Reaction of Thallium(I) Acetate–Iodine and Silver(I) Acetate–Iodine with Norborn-2-ene

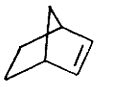
By **Richard C. Cambie, Barry G. Lindsay, Peter S. Rutledge, and Paul D. Woodgate,*** Department of Chemistry, University of Auckland, Auckland, New Zealand

The reaction of norborn-2-ene with thallium(I) acetate–iodine in several solvents has been investigated, and the products have been compared with those arising from similar treatment of norbornene with silver(I) acetate–iodine. The product distribution in each case is indicative of an ionic pathway involving initial electrophilic addition of iodine followed largely by skeletal rearrangement characteristic of the bicyclo[2.2.1]heptyl system.

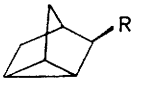
PREVIOUS work [1,2] has shown that treatment of an alkene with a thallium(I) carboxylate and iodine affords the corresponding *vic*-iodo-carboxylate in high yield. With the exception of that of 3-phenylpropene, the reactions are regiospecific, addition occurring in the Markownikov orientation. Moreover, marked differences exist between the modes of reaction of thallium(I) carboxylates and silver(I) carboxylates. No reaction occurred between the thallium(I) carboxylate, iodine, and an alkene unless all three were present, in contrast to the silver(I)-mediated systems where prior formation of the Simonini complex between the acyl hypoiodite, the silver(I) carboxylate, and iodine has been amply demonstrated. Thus, a reaction pathway in which an iodonium ion is formed from interaction of a thallium(I) species with an alkene–iodine π-complex was postulated. This work has now been extended to include norborn-2-ene (1) as substrate, since its reactivity and rearrangement under ionic conditions are well established.[3]

Treatment of bicyclo[2.2.1]hept-2-ene (norborn-2-ene) (1) with thallium(I) acetate and iodine (molar ratio 1 : 2 : 1) in various solvents afforded a range of products. The greatest number of products was obtained with carbon tetrachloride (see Table 1). No starting material remained after heating the mixture at reflux temperature for 4 h, and in all but one case pure samples of each product were obtained after exhaustive separation by preparative t.l.c. and/or preparative g.l.c.

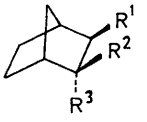
The band with the greatest R_F value on t.l.c. was a mixture (^{1}H n.m.r.) of 3-*exo*-iodotricyclo[2.2.1.0^{2,6}]-heptane (2) and 2-*exo*,3-*endo*-di-iodobicyclo[2.2.1]heptane (4). Attempted separation by multiple elution preparative t.l.c. in either hexane or n-pentane was unsuccessful owing to near-coincident R_F values. Moreover, g.l.c. analysis showed a single peak. However, molecular iodine was detected in the g.l.c. effluent, indicating thermal decomposition of (4) on the (glass) column. The presence of nortricyclanyl iodide (2) was verified by comparison of the ^{1}H n.m.r. spectrum of the mixture with that of a pure sample of (2), isolated from treatment of (1) with thallium acetate–iodine in acetic acid (Table 1). Pure (2) was stable under the g.l.c. conditions used, and its ^{1}H n.m.r. spectrum was identical

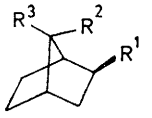


(1)



(2) R = I
(3) R = OAc





(4) R^1=R^3=I, R^2=H
(5) R^1=R^3=Br, R^2=H
(11) R^1=I, R^2=H, R^3=OAc
(12) R^1=I, R^2=H, R^3=OH
(13) R^1=I, R^2=OAc, R^3=H
(14) R^1=R^2=Br, R^3=H
(15) R^1=Cl, R^2=OH, R^3=H
(16) R^1=I, R^2=OH, R^3=H
(17) R^1=OAc, R^2=H, R^3=I
(18) R^1=Br, R^2=H, R^3=Cl
(19) R^1=Cl, R^2=H, R^3=Br

(6) R^1=R^2=I, R^3=H
(7) R^1=R^2=Br, R^3=H
(8) R^1=OAc, R^2=H, R^3=I
(9) R^1=R^3=Br, R^2=H
(10) R^1=OAc, R^2=I, R^3=H
(20) R^1=OH, R^2=I, R^3=H
(21) R^1=R^3=OAc, R^2=H
(22) R^1=R^2=OAc, R^3=H

with that reported.[4] The ^{1}H n.m.r. spectrum of (4), obtained by subtraction of the peaks due to (2), included a broad singlet at δ 2.42 assigned to the C-1 and C-4 protons, a one-proton four-line pattern at δ 3.95 assigned to the C-2 *endo*-proton, and a one-proton three-line pattern at δ 4.54 due to the C-3 *exo*-proton. Irradiation at the frequency of the C-2 *exo*-proton signal caused the apparent triplet at δ 4.54 to collapse to a doublet.

[1] R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, *J.C.S. Perkin I*, 1974, 1120.
[2] R. C. Cambie, R. C. Hayward, J. L. Roberts, and P. S. Rutledge, *J.C.S. Perkin I*, 1974, 1858, 1864.
[3] T. G. Traylor, *Accounts Chem. Res.*, 1969, **2**, 152.
[4] U. E. Diner and J. W. Lown, *Canad. J. Chem.*, 1971, **49**, 403.

