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2-Vinyl-1,1,2-trihalocyclopropanes - Valuable Five Carbon Cyclopropane and Cyclopropene Synthetic Intermediates

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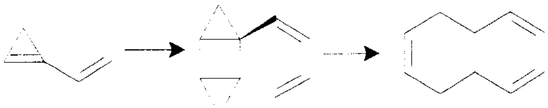
Abstract: *The dichloro- and dibromocarbene adducts of chloroprene and 2,3-dichlorobutadiene are readily dehalogenated by reaction with methyllithium to give 1-halo-2-vinylcyclopropenes which on further lithium-halogen exchange give synthetically useful 1-lithio-2-vinylcyclopropenes. Trapping of 1-lithio-2-(1-chlorovinyl)cyclopropene with methyl chloroformate leads to a very unusual cyclononadienyne.* Copyright © 1996 Elsevier Science Ltd

Despite a considerable expansion in the chemistry of cyclopropenes, and particularly in their applications in synthesis, there are very few reports of simple 1-vinylcyclopropenes.[1-3] The parent compound (1) has been obtained by gas-solid dehydrochlorination of a chlorovinylcyclopropane, but is reported to undergo dimerisation to give the formal [2+2]-cycloadduct (2) even at -40 °C; this then rearranges slowly to (3).[4*] We have recently reported that the tribromides (4) and (5) are dehalogenated in solution to cyclopropenes (6) and (7), which are rather more stable than (1), decomposing over a period of about 18 h at 20 °C.[5] We now report a simple route to 2-vinylcyclopropenes in two stages from readily available starting materials, and some examples of their trapping.

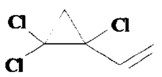


(1) (2) (3)

(4) R = CO_2Me
(5) R = CH_2OH

(6) R = CO_2Me
(7) R = CH_2OH

The addition of dichlorocarbene, generated from KOBu-t and chloroform, to chloroprene has been reported to lead to cyclopropane (**8**) together with ca. 5% of the product derived by attack at the non-chlorinated alkene.[6] In the present work, the same result was achieved when the carbene was generated under phase transfer conditions and added to chloroprene in xylene. In the same way a solution of 2,3-dichlorobutadiene in xylene was converted into (**10**) by reaction with chloroform and base under phase transfer conditions, while chloroprene and 2,3-dichlorobutadiene were converted into (**9**) and (**11**) respectively by reaction with bromoform and base under similar conditions. Although the yields of these reactions were low, the ready availability of the starting materials makes it possible to obtain large quantities of the cyclopropanes. The further addition of a second dihalocarbene to these mono-adducts is possible,[7] but in practice it occurs only slowly.



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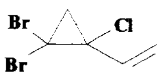

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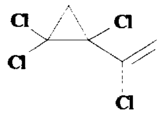

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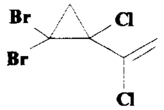
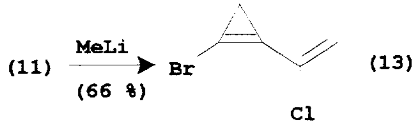


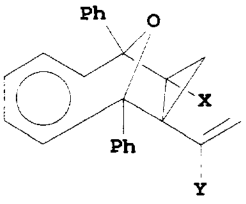
(11)

Reaction of the dibromides (**9**) or (**11**) with 1 mol. equiv. of methyllithium at -78 °C and treating with water at that temperature led to a 1,2-dehalogenation[8] to give the 1-bromo-2-vinylcyclopropenes (**12**) or (**13**) respectively:

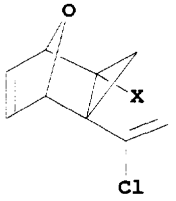


In each case, the cyclopropene could be characterised on the basis of a singlet at δ 1.6 and 1.9 respectively for the cyclopropene methylene group in the ^{1}H nmr spectrum measured at normal instrument operating temperature. Compound (**12**) decomposed on standing in $CDCl_3$ at room temperature; after 0.5 h ca. 30 % decomposition could be seen by ^{1}H nmr, and after 2 days no starting material remained and a very complex spectrum was observed. Column chromatography did lead to small quantities of largely single components, but these were not fully characterised. When (**12**) was allowed to stand in ether or benzene, similar complex mixtures were obtained. Compound (**13**) was rather more stable and, after standing for 18 h at 20 °C in $CDCl_3$ about 50% remained; after 2 days a complex mixture had been produced but the signals for (**13**) could still be seen in the ^{1}H nmr spectrum.

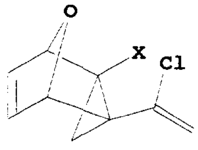
Compounds (**12**) and (**13**) could be trapped by [4+2]-cycloaddition to diphenylisobenzofuran, leading to a single product in each case, (**14a**) (46 %) and (**14b**) (49 %) respectively. The stereochemistry of the adducts was assigned by analogy with related adducts of 3,3-unsubstituted cyclopropenes with DPIBF and supported by the large chemical shift difference between the cyclopropane hydrogens in each case (0.8 and 1 ppm respectively).[9] Compound (**13**) was also trapped by [4+2]-cycloaddition to furan leading to major isomer characterised as (**15a**) (40 %) and a minor isomer (**16a**) (24 %), and to 1,3-butadiene, leading to (**17a**) (57 %). Adduct (**17a**) showed the expected AB pattern for its cyclopropane hydrogens at δ 1.5 and 1.6, and four single hydrogen signals in the alkene region, two broad singlets and two complex multiplets. The signals for the methylene groups in the six-membered ring were unusual, three hydrogens appearing as a complex multiplet at δ 2.9 - 3.1 and one as a complex doublet at δ 2.3. The furan adducts could be separated by column chromatography; the ^{1}H nmr of the major isomer included an AB pattern for the cyclopropane hydrogens centred at δ 2.5 and 1.6, while those for the minor isomer appeared at 1.99 and 1.92. Attempted reaction of the cyclopropene (**12**) with furan led only to complex products, presumably either because decomposition competes with cycloaddition or because the product is unstable.



