

Reactions of Silver(I) Acetate–Iodine and Thallium(I) Acetate–Iodine with Substituted Cyclopropanes

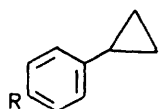
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Treatment of phenylcyclopropane with silver(I) acetate–iodine or thallium(I) acetate–iodine gives, as the major products, 1,3-disubstituted phenylpropanes resulting from cyclopropane ring opening, and in some cases, from solvolysis of intermediate iodo-acetates. Similar products are given with silver(I) trifluoroacetate–iodine but in this case aromatic iodination also occurs. Treatment of norcarane with the same reagents also results in ring opening, but here secondary products result from elimination and subsequent addition. Both substrates are less reactive than alkenes towards each reagent. Reaction mechanisms are discussed. The action of other reagent systems involving electrophilic iodine with phenylcyclopropane and norcarane is reported.

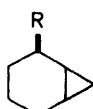
In earlier work we compared the modes of reaction of thallium(I) acetate–iodine and silver(I) acetate–iodine

we have extended our examination to phenylcyclopropane (1) and norcarane (bicyclo[4.1.0]heptane) (3).

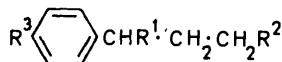
The substituted cyclopropanes were considerably less reactive than alkenes towards each reagent. Treatment of phenylcyclopropane with silver(I) acetate–iodine in acetic acid at 20 °C for 8 h gave an 81% conversion into the diacetate (5)⁴ and the iodo-acetate (6). Minor products were the hydroxy-acetates (7) and (8),^{4,5} the unsaturated acetate (17),⁶ the diol (9),^{4,7} and traces of



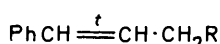
- (1) R = H
(2) R = I



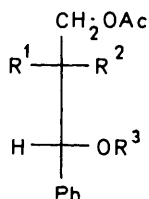
- (3) R = H
(4) R = OH



- (5) R¹ = R² = OAc, R³ = H
(6) R¹ = OAc, R² = I, R³ = H
(7) R¹ = OAc, R² = OH, R³ = H
(8) R¹ = OH, R² = OAc, R³ = H
(9) R¹ = R² = OH, R³ = H
(10) R¹ = OH, R² = I, R³ = H
(11) R¹ = I, R² = OAc, R³ = H
(12) R¹ = R² = O₂C·CF₃, R³ = H
(13) R¹ = O₂C·CF₃, R² = I, R³ = H
(14) R¹ = R² = O₂C·CF₃, R³ = I
(15) R¹ = R² = OH, R³ = I
(16) R¹ = OH, R² = OAc, R³ = I



- (17) R = OAc
(18) R = I



- (19) R¹ = R³ = H, R² = I
(20) R² = R³ = H, R¹ = I
(21) R¹ = H, R² = I, R³ = Ac
(22) R¹ = H, R² = OAc, R³ = Ac

(Prévost reaction) with some alkenes,¹ including norborn-2-ene.² In view of the similarity in chemical properties of a cyclopropane ring and an olefinic double bond,³

¹ R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, *J.C.S. Perkin I*, 1974, (a) p. 1120; (b) p. 1858; (c) p. 1864.

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

TABLE I
Products from phenylcyclopropane (% yield)

Product	AgOAc–I ₂		TlOAc–I ₂		
	HOAc ^a	CH ₂ Cl ₂ ^b	HOAc ^c	CH ₂ Cl ₂ ^d	CHCl ₃ ^e
(1)	19	5	32	54	62
(5)	21	46	5		
(7)	8	2	10		
(8)	1	29	10		
(6)	26	ca. 0.1	21	39	29
(17)	2.5	6		3	4
(9)	ca. 0.3	2			
(10)			5		
(19), (20)	Trace	Trace			

^a Molar ratio (1): AgOAc: I₂, 1:1.2:1; 8 h. ^b Molar ratio (1): AgOAc: I₂, 1:5:5; 28 h. ^c Molar ratio (1): TlOAc: I₂, 1:5:5; 72 h. ^d Molar ratio (1): TlOAc: I₂, 1:2:2; 72 h. ^e Molar ratio (1): TlOAc: I₂, 1:1:1; 72 h.

trisubstituted phenylpropanes. Repetition of the experiment for 28 h in the more easily removed solvent dichloromethane gave different ratios of the same products (Table I). Only a trace of the iodo-acetate (6) was

³ (a) M. Smith in 'Rodds Chemistry of Carbon Compounds,' vol. 2, Part A, Elsevier, Amsterdam, 1967, p. 26; (b) M. Yu Lukina, *Russ. Chem. Rev.*, 1962, **31**, 419.

⁴ (a) S. Mamedov, K. K. Shamirov, and D. N. Khydyrov, *J. Gen. Chem. (U.S.S.R.)*, 1963, **33**, 1411; (b) M. Ohara, K. Yamamoto, and K. Tanaka, *Jap. P.* 11 666, 1962 (*Chem. Abs.*, 1963, **59**, 9890).

⁵ M. Chara, K. Yamamoto, K. Tanaka, and M. Ito, *Jap. Pat.* 9078, 1962 (*Chem. Abs.*, 1963, **59**, 8658).

⁶ A. South and R. J. Ouellette, *J. Amer. Chem. Soc.*, 1968, **9**, 7064.

⁷ J. Klein and A. Medlik, *J. Amer. Chem. Soc.*, 1971, **93**, 6313.

now present and the major products were the diacetate (5) and the hydroxy-acetate (8), which were also the major products when the crude mixture from the former reaction was solvolysed with silver(I) acetate in acetic acid. Minor products from the reaction carried out in dichloromethane were the *erythro*- (19) and *threo*- (20) isomers of 3-hydroxy-2-iodo-3-phenylpropyl acetate. That the silver(I) ion did not itself play an independent role in cleavage of the cyclopropyl ring [*cf.* silver(I) ion-catalysed opening of bicyclobutanes⁸] was established when phenylcyclopropane was recovered quantitatively after being stirred with silver(I) acetate in acetic acid at 20 °C for 160 h.

Structures of the hydroxy-acetate (7) and the iodo-acetate (6) were assigned from spectral data (see Experimental section). Solvolysis of the iodo-acetate with silver(I) acetate in acetic acid resulted in quantitative conversion into a mixture of the diacetate (5) and the hydroxy-acetates (7) and (8), each arising, as expected,¹ from a 1,3-dioxan-2-ylum intermediate.⁹

The possibility that the products (7) and (8) arose by hydrolysis of the iodo-acetate (6) during work-up of the reaction of silver(I) acetate-iodine with phenylcyclopropane was eliminated when the iodo-acetate was recovered quantitatively after further subjection to work-up conditions. Moreover, when the hydroxy-acetate (8) was stirred with acetic acid at 20 °C for 48 h, a mixture of the hydroxy-acetates (7) and (8) in the ratio 1 : 5 was obtained, indicating that the former arose from solvolysis of compound (8) during the original reaction with phenylcyclopropane. However, treatment of phenylcyclopropane with a pre-formed solution of iodine(I) acetate ($I^+ OAc^-$)¹⁰ gave a mixture of composition identical with that obtained by adding iodine in acetic acid to a stirred solution of silver(I) acetate and the substrate in acetic acid. In this case it was shown that the products (5), (7), and (8) could be formed by solvolysis of the iodo-acetate (6) when the latter was treated with a pre-formed solution of iodine(I) acetate.

The reaction of phenylcyclopropane with thallium(I) acetate-iodine took place even less readily than that with silver(I) acetate-iodine; it was necessary to increase the reagent to substrate ratio from 1 : 1 to 5 : 1 and to extend the reaction time from 28 to 72 h in order to achieve a comparable level of ring cleavage in acetic acid. The major product from reactions carried out in acetic acid, dichloromethane, or chloroform (Table I) was the iodo-acetate (6). Other products from the reaction in acetic acid were the diacetate (5), the hydroxy-acetates (7) and (8), and the iodohydrin (10), whose structure followed from its i.r., ¹H n.m.r., and mass spectra (see Experimental section) and from acetylation to give the iodo-

acetate (6). However, *trans*-cinnamyl acetate (17), a minor product from the reaction in dichloromethane or chloroform, was not present in the products from the reaction in acetic acid. No reaction occurred when phenylcyclopropane was stirred with thallium(I) acetate in acetic acid at 20 °C for 27 h, with or without a catalytic amount of iodine. However, the action of iodine in glacial acetic acid alone cleaved the cyclopropane ring to give a 6% yield of 3-iodo-1-phenylpropyl acetate (6) after 27 h and low yields of both the iodo-acetate (6) (12.5%) and 3-iodo-1-phenylpropan-1-ol (10) (12.5%) after 72 h (*cf.* the molecular complex formation of cyclopropane and iodine¹¹ and the reaction in the gas phase^{3b}).

