# The Diels–Alder Route to Allylsilanes from 1-Trimethylsilylbutadienes †

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The synthesis and Diels–Alder reactions of 1-trimethylsilylbutadiene (3) and its 3-methyl (17), 3-trimethyl-silyloxy (20), 4-methyl (4), and 4-trimethylsilyl (6) derivatives are reported. The silyl group reduces somewhat the rate of the Diels–Alder reactions, and has, if anything, a small 'ortho'-directing effect on the regioselectivity in the reactions of (3) with methyl acylate, methyl propiolate, citraconic anhydride, and 2,6-dimethylbenzoquinone. The other substituent in the dienes (17), (20), and (4) is therefore the major influence on the regioselectivity in the reactions of these dienes with methyl acrylate and methyl propiolate. The products of the Diels–Alder reactions of (3), (17), and (4) are allylsilanes, which undergo clean protodesilylation with acid, and, with the acid and ester derived from the maleic anhydride adduct of (3), undergo epoxidation and sulphenylation reactions giving an allyl alcohol (33) and an allyl sulphide (37), respectively. The adducts from (20) can be hydrolysed to β-silylketones, which can be converted into enones by bromination. 1-Pentamethyldisilylbutadiene (15) is no more reactive and no more regioselective than (3). The 'ortho'-adduct (42) from the reaction of (3) and methyl propiolate aromatises with DDQ to give methyl m-trimethylsilylbenzoate (53) in high yield, in a reaction involving rearrangement of the silyl group, even though a direct dehydrogenation is an available pathway.

ALLYLSILANES are becoming well established inter-mediates in organic synthesis, because they usually react with electrophiles in the general sense of Scheme 1.[1] Allyl-metal compounds in general behave this way, but, because allyl-metal compounds are unstable with respect to 1,3-allylic rearrangement,[2] the overall regioselectivity
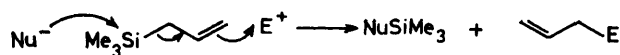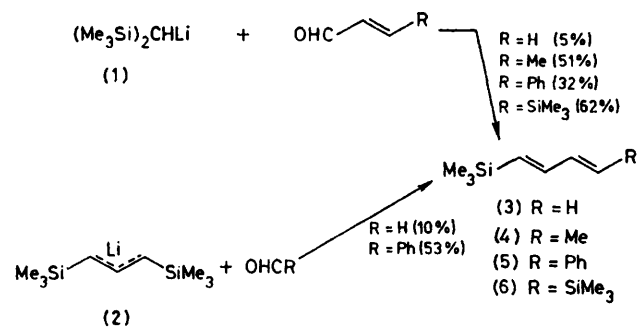

SCHEME 1

of their reactions with electrophiles is not always easy to control. Allylsilanes are uniquely useful, therefore, when a specific allylsilane can be made, for it can be relied upon not to undergo allylic rearrangement under all ordinary conditions,[3] and, furthermore, it can be expected to be stable enough to many reaction conditions to be carried through several steps before being used in the sense of Scheme 1.[4] We have, therefore, been interested in developing regioselective syntheses of allylsilanes. One such synthesis is the subject of this paper: Diels–Alder reactions of 1-silylbutadienes give adducts, which are allylsilanes. In three preliminary communications,[5-7] we reported that this reaction is a powerful method for the synthesis of functionalised allylsilanes, that the allylsilanes react with protons, peracid, and phenylsulphenyl tetrafluoroborate in the general sense of Scheme 1, and that the silyl group has only a small directing effect upon the regioselectivity of the Diels–Alder reaction. We now report the details of this work. Similar work to some of our own has also been done by Jung and Gaede.[8]

Synthesis of the Silylated Butadienes. 1-Trimethyl-silylbutadiene (3) was a known compound, which had been prepared by the dehydration of 1-trimethylsilyl-but-3-en-2-ol,[9] and by hydrosilation of but-1-en-3-yne.[10] We were unable to repeat the former, and, in order to make a variety of dienes with different substituents, we needed a more flexible method than the latter. We

therefore developed several routes to the various 1-trimethylsilylated dienes (3), (4), (5), (6), (15), (17), and (20) (Schemes 2 and 3). The methods in Scheme 2 are limited, because the organolithium reagents (1) and (2)

SCHEME 2

are apt to deprotonate enolisable aldehydes and ketones,[11] and, for less obvious reasons, the yields for the parent diene (3) were low. The methods in Scheme 3 are much more versatile, and are all based on the ready
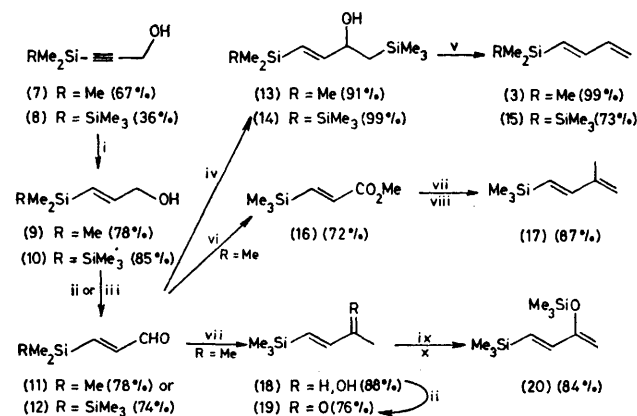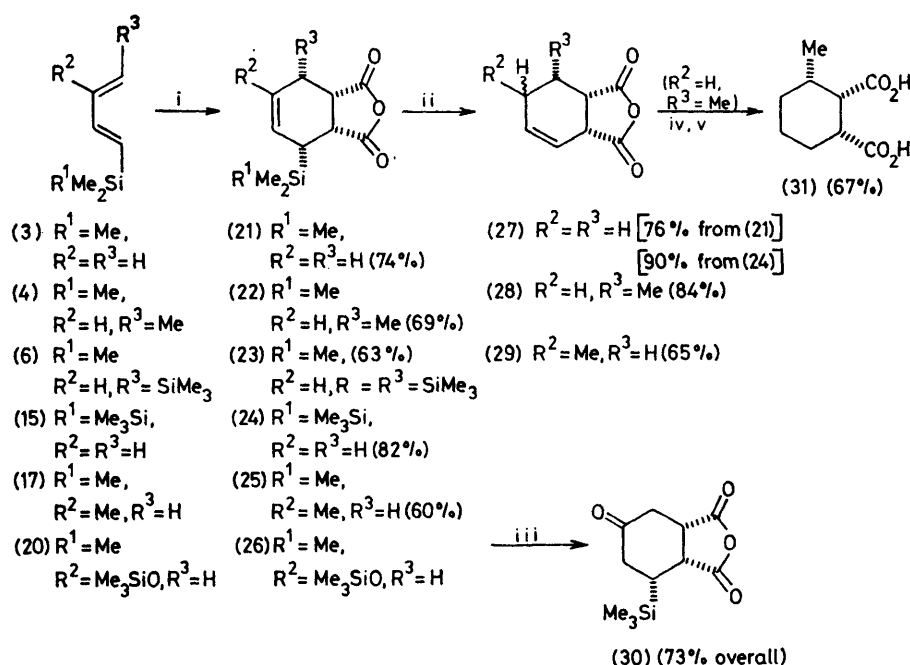