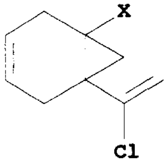
(14a) X = Br Y = H
(14b) X = Br Y = Cl
(14c) X = Cl Y = H
(14d) X = Cl Y = Cl
(14e) X = H Y = H
(14f) X = $SiMe_3$ Y = H
(14g) X = H Y = Cl
(14h) X = D Y = Cl
(14i) X = $SiMe_3$ Y = Cl



(15a) X = Br
(15b) X = Cl

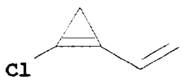


(16a) X = Br
(16b) X = Cl

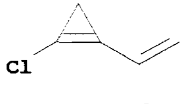


(17a) X = Br
(17b) X = Cl

In the same way, the polychlorides (**8**) and (**10**) reacted with 1 mol. equiv. of MeLi at -20 °C for 20 min to give cyclopropenes (**18**) (68 %) and (**19**) (63 %):



(18)



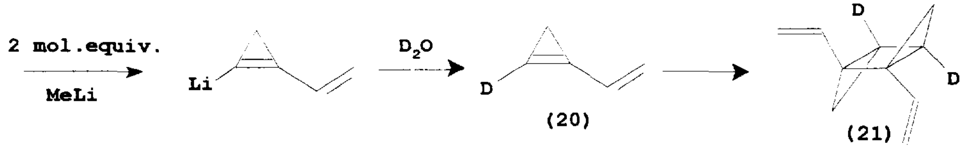
(19)

Compound (**18**) was very volatile and it was not possible to separate it completely from the solvent, ether. However, an nmr of the mixture showed only a vinyl pattern in the alkene region and a singlet at δ 1.6 apart from ether signals. The ^{13}C nmr spectrum was weak and not all the cyclopropene signals were characterised; however alkene signals were seen at δ 123.3 and 121.5. This compound decomposed relatively quickly in $CDCl_3$ at 20 °C; even after 1 h complex new signals were observed in the ^1H nmr. Compound (**19**) was rather more stable and even after 1 day at 20 °C in $CDCl_3$ about 25% remained. Once again (**18**) and (**19**) were trapped in moderate yield by addition to DPIBF, to give adducts (**14c**) and (**14d**) with ^1H nmr spectra very similar to those from the corresponding adducts of (**12**) and (**13**). Compound (**19**) was also trapped by addition to furan, and butadiene giving (**15b**) and (**16b**) in ratio ca. 5:1, and (**17b**) respectively. On chromatography of the mixture of (**15b**) and (**16b**), only (**15b**) was obtained pure.

Reaction of (**9**) with 2 mol.equiv. of MeLi at -78 to 20 °C for 5 min followed by quenching with water at low temperature gave a mixture of (**2**) and (**3**), apparently derived by dimerisation of (**1**). This was derived by formation of (**12**) from (**9**) with 1 mol.equiv.of MeLi, lithium - halogen exchange with the second mol.equiv. of MeLi to give 1-lithio-2-vinylcyclopropene,[8] and quenching of this with water. The products were characterised by comparison of the nmr spectrum of the mixture with reported data.[4] If (9) was treated with 2 mol. equiv. of MeLi and the product was quenched at -78 °C with water, decanted from the ice and then treated with DPIBF, the [4+2]-cycloadduct (**14e**) was obtained in moderate yield. The stereochemistry of this compound was assigned by analogy with other related adducts.[9] If (9) was treated with 2 mol. equiv. of MeLi as above and the volatiles were evaporated at -40 °C and 1 mm Hg, a white solid was obtained; quenching of this with water under vacuum and condensation of the volatiles produced into a trap cooled in liquid nitrogen gave (**2**) after the distillate was dissolved in $CDCl_3$ and analysed by ^1H nmr. As reported, (**2**) rearranged over a period of several weeks in $CDCl_3$ to (**3**). The structure of (3) was further supported by converting it into 1,2-divinylbenzene by reaction with DDQ.[4]

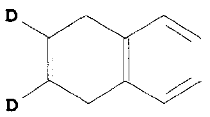
If (9) was treated as above with 2 mol. equiv. of MeLi and then the solid quenched with D_2O, the 2-deuteriovinylcyclopropene (**20**) was obtained. This was again distilled as it formed and collected at low temperature; on warming to room temperature, nmr in $CDCl_3$ showed the presence of (**21**). The spectrum was very similar to that for (**2**), except that only two signals were present in the high field region, an AB pattern at δ 1.5 and 1.2 (J 4.1 Hz). Compound (**21**) again rearranged over a period of weeks to give (**22**), the ^1H nmr spectrum of which was identical to that of (3) apart from the lack of the broad singlet for the ring alkene hydrogen at δ 5.85. Deuterium incorporation was apparently >95 % complete by nmr.

(24)



(20) (21)

Quenching of the 1-lithio-2-vinylcyclopropene with TMSCl followed by warming to room temperature gave a complex mixture. However, quenching with TMSCl at -70 °C and treatment at that temperature with DPIBF gave the adduct (**14f**) in moderate yield. This was characterised on the basis of its ^1H nmr spectrum which included signals for the vinyl and silyl groups and an AB pattern for the cyclopropane hydrogens at δ 2.5 and 1.8 (J 4.7 Hz).



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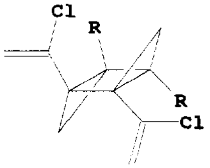
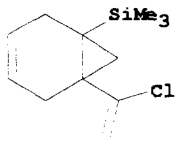


(25) R = H
(26) R = D



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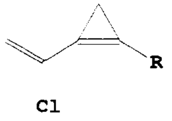
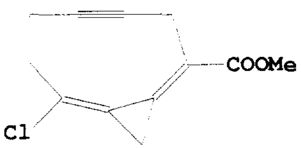


(23) R = Li
(24) R = H
(27) R = D
(28) R = $SiMe_3$

Reaction of (**11**) with 2 mol. equiv. of MeLi at -78 °C followed by warming to room temperature for 5 min and then quenching with H_2O at -78 °C, followed by addition of DPIBF led to (**14g**) together with ca. 25% of a stereoisomer, apparently by reaction of the lithiocyclopropene (**23**) with water to give (**24**) followed by cycloaddition. In the absence of DPIBF, or in the presence of furan, the dimer (**25**) was isolated. This was characterised by comparison of its ^{1}H nmr spectrum with that of **(2)**; the spectrum included two singlets in the alkene region and an ABC pattern at δ 1.7 - 2.0. This spectrum remained unchanged after a week at 20 °C. Quenching with D_2O at low temperature followed by warming to room temperature again gave the dimer **(26)** apparently derived from **(27)**. Deuteriation was essentially complete by ^{1}H nmr, a clean pair of doublets being observed in the cyclopropane region; m.s. showed over 91 % deuteration. Addition of DPIBF at low temperature followed by warming intercepted the vinylcyclopropene and led to **(14h)**, again as an ca. 5:1 mixture of stereoisomers. Once again, nmr showed essentially complete deuteration.

Quenching with TMSCl led to the cyclopropene **(28)** which was stable for several days at 20 °C; this showed four singlets in its ^{1}H nmr spectrum at δ 0.09 (9H), 1.2 (2H), 5.7 (1H) and 5.8 (1H). Trapping with DPIBF led to a single cycloadduct **(14i)** which showed a large chemical shift difference between the cyclopropane hydrogens (δ 2.70 and 1.7) in agreement with an exo-stereochemistry. Trapping with butadiene led to the adduct **(29)** in moderate yield (23 %), but reaction with furan led to a very complex mixture of products.

