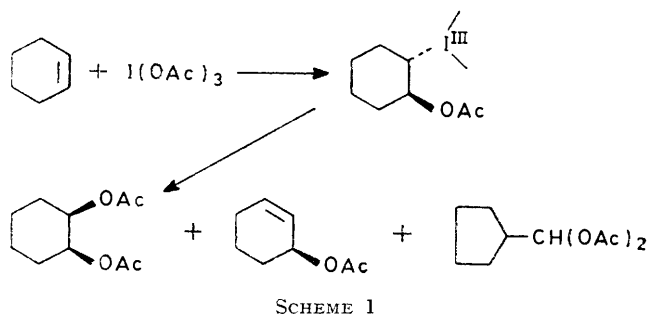


Reactions of Iodine Oxide with Alkenes

By Richard C. Cambie, Rodney C. Hayward, Barry G. Lindsay, Alice I. T. Phan, Peter S. Rutledge, and Paul D. Woodgate,* Department of Chemistry, University of Auckland, Auckland, New Zealand

The reaction of solvated iodine oxide, prepared by ozonising a solution of iodine in acetic anhydride, with alkenes has been examined. The reaction is regiospecific and leads to *vic*-iodo-acetates, iodohydrins, and iodo-ketones. In some cases di- and tri-acetates and 2,2'-di-iodo-ethers are formed. The products from norbornene are similar to those formed with thallium(I) acetate and iodine. The mode of formation of the products is discussed and the effect of non-polar solvents is investigated.

RECENTLY we have shown that the use of thallium(I) carboxylates and iodine provides an efficient method for preparing *vic*-iodo-carboxylates.^{1,2} However, this method and the Prévost and related reactions³ suffer from the disadvantage that half the added iodine is lost to the organic substrate as the insoluble metal iodide.^{4,5} In an attempt to overcome this problem the use of an ozonised solution of iodine in acetic anhydride⁶⁻⁸ has been investigated as a reagent for iodoacetylations of alkenes.⁹ Initial experiments with cyclohexene gave *trans*-2-iodocyclohexyl acetate^{1,10} (1) (46%), *trans*-2-iodocyclohexanol¹¹ (2) (26%), and 2-iodocyclohexanone (5) (19%). In the light of Buddrus' report,⁹ this result was surprising since by analogy with oxidations with Pb^{IV}, Tl^{III}, or Hg^{II},¹² the primary product of reaction with an alkene would be an iodine(III) adduct which might be expected to give the products shown in



Scheme 1. From this and later results (see below) it became clear that the reacting species is not 'iodine triacetate' but, as Beger⁶ had indicated, a solvated 'iodine oxide.' Evidence has recently been presented that the reaction of mercury(II) oxide-iodine with alkenes in aprotic solvents also proceeds *via* iodine oxide (I₂O)¹³ in a regiospecific ionic reaction initiated by attack on the double bond by positive iodine.

¹ R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, *J.C.S. Perkin I*, 1974, 1858.

² R. C. Cambie, B. G. Lindsay, P. S. Rutledge, and P. D. Woodgate, *J.C.S. Perkin I*, 1976, 845.

³ R. B. Woodward and F. V. Brutcher, *J. Amer. Chem. Soc.*, 1958, **80**, 209; S. Winstein and R. E. Buckles, *ibid.*, 1942, **64**, 2780, 2787; S. Winstein and R. M. Roberts, *ibid.*, 1953, **75**, 2297; P. S. Ellington, D. G. Hey, and G. D. Meakins, *J. Chem. Soc. (C)*, 1966, 1327; R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1967, 604; V. Dvinola, M. Adinolfi, and L. Mangoni, *Gazzetta*, 1970, **100**, 483; D. H. R. Barton, J. P. Poyser, P. G. Sammes, M. B. Hursthouse, and S. Neidle, *Chem. Comm.*, 1971, 715.

⁴ J. W. Cornforth and D. T. Green, *J. Chem. Soc. (C)*, 1970, 846.

In the work-up of the reaction of solvated iodine oxide with cyclohexene the mixture was quenched with water in order to hydrolyse the excess of acetic anhydride. Since the iodohydrin (2) may have arisen from hydrolysis of the iodo-acetate (1) during work-up, the reaction with cyclohexene was repeated with dichloromethane and n-pentane as the solvents. However, in each case appreciable amounts of the iodohydrin were still formed. Moreover, *trans*-2-iodocyclohexanol was still present when a 'non-solvated iodine oxide,' prepared by ozonising a solution of iodine in dichloromethane or n-pentane, was used. Treatment of a portion of the crude product from the latter reaction with acetic anhydride did not produce any iodo-acetate (1), implying that the latter is not formed in the reaction by acetylation of the iodohydrin. In the case where dichloromethane was the solvent a minor product was identified as 2,2'-di-iodocyclohexyl ether (6), which has been obtained previously¹³ as a product of the reaction of mercury(II) oxide-iodine with cyclohexene.

