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1,2,2-Tribromocyclopropanecarboxylic Acid and Derivatives - Valuable Intermediates for Four Carbon Cyclopropane and Cyclopropene Synthons

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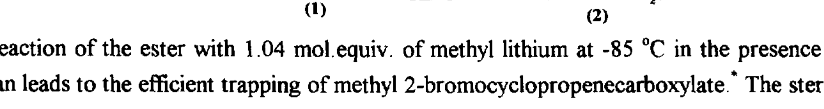
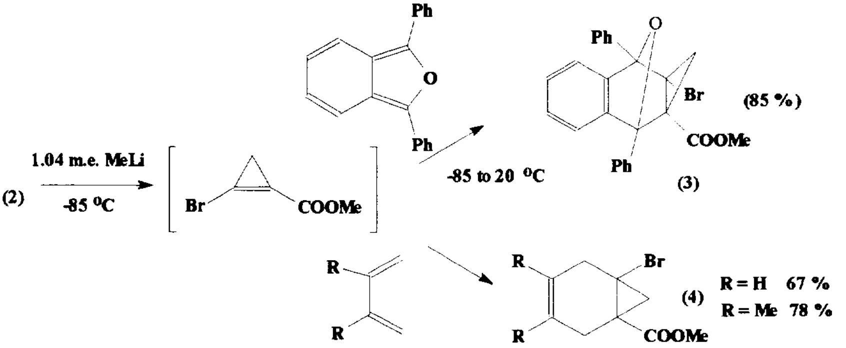
Abstract: Methyl 1,1,2-tribromocyclopropanecarboxylate is readily available by dibromocyclopropanation of methyl α-bromoacrylate. Reaction with methyllithium at low temperature provides a simple route to methyl 2-bromocyclopropene carboxylate, while modification of the ester group followed by reaction with methyllithium leads to a series of related four-carbon cyclopropenes. The tribromo-ester is also readily converted into 1,1,2,2-tetrabromocyclopropane, a valuable three-carbon cyclopropene synthon.

Although it has been known for some time that cyclopropene itself and simple 1- and 3-alkyl derivatives may be easily prepared by reaction of allyl chlorides with metal amides,[2-5] cyclopropene itself is extremely reactive and undergoes polymerisation even at -36 °C,[4] and 1-methylcyclopropene decomposes in two days in carbon tetrachloride at ambient temperature or 2 weeks neat at -20 °C.[5] There are now many routes to cyclopropenes with at least two carbon substituents on the ring or to 1-alkylcyclopropenes, and similarly to 1,2-dihalogeno- and 1-halogeno-2-trialkylsilyl-cyclopropenes,[6] and the synthetic use of such compounds has become an area of considerable interest.[7] In the same way, the chemistry of 3-alkoxycarbonylcyclopropenes, derived by addition of alkyl diazoacetates to alkynes is well described.[8] In contrast, reports of simple routes to cyclopropene-1-carboxylic acid and related four carbon synthons are rare; the dehydrobromination of t-butyl trans-2-bromocyclopropanecarboxylate with t-butoxide has been reported to proceed through the cyclopropene, but the product isolated results from *in situ* addition of t-butoxide ion.[9] We now report routes to a series of such systems, and examples of their trapping.

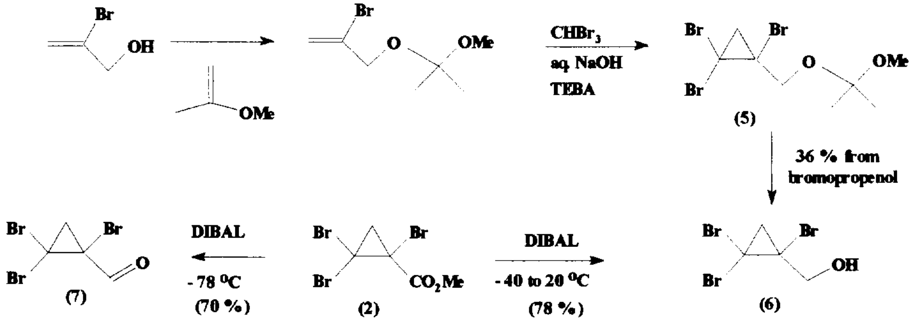
Reaction of methyl α-bromoacrylate with aqueous sodium hydroxide and bromoform under phase transfer conditions in the presence of benzyl triethylammonium chloride (TEBA) leads to the tribromo-ester (2)[10] in a reaction which may be conveniently carried out on a large laboratory scale:



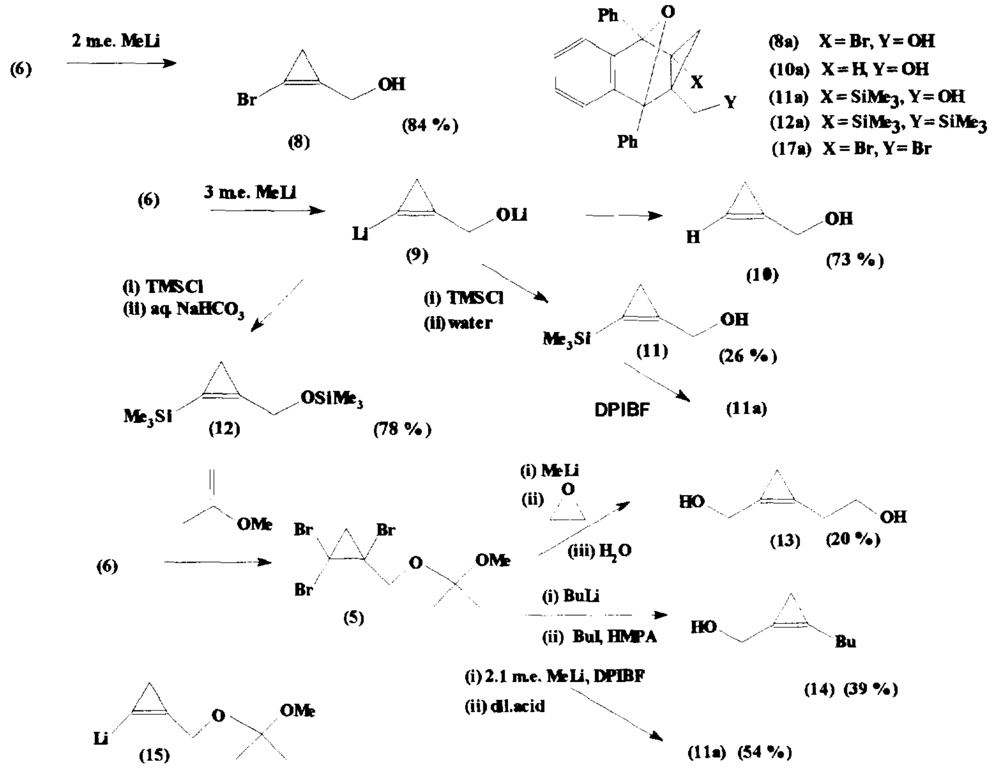
Reaction of the ester with 1.04 mol.equiv. of methyl lithium at -85 °C in the presence of diphenylisobenzofuran leads to the efficient trapping of methyl 2-bromocyclopropenecarboxylate.[*] The stereo-chemistry of the single [4+2]-cycloadduct (3) is assigned by analogy with that of other such adducts of 3,3-unsubstituted cyclopropenes with DPIBF.[11] However, unlike other cases which show a large chemical shift difference between the cyclopropane hydrogens because of the proximity of one of them to the bridge oxygen, in this case the shift difference is relatively small (ca. 0.4 ppm); nonetheless, reduction of the ester (3) gave the corresponding alcohol (see below) which did show the typical difference between the cyclopropane hydrogens.[11] It is noteable that, under these reaction conditions, the methyllithium reacts entirely by 1,2-debromination rather than by attack at the ester group. Trapping of the cyclopropene with furan leads to a mixture of exo and endo-[4+2]-cycloadducts, as is common for such cyclopropenes and, once again, the major product is assigned as that with the oxygen and cyclopropane syn.[11] The cyclopropene is also trapped in high yield by reaction with butadiene and 2,3-dimethylbutadiene, leading to (4, R = H, Me) and providing an efficient approach to functionalised derivatives of bicyclo[4.1.0]heptane-1-carboxylic acid. Converting the ester (2) into the corresponding ester of a homochiral alcohol or amide of a homochiral amine, followed by reaction with methyllithium, provides a route to homochiral derivatives of 2-bromocyclopropene- carboxylic acid; the reactions of these will be described elsewhere.