Trapping of **(23)** with methyl chloroformate led to a crystalline product characterised as **(30)** (57 %). This showed the expected ^{13}C nmr signals, including four quaternary alkene signals and two quaternary alkyne signals as well as four methylene groups. In the fully proton coupled spectrum, three of the methylene carbons showed $^1J_{CH}$ values of ca. 130 Hz, but the fourth one, that at highest field, showed a value of 167 Hz and is assigned to the cyclopropane carbon. All of the alkene and alkyne carbons appeared as narrow multiplets, suggesting long-range coupling to at least two methylene groups. In the ^{1}H nmr spectrum there was a methyl ester signal together with four multiplets at δ 3.2, 2.9, 2.4 and 1.9. The signal at δ 3.2 could be analysed as a pentuplet (J 2.1 Hz); the one at 1.9 was also a pentuplet (J 2.1 Hz). The signals at δ 2.9 and 2.4 were more complex. Irradiation at 2.4 caused the signal at 3.2 to be decoupled to a triplet but did not change the one at 1.9; it did decouple the signal at 3.0 to a broad singlet with smaller satellite lines. Irradiation at δ 2.9 had an identical effect on the signal at 2.4, but in this case decoupled the one at 1.9 to a triplet and left that at 3.2 unchanged. Irradiation at δ 3.2 decoupled the signal at 1.9 to a triplet, sharpened the signal at 2.4 removing some small couplings and did affect that at 2.9. Irradiation at δ 1.9 decoupled the signal at 3.2 to a triplet, sharpened the signal at 2.9 and left that at 2.4 unchanged. It appears therefore that the signals at δ 2.4 and 2.9 are best explained in terms of a $-CH_2-CH_2-$ group with long-range coupling of one of the methylenes (that at 2.9) to the CH_2 at 1.9 and of the other (at 2.4) to the CH_2 at 3.2; the signals at 1.9 and 3.2 also show long-range coupling to each other.



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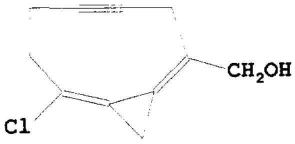

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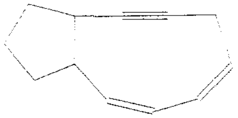
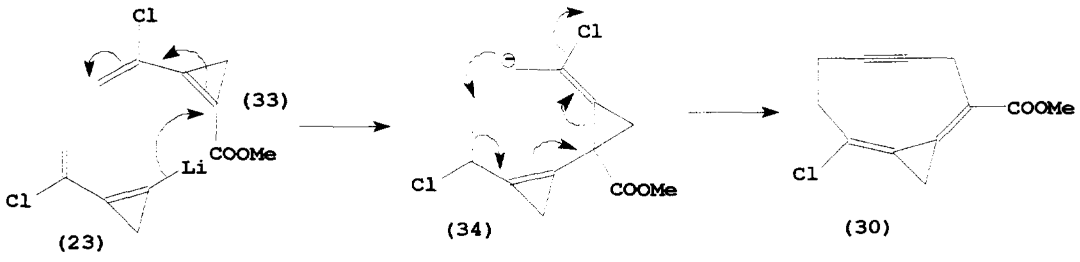
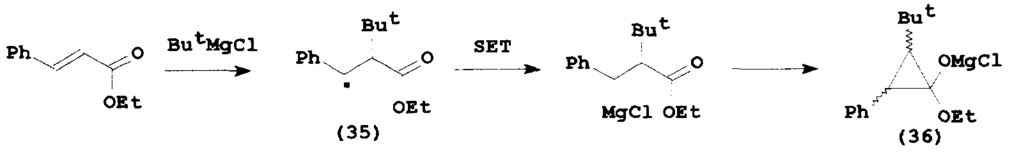


(32)

Reduction of **(30)** with DIBAL gave an alcohol **(31)**; the CH_2-group of this appeared as a singlet which rules out the presence of a $-CH_2-CO_2Me$ group in **(30)**. Further reduction of the alcohol with Li-Bu^{t}OH-THF gave two products which have not as yet been identified.

The cyclononyne **(30)** is a most unusual product - a substructure search of Chemical Abstracts reveals only one other example of a cylonona-1,3-dien-6-yne **(32)**.[10] Compound **(30)** appears to be derived from two molecules of the lithiocyclopropene **(23)** and one of methyl chloroformate, with the elimination of two molecules of lithium chloride. Since the results above show that the lithiocyclopropene can be trapped by electrophiles, it seems reasonable that the reaction is initiated by the formation of one molecule of the cyclopropene ester **(33)**; this reaction occurs relatively slowly with other cyclopropenes and it is possible therefore that the ester is relatively rapidly trapped by the second molecule of lithiocyclopropene to give **(34)**, which might cyclise as shown to produce **(30)**. There is however no direct evidence for this mechanism, and it must be said that the regiochemistry of the first addition is unusual ! However the relief of strain in going from a cyclopropene to an exocyclic allylic ion may overcome the directing effect of the ester. It should be noted that this mechanism also requires the allylic anion to be formed in a geometry suitable for cyclisation. Further experiments are required to establish the mechanism more clearly. However, it is perhaps significant that the addition of t-butylmagnesium chloride to methyl cinnamate also leads to a product derived by addition of a t-butyl group to the α-carbon of the α,β-unsaturated ester. This reaction has been explained in terms of the addition of a t-butyl radical to produce **(35)**, followed by single electron transfer to give the corresponding anion, and then cyclisation to **(36)**.[11]





The above reactions show that addition of dihalocarbenes to 2-chloro- or 2,3-dichlorobutadiene followed by reaction with one or two molecular equivalents of methyllithium provides a practical route to 1-vinylcyclopropenes, and that these are readily trapped in Diels-Alder reactions. The full chemistry of these compounds is now being examined.

We wish to thank Du Pont Ltd. for their generous gift of chloroprene and 2,3-dichlorobuta-1,3-diene.

Experimental Section

Reagents were obtained from commercial suppliers and were used without further purification unless stated. Dichloromethane was distilled over calcium hydride. Diethyl ether was distilled over sodium wire. Petrol was either of boiling point 40 - 60 or 60 - 80 °C. Both were purified by distillation. Purity of compounds was assessed by either gas liquid chromatography (glc) or by thin layer chromatography (tlc). 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) with hydrogen as carrier gas. Tlc was performed using Aldrich silica plates coated with silica gel 60 (F254). Compounds were visualised either by examination under an ultra violet 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 (solids) or as liquid films on a Perkin-Elmer 1600 FTIR spectrometer. Low resolution mass spectra were obtained using a Finnigan Mat 1020 spectrometer in EI mode. Mass measurements reported 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 using a Brucker AC250 at 250 MHz for protons and 62.5 MHz for carbon and in the latter case were either broad-band or gated decoupled.

Reactions requiring anhydrous conditions were performed using oven dried glassware (250 °C) that was cooled under a stream of either dry nitrogen or argon and were conducted under a positive atmosphere of one of these gases. Yields quoted are for the purified compounds unless otherwise stated. Solids were purified by either recrystallisation or chromatography while liquids and oils were purified either by chromatography or by distillation. All new compounds were homogeneous by tlc or by glc. The term "dried" refers to the storage of a solution of the compound over anhydrous magnesium sulphate for a few minutes.

