iodide- ($\delta_C$ 16.2 p.p.m.) groups indicated that an azidomethyl group could be readily distinguished from an iodomethyl group by this means. Stothers *et al.*[5] have shown that an inverse relationship exists between the $^1H$ and $^{13}C$ n.m.r. chemical shifts of the carbinyl atoms of the *cis*- and *trans*-t-butylcyclohexylmethanols (30) and (31). Thus, the protons of the axial group of compound (30) ($\delta_H$ 3.51) are deshielded relative to those of the equatorial group of compound (31) ($\delta_H$ 3.32), while the axial carbon atom of compound (30) ($\delta_H$ 64.2) is shielded relative to the corresponding equatorial atom of compound (31) ($\delta_C$ 68.9). In order to determine whether a similar inverse relationship existed for azidomethyl- and iodomethyl-groups we prepared the model compounds (9), (10), (11), and (12) (Scheme 1). Hydroboration of the alkene (1) followed by oxidation gave a mixture (*ca.* 1 : 1) (*cf.* for substituted methylenecyclohexanes)[6] of the androstanylmethanols (13) and (14), which were inseparable by p.l.c. [*cf.* the mixture of isomeric hydroxymethyl derivatives (35) and (36) obtained from compound (2)[7]]. However, the 3,5-dinitrobenzoate esters (15) and (16) were separated by multiple elution p.l.c. and the pure isomers (13) and (14) were recovered from subsequent alkaline hydrolysis. The stereochemistry of the alcohols (13) and (14) was assigned by $^1H$ n.m.r. spectral analysis[5,8] and confirmed by synthesis *via* an alternative route (Scheme 2).




SCHEME 1 *Reagents:* i, $B_2H_6$–$H_2O_2$–NaOH; ii, 3,5-$(O_2N)_2C_6H_3COCl$; iii, p.l.c.; iv, KOH–MeOH; v, TsCl; vi, $NaN_3$–dimethylformamide (DMF); vii, NaI–$Me_2CO$




SCHEME 2 *Reagents:* i, *m*-$ClC_6H_4CO_3H$–$Et_2O$; ii, $BF_3$–$Et_2O$–PhH; iii, $LiAlH_4$

Epoxidation of the alkene (1) gave a 1 : 3 mixture of the oxirans (37) and (38) * which, on brief treatment with boron trifluoride–diethyl ether in benzene, gave a mixture (*ca.* 1 : 3) of the aldehydes (19) and (20). Reduction of the aldehydes with lithium aluminium hydride gave a mixture of the alcohols (13) and (14). The $^1$H n.m.r. signals of the respective epoxides and aldehydes were consistent with those recorded for the corresponding cholestane derivatives.[9,10] Examination of the $^1$H n.m.r. data (Table 1) and $^{13}$C n.m.r. data (Table 2) for the model compounds shows that an inverse relationship does exist between the chemical shifts for axial and equatorial isomers of both azidomethyl- and iodomethyl-derivatives; *i.e.* the protons of an axial $CH_2X$ group are deshielded relative to those of an equatorial $CH_2X$ group, while the carbinyl carbon atom of an axial $CH_2X$ group is shielded relative to that of an equatorial $CH_2X$ group. A small, but significant, downfield shift (relative to the equatorial isomer) of the 19-H signal is also observed when the $CH_2X$ group is axial. The shift is probably associated with a small change in the conformation of ring-A since the observed 3-H–20-H coupling constant was slightly larger in the case of an axial $CH_2X$ group. Assignment of the $^{13}$C n.m.r. signals was made by comparison with the reported chemical shifts for 5α-androstane [11] with a set of self-consistent substituent-additivity values (Table 3) and, in the case of ring-A signals, from the single-frequency off-resonance decoupled (SFORD) spectra. Examination of Table 2 confirms that a clear distinction can be made between an azidomethyl group and an iodomethyl group by $^{13}$C n.m.r. spectroscopy.

Application of the above method to the iodo-azide adducts obtained from 3-methylene-5α-androstane (Tables 1 and 2) shows that while correct regiochemical assignments were made in the earlier work,[1] the stereochemistry assigned to compounds (6) and (7) should be reversed. While only one of the two possible stereoisomers containing a $CH_2N_3$ group was available, and thus assignment of stereochemistry using the inverse relationship was not possible in this case, the difference

TABLE 1

$^1$H N.m.r. data for substituted 3-methyl-5α-androstanes (δ values)

| Compound | 18-H | 19-H | 20-H (d) | $J_{3,20}$ (Hz) |
|---|---|---|---|---|
| (23) [a] | 0.70 | 0.80 | 1.01 | 7.0 |
| (24) [a] | 0.70 | 0.77 | 0.87 | 5.0 |
| (9) | 0.70 | 0.80 | 3.33 | 8.0 |
| (10) | 0.70 | 0.77 | 3.12 | 6.0 |
| (11) | 0.70 | 0.80 | 3.40 | 8.0 |
| (12) | 0.70 | 0.77 | 3.10 | 4.0 |
| (13) | 0.73 | 0.83 | 3.68 | 8.0 |
| (14) | 0.70 | 0.77 | 3.38 | 6.0 |
| (15) | 0.73 | 0.90 | 4.57 | 8.0 |
| (16) | 0.73 | 0.85 | 4.32 | 6.0 |
| (17) | 0.68 | 0.82 | 4.07 | 8.0 |
| (18) | 0.67 | 0.70 | 3.78 | 4.0 |
| (21) | 0.73 | 0.87 | 3.43 (s) | |
| (22) | 0.73 | 0.78 | 3.13 (s) | |
| (6) [b] | 0.70 | 0.84 | 3.48 (s) | |
| (7) [b] | 0.70 | 0.77 | 3.35 (s) | |
| (8) | 0.70 | 0.80 | 3.80 (s) [b] | |
| (26) | 0.73 | 0.90 | 3.77 (s) | *c* |
| (27) | 0.73 | 0.80 | 3.70 (s) | *c* |

[a] See Experimental section. [b] Incorrectly assigned in ref. 1. [c] Plus δ *ca.* 2.10 (OAc).

TABLE 3

$^{13}$C N.m.r. substituent additivity values

| | $\delta_{Me} - \delta_H$ [a] | | | |
|---|---|---|---|---|
| | *ax*-Me [b] | *eq*-Me [c] | $\delta_{CH_2I} - \delta_{Me}$ | $\delta_{CH_2N_3} - \delta_{Me}$ |
| α | 0.13 | 5.66 | −6.75 | 35.21 |
| β | 5.54 | 8.59 | 6.97 | 5.19 |
| λ | −6.49 | −0.18 | −2.17 | −4.88 |
| δ | 0.13 | −0.65 | −0.67 | −0.75 |
| ε | −0.27 | −0.27 | −0.51 | −0.26 |

[a] Data taken from H. J. Schneider and V. Hoppen, *J. Org. Chem.*, 1978, **43**, 3866. [b] $\delta_C$ 17.49 p.p.m. [c] $\delta_C$ 22.75 p.p.m.

TABLE 2

$^{13}$C N.m.r. data for substituted 3-methyl-5α-androstanes (δ values in p.p.m.). Calculated values in parentheses