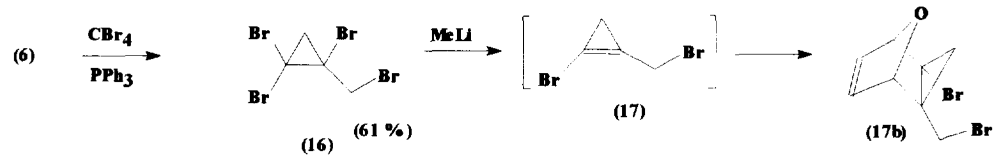
The ester (2) may be reduced to the corresponding alcohol (6) by reaction with di-isobutyl aluminium hydride at -40 to 20 °C (78 %), and to the aldehyde (7) (70 %) at -78 °C. The alcohol (6) is also obtained in three steps from 2-bromoprop-2-en-1-ol, and may in turn be oxidized to (7) with PCC (85 %):



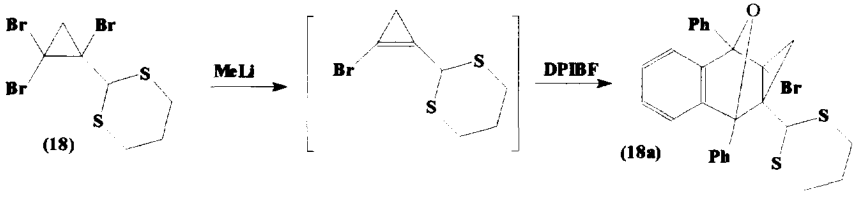
Reaction of the alcohol (6) with 2 mol.equiv. of methyllithium again leads to the corresponding bromocyclopropene (8) which again may be trapped as (8a) by reaction with DPIBF (55 % from (6)). On standing for 18 h in $CDCl_3$, this compound had decomposed to only a small extent; on further standing, a mixture of several products was obtained, the major component of which was identical by n.m.r. to 4-bromobut-2-yn-1-ol.[12] Similar rearrangements of 1-halocyclopropenes to haloalkynes have been reported.[13] Reaction of (6) with 3 mol.equiv. of methyl lithium at -78 to 20 °C followed by trapping with water leads to the cyclopropene (10) which is again trapped by addition to DPIBF to give (10a) (96 % from (6)); presumably (10) is derived by initial formation of (8) followed by lithium-halogen exchange and removal of the hydroxy proton to give (9), which is quenched by water. The cyclopropene (10) is rather less stable than (8), and had completely decomposed after standing for 18 h at ambient temperature in $CDCl_3$, leading to a complex mixture. Quenching of (9) with trimethylsilyl chloride and work up with water leads to the silane (11) which can be trapped by cycloaddition to DPIBF as (11a) (54 % from (6));[#] in contrast, work up with sat. aq. sodium bicarbonate leads to the silyl ether (12), which is once again trapped by DPIBF as (12a). Reaction of (6) with 2-methoxypropene and a trace of acid, followed by treatment with 2 mol.equiv. of methyllithium and quenching with either ethylene oxide or butyl iodide leads, after aqueous acid work-up to the cyclopropenes (13) and (14) respectively. These reactions probably occur by the formation of the lithio-cyclopropene (15), trapping of this by the electrophile and deprotection of the acetal group during work-up. In the same way, trapping of the lithiocyclopropene with trimethylsilyl chloride, followed by reaction with DPIBF again gives (11a).



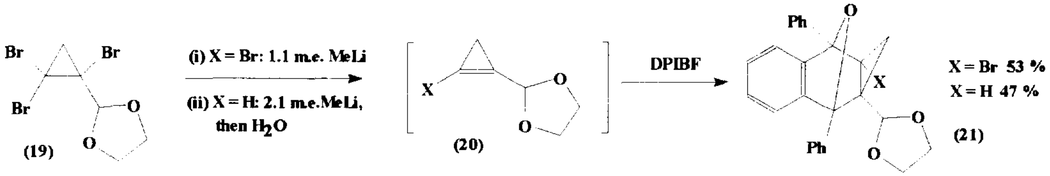
Alcohol (6) may also be brominated by reaction with carbon tetrabromide and triphenylphosphine to give (16) (61 %), which undergoes endocyclic 1,2-debromination to the cyclopropene (17) rather than exocyclic elimination to the corresponding methylene-cyclopropane or 1,3-dehalogenation on reaction with methyllithium.[14] The cyclopropene was again trapped by DPIBF as (17a) (70 %) or by furan as (17b) (79 %).



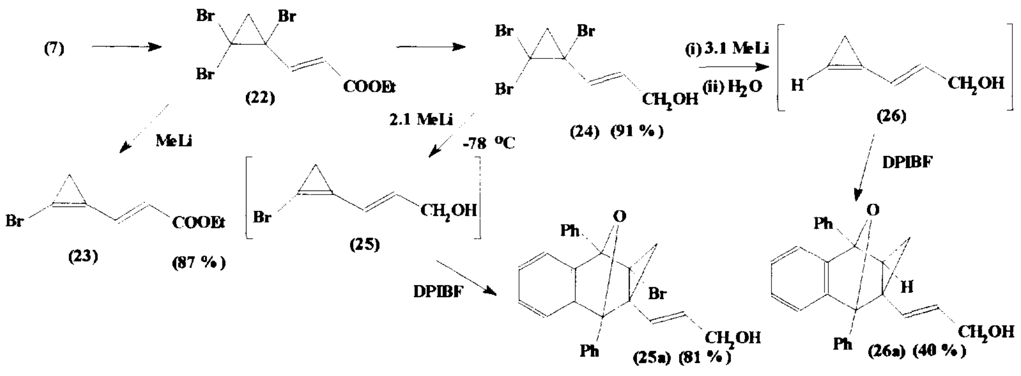
The aldehyde (7)[15] may be protected as the dithioacetal (18) which is again debrominated in high yield on reaction with methyllithium; the derived cyclopropene is trapped as a DPIBF adduct (60 %):



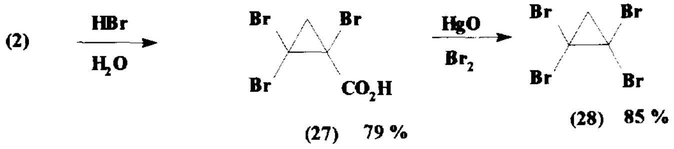
The aldehyde may also be protected as an acetal (19) using ethylene gylcol, or using a homochiral 2,3-disubstituted ethan-1,2-diol; the use of the latter in routes to homochiral cyclopropenes will be described elsewhere. Reaction of (19) with 1.1 or 2.1 mol.equiv. of methyllithium leads to the cyclopropenes (20, X = Br, H), which are again trapped in high yield with diphenylisobenzofuran:



The aldehyde also reacts with (carbethoxy)methylene triphenylphosphorane producing the α,β-unsaturated ester (22); this in turn debrominated by reaction with methyllithium at low temperature, without attack at the ester group. Reduction of (22) led to the alcohol (24) which could either be transformed into the 2-bromo- or the 2-hydrido-cyclopropene by reaction with 2.1 or 3.1 mol.equiv. of methyllithium respectively. These cyclopropenes were stable for several hours in $CDCl_3$ at 20 °C (in contrast to vinylcyclopropene itself)[16] and were once again trapped by DPIBF to give single stereoisomers of [4+2]-cycloadduct.



The above reactions illustrate the use of the ester (2) in producing a range of four-carbon cyclopropene synthons. It is also a valuable precursor of the 3-carbon synthon, 1,2-dibromocyclopropene. Hydrolysis of the ester using hydrogen bromide leads to the corresponding acid (27). This is converted into the tetrabromide (28)[17] by reaction with mercuric oxide and bromine in carbon tetrachloride, a reaction which is readily carried out on a multigram scale. Debromination of (28) with 1.1 mol.equiv. of methyl lithium has been shown to provide an efficient route to 1,2-dibromocyclopropene; the cycloaddition reactions of this and related compounds have attracted considerable interest in routes to cycloproparenes,[6] while it also undergoes ring-opening to the vinylcarbene, 1,2-dibromoprop-2-en-1-ylidene, and is debrominated to the allenic carbene, propa-1,2-dienylidene, which may be trapped by alkenes at 20 °C. [18]



We wish to thank SERC and Shell Research Ltd. for the award of a CASE studentship to MEG and Peboc plc for funding the studentship of SDH.

Experimental Section

Reagents were obtained from commercial suppliers and were used without further purification unless stated. Dichloromethane was distilled over calcium hydride. Diethyl ether and tetrahydrofuran were distilled over sodium wire. Petroleum was either of boiling point 40 - 60 °C or 60 - 80 °C and was distilled. Reactions requiring anhydrous conditions were performed using oven dried glassware (250 °C) that was cooled under either dry nitrogen or argon and the experiments were conducted under a positive atmosphere of one of these gases. Organic solutions were dried over anhydrous magnesium sulphate, and, unless stated, were evaporated at 14 mmHg. Yields quoted are for the purified compounds unless stated.