Preparation of 1,1-dihalo-2-chloro-2-(vinyl)cyclopropanes

(i) Sodium hydroxide (32.7 g) in water (33.0 ml) was added to a rapidly stirred solution of 2,3-dichloro-1,3-butadiene (10 g, in 50% xylene), cetrimide (2 g), and bromoform (31.0 g, 10.7 ml) in dichloromethane (20 ml) maintaining the temperature of the reaction below 20 °C. The reaction was stirred for 8 h, and then worked up by dilution with brine solution and extracted with dichloromethane (3 x 100 ml), the organic layer was dried and the solvent was evaporated at 14 mm Hg and 0.5 mm Hg to give a brown oil. This was treated with petrol and the solid was filtered off. Evaporation of the solvent at 14 and then 0.5 mmHg gave 1,1-dibromo-2-chloro-2-(1-chlorovinyl)cyclopropane (**11**) (7.5 g, 31 %) which showed δ_H: 5.59 (1 H, d, J 2.2 Hz), 5.56 (1 H, d, J 2.2 Hz), 2.4 (1 H, d, J 9.3 Hz), 2.2 (1 H, d, J 9.3 Hz); δ_C: 139.66, 118.80, 53.43, 37.69, 30.15; υ_{max}: 1630 cm^{-1}.

(ii) The above procedure was repeated using chloroprene in xylene for the preparation of 1,1-dibromo-2-chloro-2-vinylcyclopropane (**9**) (Found M$^+$: 257.8447. $C_5H_5Br_2Cl$ requires: 257.8446) (28 %) which showed δ_H: 6.0 (1 H, dd, J 10.2, 16.5 Hz), 5.6 (1 H, d, J 16.5 Hz), 5.4 (1 H, d, J 10.2 Hz), 2.27 (1 H, d, J 9.2 Hz), 2.18 (1 H, d, J 9.2 Hz); δ_C: 135.70, 119.54, 50.85, 36.90, 32.86; υ_{max}: 1634 cm^{-1}.

(iii) The above procedure was repeated using chloroform in place of bromoform for preparation of 1,1,2-trichloro-2-(1-chlorovinyl)cyclopropane (**10**) (29 %) (Found M^+-H: 202.8989. $C_5H_4Cl_4$-H requires: 202.8988) which showed δ_H: 5.63 (1 H, d, J 2.2 Hz), 5.61 (1 H, d, J 2.2 Hz), 2.3 (1 H, d, J 9.1 Hz), 2.1 (1 H, d, J 9.1 Hz); δ_C: 138.46, 118.94, 62.49, 53.79, 35.54; υ_{max}: 1632 cm^{-1}.

(iv) The above procedure was repeated for preparation of 1,1,2-trichloro-2-vinylcyclopropane (**8**) (28 %) (Found M^+- H: 168.9379. $C_5H_5Cl_3$ - H requires: 168.9378) which showed δ_H: 6.0 (1 H, dd, J 10.2, 16.5 Hz), 5.6 (1 H, d, J 16.5 Hz), 5.4 (1 H, d, J 10.2 Hz), 2.1 (1 H, d, J 9.0 Hz), 2.0 (1 H, d, J 9.0 Hz); δ_C: 134.08, 119.58, 63.92, 51.63, 35.03; υ_{max}: 1634 cm^{-1}.

Reaction of 1,1-dihalo-2-chloro-2-(vinyl)cyclopropanes with 1 mol.equiv. of methyllithium

Methyllithium (2.26 ml, 3.4 mmol, 1.5M) was added over 1 min. to a stirred solution of 1,1-dibromo-2-chloro-2-(1-chlorovinyl)cyclopropane (1 g, 3.4 mmol) in dry ether (15 ml) at -78 °C under an atmosphere of inert gas. The mixture was stirred for 5 min at that temperature before being quenched with water (2 ml), and the ether layer was decanted from the ice. The ice was extracted with cool ether (3 x 10 ml). Evaporation of ether at 0 °C and 14 mm Hg gave a brown oil, 2-bromo-1-(1-chlorovinyl)cyclopropene (**13**) (0.45 g, 75 %), which showed δ_H: 5.7 (1 H, br.s), 5.6 (1 H, br.s), 1.9 (2 H, s); δ_C: 130.0, 120.0, 118.74, 98.7, 19.9; υ_{max}: 1763, 1629 cm^{-1}. When the solution of the cyclopropene was allowed to stand in deuteriochloroform at 20 °C, a complex mixture was obtained.

2-Bromo-1-vinylcyclopropene (**12**) was prepared as above by reaction of 1,1-dibromo-2-chloro-2-vinylcyclopropane with methyllithium (66 %) (δ_H: 6.5 (1 H, dd, J 10.2, 17.0 Hz), 5.6 (1 H, dd, J 1.8, 10.2 Hz), 5.5 (1 H, dd, J 1.8, 17.0 Hz), 1.6 (2 H, s); δ_C (-20 C°): 123.58, 121.88, 115.42, 95.50, 15.80; υ_{max}: 1803, 1638 cm^{-1}).

2-Chloro-1-vinylcyclopropene (**18**) was prepared using the above procedure by the reaction of 1,1,2-trichloro-2-vinylcyclopropane with methyllithium but distilled at 0 °C and 14 mmHg and could not be completely separated from ether (68 % estimated yield) (δ_H: 6.5 (1 H, dd, J 10.2, 17.0 Hz), 5.6 (1 H, m), 5.5 (1 H, m), 1.6 (2 H, s); δ_C (-20 °C): 126.7, 123.30, 121.50, 109.3, 15.08).

1-Chloro-2-(1-chlorovinyl)cyclopropene (**19**) was prepared using the above procedure by the reaction of 1,1,2-trichloro-2-(1-chlorovinyl)cyclopropane with methyllithium (63 %); it showed δ_H: 5.68 (1 H, d, J 0.7 Hz), 5.57 (1 H, d, J 0.7 Hz), 1.8 (2 H, s); δ_C: 125.89, 119.99, 116.21, 112.11, 19.29; υ_{max}: 1771, 1631 cm^{-1}.

Reaction of 1,1-dibromo-2-chloro-2-vinylcyclopropane with methyllithium in the presence of diphenylisobenzofuran

(i) The above procedure was repeated using 1 mol. equiv. of methyllithium at -78 °C to *give 4-bromo-2-vinyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane* (**14a**) (46 %), m.p. 112-114 °C (Found: C 72.9, H 9.40;

$C_{25}H_{19}OBr$ requires C 72.29, H 4.61); δ_H: 7.9-7.3 (14 H, m), 5.7 (1 H, dd, J 10.6, 17.0 Hz), 5.3 (1 H, dd, J 1.3, 10.6 Hz), 5.2 (1 H, dd, J 1.3, 17.0 Hz), 2.9 (1 H, d, J 6.3 Hz), 2.1 (1 H, d, J 6.3 Hz); δ_C: 148.09, 147.97, 134.71, 133.65, 133.49, 129.29, 129.22, 129.0, 128.86, 128.58, 128.50, 127.93, 126.72, 126.66, 122.82, 121.79, 119.21, 90.68, 89.87, 51.39, 41.57, 27.14; δ_{max}: 1636 cm^{-1}.

