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# OPTICALLY ACTIVE DIHYDROPYRANS AND 3-METHYLENETETRAHYDROFURANS FROM CYCLOPROPENYLETHANOL DERIVATIVES

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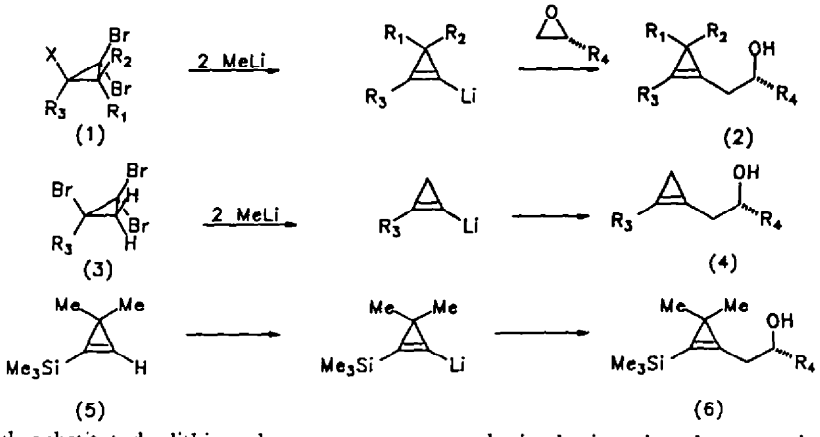
*Reaction of a number of 2-(cycloprop-1-en-1-yl)ethanol derivatives with bromine, acid or silver ion leads to ring expansion, either to 5,6-dihydro-2H-pyrans or to 3-methylenetetrahydrofurans.*

2-(Cycloprop-2-en-1-yl)ethanol derivatives undergo thermal, photochemical or metal induced rearrangement to dihydropyrans.[1] Related 2-(cycloprop-1-en-1-yl)ethanol derivatives have been prepared by ring-opening of epoxides by 1-sodiocyclopropene and are reported to add bromine rapidly, although the product(s) were not discussed.[2] We now report that this reaction leads from cyclopropenes (2), (4) and (6) to monobromo-dihydropyrans or to 3-(bromomethylene)tetrahydrofurans, that the cyclisation can also occur on reaction with acid or with silver ion, and that these reactions can be used to produce optically active heterocycles.*

The 2-(cycloprop-1-en-1-yl)ethanol derivatives were prepared by reaction of the corresponding 1-lithiocyclopropene[3] with an oxirane for 3 - 12 h at 20 °C:



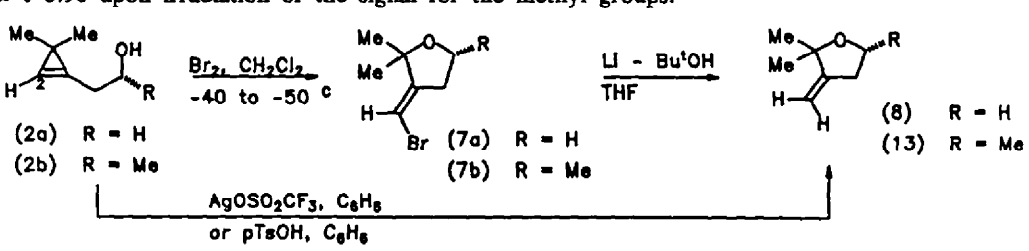

The alkyl-substituted lithiocyclopropenes were obtained *in situ* by reaction of the corresponding trihalocyclopropane with two equivalents of methyl lithium in ether.[3] The trimethylsilyl systems were prepared by reaction of the cyclopropene (5)[3] with methyl lithium and di-isopropylamine. The yields in the opening of the epoxides were, however, variable (Table 1) and the original, if less convenient, method involving sodiation of the free cyclopropene,[2] may in some cases be preferred. Compound (2f) was formed as a 1:1 mixture of diastereomers; apparently there is no diastereocontrol in the ring opening of the two enantiomers of epoxypropane by the racemic dimethyl-lithiocyclopropene.

Reaction of (2a) with bromine in $CH_2Cl_2$ for 30m at -40 °C gave (7a) (83%). Reduction of this with lithium - t-butanol - THF led to (8), which could be distinguished from an alternative product, 2,2-dimethyl-5,6-dihydro(2H)pyran on the basis of its $^{13}C$ n.m.r., which included

**Table 1 Preparation of cyclopropene substituted alcohols**

| Precursor | $R_1$ | $R_2$ | $R_3$ | Epoxide $R_4$ | Product | Yield |
|---|---|---|---|---|---|---|
| (1) | Me | Me | H | H | (2a) | 41 |
| (1) | Me | Me | H | Me | (2b) | 33 |
| (1) | Me | Me | H | (+)Me | (-)-(2b) | 29 |
| (1) | Me | Me | Me | H | (2c) | 80 |
| (1) | Me | Me | Me | Me | (2d) | 50 |
| (1) | Me | Me | Me | (-)Me | (+)-(2d) | 48 |
| (1) | Me | H | Me | H | (2e) | 58 |
| (1) | Me | H | Me | Me | (2f) | 41 |
| (3) | - | - | $Bu^t$ | H | (4a) | 78 |
| (3) | - | - | $Pr^i$ | H | (4b) | 77 |
| (5) | - | - | - | H | (6a) | 42 |
| (5) | - | - | - | (+)Me | (-)-(6b) | 34 |

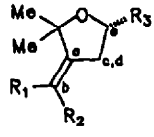
secondary and quaternary alkene carbons, and the positions of the olefinic and allylic hydrogens.[4] The E-stereochemistry of (7a) was assigned because of an n.O.e. enhancement in the alkene signal at $\delta$ 5.96 upon irradiation of the signal for the methyl groups.




Compound (8) was also obtained when (2a) was treated with either catalytic p-toluene sulphonic acid or silver trifluoromethanesulphonate in benzene for 12h at 20 °C (61, 47% respectively). In the case of the bromination of (2a), a mole of HBr is apparently generated during the reaction, but no products of protonation were observed; this may simply reflect the greater rate of the bromination reaction, in line with the relative rates of these reactions with simple alkenes.[11] When the reaction of (2c) with p-toluene sulphonic acid was carried out in acetic acid, only the corresponding acetate of the alcohol was produced!

Racemic alcohol (2b) underwent similar cyclisations, leading to (7b) (67%) and (13) (52%) respectively on treatment with bromine in dichloromethane for 30m at -50 °C or with p-TsOH in benzene for 15h at 20 °C. In the same way optically active alcohol (2b), derived from R-(+)-methyloxirane,[12] led to optically active (7b).

