Reactions of Iodine Triacetate, Iodine Trichloride, and Iodine Pentaoxide with Alkenes

By **Richard C. Cambie, David Chambers, Peter S. Rutledge,** and **Paul D. Woodgate,*** Department of Chemistry, University of Auckland, Auckland, New Zealand

Iodine triacetate has been prepared from iodine trichloride and silver acetate. Its reactions with cyclohexene, 5α-androst-2-ene, and methyl cinnamate in acetic acid are stereo- and regio-specific, leading to vicinal *trans*-iodo-acetates and *trans*-iodohydrins. The reactions of iodine trichloride with cyclohexene and 5α-androst-2-ene, and of iodine pentaoxide with cyclohexene have also been examined.

THE preparation of iodine trialkanoates has been studied by a number of workers,[1-5] the conversion of iodine(0) into iodine(III) usually being achieved by the action of an oxidising agent such as lead tetra-acetate, nitric acid, or ozone. The reaction of iodine tris(trifluoroacetate) in pentane with alkenes has been examined by Buddrus,[6] who showed that it exhibits a high degree of stereo-selectivity giving, for example, in the case of cyclo-

hexene the *cis*- and *trans*-adducts (1) and (2) in the ratio 94 : 6. However, iodine trialkanoates suffer from the disadvantages that they are sensitive to moisture and unstable to heat.[2] Moreover, it is not always clear that the reacting species is in fact an iodine trialkanoate. For example, in the case of ' iodine triacetate ' formed by ozonising a solution of iodine in acetic anhydride,[5]

[1] N. Fouqué, *Chem.-Ztg.*, 1814, **38**, 680.

[2] J. W. H. Oldham and A. R. Ubbelohde, *J. Chem. Soc.*, 1941, 368.

[3] S-J. Yeh and R. M. Noyes, *J. Org. Chem.*, 1962, **27**, 2978.

[4] M. Schmeisser, K. Dahmen, and P. Sartori, *Chem. Ber.*, 1967, **100**, 1633.

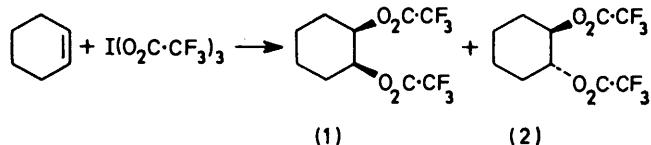[5] G. B. Bachman, G. F. Kite, S. Tuccarbasu, and G. M. Tullman, *J. Org. Chem.*, 1970, **35**, 3167.

[6] J. Buddrus, *Angew. Chem. Internat. Edn.*, 1973, **12**, 163.

we have shown that the reactive species is better regarded as a solvated iodine oxide.[7] In an attempt to circumvent this latter problem, we have investigated a

(1)   (2)

new method for preparing iodine triacetate by a non-oxidative process and have examined its products with the substrates cyclohexene, 5α-androst-2-ene, and methyl cinnamate.

In view of the known reaction delineated in equation (1),[8] iodine trichloride was treated with silver acetate

$$C_6H_5ICl_2 + 2AgOAc \longrightarrow C_6H_5I(OAc)_2 + 2AgCl \quad (1)$$

$$3AgOAc + ICl_3 \xrightarrow{\text{HOAc}} I(OAc)_3 + 3AgCl \quad (2)$$
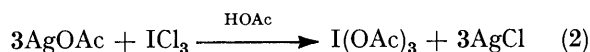
in dry acetic acid [equation (2)]. Owing to the low solubility of silver acetate in acetic acid [9] it was found necessary to re-treat the filtrate from the reaction of stoicheiometric amounts of reagents with fresh silver acetate in order to ensure complete conversion of the iodine trichloride into silver chloride. Reaction of the resulting pale yellow solution (hereafter designated iodine triacetate) with cyclohexene for 3 s gave a 4.5 : 1 mixture of the trans-iodo-acetate (3) [10,11] (45%) and the trans-iodohydrin (4) [10,12] (12%), together with a minor unidentified compound.* Extension of the reaction time resulted in an increase in the amount of iodohydrin at the expense of iodo-acetate. The iodo-acetate (3) is the initial product from the addition of iodine(I) acetate to cyclohexene in a Prévost reaction.[15] A comparative experiment showed that the iodo-acetate (3) was formed more rapidly with iodine triacetate than with iodine(I) acetate prepared from silver acetate–iodine in dry acetic acid, confirming that the iodine(III) species is a better electrophile than the iodine(I) species.

