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THE CHEMISTRY OF AN ALLYLSILANE: THE SYNTHESIS OF A PROSTAGLANDIN INTERMEDIATE AND OF LOGANIN†

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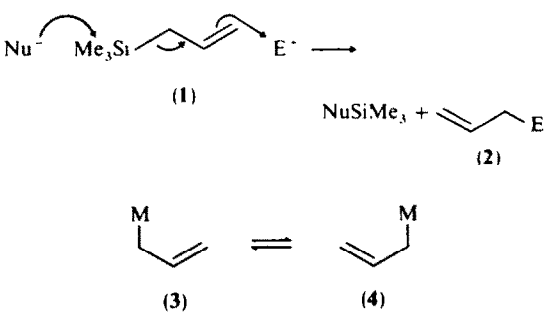
Abstract—The allylsilane 7,7-dichloro-4-*exo*-trimethylsilyl-bicyclo[3.2.0]hept-2-en-6-one (**6**) reacts regioselectively with a variety of electrophiles, and the product (**28**) of methoxymethylation can be converted into prostaglandins. Elaboration of the cyclobutanone ring of **6** in seven steps gives the allylsilane (**43**), which reacts regioselectively with chlorosulphonyl isocyanate. The product of this reaction can be converted into loganin aglucone acetate (**48**), a known intermediate in the synthesis of loganin (**49**).

In a brief paper in 1948, Sommer, Tyler and Whitmore[1] proposed that allyltrimethylsilane reacts with electrophiles in the general sense (**1** → **2**). At about the same time, it was being established that allylmetal compounds, such as the crotyl Grignard reagent, also react in this sense,[2] but that they appeared to be allylically unstable (**3** ⇌ **4**). In the intervening years, the allylic instability of metals has been well established, and many allyl-metal compounds even adopt, as their stable arrangement, a π-allyl structure which is related to the transition state for the allylic rearrangement. Because of this allylic instability, unsymmetrical allyl–metal compounds cannot be relied upon to give a single product, and there is little control over which product they will give. However, almost uniquely among metal compounds, allylsilanes are comparatively stable with respect to allylic rearrangement.[3] If, then, they can be relied upon to react in the sense (**1** → **2**), they should be useful synthetic intermediates. Furthermore, since they are comparatively unreactive, they might be expected to possess a second useful property: unlike other allyl–metal compounds, they should be able to survive a wide range of reaction conditions before their reactivity in the sense (**1** → **2**) is put to use. In this paper, we describe in full how these ideas have been combined in highly controlled syntheses of loganin (**49**) and of a well-known intermediate (**29**) in prostaglandin synthesis.[4]

Before we began this work, and during it, we and others established that unsymmetrical allylsilanes did react in the sense (**1** → **2**) with such electrophiles as the proton,[5–8] and, in the presence of Lewis acids, acetyl chloride,[6,8] acetone,[9] acetals,[10] and t-alkyl halides.[8] However, although unsymmetrical allylsilanes are evidently as regiochemically well-behaved as one could have hoped, there is a severe shortage of ways in which they can be synthesised regioselectively.[11] When they can be made easily, as here, they work well.

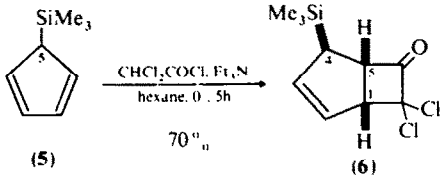


(**1**) (**2**) (**3**) (**4**)

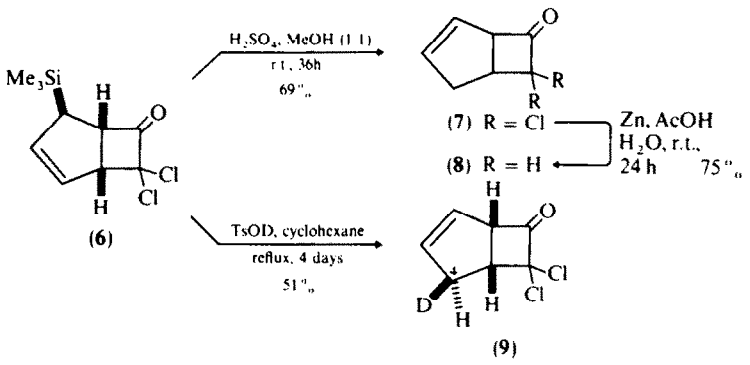
†No reprints available.

THE GENERAL CHEMISTRY OF THE ALLYLSILANE (6)

The crystalline allylsilane (**6**) used in this work was prepared in 70% yield by cycloaddition of dichloroketene to trimethylsilylcyclopentadiene (**5**),[12] which is known[13] to be largely (>90% at room temperature) the 5-isomer, as shown. The stereochemistry of the silyl group in the product (**6**) was judged to be *exo* because the PMR signal of the C-4 hydrogen is a narrow multiplet. The C-4 *exo* hydrogens in bicyclo[3.2.0]hepten-6-ones are usually[14] coupled by 6–9 Hz with the hydrogen on C-5. The similarity in chemical shift for the C-1 and C-5 hydrogens established that the regioisomer produced was the same as that for cyclopentadiene itself.[15] This was confirmed by protodesilylation (**6** → **7**) followed by dechlorination, which gave the known bicyclo[3.2.0]hept-2-en-7-one (**8**) much more conveniently than by the earlier syntheses.[16] The alternative order of events—dechlorination (**6** → **31**) followed by protodesilyation—failed in the second step. Although sulphuric acid in methanol was the best method for protodesilyation in this case, toluene-*p*-sulphonic acid also worked, and we used the latter to investigate the stereochemistry of the reaction. Using deuterated acid, we got a product (**9**) in which the PMR signal of the *exo* proton on C-4 was much diminished in intensity (*ca.* 70% d_1), and the signal of the *endo* proton was at full intensity. The reaction was therefore *syn*. Because of the *exo* bias in the bicyclic system, we are unable to say whether this is the inherently preferred stereochemistry for this type of S_E2' reaction, but Wetter *et*



(**5**) (**6**)

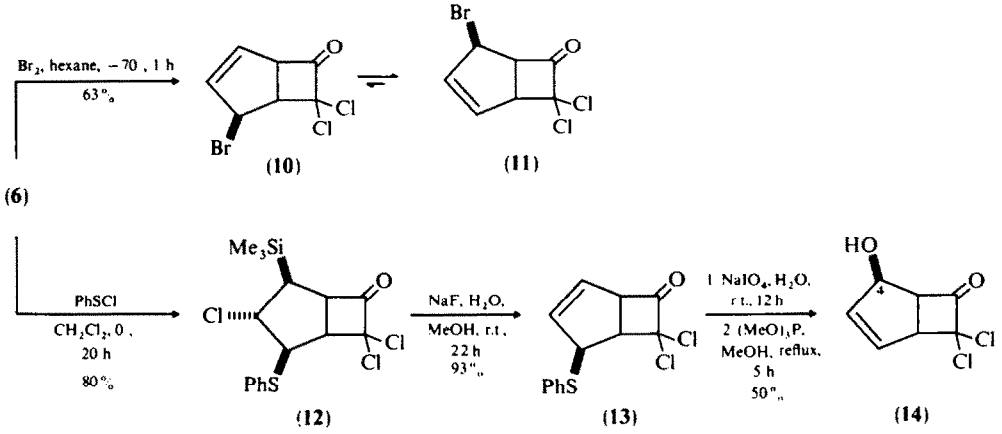


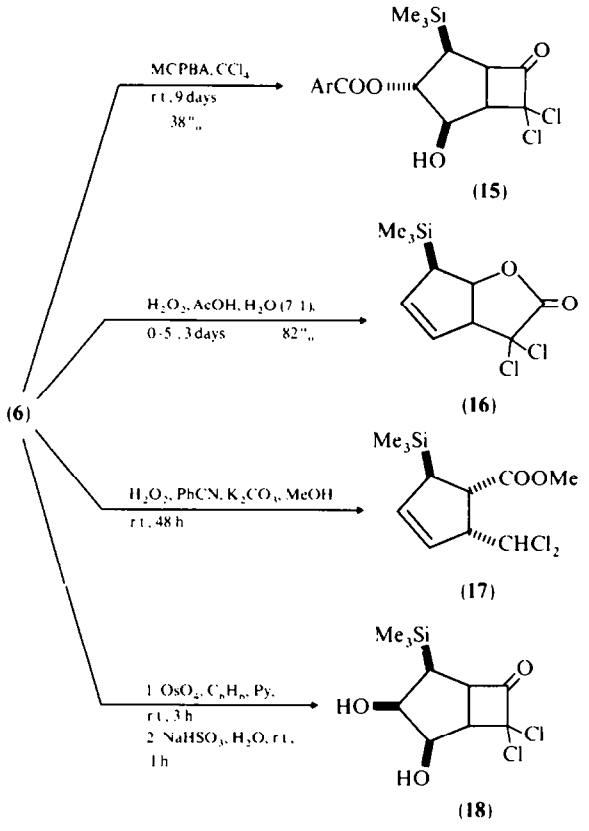
al. have recently shown that acylative desilyation in an open-chain allylsilane is also *syn*.[17]

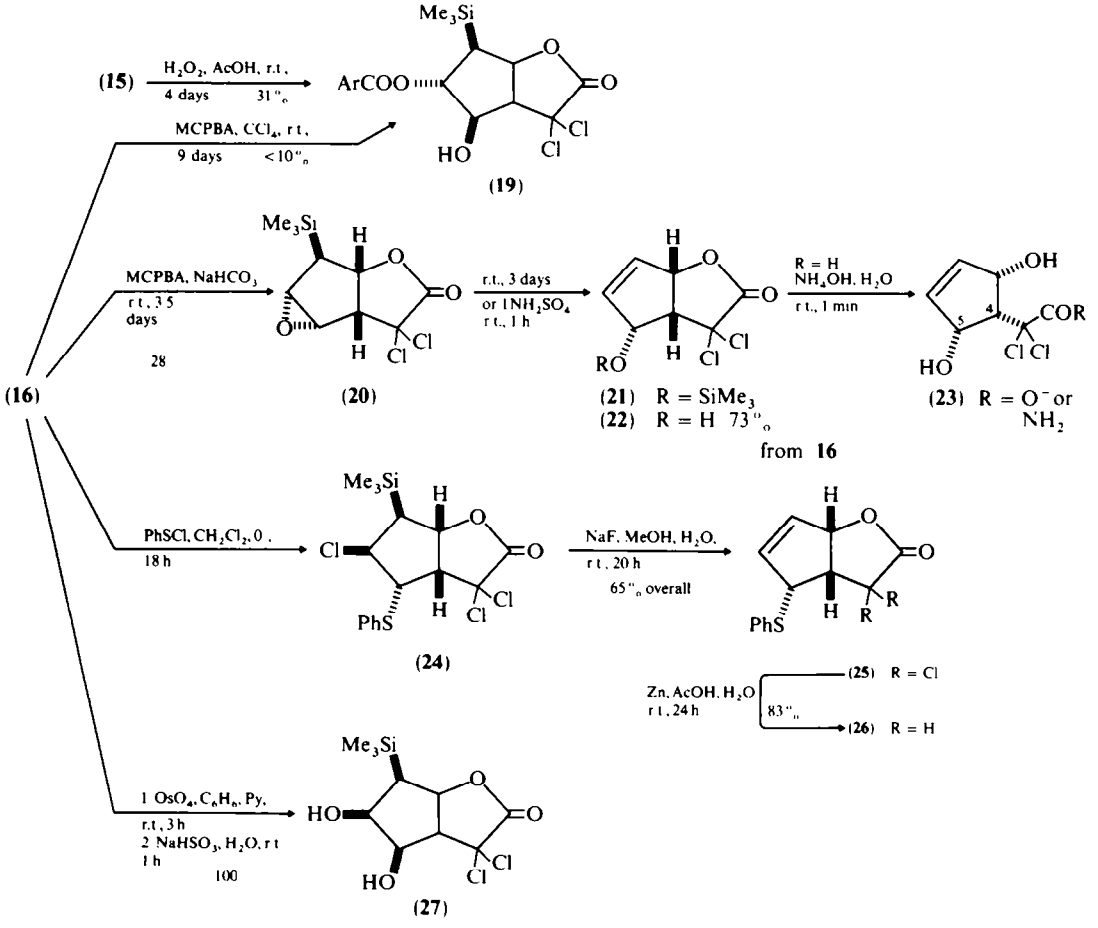
Careful, low temperature bromination of the allylsilane (**6**) gave the known[18] bromide (**10**) in 63% yield, but equilibration to its allylic isomer (**11**) was rapid and sometimes hard to avoid. Benzenesulphenylation of the allylsilane (**6**) gave the addition product (**12**) (80%), which reacted with fluoride ion to give the allylsulphide (**13**) (93%). The allylsulphide could be converted by the Mislow-Evans procedure to the allyl alcohol (**14**) (50%), the stereochemistry of which was evident from the PMR spectrum, which showed a *narrow* multiplet from the hydrogen on C-4.