| | (23) | (24) | (9) | (10) | (11) | (12) | (6) | (7) | (8) |
|---|---|---|---|---|---|---|---|---|---|
| C-1 | 33.0 (32.3) | 38.8 (38.6) | 33.0 (31.6) | 38.1 (38.4) | 32.9 (31.8) | 38.3 (38.1) | 35.3 | 34.6 | 36.5 |
| C-2 | 27.5 (27.8) | 31.0 (30.9) | 23.2 (23.0) | 26.2 (26.0) | 25.7 (25.7) | 28.8 (28.8) | 28.3 | 28.1 | 36.2 |
| C-3 | 27.4 (27.0) | 33.2 (32.6) | 33.1 (32.2) | 38.5 (37.8) | 36.6 (34.0) | 40.2 (39.5) | 62.1 | 62.5 | 61.5 |
| C-4 | 34.8 (34.7) | 37.9 (37.8) | 30.4 (29.9) | 33.0 (31.9) | 32.9 (32.6) | 35.7 (35.6) | 36.8 | 37.1 | 42.5 |
| C-5 | 39.9 (40.6) | 46.8 (46.9) | 40.7 (40.4) | 46.2 (46.2) | 40.1 (39.9) | 46.3 (46.3) | 42.9 | 41.9 | 44.0 |
| C-6 | 29.1 (29.3) | 29.0 (28.9) | 28.8 (29.1) | 28.9 (27.8) | 28.7 (28.8) | 29.1 (28.0) | 30.4 | 30.2 | 27.8 |
| C-7 | 32.6 (32.6) | 32.6 (32.6) | 32.4 (32.6) | 32.4 (32.6) | 32.4 (32.6) | 32.4 (32.1) | 32.2 | 32.2 | 32.1 |
| C-8 | 36.0 (36.0) | 36.0 (36.0) | 35.8 (36.0) | 35.9 (36.0) | 35.8 (36.0) | 35.9 (36.0) | 35.8 | 35.9 | 35.8 |
| C-9 | 55.1 (55.1) | 55.0 (55.1) | 54.6 (55.1) | 54.6 (55.1) | 54.9 (55.1) | 54.5 (55.1) | 54.5 | 54.1 | 54.0 |
| C-10 | 36.6 (36.1) | 35.9 (36.1) | 36.5 (36.3) | 36.1 (35.5) | 36.8 (36.0) | 35.8 (35.1) | 36.1 | 35.6 | 36.3 |
| C-11 | 20.8 (20.9) | 21.1 (20.9) | 20.8 (20.9) | 21.0 (20.9) | 20.8 (20.9) | 21.1 (20.9) | 21.2 | 21.1 | 21.0 |
| C-12 | 39.0 (39.0) | 39.0 (39.0) | 38.9 (39.0) | 38.9 (39.0) | 38.9 (39.0) | 38.9 (39.0) | 38.8 | 38.8 | 38.8 |
| C-13 | 40.9 (40.8) | 40.8 (40.8) | 40.8 (40.8) | 40.8 (40.8) | 40.8 (40.8) | 40.8 (40.8) | 40.8 | 40.8 | 40.8 |
| C-14 | 54.7 (54.7) | 54.6 (54.7) | 55.0 (54.7) | 54.7 (54.7) | 54.6 (54.7) | 54.6 (54.7) | 54.6 | 54.5 | 54.4 |
| C-15 | 25.5 (25.5) | 25.5 (25.5) | 25.5 (25.5) | 25.5 (25.5) | 25.5 (25.5) | 25.5 (25.5) | 25.4 | 25.5 | 25.5 |
| C-16 | 20.5 (20.5) | 20.5 (20.5) | 20.5 (20.5) | 20.5 (20.5) | 20.5 (20.5) | 20.5 (20.5) | 20.5 | 20.5 | 20.5 |
| C-17 | 40.5 (40.5) | 40.5 (40.5) | 40.4 (40.5) | 40.4 (40.5) | 40.8 (40.5) | 40.4 (40.5) | 40.4 | 40.4 | 40.4 |
| C-18 | 17.6 (17.6) | 17.6 (17.6) | 17.5 (17.6) | 17.5 (17.6) | 17.6 (17.6) | 17.6 (17.6) | 17.5 | 17.6 | 17.6 |
| C-19 | 11.7 (12.3) | 12.4 (12.3) | 11.7 (12.3) | 12.3 (12.3) | 11.5 (12.3) | 12.3 (12.3) | 11.7 | 11.6 | 13.6 |
| C-20 | 18.8 (17.5) | 22.7 (22.8) | 53.7 (52.7) | 58.0 (58.0) | 13.2 (10.7) | 16.3 (16.0) | 15.0 | 17.5 | 66.8 |

* The individual α- and β-epoxides (37) and (38) were obtained from treatment of 5α-androstan-3-one (3) with trimethylsulphoxonium iodide and sodium hydride, and with trimethylsulphonium iodide and butyl-lithium, respectively. Reaction of each of the epoxides with sodium azide in DMF gave the hydroxy-azides (21) and (22).

$\delta_{19\text{-H}} - \delta_{18\text{-H}}$ for compound (8) was 0.07 p.p.m., the same as that for the iodo-azide adduct (7) containing an equatorial iodomethyl group, but distinct from that (0.14 p.p.m.) for the isomer (6). On this basis the earlier stereochemical assignment for compound (8) is confirmed.

Further investigation of the addition of iodine(I) azide, generated by different procedures, to the alkene (1) (Table 4) showed that compounds (6) and (7) were the only adducts formed in the presence of air and that the product ratio was influenced markedly by the solvent. In the initial studies of iodine(I) azide additions to alkenes Hassner *et al.*[2,12] carried out the reactions in acetonitrile, but in our earlier work [1,13] little addition to steroidal alkenes occurred, unless diethyl ether was present as a co-solvent. It was assumed that diethyl ether merely aided solubilization of the alkenes, but the present results show that its addition causes an increase in the relative yield of compound (6). Reaction of the alkene (1) with iodine(I) azide, generated from thallium(I) azide–iodine(I) chloride in acetonitrile, gave only one iodo-azide, *viz.* compound (6), but also afforded an iodo-tetrazole, a derivative which had been isolated from the addition of iodine(I) azide to certain alkenes,[13-15] but not, hitherto, from a steroid. Since the iodo-azide adduct (7) was not detected, it is probable that the iodo-tetrazole contains a β-iodomethyl group and is therefore 1-(3β-iodomethyl-5α-androstan-3α-yl)-5-methyltetrazole (39). The iodo-azide (6) was formed as the only product when the alkene (1) was treated with *N*-iodosuccinimide and hydrazoic acid [16] in dichloromethane to give the only stereoselective method which did not require the exclusion of air found during the present study.

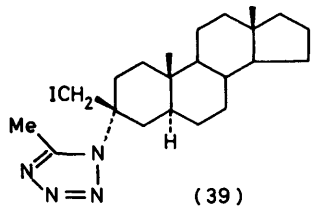
TABLE 4

Additions of iodine(I) azide to 3-methylene-5α-androstane

| Reagent | Solvent | Yield (%) | Products (rel. yields) (6) | (7) | (8) |
|---|---|---|---|---|---|
| $NaN_3$–ICl | MeCN | 83 | 52 | 48 | |
| $NaN_3$–ICl | MeCN–$Et_2O$ | 91 | 63 | 37 | |
| $NaN_3$–ICl | $CH_2Cl_2$ | 98 | 89 | 11 | |
| $TlN_3$–ICl | MeCN | 77 | 75 | | *a* |
| $TlN_3$–ICl | $CH_2Cl_2$ | 80 | 86 | 14 | |
| NIS–$HN_3$ [c] | $CH_2Cl_2$ | 69 | 100 | | |
| $NaN_3$–ICl | MeCN | 71 | | | 100 [b] |

[a] Plus the iodo-tetrazole (39) (25% rel.). [b] Under $N_2$. [c] NIS = *N*-iodosuccinimide.

Treatment of the alkene (1) with iodine(I) azide in acetonitrile under nitrogen gave the adduct (8) as the sole product. The tertiary nature of the iodide was confirmed by the facile and regioselective elimination of hydrogen iodide to give the vinyl azide (4). The regiochemistry of the addition of iodine(I) azide to the alkene (1) in the absence of oxygen suggests that this reaction proceeds *via* a radical mechanism rather than *via* an ionic mechanism as proposed earlier.[1] Radical addition of iodine(I) azide has hitherto been observed only for styrene when the reaction was carried out in pentane under nitrogen.[17] Like the addition of chlorine azide and bromine azide to alkenes in the absence of oxygen,[12b] radical addition of iodine(I) azide is assumed to involve initial attack by an azide radical (Scheme 3). Inhibition of such a pathway by oxygen may result from the formation of peroxy-radicals (*cf.* ref. 18). The high degree of stereoselectivity of the addition to the alkene (1) in the absence of oxygen can be explained (*cf.* ref. 19) using the



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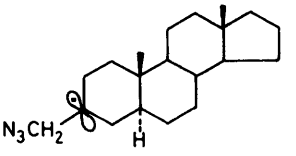

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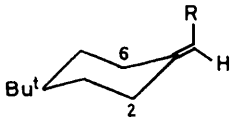
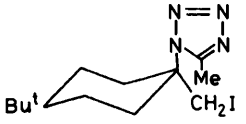


(42) R = H
(43) R = $N_3$



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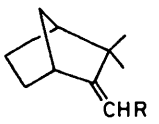
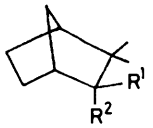
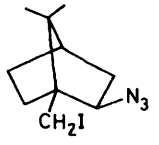


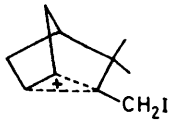
(45) R = H
(46) R = I



(47) $R^1$ = I, $R^2$ = $CH_2N_3$
(48) $R^1$ = $N_3$, $R^2$ = $CH_2I$
(49) $R^1$ = $R^2$ = H



(50)



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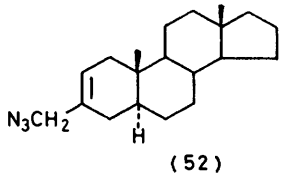

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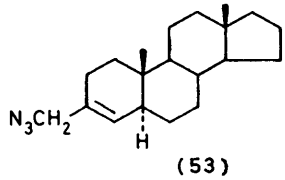
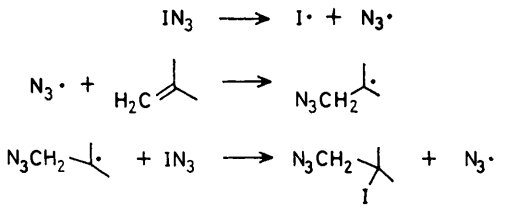


(53)

concept of torsional effects.[20] Assuming that the azido-radical (40), resulting from attack of $N_3$· at C-20 of the alkene (1), has a similar conformation to that of the t-butylcyclohexyl radical (41),[19] the conformation of ring-A will be a chair with a dihedral angle of *ca.* 22°



SCHEME 3

between the C-2β axial hydrogen and the axis of the p-orbital. Delivery of an iodine atom to the radical (40) from a pseudo-equatorial direction will result in the development of torsional interactions, since the azido-methyl group must eclipse the equatorial hydrogens at C-2 and C-4 at some stage of the reaction (Scheme 4).