Assignment of structure (4) to this di-iodide was supported by the similarity of its ^{1}H n.m.r. spectral data to those reported [5] for 2-*exo*,3-*endo*-dibromobicyclo[2.2.1]-heptane (5). In addition, the mass spectrum of the mixture of (2) and (4) showed the molecular ion due to (4) at *m/e* 347.8859 ($C_7H_{10}I_2$). Moreover, when norbornene (1) was treated with iodine in carbon tetrachloride at room temperature for 1 h, ^{1}H n.m.r. spectral analysis of the crude product showed that the *trans*, *vic*-di-iodide (4) was present in 61% yield.

A second di-iodide which was isolated in pure state, albeit in very low yield, was identified as 2-*exo*,7-*syn*-di-iodobicyclo[2.2.1]heptane (6). This compound also decomposed on g.l.c., but could be distilled *in vacuo* without decomposition. The molecular ion was observed at *m/e* 348 as required, and the ^{1}H n.m.r. spectrum was closely similar to that reported [5] for 2-*exo*,7-*syn*-dibromobicyclo[2.2.1]heptane (7).

A second tricyclic compound, 3-*exo*-acetoxytricyclo-[2.2.1.0^{2,6}]heptane (3), was also isolated in low yield, and was identified by ^{1}H n.m.r. spectral comparison and by g.l.c. comparison with an authentic sample prepared by the sulphuric acid-catalysed reaction of norborna-2,5-diene with acetic acid.[6]

The first of five iodo-acetates recovered from preparative t.l.c. was identified as 2-*exo*-acetoxy,7-*anti*-iodobicyclo[2.2.1]heptane (8). High resolution mass measurement of the molecular ion ($M^{+\cdot}$ 279.9951) agreed with the formula $C_9H_{13}IO_2$. In the ^{1}H n.m.r. spectrum a broadened singlet ($W_{\frac{1}{2}}$ 4 Hz) at δ 4.00 is characteristic of a proton on C-7; this signal shows fine splitting (*ca.* 1 Hz) due to coupling of the C-7 *syn*-proton with the C-5 *endo*- and C-6 *endo*-protons, as found for the analogous dibromide (9).[5] The chemical shift (δ 4.50) and multiplicity (dd) of a second low-field pattern defines the position of the acetate group as C-2 *exo*. In addition, the absence of further splitting of this signal from long-range coupling of the C-2 *endo*-proton with a C-7 *anti*-proton confirms the stereochemistry assigned to the C-7 iodine atom.

The C-7 stereoisomer of (8), *viz.* 2-*exo*-acetoxy-7-*syn*-iodobicyclo[2.2.1]heptane (10), was also isolated. Again, the molecular formula was confirmed by high resolution mass spectral data. The ^{1}H n.m.r. spectrum of (10) shows three important variations from that of the C-7 *anti*-stereoisomer (8). First, the broadened singlet assigned to the C-7 *anti*-proton is further upfield, appearing at δ 3.64 in the case of (10) and δ 4.00 in that of (8). This difference is expected, since in (8) the C-7 *syn*-proton is shielded by the C-2 *exo*-acetate group; this shielding cannot operate in (10) where the C-7 proton has the *anti*-stereochemistry. Secondly, the C-2 *endo*-proton in (10) resonates further downfield [δ 4.62, *cf.* δ 4.50 in (8)]. Moreover, the signal at δ 4.62 in (10) appears as an eight-line pattern as opposed to a four-line pattern in the stereoisomer (8), the additional splitting being attributable to long-range coupling of the C-7 *anti*-proton with the C-2 *endo*-proton.[7] Thirdly, the chemical shifts of the C-1 and C-4 protons in (8) are coincident, but in (10) the C-1 proton is deshielded and its signal is distinct from that of the C-4 proton. Concomitantly the observed $J_{2\text{-}endo,3\text{-}exo}$ value has increased from 3.5 in (8) to 4.4 Hz in (10). Together these data indicate a slight twisting in (10) which increases the torsion angle between the C-2 *endo*- and C-3 *exo*-protons, thereby relieving steric interaction between the iodo- and acetoxy-substituents.