(ii) The above procedure was repeated using 2 mol.equiv. of methyllithium at -78 to 20 °C, followed by quenching with H_2O to give *2-vinyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.*$0^{2,4}$*]octane* (**14e**) (68 %), m.p. 94 - 98 °C (Found: C 89.43, H 5.81; $C_{25}H_{20}O$ requires C 89.25, H 5.99); δ_H: 7.9-7.0 (14 H, m), 5.8 (1 H, dd, J 10.5, 17.1 Hz), 5.1 (1 H, dd, J 1.4, 17.1 Hz), 5.0 (1 H, dd, J 1.4, 10.5 Hz), 2.2 (1 H, br.t, J 3.5 Hz), 1.76 (1 H, dd, J 3.5, 6.8 Hz), 1.69 (1 H, dd, J 4.6, 6.8 Hz); δ_C: 151.0, 149.0, 140.1, 137.25, 136.4, 135.45, 133.0, 130.4, 129.9, 129.7, 129.2, 128.45, 128.4, 127.9, 126.7, 125.9, 121.5, 119.5, 114.9, 90.15, 88.2, 38.2, 35.9, 19.3; υ_{max}: 1661, 1602 cm^{-1}.

(iii) The above procedure was repeated using 2 mol. equiv. of methyllithium at -78 to 20 °C, followed by quenching with trimethylsilylchloride in the presence of diphenylisobenzofuran to give *4-trimethylsilyl-2-vinyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.*$0^{2,4}$*]octane* (**14f**) (47 %), m.p. 125-127 °C (Found: C 82.11, H 6.72; $C_{28}H_{28}OSi$ requires C 82.30, H 6.90) which showed δ_H: 7.7-7.2 (14 H, m), 5.8 (1 H, dd, J 10.4, 17.2 Hz), 5.2 (1 H, dd, J 1.4, 17.2 Hz), 5.1 (1 H, dd, J 1.4, 10.4 Hz), 2.5 (1 H, d, J 4.7 Hz), 1.8 (1 H, d, J 4.7 Hz), -0.3 (9 H, s); δ_C: 150.03, 149.15, 140.10, 137.77, 136.02, 135.69, 135.46, 133.05, 129.90, 129.32, 128.71, 128.39, 128.22, 127.47, 126.98, 121.89, 121.17, 114.67, 91.90, 89.56, 44.17, 30.82, 23.03, 0.56; υ_{max}: 1662 cm^{-1}.

Reaction of 2,2-dibromo-1-chloro-1-(1-chlorovinyl)cyclopropane with 1.1 mol.equiv. of methyllithium in the presence of Dienes

(i) **1,3-diphenylisobenzofuran**: Methyllithium (1.36 ml, 1.49 mmol, 1.1 mol. equiv.) was added dropwise to a stirred solution of 2,2-dibromo-1-chloro-1-(1-chlorovinyl)cyclopropane (0.4 g, 1.36 mmol) in dry ether (10 ml) in the presence of 1,3-diphenyl-isobenzofuran (0.3 g, 1.2 mmol) under nitrogen at -78 °C. The reaction mixture was allowed to reach room temperature and stirred for 18 hours, then worked up by quenching with water (2 ml) at -30 °C. The mixture was extracted with ether (3 x 15 ml), the combined ether layers were dried and the solvent was removed at 14 mm Hg to give a brown solid. The product was purified by column chromatography on silica eluting with petrol and ether (5:2) to give a white solid, *4-bromo-2-(1-chlorovinyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.*$0^{2,4}$*]octane* (**14b**) (0.3 g, 49 %), m.p. 128-130 °C (Found: C 66.84, H 4.27; $C_{25}H_{18}OBrCl$ requires C 66.76, H 4.03) which showed δ_H: 7.8-7.1 (14 H, m), 5.5 (1 H, d, J 1.5 Hz), 4.4 (1 H, d, J 1.5 Hz), 3.0 (1 H, d, J 6.2 Hz), 2.0 (1 H, d, J 6.2 Hz); δ_C: 147.40, 147.33, 136.52, 134.07, 133.17, 129.25, 129.19, 128.67, 128.50, 128.34, 127.38, 126.72, 126.30, 122.97, 122.82, 120.83, 90.42, 90.0, 51.69, 45.36, 30.54; υ_{max}: 1626, 1447 cm^{-1}.

(ii) **Furan:** The above procedure was repeated using furan (10 mol.equiv.) in place of 1,3-diphenylisobenzofuran. 2-Bromo-4-(1-chlorovinyl)-8-oxabicyclo[3.2.1.$0^{2,4}$]oct-6-ene was obtained as a 3.5:1 mixture of two isomers; chromatography on silica eluting with 5:1 petrol and ether gave the major isomer (**15a**) (0.13 g, 40 %) (Found M +

NH_4^+: 263.9791. $C_9H_8OBrCl+NH_4$ requires: 263.9790) which showed δ_H: 6.8 (1 H, dd, J 1.5, 5.6 Hz), 6.7 (1 H, dd, J 1.5, 5.6 Hz), 5.4 (1 H, d, J 1.6 Hz), 5.3 (1 H, d, J 1.6 Hz), 4.9 (1 H, d, J 1.5 Hz), 4.8 (1 H, d, J 1.5 Hz), 2.5 (1 H, d, J 6.0 Hz), 1.6 (1 H, d, J 6.0 Hz); δ_C: 139.8, 138.7, 116.6, 82.5, 79.85, 41.5, 30.8, 29.7, 20.3; υ_{max}: 1625 cm^{-1}.

The minor isomer (**16a**) (0.08 g, 24 %) showed δ_H: 6.4 (1 H, dd, J 1.7, 5.7 Hz), 6.3 (1 H, dd, J 1.7, 5.7 Hz), 5.5 (1 H, d, J 1.5 Hz), 5.4 (1 H, d, J 1.5 Hz), 5.0 (2 H, m), 1.99 (1 H, d, J 6.8 Hz), 1.92 (1 H, d, J 6.8 Hz); δ_C: 134.5, 134.2, 116.3, 88.3, 84.4, 45.7, 40.3.

(iii) **1,3-Butadiene:** The above procedure was repeated using 1,3-butadiene (10 mol. equiv.) in place of 1,3-diphenylisobenzofuran. *6-Bromo-1-(1-chlorovinyl)bicyclo[4.1.0]hept-3-ene* (**17a**) was obtained (57 %) (Found M^+: 231.9564. $C_9H_{10}BrCl$ requires: 231.9564) which showed δ_H: 5.6 (1 H, m), 5.46 (1 H, m), 5.42 (1 H, d, J 1.4 Hz), 5.3 (1 H, d, J 1.4 Hz), 2.9 (3 H, m), 2.3 (1 H, m), 1.6 (1 H, d, J 6.3 Hz), 1.4 (1 H, d, J 6.3 Hz); δ_C: 145.27, 124.11, 123.68, 115.07, 38.68, 36.08, 34.18, 29.17, 23.12; υ_{max}: 1640, 1429 cm^{-1}.

