Generation and Solution-phase Behaviour of Some 2-Halogeno-1,3-ring-fused Cyclopropenes

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The title cyclopropenes **2b** are readily formed by reaction of ring-fused β-silylated-*gem*-dihalogenocyclopropanes of the general type **1b** with tetrabutylammonium fluoride in tetrahydrofuran solution. Those halogenocyclopropenes **2b** which are fused to a seven- or eight-membered ring can be trapped with a range of 1,3-dienes and the corresponding Diels–Alder adducts **3b** are produced in high yield. In contrast, those chlorocyclopropenes which are fused to a five- or six-membered ring cannot be trapped efficiently by added diene because they each undergo rapid rearrangement to an isomeric vinyl carbene. Thus, 6-chlorobicyclo[3.1.0]hex-1(6)-ene **27** undergoes ring-expansion to carbene **28** which either inserts into the α-C–H bond of the reaction solvent tetrahydrofuran or adds to one of the double bonds of furan. In contrast, the carbene, **32**, derived by ring-cleavage of 7-chlorobicyclo[4.1.0]hept-1(7)-ene **31** reacts with chloride ion to give, after protonation, (*E*)-2-chloro-1-(chloromethylene)cyclohexane **34**. This latter result is at variance with an earlier claim that when the cyclopropene **31** is generated under vacuum gas–solid reaction conditions it rearranges, *via* a ring-expanded vinyl carbene **36**, to 2-chlorocyclohepta-1,3-diene **37**. In the present work it has been established that this claim is incorrect. X-Ray crystallographic analyses of (1′α,3′α)-(*E*)-3′-chloro-2′-(chloromethylene)cycloheptyl *p*-nitrobenzoate **54** and (1′*R*,2′*S*,3′*S*,8′*S*,9′*S*,10′*S*)-9′-chloro-13′-oxatetracyclo[8.2.1.$0^{2',8'}$.$0^{2',9'}$]tridec-11′-en-3′-yl *p*-nitrobenzoate **67** have been carried out.

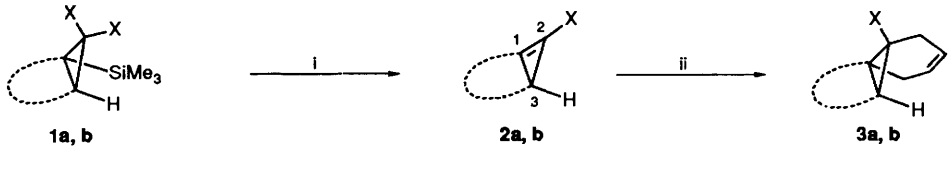
Treatment of open-chain β-trimethylsilyl-*gem*-dihalogenocyclopropanes **1a** (Scheme 1) with a fluoride ion source results in smooth elimination of the elements of trimethylsilyl halide and concomitant formation of the corresponding halogenocyclopropenes **2a**.[1] These latter compounds are effective Diels–Alder dienophiles and the derived cycloadducts **3a** have proven to be useful chemical building blocks.[2] Surprisingly, there have been only scattered reports[1,2,†] on the applications of this methodology to ring-fused systems (Series b, Scheme 1) in spite of the potential synthetic utility of the anticipated Diels–Alder adducts **3b**. The recent report[4a] by Billups *et al.* on the application of the vacuum gas–solid reaction (VGSR) technique to the production of 1,3-bridged cyclopropenes from ring-fused β-silylated halogenocyclopropanes prompts us to describe our own work regarding the generation (from silanes **1b**) and solution-phase behaviour of 2-halogeno-1,3-bridged cyclopropenes **2b**. Three key conclusions have emerged from the work described herein: (i) in many cases cyclopropenes **2b** can be trapped with a variety of dienes and high yields of the novel adducts **3b** obtained; (ii) tetrabutylammonium chloride, the by-product from the initial elimination process, can participate in subsequent and novel reactions and (iii) the report[4] that 7-chlorobicyclo[4.1.0]hept-1(7)-ene **31** rearranges to 2-chlorocyclohepta-1,3-diene **37** is incorrect.

† Recently Halton *et al.* have reported[3b] that cyclopropenes of the general type **2b**, when generated by base-promoted elimination involving ring-fused *gem*-dihalogenocyclopropanes, can be trapped (albeit in low yields) by added dienes (diphenylisobenzofuran and furan) to give the corresponding Diels–Alder adducts.

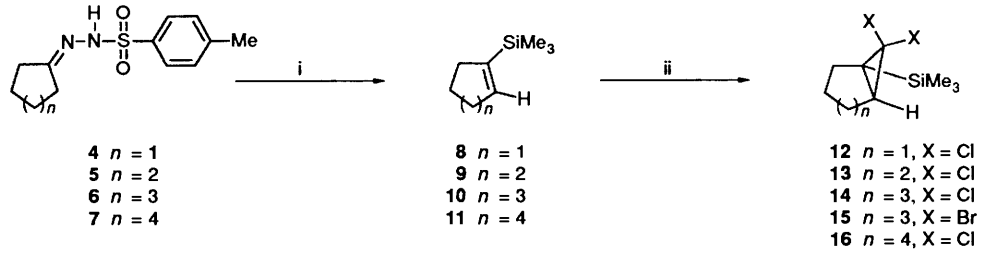
Results and Discussion

1. *Synthesis of* β-*Trimethylsilyl*-gem-*dihalogenocyclopropanes* **12–16** *and* **26**.—Syntheses of the β-trimethylsilyl-*gem*-dihalogenocyclopropanes **12–16** were achieved in a straightforward manner *via* the well established and readily generalisable reaction sequence shown in Scheme 2. Thus, the tosylhydrazones **4–7**[5] of appropriate cyclic ketones were subjected to Shapiro reaction[6] (using BuLi) and the resulting vinyl anion was quenched with chlorotrimethylsilane. The ensuing vinylsilanes **8–11** were then allowed to react with the appropriate dihalogenocarbene (generated under phase-transfer conditions) and the required adducts **12**[7]–**16** were thereby obtained in good overall yields.

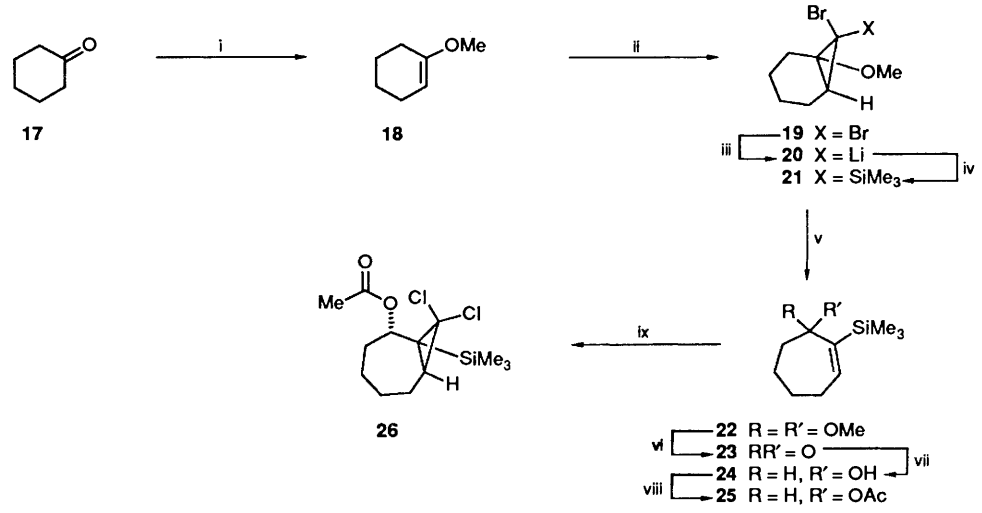
The oxygenated β-trimethylsilyl-*gem*-dihalogenocyclopropane **26** was synthesized by the route shown in Scheme 3. Thus, 1-methoxycyclohexene 18[8] was prepared by standard methods involving generation and *in situ* cracking of the dimethyl ketal of cyclohexanone **17**. Addition of dibromocarbene to olefin **18** afforded the bicyclic adduct **19**[9] as a thermally unstable oil. Treatment of compound **19** with BuLi at ~ −100 °C resulted in



Scheme 1 *Reagents:* i, fluoride ion; ii, 1,3-diene



Scheme 2 *Reagents and conditions:* i, BuLi (4 mol equiv.), 1:1 TMEDA-hexane, −45 to 0 °C, then $ClSiMe_3$ (4.2 mol equiv.); ii, CHX_3, 50% aq. NaOH, TEBAC, ~ 18 °C, 16 h



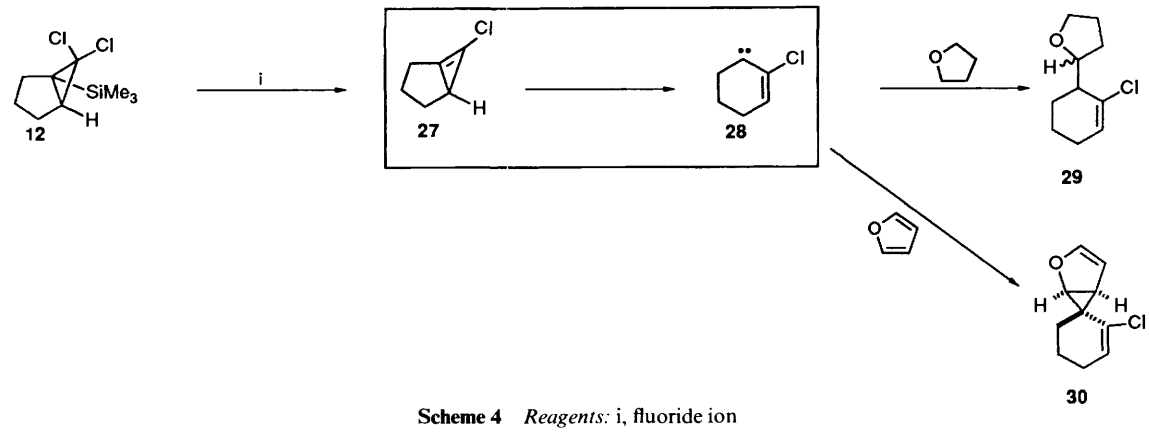
Scheme 3 *Reagents and conditions:* i, $HC(OMe)_3$, *p*-$MeC_6H_4SO_3H$, Me_3OH, reflux, 0.5 h; ii, $CHBr_3$, $Bu^tO^-K^+$, pentane, −15 °C, 0.5 h; then ~ 18 °C, 0.5 h; iii, BuLi (~ 1.1 mol equiv.), THF, −100 °C, 2 h; iv, $ClSi(Me)_3$ (3.3 mol equiv.), −95 °C, 2 h; v, K_2CO_3 (~ 6 mol equiv.), MeOH, reflux, 2 h; vi, H_2SO_4 (5% aq.), ~ 18 °C, 40 min; vii, $NaBH_4$ (~ 1.2 mol equiv.), $CeCl_3·H_2O$ (~ 1.1 mol equiv.), 0 °C, 0.5 h; viii, Ac_2O, pyridine, 0 °C, 40 h; ix, $CHCl_3$, 50% aq. NaOH, TEBAC, ~ 18 °C, 5h

formation of the corresponding *exo*-lithiated carbenoid **20**, which was trapped with chlorotrimethylsilane to afford the unstable product **21**. Reaction of compound **21** with potassium carbonate in refluxing methanol resulted in solvolytic ring-opening to give ketal **22** which was not isolated but, rather, subjected to acid-catalysed hydrolysis to give compound **23**[10] (66% overall yield from **19**). Treatment of the enone **23** with sodium borohydride and cerium trichloride[11] afforded the 1,2-reduction product **24** (97%), which was acetylated (pyridine–acetic anhydride) to give the acetate **25**. Addition of dichlorocarbene to alkene **25**, under phase-transfer conditions, gave a single adduct **26** (84% from **24**) and the illustrated (*syn*) stereochemical relationship between the trimethylsilyl and acetate moieties in this compound was established by an X-ray crystallographic study on a derivative (see below).

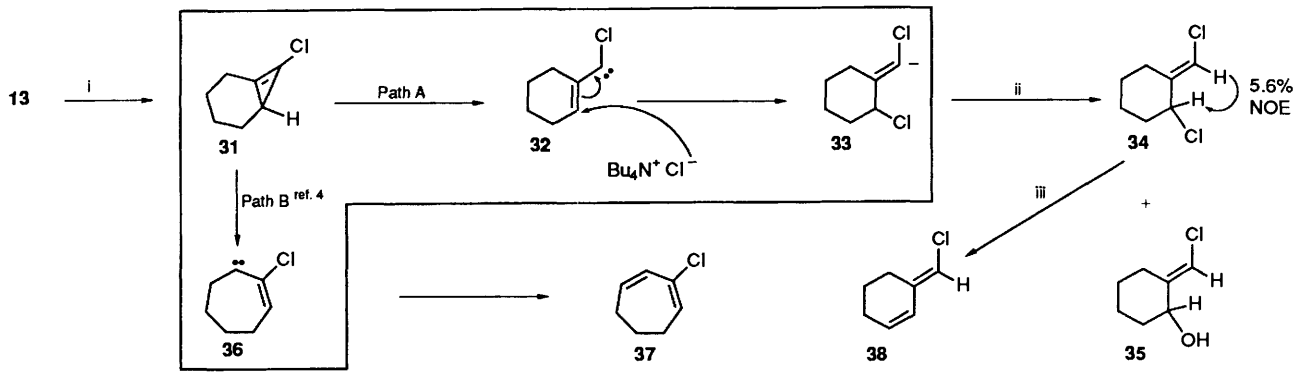
Products **12**–**16** and **26** were characterised in the usual manner and their spectroscopic properties (see Experimental section) were unexceptional.

2. *Reaction of* β-*Trimethylsilyl*-gem-*dihalogenocyclopropanes* **12**–**14**, **16** *and* **26** *with Fluoride Ion in the Absence of Diene Traps.*—Prior to developing reaction conditions for the generation and *in situ* Diels–Alder trapping of the cyclopropenes derived by treatment of the title substrates with fluoride ion, the elimination reactions were initially conducted without added trapping agent. This was done because it was anticipated that the cyclopropenes so formed might have an 'inherent reactivity' that would compete with the anticipated cycloaddition reactions. Early identification of the products derived from any such 'inherent' reactivity would then simplify analysis of the mixtures obtained when the reactions containing diene traps were run. To this end, a tetrahydrofuran (THF) solution of compound **12** was treated with tetrabutylammonium fluoride (TBAF) and the only characterisable material produced was an inseparable 4:1 mixture of two compounds tentatively identified as diastereoisomeric THF-insertion products **29** (16%). These compounds could arise (Scheme 4) *via* rearrangement of the initially formed cyclopropene **27** to the vinyl carbene **28**. Since related vinyl carbenes are known[3] to insert into the activated α-C–H bonds of THF, we suggest that an analogous process involving species **28** occurs as the final step leading to the observed products. Baird has reported[12] that the cyclopropene **27** (when generated from an alternative precursor) rearranges to the ring-expanded vinylcarbene **28**, which adds to furan giving compound **30**.[12] Consequently we treated compound **12** with TBAF in the presence of furan and thereby obtained significant quantities (58%) of adduct **30**. This result clearly lends support to the proposal that the cyclopropene **27** is generated as a result of treatment of precursor **12** with fluoride ion. It is noteworthy that no adduct derived from Diels–Alder cycloaddition between furan and compound **27** could be detected in this latter reaction, thus strongly suggesting that rearrangement of this highly strained species to the isomeric carbene is a very rapid process. As a consequence, no further attempts to trap the cyclopropene **27** in cycloaddition processes were undertaken.

Reaction of compound **13** with TBAF afforded dichloroalkene **34** (66%) as the major reaction product. Also formed in this reaction were small quantities (~ 1.5%) of the related alcohol **35**. This latter product may be an artefact resulting from hydrolysis of allylic chloride **34** during work-up. The structure of alkene **34** was supported by spectroscopic data and the illustrated double-bond geometry follows from the observation of a 5.6% nuclear Overhauser enhancement (NOE) of the signal



Scheme 4 *Reagents:* i, fluoride ion



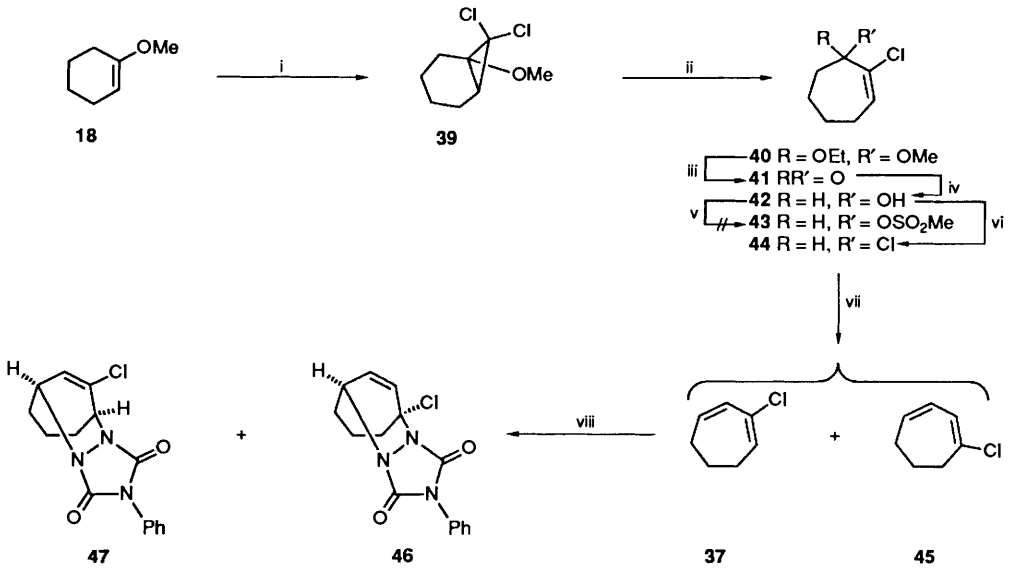
Scheme 5 *Reagents and conditions:* i, TBAF, THF; ii, proton source; iii, DBU, 75–80 °C, 10 h

(δ_H 4.69) due to the methine proton 2-H as a result of irradiation of the signal (δ_H 6.20) due to the vinylic proton. The {^{1}H}^{13}C NMR spectrum displayed the expected seven signals including those due to two vinylic carbons. An X-ray crystallographic study of a related compound (see below) generated under similar conditions provided additional support for the structure of compound **34**.

A possible mechanism for the formation of alkene **34** from precursor **13** is shown in Scheme 5 (path A). A key feature of this proposal is the ring cleavage of the initially formed 7-chlorobicyclo[4.1.0]hept-1(7)-ene **31** to the vinylcarbene **32**. This latter intermediate is then captured by chloride ion (present in soluble form as its tetrabutylammonium salt which is generated as a by-product from the initial elimination) and the resulting vinyl anion **33** is protonated (presumably by adventitious water or on aqueous work-up) to give the observed product **34**. These proposals differ significantly from the suggested[4] fate (path B, Scheme 5) of the same cyclopropene **31** when generated under VGSR conditions. Thus, Billups and co-workers have proposed that the cyclopropene **31** rearranges to the ring-expanded vinylcarbene **36** and that this latter species undergoes intramolecular C–H insertion to deliver 2-chlorocyclohepta-1,3-diene **37** as the sole isolable reaction product.

In order to cast some light on this apparent discrepancy, the alkene **34** was treated with the weakly nucleophilic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the expectation that the spectra for the resulting diene **38** (79%) would be different from the analogous data reported[4b] for the reaction product claimed to have structure **37**. However, the two sets of data were identical, indicating that one of the two structural assignments (and thence one of the two mechanistic proposals—path A or B, Scheme 5) was in error. In an attempt to resolve the matter, an unequivocal synthesis of diene **37** was undertaken. To these ends (Scheme 6) the vinyl ether **18** was treated with dichlorocarbene and the resulting adduct **39**[13] was then subjected to solvolytic ring-opening with potassium carbonate in ethanol (100 °C, sealed tube). The mixed ketal **40** thereby obtained was immediately hydrolysed and the ensuing enone **41**[14] subjected to 1,2-reduction (using cerium trichloride–sodium borohydride) to give the alcohol **42**.[15] As a prelude to an elimination, attempts were made to convert compound **42** into the corresponding mesyl derivative **43** but only a complex and uncharacterisable mixture of products was formed. In contrast, treatment of the alcohol **42** with conc. hydrochloric acid resulted in the smooth and efficient (95%) formation of the dichloro compound **44**.[16] Finally, subjection of alkene **44** to reaction with DBU in refluxing benzene afforded an inseparable ~85:15 mixture of the desired diene **37** and regioisomer **45**. Confirmation of the structures of these two dienes resulted from subjection of the mixture to reaction with the potent Diels–Alder dienophile 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) and thereby obtaining good yields of the separable and crystalline adducts **46** and **47**. Distinguishing between these two adducts was straightforward because in the 400 MHz ^{1}H NMR spectrum of the major product, **47**, one vinylic (δ_H 6.29) and two bridgehead (δ_H 5.05 and 4.99) proton resonances were observed whereas in the analogous spectrum of the minor adduct, **46**, one bridgehead and two vinylic proton resonances were apparent. These results left little doubt that diene **37** was the major product derived from reaction of compound **44** with DBU. Furthermore, the spectral properties of the mixture of dienes **37** and **45** was quite different from the analogous data obtained by Billups and Arney[4] for the end-product resulting from treatment of silane **13** under VGSR conditions with fluoride ion. Consequently, we believe that the diene product obtained by Billups *et al.* is definitely not the cyclohepta-1,3-diene **37** as claimed but is, in all likelihood, the chloromethylenecyclohexene **38**.