Multiple-elution preparative t.l.c. separated three further iodo-acetates, assigned the structures (11), (13), and (17). Irradiation at the frequency of the C-3 *endo*-proton (δ 3.55) in the ^{1}H n.m.r. spectrum of 2-*endo*-acetoxy-3-*exo*-iodobicyclo[2.2.1]heptane (11) caused the pattern due to the C-2 *exo*-proton at δ 5.28 to collapse to a doublet, the signals attributed to the C-1 and C-4 protons being unaffected. Also, irradiation at the frequency of the bridgehead protons caused the C-2 *exo*-proton signal to collapse to a doublet, the C-3 *endo*-proton signal being unaffected. The decoupling data and coupling constants are in accord with those reported [5] for 2-*exo*,3-*endo*-dibromobicyclo[2.2.1]heptane (5). Treatment of the *trans*-iodo-acetate (11) with base afforded the corresponding iodohydrin (12) only. No epoxide was detected in the crude product (^{1}H n.m.r.). The structure of the *cis*,*exo*-iodo-acetate (13) was assigned by comparison of the observed $J_{2\text{-}endo,3\text{-}endo}$, $J_{2\text{-}endo,7\text{-}anti}$, and $J_{3\text{-}endo,7\text{-}anti}$ values with those reported [8,9] for 2-*exo*,3-*exo*-dibromobicyclo[2.2.1]heptane (14) and for 2-*exo*-chloro-3-*exo*-hydroxybicyclo[2.2.1]heptane (15). Reaction of (13) with methanolic potassium carbonate gave the iodohydrin (16). The final iodo-acetate, isolated in 1% yield, was tentatively identified as 2-*exo*-acetoxy-3-*endo*-iodobicyclo[2.2.1]heptane (17), the regioisomer of (11). For the regioisomeric *trans*-bromo-chlorides (18) and (19) it has been experimentally verified [8] that *endo*-protons resonate at higher field than *exo*-protons. Similarly in (17) the C-2 proton absorbs at δ 4.60 compared with δ 5.28 in (11), and the C-3 proton signal appears at δ 3.55 in (11) compared with δ 3.95 in (17).

The last product recovered from preparative t.l.c. was the iodohydrin (20), identified by comparison with an authentic sample obtained by reduction with lithium aluminium hydride of the 2-*exo*,7-*syn*-iodo-acetate (10). The remaining 11% of the crude product consisted of four unidentified compounds.

The comparative yields obtained from the reaction of thallium(I) acetate–iodine with norbornene in acetic acid, dichloromethane, chloroform, or benzene as solvent are recorded in Table 1. When acetic acid was used as solvent, two additional compounds were isolated and

[5] D. R. Marshall, P. Reynolds-Warnhoff, E. W. Warnhoff, and J. R. Robinson, *Canad. J. Chem.*, 1971, **49**, 885.
[6] S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *J. Amer. Chem. Soc.*, 1962, **84**, 3918.
[7] J. I. Musher, *Mol. Phys.*, 1963, **6**, 93; J. Meinwald and Y. C. Meinwald, *J. Amer. Chem. Soc.*, 1963, **85**, 2514: K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, *ibid.*, 1967, **89**, 2401.
[8] P. M. Subramanian, M. T. Emerson, and N. A. Lebel, *J. Org. Chem.*, 1965, **30**, 2624.
[9] E. Tobler and D. J. Foster, *Helv. Chim. Acta*, 1965, **48**, 366.

identified (^{1}H n.m.r.[10]) as the stereoisomeric 2-*exo*,7-*anti*- and 2-*exo*,7-*syn*-diacetates, (21) and (22), respectively. A mixture of these diacetates had been prepared previously[11] by treatment of norbornene with lead tetra-acetate in acetic acid. In the present work a pure sample of each authentic diacetate was obtained by multiple-elution preparative t.l.c. of the crude product from the lead tetra-acetate reaction.

Wiberg *et al.*[12] have reported that a Woodward–Prévost reaction (silver acetate–iodine–wet acetic acid) on norbornene (1) followed by acetylation of the crude product yielded the tricyclic acetate (3) (22%) and the 2-*exo*,7-*syn*-iodo-acetate (10) (45%). They isolated these compounds from the crude product by fractional distillation, but this technique has proved inadequate in the present work for separation of the isomers (8) and (10). Moreover, the material balance was low. Using Wiberg's method, but without the subsequent acetylation step, we repeated the Woodward–Prévost reaction and compared the product distribution with that resulting from the normal Prévost method (dry acetic acid). It is noteworthy that hydroxy-acetates, the usual products of the Woodward–Prévost reaction, were not formed from norbornene as substrate, and that substantial amounts of the iodo-acetates (8) and (10) survived. Reference to Tables 1 and 2 shows that the tricyclic acetate (3) occurred in much higher yield in the silver-mediated reactions, and that none of the iodide (2) was observed. It was postulated that this acetate (3) originated *via* silver(I)-assisted solvolysis of nortricyclanyl iodide (2). Indeed, when pure (2) and silver(I) acetate were stirred in acetic acid at room temperature for 1 h, the acetate (3) was formed in quantitative yield. This implies an S_N1 mechanism proceeding *via* a carbocationic intermediate stabilized by the cyclopropyl ring.[13] Subsequent attack of the nucleophilic acetate is expected to be 99% *exo*.[3,14]

With respect to the thallium(I) acetate–iodine reactions, the product distribution implies an ionic pathway initiated by predominant *exo*-attack of electrophilic iodine at C-2 (Scheme).* The formation of the tricyclic iodide (2) requires abstraction of a C-5 proton from the cationic intermediate, presumably by acetate ion as base. This compound has been reported as a significant product (40%) from treatment of norbornene with iodonium nitrate in chloroform–pyridine.[4] The formation of the iodide (2) is analogous to the generation of allylic iodides in the diterpene series.[2] Elimination from the cationic intermediate is not a feasible pathway in the norbornyl series if the bicyclo[2.2.1]heptyl skeleton is to be retained, and the alternative ring-forming elimination occurs instead. The tricyclic acetate (3) presumably arises *via* thallium(I)-assisted solvolysis of (2),[13] albeit in low conversion: transformation of allylic iodides into allylic acetates with thallium(I) acetate and a trace of iodine has been observed in the diterpene series.[1] Formation of the 2,7-iodo-acetates (8) and (10) *via* trapping of a cationic species by nucleophilic acetate competes with the base-induced elimination, and in acetic acid higher yields of (8) and (10) are obtained. As expected the 2-*exo*,7-*syn*-stereoisomer (10) predominates.† Formation of the 2-*exo*,7-*anti*-isomer (8)

