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Reactions of Iodine(I) Acetate with Alkenes and Vicinal Diols

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Abstract

The chemoselectivities of the reactions of iodine(I) acetate and iodine(I) acetate–thallium(I) acetate with *cis*-cyclooct-5-ene-1,2-diol have been investigated. The addition of iodine(I) acetate to cycloocta-1,5-diene, for a number of reagent systems, results in products arising from both 1,2-addition and transannular pathways.

In previous work[1] we showed that iodine(I) acetate reacted not only with alkenes to afford *trans* iodo acetates, but also with vicinal diols to afford cleavage products. In order to examine the relative rates of reaction of iodine(I) acetate with double bonds and with *vic*-diols, we have examined its reaction with *cis*-cyclooct-5-ene-1,2-diol (1) (cf.[2]).

Treatment of (1) with 1 mole equiv. of the reagent prepared from silver(I) acetate and iodine returned starting material only, but treatment with 2 or 3 mole equiv. also gave (66 and 88% yield, respectively) two less polar compounds which were separated by preparative layer chromatography (p.l.c.) and identified as the isomeric bicyclic ethers (5) and (6). Of these, the kinetically preferred 9-oxabicyclo[4.2.1]nonyl isomer (6) predominated. The mass spectrum of each isomer showed a molecular ion at *m/z* 268 corresponding to the formula $C_8H_{13}IO_2$, and peaks at *m/z* 250 and 141 corresponding to the loss of H_2O and $I^{\bullet}$, respectively, while the ^1H n.m.r. spectra showed no signals due to vinyl, acetyl or aldehydic protons, but each included an exchangeable (OH) proton signal. The noise-decoupled ^{13}C n.m.r. spectrum of each compound showed eight peaks which became four doublets and four triplets in the SFORD spectrum. These signals are shown in Table 1, together with those calculated for the four possible structures formed by pathways (Scheme 1) involving transannular participation[3] of a hydroxy group on an initially formed α- or β-iodonium ion. The calculated values were determined by using data reported[4] for 9-oxabicyclo[3.3.1]nonane and 9-oxabicyclo[4.2.1]nonane and by assuming that substituent parameters

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[1] Cambie, R. C., Chambers, D., Rutledge, P. S., and Woodgate, P. D., *J. Chem. Soc., Perkin Trans. 1*, 1978, 1483.

[2] Ray, R., and Matteson, D. S., *Tetrahedron Lett.*, 1980, **21**, 449.

[3] Haufe, G., and Muhlstadt, M., *Z. Chem.*, 1979, **19**, 170.

[4] Toshimitsu, A., Aoai, T., Uemura, S., and Okano, M., *J. Org. Chem.*, 1981, **46**, 3021.

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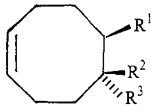
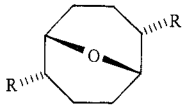
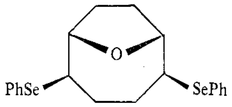


	R1	R2	R3
(1)	OH	OH	H
(2)	OH	H	H
(3)	I	H	OAc
(4)	I	H	I



(9) R = SePh
(10) R = I



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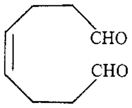

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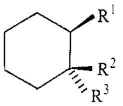
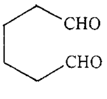
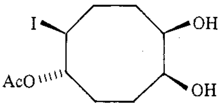


	R1	R2	R3
(14)	OH	OH	H
(15)	I	H	OAc
(16)	I	H	OH



(17)



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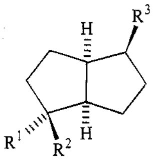
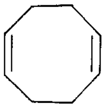
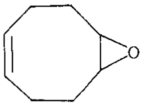


	R1	R2	R3
(19)	I	H	I
(20)	H	I	I
(21)	I	H	H
(22)	H	I	H



(18)



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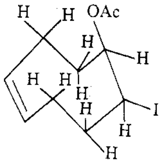