The bicyclo[5.1.0]octanyl system **14** reacted with TBAF more



Scheme 6 *Reagents and conditions:* i, Cl_3CCO_2Et, NaOMe, pentane, 0–18 °C, 16 h; ii, K_2CO_3, EtOH, 100 °C, 52 h; iii, 5% aq. H_2SO_4, THF, 18 °C, 0.5h; iv, $NaBH_4$ (2 mol equiv.), $CeCl_3 \cdot 7H_2O$ (1.1 mol equiv.), MeOH, 0 °C, 1 h; v, $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0 °C, 1 h; vi, 10 mol dm^{-3} aq. HCl, pentane, 18 °C, 0.33 h; vii, DBU (2.5 mol equiv.), C_6H_6, 80 °C, 17 h; viii, PTAD, CH_2Cl_2, 18 °C, 0.5 h

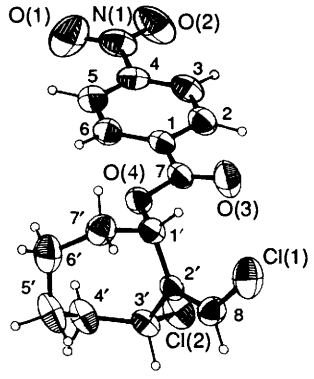


Fig. 1 ORTEP drawing of the 1'*S*, 3'*R* enantiomer of compound **54**. (Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are represented by spheres of arbitrary radius. The C symbol for the carbon atoms has been omitted).

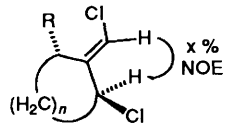
slowly than did its lower homologue **13**, and GLC analysis of the reaction mixture after eight hours at room temperature revealed the presence of two reaction products with shorter retention times than the starting material. Subsequent heating of the reaction mixture resulted in complete conversion of the more volatile product into the slightly less volatile one. The latter product was then isolated and, on the basis of spectral analysis including NOE studies, was assigned as the chloromethylenecycloheptane **48** (43%). Owing to its instability, the other product detected by GLC in the early stages of the reaction could not be isolated even when the reaction was terminated prematurely. It is believed that this early reaction product is 8-chlorobicyclo[5.1.0]oct-1(8)-ene, the cyclopropene derived from the initial elimination process.

Treatment of the oxygenated compound **26** with TBAF, under the conditions defined above, resulted in a 1 : 2 mixture of compounds **49** and **52** (52% combined yield). Hydrolysis of these products provided the corresponding alcohols, **50** and **53** respectively, which could be separated by medium-performance liquid chromatography (MPLC) and which were then independently converted into their crystalline *p*-nitrobenzoate derivatives, **51** and **54** respectively. The structure of ester **54** was secured by X-ray crystallographic analysis (Fig. 1). It is interesting to note that in the reaction of compound **26** with fluoride ion no products derived from elimination of the elements of trimethylsilyl acetate were detected, even though such a process would lead to a methylenecyclopropane, species which are generally more stable than the related 1,3-ring-fused cyclopropenes.[3] Presumably the methylenecyclopropane is not observed because its formation would require a *syn*-elimination process while the fluoride ion-induced reactions reported herein are probably *E*2 in nature and require an *anti*-periplanar relationship between the departing groups.

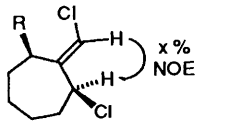
Reaction of the bicyclo[6.1.0]nonanyl system **16** with TBAF afforded the isolable but unstable cyclopropene **55** (93%), which was characterised by NMR spectroscopy (Baird has reported[17] that the bromo analogue of compound **55** can also be isolated and characterised spectroscopically). In the 100 MHz $\{^1H\}^{13}C$ NMR spectrum of compound **55** nine signals were observed including two (δ_C 116.6 and 110.0) in the region typical for sp^2-carbons associated with cyclopropenyl ring systems. In the 70 eV electron impact mass spectrum compound **55** showed the expected pair of molecular ions (at *m/z* 156 and 158) and an accurate mass measurement on the lighter of these established the formula $C_9H_{13}{}^{35}Cl$. Further evidence for the structure of compound **55** followed from the observation that this compound reacted smoothly with a variety of Diels–Alder dienes to give the expected cycloadducts (see below).

3. *Reaction of* β-*Trimethylsilyl*-gem-*dihalogenocyclopropanes* **13–16** *and* **26** *with Fluoride Ion in the Presence of Diene Traps.*—Reaction of compound **13** with TBAF in the presence of buta-1,3-diene produced only traces of the anticipated cycloadduct **56** (2.4%) and the major product remained the previously observed alkene **34** (36%). Replacement of buta-1,3-diene with furan permitted the isolation of small quantities of the Diels–Alder adduct **64** (4%) but the alkene **34** (7%) remained the predominant characterisable product. The assignment of structure **64** followed from spectral analysis and is supported by the X-ray structure of a closely related adduct formed in an analogous reaction (see below). The illustrated stereochemistry in compound **64** is consistent with the known[18] preference of cyclopropenes to add in an *exo*-fashion to furans. Compound **64** has also been prepared by Halton *et al.*[3b] and the spectral data obtained by these workers are in good agreement with those obtained here.

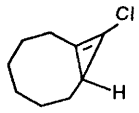
Subjection of the bicyclo[5.1.0]heptanyl systems **14**, **15** and



48 R = H, n = 4, x = 4.6
49 R = AcO, n = 4
50 R = HO, n = 4, x = 3
51 R = p-$O_2NC_6H_4CO_2$, n = 4, x = 7



52 R = AcO, x = 8
53 R = HO, x = 7
54 R = p-$O_2NC_6H_4CO_2$, x = 6



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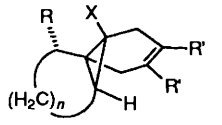
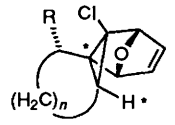
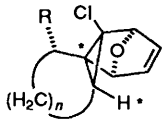


56 R = R′ = H, X = Cl, n = 3
57 R = R′ = H, X = Cl, n = 4
58 R = H, R′R′ = O[CH_2]$_2$O, X = Cl, n = 4
59 R = R′ = H, X = Br, n = 4
60 R = AcO, R′ = H, X = Cl, n = 4
61 R = AcO, R′R′ = O[CH_2]$_2$O, X = Cl, n = 4
62 R = R′ = H, X = Cl, n = 5
63 R = H, R′R′ = O[CH_2]$_2$O, X = Cl, n = 5



64 R = H, n = 3
65 R = H, n = 4
66 R = AcO, n = 4
67 R = p-$O_2NC_6H_4CO_2$, n = 4
68 R = H, n = 5



69 R = H, n = 4
70 R = AcO, n = 4
71 R = H, n = 5

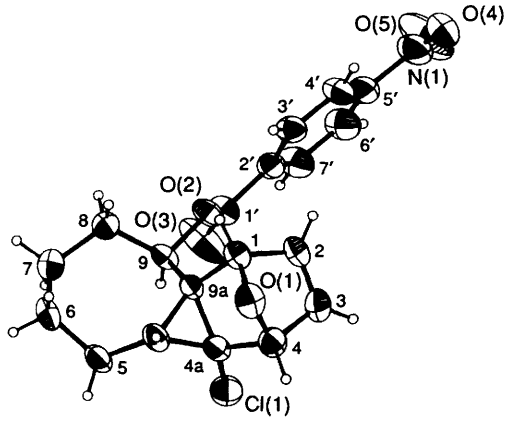


Fig. 2 ORTEP drawing of the 1*S*, 2*R*, 3*R*, 8*R*, 9*R*, 10*R* enantiomer of compound **67** (molecule A). (Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are represented by spheres of arbitrary radius. The C symbol for the carbon atoms has been omitted). Crystallographic numbering scheme is shown.

26 to the elimination conditions in the presence of buta-1,3-diene resulted in the isolation of the anticipated Diels–Alder adducts **57** (91%), **59** (78%) and **60** (97%) respectively in high yield. In the case of the reaction involving substrate **14** small amounts (6%) of the dichloroalkene **48** were also isolated. The cyclopropene derived from substrate **14** could be intercepted with 2,3-dimethylene-1,4-dioxane[19] to give adduct **58** (82%) while interception of the same cyclopropene with furan afforded both *exo*-adduct **65** (69%) and *endo*-adduct **69** (8%). Similarly, the cyclopropene derived from substrate **26** gave adducts **66** (83%) and **70** (9%) when furan was used as the trapping agent. The structure of compound **66** was established by X-ray crystallographic analysis of the derived *p*-nitrobenzoate **67** (Fig. 2). Trapping of the cyclopropene derived from **26** with 2,3-dimethylene-1,4-dioxane afforded the expected adduct **61** (98%).

Treatment of the cyclopropane **16** with TBAF in the presence of either buta-1,3-diene or 2,3-dimethylene-1,4-dioxane gave the Diels–Alder products **62** (91%) and **63** (70%), respectively, while use of furan as trapping agent afforded the expected mixture of adducts **68** (63%) and **71** (14%). Evidence for the intermediacy of the cyclopropene **55** in these conversions followed from the observation that treatment of the purified compound with the appropriate dienes gave the same adducts as previously isolated and in comparable yields.

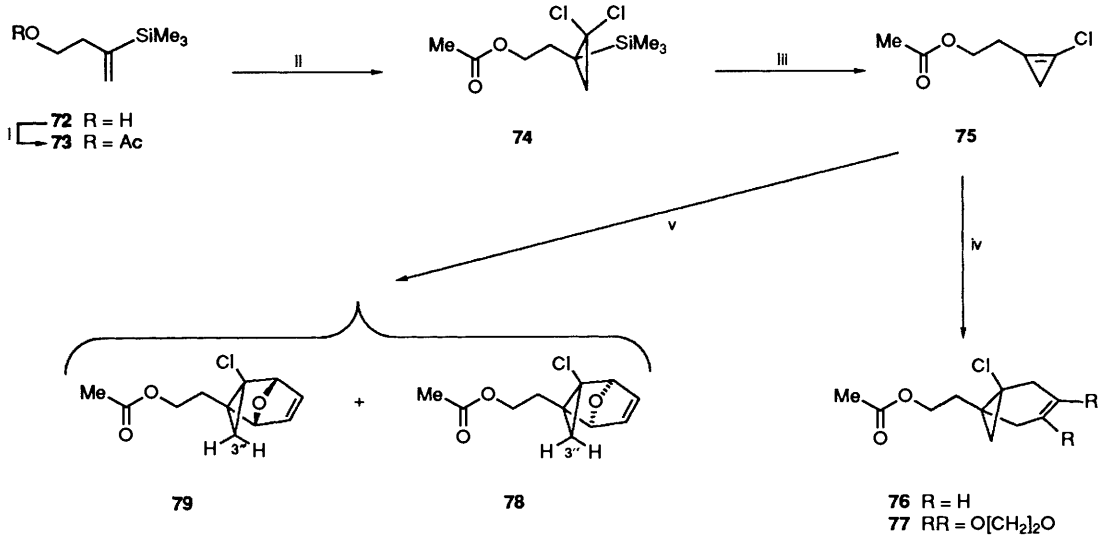
With regard to *exo*- and *endo*-adducts derived from reaction of the ring-fused cyclopropenes with furan, there are several spectroscopic trends which support the proposition that the former adducts always predominated. For example, in the {^{1}H}^{13}C NMR spectra of the minor (*endo*) adducts, the chemical shifts of the signals due to the non-chlorinated quaternary cyclopropyl carbon (C*) were found to be shielded by ~3.5 ppm in comparison with the resonances due to the analogous carbons in the major (*exo*) adducts. The origins of this trend are not clear but may be due to greater steric compression in the *endo*-adducts. In the ^{1}H NMR spectra of the *exo*-adducts the signals due to the cyclopropyl methine protons (H*) always appeared at slightly lower field than the corresponding resonances for the analogous proton in the isomeric *endo*-adducts. Another interesting trend was that in contrast to their *exo*-counterparts, the *endo*-isomers were all crystalline solids.

The conditions developed herein for the generation and Diels–Alder trapping of ring-fused cyclopropenes can be exploited equally effectively in open-chain systems (Scheme 7). For example, treatment of compound **74** (obtained by addition of dichlorocarbene to the acetate derivative, **73**, of the known[20] alcohol **72**) with TBAF in the presence of either buta-1,3-diene or 2,3-dimethylene-1,4-dioxane afforded the Diels–Alder adducts **76** (95%) and **77** (84%), respectively, of the intermediate cyclopropene **75**. When furan was used to trap the same cyclopropene the expected mixture of *endo*- and *exo*-adducts, **78** (16%) and **79** (72%) respectively, was obtained. In the absence of trapping agent the cyclopropene **75** could be isolated (97%) and when this compound was subjected to reaction with the usual set of dienes, the previously observed adducts were obtained once again. In the ^{1}H NMR spectra of the isomeric *exo*- and *endo*-adducts, **79** and **78** respectively, the chemical-shift difference between the resonances due to the non-equivalent cyclopropylmethylene protons (3″-H) was much greater ($\Delta\delta$ 1.06 *vs* 0.24 ppm) in the former compound. This observation is in accord with literature precedent[21] and is attributed to strong deshielding of 3″-H_{endo} of compound **79** by the proximate ring-oxygen.

4. *X-ray Structures of Compounds* **54** *and* **67**.—As both the compounds crystallise in centrosymmetric space groups the crystals are racemates. The molecular conformations of one enantiomeric form of compounds **54** and **67** are illustrated in

Table 1 Selected torsional angles (°) for compounds (a) **54** and (b) **67**. For compound **67**, values for molecule B follow those for molecule A. Crystallographic numbering is used.

Atoms	Angle	Atoms	Angle
(a) Compound **54**			
C(1')–C(2')–C(3')–C(4')	−32.5(5)	C(1')–C(2')–C(8)–Cl(1)	−4.8(5)
C(2')–C(3')–C(4')–C(5')	−43.8(5)	C(2')–C(1')–O(4)–C(7)	−83.9(4)
C(3')–C(4')–C(5')–C(6')	88.3(5)	C(1')–O(4)–C(7)–O(3)	3.4(5)
C(4')–C(5')–C(6')–C(7')	−73.2(5)	C(1')–O(4)–C(7)–C(1)	−175.5(5)
C(5')–C(6')–C(7')–C(1')	53.8(5)	O(4)–C(7)–C(1)–C(6)	10.2(5)
C(6')–C(7')–C(1')–C(2')	−65.5(5)	O(3)–C(7)–C(1)–C(2)	10.2(6)
C(7')–C(1')–C(2')–C(3')	79.0(4)	O(1)–N(1)–C(4)–C(5)	−2.9(6)
(b) Compound **67**			
C(1)–C(2)–C(3)–C(4)	−1.2(3)	C(9)–O(2)–C(1')–O(3)	−3.1(4)
	−0.8(3)		2.7(4)
C(2)–C(3)–C(4)–C(4a)	72.1(3)	O(3)–C(1')–C(2')–C(7')	−17.0(4)
	72.2(3)		−5.6(4)
C(3)–C(4)–C(4a)–C(9a)	−67.6(2)	C(4')–C(5')–N(1)–O(4)	−10.1(4)
	−69.5(3)		19.2(5)
C(4)–C(4a)–C(9a)–C(1)	−1.8(2)	C(4b)–C(5)–C(6)–C(7)	82.2(3)
	−0.4(2)		81.8(3)
C(4a)–C(9a)–C(1)–C(2)	70.7(2)	C(5)–C(6)–C(7)–C(8)	−62.3(4)
	69.2(2)		−62.1(4)
C(9a)–C(1)–C(2)–C(3)	−71.8(3)	C(6)–C(7)–C(8)–C(9)	64.3(4)
	−71.9(3)		63.0(4)
C(1)–O(1)–C(4)–C(3)	50.7(2)	C(7)–C(8)–C(9)–C(9a)	−82.5(3)
	51.1(2)		−82.7(3)
C(1)–O(1)–C(4)–C(4a)	−58.9(2)	C(8)–C(9)–C(9a)–C(4b)	63.5(3)
	−58.3(2)		63.8(3)
Cl(1)–C(4a)–C(4b)–C(5)	−7.1(3)	C(9)–C(9a)–C(4b)–C(5)	5.4(3)
	−4.4(4)		5.2(4)
C(1')–O(2)–C(9)–C(9a)	90.9(2)	C(9a)–C(4b)–C(5)–C(6)	−70.9(3)
	130.0(2)		−70.7(3)
C(9)–O(2)–C(1')–C(2')	177.6(2)	Cl(1)–C(4a)–C(4)–C(3)	72.6(2)
	−176.3(2)		68.4(3)



Scheme 7 *Reagents and conditions:* i, Ac_2O, pyridine, 18 °C, 4 h; ii, $CHCl_3$, 50% aq. NaOH, TEBAC, 0 °C for 20 min; then 18 °C for 3.5 h; iii, TBAF, THF, 0–5 °C, 40 min; iv, buta-1,3-diene or 2,3-dimethylene-1,4-dioxane, THF, 18 °C, 4–6 days; v, furan, THF, 18 °C, five days

Fig. 1 and Fig. 2, respectively, and the conformational details are given in Table 1. The two crystallographically independent molecules (A and B) in the structure of compound **67** adopt similar conformations apart from the orientation of the ester group at C(9) to the fused-ring systems. This difference is reflected in the torsion angle C(1')–O(2)–C(9)–C(9a) of 90.9(2)° in molecule A and 130.2(2)° in molecule B. The seven-membered rings in both the structures are in a chair form. In compound **67** the chair conformation is quite regular (asymmetry parameters[22] ΔC_s^7 being 4.4° and 4.1° in molecules A and B respectively), whereas in compound **54** there is considerable distortion from a regular chair, no doubt a consequence of the exocyclic double bond at C(2). The cyclohexene ring in compound **67** adopts a regular boat conformation with asymmetry parameters $\Delta C_s^{2,3}$ of 2.2° (A) and 0.2° (B). In each structure the nitro group lies close to its associated phenyl ring plane.

Current research efforts are directed towards exploiting Diels–Alder adducts of the general type **3b** in the chemical synthesis of various natural products. Results will be reported in due course.

Experimental

General Details.—^{1}H and ^{13}C NMR spectra were run at 400 and 100 MHz, respectively, unless otherwise specified. DEPT techniques were employed to determine the number of hydrogens attached to each carbon. Electron-impact mass spectra were recorded at 70 eV unless otherwise specified. General experimental procedures have been reported elsewhere.[23]

General Procedure for the Preparation of p-*Tolylsulfonylhydrazones* **4**–**7**.—The procedure outlined by Bertz and Dabbagh[5] was employed for the synthesis of the title hydrazones. Thus, *p*-tolylsulfonylhydrazine (1 mol equiv.) was dissolved in warm (> 50 °C) methanol (4.7 cm^3 g^{-1} of hydrazine unless otherwise specified). The appropriate ketone (1 mol equiv.) was added to the warm solution, and the mixture was swirled thoroughly to ensure complete mixing. The flask was stoppered and the mixture was kept at room temperature for 12–24 h before being refrigerated for 24–48 h. The resulting solid was collected by filtration and was washed thoroughly with chilled methanol. Drying under reduced pressure afforded the required hydrazone.

Cyclopentanone p-*Tolylsulfonylhydrazone* **4**.—Reaction of cyclopentanone (5.3 cm^3, 5.0 g, 6 mmol) with *p*-tolylsulfonylhydrazine (11.74 g, 63 mmol) in methanol (60 cm^3) at room temperature for 12 h and then in the refrigerator for 24 h gave, after filtration, the known[24] hydrazone **4** (11.92 g, 75%) as slightly yellow, clear prisms, m.p. 185–186.5 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3213, 2947, 1924, 1652, 1594, 1450, 1428, 1397, 1337, 1161, 1091 and 1033; δ_H 7.82 (2 H, br d, *J* 8.5), 7.69 (1 H, br s, NH), 7.27 (2 H, br d, *J* 8.5), 2.38 (3 H, s, Me), 2.30 (2 H, t, *J* 7.4), 2.14 (2 H, t, *J* 7.6), 1.74 (2 H, m) and 1.65 (2 H, m); δ_C 168.3, 143.9, 135.5, 129.5, 127.9, 33.4, 28.0, 24.7, 24.6 and 21.5.

Cyclohexanone p-*Tolylsulfonylhydrazone* **5**.—Reaction of cyclohexanone (8.0 cm^3, 7.58 g, 77.23 mmol) with *p*-tolylsulfonylhydrazine (14.38 g, 77 mmol) using the procedure outlined immediately above afforded hydrazone **5** (15.82 g). Concentration of the filtrate afforded a second crop (4.03 g). Recrystallisation (methanol) of the combined crops afforded hydrazone **5** (18.0 g, 88%) as prisms, m.p. 148–150 °C (decomp.) (lit.,[25] 155–158 °C); ν_{max}(KBr)/cm^{-1} 3255, 2934, 2851, 1636, 1594, 1396, 1288, 1179, 1168 and 1036; δ_H 7.83 (2 H, br d, *J* 8.5), 7.73 (1 H, br s. NH), 7.29 (2 H, br d, *J* 8.5), 2.41 (3 H, s, Me), 2.20 (4 H, m) and 1.65–1.50 (6 H, complex m); δ_C 162.7, 143.8, 135.4, 129.4, 128.0, 35.2, 26.9, 26.7, 25.6, 25.3 and 21.6.

Cycloheptanone p-*Tolylsulfonylhydrazone* **6**.—Reaction of cycloheptanone (9.5 cm^3, 9.03 g, 80.6 mmol) with *p*-tolylsulfonylhydrazine (15.0 g, 80.6 mmol) according to the procedure outlined above yielded a solid (20.43 g, 90%). Recrystallisation (methanol) of this material provided the hydrazone **6**[26] (18.54 g, 82%) as rods, m.p. 149.5–151.0 °C (decomp.): ν_{max}(KBr)/cm^{-1} 3239, 2915, 1624, 1593, 1460, 1384, 1336, 1180, 1169 and 1030; δ_H 7.83 (2 H, br d, *J* 8.3), 7.60 (1 H, br s, NH), 7.29 (2 H, br d, *J* 8.3), 2.41 (3 H, s, Me), 2.38 (2 H, m), 2.23 (2 H, m), 1.65 (2 H, m) and 1.50 (6 H, m); δ_C 164.0, 143.8, 135.5, 129.4, 127.9, 36.9, 30.4, 30.2, 30.0, 27.2, 24.2 and 21.6.