Treatment of *trans*-cinnamyl acetate (17) with either silver(I) acetate-iodine or thallium(I) acetate-iodine in dichloromethane gave as the major product, a mixture of the *erythro*- (19) and *threo*- (20) isomers of 3-hydroxy-2-iodo-3-phenylpropyl acetate in the ratio 13 : 8. Assignment of stereochemistry was made on the basis of ¹H n.m.r. spectral evidence and by analogy with the *erythro*- and *threo*-halogenohydrins of cinnamic acid.¹² The isomers (19) and (20) probably arise in the reaction rather than the expected iodo-diacetate (21) or triacetate (22), because the double bond of *trans*-cinnamyl acetate has such low reactivity that it requires a stronger nucleophile (in the form of adventitious water) than acetate ion in order to effect reaction.

In contrast to the action of silver(I) acetate and iodine(I) acetate, no solvolysis of the iodo-acetate (6) occurred when it was treated with thallium(I) acetate in acetic acid at 20 °C for 27 h or with thallium(I) acetate containing a catalytic amount of iodine. This difference is reflected in the difficulty of thallium(I) in forming amine or cyanide complexes but the relative ease of silver(I) in forming strong complexes with these ligands.¹³ The failure of thallium(I) acetate to react with the potentially labile iodo-acetate (6) and its inability to complex with alkenes¹⁴ suggests that it is not as 'soft'¹⁵ an acid as silver(I). The iodo-acetate (6) was solvolysed with thallium(III) acetate but even so only a 65% conversion into compounds (5), (7), and (8) was achieved after 74 h at 20 °C.

The pathways in Scheme 1 which proceed *via* the benzylic cation (A) offer rational routes to all the products detected from the reactions of silver(I) acetate-iodine and iodine(I) acetate with phenylcyclopropane, and are consistent with accepted views on the opening of aryl-substituted cyclopropane rings by electrophilic attack,¹⁶ *e.g.* with bromine.¹⁷ However, it is necessary to postulate a benzylic intermediate (A) and another pathway in order to explain the formation of all the products

¹³ R. O. Nilsson, *Arkiv. Kemi*, 1957, **10**, 363 (*Chem. Abs.*, 1957, **51**, 8571); F. Ya Kulba and V. E. Mironov, *Russ. J. Inorg. Chem.*, 1960, **5**, 138, 922.

¹⁴ B. T. Guran and L. B. Rogers, *J. Gas Chromatog.*, 1965, **3**, 269 (*Chem. Abs.*, 1966, **64**, 1326).

¹⁵ R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533; *Chem. in Britain*, 1967, **3**, 103.

¹⁶ C. H. DePuy, *Fortschr. Chem. Forsch.*, 1973, **40**, 73.

¹⁷ R. T. Lalonde and A. D. Debboli, *J. Org. Chem.*, 1973, **38**, 4228.

⁸ L. A. Paquette, *Accounts Chem. Res.*, 1971, **4**, 280.

⁹ J. F. King and A. D. Allbutt, *Canad. J. Chem.*, 1970, **48**, 1754; C. U. Pittman, S. P. McManus, and J. W. Larsen, *Chem. Rev.*, 1972, **72**, 357.

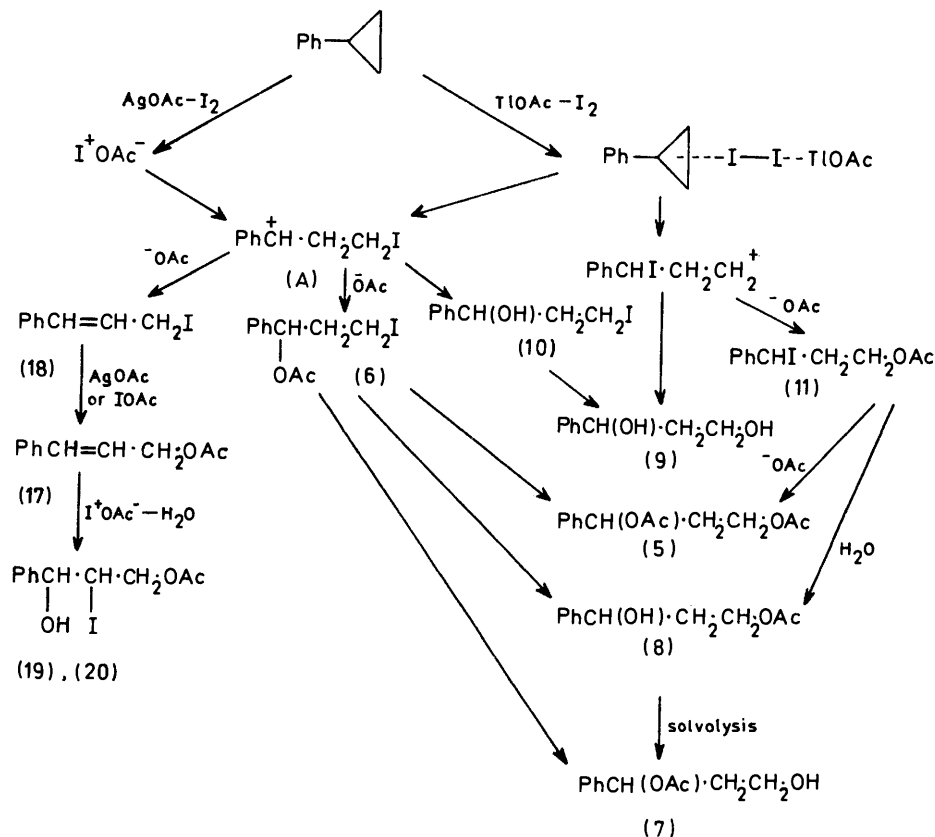
¹⁰ C. V. Wilson, *Org. Reactions*, 1957, **9**, 332.

¹¹ S. Freed and K. M. Sancier, *J. Amer. Chem. Soc.*, 1952, **74**, 1273.

¹² P. B. D. de la Mare and M. A. Wilson, *J.C.S. Perkin II*, 1973, 653.

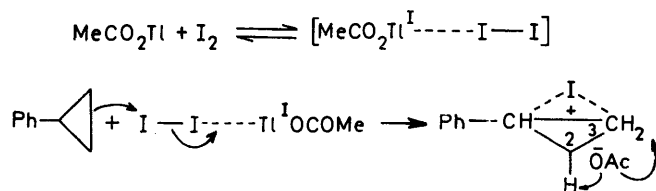
from the reaction of thallium(I) acetate-iodine with phenylcyclopropane, since the diacetate (5) and the hydroxy-acetates (7) and (8) are not formed by solvolysis of the iodo-acetate (6) with this reagent. In this case the most likely precursor of (5), (7), and (8) is the regioisomer (11) (Scheme 1). Although it was not detected

is possible that it also operates in these reactions. The products formed when dichloromethane and chloroform are the solvents may arise from a carbocation but may also be formed by a concerted reaction in which *trans*-cinnamyl iodide is produced by attack of acetate anion on a C-2 hydrogen atom (Scheme 2).



SCHEME 1

as a product of the reaction, such a benzylic iodide would be expected to be very reactive and unlikely to survive under the reaction conditions. It is suggested that the opening of the cyclopropane may proceed in a concerted manner *via* an 'edge' iodonium ion in a manner similar to that suggested earlier^{1,2} for alkenes (Scheme 2).



SCHEME 2

Nucleophilic attack at C-3 as indicated could then lead to the iodo-acetate (11) without the intermediacy of a primary carbocation. Although it is not necessary to invoke such a path for the cleavage of phenylcyclopropane with silver(I) acetate-iodine or iodine(I) acetate, it

An alternative possibility,* that thallium(I) is oxidised by iodine to thallium(III) which then cleaves the cyclopropane ring, is not favoured for reasons previously outlined,¹ and because the iodo-acetate (6) is not solvolysed with thallium(I) acetate-iodine in glacial acetic acid but is solvolysed with thallium(III) acetate in the same solvent. Moreover, Ouellette and South⁶ have reported that the reaction of an excess of phenylcyclopropane with thallium(III) acetate in anhydrous acetic acid at 75 °C gives the diacetate (5) (90%) and cinnamyl acetate (17) (10%), a product which was not obtained from the thallium(I) acetate-iodine reaction with phenylcyclopropane in acetic acid.

In an attempt to improve the amount of ring cleavage of phenylcyclopropane it was treated with thallium(I) acetate and iodine(I) chloride in acetic acid in the molar ratio 1 : 5 : 5. After 48 h this afforded a 64% conversion into a mixture which included the same products as ob-

* There is precedent for the formation of a thallium(III) species from a thallium(I) carboxylate and bromine.¹⁸

¹⁸ B. Cocton and A. Crastes de Paulet, *Bull. Soc. chim. France*, 1966, 2947; E. Goldschmidt, *Diss. Berlin*, 1903, S.45, quoted in 'Gmelin's Handbuch der Anorganischen Chemie, Vol. 38, Thallium,' Verlag Chemie, Berlin, 1940.

tained when iodine was used. In accord with the known ability of iodine(I) chloride to effect aromatic iodination,¹⁹ the reaction afforded an 18% yield of iodoaryl products.

