Pergamon

Tetrahedron 56 (2000) 1115–1125

TETRAHEDRON

A Flexible Route to [4.1.1]Propellanes

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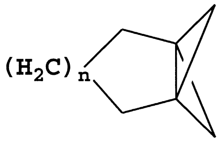
Received 22 September 1999; revised 18 November 1999; accepted 2 December 1999

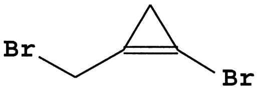
Abstract—Reaction of Diels–Alder adducts of 1-bromo-2-bromomethylcyclopropene and either 1,3-dienes or furans with *n*- or *t*-butyllithium leads to a 1,3-dehalogenation to produce [4.1.1]propellanes. The oxygen bridged propellane derived from furan reacts with a second mole equivalent of *n*-butyllithium by cleavage of the bridge with allylic rearrangement and the formation of a *cis*-2-butyl[4.1.1]propell-3-en-1-ol. Iodination of this leads to rearrangement with the production of 6-methylene-8-oxabicyclo[3.2.1]oct-2-enes. The corresponding adducts of 1-bromo-2-bromoethylcyclopropene do not undergo 1,4-debromination under the conditions examined. © 2000 Elsevier Science Ltd. All rights reserved.

There has been considerable interest in the chemistry of highly strained propellanes.[1] The parent [2.1.1]- and [3.1.1]propellanes (**1**, $n=0,1$) have been generated by dehalogenation of the corresponding 1,4-dihalobicyclo[2.1.1]hexane and 1,5-dihalobicyclo[3.1.1]heptane, respectively;[2,3] although the former propellane is detectable in a nitrogen matrix at low temperature, and the latter can be detected at somewhat higher temperatures, neither is long-lived at ambient temperature. The corresponding [4.1.1]propellane (**1**, $n=2$) has been obtained by intramolecular addition of a carbene to an alkene and is stable enough to detect at ambient temperature.[4] Although there are many examples of related propellanes in which the methylene carbons of the cyclobutane ring are bridged by a third ring, other examples with the cyclobutane methylene positions unsubstituted are relatively uncommon.[1] Related [4.1.1]- and [3.1.1]-propellanes having an additional bridge between the two methylene positions of the bicyclobutane ring have been prepared by trapping of transient 2,4-bridged bicyclo[1.1.0]but-1(3)-enes by [4+2]-cycloaddition to dienes such as diphenyl isobenzofuran[5–7] or *N*-methyl-2,4-dimethylisoindole.[8] However, trapping of the parent bicyclo[1.1.0]but-1,3-ene was not successful.[1]

We have reported that the reaction of 1,1-dibromo-2-bromomethylcyclopropanes with methyllithium leads to a 1,3-debromination and the formation of a bicyclo[1.1.0]butane.[9] This reaction has been widely used in the preparation of highly strained ring-systems, e.g. in the work of Szeimies et al.[1] We recently reported that reaction of readily available 1,1,2-tribromo-2-bromomethylcyclopropane with methyllithium leads to 1-bromo-2-bromomethylcyclopropene (**2**), which may be trapped by reaction with dienes, e.g. as the adducts (**3**) and (**5**).[10]

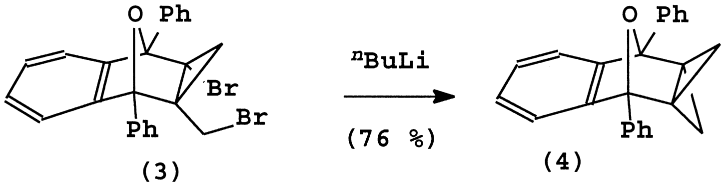


(1)



(2)

We now find that, although these adducts appear to be unreactive towards methyllithium, they react with 1 mol equiv. of *n*-butyllithium in hexane at 20°C. Thus the adduct (**3**) was converted into the propellane (**4**) in good yield[11] (Scheme 1).



Scheme 1.

Keywords: [4.1.1]propellanes; Diels–Alder adducts; cyclopropenes; 8-oxabicyclo[3.2.1]octene.

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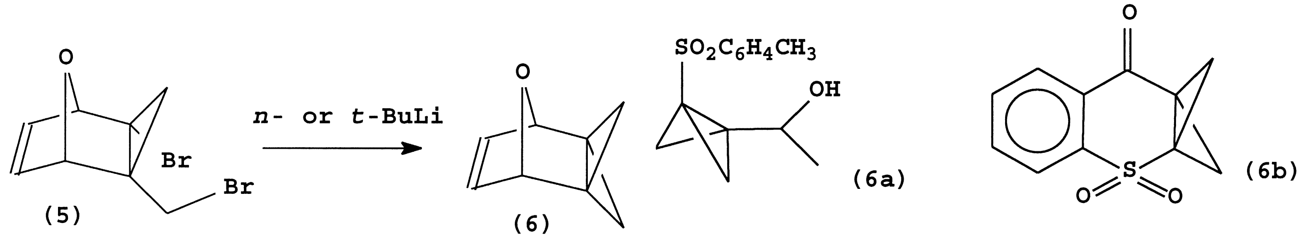
PII: S0040-4020(99)01069-8

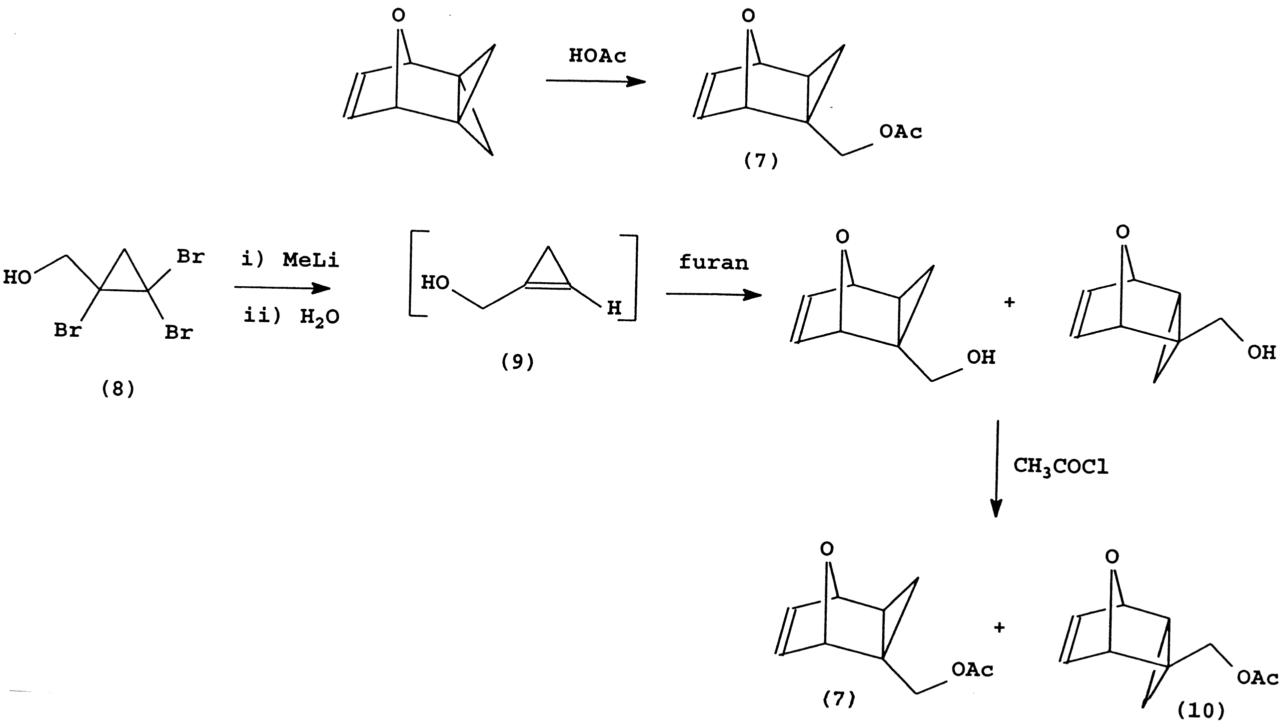


Scheme 2.

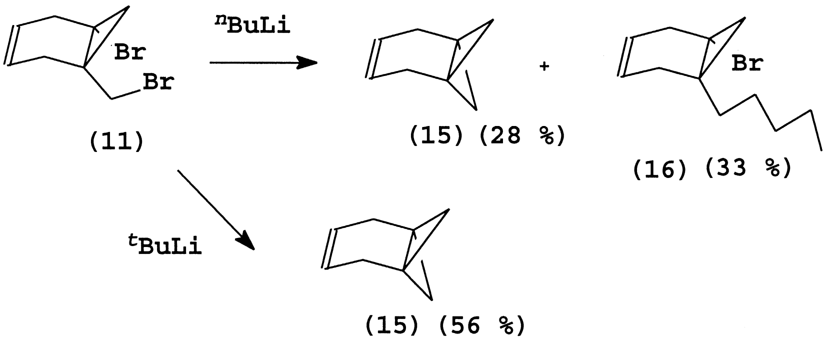
In the same way the furan (**5**)[12] was converted into (**6**) in moderate yield on reaction with 1 mol equiv. of *n*-BuLi, although with an excess of reagent the reaction was more complex (see below). A better yield (72%) was obtained on reaction with 1 mol equiv. of *t*-BuLi in pentane (Scheme 2).