Treatment of styrene, 2-phenylpropene (α -methylstyrene), 1-phenylpropene (β -methylstyrene), and methyl cinnamate with the solvated iodine oxide showed that the reagent was regiospecific in its action. Styrene afforded the iodo-acetate (7) (42%), the iodohydrin (8) (34%), and the iodo-ketone (14) (24%); α -methylstyrene gave the iodo-acetate (9) (50%), the iodohydrin (10) (12.5%), the diacetate¹⁴ (16) (10%), and the triacetate (17) (20%). Reduction of the triacetate (17) with sodium bis-(2-methoxyethoxy)aluminium hydride in benzene gave 2-phenylpropane-1,2-diol,¹⁴ presumably *via* expulsion of a primary acetate unit concomitant with neighbouring group interaction to form a 2-methyl-1,3-dioxan-2-ylum ion which is subsequently attacked by hydride. β -Methylstyrene gave the iodoacetate¹

⁵ L. Mangoni, M. Adinolfi, G. Barone, and M. Parrilli, *Tetrahedron Letters*, 1973, 4485; *Gazzetta*, 1975, **105**, 377.

⁶ M. Beger, *Chem.-Ztg.*, 1909, **33**, 1232.

⁷ G. B. Bachman, G. F. Kite, S. Tuccarbasu, and G. M. Tullman, *J. Org. Chem.*, 1970, **35**, 3167.

⁸ M. Schmeisser, K. Dahmen, and P. Sartori, *Chem. Ber.*, 1967, **100**, 1633.

⁹ J. Buddrus, *Angew. Chem. Internat. Edn.*, 1973, **12**, 163.

¹⁰ L. Birckenbach, J. Goubeau, and E. Berninger, *Ber.*, 1932, **65**, 1339.

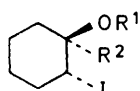
¹¹ S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *J. Amer. Chem. Soc.*, 1948, **70**, 816.

¹² J. B. Lee and M. J. Price, *Tetrahedron*, 1964, **20**, 1017.

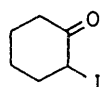
¹³ C. P. Forbes, A. Goosen, and H. A. H. Laue, *J.C.S. Perkin I*, 1974, 2346; *J. South African Chem. Inst.*, 1972, **25**, 144.

¹⁴ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1968, 994.

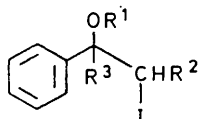
(11) (27%), the iodohydrin (12) (29%), and the iodo-ketone (15) (19%); methyl cinnamate gave methyl 3-acetoxy-2-iodo-3-phenylpropanoate (13) (45%) and



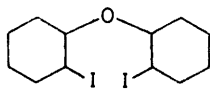
- (1) $R^1 = \text{Ac}, R^2 = \text{H}$
 (2) $R^1 = R^2 = \text{H}$
 (3) $R^1 = \text{Ac}, R^2 = \text{Me}$
 (4) $R^1 = \text{CO}\cdot\text{CF}_3, R^2 = \text{H}$



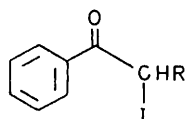
(5)



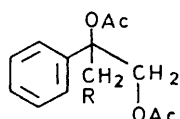
- (7) $R^1 = \text{Ac}, R^2 = R^3 = \text{H}$
 (8) $R^1 = R^2 = R^3 = \text{H}$
 (9) $R^1 = \text{Ac}, R^2 = \text{H}, R^3 = \text{Me}$
 (10) $R^1 = R^2 = \text{H}, R^3 = \text{Me}$
 (11) $R^1 = \text{Ac}, R^2 = \text{Me}, R^3 = \text{H}$
 (12) $R^1 = R^3 = \text{H}, R^2 = \text{Me}$
 (13) $R^1 = \text{Ac}, R^2 = \text{CO}_2\text{Me}, R^3 = \text{H}$



(6)

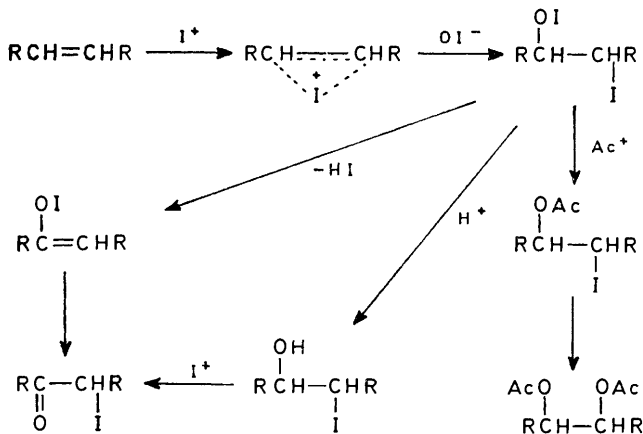


- (14) $R = \text{H}$
 (15) $R = \text{Me}$



- (16) $R = \text{H}$
 (17) $R = \text{OAc}$

starting material (55%). Although yields of individual products varied according to the reaction conditions (see below), the above results show that the reagent adds



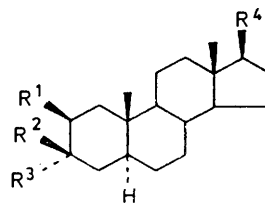
SCHEME 2

to unsymmetrical alkenes in a Markownikov manner. Formation of *trans*-adducts from cyclohexene suggests that the initial intermediate is an iodonium ion, which is

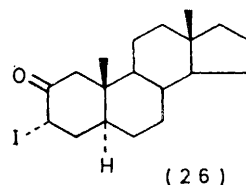
¹⁵ J. M. Evans, G. D. Meakins, Y. Morisawa, and P. D. Woodgate, *J. Chem. Soc. (C)*, 1968, 2841.

converted into a *trans*-iodo-hypoidite (Scheme 2). Protolysis would then lead to the iodohydrin, and acetolysis to the iodo-acetate and thence the diacetate. The iodo-ketones probably arise from the iodo-hypoidite *via* an ene-hypoidite as indicated, or by direct oxidation of the iodohydrin (see below).

