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Intramolecular Trapping of Esters by 1-Lithio-1-bromocyclopropanes

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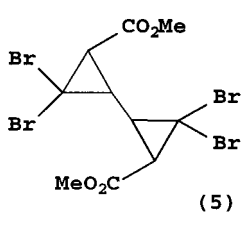
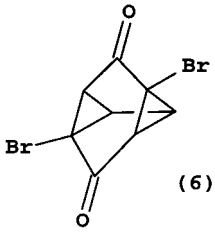
Abstract—Reaction of 2-acyloxymethyl-1,1-dibromocyclopropanes with methyllithium at −90°C leads to selective bromine–lithium exchange and intramolecular cyclisation to give a 1-bromo-3-oxabicyclo[3.1.0]hexan-2-ol.

The reaction of 1,1-dibromocyclopropanes with methyllithium is known to lead to a very rapid lithium–halogen exchange, followed in most cases by formal elimination of lithium bromide to produce a cyclopropylidene (or a related carbenoid).[1] If the reaction is carried out at low temperature or, in some cases, if there is a co-ordinating group present in the molecule, the organolithium may be trapped in intermolecular processes by reaction with electrophiles.[1] There are many examples of intramolecular trapping of the cyclopropylidene; thus insertion into CH bonds is a unique reaction of carbenes and is of considerable synthetic potential,[2,3] e.g. in the presence of monocyclic ethers,[4] sulfides[5] and amines[6] of the general structure (**1**) insertion occurs exclusively at the CH bond adjacent to the heteroatom and 5,6-related to the carbenic carbon (1,5-insertion) to give (**4**) (Scheme 1). This type of insertion was the key step in the total synthesis of the natural product 3,4-methanoproline.[7]

There are fewer cases of similar intramolecular reactions of the lithiobromides acting as nucleophiles; one such is the 1,3-elimination of BrCl from 1,1-dibromo-2-chloromethylcyclopropanes on reaction with methyllithium.[8] It is to be noted that with the related 2-(2-haloethyl)- or 2-(3-halopropyl)- systems no cyclisation is observed and only allenes derived from the cyclopropylidene are isolated.[8] In another type of process, the reaction of the tetrabromide (**5**) with methyllithium leads to the tetracyclic diketone (**6**) apparently by a double intramolecular trapping of the derived lithiobromides by the ester group in the adjacent cyclopropane ring.[9] In a rather simpler system, methyl 3-(2,2-dibromocycloprop-1-yl)propanoate is converted into 1-bromobicyclo[3.1.0]hexan-2-one by reaction with methyllithium.[10]

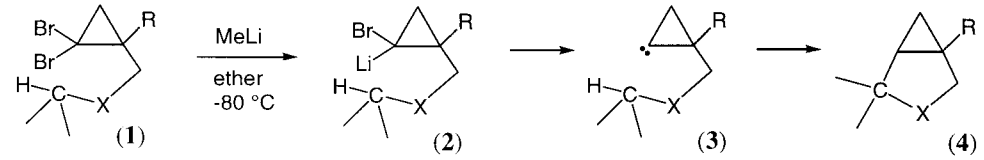


(**5**)



(**6**)

We now report that reaction of the esters (**15**), (**16**) derived from cyclopropylmethanols with methyllithium leads to the intramolecular trapping of a lithiobromocyclopropane with the formation of a five-membered ring (Scheme 3).[11] The corresponding reaction of amides will be described elsewhere.



R = H, Me; X = O, NR[1], S

Scheme 1.

Keywords: intramolecular trapping; esters; 1-lithio-1-bromocyclopropanes.
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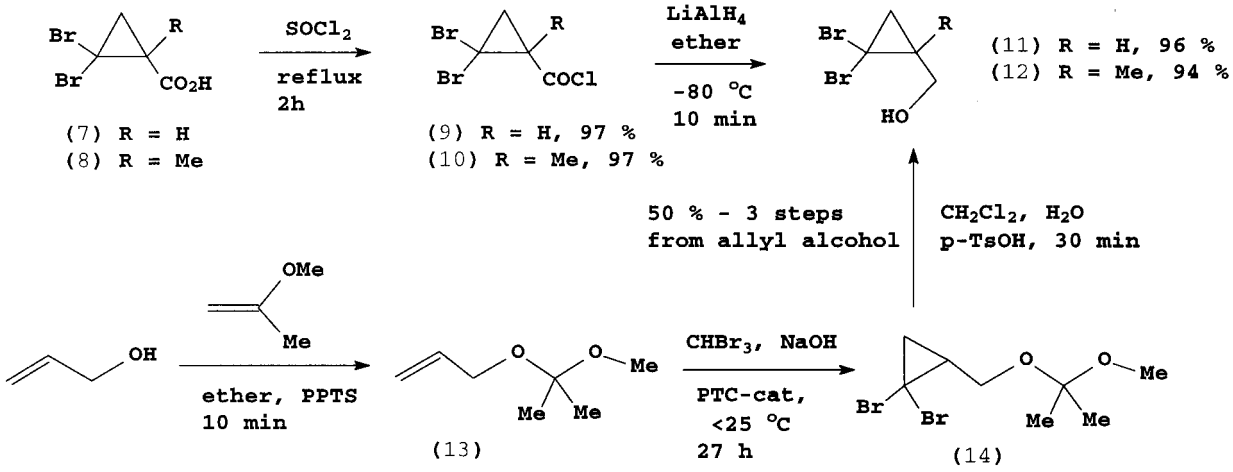


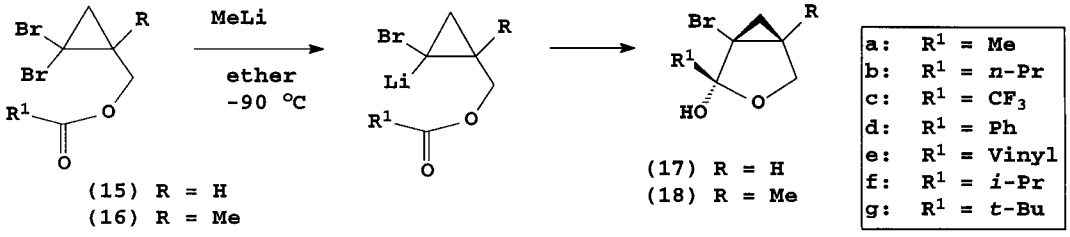
Scheme 2.

Two cyclopropanecarboxylic acids were prepared according to literature procedures,[7,12] (**8**) by the reaction of methyl methacrylate with bromoform and aqueous sodium hydroxide in the presence of a phase transfer catalyst,[13] and subsequent acid hydrolysis, and (**7**) by addition of dibromocarbene to 1,3-butadiene to give 1,1-dibromo-2-vinylcyclopropane, followed by oxidation to the acid with potassium permanganate.[14] Both acids (**7**) and (**8**) are now available in enantiomerically pure form by resolution.[14] For this work, however, racemic material was used. The acids were converted into the corresponding acid chlorides (**9**), (**10**) by reaction with thionyl chloride, and these were reduced to the alcohols (**11**), (**12**) (Scheme 2).[7]

Racemic alcohol (**11**) was also prepared by an alternative route from allyl alcohol by protection with 2-methoxypropene as (**13**), dibromocyclopropanation to give (**14**) and deprotection (50% overall yield, after distillation of the crude product).

A range of esters of general structure (**15**) and (**16**) (Scheme 3) was prepared by standard methods. Esters with R^1=methyl, trifluoromethyl and *n*-propyl were made from the alcohols (**11**), (**12**) by treatment with the corresponding acid anhydride in the presence of trimethylsilyl trifluoromethane sulfonate (TMSOTf) as catalyst.[15] The benzoates and acrylates were prepared upon treatment with the appropriate acid chloride in the presence of triethylamine, the isobutyrate and pivaloate by treatment with acid chloride in pyridine in the presence of 4-dimethylaminopyridine (DMAP) as catalyst (Table 1).

Reaction of esters (**15**), (**16**) with a slight excess of methyllithium at −90°C for 30 min, followed by quenching with



Scheme 3.

Table 1. Preparation of esters and their reactions with methyllithium in diethyl ether at −90°C

Method	R^1	R=H		R=Me	
		Ester, %	Product, %	Ester, %	Product, %
Ac_2O, TMSOTf	Me	(**15a**), 86	(**17a**), 55+(**11**), 10	(**16a**), 88	(**18a**), 60
(*n*-PrCO)$_2$O, TMSOTf	*n*-Pr	(**15b**), 92	(**17b**), 46	(**16b**), 93	(**18b**), 74
$(CF_3CO)_2O$, TMSOTf	CF_3	(**15c**), 88	(**11**), 90	–	
PhCOCl, Et_3N	Ph	(**15d**), 62	(**17d**), 64	(**16d**), 52	(**18d**), 82
CH_2=CHCOCl, Et_3N	Vinyl	(**15e**), 35	(**27**), 39	(**16e**), 44	(**18e**), 68
i-PrCOCl, Py, DMAP	*i*-Pr	–		(**16f**), 99	(**18f**), 80
t-BuCOCl, Py, DMAP	*t*-Bu	–		(**16g**), 89	(**18g**), 81

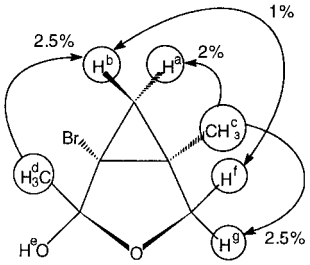


Figure 1. Proton n.O.e enhancements for (**18a**).

ammonium chloride either at low temperature or after warming to 0°C led to the hemiacetals (**17**), (**18**) (Scheme 3). The products of the intramolecular trapping are summarised in Table 1.

The formation of products (**17**) or (**18**) apparently involves a lithium–bromine exchange in (**15**) or (**16**) and cyclisation of the derived lithiocyclopropane by attack at the ester group. It is not clear whether the exchange leads stereoselectively to the *syn*-lithio-ester, or whether a more complex process occurs in which the two isomeric lithiobromides are formed and equilibrate, but only one isomer cyclises. Nonetheless, no products of intermolecular trapping of the *anti*-lithio ester were observed. It is interesting to note that reaction of 2,2-dibromocyclopropane carboxylic acid with methyllithium leads exclusively to *trans*-2-bromocyclopropane carboxylic acid, a reaction once again apparently proceeding through the *cis*-2-lithio-*trans*-2-bromo- compound.[16] Neither was there any evidence for the formation of products derived from cyclopropylidene intermediates (e.g. allenes).

In case of the trifluoroacetic acid ester (**15c**), no cyclisation took place; instead the ester was hydrolysed to the alcohol (**11**). Thus attack of methyllithium at the ester carbonyl was faster than lithium–halogen exchange. When the reaction was carried out with the acetic acid ester (**15a**) only 10% hydrolysed product was observed and the main product was the hemiacetal (**17a**). The other reactions did not afford any hydrolysis products.

