

## Reactions of Alkenes with Electrophilic Iodine in Tetramethylene Sulphone–Chloroform

By Richard C. Cambie, Wendy I. Noall, Graeme J. Potter, Peter S. Rutledge,\* and Paul D. Woodgate,  
Department of Chemistry, University of Auckland, Auckland, New Zealand

Treatment of simple alkenes with iodine and water in tetramethylene sulphone–chloroform affords high yields of *trans-vic*-iodohydrins. Use of fused sodium acetate instead of water leads to a *trans*-iodo-acetate. The tetramethylene sulphone–chloroform solvent system has been applied to other reactions involving electrophilic iodine. Reactions of alkenes with thallium(I) carboxylates and iodine(I) chloride are reported.

UNTIL recently it has generally been considered that the Prévost reaction<sup>1</sup> and its Woodward modification<sup>2</sup> require the use of a silver(I) carboxylate and iodine for the conversion of an alkene into a *trans*- or *cis-vic*-diol

<sup>1</sup> C. V. Wilson, *Org. Reactions*, 1957, **9**, 332; F. D. Gunstone, *Adv. Org. Chem.*, 1960, **1**, p. 103.

derivative. Recently, we have shown<sup>3</sup> that thallium(I) carboxylates are suitable alternatives to silver carboxy-

<sup>2</sup> R. B. Woodward and F. V. Brutcher, jun., *J. Amer. Chem. Soc.*, 1958, **80**, 209.

<sup>3</sup> R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, *J.C.S. Perkin I*, 1974, (a) p. 1858; (b) p. 1120.

lates, and Mangoni and his co-workers<sup>4</sup> have described a modification in which silver acetate is effectively replaced by potassium iodate and acetic acid. In this latter method, which is similar to that of Cornforth and Green,<sup>5</sup> the potassium iodate is thought to oxidise iodide ion to molecular iodine, thereby enhancing the rate of reaction and allowing all the original iodine to be used. We have now found that *trans*-iodohydrins can be conveniently prepared from alkenes by using iodine and water in tetramethylene sulphone–chloroform as solvent.

Treatment of cyclohexene with iodine and water in 1 : 1 tetramethylene sulphone–chloroform gave the *trans*-iodohydrin (1) in 81% yield. Although the formation of chlorohydrins and bromohydrins from reactions of dilute aqueous solutions of halogens with alkenes is a well known preparative and industrial procedure, this appears to be the first example of formation of an iodohydrin from an alkene, iodine, and water.\* Extension of the procedure to other alkenes, with a substrate–iodine–water ratio of 1 : 2.4 : 3 at 20 °C for 24 h, gave results which are summarised in Table 1. The specificity of the reaction with

rins from alkenes with *N*-bromosuccinimide in moist dimethyl sulphoxide. Although the nature of the brominating species was uncertain they showed that specific incorporation of oxygen from dimethyl [<sup>18</sup>O]-sulphoxide occurred, and therefore proposed a sequence involving a bromonium ion or a bromocarocation undergoing solvolyses by the solvent and then water. Formation of the *trans*-iodo-acetate (3) rather than the iodohydrin (1) in the present case indicates that adventitious water in the tetramethylene sulphone † was responsible for iodohydrin formation rather than a process similar to Dalton's. This was supported by the fact that treatment of cyclohexene with fused sodium acetate and iodine in commercial tetramethylene sulphone–chloroform (1 : 1) again gave the *trans*-iodohydrin (1) in 81% yield.