The ^{1}H NMR spectrum of the propellane (**4**) included four bicyclobutane hydrogens, two as double doublets at δ 3.5 (J=2.9, 7.5 Hz) and 1.8 (J=4.0, 7.5 Hz) and two as doublets at 2.0 (J=4.0 Hz), 1.86 (J=2.9 Hz). The spectrum of compound (**6**) also included four discrete bicyclobutane hydrogens showing very similar patterns, two double doublets at δ 3.2 (J=7.5, 2.7 Hz) and 2.7 (J=7.5, 3.7 Hz) and two narrow doublets at 1.8 (J=3.7 Hz) and 1.6 (J=2.7 Hz). The signals at δ 3.5 and 3.2 in the two spectra are assigned to the bicyclobutane protons adjacent to the ether oxygen; the coupling constant of 7.5 Hz is typical of a $^{4}J_{H,H}$ between the two exo-hydrogens of this ring system.[13] The signals of these two hydrogens are at much lower field than those in the parent [4.1.1]propellane.[4] Although this may be expected in the case of the hydrogen nearest to the ether oxygen, the position of the second hydrogen is more surprising. It is noteworthy that in the bicyclobutane (**6a**), the *endo*-hydrogens appear as two singlets at δ 1.3 and 1.7, while the *exo*-hydrogens appear as an AB double doublet (J=6.6 Hz) centred at δ 1.51.[14] However in (**6b**), the *endo*-hydrogens of the bicyclobutane appear as a double doublet (J=1.6, 2.2 Hz) at δ 2.13 and the *exo*-hydrogens as a similar signal at 2.99.[14] The ^{13}C NMR spectrum of compound (**6**) showed just five signals as expected from its symmetry.

It was hoped that the propellene (**6**) might be characterised by the addition of iodine across the zero-bridge.[1,15] However, on reaction with iodine in ether or chloroform, mixtures of products were obtained including in the former case the required di-iodide; these products will be described elsewhere. Treatment with ethanoic acid in chloroform for 10 min at 20°C did lead to a single product, characterised as (**7**). An identical compound was obtained on reaction of the tribromide (**8**) with 3 mol equiv. of MeLi, then water to produce the cyclopropene (**9**) in situ, trapping with an excess of furan, and then acetylation of the crude product with acetyl chloride. In this case, a minor product was the



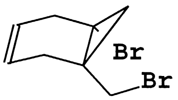
Scheme 3.



Scheme 4.

isomer (**10**); the major isomer was characterised as (**7**) by analogy with the stereochemistry of other adducts of cyclopropenes with furan.[16] In agreement, the alkene hydrogens of (**7**) appeared at lower field than those in (**10**)[17,18] and H-5 showed a 4.3 Hz coupling to cyclopropane hydrogen H-4, again seen in *endo*- but not *exo*-adducts.[19] Interestingly, one of the diastereotopic hydrogens of the acetoxymethyl group also showed additional coupling, in this case to the *endo*-cyclopropane hydrogen, H-3. No such couplings were seen in the spectrum of the major isomer. It was also observed that the cyclopropane hydrogen on C-3 *trans* to H-4 was at higher field in the spectrum of (**10**) and at lower field in that of (**7**) compared to the corresponding *cis*-hydrogen, as may be expected for the shielding effect of the alkene and the deshielding effect of the ether oxygen in the two isomers. The deshielding effect of the oxygen was, however, relatively small compared to that attributed to it in a number of related cyclopropene–furan adducts[10,18] (Scheme 3).

In order to probe this reaction further, the cycloadducts (**11**)–(**14**) of the cyclopropene (**2**), prepared in situ from 1,1,2-tribromo-2-bromomethylcyclopropane,[10] with a number of other dienes were prepared. Adduct (**11**) was obtained in 60% yield on trapping the cyclopropene (**2**) with an excess of buta-1,3-diene, while trapping with 2,5-dimethylfuran gave (**14**) (75%); in the case of 2-methylfuran, both adducts (**12**) and (**13**) were obtained in a ratio of 2.2:1 although the NMR spectra were so similar that it was not possible to identify with certainty which was the major isomer. No significant n.O.e effects could be seen to assist in this determination. Compounds (**11**)–(**14**) each showed a pair of doublets (J=6.2 Hz) for the cyclopropane protons at ca. δ 1.2 and 2.4. Such a large chemical shift difference between the protons is typical of those seen for other *exo*-adducts of cyclopropenes with furan, while in the *endo*-adducts the signals are much closer together.[10]



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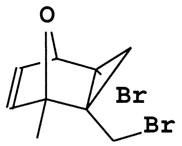
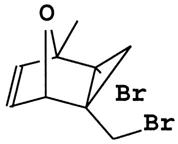
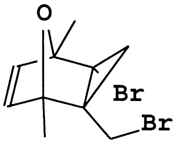


(12)

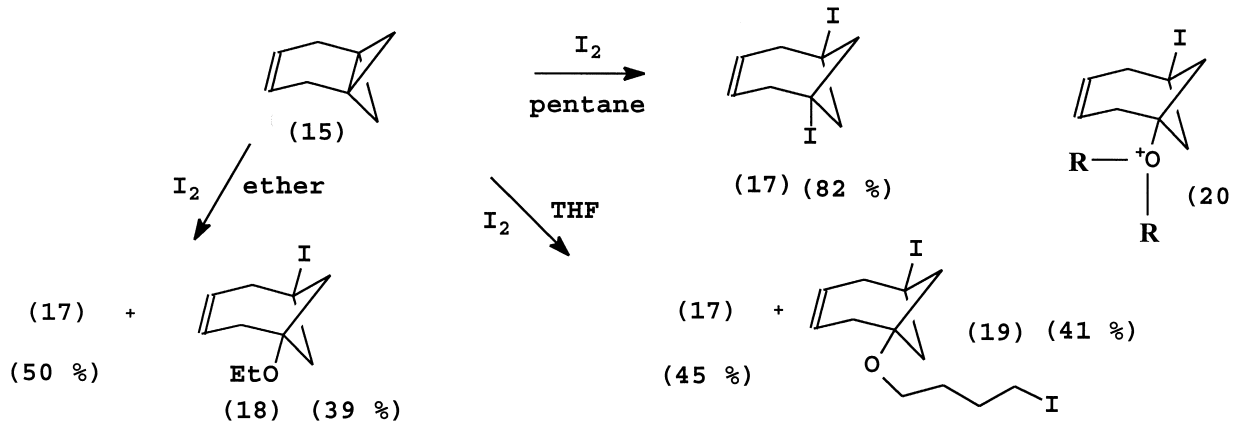


(13)

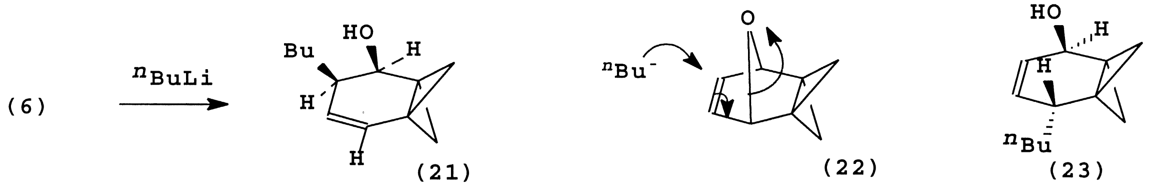


(14)

Reaction of compound (**11**), with *n*-butyllithium led to the parent [4.1.1]propell-3-ene (**15**) together with the alkylated bicycle (**16**). However, with *t*-butyllithium, the corresponding alkylation product was not observed and the propellane could readily be isolated (Scheme 4). The hydrocarbon (**15**) showed just four singlets in the ^{1}H NMR spectrum, at δ 5.5 (2 H), 2.45 (4 H), 1.4 (2 H) and 1.0 (2 H). The lack of coupling between the bicyclobutane hydrogens in this case



Scheme 5.