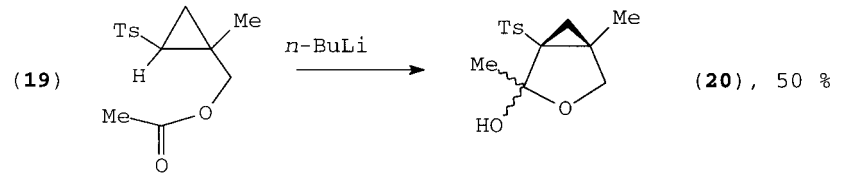
A single diastereomer was isolated from the intramolecular cyclisation in each case after chromatography; minor signals in the crude mixture could not be assigned with certainty to a second isomer. The stereochemistry at C-2 of the hemiacetal (**18a**) was assigned as that with the methyl group *endo* to the cyclopropane on the basis of n.O.e studies which established reciprocal enhancements (1%) of H^b and H^f (but not H^a and H^g), locating these protons as *endo,* an enhancement of H^b on irradiation CH_3^d, only possible if both groups are *endo*, and an enhancement of the signals for both H^a and H^g on irradiation of methyl CH_3^c, locating both protons *exo* (Fig. 1).

Confirmation of this stereochemistry came from a single crystal X-ray structure determination of the hemiacetal (**18d**) which again showed the phenyl group on the hemiacetal centre *endo* to the cyclopropane moiety.[17] The stereochemistry of other products was assigned by analogy.

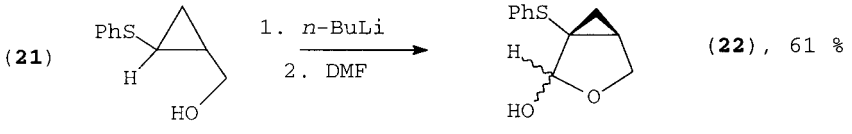
Although these reactions appear to represent the first example of such a cyclisation by reaction of 1,1-dibromides with an alkyllithium, it is known that the sulphone (**19**) reacts with *n*-butyllithium by proton removal from C-1 followed by cyclisation to give the hemiacetal (**20**, Scheme 4).[18]

A similar cyclisation occurred when 2-(hydroxymethyl)-cyclopropyl phenyl sulfide (**21**) was treated first with an excess of *n*-butyllithium and then with dimethylformamide to give the bicycle (**22**) (Scheme 5), an intermediate lithiocyclopropane apparently being trapped first as the aldehyde, which then cyclised.[19] In both cases the stereocentre of the hemiacetal was not defined although a single diastereomer was apparently obtained.

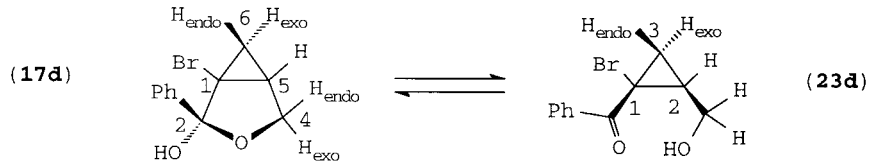
In the cases of the hemiacetals (**18a**), (**18b**), (**18d**) (see Table 1) the NMR spectra in deuterochloroform showed only the presence of the cyclic form. However, for the analogous hemiacetals (**17a**), (**17b**), (**17d**), the ^{1}H NMR spectra in deuterated solvents were more complicated and could be interpreted in terms of an equilibrium between the hemiacetal and the corresponding keto-alcohols (**23a**), (**23b**), (**23d**) (Scheme 6). The signal for the *endo* proton at C-4 in the hemiacetal (**17d**) appeared as a doublet and not a double doublet because the vicinal coupling constant is zero as the torsion angle between H_{endo}-4 and H-5 is close to 90°. The hemiacetal (**17d**) and keto-alcohol (**23d**) were readily



Scheme 4.

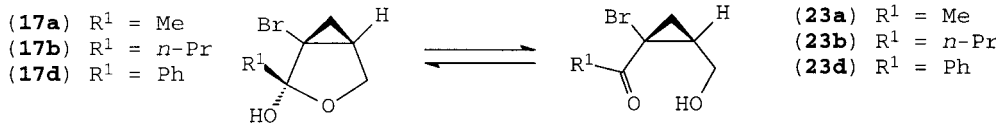


Scheme 5.



Scheme 6.

Table 2. Equilibrium hemiacetal/keto-alcohol in various deuterated solvents



R^1	Compounds	Solvent	Ratio of hemiacetal: keto-alcohol[a]
Me	(**17a**)/(**23a**)	$CDCl_3$	81: 19
		Benzene-d_6	84: 16
n-Pr	(**17b**)/(**23b**)	$CDCl_3$	58: 42
		Toluene-d_8	67: 33
Ph	(**17d**)/(**23d**)	$CDCl_3$	43: 57
		CD_3OD	58: 42
		toluene-d_8	100: 0

[a] Ratios measured after 1 h in deuterated solvent.

distinguished in the ^{13}C NMR spectrum, only the CH_2 group of the cyclopropane moiety having a comparable chemical shift, e.g. C-2 of hemiacetal (**17d**) appeared at 104.6 ppm while in the ring-opened structure (**23d**) this carbon gave a signal at 195.2 ppm.

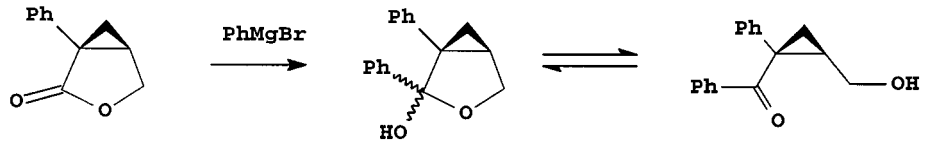
The observed ratios between those two species are summarised in Table 2 below.

Generally the equilibrium was on the side of the hemiacetal; one exception was compound (**17d**), which in deuterochloroform showed more keto-alcohol than hemiacetal present. Surprisingly, in deuterated toluene the same compound (**17d**) did not show any equilibrium at all. Thus the equilibrium position depends on structural properties of the hemiacetal—substituents on the hemiacetal centre (R^1 either Me, *n*-Pr or Ph) and group R on the cyclopropane ring (whether there is a methyl group or only a proton) and on properties of solvent (polarity and acidity). The reversibility of this equilibrium was tested with compound (**17d**). The compound was first dissolved in deuterated methanol and showed a ratio of 58: 42 in the ^1H NMR spectrum. The solvent was evaporated and the same sample was dissolved in deuterated toluene. Now only signals of the hemiacetal were present in the ^1H NMR spectrum. The solvent was evaporated and the spectrum was recorded once again in deuterated methanol. A ratio of hemiacetal to keto-alcohol almost identical to above was observed.[20]

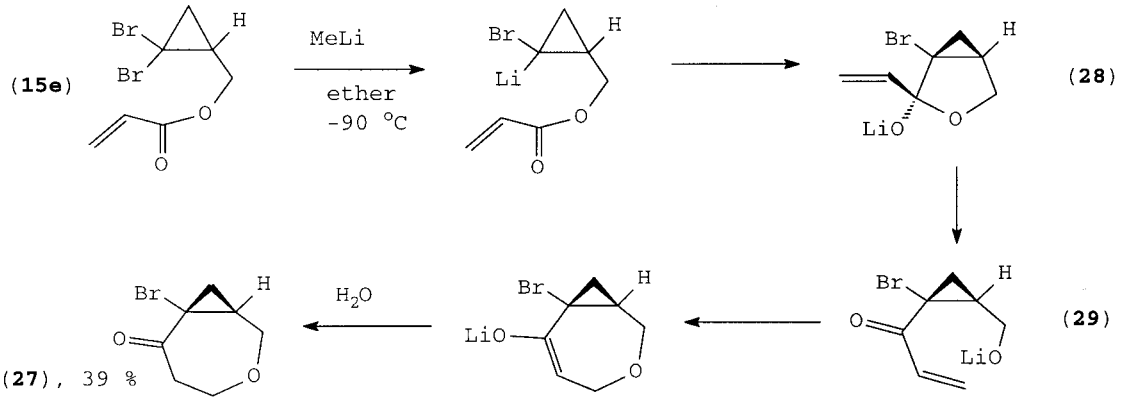
When samples of (**17a**) and (**17b**) in deuterochloroform were re-measured after one or more days, the NMR spectrum had become highly complex. It was not clear whether the compounds simply decomposed or if other diastereomers with the opposite configuration at the hemiacetal carbon were formed. A similar equilibrium has been reported in closely related acetals (**25**).[21] The bicyclic system was obtained from reaction of the lactone (**24**) with phenylmagnesium bromide (Scheme 7). The authors quoted a ratio of hemiacetal to keto-alcohol of 25 to 75 in deuterated methanol.

The reactions of esters (**15**) and (**16**) with methyllithium generally followed a similar pattern. The most significant difference was in the reaction of acrylates (**15e**) and (**16e**) with methyllithium. The ester (**16e**) gave the expected product, the hemiacetal (**18e**); however, the reaction of ester (**15e**) with methyllithium followed a rather different course, leading to the bicyclic ketone (**27**) as the sole product (Scheme 8).

This reaction may be explained in terms of initial formation of a hemiacetal species (**28**) as above, followed by ring-opening to a keto-alcohol (**29**) and recyclisation by attack of the alcoholate at the β-position of the derived α,β-unsaturated ketone. The bicyclic ketone (**27**) exhibited an unusual double carbonyl peak with maxima at 1711 and 1692 cm^{-1}; similar peaks have been reported in related



Scheme 7.



Scheme 8.

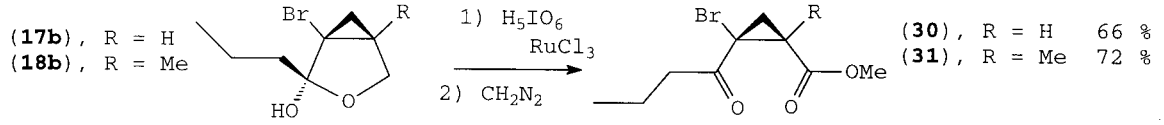
systems.[22] In the ^{13}C NMR spectrum, the carbonyl carbon gave a signal at 199.3 ppm. Peaks at 67.2 and 69.7 ppm were the signals for the CH_2 groups next to the ring-oxygen. In the ^1H NMR, the two CH_2 groups at C-4 and C-5 gave for each proton a 'ddd' multiplicity with signals at 2.04 and 2.28 ppm (2×H5) and at 2.69 and 3.20 ppm (2×H-4). In contrast to the above hemiacetal system (**17d**), both H-2 protons appeared as double doublets due to an altered torsion angle (>90° and thus non-zero vicinal coupling constants between both and the proton on C-1.