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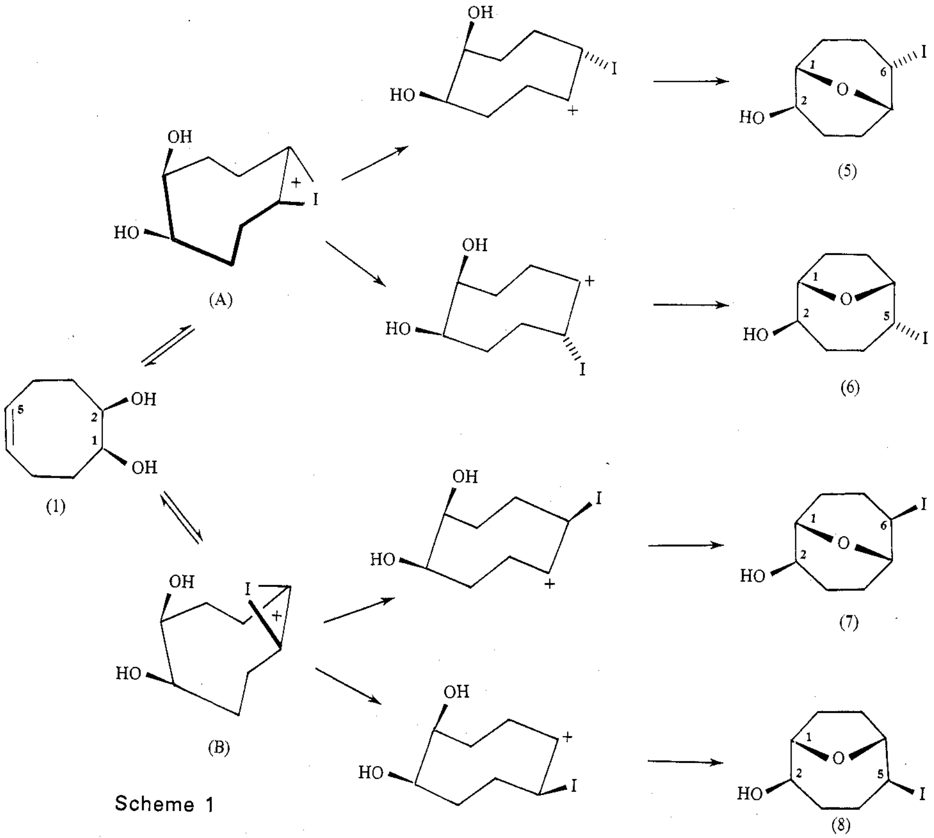

Scheme 1

for cyclohexyl systems could be applied. It was also assumed that the stereochemistry at C 2 was *exo* since the *cis* stereochemical relationship between substituents in the starting material was likely to be retained. The individual structural assignments are supported by the ^{13}C n.m.r. spectra since signals due to the bridgehead carbons of a bicyclo[4.2.1]nonyl system have been shown to occur *c.* 10 ppm downfield from those of a bicyclo[3.3.1]nonyl system.[5] Also, the observed products are analogous to those, viz. (9) and (11), from the reaction of 2 mole equiv. of phenyl selenocyanate and copper(II) chloride with (*Z*,*Z*)-cycloocta-1,5-diene in a hydroxylic solvent.[4]

Table 1. ^{13}C n.m.r. chemical shift data

Car- bon	(5) Obs.	(5) Calc.	(6) Obs.	(6) Calc.	(7) Calc.	(8) Calc.
1	72·0 (d)	71·5	83·3	80·7	70·5	81·7
2	68·1 (d)	68·3	77·5	73·2	68·3	74·2
3	29·1 (t)	23·8	31·0	31·4	22·8	25·4
4	26·8 (t)	22·8	34·9	34·4	18·3	26·4
5	70·9 (d)	69·5	35·1	38·2	74·6	46·2
6	30·2 (d)	29·6	86·2	89·7	40·3	85·7
7	31·4 (t)	31·8	31·9	32·6	26·8	26·6
8	20·2 (t)	22·8	26·0	22·6	18·3	23·6

Although neither the adduct (12) nor the cleavage product (13) was obtained, the formation of compounds (5) and (6) indicates that cleavage of a *vic*-diol is significantly slower than addition to a double bond. The formation of bicyclic ethers rather than iodo acetates reflects competition between nucleophiles which occurs after rate-determining electrophilic attack. However, since it was possible that transannular interactions were biasing the outcome of the reaction in favour of products of addition, intermolecular competition reactions were carried out with equimolar mixtures of cyclohexene and *cis*-cyclohexane-1,2-diol (14).* Treatment of the mixture with 1 or 2 mole equiv. of iodine(I) acetate at room temperature for 10 s, followed by quenching and ^{1}H n.m.r. spectral and thin-layer chromatographic (t.l.c.) analyses of the products, showed the presence of *trans*-2-iodocyclohexyl acetate (15) and unchanged diol (14), with no evidence either for the formation of hexane-1,6-dial (17) or for the presence of unchanged cyclohexene. Longer reaction time (2 min), or use of 3 mole equiv. of iodine(I) acetate, also gave the dialdehyde (17) and the diol (14) in ratios of *c.* 1 : 8 and 1 : 7 respectively; this again indicates that reaction with a double bond is faster than diol cleavage.

In earlier work,[1] we showed also that treatment of cyclohexene with thallium(I) acetate–iodine(I) chloride afforded a quantitative yield of *trans*-2-iodocyclohexyl acetate (15), but that no reaction occurred with *cis*-cyclohexane-1,2-diol (14) even after 5 days. This contrasting behaviour may be ascribed to diminished reactivity due to formation of a planar covalent complex (C) between iodine(I) acetate and

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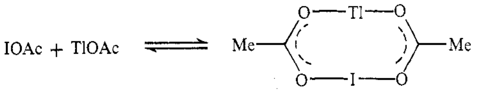
* *cis*-Cyclohex-4-ene-1,2-diol, in principle an appropriate substrate to avoid transannular reactions and so permit an evaluation of the competitive modes by intramolecular comparison, in practice proved to be unsatisfactory since water solubility and facile polymerization of the products (e.g. hex-4-ene-1,6-dial) made their recovery difficult.