Cyclooctanone p-*Tolylsulfonylhydrazone* **7**.—Reaction of cyclooctanone (5.0 g, 39.6 mmol) with *p*-tolylsulfonylhydrazine (7.38 g, 39.6 mmol) in methanol (25 cm^3) for 14 h at room temperature and then for 48 h in the freezer afforded fine needles (9.47 g). Recrystallisation (methanol) of this material afforded the hydrazone **7** (8.5 g, 73%) as large prisms, m.p. 136–139 °C (decomp.) [lit.,[27] 135.5–138.0 °C (decomp.)]; δ_H(100 MHz) 7.85 (2 H, br d, *J* 8.3), 7.29 (2 H, br d, *J* 8.1), 2.41 (3 H, s, Me), 2.39–2.16 (4 H, complex m) and 1.84–1.07 (10 H, complex m) (signal due to NH not observed); δ_C(25 MHz) 164.1, 143.7, 135.7, 129.4, 127.8, 36.1, 27.8, 27.0, 26.3, 24.9, 24.7, 23.9 and 21.5.

General Procedure for the Preparation of Vinyl Silanes **8**–**11**.—A modification of the procedure detailed by Paquette *et al.*[28] was employed. Thus, a stirred suspension of the appropriate tosylhydrazone (1 mol equiv.) in N,N,N′,N′-tetramethylethylenediamine (TMEDA) or 1 : 1 TMEDA–hexane (8 cm^3 g^{-1} of hydrazone) was cooled to −45 °C and maintained under dry nitrogen. Butyllithium (~2.5 mol dm^{-3} solution in hexanes; 4.0 mol equiv.) was added dropwise *via* a dropping funnel. The resulting deep orange-red solution was stirred at −45 °C for 1.25–1.5 h and then was allowed to warm to room temperature over a period of 2 h (evolution of N_2). When evolution of N_2 had ceased, the solution was cooled to 0 °C and chlorotrimethylsilane (4.2 mol equiv.) was added dropwise. The resulting light yellow mixture was stirred at 0 °C for 30 min and then at room temperature overnight. The reaction mixture generally darkened and turned black. The mixture was poured into a mixture of water (~40 cm^3 g^{-1} of hydrazone) and pentane (20 cm^3 g^{-1}). The organic layer was separated, and washed successively with water (4 × 20 cm^3 g^{-1}), saturated aq. $CuSO_4$ (4 × 20 cm^3 g^{-1}) and brine (2 × 20 cm^3 g^{-1}). The pentane layer was then dried, and filtered through a column of activated TLC grade neutral alumina to provide a clear, almost colourless filtrate. Concentration under reduced pressure (no heating) afforded a light yellow oil. This material, with the exception of the first case given below, consisted almost entirely of the required vinylsilane and could generally be used in the subsequent addition of dichlorocarbene without further purification. Spectroscopically pure product could be obtained by Kugelrohr distillation.

1-(*Trimethylsilyl*)*cyclopentene* **8**.—Reaction of hydrazone **4** (10.0 g, 39.63 mmol) with butyllithium (61 cm^3 of a ~2.60 mol dm^{-3} solution, 4.0 mol equiv., ~160 mmol) in TMEDA (80 cm^3) for 70 min at −40 °C, followed by addition of chlorotrimethylsilane (4.2 mol equiv., 21.10 cm^3, 166.5 mmol), afforded, after the usual work-up and alumina filtration step, a yellow filtrate. The bulk of the pentane was distilled off (Vigreaux column), and fractionation of the residue afforded the impure silane **8**, b.p. 106–134 °C (lit.,[28] 106–108 °C) in low (< 30%) yield. This material was subjected directly to addition of dichlorocarbene.

1-(*Trimethylsilyl*)*cyclohexene* **9**.—Reaction of hydrazone **5** (5.0 g, 18.77 mmol) with butyllithium (30 cm^3 of a 2.5 mol dm^{-3} solution, 75.1 mmol) in TMEDA–hexane (50 cm^3 of a 1 : 1 v/v mixture) for 1.25 h at −45 °C, followed by the addition of chlorotrimethylsilane (9.5 cm^3, 79.4 mmol) afforded, after the usual work-up, a light yellow oil. Kugelrohr distillation (b.p. 85 °C/20 mmHg) of this material afforded the title vinyl silane **9** (1.90 g, 66%) as a clear liquid (lit.,[28] b.p. 70–78 °C/33 mmHg); ν_{max}(NaCl)/cm^{-1} 2953, 2855, 1614, 1445, 1433, 1246, 1062, 938, 855 and 835; δ_H 5.98 (1 H, m, 2-H), 2.03 (4 H, m), 1.60 (4 H, m), 0.03 (9 H, s, $SiMe_3$); δ_C(22.5 MHz) 138.6 (C-1), 135.5 (C-2), 26.7, 26.5, 22.9, 22.5 and −2.3 ($SiMe_3$).

1-(*Trimethylsilyl*)*cycloheptene* **10**.—Reaction of hydrazone **6** (10 g, 35.67 mmol) with butyllithium (57 cm^3 of a 2.5 mol dm^{-3} solution, 142.68 mmol) in TMEDA (80 cm^3) for 1.25 h at −45 °C, followed by addition of chlorotrimethylsilane (19.0 cm^3, 149.9 mmol) afforded, after the usual work-up, a light yellow oil. Kugelrohr distillation (b.p. 60–65 °C/8 mmHg) of this material afforded the title vinyl silane **10** (4.38 g, 73%) as a clear liquid (lit.,[28] b.p. 94–95 °C/20 mmHg); ν_{max}(NaCl)/cm^{-1} 2919, 2848, 1615, 1447, 1258, 1246, 1053, 928, 833 and 747; δ_H 6.18 (1 H, t, *J* 6.4, 2-H), 2.18 (4 H, m), 1.76 (2 H, m). 1.42 (4 H, m)

and 0.03 (9 H, s, $SiMe_3$); δ_C 145.7 (C-1), 141.3 (C-2), 33.1, 30.4, 30.3, 27.5, 26.9 and −2.2 ($SiMe_3$).

1-(*Trimethylsilyl*)*cyclooctene* **11**.—Reaction of hydrazone **7** (11.26 g, 39.86 mmol) with butyllithium (62.7 cm^3 of a 2.62 mol dm^{-3} solution, 164.5 mmol) in TMEDA (90 cm^3) at −45 °C for 1.5 h, followed by addition of chlorotrimethylsilane (24.3 cm^3, 191.7 mmol) afforded, after the usual work-up, a light yellow oil. Kugelrohr distillation (b.p. 80 °C/10 mmHg) of this material afforded the title vinyl silane **11** (5.10 g, 70%) as a clear liquid (lit.,[29] b.p. 92–94 °C/11 mmHg); ν_{max}(NaCl)/cm^{-1} 2925, 2851, 1612, 1448, 1245, 1031, 1001, 907, 892 and 834; δ_H 6.02 (1 H, t, *J* 8.0, 2-H), 2.35 (2 H, m), 2.22 (2 H, m), 1.50 (8 H, m) and 0.10 (9 H, s, $SiMe_3$); δ_C 142.0 (C-1), 139.5 (C-2), 29.9, 29.0, 27.2, 26.9, 26.5, 26.1 and −1.4 ($SiMe_3$).

General Procedure for the Phase-transfer-catalysed Addition of Dichlorocarbene to Vinylsilanes **8**–**11**. *Formation of Bicyclic Silanes* **12**–**16**.—Sodium hydroxide (0.5 cm^3 of a 50% w/v aq. solution $mmol^{-1}$ of vinylsilane) was added in one portion to a cooled (ice–water) solution of the appropriate vinylsilane (~5–20 mmol) and triethylbenzylammonium chloride (TEBAC) (4 mg $mmol^{-1}$ of vinylsilane) in water-washed halogenoform (CHX_3) (0.81 g $mmol^{-1}$ of vinylsilane). The resulting mixture was cooled and stirred vigorously (>800 rpm) under nitrogen for *ca.* 1 h and then at room temperature overnight or until GLC analysis indicated complete consumption of the starting alkene. Occasionally, the addition of dichloromethane (2–5 cm^3) was required in order to dilute the thick reaction mixture and allow sufficiently vigorous stirring. The mixture was then poured into water (5 cm^3 $mmol^{-1}$) and extracted with dichloromethane (4 × 2.5 cm^3 $mmol^{-1}$). The combined organic extracts were washed with water (2 × 5 cm^3 $mmol^{-1}$), dried, filtered and then concentrated under reduced pressure to afford an orange oil. Kugelrohr distillation afforded the required dihalogenocarbene adduct.

(1α,5α)-6,6-*Dichloro*-1-(*trimethylsilyl*)*bicyclo*[3.1.0]*hexane* **12**.—Reaction of crude 1-(trimethylsilyl)cyclopentene **8** (2.58 g, 18.39 mmol) with chloroform (10 cm^3) and sodium hydroxide (9.2 cm^3 of a 50% w/v aq. solution) in the presence of TEBAC (65 mg) afforded a crude yellow oil (1.76 g) after work-up. Kugelrohr distillation (b.p. 100 °C/20 mmHg) gave the bicyclic adduct **12**[7] (1.20 g, 30%) as a clear oil (Found: M^+, 222.0398. Calc. for $C_9H_{16}{}^{35}Cl_2{}^{28}Si$: *M*, 222.0398); ν_{max}(NaCl)/cm^{-1} 2954, 1468, 1444, 1249, 1108, 1080, 1005, 931, 874 and 838; δ_H 2.11–1.97 (4 H, complex m), 1.87 (1 H, m), 1.78–1.66 (2 H, complex m) and 0.15 (9 H, s, $SiMe_3$); δ_C 74.2 (C-6), 41.9, 34.6 (C-1), 32.1, 28.8, 27.9 and −0.63 ($SiMe_3$); *m*/*z* (18 eV) (%) 222 (0.2) (M^+), 209 (0.3) and 207 (0.5) ($M^+ - CH_3$), 149 (2), 116 (9) and 114 (30) [$M^+ - Si(CH_3)_3 - Cl$], 79 (100) and 73 (74).

(1α,6α)-7,7-*Dichloro*-1-(*trimethylsilyl*)*bicyclo*[4.1.0]*heptane* **13**.—Reaction of 1-(trimethylsilyl)cyclohexene **9** (1.23 g, 7.95 mmol) with chloroform (5.0 cm^3) and sodium hydroxide (4.0 cm^3 of a 50% w/v aq. solution) in the presence of TEBAC (30 mg) afforded a crude orange oil (1.80 g) after work-up. Kugelrohr distillation (b.p. 100 °C/1 mmHg) gave the bicyclic adduct **13**[7] (1.58 g, 84%) as a clear oil, ν_{max}(NaCl)/cm^{-1} 2945, 2874, 2853, 1249, 881, 842 and 752; δ_H 2.02 (1H, dt, *J* 14.6 and 5.1, 6-H), 1.90 (1 H, m), 1.82 (1 H, m), 1.59–1.49 (2 H, complex m), 1.42 (1 H, m), 1.31–1.21 (2 H, complex m), 1.00–0.87 (1 H, complex m) and 0.13 (9 H, s, $SiMe_3$); δ_C 73.8 (C-7), 27.4, 22.6, 21.8 (C-1), 20.9, 19.5, 18.8 and −1.6 ($SiMe_3$).

(1α,7α)-8,8-*Dichloro*-1-(*trimethylsilyl*)*bicyclo*[5.1.0]*octane* **14**.—Reaction of 1-(trimethylsilyl)cycloheptane **10** (1.0 g, 5.94 mmol) with chloroform (5.0 cm^3) and sodium hydroxide (5.0 cm^3 of a 50% w/v aq. solution) in the presence of TEBAC (35 mg) afforded a light yellow oil (1.31 g) after work-up. Kugelrohr distillation (b.p. 70 °C/0.15 mmHg) gave the *bicyclic adduct* **14** (1.27 g, 85%) as a clear oil (Found: M^+, 250.0711. $C_{11}H_{20}{}^{35}Cl_2{}^{28}Si$ requires *M*, 250.0711); ν_{max}(NaCl)/cm^{-1} 2919, 2862, 1463, 1443, 1249, 1124, 1052, 977, 927 and 865; δ_H 2.27 (1 H, m), 2.12 (1 H, m), 1.90–1.55 (5 H, m), 1.48–1.06 (4 H, m) and 0.18 (9 H, s, $SiMe_3$); δ_C 74.9 (C-8), 36.0, 32.9, 30.4, 28.7, 28.6, 28.5 (C-1), 27.7 and −0.3 ($SiMe_3$); *m*/*z* (15 eV) (%) 250 (<1%) (M^+), 178 (<1) and 176 (<1) [$M^+ - Si(CH_3)_3 - H$], 129 (3) and 127 (9), 107 (100), 79 (66) and 73 (98).

(1α,7α)-8,8-*Dibromo*-1-(*trimethylsilyl*)*bicyclo*[5.1.0]*octane* **15**.—A mixture of the vinylsilane **10** (1.06 g, 6.3 mmol), benzene (16 cm^3), bromoform (2.8 cm^3), TEBAC (17 mg) and sodium hydroxide (9.0 cm^3 of a 50% w/v aq. solution) was stirred vigorously under nitrogen. The progress of the reaction could be followed by GLC, which indicated slow consumption of the vinylsilane (t_R 8.8 min) and formation of a single product (t_R 19.6 min). After 3 days, the mixture was worked up in the same manner as in all previous carbene-addition reactions, and subjection of the resulting brown oil (2.4 g) to chromatographic filtration (TLC-grade silica, hexane elution) afforded, after concentration of the filtrate, slightly impure *dibromide* **15** (1.29 g, 60%) as a clear oil [Found: $M^+ - Si(CH_3)_3$, 264.9227. $C_8H_{11}{}^{79}Br_2$ requires *m*/*z* 264.9227]. A spectroscopically pure sample of compound **15** was obtained by HPLC (C_{18} column; acetonitrile elution, 2.50 cm^3 min^{-1}; t_R 11.50 min); ν_{max}(NaCl)/cm^{-1} 2945, 2917, 2859, 1461, 1449, 1249, 1116, 974, 922 and 856; δ_H 2.35 (1 H, m), 2.20 (1 H, m), 1.90–1.70 (3 H, m), 1.60–1.10 (6 H, complex m) and 0.22 (9 H, s, $SiMe_3$); δ_C 50.3 (C-8), 36.9, 33.6, 32.8, 30.4, 28.6, 28.4, 28.1 (C-1) and −0.1 ($SiMe_3$); *m*/*z* (15 eV) (%) 268 (0.4), 266 (0.8) and 264 (0.4) [$M^+ - Si(CH_3)_3 - H$], 188 (5) and 186 (5) [$M^+ - Si(CH_3)_3 - Br$], 107 (81), 79 (100) and 73 (63).

(1α,8α)-9,9-*Dichloro*-1-(*trimethylsilyl*)*bicyclo*[6.1.0]*nonane* **16**.—Reaction of 1-(trimethylsilyl)cyclooctene **11** (3.0 g, 16.45 mmol) with chloroform (13.3 g) and sodium hydroxide (8.3 cm^3 of a 50% w/v aq. solution) in the presence of TEBAC (60 mg) afforded a yellow oil (4.43 g) after work-up. Kugelrohr distillation (b.p. 70 °C/0.15 mmHg) gave the required bicyclic adduct **16**[7] (3.95 g, ~91%) as a clear oil [Found: $M^+ - Si(CH_3)_3$, 191.0394 $C_9H_{13}{}^{35}Cl_2$ requires *m*/*z* 191.0394]. Since this material was not spectroscopically pure (~3% unidentified impurity), the material was subjected to flash chromatography (silica; pentane elution; R_f 0.6). Trace levels of impurity persisted in this material and an analytical sample was obtained by reversed-phase HPLC (C_{18} column; methanol elution, 2.5 cm^3 min^{-1}; t_R 10.33 min); ν_{max}(NaCl)/cm^{-1} 2924, 2859, 1465, 1447, 1249, 1170, 1147, 1074, 923 and 842; δ_H 2.03 (2 H, m), 1.70–1.30 (10 H, br complex m), 1.05 (1 H, m) and 0.21 (9 H, s, $SiMe_3$); δ_C 72.8 (C-9), 34.4, 28.4, 27.1, 26.9, 26.2, 25.9 (C-1), 25.4, 22.6 and 0.8 ($SiMe_3$); *m*/*z* (18 eV) (%) 192 (0.6) and 190 (0.8) [$M^+ - Si(CH_3)_3 - H$], 157 (0.5) and 155 (1.5) [$M^+ - Si(CH_3)_3 - HCl$], 121 (100), 93 (32), 79 (36) and 73 (86).

1-*Methoxycyclohexene* **18**.—Trimethyl orthoformate (13.0 g, 0.123 mol) was added cautiously, *via* a dropping funnel, to a solution of cyclohexanone **17** (9.8 g, 0.10 mol) and dried toluene-*p*-sulfonic acid (PTSA) (70 mg) in anhydrous methanol (16 cm^3). The mixture was refluxed under nitrogen for 30 min, and a further portion of PTSA (50 mg) was added. Distillation of the mixture (through a 20 cm long glass column packed with Fenske helices) afforded 1-methoxycyclohexene **18**[8] (8.0 g, 71%) (b.p. 138–142 °C) as a clear liquid, ν_{max}(NaCl)/cm^{-1} 2991, 2932, 2857, 1667, 1445, 1377, 1338, 1211, 1180 and 1159; δ_H (90 MHz)

4.61 (1 H, br t, *J* 4, 2-H), 3.49 (3 H, s, OMe) and 2.20–1.20 (8 H, complex m).

(1α,6α)-7,7-*Dibromo*-1-*methoxybicyclo*[4.1.0]*heptane* **19**.—A solution of potassium *tert*-butoxide was prepared by refluxing potassium metal (2.87 g, 73.4 mmol) with *tert*-butyl alcohol (90 cm^3). The excess of *tert*-butyl alcohol was removed by distillation, and the residual solid was ground under nitrogen to a fine powder. Light petroleum (15 cm^3) was added and the resulting slurry was cooled to ~ −15 °C (ice–salt-bath). A solution of 1-methoxycyclohexene **18** (8.80 g, 78.4 mmol) in light petroleum (20 cm^3) was added, followed by the dropwise addition of bromoform (18.2 g, 72 mmol) over a 1 h period. The mixture was stirred at −15 °C for a further 30 min, and then at room temperature for 30 min, before the addition of water (100 cm^3). The organic layer was separated and the aqueous portion was extracted with pentane (3 × 30 cm^3). The combined organic extracts were washed successively with water (2 × 100 cm^3), HCl (4 × 30 cm^3 of a 2 mol dm^{-3} solution), saturated aq. sodium metabisulfite (4 × 30 cm^3) and finally with saturated aq. sodium hydrogen carbonate (2 × 100 cm^3). The organic layer was dried, filtered, and then concentrated under reduced pressure (without heating) to give an orange oil. Subjection of this material to flash chromatographic purification [silica; (93:7) light petroleum–diethyl ether elution; R_f 0.5] afforded the title compound **19**[9] (14.70 g, 66%) as a clear, thermally unstable oil, ν_{max}(NaCl)/cm^{-1} 2937, 2855, 1461, 1443, 1204, 1107, 1070, 1032, 992 and 763; δ_H(90 MHz) 3.47 (3 H, s, OMe) and 2.40–1.20 (9 H, complex m); δ_C 63.8 (C-1), 53.5 (OMe), 44.4 (C-7), 34.6, 23.7, 21.0 (2 signals overlapping) and 19.9.

(1α,6α,7β)-7-*Bromo*-1-*methoxy*-7-(*trimethylsilyl*)*bicyclo*-[4.1.0]-*heptane* **21** *and* 2-(*Trimethylsilyl*)*cyclohept*-2-*enone* **23**.—To a cooled (−100 °C), vigorously stirred solution of 7,7-dibromo-1-methoxybicyclo[4.1.0]heptane **19** (3.0 g, 10.56 mmol) in dry THF (42 cm_3) was added dropwise a solution of butyllithium (7.9 cm^3 of a 1.5 mol dm^{-3} solution in hexane, 11.83 mmol) over a period of 30 min. Metallation was allowed to proceed at −95 to −100 °C for a further 1.5 h. Chlorotrimethylsilane (4.2 cm^3, 33.6 mmol) was then added cautiously to the mixture and the mixture was stirred at or below −95 °C for 2 h. After warming to room temperature the mixture was quenched with water (50 cm^3) before being extracted with diethyl ether (5 × 30 cm^3) and the combined extracts were dried, filtered, and then concentrated under reduced pressure (without heating) to afford a bright yellow oil (3.22 g). Subjection of a small portion of this material to preparative TLC (PLC) [silica; (95:5) light petroleum–diethyl ether] gave, after extraction [(95:5) light petroleum–diethyl ether] of the major band (R_f 0.65), (1α,6α,7β)-7-bromo-1-methoxy-7-(trimethylsilyl)bicyclo[4.1.0]heptane **21** as a highly unstable oil, ν_{max}(NaCl)/cm^{-1} 2934, 2854, 1462, 1445, 1246, 1202, 946, 858, 842 and 756; δ_H(90 MHz) 3.18 (3H, s, OMe), 2.09 (3 H, m), 1.58–1.27 (6 H, m) and 0.14 (9 H, s, $SiMe_3$); δ_C(22.5 MHz) 65.9 (C-1), 52.7 (OMe), 44.6 (C-7), 26.0, 24.1, 22.4, 21.5, 21.4 and −1.0 ($SiMe_3$).