**Table 2**
**Selected chemical shifts for methylenefurans**

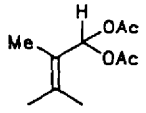


* X = Br, ** X = H, (stereochemistry uncertain)

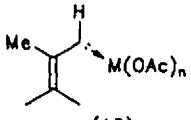
| $R_1$ | $R_2$ | $R_3$ | No | Carbon shifts a | b | Proton shifts c/d | e |
|---|---|---|---|---|---|---|---|
| H | Br | H | 7a | 153.5 | 97.5 | 2.69 | 3.95 |
| H | H | H | 8 | 156.5 | 103.6 | 2.6 | 3.8 |
| H | Br | Me | 7b | 154.6 | 97.2 | 2.82 | 4.16 |
| | | | | | | 2.22 | |
| H | H | Me | 13 | - | - | 2.66 | 4.05 |
| | | | | | | 2.26 | |
| Br | Me | H | 16* | 146.0 | 113.1 | 2.75 | 3.85 |
| H | Me | H | 16** | - | - | 2.57 | 3.79 |
| $Me_3Si$ | Br | H | 14a | - | - | 2.95 | 3.9 |
| $Me_3Si$ | H | H | | | | 2.7 | 3.7 |
| H | $Me_3Si$ | H | | 164.6 | 116.1 | 2.7 | 3.8 |

Although there are a number of reports of acid and electrophile addition to cyclopropenes,[5] few have examined the mechanism in detail. Addition can occur without rearrangement,[6] eg.,

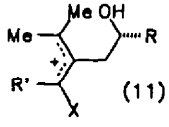
leading to 1,2-dihalocyclopropanes by halogen addition. In other cases ring-opening occurs. Addition of iodine isocyanate to 1,3,3-trimethylcyclopropene leads to an E-1-iodo-2,3-dimethylbut-1-enyl-3-amine derivative, apparently by $\pi$-attack of $I^+$ followed by ring opening to the allylic ion;[7] addition of bromine to the cyclopropene leads to 1,3-dibromo-2,3-dimethylbut-1-ene of unspecified stereochemistry.[8] In contrast, acetoxymercuration of 3,3-disubstituted cyclopropenes leads to Z-vinylmercury species,[9] although trimethylcyclopropene reacts with mercuric acetate to give (9) in a reaction formulated to involve the carbene complex (10).[10] Formally the formation of (7a) may involve attack of $Br^+$ at the less substituted end of the $\pi$-bond of (2a), cyclopropyl-allyl ring opening to give (11, R = R' = H, X = Br) and ring closure at the more substituted terminus of the allyl cation, although the detailed timing of these steps is not clear.



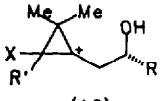
(9)



(10)



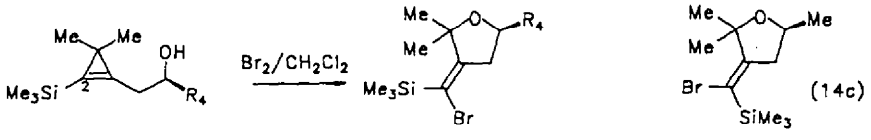
(11)



(12)

The E-stereochemistry may be controlled by a preferred outward rotation of the bromine substituent. This sequence involves at least two rotations, one bringing the three p-orbitals of the allyl system parallel, the second twisting the $CMe_2$-group approximately orthogonal to the final alkene so that cyclisation can occur. An alternative mechanism would involve attack on the back of the 2,3-cyclopropene $\sigma$-bond at C-2, leading to tertiary cationic character at C-3, concerted with attack at this position by the alcohol; this requires minimal rotational changes. Between these extremes there are a number of possibilities, the balance of which may depend on the electrophile, the substituents and the solvent. Attack on the 2,3-$\sigma$-bond at the front side of C-2 or either side of C-3 may also be possible. The full results of labelling studies to probe the mechanism and stereochemistry will be presented elsewhere.*

The cyclopropene (6a) underwent a similar cyclisation to produce (14a). The E-stereochemistry was assigned because irradiation of the $^1H$ n.m.r. signal for the trimethylsilyl group caused an n.O.e. enhancement in that for the geminal methyl. A minor product, the alkene (7a), was also obtained when (14a) was treated with hydrogen bromide in acetic acid, and is probably produced by reaction with acid generated during the bromination of (6a).[13] The regiochemistry may be explained by electrophilic attack of bromine at C-2 of (6a) leading to the development of positive charge $\beta$- to silicon, followed by ring-opening and trapping as before.



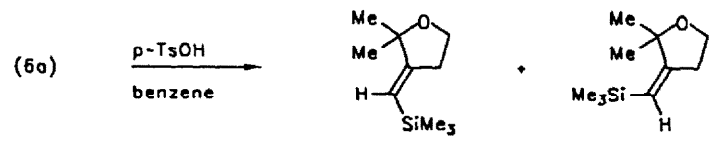
(14c)

(6a) $R_4$ = H (14a) minor product (7a)

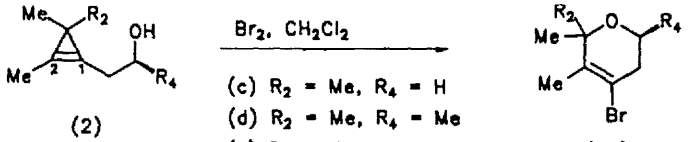
(6b) $R_4$ = Me (14b) minor products (7b), (14c)

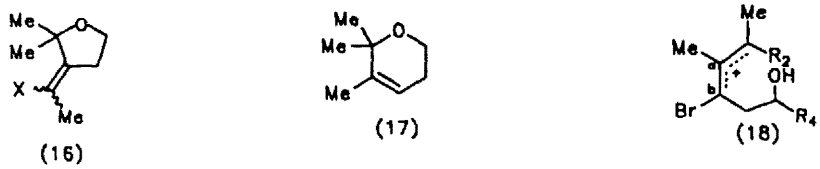
Treatment of (6a) with p-toluene sulphonic acid in benzene as above leads to a 2:1 mixture of E- and Z-3-(trimethylsilylmethylene)-2,2-dimethyltetrahydrofurans.++ It is interesting that the corresponding reaction of (5) with acid in methanol leads exclusively to E-3-methoxy-3-methyl-1-trimethylsilylbut-1-ene; the alcohol therefore exerts some intramolecular effect on

the stereochemistry.



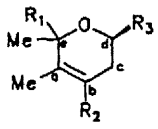

The introduction of a methyl group at C–2 of the cyclopropene caused an alternative cyclisation. Treatment of (2c) with bromine gave (15c) and (16, X = Br)[14] (ratio ca 5:1):




Reduction with Li – $^{t}$BuOH – THF led to (17) and (16, X = H); the allylic methylene group of the major isomer appeared at $\delta$ 2.04 whereas that in the minor one appeared at $\delta$ 2.57, in agreement with the assigned pyran,[4] and methylenefuran structures (N.B., shifts for (7a)).