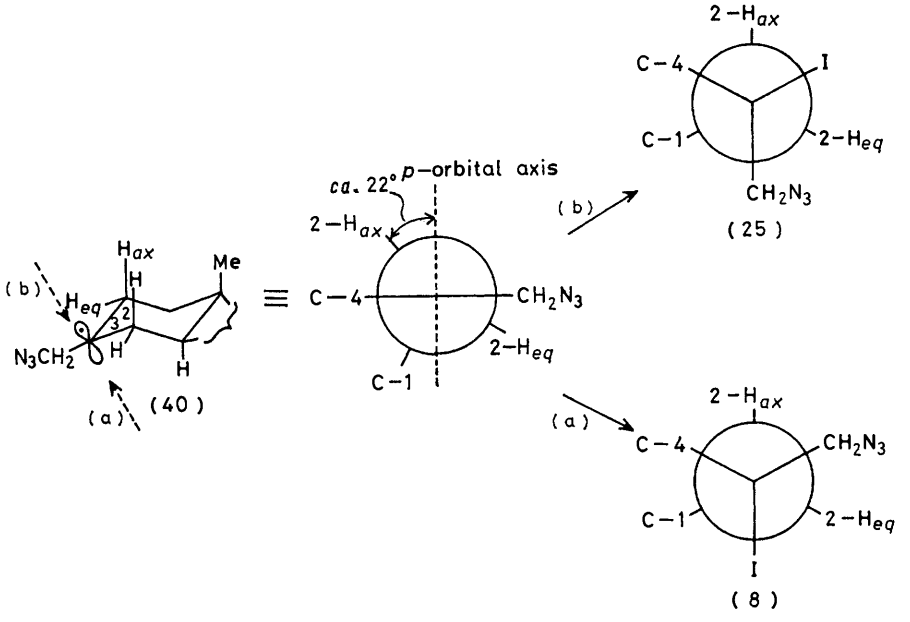
TABLE 5

Additions of iodine(I) azide to 1-methylene-4-t-butylcyclohexane

| Reagent | Solvent | Yield (%) | Products (rel. yields) (32) | (33) | (34) |
|---|---|---|---|---|---|
| $NaN_3$–ICl | MeCN | 100 | 68 | 32 | |
| $NaN_3$–ICl | MeCN–$Et_2O$ | 89 | 80 | 20 | |
| $NaN_3$–ICl | $CH_2Cl_2$ | 97 | 94 | 6 | *a* |
| $TlN_3$–ICl | MeCN | 100 | 93 | 7 | *b* |
| NIS–$HN_3$ | $CH_2Cl_2$ | 86 | 82 | | 18 |
| $NaN_3$–ICl | MeCN | 60 | | | 100 [c] |

[a] Plus unidentified product. [b] Plus the iodo-tetrazole (44) (isolated yield 24%). [c] Under $N_2$.

(33), was obtained, which were separated by p.l.c. The regiochemistry and stereochemistry of each adduct was assigned from their $^1H$ and $^{13}C$ n.m.r. parameters (Table 6). The $^{13}C$ n.m.r. chemical shifts were assigned by comparison with published data for t-butylcyclohexane [22] and by the use of SFORD spectra. Like the corresponding adducts obtained from the alkene (1), the compounds (32) and (33) may arise from attack of an




SCHEME 4 (a) Axial attack; (b) equatorial attack

For delivery of an iodine atom from a pseudo-axial direction no such interaction will result. Therefore, abstraction of I· from iodine(I) azide by the azido-methylene radical (40) should occur preferentially from the axial direction to give compound (8) as the product. An analogous result has been reported by Hassner *et al.* for the radical addition of nitryl iodide to the alkene (5).[21]

The results of the addition of iodine(I) azide to 1-methylene-4-t-butylcyclohexane (42) were similar to those obtained for the alkene (1) and are recorded in Table 5. In the presence of air a mixture of two products, *viz.* *r*-1-azido-1-iodomethyl-*t*-4-t-butylcyclohexane (32) and *r*-1-azido-1-iodomethyl-*c*-4-t-butylcyclohexane azide ion on a tertiary carbocation or by opening of α- and β-iodonium ions by an azide ion. However, the results indicate that if iodonium-ion formation does occur, electrophilic attack of iodine must occur preferentially from an axial direction. A tetrazole, obtained when the iodine(I) azide was generated from thallium(I) azide–iodine(I) chloride, was assigned the structure (44) from its $^1H$ and $^{13}C$ n.m.r. spectra, and by analogy with compound (39).

The addition of iodine(I) azide to the alkene (42) in acetonitrile under nitrogen gave a single product identified as *r*-1-azidomethyl-1-iodo-*t*-4-t-butylcyclohexane (34). Although a correct elemental analysis was not obtained and the mass spectrum failed to give a mole-

TABLE 6

$^1$H and $^{13}$C N.m.r. data for the adducts obtained from 1-methylene-4-t-butylcyclohexane ($\delta$ values)

| | (32) | (33) | (34) |
|---|---|---|---|
| $^1$H N.m.r. | | | |
| $Me_3$ | 0.90 | 0.90 | 0.90 |
| $CH_2X$ | 3.37 [a] | 3.31 [a] | 3.80 [b] |
| $^{13}$C N.m.r. (p.p.m.) | | | |
| C-1 | 61.4 | 61.6 | 61.0 |
| C-2 | 34.8 | 34.9 | 40.5 |
| C-3 | 23.6 | 23.1 | 25.0 |
| C-4 | 47.1 | 47.1 | 47.2 |
| C-5 | 23.6 | 23.1 | 25.0 |
| C-6 | 34.8 | 34.9 | 40.5 |
| C-7 | 13.9 | 17.4 | 66.7 |
| $CMe_3$ | 27.5 | 27.5 | 27.5 |
| $Me_3$ | 32.2 | 32.2 | 32.4 |

[a] X = I. [b] X = $N_3$.

cular ion, peaks in the spectrum at $m/z$ 193 and 196, corresponding to the loss of HI and $IN_2$ from the molecular ion, confirmed the presence of iodine. A singlet in the $^1$H n.m.r. spectrum at $\delta_H$ 3.80 was indicative of an azidomethyl group and this was confirmed by a signal at $\delta_C$ 66.7 in the $^{13}$C n.m.r. spectrum. The stereochemistry of the adduct at C-1 was assigned as that in structure (34) since the $^1$H and $^{13}$C n.m.r. signals of the azidomethyl group were similar to those of the iodo-azide adduct (8). Like the latter compound, the adduct (34) is assumed to arise by a radical process. Treatment of the adduct (34) with potassium t-butoxide gave the vinyl azide (43) whose structure was confirmed from the spectral parameters (see Experimental section) and by comparison of its $^{13}$C n.m.r. spectrum with that of the parent alkene (42) (Table 7). Signals at $\delta_C$ 28.9 and 32.7 p.p.m. in the

TABLE 7

$^{13}$C N.m.r. spectra of exocyclic alkenes ($\delta$ values in p.p.m.)

| | (42) | (43) |
|---|---|---|
| C-1 | 149.7 | 132.2 |
| C-2 | 35.3 | 32.7 |
| C-3 | 29.0 | 27.2 |
| C-4 | 48.0 | 48.1 |
| C-5 | 29.0 | 27.8 |
| C-6 | 35.3 | 28.9 |
| C-7 | 106.2 | 116.8 |
| $CMe_3$ | 32.4 | 32.4 |
| $Me_3$ | 27.7 | 27.6 |

spectrum of compound (43) were assigned to the C-6 and C-2 atoms, respectively, since a carbon atom α- to a double bond in a *cis*-alkene is known to be shielded relative to that in a *trans*-alkene as a result of steric interaction between the *cis*-substituents.[23]

The addition of iodine(I) azide to camphene (45) has been investigated by two groups of workers. Ranganathan *et al.*[15] reported the formation of two products, *viz.* the vinyl iodide (46) and the iodo-azide (47), while Bochwic *et al.*[24] obtained the vinyl iodide (46), the iodo-azide (48), and the rearranged product (50). The structures of the compounds obtained in both studies were assigned using $^1$H n.m.r. analyses. The data reported by the two groups for the iodo-azides (47) and (48) was identical, but Bochwic *et al.* concluded that structure (48) was correct since the adduct showed no tendency to eliminate hydrogen iodide upon treatment with base. Moreover, their isolation of the rearranged iodo-azide (50) supported the structure (48) since all of the products could then have arisen from the common carbocation (51).

In the present study, the structures (46), (48), and (50) were confirmed by repetition of the reaction and examination of the $^{13}$C n.m.r. spectra of the products. Thus, the spectra of both adducts (48) and (50) showed signals at $\delta_C$ 12.1 and 9.1 p.p.m., clearly demonstrating the presence of an iodomethyl group. Other assignments for the SFORD spectra are given in Table 8.

TABLE 8

$^{13}$C N.m.r. SFORD spectra of adducts obtained from camphene (45) ($\delta$ values in p.p.m.)

| | C-1 | C-2 | C-3 | C-4 | C-5 |
|---|---|---|---|---|---|
| (48) | 50.6 (d) | 73.1 (s) | 46.3 (s) | 48.0 (d) | 23.3 [a] (t) |
| (50) | 52.7 (s) | 68.1 (d) | 37.2 (t) | 47.2 (d) | 26.4 [a] (t) |
| | C-6 | C-7 | C-8 | C-9 | C-10 |
| (48) | 22.5 [a] (t) | 34.1 (t) | 22.5 (q) | 27.4 (q) | 12.1 (t) |
| (50) | 35.2 [a] (t) | 47.7 (s) | 19.8 (q) | 20.6 (q) | 9.1 (t) |

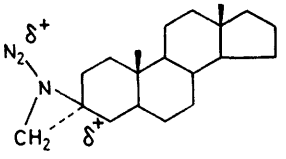
[a] May be interchanged.

