Iodo-azide Adducts of 3-Methyl-Δ^2-steroids; Structure and Solvolysis

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The action of sodium azide–iodine(I) chloride in dichloromethane on 3-methyl-5α-androst-2-ene gives a *cis*-iodo-azide as the major adduct. The major product from reaction in acetonitrile is one of ring contraction. These and other products can be rationalised as arising from a C-3 carbocation or from *trans*-diaxial opening of α- or β-iodonium ions. The effects of a crown ether and the action of thallium(I) azide–iodine are also examined. Solvolysis of the *trans*-diaxial 2β-iodo-3α-azide (10) gives *inter alia* a product where azide migration has occurred, whereas solvolysis of the *trans*-diaxial 3α-iodo-2β-azide (11) gives mainly products of elimination. The action of iodine(I) azide on 3-methylene-5α-androstane is also examined.

RECENTLY we compared the action of thallium(I) azide–iodine and sodium azide–iodine(I) chloride on a number of alkenes. These included Δ^2-steroids, which, with each reagent, gave *cis*-adducts in addition to the expected products of *trans*-addition.[1] Although a radical pathway for formation of the *cis*-adducts was not favoured, unequivocal evidence that they were formed *via* a carbocation was not adduced. One substrate examined was the diterpene isophyllocladene (8β,13β-kaur-15-ene) (1) where the action of iodine(I) azide on the trisubstituted double bond also afforded an allylic azide and a diazido-iodo-adduct but no obvious products of *cis*-addition. We have now extended our investigation of substrates with trisubstituted double bonds to 3-methyl-Δ^2-steroids, where addition of iodine(I) azide *via* α- or β-iodonium ions would be expected to lead to competition between *trans*-diaxial opening and opening dictated by formation of the more stable carbocation. In the latter case preferred attack of azide ion would be expected to occur at C-3.

The reaction of 3-methyl-5α-androst-2-ene (2) with preformed iodine(I) azide generated from sodium azide and iodine(I) chloride, in dichloromethane gave four products (Table 1), which were separated by preparative layer chromatography (p.l.c.). All showed strong azide i.r. absorption and gave elemental analyses consistent with their formulation as iodine azide adducts. The major product, m.p. 109—112°, was identified from its ^{1}H n.m.r. spectrum (Table 2) and by comparison with the adducts from 5α-androst-2-ene [1] as the *cis*-adduct 3α-azido-2α-iodo-3-methyl-5α-androstane (8). The spectrum showed the H-2 signal as a doublet of doublets, the chemical shift of which indicated that this proton was geminal to the iodo-substituent [1,2] and the $W_{1/2}$ value (19 Hz) of which showed that it was axial.[3] This was confirmed by the 19-H_3 signal, which showed a much smaller downfield shift (*ca.* 0.1 p.p.m.) relative to that in 3β-methyl-5α-androstane (δ 0.76) than expected for a 2β-iodo-substituent. However, while the chemical shift of the C-3 methyl group (δ 1.51) indicated that it was geminal to an azido-group (*cf.* δ 2.00—2.10 for a methyl group geminal to iodide [4,5]) the stereochemistry at C-3 could not be assigned unequivocally from the ^{1}H n.m.r. spectrum. This was determined from the o.r.d. curve, which showed a negative Cotton effect. Application of the octant rule for azides [6] shows that for a 3-methyl steroid a 3β-azido-group will give a positive curve whereas a 3α-azido-group will give a negative curve.†

The minor product, m.p. 159—162.5°, possessed an ^{1}H n.m.r. spectrum similar to that of the above compound and was therefore identified as 3β-azido-2α-iodo-5α-androstane (9). Its o.r.d. curve exhibited a positive Cotton effect in agreement with that predicted from the octant rule for a 3β-azido-group.

The two products with highest R_F values were identified from their ^{1}H n.m.r. spectra and by comparison with the adducts from 5α-androst-2-ene [1] as the *trans*-diaxial compounds (10) and (11). The spectrum of 3α-azido-2β-iodo-3-methyl-5α-androstane (10), m.p. 108—112°, showed its C-3 methyl signal at δ 1.65, indicating that this group was geminal to the azido-substituent. The chemical shift of the C-2 proton indicated that it was geminal to the iodo-group (*cf.* δ 4.10—4.50 for protons geminal to an azido-group in the adducts from 5α-androst-2-ene [1]); its $W_{1/2}$ value indicated that it was equatorial. The large downfield shift (0.44 p.p.m.) of the 19-H_3 signal from that of 3β-methyl-5α-androstane confirmed that the iodo-group must be in the 2β-position.[8] The o.r.d. curve was again used to assign stereochemistry at C-3 but here the difference between a 3β-azido- and a 3α-azido-3-methyl steroid is not so distinct, since from the octant rule the former would be predicted to exhibit a positive Cotton effect curve and the latter only a weak positive curve. The experimentally determined curve showed a plain positive curve which was still rising at wavelengths below 300 nm.

A signal at δ 4.13, $W_{1/2}$ 7 Hz, in the ^{1}H n.m.r. spectrum of 2β-azido-3α-iodo-3-methyl-5α-androstane (11), m.p.

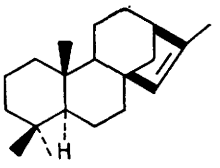
† Strong curves are obtained; a vicinal iodo-substituent has been shown to enhance the magnitude of the molecular rotation of an azide.[7]

[1] R. C. Cambie, R. C. Hayward, P. S. Rutledge, T. Smith-Palmer, and P. D. Woodgate, *J.C.S. Perkin I*, 1976, 840.
[2] F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, 1967, **89**, 2077.
[3] N. S. Bhacca and D. H. Williams, 'Application of N.M.R. Spectroscopy in Organic Chemistry,' Holden–Day, San Francisco, 1964, p. 79.
[4] M. Adinolfi, M. Parrilli, G. Barone, and L. Mangoni, *Gazzetta*, 1975, **105**, 1021.
[5] M. Parilli, G. Barone, M. Adinolfi, and L. Mangoni, *Gazzetta*, 1974, **104**, 835.
[6] C. Djerassi, A. Moscowitz, K. Ponsold, and G. Steiner, *J. Amer. Chem. Soc.*, 1967, **89**, 347.
[7] W. D. Closson and H. B. Gray, *J. Amer. Chem. Soc.*, 1963, **85**, 290.
[8] A. Hassner, J. E. Kropp, and G. J. Kent, *J. Org. Chem.*, 1969 **34**, 2628.

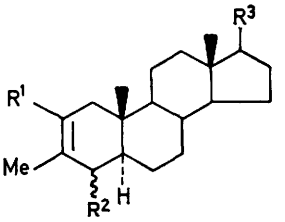
75.5—78.5°, indicated the presence of an equatorial proton geminal to the azido-substituent; thus the latter was in the 2β-position. This was confirmed by the small downfield shift of the 19-H_3 signal relative to that of 3β-methyl-5α-androstane and the chemical shift of the C-3 methyl group, which indicated that it was geminal to an iodo-group. Although it did not serve to distinguish the stereochemistry at C-3, an observed strong positive o.r.d. curve was in accord with predictions from the octant rule for a 2β-azido-3α-iodo-steroid.