All new compounds were homogeneous by tlc or by glc. Glc was conducted using a Perkin-Elmer Model F17 F.I.D. on a capillary column (30 m x 0.32 mm id Phase, DB5 split ratio of 50:1) using nitrogen as carrier gas. Tlc was performed using Aldrich silica gel 60 plates (F254). Compounds were visualised either by examination under an ultraviolet source or by exposure to iodine vapour. Column chromatography was conducted with Merck 7736 silica gel 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 using a Finnigan Mat 1020 spectrometer. Mass measurements refer to ^{79}Br and ^{35}Cl isotopes unless stated and were obtained from the Swansea Mass Spectrometry Service. Microanalyses were performed with a Carlo-Erba Model 1106 CHN analyser. Nmr spectra were recorded on a Bruker AC250 at 250 MHz for protons and 62.5 MHz for carbon and in the latter case were either broad-band or gated decoupled.

Methyl 1,2,2-tribromocyclopropanecarboxylate

Methyl acrylate (43.05 g, 0.5 mol) and dichloromethane (90 ml) were stirred at 5 °C and bromine (87.9 g, 0.55 mol) in dichloromethane (70 ml) was added dropwise over 2.5 h at 5 - 10 °C. The mixture was allowed to stand at 20 °C overnight, and then the excess of bromine was destroyed by shaking with sodium thiosulphate solution (100 ml). The organic phase was separated and the aqueous phase re-extracted with dichloromethane (2 x 20 ml). The combined organic layers were washed with sat.aq. sodium chloride (100 ml), dried and filtered to give a clear colourless solution of methyl 2,3-dibromopropionate. This was cooled to 5 °C in an ice water bath and triethylamine (60.0 g, 0.59 mol) in dichloromethane (90 ml) was added dropwise over 80 m with stirring at 5 - 10 °C. Triethylamine hydrobromide soon separated as a white solid. The mixture was stirred at ambient for 1 hour. Saturated aq. sodium chloride (150 ml) and 2N sulphuric acid (150 ml) were then added and the phases separated. The aqueous phase was re-extracted with dichloromethane (20 ml). The combined organic phases were washed with 0.2N sulphuric acid (150 ml), and then brine (200 ml) and then dried. Removal of the solvent from a small portion of the solution gave methyl 2-bromoacrylate.

Dichloromethane (140 ml) and TEBA (benzyl-triethylammonium chloride) (70 g) were stirred rapidly in an ice-bath and a solution of sodium hydroxide (160 g, 4.0 mol) in water (160 ml) was added followed by bromoform (129 g), maintaining the temperature at 10 - 15 °C. The dichloromethane solution of methyl 2-bromoacrylate was added over 30 min at such a rate that the temperature was maintained at 10 - 15 °C. The mixture was then allowed to reach a maximum of 24 °C. After 3 h, further bromoform (28.9 g) was added. When the reaction was complete by G.L.C. (ca 5.5 - 6 h), an ice-cold, half saturated solution of sodium chloride (1 L) at below 30 °C. The lower dichloromethane layer was separated and the aqueous phase was re-extracted with dichloromethane (2 x 50 ml). The combined organic phases were washed with half saturated sodium chloride solution (500 ml). The aqueous phase was re-extracted with dichloromethane (2 x 50 ml). The combined organic phases were dried, then evaporated to leave an almost black, residue. To this was added petroleum (b.p. 40 - 60, 450 ml) and the mixture was vigorously shaken for five m, when some black solid separated. The mixture was filtered through a bed of magnesium sulphate to give a pale yellow solution. Evaporation gave a reddish oil which was vacuum distilled. The fraction boiling at 65 - 90 °C at 0.2 mm Hg (86 g) was *methyl 1,2,2-tribromocyclopropanecarboxylate (2)*; an additional fraction at 90 - 110 °C (8.2 g) contained a small amount of high boiling impurity (total yield of (2) 56 % based on methyl acrylate). The ester (2) (Calculated for $C_5H_5Br_3O_2$: 333.7840. Found M: 333.7820) showed δ_H 3.9 (3 H, s), 2.77 (1 H, d, J 9.6 Hz), 2.00 (1 H, d, J 9.6 Hz); δ_C 165.7, 54.0, 38.1, 26.4, 36.1; ν_{max} 2960, 1740, 1435, 1300.

Reaction of methyl 1,2,2-tribromo-1-cyclopropanecarboxylate with methyllithium

(i) **In the presence of 2,3-dimethyl-1,3-butadiene**: Methyllithium (2.07 ml, 3.11 mmole) was added to stirred methyl 1,2,2-tribromo-1-cyclopropanecarboxylate (1.0 g, 2.96 mmole) in dry ether (10 ml) and 2,3-dimethyl-1,3-butadiene (10 mol.eq., 2.43 g) at -85 °C. The mixture was stirred for 3 h at room temperature and then quenched with water (2 ml) at -10 °C and extracted with ether (3 x 15 ml), dried and evaporated to give *1-bromo-3,4-dimethyl-6-methoxycarbonylbicyclo[4.1.0]hept-3-ene* (4, R = Me) (0.69, 78%) which was purified by chromatography eluting with petroleum and ether (5:1) ($C_{11}H_{15}BrO_2 + H_4N^+$ requires: 276.0600. Found: 276.060) which showed δ_H 3.78 (3 H, s), 3.09 (1 H, br.d, J 17.5 Hz), 2.93 (1 H, br.d, J 16.5 Hz), 2.78 (1 H, br.d, J 16.5 Hz), 2.23 (1 H, br.d, J 17.5 Hz), 1.84 (1 H, d, J 6.1 Hz), 1.6 (6 H, br.s), 1.35 (1 H, d, J 6.1 Hz); δ_C 171.4, 122.88, 122.55, 78, 52.2, 42.8, 37.6, 32.97, 32.1, 20.5, 18.87; ν_{max} 1729, 1436 cm^{-1}.

(ii) In the presence of diphenylisobenzofuran: The above procedure was repeated using DPIBF (0.9 mol. equiv.) to give *methyl 2-bromo-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octan-4-carboxylate* (3) (85 %), m.p. 63-65 °C (Found: C 67.17, H 4.55; $C_{25}H_{19}O_3Br$ requires: C 67.10, H 4.28); δ_H 7.2-7.8 (14 H, complex), 3.6 (3 H, s), 3.0 (1 H, d, J 6.0 Hz), 2.7 (1 H, d, J 6.0 Hz); δ_C 168.6, 148.56, 147.4, 134.2, 132.9, 129.24, 129.1, 129.0, 128.55, 128.5, 128.3, 126.64, 126.3, 123.55, 122.4, 91.1, 89.2, 52.08, 51.16, 42.8, 30.1; ν_{max} 1724, 1326, 980 cm^{-1}.

(iii) In the presence of 1,3-butadiene: The above procedure was repeated using 1,3-butadiene (10 mol. equiv.). *1-Bromo-6-methoxycarbonylbicyclo[4.1.0]hept-3-ene* (**4**, R = H) was obtained (67%) ($C_9H_{11}O_2Br$ requires: 248.0286 . Found M + NH_4^+: 248.0286), which showed δ_H 5.56-5.51 (1 H, m), 5.46-5.37 (1 H, m), 3.74 (3 H, s), 3.12 - 3.00 (1 H, m), 2.93 - 2.88 (2 H, m), 2.35 (1 H, ddt, J 2.2, 5.8, 17.7 Hz), 1.85 (1 H, d, J 6.4 Hz), 1.45 (1 H, d, J 6.4 Hz); δ_C 171.3, 123.7, 52.24, 36.9, 36.34, 31.8, 26.5, 20.3; ν_{max} 1733.6, 1436 cm^{-1}.

(iv) In the presence of furan: The above was repeated using furan (10 mol. equiv.) to give *2-bromo-3-methoxycarbonyl-8-oxatricyclo[3.2.1.0^{2,4}]octane* (85%) as a 3.5:1 mixture of isomers. The major isomer ($C_9H_9O_3Br$ requires: C 44.11; H 3.7; Found: C 43.7, H 3.5) showed δ_H 6.9 (1 H, dd, J 1.7, 5.7 Hz), 6.68 (1 H, dd, J 1.7, 5.7 Hz), 4.93 (1 H, d, J 1.6 Hz), 4.88 (1 H, d, J 1.6 Hz), 3.76 (3 H, s), 2.55 (1 H, d, J 6.1 Hz), 2.19 (1 H, d, J 6.1 Hz); δ_C 169.35, 140.4, 138.1, 82.0, 78.36, 52.04, 48.9, 29.95, 31.1; ν_{max} 1740, 1450 cm^{-1}. The minor isomer showed δ_H 6.41 (1 H, dd, J 1.8, 5.8 Hz), 6.33 (1 H, dd, J 1.7, 5.7 Hz), 5.55 (1 H, t, J 1.7 Hz), 5.12 (1 H, t, J 1.8 Hz), 3.85 (3 H, s), 2.54 (1 H, d, J 6.7 Hz), 2.01 (1 H, d, J 6.7 Hz); δ_C 169.56, 134.4, 133.8, 88.5, 81.7, 52.7, 47.3, 40.9, 38.1.