[5] Barrelle, M., Apparu, M., and Gey, C., *Can. J. Chem.*, 1978, **56**, 85.

thallium(I) acetate analogous to a Simonini complex[6] (Scheme 2). In view of the possibility of forming the same complex by adding thallium(I) acetate to preformed iodine(I) acetate and the consequent possibility of achieving chemoselectivity with this reagent mixture, its reaction with *cis*-cyclooct-5-ene-1,2-diol (1) was investigated.



(C)

Scheme 2

Treatment of (1) with 1, 2 or 3 mole equiv. each of iodine(I) acetate and thallium(I) acetate again afforded the bicyclic ethers (5) and (6). However, high-pressure liquid chromatography (h.p.l.c.) of the crude mixture demonstrated the presence of small amounts of two further compounds. The ^1H and ^{13}C n.m.r. spectra of the crude mixture were very similar to those of a mixture of (5) and (6) only. Although they were not isolated, the two minor components, which are obviously closely related structurally to (5) or (6), were identified provisionally as the *exo*-iodo isomers (7) and (8). Moreover, in contrast to the lack of reaction with 1 mole equiv. of iodine(I) acetate alone, use of 1 equiv. of the mixed reagents caused a marked increase in the rate of reaction; consumption of the substrate was *c.* 94% complete (^1H n.m.r.) in 5 min, and this indicates either a different mechanism or that the electrophilic step in the latter case was much faster. This could be the case if, for example, the complex (C) equilibrated to an ion pair $[I^+ Tl(OAc)_2^-]$ thereby leading to a more reactive iodine electrophile. The lower selectivity associated with the higher reactivity may account for the formation of the two minor components (7) and (8). The proposed structures (7) and (8) can arise from the bridging iodonium ion (B) (Scheme 1) which is *cis* with respect to the diol groups. Formation of (B) is less favoured than (A) since approach of the electrophile would then be sterically more hindered (cf.[4]).

When cyclohexene was treated (5 min) with iodine(I) acetate–thallium(I) acetate, a decrease in the yield of the *trans* iodo acetate (15) (31%) was observed relative to that (61%) with iodine(I) acetate alone. This could be explained by a lowering of the nucleophilicity of the acetate ion as a result of its complexing with the thallium(I) acetate. Such complexing could also account for formation of the iodohydrin (16) (20%) in the former but not in the latter reaction, since water could then compete more successfully as the nucleophile. However, a lowering of the nucleophilicity of the acetate ion cannot explain the increased rate of reaction of iodine(I) acetate–thallium(I) acetate with *cis*-cyclooct-5-ene-1,2-diol relative to that of iodine(I) acetate alone, since such a factor should not affect the rate of intramolecular attack by a hydroxy group which would be expected to be favoured over attack by acetate ion from entropy considerations. It is possible that thallium(I) acetate affects the reaction by complexing also with the *cis*-diol thereby providing a route for internal delivery of electrophilic iodine to the double bond. Thus, whether the internal nucleophile attacks a carbocationic centre or a bridging iodonium ion, both α- and β-attack by the iodine electrophile may be occurring. If complexing of the diol alters the nucleophilicity of the hydroxy group, some degree of capture of the presumably less stable product of electrophilic attack, through reversible reactions as shown in

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[6] Bunce, N. J., and Hadley, M., *Can. J. Chem.*, 1976, **54**, 2612.

Scheme 1, may be reflected in the proposed formation of (7) and (8); when thallium(I) acetate is absent, the rate of nucleophilic attack could be such that reaction via the product of α-electrophilic attack prevails (cf.[7]). Alternatively, (7) and (8) may arise from an initial iodo acetate formed by *trans* opening of the iodonium ion (B), followed by S_N2-like intramolecular substitution.

Analogous to oxyselenation[4] and oxymercuration[8] of cyclooct-4-en-1-ol (2), the reactions of *cis*-cyclooct-5-ene-1,2-diol (1) with iodine(I) acetate, with or without added thallium(I) acetate, did not go to completion in 5 min, and the product distribution reflects that of kinetic control. Since compounds (5) and (6) were found in approximately equal amounts, it is evident that they were formed at similar rates. The alternative possibility that (6) is formed first and isomerizes to (5) is less likely in view of the reaction conditions, and since Uemura *et al.*[4] have found that the analogous isomerization of (11) to (9) required refluxing for longer than 5 days.