In the spectrum of compound (48) the triplet at $\delta_C$ 34.1 p.p.m. was assigned to C-7 since the residual coupling constant [25] was greater than those associated with the other triplets (*cf.* ref. 26). Assignment of chemical shifts in the SFORD spectrum of the adduct (50) was based on the $^{13}$C n.m.r. spectrum of bornane (49),[27] that of C-3 following from its larger residual coupling constant. When the addition of iodine(I) azide to camphene was carried out in dichloromethane rather than in acetonitrile, the overall yield of the adducts (48) and (50) decreased and the vinyl iodide (46) became the major product, possibly reflecting a change in the nature of the reagent in this solvent.[28] The current results indicate that the lack of regio- and stereo-selectivity observed for the addition of iodine(I) azide to 3-methyl-$\Delta^2$-steroids,[1] 3-t-butylcyclohexene,[29] and 3-methoxycyclohexene [29] may be due to competition between ionic and radical pathways; this possibility is presently under investigation.

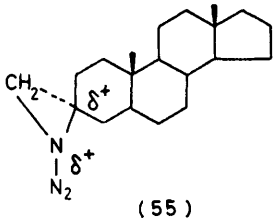
Solvolyses of certain *vic*-iodo-azides were found earlier [1] to be regio- and stereo-selective,[13] the observed retention of configuration being explained in terms of neighbouring-group participation by the azide group to give an *N*-diazonioaziridine [30] (*cf.* ref. 31). Solvolysis of the adduct (6) with silver(I) acetate in acetic acid gave a mixture of products which was partially separated by p.l.c. The least polar fraction was a mixture of 3-azidomethyl-5α-androst-2-ene (52) [1] and the corresponding $\Delta^3$-ene (53), the latter being identified by subtraction of the $^1$H n.m.r. signals of compound (52) from those of the mixture. A more polar fraction containing a 4 : 1 mixture of two acetates yielded 3β-azidomethyl-5α-androstan-3α-yl acetate (27) on fractional crystallization, while hydrolysis of the mother liquors from

crystallization afforded a mixture of 3α-azidomethyl-5α-androstan-3β-ol (21) [from the acetate (26)] and 3β-azidomethyl-5α-androstan-3α-ol (22). $^1H$ and $^{13}C$ N.m.r. chemical shifts of the latter mixture were in agreement with a composite of the spectra of the individual isomers (21) and (22) obtained earlier (Tables 1 and 2). Solvolysis of the iodo-azide (7) also gave the products (52), (53), (26), and (27), but of the latter two compounds, that containing an axial azidomethyl group, *i.e.* (26), was now the major isomer. As expected, solvolysis of the adduct (8) containing a tertiary iodide group afforded the allylic azides (52) and (53) as the major products.

The above results indicate that complete migration of the azide group occurred during the solvolysis of both compounds (6) and (7) (*cf.* ref. 1), resulting in nearly complete inversion of stereochemistry at C-3. A pathway involving neighbouring-group participation of the azide group to form the intermediates (54) and (55)



(54)



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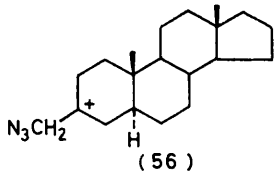

(56)

would account for this inversion. However, the allylic azides (52) and (53) may arise either from an *N*-diazonioaziridine by attack of acetate ion at 2- or 4-H, or from the C-3 carbocation (56).

## EXPERIMENTAL

I.r. spectra were recorded for solutions in $CHCl_3$ with Perkin-Elmer 237, 337, or 397 spectrophotometers. All the azides showed an i.r. absorption at ν *ca.* 2 100 $cm^{-1}$ ($N_3$). Unless otherwise stated, $^1H$ n.m.r. spectra were measured for solutions in $CDCl_3$ with a Varian T60 spectrometer (tetramethylsilane as internal reference) and $^{13}C$ n.m.r. spectra for solutions in $CDCl_3$ with a JEOL JNM–FX60 Fourier-transform instrument. Low-resolution mass spectra were determined with a Varian-MATCH7 spectrometer and high-resolution mass spectra with A.E.I. MS9 or MS30 instruments interfaced with the A.E.I. mass spectroscopy data-system DS30. T.l.c. was carried out on Keiselgel DG (Riedel de Haën) (0.5 mm thickness); preparative t.l.c. (p.l.c.) was carried out on Keiselgel $PF_{254+366}$ (Merck). Products are recorded in order of increasing $R_F$ value. Alumina used for column chromatography was P. Spence and Co., Type H material, and silica gel used for column chromatography was Keiselgel S (Riedel de Haën). G.l.c. was carried out with a Varian Aerograph series 1400 instrument [glass column (8 ft × 1/8 in o.d.) packed with 5% OV-17 on 70—80 mesh Chromosorb W]. Acetonitrile was distilled from phosphorus pentoxide immediately before use. Dichloromethane was washed with concentrated sulphuric acid and then with water until neutral, dried (anhydrous $Na_2SO_4$), fractionally distilled from phosphorus pentoxide, and stored over activated molecular sieves. Tetrahydrofuran (THF) was purified and dried by refluxing with sodium wire for 2 h, followed by fractional distillation, while dimethyl sulphoxide (DMSO) was dried over calcium hydride for 12 h and then distilled under reduced pressure from fresh calcium hydride directly onto molecular sieves which had been activated at 300 °C for 10 h. All the other solvents were purified as described in ref. 32.

Oxygen-free nitrogen refers to nitrogen which has been passed through two aqueous solutions of chromium(II) chloride, a saturated aqueous solution of lead(II) acetate, concentrated sulphuric acid (twice), and finally through a drying tube filled with potassium hydroxide pellets.

*General Procedures for the Preparation of Iodo-azides in the Presence of Air.*—(a) *From sodium azide–iodine*(I) *chloride in acetonitrile.* A solution of iodine(I) chloride (1.0 mol equiv.) in acetonitrile was added as drops over 10 min to a stirred suspension of sodium azide (2.3 mol equiv.) in acetonitrile at −10 °C (ice–methanol). The mixture was maintained at −10 °C for 20 min, the alkene was then added neat or as a solution in acetonitrile, and the mixture was warmed to 20 °C. Stirring was continued for 24 h and the mixture was worked up by addition of water and extraction with diethyl ether. The extracts were washed with aqueous sodium thiosulphate and water, dried, and the solvent was then removed.

(b) *From thallium*(I) *azide–iodine*(I) *chloride.* As for method (a), but with thallium(I) azide [33] (4.6 mol equiv.) and then removal of the thallium(I) iodide by filtration.

(c) *From sodium azide-iodine*(I) *chloride in dichloromethane.* A solution of iodine(I) chloride (1.0 mol equiv.) in dichloromethane was added to a stirred suspension of sodium azide (4.6 mol equiv.) in dichloromethane and the mixture was stirred at 20 °C for 1 h. The resulting brown suspension was cooled to 0 °C and a solution of the alkene in dichloromethane was added. This resulted in the immediate formation of a purple solution which was warmed to 20 °C, with stirring, over 45 min. The reaction was then quenched by addition of aqueous sodium thiosulphate. The dichloromethane solution was separated, washed with further sodium thiosulphate solution, dried, and the solvent was then removed.

(d) *From thallium*(I) *azide–iodine*(I) *chloride in dichloromethane.*—As for method (c), but using thallium(I) azide and work up as in method (b).

(e) *From N-iodosuccinimide–hydrazoic acid.* The alkene (1.0 mol equiv.) was added to a solution of *N*-iodosuccinimide [34] (1.5 mol equiv.) in a 40% dichloromethane solution of hydrazoic acid at 0 °C. The blood-red solution was kept at 20 °C for 1.5 h and washed successively with aqueous

sodium thiosulphate, saturated aqueous sodium hydrogencarbonate, and water. The solvent was then removed from the dried dichloromethane solution.

(f) *From sodium*(I) *azide–iodine*(I) *chloride under nitrogen.* Oxygen was displaced from a solution of iodine(I) azide in acetonitrile [prepared using procedure (a)] by bubbling oxygen-free nitrogen through it for 30 min at −10 °C. The alkene was then added as a solid or as a de-oxygenated solution in acetonitrile *via* a pressure-equalised dropping funnel and oxygen-free nitrogen was bubbled through the mixture for a further 1 h. The mixture was then stirred under the nitrogen atmosphere for 24 h and worked up as in method (a).

*Cyclohexylmethyl Toluene*-p-*sulphonate.*—Cyclohexylmethanol (1.00 g, 8.77 mmol) was treated with toluene-*p*-sulphonyl chloride (2.50 g, 13.1 mmol) in anhydrous pyridine (10 ml) at 5 °C for 24 h. Work-up gave *cyclohexylmethyl toluene*-p-*sulphonate* (1.10 g, 47%) as needles (from pentane at 0 °C), m.p. 31—32 °C (Found: C, 62.8; H, 7.8; S, 12.3. $C_{14}H_{20}SO_3$ requires C, 62.7; H, 7.5; S, 11.9%); $\nu_{max.}$ 1 360 $cm^{-1}$ ($OSO_2$); $\delta_H$ ($CCl_4$) 2.43 (s, Ar*Me*), 3.78 (d, *J* 5.0 Hz, C*H*$_2$OTs), and 7.30 and 7.73 (2d, *J* 8.0 Hz, Ar*H*); *m/z* 268 ($M^{+\cdot}$).

