

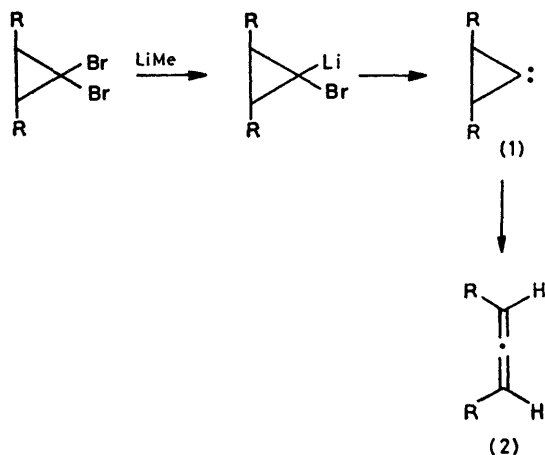
The Chemistry of Cyclopropylidenes. Part 1. Reaction of 7,7-Dibromo-3-vinylbicyclo[4.1.0]heptanes with Methyl-lithium †

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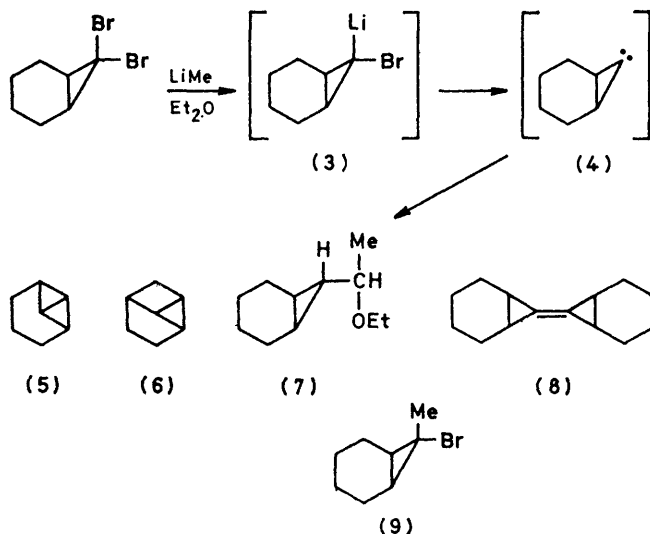
Reaction of *anti*-7,7-dibromo-3-vinylbicyclo[4.1.0]heptane (10) with LiMe, prepared from MeI and Li, leads at 25–35 °C to products derived by insertion of a cyclopropylidene into the C₃-H and C₅-H bonds, and to insertion into the solvent ether. At -40 to -50 °C, the intramolecular insertion products are replaced by *exo*-7-iodo-3-vinylbicyclo[4.1.0]heptane (29).

Reaction of *syn*-7,7-dibromo-3-vinylbicyclo[4.1.0]heptane with LiMe at 25–35 °C leads to a second iodide, (17) but at -40 to -50 °C gives a spiro-derivative (28). The latter is converted to (17) with LiI·H₂O at 25 °C and reacts exothermally with MeOH and AcOH; it rearranges on g.l.c. or on reaction with Ag⁺-C₆H₆ to (37) which on hydroxymercuration leads to (38).

THE normal reaction of the cyclopropylidene (1), ring opening to produce the allene (2),¹ can be suppressed if



the allene is made sufficiently strained and if pathways for carbene insertion or addition reactions are available.^{2,3}



Thus the reaction of 7,7-dibromobicyclo[4.1.0]heptane with methyl-lithium generates the carbene (4), or a

† A preliminary account of some of this work has already appeared (M. S. Baird, *J.C.S. Chem. Comm.*, 1974, 197).

related carbenoid, which undergoes intramolecular insertion into C-H bonds to produce (5) and (6), intermolecular insertion into the solvent ether to produce (7), or reaction with (3) to give finally the dimer (8).²

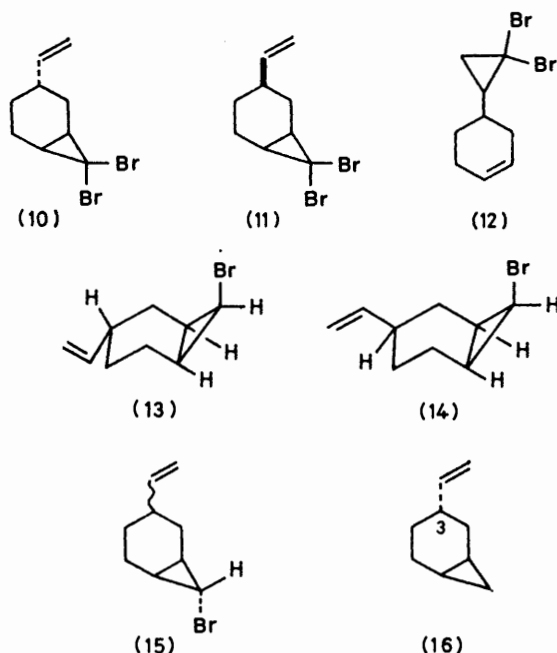
In addition, alkylation products such as (9) are sometimes observed, in yields which are dependent on the presence or absence of dissolved salts in the methyl-lithium.² In view of the potential use of these reactions in synthesis, *e.g.* in the synthesis of bicyclo[1.1.0]butanes,^{4,5} it seemed that a study of the effect of substituents on the relative rates of the various reactions involved would be of considerable value. Such studies have been reported for 3-alkyl-7,7-dibromobicyclo[4.1.0]heptanes; however, these are obtained as practically inseparable mixtures of *syn*- and *anti*-isomers from the reaction of alkylcyclohexenes and dibromocarbene, which makes the assignment of alkyl-lithium products very difficult.⁵

RESULTS AND DISCUSSION

Treatment of 4-vinylcyclohexene with dibromocarbene, generated either from $\text{KOBu}^t\text{-CHBr}_3$ in light petroleum or by phase-transfer catalysis using aqueous $\text{NaOH-CHBr}_3\text{-cetrimide}$, led to a mono-dibromocarbene adduct which was apparently a single compound by g.l.c. or t.l.c. However, the n.m.r. spectrum of the vinyl region of the product showed the presence of (10) and (11) in about equal amounts, together with a small amount of the adduct at the mono-substituted alkene, (12). The formation of equal amounts of (10) and (11) is in keeping with results in alkyl-substituted bicyclo[4.1.0]heptanes,^{4,5} and attack principally at the endocyclic alkene is in agreement with the Simmons-Smith cyclopropanation of 4-vinylcyclohexene;⁶ the result is as expected for an electrophilic carbene. Dichlorocarbene is reported to react predominantly at the endocyclic double bond of vinylcyclohexene and to give both epimers.⁷

Confirmation of the presence of both (10) and (11) was obtained by reduction of the mono-adducts with Zn-HOAc ⁸ for 3 h at 55–65 °C when the resulting *endo*-monobromides (13) and (14) could be separated; these two compounds were unusual in that their n.m.r. spectra were superimposable! Each showed the charac-

teristic triplet (J 8 Hz) at τ 6.81 of an *endo*-bromocyclopropane.⁹ In addition to (13) and (14), a minor product



was obtained, which was the *exo*-bromide (15), probably as a mixture of epimers at C-3.