1-Bromo-2-propyl-3-oxabicyclo[3.1.0]hexan-2-ol (**17b**) and its methyl analogue (**18b**) were oxidatively ring-opened using periodic acid and catalytic amounts of ruthenium trichloride, [7] to give the corresponding 2-bromo-2-butyroyl-cyclopropanecarboxylic acids, which were isolated as their methyl esters (**30**) and (**31**), Scheme 9. With hemiacetal (**18b**), the oxidation gave a higher yield of (**31**) (72%) with 2 mol equiv. than with 14 mol equiv. of periodic acid (52%). The ^{13}C NMR spectra of the products gave correct signals for the ester carbonyl in the region of 170 ppm and for the ketone at 200 ppm.

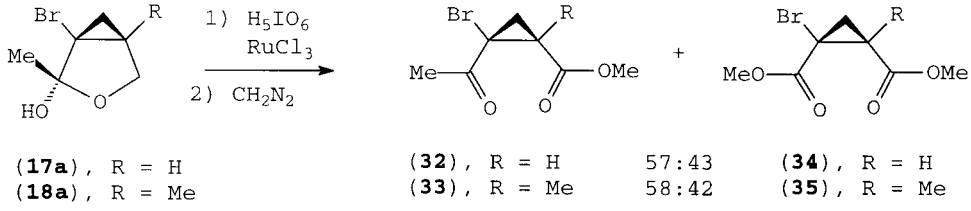
The corresponding oxidations of (**17a**) and (**18a**) afforded two products in ratio ca. 60 to 40 in each case. The major products were again the keto-esters (**32**) and (**33**); the minor products were identified as diesters (**34**)[23] and (**35**) (Scheme 10). In neither case was the mixture separated.

If the 2,2-dibromocyclopropanecarboxylic acid is regarded as the starting point of the synthesis, the overall transformation achieved is therefore a stereoselective acylation *cis* to the acid group (Scheme 11).

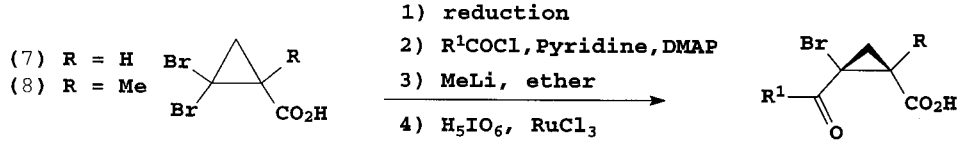
The oxidative ring-opening could also be carried out with PCC, leading in the case of (**18g**) to the keto-aldehyde (**36**), and with manganese dioxide in refluxing toluene in the



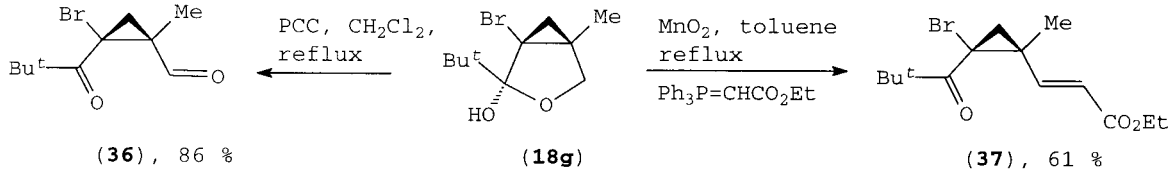
Scheme 9.



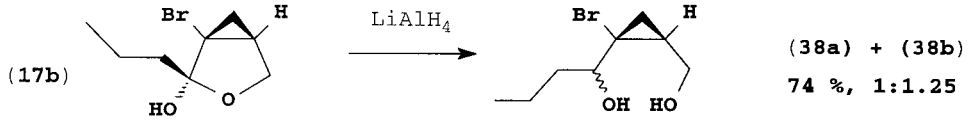
Scheme 10.



Scheme 11.



Scheme 12.



Scheme 13.

presence of ethoxycarbonyltriphenylphosphorane, when an in situ Wittig reaction was observed (Scheme 12).[24]

Reduction of the hemiacetal (**17b**), or the corresponding ring-opened hydroxyketone, with lithium aluminium hydride in ether was not stereoselective, leading to a mixture of isomeric diols (**38a**), (**38b**) (Scheme 13) which could be separated by column chromatography on silica.

The above results show that reaction of 2-acyloxymethyl-1,1-dibromocyclopropanes with methyllithium at −90°C leads to the stereoselective formation of bicyclic hemiacetals. The presence or absence of a methyl group at C-1 of the cyclopropane proved to play an important role in the outcome of the reaction and the stability of the products. Reductions and oxidations of the derived hemiacetals led to ring-opened products. Other reactions such as addition of Grignard and Wittig reagents or protection of the hydroxy-group of the hemiacetal were not successful. The applications of the bicyclic hemiacetals in the synthesis of biologically active cyclopropanes is being examined; the wide range of such compounds has recently been reviewed.[25]

General Experimental Details

Reagents were obtained from commercial suppliers (Aldrich, Lancaster) and were used without further purification unless otherwise stated. Solvents were purified when necessary using the methods suggested in 'Purification of Laboratory Chemicals' by D. D Perrin, W. L. F. Armarego and D. R. Perrin.[26] Dichloromethane was distilled over calcium hydride, diethyl ether over sodium wire. Petroleum ether was of boiling point 40–60°C unless otherwise stated. Reactions were performed using oven dried glassware (160°C) cooled under a stream of dry nitrogen or argon; the experiments were conducted under a positive atmosphere of one of these gases. Organic solutions were dried over anhydrous magnesium sulfate, and, unless stated, were evaporated at 14 mmHg. Yields quoted are for purified compounds unless otherwise stated. Any ratios given are calculated by comparing integrals of protons in the ^{1}H NMR spectra unless otherwise stated.

All new compounds were homogenous by TLC or by GLC. GLC was conducted using a Carlo Erba HRGC 5300 (F.I.D., on a capillary column). TLC was performed using Aldrich silica plates coated with silica gel 60 (F254). Compounds were visualised by examination under an ultraviolet source, by exposure to iodine vapour or by contact with phosphomolybdic acid hydrate (2% solution in ethanol) followed by heating to 180°C. Column chromatography was conducted with Fisher Scientific Silica Gel 60 under medium pressure.

Melting points are uncorrected. Infrared spectra were obtained as KBr discs or as liquid films on a Perkin Elmer 1600 FTIR spectrometer. Low resolution mass spectra were obtained on a Finnigan 8430 spectrometer. Accurate mass measurements refer to ^{79}Br for monobromides and for ^{79}Br^{81}Br for dibromides unless stated and were obtained from the Swansea Mass Spectrometry Service. Microanalyses were performed on a Carlo Erba Model 1106 CHN analyser.

NMR spectra were recorded in $CDCl_3$ unless otherwise stated on a Bruker AC250 at 250 MHz for protons and 62.9 MHz for carbon and in the latter case were broad-band decoupled; DEPT spectra were also run and the signs of signals (+ for CH, CH_3; − for CH_2) are indicated on the data for the broad-band decoupled spectrum. Those signals with no sign in such a spectrum are quaternary. When a n.O.e difference spectra was obtained from the Edinburgh University Ultra High Field NMR Service, conditions were as follows: recorded on a Bruker 360 MHz spectrometer, a total of 512 scans per FID, interleaved in blocks of 32 each with 4 'dummy scans', using Bruker program N.O.EMULT.AU; irradiation period: 7 s; 90 degree pulse, FID acquisition time: 2 s; sample stationary. Data were processed with 1 Hz line broadening.

(2,2-Dibromocyclopropyl)methanol (11).[7] 3-(1-Methoxy-1-methylethoxy)propene (11.5 g, 0.088 mol) [prepared from allyl alcohol (10 g, 0.172 mol) as described][11] was added to a mixture of bromoform (15.8 ml, 0.177 mol), dichloromethane (50 ml), *n*-hexadecyltrimethylammonium bromide (1.5 g) and triethylamine (4 drops). The mixture was stirred vigorously and sodium hydroxide (35 g, 0.883 mol) in water (35 ml) was added slowly at below

25°C. After 27 h at 20°C, brine (120 ml) was added and the mixture was extracted with dichloromethane (4×120 ml). The combined organic layers were dried and the solvent was removed. Petrol (150 ml) was added and the mixture was filtered through a layer of celite, which was washed with ether (50 ml). Removal of the solvent and distillation of unreacted bromoform at 30–40°C at 0.5 mmHg gave crude, already largely deprotected alcohol (**11**) as brown oil. To complete the deprotection, the oil was dissolved in dichloromethane (50 ml); water (25 ml) and *p*-toluenesulfonic acid (1 g) were added. After stirring for 30 min, the aqueous layer was extracted with dichloromethane (2×25 ml). The combined organic layers were washed with water (100 ml), dried and evaporated. Distillation gave (2,2-dibromocyclopropyl)methanol (**11**) (10.2 g, 50%); bp 82°C at 0.3 mmHg. Compound (**11**) was also prepared as previously described and shown to be identical by n.m.r. and i.r. to the product above.[7]

General procedure for syntheses of compounds (15a)–(15c), (16a), (16b)

A solution of alcohol (1 mmol) in dichloromethane (5 ml) was treated with the corresponding anhydride (1.1–2 mmol) at 0°C, followed by addition of trimethylsilyl trifluoromethanesulfonate (7 mg, 3 mol%). On completion, the reaction (TLC) was treated with sat. aq. $NaHCO_3$, and the aqueous phase was extracted with dichloromethane. The organic extracts were washed with aqueous $NaHCO_3$ (×3) and water, dried and the solvent evaporated. Generally, the products did not require further purification.

2,2-Dibromocyclopropylmethyl acetate (15a). (2,2-Dibromocyclopropyl)methanol (**11**) (0.6 g, 2.61 mmol) and acetic anhydride (0.27 ml, 2.87 mmol) gave *2,2-dibromocyclopropylmethyl acetate* (**15a**) (0.61 g, 86%) as a colourless oil (Found M^+: 271.8871. $C_6H_8Br_2O_2$ requires: 271.8871) which showed δ_H: 1.44 (1H, t, *J*=7.4 Hz), 1.84 (1H, dd, *J*=7.4, 10.4 Hz), 1.97 (1H, dddd, *J*=5.8, 7.4, 8.2, 10.4 Hz), 2.11 (3H, s), 4.05 (1H, dd, *J*=8.2, 11.9 Hz), 4.28 (1H, dd, *J*=5.9, 11.9 Hz); δ_C: 20.9+, 24.8, 26.8−, 28.9+, 65.8−, 170.8; ν_{max}: 2953 w, 1742 s, 1438 w, 1369 s, 1235 s, 1109 m, 1036 s, 687 s cm^{-1}; *m/z*, %: 272, 0.5; 272, 1; 270, 0.5 (M^+); 214, 6; 212, 8; 210, 5; 201, 9; 133, 5; 86, 14; 43, 100.