Use of sodium benzoate instead of sodium acetate in the reaction with cyclohexene resulted in lower yields and a mixture of *trans*-2-iodocyclohexyl benzoate (4) (25%) and *trans*-2-iodocyclohexanol (1) (8%). No reaction occurred when 5 $\alpha$ -androst-2-ene was treated with sodium benzoate–iodine in 1 : 1 tetramethylene sulphone–chloroform at 20 °C for 3 days or when the substrate was treated with sodium benzoate–iodine and a catalytic amount of silver benzoate in dry benzene in an attempt to develop the use of silver(I) salts as catalysts in the Prévost reaction. However, although *trans*-methyl cinnamate is unreactive under normal Prévost conditions it reacted with silver(I) acetate and iodine in tetramethylene sulphone–chloroform (1 : 1) (molar ratio of 1 : 3 : 2.4) to give a 34% yield of methyl 3-hydroxy-2-iodo-3-phenylpropanoate (17), identified from its spectral parameters [ $\nu_{\max}$  3 470 (OH) and 1 660 cm<sup>-1</sup> (CO);  $\delta$  3.72 (s, OMe), 3.72 (s, OH) 4.4 (d, *J* 8 Hz, CHI), 4.97 (d, *J* 7 Hz, CHOH), and 7.22 (5 H, s, Ph); *m/e* 306 (C<sub>10</sub>H<sub>11</sub>IO<sub>3</sub>), 179 (*M* – I), and 107 (PhCH:OH<sup>+</sup>)].

Since the successful reactions above occurred in both a stereospecific and a regiospecific manner, the tetramethylene sulphone–chloroform system was applied to other reactions involving electrophilic iodine. ‡ Treatment of cyclohexene with sodium azide and iodine in anhydrous tetramethylene sulphone–chloroform gave the *trans*-iodo-azide (5) in 95% yield (*cf.* ref. 10), whereas treatment of cyclohexene with sodium acetate and iodine(I) chloride in commercial tetramethylene sulphone–chloroform gave a 70% yield of the *trans*-iodo-chloride (6). Treatment of cyclohexene with

TABLE 1

Products from the iodine–water reaction

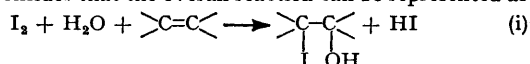
Alkene	Product	Yield (%)
Cyclohexene	(1) <sup>3a</sup>	81 <sup>a</sup>
Styrene	(13)	87
<i>trans</i> -1-Phenylpropene	(14)	24
Phenylcyclopropane	(15) <sup>15</sup>	92 <sup>b</sup>
1-Methylcyclohexene	(2) <sup>6</sup>	61
5 $\alpha$ -Androst-2-ene		0 <sup>c</sup>
Cyclohexene	(3)	55 <sup>d</sup>
Styrene	(16)	70 <sup>d</sup>

<sup>a</sup> With or without added NaOAc.3H<sub>2</sub>O. <sup>b</sup> 36 h. <sup>c</sup> Refluxing for 6 h. <sup>d</sup> Added fused NaOAc; redistilled dry tetramethylene sulphone.

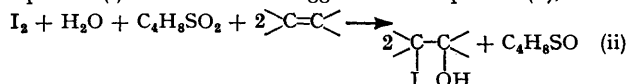
1-methylcyclohexene suggests a degree of 'concertedness' similar to that found with thallium(I) acetate and iodine<sup>3</sup> but not with silver(I) acetate and iodine or with iodine and potassium iodate.<sup>6</sup>

Treatment of cyclohexene with fused sodium acetate, iodine, and redistilled anhydrous tetramethylene sulphone gave the *trans*-iodo-acetate (3) in 55% yield. Dalton *et al.*<sup>7</sup> have reported the formation of bromohydrin

\* We consider that the overall reaction can be represented as in



equation (i). A referee has suggested that equation (ii), with the



sulphone reoxidising HI to I<sub>2</sub>, is a possible alternative. We do not favour this pathway since treatment of cyclohexene with iodine and water for 23 h at 20 °C in chloroform alone also gave a low yield (36%) of the iodohydrin (1) in addition to the *trans*-1,2-di-iodide (52%) (H. H. Lee, unpublished work). However, since we have used an excess of iodine in our reaction we cannot discount the second possibility.

† The hygroscopic nature of tetramethylene sulphone<sup>8</sup> makes it difficult to dry completely.