In order to determine if the addition of iodine triacetate exhibited regiospecificity as well as stereospecificity its reactions with 5α-androst-2-ene and methyl cinnamate were studied. With 5α-androst-2-ene it gave a moderate yield of the 3α-iodo-2β-acetate

(10) [7] along with minor unidentified products none of which were iodo-acetates. Reaction with methyl cinnamate gave low yields of the erythro-iodo-acetate (16) and erythro-iodohydrin (17) [14] but no trace of threo-products.† Assignments followed from comparison of the [1]H n.m.r. spectra of (16) and (17) with those of the corresponding erythro- and threo-chloro- [16] and bromo- [17] acetates. The stereospecificity of these reactions can be rationalised

(3) R[1]=I, R[2]=H, R[3]=OAc
(4) R[1]=I, R[2]=H, R[3]=OH
(5) R[1]=R[3]=Cl, R[2]=H
(6) R[1]=I, R[2]=H, R[3]=Cl
(7) R[1]=Cl, R[2]=H, R[3]=OAc
(8) R[1]=R[3]=OAc, R[2]=H
(9) R[1]=OAc, R[2]=OH, R[3]=H

(10) R[1]=OAc, R[2]=I
(11) R[1]=OAc, R[2]=Cl
(12) R[1]=Cl, R[2]=I
(13) R[1]=R[2]=Cl
(14) R[1]=OH, R[2]=H
(15) R[1]=R[2]=OH

(16) R = Ac
(17) R = H

(18)

(19) R = α – Cl
(20) R = β – Cl

(21)

in terms of initial formation of a bridged ion (i) with subsequent trans-diaxial opening by acetate anion (Scheme 1). In the case of 5α-androst-2-ene, formation of an α-bridged ion would occur as a result of preferential attack from the less hindered α-face. The regio-

* If incomplete conversion to iodine triacetate occurred, products of addition of the elements of Cl$_2$ (5),[13] ICl (6),[14] and ClOAc (7) were also formed. If silver salts were not removed the additional products (8) [10] and (9) [10] were formed as a result of solvolysis.
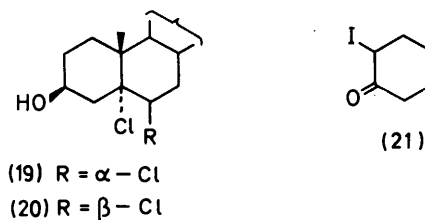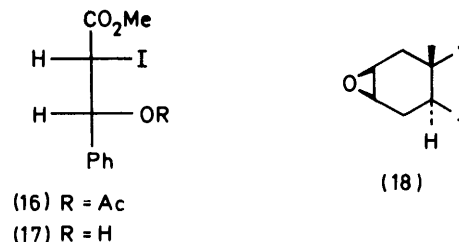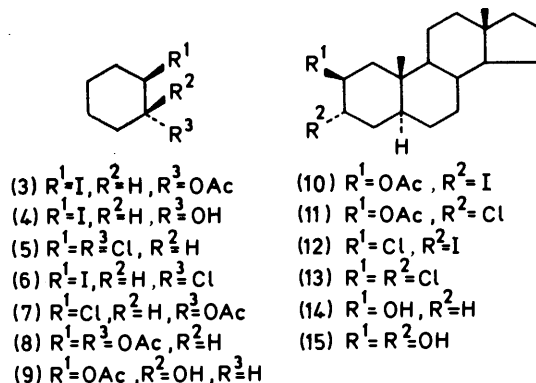
† Earlier we reported that methyl cinnamate is unreactive under normal Prévost conditions.[14] We have now found that reaction can be achieved using molar ratios of substrate to AgOAc to I$_2$ of 1 : 8 : 10, giving the erythro-iodoacetate (16) as the major product (56%).

[7] R. C. Cambie, R. C. Hayward, B. G. Lindsay, A. I. T. Phan, P. S. Rutledge, and P. D. Woodgate, J.C.S. Perkin I, 1976, 1961; F. Fichter and S. Stern, Helv. Chim. Acta, 1928, 11, 1256.

[8] N. W. Alcock and T. C. Weddington, J. Chem. Soc., 1963, 4103.

[9] W. F. Linke, 'Solubilities of Inorganic and Metal Organic Compounds,' vol. 1, 4th edn., van Nostrand, Princeton, 1958, p. 35.

[10] R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, J.C.S. Perkin I, 1974, 1858.