**Table 3**
**Selected chemical shifts for dihydropyrans**

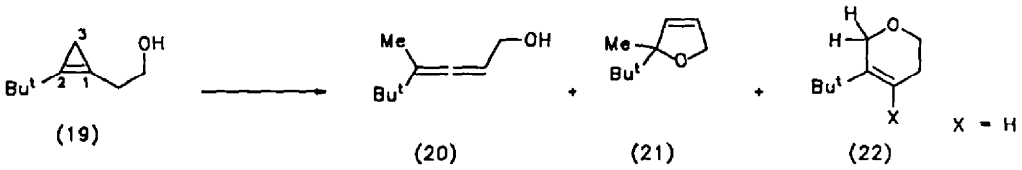


| $R_1$ | $R_2$ | $R_3$ | No | Carbon shifts a | Carbon shifts b | Proton shifts c | Proton shifts d | Proton shifts e |
|---|---|---|---|---|---|---|---|---|
| H | Br | H | 15e | 135.2 | 116.0 | 2.66<br>2.44 | 3.96<br>3.68 | 4.18 |
| H | H | H | 17 | 136.5 | 119.0 | 1.97<br>2.2 | 3.9<br>3.6 | 4.08 |
| Me | Br | Me | 15d | 137.5 | 116.4 | 2.44<br>2.35 | 3.94 | - |
| Me | Br | H | 15c | 137.9 | 116.6 | 2.55 | 3.75 | - |
| Me | H | H | 17 | - | - | 2.04 | 3.75 | |

Once again, the optically pure alcohol (2d), derived from S-(–)-methyloxirane, was converted to an optically active pyran (15d), although in low yield (32 %), while the 2,3-dimethylcyclopropene (2e) gave only the pyran (15e). In the case of the 1:1 mixture of diastereoisomers of (2f), a 2:1 mixture of diastereoisomers of the pyran (15f) was obtained; the signals for H–2 in the $^{1}$H n.m.r. of both isomers appeared as a broad quartet at $\delta$ 4.2, suggesting that both have the C–2 methyl group equatorial. The major isomer showed a sextet (J ca 6 Hz) for H–6, while the corresponding signal in the minor one was a double double quartet (J 3.9, 10.5, 6.2 Hz) at slightly higher field; the latter is therefore assigned as the *cis*-isomer, both substituents occupying equatorial positions, and the former as the *trans*-, the 6-substituent being axial.[15] The determination of the origin of each product requires the use of a single diastereoisomer of (2f). The reason that bromine apparently adds only or largely to C–1 of the $\pi$-bond in (2c–f) is not certain; however, related cyclopropene ring openings show subtle substituent effects.[16] It is not clear whether cation (18), if it is an intermediate, is formed exclusively with the geometry of

bond a–b required for cyclisation, or whether an isomerisation occurs.

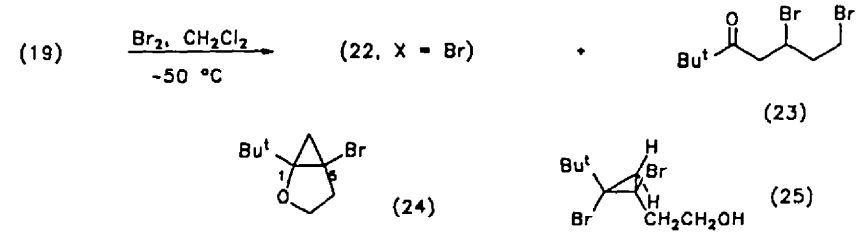
Reaction of the alcohol (19) with p-toluene sulphonic acid in benzene led to three products:



(19) (20) (21) (22) X = H

The allene (20) may arise by protonation of (19) at the methylene-end of the 1,3-$\sigma$-bond with subsequent or concurrent elimination of a allylic hydrogen. The dihydrofuran (21) may arise by acid induced ring closure of (20),[4] while (22, X = H) is apparently derived by protonation at the less hindered end of the $\pi$-bond, ring opening and cyclisation as before.

The reaction of (19) with bromine followed a different course. The origin of the ketone (23) is not certain. Addition of $Br^+$ to the less hindered end of the $\pi$-bond followed by intramolecular trapping by the alcohol could lead to (24); indeed, if the reaction was carried out in the presence of triethylamine at 0 °C, the only product was the cyclopropane (25), albeit in low yield. Protonation of the 1,5-bond of (24) at C-5 by the acid generated, and cleavage of the highly sterically hindered $\alpha$-oxycation by bromide at C-3 could in turn lead to (23).



(19) $\xrightarrow[-50\ °C]{Br_2,\ CH_2Cl_2}$ (22, X = Br) + (23)

(24) (25)

The reactions of (19) with $H^+$ and $Br^+$ therefore follow completely different courses – and can be explained in one case by $\sigma$-attack and in the other by $\pi$-attack. Once again this is in agreement with the known greater rate of reaction of bromine than a proton in reaction with $\pi$-bonds,[17] but greater rate of reaction of protons with the $\sigma$-bonds of cyclopropanes.[11]

We wish to thank the Government of Iraq for the Award of a grant to J.A-D.

## EXPERIMENTAL

Unless otherwise stated all new compounds were homogeneous by t.l.c. and/or g.l.c.; n.m.r. spectra were recorded in $CDCl_3$ solution, for $^1H$ at 200 or 300 MHz on Bruker Spectrospin instruments, and for $^{13}C$ at the corresponding carbon frequencies. Infra-red spectra were obtained on a Nicolet F.T. instrument, while mass spectra were measured on an AEI MS9 or a Kratos MS80 using the E.I. method; where mass measurements are quoted for bromine containing species, they refer to $^{79}Br$ isotope peaks. Optical rotations were measured in dichloromethane solution. All experiments involving methyl lithium were carried out under dry nitrogen. Petrol refers to the fraction boiling between 40 and 60 °C. Column chromatography was carried out over silica eluting with (a) 10:1, (b) 10:2 or (c) 20:1 petrol and ether.

### 2-(2,3,3-Trimethylcyclopropen-1-yl)ethanol (2c) and the corresponding acetate

(a) Methyl lithium (31.2 ml, 1.25 M, 2.5 mol.equiv.) was added over 5 m to a stirred solution of (1, $R_1$ = $R_2$ = $R_3$ = Me) (5.0 g, 0.015 mole) in ether (80 ml) at –40 – –50 °C. The

mixture was allowed to reach 20 °C and after 15 m was cooled again to −50 °C. Ethylene oxide (6 ml) was added and the mixture was stirred for 15 m at that temperature and then at 20 °C for 3 h, when water (10 ml) was added; the aqueous layer was washed with ether (3 x 30 ml) and the combined organic layers were washed with water (2 x 10 ml), and dried ($MgSO_4$). Removal of the solvent at 14 mmHg and flash distillation at 35 °C and 0.4 mmHg gave *2-(2,3,3-trimethylcyclopropen-1-yl)ethanol* (2c) (1.6 g, 80 %) (Found $M^+$: 126.1055. $C_8H_{14}O$ requires: 126.1045) which showed $\delta_H$ 3.74 (2 H, t, J 6 Hz), 3.42 (2H, m), 1.95 (3H, t, J 1.5 Hz), 1.05 (6H, s); $\nu_{max}$ 3342, 2928, 2853, 1047 $cm^{-1}$.

(b) Compound (2c) (0.2 g) was stirred for 24 h with acetic acid (0.1 g) in benzene (2 ml); t.l.c. showed only starting material. p-Toluene sulphonic acid (30 mg) was added; after 1 h, work up and chromatography[a] gave *2-(2,3,3-trimethyl-1-cyclopropenyl)ethyl acetate* (0.15 g) (Found $M^+$: 168.1157. $C_{10}H_{16}O_2$ requires: 168.1150) which showed $\delta_H$ 4.15 (2H, t, J 6 Hz), 2.62 (2H, br.t), 2.05 (3H, s), 1.92 (3H, narrow t), 1.01 (6H, s); $\nu_{max}$ 1744 $cm^{-1}$.