Formation of the *cis*-adduct (8) as the major product in the above reaction indicates that it arises *via* a tertiary C-3 carbocation. Thus, as expected, electrophilic attack by iodine on the double bond and attack by azide ion on the carbocation both occur predominantly from the sterically less hindered α-face. Since attack on the carbocation can also occur from the β-face, formation of the adduct (9) as a minor product is not unexpected. If attack of azide ion on an α-iodonium ion occurred either before or in competition with carbocation formation, *trans*-diaxial opening would account for formation of the adduct (11). Likewise, *trans*-diaxial attack by azide ion on a β-iodonium ion would lead to the less abundant adduct (10).

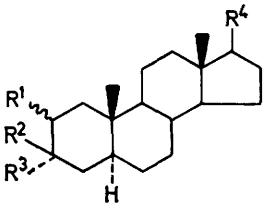
When the reaction of 3-methyl-5α-androst-2-ene with sodium azide–iodine(I) chloride was carried out in acetonitrile the products (9)—(11) were again obtained (albeit in different amounts) but, surprisingly in view of the



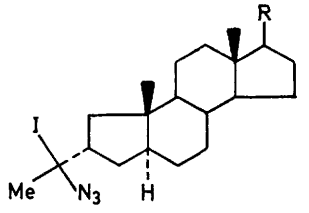
(1)



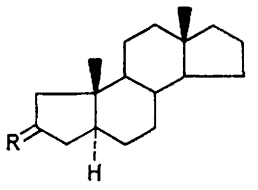
(2) $R^1 = R^2 = R^3 = H$
(3) $R^1 = R^3 = H$, $R^2 = \alpha\text{-}N_3$
(4) $R^1 = R^2 = H$, $R^3 = C_8H_{17}$
(5) $R^1 = H$, $R^2 = \alpha\text{-}N_3$, $R^3 = C_8H_{17}$
(6) $R^2 = R^3 = H$, $R^1 = N_3$
(7) $R^1 = R^3 = H$, $R^2 = \beta\text{-}N_3$



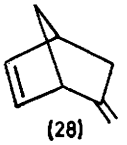
(8) $R^1 = \alpha\text{-}I$, $R^2 = Me$, $R^3 = N_3$, $R^4 = H$
(9) $R^1 = \alpha\text{-}I$, $R^2 = N_3$, $R^3 = Me$, $R^4 = H$
(10) $R^1 = \beta\text{-}I$, $R^2 = Me$, $R^3 = N_3$, $R^4 = H$
(11) $R^1 = \beta\text{-}N_3$, $R^2 = Me$, $R^3 = I$, $R^4 = H$
(12) $R^1 = \alpha\text{-}N_3$, $R^2 = I$, $R^3 = Me$, $R^4 = H$
(13) $R^1 = \alpha\text{-}I$, $R^2 = Me$, $R^3 = N_3$, $R^4 = C_8H_{17}$
(14) $R^1 = \alpha\text{-}I$, $R^2 = N_3$, $R^3 = Me$, $R^4 = C_8H_{17}$
(15) $R^1 = \beta\text{-}I$, $R^2 = Me$, $R^3 = N_3$, $R^4 = C_8H_{17}$
(16) $R^1 = \beta\text{-}N_3$, $R^2 = Me$, $R^3 = N_3$, $R^4 = C_8H_{17}$
(17) $R^1 = \alpha\text{-}N_3$, $R^2 = I$, $R^3 = Me$, $R^4 = C_8H_{17}$
(18) $R^1 = \alpha\text{-}N_3$, $R^2 = OAc$, $R^3 = Me$, $R^4 = H$
(19) $R^1 = \beta\text{-}OAc$, $R^2 = Me$, $R^3 = N_3$, $R^4 = H$
(20) $R^1 = \beta\text{-}N_3$, $R^2 = Me$, $R^3 = OAc$, $R^4 = H$
(21) $R^1 = \beta\text{-}OAc$, $R^2 = Me$, $R^3 = I$, $R^4 = C_8H_{17}$
(22) $R^1 = R^4 = H$, $R^2 = CH_2I$, $R^3 = N_3$,
(23) $R^1 = R^4 = H$, $R^2 = N_3$, $R^3 = CH_2I$,
(24) $R^1 = R^4 = H$, $R^2 = CH_2N_3$ $R^3 = I$,



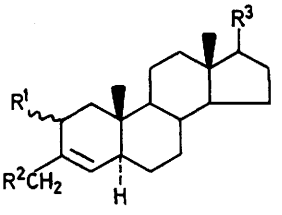
(25) R = H
(26) $R = C_8H_{17}$



(27) $R = CMeN_3$



(28)



(29) $R^1 = \beta\text{-}N_3$, $R^2 = R^3 = H$
(30) $R^1 = \beta\text{-}N_3$, $R^2 = H$, $R^3 = C_8H_{17}$
(31) $R^1 = R^3 = H$, $R^2 = N_3$
(32) $R^1 = \alpha\text{-}N_3$, $R^2 = R^3 = H$

greater polarity of acetonitrile, compound (8) was absent. The overall yield of products was lower than with dichloromethane as solvent and reaction was best achieved when the acetonitrile was purified by distillation from phosphorus pentaoxide.[2] Of three new products, the major compound, m.p. 120° (decomp. with evolution of gas), gave an elemental analysis consistent with its formulation as an iodine(I) azide adduct, but the ^{1}H n.m.r. spectrum was distinctive in that there were no low-field signals. Since there was also no downfield shift of the 19-H_3 signal no substituents could be present at C-2. However, the C-3 methyl signal showed a marked downfield shift as expected for a group geminal to iodide and the compound was therefore formulated as 2α-(1-azido-1-iodoethyl)-5α-A-norandrostane (25). The geminal disposition of the azido- and iodo-substituents explain the low stability of the compound to heat. The structure was confirmed by conversion into a vinyl azide (27) with methanolic potassium hydroxide. Compound (25) presumably arises from an α-iodonium ion by ring contraction in which the 3,4-bond migrates across the β-face to C-2 and the resulting carbocation is then attacked by azide ion. It appears that in acetonitrile the transition state energy for rearrangement is lower than that for attack of azide anion on a C-3 carbocation. Rearrangements during iodo-azide formation have been observed before[9] but a ring contraction has hitherto only been observed for methylenebornene (28).[10]

A further product, m.p. 133—137.5°, also gave analytical figures consistent with an iodine azide adduct. Its ^{1}H n.m.r. spectrum showed a doublet of doublets at δ 4.16, attributed to an axial proton geminal to an azido-group. The presence of an iodine atom at C-3 was confirmed by a marked downfield shift of the C-3 methyl signal. O.r.d. measurements do not establish the stereochemistry at C-3; thus the compound is tentatively identified as 2α-azido-3β-iodo-3-methyl-5α-androstane (12) since its formation can then be rationalised by α-attack of azide ion on an initially formed β-iodonium ion rather than by *cis*-addition to a double bond.