The reactions of these three electrophiles were therefore uneventful. Our results with oxygen electrophiles were not so straightforward. Although we were able, eventually, in this series, and in our earlier work,[7] to convert an allylsilane to an allylically rearranged allyl alcohol, this deceptively simple transformation should not always be expected to work easily. In the first place, *m*-chloroperbenzoic acid (MCPBA) alone gave, as the only isolable compound, the addition product (**15**) (30–38%). The addition of a peracid to an olefin is, of course, known,[19] but was somewhat surprising in this case in view of the ease with which a silyl group is usually lost. Presumably the elimination step is not easy because of the *syn* relationship of the silyl and epoxy groups, and because they are present in a 5-membered ring. Other peracids were no better. Buffered peracids gave, as expected, the Baeyer–Villiger product (**16**), which was most easily made, in 82% yield, using hydrogen peroxide in acetic acid. Hydrogen peroxide and benzonitrile[20] in methanolic potassium carbonate also gave a small amount of the lactone (**16**), but the major product this time was the ring-cleaved[21] ester (**17**). Our last attempt with the ketone (**6**) was to oxidise it with osmium tetroxide. The PMR spectrum of the product showed that it was the diol (**18**), but neither acid[22] nor base[23] was effective in converting **18** into an allylic alcohol. In view of the difficulties caused by the presence of a ketone group in **6**, we turned to the lactone (**16**).

This lactone also reacted with MCPBA alone to give, as a minor component of a complex mixture, the addition product (**19**), which could also be prepared by Baeyer–Villiger oxidation of the ketone (**15**). Finally, buffered MCPBA converted the lactone (**16**) into a very sensitive epoxide (**20**). Merely on standing, it rearranged to the silyl ether (**21**), which was easily hydrolysed to the alcohol (**22**). By avoiding the isolation of the epoxide, we found that we could convert the allylsilane (**16**) to the allylic alcohol (**22**) in 73% yield. *Endo* epoxidation was reasonable, since the lactone (**33**), which lacks both the silyl group and the chlorines, was known to give largely the *endo* oxide.[24] The stereochemistry was suggested by the PMR spectrum of the alcohol (**22**), and was confirmed by dissolving it in aqueous ammonia and evaporating off the solvent. The PMR spectrum of the residue (**23**) in DMSO-d_6 showed a sharp singlet (2H, δ 5.91), a sharp doublet (2H, δ 4.46, J = 6 Hz), and a sharp triplet (1H, δ 3.12, J = 6 Hz), ascribable to the olefinic, allylic, and C-4 hydrogens, respectively. The simplicity of this spectrum is a result of the plane of symmetry present in the salt (or possibly amide) (**23**). To get a spectrum as simple as this from the diastereoisomer with the C-5 hydroxyl β would need no fewer than *four* coincidences, two of chemical shift and two of coupling constants. The lactone (**16**) also reacted with benzene-sulphenyl chloride on what appears, from the PMR spectrum described below, to be the *endo* face, in contrast to the corresponding reaction of the ketone (**6**). The allyl-sulphide (**25**), produced by desilylchlorination of the first-formed adduct (**24**),




(6)
MCPBA, CCl_4
r.t., 9 days
38%
ArCOO
HO
(15)
H_2O_2, AcOH, H_2O (7:1)
0-5°, 3 days
82%
(16)
H_2O_2, PhCN, K_2CO_3, MeOH
r.t., 48 h
COOMe
$CHCl_2$
(17)
1 OsO_4, C_6H_6, Py.
r.t., 3 h
2 $NaHSO_3$, H_2O, r.t.
1 h
HO
(18)


(15)
H_2O_2, AcOH, r.t.
4 days 31%
ArCOO
MCPBA, CCl_4, r.t.
9 days <10%
(19)
(16)
MCPBA, $NaHCO_3$
r.t., 3.5 days
28
(20)
r.t., 3 days
or 1 NH_2SO_4
r.t., 1 h
(21) R = $SiMe_3$
(22) R = H 73% from 16
R = H
NH_4OH, H_2O
r.t., 1 min
(23) R = O^- or NH_2
PhSCl, CH_2Cl_2, 0°
18 h
(24)
NaF, MeOH, H_2O
r.t., 20 h
65% overall
Zn, AcOH, H_2O
r.t., 24 h
83%
(25) R = Cl
(26) R = H
1 OsO_4, C_6H_6, Py.
r.t., 3 h
2 $NaHSO_3$, H_2O, r.t.
1 h
100
(27)

showed in its PMR spectrum a large (6 Hz) coupling between the hydrogen α to the sulphur and the bridgehead hydrogen, and there was a similarly large coupling (7 Hz) in the PMR spectrum of the dechlorinated lactone (**26**). Unlike the *endo* selectivity shown in the epoxidation, the *endo* sulphenylation cannot have been caused by hydrogen-bonding of the electrophile to the lactone group. It seems likely, therefore, that the *endo* selectivity is electronic in origin, implying either that the silyl group encourages attack *anti* to itself or that the oxygen atom encourages attack *syn* to itself. In contrast, the lactone (**16**) gave the *exo* diol (**27**) with osmium tetroxide, but we were again unable to convert this product, either with acid or base (or with fluoride ion on the derived diacetate), into an allylic alcohol. In conclusion, in this section on oxygen electrophiles, we note that the successful epoxidation of an allylsilane and the subsequent formation of an allylic alcohol (**16** → **20** → **22**) took place only under *acidic* conditions, as was the case with our other example of this type of reaction.[7] It seems likely that this will prove to be a general requirement, especially in view of the entirely different course taken in a reaction observed by Hudrlik *et al.*,[25] where an allylsilane epoxide was a likely intermediate in a base-promoted reaction. Hudrlik also draws attention in this paper to the unsatisfactory level of characterization of those βγ-epoxysilanes which have been reported in the past. Except for those derived from 3-silacyclopentenes,[26] **20** is the first well-characterized βγ-epoxysilane.

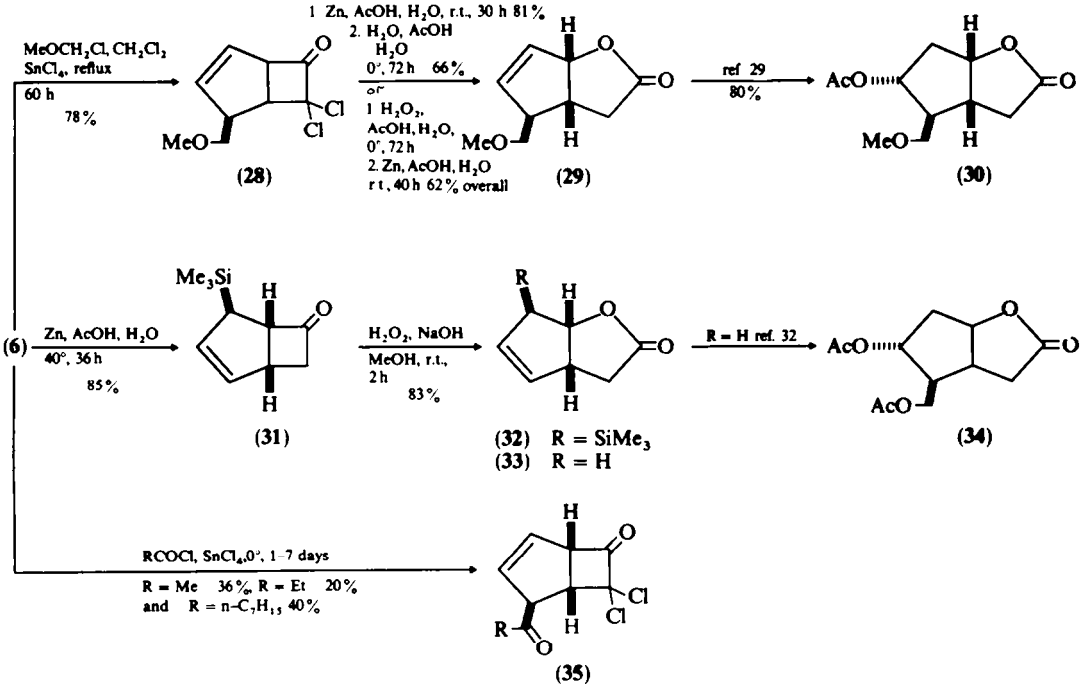
THE SYNTHESIS OF THE PROSTAGLANDIN INTERMEDIATE (29)

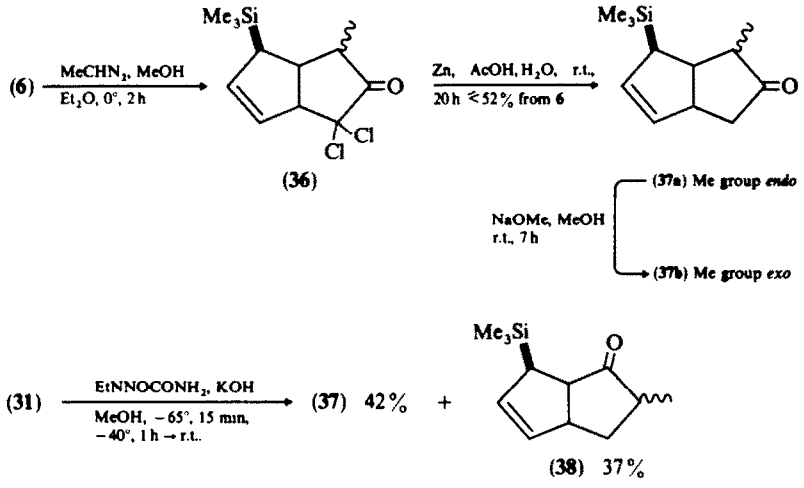
Having established that a proton and various heteroatom electrophiles reacted cleanly with our allylsilane, we turned to carbon electrophiles, of which the most interesting was chloromethyl methyl ether. It was known that alkenes react with chloromethyl methyl ether in the presence of Lewis acids to give addition, but that vinylsilanes give substitution.[27] We found that the allylsilane (**6**) reacted cleanly with choromethyl methyl ether and stannic chloride to give the ether (**28**) in 78% yield. Other Lewis acids, such as aluminium chloride, boron trifluoride and titanium tetrachloride, gave, in this case at least, inferior yields and mixtures of unidentified products. The ether (**28**) was converted in two steps into the known[28,29] lactone (**29**), which was identical with an authentic sample.[28] The conversion by oxidation followed by reduction without isolation (62% overall) was better than the alternative, reduction (81%) followed by oxidation (66%). Other variations in the order of events, such as methoxy-methylation of **16** or **31** or **32** were unsuccessful.[30] The overall yield of the lactone (**29**) from cyclopentadiene was 25%. This lactone has been converted[29] to the Corey lactone (**30**)[31] in 80% yield, and hence into A and F prostaglandins. The overall yield of the Corey lactone (**30**) by our route is 20%, by Ranganathan's route[29] 45%, and by Corey's,[31] 40%. Plainly ours is inferior in this respect. Its strength, however, is that none of our intermediates is so delicate that it demands immediate use after preparation. Scaling up should therefore be easier in our case. As it happens, a Prins reaction on the readily available lactone (**33**) has been reported[32] to give the derivative (**34**) stereo- and regioselectivity, thus doing away altogether with the need for the silyl group.