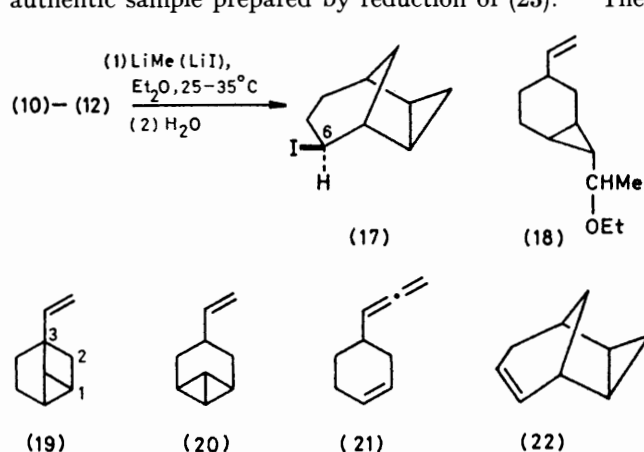
If the mixture of mono-adducts (10)–(12) was treated with *N*-bromosuccinimide (NBS) in refluxing CCl_4 , followed by brief reaction with AgClO_4 in aqueous acetone (to convert the allylic bromides into alcohols), and then column chromatography, (10) was obtained free of (12) but containing *ca.* 25% (11); apparently the allylic hydrogen of (10) is not readily removed by NBS. Reduction of enriched (10) with Zn-HOAc ⁸ gave (13) and (15) in the ratio *ca.* 5 : 1, and little (14) was observed.

Reduction of enriched (10) with sodium–liquid ammonia gave (16). Reaction of the mixed adducts (10)–(12) with sodium–liquid ammonia also gave a product which showed a single major peak on g.l.c.; this showed n.m.r. and i.r. spectra very similar to those of (16), but was presumably a mixture of epimers at C-3.

Reaction of Adducts with Methyl–lithium in the Presence of Iodides.—Reaction of the mixed monoadducts (10)–(12) with methyl–lithium (prepared from Li and MeI in ether) at 25–35 °C followed by quenching with H_2O gave a complex mixture of products.

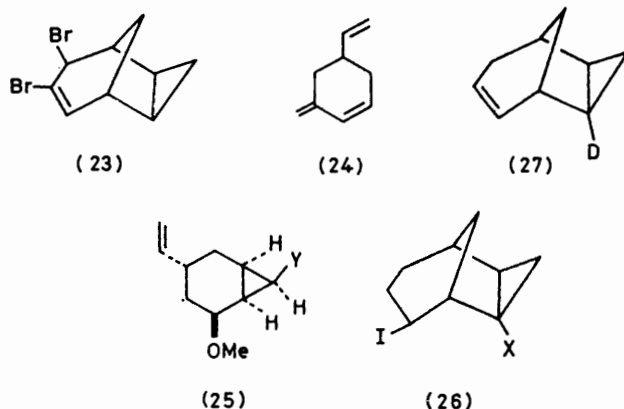
These were separated by distillation into volatile (C_9H_{12} isomers) and less volatile fractions. The latter was further separated into (17) and (18) by column chromatography or preparative g.l.c. In the n.m.r. spectrum, iodide (17) showed a 2-H multiplet at τ 9.3, consistent with the presence of a disubstituted cyclopropane, and a broad 1-H triplet at τ 5.1 for the hydrogen on C-6; there were, however, no signals in the olefinic region. Dehydroiodination of (17) with KOBu^t –DMSO gave a hydrocarbon, C_9H_{12} (88%), showing a similar

signal in the cyclopropane region; this product was characterised as (22) and shown to be identical to an authentic sample prepared by reduction of (23).¹⁰ The



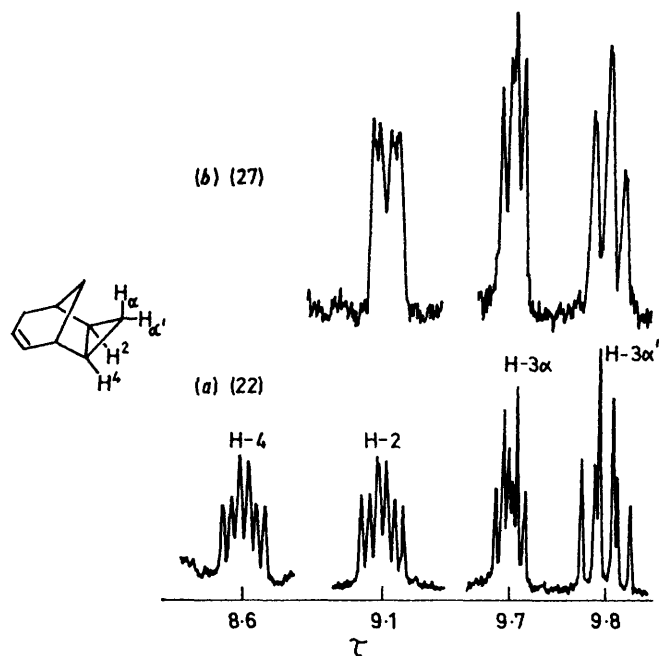
geometry at the 6-position in (17) is supported by the coupling constants and $W_{\frac{1}{2}}$ (*ca.* 8 Hz) of the methine hydrogen at that position; similar values are reported for a number of 2-iodo-9-oxabicyclo[3.3.1]nonanes^{11a} and 2-substituted bicyclo[3.3.1]nonanes.^{11b}

The volatile fraction of the reaction product was separated by preparative g.l.c. into four C_9H_{12} isomers



(ratio *ca.* 6 : 5 : 1 : 1). The first major component was readily characterised as (19) on the basis of a sharp double doublet for the $-\text{CH}=\text{}$ proton at τ 4.0 in the n.m.r. spectrum indicating the absence of a hydrogen on C-3. The two minor components were also easily characterised as the allene (21) and rearranged alkene (22). The second major component was less easy to identify, though it showed a $\text{CH}=\text{CH}=\text{CH}_2$ group in the n.m.r., together with a broad 2-H singlet at τ 7.6; however, gas chromatography under more vigorous conditions, or heating for 4 h at 70 °C with a trace of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ in CCl_4 , caused a rearrangement to a triene (24); this showed seven olefinic protons in the n.m.r. spectrum, and all remaining hydrogens were in the allylic region, though none were bis-allylic. The precursor is therefore identified as (20), by analogy with a wide variety of metal-catalysed reactions of such systems¹² [(20) did not, however, give any isomeric products on treatment

with AgClO_4 -benzene]. Bicyclo[1.1.0]butanes are known to be highly acid-labile,¹³ and accordingly (20) underwent a rapid exothermic reaction on treatment with a trace of toluene-*p*-sulphonic acid in methanol [compounds (19), (21), and (22) were unaffected by these conditions]. One major product was formed and this could be separated by preparative g.l.c. from two minor products (each *ca.* 25%); it was identified as (25, Y = H), and showed in the n.m.r. spectrum a vinyl group, cyclopropane protons at τ 9.4 and 9.8, a methyl ether, and a broad pentuplet at τ 6.28 for the hydrogen on C-2. The methoxy and vinyl groups were assigned as *trans* on steric grounds, and this was supported by the very small relative shift of the vinyl signals in the n.m.r. on addition of $[\text{Eu}(\text{fod})_3]$. Addition of toluene-*p*-sulphonic acid-MeOD to the bicyclo[1.1.0]butane (20) correspondingly



Cyclopropane signals of (a) compound (22) and (b) compound (27) at 220 MHz

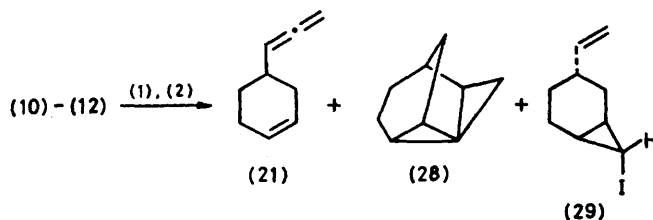
led to (25, Y = D) which showed no signal at τ 9.8. The *endo*-stereochemistry of the D-substituent was confirmed by examination of the coupling constants. Thus the signal at τ 9.8 in (25, Y = H) was a quartet (J 5 Hz).⁹ In addition the 1-H signal at τ 9.4, which appeared in the spectrum of (25, Y = H) as a double triplet (J 5 and 8.5 Hz) was reduced in the spectrum of (25, Y = D) to a triplet (J 8.5 Hz).