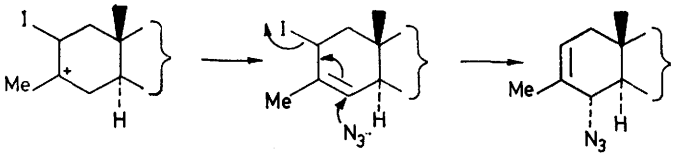
The remaining product, isolated as a pale yellow oil, showed double bond and azide i.r. absorption but was devoid of iodine. In the ^{1}H n.m.r. spectrum the C-3 methyl signal indicated that this group was adjacent to a double bond. The latter was assigned to the 2,3-position since the 19-H_3 signal showed no downfield shift, indicating the absence of substituents at C-2. A doublet at δ 3.50 with coupling constant 6 Hz was more consistent with the dihedral angle between a 4β-proton and a 5α-proton than with that between a 4α-proton and a 5α-proton,[11] and thus the compound was formulated as 4α-azido-3-methyl-5α-androst-2-ene (3). It probably arises as shown in Scheme 1.

TABLE 1

Iodo-azide adducts (% yield)

From 3-methyl-5α-androst-2-ene (2)										
Reagent	Solvent	Reaction time (h)	(2)	(11)	(10)	(3)	(9)	(12)	(8)	(25)
NaN_3–ICl	CH_2Cl_2	22	18	10	9		1		11	
NaN_3–ICl	MeCN	22	23	10	5	9	5	3		15
TlN_3–I_2	CH_2Cl_2	48	5		6	8	17		5	
NaN_3–I_2–18-crown-6	$CHCl_3$	17	4	18	24	3 *	12	5		14
TlN_3–I_2–18-crown-6	$CHCl_3$	20	2	5	21		5			
From 3-methyl-5α-cholest-2-ene (4)										
			(4)	(16)	(15)	(5)	(14)	(17)	(13)	(26)
NaN_3–ICl	CH_2Cl_2	22	17	7	5		3		2	
NaN_3–ICl	MeCN–Et_2O	22	14	2	3	†	5	†	†	3
TlN_3–I_2	CH_2Cl_2	48	10		3	†	3		†	
NaN_3–I_2–18-crown-6	$CHCl_3$	23	4	32	32	3‡	4	3		4

* Containing a trace of (29). ‡ Containing a trace of (30). † Trace.



SCHEME 1

When 3-methyl-5α-androst-2-ene was treated with thallium(I) azide and iodine in dichloromethane, compounds (8)—(10) and (3) were formed. Greater reaction of the substrate was achieved with this reagent than with sodium azide–iodine(I) chloride, but lower yields of the products were obtained owing to the formation of a yellow thallium–steroid complex which remained at the base-line in p.l.c. The use of 18-crown-6 [12] to solubilise the reagent in the reaction of 3-methyl-5α-androst-2-ene with sodium azide–iodine in chloroform gave the same products as sodium azide–iodine(I) chloride in acetonitrile. However, it also resulted in an improved overall yield and greater reproducibility, as well as an increased proportion of the *trans*-diaxial products (10) and (11). The latter compounds were unaffected by further treatment under the same conditions. Although thallium(I) has been reported to interact with 18-crown-6,[13] use of

[9] A. Hassner, *Accounts Chem. Res.*, 1971, **4**, 9.
[10] A. Hassner and J. S. Teeter, *J. Org. Chem.*, 1970, **35**, 3397.
[11] H. Conroy, 'Advances in Organic Chemistry: Methods and Results,' Interscience, New York, 1960, p. 265.
[12] P. D. Woodgate, H. H. Lee, P. S. Rutledge, and R. C. Cambie, *Synthesis*, 1977, in the press.
[13] R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet, and J. J. Christensen, *J. Amer. Chem. Soc.*, 1976, **98**, 7620.

the latter in the reaction with thallium(I) azide–iodine in dichloromethane did not improve the overall yield but it did significantly alter the relative yields of the products (see Table 1).

TABLE 2

^{1}H N.m.r. data (δ values)

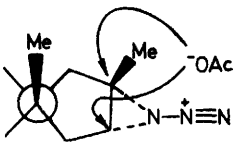
Compd.	18-H_3	19-H_3	3-Me	2-H, *etc.*
(2)	0.73	0.73	1.63	5.30 ($W_{\frac{1}{2}}$ 8 Hz, C=CH)
(8)	0.70	0.86	1.51	4.55 (dd, *J* 13, 5 Hz, CHI)
(9)	0.69	0.82	1.47	4.36 (dd, *J* 12, 5 Hz, CHI)
(10)	0.71	1.20	1.65	4.53 ($W_{\frac{1}{2}}$ 8 Hz, CHI)
(11)	0.72	0.98	2.18	4.13 ($W_{\frac{1}{2}}$ 7 Hz, CHN_3)
(25)	0.71	0.86	2.10	
(12)	0.72	0.94	1.94	4.16 (dd, *J* 12, 5 Hz CHN_3)
(3)	0.67	0.72	1.75	3.50 (d, *J* 6 Hz, 4-CHN_3), 5.52 (*J* 6 Hz, C=CH)
(29)	0.70	0.85	1.80	3.96 (d, *J* 7 Hz, CHN_3), 5.26br (s, C=CH)
(27)	0.73	0.80	1.68	
(13)	0.66	0.83	1.53	4.46 (dd, *J* 13, 5 Hz, CHI)
(14)	0.65	*ca.* 0.86	1.47	4.33 (dd, *J* 12, 5 Hz, CHI)
(15)	0.65	1.19	1.67	4.47 ($W_{\frac{1}{2}}$ 8 Hz, CHI)
(16)	0.66	0.83	2.21	4.14 ($W_{\frac{1}{2}}$ 6 Hz, CHN_3)
(26)	0.65	*ca.* 0.87	2.03	
(17)	0.65	*ca.* 0.87	1.30	4.10 ($W_{\frac{1}{2}}$ 22 Hz, CHN_3)
(5)	0.64	*ca.* 0.87	1.73	3.55 (m, 4-CHN_3), 5.25 ($W_{\frac{1}{2}}$ 5 Hz, C=CH)
(30)	0.64	*ca.* 0.87	1.73	3.93 (d, *J* 8 Hz, CHN_3), 5.50 ($W_{\frac{1}{2}}$ 12 Hz, C=CH)
(18)	0.72	0.90	1.53	4.06 (dd, *J* 12, 5 Hz, CHN_3), 2.03 (OAc)
(19)	0.72	0.94	1.29	4.79 ($W_{\frac{1}{2}}$ 6 Hz, C*H*OAc), 2.07 (OAc)
(42)	0.71	0.75	3.65 (CH_2N_3)	5.65 ($W_{\frac{1}{2}}$ 9 Hz, C=CH)
(32)	0.71	0.80	1.80	3.22 ($W_{\frac{1}{2}}$ 16 Hz, CHN_3), 5.57 ($W_{\frac{1}{2}}$ 11 Hz)
(20)	0.72	1.02	1.50	4.08 ($W_{\frac{1}{2}}$ 8 Hz, CHN_3), 1.99 (OAc)
(6)	0.72	0.80	1.62	
(7)	0.70	0.70	1.80	3.63 ($W_{\frac{1}{2}}$ 6 Hz, 4-CHN_3), 5.33 (d, *J* 6 Hz, C=CH)
(45)	0.72	0.88		4.60br (s, $C=CH_2$)
(22)	0.70	0.84	3.48 (CH_2I)	
(23)	0.70	0.77	3.31 (CH_2I)	
(24)	0.70	0.87	3.98 (CH_2N_3)	

Results similar to the above were obtained with 3-methyl-5α-cholest-2-ene (4) [14] as substrate. However, in these cases compounds were not always isolated since yields were not as high (Table 1) and greater difficulty was experienced in recovering products from p.l.c. plates.