SCHEME 3 *Reagents:* i, LiAlH₄; ii, MnO₂; iii, (C₅H₆NH⁺)₂-[Cr₂O₇]²⁻; iv, Me₃SiCH₂MgCl; v, TsOH, Et₂O; vi, MnO₂, MeOH, NaCN; vii, MeMgI; viii, MeSO₂Cl, Et₃N; ix, LDA; x, Me₃SiCl

† No reprints available.

availability of the silylated allylic alcohol (9).[12] Manganese dioxide was used for the oxidation of the alcohol (9) in this work, where we got a yield of 78%; Jung and Gaede [8] found pyridinium chlorochromate more convenient (67% yield), but we have since found that pyridinium dichromate [13] is better still, being both convenient and giving a yield of 90%.

The silylated methyl vinyl ketone (19) was prepared for this work by the method shown in Scheme 3. It is a known compound, which had been prepared by other methods.[14,15] We have since prepared it by yet another method,[16] in which 1-trimethylsilylbut-1-yn-3-one [17] is reduced with lithium aluminium hydride to give the alcohol (18), which is then oxidised with pyridinium dichromate [13] to the ketone (19). This work will be

In each case only one adduct was detected. In the case of the adduct (22), we were able to prove that it has the all-cis-stereochemistry shown; it is therefore very likely that the other adducts are also the result of reaction in the endo-sense. The diene (4) was prepared from (E)-crotonaldehyde, with the result that the double bond next to the methyl group in (4) will have the (E)-configuration. The double bond next to the silyl group also has the (E)-configuration, as we could see from the vicinal coupling constant of the hydrogen atoms (J 19 Hz). [Under our conditions, Peterson reactions of the lithium derivative (1) with aldehydes, give only the (E)-vinylsilanes, in contrast to the report that mixtures of stereoisomers are obtained.[11]] Thus the diene (6) is the (EE)-isomer and the silyl and methyl groups in the

(3) R^1 = Me,
R^2 = R^3 = H

(4) R^1 = Me,
R^2 = H, R^3 = Me

(6) R^1 = Me
R^2 = H, R^3 = SiMe$_3$

(15) R^1 = Me$_3$Si,
R^2 = R^3 = H

(17) R^1 = Me,
R^2 = Me, R^3 = H

(20) R^1 = Me
R^2 = Me$_3$SiO, R^3 = H

(21) R^1 = Me,
R^2 = R^3 = H (74%)

(22) R^1 = Me
R^2 = H, R^3 = Me (69%)

(23) R^1 = Me, (63%)
R^2 = H, R = R^3 = SiMe$_3$

(24) R^1 = Me$_3$Si,
R^2 = R^3 = H (82%)

(25) R^1 = Me,
R^2 = Me, R^3 = H (60%)

(26) R^1 = Me,
R^2 = Me$_3$SiO, R^3 = H

(27) R^2 = R^3 = H [76% from (21)]
[90% from (24)]

(28) R^2 = H, R^3 = Me (84%)

(29) R^2 = Me, R^3 = H (65%)

(31) (67%)

(30) (73% overall)

SCHEME 4 Reagents: i, maleic anhydride; ii, TsOH, C_6H_6; iii, HCl, H_2O; iv, H_2, Pd/C; v, H_2O

reported in connection with other chemistry of the ketone (19), which we have found to be a useful synthon. The diene (17) has also been prepared from (19) by Dunoguès and his co-workers.[18]

Diels–Alder Reactions with Symmetrical Dienophiles.— Each of the dienes (3), (4), (6), (15), (17), and (20) reacted smoothly with maleic anhydride to give the adducts (21)—(26) in reasonable yields (Scheme 4). The adduct (21) has been previously reported.[9] The adducts (21), (22), (24), and (25) reacted with toluene-p-sulphonic acid in refluxing benzene to give the anhydrides (27), (28), (27), and (29), respectively, as a result of protodesilylation in the sense of Scheme 1. The ease with which the double bond of a Diels–Alder adduct can be moved in this way has, we think, great potential in organic synthesis. The adduct (23) was not treated with acid but used in a different way (see below) and the adduct (26) was hydrolysed to the ketone (30).

adduct (22) must be cis. The silicon-free anhydride (28) derived from the adduct (22) was hydrogenated and hydrolysed to give the known all-cis-dicarboxylic acid (31), identical with an authentic sample.[19] The adduct (22) therefore must have the all-cis configuration.

Although we have not made exact comparisons, our general experience has been that the silylated dienes react more slowly than the corresponding dienes without a silyl group. Thus butadiene, piperylene, isoprene, and 2-methoxybutadiene typically give adducts with maleic anhydride as 10% solutions in benzene after 12—24 h at room temperature.[20] Our dienes (3), (4), and (17) needed to be heated, typically to 100 °C, neat for half an hour, and the diene (20) needed 80 °C for 10 min. Using the known [21] Arrhenius parameters for some Diels–Alder reactions, we estimate that our dienes are somewhere between $10\times$ and $1\,000\times$ less reactive than the analogous dienes without the silyl group.

We hoped that we could overcome this lack of reactivity, and hence improve the yields, by using the diene (15), which has a pentamethyldisilyl group in place of the trimethylsilyl group of the diene (3). The Si–Si bonding orbital is high in energy, and is known to be capable of overlap with π-systems; thus σ^+_p is more negative for Me_3SiMe_2Si than for Me_3Si.[22,23] If this overlap were effective in the diene (15), the energy of the highest occupied molecular orbital (HOMO) would be raised relative to that in (3), and the diene should be more reactive. In the event, the u.v. spectra of the dienes (3) and (15) were similar, and, although the disilyldiene (15) did give an adduct with maleic anhydride, the conditions were not significantly different from those needed for the simple silyldiene (3). Indeed, in a competition experiment using equimolar amounts of the dienes (3), (15), and *N*-phenylmaleimide, the monosilylated diene (3) gave more adduct than the disilylated

The reaction of phenylsulphenyl chloride on the ester (36) gave a mixture of the sulphide (37), the addition product of phenylsulphenyl chloride to the double bond of (36), and a product corresponding to the sulphide (37) but retaining the trimethylsilyl group. Although the addition product could be converted into the allyl sulphide (37) with sodium fluoride in methanol, to give an overall yield of 60%, phenylsulphenylation was much easier and more reliable with the tetrafluoroborate,[25] when we got directly a 78% yield of the sulphide (37). The by-products appeared ([1]H n.m.r.) to be a stereoisomer (9%) and the product of protodesilylation (9%).