Reaction of methyl 1,2,2-tribromocyclopropanecarboxylate with di-isobutyl aluminium hydride

(i) Di-isobutyl aluminium hydride (23.73 mmol, 23.7 ml, 1M solution in hexane) was added to a stirred solution of methyl tribromocyclopropanecarboxylate (4 g, 11.86 mmol) in dry dichloromethane (25 ml) at -40 °C under nitrogen. The mixture was allowed to reach room temperature and stirred for 30 m, when T.L.C. showed no starting material, and then quenched with sat.aq. ammonium chloride (15 ml) at -40 °C, followed by hydrochloric acid (4%, 10 ml). The cooling was removed, and the mixture stirred for 30 min. The product was extracted with dichloromethane (3 x 10 ml), and the combined organic layers were dried and evaporated to give a white solid, *(1,2,2-tribromocyclopropyl)methanol* (**6**) (2.8 g, 78 %), m.p. 86-88 °C (Found: C 15.67, H 1.99; $C_4H_5OBr_3$ requires C 15.56, H 1.63); δ_H 4.1 (1 H, dd, J 7.7, 13.0 Hz), 4.0 (1 H, dd, J 6.3, 13.0 Hz), 2.5 (1 H, dd, J 6.6, 7.4 Hz), 2.0 (1 H, d, J 9.4 Hz), 1.9 (1 H, d, J 9.4 Hz); after shaking with D_2O the ^{1}H N.M.R. showed δ_H (1 H, d, J 13.0 Hz), 4.0 (1 H, d, J 13.0 Hz), 2.09 (1 H, d, J 9.5 Hz), 2.01(1H, d, J 9.5 Hz); δ_C 70.45, 46.07, 35.71, 29.57.

(ii) Di-isobutyl aluminium hydride (2.96 ml, 2.96 mmol, 1M solution in hexene) was added to a stirred solution of methyl tribromocyclopropanecarboxylate (1 g, 2.9 mmol) in dry methylene chloride (15 ml) under nitrogen at -78 °C. The mixture was stirred for 1 hr at -78 °C followed by quenching at -78 °C with sat.aq. ammonium chloride (5 ml). Hydrochloric acid (4%, 10 ml) was added, the cooling bath removed, and the mixture stirred for 30 min. The product was extracted, dried and evaporated to give a yellow oil, 1,2,2-tribromocyclopropanecarbaldehyde (**7**) (0.63 g, 70%), identical by ^{1}H N.M.R. to that below.

1,1,2-Tribromo-2-((1-methoxy-1-methyl)ethoxymethyl)cyclopropane (5)

Dry hydrogenbromide (25.2 g, 0.31 mol, 1.1 mol.eq.) was bubbled into tetraethylammonium bromide (71.4 g, 0.34 mol, 1.2 mol.eq.) and dichloromethane (300 ml) at O °C to give a clear yellow solution. This was stirred at room temperature for 10 minutes. Propargyl alcohol (15.9g, 28 mol, 1 eq) was added slowly and the reaction stirred for 1 hour and then refluxed for 2 hours. After cooling and pouring into ether (250 ml), the precipitate was filtered through a short silica pad and washed with ether (100 ml). The combined ether layers were dried and evaporated to give *2-bromoprop-2-en-1-ol* as a brown oil. G.L.C. showed that no purification was necessary (30.4 g, 72 %) (δ_H 5.9 (1 H, dd, J 1.4, 0.9 Hz), 5.57 (1 H, dd, J 1.4, 0.9 Hz), 4.2 (2 H, t, J ca. 1.4 Hz), 3.23 (1 H, s); δ_C 132.27, 116.21, 67.36; ν_{max} 3347, 1639, 1042 cm^{-1}).

2-Methoxypropene (7.9 g, 109 mmol, 3 eq) and pyridinium toluene-4-sulphonate (catalytic amount) were added to a stirred solution of 2-bromoprop-2-en-1-ol (5 g, 36.6 mmol, 1 mol.eq.) in dry ether (60 ml) at 0 ^{0}C. An exothermic reaction was observed. After stirring at room temperature for 1 h, triethylamine (3 drops) was added and the solvent then evaporated to give *2-bromo-1-((1-methoxy-1-methyl)ethoxy)propene*, which was used unpurified in the next step and showed δ_H 5.9 (1 H, dd, J 1.4, 2.4 Hz), 5.5 (1 H, dd, J 1.4, 2.4 Hz), 4.0 (2 H, t, J 1.3 Hz), 3.2 (3 H, s), 1.35 (6 H, s).

Bromoform (14 g, 55 mmol, 1.5 mol.eq.) and cetrimide (300 mg) were added to 2-bromo-1-((1-methoxy-1-methyl)ethoxy)propene (13.9 g, 36.5 mmol) in dichloromethane (25 ml). Sodium hydroxide solution (7 ml of a 1:1 w/v solution) was added slowly at room temperature and the reaction stirred vigorously for 18 h and quenched by the addition of water (100 ml). Triethylamine (3 drops) was added and the mixture was extracted with dichloromethane (4 x 100 ml). The combined organic extracts were dried and evaporated to give a mixture of product and starting material (ratio 1 : 4). This was washed with petrol (40/60) (100 ml), filtered and evaporated and the reaction was repeated (x3) using the same conditions, reagents etc. to give *1,1,2-tribromo-2-((1-methoxy-1-methyl)ethoxymethyl)cyclopropane (5)*, which showed δ_H 3.9 (1 H, d, J 11.2 Hz), 3.7 (1 H, d, J 11.2 Hz), 3.31 (3 H, s), 2.0 (2 H, d, J 2.8 Hz), 1.41 (6 H, d, J 2.24 Hz); δ_C 70.44, 46.09, 35.70, 30,88, 29.53, 20.26, 9.69. In the absence of triethylamine this deprotected slowly to give 1,1,2-tribromocyclopropane-2-methanol in a yield of 26 % (4 steps from propargyl alcohol).

1,1,2-Tribromocyclopropane-2-methanol (6)

1,1,2-Tribromo-2-((1-methoxy-1-methyl)ethoxymethyl)cyclopropane (500 mg, 1.3 mmol) was stirred at room temperature in methanol (10 ml) and water (10 ml). p-Toluene sulphonic acid (catalytic amount) was added and after the initial exothermic reaction the mixture was stirred at room temperature for 10 m, extracted with ether (4 x 15 ml) and the combined organic extracts dried. The solvent was removed to give *1,1,2-tribromocyclopropyl-2-methanol* (**6**) (300 mg, 77 %). Chromatography on silica gel eluting with 1 : 1 ether : petrol gave a pale yellow solid identical by proton and carbon n.m.r. to that above. When this was repeated on a large scale (50 g) it was necessary to purify the product using activated charcoal.

2-Bromocyclopropene-1-methanol diphenylisobenzofuran adduct

(i) 1,1,2-Tribromocyclopropane-2-methanol (0.2g, 0.65 mmol, 1 mol.eq.) and diphenylisobenzofuran (0.17 g, 0.65 mmol, 1 mol.eq.) were dissolved in dry ether (10 ml) and stirred under argon at -78 ^{0}C. MeLi (0.86 ml, 1.3 mmol, 2 mol.eq.) was added and the reaction warmed to room temperature and stirred for 2 h. The reaction was quenched at -40 ^{0}C by the addition of water (2 ml), and the aqueous layer was separated and extracted with ether (3 x 10 ml). The combined organic extracts were dried and evaporated to give *4-bromo-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.$0^{2,4}$]octane-2-methanol* (**8a**) as a yellow solid (150 mg, 55 %) (Found: 403.053. $C_{24}H_{19}{}^{81}BrO$ requires (M - OH): 403.0522) which showed δ_H 7.8 - 7.9 (4 H, m), 7.4 - 7.5 (7 H, m), 7.3 - 7.35 (3 H, m), 3.95 (1 H, d, J 12.1 Hz), 3.8 (1 H, d, J 12.1 Hz), 2.8 (1 H, d, J 6.8 Hz), 1.84 (1 H, d, J 6.8 Hz) 1.6 (1 H, s); δ_c 156.4, 129.3, 128.7, 128.1, 121.7, 89, 62.6, 50, 39.5, 27, 20.3.

(ii) Compound (**3**) was reduced with di-isobutylaluminium hydride at -40 to 20 ^{0}C using the same method as above for the preparation of (**6**). This gave a compound identical to that in (i) in 81 % yield.

2-Bromocyclopropene-1-methanol (8)

The above experiment was repeated without the addition of diphenylisobenzofuran to give *2-bromocyclopropene-1-methanol (***8***) (84 %)* (Found M^+: 147.9524. Calculated for C_4H_5BrO: 147.9524) which showed δ_H 4.62 (2 H, s), 2.65 (1 H, s), 1.7 (2 H, s); δ_C 83.68, 64.99, 50.98, 14.25.