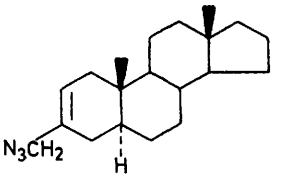
In our earlier study solvolysis of the *trans*-iodo-azide (33) derived from 1-methylcyclohexene with silver acetate in acetic acid, afforded an acetoxy-azide which was tentatively assigned the structure (34).[1] The assignment was made by analogy with that of the product (35) from solvolysis of the iodo-azide (36), but it was appreciated that since its C-2 proton signal was at higher field (δ 3.85) than expected (*viz.* δ 4.40—4.70) for a proton geminal to an acetoxy-group, the alternative structure (39) where azide migration had occurred could not be excluded. The latter was a distinct possibility since a neighbouring group effect by azide ion had been established previously for the acetolysis of *trans*-2-azidocyclohexyl tosylate (37)[15] (*cf.* ref. 16) and indeed, had also been observed for solvolysis of the iodo-azide (36) itself.[1] In order to examine further the possibility of azide migration, the *trans*-iodo-azides (10) and (11) were each solvolysed with silver acetate in acetic acid. In the case of 3α-azido-2β-iodo-3-methyl-5α-androstane (10) a mixture of products was obtained. The major fraction consisted of two isomeric azido-acetates which we were unable to separate. However, the ^{1}H n.m.r. spectrum showed that one component had an axial proton geminal to an azide group while the other had an equatorial proton geminal to an acetate group. The only reasonable structures for these

(33) R^1 = I, R^2 = Me
(34) R^1 = OAc, R^2 = Me
(35) R^1 = OAc, R^2 = H
(36) R^1 = I, R^2 = H
(37) R^1 = OTs, R^2 = H
(38) R^1 = OH, R^2 = Me

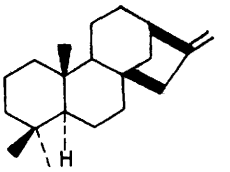
(39) R = Ac
(40) R = H



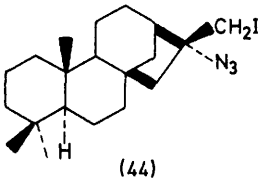
(41)



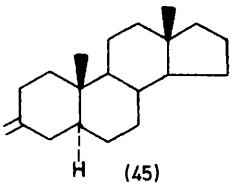
(42)



(43)



(44)



(45)

compounds are (18) and (19). They are presumably formed from a common *N*-diazonioaziridine intermediate [15,17] (41) on which attack by acetate ion occurs at both C-2 and C-3.

A further product from the solvolysis showed azide and olefinic i.r. absorption but contained no acetoxy group. This was confirmed by the ^{1}H n.m.r. spectrum, which showed an olefinic proton signal and a broad two-proton singlet at δ 3.65 attributed to an azidomethyl group, but no acetoxy or vinylic C-3 methyl signals. Of the two possible structures (42) and (31) the former is favoured

[14] D. H. R. Barton, A. da S. Campos-Neves, and R. C. Cookson, *J. Chem. Soc.*, 1956, 3500.

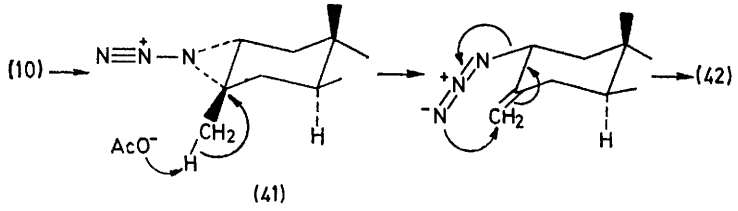
[15] A. Streitwieser and S. Pulver, *J. Amer. Chem. Soc.*, 1964, **86**, 1587.

[16] R. D. Guthrie and D. Murphy, *J. Chem. Soc.*, 1965, 6956.

[17] E. Zbiral, *Synthesis*, 1972, 285.

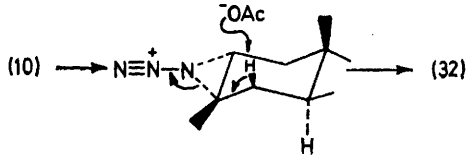
since it could then arise from the intermediate (41) as indicated in Scheme 2 (*cf.* ref. 18).

A third product from solvolysis was isomeric with the compound (42). However, its ^{1}H n.m.r. spectrum showed the presence of both an olefinic proton and a vinylic C-3 methyl group, and a signal at δ 3.22, $W_{1/2}$ 16 Hz, was



SCHEME 2

attributed to an equatorial proton geminal to an azide group. The compound was therefore tentatively assigned the structure (32) and can be envisaged as arising as in Scheme 3.



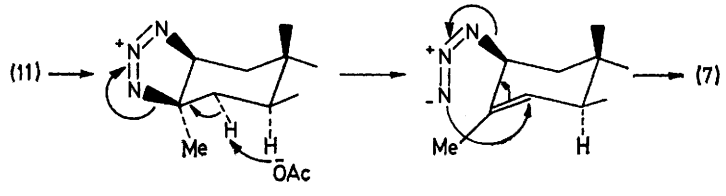
SCHEME 3

Solvolysis of 2β-azido-3α-iodo-3-methyl-5α-androstane (11) also gave a mixture from which four main products were isolated. The ^{1}H n.m.r. spectrum of the major compound showed acetate and C-3 methyl signals as well as a signal at δ 4.08 attributed to an equatorial proton geminal to an azide group. It is identified as 2β-azido-3β-methyl-5α-androstan-3-yl acetate (20). The assignment of stereochemistry at C-3 is only tentative, but if neighbouring group participation is assumed, attack by acetate ion on an *N*-diazonioaziridine similar to (41) would be expected to occur from the α-face. Since the iodo-substituent in (11) is at a tertiary centre there is no driving force for the azide group to migrate (this would lead to a secondary rather than a tertiary carbocation). A second product was identified as 3-azidomethyl-5α-androst-2-ene (42) (obtained above), and the third product tentatively identified as the unsaturated azide (6). Its i.r. spectrum showed the presence of an azido-group but the absence of an acetate group. The spectrum also showed tetrasubstituted double bond absorption ($\nu_{max.}$ 1 670 cm^{-1}), and the absence of an olefinic proton was confirmed by the ^{1}H n.m.r. spectrum, which showed no low-field signals. The compound probably arises from the tertiary carbocation formed by loss of an iodide ion.