The stereochemistry of the alcohol (33) was proved by converting it into the saturated ester (34). The corresponding ethyl ester had been reported previously;[26] so, by minor modifications of McQuillin's route, we made the methyl ester, which proved to be identical to the
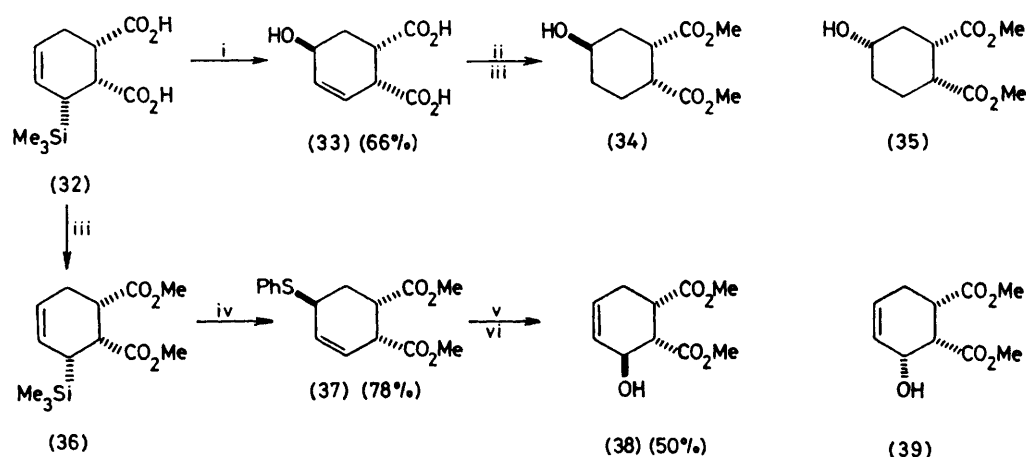
SCHEME 5 *Reagents:* i, AcOOH, H$^+$; ii, H$_2$, Pt; iii, CH$_2$N$_2$; iv, PhS$^+$[BF$_4$]$^-$; v, NaIO$_4$; vi, (MeO)$_3$PO

diene (15) (the ratio was *ca.* 3 : 2). Evidently overlap is either absent or ineffective. The pentamethyldisilyl group in the adduct (24) did not, however, interfere with the allylsilane chemistry; as reported above, the protodesilylation gave a good yield of the anhydride (27).

Reaction of Allylsilanes based on (21) *with Oxygen and Sulphur Electrophiles.*—In the course of this work, we investigated the reaction of heteroatom electrophiles on the allylsilane anhydride (21). The electrophiles were peracid, phenylsulphenyl chloride, bromine, and nitrosyl chloride. Although reactions took place, they were not easily reproducible nor were the products easily characterised. Eventually, we got clean and reproducible results from the reaction of peracetic acid on the dicarboxylic acid (32), and from phenylsulphenyl tetrafluoroborate on the corresponding ester (36) (Scheme 5). The peracid reaction was only good with unbuffered peracid, which gave the allylic alcohol (33) in 66% yield. We have drawn attention elsewhere[4] to the significance of the acidic conditions needed for this reaction, which may explain why earlier attempts to get allyl alcohols from allylsilanes[24] had led only to uncharacterised mixtures.

ester (34) prepared from (33). Furthermore, the stereoisomer (35) was also known,[27] and an authentic sample of this proved to be clearly distinguishable ([1]H n.m.r., i.r., t.l.c.) from our ester (34).

The stereochemistry of the sulphide (37) was proved by Mislow–Evans rearrangement,[28] a process which is known to be suprafacial, of the corresponding sulphoxide to give the alcohol (38). The stereoisomer (39) of this alcohol was prepared from the adduct of 1-acetoxybutadiene and maleic anhydride, which is known to be all-*cis*.[29] The two alcohols were clearly different ([1]H n.m.r., t.l.c.) and the sulphide must therefore have the structure (37). Hydrogenation of the alcohol (38) gave a saturated hydroxydiester clearly different ([1]H n.m.r., t.l.c.) from either of the esters (34) and (35), showing that 1,3-shift of the phenylthio-group[30] had not taken place before the Mislow–Evans rearrangement.

The overall stereochemistry in the reactions of the allylsilanes (32) and (36) with the two electrophiles reported here is therefore *anti*. Although *syn* has been shown to be the preferred stereochemistry in the acetylation of an open-chain allylsilane,[31] it is likely that the major factor in our case is the preference the electro-

philes will have for that side of the cyclohexene ring in (32) and (36) which has none of the substituents. The overall transformations of an allylsilane to an allyl alcohol and an allyl sulphide are powerful synthetic methods, giving in the cases reported here cyclohexenes with functionalities on five of the six atoms of the ring. The ability to obtain both allyl alcohols (33) and (38) from the same allylsilane broadens the scope of this useful intermediate. Recently, the latter type of transformation (allylsilane into the allyl alcohol with an unrearranged allyl framework) has been improved by Magnus,[32] who showed that benzeneseleninic anhydride does the whole process in one operation.

Regioselectivity of the Diels–Alder Reactions of 1-Trimethylsilylbutadiene with Unsymmetrical Dienophiles.—The Diels–Alder reaction of 1-substituted dienes with unsymmetrical dienophiles usually leads to 'ortho'-adducts. Frontier orbital theory has proved to be helpful, both in understanding this pattern [33,34] and in predicting cases where it might not be followed.[35] The silyl group is a σ-donor and a π-acceptor and does not fall into the simple C-, Z-, and Ẍ-classification of substituents.[34] For the same reason, it is not easy to use the
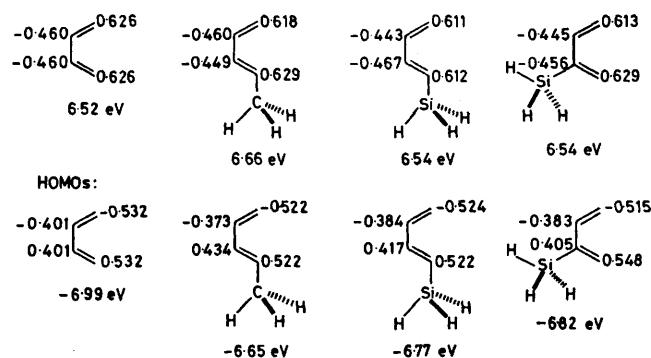