Reaction of 1,1,2-trichloro-2-vinylcyclopropane with methyllithium in the presence of 1,3-diphenylisobenzofuran

The above procedure was repeated using 1 mol.equiv. of methyllithium at 0 °C to give *4-chloro-2-vinyl-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.*$0^{2,4}$*]octane* (**14c**) (38 %), m.p. 114-116 °C (Found: C 81.23, H 5.33; $C_{25}H_{19}OCl$ requires C 80.96, H 5.16); δ_H: 7.8-7.3 (14 H, m), 5.6 (1 H, dd, J 10.7, 17.0 Hz), 5.2 (1 H, dd, J 1.1, 10.7 Hz), 5.1 (1 H, dd, J 1.1, 17.0 Hz), 2.7 (1 H, d, J 6.3 Hz), 1.9 (1 H, d, J 6.3 Hz); δ_C: 148.1, 147.7, 134.7, 133.6, 132.2, 128.9, 128.8, 128.6, 128.5, 127.5, 126.0, 122.9, 121.8, 119.1, 90.1, 90.0, 59.3, 41.8, 22.6; υ_{max}: 1637 cm^{-1}.

Reaction of 1,1,2-trichloro-2-(1-chlorovinyl)cyclopropane with methyllithium

(i) In the presence of 1,3-diphenylisobenzofuran: Methyllithium (3.7 ml, 3.77 mmol) was added to a stirred solution of 1,1,2-trichloro-2-(1-chlorovinyl)cyclopropane (0.7 g, 3.43 mmol) in dry ether (10 ml) in the presence of 1,3-diphenylisobenzofuran (0.8 g, 3.0 mmol) under nitrogen at 0 °C. The mixture was allowed to reach room temperature and stirred for 6 h, then quenched with water (2 ml) at -20 °C; the product was extracted with ether (2 x 10 ml), the combined ether layers were dried and the solvent was removed at 14 mm Hg to give a solid, which on recrystallization from petrol and dichloromethane (5:0.5) gave a yellow solid, *4-chloro-2-(1-chlorovinyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.*$0^{2,4}$*]octane* (**14d**) (0.6 g, 43 %), m.p. 142-144 °C (Found: C 74.08, H 4.47; $C_{25}H_{18}OCl_2$ requires C 74.36, H 4.20); δ_H: 7.9-7.2 (14 H, m), 5.4 (1 H, d, J 1.5 Hz), 4.3 (1 H, , J 1.5 Hz), 2.9 (1 H, d, J 6.2 Hz), 1.9 (1 H, d, J 6.2 Hz); δ_C: 147.33, 135.60, 134.14, 133.17, 129.23, 128.88, 128.76, 128.58, 128.40, 127.51, 126.85, 126.41, 122.88, 122.83, 120.97, 90.37, 89.96, 60.57, 45.51, 29.44; υ_{max}: 1626 cm^{-1}.

(ii) In the presence of furan. The above procedure was repeated using furan (10 mol. equiv.) in place of 1,3-diphenylisobenzofuran to give two isomers in ratio 4.5:1. After chromatography, one isomer, *4-Chloro-2-(1-chlorovinyl)-8-oxabicyclo[3.2.1.*$0^{2,4}$*]oct-6-ene* (**15b**) (40 %) (Found M^++H: 203.0030. $C_9H_9OCl_2$ requires:

203.0030) was isolated, which showed δ_H: 6.8 (1 H, dd, J 1.5, 5.7 Hz), 6.7 (1 H, dd, J 1.5, 5.7 Hz), 5.4 (1 H, d, J 1.6 Hz), 5.3 (1 H, d, J 1.6 Hz), 4.88 (1 H, d, J 1.5 Hz), 4.85 (1 H, d, J 1.5 Hz), 2.5 (1 H, d, 56.0 Hz), 1.6 (1 H, d, J 6.0 Hz); δ_C : 140.04, 138.29, 116.37, 81.65, 80.38, 55.56, 36.30, 29.75; υ_{max}: 1626 cm^{-1}.

(iii) In the presence of 1,3-butadiene. The above procedure was repeated using 1,3-butadiene (10 mol. equiv.) in place of 1,3-diphenylisobenzofuran. *1-(1-Chlorovinyl)-6-chlorobicyclo(4.1.0)hept-3-ene* **(17b)**, was obtained (54 %) (Found M^+: 188.0160. $C_9H_{10}Cl_2$ requires: 188.0159) which showed δ_H: 5.5 (2 H, m), 5.4 (1 H, d, J 1.4 Hz), 5.3 (1 H, d, J 1.4 Hz), 2.8 (3 H, m), 2.3 (1 H, m), 1.5 (1 H, d, J 6.1 Hz), 1.3 (1 H, d, J 6.1 Hz); δ_C: 144.0, 136.55, 124.02, 123.39, 115.25, 47.02, 37.88, 34.18, 29.59, 22.30; υ_{max}: 1644 cm^{-1}.

Dimerization of 1-vinylcyclopropene

(i) Methyllithium (10.25 ml, 15.3 mmol) was added to a stirred solution of 2,2-dibromo-1-chloro-1-vinylcyclopropane (2 g, 7.6 mmol) in dry ether (20 ml) under nitrogen at -78 °C. The reaction was allowed to reach room temperature, then cooled to -40 °C, and the ether was removed under high vacuum to give solid 1-lithio-2-vinylcyclopropane which was quenched with water at -40 °C, followed by flash distillation to give the dimer 1,2-divinyltricyclo[3.1.0.$0^{2,4}$]hexane (**2**) (0.4 g, 40 %), which showed δ_H: 5.5 (1 H, dd, J 10.4, 17.2 Hz), 5.1 (1 H, dd, J 2.0, 17.2 Hz), 4.9 (1 H, dd, J 2.0, 10.4 Hz), 1.6 (1 H, dd, J 1.7, 4.0 Hz), 1.5 (1 H, dd, J 1.7, 4.0 Hz), 1.3 (1 H, m); δ_C: 136.68, 112.69, 32.33, 30.51, 25.66; υ_{max}: 1628 cm^{-1}. The data corresponded to those reported.[4]

The dimer rearranged to 1,2-divinylcyclohexa-1,4-diene (**3**) (0.2 g, 50 %) after 4 weeks at 20 °C in $CDCl_3$; the product showed δ_H: 7.1 (1 H, dd, J 11.0, 17.2 Hz), 5.8 (1 H, s), 5.2 (1 H, dd, J 1.1, 17.2 Hz), 5.1 (1 H, dd, J 1.1, 11.0 Hz), 2.9 (2 H, s); δ_C: 133.03, 123.23, 113.33, 29.70, 26.72; υ_{max}: 1664 cm^{-1}, in agreement with the data reported for an authentic sample.[4] Reaction of the cyclohexadiene (0.1 g, 0.75 mmol) with DDQ (0.17 g, 0.75 mmol) for 0.5 h at 20 °C in $CDCl_3$, followed by filtering through silica, washing with petrol (10 ml) and evaporation of the solvent at 14 mmHg gave o-divinylbenzene (0.06 g, 61 %).