Since iodine(I) trifluoroacetate is a better source of electrophilic iodine than iodine(I) acetate^{20,21} the reaction of silver(I) trifluoroacetate-iodine with phenylcyclopropane, in dichloromethane, in the molar ratio 2.5:2.5:1, was also examined. In accord with its reactivity in electrophilic substitution the reagent gave the *p*-iodo-bistrifluoroacetate (14) in 31% yield. Other products were the bistrifluoroacetate (12) and the iodo-trifluoroacetate (13), presumably formed by pathways similar to those operating with the silver(I) acetate system. There was no indication that elimination products or addition products derived therefrom, were formed, indicating that the trifluoroacetate anion is too weak a base to participate in elimination processes. Solvolysis of the product mixture with silver(I) trifluoroacetate followed by hydrolysis gave 1-phenylpropane-1,3-diol (9) and 1-(*p*-iodophenyl)propane-1,3-diol (15). Acetylation of the diol mixture afforded the hydroxyacetates (8) and (16). Repetition of the reaction with phenylcyclopropane-thallium(I) trifluoroacetate-iodine in the molar ratio 1:1:1 gave the iodo-trifluoroacetate (13) in 50% yield. In contrast to the silver(I) trifluoroacetate reaction, no iodoaryl products were observed and like the thallium(I) acetate reaction, little solvolysis occurred, only a 4% yield of the bistrifluoroacetate (12) being formed.

Under comparable conditions norcarane (3) was less reactive than phenylcyclopropane towards both the silver and thallium systems. In acetic acid both reagents gave the iodo-acetate (23) and a difficultly separable mixture of the di-iodo-acetates (24) and (25) as the major products (Table 2) after 72 h. Minor products were the iodo-hydrin (26), the iodo-acetates (27) and (28), and the di-iodide (29), but in neither case were products of solvolysis

TABLE 2
Reactions of norcarane

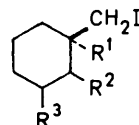
Reagent	Solvent	Reagent ratio	Products (% yield)					
			(23)	(24)	(25)	(26)	(27)	(28)
AgOAc-I ₂	HOAc	1:1.2:1.2	16	4	4	2	1	3
AgOAc-I ₂	HOAc	1:5:5	22	10	3	5	5	Trace
AgOAc-I ₂	CH ₂ Cl ₂	1:1.2:1.2	2	18	1	0.3	0.3	10
TlOAc-I ₂	HOAc	1:5:5	37	4	3	3	2	Trace

identified. Increasing the metal carboxylate-iodine-substrate ratio from 1.2:1.2:1 to 5:5:1 increased the amount of reaction without appreciably altering the product ratio. Control experiments showed that neither silver(I) acetate nor acetic acid alone cleaved the cyclopropane ring of norcarane to any appreciable extent. As with phenylcyclopropane, reaction of norcarane with preformed iodine(I) acetate gave a product composition

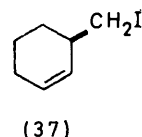
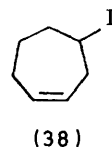
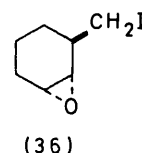
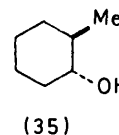
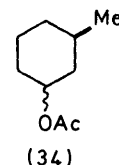
¹⁹ R. B. Sandin, W. V. Drake, and F. Leger, *Org. Synth. Coll. Vol. 11*, 1943, 196; G. H. Woollett and W. W. Johnson, *ibid.*, p. 343; V. H. Wallingford and P. A. Krueger, *ibid.*, p. 349; D. Papa, H. F. Ginsberg, I. Lederman, and V. de Camp, *J. Amer. Chem. Soc.*, 1953, **75**, 1107.

similar to that obtained when the reagent was formed *in situ*.

In the ¹H n.m.r. spectrum of *trans*-2-iodomethylcyclohexyl acetate (23) the half height width (22 Hz) of the signal at δ 4.60 indicated that the proton geminal to the



- (23) R¹ = R³ = H, R² = α-OAc
 (24) R¹ = H, R² = β-I, R³ = α-OAc
 (25) R¹ = H, R² = β-OAc, R³ = α-I
 (26) R¹ = R³ = H, R² = α-OH
 (27) R¹ = H, R² = H, R³ = β-OAc
 (28) R¹ = H, R² = H, R³ = α-OAc
 (29) R¹ = R³ = H, R² = α-I
 (30) R¹ = H, R² = OAc, R³ = I
 (31) R¹ = R³ = H, R² = OAc
 (32) R¹ = H, R² = β-I, R³ = α-OH
 (33) R¹ = R³ = H, R² = β-OAc



acetate group was in an axial position, so that the two substituents on the cyclohexane ring were both equatorial and therefore *trans*. The vicinal nature of the two substituents was shown by reduction with lithium aluminium hydride, which afforded a 95% yield of *trans*-2-methylcyclohexanol (35). Hydrolysis of the iodo-acetate (23) with potassium carbonate in aqueous methanol gave the iodo-hydrin (26) in near quantitative yield.

In addition to a single acetate signal at δ 2.05, the ¹H n.m.r. spectrum of the di-iodo-acetate (24) showed a 2-proton multiplet at δ 3.05 which was assigned to the protons of an iodomethylene group. However, although these protons were anisochronous,²² the signal was not sufficiently resolved to allow measurement of coupling constants. The regiochemistry of the secondary iodo- and acetoxy-groups was shown by acidic hydrolysis, which gave the di-iodohydrin (32) on which shift reagent studies with Eu(fod)₃ showed the presence of three protons vicinal to the hydroxy-group, and by reduction with tri-(*n*-butyl)tin hydride,²³ which gave *trans*-3-methylcyclohexyl acetate. The half height widths (7 Hz) of the signals at δ 4.60 and 5.32 of the di-iodo-acetate (24)

²⁰ R. N. Haszeldine and A. G. Sharpe, *J. Chem. Soc.*, 1952, 993; R. N. Haszeldine, *ibid.*, 1951, 584.

²¹ D. G. Hey, G. D. Meakins, and M. W. Pemberton, *J. Chem. Soc. (C)*, 1966, 1331.

²² W. B. Jennings, *Chem. Rev.*, 1975, **75**, 307.

²³ E. J. Corey and J. W. Suggs, *J. Org. Chem.*, 1975, **40**, 2554.

indicate that the protons are equatorial and hence that the substituents are axial. The *trans*-vicinal stereochemistry of the secondary iodo- and acetoxy-groups was confirmed by conversion into the *anti*-epoxide (36) with methanolic potassium carbonate. The structure of the di-iodo-acetate was confirmed by an independent synthesis of 3-iodomethylcyclohexene (37) and 4-iodocycloheptene (38) by the opening of *syn*-bicyclo[4.1.0]heptan-2-ol (4)²⁴ with aqueous hydrogen iodide.²⁵ Iodoacetylation of the alkene (37) with silver(I) acetate-iodine gave a 7 : 1 mixture of *trans*-2-iodo-*trans*-3-iodomethylcyclohexyl acetate (24) and *trans*-2-iodo-*cis*-6-iodomethylcyclohexyl acetate (25), which were separated by p.l.c.

The half height widths (8 Hz) of the signals at δ 5.10 and 4.50 in the ¹H n.m.r. spectrum of the minor di-iodo-acetate indicated equatorial protons and thus axial substituents, whence its structure (25) followed.

The structures of the two iodo-acetates (27) and (28) were established as follows. G.l.c. showed the presence of two components, and elemental analysis suggested a molecular formula of C₉H₁₅I₂O₂ which was supported by the appearance of peaks attributable to an iodo-acetate in the mass spectrum. The ¹H n.m.r. spectrum showed two low-field signals at δ 5.00 and 4.50, with half height widths of 8 and 30 Hz corresponding to equatorial and axial protons, and indicating that the isomers were epimeric about a secondary carbon atom. Also present in the ¹H n.m.r. spectrum was a partly resolved multiplet at δ 3.10 corresponding to the iodomethylene group. The isomerism of the two components of the mixture was confirmed when reduction by tri-(*n*-butyl)tin hydride²³ gave an equimolar mixture of *cis*- and *trans*-3-methylcyclohexyl acetates²⁶ (34).

The structure of the di-iodide (29) followed from its ¹H n.m.r. spectrum (see Experimental section).