[11] L. Birckenbach, J. Goubeau, and E. Berninger, Ber., 1932, 65, 1339.

[12] S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, J. Amer. Chem. Soc., 1948, 70, 816.

[13] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, 55th edn., The Chemical Rubber Co., Ohio, 1967, p. C–255.

[14] R. C. Cambie, W. I. Noall, G. J. Potter, P. S. Rutledge, and P. D. Woodgate, J.C.S. Perkin I, 1977, 222.

[15] C. V. Wilson, Org. Reactions, 1957, 9, 332; F. D. Gunstone in 'Advances in Organic Chemistry: Methods and Results,' eds. R. A. Raphael, E. C. Taylor, and H. Wynberg, Interscience, New York, 1960, vol. 1, p. 103.

[16] M. D. Johnson and M. C. Cabaleiro, J. Chem. Soc. (B), 1967, 565.

[17] M. A. Wilson and P. D. Woodgate, J.C.S. Perkin II, 1976, 141.

specificity shown in the case of 5α-androst-2-ene is a result of β-attack by a nucleophile at C-2. β-Attack at C-3 would not be favoured since, although this would ultimately lead to a more stable configuration, with equatorial substituents, the reaction must pass through a skewed [18] or boat [19] transition state. During the above process an iodine(III) species (ii) is reduced to an
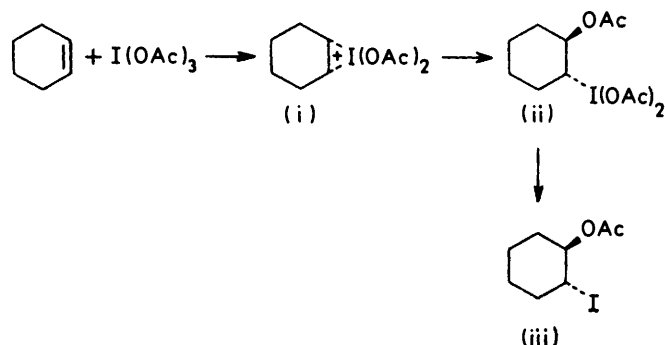
Scheme 1

iodine(I) species (iii). This may occur *via* a radical mechanism similar to that for the dissociation of (di-acetoxyiodo)benzene in acetic acid.[20] Derivatives of (dihydroxyiodo)alkanes [*e.g.* (ii)] are reported to be unstable and to undergo 1,1-elimination,[21] but no products of 1,1-elimination were detected in the present case.

Since iodine trichloride readily decomposes to iodine(I) chloride and chlorine, minor unidentified products in the above reactions could have arisen from these reagents. The action of iodine trichloride on cyclohexene and 5α-androst-2-ene was therefore examined. Reaction of cyclohexene in dry acetic acid gave the chloro-acetate (7) (43%), the iodochloride (6) (19%), the dichloride (5) (17%), and a trace (0.3%) of the iodo-acetate (3). The dichloride could not be separated from the iodochloride nor the chloro-acetate from the iodo-acetate by multiple layer chromatography but each compound was identified by g.l.c. comparison with authentic samples prepared from cyclohexene by other means. In the case of the iodo-acetate (3) and chloro-acetate (7) mixture, the latter could be separated by preferential reduction of the iodo-acetate to cyclohexyl acetate with tri-(n-butyl)tin hydride [22] and by preferential solvolysis of the iodo-acetate to the diacetate (8) with silver acetate in dry acetic acid.

Reaction of 5α-androst-2-ene with iodine trichloride gave products similar to those obtained with cyclohexene, *viz.* the 3α-chloro-2β-acetate (11) (29%) and a 1 : 1 mixture of the 3α-iodo-2β-chloride (12) (20%) and 2β,3α-dichloride (13) (20%). Although the latter mix-

ture could not be separated into its components by layer chromatography each compound was identified by comparison with an authentic sample prepared from 5α-androst-2-ene by independent means. That the chloro-acetate (11) possessed a 2β-acetoxy-group was demonstrated by reduction to 5α-androstan-2β-ol (14) [23,24] with lithium aluminium hydride. Its ^{1}H n.m.r. spectrum showed a one-proton multiplet at δ 4.96 ($W_{1/2}$ 7 Hz) indicative of an equatorial proton geminal to an acetate group,[7] and a downfield shift of the signal due to the C-19 protons to δ 0.90 characteristic of a 2β-acetoxy-group.[7] Hydrolysis with methanolic potassium hydroxide gave 2β,3β-epoxy-5α-androstane (18),[23] which afforded a quantitative yield of the 2β,3α-diol (15) [24] on treatment with perchloric acid.