2,2-Dibromocyclopropylmethyl butyrate (15b). (2,2-Dibromocyclopropyl)methanol (**11**) (2.2 g, 9.6 mmol) and butyric anhydride (1.72 ml, 10.5 mmol) gave *2,2-dibromocyclopropylmethyl butyrate* (**15b**) (2.63 g, 92%) as a colourless liquid (Found M^+: 299.9184. $C_8H_{12}Br_2O_2$ requires: 299.9184) which showed δ_H: 0.97 (3H, t, *J*=7.4 Hz), 1.45 (1H, t, *J*=7.4 Hz), 1.69 (2H, sextet, *J*=7.4 Hz), 1.84 (1H, dd, *J*=7.4, 10.4 Hz), 1.99 (1H, dddd, *J*=5.9, 7.4, 8.2, 10.4 Hz), 2.34 (2H, t, *J*=7.4 Hz), 4.05 (1H, dd, *J*=8.2, 11.9 Hz), 4.29 (1H, dd, *J*=5.9, 11.9 Hz); δ_C: 13.6+, 18.4−, 24.8, 26.8−, 29.0+, 36.0−, 65.5−, 173.4; ν_{max}: 2965 m, 2875 w, 1739 s, 1176 s, 1107 m, 686 m cm^{-1}; *m/z*, %: 302, 0.5; 300, 1; 298, 0.5 (M^+); 214, 2; 212, 6; 210, 3; 133, 5; 131, 5; 114, 10; 71, 100.

2,2-Dibromocyclopropylmethyl trifluoroacetate (15c). (2,2-Dibromocyclopropyl)methanol (**11**) (1.0 g, 4.35 mmol) and trifluoroacetic anhydride (0.67 ml, 4.78 mmol) gave *2,2-dibromocyclopropylmethyl trifluoroacetate* (**15c**) (1.5 g, 88%) as a colourless liquid (Found M^+: 325.8588. $C_6H_5Br_2F_3O_2$ requires: 325.8588) which showed δ_H: 1.57 (1H, t, *J*=7.4 Hz), 1.95 (1H, dd, *J*=7.4, 10.4 Hz), 2.09 (1H, dddd, *J*=6.5, 7.4, 7.5, 10.4 Hz), 4.45 (1H, dd, *J*=7.5, 11.7 Hz), 4.52 (1H, dd, *J*=6.5, 11.7 Hz); δ_C: 23.1, 27.0−, 28.0+, 69.2−, 114.3 (q, J_{CF} 285 Hz), 157 (q, J_{CF} 43 Hz); ν_{max}: 1789 s, 1368 s, 1333 m, 1226 s, 1168 s, 1108 s, 959 m, 775 m, 730 s, 689 s cm^{-1}; *m/z*, %: 328, 1; 326, 2; 324, 1 (M^+); 214, 41; 212, 100; 210, 37; 201, 9; 199, 13; 197, 9; 188, 10; 186, 22; 184, 10; 133, 23; 131, 26; 69, 93; 51, 29.

2,2-Dibromo-1-methylcyclopropylmethyl acetate (16a). (2,2-Dibromo-1-methylcyclopropyl)methanol (**12**) (1.7 g, 6.97 mmol) and acetic anhydride (0.72 ml, 7.67 mmol) gave *2,2-dibromo-1-methylcyclopropylmethyl acetate* (**16a**) (1.75 g, 88%) as a colourless liquid (Found M^+: 285.9027. $C_7H_{10}Br_2O_2$ requires: 285.9027) which showed δ_H: 1.45 (3H, s), 1.49 (1H, d, *J*=7.7 Hz), 1.65 (1H, d *J*=7.7 Hz), 2.12 (3H, s), 4.08 (1H, d, *J*=11.6 Hz), 4.34 (1H, d, *J*=11.6 Hz); δ_C: 20.9+, 29.7, 32.8−, 34.4, 70.2−, 170.8; ν_{max}: 2993 m, 2968 m, 2933 m, 1738 s, 1459 s, 1431 s,1387 s, 1378 s, 1364 s, 1246 s, 1162 m, 1036 s, 989 s, 851 m, 696 s cm^{-1}; *m/z*, %: 288, 0.1; 286, 0.2; 284, 0.1 (M^+); 246, 2; 244, 4; 242, 2; 228, 8; 226, 15; 224, 7; 147, 8; 145, 7; 100, 100; 72, 13; 66, 20; 65, 25.

2,2-Dibromo-1-methylcyclopropylmethyl butyrate (16b). (2,2-Dibromo-1-methylcyclopropyl)methanol (**12**) (12.2 g, 50 mmol) and butyric anhydride (15.8 g, 100 mmol) gave, after removal of excess butyric anhydride in vacuo (3 mmHg, 80°C) and distillation of the residue at 140°C and 0.3 mmHg, *2,2-dibromo-1-methyl-cyclopropylmethyl butyrate* (**16b**) (14.6 g, 46.5 mmol, 93%) as a colourless liquid (Found M^+: 313.9340. $C_9H_{14}Br_2O_2$ requires: 313.9340) which showed δ_H: 0.96 (3H, t, *J*=7.4 Hz), 1.45 (3H, s), 1.49 (1H, t, *J*=7.7 Hz), 1.65 (1H, d, *J*=7.7 Hz), 1.68 (2H, qt, *J*=7.4, 7.5 Hz), 2.35 (2H, t, *J*=7.5 Hz), 4.08 (1H, d, *J*=11.6 Hz), 4.34 (1H, d, 11.6 Hz); δ_C: 13.6+, 18.4−, 20.8+, 28.4, 32.7−, 34.4, 35.9−, 69.9−, 173.1; ν_{max}: 3077 w, 2966 s, 2934 s, 2875 m, 1738 s, 1461 s, 1431 m, 1380 m, 1356 m, 1303 m, 1282 m, 1254 s, 1173 br. s, 1090 s, 1044 s, 996 s, 695 s cm^{-1}; *m/z*, %: 316, 0.1; 314, 0.2; 312, 0.1 (M^+); 228, 1; 226, 2; 224, 1; 128, 16; 71, 100; 65, 12.

2,2-Dibromocyclopropylmethyl benzoate (15d). Benzoyl chloride (0.56 ml, 4.8 mmol) was added to a stirred solution of (2,2-dibromocyclopropyl)methanol (**11**) (1.0 g, 4.3 mmol) and triethylamine (0.67 ml, 4.8 mmol) in ether (10 ml). The mixture was stirred at room temperature for 12 h, filtered and evaporated. Chromatography on silica (petrol–ether, 3:1) gave *2,2-dibromocyclopropylmethyl benzoate* (**15d**) (900 mg, 62%) as a colourless oil (Found M^+: 333.9027. $C_{11}H_{10}Br_2O_2$ requires: 333.9027) which showed δ_H: 1.56 (1H, t, *J*=7.5 Hz), 1.91 (1H, dd, *J*=7.5, 10.4 Hz), 2.15 (1H, dddd, *J*=6.0, 7.5, 8.2, 10.4 Hz), 4.32 (1H, dd, *J*=8.2, 12.0 Hz), 4.58 (1H, dd, *J*=6.0, 12.0 Hz), 7.44–7.64 (3H, m), 8.08–8.12 (2H, m); δ_C: 24.7, 27.0−, 29.1+, 66.2−, 128. 4+, 129.7+, 133.2, 166.2; ν_{max}: 3063 w, 2952 w, 1722 s, 1602 w, 1451 m, 1341 m, 1314 m, 1270 s, 1176 m, 1111 s, 1070 m, 1026 m, 711 s, 687 m cm^{-1}; *m/z*, %: 336, 2; 334, 4; 332, 2 (M^+); 148, 8; 105, 100; 77, 28.

2,2-Dibromocyclopropylmethyl acrylate (15e). Acryloyl chloride (0.78 ml, 9.6 mmol) was added to a stirred solution of (**11**) (1.6 g, 7.7 mmol) and triethylamine (1.58 ml, 11.3 mmol) in dry ether (40 ml) at 0°C; triethylammonium chloride precipitated. After 2 h at room temperature the mixture was treated with hydrochloric acid (2%, 35 ml) to dissolve the precipitate. The aqueous layer was extracted with ether (3×40 ml) and the combined organic layers were dried and evaporated. Chromatography on silica (petrol–ether, 5:1) gave *2,2-dibromocyclopropylmethyl acrylate* (**15e**) (700 mg, 35%) as a colourless oil (Found M^+: 283.8871, $C_7H_8Br_2O_2$ requires: 283.8871) which showed δ_H: 1.48 (1H, t, *J*=7.5 Hz), 1.86 (1H, dd, *J*=7.5, 10.4 Hz), 2.04 (1H, dddd, *J*=6.0, 7.5, 8.2, 10.4 Hz), 4.16 (1H, dd, *J*=8.2, 12.0 Hz), 4.38 (1H, dd, *J*=6.0, 12.0 Hz), 5.89 (1H, dd, *J*=1.5, 10.4 Hz), 6.17 (1H, dd, *J*=10.4, 17.3 Hz), 6.47 (1H, dd, *J*=1.5, 17.3 Hz); δ_C: 24.7, 26.9−, 28.9+, 65.9−, 128.0+, 131.5−, 165.9; ν_{max}: 2953 m,1728 s, 1634 s, 1444 m, 1409 s,1394 s, 1341 m, 1294 s, 1269 s, 1185 s, 1109 s, 1058 s, 985 s, 809 s, 689 s cm^{-1}; *m/z*, %: 286, 0.5; 284, 2; 282, 0.5 (M^+); 214, 20; 212, 47; 210, 25; 133, 20; 131, 29; 98, 100; 70, 44.

2,2-Dibromo-1-methylcyclopropylmethyl benzoate (16d). Benzoyl chloride (2.86 ml, 24.6 mmol) was added to a stirred solution of (**12**) (3.0 g, 12.3 mmol) and triethylamine (3.42 ml, 24.6 mmol) in dry ether (40 ml); triethylammonium chloride precipitated. The mixture was refluxed for 24 h and then filtered. The solvent was removed; chromatography on silica (petrol–ether, 5:1) gave *2,2-dibromo-1-methylcyclopropylmethyl benzoate* (**16d**) (2.22 g, 52%) as a colourless oil (Found M^+: 347.9184. $C_{12}H_{12}Br_2O_2$ requires: 347.9184) which showed δ_H: 1.57 (3H, s), 1.58 (1H, d, *J*=7.7 Hz), 1.78 (1H, d, *J*=7.7 Hz), 4.35 (1H, d, *J*=11.6 Hz), 4.65 (1H, d, 11.6 Hz), 7.45–7.64 (3H, m), 8.09–8.13 (2H, m); δ_C: 21.1+, 28.8, 33.0−, 34.3, 70.7−, 128.5+, 129.7+, 129.8+, 133.2, 166.3; ν_{max}: 2992 w, 2964 w, 2931 w, 1721 s, 1602 w, 1451 m, 1386 w, 1314 m, 1270 s, 1175 m, 1115 s, 1070 m, 1026 m, 973 m, 710 s cm^{-1}; *m/z*, %: 348, 1 (M^+); 162, 11; 105, 100; 77, 35.