‡ The use of tetramethylene sulphone–chloroform (1 : 1) as solvent for the formation of iodo-thiocyanates and iodo-isothiocyanates with ICl–KSCN has already been reported.<sup>9</sup>

<sup>4</sup> L. Mangoni, M. Adinolfi, G. Barone, and M. Parrilli, *Gazzetta*, 1975, **105**, 377.

<sup>5</sup> J. W. Cornforth and D. T. Green, *J. Chem. Soc. (C)*, 1970, 846.

<sup>6</sup> (a) M. Parrilli, M. Adinolfi, V. Dovinola, and L. Mangoni, *Gazzetta*, 1974, **104**, 819; (b) M. Parrilli, G. Barone, M. Adinolfi, and L. Mangoni, *ibid.*, p. 835.

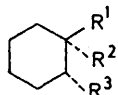
<sup>7</sup> D. R. Dalton, V. P. Dutta, and D. C. Jones, *J. Amer. Chem. Soc.*, 1968, **90**, 5498; see also, D. R. Dalton, R. C. Smith, and D. G. Jones, *Tetrahedron*, 1970, **26**, 575.

<sup>8</sup> D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals', Pergamon, Oxford, 1966.

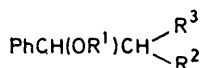
<sup>9</sup> P. D. Woodgate, H. H. Lee, P. S. Rutledge, and R. C. Cambie, *Tetrahedron Letters*, 1976, 1531.

<sup>10</sup> R. C. Cambie, R. C. Hayward, P. S. Rutledge, T. Smith-Palmer, and P. D. Woodgate, *J.C.S. Perkin I*, 1976, 840.

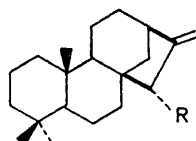
iodine and anhydrous methanol in dry tetramethylene sulphone-chloroform gave a 99% yield of the *trans*-methoxy-iodide (7)<sup>3</sup> (*cf.* ref. 11), and similar treatment of styrene gave a quantitative yield of the methoxy-iodide (18).<sup>12</sup> Use of anhydrous ethanol instead of methanol in the two previous reactions gave quantitative yields of the ethoxy-iodides (8) and (19), respectively.



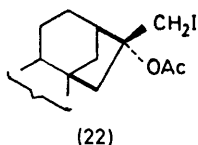
- (1)  $R^1 = I, R^2 = H, R^3 = OH$   
 (2)  $R^1 = OH, R^2 = Me, R^3 = I$   
 (3)  $R^1 = I, R^2 = H, R^3 = OAc$   
 (4)  $R^1 = I, R^2 = H, R^3 = OBz$   
 (5)  $R^1 = I, R^2 = H, R^3 = N_3$   
 (6)  $R^1 = I, R^2 = H, R^3 = Cl$   
 (7)  $R^1 = I, R^2 = H, R^3 = OMe$   
 (8)  $R^1 = I, R^2 = H, R^3 = OEt$   
 (9)  $R^1 = OAc, R^2 = Me, R^3 = I$   
 (10)  $R^1 = I, R^2 = Me, R^3 = OAc$   
 (11)  $R^1 = Me, R^2 = OAc, R^3 = OH$   
 (12)  $R^1 = Me, R^2 = OH, R^3 = OAc$



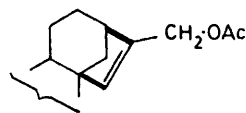
- (13)  $R^1 = R^2 = H, R^3 = I$   
 (14)  $R^1 = H, R^2 = Me, R^3 = I$   
 (15)  $R^1 = R^2 = H, R^3 = CH_2I$   
 (16)  $R^1 = Ac, R^2 = H, R^3 = I$   
 (17)  $R^1 = H, R^2 = CO_2Me, R^3 = I$   
 (18)  $R^1 = Me, R^2 = H, R^3 = I$   
 (19)  $R^1 = Et, R^2 = H, R^3 = I$