Reaction of the mixed adducts (10)–(12) with LiMe at 25–35 °C followed by quenching with D_2O rather than H_2O caused no deuterium incorporation into the ether (18) or the hydrocarbons (19)–(21). However, the iodide (17) and the hydrocarbon (22) were replaced by their deuteriated analogues (26, X = D) and (27); (26) was indeed readily dehydriodinated with KOBu^t -DMSO to (27). Each of the four cyclopropane hydrogens of (22) was shown by n.m.r. to be coupled to the other

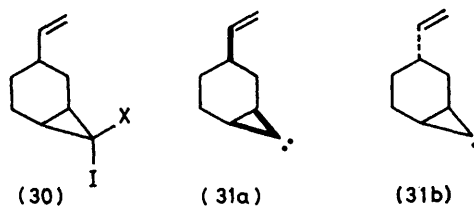
three, but not coupled appreciably to any other hydrogen. The coupling constants between *cis*- and *trans*-related hydrogens were 7 and 3.5 Hz, respectively, while the geminal coupling was 5.5 Hz; this resulted in the spectrum shown in the Figure (a). The spectrum of (27) showed no signal at 8.6, H(D)-4 being at lower field than H-2 due to the effect of the alkene; the signals for the remaining three cyclopropane hydrogens were altered correspondingly as shown in the Figure (b). The incorporation of one deuterium on D_2O quenching suggests the intermediacy of (26, X = Li) in the formation of (17) and (26, X = D).

Reaction of the mixed adducts (10)–(12) with methyl-lithium in ether at –48 to –50 °C followed by H_2O quenching gave a rather different set of products, which were once again separated into C_9H_{12} hydrocarbons and other products by distillation.

The less volatile fraction contained one major product, the iodide (29) (20%), together with several minor components (each *ca.* 5%); the iodide showed, as expected, a $\text{CH}=\text{CH}=\text{CH}_2$ group in the n.m.r. spectrum, together with a 1-H triplet (J 3.5 Hz) at τ 7.95, characteristic of the hydrogen on C-7 in an *exo*-substituted cyclo-



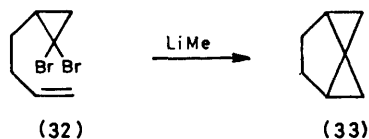
propane.⁹ Reduction of the iodide with sodium-liquid ammonia gave 3-vinylbicyclo[4.1.0]heptane, identical to that obtained above from (10). Compound (29) apparently arises by quenching of the lithio-iodocyclopropane (30, X = Li) derived from (10) by reaction with methyl-



lithium; confirmation of this was obtained by quenching the reaction mixture above with D_2O rather than H_2O , when the 7-deuterio-derivative (30, X = D) was obtained. Presumably the lithio-iodocyclopropane is obtained by halogen exchange of an initially formed lithiobromocyclopropane with iodides dissolved in the methyl-lithium; such reactions have also been observed for a number of other *gem*-dibromocyclopropanes,¹⁴ and are an extension of the known¹⁵ reduction of such compounds to 7-bromo-derivatives by reaction with alkyl-lithium at low temperature followed by quenching with water.

The volatile fractions of reaction (A) above contained

one major component, together with *ca.* 10–15% of the allene (21); the major component, which was not stable to g.l.c., showed a sharp 1-H triplet (J 6 Hz) at τ 9.98, and no signals in the olefinic region. This allowed its provisional characterisation as (28), the product of an intramolecular addition of the carbenoid [related to (31a)] to the alkene. This is analogous to the formation of (33) in the reaction of (32) with methyl-lithium.³



When the enriched single epimer (10) was treated with LiMe at 25–35 °C and the products compared to those from the combined adducts (10)–(12), it was found that there were only three major products, (19), (20), and (18). The allene (21) and rearranged alkene (22) were almost completely absent, and iodide (17) was formed in a much reduced proportion.

Treatment of the single isomer (10) with methyl-lithium at –45 °C gave only one major product, the iodide (29), although there were also several minor components present.

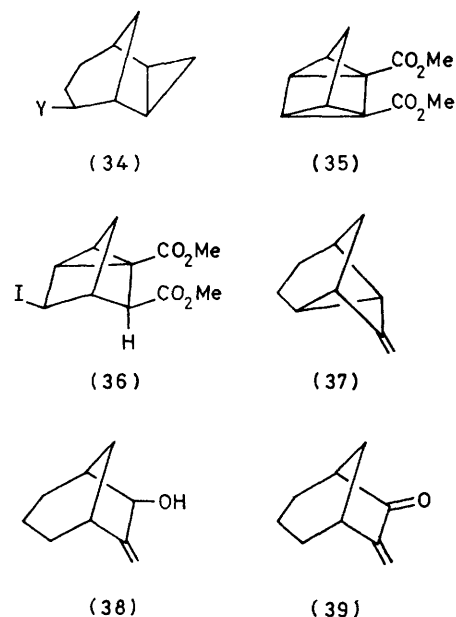
In view of the complex nature of the products and of the difficulty in separating the dibromides (10)–(12), a complete assignment of the products arising from each individual dibromide is difficult. However, it seems reasonable that the allene (21) is the sole product of reaction of (12) with methyl-lithium at 25–35 or –45 to –55 °C; (12) could also be the source of (28), but the relative yields of (21) and (28) suggest that this is not so to any great extent. The products (19) and (20) are apparently derived only from the *anti*-dibromide (10) by insertion of the carbene (31b) (or a related carbenoid) into the C₃–H and C₅–H bonds. The reason for the lack of any insertion into the C₂–H and C₄–H bonds is not immediately obvious, but the products are analogous to those from the related *anti*-3-methyl- and 3-*t*-butyl-carbenes,⁵ and an examination of Dreiding models shows that the conformation of (31b), which places the vinyl group in an equatorial position, also brings the C₃–H and C₅–H bonds relatively close to the carbene centre. The ratio of insertion at C₃ to C₅ was *ca.* 6 : 5; this is again in keeping with the 3-methyl and 3-*t*-butyl systems, and reflects the preferred insertion into a tertiary bond compared with the parent bicyclo[4.1.0]-heptan-7-ylidene, for which the ratio of (6) to (5) was 1 : 22.

The third dibromide (11) apparently leads to only one major product at low temperature, the spiro-derivative (28), and one product at 25–35 °C, the iodide (17). As will be seen below (28) can indeed be converted to (17) under the reaction conditions at 25–35 °C.

Reactions of (28).—As might be expected, (28) is a highly reactive molecule. Addition of acetic acid to a solution of (28) in CCl₄ caused complete conversion to the acetate (34, Y = OAc) (68%) in <1 min; an

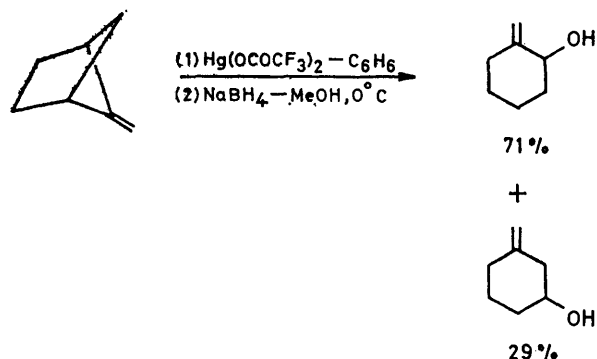
identical acetate was obtained (89%) when (17) was treated with an excess of silver acetate in acetic acid. Compound (28) also underwent an exothermic reaction with methanol to give the ether (34, Y = OMe) apparently quantitatively after *ca.* 30 min; an identical ether was obtained by treatment of (17) with silver perchlorate in methanol. More surprising is the fact that (28) was converted to (17) either on standing for 45 min with LiMe–Et₂O followed by quenching with water (44%), or on standing for 30 min with lithium iodide hydrate in ether (45%)! Presumably this accounts for the failure to observe (28), and its replacement by (17) in the reaction of the dibromocarbene adducts (10)–(12) with LiMe at 25–35 °C.