The low yield or absence of iodo-acetates in the reactions of iodine trichloride with cyclohexene and 5α-androst-2-ene in acetic acid is surprising, since iodonium ion formation is considered to be thermodynamically more favourable than chloronium ion formation. In a reaction of 5α-androst-2-ene with a mixture of iodine triacetate and iodine trichloride the ratio of chloro-acetate (11) to iodo-acetate (10) increased with time (Table), indicating that the iodo-acetate is converted into the chloro-acetate during the reaction with iodine trichloride. Such a transformation could occur as indicated (Scheme 2) *via* a 1,3-dioxolan-2-ylium ion.

Halogenoacetoxylation products

Time	Ratio of (10) to (11)
5 min	1.4 : 1
40 min	1.25 : 1
3 h	0.8 : 1
24 h	0.65 : 1
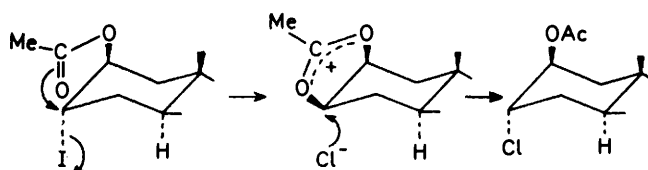
Scheme 2

The reaction of iodine(III) chloride with cholesterol has been carried out by Montignie,[25] who reported the formation of ' indefinite ' solids. Re-investigation of the reaction showed that addition occurred to give six compounds. Three of these were isolated and two were identified as the *cis*-dichloride (19) (10%) and the *trans*-dichloride (20) (22%) (*cf.* ref. 26).

Recently we showed that addition of a solvated iodine oxide, prepared by ozonising a solution of iodine in acetic anhydride, to alkenes was stereo- and regio-specific.[7] In order to determine if the polyvalent iodine species

[18] D. N. Kirk and M. P. Hartshorn, ' Steroid Reaction Mechanisms,' Elsevier, Amsterdam, 1968, p. 97.
[19] A. Hassner and C. Heathcock, *J. Org. Chem.*, 1965, **30**, 1748.
[20] R. B. Sandin and W. B. McCormack, *J. Amer. Chem. Soc.*, 1945, **67**, 2051; W. D. Johnson and J. E. Sherwood, *Austral. J. Chem.*, 1971, **20**, 2281.
[21] J. Buddrus and H. Plettenberg, *Angew. Chem. Internat. Edn.*, 1976, **15**, 436.

[22] E. J. Corey and J. W. Suggs, *J. Org. Chem.*, 1975, **40**, 2554.
[23] J. E. Gurst and C. Djerassi, *J. Amer. Chem. Soc.*, 1964, **86**, 5542.
[24] R. C. Cambie, G. J. Potter, P. S. Rutledge, and P. D. Woodgate, *J.C.S. Perkin I*, 1977, 530.
[25] E. Montignie, *Bull. Soc. chim. France*, 1929, **45**, 302.
[26] A. Zarecki, J. Wicha, and M. Kōcór, *Tetrahedron*, 1976, **32**, 559.

iodine pentaoxide would give the same products, its action on cyclohexene has been examined. Previous use of iodine pentaoxide as a reagent in organic synthesis has been limited to the dehydrogenation of Δ^1-3-oxo- and Δ^4-3-oxo-steroids [27] and the oxidation of benzenethiol.[28]

Iodine pentaoxide is sparingly soluble in acetic anhydride but initial reactions were carried out in this solvent in order to parallel the earlier work.[7] Although relative yields varied considerably depending upon the conditions, reaction with cyclohexene consistently gave trans-2-iodocyclohexyl acetate (3), 2-iodocyclohexanone (21), and trans-2-iodocyclohexanol (4), products also obtained, albeit in higher yields, with solvated iodine oxide. Reaction at 60 °C for 8 h under nitrogen (conditions which gave the best yields) afforded compounds (3), (21), and (4) in yields of 17, 22, and 5%, respectively. The iodo-ketone (21) did not appear to be derived from the iodohydrin (4) since it was not formed on further treatment of the iodohydrin with acetic anhydride in the presence or absence of iodine pentaoxide. This is in contrast to the reaction of the iodohydrin with the solvated iodine oxide, in which the iodo-ketone was formed in moderate yield after treatment for 3 h.[7] No iodo-ketone was produced when acetic anhydride was replaced by trifluoroacetic anhydride or by dimethyl sulphoxide, in which iodine pentaoxide is soluble.