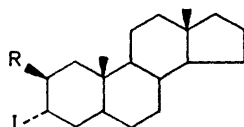
- (20)  $R = H$   
 (21)  $R = OAc$



(22)



(23)



- (24)  $R = OAc$   
 (25)  $R = Cl$   
 (26)  $R = OBz$

In earlier studies attempts were made to form an iodo-acetate from cyclohexene by using sodium acetate trihydrate and iodine(i) chloride in anhydrous dichloromethane or dry acetic acid. However, the only product identified after 2 h at 20 °C was *trans*-1-chloro-2-iodocyclohexane (6), obtained in yields of 23 and 79%, respectively. When cyclohexene was treated with thallium(i) acetate-iodine(i) chloride (1 : 2 : 1 ratio) in anhydrous dichloromethane or dry acetic acid at 20 °C for 2 h, *trans*-2-iodocyclohexyl acetate (3) was obtained in yields of 38 and 91%, respectively. Results from similar reactions with other substrates in acetic acid are given in Table 2.

*trans*-1-Chloro-2-iodocyclohexane (6) was the only

<sup>11</sup> *Cf.* C. Georgoulis and J. M. Valery, *Bull. Soc. chim. France*, 1975, 2361.

<sup>12</sup> G. Spengler and A. Weber, *Brennstoff-Chem.*, 1959, 40, 22 (*Chem. Abs.*, 1959, 53, 19937).

product formed when cyclohexene was treated with a solution obtained from stirring thallium(i) acetate and iodine(i) chloride in anhydrous dichloromethane at 20 °C for 30 min followed by removal of the residual solids. The reagent thus appeared to react in a similar manner to thallium(i) acetate-iodine in that iodoacetylation

TABLE 2

Products from the thallium acetate-iodine chloride reaction

Alkene	Product	Yield (%)
Styrene	(16) <sup>3a</sup>	86
	(9) <sup>3a</sup>	50
1-Methylcyclohexene	(10) <sup>3a</sup>	10
	(11) <sup>3a</sup>	30
	(12) <sup>3a</sup>	10
	(22) <sup>3b</sup>	59
Phyllocladene (20)	(21) <sup>3b</sup>	21
	(23) <sup>3b</sup>	20
5 $\alpha$ -Androst-2-ene	(24) <sup>14</sup>	89

occurred only when substrate and reactants were all present. However, a similar experiment with dried acetic acid as solvent gave a 91% yield of *trans*-2-iodocyclohexyl acetate (3). Thus, in acetic acid the thallium(i) acetate-iodine(i) chloride system differs from the thallium(i)-iodine system<sup>3</sup> in allowing preformation of a solution of iodine(i) acetate. The difference in mechanism of iodoacetylation is reflected in the difference in the reactions with 1-methylcyclohexene. Whereas the former system gives a product mixture similar to that obtained with silver(i) acetate and iodine,<sup>6</sup> thallium(i) acetate-iodine gives only the iodo-acetate (9), in high yield.<sup>3a</sup> The thallium(i) acetate-iodine(i) chloride system may have a synthetic advantage over silver(i) carboxylates and iodine in that iodoacetylations of less reactive olefinic bonds may be possible without silver(i)-induced solvolytic loss of the iodide.

Treatment of cyclohexene with thallium(i) benzoate and iodine(i) chloride in dichloromethane (molar ratio 1 : 1.1 : 2.5) at 20 °C for 24 h gave the iodo-chloride (6) (13%), *trans*-2-iodocyclohexyl benzoate (4) (62%), and *trans*-2-iodocyclohexanol (1) (25%). The product (1) probably arises by nucleophilic attack of adventitious water on an intermediate iodonium ion. Repetition of the reaction with a molar ratio [substrate : thallium(i) benzoate : iodine(i) chloride] of 1 : 2.5 : 2.5 in dry benzene gave an 85% yield of the *trans*-iodo-benzoate (4) as the only product (*cf.* 81% in ref. 3a). Treatment of 5 $\alpha$ -androst-2-ene with the reagents for 5 days gave starting material (36%), 2 $\beta$ -chloro-3 $\alpha$ -iodo-5 $\alpha$ -androstane (25), and the iodo-benzoate<sup>13</sup> (26) (51%).