Table 2. Reactions of cycloocta-1,5-diene (18) with IOAc systems

Entry	System[A]	Solvent	Product ratios[B] (3)	(10)	(19)+(20)	(4)	(24)
1	IOAc	HOAc	71	23	6	C	C
2	IOAc–TlOAc	HOAc	94	4	2		
3	I_2+AgOAc	CH_2Cl_2	62	14	24		
4	I_2+2AgOAc	CH_2Cl_2	74	22	4		
5	I_2+TlOAc	CH_2Cl_2	47	8	45		

[A] 1 : 1 mole ratio to (18) unless otherwise indicated (see Experimental).
[B] Determined by h.p.l.c. Retention times: (3), 9·4 min; (10), 13·3 min; (19)+(20), 26·2 min. Samples of (3), (10) and (19)+(20) were injected separately, and in mixtures of known molar composition, to determine the molar response factors used in calculating product ratios from reaction mixtures.
[C] Trace (see Experimental).

Concurrent with the above reactions, we examined the addition of iodine(I) acetate to (*Z,Z*)-cycloocta-1,5-diene (18); the common products resulting from the use of a selection of reagent systems are presented in Table 2. The least polar fraction isolated (p.l.c.) was a mixture (7 : 3) of (1α,3aα,4β,6aα)-1,4-diiodooctahydropentalene (19) and its (1α,3aβ,4α,6aβ) epimer (20), compounds which have been isolated recently from the treatment of (18) with iodine.[9] Further preparative layer chromatography of this mixture afforded the pure major isomer (19) which had ^1H and ^{13}C n.m.r. spectral properties identical with those recorded, and computer-calculated coupling constants for the ^1H spectrum were in agreement with predicted values. Reduction of the 1α,4β-diiodide (19) with lithium triethylborohydride afforded the 1α-monoiodide (21) whose structure was assigned from a comparison of the observed ^{13}C n.m.r. chemical shifts with those calculated (Table 3) for the two possible isomers (21) and (22) on the basis of data reported[10] for octahydropentalene and by assuming that

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[7] Cambie, R. C., Potter, G. J., Rutledge, P. S., and Woodgate, P. D., *J. Chem. Soc., Perkin Trans. 1*, 1977, 530.
[8] Bordwell, F. G., and Douglass, M. L., *J. Am. Chem. Soc.*, 1966, **88**, 993.
[9] Uemura, S., Fukuzawa, S., Toshimitsu, A., Okano, M., Tezuka, H., and Sawada, S., *J. Org. Chem.*, 1983, **48**, 270.
[10] Whitesell, J. K., and Mathews, R. S., *J. Org. Chem.*, 1977, **42**, 3878.

substituent parameters derived from cyclohexyl systems[11] can be applied. Reductive removal of the 1α-iodo substituent evidently does not occur, since it would require approach of the hydride species from the β-face of the molecule which is hindered as a result of the folded nature of the (3aα,6aα)-octahydropentalene skeleton.

Table 3. ^{13}**C n.m.r. chemical shifts for iodooctahydropentalenes**

Carbon	Obs. (21)	Calc. (21)	Calc. (22)	Carbon	Obs. (21)	Calc. (21)	Calc. (22)
1	34·4 (d)	37·3	45·3	4	32·4 (t)	32·3	33·3
2	39·4 (t)	39·4	35·4	5	25·6 (t)	24·4	25·4
3	32·7 (t)	34·3	29·3	6	34·1 (t)	36·3	30·3
3a	42·0 (d)	43·3	38·3	6a	56·9 (d)	56·3	52·3

endo-2,*endo*-6-Diiodo-9-oxabicyclo[3.3.1]nonane (10) was identified from its mass spectrum and ^{13}C n.m.r. spectrum (singlets only in the noise-decoupled spectrum), and from the melting point and ^{1}H n.m.r. spectrum which were identical with those recorded by Labows and Swern[12] for the sole product isolated from treatment of cycloocta-1,5-diene with iodine in methanol. The major product common to all reactions was identified as *trans*-8-iodocyclooct-4-enyl acetate (3) since the ^{1}H n.m.r. spectrum included signals at δ 5·5–5·8 attributed to olefinic hydrogens, a singlet due to an acetate methyl group, and two methine proton resonances in the region 3·0–5·0, which together were indicative of a monocyclic product of 1,2-addition. The stereochemistry was confirmed by base-catalysed solvolysis with potassium carbonate in aqueous methanol which afforded the epoxide, 9-oxabicyclo[6.1.0]non-4-ene (23), in 62% yield.

A minor product, isolated when the reaction was carried out with iodine(I) acetate alone (Prévost reaction), possessed an R_F value and ^{1}H n.m.r. and mass spectra similar to those of (3); these data indicated that the product was an isomeric iodo acetate. Its structure was assigned provisionally as *cis*-8-iodocyclooct-4-enyl acetate (24). In the ^{1}H n.m.r. spectrum, the proton geminal to the iodine atom is shifted upfield significantly (Δδ −1·35) relative to the analogous proton in the *trans* isomer (3), while the proton geminal to the acetate group is affected to a much smaller extent (Δδ −0·45). There is also a slight shift in the resonance due to the acetate methyl protons (Δδ −0·08). Moreover, the half-width of the CHOAc signal is much smaller (6 Hz) in (24) than in its isomer (3) (20 Hz). All of these data are accommodated by the *cis* isomer (24) in the conformation shown.