Cyclopropene-1-methanol diphenylisobenzofuran adduct

1,1,2-Tribromocyclopropane-2-methanol (0.553 g, 1.79 mmol, 1 mol.eq.) was stirred in dry ether (10 ml) under argon at -78 ^{0}C. MeLi (3.6 ml, 5.37 mmol, 3 mol.eq.) was added and the reaction warmed to room temperature for 5 m. The reaction was re-cooled to -78 °C when water (5 ml) was added, warmed to room temperature for 30 m, and cooled to below 0 °C to decant the ether layer from the frozen aqueous layer. The water layer was washed with ether (3 x 10 ml) and the combined organic layers were added to diphenylisobenzofuran (0.43 g, 1.59 mmol, 0.89 mol.eq.), stirred for 30 m and then evaporated to give a solid (0.58 g, 96 %); chromatography eluting with ether : petrol (1 : 2) gave *1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane-2-methanol* (**10a**) as a white solid (Found M^+: 340.1463. Calculated for $C_{24}H_{20}O_2$: 340.1463) which showed δ_H 7.6 - 7.8 (4 H, m), 7.3 - 7.6 (5 H, m), 7.0 - 7.3 (5 H, m), 3.83 (1 H, d, J 12 Hz), 3.61 (1 H, d, J 12 Hz), 2.15 (1 H, dd, J 5.2, 3.6 Hz), 1.75 (1 H, dd, J 6.8 , 3.6 Hz), 1.40 (1 H, dd, J 6.8, 5.2 Hz), 1.11 (1 H, s, OH); δ_C 14 x aromatics at 151.26 - 119.76, plus 89.66, 88.11, 62.48, 37.51, 30.51, 18.76.

Cyclopropene-1-methanol (10)

The procedure above was repeated without the addition of diphenylisobenzofuran to yield *cyclopropene-1-methanol* (**10**) (73 %) as a volatile oil which readily decomposed and showed δ_H 6.7 (1 H, pen, J 1.8 Hz), 4.5 (2 H, t, J 1.8 Hz), 2.5 (1 H, s), 1.0 (2 H, t, J 1.8 Hz); ν_{max} 3382, 1772 cm^{-1}.

2-(2-Hydroxymethylcyclopropen-1-yl)ethanol (13)

1,1,2-Tribromocyclopropane-2-methanol (1.13g, 3.66 mmol, 1 eq) was stirred at room temperature in dry ether (20 ml). 2-Methoxypropene (1.1 ml, 11 mmol, 3 eq) and pyridiniumtoluene-4-sulphonate (catalytic amount) were added and stirred for 30 m. Triethylamine (6 drops) was added and the volatile components removed under reduced pressure. The concentrate was redissolved in dry ether (20 ml), stirred under argon and cooled to -78 ^{0}C. MeLi (4.9 ml, 7.3 mmol, 2 eq) was added and the reaction warmed to room temperature for 10 m. The reaction was recooled to -78 ^{0}C and ethylene oxide (condensed) (0.94 ml, 0.64 g, 14.6 mmol, 4 eq) was added via a pre-cooled syringe. The reaction was warmed to room temperature over 18 h and quenched at -40 ^{0}C by the addition of water (20 ml). The aqueous layer was separated and extracted with ether (3 x 20 ml). The organic extracts were dried and evaporated to give an oil which was subjected to chromatography eluting with ether : petrol (1:1) to give *2-(2-hydroxymethylcyclopropen-1-yl)ethanol* (**13**) (20 %) (Found MH^+: 115.076. Calculated for $C_6H_{11}O_2$: 115.0759) which showed δ_H 4.61 (2 H, t, J 2.4 Hz), 4.2 (2 H, br.s), 3.79 (2 H, t, J 5.2 Hz), 2.65 (2 H, m), 1.05 (2 H, s); δ_C 110.36, 109.0, 60.3, 60.3, 30.05, 9.36.

2-n-Butylcyclopropen-1-ylmethanol (14)

1,1,2-Tribromocyclopropane-2-methanol (1.12g, 3.6 mmol, 1 eq) was dissolved in dry ether (15 ml) and stirred at room temperature. 2-Methoxypropene (1.04 ml, 10.8 mmol, 3 eq) and pyridinium toluene-4-sulphonate (catalytic amount) were added. After 20 m, triethylamine (6 drops) was added and the volatile components removed under vacuum. The concentrate was re-dissolved in dry ether (15 ml), stirred under argon and cooled to -78 ^{0}C. n-BuLi (5.58 ml, 7.25 mmol, 2 eq) was added and the reaction warmed to room temperature, stirred for 20 m., and then re-cooled to -78 ^{0}C. Hexamethylphoshoramide (0.6 ml, 3.6 mmol, 1 eq) was added and the reaction warmed to room temperature for 10 m. The reaction was re-cooled to -78 ^{0}C when 1-iodobutane (0.66g, 0.42 ml, 1 eq) was added and then stirred at room temperature for 18 h. Quenching at -40 ^{0}C with water (20 ml) was followed by separation of the aqueous layer. The aqueous layer was extracted with ether (3 x 20 ml) and the combined organic extracts were washed with dilute HCl (50 ml) and dried. The solvent was evaporated to give a crude oil which was subjected to chromatography eluting with ether : petrol (1 : 2) to give *2-n-butylcyclopropen-1-ylmethanol* **(14)** *(39 %)* (Found: 126.104. Calculated for $C_8H_{14}O$: 126.1045) which showed δ_H 4.55 (2 H, s), 2.24 (2 H, tt, J 7.2, 1.5 Hz), 1.9 (1 H, br.s), 1.6 (2H, br.pen, J 7.2 Hz), 1.45 (2 H, m, including J 7.2 Hz, 7.0 Hz), 0.95 (2 H, s), 0.92 (3 H, t, J 7.0 Hz); δ_C 112.96, 107.81, 58.62, 29.51, 25.58, 22.39, 13.78, 7.95.

1-Trimethylsilyl-2-(trimethysilyloxymethyl)cyclopropene

(i) 1,1,2-Tribromocyclopropane-2-methylalcohol (0.61g, 1.97 mmol, 1 eq) was stirred in dry ether (15 ml) under argon and cooled to -78 ^{0}C. MeLi (3.9 ml, 5.92 mmol, 3 eq) was added and the reaction warmed to room temperature. Trimethylsilylchloride (4 mol.eq.) was added and the reaction stirred for 1 h. Diphenylisobenzofuran (0.382g, 1.41 mmol, 0.7 eq) dissolved in a minimum of dry ether was added and the mixture stirred for 18 h. The reaction was quenched at -40 ^{0}C by the addition of sat.aq. sodium bicarbonate (5 ml), the aqueous layer was separated and extracted with ether (3 x 20 ml). The combined organic extracts were dried and evaporated to give an oil which was subjected to chromatography eluting with ether : petrol (1 : 2) to give the *2-trimethylsilyl-4-(trimethysilyloxymethyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane* **(12a)** *(89 %)* as a yellow solid (Found: 485.2332 (MH^-). Calculated for $C_{30}H_{36}Si_2O_2$: 485.2332) which showed δ_H 7.91 - 7.83 (5 H, m), 7.51 - 7.42 (5 H, m), 7.34 - 7.31 (4 H, m), 3.94 (1 H, d, J 11.1 Hz), 3.59 (1 H, d, J 11.1), 2.57 (1 H, d, J 4.3 Hz), 1.71 (1 H, d, J 4.3 Hz), 0.09 (9 H, s), -0.23 (9 H, s); δ_C 91.8, 89.5, 62.1, 42.9, 25.45, 23.55, 0.58, -0.57 (plus complex aromatics); ν_{max} 2955, 1664, 1250 cm^{-1}.

(ii) The procedure in (i) was repeated without the addition of diphenylisobenzofuran to give *1-trimethylsilyl-2-(trimethysilyloxymethyl)cyclopropene* **(12)** (78 %) which showed δ_H 4.71 (2 H, s), 0.92 (2 H, s), 0.19 (9 H, s), 0.16 (9 H, s); δ_C 133.55, 107.76, 60.55, 7.35, -0.50, -1.45; ν_{max} 2960, 1806, 1250, 842 cm^{-1}.

2-Trimethylsilyl-1-(hydroxymethyl)cyclopropene

(i) Methyllithium (1.37 ml, 1.92 m.mol) was added to stirred solution of *1,1,2-tribromo-2-((1-methoxy-1-methyl)ethoxymethyl)cyclopropane* **(5)** (prepared as above) (0.35 g, 0.91 m.mol) in dry ether at -80 ^{0}C. The mixture was allowed to reach room temperature for 5 m and then cooled to -70 ^{0}C and quenched with trimethylsilylchloride (0.28 ml, 2.3 m.ol) followed by diphenylisobenzofuran (0.2 g, 0.82 m.mol). The mixture was allowed to reach room temperature and stirred for 18 h. Water (3 ml) was added at -40 ^{0}C and the aq. layer was extracted with ether (3 x 10 ml). The combined ether layers were dried and evaporated to give a yellow solid which was treated with p-toluenesulphonic acid (10 mg) in methanol (5 ml) for 5 m and then extracted with ether, washed with sat.aq. sodium bicarbonate, dried and evaporated. Chromatography eluting with petrol and ether (1:1) gave **(11a)** (0.2 g, 54 %) which showed δ_H 7 -7.8 (14 H, m), 3.8 (1 H, d, J 12.4 Hz), 3.66 (1 H, J 12.4 Hz), 2.54 (1 H, d, J 4.6 Hz), 1.47 (1 H, d, J 4.6 Hz), -0.3 (9 H, s); δ_C 91.5, 88.7, 62.4, 43.8, 27.4, 24.0, -0.41 (plus complex aromatics); ν_{max} 3482, 1660, 1279 cm^{-1}.