TABLE 1

Products from the reaction of norborn-2-ene with thallium(I) acetate–iodine

Product	Solvent: Acetic acid	Carbon tetrachloride	Chloroform	Dichloromethane	Benzene
3-*exo*-Iodotricyclo[2.2.1.0^{2,6}]heptane (2)	35	30	88	69	43
3-*exo*-Acetoxytricyclo[2.2.1.0^{2,6}]heptane (3)	4	1		4	6
2-*exo*-Acetoxy-7-*anti*-iodobicyclo[2.2.1]heptane (8)	10	1	1	3	2
2-*exo*-Acetoxy-7-*syn*-iodobicyclo[2.2.1]heptane (10)	42	16	5	15	10
2-*exo*,7-*syn*-Diacetoxybicyclo[2.2.1]heptane (22)	1				
2-*exo*,7-*anti*-Diacetoxybicyclo[2.2.1]heptane (21)	4				
2-*exo*,3-*endo*-Di-iodobicyclo[2.2.1]heptane (4)		†	†	†	†
2-*exo*,7-*syn*-Di-iodobicyclo[2.2.1]heptane (6)		†	†	†	†
2-*endo*-Acetoxy-3-*exo*-iodobicyclo[2.2.1]heptane (11)		12	1	3 ‡	15
2-*exo*-Acetoxy-3-*exo*-iodobicyclo[2.2.1]heptane (13)		18			11
2-*exo*-Acetoxy-3-*endo*-iodobicyclo[2.2.1]heptane (17)		1		3 ‡	
2-*exo*-Hydroxy-7-*syn*-iodobicyclo[2.2.1]heptane (20)		11			6

† Present but yield not obtained; decomposed on g.l.c. ‡ Combined yield of the mixture.

TABLE 2

Products from Woodward–Prévost (A) and Prévost (B) reactions of norborn-2-ene

Product	A	B
(3)	42	30
(22)	10	6
(8)	11	16
(10)	34	47

* The non-classical *vs.* classical nature of the carbocation in this series is still the subject of debate.[15]

† The analogous 2-*exo*,7-*syn*-compound has been isolated as the major product from addition of iodine(I) chloride to norbornene.[16]

[10] W. C. Baird, jun., and M. Buza, *J. Org. Chem.*, 1968, **33**, 4105.

[11] K. Alder, F. H. Flock, and H. Wirtz, *Chem. Ber.*, 1958, **91**, 609; D. D. Tanner and P. V. Bostelen, *J. Amer. Chem. Soc.*, 1972, **94**, 3187.

[12] K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, 1957, **79**, 6256.

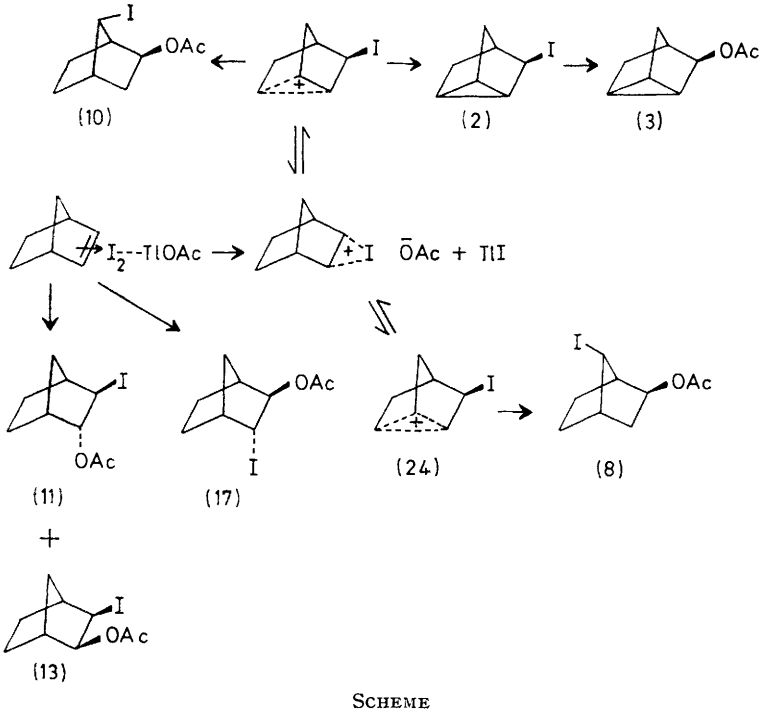
[13] G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, 1975, **97**, 1920.

[14] G. D. Sargent in 'Carbonium Ions,' vol. 3, ed. G. A. Olah and P. von R. Schleyer, Wiley, New York, 1972, p. 1099.

[15] H. C. Brown and K-T. Liu, *J. Amer. Chem. Soc.*, 1975, **97**, 600, 2469.