In order to obtain further information on the stereo-selectivity of the reagent, 5 α -androst-2-ene¹⁵ was treated with solvated iodine oxide. Reaction for 20 h at 20 °C gave 3 α -iodo-5 α -androstan-2 β -ol (18) (51%), 3 α -iodo-5 α -androstan-2 β -yl acetate (19) (16%), 3 α -iodo-5 α -androstan-2-one (26) (14%), and unchanged alkene (19%). Further treatment of the 3 α -iodo-2 β -ol (18) with the reagent for 3 h gave a 1:1 mixture of the iodo-ketone (26) and starting material, showing that the



- (18) $R^1 = \text{OH}, R^3 = \text{I}, R^2 = R^4 = \text{H}$
 (19) $R^1 = \text{OAc}, R^3 = \text{I}, R^2 = R^4 = \text{H}$
 (20) $R^1 = \text{I}, R^3 = \text{OH}, R^2 = \text{H}, R^4 = \text{C}_8\text{H}_{17}$
 (21) $R^1 = \text{OH}, R^3 = \text{I}, R^2 = \text{H}, R^4 = \text{C}_8\text{H}_{17}$
 (22) $R^1 = \text{I}, R^3 = \text{OAc}, R^2 = \text{H}, R^4 = \text{C}_8\text{H}_{17}$
 (23) $R^1 = \text{OAc}, R^3 = \text{I}, R^2 = \text{H}, R^4 = \text{C}_8\text{H}_{17}$
 (24) $R^1 = \text{OAc}, R^2 = \text{I}, R^3 = R^4 = \text{H}$
 (25) $R^1 = \text{OH}, R^2 = R^3 = R^4 = \text{H}$



(26)

iodohydrin can be oxidised directly to the iodo-ketone (*cf.* the oxidation of alcohols by acetyl hypoidite¹⁶). Compounds (18) and (19) were identified from their i.r. spectra and by comparison of their ¹H n.m.r. spectra with those of the corresponding derivatives in the cholest-2-ene series (Table I). The production of these compounds can be rationalised in terms of initial formation of an α -iodonium ion at the less hindered α -face of ring A followed by attack of the nucleophile at C-2. Attack at C-3 of the α -iodonium ion would not be favoured since although this would ultimately lead to a more stable configuration with diequatorial substituents, the reaction must pass through a boat transition state.¹⁷

For 5 α -androst-2-ene, attempts were made to relate the ratio of iodo-acetate to iodohydrin formation to the

¹⁶ T. R. Beebe, B. A. Barnes, K. A. Bender, A. D. Halbert, R. D. Miller, M. L. Ramsay, and M. W. Ridenour, *J. Org. Chem.*, 1975, **40**, 1992.

¹⁷ Cf. A. Hassner and C. Heathcock, *J. Org. Chem.*, 1965, **30**, 1748.

time of reaction, the temperature, and the method of disposing of the solvent acetic anhydride, *i.e.* by distillation or by hydrolysis with water. An increase in the

TABLE 1

¹H N.m.r. data for iodohydrins and iodo-acetates (δ values)

Compd.	H-2	H-3	19-H ₃	18-H ₃
(20) ^a	4.43 ($W_{\frac{1}{2}}$ 8 Hz)		1.13	0.63
(21) ^{a,b}	4.52 ($W_{\frac{1}{2}}$ 6 Hz)	4.32 ($W_{\frac{1}{2}}$ 6 Hz)	1.00	0.64
(18)	4.53 ($W_{\frac{1}{2}}$ 7 Hz)	4.33 ($W_{\frac{1}{2}}$ 7 Hz)	1.03	0.70
(22) ⁹	4.40 ($W_{\frac{1}{2}}$ 6 Hz)	5.15 ($W_{\frac{1}{2}}$ 6 Hz)		
(23) ^{5,a,b*}	5.14 ($W_{\frac{1}{2}}$ 8 Hz)	4.50 ($W_{\frac{1}{2}}$ 7 Hz)	0.91	0.65
(19)	5.14 ($W_{\frac{1}{2}}$ 8 Hz)	4.50 ($W_{\frac{1}{2}}$ 7 Hz)	0.94	0.70

* H-2 and H-3 assignments in ref. 5 should be reversed.

^a R. C. Cookson and J. M. Coxon, *J. Chem. Soc. (C)*, 1971, 1466. ^b D. G. Hey, G. D. Meakins, and M. L. S. Pemberton, *J. Chem. Soc. (C)*, 1966, 1331.

time or the temperature resulted in an increase in the proportion of the iodo-acetate at the expense of iodohydrin, but the ratio appeared to be independent of the method of work-up.

With cyclohexene as the substrate, trifluoroacetic anhydride was also used in place of acetic anhydride. Reaction in dichloromethane as the solvent gave six compounds, the major of which were *trans*-2-iodocyclohexanol (2) (85%) and *trans*-2-iodocyclohexyl trifluoroacetate (4) (5%). The remaining compounds were mainly mixtures of dimeric and trimeric ethers, the principal of which was bis-(2-iodocyclohexyl) ether (6).¹³ Isolation of this product indicates that the reactive

microanalytical data and molecular weight fit the formula C₁₂H₂₀I₂O equally well, and indicate that it is the bis-(2-iodocyclohexyl) ether (6).