1-(2,3,3-Trimethylcyclopropen-1-yl)propan-2-ol (2d)

(a) The above reaction was repeated using methyl lithium (26 ml) and the tribromide (5.0 g) but using 1,2-epoxypropane (1.1 ml) in place of ethylene oxide and stirring for 12 h at 20 °C; work up and chromatography[a] as before gave *1-(2,3,3-trimethylcyclopropen-1-yl)propan-2-ol* (2d) (1.14 g, 50 %) (Found $M^+$: 140.1189. $C_9H_{16}O$ requires: 140.1201) which showed $\delta_H$ 3.80 (1H, br.sextet, J ca. 6 Hz), 3.3 (1H, br.s), 2.4 (1H, ddq, J 14.2, 8.8, 1.5 Hz), 2.33 (1H, ddq, J 14.2, 8.8, 1.5 Hz), 1.79 (3H, t, J 1.5 Hz), 1.08 (3H, d, J 6.2 Hz), 0.91 (6H, s); $\nu_{max}$ 3361, 2957, 2928, 2854, 1440, 1364, 1175, 1121, 944 $cm^{-1}$.

The alcohol (0.1 g) was refluxed for 6 h with triethylamine (50 mg) and (S)-(−)-phenylethylisocyanate (0.11 g). After removal of the solvent at 14 mmHg, chromatography[b] gave the urethane as a mixture of diastereoisomers (Found $M^+$: 287.1884. Required for $C_{18}H_{25}N_2O$: 287.1885) which showed $\delta_H$ (first isomer) 7.3 (5H, br.s), 4.96 (1H, q), 4.84 (2H, br.m), 2.57 (2H, m), 1.89 (3H, br.s), 1.47 (3H, d, J 6.7 Hz), 1.33 (3H, d, J 6.2 Hz), 1.02 (6H, s); (second isomer) 7.31 (5H, br.s), 4.97 (1H, q), 4.84 (2H, br.m), 2.57 (2H, m), 1.93 (3H, br.s), 1.47 (3H, d, J 6.7 Hz), 1.33 (3H, d), 1.05 (6H, s).

(b) Reaction as in (a) using (S)-(−)-1,2-epoxypropane (1.04 g) gave (+)-(2d) (1.1 g, 48 %) (Found $M^+$: 140.1189), $[\alpha]_D^{22}$ + 15 °. The alcohol was converted into the urethane by reaction with (S)-(−)-1-phenylethylisocyanate as above (Found $M^+$: 287.1884); the $^1H$ n.m.r. showed only the signals corresponding to the second isomer obtained from the racemic alcohol.

2-(3,3-Dimethylcyclopropen-1-yl)ethan-1-ol (2a)

The above reaction was repeated using methyl lithium (32 ml, 1.5 M), 1-chloro-2,2-dibromo-3,3-dimethylcyclopropane (5.0 g) and ethylene oxide (6 ml), stirring for 3 h at 20 °C before quenching. Careful removal of the solvent at 14 mmHg and chromatography[a] gave *2-(3,3-dimethylcyclopropen-1-yl)ethan-1-ol* (2a) (0.9 g, 41 %) (Found $M^+$: 112.0883. $C_7H_{12}O$ requires: 112.0888) which showed $\delta_H$ 6.85 (1H, br.s), 3.72 (2H, t, J 6 Hz), 3.1 (1H, br.s), 2.68 (2H, br.t, J 6.5 Hz), 1.12 (6H, s); $\nu_{max}$ 3343, 2931, 1760, 1451, 1049 $cm^{-1}$.

1-(3,3-Dimethylcyclopropen-1-yl)propan-2-ol (2b)

(a) The above reaction was repeated using 1,2-epoxypropane (6 ml) in place of ethylene oxide. Work up and chromatography as above led to *1-(3,3-dimethylcyclopropen-1-yl)propan-*

*2-ol* (2b) (0.8 g, 33 %) (Found M+: 126.1052. $C_8H_{14}O$ requires: 126.1045) which showed $\delta_H$ 6.85 (1H, br.s), 4.03 (1H, sextet, J 6 Hz), 2.72 (2H, d, J 6 Hz), 2.35 (1H, br.s), 1.35 (3H, d, J 6 Hz), 1.21 (3H, s), 1.15 (3H, s); $\nu_{max}$ 3366, 2965, 2931, 1758, 1453, 1366, 735 $cm^{-1}$.

(b) Reaction as in (a) using (R)-(+)-1,2-epoxypropane (1.2 g) gave (-)-(2b) (29 %).

2-(2,3-Dimethylcyclopropen-1-yl)ethan-1-ol (2e)

The above reaction was repeated using (1, $R_1$ = $R_3$ = Me, $R_2$ = H) (5.0 g) and ethylene oxide (5 ml), stirring for 4 h at 20 °C. Work up and chromatography[b] gave *2-(2,3-dimethyl-cyclopropen-1-yl)ethan-1-ol* (1.05 g, 58 %) (2e) (Found M+: 112.0882. $C_7H_{12}O$ requires: 112.0888) which showed $\delta_H$ 3.75 (2H, t, J 6 Hz), 2.6 (2H, br.t, J 6 Hz), 2.2 (1H, br.s), 2.0 (3H, narrow m), 1.3 (1H, m), 1.0 (3H, d, J 5.0 Hz); $\nu_{max}$ 3371, 2941, 1718, 1661, 1439, 1049 $cm^{-1}$.

1-(2,3-Dimethylcyclopropen-1-yl)propan-2-ol (2f)

Reaction as above using 1,2-epoxypropane (6 ml) in place of ethylene oxide for 20 h at 20 °C, work up and chromatography[b] gave a 1:1 mixture of isomers of *1-(2,3-dimethylcyclopropen-1-yl)propan-2-ol* (2f) (0.84 g, 41 %) which was a single spot on t.l.c. (Found M+: 126.1050. $C_8H_{14}O$ requires 126.1045) and showed $\delta_H$ (first isomer) 1.23 (3H, d, 6.2 Hz), 0.96 (3H, d, J 4.5 Hz); (second isomer) 1.22 (3H, d, J 6.2 Hz), 0.95 (3H, d, J 4.5 Hz) together with overlapping signals for both isomers at 4.01 (1H, sextet, J 6.1 Hz), 2.5 (2H, m), 2.06 (1H, br.s), 1.98 (3H, t, J 1.4 Hz), 1.3 (1H, m); $\nu_{max}$ 3410, 2969, 2933, 1713, 1375, 1116, 1076, 733 $cm^{-1}$.

2-(2-(Dimethylethyl)cyclopropen-1-yl)ethan-1-ol (4a)

Methyl lithium (28.7 ml, 1.5 M) was added as above to (3, $R_3$ = $Bu^t$) (5.0 g) in ether. Ethylene oxide (6 ml) was added as above. After 3 h at 20 °C, work up and distillation gave *2-(2-(dimethylethyl)cyclopropen-1-yl)ethan-1-ol* (4a) (1.9 g, 78 %), b.p. 45 °C at 0.4 mmHg (Found M+: 140.1215. $C_9H_{16}O$ requires 140.1201) which showed $\delta_H$ 3.8 (2H, t, J 6 Hz), 2.68 (2H, t, J 6 Hz), 2.02 (1H, s), 1.15 (9H, s), 0.84 (2H, s); $\nu_{max}$ 3349, 2963, 1361, 1050 $cm^{-1}$.