T.l.c. of the final product indicated that it consisted of a mixture of two closely related compounds, shown to be 2β-azido- (29) and 4β-azido-3-methyl-5α-androst-2-ene (7) in the ratio 4 : 1 from the ^{1}H n.m.r. spectrum. The structure (7) was assigned from the similarity of the C-2 and C-4 proton signals to those of 4α-azido-3-methyl-5α-androst-2-ene (3). Compound (7) can be envisaged as arising as in Scheme 4. The greater tendency of the iodo-azide (11) to give elimination products is expected for a tertiary iodide and is similar to the behaviour noted by Mangoni and his co-workers [4] for the analogous acetoxy-iodide (21).

Identification of compound (18) as a product of solvolysis of the iodo-azide (10) suggests that the structure (34) of the solvolysis product of the iodo-azide (33)[1] should be revised to (39) and that of its hydrolysis product should be revised from (38) to (40).

In our earlier study [1] we found that the action of iodine(I) azide on the disubstituted exocyclic double bond of phyllocladene (8β,13β-kaur-16-ene) (43) gave the expected product of regiospecific addition, *viz.* (44) in 98% yield. In the present study similar treatment of the steroidal analogue 3-methylene-5α-androstane (45) in acetonitrile gave three products which were separated by p.l.c. The ^{1}H n.m.r. spectrum of the major product, m.p. 115—119°, showed a two-proton singlet at δ 3.48 attributed to an iodomethyl group. The latter appeared to have a β-configuration since the 19-H_3 signal showed a small downfield shift relative to that of 3β-methyl-5α-androstane. The compound was therefore identified as 3α-azido-3-iodomethyl-5α-androstane (22), since by analogy with the phyllocladene case attack of azide ion



SCHEME 4

[18] A. Gagneux, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, 1960, **82**, 5956.

on a C-3 tertiary carbocation would be expected to occur mainly from the less hindered α-face. The second product, m.p. 120—127°, showed a two-proton singlet at δ 3.31 in the ^{1}H n.m.r. spectrum which was also assigned to an iodomethyl group. The compound was therefore formulated as the product of β-attack of azide ion on a C-3 carbocation, *viz.* 3β-azido-3-iodomethyl-5α-androstane (**23**). The third product was an oil which showed a two-proton singlet at δ 3.98 in its ^{1}H n.m.r. spectrum. Although a proton geminal to a secondary iodo-substituent resonates further downfield than a proton geminal to a secondary azido-group,[2] available evidence indicates that protons geminal to a primary iodo-substituent resonate upfield from those geminal to a primary azido-group.[1] The compound is therefore identified as 3β-azidomethyl-3-iodo-5α-androstane (**24**), since it probably arises by anti-Markownikov opening of an α-iodonium ion rather than *via* a primary carbocation.

EXPERIMENTAL

General experimental details have been described previously.[1] ^{13}C N.m.r. spectra were measured for solutions in $CDCl_3$ with a JEOL PFT-FX60 spectrometer (tetramethylsilane as internal reference). Assignments were made according to ref. 19. O.r.d. data were determined for solutions in $CHCl_3$ with a JASCO ORD UV-5 spectrophotometer. Mass spectra were obtained with a Varian MAT CH^7 spectrometer.

Acetonitrile was distilled from phosphorus pentaoxide immediately before use. Chloroform was washed with sulphuric acid and water, dried, and then distilled from phosphorus pentaoxide. Dichloromethane was treated in a similar manner, stored over molecular sieves, and passed through a column of alumina immediately before use. Glacial acetic acid was dried by refluxing with acetic anhydride and toluene-*p*-sulphonic acid.

TABLE 3

^{13}C N.m.r. data (δ values)

	Compound					
	(20)	(11)	(10)	(9)	(25)	(27)
C-1	40.3	43.0	44.1	49.4	47.1	39.4
C-2	120.0	69.4	32.1	31.9	66.9	119.3
C-3	132.5	56.9	65.0	64.3	42.3	39.9
C-4	34.4	38.8	35.8	40.8		
C-5	41.8	45.9	41.5	41.1	44.5	41.5
C-6	28.8	27.2	27.5	27.6	32.0	28.1
C-7	32.2	32.0	32.3	38.6	35.3	35.8
C-8	36.1	35.2	35.0	35.4	35.8	32.0
C-9	54.4	54.1	55.9	54.3	54.3	54.5
C-10	35.3	35.8	36.4	40.3	37.5	35.9
C-11	21.2	21.1	21.1	21.0	21.2	21.3
C-12	39.0	38.8	38.9	38.8	38.6	38.8
C-13	40.8	40.8	40.9	40.7	40.8	40.7
C-14	54.4	53.4	54.4	53.8	54.0	54.3
C-15	25.6	25.4	25.4	25.4	25.5	25.5
C-16	20.5	20.5	20.5	20.5	20.5	20.5
C-17	40.5	40.3	40.4	40.3	40.3	40.2
C-18	17.5	17.6	17.6	17.5	17.5	17.5
C-19	11.8	14.7	15.8	12.0	14.7	12.0
C-20	23.2	35.6	30.8	29.0	61.5	124.9
C-21					27.0	16.9

* In ref. 1 steroidal products are given in order of increasing R_F value, not decreasing as stated.

[19] H. Eggert, C. L. VanAntwerp, N. S. Bhacca, and C. Djerassi, *J. Org. Chem.*, 1976, **41**, 71.

Products are recorded in order of decreasing R_F value * on p.l.c. (n-hexane).

General Procedures for the Preparation of Iodo-azides.—(a) *With sodium azide-iodine*(I) *chloride.* A solution of iodine(I) chloride (0.18 g, 1.1 mmol) in the appropriate solvent (3 ml) was added dropwise over 10 min to a stirred suspension of sodium azide (0.16 g, 2.5 mmol) in the same solvent (3 ml) in a methanol–ice bath. Iodine azide formation was indicated by the colour change reported by Hassner *et al.*[2] After 10 min, the alkene (1.0 mmol) was added, and the mixture was warmed to 20 °C. Stirring was continued overnight and the mixture was worked up by adding water and extracting with ether. The extract was washed with aqueous sodium disulphite and water, and solvent was removed from the dried solution. Products were isolated by p.l.c.

(b) *With thallium*(I) *azide–iodine.* A solution of iodine (0.32 g, 1.25 mmol) in the appropriate solvent (20 ml) was added dropwise to a stirred suspension of thallium(I) azide (0.62 g, 2.5 mmol) in a solution of the alkene (1.0 mmol) in the same solvent (10 ml). The mixture was stirred for 24 h and filtered, and the filtrate was worked up as for (a). When the reaction was carried out with thallium(I) azide (1.1 mmol) for 36 h considerable amounts of starting material remained.

(c) *With sodium azide–iodine–crown ether.* A suspension of sodium azide (0.39 g, 6.0 mmol) in a solution of 18-crown-6 (0.32 g, 1.2 mmol) and chloroform (15 ml) was stirred for 10 min and then treated with iodine (0.61 g, 2.4 mmol). The alkene (1.0 mmol) was added, and the mixture was stirred overnight. Water was added and the mixture was extracted with dichloromethane. The extract was washed with aqueous sodium disulphite, dried, and passed through a column of silica gel to remove the crown ether. Solvent was evaporated off and the products were isolated by p.l.c.