We tried to extend our route to prepare analogues of prostaglandins by using other electrophiles on the allylsilanes (**6**, **16**, **31**, and **32**). Except for acylation of **6**, which gave the appropriate ketones (**35**) in yields up to 40%, none of the usual carbon electrophiles which react with allylsilanes[11] gave identifiable products[30] (we tried acetals, methyl orthoformate, aldehydes and enones, with a variety of Lewis acids).

THE SYNTHESIS OF LOGANIN

Most of the reactions discussed above are reactions directly on the allylsilane group in **6**. However, this group should be stable to many reaction conditions which would allow elaboration of the cyclobutanone ring. For the synthesis of loganin we wanted to expand this ring regioselectively by one carbon atom, using diazoalkanes, and we hoped that the α-halogen atoms

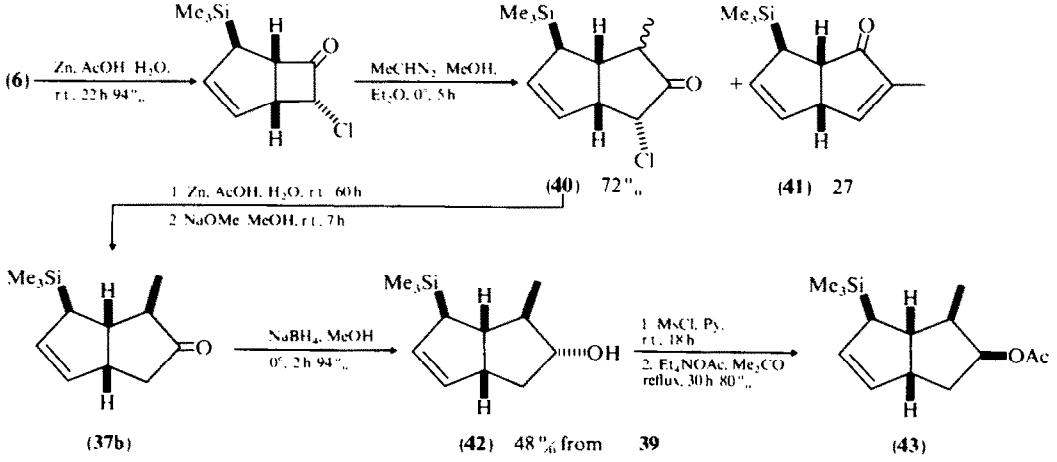


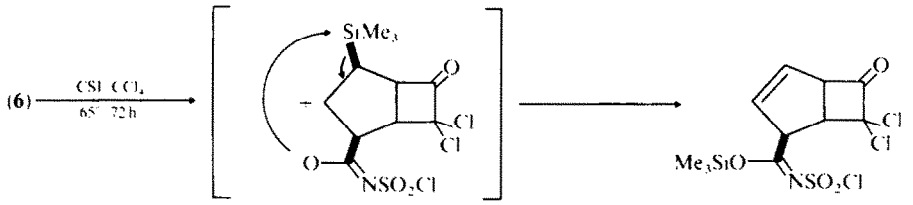


would give us the regioselectivity we wanted. This feature of our work has since been taken up and exploited in other ways.[33] The best order of events in our case took some working out. When we used the dichloroketone (**6**) itself and diazoethane in a mixture of ether and methanol, the first-formed product (**36**) was unstable. We therefore dehalogenated the crude mixture of products immediately and got the mixture of ketones (**37**) in, at best, 52% yield. However, we also got variable amounts of the dehalogenated starting material (**31**), and we could discover no convenient and reliable way of monitoring the reaction to make sure that all the starting material has been used up. The reaction was also troublesome, because the diazoethane polymerized faster than it attacked the ketone, and it had to be added in excess in batches throughout the reaction period. It was no use avoiding this problem by generating the diazoethane *in situ*, because the base used to generate the diazoethane would have opened the cyclobutanone ring (**6** → **17**). We therefore turned to the dehalogenated ketone (**31**), where we could generate the diazoethane *in situ* in methanol without trouble. The reaction with the ketone was now faster, and yields were good, but the ring expansion showed little regioselectivity, giving the mixture of ketones (**37**) in 42% yield and the mixture of ketones (**38**) in 37% yield. The preference for migration by the more-substituted carbon, slight though it was, was agreeable, and unexpected, in view of several reports[34] of higher proportions of migration by primary than by secondary alkyl groups. Although this route gave us material to work with, it was hardly satisfactory. Fortunately, the monochloroketone (**39**), easily prepared in 94% yield from the dichloroketone (**6**) by reduction with one equivalent of zinc, reacted fast enough with preformed diazoethane in ether and methanol so that only one equivalent of diazoethane was needed. The regioselectivity was reasonably high: the required ketones (**40**) were formed in 72% yield, and the by-product (**41**), from migration of the α-chloromethylene carbon, was formed in 27% yield. This was slightly disappointing in view of the report[35] that 2-chlorocyclohexanone and diazomethane gave only 2-chlorocycloheptanone.

Zinc removed the chlorine from the mixture of ketones (**40**), and the product (**37**) could then be separated chromatographically from **41**. Treatment of the mixture of stereoisomers (**37**) with sodium methoxide in methanol converted the minor isomer (**37a**), which had an *endo* methyl group, into the major (**37b**), in which the methyl group was *exo*. Sodium borohydride attacked the ketone group from the *exo* direction to give the *endo* alcohol (**42**), and the mesylate of this alcohol reacted with acetate ion to give the *exo* acetate (**43**). This reaction sequence was closely modelled on that used by Büchi in his synthesis of loganin.[36]

The right hand side of the molecule was now complete; the allylsilane function had dutifully survived seven steps, and it was time for it to perform





to order. We needed a carbon electrophile which would act overall as a methoxycarbonyl cation synthon, because we wanted the product to be the ester (**47**). Chlorosulphonyl isocyanate (CSI) appeared to have the right properties: it was known to react with alkenes; and, although the major products are usually β-lactams (70% with isobutene, for example),[37] substitution products are also formed. The presence of the silyl group ought, therefore, to tip the balance in favour of substitution, because of the ease with which the silyl group will be displaced in the zwitterionic intermediate (**44**, arrows). The model allylsilane (**6**) reacted with CSI cleanly, and the PMR spectrum of the product was entirely compatible with the structure (**45**), but we were unable to find hydrolytic conditions which gave a clean or recognisable product. With the allylsilane (**43**), the reaction with CSI was again clean, as judged by PMR, and, this time, with a lot of effort, we found conditions for the hydrolysis which were reasonably high-yielding. Simple treatment with dilute hydrochloric acid gave the amide (**46**) in 55% yield, and the amide could be converted to the ester (**47**) in 69% yield by nitrosation, hydrolysis and esterification with diazomethane. By not isolating any of the intermediates between the allylsilane (**43**) and the ester (**47**), we got an overall yield of 61%. Dunoguès *et al.*[38] have also found that allylsilanes react with CSI, and they used a pyridine work-up to get β,γ-unsaturated nitriles. This did not work in the case of **45**; nor did the procedure just described.[30]

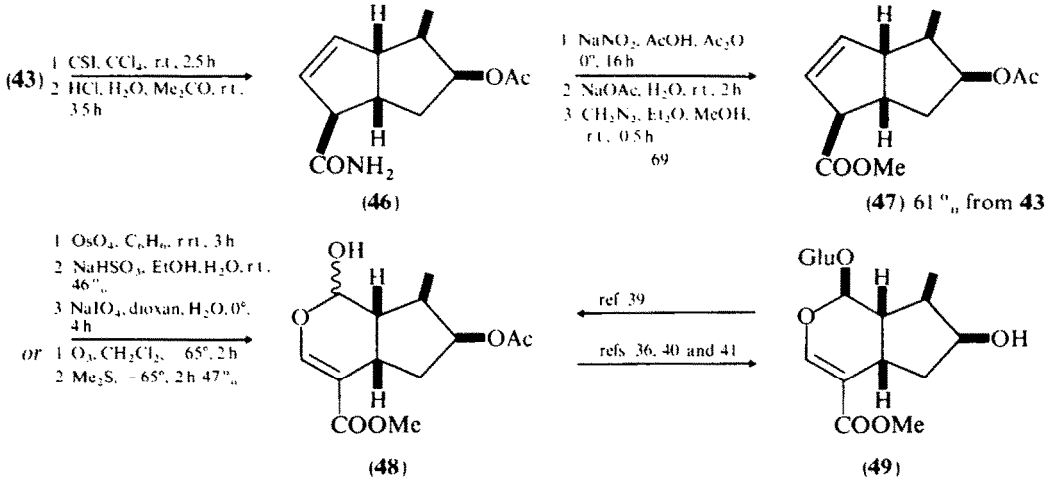
The oxidative cleavage of the double bond of **47** could be done by ozonolysis or by osmium tetroxide followed by periodate. The dialdehyde was not observed, but the hemiacetal (**48**) was isolated in 47% and 46% yields respectively. Our racemic sample was identical with an authentic, optically active sample of loganin aglucone acetate[39] prepared from loganin (**49**) itself.

This product was an intermediate in Büchi's[36] and in Uskokovic's[40] syntheses; the glycosidation step has since been improved by Tietze.[41] We have therefore completed a total synthesis of loganin; the overall yield of the intermediate (**48**) based on cyclopentadiene is 5.3%, double that of Büchi's synthesis,[36] and slightly higher† than Uskokovic's[40] (4%), both of which also began with cyclopentadiene. Our route, however, is principally interesting not for the overall yield, but for the control which the allylsilane chemistry has introduced.