2-(2-(Methylethyl)cyclopropen-1-yl)ethan-1-ol (4b)

The above reaction was repeated using methyl lithium (30.2 ml), (3, $R_3$ = $Pr^i$) (5.0g) and ethylene oxide (6 ml). Work up and distillation gave *2-(2-(methylethyl)cyclopropen-1-yl)ethan-1-ol* (4b) (1.75 g, 77 %), b.p. 40 °C at 0.4 mmHg (Found M+: 126.1042. $C_8H_{14}O$ requires 126.1045) which showed $\delta_H$ 3.78 (2H, t, J 6.7 Hz), 3.52 (1H, s), 2.69 (3H, m), 1.2 (6H, d, J 6.7 Hz), 0.85 (2H, s); $\nu_{max}$ 3344, 2963, 2867, 1464, 1050 $cm^{-1}$.

2-(3,3-Dimethyl-2-trimethylsilylcyclopropen-1-yl)ethan-1-ol (6a)

Methyl lithium (31 ml, 1.3 mol.equiv.) was added to a stirred solution of (5) (5.0 g , 0.036 mol) and di-isopropylamine (6 ml) in ether (30 ml) at -78 °C. After 5 m, the products were allowed to reach 20 °C and cooled again to -50 °C, when ethylene oxide (6 ml) was added rapidly. After 30 m at -50 °C and 16 h at 20 °C, water (20 ml) was added. The aqueous layer was washed with ether (2 x 30 ml) and the organic layer was washed with water (30 ml), 0.5 M hydrochloric acid (30 ml), saturated aq. sodium bicarbonate (30 ml) and brine (30 ml) and dried. Removal of the solvent at 14 mmHg gave a brown oil which was purified by chromatography[b] to give *2-(3,3-dimethyl-2-trimethylsilylcyclopropen-1-yl)ethan-1-ol* (6a) (2.8 g, 42 %) (Found M+: 184.1286. $C_{10}H_{20}OSi$ requires: 184.1283) which showed $\delta_H$ 0.0 (9H, s), 0.95 (6H, s), 2.55 (2H, t, J 6.5 Hz), 3.6 (2H, t, J 6.5 Hz); $\nu_{max}$ 3339, 2957, 1780, 1249, 841 $cm^{-1}$.

(-)-1-(3,3-Dimethyl-2-trimethylsilylcyclopropen-1-yl)propan-2-ol (6b)

Reaction as above using methyl lithium (15.5 ml), cyclopropene (2.5 g), di-isopropylamine (3 ml) and (R)-(+)-epoxypropane (1.3 ml) gave *(-)-1-(3,3-dimethyl-2-trimethylsilylcyclopropen-1-yl)propan-2-ol* (6b) (1.2 g, 34 %) (Found $M^+$: 198.1430. $C_{11}H_{22}OSi$ requires 198.1440) which showed $\delta_H$ 4.0 (1H, sextet, J 6.2 Hz), 2.65 (2H, d, J 6.2 Hz), 1.25 (3H, d, J 6.2 Hz), 1.1 (3H, s), 1.09 (3H, s), 0.13 (9H, s); $\nu_{max}$ 3342, 2958, 2925, 1780, 1249, 1123, 840 $cm^{-1}$; $[\alpha]_D^{22}$ -14.85°.

E-3-(Bromomethylene)-2,2-dimethyltetrahydrofuran

Bromine (0.39 g) in dichloromethane (5 ml) was added dropwise to a stirred solution of (2a) (0.25 g) in dichloromethane (5 ml) at -40 °C. After 30 m, the reactants were allowed to reach 20 °C and the solvent was removed at 14 mmHg. Chromatography[a] gave *E-3-(bromomethylene)-2,2-dimethyltetrahydrofuran* (7a) (0.35 g, 83 %) (Found $M^+$: 190.0003. $C_7H_{11}BrO$ requires 189.9993) which showed $\delta_H$ 5.96 (1H, t, J 2.7 Hz), 3.95 (2H, t, J 7.0 Hz), 2.69 (2H, dt, J 2.7, 7.0 Hz), 1.31 (6H, s); $\delta_C$ 153.5s, 97.5d, 82.3s, 63.9t, 34.0t, 27.3q; $\nu_{max}$ 3074w, 2975s, 2867m, 1649m, 1285s, 1155s, 1040s, 741m, 712m $cm^{-1}$. Irradiation of the signal at $\delta$ 1.31 caused an ca 12 % n.O.e. enhancement in the signal at $\delta$ 5.96.

E-3-(Bromomethylene)-2,2,5-trimethyltetrahydrofuran

(a) Bromine (0.41 g) in dichloromethane (5 ml) was added dropwise with stirring to (2b) (0.30 g) in dichloromethane (5 ml) at -50 °C as above. After 30 m, the mixture was allowed to reach 20 °C and the solvent was removed at 14 mmHg. Chromatography[a] on the residue gave *E-3-(bromomethylene)-2,2,5-trimethyltetrahydrofuran* (7b) (0.32 g, 67 %) (Found $M^+$: 204.0146. $C_8H_{13}BrO$ requires 204.0150) which showed $\delta_H$ 5.92 (1H, dd, J 2.1, 3.1 Hz), 4.16 (1H, d.pentuplet, J 9.4, 6.0 Hz), 2.82 (1H, ddd, J 2.1, 5.8, 16.8 Hz), 2.22 (1H, ddd, J 3.1, 9.4, 16.8 Hz), 1.36 (3H, s), 1.31 (3H, d, J 6 Hz), 1.28 (3H, s); $\nu_{max}$ 3074w, 2974s, 2929m, 1649w, 1457w, 1382m, 1282m, 1166m, 1108m, 971m $cm^{-1}$.

(b) Reaction as in (a) using (-)-(2b) (0.30 g) to give *(R)-(-)-(7b)* (0.25 g, 52 %) (Found $M^+$: 204.0146. $C_8H_{13}BrO$ requires 204.0150) which was identical by $^1H$ n.m.r. to that in (a) and showed $\delta_C$ 154.6s, 97.2d, 82.7s, 71.4d, 41.7t, 28.9q, 27.4q, 21.1q; $[\alpha]_D^{25}$ -23.63 °.

3-Methylene-2,2,5-trimethyltetrahydrofuran

Compound (2b) (0.25 g) and p-toluene sulphonic acid (0.11 g) were stirred for 15 h at 20 °C in benzene (5 ml), when no starting material remained. The products were diluted with petrol, washed with saturated aq. sodium bicarbonate and then brine, and dried. Removal of the solvent at 760 mmHg gave an oil; chromatography[b] gave *3-methylene-2,2,5-trimethyltetrahydrofuran* (13) (0.13 g, 51 %) which was one peak by g.l.c. (Found $M^+$: 126.1045. $C_8H_{14}O$ requires 126.1038) which showed $\delta_H$ 4.86 (1H, dd, J 1.63, 2.5 Hz), 4.76 (1H, dd, J 1.7, 2.8 Hz), 4.05 (1H, m), 2.66 (1H, ddt, J 1.63, 5.5, 15.4 Hz), 2.26 (1H, ddt, J 2.8, 9.59, 15.4 Hz), 1.33 (3H, s), 1.26 (3H, d, J 7 Hz), 1.26 (3H, s); $\nu_{max}$ 2972, 2931, 1449, 1366, 1176, 1037, 937, 813, 756, 669 $cm^{-1}$.