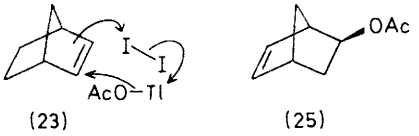
[16] G. B. Bachman, G. F. Kite, S. Tuccarbasu, and G. M. Tullman, *J. Org. Chem.*, 1970, **35**, 3167.

requires a 5,4-hydride migration to give the cation (24) followed by attack of acetate *exo* at C-5. The alternative product from the rearranged ion involves *endo*-attack of the nucleophile at C-3 which would give the *trans,vic*-iodo-acetate (11). However, whereas (8) was detected in all the solvents employed, (11) was not formed in acetic acid (Table 1); this argues against the genesis of both of these iodo-acetates from a common precursor ion. Instead compound (11) may be envisaged as arising from direct addition of 'iodine acetate' to (1) *via* a more concerted pathway which becomes operative in the less polar solvents which do not provide sufficient stabilization of the cationic species to permit hydride migration. The iodo-acetate (13) displays *cis,exo*-stereochemistry, and was detected in the products from the thallium(I) acetate–iodine reactions has suggested that the formation of such *cis*-adducts can best be explained in terms of a more concerted pathway, *e.g.* (23). The detection of (13) in the thallium(I)-mediated reaction, and not from the silver(I)-mediated reaction, therefore implies the occurrence of such a concerted pathway in the former case only, in line with previous experience [2] of the differences displayed between thallium(I) and silver(I) salts in iodocarboxylation of alkenes. Formation of the 2-*exo*-acetoxy-3-*endo*-iodide (17) requires initial attack of electrophilic iodine from the *endo*-face of the molecule; steric hindrance to approach of the reagent from this side is to be expected and is reflected in the low yield of this isomer. The most obvious pathway to compounds (21) and (22) is *via* solvolysis of either or both of the iodo-acetates (8) and (10), although both diacetates



SCHEME

in benzene or carbon tetrachloride. In order to determine whether the formation of (13) was a function of the solvent or of the metal acetate used, the reaction of norbornene with silver(I) acetate–iodine in carbon tetrachloride was investigated: ^{1}H n.m.r. spectral analysis



of the crude product showed (13) to be absent. Analogous *cis,exo*-adducts have been isolated from the reaction of (1) with certain protic acids, nitrosyl chloride, mercury(II) salts, and thallium(III) acetate. Traylor [3,17] would then be expected as products of the Prévost and Woodward–Prévost reactions, whereas only (22) was detected. The isolation of the iodohydrin (20) from the thallium(I) acetate–iodine reactions in benzene and carbon tetrachloride only, suggests that a distinct reaction pathway, perhaps involving an intermediate iodo-hypoiodite,[18] may operate in these solvents. That (20) does not arise from the presence of traces of water in these solvents can be inferred from the Woodward–Prévost reaction (wet acetic acid), where no iodohydrin was formed.

EXPERIMENTAL

General experimental details are given in ref. 2. *J* Values were obtained by first-order analysis. Analytical g.l.c. was

[17] T. G. Traylor and A. W. Baker, *Tetrahedron Letters*, 1959, No. 19, 14.

[18] C. P. Forbes, A. Goosen, and H. A. H. Laue, *J.C.S. Perkin I*, 1974, 2346.

carried out on a Varian Aerograph 1400 instrument with a glass column (8 ft, 1/8 in o.d.) packed with 3% OV-17 on 70—80 mesh Chromosorb W. For preparative g.l.c. a glass column (12 ft, 3/8 in o.d.) packed with 7% OV-17 on 70—80 mesh Chromosorb W was used.

Reaction of Thallium(I) *Acetate and Iodine with Bicyclo*-[2.2.1]*hept-2-ene* (1).—(a) *In carbon tetrachloride.* A solution of iodine (1.34 g) in carbon tetrachloride (90 ml) was added dropwise (4 h) to a stirred mixture of thallium(I) acetate (2.79 g) and bicyclo[2.2.1]hept-2-ene (0.5 g) in carbon tetrachloride (80 ml). The rate of addition was adjusted to keep the iodine colour to a minimum, and the mixture was then heated under reflux (4 h). After cooling to room temperature the mixture was filtered, and the filtrate was washed with water, aqueous sodium disulphite, and brine, and dried ($MgSO_4$). Distillation left a pale yellow oil (0.86 g) which was subjected to preparative t.l.c. (hexane–ether, 19 : 1). Percentage yields (Table 1) were calculated from the results of analytical g.l.c. on the crude product; peaks were identified by use of samples obtained from preparative t.l.c. Preparative g.l.c. gave further purification when necessary and also proof of the thermal stability of all compounds except the di-iodides (4) and (6).

(i) 3-*exo*-Iodotricyclo[2.2.1.$0^{2,6}$]heptane (2) had b.p. 35° at 0.15 mmHg (Found: $M^{+\cdot}$, 219.9760. Calc. for C_7H_9I: M, 219.9751), δ 0.70—1.70 (m, 7-*exo*-H, 2-H, 6-H, and 5-H_2), 1.90 and 2.10 (2 apparent br,s, $W_{\frac{1}{2}}$ 4 and 6 Hz, 1/2 7-*syn*-H and 1/2 7-*syn*-H plus 4-H, respectively [4]), and 3.78br (s, $W_{\frac{1}{2}}$ 3 Hz, 2-H).