The possibility that the diiodides (19) and (20) were solvolysed to (3) and (10) during reaction with an excess of silver(I) acetate (Table 2, entry 4), thereby accounting for the relative increase in yields of these products (cf. entry 3), was discounted when treatment of the mixture of compounds (19) and (20) with silver(I) acetate (2 mole equiv.)–iodine (1 mole equiv.) in dichloromethane afforded starting material together with two unidentified compounds, neither of which was (3) or (10).

From the reaction of cycloocta-1,5-diene (18) with iodine(I) acetate–thallium(I) acetate (Table 2, entry 2), the iodo acetate mixture (3) and (24) was detected in addition

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[11] Wehrli, F. W., and Wirthlin, T., 'Interpretation of ^{13}C N.M.R. Spectra' p. 45 (Heyden: London 1976).

[12] Labows, J. N., and Swern, D., *J. Org. Chem.*, 1972, **37**, 3004.

to the major products. Also present was a further diiodide which was assigned the structure (4). The latter compound readily reverted to cycloocta-1,5-diene, but the mass spectrum of the partly purified compound showed peaks at *m/z* 234 (M−HI), 128 (HI), 127 (I) and 107 (234−I), while the ^{1}H n.m.r. spectrum contained signals due to olefinic and CHI protons and a methylene envelope. Treatment of cycloocta-1,5-diene with iodine in dichloromethane[9] in the dark gave not only a mixture of the diiodides (19) and (20), but also a low yield of the unstable monocyclic diiodide (4) and unidentified products.

The reactions of (18) with preformed iodine(I) acetate and iodine(I) acetate–thallium(I) acetate may be compared with related ones reported by Labows and Swern.[12] In particular, significant amounts (Table 2) of the bicyclo[3.3.1]nonane adduct (10) and of the octahydropentalenes (19) and (20) were isolated from our reactions, whereas only the monocyclic 1,2-adducts were isolated from treatment of (18) with iodine(I) azide, iodine(I) isocyanate or iodine(I) nitrate.[12] Formation of the transannular products (10), (19) and (20) may[12] reflect greater positive charge density on carbon in the iodonium ion resulting from reaction with the iodine(I) acetate systems.

Experimental

General experimental details are given in ref.[13] High-pressure liquid chromatography was carried out on a Waters high-pressure liquid chromatograph with a U6K detector, a 6000A solvent delivery system, a 440 absorbance detector operating at 254 nm, and an R401 differential refractive index detector. Analyses were carried out on a 4 mm (internal diameter) by 10 cm C_{18} reverse-phase column, with methanol/water (7 : 3) as solvent and a flow rate of 1 ml/min. Reactions were carried out at room temperature unless otherwise stated.

cis-*Cyclooct-5-ene-1,2-diol (1)*

This was prepared by application of the method of Ray and Matteson;[2] plates (from ethyl acetate), m.p. 104–106° (lit.[14] 104–106°). δ_H 1·6–2·9, m, 8H, CH_2; 4·00, t, H 1,2; 5·00, s, 2H, OH; 5·70, t, H 5,6. The diacetate was an oil, b.p. 50°/0·65 mm (Kugelrohr). ν_{max} 3025, 2850, 1740 (OAc), 1380, 1035 cm^{-1}. δ_H 2·1, s, 6H, OAc; 1·6–3·8, m, 8H, CH_2; 5·0–5·3, m, 2H, H 1,2; 5·6–5·9, m, 2H, H 5,6.

Reaction of cis-*Cyclooct-5-ene-1,2-diol (1) with Iodine*(I) *Acetate*

Iodine (0·54 g, 2·1 mmol) was added to a suspension of silver(I) acetate (0·36 g, 2·1 mmol) in glacial acetic acid (15 ml). The mixture was stirred at room temperature for 30 min, and then an aliquot (6 ml, containing 0·86 mmol IOAc) was transferred through a syringe to a stirred solution of the diol (1) (50 mg, 0·35 mmol) in acetic acid (3 ml). The mixture was stirred for 5 min, water was added, and the pH was raised to 6 by the addition of sodium hydrogencarbonate. The mixture was saturated with sodium chloride, and extracted with dichloromethane. The dichloromethane extracts were washed with 10% aqueous sodium hydrogensulfite, and brine. Removal of the solvent from the dried extracts gave an oil (72 mg). The crude products from two reactions were combined; p.l.c. (hexane/ether 2 : 1, three elutions) gave two bands. Band (i), R_F 0·45, gave endo-*6-iodo-9-oxabicyclo[3.3.1]nonan*-exo-*2-ol* (5) (91 mg) as a waxy solid, m.p. 74–77°, b.p. 90°/0·3 mm (Kugelrohr) (Found: C, 36·4; H, 5·1. $C_8H_{13}IO_2$ requires C, 35·9; H, 4·9%). ν_{max} 3400, 1045, 1000 cm^{-1}. δ_H 1·50–2·6, m, 8H, CH_2; 3·47–3·83, m, 1H, CHI; 4·08–4·80, m, 3H, CHO. For δ_C see Table 1. *m/z* 268 (<1%, M), 250 (M−H_2O), 141 (M−I). Band (ii), R_F 0·40,

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[13] Cambie, R. C., Hayward, R. C., Lindsay, B. G., Phan, A. I. T., Rutledge, P. S., and Woodgate, P. D., *J. Chem. Soc., Perkin Trans. 1*, 1976, 1961; Cambie, R. C., Hayward, R. C., Roberts, J. L., and Rutledge, P. S., *J. Chem. Soc., Perkin Trans. 1*, 1974, 1858.