(ii) The above reaction was repeated without the addition of diphenylisobenzofuran; the mixture after the addition of TMSCl was allowed to reach room temperature and stirred for 1 h, then cooled to -40 ^{0}C and quenched with water (3 ml). The aqueous layer was extracted with ether (2 x 10 ml) and the combined organic layers were dried and evaporated to give a yellow oil *1-trimethylsilyl-2-(hydroxymethyl)cyclopropene* (**11**) (76 %) which showed δ_H 4.68 (2 H, s), 0.9 (2 H, s), 0.16 (9 H, s); ν_{max} 3334, 841 cm^{-1}.

1-Bromomethyl-1,2,2-tribromocyclopropane(16)

1,1,2-Tribromocyclopropane-2-methanol (1.0g, 3.2 mmol, 1 eq) was dissolved in dry ether (25 ml) and stirred at 0 ^{0}C under argon. Carbontetrabromide (1.4 g, 4.2 mmol, 1.3 eq) and triphenylphosphine (1.1g, 4.2 mmol, 1.3 eq) were added and reaction warmed to room temperature and stirred for 18 h. The precipitate was filtered and the filter cake washed with ether (3 x 10 ml). The combined organic layers were evaporated to give a crude solid which was subjected to column chromatography on silica gel eluting with petrol (40 / 60) to give *1-bromomethyl-1,2,2-tribromocyclopropane* (**16**) as a white solid (61 %) (Found 288.7863 (M-Br). Calculated for $C_4H_4Br_4$: 288.7863) which showed δ_H 4.07 (1 H, d, J 11.7 Hz), 3.90 (1 H, d, J 11.7 Hz), 2.17 (d,1 H, J 9.5 Hz), 2.10 (d, 1 H, J 9.5 Hz); δ_C 43.2, 42.38, 39.15, 32.02; ν_{max} 3055.8 (m), 2967.7 (m), 1734.5 (w), 1638.5 (w), 1436.0 (s), 1185.1 (s) cm^{-1}. 20 % Unreacted starting material was recovered.

1-Bromo-2-bromomethylcyclopropene

(i) 1-Bromomethyl-1,2,2-tribromocyclopropane (0.5g, 1.34 mol, 1 eq) and diphenylisobenzofuran (0.36g, 1.34 mol, 1 eq) in dry ether (15 ml) were stirred at -78 ^{0}C under argon; MeLi (0.9 ml, 1.35 mol, 1 eq) was added. The reaction was warmed to room temperature when a significant decolourisation was observed. After 10 m the reaction was quenched at -40 ^{0}C with water (2 ml). The aqueous layer was extracted with ether (2 x 15 ml) and the combined organic extracts dried and evaporated to give *4-bromo-2-bromomethyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane* (**17a**) as a white solid (0.45g, 70 %) (Found M - Br$^+$: 401.0541. Calculated for $C_{24}H_{18}Br_2O$: 401.0542) which showed δ_H 7.8 (4 H, m), 7.5 (7 H, m), 7.3 (3 H, m), 3.66 (1 H, d, J 11.9 Hz), 3.44 (1 H, d, J 11.9 Hz), 3.11 (1 H, d, J 6.6 Hz), 2.03 (1 H, d, J 6.6 Hz).

(ii) 1-Bromomethyl-1,2,2-tribromocyclopropane (1.0g, 2.69 mmol, 1 eq) and furan (0.18g, 2.69 mmol, 1 eq) were stirred in dry ether under argon and cooled to -78^{0}C. MeLi (1.8 ml, 2.69 mmol, 1 eq) was added and the reaction warmed to room temperature for 18 h and then quenched at -40 ^{0}C by the addition of water (5 ml). The aqueous layer was extracted with ether (3 x 10 ml). The combined organic extracts were dried and evaporated to give *2-bromo-4-bromomethyl-8-oxatricyclo[3.2.1.0^{2,4}]octane* (**17b**) as an oil (0.6g, 79 %) which was subjected to chromatography 1 : 1 ether : petrol (Found M$^+$: 277.8947. Calculated $C_8H_8Br_2O$: 277.8943) and showed δ_H 6.75 (1 H, dd, J 5.7, 1.5 Hz), 6.70 (1 H, dd, J 5.7, 1.5 Hz), 4.95 (1 H, d, J 1.5 Hz), 4.80 (1 H, d, J 1.5 Hz), 3.5 (1 H, dd, J 11.1, 1.37 Hz), 3.4 (1 H, d, J 11.1 Hz), 2.45 (1 H, dd, J 6.47, 1.37 Hz), 1.34 (1 H, d, J 6.47 Hz); δ_C 140.51, 138.48, 82.29, 79.56, 49.19, 35.71, 31.29, 13.83.

Oxidation of (1,2,2-tribromocyclopropyl)methanol with PCC

(1,2,2-Tribromocyclopropyl)methanol (7 g, 22.0 mmol) was added at room temperature to a stirred solution of pyridinium chlorochromate (9.76 g, 45.0 mmol) in dichloromethane (80 ml). A black colour appeared after 10 m. The reaction was stirred for 1 h, then refluxed for 1 h. The reaction was cooled, diluted with ether (150 ml), and filtered through a bed of silica. The solvent was evaporated to give a yellow oil, 1,2,2-tribromocyclopropanecarbaldehyde (7) (5.92 g, 85.1%), which showed δ_H 9.4 (1H, s), 2.8 (1H, d, J 9.4 Hz), 2.0 (1H, d, J 9.4 Hz); δ_C 189.44, 45.80, 34.77, 26.20; ν_{max} 1722, 1411 cm^{-1}; m/e 307 (M^+), 227 (M^+-Br), 147 (M^+-Br_2), 67 (M^+-Br_3).

Reaction of 1,2,2-tribromocyclopropanecarbaldehyde with 1,2-ethanediol.

1,2-Ethanediol (0.18 ml, 3.24 mmol, 5 mol.eq.) was added to a stirred solution of 1,2,2-tribromocyclopropanecarboxaldehyde (0.2 g, 0.647 mmol) and pTSA (0.012 g, 0.065 mmol, 0.1 mol.eq.) in toluene (15 ml). The mixture was refluxed for 2 h to separate the water by Dean Stark apparatus, then cooled and quenched with water (2 ml) and sat.aq. sodium bicarbonate (2 ml). The product was extracted with ether (2 x 10 ml), and the combined ether layers washed with water (10 ml), dried and evaporated. The residue was treated with petroleum (5 ml) to precipitate the product which was filtered from any excess of diol, to give *1,2,2-tribromocyclopropanecarbaldehyde ethylene acetal* (**19**) (0.13 g, 62%) ($C_6H_7O_2Br_3$ requires: C 20.54, H 2.01. Found: C 20.82, H 2.28); δ_H 4.8 (1 H, s), 4.3 (2 H, m), 4.0 (2 H, m), 2.2 (1 H, d, J 9.7 Hz), 2.0 (1 H, d, J 9.66 Hz); δ_C 106.9, 66.6, 65.85, 45.06, 34.98, 27.0; ν_{max} 1637, 1106, 732, 583 cm^{-1}.

4-Bromo-2-(2,3-dioxacyclopentyl)methyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane

Methyllithium (0.29 ml, 0.31 mmol, 1.1 M) was added to a stirred solution of 1,2,2-tribromocyclopropanecarbaldehyde ethylene acetal (0.1 g, 0.29 mmol) in dry ether (10 ml) and 1,3-diphenylisobenzo- furan (0.07 g, 0.27 mmol, 0.9 mol equiv.) at -78 ^{0}C under nitrogen. The reaction was stirred at room temperature for 18 h, and then treated with water (2 ml) at -20 ^{0}C and extracted with ether (3 x 10 ml), the combined ether layers dried and evaporated to give yellow solid, which was purified by recrystallization using 5:2 petroleum ether / ether to give a white solid, 4-bromo-2-(2,3-dioxacyclopentyl)-methyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane (**21, X = Br**) (70 mg, 53%) which showed δ_H 7.8-7.2 (14H, m), 4.8 (1H, s), 4.0-3.6 (4H, m), 2.9 (1H, d, J 6.34 Hz), 2.1 (1H, d, J 6.34 Hz) ; δ_C 147.92, 134.68, 133.31, 130.37, 129.84, 129.68, 129.31, 129.13, 128.87, 128.46, 128.34, 128.09, 127.90, 127.81, 126.39, 126.27, 123.04, 122.50, 103.87, 90.41, 89.58, 65.29, 64.54, 47.70, 38.14, 27.01 ; ν_{max} 1662, 1448, 1298, 1098, 910 cm^{-1}.