1-*Azidomethylcyclohexane* (28).—The above toluene-*p*-sulphonate (2.20 g, 8.21 mmol) in anhydrous hexamethylphosphoric triamide (11 ml) was treated with sodium azide (0.82 g, 12.62 mmol) at 80 °C for 3 h. The solution was poured into water and extracted with diethyl ether. The extract was worked up to give an oil (1.07 g) which, on distillation, gave the cyclohexane (28) (0.85 g, 75%), b.p. 184—186 °C (lit.,[3] b.p. 30—34 °C at 0.15 mmHg); $\delta_H$ ($CCl_4$) 3.11 (d, *J* 5.0 Hz, $CH_2N_3$); $\delta_C$ 25.9 (C-3 and -5), 26.3 (C-4), 30.7 (C-2 and -6), 38.2 (C-1), and 58.1 p.p.m. (C-7); *m/z* 139 ($M^{+\cdot}$).

1-*Iodomethylcyclohexane* (29).—The above toluene-*p*-sulphonate (1.5 g, 5.59 mmol) was treated with sodium iodide (1.20 g, 8.0 mmol) in refluxing anhydrous acetone (25 ml) for 24 h. Work-up gave the cyclohexane (29) (0.95 g, 76%) as an oil, b.p. 70 °C at 5 mmHg (lit.,[4] b.p. 73—74 °C at 6 mmHg); $\delta_H$($CCl_4$) 3.08 (d, *J* 6.0 Hz, $CH_2I$); $\delta_C$ 16.2 (C-7), 25.9 (C-3 and-5), 26.1 (C-4), 33.4 (C-2 and -6), and 40.0 p.p.m. (C-1); *m/z* 224 ($M^{+\cdot}$) and 97 ($M^{+\cdot}$ − İ).

3-*Methylene*-5α-*androstane* (1).—A 50% suspension of sodium hydride (1.31 g, 27.3 mmol) in mineral oil was added to a flame-dried apparatus. Oil was removed from the suspension by washing it with pentane under an atmosphere of dry nitrogen and removing the pentane with a syringe. Anhydrous DMSO (10 ml) was added to the residual powder and the suspension was stirred at 60 °C until evolution of hydrogen had ceased. The solution of sodium methylsulphinylmethylide was cooled (ice-bath), and a solution of methyltriphenylphosphonium iodide [35] (11.1 g, 36.5 mmol) in anhydrous DMSO (25 ml) was added *via* a nitrogen-flushed syringe over 5 min. The resulting dark yellow solution was stirred at 20 °C for 15 min and a solution of 5α-androstan-3-one [36] (3) (3.0 g, 11.0 mmol) in dry THF (30 ml) was added *via* a syringe over 2 min followed immediately by further THF (15 ml). The mixture was stirred under nitrogen at 60 °C for 24 h, cooled, and poured into water. The mixture was extracted with hexane, the extract was washed with water, and solvent was then removed from the dried solution. The solid was passed through an alumina column with hexane to give the androstane (1) (2.71 g, 90%) as needles, m.p. and mixed m.p. 72—74 °C (from methanol); for $\delta_H$ see ref. 1; $\delta_C$ 11.8 (C-19), 17.6 (C-18), 20.5 (C-16), 21.2 (C-11), 25.5 (C-15), 29.0 (C-6), 31.0 (C-2), 32.4 (C-7), 35.9 (C-8), 36.1 (C-10), 38.0 (C-1), 38.9 (C-12), 39.9 (C-4), 40.5 (C-17), 40.8 (C-13), 48.1 (C-5), 54.5 (C-14), 54.7 (C-9), 105.9 (C-20), and 150.0 p.p.m. (C-3).

*Hydroboration of* 3-*Methylene*-5α-*androstane* (1).—The alkene (1) (3.0 g, 11.0 mmol) was treated with diborane [generated from boron trifluoride–diethyl ether (0.45 ml, 3.64 mmol) and sodium borohydride (0.11 g, 2.91 mmol)] in anhydrous THF (30 ml) over 30 min under nitrogen. The mixture was kept at 25—30 °C for 2.5 h and the excess of hydride was destroyed by the addition of drops of water. The solution was treated with sodium hydroxide (0.5 g) in water (2 ml) and then with 30% hydrogen peroxide (10 ml) at 40 °C for 1 h. Work-up gave a clear viscous oil (3.51 g) which was a mixture of androstan-3α-ylmethanol (13) and androstan-3β-ylmethanol (14).

A solution of the oil in benzene–pyridine (2 : 1) (20 ml) was treated with 3,5-dinitrobenzoyl chloride (3.36 g, 14.6 mmol) and the mixture was heated to 80 °C for 15 min. Work-up gave a brown oil (5.72 g) which was chromatographed on deactivated silica (15% $H_2O$) and eluted with hexane–diethyl ether (4 : 1) to give a mixture of 3,5-dinitrobenzoates (3.32 g, 57%). Multiple elution by p.l.c. (hexane–diethyl ether, 19 : 1) gave (i) *androstan*-3β-*ylmethyl* 3,5-*dinitrobenzoate* (16) (1.11 g, 19%) as needles (from methanol), m.p. 141—143 °C (Found: C, 66.9; H, 7.5; N, 5.6. $C_{27}H_{36}N_2O_6$ requires C, 66.9; H, 7.5; N, 5.8%); $\nu_{max.}$ 1 730 $cm^{-1}$ (CO); for $\delta_H$ see Table 1; *m/z* 484 ($M^{+\cdot}$), 469 ($M^{+\cdot}$ − Me), 441, and 272 ($M^{+\cdot}$ − $C_7H_4N_2O_6$); and (ii) *androstan*-3α-*ylmethyl* 3,5-*dinitrobenzoate* (15) (1.18 g, 20%) as plates (from methanol), m.p. 104—107 °C (Found: C, 66.9; H, 7.8; N, 5.8. $C_{27}H_{36}N_2O_6$ requires C, 66.9; H, 7.5; N, 5.8%); $\nu_{max.}$ 1 730 $cm^{-1}$ (CO); for $\delta_H$ see Table 1; *m/z* 484 ($M^{+\cdot}$), 469 ($M^{+\cdot}$ − Me), 441, and 272 ($M^{+\cdot}$ − $C_7H_4N_2O_6$).

*Androstan*-3α-*ylmethanol* (13).—A solution of the 3,5-dinitrobenzoate (15) (1.18 g, 2.44 mmol) in methanol (30 ml) was heated under reflux with a solution of potassium hydroxide (1.36 g, 24.3 mmol) in water (3 ml) for 1 h and the methanol was removed under reduced pressure to give a residue which was extracted with diethyl ether. Work-up gave the *methanol* (13) (0.63 g, 89%) as needles (from methanol), m.p. 122—125 °C (Found: C, 82.4; H, 12.2. $C_{20}H_{34}O$ requires C, 82.7; H, 11.8%); $\nu_{max.}$ 3 600 $cm^{-1}$ (OH); for $\delta_H$ see Table 1; *m/z* 290 ($M^{+\cdot}$), 275 ($M^{+\cdot}$ − Me), and 257 ($M^{+\cdot}$ − Me − $H_2O$).

*Androstan*-3β-*ylmethanol* (14).—The 3,5-dinitrobenzoate (16) (1.11 g, 2.29 mmol) was treated with potassium hydroxide (1.29, 23.0 mmol) as above to give the *methanol* (14) (0.66 g, 96%) as needles (from methanol), m.p. 110—112 °C (Found: C, 82.8; H, 12.3. $C_{20}H_{34}O$ requires C, 82.7; H, 11.8%); $\nu_{max.}$ 3 600 $cm^{-1}$ (OH); for $\delta_H$ see Table 1; *m/z* 290 ($M^{+\cdot}$), 275 ($M^{+\cdot}$ − Me), and 257 ($M^{+\cdot}$ − Me − $H_2O$).

*Androstan*-3α-*ylmethyl Toluene*-p-*sulphonate* (17).—Toluene-*p*-sulphonyl chloride (0.29 g, 1.52 mmol) was added to a solution of androstan-3α-ylmethanol (13) (0.30 g, 1.03 mmol) in anhydrous pyridine (6 ml) at 0 °C and the solution was kept at 5 °C for 24 h. Work-up gave the *sulphonate* (17) (0.41 g, 89%) as needles (from methanol), m.p. 120—121 °C (Found: C, 73.2; H, 9.1; S, 7.2. $C_{27}H_{40}O_3S$ requires C, 72.9; H, 9.1; S, 7.2%); $\nu_{max.}$ 1 360 $cm^{-1}$ ($OSO_2$); for $\delta_H$ see Table 1; *m/z* 444 ($M^{+\cdot}$) and 272 ($M^{+\cdot}$ − $C_7H_8O_3S$).

*Androstan*-3β-*ylmethyl Toluene*-p-*sulphonate* (18).—The alcohol (14) (0.30 g, 1.03 mmol) was treated with toluene-*p*-sulphonyl chloride (0.24 g, 1.26 mmol) in dry pyridine (6 ml) as above. Work-up gave the *sulphonate* (18) (0.41 g, 89%)

as plates (from methanol), m.p. 103—105 °C (Found: C, 72.9; H, 9.4; S, 7.1. $C_{27}H_{40}O_3S$ requires C, 72.9; H, 9.1; S, 7.2%); $\nu_{max.}$ 1 360 $cm^{-1}$ ($OSO_2$); for $\delta_H$ see Table 1; *m/z* 444 ($M^{+\cdot}$) and 272 ($M^{+\cdot} - C_7H_8O_3S$).