SCHEME 6 *Parameters:* C(1)–C(2) = C(3)–C(4) = 1.35 Å; C(2)–C(3) = 1.46 Å; =C–H = 1.07 Å; sat. –C–H = 1.08 Å; Si–H = 1.48 Å; Si–C = 1.865 Å; tetrahedral bond angles 109.5°; trigonal bond angles 120.0°; =C–CH₃ = 1.488 Å

non-mathematical arguments for predicting [36] the effect of a silyl group on the energies and coefficients of the frontier orbitals. Paterson, therefore, calculated for us the energies and coefficients of the frontier orbitals of 1- and 2-silylbutadiene, and, for comparison using the same Gaussian 70 program,[37] those for butadiene and *trans*-piperylene as well. His results are shown in Scheme 6. These numbers are, of course, dependent upon the geometry and other parameters chosen, and are not necessarily the best values. They are, however, indicative of the trend we wanted to know about. The main result is that the HOMO of the 1-silyldiene is polarised only to a very small extent. This implies that the regioselectivity in Diels–Alder reactions will be low, whether that regioselectivity is principally controlled by primary [33,34] or by secondary [38] overlap. If there is any regioselectivity, the prediction is that the 'ortho'-adduct will be the major product with the usual dienophiles, unless steric factors outweigh the effect of orbital overlap.

The calculation also indicates that the energy of the HOMO will be raised relative to that of butadiene, and this should imply that the silyldiene will be the more reactive; we have already shown above that this is not the case.

We carried out Diels–Alder reactions between the diene (3) and the unsymmetrical dienophiles, methyl acrylate,
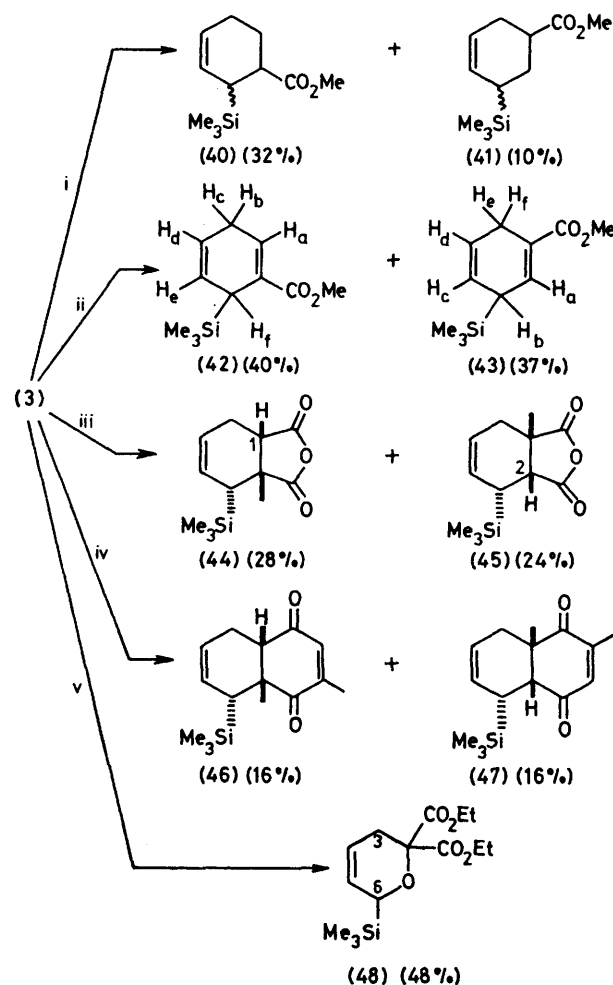

SCHEME 7 *Reagents:* i, CH₂=CHCO₂Me, 150 °C, 24 h; ii, HC≡CCO₂Me, 150 °C, 40 h; iii, citraconic anhydride, 100 °C, 72 h; iv, 2,6-dimethylbenzoquinone, 140 °C, 24 h; v, (EtO₂C)₂-CO, 150 °C, 40 h

methyl propiolate, citraconic anhydride, 2,6-dimethylbenzoquinone,[39] and diethyl oxomalonate,[40] getting in each case but the last mixtures of regioisomers, as shown in Scheme 7. On the whole, 'ortho'-adducts are the major products, but the degree of regioselectivity is low. This is disappointing in view of the comparatively greater regioselectivity shown by *trans*-piperylene, even though the calculation shows this diene to be even less polarised than the silyldiene. Evidently the frontier orbital effects on both regioselectivity and reactivity are not the whole story. No doubt steric effects counter them, but even these cannot explain all our results.

*Methyl acrylate.* Methyl acrylate gave a 42% yield of

a mixture of four adducts. This was revealed by the addition of 7% of Eu(fod)$_3$, which caused the methoxy-singlet to break up into four singlets, two of which had moved substantially downfield (by 49 and 40 Hz) and two of which had moved much less (by 22 and 18 Hz). These four singlets integrated in the ratio 1 : 1 : 3 : 3, respectively. Assuming that the latter pair are the 'ortho'-adducts (40) for which the silyl group might hinder complexation of the europium, and the former pair are the 'meta'-adducts (41), the 'ortho' : 'meta' ratio is 3 : 1, and there is negligible endo-selectivity for either regioisomer (indicating incidentally that secondary overlap is not an important factor in determining regio-selectivity[41]). This tentative conclusion was confirmed by protodesilylation (Scheme 8), where we obtained a

SCHEME 8   *Reagent*: i, TsOH, C$_6$H$_6$
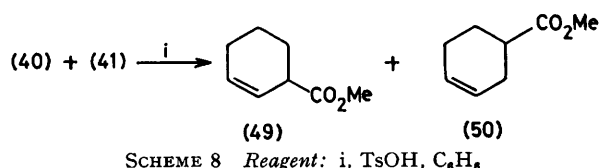
mixture of two esters (49) and (50) from (40) and (41) respectively, in 87% yield and a ratio of 3 : 1. The ratio was measured by integration of the olefinic signals in the ^{1}H n.m.r. spectrum, those of the ester (49) occurring at δ 5.68 and those of the ester (50) at δ 5.58. Authentic samples of these esters were prepared in order to make the assignments confidently. Thus, the 'ortho' : 'meta' ratio appears to be 3 : 1. This result is the only one where our observations and those of Jung and Gaede are significantly different. They found the 'meta'-adducts to be the major products with acrylonitrile and with acrolein. It is unlikely that the differences in the dienophiles are responsible. It is possible either that the ratio has been affected by the chromatography used by both groups to isolate the mixtures of adducts, or that one of the methods of analysis is in error (the methods used were very different). Our result has the virtue that it is consistent with our later observations on the regio-selectivity shown by the dienes (17) and (4).