EXPERIMENTAL

7,7-Dichloro-4-exo-trimethylsilylbicyclo[3.2.0]hept-2-en-6-one (**6**). A solution of dichloroacetyl chloride (29.5 g, 0.2 mol) in dry hexane was added dropwise over 2 hr to a stirred mixture of 5-trimethylsilylcyclopentadiene[12] (20.6 g, 0.15 mol) and triethylamine (20.2 g, 0.2 mol) in dry hexane (300 ml) at 0°C under nitrogen. After stirring at 0–5° for an additional 3 hr, the mixture was poured into water (500 ml). The hexane layer was separated, dried ($MgSO_4$) and the solvent evaporated. Distillation gave the adduct (**6**) (26.1 g; 70%), b.p. 71–3°/0.3 mm Hg (Found: C, 48.0; H, 5.7. $C_{10}H_{14}Cl_2OSi$ requires: C, 48.2; H, 5.7%), ν_{max} (film) 1804s and 1594w cm^{-1}, δ (CCl_4) 0.02 (9 H, s, $SiMe_3$), 2.46 (1 H, m, Me_3SiCH), 4.0 (2 H, m, bridgehead H's), and 5.65 and 5.96 (each 1 H, m, CH=CH).

6,6-Dichlorobicyclo[3.2.0]hept-2-en-7-one (**7**). A solution of the silane (**6**) (3.5 g) in a mixture of sulphuric acid (50 ml) and methanol (50 ml) was kept at room temperature for 36 hr. The mixture was poured into cold water (300 ml) and extracted with chloroform (3 × 40 ml) to give the ketone (**7**) (1.7 g, 69%), b.p. 55–6°/0.65 mm Hg (Found: C, 47.35; H, 3.6.



†This synthesis, however, was of optically active loganin aglucone acetate.

$C_7H_6Cl_2O$ requires: C, 47.5; H, 3.4%), ν_{max} (film) 1800s and 1604w cm^{-1}, δ (CCl_4) 2.62 2.88 (1 H, ddm, *J* 19 and 8 Hz, C-4 *exo* H), 2.95–3.16 (1 H, dm, *J* 19 Hz, *endo* C-4 H), 3.48 (1 H, *dt*, *J* 8 and 2 Hz, C-5 H), 4.54 (1 H, m, C-1 H), and 5.63 and 5.90 (each 1 H, m, CH=CH).

Bicyclo[3.2.0]*hept-2-en-7-one* (**8**). The ketone (**7**) (1.7 g) was stirred with zinc powder (7 g, excess) in a mixture of acetic acid (40 ml) and water (5 ml) at room temperature for 24 hr. The inorganic solids were filtered off and washed with chloroform (50 ml). The combined filtrate and washings were washed with water (3 × 150 ml) and then with sodium hydrogen carbonate solution. The chloroform layer was separated, dried ($MgSO_4$), and evaporated, and the residue distilled to give the ketone (**8**) (0.8 g, 75%), b.p. 56 /15 mm Hg (Found: C, 77.5; H, 7.4. Calc. for C_7H_8O: C, 77.75; H, 7.5%), ν_{max} (film) 1775s and 1602w cm^{-1} (lit.[16] 1780 cm^{-1}), δ (CCl_4) 2.2 3.5 (5 H, m), 4.2 (1 H, m, C-1 H), and 5.6 and 5.85 (each 1 H, m, CH=CH), λ_{max} (cyclohexane) 296, 306, and 317 nm (ε 128, 142, and 100), [lit.[16] 297, 306, and 317 nm (ε 142, 160, and 112)], *m/z* 108 (M^+) and 66 (base; $M^+ - CH_2CO$) (lit.[16], same observations) 2,4-dinitrophenylhydrazone, needles (from ethanol), m.p. 149–150° (lit.[16] 149–151°).

6,6-*Dichloro*-4-*exo*-*deuteriobicyclo*[3.2.0]*hept-2-en-7-one* (**9**). The water of crystallisation of toluene-*p*-sulphonic acid monohydrate (0.8 g, 4 mmol) was first removed by azeotropic distillation with dry cyclohexane. Deuterium oxide (2 g) was added to the dry mixture and stirred for 5 min. The acid was dried again by azeotropic removal of water using dry cyclohexane. Another 2 g of deuterium oxide was again added and the removal of water repeated, until about 10 ml of cyclohexane finally remained. The silane (**6**) (0.15 g, 0.6 mmol) was added and the mixture heated under reflux with stirring for 4 days. The charred substances and excess acid were filtered off. The filtrate was washed with water and then evaporated. The residue, after purification by tlc on silica gel (benzene, R_F 0.4), gave an oil (54 mg, 51%) in which the PMR signal at δ 2.62 2.88 was much reduced in intensity, indicating a composition of about 70% of (**9**) and 30% of (**7**).

4-exo-*Bromo*-6,6-*dichlorobicyclo*[3.2.0]*hept-2-en-7-one* (**10**). Bromine (1.6 g, 10 mmol) in dry hexane (4 ml) was added dropwise over 0.5 hr to a solution of the silane (**6**) (2.5 g, 10 mmol) in hexane (11 ml) at −70°, and the mixture stirred for an additional 0.5 hr at −70°. The precipitate was quickly separated from the cold solution and washed with 5 ml of cold hexane (−70°) to give pure bromide (**10**) (1.6 g; 63%). A sample was recrystallised to give prisms, m.p. 71 2° (from hexane) (Found: C, 32.8; H, 2.3. $C_7H_3BrCl_2O$ requires: C, 32.9; H, 2.0%), ν_{max} (KBr) 1805s and 1594w cm^{-1}, δ (CCl_4) 3.88 (1 H, d, *J* 6.5 Hz, C-5 H), 4.80 (1 H, m, C-1 H), 5.33 (1 H, m, BrCH), and 5.92 and 6.18 (each 1 H, m, CH=CH).

2-exo-*Phenylthio*-3-endo-7,7-*trichloro*-4-exo-*trimethylsilylbicyclo*-[3.2.0]*heptan*-6-*one* (**12**). Phenylsulphenyl chloride (1.50 g, 10 mmol) was added to a solution of the silane (**6**) (2.50 g, 10 mmol) in dry dichloromethane (40 ml), and the mixture kept at 0–3° for 20 hr. After evaporation of solvent, the residue was crystallised from light petroleum (b.p. 40–60°) to give the adduct (**12**) (3.2 g, 80%) as needles, m.p. 85–6° (Found: C, 48.7; H, 4.7. $C_{16}H_{19}Cl_3OSSi$ requires: C, 48.8; H, 4.9%), ν_{max} (KBr) 1804s cm^{-1}, δ (CCl_4) 0.10 (9 H, s, $SiMe_3$), 1.74 (1 H, m, Me_3SiCH), 3.18 (1 H, m), 3.65 (3 H, m), and 7.32 and 7.53 (3 H + 2 H, m, ArH).

6,6-*Dichloro*-4-exo-*phenylthiobicyclo*-[3.2.0]*hept*-2-*en*-7-*one* (**13**). Sodium fluoride (800 mg) in water (15 ml) was added to a solution of the adduct (**12**) (1.36 g) in methanol (50 ml) and the mixture stirred at room temperature for 22 hr. After evaporating off most of the methanol, the residue was extracted with ether (40 ml), the ether dried (Na_2SO_4), and evaporated to give the sulphide (**13**) (0.90 g, 93%) as prisms, m.p. 56–7° (light petroleum, b.p. 40–60°) (Found: C, 54.5; H, 3.4; Cl, 24.9; S, 11.0. $C_{13}H_{10}Cl_2OS$ requires: C, 54.75; H, 3.5; Cl, 24.9; S, 11.2%), ν_{max} (KBr) 1800s and 1602w cm^{-1}, δ (CCl_4) 3.58 (1 H, d, *J* 7 Hz, C-5 H), 4.28 (1 H, m, C-1 H), 4.62 (1 H, m, $PhSCH$), 5.70 and 5.96 (each 1 H, m, CH=CH), and 7.30 (5 H, m, ArH).

7,7-*Dichloro*-4-exo-*hydroxybicyclo*[3.2.0]*hept*-2-*en*-6-*one* (**14**). Sodium metaperiodate (0.71 g, 3.3 mmol) in water (10 ml) was added dropwise to an ice-cold solution of the sulphide (**13**) (0.9 g, 3.2 mmol) in methanol (40 ml). The mixture was stirred at 0° for 2 hr and then at room temperature overnight. Methanol was evaporated off and the aqueous residue extracted with ether (20 ml). The extract was washed with water, dried (Na_2SO_4), evaporated, and the residue purified through a column (SiO_2; 30 g) eluting with dichloromethane-ether (1:1) to give a mixture of two diastereoisomers of the sulphoxide [0.86 g, 90%; R_f (ether) 0.33], ν_{max} (CCl_4) 1814s and 1058s cm^{-1}, δ ($CDCl_3$) 3.80 (1 H, m), 4.2 4.7 (2 H, m), 5.60, 6.04 (total 2 H, m, CH=CH), and 7.56, 7.64 (total 5 H, s, ArH), *m/z* 304, 302, 300 (M^+). The sulphoxide (0.58 g, 1.9 mmol) was heated with trimethyl phosphite (0.28 g, 2.2 mmol) in methanol (10 ml) under reflux for 5 hr. After evaporation of solvent, the residue was purified by tlc (SiO_2; ether; R_f 0.7) to give the alcohol (**14**) (0.19 g, 50%), liquid, ν_{max} (CCl_4) 3590m, 3400br, and 1810 cm^{-1}, δ (CCl_4) 2.80 (1 H, br, OH), 4.12 (2 H, m, bridge-head H's), 4.93 (1 H, m, $HOCH$), and 6.13 (2 H, m, CH=CH). The alcohol (14) was characterised as its dimethyl(trityl)silyl ether,[42] prisms (hexane), m.p 140–1°. (Found: C, 68.0; H, 5.3; Cl, 14.1. $C_{28}H_{26}Cl_2O_2Si$ requires: C, 68.2; H, 5.3; Cl, 14.4%), ν_{max} (CCl_4) 1808s and 1595m cm^{-1}, δ (CCl_4) 0.26 (6 H, sm, $SiMe_2$), 3.35 (1 H, d, *J* 6.5 Hz, C-5 H), 3.94 (1 H, m, C-1 H), 4.64 (1 H, m, $SiOCH$), 5.55 and 5.82 (each 1 H, m, CH=CH), and 7.12 (15 H, m, ArH).

7,7-*Dichloro*-2-exo-*hydroxy*-6-*oxo*-4-exo-*trimethylsilylbicyclo*[3.2.0]*hept*-3-endo-*yl*-3-*chlorobenzoate* (**15**). A solution of **6** (250 mg, 1 mmol) and *m*-chloroperbenzoic acid (300 mg) in carbon tetrachloride (20 ml) was stirred at room temperature for 9 days. The resultant mixture was washed with 5% sodium hydroxide solution and water. The organic layer was separated, dried (Na_2SO_4) and evaporated, and the residue separated by tlc on silica gel (CH_2Cl_2). Besides 36 mg recovery of the starting silane, the only identified product was the benzoate (**15**) (137 mg, 38% based on consumed starting silane), prisms, m.p. 126 7° [from light petroleum (60 80°)] (Found: C, 48.4; H, 4.5; Cl, 25.2. $C_{17}H_{19}Cl_3O_4Si$ requires: C, 48.4; H, 4.5; Cl, 25.2%), ν_{max} (KBr) 3490s, 1810s, and 1692s cm^{-1} δ (CCl_4) 0.15 (9 H, s, $SiMe_3$), 1.98 (1 H, dd, *J* 3 and 2 Hz, Me_3SiCH), 3.38 (1 H, d, *J* 8.5 Hz, C-1 H), 3.65 (1 H, d, *J* 3 Hz, OH), 4.03 (1 H, dd, *J* 8.5 and 3 Hz, C-5 H), 4.62 (1 H, m, C-2 H), 5.26 (1 H, t, *J* 3 Hz, C-3 H), and 7.1–7.7 (4 H, m, aromatic).