3α-*Azidomethyl-5α-androstane* (9).—The toluene-*p*-sulphonate (17) (0.12 g, 0.27 mmol) was treated with sodium azide (26 mg, 0.40 mmol) in anhydrous hexamethylphosphoric triamide (5 ml) at 80 °C for 2 h. The solution was poured into water and worked up to give an oil (83 mg) which crystallized from acetone at −78 °C to give the *androstane* (9) (29 mg, 34%) as plates, m.p. 34—36 °C (Found: C, 76.6; H, 10.9; N, 12.7. $C_{20}H_{33}N_3$ requires C, 76.2; H, 10.5; N, 13.3%); for $\delta_H$ see Table 1; for $\delta_C$ see Table 2; *m/z* 315 ($M^{+\cdot}$), 287 ($M^{+\cdot} - N_2$), and 272 ($M^{+\cdot} - HN_3$).

3β-*Azidomethyl-5α-androstane* (10).—The toluene-*p*-sulphonate (18) (0.12 g, 0.27 mmol) was treated with sodium azide (26 mg, 0.40 mmol) in anhydrous hexamethylphosphoric triamide (5 ml) as above. Crystallization of the oily product (80 mg) from acetone at −78 °C gave the *androstane* (10) (27 mg, 32%) as rods, m.p. 31—34 °C (Found: C, 76.1; H, 11.1; N, 13.1. $C_{20}H_{33}N_3$ requires C, 76.1; H, 10.5; N, 13.3%); for $\delta_H$ see Table 1; for $\delta_C$ see Table 2; *m/z* 315 ($M^{+\cdot}$), 287 ($M^{+\cdot} - N_2$), and 272 ($M^{+\cdot} - HN_3$).

3α-*Iodomethyl-5α-androstane* (11).—A solution of the toluene-*p*-sulphonate (17) (0.12 g, 0.27 mmol) and sodium iodide (60 mg, 0.40 mmol) in anhydrous acetone (8 ml) was heated under reflux for 24 h. The solvent was removed under reduced pressure, the residue was extracted with diethyl ether, and the extract was worked up to give the *androstane* (11) (77 mg, 71%) as needles (from methanol), m.p. 120—125 °C (Found: $M^{+\cdot}$, 400.1597. $C_{20}H_{33}I$ requires *M*, 400.1626); for $\delta_H$ see Table 1; for $\delta_C$ see Table 2; *m/z* 385.1338 ($M^{+\cdot} - \dot{M}e$), 273.2537 ($M^{+\cdot} - \dot{I}$), 259.2466 ($M^{+\cdot} - \dot{C}H_2I$).

3β-*Iodomethyl-5α-androstane* (12).—The toluene-*p*-sulphonate (18) (0.10 g, 0.23 mmol) was treated with sodium iodide (50 mg, 0.33 mmol) in anhydrous acetone (8 ml) as above. Work-up gave the *androstane* (12) (69 mg, 64%) as needles (from methanol), m.p. 90—93 °C (Found: $M^{+\cdot}$, 400.1628. $C_{20}H_{33}I$ requires *M*, 400.1626); for $\delta_H$ see Table 1; for $\delta_C$ see Table 2; *m/z* 273.2554 ($M^{+\cdot} - \dot{I}$).

3α-*Methyl-5α-androstane* (23).—The toluene-*p*-sulphonate (17) (0.10 g, 0.23 mmol) was heated under reflux with lithium aluminium hydride (17 mg, 0.45 mmol) in anhydrous THF (8 ml) for 24 h. Work-up afforded an oily solid (65 mg) which was percolated through a column of alumina (pentane) to give the *androstane* (23) (50 mg, 79%) as needles, m.p. 62—67 °C (Found: C, 87.3; H, 12.6. $C_{20}H_{34}$ requires C, 87.5; H, 12.5%); for $\delta_H$ see Table 1; for $\delta_C$ see Table 2; *m/z* 274.2661 ($M^{+\cdot}$) and 259.2417 ($M^{+\cdot} - \dot{M}e$).

3β-*Methyl-5α-androstane* (24).—The toluene-*p*-sulphonate (18) (0.10 g, 0.23 mmol) was treated with lithium aluminium hydride (20 mg, 0.53 mmol) as above. Work-up gave the *androstane* (24) (55 mg, 89%) as plates, m.p. 56—60 °C (Found: C, 87.1; H, 12.9. $C_{20}H_{34}$ requires C, 87.5; H, 12.5%); for $\delta_H$ see Table 1; for $\delta_C$ see Table 2; *m/z* 274.2651 ($M^{+\cdot}$) and 259.2380 ($M^{+\cdot} - \dot{M}e$).

(3R)-*Spiro*-(5α-*androstane*-3,2′-*oxiran*) (37).—Sodium hydride (58 mg, 2.42 mmol) was treated with trimethylsulphoxonium iodide (0.52 g, 2.37 mmol) in THF (25 ml) at 70 °C for 2 h under nitrogen. A solution of 5α-androstan-3-one (3) (0.50 g, 1.83 mmol) in THF (10 ml) was added and the mixture was stirred at 20 °C overnight, poured into water, and then extracted with diethyl ether. The extract was worked up to give a yellow solid (0.53 g) which was chromatographed on deactivated silica (10% $H_2O$) and eluted with hexane–diethyl ether (4 : 1) to give the *oxiran* (37) (0.41 g, 77%) as plates (from methanol), m.p. 94—99 °C (Found: C, 83.15; H, 11.5. $C_{20}H_{32}O$ requires C, 83.3; H, 11.2%); $\nu_{max.}$ 1 375 and 920 $cm^{-1}$ (epoxide); $\delta_H$ 0.73 (s, 18-H), 0.90 (s, 19-H), and 2.63 (s, $OCH_2$).

(3S)-*Spiro*-(5α-*androstane*-3,2′-*oxiran*) (38).—Butyllithium (0.14 g, 2.19 mmol) was added as drops to a stirred suspension of trimethylsulphonium iodide (0.49 g, 2.37 mmol) in anhydrous THF (25 ml) under nitrogen at 0 °C. The mixture was stirred for 5 min, 5α-androstan-3-one (3) (0.50 g, 1.83 mmol) was added, and the suspension was maintained at 0 °C for 30 min and then warmed to 20 °C over 1 h. The mixture was poured into water and then extracted with diethyl ether. Work-up gave a pale yellow solid (0.53 g) which was chromatographed on deactivated silica (5% $H_2O$) and eluted with hexane–diethyl ether (4 : 1) to give a mixture of epoxides (0.25 g, 48%). Fractional crystallization from pentane at −78 °C gave (i) the *oxiran* (38) (91 mg, 17%) as plates (from aqueous methanol), m.p. 152—155 °C (Found: C, 83.3; H, 11.3. $C_{20}H_{32}O$ requires C, 83.3; H, 11.2%); $\nu_{max.}$ 1 360 and 915 $cm^{-1}$ (epoxide); $\delta_H$ 0.73 (s, 18-H), 0.90 (s, 19-H), and 2.60 (s, $W_{\frac{1}{2}}$ 1.5 Hz, $OCH_2$); and (ii) impure (3*R*)-spiro-(5α-androstane-3,2′-oxiran) (37) (0.17 g, 31%), m.p. 82—88 °C (from methanol), containing *ca.* 20% of the β-epoxide (38) ($^1H$ n.m.r. spectral analysis).

*Epoxidation of* 3-*Methylene-5α-androstane* (1).—A solution of the alkene (1) (0.30 g, 1.10 mmol) in anhydrous diethyl ether (10 ml) was treated with *m*-chloroperbenzoic acid (0.45 g, 2.61 mmol) at 20 °C for 23 h. The solution was washed successively with saturated sodium hydrogensulphite, saturated sodium hydrogencarbonate, and water, dried, and the solvent was removed to give an oily solid (0.43 g). Chromatography on deactivated alumina (10% $H_2O$) and elution with hexane–diethyl ether (4 : 1) gave a 3 : 1 mixture (0.30 g, 93%) of (3*R*)-spiro-(5α-androstane-3,2′-oxiran) (37) and (3*S*)-spiro-(5α-androstane-3,2′-oxiran) (38) ($^1H$ n.m.r. spectral and t.l.c. analyses).

3α- *and* 3β-*Formylandrostanes* (19) *and* (20).—The epoxide mixture of compounds (37) and (38) (3 : 1) (0.30 g) was treated with freshly distilled boron trifluoride–diethyl ether (0.3 ml) in anhydrous benzene (3 ml) at 20 °C for 1 min. Water was added and the benzene solution was worked up to give a yellow oil (0.26 g) which was chromatographed on silica. Elution with hexane–diethyl ether (4 : 1) gave an oil (0.15 g, 52%) which was a mixture (1 : 1.2) of the androstane (19); $\delta_H$ 0.70, (s, 18-H), 0.77 (s, 19-H), and 9.73 (s, $W_{\frac{1}{2}}$ 1.5 Hz, CHO); and the androstane (20); $\delta_H$ 0.70 (s, 18-H), 0.80 (s, 19-H), 9.61 (d, *J* 2.0 Hz, CHO).

The aldehyde mixture (0.15 g, 0.52 mmol) was heated under reflux with lithium aluminium hydride (40 mg, 1.05 mmol) in anhydrous diethyl ether (4 ml) for 1 h. Work-up gave a 1 : 2.7 mixture (0.13 g, 90%) of the methanols (13) and (14) ($^1H$ n.m.r. spectral analysis).