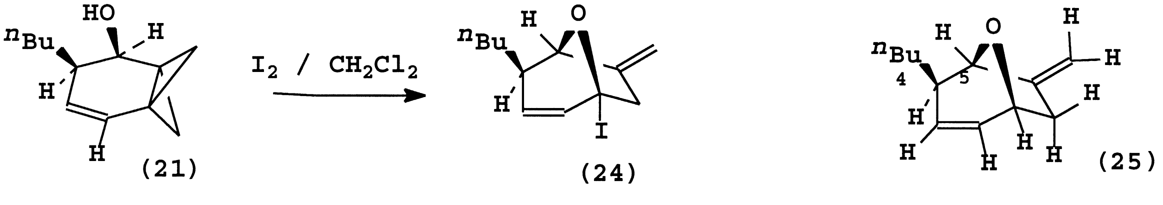
Scheme 6.

is surprising, but entirely in agreement with the corresponding signals for the hydrogens of [4.1.1]propellane itself, the bicyclobutane hydrogens of which are reported to occur at δ 0.82 and 1.43.[4] It also showed just the expected four signals in its ^{13}C NMR spectrum, including one in the alkene region and one at δ 0.5; once again this can be compared with the signals in [4.1.1]propellane which are reported to occur at 39.9, 23.3, 20.0 and 2.0.[4] As noted earlier,[4] these chemical shifts are somewhat different from those reported for [3.1.1]propellane.[3] The hydrocarbon (**15**) was characterised by reaction with iodine in pentane by 1,3-addition to give the diiodide (**17**) (Scheme 5). Compound (**17**) also showed just four signals in its ^{13}C NMR spectrum, in this case including one in the alkene region, one at 60.1 which was coupled to all the hydrogens appearing at both 3.1 and 3.7, and one at δ 15.9. The ^{1}H NMR spectrum included a narrow triplet at δ 5.2, coupled to a four hydrogen doublet at 2.9, and two pairs of hydrogens at δ 3.7 and 3.1; these appeared at first sight to be a pair of doublets with additional splitting, but are assigned as an AA′BB′ system for the *exo*- and *endo*-bicyclobutane hydrogens. Similar patterns were observed for all the bicyclobutanes described below having a plane of symmetry through the cyclobutane bridgehead carbons.

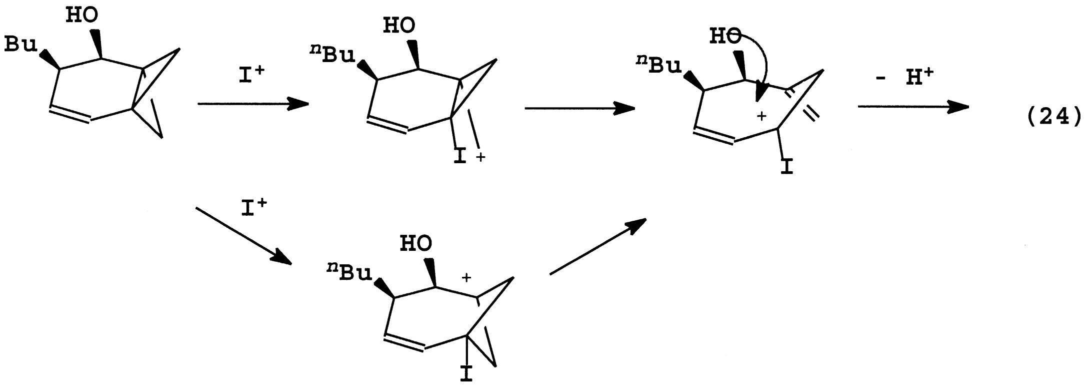
When the addition was carried out in either ether or tetrahydrofuran, the ethers (**18**) and (**19**) were obtained in addition to (**17**). The ethers each showed two non-equivalent alkene hydrogens in the ^{1}H NMR spectrum, with a vicinal coupling of 12.3 Hz, and two alkene signals in the ^{13}C NMR spectrum. The ^{1}H NMR spectra included AA′BB′ systems very similar to that observed for (**17**), and the two pairs of allylic hydrogens appeared as narrow multiplets at 2.23 and 3.0 in each case. The ^{13}C NMR spectra each included common signals for the cyclobutane bridgehead carbons at 76.3 and 26.8, and 76.4 and 26.5, respectively. These ethers were presumably derived by formation of an intermediate oxonium ion such as (**20**) followed by nucleophilic substitution at the α-carbon, leading to dealkylation in the case of (**18**) and ring-opening in the case of (**19**).

Although compound (**4**) was stable to reaction with a second mole equivalent of *n*-butyllithium, compound (**6**) reacted rapidly under these conditions by opening of the furan ring without reaction at the bicyclobutane moiety, leading to the alcohol (**21**), apparently derived by ring-opening as in (**22**). It was difficult to distinguish the product absolutely by NMR from structures such as (**23**) in which an alternative mode of furan opening had occurred, because coupling constants in the cyclohexenol were small (Scheme 6). The ^{13}C NMR spectrum of (**21**) included the expected 12 signals, including two in the alkene region and two quaternary carbons at δ 12.0 and 1.9. The ^{1}H NMR spectrum showed two alkene hydrogens, with a vicinal coupling constant of 9.2 Hz; each of them also showed additional small couplings, in one case to two hydrogens, in the other to one; this provided some evidence that (**21**) and not (**23**) was the correct structure. The methine hydrogen of the alcohol showed a 3.9 Hz coupling to one proton; irradiation of a broad signal at δ 1.98 caused this hydrogen to be decoupled, again suggesting structure (**21**). However, the signal for this methine hydrogen also appeared to show a small coupling to one of the alkene hydrogens.[20] Given the size of the coupling constants and the possibilities for long range coupling in this ring system, the structure (**21**) was confirmed by chemical means (see below),[21] and through an unusual oxidation to 3-butylbicyclo[4.1.1]oct-3-en-2,4-dione.[22] As in the case of compound (**6**), the four bicyclobutane hydrogens of (**21**) are non-equivalent; only two of them could be positively identified, appearing as two double doublets (J=6.8, 1.6 Hz and J=6.8, 2.8 Hz) at δ 2.1 and 1.82. These are assigned as before to the two *exo*-hydrogens of the bicyclobutane, showing a W-coupling between them of 6.8 Hz. A third bicyclobutane proton was provisionally assigned to a doublet (J=2.8 Hz) which appeared as part of a complex high field signal.

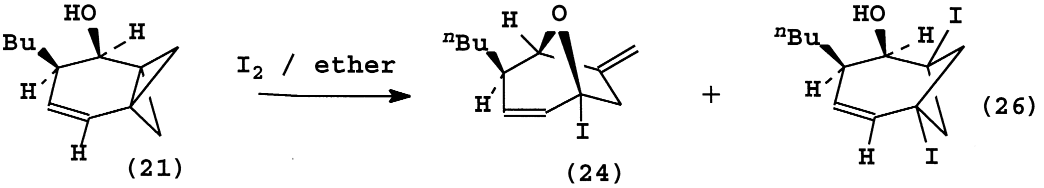
Compound (**21**) reacted with iodine in ether or dichloromethane to give a mixture of two ethers (**24**) and (**25**). The structure of (**24**) was confirmed by reduction to (**25**) on reaction with Li-^{t}BuOH–THF (Scheme 7). The stereochemistry of the butyl group was assigned on the basis of the



Scheme 7.



Scheme 8.

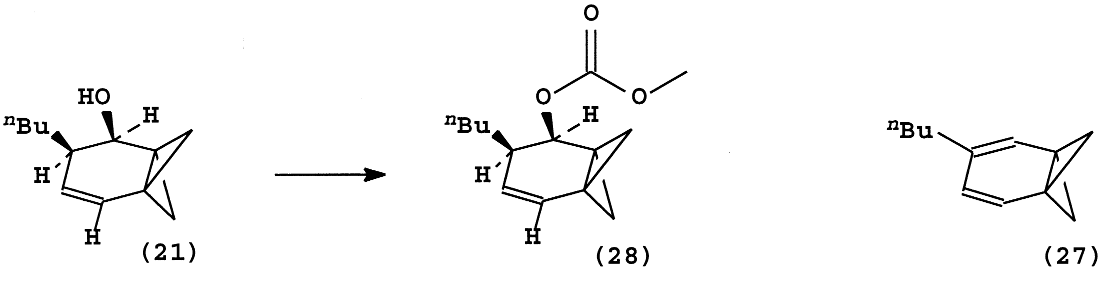


Scheme 9.