Rationalisation of the formation of (24) and (25) requires a sequence in which iodine(I)-induced cleavage of the cyclopropyl ring is accompanied or followed by elimination of a proton and then addition of the elements of iodine(I) acetate to the resulting alkene (37). The intermediacy of (37) has analogy in the cleavage of norcarane by other reagents.^{27,28} The stereospecificity reflected in the formation of *trans*-2-iodomethylcyclohexyl acetate (23) but not the *cis*-isomer (33) indicates that a free carbocation is not involved. Concerted attack of iodine(I) acetate or of thallium(I) acetate and iodine, similar to that proposed by Lalonde²⁹ for the reaction of norcarane with acetic acid, would account for this specificity. Presumably the iodo-acetates (27) and (28) result from non-stereospecific addition of acetate to a carbo-

cation, formed by a hydride migration concerted with the cleavage of the cyclopropane ring.

The di-iodide (29) presumably arises by opening of the cyclopropane ring of norcarane with molecular iodine. However, although treatment of norcarane with iodine in acetic acid at 20 °C for 76 h resulted in cleavage of the cyclopropane ring, the ¹H n.m.r. spectrum of the crude product mixture showed no evidence for the presence of compounds containing an iodomethyl group.

Reactions of phenylcyclopropane and norcarane with other reagent systems involving electrophilic iodine were also examined. Treatment of phenylcyclopropane for 1 week with iodine and potassium iodate in glacial acetic acid³⁰ (ratio 1.3 : 2 : 1) afforded the iodo-acetate (6) (77%), the iodohydrin (10) (5%), and cinnamyl iodide (18) (4%). Although it was not isolated, the last (18) was detected from the ¹H n.m.r. spectrum of the crude product which showed a multiplet at δ 3.10 due to the protons of an iodomethylene group, a multiplet at δ 6.63 due to olefinic protons, and a singlet at δ 7.30 due to the aromatic protons. Its presence was substantiated when solvolysis of the crude product with silver(I) acetate gave *trans*-cinnamyl acetate (17) in addition to compounds (5), (7), and (8). The absence of solvolysis products in the original product is in keeping with their absence in products from the reaction of iodine and potassium iodate with cholest-2-ene.³⁰ Treatment of phenylcyclopropane with iodine and potassium iodate (1.35 : 2 : 1 molar ratio) in dilute sulphuric acid³¹ and dioxan gave the iodohydrin (10)³² in 68% yield but no product was isolated from treatment with mercury(II) oxide and iodine in carbon tetrachloride. The reaction of norcarane with iodine and potassium iodate in acetic acid for 72 h (ratio 4 : 2 : 1) gave the iodo-acetate (23) (20%), the di-iodo-acetates (24) and (25) (16%), and the iodo-acetates (27) and (28) (5%). Use of iodine and potassium iodate in sulphuric acid and dioxan gave low yields of the iodohydrin (26) (3%) and the di-iodide (29) (6%).

Recently we found that the reaction of ozonised iodine in acetic anhydride on alkenes is regiospecific, leading to *vic*-iodo-acetates, iodohydrins, and iodo-ketones.³³ Treatment of phenylcyclopropane with a 10 molar excess of 'iodine oxide' in acetic anhydride gave the iodo-acetate (6) (16%), the diacetate (5) (13%), the iodohydrin (10) (9%), the hydroxy-acetates (7) (2%) and (8) (6%), and (4-iodophenyl)cyclopropane (2) (7%). The structure of the compound (2) was assigned from its ¹H n.m.r. and mass spectra. Treatment of norcarane with solvated 'iodine oxide' gave the iodo-acetate (23) (9%), a mixture of the di-iodo-acetates (24) and (25) (8%), a mixture of the iodo-acetates (27) and (28) (10%), a trace of the di-

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²⁵ M. Julia, S. Julia, and R. Guegan, *Bull. Soc. chim. France*, **1960**, 1072.

²⁶ G. A. C. Gough, H. Hunter, and J. Kenyon, *J. Chem. Soc.*, **1926**, 2052; H. L. Goering and C. Serres, *J. Amer. Chem. Soc.*, **1952**, **74**, 5908.

²⁷ R. T. Lalonde and L. S. Forney, *J. Amer. Chem. Soc.*, **1963**, **85**, 3767.

²⁸ R. T. Lalonde, *J. Org. Chem.*, **1962**, **27**, 2275; R. T. Lalonde and M. A. Tobias, *J. Amer. Chem. Soc.*, **1964**, **86**, 4068.

²⁹ R. T. Lalonde and M. A. Tobias, *J. Amer. Chem. Soc.*, **1963**, **85**, 3771.

³⁰ L. Mangoni, M. Adinolfi, G. Barone, and M. Parrilli, *Gazzetta*, **1975**, **105**, 377.

³¹ J. W. Cornforth and D. T. Green, *J. Chem. Soc. (C)*, **1970**, 846.

³² R. C. Cambie, W. I. Noall, G. J. Potter, P. S. Rutledge, and P. D. Woodgate, preceding paper.

³³ 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.

iodohydrin (32), and small amounts of unidentified products.

EXPERIMENTAL

General experimental details are given in refs. 1b and 2.

General Procedures for Work-up of Metal Carboxylate-Iodine Reactions.—(a) *With aprotic solvents.* The reaction mixture was diluted with an equal volume of the solvent and then washed successively with water, saturated aqueous sodium hydrogen carbonate, water, saturated aqueous sodium disulphite, water, and saturated aqueous sodium chloride. The mixture was dried (MgSO_4) and evaporated *in vacuo* at room temperature.

(b) *With acetic acid as solvent.* The reaction mixture was diluted with an equal volume of water and extracted twice with ether. The combined extracts were washed with saturated aqueous sodium hydrogen carbonate until bubbling ceased and then treated as in (a).

Reaction of Phenylcyclopropane with Silver(I) Acetate—Iodine.—(a) *In acetic acid.* Iodine (2.8 g, 11.0 mmol) in glacial acetic acid (15 ml) was added dropwise to a stirred suspension of silver(I) acetate (2.12 g, 12.7 mmol) in phenylcyclopropane³⁴ (1.3 g, 11.0 mmol) and glacial acetic acid (40 ml). The mixture was stirred at 20 °C for 8 h and worked up by method (b) to give a yellow oil (2.78 g), which was separated by p.l.c. into (i) phenylcyclopropane (19%); (ii) 1-phenylpropane-1,3-diyl diacetate (5) (21%), b.p. 103° at 0.01 mmHg (lit.^{4a} 153–155° at 5 mmHg; lit.^{4b} 135–138° at 3 mmHg), ν_{max} 1720 cm^{-1} (OAc), δ 2.00 (s, OAc), 2.05 (s, OAc), 2.20 [m, J 3.2 Hz (from decoupling), 2- H_2], 4.10 [m, $J_{2,3}$ 6 Hz (from decoupling), 3- H_2], and 5.80 [t, $J_{1,2}$ 6 Hz (from decoupling), 1-H], m/e 236 (M^{+}), 193 ($M-\text{Ac}$), 177 ($M-\text{OAc}$), 176 ($M-\text{HOAc}$), and 116 ($M-2 \text{HOAc}$); (iii) 3-hydroxy-1-phenylpropyl acetate (7) (8%), b.p. 90–95° at 0.1 mmHg, ν_{max} 3600–3300 (OH) and 1720 cm^{-1} (OAc), δ 2.00 (s, OAc), 2.30 (m, 2- H_2), 3.65 (t, $J_{2,3}$ 6 Hz, 3- H_2), 6.00 (t, $J_{1,2}$ 6 Hz, 1-H), and 7.35 (s, ArH); (iv) 3-hydroxy-3-phenylpropyl acetate (8) (1%), b.p. 90° at 0.1 mmHg (lit.^{4a} 144–146° at 5 mmHg; lit.⁵ 116–118° at 0.25 mmHg), ν_{max} 3400 (OH) and 1725 cm^{-1} (OAc), δ 2.00 (s, OAc), 2.20 (m, 2- H_2), 2.70 (m, $W_{1/2}$ 11 Hz, OH), 4.20 (m, 1- H_2), 4.80 (t, $J_{1,2}$ 6 Hz, 3-H), and 7.30 (s, ArH), m/e 194 (M^{+}), 177 ($M-\text{OH}$), 176 ($M-\text{H}_2\text{O}$), 135 ($M-\text{OAc}$), and 134 ($M-\text{HOAc}$) [acetylation (acetic anhydride–pyridine; 20 °C; 3 h) gave the diacetate (5) in quantitative yield]; (v) 3-iodo-1-phenylpropyl acetate (6) (26%), b.p. 135° at 0.1 mmHg (Found: C, 44.0; H, 4.3; I, 40.5. $\text{C}_{11}\text{H}_{13}\text{IO}_2$ requires C, 43.4; H, 4.3; I, 41.8%), ν_{max} 1725 cm^{-1} (OAc), δ 2.00 (s, OAc), 2.30 (m, 2- H_2), 3.10 [m, $J_{2,3}$ 6 Hz (from decoupling), 3- H_2], 5.80 (t, $J_{1,2}$ 6 Hz, 1-H), and 7.30 (s, ArH), m/e 304 (M^{+}), 245 ($M-\text{OAc}$), 244 ($M-\text{HOAc}$), and 176 ($M-\text{HI}$); (vi) *trans*-cinnamyl acetate (17) (2.5%), identical (by i.r., u.v., n.m.r., and mass spectra) with an authentic sample, ν_{max} 1735 cm^{-1} (ester CO), λ_{max} (EtOH) 215 (ϵ 126 000), 256 (ϵ 32 700), and 263 nm (ϵ 26 300), δ (CCl_4) 2.00 (s, OAc), 4.60 (d, $\text{CH}_2\text{-OAc}$), 5.9–6.8 (m, $\text{CH}=\text{CH}$), and 7.30 (s, ArH), m/e 176 (M^{+}), 117 ($M-\text{OAc}$), and 116 ($M-\text{HOAc}$); (vii) 1-phenylpropane-1,3-diol (9) (0.3%), oil, δ (CCl_4) 1.90 (m, 2- H_2), 3.60 (t, 3- H_2), 4.90 (t, 1-H), and 7.30 (s, ArH), identical with an authentic sample;⁴ and (viii) traces of trisubstituted phenylpropanes (see later).