There is indeed a precedent for the ring opening of strained cyclopropanes by reaction with iodide ion, particularly when the resulting anion can be stabilised by substituents.¹⁶ Thus (35) is converted to the *exo*-iodide (36).



As stated above, (28) was also unstable to g.l.c., giving a single major volatile product which was shown to be a further C₉H₁₂ isomer. The same product was obtained (50%) when (28) was set aside for 18 h with a trace of silver perchlorate in benzene. The 220-MHz ¹H n.m.r. spectrum of the product showed two slightly non-equivalent hydrogens of an exocyclic methylene group at τ 5.68 and 5.70, a broad 2-H singlet at τ 7.31 and two 1-H signals at τ 7.72 and 7.85, the former as a broad doublet. The remaining hydrogens appeared as a complex set of signals between τ 8.3 and 8.7, apart from a 1-H doublet (J 11 Hz) at τ 8.84. The presence of i.r. bands at 1 685 and 925 cm⁻¹, in positions very close to those reported for a range of 5-methylene-bicyclo[2.1.1]hexane derivatives,¹⁷ supported the assignment of structure (37). Attempted ozonolysis of (37), oxidation with alkaline KMnO₄, or reaction with

$\text{Br}_2\text{-CCl}_4$ led to complex product mixtures; 5-methylenebicyclo[2.1.1]hexanes are also reported to lead to complex product mixtures in these reactions.¹⁷ However, reaction of the hydrocarbon with mercury trifluoroacetate in benzene¹⁸ gave a single product (38) (74%), showing two signals for the non-equivalent protons of an exocyclic methylene group, a broad singlet for H-6 at τ 5.86, two broad 1-H singlets at τ 7.8 and 7.9, a complex set of signals at τ 8—8.6, and a hydroxy hydrogen. The chemical shifts for (38) are similar to those reported for *exo*-2-hydroxy-3-methylenebicyclo[2.2.1]heptane.¹⁹ Addition of $[\text{Eu}(\text{fod})_3]$ to a CCl_4 solution of the alcohol caused one of the alkene hydrogens to shift very rapidly downfield, only the CH-OH signals



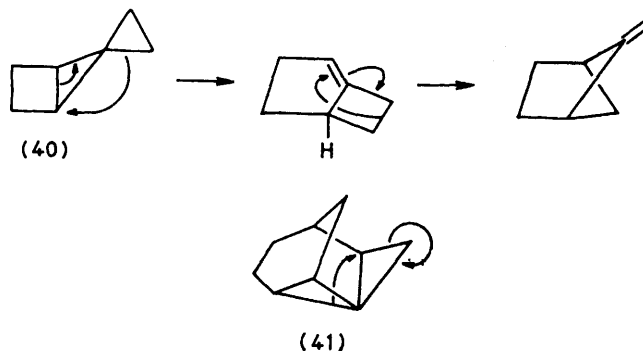
moving more quickly. The second alkene signal, however, moved only very slowly. The formation of the alcohol (38) does, in fact, have some precedent in the corresponding reaction of 5-methylenebicyclo[2.1.1]hexane itself,¹⁸ which, at 0 °C, leads predominantly to 2-methylenecyclohexanol.

Oxidation of (38) with $\text{MnO}_2\text{-CCl}_4$ at 25 °C gave a single product, the ketone (39); again, the n.m.r. spectrum showed two non-equivalent hydrogens on an exocyclic methylene group, together with two broad 1-H signals at τ 7.35 and 7.75. Addition of $[\text{Eu}(\text{fod})_3]$ caused a rapid downfield shift of one of the alkene hydrogens and the signal at τ 7.75, but the second alkene hydrogen and the signal at τ 7.35 moved only very slowly. The chemical shifts in (39) are again close to those reported for 3-methylenebicyclo[2.2.1]heptan-2-one.²⁰

The rearrangement of (28) to (37) can be thought of formally as a shift of four electrons as in (41), though the reaction is probably non-concerted. The spiro-pentane derivative (40) is reported to rearrange in an analogous manner.²¹

Reaction of Adducts with Methyl-lithium in the Absence of Iodides.—When the mixed adducts (10)—(12) were treated with commercial methyl-lithium, containing no dissolved iodide ion but bromide ion instead, a complex mixture of volatile components consisting of (19)—(21), (28), and probably a trace of (22) was obtained. The less volatile fraction consisted of the ether (18) together with a minor component, probably 7-bromo-7-methyl-3-vinylbicyclo[4.1.0]heptane. Treatment of the complex mix-

ture of C_9H_{12} isomers with methanol at 25—35 °C caused rapid reaction of the spiro-compound (28) to give the tricyclic ether (34, Y = OMe) (20% overall); this could be separated from the remaining C_9H_{12} isomers by flash-



distillation. Treatment of the distillate with methanol and a trace of toluene-*p*-sulphonic acid at 25—35 °C converted the bicyclo[1.1.0]butane (20) into the methyl ether (25, Y = H) (ca. 13%).

EXPERIMENTAL

Methyl-lithium was used as a solution in diethyl ether, either obtained from Ventron Ltd., or prepared from lithium and methyl iodide.

Mass spectra were obtained on an MS-9 spectrometer. N.m.r. spectra were obtained at 60 MHz on a Varian EM360 and at 90 MHz on a Bruker spectrometer; spectra at 220 MHz were run at PCMU, Harwell.

7,7-Dibromo-3-vinylbicyclo[3.1.0]heptanes.—(a) 4-Vinylcyclohexene (25 g) was stirred with bromoform (70 g) and cetrimide (500 mg), and NaOH (50 g) in water (50 ml) was added during 30 min, keeping the temperature below 60 °C. The products were stirred for 18 h at 50—60 °C, and then water (100 ml) and light petroleum (250 ml, b.p. 40—60 °C) were added. The organic layer was separated and the aqueous layer extracted with light petroleum (150 ml). The combined organic layers were washed with water (4 × 150 ml), dried (MgSO_4), and the solvent removed at reduced pressure. The residue was distilled to give the dibromides (10)—(12) at 100—105 °C and 2.5 mmHg (40 g, 62%) (Found: C, 38.75; H, 4.50. $\text{C}_9\text{H}_{12}\text{Br}_2$ requires C, 38.6; H, 4.3%); ^1H n.m.r., τ 4.35 (16 lines, separations 18, 10, 5, and 2 Hz, 1 H), 4.9—5.3 (complex, 2 H), 7.6—9.2 (complex, 9 H); ν_{max} , 1 640m, 920s, and 738s.

(b) The diene (25 g) and KOBu^b [potassium (19 g) was dissolved in Bu^tOH (500 ml) and the solvent was then removed at 14 mmHg, and then 1 mmHg at 60 °C)] were stirred with light petroleum (500 ml, b.p. 30—40 °C) in an ice-bath; bromoform (115 g) was added during 2.5 h and the products were stirred for 18 h at 20 °C and then poured into water (300 ml). The aqueous layer was extracted with light petroleum (2 × 100 ml), and the combined organic layers were washed with water (2 × 100 ml), dried (MgSO_4), and the solvent removed at 14 mmHg and then at 1 mmHg to give the crude dibromides (56 g).