2,2-Dibromo-1-methylcyclopropylmethyl acrylate (16e). Acryloyl chloride (0.90 ml, 11.0 mmol) was treated with (**12**) (2.5 g, 10.2 mmol) and triethylamine (2.86 ml, 20.5 mmol) in dry ether (40 ml) at 0°C as for (**15e**). Chromatography on silica (petrol–ether, 5:1) gave *2,2-dibromo-1-methyl-cyclopropylmethyl acrylate* (**16e**) (1.3 g, 44%) as a colourless oil (Found M^+: 297.9027. $C_8H_{10}Br_2O_2$ requires: 297.9027) which showed δ_H: 1.44 (3H, s), 1.48 (1H, d, *J*=7.7 Hz), 1.65 (1H, d, *J*=7.7 Hz), 4.15 (1H, d, *J*=11.7 Hz), 4.41 (1H, d, 11.7 Hz), 5.85 (1H, dd, *J*=1.5, 10.3 Hz), 6.15 (1H, dd, *J*=10.3, 17.3 Hz), 6.44 (1H, dd, *J*=1.5, 17.3 Hz); δ_C: 20.9+, 28.6, 32.9−, 34.3, 70.2−, 128.0+, 131.4−, 165.6; ν_{max}: 2993 w, 2966 w, 2933 w, 1727 s, 1634 m, 1458 m, 1407 s, 1384 m, 1295 s, 1268 s, 1185 s, 1058 s, 1033 m, 985 s, 808 m, 695 s cm^{-1}; *m/z*, %: 300, 1; 298, 2; 296, 1 (M^+); 228, 16; 226, 32; 224, 19; 188, 8; 186, 14; 184, 8; 147, 22; 145, 18; 112, 100; 107, 16.

2,2-Dibromo-1-methylcyclopropylmethyl isobutyrate (16f). A solution of (**12**) (3.66 g, 15.0 mmol) and 4-dimethylaminopyridine (183 mg, 1.5 mmol) in dry pyridine (35 ml) was treated with isobutyryl chloride (2.4 ml, 22.5 mmol) at room temperature. The mixture was stirred for 2 h at 60°C then poured into cold water (150 ml) and extracted with ether (2×50 ml). The combined extracts were washed with 5% hydrochloric acid (2×100 ml), water (50 ml), dried and the solvent was evaporated to yield *2,2-dibromo-1-methylcyclopropylmethyl isobutyrate* (**16f**) (4.67 g, 14.8 mmol, 99%) as a colourless liquid which was one spot by t.l.c. (Found $M+NH_4^+$: 329.9704. $C_9H_{18}Br_2NO_2$ requires: 329.9702) which showed δ_H: 1.15 (6H, d, *J*=7.0 Hz), 1.40 (3H, s), 1.44 (1H, d, *J*=7.7 Hz), 1.61 (1H, d, *J*=7.7 Hz), 2.57 (1H, heptet, *J*=7.0 Hz), 4.02 (1H, d, *J*=11.6 Hz), 4.29 (1H, d, *J*=11.6 Hz); δ_C: 19.0+, 20.9+, 28.6, 32.8−, 33.9+, 34.4, 70.0−, 176.8; ν_{max}: 2973 s, 2934 m, 2875 w, 1737 br. s, 1469 m, 1389 m, 1257 m, 1189 s, 1152 s, 1075 m, 1033 m, 990 m, 695 m cm^{-1}; *m/z*, % (CI, NH_3): 334, 50; 332, 100; 330, 48 ($M+NH_4^+$); 316, 14; 314, 26; 312, 14 (M^+); 229, 7; 228, 12; 227, 12; 226, 18; 225, 8; 224, 13; 147, 12; 145, 11; 138, 25; 105, 36.

2,2-Dibromo-1-methylcyclopropylmethyl pivaloate (16g). A solution of (**12**) (3.66 g, 15.0 mmol) and 4-dimethylaminopyridine (183 mg, 1.5 mmol) in dry pyridine (35 ml) was treated with pivaloyl chloride (3.7 ml, 30 mmol) at room temperature. The mixture was stirred for 2 h at 55°C; work up as above and distillation afforded *2,2-dibromo-1-methylcyclopropylmethyl pivaloate* (**16g**) (4.4 g, 13.3 mmol, 89%) as a colourless liquid (Found $M+NH_4^+$: 343.9858. $C_{10}H_{20}Br_2NO_2$ requires: 343.9861), bp 140°C (0.3 mmHg), δ_H: 1.19 (9 H, s), 1.41 (3H, s), 1.45 (1H, d, *J*=7.7 Hz), 1.65 (1H, d, *J*=7.7 Hz), 4.01 (1H, d, *J*=11.6 Hz), 4.28 (1H, d, *J*=11.6 Hz); δ_C: 20.9+, 27.2+, 28.7, 32.8−, 34.3, 38.8, 70.1−, 178.1; ν_{max}: 2971 s, 2933 m, 2872 m, 1732 br.s, 1480 m, 1459 m, 1284 s, 1154 br.s, 1035 m, 986 m, 695 m cm^{-1}; *m/z*, % (CI, NH_3): 348, 6; 346, 9; 344, 5 ($M+NH_4^+$); 330, 17; 328, 34; 326, 15 (M^+); 249, 4; 247, 4; 246, 4; 244, 6; 229 46; 227, 40; 226, 52; 224, 46; 186, 12; 142, 88; 102, 100.

1-Bromo-2-methyl-3-oxabicyclo[3.1.0]hexan-2-ol (17a). Methyllithium in ether (1.13 ml, 1.70 mmol, 1.5 M) was added dropwise with stirring to 2,2-dibromocyclopropylmethyl acetate (**15a**) (420 mg, 1.54 mmol) in ether (10 ml) at −90°C. After 45 min the solution was allowed to warm to −75°C. Sat. aq. NH_4Cl (5 ml) was added and the aqueous layer was extracted with ether (2×10 ml). The combined organic layers were dried and evaporated. Chromatography on silica (petrol–ether, 1:1) gave a mixture of *1-bromo-2-methyl-3-oxabicyclo[3.1.0]hexan-2-ol* (**17a**) (55%) and *(2,2-dibromocyclopropyl)methanol* (**11**) (10%) (200 mg, ratio 83:17). Compound (**17a**) showed ν_{max}: 3389 br. s, 2991 m, 2939 m, 2884 m, 1698 m, 1430 m, 1382 m, 1361 m, 1328 m, 1252 m, 1214 m, 1160 s, 1093 s, 1044 s, 976 s, 949 s, 869 m, 791 m cm^{-1}; *m/z*, %: 177, 27; 175, 38 (M^+-OH); 131, 2; 53, 16; 43, 100. M^+ was not observed. In solution, an equilibrium between (**17a**) and 1-(1-bromo-2-hydroxymethylcyclopropyl)ethanone (**23a**) was observed by NMR; ratio (**17a**) to (**23a**) in $CDCl_3$, 81:19; in benzene-d_6, 84:16. Hemiacetal (**17a**) showed δ_H: 0.97 (1H, dd, *J*=5.0, 5.7 Hz), 1.19 (1H, dd, *J*=5.7, 8.4 Hz), 1.48 (3H, s), 1.96 (1H, ddd, 2.8, 5.0, 8.4 Hz), 2.90 (1H, s), 3.67 (1H, d, *J*=8.6 Hz), 4.13 (1H, dd, *J*=2.8, 8.6 Hz); δ_C (benzene-d_6): 18.5−, 21.2+, 25.3+, 39.6, 65.9−, 103.7. Keto-alcohol

(**23a**) showed δ_H: 2.13 (1H, m), 2.57 (3H, s), 3.34 (1H, dd, J=9.1, 12.0 Hz), all other peaks underneath alcohol (**11**) peaks; δ_C (benzene-d_6): 22.5−, 30.0+, 37.0, 37.4+, 59.8−, CO peak not detected.

1-Bromo-2-propyl-3-oxabicyclo[3.1.0]hexan-2-ol (17b). 1.5 M Methyllithium in ether (1.22 ml, 1.83 mmol) was added dropwise to 2,2-dibromocyclopropylmethyl butyrate (**15b**) (500 mg, 1.67 mmol) in ether (10 ml) at −90°C. The solution was stirred for 1 h at −90°C and quenched with water (5 ml). The aqueous layer was extracted with ether (2×10 ml). The combined organic layers were dried and evaporated. Chromatography on silica (petrol–ether, 1:1) gave *1-bromo-2-propyl-3-oxabicyclo[3.1.0]hexan-2-ol* (**17b**) (170 mg, 46%) as a white solid, mp 51–53°C (Found: M^+, 220.0099. $C_8H_{13}BrO_2$ requires: 220.0099. Found: C 43.9, H 6.0. $C_8H_{13}BrO_2$ requires: C 43.46, H 5.93) showed ν_{max}: 3362 br.s, 2959 s, 2932 s, 2874 m, 1696 w, 1458 m, 1408 m, 1338 m, 1240 m, 1151 s, 1110 s, 1070 m, 1046 s, 1002 s, 973 s, 945 s, 882 s, 710 m cm^{-1}; *m/z*, %: 222, 5; 221, 3, 220, 3 (M^+); 205, 60; 203, 66; 179, 41; 177, 30; 134, 24; 99, 20; 97, 16; 71, 42; 69, 20; 53, 100. In solution, an equilibrium between (**17b**) and 1-(1-bromo-2-hydroxymethylcyclopropyl)-butan-1-one (**23b**) was observed by NMR; ratio (**17b**) to (**23b**) in $CDCl_3$, 58:42; in toluene-d_8, 67:33. The hemiacetal (**17b**) showed δ_H: 0.94 (3H, t, J=7.2 Hz), 1.03 (1H, dd, J=4.8, 6.0 Hz), 1.22 (1H, dd, J=6.0, 8.5 Hz), 1.45–1.85 (4H, m), 1.92 (1H, ddd, 2.8, 4.8, 8.5 Hz), 2.67 (1H, s), 3.66 (1H, d, J=8.6 Hz), 4.13 (1H, dd, J=2.8, 8.6 Hz); δ_C (toluene-d_8): 15.4+, 17.9−, 19.4−, 25.9+, 38.6−, 40.6, 66.6−, 105.2. The keto-alcohol (**23b**) showed δ_C (toluene-d_8): 14.4+, 18.7−, 22.6−, 37.7+, 38.9, 44.4−, 60.6−, 204.6.