3β-*Azidomethyl-5α-androstan-3α-ol* (22).—Sodium azide (80 mg, 1.23 mmol) was added to a solution of the β-epoxide (37) (70 mg, 0.24 mmol) in anhydrous dimethylformamide (DMF) (5 ml) and the mixture was kept at 80 °C for 10 h. Water was added and the solution was then extracted with diethyl ether. The extract was worked up to give the *alcohol* (22) (60 mg, 75%) as plates (from methanol), m.p. 115—120 °C (Found: C, 72.3; H, 10.1; N, 12.6. $C_{20}H_{33}N_3O$ requires C, 72.5; H, 10.0; N, 12.7%); $\nu_{max.}$ 3 600 $cm^{-1}$ (OH); for $\delta_H$ see Table 1; $\delta_C$ 11.2 (C-19), 17.6 (C-18), 20.5

(C-16), 21.0 (C-11), 25.5 (C-15), 28.5 (C-6), 30.8 (C-2), 32.3 (C-7), 33.4 (C-1), 35.9 (C-8), 36.0 (C-10), 37.7 (C-4), 38.9 (C-12), 40.4 (C-5), 40.5 (C-17), 40.8 (C-13), 54.4 (C-14), 54.5 (C-9), 62.9 (C-20), and 71.8 p.p.m. (C-3); *m/z* 302.2507 ($M^{+\cdot}$ — $HN_2$), 289.2500 ($M^{+\cdot}$ — $N_3$), and 288.2317 ($M^{+\cdot}$ — Me — $N_2$).

Treatment of the azido-alcohol (22) (53 mg, 0.16 mmol) with acetic anhydride (0.03 ml) and 4-*NN*-dimethylaminopyridine (2 mg) in triethylamine (0.04 ml) at 20 °C for 27 h gave the 3β-*azidomethyl-5α-androstan-3α-yl acetate* (27) (49 mg, 82%) as rods (from methanol), m.p. 81—82 °C (Found: C, 70.9; H, 9.8; N, 11.4. $C_{22}H_{35}N_3O_2$ requires C, 70.7; H, 9.5; N, 11.3%); $\nu_{max.}$ 1 710 $cm^{-1}$ (CO); for $\delta_H$ see Table 1; $\delta_C$ 11.7 (C-19), 17.5 (C-18), and 56.8 p.p.m. (C-20); *m/z* 345 ($M^{+\cdot}$ — $N_2$), 317 ($M^{+\cdot}$ — $CH_2N_3$), 285 ($M^{+\cdot}$ — $N_2$ — HOAc), 275 ($M^{+\cdot}$ — $CH_2N_3$ — $CH_2CO$), 270 ($M^{+\cdot}$ — $N_2$ — HOAc — Me), and 257 ($M^{+\cdot}$ — $CH_2N_3$ — $CH_2CO$ — $H_2O$).

*3α-Azidomethyl-5α-androstan-3β-ol* (21).—The α-epoxide (38) (50 mg, 0.1 mmol) was treated with sodium azide (80 mg, 1.23 mmol) in anhydrous DMF (8 ml) at 90 °C for 48 h. Work-up gave an oily solid (59 mg) which, on p.l.c. (hexane–diethyl ether, 4 : 1) afforded (i) the androstan-3β-ol (21) (33 mg, 58%) as needles (from pentane), m.p. 123—125 °C; $\nu_{max.}$ 3 600 $cm^{-1}$ (OH); for $\delta_H$ see Table 1; *m/z* 303 ($M^{+\cdot}$ — $N_2$) and 275 ($M^{+\cdot}$ — $CH_2N_3$); and (ii) the starting epoxide (8 mg, 16%).

*3α-Azidomethyl-5α-androstan-3β-yl acetate* (26), prepared as for compound (27), crystallized from methanol as needles (76% yield), m.p. 74—77 °C (Found: C, 70.7; H, 9.6; N, 10.9. $C_{22}H_{35}N_3O_2$ requires C, 70.7; H, 9.5; N, 11.3%); $\nu_{max.}$ 1 710 $cm^{-1}$ (CO); for $\delta_H$ see Table 1; $\delta_C$ 12.1 (C-19), 17.5 (C-18), and 53.0 p.p.m. (C-20).

*Addition of Iodine*(I) *Azide to 3-Methylene-5α-androstane* (1).—Reagents, solvents, and yields are given in Table 4.

3β-Azido-3α-iodomethyl-5α-androstane (6) crystallized from methanol as needles, m.p. 108—110 °C (incorrectly assigned in ref. 1); for $\delta_H$ see Table 1; for $\delta_C$ see Table 2; *m/z* 441 ($M^{+\cdot}$), 399 ($M^{+\cdot}$ — $N_3$), 286 ($M^{+\cdot}$ — $IN_2$), and 272 ($M^{+\cdot}$ — $IN_3$).

3α-Azido-3β-iodomethyl-5α-androstane (7) crystallized from methanol as plates, m.p. 123—128 °C (incorrectly assigned in ref. 1); for $\delta_H$ see Table 1; for $\delta_C$ see Table 2; *m/z* 441 ($M^{+\cdot}$), 399 ($M^{+\cdot}$ — $N_3$), 286 ($M^{+\cdot}$ — $IN_2$), and 272 ($M^{+\cdot}$ — $IN_3$).

1-(3β-Iodomethyl-5α-androstan-3α-yl)-5-methyltetrazole (39) crystallized from aqueous methanol as *needles*, m.p. 185—186 °C (Found: C, 55.1; H, 7.8; N, 11.8. $C_{22}H_{35}IN_4$ requires C, 54.8; H, 7.8; N, 11.8%); $\nu_{max.}$ 1 430 $cm^{-1}$ (tetrazole); $\delta_H$ 0.70 (s, 18-H), 0.90 (s, 19-H), 2.73 (s, Me), and 3.47 (s, $CH_2I$); *m/z* 482 ($M^{+\cdot}$), 467 ($M^{+\cdot}$ — Me), 454 ($M^{+\cdot}$ — $N_2$), 439 ($M^{+\cdot}$ — $N_2$ — Me), 399 ($M^{+\cdot}$ — $C_2H_3N_4$), 384 ($M^{+\cdot}$ — Me — $C_2H_3N_4$), 355 ($M^{+\cdot}$ — I — HCN), and 272 ($M^{+\cdot}$ — I — $C_2H_3N_4$).

3β-Azidomethyl-3α-iodo-5α-androstane (8) crystallized from methanol as *needles*, m.p. 59—61 °C; for $\delta_H$ see Table 1; for $\delta_C$ see Table 2; *m/z* 286.2531 ($M^{+\cdot}$ — $IN_2$), and 272.2486 ($M^{+\cdot}$ — $IN_3$).

*3-(1-Azidoethylidene)-5α-androstane* (4).—The iodo-azide (8) (80 mg, 0.18 mmol) was treated with potassium t-butoxide (24 mg, 0.21 mmol) in anhydrous diethyl ether (2 ml) at 20 °C and the mixture was poured into water and extracted with diethyl ether. The extract was washed with water and saturated aqueous sodium chloride and the solvent was removed to give an oil (54 mg) which was percolated in hexane through a column of alumina to give the *androstane* (4) (37 mg, 65%) as an oil (Found: $M^{+\cdot}$, 313.2585. $C_{20}H_{31}N_3$ requires *M*, 313.2517); $\nu_{max.}$ 1 650 $cm^{-1}$ (C=C); $\delta_H$ 0.70 (s, 18-H), 0.83 (s, 19-H), and 5.92 (s, C=CHN$_3$); *m/z* 285.2461 ($M^{+\cdot}$ — $N_2$) and 270.2158 ($M^{+\cdot}$ — $N_2$ — Me).

*1-Methylene-4-t-butylcyclohexane* (42).—Compound (42) was prepared (98%) from 4-t-butylcyclohexanone by a Wittig reaction as an oil, b.p. 56—60 °C at 8 mmHg (lit.,[37] b.p. 78—80 °C at 18 mmHg); $\delta_H$ 0.90 (s, $CMe_3$) and 4.53br (s, $C=CH_2$); for $\delta_C$ see Table 7.

*Addition of Iodine*(I) *Azide to 1-Methylene-4-t-butylcyclohexane* (42).—Reagents, solvents, and yields are given in Table 5.

*r*-1-Azido-1-iodomethyl-*t*-4-t-butylcyclohexane (32) was obtained as an *oil*, b.p. 119 °C (Kugelrohr) at 0.55 mmHg (Found: C, 41.1; H, 6.5; N, 13.5. $C_{11}H_{20}IN_3$ requires C, 41.1; H, 6.3; N, 13.1%); for $\delta_H$ and $\delta_C$ see Table 6; *m/z* 293 ($M^{+\cdot}$ — $N_2$), 279 ($M^{+\cdot}$ — $N_3$), 264 ($M^{+\cdot}$ — $CMe_3$), 236 ($M^{+\cdot}$ — $CMe_3$ — $N_2$), 194 ($M^{+\cdot}$ — I), 166 ($M^{+\cdot}$ — $IN_2$), and 152 ($M^{+\cdot}$ — $IN_3$).