2,2-Dimethyl-3-methylenetetrahydrofuran

(a) Compound (2a) (0.3 g) was stirred for 12 h at 20 °C with silver trifluoromethane sulphonate (0.3 g) in benzene (10 ml), when t.l.c. showed that no starting material remained. Removal of the solvent at 760 mmHg, and chromatography[b] gave *3-methylene-2,2-dimethyltetrahydrofuran* (8) (0.14 g, 47 %) (Found $M^+$: 112.0867. $C_7H_{12}O$ requires 112.0888) which

showed $\delta_H$ 4.91 (1H, t, J 2.15 Hz), 4.79 (1H, t, J 2.35 Hz), 3.8 (2H, t, J 6.9 Hz), 2.6 (2H, tt, J 2.2, 6.9 Hz), 1.29 (6H, s); $\nu_{max}$ 3077w, 2974s, 2929m, 2860m, 1664w, 1360m, 1160s, 1042s, 886m cm $^{-1}$; m/z 97 ($M^+ - CH_3$); $\delta_C$ 156.5s, 103.6t, 81.3s, 64.4t, 33.3t, 27.7q. Irradiation of the signal at $\delta$ 1.29 caused an ca 10 % n.O.e. enhancement only in the alkene signal at $\delta$ 4.79, with no enhancement in that at $\delta$ 4.91.

(b) The above reaction was repeated using p.toluene sulphonic acid (0.15 g) in place of the silver salt. Work up gave (8) (0.18 g, 61 %) identical by n.m.r. and i.r. to that obtained in (a).

(c) Lithium metal (100 mg) was stirred with (7a) (0.5 g) and t-butanol (1.0 ml) in tetrahydrofuran (10 ml). After 5 m, an exothermic reaction began; this was controlled by cooling so that the mixture refluxed gently over a period of 1 h. After a further 2 h at 20 °C, the products were poured into ice-water and extracted with ether (5 x 10 ml). The combined organic layers were washed with water (10 ml) and brine (20 ml), and dried; the solvent was removed carefully at 760 mmHg to give (8) (0.21 g, 71 %) identical to that obtained above.

2,2-Dimethyl-E-3-(2-bromo-2-trimethylsilylmethylene)tetrahydrofuran

(a) Bromine (0.48 g) in dichloromethane (5 ml) was added to (6a) (0.5 g) in dichloromethane (5 ml) as above. Work up and chromatography[a] gave *2,2-dimethyl-E-3-(2-bromo-2-trimethylsilylmethylene)tetrahydrofuran* (14a) (0.38 g, 53 %) (m/z 247 ($M^+$ - Me), 189 ($M^+$ - $SiMe_3$), 183 ($M^+$ - Br)) which showed $\delta_H$ 3.9 (2H, t, J 6 Hz), 2.95 (2H, t, J 6 Hz), 1.4 (6H, s), 0.34 (9H, s); $\nu_{max}$ 2975s, 2863m, 1600w, 1251s, 1148m, 1056s, 878s, 843s, 734m cm $^{-1}$. The E-stereochemistry was assigned because irradiation of the signal at $\delta$ 1.4 caused an ca 2 % n.O.e. enhancement in the signal at 0.34. A second product (40 mg, 8 %) was identical to (7a).

(b) Compound (14a) (50 mg) was stirred for 1 h with 48 % hydrogen bromide in acetic acid (2 ml) in tetrahydrofuran (2 ml), when t.l.c. showed no starting material remained. The mixture was washed with saturated aq. sodium bicarbonate and extracted with ether (3 x 5 ml). Removal of the solvent from the dried organic layer at 14 mmHg gave an oil which gave one peak on g.l.c. This was collected and shown to be identical to (7a) obtained above.

E- and Z-2,2-Dimethyl-3-(trimethylsilylmethylene)tetrahydrofurans

Compound (6a) (0.4 g) was stirred for 3.5 h at 20 °C with p.toluene sulphonic acid (0.12 g) in benzene (5 ml). Work up and chromatography[a] gave a 2:1 mixture of isomers (0.21 g, 53 %) as an oil which were separated by preparative g.l.c. The first was *2,2-dimethyl-E-3-(trimethylsilylmethylene)tetrahydrofuran* (Found $M^+$: 184.1290. $C_{10}H_{20}OSi$ requires 184.1283) which showed $\delta_H$ 5.12 (1H, t, J 2 Hz), 3.8 (2H, t, J 7 Hz), 2.67 (2H, dt, J 2, 7 Hz), 1.2 (6H, s), 0.1 (9H, s); $\delta_C$ 164.6s, 116.1d, 82.8s, 64.3t, 32.6t, 27.4q, -0.5q; $\nu_{max}$ 2972, 1634, 1376, 1247, 1154, 1073, 869, 843 cm$^{-1}$. Irradiation of the signal at $\delta$ 1.2 caused an ca. 13 % enhancement in that at $\delta$ 5.12, and none in that at 0.1. The second was *2,2-dimethyl-Z-3-(2-trimethylsilylmethylene)tetrahydrofuran* (Found $M^+$: 184.1296) which showed $\delta_H$ 5.4 (1H, t, J 2 Hz), 3.7 (2H, t, J 7 Hz), 2.7 (2H, dt, J 2, 7 Hz), 1.34 (6H, s), 0.14 (9H, s); $\nu_{max}$ 2970, 1629, 1377, 1360, 1249, 1148, 1047, 839 cm$^{-1}$. Irradiation of the signal at $\delta$ 1.34 caused a 4 % enhancement in that at 0.14, but none in that at 5.4; irradiation at 0.14 caused an equal enhancement at 1.34.

Reaction of 3-(2-trimethylsilyl-3,3-dimethylcyclopropen-1-yl)propan-2-ol with bromine

Bromine (0.41 g) in dichloromethane (5 ml) was added over 5 m to the alcohol (0.5 g) in dichloromethane (5 ml) at - 40 °C as above. Work up and chromatography[a] gave an oil (0.34 g,

49 %) which was a mixture of E- and Z-3-(2-bromo-2-trimethylsilylmethylene)-2,2,5-trimethyltetrahydrofurans in ratio 5:1 (Found: M+: 276.0521. $C_{11}H_{21}BrOSi$ requires: 276.0545) which showed $\delta_H$ (major) 4.1 (1H, m), 3.04 (1H, dd, J 4.45, 17.4), 2.43 (1H, dd, J 10.2, 17.4), 1.47 (3H, s), 1.38 (3H, s), 1.27 (3H, d, J 6.0 Hz), 0.33 (9H, s); (minor) 4.1 (1H, m), 2.71 (1H, dd, J 4.8, 15.3 Hz), 2.17 (1H, dd, J 10.5, 15.4 Hz), 1.58 (3H, s), 1.5 (3H, s), 1.27 (3H, d, J 6.0 Hz), 0.24 (9H, s); $\nu_{max}$ 2973, 2932, 1600, 1382, 1249, 1162, 1116, 1056, 971, 868, 842, 763, 695. The major isomer was characterised as E- because irradiation of the signal at $\delta$ 0.33 caused 2.5 and 1.9 % enhancements in the signals at $\delta$ 1.47 and 1.38; irradiation at $\delta$ 0.24 caused no enhancement in the signals of the minor isomer. In addition, a minor product was (7b) (0.05 g, 10 %) which was identical by n.m.r. to that obtained above.