(d) *With thallium*(I) *azide–iodine–crown ether.* A suspension of thallium(I) azide (1.48 g, 6.0 mmol) in a solution of 18-crown-6 (0.32 g, 1.2 mmol) in dichloromethane (15 ml) was stirred for 10 min and then treated with iodine (0.61 g, 2.4 mmol). The alkene (1.0 mmol) was added and the mixture was stirred overnight. The precipitate was filtered off and dichloromethane was added to the filtrate. The solution was then worked up as in (c).

3-Methyl-5α-androst-2-ene (2).—5α-Androstan-3-one [20] (2.0 g, 7.3 mmol) and methylmagnesium iodide (3.6 g, 21.9 mmol) were heated under reflux in dry ether for 3 h to give a mixture of C-3 epimers of 3-methyl-5α-androstan-3-ol (1.93 g). The mixture (1.5 g) was heated under reflux with perchloric acid (66%, 0.5 ml) in acetic acid (100 ml) for 30 min. It was then worked up and the crude product in hexane was percolated through a column of alumina. Recrystallization from methanol–acetone (1 : 10) gave *3-methyl-5α-androst-2-ene* (78%) as needles, m.p. 76.5—78° (Found: C, 88.2; H, 11.8. $C_{20}H_{32}$ requires C, 88.3; H, 11.9%), $\nu_{max.}$ 1 665 cm^{-1} (trisubst. C=C).

A minor signal at δ 5.03 in the ^{1}H n.m.r. spectrum was attributed to the 4-H of 3-methyl-5α-androst-3-ene (*cf.*

[20] V. Prelog, L. Ruzicka, P. Mesiter, and P. Wieland, *Helv. Chim. Acta*, 1945, **28**, 618.

ref. 21). Integration of the low-field olefinic proton signals indicated 10% of the 3-ene in the product after percolation through alumina, decreasing to 5% after one recrystallization. If the reaction time was increased a further impurity appeared which was difficult to remove.

3-*Methyl*-5α-*androstane*.—3-Methyl-5α-androst-2-ene (80 mg, 0.18 mmol) was hydrogenated over 10% palladium–charcoal (60 mg) in ethanol (10 ml) at 45 lb in^{-2} overnight. Work-up and percolation of the product in hexane through a column of alumina gave a 1 : 5 mixture of 3α- *and* 3β-*methyl*-5α-*androstane* (60 mg), which crystallized from methanol–ether as plates, m.p. 51—59° (Found: C, 87.4; H, 12.5. $C_{20}H_{34}$ requires C, 87.5; H, 12.5%), δ 0.71 (s, 18-H_3), 0.76 (s, 19-H_3), 0.84 (s, 3α-Me), and 0.92 (s, 3β-Me).

Iodo-azides of 3-*Methyl*-5α-*androst*-2-*ene*.—(a) *Using method* (a) *in dichloromethane*. P.l.c. of the product (0.31 g) gave (i) starting material (50 mg); (ii) 2β-*azido*-3α-*iodo*-3-*methyl*-5α-*androstane* (11) (45 mg), which crystallized from methanol–ether as needles, m.p. 75.5—78.5° (Found: C, 54.7; H, 7.4; I, 29.1; N, 9.6. $C_{20}H_{32}IN_3$ requires C, 54.4; H, 7.3; I, 28.8; N, 9.5%), $\nu_{max.}$ 2 100 cm^{-1} (N_3), *m/e* 441 ($M^{+\cdot}$), 413 ($M - N_2$), 399 ($M - N_3$), and 286 ($M - IN_2$), o.r.d. (*c* 0.78) $[\phi]_{589}$ +650°, $[\phi]_{450}$ +1 260°, $[\phi]_{316}$ +4 270°, and $[\phi]_{300}$ +3 890°; (iii) 3α-*azido*-2β-*iodo*-3-*methyl*-5α-*androstane* (10) (40 mg), needles (from methanol–ether), m.p. 108—112° (Found: C, 54.8; H, 7.3; N, 9.3. $C_{20}H_{32}IN_3$ requires C, 54.4; H, 7.3; N, 9.5%), $\nu_{max.}$ 2 100 cm^{-1} (N_3), o.r.d. (*c* 0.11) $[\phi]_{589}$ +970°, $[\phi]_{450}$ +1 330°, and $[\phi]_{300}$ +3 040°; (iv) 3β-*azido*-2α-*iodo*-3-*methyl*-5α-*androstane* (9) (5 mg), needles (from methanol–ether), m.p. 159—162.5° (Found: C, 54.6; H, 7.3; I, 28.6; N, 9.5. $C_{20}H_{32}IN_3$ requires C, 54.4; H, 7.3; I, 28.8; N, 9.5%), $\nu_{max.}$ 2 100 cm^{-1} (N_3), *m/e* 427 (M — N), 399 ($M - N_3$), 384 (M — Me — N_3), and 286 ($M - IN_2$), o.r.d. (*c* 0.50) $[\phi]_{589}$ +240°, $[\phi]_{450}$ +500°, $[\phi]_{314}$ +230°, and $[\phi]_{300}$ +2 160°; and (v) 3α-*azido*-2α-*iodo*-3-*methyl*-5α-*androstane* (8) (50 mg), needles (from methanol–ether), m.p. 109—112° (Found: C, 54.6; H, 7.4; N, 9.9. $C_{20}H_{32}IN_3$ requires C, 54.4; H, 7.3; N, 9.5%), $\nu_{max.}$ 2 100 cm^{-1} (N_3), o.r.d. (*c* 0.88) $[\phi]_{589}$ −140°, $[\phi]_{450}$ −310°, $[\phi]_{314}$ −2 100°, and $[\phi]_{300}$ −1 625°.

(b) *Using method* (a) *in acetonitrile*. P.l.c. of the product (0.31 g) gave (i) starting material (62 mg); (ii) 2β-azido-3α-iodo-3-methyl-5α-androstane (11) (43 mg); (iii) 3α-azido-2β-iodo-3-methyl-5α-androstane (10) (22 mg); (iv) 4α-azido-3-methyl-5α-androst-2-ene (3) (27 mg), pale yellow oil, $\nu_{max.}$ 2 100 (N_3) and 1 670 cm^{-1} (C=C); (v) 3β-azido-2α-iodo-3-methyl-5α-androstane (9) (22 mg); (vi) 2α-*azido*-3β-*iodo*-3-*methyl*-5α-*androstane* (12) (13 mg), plates (from methanol–ether), m.p. 133—137.5° (Found: C, 54.6; H, 7.4; N, 9.2. $C_{20}H_{32}IN_3$ requires C, 54.4; H, 7.3; N, 9.5%), $\nu_{max.}$ 2 100 cm^{-1} (N_3), o.r.d. (*c* 0.74) $[\phi]_{589}$ −186°, $[\phi]_{450}$ −372°, and $[\phi]_{324}$ −2 108°; and (vii) 2α-(1-*azido*-1-*iodoethyl*)-5α-A-*norandrostane* (25) (64 mg), needles (from methanol–ether), m.p. 120° (decomp. with evolution of gas) (Found: C, 54.7; H, 7.3; N, 9.7. $C_{20}H_{32}IN_3$ requires C, 54.4; H, 7.3; N, 9.5%), $\nu_{max.}$ 2 100 cm^{-1} (N_3), *m/e* 441 ($M^{+\cdot}$), 412 ($M - HN_2$), 399 ($M - N_3$), and 286 ($M - IN_2$), o.r.d. (*c* 0.62) $[\phi]_{589}$ 0°, $[\phi]_{450}$ 0°, $[\phi]_{320}$ +1 367°, and $[\phi]_{310}$ +1 070°.