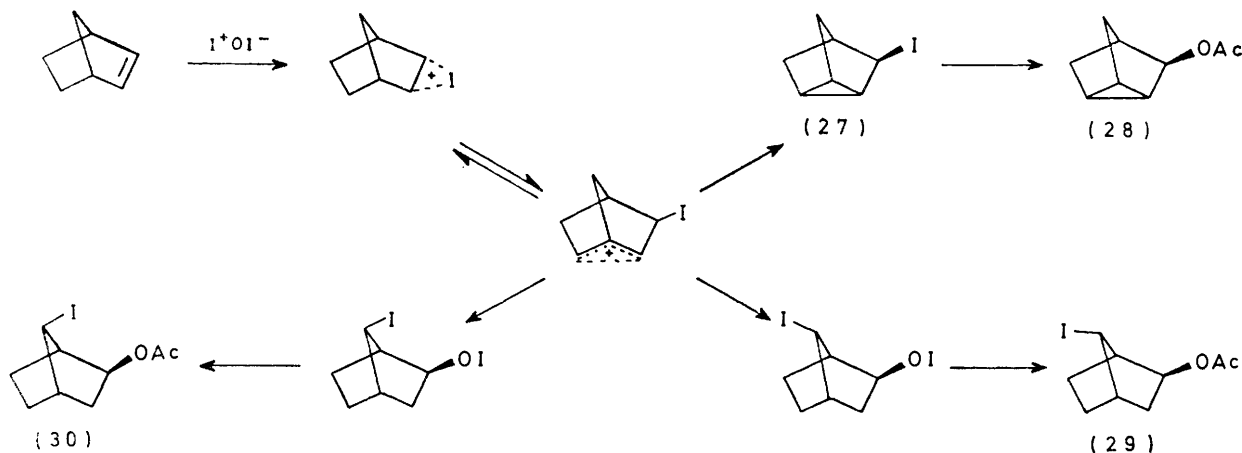
Treatment of norborn-2-ene with solvated iodine oxide in three different solvents gave the results outlined in Table 2. The products differed from those obtained from the action of iodine or iodine-acetic anhydride on norbornene, *viz.* the *trans*-di-iodide (34), a monoacetate, and a di-iodide tentatively identified as 2-*exo*,7-*syn*-di-iodobicyclo[2.2.1]heptane (33), but were similar to those obtained from the action of thallium(I) acetate-iodine on norbornene.² They are believed to

TABLE 2

Products (%) from reaction of norborn-2-ene with solvated iodine oxide in three different solvents

Compound	Ac ₂ O	CH ₂ Cl ₂	Me[CH ₂] ₃ Me
3- <i>exo</i> -Iodotricyclo[2.2.1.0 ^{2,6}]-heptane (27)	20	59	40
3- <i>exo</i> -Acetoxytricyclo[2.2.1.0 ^{2,6}]-heptane (28)	2.5	4.5	4.5
2- <i>exo</i> -Acetoxy-7- <i>anti</i> -iodobicyclo[2.2.1]heptane (29)	10	6.4	8
2- <i>exo</i> -Acetoxy-7- <i>syn</i> -iodobicyclo[2.2.1]heptane (30)	19	7	16
2- <i>exo</i> -7- <i>anti</i> -Diacetoxybicyclo[2.2.1]heptane (31)	14	4	8
2- <i>exo</i> -7- <i>syn</i> -Diacetoxybicyclo[2.2.1]heptane (32)	34	8	18

arise in a manner (Scheme 3) similar to that detailed for the latter reaction.² The suggested ionic mechanism is consistent with the observed product distribution and

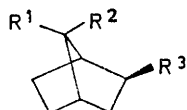


SCHEME 3

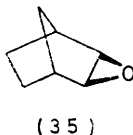
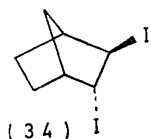
species generated by treatment of molecular iodine with ozone in the presence of acid anhydrides may be more correctly represented as a solvated iodine oxide than as triacyliodine(III).⁷ Goosen *et al.*¹³ explained the formation of the di-iodo-ether (6) by attack of iodine oxide or a hypoiodite anion on an initially formed iodonium ion, followed by regiospecific attack on the resulting iodo-hypoiodite by a further iodonium ion. Birckenbach *et al.*¹⁰ described the formation of an unidentified product, given the formula C₁₁H₁₈I₂O₂, from the action of iodine and silver iodate on cyclohexene. However the reported

supports the conclusion of Goosen *et al.*¹³ that the reaction of iodine oxide with alkenes proceeds *via* an ionic pathway. The origin of the diacetates (31) and (32) is uncertain, but they probably arise by solvolysis of the corresponding iodo-acetates. The possibility of their genesis *via* the 2-*exo*,3-*exo*-epoxide (35) as a result of peroxyacetic acid formation when ozone is passed through acetic anhydride was discounted when g.l.c. of the crude product from treatment of norbornene with ozonised acetic anhydride showed mainly starting material but no diacetates.