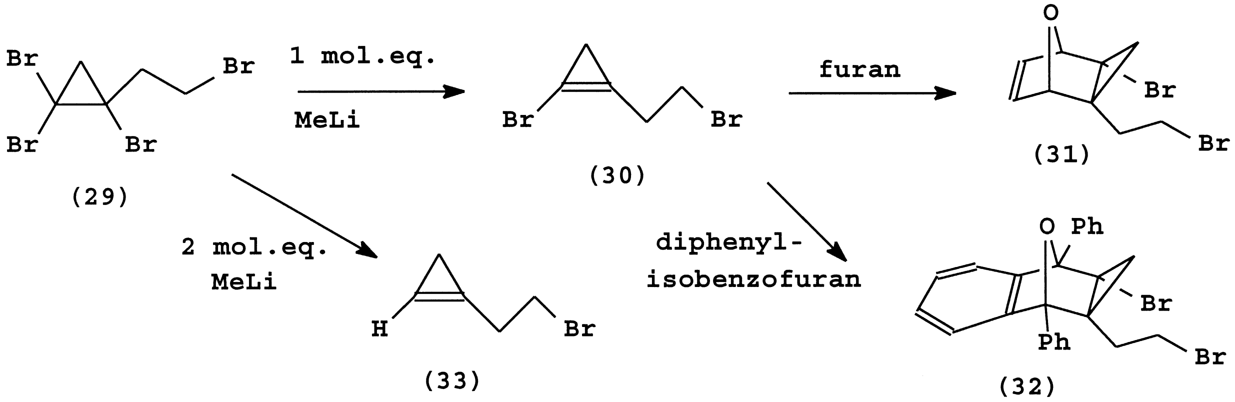
very small coupling constant between H-4 and the bridgehead proton H-5, typical of that for an *exo*-3-substituted compound.[23] The formation of (**24**) may occur either through formal addition of iodine to an external cyclopropane bond to generate a cyclopropylmethyl cation or by similar addition to the bicyclobutane bridge bond, in either case followed by (or concerted with) rearrangement (Scheme 8). When the iodination of (**21**) was carried out in ether solution, the diiodide (**26**) was obtained as a minor product, together with (**24**) (Scheme 9). Compound (**26**) showed four different bicyclobutane hydrogens in the ^{1}H NMR spectrum, including a double doublet (J=6.8, 12.4 Hz) and a doublet (J=11.8 Hz) as well as a two hydrogen multiplet. The larger coupling constants presumably correspond to geminal-couplings and are similar in value to others reported in four membered rings.

The elimination of water from (**21**) would, formally at least, lead to the unusual homonorcaradiene (**7**). In order to try to carry out such an elimination the alcohol (**21**) was first treated with triphenylphosphine and bromine in order to try to prepare the corresponding bromide; this reaction was, however, not successful, leading to a complex mixture. The alcohol was successfully converted into the carbonate (**28**) by reaction with methyl chloroformate. However attempted elimination of the elements of carbon dioxide and methanol by reaction with sodium methoxide or lithium bistrimethylsilylamide again led to complex product mixtures (Scheme 10).

The 1,3-elimination of bromine observed in the above reactions suggested that it might be possible to achieve the corresponding 1,4-elimination, leading to the formation of bridged bicyclo[2.1.0]pentanes. The adducts of 1-(2-bromoethyl)cyclopropene (**30**) with furan and diphenylisobenzofuran were therefore prepared by in situ generation of the cyclopropene from 2-(2-bromoethyl)-1,1,2-tribromocyclopropane (**29**) (Scheme 11). Compound (**31**) was obtained as a mixture of *exo*- (major) and *endo*-adducts as is common for cyclopropene adducts of furan.[10] These could be distinguished because the chemical shift difference between the cyclopropane protons was larger in the *exo*-isomer. The 2-H-cyclopropene (**33**) was also prepared and trapped with diphenylisobenzofuran. Neither of the adducts (**31**) or (**32**) underwent 1,4-dehalogenation on reaction with *n*-butyllithium.



Scheme 10.



Scheme 11.

Experimental

Reagents were obtained from commercial suppliers and were used without further purification unless stated. Dichloromethane was distilled over calcium hydride. *n*-Butyllithium was obtained as a 1.6 M solution in hexane (Aldrich) and the molarity was checked by titration with diphenyl acetic acid. *t*-Butyllithium was obtained as a 1.7 M solution in pentane (Aldrich). 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 FID on a capillary column (30 m×0.32 mm i.d. 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 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.

2,5-Diphenyl-3,4-benzo-2,5-epoxy[4.1.1.0^{1,6}]octane. *n*-Butyllithium (0.42 ml, 0.59 mmol, 1.1 mol equiv.) was added to a stirred solution of 2-bromo-4-bromomethyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane (**3**)[10] (0.26 g, 0.53 mmol) in dry ether (7 ml) under nitrogen at −78°C. The mixture was allowed to reach 0°C before cooling to −40°C and quenching with water (2 ml). After extraction with ether (3×10 ml), the combined ether layers were dried and evaporated to give a thick yellow oil, *2,5-diphenyl-3,4-benzo-2,5-epoxy[4.1.1.0^{1,6}]octane* (**4**) (0.13 g, 76%) (Found M$^+$: 322.1358. $C_{24}H_{18}O$: requires 322.1357); δ_H: 7.8–7.0 (14 H, m), 3.5 (1 H, dd, J=2.9, 7.5 Hz), 2.0 (1 H, d, J=4.0 Hz), 1.86 (1 H, d, J=2.9 Hz), 1.8 (1 H, dd, J=4.0, 7.5 Hz); δ_C: 146.8, 137.0, 128.6, 128.4, 128.2, 128.0, 127.0, 124.7, 120.4, 92.8, 62.05, 49.5, 26.4 (together with some minor signals in the aromatic region); ν_{max}: 2925, 1662, 1447, 1297 cm^{-1}.

Reaction of 2-bromo-4-bromomethyl-8-oxatricyclo-[3.2.1.0^{2,4}]oct-6-ene with butyllithium. (a) *n*-Butyllithium (1.3 ml, 1.96 mmol, 1.1 mol equiv.) was added to a stirred solution of 2-bromo-4-bromomethyl-8-oxatricyclo [3.2.1.0^{2,4}]-oct-6-ene (**5**)[10,12] (0.5 g, 1.7 mmol) in dry ether (10 ml) under nitrogen at −78°C. The mixture was allowed to reach 10°C, before quenching with water (3 ml) at −40°C. The solvent was evaporated and the product was distilled at 0.1 mmHg into a cold receiver to give a colourless oil, *2,5-epoxytricyclo[4.1.1.0^{1,6}]oct-4-ene* (**6**) (92 mg, 43%) which showed δ_H: 6.1 (2 H, br, s), 4.8 (2 H, br, s), 3.2 (1 H, dd, J=2.7, 7.5 Hz), 2.7 (1 H, dd, J=3.7, 7.5 Hz), 1.8 (1 H, d, J=3.7 Hz), 1.6 (1 H, d, J=2.7 Hz); δ_C: 132.8, 80.7, 61.8, 52.6, 29.3; ν_{max}: 2956, 1660, 1465 cm^{-1}; *m/z* 120, 119, 91. This compound was characterised as its adduct with ethanoic acid (see below).

(b) The above reaction was repeated using the same conditions except that *n*-butyllithium was replaced by *t*-butyllithium, to give (**6**) (0.15 g, 72%).

(c) *n*-Butyllithium (36.8 ml, 0.04 mol, 2.1 mol equiv.) was added dropwise to a stirred solution of 2-bromo-4-bromomethyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (5.5 g, 0.01 mol) in dry ether (40 ml) under nitrogen at −78°C. The solution was allowed to reach 10°C, before quenching with water (5 ml) at −40°C. The product was further extracted with ether (3×20 ml), and the combined organic layers were dried and the solvent was evaporated to give a thick yellow oil, *2-hydroxy-3-butyltricyclo[4.1.1.0^{1,6}]oct-4-ene* (**21**) (3.2 g, 94%) (Found M$^+$: 178.1358. $C_{12}H_{18}O$ requires 178.1357) which showed δ_H: 6.2 (1 H, ddd, J=0.8, 2.95, 9.2 Hz), 5.5 (1 H, dd, J=2.3, 9.2 Hz), 4.6 (1 H, dd, J=3.9, 6.6 Hz), 2.0 (1 H, dd, J=1.6, 6.8 Hz), 1.9 (1 H, m), 1.8 (1 H, dd, J=2.8, 6.8 Hz), 1.6–1.3 (8 H, m), 1.2 (OH, br), 0.92 (3 H, t, J=7.0 Hz); δ_C: 131.7d, 126.2d, 66.1d, 41.3t, 39.8t, 37.8d, 31.2t, 30.0t, 22.8t, 14.0d, 12.0s, 1.9s; ν_{max}: 3428, 2928, 1610, 1465 cm^{-1}; m/z: M$^+$ (177.9), 120.9 (M$^+-C_4H_9$). After shaking with D_2O the signal at δ 4.6 changed to a doublet with coupling constant 3.8 Hz.[20]