8,8-*Dichloro*-6-*oxa*-4-exo-*trimethylsilylbicyclo*[3.3.0]*oct*-2-*en*-7-*one* (**16**). A mixture of **6** (5 g, 20 mmol), hydrogen peroxide (4.5 ml, 100 vols) and water (10 ml) in acetic acid (70 ml) was kept at 0–5° for 3 days, then poured into water (800 ml), and extracted with ether (100 ml). The ethereal extract was washed with sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated to give the lactone (**16**) (4.38 g, 82%) as prisms, m.p. 69 70° (from light petroleum, b.p. 60 80°) (Found: C, 45.5, H, 5.4. $C_{10}H_{14}Cl_2O_2Si$ requires: C, 45.3; H, 5.3%), ν_{max} (CCl_4) 1805s cm^{-1}, δ (CCl_4) 0.03 (9 H, s, $SiMe_3$), 2.42 (1 H, m, Me_3SiCH), 3.85 (1 H, m, CCl_2CH), 5.02 (1 H, d, *J* 4.5 Hz, CO_2CH), and 5.55 and 5.94 (each 1 H, m, CH=CH).

Methyl 2-(*Dichloromethyl*)-5-*trimethylsilylcyclopent*-3-*enecarboxylate* (**17**). A mixture of **6** (0.25 g, 1 mmol), benzonitrile (103 mg, 1 mmol), hydrogen peroxide (30 mg, 100 vols) and potassium hydrogen carbonate (20 mg) in methanol (5 ml) was stirred under nitrogen at room temperature for 48 h. The inorganic solid was filtered off and the filtrate evaporated. The residue (0.20 g) was purified by tlc on silica gel (CH_2Cl_2) to give, among other products, the ester to which we ascribe, by analogy,[21] the structure **17**, ν_{max} (CCl_4) 1736s cm^{-1}, δ (CCl_4) −0.4 (9 H, s, $SiMe_3$), 2.26 (1 H, m, Me_3SiCH), 3.08 (1 H, dd, *J* 9 and 5 Hz), *ca.* 3.4 (1 H, m), 3.58 (3 H, s, CO_2Me), 5.58 and 5.80 (each 1 H, m, CH=CH), and 6.01 (1 H, d, *J* 8 Hz, $CHCl_2$)

7,7-*Dichloro*-2,3-exo-*dihydroxy*-4-exo-*trimethylsilylbicyclo*[3.2.0]*heptan*-6-*one* (**18**) The silane (0.20 g, 0.8 mmol)

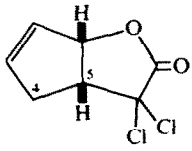
and osmium tetroxide (0.20 g, 0.8 mmol) in benzene (10 ml) were mixed with a catalytic amount of pyridine and stirred at room temperature for 3 hr. The benzene was evaporated off and the residue was taken up in ethanol (10 ml). A solution of sodium metabisulphite (1.5 g) in water (10 ml) was added and the mixture stirred at room temperature for 1 hr, diluted with water (100 ml) and extracted with ether (3 × 40 ml). The residue from the extracts was purified by tlc on silica gel (ether) to give the diol (**18**), ν_{max} (film) 3700–3050 br and 1805s cm^{-1}, δ (CCl_4) 0.10 (9 H, s, $SiMe_3$), 1.38 (1 H, dd, *J* 8 and 3 Hz, Me_3SiCH), 3.36 (3 H, br m, OH, C-1 H), 3.98 (1 H, t, *J* 8 Hz, C-3 H), and 4.27 (2 H, m, C-2 and C-5 H), *m/z* 283 (M^+, not detectable), 265 (M^+-H_2O).

Reaction of the m-*chlorobenzoate* (**15**) *with hydrogen peroxide.* A solution of **15** (69 mg)and hydrogen peroxide (0.2 ml, 100 vols) in acetic acid (2 ml) was kept at room temperature for 4 days. The mixture was taken up in ether and washed with water. The ether layer was separated and purified by tlc on silica gel (CH_2Cl_2) to obtain a product (23 mg, 32%) which was assigned structure (**19**), ν_{max} (KBr) 3640–3300br, 1805s, and 1715s cm^{-1}, δ (CCl_4) 0.20 (9 H, s, $SiMe_3$), 1.94 (1 H, m, Me_3SiCH), 3.25 (1 H, t, *J* 6 Hz, CCl_2CH), 3.35 (1 H, br, OH), 4.35 (1 H, m), 4.94 (1 H, dm, *J* 6 Hz), 5.18 *J* 1 H, t, *J* 5 Hz), 7.3–7.9 (4 H, m, aromatic), *m/z* 440, 438, 436 (M^+, weak), 425, 423, 421 (M^+-CH_3). The same product was obtained in < 10% yield from the reaction of **16** with MCPBA alone.

8,8-*Dichloro*-2,3-*endo*-*epoxy*-6-*oxa*-4-exo-*trimethylsilyl*-*bicyclo*[3.3.0]*octan*-7-*one* (**20**). The lactone (**16**) (500 mg, 1.9 mmol) and *m*-chloroperbenzoic acid (650 mg) in dry dichloromethane (20 ml) were stirred with sodium hydrogen carbonate (8 g, large excess) at room temperature for 3.5 days. The salts were filtered off and washed thoroughly with dry dichloromethane (stirred with sodium hydrogen carbonate before use). The filtrates were evaporated and purified by tlc on silica gel (benzene) (R_f 0.22; 0.15 g, 28%). An analytical sample was obtained by recrystallization from ether-hexane at room temperature, to give the epoxide (**20**) as leaflets, m.p. 70–1° (Found: C, 42.7; H, 4.8. $C_{10}H_{14}Cl_2O_3Si$ requires: C, 42.7; H, 5.0%), ν_{max} (KBr) 1798s cm^{-1}, δ (CCl_4) 0.12 (9 H, s, $SiMe_3$), 2.08 (1 H, s, Me_3SiCH), 3.38 (1 H, dd, *J* 5.5 and 2 Hz, CCl_2CH), 3.56 and 3.70 (each 1 H, m, OCH), and 4.82 (1 H, d, *J* 5.5 Hz, CO_2CH). The mother liquor was composed mainly of two components. After separation by tlc on silica gel (CH_2Cl_2), the slower running component (R_f about 0.15) was identified by PMR as the alcohol (**22**); the fastest running one (R_f about 0.6) was the trimethylsilyl ether (**21**), a liquid, ν_{max} (film) 1805s cm^{-1}, δ (CCl_4) 0.12 (9 H, s, $SiMe_3$), 3.14 (1 H, t, *J* 5.5 Hz, CCl_2CH), 4.78 (1 H, dd, *J* 5.5 and 2 Hz, Me_3SiOCH), 5.18 (1 H, dd, *J* 5 and 2 Hz, CO_2CH), and 6.27 (2 H, m, CH=CH).

6,6-*Dichloro*-4-endo-*hydroxy*-8-*oxabicyclo*[3.3.0]*oct*-2-*en*-7-*one* (**22**). The lactone (**16**) (530 mg, 2 mmol) was treated with *m*-chloroperbenzoic acid (680 mg) in dry dichloromethane (20 ml) in the presence of sodium hydrogen carbonate (8 g), as in the preparation of the epoxide (**20**) above. The epoxide was not separated but the crude residue was stirred with dilute sulphuric acid at room temperature for 1 hr. The resultant mixture was extracted with dichloromethane (50 ml), washed rapidly with sodium hydrogen carbonate solution, quickly separated, dried (Na_2SO_4), and evaporated. The residue was stirred in sodium hydrogen carbonate solution (30 ml) for 2 hr and the insoluble substances were filtered off. The aqueous filtrate was acidified and then extracted with ether (2 × 20 ml). The ether layer was separated, dried (Na_2SO_4), evaporated and distilled (0.05 mm; bath temp 80–90°) to give the alcohol (**22**) as an oil (306 mg, 73%) (Found: C, 40.0; H, 3.1; Cl, 34.1 $C_7H_5Cl_2O_3$ requires: C, 40.2; H, 2.9; Cl, 33.9%), ν_{max} (film) 36–3100br and 1806s cm^{-1}, δ ($CDCl_3$) 2.48 (1 H, br, OH), 3.29 (1 H, t, *J* 5 Hz, CCl_2CH), 4.94 (1 H, dd, *J* 5.5 and 2.5 Hz, $HOCH$), 5.32 (1 H, dd, *J* 5 and 2.5 Hz, CO_2CH), 6.35 (1 H, dm, J 5.5 Hz, CH=CH), and 6.72 (1 H, dd, J 5.5 and 2.5 Hz, CH=CH). The lactone (**22**) was dissolved in aqueous ammonia and the solvent evaporated. The residue of the ammonium salt (**23**) (or possibly the corresponding amide) showed δ (DMSO-d_6) 3.12 (1 H, t, *J* 6 Hz, $CHCCl_2$), 4.46 (2 H, d, *J* 6 Hz, $CHOH$) and 5.91 (2 H, s, CH=CH).

6,6-*Dichloro*-8-*oxabicyclo*[3.3.0]*oct*-2-*en*-7-*one* (**50**). This lactone was prepared from **7** (107 mg) in the same way that **16** was prepared from **6**. The product (85 mg, 72%) was distilled (0.05 mm; bath temp 45–50°) to give the *lactone* (**50**) (Found: C, 43.4; H, 3.25; Cl, 36.6. $C_7H_6Cl_2O_2$ requires: C, 43.55; H 3.1; Cl, 36.7%), ν_{max} (film) 1890s and 1615w cm^{-1}, δ (CCl_4, 2.68 and 2.82 (each 1 H, m, CH_2), 3.61 (1 H, dt, *J* 8, 8, and 6 Hz, CCl_2CH), 5.42 (1 H, dm, *J* 6 Hz, CO_2CH), and 5.98 and 6.22 (each 1 H, m, CH=CH). It was prepared as a model compound, to give us coupling constants from the bridgehead proton on C-5 to each of the protons on C-4. We hoped to use these values in the assignment of configuration at C-4 of **22**, where the coupling constant between the protons on C-4 and C-5 was about 5.5 Hz. However, the PMR spectrum of **50**, as reported above, shows a remarkable example of *virtual* coupling, giving the impression that the coupling constant both to the *exo* and the *endo* protons on C-4 is 8 Hz.