EXPERIMENTAL

General experimental details are given in ref. 7. [13]C N.m.r. spectra were measured for solutions in $CDCl_3$ with a JEOL JNM-FX60 Fourier transform spectrometer.

Iodine Triacetate.—Iodine trichloride (8.0 g, 34 mmol) [containing 96% of an iodine(III) species (from titration with thiosulphate)] was stirred with dried silver acetate (21 g, 126 mmol) to dried acetic acid (150 ml) at 20 °C for 30 min. The yellow suspension was centrifuged and filtered under nitrogen. The filtrate was re-treated twice with silver acetate (8 and 3.5 g) for 1 h and 20 min and the mixture was centrifuged and filtered under nitrogen to give a pale yellow solution which was stored under nitrogen in the dark. The molarity of the solution was determined by titration with sodium thiosulphate.

Reaction of Cyclohexene with Iodine Triacetate.—Cyclohexene (82 mg, 1 mmol) was added under nitrogen to a stirred solution of iodine triacetate (5 ml, 1.01 mmol) at 20 °C and the reaction was quenched with ice–water after 3 s. The mixture was extracted with ether and the extracts were washed successively with water, saturated aqueous sodium hydrogen carbonate, water, saturated aqueous sodium disulphite, and brine. Removal of solvent from the dried solution under reduced pressure gave an oil (0.13 g) containing (t.l.c., g.l.c., and n.m.r. analysis) a 4.5 : 1 mixture of trans-2-iodocyclohexyl acetate (3) [10,11] and trans-2-*iodocyclohexanol* (4).[10,12] A third, minor product was not identified.

The ratio of (3) to (4) after reaction for 10 s was 3 : 1 and after 3 min was 1.4 : 1.

Reaction of Cyclohexene with Iodine Trichloride.—(a) *In acetic acid.* Cyclohexene (82 mg, 1 mmol) was added under

[27] N. V. Organon, Neth. Pat. 90,039/1949 (*Chem. Abs.*, 1960, **55**, 14,310).

nitrogen to a solution of iodine trichloride (0.24 g, 1.01 mmol) in acetic acid (5 ml) and the mixture was stirred at 20 °C for 3 s. Work-up gave an oil (0.27 g) containing (p.l.c., g.l.c., and n.m.r. analysis) (i) *trans*-1,2-dichloro-cyclohexane (5) [13] (26 mg); (ii) *trans*-2-chlorocyclohexyl acetate (7) (78 mg), identical with a sample prepared from cyclohexene by the action of chlorine acetate, $\nu_{max.}$ (film) 1 740 and 1 230 cm^{-1} (OAc), δ 2.01 (s, OAc), 3.76 (6-line pattern, CHCl), and 4.70 (m, CHOAc), m/e 176 ($M^{+\cdot}$), 141 ($M^{+\cdot}$ − Cl), 140 ($M^{+\cdot}$ − HCl), 134 ($M^{+\cdot}$ − CH_2CO), and 116 ($M^{+\cdot}$ − HOAc); (iii) *trans*-1-chloro-2-iodocyclohexane (6) [14] (48 mg); (iv) *trans*-2-iodocyclohexyl acetate (3) (1 mg); and (v) minor unidentified compounds.

(b) *In carbon tetrachloride.* Cyclohexene (0.20 g, 2.44 mmol) was added to a solution of iodine trichloride (0.57 g, 2.44 mmol) in carbon tetrachloride (20 ml) and the mixture was stirred at 20 °C for 6 days. Work-up gave an oil which after layer chromatography (hexane) gave *trans*-1-chloro-2-iodocyclohexane (85 mg, 14%) and *trans*-1,2-dichloro-cyclohexane (51 mg, 13%).

Separation of trans-2-*Chlorocyclohexyl Acetate from the Iodo-acetate* (3).—(a) *By reduction.* Tri-(n-butyl)tin hydride (0.24 ml, 0.83 mmol) was added to a *ca.* 1 : 1 mixture (0.12 g) of *trans*-2-chlorocyclohexyl acetate and *trans*-2-iodocyclo-hexyl acetate in dry ether (3 ml). A small amount of 2,2'-azobis-(2-methylpropiononitrile) was added and a slow stream of dry nitrogen was passed over the solution, which was stirred at 20 °C for 3 h. Oxalic acid (60 mg) was added and the mixture was stirred for 5 min. Dichloro-methane (50 ml) was added and the solution was washed with saturated aqueous sodium hydrogen carbonate and dried. Removal of solvent gave a 1 : 1 mixture of *trans*-2-chlorocyclohexyl acetate and cyclohexyl acetate (g.l.c. analysis).