The reaction was repeated with phenylcyclopropane (4.24 mmol) and the product (0.80 g) was stirred with silver(I) acetate (0.38 g, 2.3 mmol) and glacial acetic acid (10 ml) at 20 °C for 20 h. Work-up gave a pale yellow oil (0.65 g)

which was separated by p.l.c. into 1-phenylpropane-1,3-diyl diacetate (5.5%), 3-hydroxy-3-phenylpropyl acetate (22.5%), 3-hydroxy-1-phenylpropyl acetate (4.5%), and a mixture of *erythro*- and *threo*-3-hydroxy-2-iodo-3-phenylpropyl acetates (19) and (20) (1%), b.p. 122–125° at 0.04 mmHg, ν_{max} 3450 (OH), 1735 (OAc), and 1720 cm^{-1} (OAc), δ (CCl_4) 1.97 (s, OAc), 2.69 (s, OH, exchanged with D_2O), 3.70 (m, 2-H), 4.40 (m, 1- H_2), 4.96 (m, 3-H), and 7.40 (s, ArH) and 1.97 (s, OAc), 3.6 (m, 2-H), 4.40 (m, 1- H_2), 4.85 (m, 3-H), and 7.34 (s, ArH), m/e 320 (M^{+}), 261 ($M-\text{OAc}$), 260 ($M-\text{HOAc}$), 193 ($M-\text{I}$), and 133 ($M-\text{I}-\text{HOAc}$).

(b) *In dichloromethane.* Iodine (4.3 g, 17 mmol) in anhydrous dichloromethane (30 ml) was added dropwise to a stirred suspension of silver(I) acetate (2.82 g, 17 mmol) and phenylcyclopropane (0.40 g, 3.4 mmol). The mixture was stirred at 20 °C for 28 h and worked up by method (a) to give a red oil (0.97 g). Analysis by n.m.r., t.l.c., and g.l.c. showed the presence of phenylcyclopropane (5%), 1-phenylpropane-1,3-diyl diacetate (46%), 3-hydroxy-1-phenylpropyl acetate (2%), 3-hydroxy-3-phenylpropyl acetate (29%), 3-iodo-1-phenylpropyl acetate (0.1%), *trans*-cinnamyl acetate (6%), and 1-phenylpropane-1,3-diol (2%). G.l.c. indicated the presence of traces of the *erythro*- and *threo*-isomers of 3-hydroxy-2-iodo-3-phenylpropyl acetate, (19) and (20).

Solvolyses of 3-Iodo-1-phenylpropyl Acetate.—(a) *With silver(I) acetate and acetic acid.* The iodo-acetate (6) (56 mg, 0.18 mmol), silver(I) acetate (30 mg, 0.18 mmol), and glacial acetic acid were stirred at 20 °C for 18 h. Removal of silver iodide and work-up gave a liquid (40 mg) containing (n.m.r. analysis) the diacetate (5) and the hydroxy-acetates (7) and (8).

(b) *With acetic acid.* The iodo-acetate (6) (50 mg, 0.16 mmol) was heated under reflux with 'wet' acetic acid (5 ml) for 5 h. Work-up gave an oil (50 mg) containing (n.m.r. and t.l.c. analysis) starting material (68%) and a mixture (32%) of the diacetate (5) and the hydroxy-acetates (7) and (8).

(c) *With iodine(I) acetate.* Iodine was added to a stirred suspension of silver acetate (65 mg, 0.39 mmol) in dried acetic acid (10 ml) until the iodine colour persisted. Stirring was continued for 30 min after which time the precipitate was filtered off.* 3-Iodo-1-phenylpropyl acetate (0.10 g, 0.33 mmol) was added to the filtrate and stirring was continued at 20 °C for 5 h. Standard work-up (b) gave an orange oil (94 mg). Analysis by n.m.r. and g.l.c. showed the presence of 3-iodo-1-phenylpropyl acetate (76%), 1-phenylpropane-1,3-diyl diacetate (15%), cinnamyl acetate (9%), and a trace of 3-hydroxy-3-phenylpropyl acetate.

(d) *With thallium(III) acetate and acetic acid.* The iodo-acetate (0.10 g, 0.33 mmol) was stirred with thallium(III) acetate (0.15 g, 0.39 mmol) in acetic acid at 20 °C for 74 h. Work-up gave an oil which contained (n.m.r. and t.l.c. analysis) 65% of the diacetate (5) and hydroxy-acetates (7) and (8), and 35% of starting material. Repetition of the reaction at 80 °C for 4.5 h gave a product containing the diacetate (5) (35%) and the hydroxy-acetates (7) and (8) (65%).

Solvolysis of 3-Hydroxy-3-phenylpropyl Acetate.—The hydroxy-acetate (8) (40 mg, 0.2 mmol) was stirred with acetic acid (5 ml) at 20 °C for 45 h. Work-up gave a product containing (n.m.r. analysis) starting material (81%) and 3-hydroxy-1-phenylpropyl acetate (16%).

* Atomic absorption analysis of the filtrate showed a silver content of 0.05 ± 0.01 p.p.m., indicating that the solvolysis was unlikely to be initiated by silver(I)-induced heterolysis.

³⁴ R. J. Petersen and P. S. Skell, *Org. Synth.*, 1967, **47**, 98.

Reaction of Phenylcyclopropane with Thallium(I) Acetate-Iodine.—(a) *In acetic acid.* Iodine (5.45 g, 21.4 mmol) in glacial acetic acid (10 ml) was added dropwise to a suspension of thallium(I) acetate (5.65 g, 21.4 mmol) and phenylcyclopropane (0.51 g, 4.3 mmol) in glacial acetic acid (90 ml). The mixture was stirred at 20 °C for 72 h and worked up by method (b) to give a red oil (1.24 g), which was shown (n.m.r. and t.l.c. analysis) to contain phenylcyclopropane (32%), 1-phenylpropane-1,3-diyl diacetate (5) (5%), 3-hydroxy-1-phenylpropyl acetate (7) (10%), 3-hydroxy-3-phenylpropyl acetate (8) (10%), 3-iodo-1-phenylpropyl acetate (6) (21%), 3-iodo-1-phenylpropan-1-ol (10) (5%), needles, m.p. 32.5–33°, b.p. 146–148° at 0.5 mmHg (decomp.) (Found: C, 41.4; H, 4.4; I, 48.7. $C_9H_{11}IO$ requires C, 41.4; H, 4.1; I, 48.3%), ν_{max} 3400 cm^{-1} (OH), δ 2.20 (m, $W_{1/2}$ 7.5 Hz, 2- H_2), 3.30 (m, 3- H_2), 4.0 (s, OH, exchanged with D_2O), 4.80 (t, $J_{1,2}$ 6 Hz, 1-H), and 7.30 (s, ArH), m/e 262 (M^+), 245 ($M-OH$), 234 ($M-C_2H_4$) or ($M-CO$), 208.9 ($m^* 262 \rightarrow 234$), 155 (C_2H_4I), 134 ($M-HI$), 107 ($M-C_2H_4I$), 79 ($M-C_2H_4-CO$), 77 (aryl), and 58.5 ($m^* 107 \rightarrow 79$). Acetylation with acetic acid and acetic anhydride (20 °C; 24 h) gave the acetate (6) (32%). Minor unidentified products were also obtained from the above reaction. Increased amounts of starting material were obtained from reactions carried out for shorter periods.

(b) *In dichloromethane.* Iodine (0.21 g, 0.84 mmol) in anhydrous dichloromethane (30 ml) was added dropwise (15 min) to a stirred suspension of thallium(I) acetate (0.22 g, 0.84 mmol) and phenylcyclopropane (50 mg, 0.42 mmol) in anhydrous dichloromethane (10 ml). The mixture was heated under reflux for 72 h and worked up by method (a) to give a yellow oil (0.23 g). Analysis by n.m.r., g.l.c., and g.l.c.–mass spectrometry showed the presence of phenylcyclopropane (54%), 3-iodo-1-phenylpropyl acetate (39%), *trans*-cinnamyl acetate (3%), and two minor, unidentified compounds (4%).