As pointed out by Goosen *et al.*,¹³ although direct evidence for its reality is still lacking, the existence of iodine oxide as a reactive intermediate has been suggested before.^{18,19} Schmeisser and Brandle²⁰ have reported that the passage of ozone through a solution of iodine in carbon tetrachloride or chloroform from -78°C to room temperature gives tetraiodine ennea-oxide, I_4O_9 . Although no definitive structural evidence



- (29) $\text{R}^1 = \text{I}, \text{R}^2 = \text{H}, \text{R}^3 = \text{OAc}$
 (30) $\text{R}^1 = \text{H}, \text{R}^2 = \text{I}, \text{R}^3 = \text{OAc}$
 (31) $\text{R}^1 = \text{OAc}, \text{R}^2 = \text{H}, \text{R}^3 = \text{OAc}$
 (32) $\text{R}^1 = \text{H}, \text{R}^2 = \text{R}^3 = \text{OAc}$
 (33) $\text{R}^1 = \text{H}, \text{R}^2 = \text{R}^3 = \text{I}$



is available, this yellow hygroscopic solid is usually formulated as $\text{I}(\text{IO}_3)_3$ since it reacts with water to form iodine and iodic acid.

An attempt was made in the present study to determine the stoichiometry by analysing the reaction of cyclohexene (2 mol) with the reagent prepared from iodine (1 mol) and ozone in carbon tetrachloride. ^1H N.m.r. analysis of samples taken after 19, 23, and 42 h, at room temperature, showed a constant ratio of residual cyclohexene to products (29:71). That the reagent had been consumed almost completely was indicated by the production of only a faint iodine colour when the mixture was quenched with water. The ratio of unchanged cyclohexene to products indicates that 1.5 mol of electrophilic iodine are generated by treatment of 1 mol of molecular iodine with ozone. Preparative t.l.c. gave 2-iodocyclohexanol (2) (58% based on iodine) and the dimeric ether (6) (2.5%).

EXPERIMENTAL

I.r. spectra were recorded for solutions in CHCl_3 or CCl_4 with a Perkin-Elmer 237 or 337 spectrophotometer. Unless otherwise indicated, n.m.r. spectra were measured for solutions in CDCl_3 with a Varian T60 spectrometer (tetramethylsilane as internal reference). Low resolution mass spectra were obtained with a Varian MAT CH7 spectrometer operating at 70 or 12 eV, and high resolution spectra with an A.E.I. MS9 instrument interfaced with the A.E.I. mass spectroscopy data system DS30. T.l.c. was carried out on plates of Kieselgel DG (Riedel-de Haen); preparative t.l.c. (p.l.c.) was carried out on 1 mm thick plates of Kieselgel

¹⁸ M. Akhtar and S. Marsh, *J. Chem. Soc. (C)*, 1966, 937.

¹⁹ C. P. Forbes, A. Goosen, and H. A. H. Laue, *J. South African Chem. Inst.*, 1972, **25**, 328.

$\text{PF}_{254+366}$ (Merck). G.l.c. was carried out with a Varian Aerograph series 1400 instrument [glass column (8 ft \times 1/8 in o.d.) packed with 3% OV-17 on 70–80 mesh Chromosorb W]. For preparative g.l.c. a glass column (12 ft \times 3/8 in o.d.) packed with 7% OV-17 on 70–80 mesh Chromosorb W was used. Ozone was generated in a British Oxygen Co. Mark II ozoniser. All solvents were purified according to ref. 21.

Solvated Iodine Oxide.—Ozone-enriched oxygen was passed through a solution of iodine (0.67 g, 2.6 mmol) in freshly distilled acetic anhydride (19 ml) at 0°C until all traces of iodine had disappeared. The resulting yellow suspension of solvated iodine oxide (2.6 mmol) was flushed with dry nitrogen until no ozone could be detected (starch-iodide paper) in the effluent.

The non-solvated reagent was prepared by replacing the acetic anhydride with dichloromethane (35 ml).

Reaction of Cyclohexene with Solvated Iodide Oxide.—

(a) *In acetic anhydride.* Cyclohexene (1.62 g, 19.8 mmol) was added dropwise to a stirred suspension of solvated iodine oxide (19.8 mmol, based on iodine ozonised) in acetic anhydride (50 ml) in the absence of light. The mixture was stirred at 20°C for 24 h and then poured into ice-water with rapid stirring. When hydrolysis of the acetic anhydride was complete (*ca.* 1 h), the mixture was extracted with ether and the extract was washed with water, sodium thiosulphate solution, saturated aqueous sodium hydrogen carbonate, and brine. Solvent was removed from the dried solution to give a pale yellow oil (3.96 g), which was separated by p.l.c. (hexane-ether, 95:5) into (decreasing R_F) (i) *trans*-2-iodocyclohexyl acetate (1) (46%) (i.r. and ^1H n.m.r. spectra¹), *m/e* 268 (M^+ , $\text{C}_8\text{H}_{12}\text{IO}_2$); (ii) 2-iodocyclohexanone (5) (19%), ν_{max} 1705 cm^{-1} (CO), δ 3.18 (m, $W_{\frac{1}{2}}$ 38 Hz, 6 α -H) and 4.60br (s, $W_{\frac{1}{2}}$ 11 Hz, 2-H) *m/e* 224 (M^+ , $\text{C}_6\text{H}_9\text{IO}$); and (iii) *trans*-2-iodocyclohexanol (2) (26%) (i.r. and n.m.r. spectra¹), *m/e* 226 (M^+ , $\text{C}_6\text{H}_{11}\text{IO}$).