Reaction of 2,2-dibromocyclopropylmethyl trifluoroacetate (15c) with methyllithium

Methyllithium in ether (0.61 ml, 0.97 mmol, 1.5 M) was added dropwise to 2,2-dibromocyclopropylmethyl trifluoroacetate (**15c**) (300 mg, 0.92 mmol) in ether (15 ml) at −90°C as above. The solution was stirred for 30 min at −90°C then warmed to 0°C over 30 min and quenched with sat. aq. NH_4Cl (5 ml). The aqueous layer was extracted with ether (2×10 ml). The combined organic layers were dried and evaporated to give *(2,2-dibromocyclopropyl)-methanol* (**11**) (190 mg, 90%) as a colourless oil, identical by NMR and IR to the material prepared above and to that reported.[7]

1-Bromo-2-phenyl-3-oxabicyclo[3.1.0]hexan-2-ol (17d). 1.5 M Methyllithium in ether (0.72 ml, 1.09 mmol) was added dropwise to 2,2-dibromocyclopropylmethyl benzoate (**15d**) (300 mg, 0.90 mmol) in ether (10 ml) at −90°C. The solution was stirred for 40 min at below −80°C. Water (5 ml) was added and the aqueous layer was extracted with ether (2×10 ml). The combined organic layers were dried and evaporated. Chromatography on silica (petrol–ether, 1:1) gave *1-bromo-2-phenyl-3-oxabicyclo[3.1.0]-hexan-2-ol* (**17d**) (146 mg, 64%) as a white solid, mp 141°C (Found: C 51.9, H 4.3. $C_{11}H_{11}BrO_2$ requires: C 51.79, H 4.35) which showed ν_{max}: 3360 br. s, 3091 m, 2948 m, 2887 s, 1451 m, 1411 s, 1333 m, 1240 s, 1222 s, 1145 s, 1092 s, 1077 s, 1056 s, 1045 s, 1017 s, 1000 s, 954 s, 932 m, 884 s, 785 m, 762 s, 705 s cm^{-1}; *m/z*, %: 256, 9; 254, 4 (M^+); 239, 4; 237, 4; 175, 12; 134, 25; 132, 17; 105, 100; 77, 42; 53, 77. In solution, an equilibrium between (**17d**) and (1-bromo-2-hydroxymethylcyclopropyl)phenyl methanone (**23d**) was observed; ratio (**17d**) to (**23d**) in $CDCl_3$, 43:57; in CD_3OD, 58:42; in toluene-d_8, 100:0; (**17d**) showed δ_H (CD_3OD): 1.03 (1H, dd, J=5.1, 6.0 Hz), 1.10 (1H, dd, J=6.0, 8.4 Hz), 2.07 (1H, ddd, 2.9, 5.1, 8.4 Hz), 3.86 (1H, d, J=8.5 Hz), 4.30 (1H, dd, J=2.9, 8.5 Hz), 7.30–7.40 (3H, m), 7.59–7.65 (2H, m); δ_C (CD_3OD): 19.7−, 27.8+, 42.1, 67.8−, 104.6, 127.9+, 129.0+, 129.6+, 141.0. Compound (**23d**) showed δ_H (CD_3OD): 1.46 (1H, dd, J=6.6, 9.9 Hz), 1.70 (1H, dd, J=6.6, 7.4 Hz), 2.24 (1H, ddd, 6.6, 7.4, 9.9 Hz), 3.43 (2H, d, J=6.6 Hz) 7.38–7.56 (3H, m), 8.07–8.11 (2H, m); δ_C (CD_3OD): 18.9−, 34.3+, 35.0, 61.6−, 129.6+, 131.3+, 134.8+, 136.8, 195.2.

7-Bromo-3-oxabicyclo[5.1.0]octan-6-one (27). Methyllithium in ether (0.96 ml, 1.39 mmol, 1.5 M) was added dropwise to a 2,2-dibromocyclopropylmethyl acrylate (**15e**) (330 mg, 1.16 mmol) in ether (10 ml) at −90°C. After stirring for 50 min at below −80°C, work up as above and chromatography on silica (petrol–ether, 2:1) gave *7-bromo-3-oxabicyclo[5.1.0]octan-6-one* (**27**) (92 mg, 39%) as a white solid, mp 31°C (Found M^+: 203.9786. $C_7H_9BrO_2$ requires: 203.9786) which showed δ_H (benzene-d_8): 1.21 (1H, dd, J=5.8, 9.1 Hz), 1.40 (1H, dddd, J=2.5, 4.3, 7.7, 91 Hz), 1.49 (1H, dd, J=5.8, 7.7 Hz), 2.04 (1H, ddd, J=4.3, 10.6, 13.5 Hz), 2.28 (1H, ddd, J=2.3, 5.0, 13.5 Hz), 2.69 (1H, ddd, J=2.3, 10.6, 12.4 Hz), 3.20 (1H, ddd, J=4.3, 5.0, 12.4 Hz), 3.21 (1H, dd, J=2.5, 13.6 Hz), 3.28 (1H, dd, J=4.3, 13.6 Hz); δ_C (benzene-d_8): 23.2−, 29.8+, 42.3, 43.2−, 67.2−, 69.7−, 199.3; ν_{max}: 2937 w, 2862 m, 1711 m, 1692 s, 1294 m, 1261 m, 1166 m, 1141 s, 1034 m, 904 cm^{-1}; *m/z*, %: 206, 5; 204, 4 (M^+); 178, 5; 176, 12; 148, 9; 146, 10; 133, 10; 125, 70; 97, 18; 69, 75, 53, 100.

1-Bromo-2,5-dimethyl-3-oxabicyclo[3.1.0]hexan-2-ol (18a). Methyllithium in ether (1.37 ml, 2.06 mmol, 1.5 M) was added dropwise to 2,2-dibromo-1-methylcyclopropylmethyl acetate (**16a**) (490 mg, 1.70 mmol) in ether (10 ml) at −90°C. Work up as above and chromatography on silica (petrol–ether, 2:1) gave (**16a**) (60 mg) and a colourless oil, *1-bromo-2,5-dimethyl-3-oxabicyclo[3.1.0]hexan-2-ol* (**18a**) (186 mg, 52% [60% based on recovered starting material]) (Found M^+: 205.9942. $C_7H_{11}BrO_2$ requires: 205.9942) which showed δ_H: 0.89 (1H, d, J=5.9 Hz), 1.10 (1H, d, J=5.9 Hz), 1.35 (3H, s), 1.50 (3H, s), 3.14 (1H, br. s), 3.72 (1H, d, J=8.4 Hz), 3.88 (1H, d, J=8.4 Hz); δ_C: 15.2+, 21.9+, 23.8−, 28.1, 47.4, 70.8−, 104.5; ν_{max}: 3397 br. s, 2954 m, 2933 m, 2878 m, 1446 m, 1389 m, 1315 m, 1212 m, 1171 s, 1077 s, 997 s, 952 s, 883 s, 807 m, 754 m cm^{-1}; *m/z*, %: 208, 2; 206, 2 (M^+); 193, 21; 191, 20; 175, 6; 173, 4; 151, 12; 149, 11; 148, 13; 146, 10; 127, 16; 67, 100.

1-Bromo-5-methyl-2-propyl-3-oxabicyclo[3.1.0]hexan-2-ol (18b). Methyllithium in ether (22.3 ml, 33.4 mmol, 1.5 M) was added to 2,2-dibromo-methylcyclopropylmethyl butyrate (**16b**) (10.00 g, 31.8 mmol) in ether (150 ml) at −90°C over 5 min. The solution was stirred for 30 min at −90°C then warmed to 0°C for 30 min. Work up as above gave crude *1-bromo-5-methyl-2-propyl-3-oxabicyclo[3.1.0]-*

hexan-2-ol (**18b**) (7.75 g, 99%). For analytical purposes, chromatography of 1.14 g of crude product on silica (petrol–ether, 1:1) gave pure (**18b**) (840 mg, 74%) as a white solid, mp 49–51°C (Found M^+: 234.0255. $C_9H_{15}BrO_2$ requires: 234.0255. Found: C 46.5, H 6.5. $C_9H_{15}BrO_2$ requires: C 45.98, H 6.43) which showed δ_H: 0.91 (1H, d, *J*=6.0 Hz), 0.96 (3H, t, *J*=7.2 Hz), 1.18 (1H, d, *J*=6.0 Hz), 1.35 (3H, s), 1.40–1.95 (4H, m), 2.65 (1H, s), 3.73 (1H, d, *J*=8.4 Hz), 3.88 (1H, d, *J*=8.4 Hz); δ_C: 14.4+, 15.2+, 16.7−, 23.9−, 27.3, 38.1−, 47.2, 70.7−, 105.4; ν_{max}: 3425 br. s, 2961 s, 2931 s, 2873 s, 1456 s, 1390 s, 1315 m, 1294 m, 1267 m, 1245 m, 1162 s, 1127 m, 1103 m, 1086 m, 1039 s, 1011 s, 954 s, 909 m, 880 m, 859 m, 804 m, 755 m cm^{-1}; *m/z*, %: 236, 6; 234, 8 (M^+), 193, 29; 191, 41; 179, 6; 177, 6; 148, 12; 146, 12; 111, 41; 86, 26; 84, 43; 71, 42; 67, 100; 43, 58; 41, 90.

1-Bromo-5-methyl-2-phenyl-3-oxabicyclo[3.1.0]hexan-2-ol (18d). Methyllithium in ether (2.77 ml, 3.60 mmol, 1.5 M) was added dropwise to 2,2-dibromo-1-methylcyclopropylmethyl benzoate (**16d**) (1.0 g, 2.87 mmol) in ether (25 ml) at −90°C. The solution was stirred for 20 min at −90°C and quenched with sat. aq. NH_4Cl (10 ml). Work up as above and recrystallisation from ethyl acetate gave *1-bromo-5-methyl-2-phenyl-3-oxabicyclo-[3.1.0]hexan-2-ol* (**18d**) (631 mg, 82%) as a white solid, mp 142°C (Found: C 53.63, H 4.90. $C_{12}H_{13}BrO_2$ requires: C 53.55, H 4.87) which showed δ_H: 0.81 (1H, d, *J*=6.2 Hz), 1.17 (1H, d, *J*=6.2 Hz), 1.39 (3H, s), 3.92 (1H, d, *J*=8.4 Hz), 4.05 (1H, d, *J*=8.4 Hz), 7.33–7.36 (3H, m), 7.62–7.65 (2H, m); δ_C: 15.6+, 23.8−, 28.6, 48.1, 71.2−, 104.2, 126.2+, 128.5+, 128.8+, 139.4; ν_{max}: 3354 s, 2966 m, 2931 m, 2876 s, 1448 s, 1411 s, 1323 m, 1275 s, 1165 s, 1071 s, 1015 s, 954 s, 920 s, 878 s, 768 s, 752 s, 702 s, 655 s, 596 m cm^{-1}; *m/z*, %: 270, 5; 268, 3 (M^+), 253, 4; 251, 5; 162, 12; 148, 18; 115, 15; 105, 30; 77, 100; 65, 32; 51, 32.