#### EXPERIMENTAL

General experimental details are given in refs. 3 and 14.

*General Procedure for Iodohydrin Formation in Tetramethylene Sulphone-Chloroform.*—Iodine (2.4 equiv.) was added over 1 h to a stirred solution of water (3 equiv.) in tetra-

<sup>13</sup> G. J. Potter, M.Sc. Thesis, University of Auckland, 1976.

<sup>14</sup> 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.

methylene sulphone (10 ml) and chloroform (10 ml). The alkene (1 equiv.) was added to the cooled (0 °C) solution, and the mixture was stirred at 20 °C for 24 h. The mixture was then poured into water and extracted with ether. The extracts were washed repeatedly with water and then successively with saturated aqueous sodium hydrogen carbonate, water, saturated aqueous sodium disulphite, water, and saturated aqueous sodium chloride. The mixture was dried ( $\text{MgSO}_4$ ) and the solvent was removed *in vacuo* at room temperature. In general, products were identified by direct comparison (t.l.c., n.m.r., and g.l.c.) with samples obtained in previous work.<sup>3</sup> For most reactions yields have not been optimised.

Cyclohexene gave *trans*-2-iodocyclohexanol<sup>3a</sup> (81%); styrene gave 2-iodo-1-phenylethanol (13) (87%),  $\delta$  ( $\text{CCl}_4$ ) 3.20 (s, OH exchanged with  $\text{D}_2\text{O}$ ), 3.30 (m, 2- $\text{H}_2$ ), 4.65 (m, 1-H), and 7.20 (s, ArH), and starting material (13%); phenylcyclopropane (36 h) gave 3-iodo-1-phenylpropanol<sup>15</sup> (92%) and starting material (5%); *trans*-1-phenylpropene gave 2-iodo-1-phenylpropanol (14) (24%) and starting material (72%); and 1-methylcyclohexene gave *t*-2-iodo-1-methylcyclohexan-*r*-1-ol<sup>6</sup> (2) (61%),  $\delta$  ( $\text{CCl}_4$ ) 1.39 (s, Me), 1.05–2.38 (m, 3-, 4-, 5-, and 6-H), 2.20 (s, OH, exchanged with  $\text{D}_2\text{O}$ ), and 4.30 (m, 2-H).

**Reactions of Alkenes with Sodium Salts in Tetramethylene Sulphone–Chloroform.**—(a) *With sodium acetate trihydrate.* Cyclohexene (1 equiv.) was added to a stirred suspension of sodium acetate trihydrate (3 equiv.) and iodine (2.4 equiv.) in tetramethylene sulphone–chloroform (1 : 1) as above. Work-up gave *trans*-2-iodocyclohexanol (81%).

(b) *With fused sodium acetate.* Cyclohexene (1 equiv.), fused sodium acetate (3 equiv.), and iodine (2.4 equiv.) in anhydrous tetramethylene sulphone–chloroform gave *trans*-2-iodocyclohexyl acetate<sup>3a</sup> (3) (55%); styrene gave 2-iodo-1-phenylethyl acetate<sup>3a</sup> (16) (70%), starting material (20%), and a minor unidentified product.

(c) *With sodium benzoate.* Cyclohexene (1 equiv.) was added to a stirred solution of sodium benzoate (3 equiv.) and iodine (2.4 equiv.) in tetramethylene sulphone–chloroform (1 : 1) as above. Work-up and p.l.c. gave *trans*-2-iodocyclohexyl benzoate (4) and *trans*-2-iodocyclohexanol in the ratio 3 : 1.