4-Bromo-2,2,3-trimethyl-5,6-dihydro[2H]pyran

(a) Bromine (0.69 g) in dichloromethane (5 ml) was added to (2e) (0.5 g) in dichloromethane (5 ml) as above. Work up and column chromatography[a] gave an oil (0.41 g, 47 %) (Found M+: 204.0164. $C_8H_{13}BrO$ requires 204.0150) which was one peak by g.l.c., but was an ca. 5:1 mixture of 4-bromo-2,2,3-dimethyl-5,6-dihydro[2H]pyran which showed $\delta_H$ 3.75 (2H, t, J 7 Hz), 2.55 (2H, tq, J 7, 2 Hz), 1.83 (3H, t, J 2 Hz), 1.35 (6H, s); $\delta_C$ 137.9s, 116.6s, 60.0t, 36.8t, 26.0q, 19.0q, and 3-(1-bromoethylidene)-2,2-dimethyltetrahydrofuran which showed $\delta_H$ 3.85 (2H, t, J 7 Hz), 2.75 (2H, tq, J 7, 2 Hz), 2.37 (3H, t, J 2 Hz), 1.4 (6H, s); $\delta_C$ 146s, 113.1s, 81.6s, 38.9t, 26.0q (the remaining signals were presumably underneath those of the major isomer). The mixture showed $\nu_{max}$ 2976s, 2930s, 2869m, 1656w, 1276m, 1095s, 724w $cm^{-1}$.

(b) Lithium metal (150mg) was stirred with the mixture obtained above (0.5 g) and t-butanol (1.0 g) in tetrahydrofuran (10 ml). After 5 m, an exothermic reaction ensued which was controlled by cooling so that a gentle refluxing occurred for 1 h. The products were refluxed for 1 h and stirred at 20 °C for 2 h, poured into ice water and extracted with ether (5 x 20 ml). The combined organic layers were washed with water (3 x 10 ml) and brine (20 ml), and dried and the solvent was removed by careful distillation at 760 mmHg. Chromatography[a] of the residue gave an oil (0.21 g, 71 %) which gave one peak on g.l.c. but was an ca. 5:1 mixture of two components (Found M+: 126.1039. $C_8H_{14}O$ requires 126.1045). The major component was *2,2,3-trimethyl-5,6-dihydro[2H]pyran* (17) (Found M+: 126.1039. $C_8H_{14}O$ requires 126.1045) which showed $\delta_H$ 5.4 (1H, m), 3.75 (2H, t, J 5.5 Hz), 2.04 (2H, m), 1.64 (3H, m), 1.28 (6H, s); $\nu_{max}$ 2974, 2923, 1451, 1217, 1094, 1052 $cm^{-1}$. The minor component, provisionally characterised as either E- or Z-3-ethylidene-2,2-dimethyltetrahydrofuran (16, X = H) and showed $\delta_H$ 5.37 (1H, tq, J 2, 7.3 Hz), 3.79 (2H, t, J 5.5 Hz), 2.57 (2H, m), 1.59 (3H, m), 1.38 (6H, s).

4-Bromo-2,3,6-trimethyl-5,6-dihydro[2H]pyran

Bromine (0.66 g) in dichloromethane (5 ml) was added to (2f) (0.5 g) in dichloromethane (5 ml) as above. Chromatography[a] gave cis- and trans-4-bromo-2,3,6-trimethyl-5,6-dihydro-[2H]pyran (0.3 g, 37 %) (Found M+: 204.0157. $C_8H_{13}BrO$ requires 204.0150). These appeared as two peaks on capillary g.l.c. but could not be separated by preparative g.l.c. The mixture showed $\delta_H$ (major isomer) 4.2 (1H, m), 4.01 (1H, sextet, J ca.6.5 Hz), 2.4 (2H, m), 1.75 (3H, narrow t), 1.32 (3H, d, J 6.6 Hz), 1.21 (3H, d, J 6.2 Hz); (minor isomer) 4.2 (1H, m), 3.72 (1H, ddq, J 3.9, 10.5, 6.2 Hz), 2.4 (2H, m), 1.75 (3H, narrow t), 1.27 (3H, d, J 6.6 Hz), 1.22 (3H, d, J 6.1 Hz); $\nu_{max}$ 2976, 2931, 1668, 1445, 1382, 1212, 910, 734 $cm^{-1}$.

4-Bromo-2,3-dimethyl-5,6-dihydro[2H]pyran

Bromine (0.72 g) in dichloromethane (5 ml) was added to (2e) (0.5 g) in dichloromethane (5 ml) as above. Work up and chromatography[a] gave *4-bromo-2,3-dimethyl-5,6-dihydro-[2H]pyran* (0.41 g, 48 %) (Found $M^+$: 190.0010. $C_7H_{11}BrO$ requires 189.9993) showed $\delta_H$ 4.18 (1H, br.q, J 6.6 Hz), 3.96 (1H, dddd, J 0.4, 3.9, 5.4, 11.2 Hz), 3.68 (1H, ddd, J 11.2, 8.3, 4.3 Hz), 2.66 (1H, v.complex d, J 14.0 Hz), 2.44 (1H, v.complex d, J 14.0 Hz), 1.75 (3H, ddd, 0.95, 1.7, 2.2 Hz), 1.28 (3H, d, J 6.6 Hz); $\delta_C$ 135.15s, 116.0s, 74.8d, 63.4t, 36.5t, 19.36q, 18.84q; $\nu_{max}$ 2977m, 2934m, 2858m, 1666w, 1374m, 1267m, 1121s, 1073m, 871w, 786w $cm^{-1}$.

2,3-Dimethyl-5,6-dihydro[2H]pyran

Lithium metal (100mg) was added to a stirred solution of 4-bromo-2,3-dimethyl-5,6-dihydro[2H]pyran (0.5 g) and t-butanol (1.0 g) in tetrahydrofuran (10 ml). After 5 m, an exothermic reaction ensued which was controlled by cooling so that a gentle refluxing occurred for 1 h. The products were refluxed for 1 h, stirred at 20 °C for 2 h, and then poured into ice water and extracted with ether (5 x 10 ml). The combined organic layers were washed with water (10 ml) and brine (20 ml), and dried and the solvent was removed at 760 mmHg to give *2,3-dimethyl-5,6-dihydro[2H]pyran* (0.19 g, 67 %). An analytical sample was obtained by preparative g.l.c. (Found $M^+$: 112.0867. $C_7H_{12}O$ requires 112.0888) which showed $\delta_H$ 5.5 (1H, m, $W_{1/2}$ 7 Hz), 4.08 (1H, br.q, J 6.5 Hz), 3.9 (1H, ddd, J 3.7, 5.4, 11.1 Hz, further split into t, J ca. 0.5 Hz), 3.6 (1H, ddd, J 4.2, 8.7, 11.1 Hz), 2.2 (1H, complex), 1.97 (1H, complex), 1.61 (3H, narrow m), 1.25 (3H, d, J 6.5 Hz); $\delta_C$ 136.5s, 119.0d, 72.5d, 62.0t, 25.3t, 19.0q, 18.8q; $\nu_{max}$ 2970s, 2940m, 1710w, 1443m, 1372m, 1116s, 1081m, 1046m, 889w, 861m $cm^{-1}$.