1-Bromo-5-methyl-2-vinyl-3-oxabicyclo[3.1.0]hexan-2-ol (18e). Methyllithium in ether (0.65 ml, 0.84 mmol, 1.3 M) was added dropwise to 2,2-dibromo-1-methylcyclopropylmethyl acrylate (**16e**) (200 mg, 0.67 mmol) in ether (10 ml) at −90°C. The solution was stirred for 40 min at below −80°C. Work up as above and chromatography on silica (petrol–ether, 1:5) gave *1-bromo-5-methyl-2-vinyl-3-oxabicyclo[3.1.0]hexan-2-ol* (**18e**) (100 mg, 68%) as a white solid, mp 63°C which showed δ_H: 1.44 (3H, s), 1.48 (1H, d, *J*=7.7 Hz), 1.65 (1H, d, *J*=7.7 Hz), 4.15 (1H, d, *J*=11.7 Hz), 4.41 (1H, d, 11.7 Hz), 5.85 (1H, dd, *J*=1.5, 10.3 Hz), 6.15 (1H, dd, *J*=10.3, 17.3 Hz), 6.44 (1H, dd, *J*=1.5, 17.3 Hz); δ_C: 20.9+, 28.6, 32.9−, 34.3, 70.2−, 128.0+, 131.4−, 165.6; ν_{max}: 3340 br. s, 2962 m, 2885 m, 1419 m, 1389 w, 1214 m, 1176 s, 1088 m, 1044 s, 1021 m, 983 s, 954 m, 039 s, 880 m, 803 m, 760 m, 681 m, 502 m cm^{-1}; *m/z*, %: 221, 4; 220, 5; 219, 5 (M^+); 218, 7; 217, 40; 215, 60; 203, 25; 201, 37; 137, 98; 108, 84; 67, 52; 55, 100; 53, 53. It was not possible to obtain good CHN values for (**18e**).

1-Bromo-2-isopropyl-3-oxabicyclo[3.1.0]hexan-2-ol (18f). 1.5 M Methyllithium in ether (11.7 ml, 1.2 mol equiv.) was added dropwise to 2,2-dibromo-1-methylcyclopropylmethyl isobutyrate (**16f**) (4.59 g, 14.6 mmol) in ether (100 ml) at −90°C over 10 min. The solution was allowed to reach 0°C over 30 min then worked up as above. Chromatography on silica (80 g, petrol–ether, 75:25) gave *1-bromo-2-isopropyl-3-oxabicyclo[3.1.0]hexan-2-ol* (**18f**) (2.73 g, 11.6 mmol, 80%) as a colourless oil (Found MH^+: 235.0331. $C_9H_{16}BrO_2$ requires: 235.0334) which showed δ_H: 0.91 (1H, d, *J*=6.0 Hz), 0.98 (3H, d, *J*=6.9 Hz), 1.09 (3H, d, *J*=6.9 Hz), 1.22 (1H, d, *J*=6.0 Hz), 1.28 (3H, s), 2.03 (1H, qq, *J*=6.9, 6.9 Hz), 2.61 (1H, s), 3.67 (1H, d, *J*=8.4 Hz), 3.81 (1H, d, *J*=8.4 Hz); δ_C: 15.6+, 17.4+, 17.7+, 23.3−, 27.0, 34.8+, 46.1, 70.6−, 106.5; ν_{max}: 3462 br. s, 2968 s, 2931 s, 2876 s, 1472 m, 1388 m, 1316 w, 1162 m, 1066 s, 1017 s, 944 s cm^{-1}; *m/z*, % (CI, NH_3): 252, 4; 250, 3; 237, 2; 235, 3 (MH^+); 219, 94; 217, 100; 155, 2; 111, 2.

1-Bromo-2-*t*-butyl-3-oxabicyclo[3.1.0]hexan-2-ol (18g). Methyllithium in ether (9.6 ml, 1.2 mol equiv., 1.5 M) was added dropwise to 2,2-dibromo-1-methylcyclopropylmethyl pivaloate (**16g**) (3.94 g, 12.0 mmol) in ether (60 ml) at −90°C over 10 min. The solution was allowed to reach 0°C over 30 min; quenching and work-up as above gave *1-bromo-2-t-butyl-3-oxabicyclo[3.1.0]hexan-2-ol* (**18g**) (2.4 g, 9.7 mmol, 81%) as a colourless oil (Found MH^+: 249.0488. $C_{10}H_{18}BrO_2$ requires: 249.0490) which showed δ_H: 0.98 (1H, d, *J*=6.2 Hz), 1.10 (9H, s), 1.28 (3H, s), 1.42 (1H, d, *J*=6.2 Hz), 2.56 (1H, s), 3.68 (1H, d, *J*=8.4 Hz), 3.80 (1H, d, *J*=8.4 Hz); δ_C: 13.1+, 25.8−, 26.1, 39.8, 44.8, 70.3−, 107.4; ν_{max}: 3498 br. s, 3081 w, 2961 s, 2875 s, 1486 s, 1463 s, 1396 s, 1365 s, 1249 m, 1214 m, 1167 m, 1079 s, 1050 s, 1006 s, 954 s, 868 m, 754 m cm^{-1}; *m/z*, % (CI, NH_3): 250, 4; 248, 7 (M^+); 234, 9; 233, 87; 231, 100; 210, 6; 208, 6; 193, 40; 191, 42; 175, 9; 173, 7; 146, 18; 111, 52.

2-Bromo-2-butyrylcyclopropanecarboxylic acid methyl ester (30). Water (3 ml), periodic acid (1.5 g, 6.56 mmol) and ruthenium trichloride hydrate (5 mg, 0.05 mol equiv.) were added to 1-bromo-2-propyl-3-oxabicyclo[3.1.0]hexan-2-ol (**17b**) (100 mg, 0.45 mmol) in carbon tetrachloride (2 ml) and acetonitrile (2 ml). The mixture was refluxed for 12 h. Water (5 ml) was added, the mixture was extracted with ether (3×10 ml), the combined organic layers were washed with water (2×20 ml), dried and concentrated to ca. 6 ml and a solution of diazomethane in ether was added. The solvent and excess diazomethane were removed. Chromatography on silica (petrol–ether, 5:1) gave *methyl 2-bromo-2-butyrylcyclopropane carboxylate* (**30**) (74 mg, 66%) as a colourless oil which showed δ_H: 0.90 (3H, t, *J*=7.3 Hz), 1.61 (2H, sextet, *J*=7.3 Hz), 1.62 (1H, dd, *J*=7.0, 9.4 Hz), 2.12 (1H, t, *J*=7.0 Hz), 2.45 (1H, dd, *J*=7.0, 9.4 Hz), 2.55 (1H, td, *J*=7.3, 17.8 Hz), 2.89 (1H, td, *J*=7.3, 17.8 Hz), 3.68 (3H, s); δ_C: 13.5+, 17.2−, 21.9−, 31.8+, 37.4, 41.7−, 52.5+, 168.9, 200.1; ν_{max}: 2963 s, 2877 m, 1732 s, 1439 s, 1373 s, 1273 m, 1207 s, 1181 s, 1141 s, 1066 m, 1009 m, 936 m, 915 m, 733 s cm^{-1}; *m/z*, %: 222, 56; 220, 6 (M^+−CO); 205, 2; 203, 2; 169, 9; 149, 7; 98, 7; 81, 9; 71, 57; 59, 23; 55, 19; 43, 100 (M^+ was not observed).

2-Bromo-2-butyryl-1-methylcyclopropanecarboxylic acid methyl ester (31). (a) Water (0.6 ml), periodic acid (202 mg, 0.88 mmol) and ruthenium trichloride hydrate (2 mg, 0.02 mol equiv.) were added to 1-bromo-5-methyl-

2-propyl-3-oxabicyclo[3.1.0]hexan-2-ol (**18b**) (99 mg, 0.42 mmol) in carbon tetrachloride (0.6 ml) and acetonitrile (0.6 ml). The mixture was refluxed for 30 min, when it was black, then extracted with ether (3×3 ml). The combined organic layers were dried and evaporated to give *2-bromo-2-butyryl-1-methylcyclopropanecarboxylic acid*, as a colourless oil (100 mg, 0.40 mmol, 80% pure by ^{1}H NMR), which showed: δ_H: 0.89 (3H, t, J=7.4 Hz), 1.26 (1H, d, J=6.6 Hz), 1.20–1.80 (2H, m), 1.62 (3H, s), 2.35 (1H, d, J=6.6 Hz), 2.54 (1H, dt, J=17.8, 7.3 Hz), 2.86 (1H, dt, J=17.8, 7.3 Hz), 10.42 (1H, s); δ_C: 13.5+, 17.3−, 19.4+, 28.1−, 32.0, 41.6−, 47.6, 176.4, 201.0; ν_{max}: 3376 br. m, 3093 w, 2966 m, 2935 m, 2876 w, 1723 s, 1704 s, 1456 m, 1417 w, 1296 m, 1200 m, 930 m cm^{-1}. Attempts to purify the crude acid failed; it was dissolved in ether (1 ml) and a solution of diazomethane in ether was added. The solvent and excess diazomethane were removed. Chromatography on silica (3 g, petrol–ether, 3:1) gave *methyl 2-bromo-2-butyryl-1-methylcyclopropane carboxylate* (**31**) (79 mg, 72% based on (**18b**)) as a colourless oil (Found M^+: 262.0205. $C_{10}H_{15}BrO_3$ requires: 262.0205) which showed δ_H: 0.98 (3H, t, J=7.4 Hz), 1.26 (1H, d, J=6.5 Hz), 1.63 (2H, sextet, J=7.4 Hz), 1.68 (3H, s), 2.41 (1H, d, J=6.5 Hz), 2.60 (1H, td, J=7.4, 17.8 Hz), 2.92 (1H, td, J=7.4, 17.8 Hz), 3.68 (3H, s); δ_C: 13.6+, 17.3−, 19.9+, 27.9−, 33.0, 41.9−, 47.1, 52.5+, 176.4, 201.6; ν_{max}: 2963 m, 1732 s, 1456 m, 1436 m, 1303 s, 1199 s, 1166 s cm^{-1}; *m/z*, %: 264, 16; 262, 17 (M^+), 233, 6; 203, 9; 183, 100; 175, 10; 173, 10; 124, 11; 71, 33; 53, 17.

(b) Water (3 ml), periodic acid (2.8 g, 12.3 mmol) and ruthenium trichloride hydrate (9 mg, 0.05 mol equiv.) were added to (**18b**) (200 mg, 0.85 mmol) in carbon tetrachloride (2 ml) and acetonitrile (2 ml). The mixture was refluxed for 12 h. Water (5 ml) was added, the mixture was extracted with ether (3×10 ml), the combined organic layers were washed with water (2×20 ml) and dried. The solvent was removed to give *2-bromo-2-butyryl-1-methylcyclopropanecarboxylic acid*. Crude acid was dissolved in ether (10 ml) and treated with diazomethane in ether as in (a) to give (**31**) (116 mg, 52%), identical to that above.