(b) *In dichloromethane.* Solvated iodine oxide, prepared from ozone, iodine (0.96 g, 3.8 mmol), and acetic anhydride (1.16 g, 11.3 mmol), in dichloromethane (35 ml) was stirred with cyclohexene (0.67 g, 8.2 mmol) at 20°C for 24 h. Work-up as above gave a pale yellow oil (1.3 g) which contained (g.l.c. analysis) (i) *trans*-2-iodocyclohexyl acetate (19%); (ii) 2-iodocyclohexanone (20%); and (iii) *trans*-2-iodocyclohexanol (61%).

(c) *In n-pentane.* Cyclohexene (0.50 g, 6.1 mmol) was treated with solvated iodine oxide (6.1 mmol) in *n*-pentane (35 ml) and the mixture was heated under reflux for 3 days. Work-up as above gave a pale yellow oil (1.52 g) which contained (^1H n.m.r. analysis) *trans*-2-iodocyclohexyl acetate (86%) and *trans*-2-iodocyclohexanol (14%).

(d) *In n-pentane-trifluoroacetic anhydride.* Solvated iodine oxide, prepared from ozone, iodine (0.67 g, 2.6 mmol), and trifluoroacetic anhydride (1.67 g, 0.80 mmol), in *n*-pentane (40 ml) was stirred with cyclohexene (0.43 g, 5.2 mmol) at 20°C for 20 h. Work-up as above followed by p.l.c. (hexane-ether, 95:5) gave (i) *bis*-(2-iodocyclohexyl) ether (6) (<5%) as an oil (Found: M^+ , 433.9628. $\text{C}_{12}\text{H}_{20}\text{I}_2\text{O}$ requires M , 433.9608), ν_{max} 1074 cm^{-1} (COC), δ 3.60 (m, $W_{\frac{1}{2}}$ 14 Hz, 1- and 1'-H) and 4.09 (m, $W_{\frac{1}{2}}$ 36 Hz, 2- and 2'-H); (ii) *trans*-2-iodocyclohexyl trifluoroacetate (4) (5%), ν_{max} 1785 cm^{-1} (OCOCF₃), δ 4.18 (sext, $J_{1,2} =$

²⁰ M. Schmeisser and K. Brandle, *Adv. Inorg. Chem. Radiochem.*, 1963, **5**, 78.

²¹ D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, Oxford, 1966.

$J_{2,3ax} = 10$, $J_{2,3eq} 5$ Hz, 2-H) and 5.02 (sext, $J_{1,2} = J_{1,6ax} = 10$, $J_{1,6eq} 5$ Hz, 1-H), m/e 322 (M^+ , $C_8H_{10}F_3IO_2$); (iii) a mixture containing dimeric and trimeric ethers; (iv) *trans*-2-iodocyclohexanol (85%).

Reaction of Cyclohexene with Non-solvated Iodine Oxide.—(a) *In dichloromethane.* Cyclohexene (0.22 g, 2.7 mmol) was shaken with non-solvated iodine oxide (2.7 mmol) in dichloromethane (30 ml) at 20 °C for 12 h. Work-up gave a yellow oil (0.54 g) which contained (1H n.m.r. analysis) (i) *trans*-2-iodocyclohexanol (80%); (ii) starting material (1%); (iii) bis-(2-iodocyclohexyl) ether (5%); and (iv) two unidentified compounds (<5%).

(b) *In carbon tetrachloride.* Cyclohexene (0.50 g, 6.1 mmol) was shaken with non-solvated iodine oxide (from iodine, 0.77 g, 3.05 mmol) at 20 °C for 43 h. 1H N.m.r. analysis showed the ratio of cyclohexene to products to be 21 : 79. Work-up gave *trans*-2-iodocyclohexanol (58%) and bis-(2-iodocyclohexyl) ether (2.5%).

Reaction of Styrene with Solvated Iodine Oxide.—(a) *In acetic anhydride.* Styrene (0.72 g, 6.9 mmol) was stirred with solvated iodine oxide (6.9 mmol) in acetic anhydride (45 ml) in the absence of light at 20 °C for 3 h. Work-up gave a pale yellow oil (1.29 g) which contained (1H n.m.r. analysis) (i) 2-iodoacetophenone (14) (24%), ν_{max} 1 680 cm^{-1} (conj. CO), λ_{max} (EtOH) 252 nm, δ (CCl_4) 4.26 (s, 2-H₂), 7.44 (m, $W_{\frac{1}{2}}$ 6 Hz, 3'- and 4'-ArH), and 7.92 (m, $W_{\frac{1}{2}}$ 12 Hz, 2'- and 6'-ArH), m/e 246 (M^+ , C_8H_7IO); (ii) 2-iodo-1-phenylethyl acetate (7) (42%), ν_{max} 1 750 cm^{-1} (CO), δ (CCl_4) 3.47 (d, J 7 Hz, 2-H₂), 5.90 (t, J 7 Hz, 1-H), and 7.34 (s, ArH), m/e 231 (M^+ - OAc); and (iii) 2-iodo-1-phenylethanol (8) (34%), ν_{max} 3 450 cm^{-1} (OH), δ (CCl_4) 2.27br (s, $W_{\frac{1}{2}}$ 14 Hz, OH, exchanged with D_2O), 3.35 (m, $W_{\frac{1}{2}}$ 12 Hz, 2-H₂), 4.76 (m, $W_{\frac{1}{2}}$ 14 Hz, 1-H), and 7.32 (s, ArH), m/e 121 (M^+ - I).