2-Acetoxymethyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-enes. (i) 1,1,2-Tribromocyclopropane-2-methanol (5 g, 0.0162 mol) was stirred in dry ether (60 ml) under nitrogen at −78°C. Methyllithium (34.5 ml, 1.5 M, 0.0517 mol) was added and the reaction was warmed to room temperature for 15 min, re-cooled to −30°C and treated with water (5 ml). The mixture was allowed to reach room temperature and cooled to below 0°C, when the ether layer was decanted from the frozen aqueous layer. The water layer was washed with ether (3×10 ml) and the combined organic layers were added to furan (11.0 g, 0.162 mol). The mixture was stirred for 24 h and then evaporated to give an oil. The ^{1}H NMR of this showed two major products in ratio ca. 2:1. The crude product was dissolved in ether (30 ml) and stirred with acetyl chloride (1.6 ml, 1.75 g, 22.3 mmol) and triethylamine (3.3 ml, 2.4 g, 23 mmol) at 0°C. After 1 h at room temperature, the product was quenched with water (10 ml) and extracted with ether (2×30 ml). The combined organic layers were dried and evaporated to give an oil which again showed two major products in ratio ca. 3:2 by NMR. These were separated by chromatography eluting with 2:1 ether/petrol. The major product (**7**) (Found M$^+-$MeCO: 138.0667. Calculated for $C_8H_{10}O_2$: 138.0680) (1.5 g, 52%) showed δ_H: 6.6 (1 H, dd, J=5.7, 1.6 Hz), 6.5 (1 H, dd, J=5.7, 1.6 Hz), 4.6 (1 H, dd, J=11.7, 1.5 Hz), 4.2 (1 H, dd, J=12, 1.3 Hz), 3.8 (1 H, d, J=12 Hz), 2.0 (3 H, s), 1.7 (1 H, ddd, J=5, 3.6, 1.3 Hz), 1.1 (1 H, dd, J=6.8, 3.6 Hz), 0.9 (1 H, dd, J=6.8, 5.0 Hz); ν_{max}: 2956, 1736, 1654 cm^{-1}. The minor isomer (**10**) (0.5 g, 17%) showed δ_H: 6.15 (1 H, dd, J=5.8, 1.7 Hz), 6.00 (1 H, dd, J=5.7, 1.7 Hz), 4.9 (1 H, dt, J=4.3, 1.7 Hz), 4.8 (1 H, t, J=1.7 Hz), 4.5 (1 H, dd, J=11.75, 1.1 Hz), 4.1 (1 H, d, J=11.7 Hz), 2.0 (3 H, s), 1.8 (1 H, ddd, J=7.1, 4.3, 3.6 Hz), 1.2 (1 H, dd, J=7.1, 5.8 Hz), 1.01 (1 H, ddd, J=5.8, 3.6, 1.1 Hz); δ_C: 171.2, 131.9, 131.1, 81.4, 79.5, 68.0, 33.8, 21.9, 21.0, 9.1; ν_{max}: 2999, 738 cm^{-1}.

(ii) Ethanoic acid (ca. 50 mg) was added to a stirred solution of the tricycle (**6**) (0.2 g, 1.66 mmol) in chloroform (4 ml) at room temperature. After 10 m, an NMR spectrum showed that no starting material remained. The mixture was quenched with saturated aqueous sodium bicarbonate and extracted with dichloromethane (3×10 ml). After drying and evaporation the product was purified by column chromatography eluting with 5:2 petrol/ether to give *2-acetoxymethyl-exo-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene* (**7**) as a colourless oil (0.18 g, 60%) identical by TLC and ^{1}H NMR to that above (δ_C: 171.1, 139.0, 138.6, 78.6, 77.8, 68.0, 32.9, 26.3, 21.5, 20.9.

Adducts of 1-bromo-2-bromomethylcyclopropene. (i) Methyllithium (4.0 ml, 5.6 mmol) was added dropwise to a stirred solution of 1-bromomethyl-1,2,2-tribromocyclopropane (1.9 g, 5.1 mmol) in dry ether (20 ml) under argon at −78°C. The reaction was allowed to reach 0°C before quenching with water (4 ml) at −50°C. The aqueous layer was extracted with ether (3×15 ml) and the combined organic layers were dried and filtered. An excess of 2,5-dimethylfuran was added to the filtrate and stirred overnight. Evaporation of the solvent gave a yellow oil, which on chromatography eluting with petrol and ether (5:1) gave a colourless oil, *2-bromo-3-bromomethyl-4,7-dimethyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene* (**14**) (Found M$^+-$Br: 227.0072. $C_{10}H_{12}BrO$ requires: 227.0063) (1.2 g, 75%) which showed δ_H: 6.5 (1 H, d, J=5.4 Hz), 6.4 (1 H, d, J=5.4 Hz), 3.5 (1 H, d, J=11.6 Hz), 3.4 (1 H, d, J=11.6 Hz), 2.4 (1 H, d, J=6.2 Hz), 1.58 (3 H, s), 1.56 (3 H, s), 1.2 (1 H, d, J=6.2 Hz); δ_C: 143.58, 142.22, 88.01, 87.07, 57.94, 41.12, 35.26, 31.24, 16.32, 14.74; ν_{max}: 2977, 1567 cm^{-1}; m/z: 227/229 (M$^+-$Br), 147 (M$^+-Br_2$).

(ii) The above procedure was repeated using an excess of 2-methylfuran to give two isomers *2-bromo-3- bromomethyl-7-methyl-8-oxatricyclo[3.2.1.0^{2,4}]octane* (**12**, **13**) (50%) in ratio 2.2:1. The major isomer was separated by recrystallisation from petrol and ether to give a colourless solid, mp 58–60°C (Found: C, 36.6; H, 3.6. $C_9H_{10}Br_2O$ requires: C, 36.77; H, 3.24) which showed δ_H: 6.73 (1 H, dd, J=1.5, 5.6 Hz), 6.5 (1 H, d, J=5.6 Hz), 4.73 (1 H, d, J=1.6 Hz), 3.5 (2 H, m), 2.4 (1 H, dd, J=1.3, 6.3 Hz), 1.62 (3 H, s), 1.2 (1 H, d, J=6.3 Hz); δ_C: 143.5, 138.8, 89.4, 79.2, 54.0, 40.1, 35.9, 31.3, 14.7. The minor isomer, purified by chromatography (Found M$^+-$Br: 212.9915. $C_9H_{10}BrO$ requires: 212.9909) showed δ_H: 6.64 (1 H, dd, J=1.5, 5.6 Hz), 6.5 (1 H, d, J=5.6 Hz), 4.76 (1 H, d, J=1.6 Hz), 3.4 (2 H, m), 2.43 (1 H, m), 1.6 (3 H, s), 1.3 (1 H, d, J=6.3 Hz); δ_C: 141.95, 140.7, 87.5, 81.2, 53.20, 40.05, 38.5, 35.11, 16.1; ν_{max}: 2929, 1560.5 cm^{-1}; m/z: 277/279/281 (M$^+-CH_3$), 213/215 (M$^+-$Br).

(iii) Methyllithium (2.95 ml, 4.43 mmol) was added to a stirred solution of 1-bromomethyl-1,2,2-tribromocyclopropane (1.5 g, 4.03 mmol) in dry ether (15 ml) under nitrogen at −78°C. The mixture was allowed to reach 0°C, then cooled again to −60°C and quenched with water (3 ml). The ether layer was decanted from the ice, the ice was washed with ether (3×10 ml), and an excess of buta-1,3-diene was added to the combined ether layers. The mixture was allowed to reach room temperature and stirred for 18 h. Evaporation of the solvent gave *6-bromo-1-bromomethylbicyclo[4.1.0]hept-3-ene* (**11**) (0.6 g, 60%) (Found M$^+$: 263.899 $C_8H_{10}Br_2$ requires 263.914) which showed δ_H: 5.4 (2 H, m), 3.8 (1 H, d, J=10.3 Hz), 3.6 (1 H, d, J=10.3 Hz), 2.8 (2 H, m), 2.5 (2 H, m), 1.4 (1 H, d, J=6.2 Hz), 1.0 (1 H, d, J=6.2 Hz); δ_C: 124.33, 123.98, 44.22, 42.77, 37.0, 28.70, 26.69, 23.65; ν_{max}: 2924, 1661, 1431 cm^{-1}.

Reaction of 6-bromo-1-bromomethylbicyclo[4.1.0]hept-3-ene with butyllithium. (a) *n*-Butyllithium (7.78 ml, 11 mmol) was added to a stirred solution of 6-bromo-1-bromomethyl-bicyclo[4.1.0]hept-3-ene (2 g, 7.52 mmol) in dry ether (25 ml) at −90°C under nitrogen. The reaction was allowed to reach room temperature for 2 h. When GLC showed no starting material was left, the products were quenched with water (5 ml) and the aqueous layer was extracted with ether (2×15 ml). The combined organic layers were dried and the solvent was removed at −5°C and 14 mmHg. The volatiles were flash distilled under reduced pressure to give tricyclo[4.1.1]oct-3-ene (**15**) (0.22 g, 28%) (see below). The residue was purified by Kugelrohr distillation to give 1-bromo-6-pentylbicyclo[4.1.1.0^{1,6}]hept-3-ene (**16**) (0.6 g, 33%), which showed δ_H: 5.35 (1 H, m), 5.2 (1 H, m), 2.75 (2 H, br, m), 2.5 (1 H, m), 2.2 (2 H, m), 1.5 (2 H, m), 1.2 (6H, br.m), 1.05 (1H, d, J=6.6 Hz), 0.75 (3H, t, J=7.0 Hz), 0.65 (1H, d, J=6.6 Hz); δ_C: 124.6 (d), 124.3 (d), 43.7 (s), 38.9 (t), 37.65 (t), 32.0 (t), 29.2 (t), 26.0 (t), 25.7 (s), 22.6 (t), 22.16 (t), 14.1 (q); ν_{max}: 1465, 1091, 1051, 666 cm^{-1}; m/z: 244:242 (M^+), 163 ($M^+ - Br$), 173 ($M^+ - C_5H_{11}$).