2-Acetyl-2-bromocyclopropanecarboxylic acid methyl ester (32) and 1-bromocyclopropane-1,2-dicarboxylic acid dimethyl ester (34). Water (3 ml), periodic acid (1.6 g, 7.25 mmol) and ruthenium trichloride hydrate (5 mg, 0.05 mol equiv.) were added to 1-bromo-2-methyl-3-oxabicyclo[3.1.0]hexan-2-ol (**17a**) (100 mg, 0.52 mmol) in carbon tetrachloride (2 ml) and acetonitrile (2 ml). The mixture was refluxed for 12 h. Water (5 ml) was added, the mixture was extracted with ether (3×10 ml), the combined organic layers were washed with water (2×20 ml) and dried. The volume was reduced to ca. 10 ml and a solution of diazomethane in ether was added. The solvent and excess diazomethane were removed to give *methyl 2-acetyl-2-bromocyclopropane carboxylate* (**32**) and dimethyl 1-bromocyclopropane-*cis*-1,2-dicarboxylate (**34**) (98 mg in total, compounds not separated, ratio by GLC, 57:43). The data of (**34**) were identical to those reported.[23] Compound (**32**) showed δ_H: 1.64 (1H, dd, J=6.7, 9.6 Hz), 2.12 (1H, dd, J=6.7, 7.3 Hz), 2.39 (3H, s), 2.47 (1H, dd, J=7.3, 9.6 Hz), 3.68 (1H, s); δ_C: 27.4+, 21.9−, 31.8+, 37.6, 52.5+, 169.1, 197.7; *m/z*, % (GC/MS): 207, 0.5; 205, 0.5 (M^+-CH_3); 191, 7; 189, 13; 163, 24; 141, 100; 99, 67; 82, 18; 59, 20; 53, 19.

2-Acetyl-2-bromo-1-methylcyclopropanecarboxylic acid methyl ester (33) and 1-bromo-2-methylcyclopropane-1,2-dicarboxylic acid dimethyl ester (35). Water (3 ml), periodic acid (2.77 g, 12.17 mmol) and ruthenium trichloride hydrate (9 mg, 0.05 mol equiv.) was added to 1-bromo-2,5-dimethyl-3-oxabicyclo[3.1.0]-hexan-2-ol (**18a**) (180 mg, 0.87 mmol) in carbon tetrachloride (2 ml) and acetonitrile (2 ml). The mixture was refluxed for 12 h. Work up as above gave a mixture of *methyl 2-acetyl-2-bromo-1-methylcyclopropane carboxylate* (**33**) and *dimethyl 1-bromo-2-methylcyclopropane-1,2-dicarboxylate* (**35**) (194 mg in total, compounds not separated, ratio by GLC, 58:42) (ν_{max}: 1789 m, 1735 s cm^{-1}). Compound (**33**) showed δ_H: 1.21 (1H, d, J=6.6 Hz), 1.63 (3H, s), 2.34 (1H, d, J=6.6 Hz), 2.39 (3H, s), 3.64 (1H, s); *m/z*, %: 235, 0.1; (M^+); 221, 0.1; 205, 5; 177, 8; 176, 13; 175, 13; 174, 8; 155, 100; 96, 37; 53, 33. Compound (**35**) showed δ_H: 1.26 (1H, d, J=6.6 Hz), 1.58 (3H, s), 2.33 (1H, d, J=6.6 Hz), 3.63 (3H, s), 3.71 (1H, s); *m/z*, %: 252, 6; 250, 3 (M^+); 221, 23; 220, 18; 219, 24; 218, 31; 192, 40; 190, 23; 175, 20; 171, 100, 139, 25; 112, 30; 111, 30; 83, 33; 69, 25; 59, 44; 53, 84. The mixture showed δ_C: 19.4+, 19.8+, 27.4+, 27.9−, 28.4−, 31.9, 33.2, 38.8, 46.7, 52.6+, 52.6+, 53.4+, 168.1, 170.9, 171.0, 199.4.

1-Bromo-1-(1-keto-*2,2*-dimethylpropanyl)-2-methyl-2-formylcyclopropane (36). A solution of 1-bromo-2-*t*-butyl-3-oxabicyclo[3.1.0]hexan-2-ol (**18g**) (125 mg, 0.50 mmol) in dry dichloromethane (1 ml) was added to a solution of PCC (162 mg, 0.75 mmol) in dichloromethane (10 ml). The mixture was refluxed for 15 h. Ether (10 ml) was added and the solution was columned through silica (10 g, 4:6 ether:-petrol) to yield a mixture of *1-bromo-1-(1-keto-2,2-dimethylpropanyl)-2-methyl-2-formylcyclopropane* (**36**) and starting material (it was not possible to separate the two compounds) (107 mg, 0.43 mmol, 86% total) as a colourless oil (ratio (**36**) to (**18g**) 90:10 by ^{1}H NMR) which showed δ_H: 1.27 (9H, s), 1.42 (1H, d, J=7.1 Hz), 1.60 (3H, s), 2.41 (1H, d, J=7.1 Hz), 8.91 (1H, s); δ_C: 18.4+, 26.5, 28.7+, 29.7−, 44.2, 46.1, 177.5+, 205.2; ν_{max}: 3084 w, 2968 s, 2933 m, 2872 m, 1717 s, 1696 s, 1479 m, 1459 m, 1366 m, 1155 m, 1087 m, 1002 m, 992 m, 945 m, 895 m cm^{-1}; *m/z*, % (CI, NH_3): 266, 7; 264, 10; 250, 12; 249, 84; 248, 13; 247, 100 (MH^+); 219, 8; 217, 10; 167, 14; 139, 4; 111, 4.

1-Bromo-1-(1-keto-2,2-dimethylpropanyl)-2-methyl-2-(*trans*-2-ethoxycarbonylvinyl)cyclopropane (37). Activated manganese dioxide (0.3 g, 3.4 mmol) was added to a stirred solution of (**18g**) (249 mg, 1.00 mmol) and ethoxycarbonylmethylenetriphenylphosphorane (418 mg, 1.2 mmol) in dry toluene (25 ml) and the mixture was heated to reflux. Two further portions of manganese dioxide (0.3 g each) were added after 45 and 90 min. In 4 h, glc showed that 40% of starting material was consumed. After 30 h, a further portion of manganese dioxide (0.5 g) and ethoxycarbonylmethylenetriphenylphosphorane (418 mg, 1.2 mmol) were added. After 18 h more at reflux, the cooled mixture was passed through celite (5 g, washing with ether-petrol, 1:1). The crude product was columned on silica to yield starting material (47 mg, 0.19 mmol) and *1-bromo-1-(1-keto-2,2-*

dimethylpropanyl)-2-methyl-2-(trans-2-ethoxycarbonylvinyl)-cyclopropane (**37**) (193 mg, 0.61 mmol, 61%) as a colourless liquid (Found MH^+: 317.0754. $C_{14}H_{22}BrO_3$ requires: 317.0752) which showed δ_H: 1.24 (3H, t, J=7.1 Hz), 1.25 (9H, s), 1.27 (1H, d, J=6.8 Hz), 1.58 (3H, s), 2.11 (1H, d, J=6.8 Hz), 4.12 (1H, dq, J=10.9, 7.1 Hz), 4.18 (1H, dq, J=10.9, 7.1 Hz), 5.88 (1H, d, J=15.6 Hz), 6.24 (1H, d, J=15.6 Hz); δ_C: 14.2+, 19.1+, 26.5, 28.1+, 29.9−, 44.0, 46.4, 60.5−, 121.6+, 148.6+, 165.7, 207.5; ν_{max}: 2983 s, 2934 m, 2908 m, 2873 m, 1720 s, 1693 s, 1644 s, 1479 m, 1462 m, 1394 m, 1366 s, 1315 s, 1266 s, 1242 m, 1180 s, 1063 m, 1037 s, 997 s, 955 m, 868 m cm^{-1}; *m/z*, % (CI, NH_3): 318 (44), 316 (54), 272 (14), 270 (32), 237 (28), 191 (68), 186 (100), 135 (60), 120 (80), 108 (64), 107 (81).

1-(1-Bromo-2-hydroxymethylcyclopropyl)butan-1-ol (38). 1-Bromo-2-propyl-3-oxabicyclo[3.1.0]hexan-2-ol (**17b**) (60 mg, 0.27 mmol) in ether (8 ml) was added dropwise to a suspension of $LiAlH_4$ (23 mg, 6.0 mmol) in ether (8 ml) at −80°C. The mixture was stirred for 1 h at −70°C and then allowed to warm to room temperature. Work-up as above and chromatography on silica (petrol–ether, 1:5) gave two diastereomers of *1-(1-bromo-2-hydroxymethylcyclopropyl)-butan-1-ol* (**38**) (total 45 mg, 74%). Diastereomer (**38a**) (fraction 1; 20 mg), a white solid, mp 72°C (Found: C 43.5, H 6.8. $C_8H_{15}BrO_2$ requires: C 43.07, H 6.78) showed δ_H: 0.81 (1H, t, J=6.7 Hz), 0.93 (3H, t, J=7.4 Hz), 1.42 (2H, sextet, J=7.4 Hz), 1.44 (1H, dd, J=6.7, 9.6 Hz), 1.61–1.80 (2H, m), 1.91 (1H, dddd, J=5.8, 6.7, 9.6, 10.9 Hz), 3.10 (1H, t, 6.6 Hz), 3.27 (1H, dd, 10.9, 12.1 Hz), 4.04 (1H, dd, 5.8, 12.1 Hz); δ_C: 14.1+, 18.6−, 20.1−, 29.4+, 38.4−, 43.9, 63.0−, 74.7+; ν_{max}: 3320 br. s, 2953 s, 2913 m, 2868 m, 1464 m, 1376 m, 1332 s, 1268 w, 1166 m, 1145 m, 1111 s, 1080 s, 1028 s, 969 m, 840 m, 628 m cm^{-1}; *m/z*, %: 207, 100; (M^+−OH); 128, 46; 127, 53; 85, 48; 55, 25. Diastereomer (**38b**) (colourless oil; 25 mg; fraction 2) showed δ_H: 0.92 (3H, t, J=7.2 Hz), 1.0 (1H, t, J=7.0 Hz), 1.39 (1H, dd, J=7.0, 9.9 Hz), 1.43–1.58 (2H, m), 1.60–1.78 (2H, m), 1.89 (1H, ddd, J=7.0, 7.3, 9.9 Hz), 3.18 (1H, dd, 3.5, 9.0 Hz), 3.65 (1H, dd, 7.3, 11.6 Hz), 3.71 (1H, dd, 7.0, 11.6 Hz); δ_C: 14.0+, 18.9−, 20.0−, 30.3+, 39.0−, 45.2, 61.5−, 74.7+; ν_{max}: 3354 br. s, 2959 s, 2872 s, 1640 w, 1445 m, 1380 m, 1313 m, 1256 m, 1158 m, 1108 m, 1074 m, 1036 s cm^{-1}; *m/z*, %: 207, 0.4; 205, 0.8 (M^+−OH); 181, 3; 179, 5; 163, 17; 137, 16; 107, 15; 81, 23; 73, 16; 69, 16; 53, 46; 43, 100 (M^+ was not observed).

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