The experiment was repeated with styrene (0.31 g, 3.0 mmol) and solvated iodine oxide (3.0 mmol) in acetic anhydride (10 ml) for 12 h. Work-up gave a product (0.67 g) containing the iodo-ketone (14) (13%), the iodo-acetate (7) (78%), and the iodo-alcohol (8) (9%). When the reaction was carried out for 24 h the yield of iodo-acetate (7) was 88%.

(b) *In dichloromethane.* Solvated iodine oxide prepared from ozone, iodine (0.88 g, 3.5 mmol), and acetic anhydride (1.06 g, 10.4 mmol) in dichloromethane (35 ml) was stirred with styrene (0.72 g, 6.9 mmol) at 20 °C for 1.5 h. Work-up gave a product containing >90% of starting material.

Reaction of 2-Phenylpropene with Solvated Iodine Oxide.—2-Phenylpropene (0.81 g, 6.9 mmol) was added dropwise to a stirred suspension of solvated iodine oxide (6.9 mmol) in acetic anhydride (45 ml). The mixture was stirred at 20 °C for 3 h and worked up to give a gum which contained (p.l.c. and 1H n.m.r. analysis) (i) 1-iodo-2-phenylpropan-2-ol (10) (12.5%), δ (CCl_4) 1.66 (s, Me), 2.34br (s, $W_{\frac{1}{2}}$ 5 Hz, OH, exchanged with D_2O), 3.58 (s, 1-H₂), and 7.30 (m, $W_{\frac{1}{2}}$ 4 Hz, ArH), m/e 262 (M^+ , $C_9H_{11}IO$); (ii) 2-phenylpropane-1,2-diyl diacetate (16) (10%), ν_{max} 1 745 cm^{-1} (OAc), δ 1.84 (s, Me), 1.98 (s, OAc), 2.04 (s, OAc), 4.32 (s, 1-H₂), and 7.30 (s, ArH), m/e 236 (M^+ , $C_{13}H_{16}O_4$); (iii) 2-iodo-1-methyl-1-phenylethyl acetate (9) (50%), δ (CCl_4) 1.97 (s, Me), 2.10 (s, OAc), 3.80 (s, 1-H₂), and 7.25 (s, ArH); and (iv) 2-phenylpropane-1,2,3-triyl triacetate (17) (20%) (Found: M^+ , 294.1123. $C_{15}H_{18}O_6$ requires M , 294.1101), ν_{max} 1 750 cm^{-1} (OAc), δ 1.83 (s, OAc), 2.03 (s, OAc), 2.08 (s, OAc), 4.42 (s, CH_2 ·OAc), 4.49 (s, CH_2 ·OAc), and 7.32 (s, ArH).

Reduction of 2-Phenylpropane-1,2,3-triyl Triacetate.—

Sodium bis-(2-methoxyethoxy)aluminium hydride in benzene (0.18 ml, 0.94 mmol) was added to a stirred solution of the triacetate (17) (80 mg, 0.27 mmol) in dry benzene (5 ml) under dry nitrogen. On completion of the exothermic reaction, saturated aqueous sodium sulphate was added and the mixture worked up in the normal manner to give 2-phenylpropane-1,2-diol (30 mg) (i.r. and 1H n.m.r. spectra ¹⁴).

Reaction of 1-Phenylpropene with Solvated Iodine Oxide.—1-Phenylpropene (0.81 g, 6.9 mmol) was added dropwise to a stirred suspension of solvated iodine oxide (6.9 mmol) in acetic anhydride (45 ml). The mixture was stirred at 20 °C for 12 h and worked up to give a gum which contained (p.l.c. analysis) (i) 2-iodopropiophenone (15) (19%), ν_{max} 1 680 cm^{-1} (conj. CO), δ 2.10 (d, J 7 Hz, Me), 5.52 (q, J 7 Hz, 2-H), 7.52 (m, $W_{\frac{1}{2}}$ 13 Hz, 3'- and 5'-H), and 7.56 (m, $W_{\frac{1}{2}}$ 7 Hz, 2', 4', and 6'-H), m/e 260 (M^+ , C_9H_9IO); (ii) 2-iodo-1-phenylpropyl acetate (11) (27%), ν_{max} 1 740 cm^{-1} (OAc), δ 1.84 (d, $J_{2,3}$ 7 Hz, Me), 2.18 (s, OAc), 4.46 (q × d, $J_{2,3}$ 7, $J_{1,2}$ 6 Hz, 2-H), 5.90 (d, $J_{1,2}$ 6 Hz, 1-H), and 7.40 (s, ArH), m/e 262 (M^+ - COMe); and (iii) 2-iodo-1-phenylpropan-1-ol (12) (29%), ν_{max} 3 500 cm^{-1} (OH), δ 1.74 (d, J 6 Hz, Me), 2.40br (s, $W_{\frac{1}{2}}$ 7 Hz, OH, exchanged with D_2O), 4.58 (m, $W_{\frac{1}{2}}$ 14 Hz, 2-H), 4.97 (d, J 4 Hz, 1-H), and 7.36 (s, ArH), m/e 245 (M^+ - OH).