(ii) 2-*exo*,3-*endo*-Di-iodobicyclo[2.2.1]heptane (4), inseparable from (2), decomposed in g.l.c. (Found: $M^{+\cdot}$, 347.8859. Calc. for $C_7H_{10}I_2$: M, 347.8876); δ [obtained by subtraction of the resonances due to (2)] 0.90—2.30 (m, 5-, 6-, and 7-H_2), 2.42br (s, $W_{\frac{1}{2}}$ 14 Hz, 1- and 4-H), 3.95 (four lines, $J_{2\text{-}endo,3\text{-}exo}$ 4, $J_{2\text{-}endo,7\text{-}anti}$ 3 Hz, 2-*endo*-H), and 4.54 (three lines, $W_{\frac{1}{2}}$ 15 Hz, $J_{3\text{-}exo,2\text{-}endo}$ 4, $J_{3\text{-}exo,4}$ 4 Hz, 3-*exo*-H).

(iii) 2-*exo*,7-*syn*-Di-iodobicyclo[2.2.1]heptane (6) had b.p. 55° at 0.20 mmHg, *m/e* 348 ($M^{+\cdot}$, $C_7H_{10}I_2$), δ 1.00—3.00 (m, 1-H, 4-H, 3-H_2, 5-H_2, and 6-H_2), and 3.78 (m, $W_{\frac{1}{2}}$ 18 Hz, 7-*anti*- and 2-*endo*-H).

(iv) 3-*exo*-Acetoxytricyclo[2.2.1.$0^{2,6}$]heptane (3) had b.p. 48° at 0.7 mmHg, *m/e* 152 ($M^{+\cdot}$, $C_9H_{12}O_2$), $\nu_{max.}$ 1 710 and 1 235 cm^{-1} (OAc), δ 1.00—2.40 (m, 1-H, 2-H, 5-H_2, 6-H, and 7-*anti*-H), 1.66 and 1.95 (2 apparent br,s, $W_{\frac{1}{2}}$ 3 and 4 Hz, 1/2 7-*syn*-H and 1/2 7-*syn*-H plus 4-H plus OAc, respectively), and 4.56br (s, $W_{\frac{1}{2}}$ 4 Hz, 2-H).

(v) 2-*exo*-Acetoxy-7-*anti*-iodobicyclo[2.2.1]heptane (8) had b.p. 85° at 0.2 mmHg (Found: $M^{+\cdot}$, 279.9951. Calc. for $C_9H_{13}IO_2$: M, 279.9962), $\nu_{max.}$ 1 740 and 1 260 cm^{-1} (OAc), δ 0.90—1.80 (m, 3-, 5-, and 6-H_2), 2.00 (s, OAc), 2.40br (s, $W_{\frac{1}{2}}$ 8 Hz, 1- and 4-H), 4.00br (s, $W_{\frac{1}{2}}$ 4 Hz, 7-*syn*-H), and 4.50 (dd, $W_{\frac{1}{2}}$ 10.5 Hz, $J_{2\text{-}endo,3\text{-}endo}$ 7.6, $J_{2\text{-}endo,3\text{-}exo}$ 3.5 Hz, 2-H).

(vi) 2-*exo*-Acetoxy-7-*syn*-iodobicyclo[2.2.1]heptane (10) had b.p. 101—105° at 0.75 mmHg (Found: $M^{+\cdot}$ 279.9914. Calc. for $C_9H_{13}IO_2$: 279.9962), $\nu_{max.}$ 1 720 and 1 242 cm^{-1} (OAc), δ 0.90—1.80 (m, 3-, 5-, and 6-H_2), 2.00 (s, OAc), 2.38br (s, $W_{\frac{1}{2}}$ 6 Hz, 4-H), 2.58br (s, $W_{\frac{1}{2}}$ 6 Hz, 1-H), 3.64br (s, $W_{\frac{1}{2}}$ 4 Hz, 7-*anti*-H), and 4.62 (eight lines, $W_{\frac{1}{2}}$ 15 Hz, $J_{2\text{-}endo,3\text{-}endo}$ 7.5, $J_{2\text{-}endo,3\text{-}exo}$ 4.4, $J_{2\text{-}endo,7\text{-}anti}$ 1.3 Hz, 2-H).

(vii) 2-*endo*-Acetoxy-3-*exo*-iodobicyclo[2.2.1]heptane (11) had b.p. 44° at 0.3 mmHg (Found: $M^{+\cdot}$, 279.9963. Calc. for $C_9H_{13}IO_2$: M, 279.9962), $\nu_{max.}$ 1 745 and 1 228 cm^{-1} OAc), δ 0.90—2.20 (m, 5-, 6-, and 7-H_2), 2.04 (s, OAc), 2.58br (s, $W_{\frac{1}{2}}$ 8 Hz, 1- and 4-H), 3.55 (three lines, $W_{\frac{1}{2}}$ 8 Hz, $J_{3\text{-}endo,2\text{-}exo}$ 2.9, $J_{3\text{-}endo,7\text{-}anti}$ 2.7 Hz, 3-*endo*-H), and 5.28 (m, $W_{\frac{1}{2}}$ 10 Hz, $J_{2\text{-}exo,1}$ 4.7, $J_{2\text{-}exo,3\text{-}endo}$ 2.9 Hz, 2-*exo*-H).