2-(2,3-Dioxacyclopentyl)methyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane

Methyllithium (0.82 ml, 0.90 mmol, 1.1 M, 2.1 mol equiv.) was added to a stirred solution of 1,2,2-tribromocyclopropane carbaldehyde ethylene acetal (0.15 g, 0.43 mmol) in dry ether (8 ml) at -78 ^{0}C. The solution was allowed to reach room temperature and stirred for 5 min. before cooling to -60 ^{0}C and quenching with water (3 ml). The ether layer was decanted from the ice and added to 1,3-diphenyliso-benzofuran (0.11 g, 0.38 mmol) and stirred for 12 h and then evaporated andrecrystallized using petroleum ether / ether (5:2) to give a white solid, *2-(2,3-dioxacyclopentyl)methyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo- [3.2.1.0^{2,4}]octane* (**21, X = H**) (76 mg, 47%) ($C_{26}H_{22}O_3$ requires: C 81.65, H 5.80. Found: C 81.52, H 6.06) which showed δ_H 7.8-7.1 (14H, m), 4.9 (1H,s), 3.9(1H, dd, J 6.5, 13.9 Hz), 3.7 (3H, m), 2.1 (1H, dd, J 4.15, 8.7 Hz), 2.0 (1H, dd, J 4.0, 6.7 Hz), 1.6 (1H, dd, J 4.8, 6.7 Hz) ; δ_C 148.34, 136.14, 134.85, 132.91,130.27, 129.71, 129.55, 129.37, 128.70, 128.30, 128.23, 128.08, 127.78, 126.76, 126.32, 125.82, 121.34, 119.56, 102.20, 89.90, 87.86, 65.32, 64.16, 36.87, 32.04, 16.33 ; ν_{max} 1662, 1449, 1302, 1101, 909 cm^{-1}.

Reaction of 1,2,2-tribromocyclopropanecarboxaldehyde with 1,3-propane dithiol.

1,3-Propanedithiol (3.2 mmol, 0.2 ml) was added to a stirred solution of 1,2,2-tribromocyclopropane carbaldehyde (0.2 g, 0.65 mmol) and PTSA (0.012 g, 0.065 mmol) in toluene (10 ml). The mixture was refluxed for 1.5 hr to separate the water by Dean Stark apparatus and then cooled and quenched with water (3 ml) and sat. aq. sodium bicarbonate (1 ml). The product was extracted with ether (2 x 10 ml), the combined ether layers were washed with water (10 ml), dried and evaporated. The residue was treated with petroleum ether (5 ml) to precipitate the product which was filtered from any excess of dithiol, to give *1,2,2-tribromo-1-(2,6-dithiocyclohexyl)cyclopropane* **(18)** (0.15 g, 60%), m.p. 112-114 °C (Found: C 21.28; H 2.32; $C_7H_9Br_3S_2$ requires C 21.17, H 2.28); δ_H 4.1 (1H, s), 3.0 (4H, m), 3.0 (4H, m), 2.15 (1H, m), 2.1 (2H, s), 1.9 (1H, m); δ_C 58.96, 45.75, 39.34, 32.18, 31.19, 30.47, 25.19; ν_{max} 1417.6, 1026.9 cm^{-1}.

4-Bromo-2-(2,6-dithiocyclohexyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane

Methyllithium (0.5 ml, 0.55 mmol, 1.1M) was added to a stirred solution of 1,2,2-tribromo-1-(2,6-dithiocyclohexyl)cyclopropane (0.2 g, 0.5 mmol) in dry ether (10 ml) and 1,3-diphenylisobenzofuran (0.12 g, 0.45 mmol) at -78 °C under nitrogen. The reaction was allowed to reach room temperature and stirred for 5 h. The product was quenched with water (2 ml) and -20 °C and extracted with ether (3 x 15 ml); the combined ether layers were dried and evaporated to give a yellow solid, which was recrystallized from 5:2 petroleum ether/ether to give a white solid, *4-bromo-2-(2,6-dithiocyclohexyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane* **(18a)** (0.15 g, 60%), m.p. 126-128 °C (Found: C 63.73, H 4.66; $C_{27}H_{23}BrOS_2$ requires C 63.89, H 4.56); δ_H 7.9-7.2 (14H, m), 4.0 (1H, s), 2.9 (1H, d, J 6.5 Hz), 2.7 (4H, m), 2.0 (1H, m), 1.7 (1H, d, J 6.5 Hz), 1.6 (1H, m); δ_C 148.0, 147.13, 140.0, 137.19, 134.53, 133.54, 133.0, 130.40, 129.84, 129.21, 128.75, 128.13, 127.12, 126.78, 126.16, 125.08, 124.39, 122.36, 89.88, 88.94, 53.39, 51.41, 41.84, 32.95, 32.11, 25.63; ν_{max} 1660.4 cm^{-1}.

Ethyl 3-(1,2,2-tribromocycloprop-1-enyl)prop-E-2-en-1-oate

To a stirred solution of 1,2,2-tribromocyclopropane carbaldehyde (2.5 g, 8.1 mmol) in toluene (50 ml), carboethoxymethylene triphenylphosphorane (4.25 g, 12.21 mmol) was added at room temperature. The mixture was then refluxed for 3.5 h, then the solvent was evaporated to give a thick oil which treated with petroleum (b.p. 40 - 60 °C). The precipitate was filtered off, evaporation of the solvent gave a brown oil which purified by column chromatography eluting with petroleum ether/ether (5:2) to give *ethyl 3-(1,2,2-tribromocyclo- prop-1-enyl)prop-E-2-en-1-oate* **(22)** (2.8 g, 91 %) (Found M + NH_4^+: 393.8482. Calculated for $C_8H_9{}^{79}Br^{81}BrO_2+NH_4^+$: 393.9478) which showed δ_H 6.9 (1H, d, J 15.0 Hz), 6.2 (1H, d, J 15.0 Hz), 4.2 (2H, q, J 7.1 Hz), 2.3 (1H, d, J 9.4 Hz), 2.2 (1H, d, J 9.4 Hz), 1.3 (3H, t, 7.1 Hz); δ_C 165.34, 145.41, 126.13, 60.98, 40.09, 38.47, 31.21, 14.20; ν_{max} 1718.6, 1649.0 cm^{-1}; m/e 337 (M^+), 305, 304 (M^+-$C_3H_5O_2$), 224 (305-Br).

Ethyl 3-(2-bromocyclopropenyl)prop-E-2-en-oate

(i) Methyl lithium (0.4 ml, 1.3M, 0.53 mmol) was added to a stirred solution of ethyl 3-(1,2,2-tribromocycloprop-2-yl)prop-E-2-en-1-oate (0.2 g, 0.53 mmol) in dry ether (5 ml) at -78 °C under a nitrogen atmosphere. The reaction was allowed to reach -40 °C, cooled again to -70 °C and quenched with water (3 ml), and the ether layer was then decanted from the ice., which was extracted with cold ether (2 x 10 ml). Evaporation of the ether at 0 °C gave ethyl 3-(2-bromocyclopropenyl)prop-E-2-en-oate **(23)** (0.1 g, 87 %) which showed δ_H 7.4 (1H, d, J 15.4 Hz), 6.0 (1H, d, J 15.3 Hz), 4.2 (2H, q, 7.1 Hz), 1.7 (2H, s), 1.3 (3H, t, J 7.2 Hz); δ_C 166.3, 127.9, 126.2, 112.67, 105.4, 60.8, 16.4, 14.3; ν_{max} 1794.0, 1711.7, 1614.4 cm^{-1}. This decomposed slowly in deuterochloroform at ambient temperature to give a complex mixture; ca. 50 % remained after 18 h.

(ii) Diphenylisobenzofuran (0.11 g, 0.41 mmol) was added to a stirred solution of ethyl 3-(2-bromocyclopropenyl)prop-2-en-oate in ether (5 ml) at room temperature. The reaction was stirred for 6 hours, then the solvent was removed at 14 mm Hg to give a yellow solid which was purified by column chromatography on silica eluting with petroleum ether and ether 5:2, which gave *ethyl 4-bromo-2-(3-prop-E-2-enoyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0*^{2,4}*]octane* (0.15 g, 68 %) (m.p. 58-60 °C) (Found: C 69.07, H 4.80; $C_{28}H_{23}O_3Br$ requires C 69.00, H 4.76); δ_H 7.8-7.2 (14H, m), 6.8 (1H, d, J 15.7 Hz), 5.8 (1H, d, J 15.8 Hz), 4.1 (2H, q, 7.1 Hz), 3.0 (1H, d, J 6.4 Hz), 2.1 (1H, d, J 6.4 Hz), 1.2 (3H, t, J 7.2 Hz); δ_C 165.8, 147.68, 147.38, 144.24, 133.81, 133.04, 130.36, 129.82, 129.33, 129.28, 129.08, 128.81, 128.68, 128.55, 128.32, 127.08, 126.80, 123.70, 122.83, 122.04, 90.78, 89.93, 60.52, 52.84, 40.74, 29.70, 14.20; ν_{max} 1716.9, 1648 cm^{-1}.