Methyl propiolate. Methyl propiolate gave a mixture of two adducts which were separated by column chro-matography to give 40% of the 'ortho'-adduct (42) and 37% of the 'meta'-adduct (43). Structures were assigned to these adducts from their ^{1}H n.m.r. spectra, using the europium shift reagent and double irradiation (see Experimental section). The methoxy-signal of the unambiguously assigned 'ortho'-adduct (42) was shifted less than that of the 'meta'-adduct (43), supporting there-fore the argument tentatively used in the case of the methyl acrylate adducts above. The assignments of structure were the same as those made by Jung and Gaede, and the spectra were identical.[42] We attach no significance to the difference between our ratio for the two isomers (40 : 37) and the ratio obtained by Jung and Gaede (21 : 26); we both agree on the general observ-ation that the regioisomers are formed in nearly equal amounts.

Jung and Gaede aromatised the adducts (42) and (43) to methyl ortho- and meta-trimethylsilylbenzoate, re-spectively, using palladium in refluxing cumene. We also aromatised the adducts, but, using dichlorodicyano-benzoquinone (DDQ), got an entirely different, useless, unexpected, and remarkable result. *Both* adducts separately gave the *same* aromatic product, methyl m-trimethylsilylbenzoate (53), in high yield (Scheme 9). At the time we did this reaction, we had no precedent even for the unexceptionable aromatisation (43) ⟶ (53) (Scheme 9). Following the usually accepted mechanism for DDQ dehydrogenations,[43] one would expect the cation (54) to be formed, at which point either a hydrogen or a silyl group could be lost, to give either (53) or methyl benzoate itself. The counter ion to the cation (54) will be an enolate or phenolate derived from DDQ, and, therefore, since oxygen nucleophiles usually select a silyl group rather than a proton, when both are available, the silyl group might well have been removed here. Since we did our work, cases in which a silyl group was selectively removed in similar

SCHEME 9
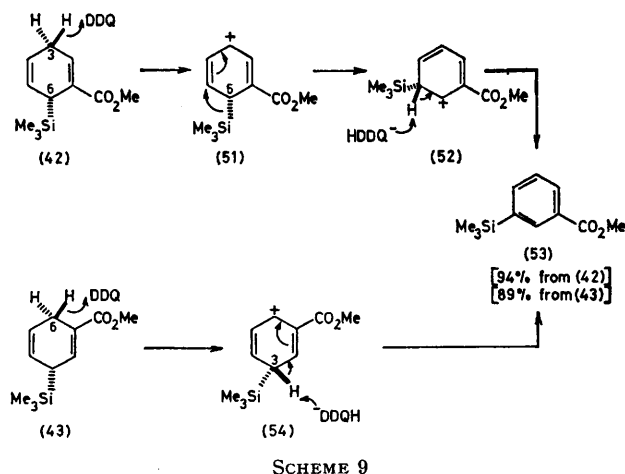
circumstances have been reported. One was the oxid-ation of the dihydroacenaphthylene (55), using DDQ, which gave 1-trimethylsilylacenaphthylene (56),[44] and another was the oxidation of the cyclohexadiene (57) with chloranil, which gave mainly the trimethylsilyl xylene (58).[45] Why then did our adduct (43) lose only hydrogen? The answer to this first puzzle lies in some work we did some time ago but have never published.[46] We found that the DDQ oxidation of trans-3,6-dideuteriocyclohexa-1,4-diene[47] was com-pletely syn stereoselective, causing the loss only of HD. This might have been because the whole process is cyclic and concerted, as Rocek has suggested,[48] but we found evidence that the reaction is still stepwise. Whether the reaction is concerted or stepwise, the groups that are lost in this DDQ oxidation are cis to each other. If the silyl groups in (55) and (57) are trans, as they are likely to be, then the loss of H and SiMe$_3$ is accounted for. Like-wise, in our case (43), if the hydrogen atom on C-6 on the less hindered side of the molecule is removed first,

then the second group to be removed will be the *hydrogen* on C-3, which was *cis* to it, and not the silyl group which was *trans*. That leaves the dehydrogenation with the rearrangement (42) ⟶ (53) to be accounted for. In this case it is not quite so obvious which hydrogen will be removed first. The hydrogen on C-6 is α to a silyl group and comparatively hindered but the hydrogen on C-3 is conjugated to a methoxycarbonyl group. It seems that the latter is in fact the hydrogen lost, giving the high-energy cation (51). Apparently, this cation rearranges
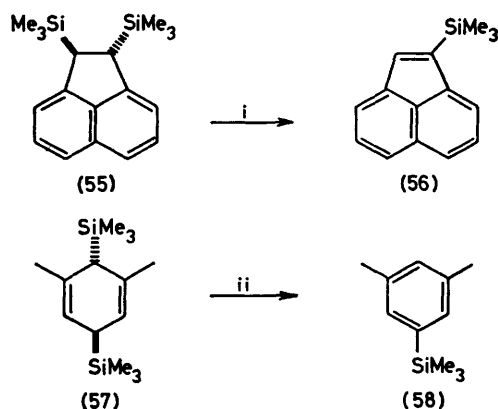
SCHEME 10   *Reagents:* i, DDQ; ii, *p*-chloranil

to a cation (52), which is no longer conjugated to the methoxycarbonyl group, faster than it loses the hydrogen on C-6. The new cation (52) then loses hydrogen. If the original hydrogen taken from C-3 by the DDQ is the one on the less hindered side of the molecule, as shown in (42) (Scheme 9), then the loss of hydrogen from the re-arranged cation may again be the result of the overall *cis* removal of groups preferred by DDQ. Rearrange-ments in DDQ oxidations are well known in cases where straightforward dehydrogenation is not possible,[49] and rearrangements of silyl groups are also well known.[50] The dehydrogenation with rearrangement (42) ⟶ (53) is the first example of a rearrangement in a DDQ oxid-ation when there is a straightforward dehydrogenation available. It therefore provides evidence against the concerted mechanism.

Citraconic anhydride. Citraconic anhydride gave a mixture of two adducts (44) and (45), which were sepa-rated (t.l.c.) as the corresponding dicarboxylic acids, which were obtained in 28% and 24% yield overall. The anhydrides were then reformed and identified by their [1]H n.m.r. spectra. In particular, the 'ortho'-isomer (44) had the hydrogen on C-1 as a double doublet, and the 'meta'-isomer (45) had the hydrogen on C-2 as a doublet.