(b) *t*-Butyllithium in pentane (5.7 ml, 8.3 mmol, 1.1 equiv.) was added to a stirred solution of 6-bromo-1-bromomethylbicyclo[4.1.0]hept-3-ene (2 g, 7.52 mmol) in dry pentane (25 ml) at −90°C, under nitrogen. The mixture was allowed to reach room temperature for 1 h, when GLC showed no starting material was left, then cooled to −30°C and quenched with water (3 ml). The organic layer was separated and the aqueous layer was extracted with pentane (2×15 ml). The organic layers were dried and the solvent was evaporated at −5°C and 14 mmHg; flash distillation at 0.5 mmHg then gave tricyclo[4.1.1.0^{1,6}]oct-3-ene (**15**) (0.45 g, 56%) (the crude yield was estimated as 95% by GLC), which showed δ_H: 5.5 (2 H, br.s), 2.45 (4 H, br.s), 1.45 (2 H, s), 1.04 (2 H, s); δ_C: 121.9, 39.7, 22.3, 0.5; m/z: 106 (M^+), 91 ($M^+ - 15$); ν_{max}: 1426, 1225 cm^{-1}. The product was essentially unchanged after 16 h at 20°C in $CDCl_3$. This was characterised as its adduct with iodine (see below).

Reaction of tricyclo[4.1.1.0^{1,6}]oct-3-ene with iodine. (a) Iodine (0.53 g, 2.1 mmol) in dry pentane (30 ml) was added to a stirred solution of tricyclo[4.1.1.0^{1,6}]oct-3-ene (0.2 g, 1.88 mmol) in pentane (10 ml) at −90°C. The reaction was warmed to room temperature for 2 h before quenching with sodium thiosulphate solution (15 ml). The product was extracted with pentane (2×15 ml). The organic layers were dried and evaporated to give a brown oil *1,6-diiodobicyclo[4.1.1]oct-3-ene* (0.55 g, 82%) (**17**) (Found M^+: 359.8873. $C_8H_{10}I_2$ requires: 359.8872) which showed δ_H: 5.22 (2 H, t, J=1.6 Hz), 3.7 (2 H, br.dd, J=3.4, 10.6 Hz), 3.1 (2 H, br.dd, J=3.5, 10.6 Hz), 2.9 (4 H, d, J=1.6 Hz); δ_C: 126, 60.2, 49.3, 15.9. The carbon signal at 60.2 was coupled to the hydrogen signal at 3.19 and 3.7, while that at 49.3 was coupled to the hydrogens at 2.9; m/z: 360 (M^+), 233 ($M^+ - I$), 205 ($233 - 2CH_2$).

(b) Iodine (0.86 g, 3.4 mmol) in dry ether (45 ml) was added to a stirred solution of tricyclo[4.1.1.0^{1,6}]oct-3-ene (0.3 g, 2.83 mmol) in dry ether (10 ml) at −90°C. The reaction was stirred for 2 h at ambient temperature before quenching with aqueous sodium thiosulphate (10 ml). Work up as before gave two products which were separated by chromatography on silica eluting with petroleum and ether (5:0.50) to give 1,6-diiodobicyclo[4.1.1]oct-3-ene (**17**) (0.51 g, 50%) and *1-iodo-6-ethoxybicyclo[4.1.1]oct-3-ene* (0.31 g, 39%) (**18**) (Found $M^+ - I$: 151.1123. $C_{10}H_{15}O$ requires: 151.1113) which showed δ_H: 5.46 (1 H, sex.d, J=12.3 Hz), 5.2 (1 H, sex.d, J=12.3 Hz), 3.34 (2 H, q, J=7.0 Hz), 3.05 (2 H, complex, incl. d, J=9.9 Hz), 3.0 (2 H, br.s), 2.71 (2 H, complex incl. d, J=9.9 Hz), 2.23 (2 H, br.s), 1.15 (3 H, t, J=7.0 Hz); δ_C: 125.9d, 123.2d, 76.3s, 58.3t, 51.9t, 48.8t, 37.1t, 26.8s, 15.9q; ν_{max}: 1663, 1421, 1127, 1054, 988, 776 cm^{-1}; m/z: M^+ (278), 151 ($M^+ - I$), 105 ($151 - C_2H_5OH$).

(c) Iodine (0.57 g, 2.26 mmol) in dry THF (30 ml) was added to a stirred solution of tricyclo[4.1.1.0^{1,6}]oct-3-ene (0.2 g, 1.88 mmol) in THF (10 ml) at −90°C. The reaction was stirred for 2 h at room temperature before quenching with aqueous sodium thiosulphate (10 ml). Work up as before gave a brown residue; chromatography on silica eluting with petroleum and ether (5:0.5) gave 1,6-diiodobicyclo[4.1.1]oct-3-ene (**13**) (0.31 g, 45%) and *1-iodo-6-(1-iodobutoxy)bicyclo[4.1.1]oct-3-ene* (**15**) (0.33 g, 41%) (Found: C, 33.6; H, 4.3. $C_{12}H_{18}I_2O$ requires: C, 33.35; H, 4.19) which showed δ_H: 5.4 (1 H, d.m, J=12.3 Hz), 5.2 (1 H, d.m, J=12.3 Hz), 3.31 (2 H, t, J=6.2 Hz), 3.2 (2 H, t, J=6.9 Hz), 3.0 (4 H, m), 2.7 (2 H, complex d, incl. J=9.9 Hz), 2.23 (2 H, br.s), 1.9 (2 H, m), 1.6 (2 H, m); δ_C: 126, 123, 76.4, 61.8, 51.8, 48.7, 37.1, 31.1, 30.4, 26.5, 20.3, 6.7; ν_{max}: 1660, 1430 cm^{-1}.

Reaction of 2-hydroxy-3-butyltricyclo[4.1.1.0^{1,6}]oct-4-ene with iodine in dichloromethane. 2-Hydroxy-3-butyltricyclo[4.1.1.0^{1,6}]oct-4-ene (**21**) (1.2 g, 6.74 mmol) was stirred in dry dichloromethane (30 ml) at −90°C. Iodine (2.1 g, 8.1 mmol) in dichloromethane (75 ml) was added dropwise over 0.5 h. The mixture was allowed to reach room temperature, stirred for 1 h and then quenched with saturated aqueous sodium thiosulphate (10 ml). The product was extracted with dichloromethane (3×20 ml) and the combined organic layers were dried and evaporated to give a brown oil, which showed two peaks by GLC in ratio 5:10. Chromatography on silica eluting with 5:1 petroleum and ether gave 1-iodo-4-butyl-6-methylene-8-oxabicyclo[3.2.1]oct-2-ene as the major product (**24**) (1.1 g, 54%) which showed δ_H: 6.35 (1 H, dd, J=1.5, 9.8 Hz), 5.25 (1 H, ddd, J=2.0, 4.3, 9.8 Hz), 5.1 (1 H, m), 5.0 (1 H, m), 4.55 (1 H, br.s), 3.23 (1 H, d of narrow m, J=15 Hz), 3.1 (1 H, d of narrow m, J=15 Hz), 1.7 (1 H, m), 1.64–1.5 (2 H, m), 1.4–1.15 (4 H, m), 0.9 (3 H, t, J=7.2 Hz); δ_C: 150.4 (s), 138.8 (d), 128 (d), 106.4 (t), 82.8 (d), 67.7 (s), 56 (t), 44 (d), 32.8 (t), 29.4 (t), 22.7 (t), 14 (q); ν_{max}: 1667, 1621, 1465, 1233, 968 cm^{-1}; m/z 304 (M^+), 177 ($M^+ - I$). This was characterised by reduction to (**25**).