(c) *Preparation of enriched* (10). The mixed adducts (10)—(12) (10 g) were refluxed in CCl_4 (75 ml) with *N*-bromosuccinimide (7 g) and dibenzoyl peroxide (100 mg) for 2 h. The products were cooled, filtered, and the filtrate

washed with water (3×50 ml), dried (MgSO_4) and the solvent removed at reduced pressure. The resulting oil was dissolved in 95% aqueous acetone (25 ml) and treated with AgClO_4 (5 g) in the same solvent (10 ml). There was an immediate heavy precipitate. The products were stirred for 15 min, poured into water (100 ml), and extracted with ether (2×50 ml). The combined organic layers were washed with water (2×50 ml), dried (MgSO_4), and the solvent removed at 14 mmHg. The residue was chromatographed through alumina, the required dibromide (10) (4.6 g) being rapidly eluted with light petroleum (b.p. 40–60 °C). Further elution with ethyl acetate gave a complex product mixture.

The n.m.r. spectrum of (10) was practically identical to that of the mixed adducts, apart from the olefinic region which showed a signal at τ 4.35 (ddd, J 18, 10, and 5 Hz, 1 H). An overlapping signal with identical couplings was also observed; this was due to the presence of ca. 25% of (11).

3-Vinylbicyclo[4.1.0]heptane.—(a) The anti-dibromide (10) (500 mg) in ether (5 ml) was added dropwise during ca. 1 min to sodium (1 g) in liquid ammonia (20 ml). After stirring for 10 min, excess of sodium was destroyed by addition of solid NH_4Cl ; water (10 ml) and ether (20 ml) were then carefully added and, after allowing the products to reach ambient temperature, the ether layer was separated, washed with water (2×10 ml), dried, and the solvent removed at 14 mmHg and 20 °C. The residue was flash-distilled to give a colourless oil, trans-3-vinylbicyclo[4.1.0]heptane (16) (152 mg, 71%) at 20–30 °C and 1 mmHg; τ 4.3 (ddd, J 19, 10, and 6 Hz, 1 H), 4.9–5.3 (complex, 2 H), 7.5–9.6 (complex, 10 H), and 10.0 (complex, 1 H); ν_{max} 1 640m, 1 025m, 1 000m, and 920s.

The residue contained at least six components by g.l.c.

(b) *exo*-7-Iodo-3-vinylbicyclo[4.1.0]heptane (see below) was reduced as in (a). A single product was observed, which was identical by n.m.r. to that obtained in (a).

(c) The mixed dibromides (5 g) in ether (25 ml) were reduced as above with Na (4 g) in liquid NH_3 (75 ml). Flash-distillation after work-up gave a distillate (1.15 g, 53%) which showed an n.m.r. practically identical to that in (a), apart from a broadening and increase in complexity of the signal at τ 4.3. The residue (ca. 1 g) again consisted of at least six peaks on g.l.c.

7-Bromo-3-vinylbicyclo[4.1.0]heptanes.—(a) *trans*-7,7-Dibromo-3-vinylbicyclo[4.1.0]heptane (10) (400 mg) was stirred for 2 h at 50–55° with zinc (2.0 g) and acetic acid (10 ml). The products were poured into ether (20 ml) and saturated aqueous sodium carbonate (40 ml), and the ether layer separated. The aqueous layer was washed with ether (15 ml), and the combined organic layers washed with aqueous Na_2CO_3 (20 ml), dried (MgSO_4), and the solvent removed at 14 mmHg to leave a colourless oil (164 mg, 57%), which consisted of two components in the ratio ca. 1 : 5 by g.l.c. (6 ft Carbowax, 150 °C); these were separated and found to be *exo*-trans-7-bromo-3-vinylbicyclo[4.1.0]heptane (15) (Found: M^+ , 200.020 0. $\text{C}_9\text{H}_{13}\text{Br}$ requires M , 200.020 1); τ 4.3 (ddd, J 18, 10.5, and 6 Hz, 1 H), 4.9–5.3 (complex, 2 H), 7.5 (t, J 3 Hz, 1 H), and 7.7–8.8 (complex, 9 H); ν_{max} 1 640s and 920s; and *endo*-trans-7-bromo-3-vinylbicyclo[4.1.0]heptane (13) (Found: M^+ , 200.022 0. $\text{C}_9\text{H}_{13}\text{Br}$ requires M , 200.020 1); τ 4.31 (ddd, J 18, 10.5, and 6 Hz, 1 H), 4.9–5.3 (complex, 2 H), 6.81 (t, J 8 Hz, 1 H), and 7.5–9.1 (complex, 9 H); ν_{max} 920s, 1 000m, and 1 640m.

(b) The mixed dibromides (5.0 g) were reduced as above with zinc (20 g) in acetic acid (80 ml) for 3 h at 55–65 °C. Work-up and distillation gave a colourless oil (2.1 g, 59%), b.p. 72–76 °C at 2 mmHg. G.l.c. (as above) showed this to consist of three components in the ratio ca. 2 : 5 : 4. The first component showed an n.m.r. spectrum very similar to component one above, but presumably was a mixture of *cis*- and *trans*-*exo*-monobromides (15). The second component was identical to the second component above. The third component was *endo*-*cis*-7-bromo-3-vinylbicyclo[4.1.0]heptane (14) (Found: M^+ , 200.019 0. $\text{C}_9\text{H}_{13}\text{Br}$ requires M , 200.020 1) which showed an n.m.r. spectrum effectively identical to that of the *endo*-*trans*-7-bromo-3-vinyl isomer (indeed, a mixture of the two isomers showed no splitting of peaks in the characteristic region below τ 7); ν_{max} 920s, 1 000m, and 1 640m (small changes in the fingerprint region from the *trans*-isomer).

Reaction of 7,7-Dibromo-3-vinylbicyclo[4.1.0]heptanes with LiMe.—(a) At –49 to –52 °C. The dibromides (3.0 g) were stirred in ether (50 ml) at –40 to –52 °C and an excess of LiMe (25 ml, from MeI and Li) was added over a period of 5 min. Water (15 ml) was added dropwise; after an initial vigorous reaction in which the temperature reached –35 °C the system was allowed to warm to –20 °C to facilitate extraction. The organic layer was washed with water (2×15 ml), dried (MgSO_4), and the solvent removed at 14 mmHg without heating. Flash-distillation at ca. 40 °C and 1 mmHg gave a colourless oil (587 mg, 46%) which consisted of one major (ca. 80%) and two minor peaks on g.l.c. (6 ft Apiezon, 130 °C). The major component rearranged on g.l.c. (see later) but was characterised as the *spiro*-compound (28); τ 7.4–9.0 (complex, 10 H), 9.30 (t, J 5 Hz, 1 H) and 9.98 (t, J 6 Hz, 1 H); ν_{max} 3 040 (sh), 3 020 (sh), 820s, and 730s; m/e 120 (M^+) (40%) and 79 (100). One of the minor components (which accounted for all the other n.m.r. signals) was 4-propadienylcyclohexene (see below).

The residue of the flash-distillation above was further distilled at 65–68 °C and 1 mmHg to give a pale yellow oil (526 mg, 20%), and a thick gummy residue (420 mg). The distillate was one major peak on g.l.c. (2 ft Apiezon, 130 °C) which was characterised as 7-iodo-3-vinylbicyclo[4.1.0]heptane (29) (Found: M^+ , 248.005 5. Calc. for $\text{C}_9\text{H}_{13}\text{I}$: M , 248.006 4); τ 4.32 (ddd, J 18, 10, and 5 Hz, 1 H), 4.8–5.3 (complex, 2 H), 7.95 (t, J 3.5 Hz, 1 H), 7.5–9.1 (complex, 9 H); ν_{max} 3 080w, 3 020w, 1 640m, and 916s.