(**50**)

6,6-*Dichloro*-8-*oxa*-4-exo-*phenylthiobicyclo*[3.3.0]*oct*-2-*en*-7-*one* (**25**). Phenylsulphenyl chloride (300 mg, 2 mmols) was added to a solution of the silane (**16**) (530 mg, 2 mmols) in dichloromethane (5 ml) and the mixture kept at 0–3° for 18 hr. The resultant solution was evaporated to give the adduct (**24**), δ (CCl_4), 0.32 (9 H, s, $SiMe_3$), 2.38 (1 H, m, Me_3SiCH), 3.85 (1 H, d, *J* 7 Hz)m 4.15 (1 H, t, *J* 7 Hz), 4.8–5.2 (2 H, m), and 7.42 (5 H, m, ArH). The adduct was kept in methanol (30 ml) and water (10 ml) with sodium fluoride (400 mg) at room temperature for 20 hr. After removal of most of the methanol, the residue was extracted with ether. The ether layer was dried (Na_2SO_4) and evaporated, and the residue was purified by tlc (SiO_2; benzene; R_f 0.3) to give the sulphide (**25**) (0.39 g, 65%), ν_{max} (CCl_4) 1805 cm^{-1}, and 1585w cm^{-1}, δ (CCl_4) 3.70 (1 H, dd, *J* 7.5 and 6 Hz, C–5 H), 4.36 (1 H, dm, *J* 6 Hz, $PhSCH$), 5.30 (1 H, dm, *J* 6 Hz, CO_2CH), 5.9 (1 H, dm, *J* 6 Hz, CH=CH), 6.24 (1 H, dd, *J* 5.5 and 2 Hz, CH=CH), and 7.3 (5 H, m, ArH), *m/z* 304, 302, 300 (M^+).

8-*Oxa*-4-exo-*phenylthiobicyclo*[3.3.0]*oct*-2-*en*-7-*one* (**26**). The sulphide (**25**) (300 mg, 1 mmol) was stirred with zinc powder (2 g) in a mixture of acetic acid (10 ml) and water (0.5 ml) at room temperature for 24 hr. The inorganic solid was removed by filtration and washed with ether (30 ml). The combined filtrate and washings were washed with water (2 × 70 ml), dried (Na_2SO_4) and evaporated to give the sulphide (**26**) (190 mg, 83%) as leaflets, m.p. 63–5° (CH_2Cl_2–hexane) (Found: C, 67.0; H, 5.3; S, 13.7. $C_{13}H_{12}O_2S$ requires: C, 67.2; H, 5.2; S, 13.8%), ν_{max} ($CHCl_3$) 1780s cm^{-1}, δ (CCl_4) 2.45 (1 H, dd, *J* 10.5 and 18 Hz, CH_AH_BCO), and 2.86 (1 H, dd, *J* 7 and 18 Hz, CH_AH_BCO), 3.38 (1 H, m, C–5 H), 4.42 (1 H, dm, *J* 7 Hz, SCH), 5.32 (1 H, dm, *J* 7.5 Hz, CO_2CH), 6.00 (2 H, s, CH=CH), and 7.26 (5 H, m, ArH).

8,8-*Dichloro*-2,3-exo-*dihyaroxy*-6-*oxa*-4-exo-*trimethylsilyl*-*bicyclo*[3.3.0]*octan*-7-*one* (**27**). The procedure was the same as that in the preparation of the diol (**18**). The lactone (**16**) (100 mg) reacted with osmium tetroxide (100 mg) to give the diol (**27**) (100 mg, 100%) as leaflets, m.p. 155° (from CCl_4 or ether–hexane) (Found: C, 40.4; H, 5.3; Cl, 23.8. $C_{10}H_{16}Cl_2O_4Si$ requires: C, 40.14; H, 5.4; Cl, 23.7%), ν_{max} (KBr) 3650–3250br and 1798s cm^{-1}, δ ($CDCl_3$) 0.17 (9 H, s, $SiMe_3$), 1.64 (1 H, dd, *J* 10 and 3.5 Hz, Me_3SiCH), 3.07 (1 H, dd, *J* 5 and 3.5 Hz, CCl_2CH), 3.23 (2 H, s, OH), 4.07 (1 H, dd, *J* 10 and 3.5 Hz, C–2 H), 4.28 (1 H, t, *J* 3.5 Hz, C–3 H), and 4.76

(1 H, dd, *J* 5 and 3.5 Hz, CO_2CH). The diol was further characterised as its diacetate, 2,3-exo-diacetoxy-7,7-dichloro-4-exo-trimethylsilyl[3.2.0]heptan-6-one (90%) as plates, m.p. 124–6° (hexane) (Found: C, 45.55; H, 5.4; Cl, 19.5. $C_{14}H_{20}Cl_2O_5Si$ requires: C, 45.8; H, 5.5; Cl, 19.3%), ν_{max} (CCl_4) 1804s and 1746s cm^{-1}, δ (CCl_4) 0.0 (9 H, s, $SiMe_3$), 1.57 (1 H, dd, *J* 8 and 4 Hz, Me_3SiCH), 1.88 and 1.92 (each 3 H, s, OAc), 3.30 (1 H, dd, *J* 9.5 and 7.5 Hz, C–1 H), 3.96 (1 H, t, *J* 9.5 Hz, C–5 H), 5.18 (1 H, dd, *J* 7.5 and 4 Hz, C–2 H), and 5.44 (1 H, t, *J* 4 Hz, C–3 H).

6,6-*Dichloro*-4-exo-*methoxymethylbicyclo*[3.2.0]*hept*-2-*en*-7-*one* (**28**). A mixture of **6** (5.0 g, 20 mmol), chloromethyl methyl ether (2.0 g, 25 mmol), and stannic chloride (10 ml, excess) in dry dichloromethane (70 ml) was heated under reflux under nitrogen for 60 hr. The mixture was poured into a mixture of crushed ice and conc. hydrochloric acid and the organic layer dried (Na_2SO_4) and evaporated. The residue was taken up in carbon tetrachloride, filtered and the filtrate distilled to give the ether (**28**) (3.45 g, 78%), b.p. 65–8°/0.03 mm (Found: C, 48.6; H, 4.6; Cl, 32.45. $C_9H_{10}Cl_2O_2$ requires: C, 48.9; H, 4.6; Cl, 32.1%), ν_{max} (film) 1805s and 1604w cm^{-1}, δ (CCl_4) 3.15–3.60 (7 H, m, with a singlet at 3.35), 4.55 (1 H, m, C–1 H), and 5.82 (2 H, m, CH=CH). The use of the harmless dimethoxymethane in place of chloromethyl methyl ether gave the same product but in only 15% yield (R. V. Williams).

4-exo-*Methoxymethylbicyclo*[3.2.0]*hept*-2-*en*-7-*one*. The ether (**28**) (2.50 g) was stirred with zinc powder (10 g) in an acetic acid–water mixture (30 ml: 2 ml) at room temperature for 30 hr. The inorganic solids were filtered off and washed with ether. The combined filtrate and washings were washed with water (2 × 200 ml) then with sodium hydrogen carbonate solution. The ether layer was dried (Na_2SO_4), and evaporated, and the residue distilled to give the ether (1.40 g, 81%), b.p. 45–8°/0.25 mm (Found: C, 71.0; H, 8.0. $C_9H_{12}O_2$ requires: C, 71.0; H, 8.0%), ν_{max} (film) 1775s and 1600w cm^{-1}, δ (CCl_4) 2.50–3.45 (9 H, m, with a singlet at 3.26), 4.18 (1 H, m, C–1 H) and 5.74 (2 H, m, CH=CH).

4-exo-*Methoxymethyl*-8-*oxabicyclo*[3.3.0]*oct*-2-*en*-7-*one* (**29**). *Method A*. The ketone described immediately above (880 mg, 5.8 mmol), hydrogen peroxide (1 ml, 100 vols), and water (2 ml) were kept in acetic acid (15 ml) at 0–3° for 72 hr. The mixture was taken up in ether (30 ml) and the solution washed with water (3 × 100 ml). The residue from the dried (Na_2SO_4) ether layer was crystallised to give the lactone (**29**) (640 mg, 66%) as plates, m.p. 29–30° (cold hexane) (Found: C, 64.1; H, 7.2. Calc. for $C_9H_{12}O_3$: C, 64.3; H, 7.2%), ν_{max} ($CHCl_3$) 1770s cm^{-1}, δ (CCl_4) 2.40 (1 H, m), 2.90 (3 H, m), 3.36 (5 H, m, with a singlet at 3.36, $MeOCH_2$), 5.55 (1 H, m, CO_2CH) and 6.02 (2 H, m, CH=CH), *m/z* 168 (M^+). This compound was identical (PMR, solution IR, tlc) with an authentic sample[28] of optically active lactone.

Method B. The ketone (**28**) (470 mg, 2.1 mmol), hydrogen peroxide (0.9 ml, 100 vols), and water (2 ml) in acetic acid (15 ml) were kept at 0–3° for 3 days. The mixture was taken up in ether (20 ml) and the solution washed with water (3 × 70 ml). The ether layer was dried (Na_2SO_4), and evaporated to give the lactone, ν_{max} (film) 1800s and 1620w cm^{-1}, δ (CCl_4) 3.05–3.65 (7 H, m, with a singlet at 3.40), 5.50 (1 H, m, CO_2CH), and 6.00 and 6.20 (each 1 H, m, CH=CH), which was then stirred with zinc powder (6 g) in an acetic acid–water mixture (15 ml: 0.5 ml) at room temperature for 40 h. The inorganic solids were filtered off and washed with ether. The combined filtrate and washings were washed with water (3 × 70 ml), dried (Na_2SO_4), and evaporated. The residue was crystallised from cold hexane to give the lactone (**29**) (220 mg, 62%), identical with the sample prepared by method A. A distillation of the crude product (0.02 mm, bath temp 70–85°) was found to be helpful when crystallisation was difficult.

4-exo-*Trimethylsilylbicyclo*[3.2.0]*hept*-2-*en*-6-*one* (**31**). The ketone (**6**) (10.0 g, 0.04 mol) was stirred with zinc powder (20 g) in a mixture of acetic acid (100 ml) and water (5 ml) at 40° for 36 hr. The inorganic solids were filtered off, and washed with ether (200 ml). The combined filtrate and washings were washed with water (3 × 250 ml) and with sodium hydrogen carbonate solution. The ether layer was dried (Na_2SO_4) and evaporated and the residue distilled to give the ketone (**31**), (6.1 g, 85%), b.p. 43–5°/0.05 mm, 72–3°/3 mm (Found: C, 66.9; H, 9.1. $C_{10}H_{16}OSi$ requires: C, 66.6; H, 9.0%), ν_{max} (film) 1776s and 1592w cm^{-1}, δ (CCl_4) −0.04 (9 H, s, $SiMe_3$), 2.30 (1 H, m, Me_3SiCH), 2.5–2.85 (1 H, m, C–1 H), 3.15–3.45 (2 H, m), 3.64 (1 H, m), and 5.68 (2 H, m, CH=CH). The ketone was also characterised as its ethylene glycol acetal, 4-exo-*trimethylsilylbicyclo*[[3.2.0]*hept*-2-*en*-6-*one ethyleneglycol acetal*: the ketone (**31**) (3.24 g, 18 mmol), triethyl orthoformate (2.7 g, 18 mmol) and toluene-*p*-sulphonic acid (0.1 g) in dry ethylene glycol (35 g) were kept at room temperature for 24 hr; potassium hydroxide was added and the mixture poured into water (150 ml) and extracted with chloroform (3 × 40 ml) to give the acetal (3.3 g, 82%), b.p. 64–6°/0.7 mm (Found: C, 64.5; H, 8.8. $C_{12}H_{20}O_2Si$ requires: C, 64.2; H, 9.0%), ν_{max} (film) 1596w cm^{-1}, δ (CCl_4) −0.10 (9 H, s, $SiMe_3$), 1.95–2.15 (2 H, m), 2.4–2.7 (1 H, m), 2.92 (2 H, m), 3.72 (4 H, m, OCH_2), and 5.58 (2 H, m, CH=CH).