(b) *By solvolysis.* A mixture of compounds (3) and (7) (37 mg) was stirred with dried silver acetate (30 mg) in dried acetic acid (0.25 ml) at 110 °C for 6.5 h. Work-up gave a mixture of *trans*-2-chlorocyclohexyl acetate and *trans*-1,2-cyclohexyl diacetate (8),[10] $\nu_{max.}$ 1 734 and 1 243 cm^{-1} (OAc), δ 1.97 (s, 2 OAc), and 4.74 (m, $W_{1/2}$ 12 Hz, 2 CHOAc), m/e 200 ($M^{+\cdot}$), 158 ($M^{+\cdot}$ − CH_2CO), 157 ($M^{+\cdot}$ − $COCH_3$), and 140 ($M^{+\cdot}$ − HOAc).

2β,3α-*Dichloro-5α-androstane* (13).—Chlorine was bubbled through a solution of 5α-androst-2-ene [29] (72 mg) in dichloro-methane (10 ml) at 20 °C for 5 min. Work-up and layer chromatography (hexane) gave 2β,3α-*dichloro-5α-androstane* (35 mg, 35%), which crystallized from ethanol–ether as needles, m.p. 126.5—127.5° (Found: C, 69.5; H, 8.9. $C_{19}H_{30}Cl_2$ requires C, 69.2; H, 9.2%), δ 0.69 (s, 18-H_3), 1.08 (s, 19-H_3), and 4.37 (m, $W_{1/2}$ 6 Hz, 2α- and 3β-H), m/e 328 ($M^{+\cdot}$) and 313 ($M^{+\cdot}$ − Me).

2β-*Chloro-3α-iodo-5α-androstane* (12).—Iodine(I) chloride (41 mg, 0.26 mmol) in dichloromethane (5 ml) was added dropwise to a solution of 5α-androst-2-ene (66 mg, 0.26 mmol) in dichloromethane (2 ml) and the mixture was stirred at 20 °C for 5 min. Work-up and layer chromato-graphy (pentane) gave light-sensitive 2β-*chloro-3α-iodo-5α-androstane* (64 mg, 60%), which crystallized from ether–hexane as needles, m.p. 126—130° (Found: C, 54.3; H, 7.3; Cl, 8.3; I, 30.2. $C_{19}H_{30}ClI$ requires C, 54.2; H, 7.2; Cl, 8.3; I, 30.2%), δ 0.69 (s, 18-H_3), 1.10 (s, 19-H_3), 4.59

[28] T. Mukaiyama and T. Endo, *Bull. Chem. Soc. Japan*, 1967, **40**, 2388.
[29] J. M. Evans, G. D. Meakins, Y. Morisawa, and P. D. Woodgate, *J. Chem. Soc.* (C), 1968, 2841.

(m, $W_{1/2}$ 7 Hz, CHCl *), and 4.84 (m, $W_{1/2}$ 7 Hz, CHI *), m/e 420 ($M^{+\cdot}$), 405 ($M^{+\cdot}$ — Me), 369 ($M^{+\cdot}$ — Me — HCl), and 293 ($M^{+\cdot}$ — I).

3α-Chloro-5α-androstan-β-yl Acetate (11).—A mixture of mercury(II) acetate (35 g) and a solution of chlorine (7.29 g) in acetic acid (100 ml) was stirred at 20 °C overnight and then distilled under reduced pressure. 5α-Androst-2-ene (0.26 g) was added to the distillate (20 ml) and the mixture was stirred at 20 °C for 10 min. Most of the solvent was removed under reduced pressure and the residue was worked up in the normal manner. Layer chromatography gave *3α-chloro-5α-androstan-2β-yl acetate* (0.16 g, 46%), which crystallized from ethanol as needles, m.p. 129—130° (Found: C, 71.8; H, 9.5. $C_{21}H_{33}ClO_2$ requires C, 71.5; H, 9.4%), $\nu_{max.}$ 1 746 and 1 229 cm^{-1} (OAc), δ_H 0.68 (s, 18-H_3), 0.90 (s, 19-H_3), 1.97 (s, OAc), 4.10 (m, $W_{1/2}$ 7 Hz, CHCl), and 4.96 (m, $W_{1/2}$ 7 Hz, CHOAc), m/e (no $M^{+\cdot}$) 293 ($M^{+\cdot}$ — OAc), 292 ($M^{+\cdot}$ — HOAc), 277 ($M^{+\cdot}$ — HOAc — Me), 258 ($M^{+\cdot}$ — ClOAc), and 257 ($M^{+\cdot}$ — HOAc — Cl), δ_C 14.2 (C-19), 17.6 (C-18), 20.5 (C-16), 21.0 (C-11), 21.2 (CH_3CO), 25.5 (C-15), 27.8 (C-6), 32.3 (C-7), 32.3 (C-4), 35.5 (C-8), 35.9 (C-10), 36.3 (C-1), 39.0 (C-12), 39.0 (C-5), 40.5 (C-17), 40.9 (C-13), 54.5 (C-14), 55.1 (C-9), 57.7 (C-3), 73.2 (C-2), and 169.3 (CO).