(ii) The procedure in (i) was repeated but quenching with D_2O instead of H_2O to give 4,5-dideuterio-1,2-divinyltricyclo[3.1.0.$0^{2,4}$]hexane (**21**) (40%); δ_H: 5.5 (1 H, dd, J 10.4, 17.2 Hz), 5.2 (1 H, dd, 2.0, 17.2 Hz), 4.9 (1 H, dd, J 2.0, 10.4 Hz), 1.5 (1 H, d, J 4.1 Hz), 1.2 (1 H, d, J 4.1 Hz); δ_C: 136.69, 112.70, 31.57, 30.41, 20.28; υ_{max}: 1627 cm^{-1}. This rearranged over 4 weeks at at 20 °C in $CDCl_3$ to give 4,5-dideuterio-1,2-divinylcyclohexa-1,4-diene (**22**) (50 %) which showed δ_H: 7.0 (1 H, dd, J 11.0, 17.2 Hz), 5.1 (1 H, dd, J 1.0, 17.2 Hz), 5.0 (1 H, dd, J 1.0, 11.0 Hz), 2.8 (2 H, s); δ_C: 133.02, 113.35, 31.91, 29.68, 26.56; υ_{max}: 1636 cm^{-1}.

Reaction of 1,1-dibromo-2-chloro-2-(1-chlorovinyl)cyclopropane with 2.1 mol.equiv. of methyllithium in the presence of 1,3-diphenylisobenzofuran

(i) Methyllithium (2.59 ml, 2.85 mmol) was added with stirring to 1,1-dibromo-2-chloro-2-(1-chlorovinyl)-cyclopropane (0.4 g, 1.36 mmol) in dry ether (10 ml) at -78 °C. The mixture was allowed to reach room temperature before cooling to -78 °C, and quenching with water (2 ml). The ether layer was decanted from the ice. The ice was washed with cool ether (2 x 10 ml), and 1,3-diphenylisobenzofuran (0.3 g, 1.2 mmol) was added at -70 °C to the combined ether layers. These were allowed to reach room temperature and stirred for 18 h, and evaporated to give a yellow solid, the NMR spectrum of which showed two isomers in ratio 4:1. Recrystallization from petrol and ether (5:1) gave one isomer of *2-(1-chlorovinyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane* (**14g**) (0.2 g, 40 %), m.p. 132 - 134 °C (Found: C 81.23, H 5.46; $C_{25}H_{19}OCl$ requires: C 80.96, H 5.16) which showed δ_H: 7.8-7.1 (14 H, m), 5.2 (1 H, d, J 1.7 Hz), 4.8 (1 H, d, J 1.7 Hz), 2.4 (1 H, dd, J 4.2, 5.0 Hz), 2.2 (1 H, dd, J 4.2, 7.0 Hz), 1.9 (1 H, dd, J 5.0, 7.0 Hz); δ_C: 150.80, 147.63, 140.04, 137.21, 135.91, 134.23, 129.73, 128.64, 128.46, 127.85, 126.33, 125.83, 123.02, 121.34, 116.18, 112.08, 90.24, 88.01, 41.65, 34.75, 20.51; υ_{max}: 1661 cm^{-1}.

(ii) The above procedure was repeated and the reaction was quenched with D_2O instead of H_2O. *4-Deuterio-2-(1-chlorovinyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]octane* (**14h**) was obtained (66 %); the crude product showed two isomers in (4.3:1) by ^{1}H nmr; recrystallisation from petrol and ether gave one isomer, m.p. 138 - 140 °C (Found: C 80.82, H 4.63; $C_{25}H_{18}OClD$ requires C 80.96, H 4.90); δ_H: 7.8-7.1 (14 H, m), 5.2 (1 H, d, J 1.7 Hz), 4.9 (1 H, d, J 1.7 Hz), 2.4 (1 H, d, J 5.1 Hz), 2.0 (1 H, d, J 5.1 Hz); δ_C: 150.79, 147.65, 140.05, 137.22, 135.03, 134.25, 133.04, 130.41, 129.31, 129.0, 128.63, 128.51, 128.38, 127.83, 126.52, 125.82, 122.63, 119.75, 116.16, 112.06, 90.24, 87.94, 41.57, 29.73, 21.12; υ_{max}: 1664 cm^{-1}.

Dimerization of 1-(1-Chlorovinyl)cyclopropene

(i) A solution of 1,1-dibromo-2-chloro-2-(1-chlorovinyl)cyclopropane (1 g, 3.4 mmol) in dry ether (15 ml) was treated with methyllithium (8.07 ml, 2.1 mol. equiv.) at -78 °C under nitrogen. The reaction mixture was allowed to reach room temperature, then cooled again to -70 °C and quenched with water (2 ml). After extraction with ether (3 x 15 ml), the combined ether layers were dried and evaporated at 14 mm Hg to give *1,2-bis(1-chlorovinyl)-tricyclo[3.1.0.0^{2,4}]hexane* (**25**) (0.3 g, 50 %) (Found M^+: 200.0160. $C_{10}H_{10}Cl_2$ requires: 200.0159) which showed δ_H: 5.4 (1 H, d, J 1.4 Hz), 5.2 (1 H, d, J 1.4 Hz), 1.9 (1 H, dd, J 2.2, 4.2 Hz), 1.7 (1 H, dd, J 1.8, 6.0 Hz), 1.6 (1 H, dd, J 2.2, 4.6 Hz); δ_C: 139.31, 111.99, 34.13, 29.42, 25.57; υ_{max}: 1621. Generation of the cyclopropene in the presence of an excess of furan gave only the above dimer.

(ii) The above procedure was repeated and the reaction was quenched with D_2O instead of H_2O to give *4,5-dideuterio-1,2-bis(1-chlorovinyl)tricyclo[3.1.0.0^{2,4}]hexane* (**26**) (44.5 %) (Found M^+: 202.0285. $C_{10}H_8D_2Cl_2$ requires: 202.0285) which showed δ_H: 5.4 (1 H, d, J 1.4 Hz), 5.2 (1 H, d, J 1.4 Hz), 1.7 (1 H, d, J 4.7 Hz), 1.6 (1 H, d, J 4.7 Hz); δ_C: 139.31, 112.0, 34.0, 29.68, 29.80; υ_{max}: 1621 cm^{-1}.

Preparation of 1-trimethylsilyl-2-(1-chlorovinyl)cyclopropene

(i) Methyllithium (6.49 ml, 7.1 mmol) was added to a stirred solution of 2,2-dibromo-1-chloro-1-(1-chlorovinyl)cyclopropane (1 g, 3.4 mmol) in dry ether (10 ml) at -78 °C under nitrogen. The mixture was allowed to reach room temperature, then cooled down to -50 °C and quenched with trimethylsilyl chloride (0.8 ml, 6.8 mmol). The reaction was allowed to reach room temperature and stirred for 30 min before quenching with water (3 ml) at -40 °C, then the water layer was extracted with ether (3 x 10 ml), the combined ether layers were dried and the solvent was removed at 5 °C and 14 mm Hg to give an oil, 1-trimethylsilyl-2-(1-chloroethylene)cyclopropene (**28**) (0.35 g, 60 %), which showed δ_H: 5.8 (1 H, s), 5.72 (1 H, s), 1.2 (2 H, s), 0.09 (9 H, s); δ_C: 132.77, 129.51, 119.82, 29.68, 11.01, -1.39; υ_{max}: 2957, 1781, 1589, 1250 cm^{-1}.