(c) *Using method* (b) *in dichloromethane*. P.l.c. of the product (0.40 g) gave (i) starting material (15 mg); (ii) 3α-azido-2β-iodo-3-methyl-5α-androstane (10) (28 mg); (iii) 4α-azido-3-methyl-5α-androst-2-ene (3) (24 mg); (iv) 3β-azido-2α-iodo-3α-methyl-5α-androstane (9) (77 mg); and (v) 3α-azido-2α-iodo-3-methyl-5α-androstane (8) (20 mg).

Use of chloroform as the solvent gave starting material (0.15 g) and 3β-azido-2α-iodo-3-methyl-5α-androstane (9) (18 mg) as the only identified products.

(d) *Using method* (c) *in chloroform*. P.l.c. of the product (0.45 g) gave (i) starting material (12 mg); (ii) 2β-azido-3α-iodo-3-methyl-5α-androstane (11) (78 mg); (iii) 3α-azido-2β-iodo-3-methyl-5α-androstane (10) (0.11 g); (iv) a mixture (13 mg) of 4α-azido-3-methyl-5α-androst-2-ene (3) and 2β-azido-3-methyl-5α-androst-3-ene (29); (v) 3β-azido-2α-iodo-3-methyl-5α-androstane (9) (51 mg); (vi) 2α-azido-3β-iodo-3-methyl-5α-androstane (12) (22 mg); and (vii) 3α-(1-azido-1-iodoethyl)-5α-A-norandrostane (25) (61 mg).

(e) *Using method* (d) *in chloroform*. P.l.c. of the product (0.49 g) gave (i) starting material (10 mg); (ii) 2β-azido-3α-iodo-3-methyl-5α-androstane (11) (22 mg); (iii) 3α-azido-2β-iodo-3-methyl-5α-androstane (10) (91 mg); and (iv) 3β-azido-2α-iodo-3-methyl-5α-androstane (9) (20 mg).

Similar results were obtained using dichloromethane as the solvent.

2-(1-*Azidoethylidene*)-5α-A-*norandrostane* (27).—The iodo-azide (25) (0.15 g, 0.33 mmol) was stirred with potassium hydroxide (0.19 g, 3.3 mmol) in a 1 : 1 mixture of methanol–tetrahydrofuran (6 ml) for 30 min. Work-up gave an orange oil which was dissolved in hexane and percolated through a column of alumina to give 2-(1-*azidoethylidene*)-5α-A-*norandrostane* which crystallized from acetone–methanol (10 : 1) as plates (90 mg, 87%), m.p. 92—93° (Found: C, 76.4; H, 10.0; N, 13.2. $C_{20}H_{31}N_3$ requires C, 76.6; H, 10.0; N, 13.4%), $\nu_{max.}$ 2 100 (N_3) and 1 670 cm^{-1} (C=C), *m/e* 313 ($M^{+\cdot}$), 285 ($M - N_2$), 270 ($M - N_2$ — Me), and 256 ($M - N_3$ — Me).

Iodo-azides of 3-*Methyl*-5α-*cholest*-2-*ene* (4).—(a) *Using method* (a) *in dichloromethane*. P.l.c. of the product (0.24 g) gave (i) starting material (64 mg); (ii) 2β-*azido*-3α-*iodo*-3-*methyl*-5α-*cholestane* (16) (41 mg), needles (from methanol–ether), m.p. 76.5—79° (Found: C, 61.3; H, 8.9; N, 7.8. $C_{28}H_{48}IN_3$ requires C, 60.8; H, 8.8; N, 7.6%), $\nu_{max.}$ 2 100 cm^{-1} (N_3); (iii) 3α-*azido*-2β-*iodo*-3-*methyl*-5α-*cholestane* (15) (25 mg), needles (from methanol–ether), m.p. 86.5—88° (Found: C, 60.8; H, 8.5; N, 7.6. $C_{28}H_{48}IN_3$ requires C, 60.8; H, 8.8; N, 7.6%), $\nu_{max.}$ 2 100 cm^{-1} (N_3); (iv) 3β-*azido*-2α-*iodo*-3-*methyl*-5α-*cholestane* (14) (19 mg), needles (from methanol–ether), m.p. 149—153.5° (Found: C, 61.1; H, 8.7; N, 7.9. $C_{28}H_{48}IN_3$ requires C, 60.8; H, 8.7; N, 7.6%), $\nu_{max.}$ 2 100 cm^{-1} (N_3); (v) 3α-*azido*-2α-*iodo*-3-*methyl*-5α-*cholestane* (13) (13 mg), needles (from methanol–ether), m.p. 109—115° (Found: C, 60.6; H, 8.6; N, 7.5. $C_{28}H_{48}IN_3$ requires C, 60.8; H, 8.8; N, 7.6%), $\nu_{max.}$ 2 100 cm^{-1} (N_3).

(b) *Using method* (a) *in acetonitrile–dry ether* (1 : 1). P.l.c. of the product (0.22 g) gave (i) starting material (56 mg); (ii) 2β-azido-3α-iodo-3-methyl-5α-cholestane (16) (12 mg); (iii) 3α-azido-2β-iodo-3-methyl-5-cholestane (15) (16 mg); (iv) 4α-azido-3-methyl-5α-cholest-2-ene (5) (trace); (v) 3β-azido-2α-iodo-3-methyl-5α-cholestane (14) (25 mg); (vi) 2α-azido-3β-iodo-3-methyl-5α-cholestane (17) (trace); and 2α-(1-*azido*-1-*iodoethyl*)-5α-A-*norcholestane* (26) (14 mg), plates (from methanol–ether), m.p. 136.5—139° (decomp.) (Found: C, 60.6; H, 9.1; N, 7.8. $C_{28}H_{48}IN_3$ requires C, 60.8; H, 8.8; N, 7.6%), $\nu_{max.}$ 2 100 cm^{-1} (N_3).

(c) *Using method* (b) *in dichloromethane*. P.l.c. of the product (0.32 g) gave (i) starting material (38 mg); (ii)

[21] M. Adinolfi, M. Parrilli, G. Barone, and L. Mangoni, *Steroids*, 1975, **26**, 169.

3α-azido-2β-iodo-3-methyl-5α-cholestane (15) (14 mg); (iii) 4α-azido-3-methyl-5α-cholest-2-ene (5) (trace); (iv) 3β-azido-2α-iodo-3-methyl-5α-cholestane (14) (17 mg); and (v) 3α-azido-2α-iodo-3-methyl-5α-cholestane (13) (trace).