Reduction of the Chloro-acetate (11).—A solution of the chloro-acetate (11) (52 mg) in dry ether was heated under reflux with lithium aluminium hydride (0.25 g) for 2 h. Work-up gave 5α-androstan-2β-ol (14) (100%), m.p. and mixed m.p. 148—150°.[24]

Hydrolysis of the Chloro-acetate (11).—The chloro-acetate (11) (56 mg) was stirred with 2% potassium hydroxide in methanol (0.5 ml) at 20 °C for 48 h. Work-up gave 2β,3β-epoxy-5α-androstane (18) [23] (30 mg, 81%).

The epoxide was stirred with aqueous 20% perchloric acid (0.5 ml) and acetone (5 ml) at 20 °C for 20 h. Work-up gave 5α-androstane-2β,3α-diol (15) (32 mg, 100%), which crystallized from methanol as plates, m.p. and mixed m.p. 195—198° (correct ^{1}H n.m.r. and mass spectra).[24]

Reaction of 5α-Androst-2-ene with Iodine Triacetate.— Iodine triacetate (6 ml, 0.93 mmol) was added under nitrogen to 5α-androst-2-ene (0.20 g, 0.75 mmol) and the mixture was stirred at 20 °C for 1.5 h. Work-up as for cyclohexene gave an oil (0.26 g) which after layer chromatography yielded (i) 3α-iodo-5α-androstan-2β-yl acetate (10) [7] (0.18 g, 51%), δ_C 14.8 (C-19), 17.6 (C-18), 20.5 (C-16), 20.9 (C-11), 21.2 (CH_3CO), 25.5 (C-15), 27.5 (C-6), 31.0 (C-4), 32.1 (C-7), 33.8 (C-3), 35.3 (C-8), 36.2 (C-1), 36.4 (C-10), 38.8 (C-12), 40.4 (C-17), 40.8 (C-13), 42.0 (C-5), 54.4 (C-14), 55.0 (C-9), 74.3 (C-2), and 169.5 (CO); and (ii) minor unidentified products.

Reaction of 5α-Androst-2-ene with Iodine Trichloride.— 5α-Androst-2-ene (0.15 g, 0.57 mmol) was added under nitrogen to iodine trichloride (0.13 g, 0.57 mmol) in acetic acid (5 ml) and the mixture was stirred at 20 °C for 3 min. Work-up yielded an oil (0.19 g) which after layer chromatography gave (i) 2β,3α-dichloro-5α-androstane (13) (20%); (ii) 2β-chloro-3α-iodo-5α-androstane (12) (20%); and (iii) 3α-chloro-5α-androstan-2β-yl acetate (11) (29%).

Reaction of Methyl Cinnamate with Iodine Triacetate.— Iodine triacetate (5 ml, 1.01 mmol) was added under nitrogen to *trans*-methyl cinnamate (0.16 g, 1 mmol) and the mixture was stirred at 20 °C for 9 h. Work-up gave an oil which contained (layer chromatography and n.m.r. analysis) (i) starting material (86 mg, 53%); (ii) methyl

erythro-3-acetoxy-2-iodo-3-phenylpropanoate (16) (20 mg, 6%), b.p. 143° at 0.35 mmHg, $\nu_{max.}$ 1 745 and 1 215 cm^{-1} (OAc), δ 1.96 (s, OAc), 3.76 (s, OMe), 4.52 (d, J 10.5 Hz, CHI), 6.04 (d, J 10.5 Hz, CHOAc), and 7.35 (s, ArH), m/e 348 ($M^{+\cdot}$), 288 ($M^{+\cdot}$ — HOAc), and 220 ($M^{+\cdot}$ — HI); and (iii) methyl *erythro*-3-hydroxy-2-iodo-3-phenylpropanoate (17) (39 mg, 13%) (correct ^{1}H n.m.r. and mass spectra [14]).