2,6-Dimethylbenzoquinone. 2,6-Dimethylbenzoqui-none gave a mixture of two adducts (46) and (47) in a ratio, measured by integration of the saturated *C*-methyl singlets, of 1 : 1. The separate isomers were obtained, the former by using an excess of diene, followed by chro-matography [the excess of diene apparently consuming the isomer (47) as a mixture of 2 : 1 adducts], and the latter by Lewis-acid catalysed reaction (see below). The

[1]H n.m.r. spectra were definitive, the hydrogen on C-1 in (46) giving rise to a double doublet and the hydrogen on C-2 of (47) giving rise to just a doublet.

Diethyl oxomalonate. The strongly polarised dieno-phile diethyl oxomalonate was the only one to give a single adduct (48). The structure was clear from the [1]H n.m.r. spectrum, which showed a signal for the single hydrogen on C-6 at δ 4.2 and a two-proton multiplet for the hydrogens on C-3 centred at δ 2.5. It is perhaps significant that this is the only dienophile of the ones we tried in which steric effects and the electronic effects co-operate instead of opposing each other.
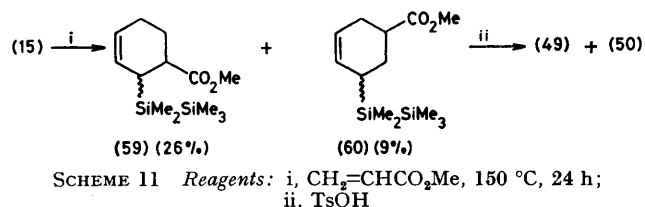
Lewis-acid catalysis. In the hope that Lewis acid might accelerate the reactions and improve the regio-selectivity, we repeated the reactions in the presence of boron trifluoride–ether. They were all faster, but the effect was not particularly useful. Dimethyl acrylate gave (40) and (41) in equal amounts in only 19% yield; however, the addition of Eu(fod)$_3$ to the n.m.r. tube containing the mixture of adducts split the methoxy-singlet only into two, indicating perhaps that, even though the regioselectivity had been reduced, the *endo*-selectivity had been increased. Methyl propiolate gave only the adduct (42) in 20% yield. Citraconic anhydride gave the adducts (44) and (45) in 34 and 31% yield, and dimethylbenzoquinone gave only the adduct (47). These reproducible, but confusing and inconsistent results were not pursued exhaustively. It is more than likely that the Lewis acid is responsible for decomposing some of the adducts.

In contrast to these results, Batt and Ganem have found that 2-triethylsilylbutadiene does show a useful degree of regioselectivity in Lewis-acid-catalysed Diels–Alder reactions.[51] This may be because the products are vinylsilanes, instead of being allylsilanes, and are there-fore more stable to the reaction conditions. It is also possible that 2-silyldienes are inherently more polarised than 1-silyldienes; Paterson's calculation (Scheme 6) supports this possibility and correctly accounts for the regioselectivity observed.

In the hope that we could overcome the low level of regioselectivity shown by the diene (3), we tested the regioselectivity of the diene (15). If the silicon–silicon bond in the diene (15) were to overlap effectively with the orbitals of the conjugated diene, the coefficients in the HOMO at C-2 and C-4 would be raised relative to those at C-1 and C-3, and the regioselectivity should be increased. In the event, the diene (15) reacted with methyl acrylate to give a mixture of adducts (59) and (60) (Scheme 11) in 35% yield. Protodesilylation of this mixture gave the esters (49) and (50) in nearly quanti-tative yield, but the ratio was 3 : 1, exactly as it had been for the corresponding reaction of the diene (3). Evi-dently the regioselectivity of the diene (15) was the same as that of the diene (3).

Regioselectivity of the Diels–Alder Reactions of Sub-stituted 1-*Trimethylsilylbutadienes with Unsymmetrical Dienophiles.*—It is evident from our results, and those of Jung and Gaede, that the simple 1-silyldiene (3) is not

often going to give a synthetically useful result with an unsymmetrical dienophile. From one point of view, this is a disappointing conclusion. However, since the trimethylsilyl group exerts little directing effect, any other substituent on the diene should exert its directing effect more or less unimpeded. The regioselectivity

$$(15) \xrightarrow{i} + \xrightarrow{ii} (49) + (50)$$

(59) (26%)   (60) (9%)