(d) *Using method* (c) *in chloroform*. P.l.c. of the product (0.49 g) gave (i) starting material (15 mg); (ii) 2β-azido-3α-iodo-3-methyl-5α-cholestane (16) (0.18 g); (iii) 3α-azido-2β-iodo-3-methyl-5α-cholestane (15) (0.18 g); (iv) a mixture (12 mg) of 4α-azido-3-methyl-5α-cholest-2-ene (5) and 2β-azido-3-methyl-5α-androst-3-ene (30); (v) 3β-azido-2α-iodo-3-methyl-5α-cholestane (14) (23 mg); (vi) 2α-azido-3β-iodo-3-methyl-5α-cholestane (17) (15 mg), plates (from methanol–ether), m.p. 80—84°, $\nu_{max.}$ 2 100 cm^{-1} (N_3); and (vii) 2α-(1-azido-1-iodoethyl)-5α-A-norcholestane (26) (23 mg).

Solvolysis of 3α-*Azido*-2β-*iodo*-3-*methyl*-5α-*androstane*.—A solution of the iodo-azide (10) (0.50 g, 1.13 mmol) in dry acetic acid (25 ml) was stirred with silver acetate (0.21 g, 1.25 mmol) at 20 °C for 1 h and then warmed on a water-bath for 30 min. Silver iodide was filtered off, the product was extracted into ether, and the extract was washed with water and saturated aqueous sodium hydrogen carbonate. Solvent was removed from the dried solution to give a yellow oil which was separated by p.l.c. into (i) 2α-*azido*-3-*methyl*-5α-*androst*-3-*ene* (32) (20 mg), needles (from methanol–ether), m.p. 75—77° (Found: C, 76.8; H, 10.1; N, 13.4. $C_{20}H_{31}N_3$ requires C, 76.6; H, 10.0; N, 13.4%), $\nu_{max.}$ 2 100 cm^{-1} (N_3), o.r.d. (*c* 0.97) $[\phi]_{589}$ 0°, $[\phi]_{450}$ −286°, and $[\phi]_{300}$ −2 383°; (ii) 3-*azidomethyl*-5α-*androst*-2-*ene* (42) (30 mg), plates (from methanol–ether), m.p. 59—61° (Found: C, 76.7; H, 9.9; N, 13.0. $C_{20}H_{31}N_3$ requires C, 76.6; H, 10.0; N, 13.4%), $\nu_{max.}$ 2 100 (N_3) and 1 655 cm^{-1} (C=C), o.r.d. (*c* 0.80) $[\phi]_{589}$ +306°, $[\phi]_{450}$ +535°, and $[\phi]_{300}$ +1 530°; (iii) a mixture (0.15 g) of 3α-*azido*-3-*methyl*-5α-*androstan*-2β-*yl acetate* (19) and 2α-*azido*-3α-*methyl*-5α-*androstan*-3-*yl acetate* (18) which crystallized from methanol–ether as plates, m.p. 94—126° (Found: C, 70.8; H, 9.6; N, 11.4. $C_{22}H_{35}N_3O_2$ requires C, 70.7; H, 9.5; N, 11.3%), $\nu_{max.}$ 2 100 (N_3) and 1 730 cm^{-1} (OAc).

Solvolysis of 2β-*Azido*-3α-*iodo*-3-*methyl*-5α-*androstane*.—A solution of the iodo-azide (11) (0.47 g, 1.1 mmol) in dry acetic acid (6 ml) was stirred with silver acetate (0.20 g, 1.2 mmol) as above. Work-up and p.l.c. gave (i) 2-azido-3-methyl-5α-androst-2-ene (6) (51 mg), pale yellow oil, $\nu_{max.}$ 2 100 (N_3) and 1 665 cm^{-1} (C=C); (ii) a 1 : 4 mixture (40 mg) of 4β-*azido*-3-*methyl*-5α-*androst*-2-*ene* (7) and 2β-*azido*-3-*methyl*-5α-*androst*-3-*ene* (29) (Found: C, 76.9; H, 9.9. $C_{20}H_{31}N_3$ requires C, 76.6; H, 10.0%); (iii) 2β-*azido*-3β-*methyl*-5α-*androstan*-3-*yl acetate* (20) (58 mg) which crystallized from methanol–ether as plates, m.p. 101.5—104.5° (Found: C, 70.9; H, 9.6; N, 10.9. $C_{22}H_{35}N_3O_2$ requires C, 70.7; H, 9.45; N, 11.3%), $\nu_{max.}$ 2 100 (N_3) and 1 720 cm^{-1} (OAc), *m/e* 285 (M − Ac − HN_2) and 43 (Ac^+), o.r.d. (*c* 1.23) $[\phi]_{589}$ +350°, $[\phi]_{450}$ +613°, and $[\phi]_{300}$ +1 775°; and (iv) 3-azidomethyl-5α-androst-2-ene (42) (15 mg).

3-*Methylene*-5α-*androstane* (45).—Triphenylmethylphosphonium bromide [22] (0.71 g, 2.0 mmol) was stirred with n-butyl-lithium (1.2 ml of a 15% hexane solution) in dry ether (6 ml) for 4 h under nitrogen. 5α-Androstan-3-one (0.55 g, 2.0 mmol) in dry ether (3 ml) was added and the mixture was heated under reflux overnight. The mixture was worked up and passed through a column of alumina in hexane to give 3-*methylene*-5α-*androstane* (0.10 g, 18%) as needles, m.p. 71.5—72.5° (lit.,[23] 89—90°) (Found: C, 88.05; H, 12.1. $C_{20}H_{32}$ requires C, 88.2; H, 11.8%).

Reaction of 3-*Methylene*-5α-*androstane with Iodine*(I) *Azide*.—The alkene (45) (0.14 g, 0.5 mmol) was treated with iodine(I) azide in acetonitrile (6 ml) as in method (a) above. P.l.c. of the product (0.18 g) gave (i) 3β-*azido*-3-*iodomethyl*-5α-*androstane* (23) (21 mg, 10%), needles (from methanol–ether), m.p. 120—127° (Found: C, 54.7; H, 7.2; I, 29.0; N, 9.9. $C_{20}H_{32}IN_3$ requires C, 54.4; H, 7.3; I, 28.8; N, 9.5%), $\nu_{max.}$ 2 100 cm^{-1} (N_3), o.r.d. (*c* 0.66) $[\phi]_{589}$ +140°, $[\phi]_{450}$ +200°, $[\phi]_{314}$ +500°, and $[\phi]_{305}$ +470°; (ii) 3β-azidomethyl-3α-iodo-5α-androstane (24) (29 mg, 13%), $\nu_{max.}$ 2 100 cm^{-1} (N_3); and (iii) 3α-*azido*-3-*iodomethyl*-5α-*androstane* (22) (69 mg, 31%), needles (from methanol–ether), m.p. 115—119° (Found: C, 54.3; H, 7.3; I, 29.1; N, 9.5. $C_{20}H_{32}IN_3$ requires C, 54.4; H, 7.3; I, 28.8; N, 9.5%), $\nu_{max.}$ 2 100 cm^{-1} (N_3), o.r.d. (*c* 0.91) $[\phi]_{589}$ +130°, $[\phi]_{450}$ +180°, and $[\phi]_{305}$ +320°.

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