The bulk of compound **21** was dissolved in dry methanol (30 cm^3) and refluxed with anhydrous potassium carbonate (8.87 g, 63 mmol) for 2 h. The cooled reaction mixture was poured into water (200 cm^3), and then extracted with diethyl ether (4 × 50 cm^3). The combined organic extracts were dried, filtered, and then concentrated under reduced pressure to give a crude brown oil. This oil was dissolved in THF (20 cm^3) and was treated with H_2SO_4 (20 cm^3 of a 5% aq. solution). After being stirred at room temperature for 40 min, the mixture was poured into water (150 cm^3) and extracted with diethyl ether (4 × 50 cm^3). The combined organic phases were washed with saturated aq. sodium hydrogen carbonate (1 × 50 cm^3) before being dried, filtered, and then concentrated under reduced pressure to a dark yellow oil (1.91 g). Subjection of this material to PLC [silica; (84:16) light petroleum–diethyl ether] and extraction (diethyl ether) of the resulting chromophoric band (R_f 0.6) afforded the title enone **23**[10] (1.27 g, 66%) as a clear oil, ν_{max}(NaCl)/cm^{-1} 2939, 1660, 1592, 1363, 1245, 1205, 1184, 1171 and 840; δ_H(90 MHz) 6.71 (1 H, t, *J* 5.5, 3-H), 2.65–2.30 (4 H, m), 1.85–1.60 (4 H, m) and 0.09 (9 H, s, $SiMe_3$); δ_C(22.5 MHz) 209.2 (C-1), 150.0 (C-3), 147.0 (C-2), 43.3, 30.7, 24.8, 22.3 and −1.4 ($SiMe_3$); *m*/*z* (%) 182 (20) (M^+), 167 (100) ($M^+ - CH_3$), 154 (14) (M^+ − CO), 139 (14) ($M^+ - CH_3$ − CO), 75 (98) and 73 (52).

2-(*Trimethylsilyl*)*cyclohept*-2-*enol* **24**.—To a cooled (ice-bath), magnetically stirred solution of the enone **23** (307 mg, 1.7 mmol) and $CeCl_3 \cdot 7H_2O$ (0.65 g, 1.84 mmol) in methanol (10 cm^3) was added sodium borohydride (80 mg, 2.1 mmol) in four equal portions. The resulting mixture was stirred for 30 min on the ice-bath before being poured into water (50 cm^3). The mixture was extracted with dichloromethane (5 × 20 cm^3) and the combined extracts were dried, filtered, and then concentrated under reduced pressure to provide the *title compound* **24** (300 mg, 97%) as a spectroscopically pure, clear oil which was homogeneous by TLC (R_f 0.6, dichloromethane) (Found: M^+, 184.1282. $C_{10}H_{20}O^{28}Si$ requires *M*, 184.1283); ν_{max}(NaCl)/cm^{-1} 3440, 2921, 2850, 1608, 1444, 1342, 1244, 1068, 1031, 837 and 753; δ_H 6.10 (1 H, t, *J* 6.5, 3-H), 4.63 (1 H, br s, 1-H), 2.23 (1 H, m), 2.09 (1 H, m), 1.99–1.87 (1 H, complex m), 1.69 (3 H, complex m), 1.56 (1 H, m), 1.49 (1 H, m), 1.26 (1 H, m) and 0.11 (9 H, s, $SiMe_3$); δ_C 150.5 (C-2), 139.8 (C-3), 74.9 (C-1), 37.1, 29.9, 28.0, 25.9 and −0.17 ($SiMe_3$); *m*/*z* (%) 184 (3) (M^+), 183 (10) (M^+ − H), 167 (11) (M^+ − OH), 166 (60) ($M^+ - H_2O$) and 73 (100).

2′-(*Trimethylsilyl*)*cyclohept*-2′-*enyl Acetate* **25**.—Acetic anhydride (2.3 cm^3, 24.4 mmol) was added in one portion to a stirred solution of the alcohol **24** (1.30 g, 7.1 mmol) in pyridine (6 cm^3). 4-(Dimethylamino)pyridine (20 mg) was added and the stoppered reaction vessel was placed in a refrigerator for 40 h. The mixture was poured into water (200 cm^3) and extracted with dichloromethane (5 × 40 cm^3). The combined extracts were washed successively with HCl (2 × 100 cm^3 of a 2 mol dm^{-3} aq. solution), saturated aq. sodium hydrogen carbonate (1 × 50 cm^3) and water (1 × 50 cm^3) before being dried, filtered, and then concentrated under reduced pressure to afford a bright yellow oil. Subjection of this material to PLC (silica; dichloromethane) and subsequent extraction (dichloromethane) of the major band (R_f 0.7) afforded the *title compound* **25** (1.45 g, 91%) as a clear oil (Found: M^+, 226.1390. $C_{12}H_{22}O_2{}^{28}Si$ requires *M*, 226.1390); ν_{max}(NaCl)/cm^{-1} 2925, 2853, 1736, 1609, 1445, 1371, 1244, 1199, 1135, 1027 and 837; δ_H 6.15 (1 H, ddd, *J* 2.0, 6.8 and 6.9, 3′-H), 5.68 (1 H, br d, *J* 10.0, 1′-H), 2.25 (1 H, m), 2.13 (1 H, m), 2.05 (3 H, s, OAc), 1.87 (1 H, m), 1.74 (2 H, m), 1.60 (2 H, m), 1.23 (1 H, m) and 0.08 (9 H, s, $SiMe_3$); δ_C 170.1 (OCOMe), 146.5 (C-2′), 140.7 (C-3′), 77.8 (C-1′), 33.9, 29.7, 28.1, 25.5, 21.6 and −0.5 ($SiMe_3$); *m*/*z* (%) 226 (6) (M^+), 211 (6) ($M^+ - CH_3$), 183 (21) ($M - COCH_3$), 117 (82) and 73 (100).

(1′α,2′α,7′α)-8′,8′-*Dichloro*-1′-(*trimethylsilyl*)*bicyclo*[5.1.0]-*octan*-2′-*yl Acetate* **26**.—To a cooled (ice-bath), magnetically stirred solution of the acetate **25** (5.0 g, 16.2 mmol) and TEBAC (88 mg) in chloroform (17.9 g) was slowly added, down a condenser, sodium hydroxide (11.0 cm^3 of a 50% w/v aq. solution). The mixture was stirred vigorously (> 800 rpm) at room temperature for 5 h, then was poured into water (400 cm^3) and extracted with dichloromethane (4 × 80 cm^3). The combined extracts were washed with water (2 × 250 cm^3), dried, filtered, and then concentrated under reduced pressure to afford a slightly yellow oil (6.71 g). Subjection of this material to MPLC [silica; (93:7) light petroleum–diethyl ether] afforded,

after concentration of the appropriate fractions, a clear oil which crystallised upon storage. Recrystallisation (methanol) of this material afforded the *title ester* **26** (6.29 g, 92%) as rhomboids, m.p. 67.5–69.0 °C (Found: C, 50.8; H, 7.1; Cl, 22.9. $C_{13}H_{22}Cl_2O_2Si$ requires C, 50.6; H, 7.2; Cl, 22.7%); ν_{max}(KBr)/cm^{-1} 2938, 2909, 2851, 1731, 1446, 1420, 1371, 1360, 1242 and 1205; δ_H 4.97 (1 H, dd, *J* 10.1 and 2.0, 2′-H), 2.32 (1 H, m), 2.06 (3 H, s, OAc), 1.90–1.70 (5 H, complex m), 1.35 (2 H, m), 1.20 (1 H, m) and 0.27 (9 H, s, $SiMe_3$); δ_C 169.2 (C, OCOMe), 78.6 (CH, C-2′), 72.1 (C, C-8′), 35.7 (CH_2), 34.8 (CH, C-7′), 32.0 (C, C-1′), 27.8 (CH_2), 27.3 (CH_2), 26.6 (CH_2), 21.3 (CH_3, OCO*Me*) and 1.5 (CH_3, $SiMe_3$); *m*/*z* (15 eV) (%) 295 (1) and 293 (2) ($M^+ - CH_3$), 275 (9) and 273 (27) ($M^+ - Cl$), 183 (37), 141 (27), 73 (86) and 43 (100).

General Procedure for the Reaction of β,β-*Dichloro(trimethylsilyl)cyclopropanes* **12–16** *and* **26** *with TBAF*.—A solution of the appropriate β,β-dichloro(trimethylsilyl)cyclopropane (1.0 mol equiv.) in dry THF (2–5 cm^3 mmol^{-1} of cyclopropane) was maintained under dry nitrogen and cooled in an ice–water-bath. A solution of TBAF (1.0–1.5 mol equiv.) in THF (1 cm^3 mmol^{-1}) was added dropwise over a period of *ca.* 10 min. The reaction mixture was stirred at 0 to 5 °C until GLC analysis indicated complete consumption of the starting material. The mixture was poured into water (50 cm^3 mmol^{-1}) and extracted with dichloromethane (3 × 30 cm^3). The combined extracts were washed with water (1 × 40 cm^3) before being dried, filtered, and then concentrated under reduced pressure (without heating) to afford the crude product mixture. This material was purified as indicated below to afford the observed product(s).

2′-(2-*Chlorocyclohex*-2-*enyl*)*tetrahydrofuran* **29**.—A solution of the silane **12** (500 mg, 2.24 mmol) in THF (7 cm^3) was treated with TBAF (3.4 cm^3 of a 1.0 mol dm^{-3} solution in THF, 3.4 mmol, 1.5 mol equiv.). The resulting mixture was stirred at room temperature for 12 h. The prescribed work-up (see above) afforded an orange oil (330 mg). Flash chromatography of this material (silica; dichloromethane) afforded, after concentration of the appropriate fractions (R_f 0.4), impure compound **29** (89 mg, 21%) as an unstable, slightly yellow oil. Further purification *via* HPLC [μ-Porasil; (2:98) ethyl acetate–hexane elution, 2.0 cm^3 min^{-1}) afforded the title compounds **29** (67 mg, 16%) 1:4 ratio of diastereoisomers) as a clear oil, δ_H (major isomer) 5.95 (1 H, td, $J_{1,6}$ 4.2 and $J_{1,3}$ 1.5, 1-H), 4.23 (1 H, ddd, *J* 8.3, 6.6 and 4.6, 2′-H), 3.84 (1 H, td, J_{gem} 8.3, $J_{5',4'}$ 6.8, 5′-H), 3.73 (1 H, dt, J_{gem} 8.6, $J_{5',4'}$ 6.6, 5′-H), 2.35 (1 H, m) and 2.15–1.40 (10 H, complex m); δ_H(minor isomer—partial) 5.90 (1 H, td, $J_{1,6}$ 4.2 and $J_{1,3}$ 1.7, 1-H), 4.34 (1 H, m, 2′-H), 3.90 (1 H, m, 5′-H) and 2.75 (1 H, m); δ_C(major isomer) 127.7, 127.3, 78.9, 68.0, 44.7, 29.2, 26.4, 26.3, 24.5(1) and 19.4; δ_C(minor isomer) 133.4, 133.2, 80.1, 68.6, 43.7, 26.5, 26.0, 24.4(7) and 20.2 (one peak obscured).

(1′α,5′α)-2-*Chlorospiro*{*cyclohex*-2-*ene*-1,6′-[2′]*oxabicyclo*-[3.1.0]*hex*-3′-*ene*} **30**.—A solution of the silane **12** (250 mg, 1.12 mmol) in furan (5 cm^3) was treated with TBAF (1.7 cm^3 of a 1.0 mol dm^{-3} solution in THF, 1.7 mmol). The resulting mixture was stirred at room temperature for four days. The prescribed work-up afforded an orange oil (195 mg), which was subjected to flash chromatograhy (silica; hexane) and gave, after concentration of the appropriate fractions (R_f 0.45), the adduct **30**[12] (118 mg, 58%) as a clear oil (Found: M^+, 182.0498. Calc. for $C_{10}H_{11}{}^{35}ClO$: *M*, 182,0498); ν_{max}(NaCl)/cm^{-1} 2925, 1631, 1589, 1440, 1244, 1144, 1074, 964, 947 and 731; δ_H 6.38 (1 H, dd, $J_{3',4'}$ 2.1 and $J_{3',5'}$ 0.6, 3′-H), 5.93 (1 H, t, $J_{3,4}$ 4.3, 3-H), 5.16 (1 H, t, $J_{4',3'} = J_{4',5'}$ = 2.9, 4′-H), 4.75 (1 H, br d, $J_{1',5'}$ 6.0, 1′-H), 2.78 (1 H, dd, $J_{5',1'}$ 6.0, $J_{5',4'}$ 2.9, 5′-H), 2.17 (2 H, m, 4-H_2), 1.60 (2 H, m), 1.42 (1 H, m) and 1.34 (1 H, m); δ_C 148.0 (CH, C-3), 133.4 (C, C-2), 124.8 (CH, C-3′), 101.5 (CH, C-4′), 69.3 (CH, C-1′), 32.8 (CH, C-5′), 26.9 (CH_2), 21.0 (CH_2), 20.4 (CH_2) and 18.2 (C, C-1); *m*/*z* (%) 184 (16) and 182 (32) (M^+), 147 (95) ($M^+ - Cl$), 129 (30), 119 (50), 117 (45) and 91 (100).

(E)-1-*Chloro*-2-(*chloromethylene*)*cyclohexane* **34** *and* (E)-2-(*Chloromethylene*)*cyclohexanol* **35**.—Treatment of a THF (10 cm^3) solution of the cyclopropane **13** (2.0 g, 8.43 mmol) with TBAF (11 cm^3 of a 1.0 mol dm^{-3} solution in THF, 11 mmol, 1.2 mol equiv.) for 1.5 h at 0–5 °C afforded an orange oil (1.36 g) after work-up. Subjection of this material to MPLC (silica; hexane) afforded two components. Concentration of the fractions containing the more mobile component (R_f 0.6) afforded a mixture of compounds (by GLC and NMR analysis), while concentration of the fractions containing the less mobile material (R_f 0.5) afforded *alkene* **34** (608 mg. 44%) as a clear oil (Found: M^+, 164.0160. $C_7H_{10}{}^{35}Cl_2$ requires *M*, 164.0160); ν_{max}(NaCl)/cm^{-1} 2940, 2860, 1632, 1444, 1437, 1340, 1299, 1136, 979 and 803; δ_H 6.20 (1 H, br d, *J* 1.7, 1′-H), 4.69 (1 H, br t, *J* 3.6, 2-H), 2.62 (1 H, dt, *J* 14.2 and 4.2), 2.37 (1 H, m), 2. 10–1.70 (4 H, complex m), 1.55 (1 H, m) and 1.45–1.30 (1 H, complex m); δ_C 140.7 (C, C-1), 114.2 (CH, C-1′), 62.0 (CH, C-2), 36.3 (CH_2), 25.7 (CH_2), 24.3 (CH_2) and 21.0 (CH_2); *m*/*z* (%) 168 (16), 166 (13) and 164 (2) (M^+), 131 (29) and 129 (100) ($M^+ - Cl$), 93 (86) ($M^+ - Cl - HCl$) and 77 (33).

In a second experiment, conducted on a larger scale (3.0 g of silane precursor **13**), and where the TBAF solution was added more slowly (over *ca.* 2.5 h), it was possible to isolate, in addition to dichloride **34** (1.39 g, 66%), a minor, more polar component [R_f (dichloromethane) 0.25], which was found to be the *alcohol* **35** (31 mg, 1.7%) and which was obtained as a clear oil (Found: M^+, 146.0498. $C_7H_{11}{}^{35}ClO$ requires *M*, 146.0498); ν_{max}(NaCl)/cm^{-1} 3340, 2935, 2857, 1642, 1445, 1339, 1077, 989 and 889; δ_H 6.10 (1 H, dd, *J* 1.2 and 2.4, 1′-H), 4.17 (1 H, m, 1-H), 2.67 (1 H, m), 2.09 (1 H, m), 1.92–1.78 (2 H, complex m), 1.65 (1 H, br s, OH) and 1.62–1.41 (5 H, complex m); δ_C 143.5 (C-2), 110.9 (C-1′), 72.1 (C-1), 36.1, 26.3, 26.1 and 22.8; *m*/*z* (%) 148 (< 1) and 146 (2) (M^+), 130 (< 1) and 128 (3) ($M^+ - H_2O$), 111 (100) ($M^+ - Cl$) and 93 (29) ($M^+ - Cl - H_2O$).

(E)-3-(*Chloromethylene*)*cyclohexene* **38**.—Treatment of the dichloride **34** (750 mg, 4.54 mmol) with DBU (1.73 g, 11.35 mmol, 2.5 mol equiv.) under nitrogen at 75–80 °C for 10 h afforded a viscous orange mixture. Addition of pentane resulted in the precipitation of copious quantities of a tan solid. The suspension thus obtained was subjected to chromatographic filtration (silica; pentane) to afford a filtrate. Careful concentration of this solution afforded the *diene* **38** (463 mg, 79%) as a clear, unstable oil (Found: M^+, 128.0393. $C_7H_9{}^{35}Cl$ requires *M*, 128.0393); ν_{max}(NaCl)/cm^{-1} 2928, 1434, 1351, 1051, 834 and 794; δ_H 6.06 (1 H, dt with further coupling, $J_{2,1}$ 9.9, $J_{2,6}$ 2.0, 2-H), 5.91 (1 H, br s, 1′-H), 5.85 (1 H, dt, $J_{1,2}$ 9.9, $J_{1,6}$ 4.2, 1-H), 2.45 (2 H, m), 2.13 (2 H, m) and 1.70 (2 H, m); δ_C 137.5 (C, C-3), 130.1 (CH), 126.4 (CH), 114.2 (CH), 25.4 (CH_2), 25.2 (CH_2) and 21.5 (CH_2): *m*/*z* (%) 130 (15) and 128 (45) (M^+), 115 (3.5) and 113 (10) ($M^+ - CH_3$), 93 (100) ($M^+ - Cl$), 91 (70), 79 (86), 77 (80) and 65 (24).

(1α,6α)-7,7-*Dichloro*-1-*methoxybicyclo*[4.1.0]*heptane* **39**.—A magnetically stirred slurry of sodium methoxide [prepared by reaction of sodium (6.2 g, 270 g-atom) with an excess of anhydrous methanol] in dry pentane (150 cm^3) and containing 1-methoxycyclohexene **18** (7.6 g, 67.5 mmol) was cooled in an ice–water-bath and maintained under nitrogen. Ethyl trichloroacetate (51.7 g, 38 cm^3, 270 mmol) was added dropwise (dropping funnel). After the addition was complete (*ca.* 1.5 h) the cooling bath was removed. The resulting pale brown slurry was stirred overnight, then poured into water (600 cm^3). Extraction with light petroleum (3 × 75 cm^3), followed by washing of the

combined organic extracts with water (3 × 500 cm^3), drying, filtration and then concentration under reduced pressure afforded an orange oil (14.63 g). Subjection of this material to MPLC (silica; dichloromethane) afforded, after concentration of the appropriate fractions (R_f 0.6), the dichlorocarbene adduct[13] **39** (11.85 g, 90%) as a clear oil (Found: $M^+ - Cl$, 159.0577. Calc. for $C_8H_{12}{}^{35}ClO$: $M - Cl$, 159.0577); ν_{max}(NaCl)/cm^{-1} 2940, 1462, 1444, 1206, 1109, 1073, 997, 917, 816 and 717; δ_H(90 MHz) 3.41 (3 H, s, OMe) and 2.20–1.10 (9 H, complex m); δ_C(22.5 MHz) 69.1 (C-7), 64.7 (C-1), 54.1 (OMe), 33.2, 22.9, 21.0, 20.1 and 19.1; *m/z* (%) 193 (10) ($M^+ - H$), 167 (9) and 165 (12), 161 (35) and 159 (100) ($M^+ - Cl$) and 123 (16) ($M^+ - Cl - HCl$).

2-*Chlorocyclohept*-2-*enone* **41**.—A mixture of the dichloride **39** (4.0 g, 20.5 mmol), potassium carbonate (16.8 g, 121.6 mmol) and anhydrous ethanol (20 cm^3) was heated in a sealed glass tube at 100 °C for 52 h. After cooling, the mixture was poured into water (200 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined extracts were washed with brine (2 × 100 cm^3) before being dried, filtered, and then concentrated under reduced pressure to afford an orange oil (4.3 g). This material was taken up in THF (20 cm^3) and treated with H_2SO_4 (20 cm^3 of a 5% aq. solution). After the mixture had been stirred for 0.5 h at room temperature, TLC analysis (dichloromethane) indicated complete conversion of the non-chromophoric ketal **40** (R_f 0.6) into the strongly chromophoric enone **41** (R_f 0.5). The reaction mixture was poured into water (100 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined extracts were washed successively with saturated aq. $NaHCO_3$ (1 × 100 cm^3) and brine (3 × 100 cm^3). The organic phase was dried, filtered, and then concentrated under reduced pressure to afford a light yellow oil (3.72 g). Subjection of this material to MPLC (silica; dichloromethane) afforded two fractions (R_f 0.5 and 0.6).

Concentration of the fraction containing the less mobile component afforded the previously reported[14] and unstable enone **41** (2.11 g, 87% at 81% conversion) as a slightly yellow, sweet smelling oil (Found: M^+, 144.0341. Calc. for $C_7H_9{}^{35}ClO$: M, 144.0342); ν_{max}(NaCl)/cm^{-1} 2941, 1681, 1604, 1452, 1342, 1166, 963, 915, 895 and 732; δ_H(90 MHz) 7.01 (1 H, t, $J_{3,4}$ 6.6, 3-H), 2.75–2.20 (4 H, complex m) and 1.90–1.60 (4 H, complex m); δ_C(22.5 MHz) 195.6 (C-1), 143.9 (C-3), 135.0 (C-2), 41.5, 27.6, 24.6 and 20.8; *m/z* (%) 146 (22) and 144 (68) (M^+), 117 (5) and 115 (15) ($M^+ - CHO$), 109 (15) ($M^+ - Cl$) and 81 (100).

Concentration of the fraction containing the more mobile material afforded starting material **39** (770 mg, 19%) identical in all respects with an authentic sample.