(b) At 25–35 °C. The dibromides (5.0 g) in ether (25 ml) were stirred at 25–35 °C and LiMe (20 ml, as above) was added cautiously. The first few drops caused a vigorous reaction and the formation of a white solid; when the reaction had subsided further addition again caused vigorous refluxing. The products were allowed to stand for 5 min and were then carefully quenched with water (25 ml). The organic layer was separated and the aqueous layer washed with ether (2×20 ml). The combined organic layers were dried (MgSO_4) and the solvent removed at reduced pressure without heating. Flash-distillation at 25–27 °C and 1 mmHg gave a colourless oil (1.07 g, 50%); a second fraction (1.43 g) was obtained at 77–80 °C, leaving only a small residue.

The second fraction was separated into two components by elution down CC-7 silica using light petroleum (b.p. 60–80 °C). The faster running component (1.1 g, 25%) was 6-iodotricyclo[3.3.1.0^{2,4}]nonane (17) (Found: M^+ , 248.004 5. Calc. for $\text{C}_9\text{H}_{13}\text{I}$: M , 248.006 4); τ 5.1 (br t,

J ca. 4 Hz, 1 H), 7.0—9.0 (complex, 10 H), and 9.25 (complex, 2 H); ν_{\max} . 3 075w, 3 020m, 860m, 825m, 810m, and 795m.

The second component (150 mg, 5%) was the *ether-insertion product* (18) (Found: M^+ , 194.167 9. $C_{13}H_{22}O$ requires M , 194.167 1); τ 4.3 (ddd, *J* 18, 10, and 5 Hz, 1 H), 5.15 (complex, 2 H), 4.6 (q, *J* 7 Hz, 2 H), 6.4 (q, *J* 6.5 Hz, 1 H), and 7.7—9.8 (complex, 16 H); ν_{\max} . 1 645m, 1 120vs, and 920s.

The volatile fraction of the distillate was separated into four components in the ratio ca. 6:5:1:1 on g.l.c. (2-ft silicone oil, 55 °C). The first component was 3-vinyltricyclo[4.1.0.0^{2,7}]heptane (19) (Found: M^+ , 120.094 9. C_9H_{12} requires M , 120.093 9); τ 4.0 (dd, *J* 17.5 and 10 Hz, 1 H), 4.8—5.2 (complex, 2 H), 7.6—8.2 (complex, 4 H), and 8.2—8.8 (5 H); ν_{\max} . 1 640m, 915s, 989m, 800m, 775m, and 720m. The second was 4-vinyltricyclo[4.1.0.0^{2,7}]heptane (20) (Found: M^+ , 120.093 8. C_9H_{12} requires M , 120.093 9); τ 4.4 (ddd, *J* 18, 10, and 6 Hz, 1 H), 4.8—5.4 (complex, 2 H), 7.6 (br s, 2 H), and 7.8—9.2 (complex, 7 H); ν_{\max} . 3 000m, 1 645m, 1 000m, 918s, and 920s. The third peak was tricyclo[3.3.1.0^{2,4}]non-6-ene (22) (see later); the fourth was 4-propadienylcyclohexene (21) (Found: M^+ , 120.094 2. C_9H_{12} requires M , 120.093 9); τ 4.4 (br s, 2 H), 4.97 (q, *J* 8 Hz, 1 H), 5.4 (dd, *J* 7 and 2.5 Hz, 2 H), and 7.6—8.7 (complex, 7 H); ν_{\max} . 1 965m, 1 655w, 870m, 850s, and 800m.

(c) At 25—35 °C with D_2O work-up. The dibromides (10 g) were stirred in Et_2O (30 ml) at 25—35 °C and LiMe (60 ml, as above) was added during 2—3 min. The products were allowed to stand for 2 min and D_2O (7.5 ml) was added dropwise; there was an initial vigorous reaction, a pause, and then a second more vigorous reaction. The products were worked-up as before and distilled to give a volatile fraction (2.1 g, 49%) and a residue (3.1 g). The latter was separated by elution through CC-7 (15 g) using light petroleum followed by 20% benzene in light petroleum. The former solvent eluted exo-4-deuterio-6-iodotricyclo[3.3.1.0^{2,4}]nonane (26) (2.7 g, 30%) (Found: M^+ , 249.009 2. $C_9H_{12}DI$ requires M , 249.012 7); τ 5.1 (br t, *J* ca. 4 Hz, 1 H), 7.9—9.0 (m, 9 H), and 9.25 (complex, 2 H); ν_{\max} . 3 070w, 3 020m, 915m (br), 865m, 845m, 793m, and 690m. The latter solvent eluted the *ether-insertion product* (18) (306 mg, 5%).

The volatile distillate was separated into four components by g.l.c. (2-ft silicone oil, 55 °C); the first, second, and fourth components were identical to those in (b) and did not contain any deuterium (mass spectrometry). The third component was exo-4-deuterio-tricyclo[3.3.1.0^{2,4}]non-6-ene (27) (see below).

(d) At -50 °C with D_2O work-up. The dibromides (3.0 g) in ether (25 ml) were stirred at -48 to -50 °C and methyl-lithium (16 ml, as above) was added during 10 min. The products were quenched with D_2O (5 ml) below -30 °C, allowed to warm to 20 °C, then washed with water (2 × 15 ml), dried ($MgSO_4$), and the solvent removed at 20 °C. Flash-distillation gave a volatile fraction (474 mg, 37%) at 24—26 °C and a second fraction (600 mg) at 70—75 °C and 1 mmHg, together with a small residue (100 mg). The second fraction was one major peak on g.l.c.; this was collected and characterised as 7-deuterio-7-iodo-3-vinylbicyclo[4.1.0]heptane (30; X = D) (Found: M^+ , 249.007 9. $C_9H_{12}DI$ requires M , 249.012 7); τ 4.3 (ddd, *J* 18, 10, and 5 Hz, 1 H), 4.9—5.3 (complex, 2 H), and 7.5—9.5 (complex, 9 H); ν_{\max} . 3 070w, 3 010m, 1 640w, 915m, 793m, and 740m.

The volatile fraction was spiro-compound (28), with no apparent deuterium incorporation by mass spectroscopy, together with ca. 10% of (21).

(e) The dibromides (5 g) in ether (10 ml) were treated with methyl-lithium (15 ml, 2M, Ventron) during 5 min at 25—35 °C. The products were quenched with water (10 ml), separated, and the organic layer washed with water (2 × 10 ml), dried ($MgSO_4$), and the solvent removed at 14 mmHg and room temperature. The products were flash-distilled at below 40 °C (1 mmHg) (1.6 g), leaving a residue (742 mg). G.l.c. showed the volatile fraction to contain (19)—(21) in ratios very similar to those from (a), but only a trace of (22); in addition ca. 20% of the product was the spiro-compound (28); this was confirmed by the characteristic high-field n.m.r. signal at τ 9.9.

The residue consisted of two major peaks on g.l.c., in the ratio ca. 1:3. Elution down alumina (15 g) using light petroleum (b.p. 40—60 °C) gave a brominated hydrocarbon (200 mg) and the ether-insertion product (18) (300 mg). The bromo-hydrocarbon showed M^+ at *m/e* 214/216, n.m.r. τ 4.2 (ddd, *J* 6, 9, and 17 Hz, 1 H), 4.8—5.2 (complex, 2 H), 7.2—9.2 (complex, 9 H), and 8.15 (br s, 3 H), and was characterised as 7-bromo-7-methyl-3-vinylbicyclo[4.1.0]-heptane.

Reaction of anti-7,7-Dibromo-3-vinylbicyclo[4.1.0]heptane with LiMe.—(a) At 25—35 °C. The enriched anti-dibromide (10) (0.5 g) was stirred in ether (10 ml) at 25—35 °C and LiMe (10 ml, from Li and MeI) was added during 2 min. Water (10 ml) was carefully added and the organic layer was separated and washed with more water (10 ml). After drying ($MgSO_4$) and removal of the solvent the organic residue was flash-distilled at 20—30 °C and 2.5 mmHg to give a ca. 5:6 mixture of 3-vinyltricyclo[4.1.0.0^{2,7}]heptane (19) and 4-vinyltricyclo[4.1.0.0^{2,7}]heptane (20) (110 mg, 51%). The residue (62 mg) contained a complex mixture of components, but the major peak corresponded in R_T to the ether-insertion compound (18).