[14] Jernow, J. L., Gray, D., and Closson, W. D., *J. Org. Chem.*, 1971, **36**, 3511.

gave *endo*-5-iodo-9-oxabicyclo[4.2.1]nonan-*exo*-2-ol (6) (40 mg) as an unstable oil. ν_{max} 3400, 1040, 1000 cm^{-1}. δ_H 1·50–2·60, m, 8H, CH_2; 3·48–3·85, m, 1H, CHI; 4·05–4·85, m, 3H, CHO. For δ_C see Table 1. *m/z* 268 (< 1% M), 250 (M – H_2O), 141 (M – I).

Use of a reagent to substrate ratio of 3 : 1 gave the same products, whereas use of a ratio of 1 : 1 returned starting material (41 mg, 82%).

Reaction of cis-*Cyclooct-5-ene-1,2-diol (1) with Iodine*(I) *Acetate and Thallium*(I) *Acetate*

Preformed iodine(I) acetate (3 ml, containing 0·70 mmol) and thallium(I) acetate (0·18 g, 0·70 mmol) were stirred together for 2 min and added to a solution of the diol (1) (0·10 g, 0·70 mmol) in acetic acid (3 ml). The mixture was stirred for 5 min and worked up as above. T.l.c., h.p.l.c., and ^1H and ^{13}C n.m.r. spectral analyses showed the presence of (5), (6), and two minor products assumed to be (7) and (8); attempted purification of (7) and (8) by p.l.c. was unsuccessful.

Similar results were obtained with reagent to substrate ratios of 2 : 1 and 3 : 1.

Competition Reactions Between Cyclohexene and cis-*Cyclohexane-1,2-diol (14) for Iodine*(I) *Acetate*

Preformed iodine(I) acetate solution (4·4 ml, containing 1·0 mmol) was added to a solution of cyclohexene (70 mg, 0·86 mmol) and *cis*-cyclohexane-1,2-diol (14) (0·10 g, 0·86 mmol) in acetic acid (3 ml), and the mixture was stirred for 10 s, diluted with water, and neutralized with aqueous sodium hydroxide. The mixture was then saturated with sodium chloride and continuously extracted with ether. Removal of solvent from the dried extract gave a solid (0·14 g) containing *cis*-cyclohexane-1,2-diol (14) and *trans*-2-iodocyclohexyl acetate (15) (^1H n.m.r. spectral and t.l.c. analyses).

Use of 2 mole equiv. of iodine(I) acetate for 10 s gave the same product mixture (0·22 g). Extension of the reaction time to 2 min gave a mixture (0·40 g) which now included hexane-1,6-dial (17),[1] the ratio of diol (14) to dialdehyde (17) being 7 : 1. Use of 3 mole equiv. of iodine(I) acetate for 10 s also gave the latter mixture (0·32 g) in which the ratio of (14) to (17) was 8 : 1.