The minor product *4-butyl-6-methylene-8-oxabicyclo[3.2.1]oct-2-ene* (**25**) (0.33 g, 38%) (Found $M + NH_4^+$: 196.1701. Calculated for $[C_{12}H_{18}O + NH_4]^+$: 196.1701) showed δ_H: 5.9 (1 H, ddd, J=1.6, 4.2, 9.8 Hz), 5.56 (1 H, ddd, J=1.6, 4.2, 9.8 Hz), 5.1 (1 H, br.d, J=2.1 Hz), 5.03 (1 H, br.s), 4.55 (1 H, br.s), 4.48 (1 H, br.d, J=15 Hz), 2.6 (1 H, dm, J=15.0 Hz), 2.5 (1 H, br.d, J=15.0 Hz), 1.82 (1 H, m), 1.7–1.3 (6 H, br.m), 0.92 (3 H, t, J=6.7 Hz); δ_C: 152.6 (s), 131.3 (d), 128.3 (d), 106.14 (t), 80.45 (d), 73.75 (d), 45.13 (d), 41.5 (t), 33.4 (t), 29.5 (t), 22.8 (t), 14.1 (q); ν_{max}: 1666, 1465, 1024 cm^{-1}; m/z: 178 (M^+), 149 ($M^+ - CHO$), 121 ($M^+ - C_4H_9$).

Reduction of 1-iodo-4-butyl-6-methylene-8-oxabicyclo[3.2.1]oct-2-ene with lithium-^{t}butanol-THF. Lithium (150 mg) was added to 1-iodo-4-butyl-6-methylene-8-

oxabicyclo[3.2.1]oct-2-ene (**24**) (0.5 g, 1.6 mmol) in *t*-butanol (1.2 g, 16 mmol) and tetrahydrofuran (10 ml). The mixture was stirred for 16 h at room temperature, when GLC showed no starting material, then the products were poured into ice water (20 ml) and extracted with ether (3×15 ml). The organic layer was washed with water (2×10 ml) and then with saturated brine (15 ml). The organic layer was dried and the solvent was evaporated to give an oil, 4-butyl-6-methylene-8-oxabicyclo[3.2.1]oct-2-ene (**25**) (0.27 g, 94%), which was pure by NMR and identical to the above product.

Reaction of 2-hydroxy-3-butyltricyclo[4.1.1.0^{1,6}]oct-4-ene with iodine in ether. The above procedure was repeated using dry ether as a solvent to give a mixture of two products in ratio 5:1. This was separated by column chromatography on silica, eluting with petrol/ether (5:0.5) to give *1,6-diiodo-3-butyl-2-hydroxybicyclo[4.1.1]oct-4-ene* (**26**) (0.64 g, 22%), mp 70–72°C (Found: C 33.78, H 4.1; $C_{12}H_{18}OI_2$ requires: C 33.34, H 4.2) which showed δ_H: 6.36 (1 H, dd, J=2.4, 11.5 Hz), 4.95 (1 H, dd, J=1.6, 11.5 Hz), 4.58 (1 H, d, J=3.94 Hz), 3.8 (1 H, dd, J=6.8, 12.4 Hz), 3.62–3.53 (2 H, m), 3.42 (1 H, d, J=11.8 Hz), 2.86 (1 H, br.m), 2.1 (1 H, br.s), 1.5 (2 H, m), 1.33 (4 H, br.m), 0.93 (3 H, t, J=6.5 Hz). On irradiation at δ 2.86, the signals at δ 6.36 and δ 4.95 changed to a doublet with coupling constant 11.5 Hz; δ_C: 141.8 (d), 128 (d), 83.1 (d), 59.2 (t), 57.8 (t), 40.8 (d), 39.7 (s), 32.4 (t), 29.7 (t), 27.3 (s), 22.7 (t), 14.1 (q); ν_{max}: 3486 cm^{-1}. The second product was 1-iodo-4-butyl-6-methylene-8-oxabicyclo-[3.2.1]oct-2-ene (**24**) (1.25 g, 61%).

Attempted deiodination of 1,6-diiodo-3-butyl-2-hydroxybicyclo[4.1.1]oct-4-ene. *n*-Butyllithium (0.27 ml, 0.4 mmol, 1.5 M) was added to a stirred solution of (**26**) (150 mg, 0.33 mmol) in ether (7 ml) at −78°C under nitrogen. The reaction was allowed to reach room temperature for 15 min before being quenched with saturated aqueous ammonium chloride (2 ml). The product was extracted with ether (2×5 ml), the combined organic layers were dried and evaporated to give a crude product. The NMR spectrum of this showed it to be a complex mixture.

Reaction of 2-hydroxy-3-butyltricyclo[4.1.1.0^{1,6}]oct-4-ene with triphenylphosphine/bromine. Bromine (0.427 g, 2.67 mmol) in dry dichloromethane (5 ml) was added dropwise with stirring to triphenylphosphine (0.7 g, 2.67 mmol) in dry dichloromethane (20 ml) at −10°C. After an additional 10 min, a solution of alcohol (0.45 g, 2.5 mmol) and pyridine (0.211 g, 2.67 mmol) in dichloromethane (5 ml) was added at −10°C. The mixture was stirred for 2 h at −10°C and 5 h at rt. After evaporation of the solvent the residue was treated with pentane, filtered and evaporated to give a dark residue which was very complicated by ^{1}H NMR.

O-Methoxycarbonyl-2-hydroxy-3-butyltricyclo-[4.1.1.0^{1,6}]oct-4-ene. Methyllithium (2.78 ml, 4.17 mmol) was added to a stirred solution of 2-hydroxy-3-butyltricyclo[4.1.1.0^{1,6}]oct-4-ene (0.61 g, 3.4 mmol) in dry ether (20 ml) at −80°C. The mixture was allowed to reach room temperature for 15 min, then cooled to −30°C and quenched with methyl chloroformate (0.58 ml, 7.5 mmol). The mixture was allowed to reach room temperature for 0.5 h, before quenching with saturated aqueous sodium bicarbonate (10 ml). The aqueous layer was extracted with ether (2×15 ml). The combined organic layers were dried and evaporated to give a pale yellow oil *O-methoxycarbonyl-2-hydroxy-3-butyltricyclo[4.1.1.0^{1,6}]oct-4-ene* (**28**) (0.73 g, 91.3%) (Found M$^+$: 236.1406. $C_{14}H_{20}O_3$ requires: 236.1403) which showed δ_H: 6.1 (1 H, dd, J=2.8, 9.3 Hz), 5.58 (1 H, dd, J=2.7, 9.3 Hz), 5.43 (1 H, d, J=4.4 Hz), 3.7 (3 H, s), 2.1 (1 H, br.m), 1.84 (1 H, dd, J=1.5, 6.7 Hz), 1.78 (1 H, dd, J=2.2, 6.7 Hz), 1.6–1.2 (7 H, m), 1.16 (1 H, s), 0.84 (3 H, t, J=7.0 Hz); δ_C: 155.47, 131.9, 125.23, 73.5, 54.7, 41.6, 40.5, 36.3, 30.78, 29.95, 22.65, 13.9, 9.31, 3.44; ν_{max}: 1750, 1265 cm^{-1}.

Reaction of (28) with base. (a) Sodium bis (trimethylsilyl) amide (3.48 ml, 3.48 mmol) was added to a stirred solution of (**28**) (0.52 g, 2.32 mmol) in dry THF (10 ml) at −80°C under nitrogen. The mixture was allowed to reach room temperature and stirred for 3 h, when TLC showed no starting material. The products were cooled to −50°C, and quenched with saturated aqueous ammonium chloride (5 ml) and diluted with ether (15 ml). The organic layer was separated, and the aqueous layer was extracted with ether (10 ml). The combined organic layers were washed with 2 M hydrochloric acid, dried and evaporated to give a dark residue which was very complicated by ^{1}H NMR.

(b) Compound (**28**) (0.65 g, 2.9 mmol) in THF (5 ml) was added with stirring to sodium methoxide prepared from sodium (1.0 g) and methanol (25 ml). After 2 h, TLC showed no starting material. The products were treated with water (15 ml) and extracted with dichloromethane (2×15 ml), the organic layer was dried, and the solvent was removed at 14 mmHg to give 2-hydroxy-3-butyltricyclo[4.1.1.0^{1,6}]oct-4-ene (0.41 g, 80%).

1-Bromoethyl-1,2,2-tribromocyclopropane. 1,1,2-Tribromocyclopropane-2-ethanol (3.0 g, 97 mmol) was dissolved in dry ether (60 ml) and stirred at 0°C under argon. Carbon tetrabromide (4.8 g, 14.6 mmol) and triphenylphosphine (3.8 g, 14.6 mmol) were added and the reaction warmed to room temperature and stirred for 2 h. TLC in petroleum then showed no starting material. The resulting precipitate was filtered and the filter pad was washed with ether (3×15 ml). The combined organic layers were reduced under vacuum to give a crude oil which was subjected to chromatography on silica eluting with petroleum (bp 40–60°C). *1-Bromoethyl-1,2,2-tribromocyclopropane* (**29**) was obtained as a colourless oil (2.7 g, 73%) (Found M$^+$: 381.69999. $C_5H_6Br_4$ requires 381.7202) which showed δ_H: 3.6 (2 H, m), 2.5 (2 H, m), 1.9 (2 H, s); δ_C: 44.13, 43.65, 38.02, 31.25, 29.39; ν_{max}: 2967, 1439, 1216 cm^{-1}.