(b) At -40 to -50 °C. The anti-dibromide (0.5 g) was stirred in ether (10 ml) at -40 to -50 °C and LiMe (10 ml) added as above. After quenching at below -20 °C the products were worked-up as in (a). G.l.c. showed very little in the C_9H_{12} region, and instead two peaks at longer R_T . Distillation at 82—88 °C and 2.5 mmHg gave a mixture of 7-iodo-3-vinylbicyclo[4.1.0]heptane (29) and an unidentified product (ca. 5:1, 143 mg), together with several minor peaks.

exo-Tricyclo[3.3.1.0^{2,4}]non-6-ene.—6-Iodotricyclo[3.3.1.0^{2,4}]nonane (17) (185 mg) was added to $KOBu^t$ (600 mg) in DMSO (4 ml) and set aside for 16 h at 25 °C. The products were poured into water (30 ml), extracted with ether (2 × 25 ml) and the combined organic layers were washed with water (3 × 15 ml), dried ($MgSO_4$), and the solvent removed at 14 mmHg and 20 °C. Flash-distillation at 25 °C and 1 mmHg gave exo-tricyclo[3.3.1.0^{2,4}]non-6-ene (22) (79 mg, 88%); τ 3.98 (m, 1 H), 4.70 (m, 1 H), 7.8 (m, 3 H), 8.05 (d,d *J* 17, 3.5, and 2.5 Hz, 1 H), 8.60 (td, *J* 7 and 3.5 Hz, 1 H), 8.75 (m, 2 H), 9.10 (td, *J* 7 and 3.5 Hz, 1 H), 9.68 (dt, *J* 5.5 and 3.5 Hz, 1 H), and 9.84 (td, *J* 7.5 and 6 Hz, 1 H); ν_{\max} . 3 070w, 3 030s, 1 660w, 1 635w, 987m, 930m, 870m (br), 937m, and 806s.

exo-4-Deuteriotricyclo[3.3.1.0^{2,4}]non-6-ene.—The 4-deuterio-iodide (1.5 g) was set aside for 16 h with $KOBu^t$ (2.0 g) in DMSO (10 ml) at 20 °C. The products were extracted as before to give as the sole volatile product exo-4-deuteriotricyclo[3.3.1.0^{2,4}]non-6-ene (27) (596 mg,

79%) (Found: M^+ , 121.099 9. $C_9H_{11}D$ requires M , 121.100 2); τ 4.0 (br dd, J 9 and 6.5 Hz, 1 H), 4.7 (br d, J 9 Hz, 1 H), 7.8 (m, 2 H), 8.05 (dt, J 17 and 2.5 Hz, 1 H), 8.74 (m, 2 H), 9.08 (dd, J 8 and 3 Hz, 1 H), 9.68 (dd, J 5.5 and 3.5 Hz, 1 H), and 9.88 (br t, J 6.5 Hz, 1 H); ν_{\max} 3 070w, 3 020m, 960m, 950m, 930m, 905m, 875m (br), and 840m.

There was a small residue (140 mg); the n.m.r. of this was complex, but showed a weak vinyl set (also present to a small extent in the starting iodide).

exo-6-Methoxytricyclo[3.3.1.0^{2,4}]nonane.—(a) 6-Iodotri-cyclo[3.3.1.0^{2,4}]nonane (300 mg) was stirred in methanol (2 ml) and $AgClO_4$ (600 mg) in methanol (2 ml) was added dropwise during 3–4 min. A slight exothermic reaction occurred and a heavy precipitate appeared. After 10 min, the products were poured into water (20 ml) and extracted with ether (2×15 ml). The combined organic layers were washed with water (2×10 ml), dried ($MgSO_4$), and the solvent removed at reduced pressure to leave a colourless oil (162 mg), which was practically pure by n.m.r. Flash-distillation at 40 °C and 1 mmHg gave *exo-6-methoxy-tricyclo[3.3.1.0^{2,4}]nonane* (34; $Y = OMe$) (102 mg, 64%) (Found: M^+ , 152.119 5. $C_{10}H_{16}O$ requires M , 152.120 1); τ 4.75 (s, 3 H) (superimposed on m, 1 H), 7.5–8.0 (complex, 3 H), 8.0–8.7 (complex, 5 H), 9.05 (dd, J 6.5 and 4 Hz, 2 H), and 9.6 (m, 2 H); ν_{\max} 1 115s and 1 098s.

(b) An n.m.r. solution of the spiro-compound (28) in CCl_4 was treated with methanol (3 drops). There was an immediate reaction. Removal of the excess of methanol gave the above ether, apparently as the sole product.

6-Acetoxytricyclo[3.3.1.0^{2,4}]nonane.—(a) 6-Iodotri-cyclo[3.3.1.0^{2,4}]nonane (300 mg) in acetic acid (2 ml) was treated with stirring with $AgOAc$ (600 mg) in acetic acid (2 ml). After 30 min the products were poured into water (50 ml), extracted with ether (2×30 ml) and the combined organic layers washed with saturated aqueous $NaHCO_3$ (2×25 ml), dried ($MgSO_4$), and the solvent removed at reduced pressure. Distillation of the residue (201 mg) at 65 °C and 1 mmHg gave *6-acetoxytricyclo[3.3.1.0^{2,4}]nonane* (194 mg, 89%) (Found: C, 73.45; H, 8.90%; M^+ , 180.115 1. $C_{11}H_{16}O_3$ requires C, 73.3; H, 8.9%; M , 180.115 0); τ 5.22 (br t, J ca. 4 Hz, 1 H), 8.05 (s, 3 H), 7.7–9.4 (complex, 10 H), and 9.6 (m, 2 H); ν_{\max} 3 080w, 3 020m, 1 735s, and 1 035s.

(b) The spiro-compound (28) (152 mg) in CCl_4 (1 ml) was treated dropwise with acetic acid (200 mg); there was an immediate exothermic reaction and the n.m.r. spectrum showed complete disappearance of the starting material after ca. 30 s. The products were poured into saturated aqueous $NaHCO_3$ (10 ml) and extracted with ether (2×10 ml). The combined organic layers were dried ($MgSO_4$) and the solvent removed at 14 mmHg to leave the acetate (155 mg, 68%).

3-Methylene-5-vinylcyclohexene.—(a) When an attempt was made to separate 4-vinyltricyclo[4.1.0.0^{2,7}]heptane (20) from other volatile products by g.l.c. through a 7-ft Apiezon column at 120 °C a rearrangement occurred and a single major new product was collected; the same product was obtained when pure (20) was injected under these conditions. It was characterised as *3-methylene-5-vinylcyclohexene* (24) (Found: M^+ , 120.094 0. C_9H_{12} requires M , 120.093 0); τ 3.95 (d, J 10 Hz, 1 H), 4–4.5 (complex, 2 H), 4.9–5.4 (complex, 4 H), and 7.5–8.2 (complex, 5 H); ν_{\max} 3 080m, 3 040m, and 1 640m. When the signal at τ 7.5–8.2 was irradiated (at τ 7.9), the signal at τ 4–4.5

was partially decoupled to produce a doublet, J 10 Hz, superimposed on other signals.

(b) Compound (20) (ca. 25 mg) was set aside for 18 h with $\{[Rh(CO)_2Cl]_2\}$ (5 mg) in benzene (0.5 ml). N.m.r. showed complete disappearance of the starting material and the formation of 3-methylene-5-vinylcyclohexene, which was purified by g.l.c.