(viii) 2-*exo*-Acetoxy-3-*exo*-iodobicyclo[2.2.1]heptane (13) had b.p. 45—50° at 0.15 mmHg (Found: $M^{+\cdot}$, 279.9947. Calc. for $C_9H_{13}IO_2$: M, 279.9962), $\nu_{max.}$ 1 742 and 1 225 cm^{-1} (OAc), δ 0.90—2.40 (m, 5-, 6-, and 7-H_2), 2.04 (s, OAc), 2.18br (s, $W_{\frac{1}{2}}$ 7 Hz, 1-H), 2.60br (s, $W_{\frac{1}{2}}$ 7 Hz, 4-H), 4.12 (dd, $J_{3\text{-}endo,2\text{-}endo}$ 6.7, $J_{3\text{-}endo,7\text{-}anti}$ 1.7 Hz, 3-*endo*-H), and 4.40 (dd, $J_{2\text{-}endo,3\text{-}endo}$ 6.7, $J_{2\text{-}endo,7\text{-}anti}$ 2.3 Hz, 2-*endo*-H).

(ix) 2-*exo*-Acetoxy-3-*endo*-iodobicyclo[2.2.1]heptane (17) had b.p. 80—85° at 0.9 mmHg, *m/e* 280 ($M^{+\cdot}$, $C_9H_{13}IO_2$), $\nu_{max.}$ 1 745 and 1 228 cm^{-1} (OAc), δ 1.00—2.60 (m, 1-H, 4-H, 5-H_2, 6-H_2, and 7-H_2), 2.00 (s, OAc), 3.95 (m, $W_{\frac{1}{2}}$ 10 Hz, 3-*exo*-H), and 4.60 (m, $W_{\frac{1}{2}}$ 9 Hz, 2-*endo*-H).

(x) 2-exo-*Hydroxy*-7-syn-*iodobicyclo*[2.2.1]*heptane* (20) had m.p. 52° (sublimed) (Found: C, 35.2; H, 4.6. $C_7H_{11}O$ requires C, 35.3; H, 4.6%), $\nu_{max.}$ 3 480 and 1 088 cm^{-1} (OH), δ 0.90—2.20 (m, 3-, 5-, and 6-H_2), 1.90 (s, exchangeable on deuteriation, OH), 2.42br (s, $W_{\frac{1}{2}}$ 6.5 Hz, 1- and 4-H), and 3.70br (s, $W_{\frac{1}{2}}$ 5 Hz, 2-*endo*- and 7-*anti*-H).

(b) *In acetic acid.* A solution of iodine (1.34 g) in acetic acid (80 ml) was added dropwise (35 min) to a stirred mixture of bicyclo[2.2.1]hept-2-ene (0.5 g) and thallium(I) acetate (2.79 g) in acetic acid (70 ml) at room temperature. The mixture was then stirred at 80 °C (3 h). In this case two additional products were isolated (Table 1).

(i) 2-*exo*,7-*syn*-Diacetoxybicyclo[2.2.1]heptane (22) had b.p. 65—70° at 0.35 mmHg, *m/e* 212 ($M^{+\cdot}$, $C_{11}H_{16}O_4$), $\nu_{max.}$ 1 725 and 1 240 cm^{-1} (OAc), δ 0.90—2.10 (m, 3-, 5-, and 6-H_2), 1.92 (s, OAc), 1.98 (s, OAc), 2.10br (s, $W_{\frac{1}{2}}$ 7 Hz, 4-H), 2.42br (s, $W_{\frac{1}{2}}$ 7 Hz, 1-H), and 4.58 (m, 2-*endo*- and 7-*anti*-H).

(ii) 2-*exo*,7-*anti*-Diacetoxybicyclo[2.2.1]heptane (21) had b.p. 65—70° at 0.35 mmHg, *m/e* 212 ($M^{+\cdot}$, $C_{11}H_{16}O_4$), $\nu_{max.}$ 1 730 and 1 240 cm^{-1} (OAc), δ 0.80—2.20 (m, 3-, 5-, and 6-H_2), 2.00 (s, 2 × OAc), 2.25br (s, $W_{\frac{1}{2}}$ 8 Hz, 1- and 4-H), and 4.52 (dd, $W_{\frac{1}{2}}$ 13 Hz, $J_{2\text{-}endo,3\text{-}endo}$ 7, $J_{2\text{-}endo,6\text{-}endo}$ 3.3 Hz, 2-*endo*-H), and 4.90br (s, $W_{\frac{1}{2}}$ 4 Hz, 7-*syn*-H).

(c) *In chloroform.* The addition time was 30 min and the reflux time 25 min.

(d) *In dichloromethane.* The addition time was 45 min, and the mixture was then stirred at room temperature for 10 min.

(e) *In benzene.* The addition time was 2 h and the reflux time 1.5 h.