Reaction of Methyl Cinnamate with Solvated Iodine Oxide.—Methyl cinnamate (0.50 g, 3.1 mmol) was stirred with a suspension of solvated iodine oxide (3.1 mmol) in acetic anhydride at 20 °C for 48 h. Work-up gave a product (0.55 g) which contained (1H n.m.r. analysis) methyl 3-acetoxy-2-iodo-3-phenylpropanoate (13) (44%), δ 1.91 (s, OAc), 3.72 (s, OMe), 4.68 (d, $J_{2,3}$ 11 Hz, 2-H), 6.15 (d, $J_{2,3}$ 11 Hz, 3-H), and 7.41 (s, ArH), and starting material (55%).

Reaction of 5 α -Androst-2-ene with Solvated Iodine Oxide.—5 α -Androst-2-ene (0.10 g, 0.4 mmol) was stirred with a suspension of solvated iodine oxide (0.4 mmol) in acetic anhydride (10 ml) at 20 °C for 8 h. Work-up gave a product which contained (1H n.m.r. and p.l.c. analysis) (i) starting material (36%), (ii) 3 α -iodo-5 α -androstan-2 β -yl acetate (19) (9%), m.p. 137° (from pentane-ether) (Found: C, 56.9; H, 7.6. $C_{21}H_{33}IO_2$ requires C, 56.7; H, 7.5%), ν_{max} 1 750 cm^{-1} (OAc), δ (CCl_4) 0.70 (s, 18-H₃), 0.94 (s, 19-H₃), 1.98 (s, OAc), 4.50 (m, $W_{\frac{1}{2}}$ 7 Hz, 3-H), and 5.14 (m, $W_{\frac{1}{2}}$ 8 Hz, 2-H), and (iii) 3 α -iodo-5 α -androstan-2 β -ol (18) (22%), m.p. 129–130° (from pentane-ether) (Found: C, 57.2; H, 7.9. $C_{19}H_{31}IO$ requires C, 56.7; H, 7.8%), ν_{max} 3 620 cm^{-1} (OH), δ (CCl_4) 0.70 (s, 18-H₃), 1.00 (s, 19-H₃), 4.28 (m, $W_{\frac{1}{2}}$ 6 Hz, 2-H), and 4.47 (m, $W_{\frac{1}{2}}$ 6 Hz, 3-H).

Repetition of the reaction for 20 h gave (i) starting material (19%); (ii) 3 α -iodo-5 α -androstan-2 β -yl acetate (16%); (iii) 3 α -iodo-5 α -androstan-2-one (26) (14%), needles, m.p. 146–148° (from pentane-ether) (Found: M^+ 400.1264. $C_{19}H_{29}IO$ requires M , 400.1265), ν_{max} 1 700 cm^{-1} (CO), δ 0.75 (s, 18, 19-H₃), 2.30 (d × d, J 14.5, 1.5 Hz, 1 β -H), 3.09 (d, J 14.5 Hz, 1 α -H), and 4.63br (s, $W_{\frac{1}{2}}$ 7 Hz, 3-H); and (iv) 3 α -iodo-5 α -androstan-2 β -ol (51%).

The reaction was repeated at 60–70 °C for 12 h and the acetic anhydride was distilled off *in vacuo*. Work-up gave a product containing (1H n.m.r. and p.l.c. analysis) starting material (14%) and 3 α -iodo-5 α -androstan-2 β -yl acetate (50%).

Reaction for 18 h with the removal of acetic anhydride by distillation gave starting material (43%), and compounds (19) and (18) in 1 : 1 ratio.

3 α -Iodo-5 α -androstan-2 β -ol was stirred with solvated iodine oxide (1 equiv.) at 20 °C for 3 h. Work-up gave a product containing (¹H n.m.r. and p.l.c. analysis) a 1 : 1 mixture of starting material and 3 α -iodo-5 α -androstan-2-one.

Reaction of Bicyclo[2.2.1]hept-2-ene with Solvated Iodine Oxide.—(a) *In acetic anhydride.* Norbornene (0.47 g, 5.0 mmol) was added to a stirred suspension of solvated iodine oxide (5.0 mmol) in acetic anhydride (19 ml). The mixture was stirred at 20 °C for 4 h and worked up in the usual manner to yield a pale yellow oil (1.3 g); for analysis of the products see Table 2.

(b) *In dichloromethane.* Norbornene (0.50 g, 5.3 mmol) was stirred with solvated iodine oxide (5.3 mmol) in dichloromethane (35 ml) at 20 °C for 1.5 days. Work-up gave a yellow oil (1.1 g); for analysis see Table 2.

(c) *In n-pentane.* Norbornene (0.50 g, 5.3 mmol) was

stirred with solvated iodine oxide (5.3 mmol) in n-pentane (35 ml) at 20 °C for 12 h. Work-up gave a yellow oil (1.48 g); for analysis see Table 2.

Reaction of Iodine with Bicyclo[2.2.1]hept-2-ene.—Iodine (1.34 g, 5.3 mmol) and norbornene (0.50 g, 5.3 mmol) were shaken in carbon tetrachloride (20 ml) for 1 h. The mixture was worked up as above to give a yellow oil which contained (¹H n.m.r. analysis) (i) *trans-2-exo,3-endo*-di-iodo-bicyclo[2.2.1]heptane (34) (61%), (ii) starting material (9%), and (iii) unidentified material (30%).

Repetition of the reaction with addition of acetic anhydride (5 ml, 5.3 mmol), for 6 days, gave mainly starting material, an unidentified monoacetate, and 2-*exo,7-syn*-di-iodobicyclo[2.2.1]heptane (33).

The substrate was recovered (95%) after treatment with ozonised acetic anhydride.

[6/389 Received, 25th February, 1976]