2-Methoxy-4-vinylbicyclo[4.1.0]heptane.—(a) The mixture of volatile products from the reaction of the mixed di-bromides (10)–(12) with $LiMe-MeI$ at 25–35 °C (100 mg) in methanol (250 mg) was treated with toluene-*p*-sulphonic acid (2 mg). G.l.c. showed rapid reaction of the second component (4-vinyltricyclo[4.1.0.0^{2,7}]heptane) and its complete replacement after 15 min by one major and two minor products at longer R_T . The major product was collected and characterised as *2-methoxy-4-vinylbicyclo[4.1.0]heptane* (25; $Y = H$) (Found: M^+ , 152.120 7. $C_{10}H_{16}O$ requires M , 152.120 1) which showed τ 4.37 (ddd, J 18, 10, and 6 Hz, 1 H), 5.0–5.25 (complex, 2 H), 6.28 (quin, J 5.5 Hz, 1 H), 6.7 (s, 3 H), 7.9–8.5 (complex, 3 H), 8.7–9.1 (complex, 3 H), 9.3 (br dd, J 13 and 11 Hz, 1 H), 9.4 (dt, J 5 and 8, 5 Hz, 1 H), and 9.8 (q, J 5 Hz, 1 H); ν_{\max} 1 100vs.

(b) The mixed dibromides (5.0 g) in ether (50 ml) were treated with $LiMe$ (25 ml, 2M, Alfa Inorganics) during 5 min at 25–35 °C. The products were quenched with water (50 ml), washed with more water (2×50 ml), dried ($MgSO_4$), and the solvent removed at 14 mmHg; the residue was separated by distillation into a volatile fraction (at 28–32 °C and 1 mmHg) (1.62 g, 76%), and a less volatile fraction (at 60–70 °C) (470 mg) and a residue (250 mg). The second fraction consisted of the ether-insertion compound (18) and 7-bromo-7-methyl-3-vinylbicyclo[4.1.0]-heptane in the ratio ca. 3 : 1 by g.l.c.

The volatile fraction contained (by g.l.c.) the spiro-compound (28) together with (19)–(21), but no (17) was observed. Compound (28) was removed by reaction either with $MeOH$ or $LiH \cdot H_2O$. (i) The mixture (1.6 g) was treated with $MeOH$ (2.5 ml); an exothermic reaction occurred. After 15 min the products were flash-distilled at 1 mmHg, together with methanol. A colourless oil remained (551 mg, 20%), which was *6-methoxytricyclo[3.3.1.0^{2,4}]nonane* (see above). The distillate was treated with toluene-*p*-sulphonic acid (2 mg); a second exothermic reaction occurred, and g.l.c. showed that (20) had reacted. After a further 15 min the products were again flash-distilled to give a volatile fraction containing (19) and (21) and methanol, and a second fraction (452 mg, 16%), at 60–70 °C and 1 mmHg which contained three components in the ratio ca. 1 : 6 : 2. The major component was collected by g.l.c. and found to be *2-methoxy-4-vinylbicyclo[4.1.0]-heptane* (25; $Y = H$). (ii) The mixture (1.5 g) was treated with $LiH \cdot H_2O$ (2.2 g) in ether (10 ml). After 5 h the products were washed with water (2×10 ml), dried ($MgSO_4$), and the solvent removed carefully at 14 mmHg. Flash-distillation gave a mixture of (19)–(21) (635 mg) and a residue which was (17) by n.m.r. and g.l.c. (755 mg, 17%).

7-Deuterio-2-methoxy-4-vinylbicyclo[4.1.0]heptane (25; $Y = D$).—Experiment (i) as above was repeated using CH_3OD in place of CH_3OH giving (25; $Y = D$) (Found: M^+ , 153.125 8. $C_{10}H_{15}DO$ requires M , 153.120 4); τ 4.38 (ddd, J 18, 10, and 6 Hz, 1 H), 4.9–5.2 (complex, 2 H), 6.28 (quintet, J 5.5 Hz, 1 H), 6.7 (s, 3 H), 7.8–8.6 (complex, 3 H), 4.7–9.1 (complex, 3 H), 9.3 (dd, J 11 and 13 Hz, 1 H), and 9.4 (t, J 8.5 Hz, 1 H); ν_{\max} 1 640m, 1 095vs, and 915s.

Conversion of Spiro-compound (28) to Iodide (17).—

(a) The spiro-compound (28) (60 mg) in ether (5 ml) was treated with methyl-lithium (2 ml, from Li and MeI). After 45 min at 20 °C, water (10 ml) was added. The organic layer was dried (MgSO₄) and the solvent removed to leave the iodide (17) (55 mg, 44%).

(b) The spiro-compound (50 mg) was set aside for 30 min with lithium iodide hydrate (100 mg) in ether (1 ml); ether (10 ml) and water (10 ml) were then added and the organic layer was separated, dried, and the solvent removed at 14 mmHg to leave the iodide (17) (46 mg, 45%).

8-Methylenetricyclo[4.2.0.0^{2,7}]octane (37).—(a) G.l.c. of the spiro-compound (28) even with very low injector (ca. 60 °C), detector, and column temperatures, caused a rearrangement to the tricyclic derivative (37) (*M*⁺, 120.094 2. C₉H₁₂ requires *M*, 120.093 9); τ 5.68 (s, 1 H), 5.70 (s, 1 H), 7.31 (br s, 2 H), 7.72 (br d, 1 H), 7.85 (br s, 1 H), 8.3 (m, 2 H), 8.5 (m, 3 H), and 8.84 (d, *J* 11 Hz, 1 H); ν_{max} 3 080m, 3 040m, 1 685m, 925m, and 865s.

(b) Compound (28) (2.5 g) [containing ca. 10% (21)] was set aside overnight in benzene (2.5 ml) with silver perchlorate (100 mg). The solvent was removed carefully at 14 mmHg and the residue was flash-distilled at 25–35 °C and 1 mmHg to give a colourless oil (1.25 g) which was largely (37) (ca. 50%) by n.m.r. and g.l.c., together with unreacted allene.

5-Hydroxy-6-methylenebicyclo[3.2.1]octane (38).—8-Methylenetricyclo[4.2.0.0^{2,7}]octane (37) (70 mg, g.l.c. pure) in benzene (2 ml) was treated with mercury trifluoroacetate (1.1 mol. equiv.) in benzene (2 ml) and stirred for 4 h at 25 °C. The solvent was removed at reduced pressure and the residue extracted between ether and water (both 15 ml). The organic layer was dried, and the solvent removed at reduced pressure. G.l.c. (7-ft Apiezon, 100 °C) showed only one peak, which was collected and characterised as the alcohol (38) (60 mg, 74%) (Found: *M*⁺, 138.104 0. Calc. for C₉H₁₄O: *M*, 138.104 5); τ 4.98 (n.m., 1 H), 5.86 (br s, 1 H), 7.8 (br s, 1 H), 7.9 (br s, 1 H), 8.0–8.6 (complex, 8 H), and 7.5 (s, 1 H, OH); ν_{max} 3 500s (br), 1 660m, and 900s.

6-Methylenebicyclo[3.2.1]octan-5-one (39).—The above alcohol (38) (ca. 30 mg) was stirred with activated manganese dioxide (100 mg) in carbon tetrachloride (2 ml). After 45 min, n.m.r. showed complete reaction of the starting material and the appearance of new signals attributable to one product. G.l.c. (2-ft Apiezon, 100 °C) showed only one product, which was collected and characterised as the ketone (39) (Found: *M*⁺, 136.089 4. Calc. for C₉H₁₂O: *M*, 136.088 8); τ 4.28 (n.m., 1 H), 5.03 (n.m., 1 H), 7.36

(br s, 1 H), and 7.6–8.8 (complex, 10 H); ν_{max} 1 710s and 1 630m.

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