(c) *In chloroform.* The above experiment was repeated with iodine (0.11 g, 0.42 mmol) in anhydrous chloroform (20 ml), and thallium(I) acetate (0.11 g, 0.42 mmol) and phenylcyclopropane (50 mg, 0.42 mmol) in anhydrous chloroform (10 ml). Work-up gave a yellow oil (69 mg) which contained phenylcyclopropane (62%), 3-iodo-1-phenylpropyl acetate (29%), *trans*-cinnamyl acetate (4%), and five minor, unidentified products (5%).

Reaction of Phenylcyclopropane with Iodine and Acetic Acid.—Phenylcyclopropane (0.25 g, 2.12 mmol) was treated with iodine (0.54 g, 2.12 mmol) in glacial acetic acid (30 ml) at 20 °C for 72 h in the absence of silver(I) acetate. Work-up gave phenylcyclopropane (72%), 3-iodo-1-phenylpropyl acetate (6) (12.5%), and 3-iodo-1-phenylpropan-1-ol (10) (12.5%). Only the iodo-acetate (6) (6%) was observed after 27 h.

erythro- and threo-Isomers of 3-Hydroxy-2-iodo-3-phenylpropyl Acetate, (19) and (20).—(a) Iodine (0.83 g, 3.3 mmol) in anhydrous dichloromethane (60 ml) was added dropwise (30 min) to a stirred suspension of *trans*-cinnamyl acetate⁶ (0.50 g, 3.9 mmol) and silver(I) acetate (0.65 g, 3.9 mmol) in anhydrous dichloromethane (10 ml) and the mixture was stirred at 20 °C for 50 h. Work-up by method (a) gave a yellow oil (0.74 g) which was separated by p.l.c. into *trans*-cinnamyl acetate (8.5%) and a 13 : 8 mixture of the *erythro*- and *threo*-isomers of 3-hydroxy-2-iodo-3-phenylpropyl acetate (24%).

(b) The above experiment was repeated with iodine (0.72 g, 2.8 mmol), *trans*-cinnamyl acetate (0.50 g, 3.9 mmol), and

thallium(I) acetate (0.90 g, 3.4 mmol) in anhydrous dichloromethane (70 ml) for 72 h. Work-up gave a yellow oil (0.68 g) of composition identical (by n.m.r., t.l.c., and g.l.c.) with that of the oil obtained in (a).

Reaction of Phenylcyclopropane with Thallium(I) Acetate—Iodine(I) Chloride.—Iodine(I) chloride (1.37 g, 8.4 mmol) in dry acetic acid (2 ml) was added dropwise (30 min) to a stirred suspension of thallium(I) acetate (2.21 g, 8.4 mmol) in dry acetic acid (8 ml) and the mixture was stirred at 20 °C for 30 min. Phenylcyclopropane (0.20 g, 1.68 mmol) was added and the stirring continued for 48 h. Work-up gave an orange oil (0.39 g) which contained (n.m.r. and g.l.c. analysis) 3-hydroxy-1-phenylpropyl acetate (1%), 1-phenylpropane-1,3-diyl diacetate (9%), 3-hydroxy-3-phenylpropyl acetate (10%), 3-iodo-1-phenylpropyl acetate (15%), 3-iodo-1-phenylpropan-1-ol (11%), and several minor products including iodoaryl compounds (18%).

Reaction of Phenylcyclopropane with Silver(I) Trifluoroacetate-Iodine.—Iodine (2.14 g, 8.4 mmol) in anhydrous dichloromethane (10 ml) was added to a stirred suspension of silver(I) trifluoroacetate (1.86 g, 8.4 mmol) and phenylcyclopropane (0.40 g, 3.4 mmol) in dichloromethane. The mixture was stirred at 20 °C for 48 h and worked up by method (a) to give a yellow oil (1.17 g) which contained (n.m.r., t.l.c., and g.l.c. analysis) 3-iodo-1-phenylpropyl trifluoroacetate (13) (36%), δ (CCl_4) 2.40 (m, 2- H_2), 3.10 (m, 3- H_2), 6.00 (t, 1-H), and 7.40 (s, ArH); 1-phenylpropane-1,3-diyl bistrifluoroacetate (12) (33%), δ (CCl_4) 2.40 (m, 2- H_2), 4.40 (m, 3- H_2), 6.00 (t, 1-H), and 7.40 (s, ArH); 1-(4-iodophenyl)propane-1,3-diyl bistrifluoroacetate (14) (31%), δ (CCl_4) 2.40 (m, 2- H_2), 4.40 (m, 3- H_2), 6.00 (t, 1-H), 7.10 (d, J 6 Hz, 2'- and 6'- H_2), and 7.76 (d, J 6 Hz, 3'- and 5'- H_2).

A portion of the crude product (0.60 g) was stirred with silver(I) trifluoroacetate (0.37 g, 1.68 mmol) in anhydrous dichloromethane at 20 °C for 72 h. Work-up by method (a) gave an oil (0.65 g) which contained (n.m.r. analysis) 1-phenylpropane-1,3-diyl bistrifluoroacetate (12), 1-(4-iodophenyl)propane-1,3-diyl bistrifluoroacetate (14), and a minor, unidentified compound. The crude product (0.23 g) was stirred with ethanolic 2% potassium hydroxide (30 ml) at 20 °C for 12 h. Work up and preparative g.l.c. gave 1-phenylpropane-1,3-diol (9) (62%) and 1-(4-iodophenyl)propane-1,3-diol (15) (35%), δ 1.90 (m, 2- H_2), 3.60 (m, 3- H_2), 4.90 (t, 1-H), 7.10 (d, J 8 Hz, 2'- and 6'- H_2), and 7.65 (d, J 8 Hz, 3- and 5- H_2), along with minor products.

Acetylation of the diol mixture (34 mg) in acetic acid (0.21 ml) with acetic anhydride (0.64 ml) at 20 °C for 24 h gave a mixture (47 mg) of 3-hydroxy-3-phenylpropyl acetate (8) and 3-hydroxy-3-(4-iodophenyl)propyl acetate (16), δ 2.00 (s, OAc), 2.20 (m, 2- H_2), 2.70 (m, $W_{1/2}$ 11 Hz, OH), 4.20 (m, 1- H_2), 4.80 (t, $J_{1,2}$ 6 Hz, 3-H), 7.13 (d, 2'- and 6'-H), and 7.60 (d, 3'- and 5'-H).

Reaction of Phenylcyclopropane with Thallium(I) Trifluoroacetate-Iodine.—Iodine (0.43 g, 1.7 mmol) in anhydrous dichloromethane (30 ml) was added dropwise to a stirred suspension of thallium(I) trifluoroacetate (0.54 g, 1.7 mmol) and phenylcyclopropane (0.20 g, 1.7 mmol) in anhydrous dichloromethane (10 ml). The mixture was heated under reflux for 72 h and worked up by method (a) to give an orange oil (0.39 g) which contained (n.m.r. and g.l.c. analysis) phenylcyclopropane (45%), 3-iodo-1-phenylpropyl trifluoroacetate (13) (50%), 1-phenylpropane-1,3-diyl bistrifluoroacetate (12) (4%), and a minor, unidentified product.