(d) *With sodium azide.* Iodine (0.61 g, 2.4 mmol) was added over 1 h to a stirred and cooled suspension of sodium azide (0.20 g, 3.0 mmol) in a mixture of dry tetramethyl sulphone (5 ml) and anhydrous chloroform (5 ml). The suspension was stirred at 0 °C for 1 h, cyclohexene (82 mg, 1.0 mmol) was added, and the mixture was stirred at 20 °C for 24 h. Work-up gave *trans*-1-azido-2-iodocyclohexane (5) (95%) and a minor unidentified product.

**Reaction of *trans*-Methyl Cinnamate with Silver(I) Acetate–Iodine in Tetramethylene Sulphone–Chloroform.**—Iodine (0.61 g, 2.4 mmol) was added over 1 h to a stirred and cooled slurry of silver(I) acetate (0.50 g, 3.0 mmol) in anhydrous tetramethylene sulphone (8 ml) and anhydrous chloroform (8 ml). The suspension was stirred at 0 °C for 1 h, *trans*-methyl cinnamate (0.16 g, 1.0 mmol) was added, and the mixture was stirred at 20 °C for 24 h. Work-up as for iodohydrin formation gave an orange oil (0.22 g), which was purified by p.l.c. to give methyl 3-hydroxy-2-iodo-3-phenylpropanoate (14) (49 mg, 34%), crystals,  $\nu_{\text{max}}$  3 470 (OH) and 1 660  $\text{cm}^{-1}$  (ester CO),  $\delta$  ( $\text{CCl}_4$ ) 3.72 (s, OMe), 3.72 (s, OH,

exchanged with  $\text{D}_2\text{O}$ ), 4.40 (d,  $J$  8 Hz, 2-H), 4.97 (d,  $J$  7 Hz, 3-H), and 7.22 (s, ArH),  $m/e$  306 ( $M^{++}$ ), 199 [ $\text{CH}(\text{I})\text{CO}_2\text{Me}^+$ ], 179 ( $M - \text{I}$ ), and 107 ( $\text{PhCH}=\text{OH}^+$ ).

**Reaction of Cyclohexene with Sodium Acetate Trihydrate and Iodine(I) Chloride.**—(a) *In acetic acid.* Iodine(I) chloride (0.16 g, 1.0 mmol) in dried acetic acid (0.5 ml) was added dropwise over 20 min to a stirred suspension of sodium acetate trihydrate (82 mg, 0.6 mmol) in dry acetic acid (4.5 ml). The suspension was stirred at 20 °C for 30 min, cyclohexene (82 mg, 1.0 mmol) was added, and the mixture was stirred at 20 °C for 2 h. Work-up gave *trans*-1-chloro-2-iodocyclohexane (79%).

(b) *In dichloromethane.* Repetition of the above experiment in dichloromethane gave *trans*-1-chloro-2-iodocyclohexane (23%) and two minor unidentified products.

(c) *In tetramethylene sulphone–chloroform.* Iodine(I) chloride (0.39 g, 2.4 mmol) in tetramethylene sulphone (1 ml) and anhydrous chloroform (1 ml) was added dropwise over 1 h to a stirred and cooled slurry of sodium acetate trihydrate (0.25 g, 1.8 mmol) in tetramethylene sulphone (10 ml) and chloroform (10 ml). The suspension was cooled at 0 °C for 1 h, cyclohexene (82 mg, 1.0 mmol) was added, and the mixture was stirred at 20 °C for 24 h. Work-up gave *trans*-1-chloro-2-iodocyclohexane (70%).