*r*-1-Azido-1-iodomethyl-*c*-4-t-butylcyclohexane (33) was obtained as an *oil*, b.p. 112 °C (Kugelrohr) at 0.3 mmHg (Found: C, 41.2; H, 6.4; N, 13.6. $C_{11}H_{20}IN_3$ requires C, 41.1; H, 6.3; N, 13.1%); for $\delta_H$ and $\delta_C$ see Table 6; *m/z* 321 ($M^{+\cdot}$), 293 ($M^{+\cdot}$ — $N_2$), 279 ($M^{+\cdot}$ — $N_3$), 264 ($M^{+\cdot}$ — $CMe_3$), 236 ($M^{+\cdot}$ — $CMe_3$ — $N_2$), 194 ($M^{+\cdot}$ — I), 166 ($M^{+\cdot}$ — $IN_2$), and 152 ($M^{+\cdot}$ — $IN_3$).

1-(*r*-1-Iodomethyl-*t*-4-t-butylcyclohexanyl)-5-methyltetrazole (44) crystallized from aqueous methanol as *plates*, m.p. 106—109 °C (Found: C, 43.3; H, 6.7; N, 15.8. $C_{13}H_{23}IN_4$ requires C, 43.1; H, 6.4; N, 15.5%); $\nu_{max.}$ 1 450 $cm^{-1}$ (tetrazole); $\delta_H$ 0.83 (s, $Me_3$), 2.73 (s, Me), and 3.47 (s, $CH_2I$); $\delta_C$ 12.5 (C-9), 17.1 (C-7), 23.2 (C-3 and -5), 27.3 ($Me_3$), 32.1 ($CMe_3$), 35.9 (C-2), 35.9 (C-6), 47.1 (C-4), 63.9 (C-1), and 151.4 p.p.m. (C-8); *m/z* 362 ($M^{+\cdot}$), 305 ($M^{+\cdot}$ — $CMe_3$), 263 ($M^{+\cdot}$ — $CMe_3$ — $N_3$), 235 ($M^{+\cdot}$ — I), 222 ($M^{+\cdot}$ — $CMe_3$ — $N_3$ — $C_2H_3N$), 207 ($M^{+\cdot}$ — $IN_2$), 179 ($M^{+\cdot}$ — I — $CH_2N_3$), and 151 ($M^{+\cdot}$ — I — $CH_2N_3$ — $H_2CN$).

*r*-1-Azidomethyl-1-iodo-*t*-4-t-butylcyclohexane (34) was obtained as a pale yellow *oil*, b.p. 84 °C (Kugelrohr) at 0.03 mmHg; for $\delta_H$ and $\delta_C$ see Table 6; *m/z* 193 ($M^{+\cdot}$ — HI), 166 ($M^{+\cdot}$ — $IN_2$), 165 ($M^{+\cdot}$ — HI — $N_2$), and 150 ($M^{+\cdot}$ — HI — $N_2$ — Me).

*1-Azidoethylidene-4-t-butylcyclohexane* (43).—The iodo-azide (34) (0.24 g, 0.75 mmol) was treated with potassium t-butoxide (0.13 g, 1.16 mmol) in anhydrous diethyl ether (5 ml) at 20 °C for 21 h. Work-up gave a pale yellow oil (0.14 g) which, on p.l.c. (hexane), afforded the *t-butylcyclohexane* (43) (0.14 g, 95%) as an oil, b.p. 82 °C (Kugelrohr) at 0.05 mmHg (Found: C, 68.8; H, 10.2; N, 21.3. $C_{11}H_{19}N_3$ requires C, 68.4; H, 9.9; N, 21.7%); $\nu_{max.}$ 1 660 $cm^{-1}$ (C=C); $\delta_H$ 0.87 (s, $CMe_3$), 5.87 (s, $W_{\frac{1}{2}}$ 4.0 Hz, C=CH); for $\delta_C$ see Table 6; *m/z* 193 ($M^{+\cdot}$), 165 ($M^{+\cdot}$ — $N_2$), and 150 ($M^{+\cdot}$ — $N_2$ — Me).

*Treatment of 3,3-Dimethyl-2-methylenenorbornane with Iodine*(I) *Azide*.—(a) *In acetonitrile*. Camphene (45) (0.30 g, 2.21 mmol) was treated with iodine(I) azide in acetonitrile (20 ml) as in procedure (a) above. Work-up gave a yellow oil (0.48 g) which was chromatographed on silica. Elution with hexane gave two fractions, the least polar of which was pure 2-(1-iodoethylidene)-3,3-dimethylnorbornane[24] (46) (0.15 g, 25%); $\delta_H$ ($CCl_4$) 1.10br (s, 2 × Me), 2.13, 3.05 (2m, bridgehead H), and 5.50 (s, C=CHI). The other fraction (0.12 g) was a mixture ($^1H$ n.m.r. spectroscopy and t.l.c.) of two products. P.l.c. (hexane) gave (i) 2-*exo*-azido-2-*endo*-

iodomethyl-3,3-dimethylnorbornane [24] (48) (16 mg); $\delta_H$ ($CCl_4$) 1.03, 1.17 (2s, 2 × Me), 2.07, 2.50 (2m, bridgehead H), and 3.47 (dd, *J* 10.0 Hz, $CH_2I$); for $\delta_C$ see Table 7; and (ii) 2-*exo*-azido-10-iodobornane [24] (50) (5 mg); $\delta_H$ 0.93, 0.97 (2s, 2 × Me), 3.25 (dd, *J* 10.0 Hz, $CH_2I$), and 3.63 (m, $W_{\frac{1}{2}}$ 14 Hz, $CHN_3$); for $\delta_C$ see Table 8.

Elution of the column with diethyl ether gave a mixture of unidentified tetrazoles (62 mg).

(b) *In dichloromethane.* Camphene (45) (0.30 g, 2.21 mmol) was treated with iodine(I) azide (2.43 mmol) in dichloromethane (20 ml) as in procedure (c) above. Work-up afforded a yellow oil (0.55 g) which was chromatographed on silica to give (i) 2-(1-iodoethylidene)-3,3-dimethylnorbornane (46) (0.19 g, 33%); (ii) the norbornane (48) (0.23 g, 35%); and (iii) the bornane (50) (69 g, 10%).

*Solvolysis of* 3β-*Azido*-3α-*iodomethyl*-5α-*androstane* (6).—A solution of the iodo-azide (6) (0.35 g, 0.79 mmol) in acetic acid (10 ml) was stirred with silver(I) acetate (0.16 g, 0.95 mmol) at 100 °C for 1 h. Silver(I) iodide was filtered off, the filtrate was extracted with diethyl ether, and the extract was washed with water and saturated aqueous sodium hydrogencarbonate until neutral. The solvent was removed from the dried solution to give an oil (0.30 g) which, on p.l.c. (hexane–diethyl ether, 4 : 1), afforded (i) an oil (71 mg) which was a mixture (2 : 1) ($^1$H n.m.r. spectroscopy) of 3-azidomethyl-5a-androst-2-ene (52) (correct i.r. and $^1$H n.m.r. spectra [1]) and 3-azidomethyl-5α-androst-3-ene (53); $\nu_{max.}$ 1 700 $cm^{-1}$ (C=C); $\delta_H$ 0.70 (s, 18-H), 0.73 (s, 19-H), 3.63br (s, $CH_2N_3$), and 5.30 (m, $W_{\frac{1}{2}}$ 4.0 Hz, C=CH); and (ii) an oil (0.15 g) which was a mixture (4 : 1) of two compounds ($^1$H n.m.r. spectroscopy) which crystallized from methanol at 0 °C to give the 3α-acetate (27) (42 mg) as rods (from methanol), m.p. and mixed m.p. 81—82 °C (correct i.r. and $^1$H n.m.r. spectra).

The mother liquors obtained from the crystallization contained the 3β-acetate (26) (correct i.r. and $^1$H n.m.r. spectra).

*Solvolysis of* 3α-*Azido*-3β-*iodomethyl*-5α-*androstane.*—A solution of the iodo-azide (7) (0.18 g, 0.41 mmol) was treated with silver(I) acetate (0.10 g, 0.60 mmol) in acetic acid (5 ml) as above. Work-up gave an oil (0.14 g) which was separated into (i) a mixture (5 : 2) (44 mg) of 3-azidomethyl-5α-androst-2-ene (52) and 3-azidomethyl-5α-androst-3-ene (53) ($^1$H n.m.r. spectral analysis), and (ii) a mixture (1 : 3) (63 mg) of the 3β- and 3α-acetates (26) and (27).

*Solvolysis of* 3β-*Azidomethyl*-3α-*iodo*-5α-*androstane.*—The iodo-azide (8) (0.10 g, 0.23 mmol) was treated with silver(I) acetate (60 mg, 0.36 mmol) in acetic acid (5 ml) at 80 °C as above. Work-up gave an oil (65 mg) consisting mainly of a mixture (2 : 1) of 3-azidomethyl-5α-androst-2-ene (52) and 3-azidomethyl-5α-androst-3-ene (53) (t.l.c. and $^1$H n.m.r. spectral analyses).

*Hydrolysis of the* 3-*Azidomethyl*-5α-*androstan*-3-*yl Acetates.*—A mixture (1 : 1) of the acetates (26) and (27) (0.12 g, 0.32 mmol) in methanol (5 ml) was heated under reflux with a solution of potassium hydroxide (90 mg, 1.6 mmol) in water (0.5 ml) for 3 h. Methanol was removed under reduced pressure and the residue was extracted with diethyl ether. Work-up gave a mixture (1 : 1) of the 3β- and 3α-alcohols (21) and (22) as an oily solid (85 mg) (correct i.r. and $^1$H n.m.r. spectra).

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