Reaction of Norcarane with Silver(I) Acetate-Iodine.—(a) Iodine (3.17 g, 12.5 mmol) was added to a stirred suspension of silver(I) acetate (2.1 g, 12.5 mmol) in acetic acid (100 ml) and the resulting mixture was stirred for 15 min. Norcarane³⁵ (1.0 g, 10.4 mmol) was added all at once and the mixture was stirred for 72 h and worked up by method (b) to give a pale yellow oil (0.65 g), which was separated by p.l.c. into (i) *trans*-2-iodo-*trans*-3-iodomethylcyclohexyl acetate (24) (3%), crystals, m.p. 67–68° (Found: C, 26.8; H, 3.6%; M^+ , 407.9084. $C_9H_{14}I_2O_2$ requires C, 26.5; H, 3.5%; M , 407.9074), $\nu_{\max.}$ (CCl₄) 1735 cm⁻¹ (OAc), δ 2.05 (s, OAc), 2.25 (m, $W_{1/2}$ 16 Hz, 3-H), 3.05 (m, CH₂I), 4.60 (m, $W_{1/2}$ 7 Hz, 2-H), and 5.20 (m, $W_{1/2}$ 7 Hz, 1-H), m/e 408 (M^+), 349 (M -OAc), 347.8873 (M -HOAc, 347.8876), 281 (M -I), 221 (M -I-HOAc), 154.9371 (C_8H_9I , 154.9360), 95 (M -2I-OAc), 94 (M -2I-HOAc), and 93 (M -2HI-OAc); (ii) *trans*-2-iodo-*cis*-6-iodomethylcyclohexyl acetate (25) (1%), $\nu_{\max.}$ (film) 1740 (C=O) and 1220 cm⁻¹ (C-O), δ (CCl₄) 2.06 (s, OAc), 2.95 (d, $J_{\text{obs.}}$ 2 Hz, CHI), 3.06 (d, $J_{\text{obs.}}$ 3 Hz, CHI), 4.50 (m, $W_{1/2}$ 8 Hz, 2-H), and 5.10 (m, $W_{1/2}$ 8 Hz, 1-H); (iii) *trans*-2-iodomethylcyclohexyl acetate (23) (16%), b.p. 138–142° at 0.5 mmHg (Found: C, 38.0; H, 5.1; I, 43.4. $C_9H_{15}IO_2$ requires C, 38.3; H, 5.3; I, 45.0%), $\nu_{\max.}$ 1730 cm⁻¹ (OAc), δ 2.10 (s, OAc), 3.20 (m, CH₂I), and 4.60 (m, $W_{1/2}$ 22 Hz, 1-H), m/e 282 (M^+), 223 (M -OAc), 222 (M -HOAc), 155 (M -I), and 154 (M -HI); (iv) *trans*-2-iodomethylcyclohexanol (26) (4%), identical (i.r. and n.m.r.) with an authentic sample (see later); (v) a mixture (3%) of *cis*-3-iodomethylcyclohexyl acetate (27) and *trans*-3-iodomethylcyclohexyl acetate (28), b.p. 97–96° at 0.3 mmHg (Found C, 38.0; H, 5.5; I, 45.6. $C_9H_{15}IO_2$ requires C, 38.3; H, 5.4; I, 45.0%), δ (CCl₄) 2.05 (s, OAc), 3.10 (dd, $J_{\text{obs.}}$ 2 and 5 Hz, CH₂I), 4.50 [m, $W_{1/2}$ 30 Hz, 2-H of (28)], and 5.00br [s, $W_{1/2}$ 8 Hz, 2-H of (27)], m/e 282 (M^+), 222 (M -HOAc), and 155 (M -HI); and (vi) *trans*-2-iodomethylcyclohexyl iodide (29) (3%), δ (CCl₄) 3.50br (s, $W_{1/2}$ 4 Hz, CH₂I) and 4.10br (s, $W_{1/2}$ 15 Hz, 1-H).

(b) The reaction was repeated with iodine (12.85 g, 50 mmol) in acetic acid (60 ml), silver(I) acetate (8.4 g, 50 mmol), and norcarane (1.0 g, 10 mmol) in acetic acid (35 ml) for 72 h. Work-up gave an orange oil (1.0 g) which was separated into the same products as in (a) and in the ratios given in Table 2.

(c) Norcarane (0.25 g, 2.5 mmol) in glacial acetic acid (2 ml) was added dropwise to a stirred solution of iodine(I) acetate, formed by adding iodine (0.76 g, 3 mmol) in glacial acetic acid to silver(I) acetate (0.50 g, 3 mmol) in acetic acid (20 ml) and filtering off the resulting silver iodide. The mixture was stirred for 20 h and worked up to give a yellow oil (0.26 g) with a composition similar to that of the product formed in (a).

(d) The reaction was repeated with a 1 : 1.2 : 1.2 ratio of norcarane, silver(I) acetate, and iodine in anhydrous dichloromethane for 75 h. Work up gave an oil which was separated into the same products as in (a) and in the ratio given in Table 2.

Reaction of Norcarane with Thallium(I) Acetate-Iodine.—Norcarane (0.5 g, 5.2 mmol) was added to a stirred suspension of iodine (6.6 g, 26 mmol) and thallium(I) acetate (6.8 g, 26 mmol) in acetic acid (100 ml) and the mixture was stirred for 72 h. Work-up by method (b) gave a yellow oil (0.8 g) which was separated by p.l.c. into the same products as in (a) of the previous experiment (Table 2).

³⁵ R. J. Rawson and I. T. Harrison, *J. Org. Chem.*, 1970, **35**, 2057; R. D. Smith and H. E. Simmons, *Org. Synth.*, 1961, **41**, 72.

Reduction of *trans*-2-Iodomethylcyclohexyl Acetate.—The iodo-acetate (23) (0.14 g, 5 mmol) was reduced with lithium aluminium hydride (0.30 g, 8 mmol), in dry ether (30 ml). Work-up gave *trans*-2-methylcyclohexanol (55 mg, 95%).³⁶

Hydrolysis of *trans*-2-Iodomethylcyclohexyl Acetate.—The iodo-acetate (23) (75 mg, 2.7 mmol) was added to a stirred suspension of potassium carbonate (75 mg, 5.3 mmol) in methanol (9 ml)-water (1 ml). The mixture was stirred for 3 h and extracted with ether. Work-up of the extract gave *trans*-2-iodomethylcyclohexanol (26) (62 mg, 98%) as a clear mobile liquid, b.p. 73–76° at 1.5 mmHg (Found: C, 34.9; H, 5.7; I, 52.6. $C_7H_{13}IO$ requires C, 35.0; H, 5.5; I, 52.9%), $\nu_{\max.}$ (film) 3500–3300 cm⁻¹ (OH), δ (CCl₄) 3.40 (d, $J_{\text{obs.}}$ 4 Hz, CH₂I), 3.30 (m, $W_{1/2}$ 14 Hz, 1-H), and 2.50br (s, OH, exchanged with D₂O), m/e 240 (M^+), 222 (M -H₂O), 113 (M -I), 95 (M -I-H₂O), 69 ($C_5H_9^+$), 67 ($C_5H_7^+$), 57 ($C_4H_9^+$), 55 ($C_4H_7^+$), 53.2 (m^* 240 → 113), 79.9 (m^* 113 → 95), 47.2–47.1 (m^* 95 → 67, 69 → 57), and 31.8 (m^* 95 → 55).

Hydrolysis of *trans*-2-Iodo-*trans*-3-iodomethylcyclohexyl Acetate.—The di-iodo-acetate (24) (0.12 g, 0.3 mmol) was stirred with methanol (25 ml) containing concentrated hydrochloric acid (0.25 ml) at 20 °C for 185 h. Water (100 ml) was added and the mixture was extracted with ether. Work-up of the extract gave *trans*-2-iodo-*trans*-3-iodomethylcyclohexanol (32) (0.11 g, 98%), as a clear oil, $\nu_{\max.}$ (film) 3500–3300 cm⁻¹ (OH), δ (CCl₄) 2.25 (s, OH, exchanged with D₂O), 3.05 (m, $W_{1/2}$ 10 Hz, CH₂I), 4.25 (m, $W_{1/2}$ 7 Hz, 1-H), and 4.45br (s, $W_{1/2}$ 7 Hz, 2-H), m/e 366 (M^+), 239 (M -I), 221 (M -I-H₂O), 111 (M -I-HI), and 93 (M -I-HI-H₂O).

***anti*-2-Iodomethyl-7-oxabicyclo[4.1.0]heptane (36).**—Potassium carbonate (7.5 g, 54 mmol) was added to a stirred solution of the di-iodo-acetate (24) (0.11 g, 0.3 mmol) in methanol (9 ml)-water (1 ml)-ether (1 ml). The mixture was stirred at 20 °C for 3 h, diluted with water (10 ml), and extracted with ether. Work-up of the extract gave *anti*-2-iodomethyl-7-oxabicyclo[4.1.0]heptane (55 mg, 85%) as a clear oil, $\nu_{\max.}$ (film) 1270 and 820 cm⁻¹ (epoxide), δ (CCl₄) 2.80 (d, $J_{\text{obs.}}$ 4 Hz, 1-H), 3.05 (m, $W_{1/2}$ 8 Hz, 6-H), and 3.25 (dd, $J_{\text{obs.}}$ 3 and 6 Hz, CH₂I).

Reaction of *syn*-Bicyclo[4.1.0]heptan-2-ol with Aqueous Hydrogen Iodide.—Freshly distilled aqueous 57% hydrogen iodide (0.45 ml, 2.0 mmol) was added to *syn*-bicyclo[4.1.0]heptan-2-ol²⁴ (0.15 g, 1.34 mmol). The mixture was stirred at 20 °C for 15 min and extracted with ether. Analytical g.l.c. (on QF-1 at 40 °C) showed the presence of two products in the ratio 10 : 1. Work-up of the extract and fractional distillation gave a red oil (0.17 g) which was separated by p.l.c. and g.l.c. into 3-iodomethylcyclohexene (37), δ (CCl₄) 3.10 (d, J 6 Hz, CH₂I) and 5.65 (m, 1,2-H), m/e 222 (M^+), 221 (M -H), 95 (M -I), 66 (M -C₂H₅I), and 55 (M -C₃H₄I), and 4-iodocycloheptene (38), δ 2.85 (t, J 6 Hz, 3-H), 4.35 (m, 4-H), and 5.65 (m, 1- and 2-H), in the ratio 3 : 2.