6-*Oxa*-4-exo-*trimethylsilylbicyclo*[3.3.0]*oct*-2-*en*-7-*one* (**32**). The ketone (**31**) (1.35 g, 7.5 mmol), hydrogen peroxide (15 ml, 20 vols) and sodium hydroxide (0.4 g, 10 mmol) in methanol (50 ml) were kept at room temperature for 2 hr. The mixture was acidified and most of the solvent was evaporated. The residue was taken up in ether, washed with water and evaporated to give the lactone (**32**) (1.31 g, 83%), as plates, m.p. 52–3° (from hexane) (Found: C, 61.1; H, 8.2. $C_{10}H_{16}O_2Si$ requires: C, 61.2; H, 8.2%), ν_{max} (KBr) 1775s and 1596w cm^{-1}, δ (CCl_4) −0.07 (9 H, s, $SiMe_3$), 2.20 (1 H, m, Me_3SiCH), 2.16–2.33 (1 H, dm, *J* 18 Hz, CH_AH_BCO), 2.47–2.73 (1 H, dd, *J* 18 and 8 Hz, CH_AH_BCO), 3.26 (1 H, m, C–1 H), 4.82 (1 H, d, *J* 5.5 Hz, CO_2CH), 5.34 (1 H, dt, *J* 5 and 2 Hz, CH=CH), 5.68 (1 H, m, CH=CH).

4-exo-*Acetyl*-6,6-*dichlorobicyclo*[3.2.0]*hept*-2-*en*-7-*one* (**35**, R=Me). Stannic chloride (7 ml) was added dropwise to a solution of the silane (**6**) (5.0 g) in acetyl chloride (20 ml) at room temperature and kept at 0–3° for 24 hr. The mixture was then poured into an ice–water mixture and extracted with light petroleum (60–80°). Column chromatography on silica gel eluting with light petroleum (40–60°)–dichloromethane (3:1) removed a mixture of by-products, and elution with light petroleum (40–60°)–dichloromethane (1:1) then gave the ketone (**35**, R=Me) (1.6 g, 36%) as prisms, m.p. 66–7° (cold hexane) (Found: C, 49.4; H, 3.7; Cl, 32.5. $C_9H_8Cl_2O_2$ requires: C, 49.35; H, 3.7; Cl, 32.4%), ν_{max} (KBr) 1805s, 1712s, and 1605w cm^{-1}, δ (CCl_4) 2.27 (3 H, s, COMe), 4.05 (2 H, m, MeCOCH and C–5 H), 4.60 (1 H, m, C–1 H), and 5.08 and 6.08 (each 1 H, m, CH=CH).

6,6-*Dichloro*-4-exo-*propanoylbicyclo*[3.2.0]*hept*-2-*en*-7-*one* (**35**, R=Et). In a similar preparation (by R. V. Williams), the allylsilane (**6**) (0.25 g), propanoyl chloride (0.5 ml) and stannic chloride (0.5 ml) were kept at 0° for 1 week to give the ketone (**35**, R=Et) (0.48 g, 20%), ν_{max} (CCl_4) 1815 and 1725 cm^{-1}, δ (CCl_4) 1.05 (3 H, t, *J* 6 Hz, CH_3), 2.55 (2 H, q, *J* 6 Hz, CH_3CH_2CO), 4.0 (2 H, m, other ring protons), 4.55 (1 H, m, CHCOEt), 5.80 and 6.15 (each 1 H, m, HC=CH). (Found: M^+, 232.0047, $C_{10}H_{10}O_2{}^{35}Cl_2$ requires M, 232.0058), *m/z* 232 (7.5%, M^+), 203 (10, M–Et), 175 (73, M–EtCO) and 57 (100, $M-C_7H_5OCl_2$).

6,6-*Dichloro*-4-exo-*octanoylbicyclo*[3.2.0]*hept*-2-*en*-7-*one* (**35**, R=n-C_7H_{15}). In a similar preparation (by R. V. Williams), the allylsilane (**6**) gave the ketone (**35**, R=n-C_7H_{15}) (40%), ν_{max} (CCl_4) 1820 and 1725 cm^{-1}, δ 0.5 (3 H, t, CH_3), 1.15–1.80 (10 H, m, remaining CH_2's), 2.5 (2 H, t, CH_2CO–), 3.9–4.1 (2 H, m remaining ring protons), 4.6 (1 H, m, $CHCOCH_2$–), 5.78 and 6.04 (each 1 H, m, HC=CH) (Found: M^+, 302.0842. $C_{15}H_{20}O_2{}^{35}Cl_2$ requires M 302.0840) *m/z* 302 (M^+, 12%), 175 (16, M-octanoyl) and 127 (100, $M-C_7H_5OCl_2$).

6-exo-*Methyl*-4-exo-*trimethylsilylbicyclo*[3.3.0]*oct*-2-*en*-7-*one* (**37**). *Method A*. An ethereal solution of diazoethane

(50 ml, prepared from 4.5 g of N-ethyl-N-nitrosourea, washed with water before use) was added to an ice-cold solution of **6** (1.0 g, 4 mmol) in methanol (10 ml) and kept at 0° for 1 hr. Most of the solvent was evaporated off, the residue was dissolved in methanol (10 ml) and ethereal diazoethane (40 ml, from 4 g of N-ethyl-N-nitrosourea) was again added and the mixture kept at 0° for 1 hr. The solvents were evaporated and the residue taken up in light petroleum (40–60°) and the insoluble polymers filtered off. The residue from the filtrate, [**36**, ν_{max} (film) 1780 cm^{-1}] was stirred with zinc powder (3 g) and water (1 ml) in acetic acid (20 ml) at room temperature for 20 h. Similar work-up as in previous dechlorinations and chromatography on a silica gel column gave the mixture of diastereoisomers (**37**) (430 mg, 52%). After equilibration with sodium methoxide, this mixture gave **37b**, identical with a sample prepared by Method B.

Method B. Aqueous potassium hydroxide (50 ml, 30%) was added to a mixture of N-ethyl-N-nitrousourea (18 g) and the ketone (**31**) (5.6 g, 31 mmol) in methanol (300 ml) at −65°. The mixture was stirred at −65° for 15 min, then at −40° to −45° for 1 hr, and finally allowed to warm to room temperature. Most of the solvent was evaporated off, the residue partitioned between ether and water, the ether layer dried (Na_2SO_4), evaporated, and the residue chromatographed on a column (silica gel, 180 g), eluting with light petroleum (40–60°)-dichloromethane (5:1) to give the mixture of diastereoisomers of 7-methyl-4-exo-trimethylsilylbicyclo[3.3.0]oct-2-en-6-one (**38**) (2.4 g, 37%), b.p. 52–5°/0.02 mm (Found: C, 69.4; H, 9.96. $C_{12}H_{20}OSi$ requires: C, 69.2; H, 9.7%), ν_{max} 1740s and 1600w cm^{-1}, $\delta(CCl_4)$ −0.04 (9 H, s, $SiMe_3$), 1.0 (3 H, d, *J* 6.5 Hz, Me), 1.4–2.6 (5 H, m), 3.26 (1 H, m, C-1 H), and 5.4 and 5.6 (each 1 H, m, CH=CH). Further elution with light petroleum (40–60°)-dichloromethane (3:1) gave the mixture of diastereoisomers (**37**), which was stirred under nitrogen in a solution of sodium methoxide in methanol (0.7 M, 100 ml) at room temperature for 7 hr. The mixture was neutralised under nitrogen at 0° with dilute hydrochloric acid and the solvent evaporated. The residue was taken up in ether, washed with water, dried (Na_2SO_4), and evaporated. Distillation of the residue gave the ketone (**37b**) (2.7 g, 42%), b.p. 55–8°/0.02 mm (Found: C, 69.3; H, 9.9. $C_{12}H_{20}OSi$ requires C, 69.2; H, 9.7%), ν_{max} 1740s and 1600w cm^{-1}, $\delta(CCl_4)$ −0.12 (9 H, s, $SiMe_3$), 0.96 (3 H, d, *J* 7 Hz, Me), 1.85 (2 H, m), 2.24 (3 H, m), 3.18 (1 H, m, C-1 H), and 5.50 and 6.65 (each 1 H, m, CH=CH).

7-endo-*Chloro*-4-exo-*trimethylsilylbicyclo*[3.2.0]*hept*-2-*en*-6-*one* (**39**). The ketone (**6**) (10.0 g, 40 mmol), zinc powder (2.9 g, 44 mmol), and water (2 ml) in acetic acid (50 ml) were stirred at room temperature for 22 hr. The inorganic salts were filtered off and washed with ether (50 ml). The combined filtrate and washings were washed with water (3 × 250 ml) and then with sodium hydrogen carbonate solution. Distillation gave the ketone (**39**) (8.0 g, 94%), b.p. 60–3°/0.01 mm (Found: C, 56.47; H, 6.95. $C_{10}H_{15}OClSi$ requires: C, 55.93; H, 7.04%), ν_{max} (film) 1800s and 1600w cm^{-1}, $\delta(CCl_4)$ −0.05 (9 H, s, $SiMe_3$), 2.35 (1 H, m, Me_3SiCH), 3.5–3.9 (2 H, m, bridgehead H's), 4.98 (1 H, dd, *J* 8, 3.5 Hz, C-7 H), and 5.60 and 5.80 (each 1 H, m, CH=CH).

6-exo-*Methyl*-4-exo-*trimethylsilylbicyclo*[3.3.0]*oct*-2-*en*-7-endo-*ol* (**42**). *Method A.* Sodium borohydride (450 mg, 12 mmol) was added to a solution of the ketone (**37b**) (2.40 g, 11.5 mmol) in methanol (100 ml) at 0°. After stirring at 0° for 2 hr, the mixture was acidified with acetic acid. The solvent was evaporated off and the residue taken up in ether. The solution was washed with water, dried (Na_2SO_4), and evaporated. The residue was crystallised from cold aqueous methanol to give the alcohol (**42**) (2.1 g, 88%), needles, m.p. 74–6° (Found: C, 68.4; H, 10.8. $C_{12}H_{22}OSi$ requires: C, 68.5; H, 10.5%), ν_{max} (nujol) 3300br cm^{-1}, $\delta(CCl_4)$ −0.05 (9 H, s, $SiMe_3$), 0.97 (3 H, d, *J* 6.5 Hz, Me), 1.1–1.5 (2 H, m), 1.6–2.35 (3 H, m), 2.83 (1 H, m, C-1 H), 3.42 (2 H, m, CHOH), and 5.51 (2 H, s, CH=CH). A further 120 mg (4%) was obtained from the mother liquor after preparative tlc (SiO_2, CH_2Cl_2, R_f 0.15).