Reaction of ethyl 3-(1,2,2-tribromocycloprop-1-ayl)prop-E-2-en-1-oate with DIBAL

To a stirred solution of ethyl-3-(1,2,2-tribromocyclopropyl)prop-E-2-en-1-oate (0.5 g, 1.32 mmol) in dry toluene (20 ml) was added a solution of 1.0M DIBAL in toluene (2.65 ml) at -40 °C. The mixture was allowed to reach room temperature and stirred for 30 m, when T.L.C. in petroleum ether/ether (5:2) showed no starting material. The mixture was treated with a sat.aq. ammonium chloride (20 ml) at -40 °C. Hydrochloric acid (4%, 40 ml) was added, the cooling bath removed, and the mixture stirred for 30 m. The mixture was extracted with methylene chloride (4 x 15 ml), and the extracts were dried and evaporated to give a yellow oil. Column chromatography eluting with petroleum ether and ether (5:2) gave 3-(1,2,2-tribromocyclopropyl)-E-2-propen-1-ol (**24**) (0.4 g, 91 %), which showed δ_H 6.0 (1H, d, J 15.0 Hz), 5.9 (1H, d, J 15.0 Hz), 4.28 (1H, d, J 14.1 Hz), 4.21 (1H, d, J 14.1 Hz), 2.2 (1H, d, J 9.3 Hz), 2.15 (OH, br, s), 2.10 (2H, d, J 9.3 Hz); δ_C 135.02, 130.32, 62.16, 41.61, 37.07, 32.46; ν_{max} 3347.3, 1661.4 cm^{-1}; m/e 305 (M^+), 303 (M^+-CH_2OH), 224 (303-Br), 145 (224-Br).

4-Bromo-2-(3-hydroxyprop-E-1-en-1-yl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane

(i) Methyllithium (1.82 ml, 2.19 mmol, 2.1 mol. equiv.) was added dropwise to a stirred solution of 3-(1,2,2-tri-bromocyclopropyl)-E-2-propen-1-ol (0.35 g, 1.04 mmol) in dry ether (10 ml) in the presence of 1,3-diphenyl-isobenzofuran (0.25 g, 0.94 mmol) under nitrogen at -78 °C. The reaction mixture was allowed to reach room temperature and stirred at that temperature for 4 hours, then worked up by quenching with water (3 ml) and -20 °C. The product was extracted with ether (3 x 10 ml), dried and evaporated to give a yellow solid. This was purified by column chromatography eluting with petroleum ether and ether (5:2) to give a white solid, *4-bromo-2-(3-hydroxyprop-E-1-en-1-yl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0*^{2,4}*]octane* (**25a**) (0.37 g, 80.4 %), m.p. 74-76 °C (Found: C 70.39, H 4.72; $C_{26}H_{21}O_2Br$ requires C 70.26, H 4.75); δ_H 7.9-7.2 (14 H, m), 5.8 (1 H, dt, 5.5, 15.5 Hz), 5.5 (1 H, d, J 15.5 Hz), 4.1 (1 H, d, J 1.0 Hz), 4.0 (1 H, d, J 1.0 Hz), 2.9 (1 H, d, J 6.3 Hz), 2.0 (1 H, d, J 6.3 Hz); δ_C 147.92, 134.48, 134.0, 133.48, 129.86, 129.21, 129.0, 128.87, 128.52, 127.04, 126.71, 126.62, 122.80, 121.82, 90.60, 89.88, 63.20, 51.61, 40.20, 27.72; ν_{max} 3421, 1665 cm^{1}.

(ii)Methyllithium (0.84 ml, 0.92 mmol, 3.1 mol. equiv.) was added to a stirred solution of 3-(1,2,2-tribromocyclopropyl)-2-propene-1-ol (0.1 g, 0.29 mmol) in dry ether at -78 °C. The solution was allowed to reach room temperature and stirred for 5 min before cooling to -60 °C and quenching with water (2 ml). The ether layer was decanted from the ice and added to 1,3-diphenylisobenzofuran (0.07 g, 0.26 mmol). The ether solution was stirred for 3 h at room temperature then the solvent was removed at 14 mm Hg to give yellow solid, which purified by column chromatography eluting with petroleum ether and ether (5:2) to give a yellow solid of *2-(3-hydroxyprop-E-1-en-1-yl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane* (**26a**) (0.04 g, 40%), m.p. 58-60 °C (Found: C 85.42, H 5.83; $C_{26}H_{22}O_2$ requires C 85.22, H 6.05), δ_H 7.7-7.0 (14H, m), 5.69 (1H, d, J 15.3 Hz), 5.62 (1H, dd, J 4.5, 15.5 Hz), 4.0 (2H, d, 4.5 Hz), 2.2 (1H, dd, J 3.7, 4.9 Hz), 1.7 (1H, dd, J 3.7, 6.8 Hz), 1.6 (1H, dd, J 4.9, 6.8 Hz); δ_C 150.97, 148.84, 136.28, 135.23, 130.28, 129.56, 129.24, 128.75, 128.50, 128.40, 127.87, 126.37, 125.92, 121.52, 119.60, 90.19, 88.24, 63.45, 36.94, 35.74, 19.80; ν_{max} 3394.0, 1662.6 cm^{-1}.

1,2,2-tribromocyclopropane carboxylic acid

Methyl (1,1,2-tribromocyclopropyl) formate (94.2 g) was vigorously stirred with 48% hydrobromic acid (350 ml) and heated under a Claisen still head in an oil bath to a temperature of 152 °C. The heating was adjusted until the vapour temperature in the still head reached 120°C, and thereafter maintained under gentle air reflux for 2.5 h. The mixture was diluted with water (200 ml) and cooled to 30 °C. Dichloromethane (200 ml) was added and the mixture stirred until all the solid had dissolved. The aqueous phase was re-extracted with dichloro-methane (3 x 50 ml). The combined organic phases were washed with sat.aq. sodium chloride(100 ml), dried and decolorised with charcoal (2 g), and then evaporated to give *1,2,2-tribromocyclopropane carboxylic acid* (**27**) (71.6 g, 79 %) as a cream solid (Found: C, 14.90; H, 0.48. $C_4H_3Br_3O$ requires: C, 14.88; H, 0.94) which showed δ_H (DMSO) 2.18 (1 H, d, J 9 Hz), 2.6 (1 H, d, J 9 Hz), 5.8 (1 H, br.s); δ_C (CD_2Cl_2) 169.9, 38.23, 36.8, 26.5.

1,1,2,2-Tetrabromocyclopropane

1,2,2-Tribromocyclopropanecarboxylic acid (72.08 g, 0.233 mol) was heated to reflux while mechanically stirred with carbon tetrachloride (850 ml) and red mercuric oxide (63 g, 0.29 mol). Bromine (45 g, 0.28 mol) in carbon tetrachloride (180 ml) was added dropwise over a period of 2.5 h. The mixture was refluxed a further 2.5 h, allowed to cool overnight and filtered. The filtrate was concentrated under vacuum. The residue was dissolved in petroleum b.p. 40 - 60° (250 ml) when more salts were precipitated. These were removed by filtration. The clear solution was then run through a short column of silica gel (100 g) in a glass sintered funnel, followed by a wash with petroleum (200 ml). The petroleum was distilled of, finally under vacuum, to leave pure 1,1,2,2-tetrabromo-cyclopropane (**28**) (67.9 g, 85%)[17] which showed δ_H 2.39 (s); δ_C 31.4, 43.6; ν_{max} 3073, 1000 cm^{-1}.

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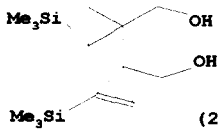
* If the reaction was carried out in the absence of diphenylisobenzofuran, it became very dark on warming to room temperature and evaporation of the solvent gave a complex product. If the ether solution was allowed to reach -40 to -35 °C, and then treated with DPIBF a 55 % yield of (3) was isolated, while if the temperature was allowed to reach -15 to -20 °C, the yield was reduced to 15 %.

\# Addition of the cyclopropene to DPIBF competed with a dimerisation through an ene-type reaction to give (29) (δ_H 7.7 (1H, s),3.45 (1 H, d, J 10.6 Hz), 3.3 - 3.4 (m, 3 H), 0.5 (1H, dd, J 3.7, 10.1 Hz), 0.4 (1 H, dd, J 3.7, 7.8 Hz), -0.01 (9 H, s), -0.53 (1H, dd, J 7.8, 10.1 Hz). The stereochemistry of (29) is assigned provisionally on the basis of an endo-transition state controlled by the size of the silyl-substituents (Baird, M.S.; Hussain, H.H.; Clegg, W. *J.Chem.Res.*, 1988, 110S).



(29)

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