Reaction of Methyl Cinnamate with Silver Acetate–Iodine.— Freshly ground iodine (1.82 g, 7.2 mmol) was added over 1 h at 20 °C to a stirred suspension of silver acetate (1.0 g, 6 mmol) in acetic acid (17 ml). After 30 min, *trans*-methyl cinnamate (0.12 g, 0.74 mmol) was added and the stirring was continued at 20 °C for 14 h. Work-up gave an oil (0.24 g) which after layer chromatography yielded methyl *erythro*-3-acetoxy-2-iodo-3-phenylpropanoate (16) (0.14 g) and two minor unidentified products.

Reaction of Cholesterol with Iodine Trichloride.—Cholesterol (0.20 g, 0.5 mmol) was added to a solution of iodine trichloride (0.24 g, 1.01 mmol) in carbon tetrachloride (10 ml) and the mixture was stirred at 20 °C for 2 h. Work-up gave an oil (0.27 g) which after layer chromatography yielded 5α,6α-dichloro-5α-cholestan-3β-ol (19) (23 mg, 10%), $\nu_{max.}$ 3 583 cm^{-1} (OH), δ 0.65 (s, 18-H_3), 1.16 (s, 19-H_3), and 4.24 (t, 6β-H), m/e 456 ($M^{+\cdot}$), 420 ($M^{+\cdot}$ — HCl), and 384 ($M^{+\cdot}$ — 2HCl), and 5α,6β-dichloro-5α-cholestan-3β-ol (20) (51 mg, 22%), $\nu_{max.}$ 3 621 cm^{-1} (OH), δ 0.72 (s, 18-H_3), 1.37 (s, 19-H_3), and 4.31 (m, 6α-H), m/e 456 ($M^{+\cdot}$), 420 ($M^{+\cdot}$ — HCl), and 384 ($M^{+\cdot}$ — 2HCl).

Reaction of Cyclohexene with Iodine Pentaoxide.—(a) *In acetic anhydride.* Iodine pentaoxide (1.02 g, 3.1 mmol) (dried at 114 °C under reduced pressure for 14 h) was added to freshly distilled acetic anhydride (20 ml) and the mixture was stirred at 20 °C for 10 min, whereupon *ca.* half the iodine pentaoxide had dissolved. Cyclohexene (0.25 g, 3.1 mmol) was added and the suspension was stirred under dry nitrogen at 60 °C for 8 h. The reaction was quenched with ice–water. Work-up yielded an orange oil (0.51 g) which was separated by layer chromatography into *trans*-2-iodocyclohexyl acetate (3) (0.14 g), 2-iodocyclohexanone (21) [7] (0.15 g), and *trans*-2-iodocyclohexanol (4) (36 mg).

(b) *In dimethyl sulphoxide.* The above experiment was repeated with iodine pentaoxide (1.02 g), cyclohexene (0.50 g, 6.1 mmol), and freshly distilled dimethyl sulphoxide (20 ml). Work-up gave an oil (0.37 g) which after layer chromatography afforded *trans*-2-iodocyclohexanol (0.28 g, 40%) and two minor unidentified products.

(c) *In acetic anhydride–dimethyl sulphoxide.*[30] The above experiment was repeated with iodine pentaoxide (1.02 g) and cyclohexene (0.25 g), in acetic anhydride (10 ml) and dimethyl sulphoxide (6.6 ml). Work-up gave a brown oil which contained at least nine products, the major one of which was *trans*-2-iodocyclohexyl acetate.

(d) *In trifluoroacetic anhydride.* The above experiment was repeated with iodine pentaoxide (0.41 g, 1.22 mmol), cyclohexene (0.10 g, 1.22 mmol), and trifluoroacetic anhydride (8 ml). Work-up gave an oil (82 mg) which after layer chromatography (hexane–ether, 7 : 3) gave *trans*-2-iodocyclohexyl trifluoroacetate [10] (23 mg, 6%).

* Assignments in ref. 24 should be reversed.

[30] J. D. Albright and L. Goldman, *J. Amer. Chem. Soc.*, 1967, **89**, 2416.