Iodoacetylation of 3-Iodomethylcyclohexene.—Silver(I) acetate (0.75 g, 4.5 mmol) was added to a solution of iodine (1.14 g, 4.5 mmol) in acetic acid (50 ml) and the mixture was stirred at 20 °C for 15 min. A solution of 3-iodomethylcyclohexene (0.90 g, 4.1 mmol) and 4-iodocycloheptene (90 mg, 0.41 mmol) in dry ether (50 ml) was added and the mixture was stirred at 20 °C for 12 h. Work-up gave a pale red oil (1.5 g) which was separated by p.l.c. into (i) *trans*-2-iodo-*trans*-3-iodomethylcyclohexyl acetate (1.07 g), m.p.

³⁶ J. W. Huffman and J. T. Charles, *J. Amer. Chem. Soc.*, 1968, **90**, 6486.

67—68° (identical i.r., n.m.r., and mass spectra); (ii) *trans*-2-iodo-*cis*-6-iodomethylcyclohexyl acetate (0.17 g) (identical i.r. and n.m.r. spectra); and (iii) an inseparable mixture of di-iodo-acetates of cycloheptane (0.14 g), δ (CCl₄) 2.05 (s, OAc), 4.50 (m, CHI), and 5.10 (m, CH-OAc).

If a small amount of water was added to the reaction mixture, small amounts ($\leq 10\%$) of *trans*-2-iodo-*trans*-3-iodomethylcyclohexanol (32) were also formed.

Reductions with Tri-(n-butyl)tin Hydride.—(a) Of *trans*-2-iodo-*trans*-3-iodomethylcyclohexyl acetate. Tri-(n-butyl)tin chloride (12 mg, 0.04 mmol) was added to a stirred solution of the di-iodo-acetate (24) (40 mg, 0.1 mmol) in freshly dried and distilled ethanol. The solution was flushed with nitrogen and sodium borohydride (15 mg, 0.4 mmol) was added. The mixture was irradiated with a 100 W mercury lamp while it was agitated with bubbling dry nitrogen for 40 min. An excess of oxalic acid was added, followed by ether (25 ml) and saturated aqueous sodium hydrogen carbonate (50 ml). The ether layer was separated and washed with saturated aqueous sodium chloride and dried. Removal of solvent gave *trans*-3-methylcyclohexyl acetate²⁶ as an oil (60%).

(b) Of the iodo-acetates (27) and (28). Similar treatment of the iodo-acetates (65 mg, 0.23 mmol) with tri-(n-butyl)tin hydride (15 mg, 0.05 mmol) and sodium borohydride (20 mg, 0.5 mmol) gave a pale yellow oil, shown by g.l.c. and ¹H n.m.r. to contain *cis*-3-methylcyclohexyl acetate, δ (CCl₄) 1.95 (s, OAc), 4.60 (m, $W_{1/2}$ 22 Hz, CH-OAc), and *trans*-3-methylcyclohexyl acetate, δ (CCl₄) 2.00 (s, OAc) and 5.00 (m, $W_{1/2}$ 6 Hz, CH-OAc), and alkyltin compounds. No 2-methylcyclohexyl acetates were detected.

Reaction of Phenylcyclopropane with Potassium Iodate-Iodine.—(a) Iodine (1.27 g, 5.0 mmol) and potassium iodate (0.47 g, 2.5 mmol) in glacial acetic acid (60 ml) were heated until the iodine had dissolved. Phenylcyclopropane (0.40 g, 3.38 mmol) was added to the cooled solution and the mixture was stirred at 20 °C for 1 week. Work-up by method (b) gave a yellow oil (0.64 g) which contained (n.m.r., t.l.c., and g.l.c. analysis) phenylcyclopropane (14%), 3-iodo-1-phenylpropyl acetate (77%), 3-iodo-1-phenylpropan-1-ol (5%), and cinnamyl iodide (18) (4%).

Reaction for 72 h gave phenylcyclopropane (32%), 3-iodo-1-phenylpropyl acetate (60%), and cinnamyl iodide (8%).

A portion (0.15 g) of the crude product from the latter experiment was heated under reflux with silver(I) acetate (0.83 g, 4.95 mmol) in glacial acetic acid (5 ml) and water (0.05 ml) for 4 h. Work-up by method (b) gave a yellow oil (77 mg) which contained (n.m.r. and g.l.c. analysis) phenylcyclopropane (13%), 3-hydroxy-1-phenylpropyl acetate (9%), 1-phenylpropane-1,3-diyl diacetate (27%), 3-hydroxy-3-phenylpropyl acetate (38%), 3-iodo-1-phenylpropyl acetate (4%), *trans*-cinnamyl acetate (4%), and six minor products (5%).

(b) Iodine (1.27 g, 5.0 mmol) and potassium iodate (0.47 g, 2.5 mmol) in aqueous 20% sulphuric acid (0.2 ml) were

added to a suspension of phenylcyclopropane (0.40 g, 3.38 mmol) in water (25 ml) and dioxan (25 ml), and the mixture was stirred at 20 °C for 1 week. The solution was shaken with sodium disulphite until colourless and then sodium chloride was added. The mixture was extracted with ether and worked up by method (a) to give an orange oil (1.13 g). P.l.c. yielded 3-iodo-1-phenylpropan-1-ol (68%).

Reaction of Phenylcyclopropane with Solvated Iodine Oxide.—Phenylcyclopropane (0.10 g, 0.84 mmol) was added to a stirred suspension of 'solvated iodine oxide' (8.4 mmol) in acetic anhydride (10 ml). The reaction was quenched by pouring into ice-water and stirring (30 min). Work-up by method (b) gave an oil (0.23 g) which was separated by p.l.c. into 3-iodo-1-phenylpropyl acetate (16%), 1-phenylpropane-1,3-diyl diacetate (13%), 3-iodo-1-phenylpropan-1-ol (9%), 4-iodophenylcyclopropane (2) (7%), δ (CCl₄) 0.62—1.0 (m, CH₂), 1.63 (m, CH), 6.66 (d, J 7 Hz, 2'- and 6'-ArH), and 7.40 (d, J 7 Hz, 3- and 5-ArH), m/e 244 (M^+), 117 ($M-I$), 115 ($M-I-H_2$), 113.03 (m^* 117 \rightarrow 115), and 56.5 (m^* 244 \rightarrow 117), 3-hydroxy-3-phenylpropyl acetate (6%), 3-hydroxy-1-phenylpropyl acetate (2%), and several minor products.

Little cleavage of the ring occurred when the reaction was carried out in anhydrous carbon tetrachloride at 20 °C for 72 h.

Reaction of Norcarane with Potassium Iodate-Iodine.—(a) A solution of iodine (1.32 g, 5.2 mmol) and potassium iodate (0.56 g, 2.6 mmol) in glacial acetic acid (50 ml) was added to norcarane (1.0 g, 10.4 mmol) in glacial acetic acid (20 ml) and the mixture was stirred at 20 °C for 72 h. Work-up by method (b) gave an orange oil (1.24 g) which contained (n.m.r. and g.l.c. analysis) norcarane (23%), *trans*-2-iodomethylcyclohexyl acetate (20%), *trans*-2-iodo-*trans*-3-iodomethylcyclohexyl and *trans*-2-iodo-*cis*-6-iodomethylcyclohexyl acetates (24) and (25) (16%), *cis*-3-iodomethylcyclohexyl and *trans*-3-iodomethylcyclohexyl acetates (27) and (28) (5%), and an unidentified compound (7%).

(b) A solution of norcarane in water-dioxan (1:1) was treated with iodine and potassium iodate (molar ratio 4:2:1) in aqueous 20% sulphuric acid, as for phenylcyclopropane, for 3 h. Work-up gave *trans*-2-iodomethylcyclohexanol (3%), *trans*-2-iodomethylcyclohexyl iodide (6%), and starting material, together with traces of unidentified compounds.

Reaction of Norcarane with Solvated Iodine Oxide.—Norcarane (1.0 g, 10.4 mmol) in acetic anhydride (10 ml) was added to a stirred solution of 'solvated iodine oxide' (10.4 mmol) in acetic anhydride (58 ml). The mixture was stirred at 20 °C for 2 h and worked up by method (b) to give an orange oil (0.52 g), which was separated by p.l.c. into *trans*-2-iodomethylcyclohexyl acetate (9%), a mixture of *trans*-2-iodo-*trans*-3-iodomethylcyclohexyl and *trans*-2-iodo-*cis*-6-iodomethylcyclohexyl acetates (8%), a mixture of *cis*- and *trans*-3-iodomethylcyclohexyl acetates (10%), a trace of the di-iodohydrin (32), and traces of unidentified products.