**Preparation of Iodo-alkoxides.**—Iodine (2.4 equiv.) was added to a stirred mixture of anhydrous methanol (or ethanol) (10 ml) and anhydrous tetramethylene sulphone (10 ml) with cooling (0 °C). The mixture was stirred at 20 °C for 1 h, the alkene (1 equiv.) was added, and stirring was continued at 20 °C for 24 h. Cyclohexene gave *trans*-1-iodo-2-methoxycyclohexane<sup>3a</sup> (7) (99%) and *trans*-1-ethoxy-2-iodocyclohexane (8) (100%) (Found: C, 38.3; H, 6.1; I, 49.5.  $\text{C}_8\text{H}_{15}\text{IO}$  requires C, 37.8; H, 6.0; I, 49.9%),  $\delta$  1.23 (t,  $\text{CH}_3\cdot\text{CH}_2$ ), 3.57 (q,  $\text{O}\cdot\text{CH}_2\cdot\text{CH}_3$ ), 3.57 (m, 2-H), and 4.07 (m, 1-H); styrene gave 2-iodo-1-methoxy-1-phenylethane<sup>12</sup> (18) (100%),  $\delta$  ( $\text{CCl}_4$ ) 3.25 (s, OMe), 3.25 (m, 2- $\text{H}_2$ ), 4.20 (t, 1-H), and 7.3 (s, ArH), and 2-iodo-1-ethoxy-1-phenylethane (19) (100%) (Found: C, 43.5; H, 4.7; I, 45.7.  $\text{C}_{10}\text{H}_{13}\text{IO}$  requires C, 43.5; H, 4.75; I, 46.0%),  $\delta$  1.23 (t,  $\text{CH}_3\cdot\text{CH}_2$ ), 3.45 (q,  $\text{OCH}_2\cdot\text{CH}_3$ ), 3.45 (m, 1-H), 4.40 (t, 2-H), and 7.37 (s, ArH).

**Iodocarboxylations.**—(a) *With thallium(I) acetate–iodine(I) chloride.* A solution of iodine(I) chloride (1 equiv.) in dry acetic acid (1 ml) was added dropwise over 20 min to a stirred suspension of thallium(I) acetate (2 equiv.) in dry acetic acid (4 ml). The suspension was stirred at 20 °C for 30 min, the alkene (1 equiv.) was added, and the mixture was stirred at 20 °C for 2 h. The reactions were worked up as for iodocarboxylations with iodine.<sup>3a</sup> The results are summarised in Table 2.

(b) *With thallium(I) benzoate–iodine(I) chloride.* A solution of iodine(I) chloride (1.1 equiv.) in dry benzene was added slowly (30 min) to a stirred and cooled (0 °C) slurry of thallium(I) benzoate (2.5 equiv.) in benzene (20 ml). After 15 min cyclohexene (1.1 equiv.) was added, and the mixture was stirred at 20 °C for 24 h. Work-up gave *trans*-2-iodocyclohexyl benzoate<sup>3a</sup> (30%). The experiment was repeated using dichloromethane as the solvent. Work-up gave *trans*-1-chloro-2-iodocyclohexane (13%), *trans*-2-iodocyclohexyl benzoate (62%), and *trans*-2-iodocyclohexanol (25%).

Repetition of the reaction in dry benzene with a molar ratio [substrate : thallium(I) benzoate : iodine(I) chloride] of 1 : 2.5 : 2.5 gave *trans*-2-iodocyclohexyl benzoate (85%).

5 $\alpha$ -Androst-2-ene (1 equiv.) was treated with iodine(I)

<sup>15</sup> P. H. Atkinson, R. C. Cambie, G. Dixon, W. I. Noall, P. S. Rutledge, and P. D. Woodgate, following paper.

chloride (2.5 equiv.) and thallium(I) benzoate (2.5 equiv.) in benzene for 5 days. Work-up and p.l.c. gave starting material (36%), 2 $\beta$ -chloro-3 $\alpha$ -iodo-5 $\alpha$ -androstane (25) (13%), needles (from MeOH), m.p. 126—130°,  $\delta$  0.70 (s, 18-H<sub>3</sub>), 1.13 (s, 19-H<sub>3</sub>), 4.66 (m,  $W_{\frac{1}{2}}$  7 Hz, 3-H), and 4.86 (m,  $W_{\frac{1}{2}}$  7 Hz, 2-H), and 3 $\alpha$ -iodo-5 $\alpha$ -androstan-2 $\beta$ -yl benzoate <sup>13</sup> (26) (51%).

[6/847 Received, 3rd May, 1976]

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