A sample of enone **41** was converted into the corresponding 2,4-dinitrophenylhydrazone under standard conditions. Thus, 2,4-dinitrophenylhydrazine (250 mg, 1.26 mmol) was suspended in methanol (5 cm^3) then treated with conc. H_2SO_4 (0.5 cm^3). The resulting mixture was filtered through a plug of cotton wool to give a clear, yellow solution. A solution of enone **41** (110 mg, 0.76 mmol) in methanol (2 cm^3) was added to the hydrazine solution and crystals soon separated from the deep orange solution. After 1 h, filtration afforded small, bright orange crystals. Recrystallisation (ethanol) gave analytically pure *hydrazone* (195 mg, 80%) as lustrous, bright orange, prismic plates, m.p. 152–154 °C (lit.,[14b] 198–199 °C for a red-purple solid) (Found: C, 48.3; H, 4.0; N, 17.4; Cl, 11.1. $C_{13}H_{13}ClN_4O_4$ requires C, 48.1; H, 4.0; N, 17.3; Cl, 10.9%); ν_{max}(KBr)/cm^{-1} 3311, 1618, 1591. 1514, 1502, 1414, 1331 and 1130; δ_H 11.30 (1 H, br s, NH), 9.11 (1 H, d, $J_{3',5'}$ 2.6, 3'-H), 8.35 (1 H, ddd, $J_{5,6'}$ 9.5, $J_{5',3'}$ 2.6 and $J_{5',NH}$ 0.7, 5'-H), 8.07 (1 H, d, $J_{6',5'}$ 9.5, 6'-H), 6.54 (1 H, t, $J_{3,4}$ 6.6, 3-H), 2.73 (2 H, m), 2.39 (2 H, m), 1.95 (2 H, m) and 1.79 (2 H, m); δ_C 153.3, 144.8, 138.7, 136.1, 130.7, 130.1, 130.0, 123.2, 117.2, 28.1, 27.1, 24.7 and 22.2; *m/z* (%) 326 (35) and 324 (100) (M^+), 289 (2) ($M^+ - Cl$) and 91 (36).

2-*Chlorocyclohept*-2-*enol* **42**.—Cerium trichloride heptahydrate (5.98 g, 16.05 mmol) was added to a solution of the enone **41** (2.11 g, 14.59 mmol) in methanol (65 cm^3). After being stirred at ambient temperature for 10 min, the solution was cooled to 0 °C (ice-bath), and sodium borohydride (1.11 g, 29.2 mmol) was added in portions during 30 min. The reaction mixture was stirred on the ice-bath for a further 1 h, by which time TLC analysis (dichloromethane) indicated complete conversion of the chromophoric enone (R_f 0.5) into the more polar (R_f 0.3) and non-chromophoric alcohol **42**. The reaction mixture was poured into water (200 cm^3) and extracted with dichloromethane (4 × 50 cm^3). The combined extracts were washed with water (2 × 100 cm^3) before being dried, filtered, and then concentrated under reduced pressure to afford alcohol **42**[15] (1.65 g, 78%) as a slightly yellow oil (Found: M^+, 146.0498. Calc. for $C_7H_{11}{}^{35}ClO$: M, 146.0498). This material was homogeneous by TLC and was used as obtained in the next step. A spectroscopically pure sample of compound **42** was obtained using flash chromatography (silica; dichloromethane), ν_{max}(NaCl)/cm^{-1} 3381, 2931, 2859, 1642, 1444, 1084, 1069, 1000, 899 and 870; δ_H 6.03 (1 H, t, J 6.6, 3-H), 4.35 (1 H, m, 1-H), 2.62 (1 H, br d, J 3.7, OH) 2.20 (1 H, m), 2.10 (1 H, m), 1.95–1.75 (3 H, complex m) and 1.65–1.50 (3 H, complex m); δ_C 137.3 (C-2), 130.0 (C-3), 74.1 (C-1), 32.1, 26.3, 25.9 and 23.0; *m/z* (%) 146 (7) (M^+), 130 (14) and 128 (40) ($M^+ - H_2O$), 117 (13), 111 (76) ($M^+ - Cl$), 104 (25), 93 (100) ($M^+ - H_2O - Cl$) and 67 (47).

1,7-*Dichlorocycloheptene* **44**.—Hydrochloric acid (9.5 cm^3; 10 mol dm^{-3}) was added to a solution of the alcohol **42** (1.65 g, 11.25 mmol) in pentane (2.5 cm^3). The resulting mixture was stirred vigorously at room temperature for 20 min. After this time TLC analysis (dichloromethane) indicated complete conversion of the alcohol **42** (R_f 0.3) into the dichloride **44** (R_f 0.8). The reaction mixture was poured into water (100 cm^3) and extracted with pentane (3 × 30 cm^3). The combined extracts were washed with brine (2 × 50 cm^3), before being dried and filtered. Concentration of the solution under reduced pressure (no heating) afforded the known[16] dichloride **44** (1.70 g, 92%) as a clear, spectroscopically pure oil (Found: M^+, 164.0159. Calc. for $C_7H_{10}{}^{35}Cl_2$: M, 164.0160); ν_{max}(NaCl)/cm^{-1} 2934, 2860, 1642, 1444, 1429, 1355, 1253, 963, 925, 916, 861 and 839; δ_H 6.09 (1 H, t, $J_{1,7}$ 6.5, 1-H), 4.73 (1 H, m, 3-H), 2.30–2.10 (2 H, complex m), 2.10–2.00 (3 H, complex m), 1.85 (1 H, m), 1.78 (1 H, m) and 1.50 (1 H, m); δ_C 133.8 (C-1 and C-2 overlapping), 65.3 (C-3), 33.3, 26.9, 25.9 and 23.5; *m/z* (%) 168 (3), 166 (11) and 164 (20) (M^+), 131 (50), 130 (8) and 128 (20) ($M^+ - HCl$), 93 (100) ($M^+ - Cl - HCl$), 91 (31) and 77 (33).

1-*Chlorocyclohepta*-1,3-*diene* **45** *and* 2-*Chlorocyclohepta*-1,3-*diene* **37**.—A solution of the dichloride **44** (300 mg, 1.8 mmol) and DBU (770 mm^3, 4.5 mmol) in anhydrous benzene (5 cm^3) was heated at reflux under nitrogen for 17 h. GLC analysis after this time indicated that ~10% of starting material remained. A further aliquot (300 mm^3) of DBU was added and the mixture was heated for a further 5.25 h before being allowed to cool. Addition of pentane (15 cm^3) resulted in DBU · HCl being precipitated. The suspension was filtered through a 3 cm pad of flash-chromatography-grade silica gel, and the solids thus retained were washed well with pentane. Careful rotary evaporation of the combined filtrates afforded a volatile and slightly yellow oil. NMR analysis revealed an inseparable 85:15 mixture of the isomeric dienes **37** and **45** (156 mg, 63% combined) respectively (Found: M^+, 128.0393. $C_7H_9{}^{35}Cl$ requires M, 128.0393). Compounds **37** and **45** were found to polymerise within minutes if kept neat.

Spectral data for 2-chlorocyclohepta-1,3-diene **37**: δ_H 6.05 (1 H, m), 5.91–5.84 (2 H, complex m), 2.37–2.26 (4 H, complex m) and 1.89–1.82 (2 H, complex m); δ_C 135.0 (CH), 130.4 (CH), 128.9 (C, C-2), 128.3 (C), 31.0 (CH_2), 29.9 (CH_2) and 25.9 (CH_2).

Spectral data for 1-chlorocyclohepta-1,3-diene **45**: δ_H 6.10 (1 H, m), 5.81 (1 H, m), 5.61 (1 H, m), 2.73 (2 H, m), 2.32 (2 H, m) and 1.90 (2 H, m); δ_C 138.1 (C, C-1), 134.0 (CH), 123.7 (CH), 122.5 (CH), 40.3 (CH_2), 30.5 (CH_2) and 24.4 (CH_2).

Spectral data for diene mixture: ν_{max}(NaCl)/cm^{-1} 3033, 2929, 1632, 1477, 1447, 1432 and 929; *m/z* (%) 130 (15) and 128 (45) (M^+), 93 (100) (M^+ – Cl), 91 (63) and 77 (84).

Reaction of 1- *and* 2-*Chlorocyclohepta*-1,3-*diene with PTAD. Formation of Adducts* **46** *and* **47**.—Treatment of dichloride **44** (0.50 g, 3.03 mmol) with DBU (910 mm^3, 2 mol equiv., 6.06 mmol) at 80 °C for 40 min in the absence of solvent gave an orange viscous syrup. After chromatographic filtration (silica; pentane) and rotary evaporation, an oil (312 mg) was obtained. This oil was immediately taken up in dichloromethane (5 cm^3) and treated portionwise with PTAD (total ~ 390 mg) until the crimson colour of excess dienophile persisted in the solution. Removal of the solvent under reduced pressure, and subjection of the residue to MPLC [silica; (3:7) ethyl acetate–hexane] afforded two major components (R_f 0.4 and 0.1).

Concentration of the fractions containing the less polar material gave a solid. Recrystallisation (ethyl acetate–cyclohexane) of this material afforded the *major adduct* **47** (482 mg, 52%) as prisms, m.p. 196.5–197.5 °C (Found: C, 59.1; H, 4.8; N, 13.8; Cl, 11.9. $C_{15}H_{14}ClN_3O_2$ requires C, 59.3; H, 4.7; N, 13.8; Cl, 11.7%); ν_{max}(KBr)/cm^{-1} 2934, 1762, 1702, 1412, 1268, 1138, 757, 720 and 690; δ_H 7.55–7.40 (4 H, complex m, ArH), 7.35 (1 H, m, ArH), 6.29 (1 H, dd, $J_{3,4}$ 7.1, $J_{3,1}$ 1.7, 3-H), 5.05 (1 H, m, 1- or 4-H), 4.99 (1 H, m, 4- or 1-H), 2.15 (1 H, m), 2.03–1.78 (4 H, complex m) and 1.65 (1 H, m); δ_C 151.5 (C=O), 151.4 (C=O), 132.0, 131.5, 129.0, 128.1, 125.5, 124.0, 57.6 (C-1 or -4), 51.2 (C-4 or -1), 29.0, 27.5 and 19.9; *m/z* (%) 305 (22) and 303 (62) (M^+), 268 (100) (M^+ – Cl) and 149 (75).

Concentration of the fractions containing the more polar material afforded a solid, which upon recrystallisation (ethyl acetate–cyclohexane) afforded the *minor adduct* **46** (103 mg, 11%) as rods, m.p. 165.0–166.5 °C (Found: C, 59.4; H, 4.9; N, 13.9%); ν_{max}(KBr)/cm^{-1} 2946, 1767, 1711, 1556, 1501, 1402, 1266, 1133, 913 and 751; δ_H 7.53 (2 H, m, ArH), 7.47 (2 H, m, ArH), 7.37 (1 H, m), 6.45 (1 H, dd, $J_{3,2}$ 9.5, $J_{3,4}$ 7.1, 3-H), 6.31 (1 H, dd, $J_{2,3}$ 9.5, $J_{2,4}$ 1.0, 2-H), 4.94 (1 H, m, 4-H), 2.72 (1 H, m), 2.36 (1 H, m), 1.95 (1 H, m) and 1.75–1.60 (3 H, complex m); δ_C 151.4, 149.1, 133.7, 131.2, 129.1, 128.2, 127.3, 125.5, 77.2, 51.8, 39.4, 27.0 and 20.5; *m/z* (%) 305 (10) and 303 (27) (M^+), 268 (9) (M^+ – Cl), 263 (100), 236 (24) and 178 (84).

(E)-1-*Chloro*-2-(*chloromethylene*)*cycloheptane* **48**.—A THF (10 cm^3) solution of the cyclopropane **14** (500 mg, 1.99 mmol) was treated with a solution of TBAF (940 mg, 2.99 mmol, 1.5 mol equiv.) in THF (5 cm^3) for 30 min at 0–5 °C, and then at room temperature for 8 h. At this time GLC analysis indicated that all starting material had been consumed. Two products (t_R 9.1 and 14.4 min) were detected by GLC. The reaction mixture was heated at reflux for 12 h (with significant decomposition) which resulted in complete conversion of the more volatile product into the less volatile one. The resulting deep orange solution was subjected to the usual work-up and afforded a reddish oil (338 mg). Subjection of this material to flash chromatography (silica; hexane) afforded, after concentration of the appropriate fractions (R_f 0.5), the *title alkene* **48** (153 mg, 43%) as a clear oil (Found: M^+, 178.0316. $C_8H_{12}{}^{35}Cl_2$ requires M, 178.0316); ν_{max}(NaCl)/cm^{-1} 2928, 2854, 1626, 1462, 1452, 1353, 1296, 1210, 1018, 744 and 689; δ_H 6.21 (1 H, s, 1′-H), 4.63 (1 H, dd, *J* 6.4 and 9.0, 2-H), 2.67 (1 H, m), 2.33 (1 H, m), 2.22 (1 H, ddd, *J* 14.1, 11.3 and 2.2), 1.97–1.82 (2 H, complex m), 1.79–1.67 (2 H, complex m), 1.51–1.37 (2 H, complex m) and 1.24–1.13 (1 H, complex m); δ_C 143.7 (C, C-1), 118.8 (CH, C-1′), 63.4 (CH, C-2), 38.0 (CH_2), 30.2 (CH_2), 26.7 (CH_2), 26.0 (CH_2) and 24.5 (CH_2); *m/z* (%) 182 (3), 180 (20) and 178 (30) (M^+), 145 (27) and 143 (80) (M^+ – Cl), 107 (100) (M^+ – Cl – HCl), 95 (30) and 69 (61).

(1′α,3′α)-(E)-3′-*Chloro*-2′-(*chloromethylene*)*cycloheptyl Acetate* **52** *and* (1′α,3′β)-(E)-3′-*Chloro*-2′-(*chloromethylene*)*cycloheptyl Acetate* **49**.—A solution of the silane **26** (1.0 g, 3.23 mmol) in THF (14 cm^3) was treated with TBAF (1.14 g, 3.6 mmol, 1.1 mol equiv.) and the resulting mixture was heated at 40 °C for 16 h. After the usual work-up, a yellow oil (690 mg) was obtained. Subjection of this material to flash chromatography (silica; dichloromethane) afforded, after concentration of the appropriate fractions (R_f 0.6), a 2:1 mixture of diastereoisomeric acetates **52** and **49** respectively (396 mg, 52% combined) which partially crystallised on storage. Recrystallisation (hexane) of this material afforded *product* **52** as cubes, m.p. 81–82 °C (Found: C, 50.9; H, 6.1; Cl, 30.0. $C_{10}H_{14}Cl_2O_2$ requires C, 50.7; H, 6.0; Cl, 29.9%); ν_{max}(KBr)/cm^{-1} 3079, 2948, 2925, 1735, 1619, 1454, 1371, 1269, 1240, 1198, 1049, 697 and 635; δ_H 6.32 (1 H, 1″-H), 6.12 (1 H, ddd, *J* 6.5, 4.4 and 1.0, 1′-H), 4.64 (1 H, dd, *J* 10.0 and 6.8, 3′-H), 2.34 (1 H, m), 2.22 (1 H, m), 2.16–2.09 (1 H, complex m), 2.11 (3 H, s, OAc), 1.84 (1 H, m), 1.70 (2 H, m), 1.60 (1 H, m) and 1.25–1.12 (1 H, complex m); δ_C 170.0 (C, OCOMe), 140.5 (C, C-2′), 122.2 (CH, C-1″), 70.3 (CH, C-1′), 61.3 (CH, C-3′), 37.3 (CH_2), 31.6 (CH_2), 25.1 (CH_2), 24.9 (CH_2) and 21.2 (CH_3, OCO*Me*); *m/z* (FAB) (%) 239 (25) and 237 (35) ($M + H)^+$, 201 (15) and 199 (20) (M^+ – HCl – H), 131 (100), 91 (100) and 73 (98).

The minor isomer **49** proved to be inseparable from the remaining major isomer.

(1α,3α)-(E)-3-*Chloro*-2-(*chloromethylene*)*cycloheptanol* **53** *and* (1α,3β)-(E)-3-*Chloro*-2-(*chloromethylene*)*cycloheptanol* **50**.—A mixture of acetates **52** and **49** (247 mg, 1.04 mmol) and anhydrous potassium carbonate (485 mg, 3.51 mmol) in methanol (5 cm^3) was stirred under nitrogen at room temperature for 14 h. The mixture was diluted with water (30 cm^3) and extracted with dichloromethane (3 × 30 cm^3). The combined extracts were washed with water (2 × 100 cm^3) before being dried, filtered, and then concentrated under reduced pressure to afford a brown oil. This material was subjected to flash chromatography (silica; dichloromethane) and afforded, after concentration of the appropriate fractions (R_f 0.4), a mixture of alcohols **53** and **50** (133 mg, 66%). Subjection of this mixture to HPLC [μ-Porasil; (1:9) ethyl acetate–hexane, 2.0 cm^3 min^{-1}] afforded two components (t_R 9.4 and 13.5 min).

Concentration of the fractions containing the more mobile component afforded the *alcohol* **53** as a clear oil (Found: M^+ – Cl, 159.0577. $C_8H_{12}{}^{35}ClO$ requires *m/z*, 159.0577); ν_{max}(NaCl)/cm^{-1} 3424, 2927, 2852, 1605, 1453, 1105, 1005, 785, 742 and 694; δ_H 6.26 (1 H, m, 1′-H), 5.15 (1 H, br d, *J* 4.4, 1-H), 4.68 (1 H, dd, *J* 9.0 and 6.4, 3-H), 2.38–2.28 (1 H, complex m), 2.27–2.18 (1 H, complex m), 2.10 (2 H, m), 1.80 (2 H, m), 1.75–1.50 (2 H, complex m) and 1.25 (1 H, m); δ_C 144.1 (C-2), 120.8 (C-1′), 69.5 (C-1), 62.7 (C-3), 37.4, 33.7, 25.3 and 24.4; *m/z* (15 eV) (%) 161 (19) and 159 (60) (M^+ – Cl) and 123 (100) (M^+ – HCl – Cl).

Concentration of the fractions containing the less mobile component afforded the *alcohol* **50** as a clear oil (Found: M^+, 194.0265. $C_8H_{12}{}^{35}Cl_2O$ requires *M*, 194.0265); ν_{max}(NaCl)/cm^{-1} 3400, 2933, 2856, 1627, 1340, 1258, 1025 and 839; δ_H 6.53 (1 H, br s, 1′-H), 4.96 (1 H, br dd, *J* 7.8 and 4.9, 1-H), 4.81 (1 H, ddd, *J* 9.2, 4.3 and 1.0, 3-H), 2.35 (1 H, m), 2.10 (2 H, m), 1.85 (1 H, m), 1.80–

1.68 (3 H, complex m), 1.55 (1 H, m) and 1.35 (1 H, m); δ_C 144.9 (C-2), 120.7 (C-1'), 68.1 (C-1), 59.7 (C-3), 39.7, 33.4, 26.0 and 23.1; *m/z* (%) 161 (18) and 159 (57) ($M^+ - Cl$) and 123 (100) ($M^+ - Cl - HCl$).

(1'α,3'β)-(E)-3'-*Chloro*-2'-(*chloromethylene*)*cycloheptyl* p-*Nitrobenzoate* **51**.—*p*-Nitrobenzoyl chloride (82 mg, 0.441 mmol) was added to a solution of alcohol **50** (43 mg, 0.220 mmol) in pyridine (2 cm^3), and the resulting mixture was stirred at room temperature for 24 h. The mixture was diluted with water (30 cm^3) and extracted with dichloromethane (3 × 30 cm^3). The combined extracts were washed successively with HCl (3 × 30 cm^3 of a 2 mol dm^{-3} aq. solution), then with water (2 × 30 cm^3) before being dried, filtered, and then concentrated under reduced pressure to afford a yellow solid. Subjection of this material to flash chromatograhy (silica; dichloromethane) afforded, after concentration of the appropriate fractions (R_f 0.6), a solid. Recrystallisation (diethyl ether–pentane) of this material afforded *benzoate* **51** (76 mg, 92%) as rods, m.p. 114.5–115 °C (Found: C, 52.6; H, 4.4; Cl, 20.6; N, 4.1. $C_{15}H_{15}Cl_2NO_4$ requires C, 52.3; H, 4.4; Cl, 20.6; N, 4.1%); ν_{max}(KBr)/cm^{-1} 3102, 2932, 1719, 1603, 1522, 1345, 1317, 1281, 1104, 874, 868 and 720; δ_H 8.29 (2 H, d, *J* 9.0), 8.21 (2 H, d, *J* 9.0), 6.64 (1 H, br d, *J* 0.7, 1''-H), 6.21 (1 H, dd, *J* 7.3 and 3.9, 1'-H), 4.84 (1 H, ddd, *J* 8.3, 4.4 and 1.0, 3'-H), 2.35 (1 H, m), 2.15 (1 H, m), 2.10–1.95 (2 H, complex m), 1.87–1.66 (2 H, complex m) and 1.65–1.50 (2 H, complex m); δ_C 163.3, 150.6, 140.3, 135.3, 130.8, 123.6, 123.4, 72.1 (C-1'), 60.2 (C-3'), 38.9, 31.0, 24.9 and 23.8; *m/z* (15 eV) (%) 310 (21) and 308 (63) ($M^+ - Cl$), 272 (12) ($M^+ - HCl - Cl$), 150 (83) ($M^+ - Cl_2 - C_6H_4NO_2$), 143 (24) and 141 (83) and 123 (100) ($HO_2CC_6H_4NO_2^+$).