Method B. Ethereal diazoethane (0.04 M, 150 ml) was added to an ice-cooled solution of the ketone (**39**) (1.08 g, 5 mmol) in methanol (20 ml) and the mixture kept at 0° for 5 hr. Excess diazoethane was decomposed with acetic acid and the solvent was evaporated. The residue was dissolved in light petroleum (40–60°), filtered, and washed with water. After evaporation of solvent, the residue was stirred with zinc powder (1.5 g) and water (1 ml) in acetic acid (20 ml) at room temperature for 60 hr. The inorganic solids were filtered off and washed with ether (25 ml). The combined filtrate and washings were washed with water (3 × 70 ml) and sodium hydrogen carbonate solution, and then evaporated. The residue was purified by column chromatography on silica gel. Elution with light petroleum (40–60°)-dichloromethane (6:1) gave a compound assigned as **41** (280 mg, 27%), ν_{max} (film) 1712s, 1640w, and 1608w cm^{-1}, $\delta(CCl_4)$ 0.08 (9 H, s, $SiMe_3$), 1.74 (3 H, t, *J* 1.5 Hz, Me), 2.05 (1 H, m, Me_3SiCH), 2.75 (1 H, ddm, *J* 6.5 and 4 Hz, HCCO), 3.71 (1 H, m, allylic H), 5.56 (2 H, m, CH=CH), and 7.24 (1 H, m, CMe=CH), *m/z* 206 (M^+). Further elution with light-petroleum (40–60°)-dichloromethane (3:1) gave the mixture of ketones (**37**) (760 mg, 72%), which was equilibrated with sodium methoxide (1.2 g) in methanol (40 ml) at room temperature to give the ketone (**37b**). The crude **37b** was reduced with sodium borohydride (150 mg) in methanol (30 ml) at 0° as described under Method A, above, and the product crystallised from cold aqueous methanol to give the *endo* alcohol (500 mg, 48% based on **39**) identical to the sample prepared above.

6-exo-*Methyl*-4-*trimethylsilylbicyclo*[3.3.0]*oct*-2-*en*-7-exo-*yl Acetate* (**43**). Methanesulphonyl chloride (1.6 g) was added dropwise to a solution of the alcohol (**42**) (2.58 g, 12.3 mmol) in dry pyridine (20 ml). The mixture was stirred at room temperature for 18 hr and then diluted with dry ether (40 ml). The salts were removed by filtration and washed with dry ether. The combined filtrates were evaporated and the residue was filtered through a silica gel column (30 g) with dichloromethane to give the methanesulphonate, ν_{max} (film) 1602w, 1350s, and 1165s cm^{-1}, $\delta(CCl_4)$ −0.1 (9 H, s, $SiMe_3$), 1.0 (3 H, d, *J* 5.5 Hz, Me), 1.3–3.0 (6 H, m), 2.8 (3 H, s, O_3SMe), 4.3 (1 H, m, SO_3CH), and 5.5 (2 H, m, CH=CH). The methanesulphonate was heated with tetraethylammonium acetate (23 g) in dry acetone under reflux under a dry atmosphere for 30 hr. The solvent was evaporated and the residue taken up in dichloromethane. The solution was washed twice with water (200 ml) containing a few ml of acetic acid, dried (Na_2SO_4), and evaporated. The residue was chromatographed on a silica gel column. After the separation of a small amount of a by-product (R_f 0.9, CH_2Cl_2) by elution with light petroleum (40–60°), a major fraction was eluted with dichloromethane and distilled to give the acetate (**43**) (2.46 g, 80%), b.p. 65–8°/0.01 mm (Found: C, 66.8; H, 9.65. $C_{14}H_{24}O_2Si$ requires: C, 66.6; H, 9.6%), ν_{max} (film) 1742s and 1605w cm^{-1}, $\delta(CCl_4)$ −0.04 (9 H, s, $SiMe_3$), 0.90 (3 H, d, *J* 7 Hz, Me), 1.6 (3 H, m), 1.88–2.26 (4 H, m, with a singlet at 2.00), 3.12 (1 H, m, C-1 H), 5.06 (1 H, m, AcOCH), and 5.42 (2 H, m, CH=CH).

Reaction of chlorosulphonyl isocyanate with the allylsilane (**6**). (R. V. Williams) CSI (0.1 ml) was added to the allylsilane (**6**) (0.25 g) in dry carbon tetrachloride (0.5 ml) under nitrogen and the mixture kept at 65° for 72 hr. The PMR spectrum of the mixture now indicated the clean formation of **45**: δ 0.35 (9 H, s, $SiMe_3$), 3.55–4.25 (2 H, m, remaining ring protons), 4.50 (1 H, m, –CHCO–), and 5.90 (2 H, m, HC=CH).

2-exo-*Carbamoyl*-6-exo-*methylbicyclo*[3.3.0]*oct*-3-*en*-7-exo-*yl Acetate* (**46**). Chlorosulphonyl isocyanate (1 ml, 11 mmol) was added dropwise to a solution of the allylsilane (**43**) (2.34 g, 9.3 mmol) in dry carbon tetrachloride (5 ml) at 0°. The mixture was kept at 0° for 15 min and then at room temperature for 2.5 hr. The reaction was observed (PMR) to give the analogous adduct, δ 0.3 (9 H, s, $SiMe_3$), 1.0 (3 H, d, *J* 7 Hz), 1.2–3.0 (8 H, m, with a singlet at 1.9), 4.3 (1 H, m), 4.65 (1 H, m), 5.5 and 6.0 (each 1 H, m, CH=CH). The solvent was

evaporated off, the residue dissolved in a mixture of acetone (25 ml), water (10 ml) and 3N hydrochloric acid (2 ml), kept at room temperature for 3.5 h, and then extracted with dichloromethane (6 × 15 ml). The residue from the extracts was crystallised from diisopropyl ether, to give the amide (**46**) (1.14 g, 55%), m.p. 130–6°. (Found: C, 64.25; H, 7.65; N, 6.05. $C_{12}H_{17}NO_3$ requires: C, 64.55; H, 7.68; N, 6.27%), ν_{max} ($CHCl_3$) 3525, 3410, 1725s, and 1680s cm^{-1}, δ ($CDCl_3$) 1.0 (3 H, d, *J* 7 Hz, Me), 1.45–2.35 (7 H, m, with a singlet at 2.02), 3.02 and 3.15 (each 1 H, m, allylic H), 5.12 (1 H, q, *J* 8 Hz, 4.5 Hz, AcOCH), 5.60, 5.85 (each 1 H, m, CH=CH), and 6.05 (2 H, broad, NH_2), *m/z*, 223 (M^+, weak) and 206 ($M^+ - NH_3$).

2-exo-*Carbomethoxy*-6-exo-*methylbicyclo*[3.3.0]*oct*-3-*en*-7-exo-*yl acetate* (**47**). *Method A.* Sodium nitrite (4 g) was added in small portions over 1.5 h to the amide (**46**) (560 mg) in acetic acid (2.5 ml) and acetic anhydride (12 ml) at 0° and the mixture kept at 0–3° for 16 hr. Cold saturated aqueous sodium acetate solution (20 ml) was added to the precipitated solid and the mixture stirred in an ice bath for 0.5 hr, and then at room temperature for 2 hr. The mixture was extracted with dichloromethane (5 × 20 ml), and the extracts evaporated. The residue was dissolved in methanol and excess ethereal diazomethane added. After 0.5 hr at room temperature, the excess diazomethane was decomposed with acetic acid, the mixture was washed with water, dried (Na_2SO_4), and evaporated. The carbon tetrachloride-soluble part of the residue was purified by tlc (SiO_2, ether, R_f 0.6) followed by distillation (bath temperature (130–140°, 0.07 mm) to give the ester (**47**) (410 mg, 69%) (Found: C, 65.44; H, 7.85. $C_{13}H_{18}O_4$ requires: C, 65.5; H, 7.6%), ν_{max} (film) 1740s cm^{-1} δ (CCl_4) 0.96 (3 H, d, *J* 7 Hz, Me), 1.38–2.24 (7 H, m, with a singlet at 1.96), 2.95, 3.08 (each 1 H, m, allylic H), 3.60 (3 H, s, OMe), 5.03 (1 H, q, *J* 8 and 4 Hz, AcOCH), 5.52 and 5.75 (each 1 H, m, CH=CH).

Method B. Chlorosulphonyl isocyanate (500 mg, 3.5 mmol) was added dropwise to the silane (**43**) (715 mg, 2.8 mmol) in carbon tetrachloride (1.2 ml) at 0°. After keeping at 0° for 10 min and then at room temperature for 2.5 hr, the solvent was evaporated off. The residue was stirred at 0° with acetic acid (3 ml) in acetic anhydride (15 ml), and sodium nitrite (4.5 g) added in portions over 1 hr. The mixture was kept under nitrogen at 0–3° for 16 hr, and the precipitate separated. Sodium acetate (10 g) in water (25 ml) was added at 0° to the precipitate; the mixture was stirred at 0° for 2 hr, then at room temperature for 3 hr, and then extracted with dichloromethane (5 × 25 ml), and the residue treated with diazomethane and purified as above to give the ester (**47**) (410 mg, 61%).

Methyl 6α-*Acetoxy*-7α-*methyl*-1-*hydroxy*-1,4aα,5,6,7,7aα-*hexahydrocyclopenta*[c]*pyran*-4-*carboxylate* (**48**). *Method A.* The diester (**47**) (4 mg, 0.04 mmol) was stirred with osmium tetroxide (100 mg, 0.4 mmol) in benzene (4 ml) at room temperature for 3 hr. After evaporation of solvent, the residue was taken up in 95% ethanol (10 ml). Sodium metabisulphite (1.5 g) in water (5 ml) was added and the mixture was stirred at room temperature for 3 hr. The mixture was extracted with ether (6 × 15 ml) and the extracts were dried and evaporated to give the crude diol, ν_{max} (film) 3440br and 1730s cm^{-1}, δ ($CDCl_3$) 1.04 (3 H, d, *J* 6 Hz, Me), 1.4–2.7 (7 H, m, with a singlet at 2.04), 3.22 (1 H, m), 3.70 (3 H, s, CO_2Me); 3.80 (1 H, m), 4.37 (1 H, m), 5.18 (4 H, m, CHOH). The diol was dissolved in 70% aqueous dioxan, (6 ml) and this solution added dropwise over 10 min to an ice-cold solution of sodium metaperiodate (95 mg, 0.44 mmol) in 50% aqueous dioxan (6 ml), and stirred at 0° for 4 hr. The solvent was evaporated and the residue dissolved in chloroform (10 ml), washed with water (5 ml), dried (Na_2SO_4), and evaporated. The residue was purified by tlc [SiO_2, EtOAc–benzene (1:2)] to give loganin aglucone acetate (**48**) (50 mg, 46%), a viscous liquid, ν_{max} ($CHCl_3$) 3600m, 3495br, 1735s, 1710s, and 1640s cm^{-1}, δ ($CDCl_3$) 1.07 (3 H, d, *J* 6.5 Hz, Me), 1–2.5 (4 H, m), 2.06 (3 H, s, OAc), 3.12 (1 H, m), 3.71 (3 H, s, CO_2Me), 4.4 (1 H, br, OH), 5.00 (1 H, d, *J* 5 Hz), 5.20 (1 H, m), and 7.41 (1 H, dm, *J* 1 Hz, C=CH). This compound was identical (tlc, solution IR, and PMR) with loganin aglucone monoacetate,[39] which we prepared from loganin.

Method B. The diester (**47**) (120 mg, 0.5 mmol) in dry dichloromethane (20 ml) was cooled to −65°C. Dry ozone was bubbled through this solution at a flow rate of *ca.* 10 l/hr until the solution became faintly blue. Dry oxygen was then passed through the solution to flush off any excess ozone. Dimethyl sulphide (1 ml) was then added dropwise and the mixture kept at −65° for 2 hr, then at 0° for 1 hr, and room temperature for 1 hr. The solvent and excess reagent were evaporated and the residue purified by tlc to give **48** (79 mg, 47%).

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