(ii) **Trapping with DPIBF**: Methyllithium (6.49 ml, 7.1 mmol) was added with stirring to 2,2-dibromo-1-chloro-1-(1-chlorovinyl)cyclopropane (1 g, 3.4 mmol) in dry ether (15 ml) at -78 °C. The solution was allowed to reach room temperature, cooled to -50 °C and quenched with trimethylsilyl chloride (10.8 ml, 6.8 mmol). After 10 min at that temperature, 1,3-diphenylisobenzofuran (0.8 g, 3.06 mmol) was added; the mixture was stirred at room temperature for 18 h, quenched with water (3 ml) at -40 °C and extracted with ether (3 x 15 ml). The combined ether layers were dried and evaporated at 14 mmHg to give a brown solid. Chromatography on silica eluting with 5:2 petrol and ether gave *4-trimethylsilyl-2-(1-chlorovinyl)-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.*$0^{2,4}$*]octane* (**14i**) (0.5 g, 33 %), m.p. 138 - 142 °C (Found: C 76.11, H 6.28; $C_{28}H_{27}OClSi$ requires: C 75.91, H 6.14); δ_H: 8.1-7.2 (14 H, m), 5.4 (1 H, d, J 1.1 Hz), 5.1 (1 H, d, J 1.1 Hz), 2.7 (1 H, d, J 4.6 Hz), 1.7 (1 H, d, J 4.6 Hz), 0.2 (9 H, s); δ_C: 149.86, 148.64, 143.83, 140.80, 137.28, 136.0, 135.1, 133.0, 131.74, 130.44, 129.03, 128.72, 128.42, 128.32, 126.98, 125.80, 123.36, 122.25, 121.90, 120.26, 119.38, 91.17, 89.09, 48.90, 33.17, 29.82, 2.14; υ_{max}: 1660 cm^{-1}.

(iii) **Trapping with 1,3-butadiene:** The above procedure was repeated using 1,3-butadiene (10 mol. equiv.) in place of 1,3-diphenylisobenzofuran. 1-(1-Chlorovinyl)-6-trimethylsilylbicyclo[4.1.0]hept-3-ene (**29**) was obtained (43 %) which showed δ_H: 5.5 (2 H, m), 5.21 (1 H, d, J 0.8 Hz), 5.17 (1 H, d, J 0.8 Hz), 2.7 (1 H, m), 2.2 (3 H, m), 1.0 (1 H, d, J 3.8 Hz), 0.8 (1 H, d, J 3.8 Hz), 0.04 (9 H, s); δ_C: 147.88, 123.17, 123.27, 113.44, 34.02, 29.39, 26.23, 17.39,m -1.30; υ_{max}: 1632 cm^{-1}.

(iv) **Trapping with furan:** The above procedure was repeated using furan (10 mol. equiv.) in place of 1,3-diphenylisobenzofuran; no adduct was obtained, but instead a complicated mixture was isolated.

Reaction of 1,1-dibromo-2-chloro-2-(1-chlorovinyl)cyclopropane with methyllithium in the presence of methyl chloroformate

Methyllithium (4.5 ml, 5.0 mmol, 1.1M) was added with stirring to 1,1-dibromo-2-chloro-2-(1-chlorovinyl)-cyclopropane (0.7 g, 2.3 mmol) in dry ether (10 ml) at -78 °C under nitrogen. The reaction was allowed to reach room temperature for 10 min, cooled to -50 °C, and added to methyl chloroformate (1.87 ml) in ether (10 ml), at below 30 °C. After 18 h at room temperature, the mixture was cooled to -30 °C and quenched with water. The aq. layer was extracted with ether (3 x 10 ml), the combined ether layers were dried and evaporated at 14 mm Hg to give a brown solid. Chromatography on silica eluting with 5:1 petrol/ether gave *methyl 8-chlorobicyclo[7.1.0]deca-1,8-dien-4-yn-2-carboxylate* (**30**) (0.3 g, 57 %), m.p. 104 - 106 °C (Found: C 64.46, H 4.85; $C_{12}H_{11}O_2Cl$ requires:

C 64.72, H 4.97); δ_H: 3.8 (3 H, s), 3.2 (2 H, m), 2.9 (2 H, m), 2.4 (2 H, m), 1.9 (2 H, p, J 2.0 Hz); δ_C: 167.0, 132.86, 131.72, 117.05, 114.88, 87.39, 83.40, 52.0, 38.45, 22.47, 17.40, 14.49; υ_{max}: 1765, 1700 cm^{-1}.

8-Chlorobicyclo[7.1.0]deca-1,8-dien-4-yn-2-methanol

Diisobutylaluminium hydride (1.35 ml, 1.35 mmol, 1 M in hexane) was added to a stirred solution of methyl 8-chlorobicyclo[7.1.0]deca-1,8-dien-4-yn-2-carboxylate (0.15 g, 0.67 mmol) in dry methylene chloride (10 ml) at -40 °C under nitrogen. The mixture was allowed to reach room temperature and stirred for 30 min, when tlc showed no starting material, and then quenched with sat.aq. ammonium chloride (3 ml) at -40 °C. Hydrochloric acid (4%, 5 ml) was added, the cooling bath removed, and the mixture was stirred for 30 m and then extracted with methylene chloride (2 x 10 ml). The extracts were dried and evaporated at 14 mm Hg to give yellow solid. Chromatography on silica eluting with 5:2 petrol and ether gave a white solid, *8-chlorobicyclo[7.1.0]deca-1,8-dien-4-yn-2-methanol* **(31)** (0.12 g, 92 %), m.p. 92 - 94 °C (Found: C, 67.69; H, 5.42; $C_{11}H_{11}OCl$ requires: C, 67.87; H, 5.69) which showed δ_H: 4.2 (2 H, br, s), 3.0 (2 H, br.s), 2.8 (2 H, t, J 6.0 Hz), 2.4 (2 H, m), 1.6 (1 H, br.s), 1.5 (2 H, br, s); δ_C: 126.32, 125.83, 117.70, 115.41, 87.66, 83.54, 65.70, 37.99, 23.32, 17.64, 10.49; υ_{max}: 3331, 1628 cm^{-1}.

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* The formation of tricyclo[3.1.0.0^{2,4}]hexanes by dimerisation of transient 1-alkenylcyclopropene-3-carboxylates has been decribed [Shapiro, E.A.; Kalinin, A.V.; Ugrak, B.I.; Nefedov, O.M. *J.Chem.Soc., Perkin Trans.II*, **1994**, 709] while a 1-alkenyl-2-trimethylsilylcyclopropene-3-carboxylate may be isolated [Shapiro, E.A.; Kalinin, A.V.; Platonov, D.N.; Nefedov, O.M. *Izv.Akad.Nauk SSSR, Ser.Khim.*, **1993**, 1248.

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