(1'α,3'α)-(E)-3'-*Chloro*-2'-(*chloromethylene*)*cycloheptyl* p-*Nitrobenzoate* **54**.—*p*-Nitrobenzoyl chloride (103 mg, 0.554 mmol) was added to a solution of the alcohol **53** (54 mg, 0.277 mmol) in pyridine (2 cm^3), and the resulting mixture was stirred at room temperature for 24 h before being diluted with water (30 cm^3) and extracted with dichloromethane (3 × 30 cm^3). The combined extracts were washed successively with HCl (3 × 30 cm^3 of a 2 mol dm^{-3} aq. solution), then water (2 × 30 cm^3) before being dried, filtered, and then concentrated under reduced pressure to afford a yellow solid. Subjection of this material to flash chromatography (silica; dichloromethane) afforded, after concentration of the appropriate fractions (R_f 0.6), a solid. Recrystallisation (diethyl ether–pentane) of this material afforded the *title compound* **54** (83 mg, 87%) as rods, m.p. 118–118.5 °C (Found: C, 52.6; H, 4.4; N, 4.1; Cl, 20.8. $C_{15}H_{15}Cl_2NO_4$ requires C, 52.3; H, 4.4; N, 4.1; Cl, 20.6%); ν_{max}(KBr)/cm^{-1} 2930, 1723, 1603, 1525, 1341, 1303, 1282, 1262, 1112 and 1102; δ_H 8.31 (2 H, d, *J* 9.3), 8.27 (2 H, d, *J* 9.3), 6.41 (1 H, m, 1''-H), 6.39 (1 H, m, 1'-H), 4.73 (1 H, dd, *J* 10.0 and 6.7, 3'-H), 2.45 (1 H, m), 2.35–2.20 (2 H, complex m), 1.90 (1 H, m), 1.83–1.67 (3 H, complex m) and 1.25 (1 H, m); δ_C 163.7, 150.5, 139.9, 135.6, 130.9, 123.6, 123.0, 72.3 (C-1'), 61.2 (C-3'), 37.6, 31.6, 25.2 and 24.9; *m/z* (%) 310 (3) and 308 (9) ($M^+ - Cl$), 272 (4) ($M^+ - Cl - HCl$) and 150 (100).

9-*Chlorobicyclo*[6.1.0]*non*-1(9)-*ene* **55**.—A solution of compound **16** (500 mg, 1.88 mmol) in THF (5 cm^3) maintained at 0–5 °C was treated with a solution of TBAF (640 mg, 2.03 mmol, 1.1 mol equiv.) in THF (5 cm^3). After the mixture had been stirred at 0–5 °C for 45 min, a further portion (100 mg, 0.32 mmol) of TBAF was added and stirring was continued at room temperature for a further 3.25 h. The usual work-up afforded a light yellow and very unstable oil, which was subjected to flash chromatographic purification (silica; hexane). Concentration of the appropriate fractions (R_f 0.6) afforded the *title compound* **55** (274 mg, 93%) as a clear oil (Found: M^+, 156.0706. $C_9H_{13}{}^{35}Cl$ requires *M*, 156.0706); ν_{max}(NaCl)/cm^{-1} 2919, 2847, 1839, 1455, 1445, 1065, 1036, 1020 and 871; δ_H 2.70 (1 H, ddd, *J* 14.8, 5.8 and 3.9), 2.19 (1 H, m), 2.11 (1 H, td, *J* 3.4 and 1.2), 1.88–1.78 (1 H, complex m) and 1.67–1.19 (9 H, complex m); δ_C 116.6 (C-1 or -9), 110.0 (C-9 or -1), 30.2, 29.5, 28.5, 25.0, 24.9, 24.6 and 19.8; *m/z* (%) 158 (< 1) and 156 (2) (M^+), 121 (44) ($M^+ - Cl$), 93 (52) ($M^+ - Cl - C_2H_4$) and 79 (100).

General Procedure for the Reaction of β,β-*Dichloro*-(*trimethylsilyl*)*cyclopropanes* **13–16** *and* **26** *with TBAF in the Presence of Buta*-1,3-*diene*.—A solution (1 cm^3 $mmol^{-1}$ in dry THF) or neat quantity (1 mol equiv.) of the appropriate cyclopropane was placed in an Ace™ Pressure Tube. The tube was immersed in liquid nitrogen and a solution of TBAF (1.0–1.5 mol equiv.) in THF (1–2 cm^3 $mmol^{-1}$) was added. Buta-1,3-diene (~ 2–3 cm^3) was then condensed into the tube, which was sealed while the contents were still frozen. The mixture was allowed to warm to room temperature and the resulting solution was stirred at room temperature for the period indicated (NB: when the volume of buta-1,3-diene exceeds the volume of THF the reaction mixture may be non-homogeneous at room temperature). The mixture was then refrozen, the tube unsealed, and the thawed contents were poured into water. The mixture was extracted with dichloromethane and the combined extracts were dried, filtered, and then concentrated under reduced pressure to yield the crude product mixture. Purification as described below yielded the required product(s).

(1S,6S,7S)-6-*Chlorotricyclo*[5.4.0.0^{1,6}]*undec*-3-*ene* **56** *and* (E)-1-*Chloro*-2-(*chloromethylene*)*cyclohexane* **34**.—Reaction of (1α,6α)-7,7-dichloro-1-(trimethylsilyl)bicyclo[4.1.0]heptane **13** (250 mg, 1.05 mmol) with TBAF (1.13 cm^3 of a 1.0 mol dm^{-3} solution in THF, 1.13 mmol) in the presence of buta-1,3-diene (~ 1 cm^3) for 27 h at room temperature afforded a yellow, sweet smelling oil (182 mg) on work-up. This material was subjected to MPLC (silica; light petroleum) and afforded two major components (R_f 0.4 and 0.5).

Concentration of the fractions containing the more polar component afforded the dichloroalkene **34** (63 mg, 36%), which was identical in all respects with the material obtained earlier.

Concentration of the fractions containing the less polar component afforded an oil, which was subjected to further purification by reversed-phase HPLC (C_{18} column; acetonitrile elution, 2.0 cm^3 min^{-1}) and afforded, after concentration of the appropriate fraction (t_R 11.8 min), the *adduct* **56** (5 mg, 2.4%) as a clear oil (Found: M^+, 182.0862. $C_{11}H_{15}{}^{35}Cl$ requires *M*, 182.0862); ν_{max}(NaCl)/cm^{-1} 2932, 2866, 1659, 1461, 1443 and 1079; δ_H 5.50–5.41 (2 H, complex m, 3- and 4-H), 2.87–2.78 (1 H, complex m), 2.74–2.66 (1 H, complex m), 2.31 (2 H, m), 1.94–1.83 (2 H, complex m), 1.62–1.52 (3 H, complex m), 1.49–1.37 (2 H, complex m) and 1.34–1.13 (2 H, complex m); δ_C 124.6 (C-3 or -4), 124.4 (C-4 or -3), 54.6 (C-6), 36.5, 34.4, 27.8, 21.9 (C-1), 21.8, 21.7, 19.1 and 18.7; *m/z* (%) 184 (9) and 182 (26) (M^+), 147 (86) ($M^+ - Cl$), 105 (54) and 91 (100) ($C_7H_7^+$).

(1S,6S,7S)-6-*Chlorotricyclo*[5.5.0.0^{1,6}]*dodec*-3-*ene* **57**.—Reaction of compound **14** (1.50 g, 5.97 mmol) with TBAF (2.83 g, 8.96 mmol) in THF (8 cm^3) in the presence of buta-1,3-diene (~ 6 cm^3) gave a two-phase mixture,* which was stirred at room temperature for six days. The orange oil (1.40 g) obtained after work-up was subjected to flash chromatography (silica;

* In some subsequent runs a homogeneous reaction mixture was obtained. In these cases some of the dichloroalkene **48** was formed. For example, one run produced the adduct **57** in 73% yield along with **48** in 15% yield.

light petroleum) and afforded, after concentration of the appropriate fractions (R_f 0.55), the *title compound* **57** (1.07 g, 91%) as a clear oil (Found: M^+, 196.1017. $C_{12}H_{17}{}^{35}Cl$ requires *M*, 196.1019); ν_{max}(NaCl)/cm^{-1} 3030, 2948, 2918, 2861, 1660, 1462, 1441, 1431, 1021 and 753; δ_H 5.48 (2 H, m, 3- and 4-H), 2.79 (2 H, m), 2.57 (1 H, d, *J* 19.0), 2.11 (1 H, d, *J* 16.0), 1.99 (1 H, m), 1.92–1.70 (5 H, complex m), 1.55–1.39 (2 H, complex m) and 1.36–1.15 (3 H, complex m); δ_C 124.5 (CH, C-3 or -4), 123.9 (CH, C-4, or -3), 57.1 (C, C-6), 35.9 (CH_2), 33.1 (CH_2), 32.4(4) (CH_2), 32.3(8) (CH_2), 28.7 (CH_2), 28.2 (C, C-1), 26.9 (CH_2), 26.8 (CH, C-7) and 26.0 (CH_2); *m*/*z* (%) 198 (8) and 196 (27) (M^+), 161 (100) (M^+ − Cl) and 160 (43) (M^+ − HCl).

(1S,6S,7S)-6-*Bromotricyclo*[5.5.0.0^{1,6}]*dodec*-3-*ene* **59**.— Reaction of (1α,7α)-8,8-dibromo-1-(trimethylsilyl)bicyclo[5.1.0]-octane **15** (1.0 g, 2.94 mmol) with TBAF (1.45 g, 4.6 mmol) in THF (5 cm^3) in the presence of buta-1,3-diene (~ 5 cm^3) for four days at room temperature afforded a brown oil (860 mg) after work-up. Purification of this material *via* flash chromatograhy (silica; light petroleum) afforded, after concentration of the appropriate fractions (R_f 0.5), the adduct **59** (575 mg, 78%) as a clear oil which was slightly impure as determined by NMR analysis. Subjection of this material to reversed-phase HPLC (C_{18} column; acetonitrile elution, 2.0 cm^3 min^{-1}, t_R 14.12 min) afforded a spectroscopically pure sample of *adduct* **59** (Found: M^+, 240.0514. $C_{12}H_{17}{}^{79}Br$ requires *M*, 240.0514); ν_{max}(NaCl)/cm^{-1} 3029, 2917, 2858, 1659, 1461, 1218, 1119, 1021, 973, 907 and 858; δ_H 5.52 (1 H, m, 3- or 4-H), 5.40 (1 H, m, 4- or 3-H), 2.96 (1 H, m), 2.55 (1 H, d, *J* 18), 2.16–2.01 (2 H, m), 1.92–1.68 (6 H, complex m), 1.57–1.17 (4 H, complex m) and 1.09 (1 H, dd, *J* 10.1 and 6.9, 7-H); δ_C 124.5 (C, C-3 and -4 overlapping), 55.1 (C, C-6), 38.1 (CH_2), 36.1 (CH_2), 32.4 (CH_2), 32.1 (CH_2), 29.6 (CH_2), 28.5 (CH_2), 28.1 (C, C-1), 26.8 (CH, C-7) and 26.0 (CH_2); *m*/*z* (%) 242 (7) and 240 (9) (M^+), 161 (100) (M^+ − Br) and 133 (23) (M^+ − Br − CH_2=CH_2).

(1′S,6′S,7′S,12′S)-6′-*Chlorotricyclo*[5.5.0.0$^{1',6'}$]*dodec*-3′-*en*-12′-*yl Acetate* **60**.—Reaction of compound **26** (500 mg, 1.62 mmol) with TBAF (537 mg, 1.70 mmol) in THF (5.5 cm^3) in the presence of buta-1,3-diene (~ 2–3 cm^3) for three days afforded a slightly yellow, viscous oil (620 mg). Subjection of this material to PLC (silica; dichloromethane) afforded a single major band (R_f 0.8), which upon extraction (dichloromethane) afforded the *adduct* **60** (402 mg, 97%) as a clear oil (Found: M^+ − Cl, 219.1384. $C_{14}H_{19}O_2$ requires *m*/*z* 219.1385); ν_{max}(NaCl)/cm^{-1} 2976, 2927, 2851, 1736, 1661, 1442, 1362, 1242, 1024 and 961; δ_H 5.57 (1 H, m, 3′- or 4′-H), 5.47 (1 H, m, 4′-or 3′-H), 5.10 (1 H, d, *J* 11, 12′-H), 2.91–2.68 (3 H, m), 2.37 (1 H, m), 2.10–2.00 (1 H, complex m), 2.05 (3 H, s, OAc), 1.95–1.72 (4 H, complex m), 1.56–1.40 (2 H, complex m) and 1.30–1.16 (2 H, m); δ_C 169.9 (C, OCOMe), 124.1 (CH, C-3′ or -4′), 123.1 (CH, C-4′ or -3′), 74.6 (CH, C-12′), 55.1 (C, C-6′), 35.7 (CH_2), 32.3 (CH_2), 30.1 (C, C-1′), 27.6 (CH_2), 27.0 (CH_2), 26.0 (CH_2, C-7′), 25.9 (CH_2), 25.0 (CH_2) and 21.4 (CH_3, OCO*Me*); *m*/*z* (%) 226 (3), 218 (1) (M^+ − HCl), 158 (43), 117 (91) and 91 (100) ($C_7H_7^+$).

(1S,8S,9S)-9-*Chlorotricyclo*[6.5.0.0^{1,9}]*tridec*-11-*ene* **62**.— Treatment of a THF (6 cm^3) solution of compound **16** (0.50 g, 1.88 mmol) with TBAF (890 mg, 2.82 mmol) in the presence of buta-1,3-diene (~ 3.0 cm^3) gave a homogeneous mixture, which was stirred at room temperature for five days. The light yellow oil (416 mg) obtained after work-up was purified by flash chromatography (silica; light petroleum) which, after concentration of the appropriate fractions (R_f 0.6), afforded the title compound **62** (362 mg, 91%) as a clear oil which was contaminated with a small amount (< 5%) of unchanged cyclopropene **55**. Subjection of this material to reversed-phase HPLC (C_{18} column; acetonitrile, 2.0 cm^3 min^{-1}, t_R 15.14 min) afforded a spectroscopically pure sample of *adduct* **62** (Found: M^+, 210.1175. $C_{13}H_{19}{}^{35}Cl$ requires *M*, 210.1175); ν_{max}(NaCl)/cm^{-1} 3030, 2969, 2921, 2857, 1660, 1466, 1447, 1217, 1093, 1079 and 950; δ_H 5.55–5.42 (2 H, complex m, 11- and 12-H), 2.83 (1 H, dm, *J* 19.0), 2.71 (1 H, dm, *J* 19.0), 2.47 (1 H, dm, *J* 17.0), 2.14 (1 H, dm, *J* 17.0), 1.90–1.25 (12 H, complex m) and 0.88 (1 H, dd, *J* 11.0 and 3.0, 8-H); δ_C 124.2 (CH, C-11 or -12), 123.7 (C, C-12 or -11), 53.4 (C, C-9), 35.9 (CH_2), 30.5 (CH_2), 29.7 (CH_2), 28.5 (CH_2), 26.3 (CH_2, two signals overlapping), 25.4 (CH, C-8), 25.1 (CH_2), 25.0 (C, C-1) and 24.0 (CH_2); *m*/*z* (%) 212 (6) and 210 (19) (M^+), 175 (39) (M^+ − Cl), 105 (42) and 91 (100).

General Procedure for the Reaction of β,β-*Dichloro*-(*trimethylsilyl*)*cyclopropanes* **13**–**16** *and* **26** *with TBAF in the Presence of Furan*.—A solution of the appropriate β,β-dichloro(trimethylsilyl)cyclopropane (1.0 mol equiv.) in freshly distilled furan (4–8 cm^3 mmol^{-1}) was stirred magnetically while being maintained under dry nitrogen, and cooled on an ice-water-bath. TBAF (as a 1.0 mol dm^{-3} solution in THF, 1.5 mol equiv.) was added dropwise over a period of *ca.* 10 min. The mixture was stirred on the ice-bath for 1 h. The reaction vessel was then stoppered, and maintained at room temperature for the specified time, then diluted with water and extracted with dichloromethane. The combined extracts were washed twice with water, and dried, filtered, and then concentrated under reduced pressure to afford the crude product which, upon subjection to flash chromatography, afforded spectroscopically pure material.

(1R,2R,7S,8S,9S)-8-*Chloro*-12-*oxatetracyclo*[7.2.1.0^{2,7}0^{2,8}]-*dodec*-10-*ene* **64** *and* (E)-1-*Chloro*-2-(*chloromethylene*)*cyclohexane* **34**.—Treatment of a solution of the silane **13** (540 mg, 2.28 mmol) in furan (10 cm^3) with TBAF (3.4 cm^3 of a 1.0 mol dm^{-3} solution in THF, 3.42 mmol) gave a deep red solution, which was maintained at 5 °C for 24 h, and then at room temperature for four days. The usual work-up afforded a bright yellow oil (315 mg). Subjection of this material to MPLC [silica, (5:95) diethyl ether–light petroleum] afforded two components (R_f 0.7 and 0.35).

Concentration of the fractions containing the less polar component afforded a clear oil (137 mg). GLC analysis of this material established that it was a 3:1 mixture of substrate **13** (21% recovery) and dichloride **34** (7%).

Concentration of the fractions containing the more polar material afforded the title adduct **64** (18 mg, 4%) as an oil. To remove trace impurities in this material it was subjected to reversed-phase HPLC (C_{18} column; acetonitrile, 2.0 cm^3 min^{-1}, t_R 9.08 min^{-1}) and a spectroscopically pure sample of *adduct* **64** was thereby obtained (Found: M^+ − H_2O, 178.0549. $C_{11}H_{11}{}^{35}Cl$ requires *m*/*z*, 178.0549); ν_{max}(NaCl)/cm^{-1} 2994, 2937, 2853, 1556, 1460, 1444, 1295, 1035, 1008, 924, 911 and 704; δ_H 6.66 (2 H, m, 10- and 11-H), 4.76 (1 H, s, 1- or 9-H), 4.47 (1 H, d, *J* 1.2, 9- or 1-H), 2.26 (1 H, dd, *J* 9.0 and 2.4, 7-H), 1.95 (1 H, m), 1.78 (1 H, m), 1.45 (1 H, m), 1.35 (4 H, m) and 1.30–1.15 (1 H, complex m); δ_C 138.2 (C-10 or -11), 137.7 (C-11 or -10), 82.4 (C-1 or -9), 81.8 (C-9 or -1), 60.4 (C-8), 31.8 (C-2), 27.1, 21.3, 21.0, 20.9 and 19.5; *m*/*z* (%) 169 (8), 167 (28) (M^+ − CHO), 161 (26) (M^+ − Cl), 127 (33) and 125 (100).

(1R,2R,8S,9S,10S)-9-*Chloro*-13-*oxatetracyclo*[8.2.1.0^{2,8}.0^{2,9}]-*tridec*-11-*ene* **65**, (1S,2R,8S,9S,10R)-9-*Chloro*-13-*oxatetracyclo*-[8.2.1.0^{2,8}.0^{2,9}]*tridec*-11-*ene* **69** *and* (E)-1-*Chloro*-2-(*chloromethylene*)*cycloheptane* **48**.—Treatment of a solution of the silane **14** (3.0 g, 11.94 mmol) in furan (40 cm^3) with TBAF (21.5 cm^3 of a 1.0 mol dm^{-3} solution in THF, 21.5 mmol) afforded an orange solution, which was maintained at room temperature for

six days. The usual work-up afforded a dark orange oil. Subjection of this material to MPLC [silica; (7.5:92.5) diethyl ether–light petroleum] afforded three major components (R_f 0.5, 0.4 and 0.1).

Concentration of the fractions containing the least mobile component afforded the *adduct* **65** (1.74 g, 69%) as a clear oil (Found: M^+, 210.0811. $C_{12}H_{15}{}^{35}ClO$ requires *M*, 210.0811); ν_{max}(NaCl)/cm^{-1} 2997, 2919, 2850, 1555, 1461, 1296, 1014, 919, 837, 786 and 708; δ_H 6.72 (1 H, dd, *J* 5.6 and 1.5, 11-or 12-H), 6.66 (1 H, dd, *J* 5.7 and 1.5, 12- or 11-H), 4.77 (1 H, d, *J* 1.4, 1- or 10-H), 4.70 (1 H, d, *J* 1.4, 9- or 1-H), 2.23 (1 H, dd, *J* 9.2 and 6.6, 8-H), 1.86 (2 H, m), 1.81 (2 H, m) and 1.60–1.09 (6 H, complex m); δ_C 139.7 (CH, C-11 or -12), 139.3 (CH, C-12 or -11), 81.3 (CH, C-1 or -10), 80.5 (CH, C-10 or -1), 63.8 (C, C-9), 38.6 (C, C-2), 34.6 (CH, C-8), 32.6 (CH_2), 28.5 (CH_2), 27.9 (CH_2), 26.9 (CH_2) and 25.5 (CH_2); *m*/*z* (20 eV) (%) 183 (5) and 181 (15) (M^+ − CHO), 175 (12) (M^+ − Cl), 127 (35) and 125 (100).

Concentration of the fractions containing the component of intermediate mobility afforded a light yellow solid, recrystallisation (pentane) of which gave the *minor adduct* **69** (197 mg, 8%) as plates, m.p. 51.5–52.5 °C (Found: M^+, 210.0811; C, 68.6; H, 7.5; Cl, 17.1%. $C_{12}H_{15}{}^{35}ClO$ requires *M*, 210.0811; C, 68.4; H, 7.2; Cl, 16.8%); ν_{max}(NaCl)/cm^{-1} 2985, 2919, 2849, 1461, 1448, 1440, 1304, 1130, 992, 868 and 845; δ_H 6.28 (1 H, dd, *J* 5.7 and 1.8, 11- or 12-H), 6.20 (1 H, dd, *J* 5.9 and 1.7, 12- or 11-H), 4.92 (1 H, t, *J* 2, 1- or 10-H), 4.73 (1 H, t, *J* 2, 10- or 1-H), 2.08 (1 H, dd, *J* 15.5 and 7.5), 1.91–1.58 (6 H, complex m) and 1.45–1.10 (4 H, complex m); δ_C 134.2 (CH, C-11 or -12), 131.7 (CH, C-12 or -11), 88.5 (CH, C-1 or -9), 86.6 (CH, C-9 or -1), 62.4 (C, C-9), 46.1 (CH, C-8), 34.8 (C, C-2), 32.1 (CH_2), 28.3 (CH_2), 27.9 (CH_2) (two signals overlapping) and 26.5 (CH_2); *m*/*z* (%) 212 (0.7) and 210 (2) (M^+), 175 (62) (M^+ − Cl), and 127 (33) and 125 (100).