Reaction of Cycloocta-1,5-diene (18) with Iodine and Silver(I) *Acetate*

(A) *Use of a 1 : 1 : 2 mole ratio.*—A stirred suspension of silver(I) acetate (3·08 g, 18·5 mmol) and the diene (18) (1·00 g, 9·24 mmol) in dichloromethane (30 ml) was treated with iodine (2·35 g, 9·24 mmol) under N_2 at room temperature for 40 min, and the mixture was then filtered. The filtrate was washed successively with dilute aqueous sodium hydrogensulfite, water, saturated aqueous sodium hydrogencarbonate, water, and saturated brine. Solvent was removed from the dried solution to give a pale yellow oil (1·62 g) which was separated by p.l.c. (hexane/ether 9 : 1) into four bands. Band (i), R_F 0·70, gave a mixture (7 : 3, ^{13}C n.m.r. analysis) of (1α,3aα,4β,6aα)-1,4-diiodooctahydropentalene (19) and (1α,3aβ,4α,6aβ)-1,4-diiodooctahydropentalene (20). Crystallization from hexane gave the major isomer (19) as needles, m.p. 77° (lit.[9] 79–80°) (Found: C, 26·7; H, 3·7. Calc. for $C_8H_{12}I_2$: C, 26·5; H, 3·3%). ν_{max} 3020, 1220, 1040 cm^{-1}. δ_H 1·4–2·5, m, 8H, CH_2; 2·5–2·8, m, $W_{h/2}$ 10 Hz, CH; 2·8–3·1, m, $W_{h/2}$ 10 Hz, CH; 4·1–4·8, m, 2H, CHI. δ_C 30·6, t, C 6; 31·1, d, C 4; 32·2, d, C 1; 34·4, t, C 3; 36·9, t, C 2; 39·9, t, C 5; 47·9, d, C 6a; 54·6, d, C 3a. *m/z* 362 (M), 235 (M – I), 254 (I_2), 207 (235 – C_2H_4), 128 (HI), 127 (I), 107 (235 – HI), 79 (107 – C_2H_4). Band (ii), R_F 0·48, crystallized from hexane to give *endo*-2,*endo*-6-diiodo-9-oxabicyclo[3.3.1]nonane (10) as plates (0·18 g), m.p. 117–120° (lit.[12] 124°) (Found: C, 25·5; H, 3·3; I, 66·4. Calc. for $C_8H_{12}I_2O$: C, 25·4; H, 3·3; I, 67·2%). ν_{max} 2945, 1490, 1340, 1110, 1030 cm^{-1}. δ_H 1·9–3·0, m, 8H, CH_2; 3·9–4·2, m, 2H, CHI; 4·4–4·9, m, 2H, CHO. δ_C 28·8, t, C 3,7, J_R 31 Hz; 29·6, d, C 2,6, J_R 24 Hz; 33·1, t, C 4,8, J_R 32 Hz; 70·4, d, C 1,5, J_R 31 Hz. *m/z* 378 (M), 251 (M – I), 223 (251 – C_2H_4), 205 (223 – H_2O), 127 (I), 124 (M – 2I), 123 (124 – H), 105 (123 – H_2O), 95 (123 – C_2H_4). Band (iii), R_F 0·38, gave *cis*-8-iodocyclooct-4-enyl acetate (24) as an oil (0·12 g). ν_{max} 3090, 3040, 1715 cm^{-1}. δ_H 1·2–2·8, m, 8H, CH_2; 2·03, s, 3H, OAc; 3·0–3·5, m, $W_{h/2}$ 20 Hz, CHI; 4·9, m, $W_{h/2}$ 6 Hz, CHO; 5·4–5·7, m, CH=C. *m/z* 294 (M), 251 (M – CH_3CO), 167 (M – I), 107 (167 – HOAc). Band (iv), R_F 0·35, was distilled to give trans-*8-iodocyclooct-4-enyl acetate* (3) as a clear oil, b.p. 50°/0·7 mm (Kugelrohr) (Found: C, 40·9; H, 5·2; I, 43·1. $C_{10}H_{15}IO_2$ requires C, 40·8; H, 5·1; I, 43·2%). ν_{max} 3020, 1730, cm^{-1}. δ_H 1·2–2·8, m, 8H, CH_2; 2·11, s, 3H, OAc; 4·4–4·8, m, $W_{h/2}$ 20 Hz, CHI; 5·1–5·4, m, $W_{h/2}$ 20 Hz, CHO; 5·5–5·8, m, 2H, CH=C. δ_C 21·4, d, C 1; 23·7, t, C 2; 26·9, t, C 3; 30·4, t, C 6; 36·0, d, C 8; 36·3, t, C 7; 76·9, q, CH_3; 126·8, d, C 5; 129·5, d, C 4; 169·3, s, C=O. *m/z* 294 (M), 293 (M – H), 279 (M – CH_3), 251 (M – CH_3CO), 233 (293 – HOAc), 167 (M – I), 124 (167 – CH_3CO), 107 (167 – HOAc), 79 (107 – C_2H_4).

(B) *Use of a 1 : 1 : 1 mole ratio.*—Silver(I) acetate (0·31 g, 1·85 mmol), iodine (0·47 g, 1·85 mmol) and cycloocta-1,5-diene (0·20 g, 1·85 mmol) were treated as in (A) to give a pale yellow oil which was shown by h.p.l.c. to contain the products above (Table 2, entry 3).

(1α,3aα,6aα)-1-Iodooctahydropentalene (21)

Lithium triethylborohydride (1·7 ml of a 1·0 M solution in tetrahydrofuran containing 0·18 g, 1·7 mmol) was added slowly to a solution of the diiodide (19) (0·25 g, 0·7 mmol) in dried ether (10 ml) under N_2, and the mixture was stirred at room temperature for 22 h. Saturated aqueous ammonium chloride was added and the mixture was washed twice with saturated brine. Removal of solvent from the dried organic layer gave *(1α,3aα,6aα)-1-iodooctahydropentalene* as an oil (98 mg, 59%), b.p. 100–110°/760 mm (Kugelrohr) (Found: C, 40·5; H, 5·7. $C_8H_{13}I$ requires C, 40·7; H, 5·6%). δ_H 1·1–3·1, m, 12H, CH_2 and CH; 3·9, m, $W_{h/2}$ 8 Hz, CHI. For δ_C see Table 3. *m/z* 236 (M), 235 (M−H), 127 (I), 109 (M−I), 107 (235−HI), 81 (109−C_2H_4).