4-Bromo-2,2,3,6-tetramethyl-5,6-dihydro[2H]pyran

(a) Bromine (0.25 g) in dichloromethane (5 ml) was added to (2d) (0.2 g) in dichloromethane (5 ml) as above. Work up and chromatography[a] gave *4-bromo-2,2,3,6-tetramethyl-5,6-dihydro[2H]pyran* (15d) (0.105 g, 32 %) (Found $M^+$: 218.0313. $C_9H_{15}BrO$ requires 218.0306) which showed $\delta_H$ 3.94 (1H, complex m), 2.44 (1H, complex), 2.35 (1H, complex d, J 15 Hz), 1.79 (3H, dd, J 1.5, 2.4 Hz), 1.32 (3H, s), 1.30 (3H, s), 1.19 (3H, d, J 6.1 Hz); $\delta_C$ 137.5s, 116.4s, 77.0s, 65.3d, 44.2t, 28.3q, 24.5q, 21.3q, 18.9q; $\nu_{max}$ 2976, 1668, 1445, 1382, 1360, 1212, 910, 734 $cm^{-1}$.

(b) Reaction as in (a) above using (S)-(+)-(2d) gave *(+)*-(15d) (0.10 g, 33 %) (Found $M^+$: 218.0313. $C_9H_{15}BrO$ requires 218.0306), $[\alpha]_D^{22}$ +115 °.

Reaction of 2-(2-(dimethylethyl)cyclopropen-1-yl)ethanol with acid

Compound (4a) (1.0 g) was stirred for 12 h at 20 °C with p.toluene sulphonic acid (0.4 g) in benzene (10 ml). Work up as above gave an oil which was flash distilled at 20 °C and 14 mmHg to give *2-methyl-2-t-butyl-2,5-dihydrofuran* (0.1 g, 10 %) which showed $\delta_H$ 5.7 (2H, narrow m), 4.65 (1H, d, J 21 Hz), 4.60 (1H, ddd, J 21, 0.7, 1.5 Hz), 1.2 (3H, s), 0.9 (9H, s); $\delta_C$ 132.5d, 125.3d, 95.2s, 75.2t, 38.0s, 25.7q, 21.6t; $\nu_{max}$ 3078w, 2963s, 2871s, 2842m, 1365m, 1084s, 1038m, 712m $cm^{-1}$. The residue was separated into two components by chromatography.[a] The first was *3-t-butyl-5,6-dihydro[2H]pyran* (0.18 g, 18 %) (Found $M^+$: 140.1215. $C_9H_{16}O$ requires: 140.1201) which showed $\delta_H$ 5.5 (1H, m), 4.15 (2H, m), 3.68 (2H, t, J 6.0 Hz), 2.15 (2H, m), 1.05 (9H, s); $\nu_{max}$ 2964s, 2907m, 1689, 1464, 1364, 1112, 911 $cm^{-1}$. The second was *4,5,5-trimethylhexa-2,3-dien-1-ol* (0.35 g, 35 %) (Found $M^+$: 140.1208) which showed $\delta_H$ 5.22 (1H, m), 4.05 (2H, d, J 6 Hz), 1.7 (3H, d, J 3 Hz), 1.42 (1H, br.s), 1.02 (9H, s); $\nu_{max}$ 3347br.s, 2964s, 2869m, 1960w,

1362m, 1012m, 735m $cm^{-1}$. Irradiation at $\delta$ 1.7 reduced the signal at 5.22 to a triplet (J 6 Hz).

Reaction of 2-(2-(dimethylethyl)cyclopropen-1-yl)ethanol with bromine

Bromine (1.14 g) in dichloromethane (5 ml) was added as before to (4a) (1.0 g) in dichloromethane (5 ml). Work up and chromatography[c] gave two products. The first was *4-bromo-3-(dimethylethyl)-5,6-dihydro[2H]pyran* (0.28 g, 18 %) (Found $M^+$: 218.0294. $C_9H_{15}BrO$ requires: 218.03060) which showed $\delta_H$ 4.18 (2H, t, J 2.5 Hz), 3.68 (2H, t, 5.7 Hz), 2.62 (2H, tt, J 2.5, 5.7 Hz), 1.26 (9H, s); $\nu_{max}$ 1671, 1255, 1111, 1049, 759 $cm^{-1}$. The second was *5,7-dibromo-2,2-dimethylheptan-3-one* (1.3 g, 61 %) (Found $M^+$: 297.9556. $C_9H_{16}Br_2O$ requires: 297.9556) which showed $\delta_H$ 3.65 (1H, br.pent, J ca.6.3 Hz), 3.55 (1H, dd, J 7.0, 9.9 Hz), 3.42 (1H, br.dt, J 10.4, 6.8 Hz), 3.31 (2H, m), 2.23 (1H, dq, J 14.7, 7.0 Hz), 2.06 (1H, dq, J 14.7, 6.8 Hz), 1.22 (9H, s); $\delta_C$ 214.7s, 46.3d, 44.8s, 34.8t, 31.7t, 30.1t, 26.4q; $\nu_{max}$ 2970, 2909, 1703, 1478, 654 $cm^{-1}$.

3-Methoxy-3-methyl-1-trimethylsilylbut-1-ene

3,3-Dimethyl-1-trimethylsilylcyclopropene (0.5 g) was stirred for 48 h at 20 °C with p.toluene sulphonic acid (0.13 g) and methanol (2 ml) in dry benzene (6 ml). T.l.c. then showed complete reaction. The products were washed with saturated aq. sodium bicarbonate and the aqueous layer was extracted with ether (3 x 15 ml), dried and the solvent removed carefully at 760 mmHg. The residue was *E-3-methoxy-3-methyl-1-trimethylsilylbut-1-ene* (0.38 g, 62 %) (m/z 141 ($M^+$ - OMe)) which showed $\delta_H$ 5.97 (1H, d, J 19.2 Hz), 5.76 (1H, d, J 19.2 Hz), 3.14 (3H, s), 1.2 (6H, s), 0.07 (9H, s); $\nu_{max}$ 2976, 2957, 2167, 1735, 1618, 1461, 1375, 1249, 1076 $cm^{-1}$.

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* For a preliminary account of this see J.R.AlDulayymi and M.S.Baird, *Tetrahedron Letters*, 1989, 253.

++ After 4 days in deuteriochloroform at 20 °C, the E- isomer had 50 % rearranged to 2,2-dimethyl-3-(trimethylsilylmethyl)-2,5-dihydrofuran. Under the same conditions, the Z-isomer rearranged to a 1:2:1 mixture of itself, the E-isomer and the dihydrofuran. Presumably both processes occur by protonation of the exocyclic alkene by traces of acid in the solvent, to generate a tertiary cation $\beta$- to silicon, followed by alternative deprotonations. Such a process could clearly occur in the reaction of (6a) with acid, altering the E/Z-ratio in favour of the E-form. However, since less than 5 % of the dihydrofuran was observed in this process and the ratio was 2:1, the isomerisation is apparently not occurring to a major extent under the reaction conditions. A full account of the isomerisation will be provided elsewhere.