Concentration of the fractions containing the most mobile component, followed by subjection of this material to flash chromatography (silica; light petroleum) afforded, after concentration of the appropriate fractions (R_f 0.5), dichloroalkene **48** (123 mg, 6%) which was identical in all respects with material obtained previously.

(1′R,2′S,3′S,8′S,9′S,10′S)-9′-*Chloro*-13′-*oxatetracyclo*-[8.2.1.0$^{2',8'}$.0$^{2',9'}$]*tridec*-11′-*en*-3′-*yl Acetate* **66** *and* (1′S,2′S,-3′S,8′S,9′S,10′R)-9′-*Chloro*-13′-*oxatetracyclo*[8.2.1.0$^{2',8'}$.0$^{2',9'}$]-*tridec*-11′-*en*-3′-*yl Acetate* **70**.—Treatment of a solution of the silane **26** (1.0 g, 3.23 mmol) in furan (20 cm^3) with TBAF (4.85 cm^3 of a 1.0 mol dm^{-3} in THF, 4.85 mmol) afforded a yellow solution, which was stirred at room temperature for 30 h. The usual work-up afforded a pale yellow oil (890 mg). Subjection of this material to flash chromatography [silica; (5:95) diethyl ether–dichloromethane] afforded two major components (R_f 0.6 and 0.3).

Concentration of the fractions containing the more mobile component afforded *adduct* **66** (722 mg, 83%) as a clear oil (Found: M^+ − CH_3CO_2H − CHO, 179.0627. $C_{11}H_{12}{}^{35}Cl$ requires *m*/*z*, 179.0627); ν_{max}(NaCl)/cm^{-1} 2998, 2927, 2853, 1736, 1558, 1449, 1372, 1238, 1039, 1024, 915 and 718; δ_H 6.65 (1 H, dd, *J* 5.6 and 1.7, 11′- or 12′-H), 6.53 (1 H, dd, *J* 5.6 and 1.7, 12′- or 11′-H), 4.82 (1 H, br d, *J* 10, 3′-H), 4.78 (1 H, d, *J* 1.7, 1′- or 10′-H), 4.76 (1 H, d, *J* 1.7, 10′- or 1′-H), 2.32–2.25 (1 H, complex m), 2.02 (3 H, s, OAc), 2.00–1.75 (4 H, complex m), 1.45 (1 H, m) and 137–1.18 (3 H, complex m); δ_C 168.9 (C, *O*COMe), 140.7 (CH, C-11′ or -12′), 135.6 (CH, C-12′ or -11′), 81.5 (CH, C-1′ or -10′), 78.6 (CH, C-10′ or -1′), 70.2 (CH, C-3′), 62.4 (C, C-9′), 41.1 (C, C-2′), 36.1 (CH_2), 33.3 (CH, C-8′), 27.6 (CH_2), 26.3 (CH_2), 26.2 (CH_2) and 21.5 (CH_3, OCO*Me*); *m*/*z* (FAB) (%) 401 (2) and 399 (6) ([M + thioglycerol + Na]$^+$); *m*/*z* (15 eV) (%) 181 (18) and 179 (52) (M^+ − CH_3CO_2H − CHO) and 145 (100).

Concentration of the fractions containing the less mobile component afforded a solid, recrystallisation (diethyl ether–pentane) of which afforded *adduct* **70** (81 mg, 9%) as needles, m.p. 97–98 °C (Found: M^+, 268.0866; C, 62.7; H, 6.2; Cl, 13.4%. $C_{14}H_{17}{}^{35}ClO_3$ requires *M*, 268.0866; C, 62.6; H, 6.4; Cl, 13.2%); ν_{max}(KBr)/cm^{-1} 2932, 1730, 1460, 1446, 1372, 1360, 1243, 1235, 1024, 880 and 855; δ_H 6.35 (1 H, dd, *J* 5.8 and 1.8, 11′- or 12′-H), 6.22 (1 H, dd, *J* 5.9 and 1.8, 12′-or 11′-H), 5.24 (1 H, br t, *J* 1.8, 3′-H), 5.01 (1 H, br d, *J* 10.4, 1′- or 10′-H), 4.92 (1 H, br t, *J* 1.8, 10′- or 1′-H), 2.09 (3 H, s, OAc), 1.90 (2 H, m), 1.85–1.60 (4 H, complex m), 1.45 (1 H, m), 1.30 (1H, m) and 1.13 (1 H, m); δ_C 169.7 (C, OCOMe), 134.1 (CH, C-11′ or -12′), 133.1 (CH, C-12′ or -11′), 87.7 (CH, C-1′ or -10′), 80.8 (CH, C-10′ or -1′), 70.3 (CH, C-3′), 60.7 (C, C-9′), 44.6 (CH, C-8′), 37.5 (C, C-2′), 35.8 (CH_2), 27.6 (CH_2), 26.4 (CH_2), 26.1 (CH_2) and 21.3 (CH_3, OCO*Me*); *m*/*z* (18 eV) (%) 233 (25) (M^+ − Cl), 181 (20) and 179 (54) (M^+ − CH_3CO_2H − CHO) and 173 (100) (M^+ − Cl − CH_3CO_2H).

(1′R,2′S,3′S,8′S,9′S,10′S)-9′-*Chloro*-13′-*oxatetracyclo*-[8.2.1.0$^{2',8'}$.0$^{2',9'}$]*tridec*-11′-*en*-3′-*yl* p-*Nitrobenzoate* **67**.—A solution of acetate **66** (377 mg, 1.40 mmol) in methanol (15 cm^3) was treated with anhydrous potassium carbonate (390 mg, 2.80 mmol). The suspension was stirred at room temperature until TLC analysis [silica; dichloromethane, R_f (acetate) 0.5, R_f (alcohol) 0.2] indicated that hydrolysis was complete (6 h). The reaction mixture was then poured into water (100 cm^3) and extracted with diethyl ether (4 × 25 cm^3). The combined extracts were dried, filtered, and then concentrated under reduced pressure to afford a solid (313 mg). Subjection of this material to flash chromatography [silica; (5:95) diethyl ether–dichloromethane] afforded, after concentration of the appropriate fractions (R_f 0.5), (1R,2S,-3S,8S,9S,10S)-9-*chloro*-13-*oxatetracyclo*[8.2.1.0^{2,8}.0^{2,9}]*tridec*-11-*en*-3-*ol* (292 mg, 92%). Recrystallisation (diethyl ether–light petroleum) of this material afforded the analytically pure alcohol as clear cubes, m.p. 96–97 °C (Found: C, 63.4; H, 6.9; Cl, 15.9. $C_{12}H_{15}ClO_2$ requires C, 63.6; H, 6.7; Cl, 15.6%); ν_{max}(KBr)/cm^{-1} 3393, 2998, 2921, 2851, 1556, 1450, 1336, 1298, 1065, 1003, 914, 720, 623 and 484; δ_H 6.80 (1 H, dd, *J* 5.6 and 1.7, 11- or 12-H), 6.58 (1 H, dd, *J* 5.6 and 1.7, 12- or 11-H), 4.81 (1 H, d, *J* 1.7, 1- or 10-H), 4.72 (1 H, d, *J* 1.7, 10- or 1-H), 3.73 (1 H, dt, *J* 11.0 and 2.7, 3-H), 2.21 (1 H, dd, *J* 11.6 and 6.8, 8-H), 2.05–1.80 (4 H, complex m), 1.75 (1 H, m), 1.51 (1 H, d, *J* 3.2, OH) and 1.35–1.10 (3 H, complex m); δ_C 141.4 (CH, C-11 or -12), 135.9 (CH, C-12 or -11), 81.5 (CH, C-1 or -10), 78.8 (CH, C-10 or -1), 68.6 (CH, C-3), 62.8 (C, C-9), 42.3 (C, C-2), 38.0 (CH_2), 33.1 (CH, C-2), 28.0 (CH_2) and 26.1 (CH_2, two signals overlapping); *m*/*z* (15 eV) (%) 191 (9) (M^+ − Cl), 181 (31) and 179 (100) (M^+ − CHO − H_2O), 145 (78), 141 (37) and 125 (47).

The alcohol (97 mg, 0.43 mmol) obtained above was dissolved in dry pyridine (5 cm^3) and *p*-nitrobenzoyl chloride (88 mg, 0.473 mmol) was added in one portion. The solution was stirred under nitrogen for 7.5 h, at which time further *p*-nitrobenzoyl chloride (88 mg, 0.473 mmol) was added, and the mixture was then stirred at room temperature overnight. The reaction mixture was poured into water (50 cm^3) and extracted with dichloromethane (4 × 30 cm^3). The combined extracts were washed successively with HCl (3 × 50 cm^3 of a 2 mol dm^{-3} aq. solution) and water (2 × 50 cm^3), before being dried, filtered, and then concentrated under reduced pressure to afford a slightly yellow solid (171 mg). Subjection of this material to flash chromatography (silica; dichloromethane) afforded, after concentration of the appropriate fractions (R_f 0.6), a solid. Recrystallisation (diethyl ether–pentane) of this material afforded the *ester* **67** (147 mg, 91%) as cubes, m.p. 145.5–146.5 °C (Found: C, 60.7; H, 5.0; Cl, 9.7; N, 3.8. $C_{19}H_{18}ClNO_5$ requires C, 60.7; H, 4.8; Cl, 9.4; N, 3.7%); ν_{max}(KBr)/cm^{-1} 3109, 3011, 2923, 2861, 1722, 1605, 1595, 1522, 1347, 1269, 1116, 1102 and 1093; δ_H 8.33 (2 H, d, *J* 9.0), 8.20 (2 H, d, *J* 9.0), 6.52 (2 H, m,

11'- and 12'-H), 5.22 (1 H, br d, *J* 10.3, 3'-H), 4.90 (1 H, br s, 1'- or 10'-H), 4.81 (1 H, br s, 10'- or 1'-H), 2.35 (1 H, m), 2.20–1.85 (5 H, complex m), 1.60–1.45 (1 H, m) and 1.45–1.30 (2 H, complex m); δ_C 162.8, 150.5, 140.0, 136.8, 135.8, 130.6, 123.7, 81.5 (C-1' or -10'), 78.4 (C-10' or -1'), 72.0 (C-3'), 62.4 (C-9'), 41.1 (C-2'), 36.3, 33.5, 27.6, 26.3 and 26.0; *m/z* (%) 340 (3) ($M^+ - Cl$), 313 (3), 311 (3), 181 (29), 179 (73) and 150 (100).

(1R,2R,9S,10S,11S)-10-*Chloro*-14-*oxatetracyclo*-[9.2.1.$0^{2,9}$.$0^{2,10}$]*tetradec*-12-*ene* **68** *and* (1S,2R,9S,10S,11R)-10-*Chloro*-14-*oxatetracyclo*[9.2.1.$0^{2,10}$]*tetradec*-12-*ene* **71**.—Treatment of a solution of the silane **16** (0.50 g, 1.88 mmol) in furan (10 cm^3) with TBAF (2.82 cm^3 of a 1.0 mol dm^{-3} solution in THF, 2.82 mmol) resulted in a yellow solution, which was maintained at room temperature for five days. The usual work-up afforded an orange oil (0.53 g). Subjection of this material to flash chromatography [silica; (93:7) light petroleum–diethyl ether] afforded three components (R_f 0.7, 0.4 and 0.15).

Concentration of the fractions containing the least polar component afforded an oil (130 mg). GLC analysis of this material indicated that it consisted of a ~2:1 mixture of cyclopropene **55** (14%) (see above) and starting silane **16** (7% recovery).

Concentration of the fractions containing the component of intermediate mobility afforded the *adduct* **68** (265 mg, 63%) as a clear oil (Found: M^+, 224.0968. $C_{13}H_{17}{}^{35}ClO$ requires *M*, 224.0968); ν_{max}(NaCl)/cm^{-1} 2993, 2922, 2853, 1555, 1466, 1446, 1296, 1018, 917 and 804; δ_H 6.68 (1 H, dd, *J* 5.7 and 1.4, 12- or 13-H), 6.65 (1 H, dd, *J* 5.7 and 1.4, 13- or 12-H), 4.78 (1 H, d, *J* 1.4, 1- or 11-H), 4.65 (1 H, d, *J* 1.4, 11- or 1-H), 2.00 (1 H, dd, *J* 12.2 and 3.7, 9-H), 1.81 (1 H, m) and 1.70–1.20 (11 H, complex m); δ_C 138.7 (CH, C-12 or -13), 138.3 (CH, C-13 or -12), 81.1 (CH, C-1 or -11), 80.1 (CH, C-11 or -1), 58.3 (C, C-10), 35.9 (C, C-2), 33.0 (CH, C-9), 28.7 (CH_2), 27.4 (CH_2), 26.6 (CH_2), 26.2 (CH_2), 25.4 (CH_2) and 22.1 (CH_2); *m/z* (20 eV) (%) 206 (2) ($M^+ - H_2O$), 197 (21) and 195 (45) ($M^+ - CHO$), 189 (63) ($M^+ - Cl$), 153 (82), and 141 (36) and 139 (100).

Concentration of the fractions containing the least mobile component afforded a waxy solid. Recrystallisation (pentane) of this material afforded *adduct* **71** (58 mg, 14%) as prisms, m.p. 64–65 °C (Found: C, 69.5; H, 7.5; Cl, 16.1. $C_{13}H_{17}ClO$ requires C, 69.5; H, 7.6; Cl, 15.8%); ν_{max}(KBr)/cm^{-1} 2959, 2925, 2906, 1464, 1444, 1299, 1243, 965, 869 and 728; δ_H 6.32 (1 H, dd, *J* 5.8 and 2.0, 12- or 13-H), 6.19 (1 H, dd, *J* 5.8 and 2.0, 13- or 12-H), 4.93 (1 H, t, *J* 2.0, 1- or 11-H), 4.79 (1 H, t, *J* 2.0, 11- or 1-H), 1.98 (1 H, m), 1.80–1.50 (5 H, complex m) and 1.50–1.20 (7 H, complex m); δ_C 133.5 (C-12 or -13), 132.2 (C-13 or -12), 88.8 (C-1 or -11), 83.9 (C-11 or -1), 58.7 (C-10), 44.4 (C-9), 32.0 (C-2), 28.2, 27.5, 26.5, 26.4, 24.5 and 24.1; *m/z* (%) 226 (0.4) and 224 (1.2) (M^+), 189 (68) ($M^+ - Cl$), 127 (33), 125 (100) and 91 (84) ($C_7H_7^+$).

2,3-*Dimethylene*-1,4-*dioxane*.—Yellow mercury(II) oxide (48.6 g, 0.224 mol) was dissolved in a mixture of HNO_3 (70% w/w; 60 cm^3) and water (30 cm^3). When dissolution was complete, additional water (20 cm^3) and ethylene glycol (100 cm^3) were added cautiously. The mixture was cooled to 20 °C using a cold-water-bath, and buta-1,3-diene was bubbled through the magnetically stirred solution at about 5 bubbles s^{-1} for 4 h. During this time, a light grey precipitate formed. The resulting suspension was cooled to −5 °C, and the solid was collected and dried at the pump (5 h) to give 2,3-bis-(nitratomercuriomethyl)-1,4-dioxane as a grey solid (62.7 g, 86%). This material was dissolved in 10% aq. sodium hydroxide (400 cm^3). Addition of aq. potassium iodide (26.6 g in 100 cm^3) resulted in rapid precipitation of a grey solid. After the mixture had been stirred for 2 h, the precipitate was collected and dried at ~50 °C overnight to afford 2,3-bis(iodomercuriomethyl)-1,4-dioxane (57.5 g) as a grey powder, m.p. ~180 °C. This material was stirred vigorously at reflux with a mixture of chloroform (174 cm^3), water (43 cm^3) and iodine (39.8 g) for 12 h. An intensely fluorescent orange-pink mixture was obtained. Upon cooling, the mixture was transferred to a separating funnel and treated with 10% aq. sodium thiosulfate (500 cm^3), resulting in a discharge of the fluorescent colour. The organic layer was washed successively with further 10% thiosulfate (2 × 400 cm^3) and 10% aq. potassium iodide (250 cm^3). The chloroform layer was washed with water (1 × 300 cm^3) and dried, filtered, and then concentrated under reduced pressure to afford an off-white solid. Recrystallisation (methanol) gave a mixture of *cis*- and *trans*-2,3-bis(iodomethyl)-1,4-dioxane[30] (19.6 g, 24% from HgO). Further recrystallisation of this material gave pure *trans*-2,3-bis(iodomethyl)-1,4-dioxane as prisms, m.p. 89–90 °C (Found: M^+, 367.8774. Calc. for $C_6H_{10}{}^{127}I_2O_2$: *M*, 367.8774); ν_{max}(KBr)/cm^{-1} 2956, 2853, 1421, 1407, 1340, 1266, 1194 and 1127; δ_H 3.80 (4 H, m), 3.25 (2 H, m) and 3.20–3.10 (4 H, m); δ_C 77.5 (OCH), 66.9 (OCH_2) and 4.5 (CH_2I); *m/z* (%) 368 (0.6) (M^+), 241 (0.6) ($M^+ - I$) and 73 (100).

A solution of *cis*- and *trans*-2,3-bis(iodomethyl)-1,4-dioxane (1 mol equiv.) in anhydrous benzene (4 cm^3 g^{-1}) was treated in one portion with DBU (2 mol equiv.). The resulting clear solution was stirred at room temperature for 15–20 h, during which time a thick precipitate of DBU hydroiodide was formed. The reaction mixture was then diluted with an equal volume of pentane and filtered. The solids thus retained were washed with 1:1 benzene–pentane and the combined filtrates were concentrated under reduced pressure (to about one quarter of the original volume of benzene used) to give a solution of the title diene, which was used immediately in the subsequent Diels–Alder reactions.

General Procedure for the Reaction of β,β-*Dichloro*-(*trimethylsilyl*)*cyclopropanes* **13–16** *and* **26** *with TBAF in the Presence of* 2,3-*Dimethylene*-1,4-*dioxane*.—A mixture of the appropriate cyclopropane (1 mol equiv.) and the title diene (~2–3 mol equiv. as a solution in benzene) were cooled on an ice-bath and stirred under nitrogen. TBAF (~1.5 mol equiv. as a 1.0 mol dm^{-3} solution in THF) was added over a period of 10 min. The cooling bath was removed after 30 min, and the solution was stirred at room temperature for the specified time. Work-up consisted of dilution of the reaction mixture with water, extraction with dichloromethane, and washing of the combined extracts with water. The extracts were dried, filtered, and then concentrated under reduced pressure. Subjection of the material thus obtained to chromatographic filtration [silica; dichloromethane or (5:95) diethyl ether–dichloromethane] afforded, after concentration of the filtrate, material which was subsequently purified by flash chromatography and/or recrystallisation.

(1S,10S,11S)-10-*Chloro*-4,7-*dioxatetracyclo*[8.6.0.$0^{1,11}$.$0^{3,8}$]-*hexadec*-3(8)-*ene* **58** *and* (E)-1-*Chloro*-2-(*chloromethylene*)*cycloheptane* **48**.—Reaction of the silane **14** (3.0 g, 11.94 mmol) with 2,3-dimethylene-1,4-dioxane (~23.9 mmol) and TBAF (18 cm^3 of a 1.0 mol dm^{-3} solution in THF, 18 mmol) in benzene (15 cm^3) for four days afforded, after the usual work-up, a pale yellow oil (3.89 g). Subjection of this material to flash chromatography (silica; dichloromethane) afforded two components (R_f 0.85 and 0.5).

Concentration of the fractions containing the more polar material afforded a light yellow solid. Recrystallisation (light petroleum) of this material gave the *adduct* **58** (2.48 g, 82%) as rectangular, opaque prisms, m.p. 61–62 °C (Found: C, 66.0; H, 7.7; Cl, 14.2. $C_{14}H_{19}ClO_2$ requires C, 66.0; H, 7.5; Cl, 13.9%); ν_{max}(KBr)/cm^{-1} 2978, 2917, 2847, 1720, 1456, 1444, 1324, 1278, 1198 and 1135; δ_H 4.00 (4 H, m, OCH_2CH_2O), 2.95 (1 H, dt, *J*

15.9 and 2.5, 2- or 9-H), 2.80 (1 H, br dt, *J* 15.9 and 1.7, 9- or 2-H), 2.50 (1 H, br d, *J* 16.1, 9-H or 2-H), 2.31 (1 H, dt, *J* 16.1 and 2.2, 9- or 2-H), 2.00 (1 H, p, *J* 6.8), 1.92–1.70 (5 H, complex m) and 1.55–1.16 (5 H, complex m); δ_C 127.2 (C-3 or -8), 126.3 (C-8 or -3), 64.5 (OCH_2CH_2O), 64.4 (OCH_2CH_2O), 55.7 (C-10), 37.3, 33.9, 33.0, 32.3, 29.0 (C-1), 28.5, 27.8, 26.6 and 26.2; *m/z* (%) 256 (32) and 254 (100) (M^+), 219 (60) ($M^+ - Cl$), 218 (45) ($M^+ - HCl$) and 149 (84).

Concentration of the fractions containing the less polar material afforded an oil (340 mg). Subjection of this material to flash chromatography (silica; light petroleum) afforded, after concentration of the appropriate fractions (R_f 0.5), the dichloroalkene **48** (158 mg, 7.4%), which was identical in all respects with the material obtained previously.