Solvolysis of trans-*8-Iodocyclooct-4-enyl Acetate (3)*

A solution of the iodo acetate (3) (0·49 g, 0·17 mmol) in water (1 ml) and methanol (1·5 ml) was treated with potassium carbonate (0·46 g, 0·33 mmol), and the mixture was stirred overnight at room temperature. The mixture was poured into water (10 ml), extracted with dichloromethane (3 × 10 ml), and the extract was washed with dilute aqueous sodium hydrogensulfite, water, and saturated brine. Removal of solvent from the dried solution gave 9-oxabicyclo[6.1.0]non-4-ene (23) as a pale yellow oil (13 mg; 62%). The ^1H n.m.r. spectrum (δ_H 1·7–2·5, m, 4H, CH_2; 3·1, m, $W_{h/2}$ 10 Hz, 2H, CHO; 5·6, m, $W_{h/2}$ 9 Hz, 2H, CH=C) was identical with that of a sample, b.p. 46–50°/2 mm (lit.[15] 95–100°/10 mm), prepared (79%) by oxidation of cycloocta-1,5-diene with *m*-chloroperbenzoic acid in dichloromethane.

Reaction of Cycloocta-1,5-diene (18) with Iodine and Thallium(I) *Acetate*

Thallium(I) acetate (0·61 g, 2·31 mmol) and iodine (0·59 g, 2·31 mmol) were added to a solution of the diene (18) (0·25 g, 2·31 mmol) in dichloromethane (25 ml), and the mixture was stirred for 25 min. Workup gave an oil (0·40 g) which was separated by p.l.c. (hexane/ether 9 : 1) into: (i) (1α,3aα,4β,6aα)- and (1α,3aβ,4α,6aβ)-1,4-diiodooctahydropentalene (19) and (20) (0·14 g, 17%); (ii) *endo*-2,*endo*-6-diiodo-9-oxabicyclo[3.3.1]nonane (10) (9 mg, 1%); (iii) *trans*-8-iodocyclooct-4-enyl acetate (3) (66 mg, 10%). H.p.l.c. analysis showed the presence of additional products, including (4) and (24).

Reaction of Cycloocta-1,5-diene (18) with Preformed Iodine(I) *Acetate*

The diene (18) (0·20 g, 1·85 mmol) was added to a solution of preformed iodine(I) acetate in acetic acid (4·5 ml, containing 0·41 g, 2·22 mmol), and the mixture was stirred at room temperature for 5 min. Water was added followed by dichloromethane (10 ml) and aqueous sodium hydroxide (10 ml, containing 3·1 g). Workup gave an oil (0·13 g) containing the compounds (3), (10) and (19)+(20) (Table 2, entry 1), and the minor products (4) and (24).

Repetition of the reaction with added thallium(I) acetate (0·58 g, 2·22 mmol) gave similar results (Table 2, entry 2 for major products).

Reaction of Cycloocta-1,5-diene (18) with Iodine

The diene (18) (0·10 g, 0·92 mmol) was added to a solution of iodine (0·23 g, 0·92 mmol) in dichloromethane (15 ml), and the mixture was kept in the dark for 24 h. Workup gave an oil (0·17 g) containing the diiodides (4), (19) and (20), and unidentified products (h.p.l.c. analysis).

Repetition of this reaction* according to the reported[9] conditions afforded a mixture containing (19) and (20) in a ratio (^{13}C n.m.r. analysis) of 65 : 35 (cf.[9] 50 : 50).

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[15] Anderson, R. J., and Henrick, C. A., *J. Am. Chem. Soc.*, 1975, **97**, 4327.

Reactions of Cyclohexene

(A) *With iodine*(I) *acetate*.—A solution of iodine(I) acetate was prepared from freshly ground iodine (0·85 g, 3·34 mmol) and silver(I) acetate (0·56 g, 3·34 mmol) in glacial acetic acid (11 ml). The mixture was stirred for 10 min and then centrifuged to yield a yellow precipitate of silver(I) iodide and a red-brown supernatant. Rapid addition of cyclohexene (81 mg, 0·98 mmol) to an aliquot (4 ml, 1·21 mmol) of this solution of iodine(I) acetate resulted in immediate loss of colour. The mixture was stirred at room temperature for 10 s and ice-water was then added. Workup yielded *trans*-2-iodocyclohexyl acetate (15) (0·16 g, 61%).

(B) *With iodine*(I) *acetate and thallium*(I) *acetate*.—A portion (4 ml, 1·21 mmol) of the above solution of iodine(I) acetate was added to thallium(I) acetate (0·32 g, 1·21 mmol) under an atmosphere of nitrogen, and the mixture was stirred at room temperature for 2 min. Cyclohexene (81 mg, 0·98 mmol) was then added rapidly and stirring was continued for 10 s, followed by the addition of ice-water. Workup gave an oil (0·13 g) composed (^{1}H n.m.r.) of *trans*-2-iodocyclohexyl acetate (15) (83 mg, 31%) and *trans*-2-iodocyclohexanol (16) (45 mg, 20%).

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