1-Bromo-2-bromoethylcyclopropene. Methyllithium (1.51 ml, 2.27 mmol, 1.1 mol equiv.) was added to a stirred solution of 1-bromoethyl-1,2,2-tribromocyclopropane (0.8 g, 2.07 mmol) in dry ether (10 ml) under nitrogen at −78°C. The mixture was allowed to reach 0°C, cooled again to −40°C and quenched with water (2 ml). After extraction with ether (3×10 ml), the combined ether layers were dried and the solvent was removed at 14 mmHg to give

1-bromo-2-(2-bromoethyl)cyclopropene (**30**) (0.4 g, 87%) (Found M^+: 223.8836. $C_5H_6Br_2$ requires 223.8836); δ_H: 3.5 (2 H, t, J=7.0 Hz), 3.0 (2 H, t, J=7.0 Hz), 1.5 (2 H, s); δ_C: 115.37, 94.87, 29.29, 27.88, 17.02; ν_{max}: 2882, 1838, 1268 cm^{-1}.

1-Bromo-2-bromoethylcyclopropene diphenylisobenzofuran adduct. Methyllithium (0.94 ml, 1.42 mmol, 1.1 mol equiv.) was added to 1-bromoethyl-1,2,2-tribromocyclopropane (0.5 g, 1.29 mmol) and diphenylisobenzofuran (0.38 g, 1.92 mmol) stirred in dry ether (15 ml) under nitrogen at −78°C. The mixture was then stirred overnight at room temperature. After quenching with water (2 ml) at −40°C and extracting with ether (3×15 ml), the combined ether layers were dried and evaporated to give a yellow oil, *4-bromo-2-bromoethyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo-[3.2.1.0^{2,4}]octane* (**32**) (0.48 g, 77%) (Found M^+: 493.9881. $C_{25}H_{20}Br_2O$ requires: 493.9880); δ_H: 8.0–7.0 (14 H, m), 3.3 (2 H, m), 2.9 (1 H, d, J=6.6 Hz), 2.2 (1 H, ddd, J=6.3, 9.5, 15.4 Hz), 1.9 (1 H, ddd, J=6.3, 9.4, 15.5 Hz), 1.8 (1 H, d, J=6.6 Hz); δ_C: 90.53, 89.88, 49.68, 36.95, 32.68, 30.41, 28.35 (plus complex aromatics); ν_{max}: 1660, 1447, 1295 cm^{-1}.

2-Bromo-4-bromoethyl-8-oxatricyclo [3.2.1.0^{2,4}]oct-6-ene. An excess of furan was added to a stirred solution of 1-bromo-2-bromoethylcyclopropene (0.2 g, 0.88 mmol) in ether (7 ml) at room temperature. The reaction was stirred at that temperature for five days, then the solvent was removed at 14 mmHg to give a yellow oil, *2-bromo-4-bromoethyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene* (**31**) (0.18 g), which showed two isomers in ratio 3.5: 1. Chromatography on silica eluting with 5:2 petroleum and ether gave the major isomer (0.1 g, 38%) (Found $M+H^+$: 292.9177. $C_9H_{10}Br_2O+H^+$ requires: 292.9176) which showed δ_H: 6.69 (1 H, dd, J=1.6, 5.7 Hz), 6.62 (1 H, dd, J=1.5, 5.7 Hz), 4.87 (1 H, d, J=1.4 Hz), 4.81 (1 H, d, J=1.5 Hz), 3.5 (2 H, m), 2.2 (1 H, dd, J=1.14, 6.3 Hz), 2.0 (2 H, m), 1.1 (1 H, d, J=6.2 Hz); δ_C: 139.83, 138.38, 81.35, 79.49, 46.62, 34.90, 33.68, 31.55, 28.91; ν_{max}: 2998, 1618, 1296 cm^{-1}. The minor isomer (0.03 g, 11.5%) showed δ_H: 6.3 (1 H, dd, J=1.7, 5.6 Hz), 6.2 (1 H, dd, J=1.7, 5.8 Hz), 5.01 (1 H, t, J=1.8 Hz), 4.9 (1 H, t, J=1.8 Hz), 3.5 (2 H, dt, J=1.5, 7.6 Hz), 2.4 (1 H, m), 2.2 (2 H, m), 1.7 (1 H, d, J=6.8 Hz), 1.4 (1 H, d, J=6.8 Hz); δ_C: 134.08, 132.79, 88.58, 83.66, 45.59, 39.78, 35.28, 32.05, 31.25.

2-(2-Bromoethyl)cyclopropene diphenylisobenzofuran adduct. Methyllithium (1.45 ml, 2.17 mmol, 2.1 mol equiv.) was added to a stirred solution of 2-bromo-ethyl-1,2,2-tribromocyclopropane (0.4 g, 1.03 mmol) in dry ether (10 ml) under nitrogen 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 (0.25 g, 0.93 mmol). After 18 h the solvent was removed at 14 mmHg to give a thick yellow oil (0.3 g, 70%), *2-(2-bromoethyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane* (**32**) (Found $M+H^+$: 417.0854 $C_{25}H_{21}BrO+H^+$ requires 417.0853); δ_H: 8.0–7.0 (14 H, m), 2.9 (2 H, m), 2.3 (1 H, ddd, J=6.0, 9.6 15.0 Hz), 2.2 (1 H, dd, J=3.7, 5.4 Hz), 1.9 (1 H, ddd, J=6.1, 10.0, 15.0 Hz), 1.7 (1 H, dd, J=3.6, 6.9 Hz), 1.3 (1 H, dd, J=5.4, 6.9 Hz); δ_C: 90.50, 88.28, 34.72, 32.62, 30.23, 30.20, 19.34 (plus complex aromatics); ν_{max}: 1663, 1442, 1096 cm^{-1}.

1-(2-Bromoethyl)cyclopropene. The experimental procedure was repeated as for the previous reaction without the addition of diphenylisobenzofuran to give *2-(2-bromoethyl)cyclopropene* (**33**) (0.08 g, 47%) which showed δ_H: 6.6 (1 H, br.s), 3.5 (2 H, t, J=6.8 Hz), 3.0 (2 H, t, J=6.8 Hz), 0.9 (2 H, d, J=1.6 Hz).

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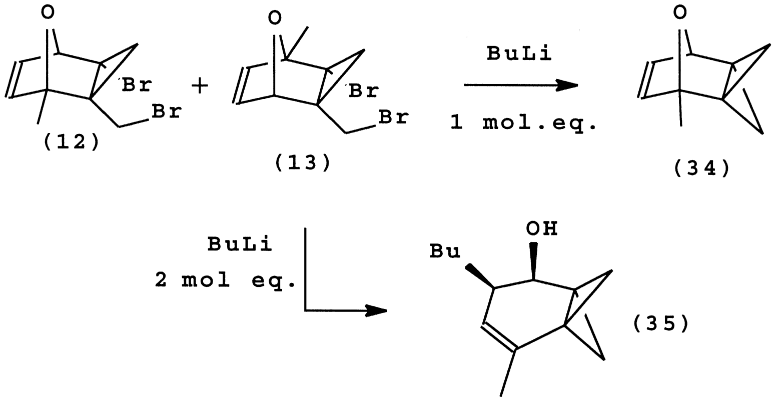
20. Irradiation of the signal at δ 1.9 reduced those at 6.2, 5.5 and 4.6 to doublets or broad doublets. Irradiation at δ 1.8 reduced the signal at 2.1 to a broad singlet and a doublet at 1.3 to a singlet and appeared not to affect any other signals. Irradiation at δ 2.1 reduced the signal at 1.8 to a narrow doublet and no other changes could be observed. Irradiation at δ 6.2 or 5.5 caused the second of these signals to be reduced to broad singlets but led to little change

elsewhere in the spectrum, while irradiation at δ 4.6 sharpened to a small extent the signal at 1.9. We thank the EPSRC NMR service in Edinburgh for obtaining these spectra at 600 MHz.

21. In order to establish the structure, the corresponding reactions of adduct (**14**) were examined. This was unreactive to *n*-butyllithium. However, treatment of an ca. 1:1 mixture of the adducts (**12**) and (**13**) with 1 mol equiv. of *n*-butyllithium led to the reaction of one isomer, to give a product provisionally characterised as (**34**); the second isomer remaining unchanged. However, treatment of the mixture of (**12**) and (**13**) with 2.1 mol equiv. of *n*-butyllithium resulted in both of them reacting; the alcohol (**35**) was then isolated. This results from attack as in (**22**) and could be clearly distinguished from the products of possible attack at other positions since it showed just one alkene hydrogen (a broad singlet) in its ^{1}H NMR spectrum.



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