(1′S,10′S,11′S,16′S)-10′-*Chloro*-4′,7′-*dioxatetracyclo*-[8.6.0.0$^{1',11'}$.0$^{3',8'}$]*hexadec*-3′(8′)-*en*-16′-*yl Acetate* **61**.—Reaction of the silane **26** (1.0 g, 3.23 mmol) with 2,3-dimethylene-1,4-dioxane (~6.5 mmol) and TBAF (4.85 cm^3 of a 1.0 mol dm^{-3} solution in THF, 4.85 mmol) in benzene (7 cm^3) for three days afforded, after the usual work-up, a pale yellow oil. Subjection of this material to flash chromatography (silica; dichloromethane) afforded, after concentration of the appropriate fractions (R_f 0.74), a light yellow solid. Recrystallisation of this material (diethyl ether–hexane) afforded *adduct* **61** (919 mg, 98%) as large prisms, m.p. 133–134.5 °C (Found: C, 61.4; H, 6.5; Cl, 11.6. $C_{16}H_{21}ClO_4$ requires C, 61.4; H, 6.8; Cl, 11.3%); ν_{max}(KBr)/cm^{-1} 2919, 2874, 2852, 1727, 1453, 1441, 1365, 1244, 1197, 1021, 910 and 885; δ_H 5.00 (1 H, d, *J* 11.2, 16′-H), 4.02 (4 H, m, OCH_2CH_2O), 2.98 (1 H, dt, *J* 15.6 and 2.5, 2′- or 9′-H), 2.91 (1 H, br dt, *J* 15.9 and 2.2, 9′- or 2′-H), 2.82 (1 H, dt, *J* 15.6 and 1.7, 2′- or 9′-H), 2.30 (1 H, br dt, *J* 15.9 and 1.7, 9′- or 2′-H), 2.06 (1 H, m), 2.04 (3 H, s OAc), 1.90–1.70 (4 H, complex m), 1.45 (2 H, m) and 1.25 (2 H, m); δ_C 169.8 (*O*C*O*Me), 127.0 (C-3′ or -8′), 125.7 (C-8′ or -3′), 74.3 (C-16′), 64.5 (OCH_2CH_2O), 64.4 (OCH_2CH_2O), 53.8 (C-10′), 37.1, 32.6, 30.9 (C-1′), 27.6, 27.1, 26.9, 26.7, 25.8 and 21.3 (OCO*Me*); *m/z* (%) 314 (2) and 312 (8) (M^+), 254 (6) and 252 (20) ($M^+ - CH_3CO_2H$), 217 (81) ($M^+ - CH_3CO_2H - Cl$), 203 (19), 175 (19) and 149 (100).

(1S,10S,11S)-10-*Chloro*-4,7-*dioxatetracyclo*[8.7.0.0^{1,11}.0^{3,8}]-*heptadec*-3(8)-*ene* **63**.—Reaction of the silane **16** (0.5 g, 1.87 mmol) with 2,3-dimethylene-1,4-dioxane (~6 mmol) and TBAF (2.82 cm^3 of a 1.0 mol dm^{-3} solution in THF, 2.82 mmol) in benzene (3.5 cm^3) for five days afforded, after the usual work-up, a pale yellow oil (1.05 g). Subjection of this material to flash chromatography [silica; (7:93) diethyl ether–light petroleum] afforded, after concentration of the appropriate fractions (R_f 0.3), a solid. Recrystallisation (hexanes) of this material afforded the *adduct* **63** (335 mg, 70%) as opaque prisms, m.p. 90–94 °C (Found: C, 66.9; H, 8.3; Cl, 13.3. $C_{15}H_{21}ClO_2$ requires C, 67.0; H, 7.9; Cl, 13.2%); ν_{max}(KBr)/cm^{-1} 2962, 2916, 2845, 1719, 1473, 1453, 1431, 1277, 1197, 1189, 914 and 889; δ_H 4.00 (4 H, m, OCH_2CH_2O), 2.92 (1 H, dt, *J* 15.9 and 2.6, 2-or 9-H), 2.81 (1 H, dt, *J* 15.9 and 1.7, 2- or 9-H), 2.40 (1 H, br dt, *J* 16.4 and ~2.0, 9- or 2-H), 2.33 (1 H, br dt, *J* 16.4 and 2.0, 9- or 2-H), 1.90 (1 H, m) 1.75–1.20 (11 H, complex m) and 0.90 (1 H, m); δ_C 127.1 (C, C-3 or -8), 126.1 (C, C-8 or -3), 64.5 (CH_2, OCH_2), 64.4 (CH_2, OCH_2), 51.9 (C, C-10), 37.3 (CH_2), 32.2 (CH_2), 29.5 (CH_2), 28.3 (CH_2), 26.3(2) (CH, C-11), 26.2(5) (CH_2), 26.2 (CH_2), 25.8 (C, C-1), 25.2 (CH_2) and 23.8 (CH_2); *m/z* (%) 270 (30) and 268 (91) (M^+), 233 (49) ($M^+ - Cl$), 232 (32) ($M^+ - HCl$), 175 (25), 163 (16) and 149 (100).

3′-(*Trimethylsilyl*)*but*-3′-*enyl Acetate* **73**.—A mixture of the alcohol **72**[20] (314 mg, 2.18 mmol), acetic anhydride (0.7 cm^3, 7.42 mmol) and pyridine (2.0 cm^3) was stirred at room temperature for 4 h before being quenched with water (40 cm^3) and extracted with dichloromethane (3 × 30 cm^3). The combined extracts were washed with 2 mol dm^{-3} HCl (2 × 40 cm^3), saturated aq. sodium hydrogen carbonate (1 × 50 cm^3) and water (50 cm^3), before being dried, filtered, and then concentrated under reduced pressure to give a slightly yellow oil. Subjection of this material to flash chromatography (silica; dichloromethane) afforded, after concentration of the appropriate fractions (R_f 0.7), the title acetate **73** (335 mg, 97%) as a clear oil, ν_{max}(NaCl)/cm^{-1} 2955, 1743, 1383, 1363, 1247, 1034, 929, 837 and 758; δ_H 5.62 (1 H, m, 4′-H), 5.41 (1 H, m), 4.12 (2 H, t, *J* 7.3, 1′-H_2), 2.44 (2 H, tt, *J* 7.6 and 1.3, 2′-H_2), 2.03 (3 H, s, OAc) and 0.09 (9 H, s, $SiMe_3$); δ_C 171.0 (*O*C*O*Me), 147.8 (C-3′), 126.5 (C-4′), 63.9 (C-1′), 34.5 (C-2′), 21.0 (OCO*Me*) and −1.7 ($SiMe_3$); *m/z* (15 eV) (%) 171 (40) ($M^+ - CH_3$), 129 (100) and 117 (72).

2′-[2″,2″-*Dichloro*-1″-(*trimethylsilyl*)*cyclopropyl*]*ethyl Acetate* **74**.—A solution of alkene **73** (270 mg, 1.45 mmol) and TEBAC (10 mg) in chloroform (1.5 cm^3) was cooled to 0 °C. The mixture was treated with NaOH (1.0 cm^3 of a 1:1 w/v aq. solution) and stirred at 0 °C for 20 min, and for a further 3.5 h at room temperature. The mixture was then diluted with water (40 cm^3) and extracted with dichloromethane (4 × 20 cm^3). The combined extracts were washed with water (2 × 40 cm^3), dried, filtered, and then concentrated under reduced pressure to give a slightly yellow oil (310 mg). Kugelrohr distillation (b.p. 100 °C/0.4 mmHg) afforded the *title compound* **74** (272 mg, 70%) as a clear oil (Found: M^+, 268.0453. $C_{10}H_{18}{}^{35}Cl_2{}^{28}O_2Si$ requires *M*, 268.0453); ν_{max}(NaCl)/cm^{-1} 2957, 2901, 1744, 1457, 1433, 1390, 1365, 1251, 1041, 845 and 745; δ_H 4.27 (1 H, ddd, *J* 11.0, 9.5, and 5.6, 1′-H), 4.12 (1 H, ddd, *J* 11.0, 9.3 and 6.2, 1′-H), 2.20 (1 H, ddd, *J* 14.3, 9.1 and 5.4, 2′-H), 2.04 (3 H, s, OAc), 1.61 (1 H, ddd, *J* 14.3, 9.4 and 6.3, 2′-H), 1.52 (1 H, d, *J* 6.1, 3″-H), 1.16 (1 H, d, *J* 6.1, 3″-H) and 0.18 (9 H, s, $SiMe_3$); δ_C 170.7 (C, *O*C*O*Me), 67.1 (C, C-2′), 62.5 (CH_2, C-1′), 34.7 (CH_2, C-2′), 30.3 (CH_2, C-3″), 22.8 (C, C-1″), 20.9 (CH_3, OCO*Me*) and −0.6 (CH_3, $SiMe_3$); *m/z* (15 eV) (%) 215 (< 1), 213 (4) and 211 (7), 183 (10) ($M^+ - CH_3 - Cl_2$), 172 (23), 101 (90) and 73 (100).

2′-(2″-*Chlorocycloprop*-1″-*enyl*)*ethyl Acetate* **75**.—Treatment of a solution of the cyclopropane **74** (259 mg, 0.96 mmol) in dry THF (7.0 cm^3) with a solution of TBAF (455 mg, 1.44 mmol, 1.5 mol equiv.) in THF (5 cm^3) at 0–5 °C for 40 min afforded, after the usual work-up, the *title cyclopropene* **75** (150 mg, 97%) as a clear, pungent smelling and slightly yellow oil (Found: M^+, 160.0291. $C_7H_9{}^{35}ClO_2$ requires *M*, 160.0291); ν_{max}(NaCl)/cm^{-1} 2970, 1852, 1744, 1384, 1238 and 1039; δ_H 4.25 (2 H, t, *J* 6.7, 1′-H_2), 2.74 (2 H, t, *J* 6.7, 2′-H_2), 2.04 (3 H, s, OAc) and 1.53 (2 H, s, 3″-H_2); δ_C 170.8 (*O*C*O*Me), 108.8 (C-1″ or -2″), 107.4 (C-2″ or -1″), 61.1 (C-1′), 24.9, 20.8 (OCOMe) and 16.4; *m/z* (%) 162 (0.3) and 160 (1.1) (M^+), 125 (29) ($M^+ - Cl$), 120 (5) and 118 (16) ($M^+ - C_2H_2O$), 102 (22) and 100 (68) ($M^+ - C_2H_2O - H_2O$) and 65 (100).

The cyclopropene **75** was found to be unstable as the neat liquid, but survived in solution for a number of days with little decomposition.

2′-{(1″α,6″α)-6″-*Chlorobicyclo*[4.1.0]*hept*-3″-*en*-1″-*yl*}*ethyl Acetate* **76**.—Reaction of the cyclopropane **74** (300 mg, 1.11 mmol) in THF (1 cm^3) with TBAF (1.67 cm^3 of a 1.0 mol dm^{-3} solution in THF, 1.67 mmol), in the presence of buta-1,3-diene (~2 cm^3) for six days at room temperature afforded a light yellow oil (255 mg) after work-up. Subjection of this material to flash chromatography [silica; (1:9) diethyl ether–light petroleum) afforded, after concentration of the appropriate fractions (R_f 0.3), the *title adduct* **76** (225 mg, 95%) as a clear oil (Found: $M^+ - CH_3CO_2H$, 154.0549. $C_{11}H_{15}{}^{35}ClO_2$ requires *m/z*, 154.0549); ν_{max}(NaCl)/cm^{-1} 2903, 1739, 1659, 1433, 1365, 1237, 1034 and 669; δ_H 5.48 (2 H, m, 3″- and 4″-H), 4.25 (2 H, td, *J* 6.6

and 1.5, 1'-H_2), 2.84 (1 H, dm, *J* 17.0, 2''- or 5''-H), 2.70 (1 H, dm, *J* 17.0, 2''- or 5''-H), 2.35 (2 H, m, 2 × 5''-or 2''-H), 2.05 (3 H, s, OAc), 2.03 (2 H, m, 2'-H_2), 1.16 (1 H, d, *J* 5.9, 7''-H_{endo}) and 0.78 (1 H, d, *J* 5.9, 7''-H_{exo}); δ_C 171.1 (C, *O*COMe), 124.2 (CH, C-3'' or -4''), 124.0 (CH, C-4'' or -3''), 62.4 (CH_2, C-1'), 48.7 (C, C-6''), 35.2 (CH_2), 34.6 (CH_2), 29.7 (CH_2), 23.9 (C, C-1''), 21.1 (CH_2) and 21.0 (CH_3, OCO*Me*); *m/z* (15 eV) (%) 156 (8) and 154 (12) ($M^+ - CH_3CO_2H$), 118 (100) ($M^+ - CH_3CO_2H - HCl$), 105 (23) and 91 (88) ($C_7H_7^+$).

2'-{(3''α,5''α)-5''-*Chloro*-8'',11''-*dioxatricyclo*[5.4.0.0$^{3'',5''}$]*undec*-1''(7'')-*en*-3''-*yl*}*ethyl Acetate* **77**.—Reaction of the silane **74** (1.0 g, 3.71 mmol) with 2,3-dimethylene-1,4-dioxane (~12.8 mmol) and TBAF (5.57 cm^3 of a 1.0 mol dm^{-3} solution in THF, 5.57 mmol) in benzene (5 cm^3) for four days afforded, after the usual work-up, a pale yellow oil (2.36 g). Subjection of this material to flash chromatograhy [silica; (5:95) diethyl ether–dichloromethane] afforded, after concentration of the appropriate fractions (R_f 0.60), the *adduct* **77** (852 mg, 84%) as a clear, viscous oil (Found: M^+, 272.0815. $C_{13}H_{17}{}^{35}ClO_4$ requires *M*, 272.0815); ν_{max}(NaCl)/cm^{-1} 2909, 1735, 1719, 1366, 1276, 1233, 1200, 1130, 1050, 915 and 886; δ_H 4.24 (2 H, m, 1'-H_2), 3.99 (4 H, m, OCH_2CH_2O), 2.92 (1 H, br d, *J* 15.9, 2''- or 6''-H), 2.81 (1 H, br d, *J* 15.9, 6''- or 2''-H), 2.54 (1 H, d, *J* 16.1, 2''- or 6''-H), 2.27 (1 H, d, *J* 16.1, 6''- or 2''-H), 2.05 (3 H, s, OAc), 1.98 (2 H, br t, *J* 7.0, 2'-H_2), 1.17 (1 H, d, *J* 5.7, 4''-H) and 0.85 (1 H d, *J* 5.7, 4''-H); δ_C 171.0 (C, *O*COMe), 126.9 (C, C-1'' or -7''), 126.2 (C, C-7'' or -1''), 64.4(4) (CH_2, OCH_2CH_2O), 64.3(7) (CH_2, OCH_2CH_2O), 62.3 (CH_2, C-1'), 47.3 (C, C-5''), 36.5 (CH_2, C-2'' or C-6''), 34.4 (CH_2, C-2'), 31.2 (CH_2, C-6'' or -2''), 24.4 (C, C-3''), 21.7 (CH_2, C-4'') and 21.0 (CH_3, OCO*Me*); *m/z* (%) 274 (16) and 272 (50) (M^+), 214 (4) and 212 (13) ($M^+ - CH_3CO_2H$), and 177 (100) ($M^+ - CH_3CO_2H - Cl$).

2'-{(1''α,2''α,4''α,5''α)-4''-*Chloro*-8''-*oxatricyclo*[3.2.1.0$^{2'',4''}$]*oct*-6''-*en*-2''*yl*}*ethyl Acetate* **78** *and* 2'-{(1''β,2''α,4''α,5''β)-4''-*Chloro*-8''-*oxatricyclo*[3.2.1.0$^{2'',4''}$]*oct*-6''-*en*-2''-*yl*}*ethyl Acetate* **79**.—Treatment of a solution of the silane **74** (0.50 g, 1.86 mmol) in furan (10 cm^3) with TBAF (2.8 cm^3 of a 1.0 mol dm^{-3} solution in THF, 2.8 mmol) at room temperature for five days gave, after the prescribed work-up, a yellow oil (441 mg). Subjection of this material to flash chromatography [(2:98) diethyl ether–dichloromethane] yielded two components (R_f 0.5 and 0.3).

Concentration of the fractions containing the less mobile component afforded *adduct* **78** (67 mg, 16%) as a clear oil (Found: $M^+ - Cl$, 193.0865. $C_{11}H_{13}{}^{35}ClO_3$ requires *M* – Cl, 193.0865); ν_{max}(NaCl)/cm^{-1} 2993, 2960, 1735, 1365, 1242, 1049, 863 and 731; δ_H 6.34 (1 H, dd, *J* 5.8 and 1.7, 6''- or 7''-H), 6.21 (1 H, dd, *J* 5.6 and 1.7, 7''- or 6''-H), 4.94 (1 H, t, *J* 2.0, 1''- or 5''-H), 4.89 (1 H, t, *J* 2.0, 5''- or 1''-H), 4.35 (1 H, dt, *J* 11.0 and 6.5, 1'-H), 4.17 (1 H, dt, *J* 11.0 and 6.6, 1'-H), 2.24 (1 H, m, 2'-H), 2.04 (3 H, s, OAc), 1.90 (1 H, dt, *J* 14.7 and 6.6, 2'-H), 1.59 (1 H, dd, *J* 6.6 and 1.2, 3''-H) and 1.35 (1 H, d, *J* 6.6, 3''-H); δ_C 170.8 (C, *O*COMe), 134.4 (CH, C-6'' or -7''), 133.0 (CH, C-7'' or -6''), 87.6 (CH, C-1'' or C-5''), 83.9 (CH, C-5'' or -1''), 63.1 (CH_2, C1'), 55.2 (C, C-4''), 38.5 (CH_2, C-3''), 30.4 (C, C-2''), 29.4 (CH_2, C-2') and 20.9 (CH_3, OCO*Me*); *m/z* (%) 193 (2) ($M^+ - Cl$), 141 (34) and 139 (100) ($M^+ - CH_3CO_2H - CHO$), 133 (24), and 105 (28) and 103 (61).

Concentration of the fractions containing the more mobile component afforded *adduct* **79** (304 mg, 72%), as a clear oil (Found: $M^+ - Cl$, 193.0865); ν_{max}(NaCl)/cm^{-1} 2999, 1738, 1364, 1296, 1237, 1051, 926 and 875; δ_H 6.73 (1 H, dd, *J* 5.7 and 1.5, 6''- or 7''-H), 6.70 (1 H, dd, *J* 5.7 and 1.5, 7''- or 6''-H), 4.85 (1 H, d, *J* 1.5, 1''- or 5''-H), 4.73 (1 H. d, *J* 1.5, 5''- or 1''-H), 4.30 (1 H, dt, *J* 11.0 and 5.6, 1'-H), 4.16 (1 H, ddd, *J* 11.0, 8.3 and 5.8, 1'-H), 2.15 (1 H, dd, *J* 6.1 and 1.5, 3''-H), 2.09 (3 H, s, OAc), 1.81 (1 H, m, 2'-H), 1.63 (1 H, dt, *J* 15.1 and 5.7, 2'-H) and 1.09 (1 H, d, *J* 6.1, 3''-H); δ_C 170.8 (C, *O*COMe), 139.2 (CH, C-6'' or -7''), 138.9 (CH, C-7'' or -6''), 80.6 (CH, C-1'' or -5''), 80.5 (CH, C-5'' or -1''), 63.7 (CH_2, C-1'), 55.2 (C, C-4''), 34.0 (C, C-2''), 27.9 (CH_2, C-2'), 27.3 (CH_2, C-3'') and 21.0 (CH_3, OCO*Me*); *m/z* (FAB) (%) 361 (15) and 359 (35) (M^+ + thioglycerol + Na), 339 (6) and 337 (10) (M^+ + thioglycerol + H), and 321 (38) 319 (100) (M^+ + thioglycerol + H − H_2O).

Single-crystal X-Ray Diffraction Analyses of Compounds **54** *and* **67**.—*Crystal data.* Compound **54**; $C_{15}H_{15}Cl_2NO_4$, *M* = 344.2, monoclinic, space group $P2_1/n$, *a* = 8.574(1), *b* = 8.432(1), *c* = 21.914(3) Å, β = 98.30(1)°, *V* = 1567.7(5) $Å^3$, *F*(000) = 712, *Z* = 4, D_m = 1.451(5), D_c = 1.458 g cm^{-3}, μ = 37.4 cm^{-1}, (Cu-Kα). Final *R* = 0.052, R_w = 0.062 for 1880 terms ($I \geq 2\sigma I$), *w* = 0.92/($\sigma^2|F| + 0.0005|F|^2$), *S* = 1.96 (259 parameters).

Compound **67**; $C_{19}H_{18}ClNO_5$, *M* = 375.8, triclinic, space group $P\bar{1}$ (confirmed on refinement), *a* = 11.836(2), *b* = 8.953(1), *c* = 17.127(3) Å, α = 101.24(1), β = 91.80(1)°, γ = 98.04(1)°, *V* = 1759.4(6) $Å^3$, *F*(000) = 784, *Z* = 4, D_m = 1.409 (5), D_c = 1.419 g cm^{-3}, μ = 21.5 cm^{-1}, (Cu-Kα). Final *R* = 0.039, R_w = 0.051 for 3930 terms ($I \geq 2\sigma I$), w = 1.216/($\sigma^2|F| + 0.0005|F|^2$), *S* = 1.16 (317 parameters).

Data collection and processing. Integrated intensities were recorded on a Rigaku-AFC diffractometer at 291(1) K with Cu-Kα radiation (graphite crystal monochromator, λ = 1.5418 Å), by a Θ/2Θ scan to $2\Theta_{max}$ 130°, yielding 2704 and 5978 unique terms for compounds **54** and **67**, respectively. The intensities were corrected for Lorentz and polarisation effects and for absorption [transmission factors 0.4305–0.5584 (**54**) and 0.5003–0.7418 (**67**)]. The structure was solved by direct methods (SHELXS-86)[31] and refined with SHELX-76,[32] the function minimised was $\Sigma w(|F_o| - |F_c|)^2$. The C, Cl, N and O atoms were given anisotropic temperature factors and the H atoms were given individual isotropic temperature factors, the atomic co-ordinates of the latter being refined. The parameters for compound **67** were refined in two blocks whereas full-matrix refinement was used for compound **54**. An isotropic extinction correction of the form $F_c = F(1 - 6.4 \times 10^{-6}|F|^2 \sin\Theta)$ was applied to the calculated structure amplitudes of compound **67**. At convergence $(\Delta\rho)_{max}$, $(\Delta\sigma)_{min}$ = +0.32, −0.38 e $Å^3$ (**54**) and +0.25, −0.27 e $Å^3$ (**67**).*

* *Supplementary data:* Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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