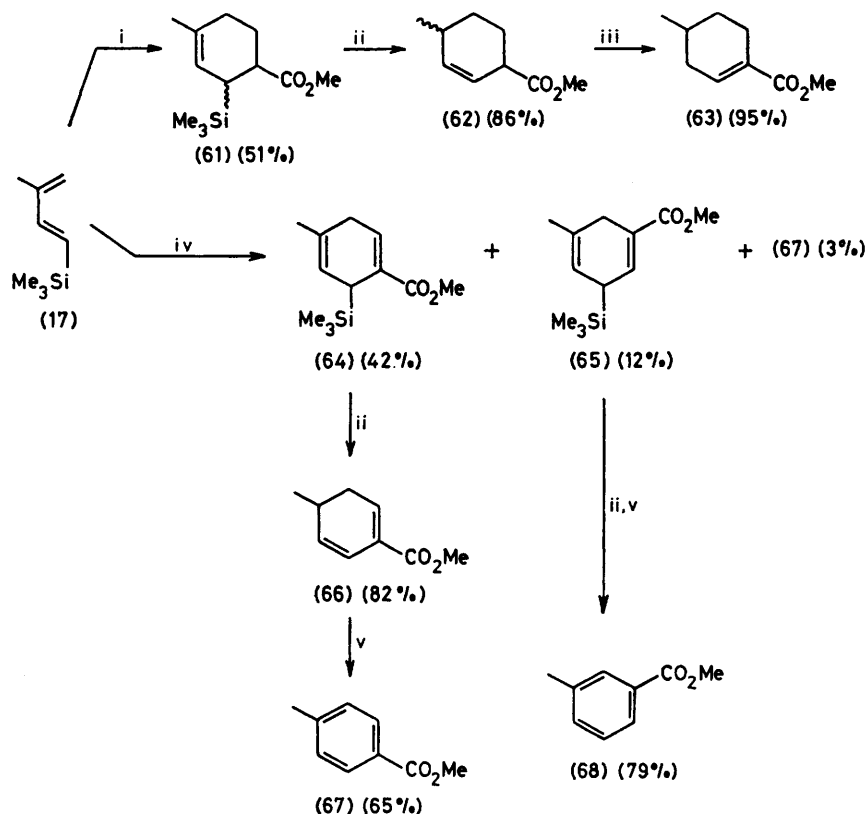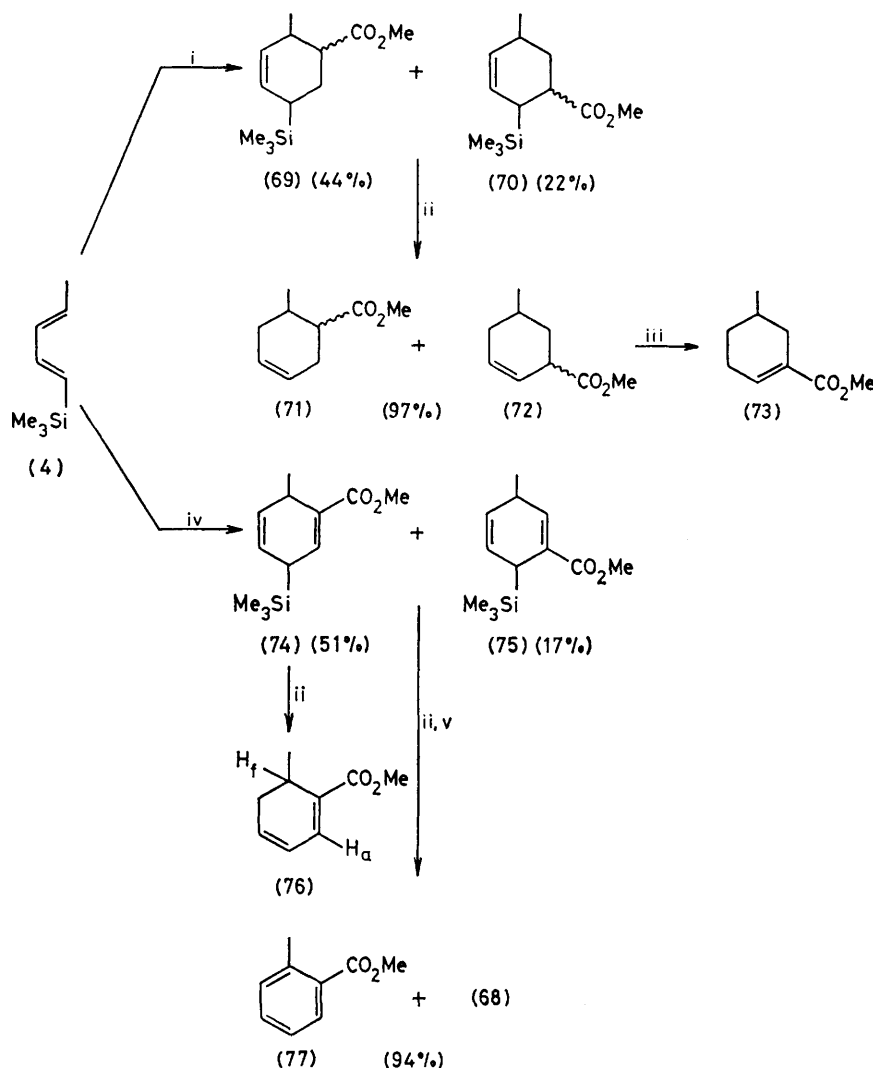SCHEME 11   *Reagents:* i, $CH_2=CHCO_2Me$, 150 °C, 24 h; ii, TsOH

shown by substituted dienes is rather well understood, which means that it should be easy to predict what the regioselectivity will be for the corresponding silylated diene. We have tested this idea by carrying out Diels–Alder reactions between the methylated silyldienes (17) and (4) and methyl acrylate and methyl propiolate. In each case, the methyl group is the dominant influence on the regioselectivity (Schemes 12 and 13). Furthermore, the regioselectivity shown by the 3-methyl-1-silyldiene (17), where the '*para*'-directing effect of the methyl group and the mild '*ortho*'-directing effect of the silyl group co-operate, is greater than the regioselectivity shown by the 4-methyl-1-silyldiene (4), where the two groups oppose each other. This observation supports

our earlier statement that the 1-silyl group is, if anything, mildly '*ortho*'-directing.

3-Methyl-1-trimethylsilylbutadiene (17) *and methyl acrylate.* The diene (17) and methyl acrylate gave a mixture of two adducts in 51% yield. These proved to be stereoisomers (61) rather than regioisomers, since protodesilylation gave a mixture of two products (62) in nearly equal amounts, both of which isomerised in base to the conjugated ester (63) in high yield. There was no sign of the regioisomers, and no obvious reason why, if they had been formed, they should have been selectively decomposed in the work-up. We conclude that this Diels–Alder reaction is more regioselective than the reaction between isoprene and methyl acrylate, which gives the '*para*'- and '*meta*'-adducts in a ratio of 4 : 1.[52]

3-Methyl-1-trimethylsilylbutadiene (17) *and methyl propiolate.* The diene (17) and methyl propiolate gave a mixture of regioisomers (64) and (65), and a little methyl *p*-toluate (67), which were separated by t.l.c. Protodesilylation of the major product (64) (42%) gave the unsaturated ester (66) in 82% yield, aromatisation of which with DDQ gave methyl *p*-toluate (67). Protodesilylation of the minor product (65) (12%) followed by aromatisation with DDQ gave methyl *m*-toluate (68). Direct oxidation of the major product (64) with DDQ again caused rearrangement; the products, as judged from the ^{1}H n.m.r. spectrum of the mixture, were the aromatic ester which had rearranged, methyl 4-methyl-3-trimethylsilylbenzoate, and the aromatic ester which

(61) (51%)   (62) (86%)   (63) (95%)

(17)   (64) (42%)   +   (65) (12%)   + (67) (3%)

(66) (82%)   (68) (79%)

(67) (65%)

SCHEME 12   *Reagents:* i, $CH_2=CHCO_2Me$, 150 °C, 24 h; ii, TsOH, C_6H_6; iii, NaOMe, MeOH; iv, $HC\equiv CCO_2Me$, 150 °C, 22 h; v, DDQ

SCHEME 13   *Reagents:* i, $CH_2=CHCO_2Me$, 140 °C, 48 h; ii, TsOH, C_6H_6; iii, NaOMe, MeOH; iv, $HC\equiv CCO_2Me$, 130 °C, 48 h; v, DDQ

had not, methyl 4-methyl-2-trimethylsilylbenzoate, in a ratio of 3 : 1. The overall regioselectivity, allowing for the aromatic product (67), is 79 : 21, which in this case is probably less than that for the corresponding reaction between isoprene and methyl propiolate, where the 'para'-isomer was obtained in 73% yield and was the only product isolated.[53]