Treatment of 2-endo-*Acetoxy*-3-exo-*iodobicyclo*[2.2.1]*heptane* (11) *with Base.*—The iodo-acetate (11) (24 mg) and potassium carbonate (23 mg) were shaken (6 h) in aqueous methanol (1 : 1; 10 ml). Work-up yielded 2-*endo*-hydroxy-3-*exo*-iodobicyclo[2.2.1]heptane (12) as an oil (19 mg), *m/e* 238 ($M^{+\cdot}$, $C_7H_{11}IO$), $\nu_{max.}$ 3 430 and 1 115 cm^{-1} (OH), δ 1.00—2.40 (m, 4-H, 5-H_2, and 7-H_2), 1.85br (s, exchangeable on deuteriation, OH), 2.50br (s, $W_{\frac{1}{2}}$ 7 Hz, 1-H), 3.44 (three lines, $W_{\frac{1}{2}}$ 8 Hz, $J_{3\text{-}endo,2\text{-}exo}$ 2.9, $J_{3\text{-}endo,7\text{-}anti}$ 2.7 Hz, 3-*endo*-H), and 4.70 (m, $W_{\frac{1}{2}}$ 10 Hz, 2-*exo*-H).

Treatment of 2-exo-*Acetoxy*-3-exo-*iodobicyclo*[2.2.1]*heptane* (13) *with Base.*—2-*exo*-Acetoxy-3-*exo*-iodobicyclo[2.2.1]-heptane (13) (11 mg) and potassium carbonate (10 mg) were shaken (18 h) in aqueous methanol (1 : 1; 10 ml). Work-up afforded 2-*exo*-hydroxy-3-*exo*-iodobicyclo[2.2.1]heptane (16) (7 mg), *m/e* 238 ($M^{+\cdot}$, $C_7H_{11}IO$), δ 0.90—2.70 (m, 1-H and 4-H, 5-H_2, 6-H_2, and 7-H_2), 3.28 (dd, $J_{2\text{-}endo,3\text{-}endo}$ 6, $J_{2\text{-}endo,7\text{-}anti}$ 2 Hz, 2-*endo*-H), and 4.19 (dd, $J_{3\text{-}endo,2\text{-}endo}$ 6, $J_{3\text{-}endo,7\text{-}anti}$ 2.5 Hz, 3-*endo*-H).

Reduction of 2-exo-*Acetoxy*-7-syn-*iodobicyclo*[2.2.1]*heptane*

(10).—A solution of the iodo-acetate (10) (160 mg) in ether (0.5 ml) was added to a stirred suspension of lithium aluminium hydride (63 mg) in ether (15 ml) and the mixture was heated under reflux (4 h). Work-up gave an oil (140 mg) from which pure 2-*exo*-hydroxy-7-*syn*-iodobicyclo-[2.2.1]heptane (20) (120 mg), m.p. 52°, was isolated by sublimation at 44 °C and 0.65 mmHg.

Reaction of Lead Tetra-acetate with Bicyclo[2.2.1]*hept*-2-*ene*.[11]—A solution of norborn-2-ene (1.0 g) in acetic acid (10 ml) was added to a stirred suspension of lead tetra-acetate (8.9 g) in acetic acid (65 ml). The mixture was stirred at room temperature (18 h), and then water (150 ml) was added. Extraction into dichloromethane and work-up yielded an oil (2.10 g) which was subjected to preparative t.l.c. in hexane–ether (9 : 1; three elutions) to give 3-*exo*-acetoxytricyclo[2.2.1.$0^{2,6}$]heptane (3) (160 mg, 10%), and a mixture of the diacetates (21) and (22) (1.8 g, 80%). This mixture was subjected again to preparative t.l.c. in hexane–ether (19 : 1; seven elutions) to give pure samples of the 2-*exo*-7-*anti*-diacetate (21) (1.25 g, 55%) and of the 2-*exo*-7-*syn*-diacetate (22) (0.55 g, 24%).

Addition of Acetic Acid to Bicyclo[2.2.1]*hepta*-2,5-*diene*.[6]—Bicyclo[2.2.1]hepta-2,5-diene (1.67 g) was added to acetic acid (4.35 ml) containing aqueous 40% sulphuric acid (0.1 ml), and the solution was shaken for 4 days at room temperature. Work-up gave an oil (2.6 g) which after preparative t.l.c. in hexane–ether (97 : 3; one elution) yielded a 1 : 1 mixture (2.4 g, 88%) of 2-*exo*-acetoxybicyclo[2.2.1]-hept-5-ene (25) and 3-*exo*-acetoxytricyclo[2.2.1.$0^{2,6}$]heptane (3). The bicyclic alkene (25) was removed by extraction into aqueous 20% silver nitrate, leaving pure nortricyclanyl acetate (3) (1.2 g, 44%).

Reaction of Silver(I) *Acetate and Iodine with Bicyclo*[2.2.1]-*hept*-2-*ene*.—(a) *In anhydrous acetic acid*. Iodine (1.34 g) was added in portions (2 h) to a stirred suspension of silver(I) acetate (2.21 g) and norborn-2-ene (0.5 g) in anhydrous acetic acid (15 ml). The mixture was heated at 100 °C (1.5 h), then cooled and worked up to give an oil (1.34 g). Preparative t.l.c. and analysis of the products as before gave the compounds listed in Table 2.

(b) *In wet acetic acid*.[12] The above reaction was repeated with acetic acid (15.9 ml)–water (0.15 ml) as solvent to give the product distribution recorded in Table 2.

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