1-Trimethylsilylpentadiene (4) *and methyl acrylate.* The diene (4) and methyl acrylate gave a mixture of adducts (69) and (70) in 66% yield. Protodesilylation gave the esters (71) and (72) in 97% yield. The C-methyl region in the [1]H n.m.r. spectrum showed four closely spaced doublets, indicating that all four possible products were present, but the olefinic region showed only two fairly narrow multiplets, one centred at δ 5.64 and the other at δ 5.77. These signals integrated in the ratio 2 : 1, and it seemed likely, from our experience with the esters (49) and (50), that they represented the signals of the regio-isomers (71) and (72), respectively. This tentative conclusion was confirmed by treating the mixture with

sodium methoxide. After this treatment, the C-methyl region of the [1]H n.m.r. spectrum changed from four to three doublets, the O-methyl signal split into two closely spaced singlets, the signal at δ 5.64 remained unchanged, the signal at δ 5.77 disappeared, and a new signal with half the intensity of that at δ 5.77 grew at δ 6.97. These changes are consistent with the ester (72) changing to the conjugated ester (73) and the other ester (71) remaining unchanged, except perhaps in the proportion of the two stereoisomers. The overall regioselectivity of 67 : 33 in favour of the isomers which are *ortho* with respect to the relationship of the methyl and methoxycarbonyl groups, is less than that for the corresponding reaction of piperylene with methyl acrylate, where the ratio is 82 : 18.[54]

1-Trimethylsilylpentadiene (4) *and methyl propiolate.* The diene (4) and methyl propiolate gave a mixture of adducts (74) and (75) in 68% yield. These were not easily separated, but we did get a chromatographic fraction rich (9 : 1) in the major isomer (74). Proto-

desilylation of the enriched sample gave a mixture rich in the ester (76), which was identifiable as such by its ¹H n.m.r. spectrum; in particular, the signal from H_f was not coupled significantly to the signal from H_a, as the corresponding signals would have been in the isomer derived from (75). Protodesilylation of the original mixture of adducts (74) and (75), followed by oxidation with DDQ gave a mixture of methyl o-toluate (77) and methyl m-toluate (68) in 94% yield and in a ratio of 3 : 1, as judged by integration of the O-methyl singlets. The overall regioselectivity of 3 : 1 is again probably less than that for the corresponding reaction of piperylene with methyl propiolate, where only the ortho-adduct was isolated in 71% yield.[53]

Diels–Alder Reactions of the 1-*Silyl*-3-*silyloxydiene* (20).—After our experience with the methyl-substituted dienes (17) and (4), it was possible to predict with some confidence, since the silyloxy-group is notable [55] for the
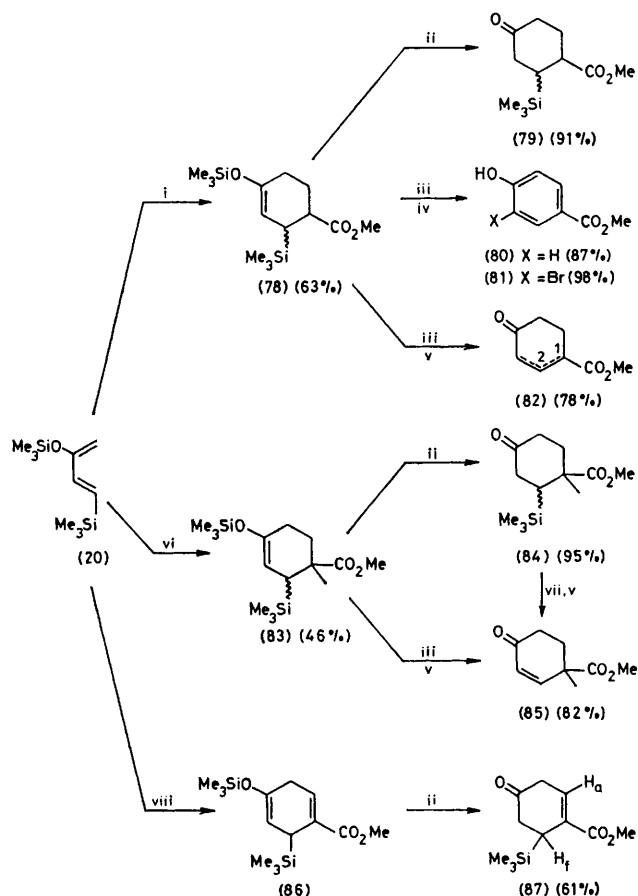
SCHEME 14 *Reagents:* i, CH₂=CHCO₂Me, 120 °C, 40 h; ii, HCl, H₂O, THF; iii, NBS, THF; iv, DMSO; v, CsF, DMF; vi, CH₂=CMeCO₂Me, 130 °C, 64 h; vii Br₂; viii, HC≡CCO₂Me, 120 °C, 65 h

high level of regioselectivity that it imparts, that the silyloxydiene (20) would show a high level of regioselectivity. This it did, giving with methyl acrylate, methyl methacrylate and methyl propiolate only the adducts in which the silyloxy-group is '*para*' to the ester group (Scheme 14).

1-*Trimethylsilyl*-3-*trimethylsilyloxybutadiene* (20) *and methyl acrylate.* The diene (20) and methyl acrylate gave a mixture of two adducts. Addition of Eu(fod)₃ to the ¹H n.m.r. tube split the O-methyl signal into two singlets in the ratio 2 : 1. Mild hydrolysis gave a mixture of two ketones (79), in which the O-methyl groups again appeared as two sharp singlets in the ratio 2 : 1 in the ¹H n.m.r. spectrum. Bromination of the mixture of adducts with N-bromosuccinimide (NBS) gave a mixture of α-bromoketones, which readily lost the silyl and bromo groups in DMSO. The product was the phenol (80), evidently the result of over-oxidation. Nevertheless, the overall yield of 87% showed that both adducts must have the silyloxy-group and the ester group '*para*', and that they differ only in stereochemistry. Bromination of the mixture of adducts with two equivalents of NBS and treatment of the products with dimethyl sulphoxide (DMSO) gave the corresponding bromophenol (81). Finally, bromination with one equivalent of NBS followed by desilylbromination with fluoride ion in dimethylformamide (DMF), gave a mixture of unsaturated ketoesters (82) without concomitant aromatisation. Because of their ready interconvertibility, these products were a little difficult to handle, and were not fully characterised.

1-*Trimethylsilyl*-3-*trimethylsilyloxybutadiene* (20) *and methyl methacrylate.* To avoid the problems caused by the interconversion of the two ketoesters (82), we carried out the corresponding series of reactions with methyl methacrylate. We again got a mixture of stereoisomeric adducts (83) in a ratio of 3 : 2 [as estimated in the ¹H n.m.r. spectrum by the addition of Eu(fod)₃, and directly in the ¹H n.m.r. spectrum of the hydrolysis product (84)]. Bromination and dissolution of the bromoketones in DMSO cleanly gave the ketoester (85) in 82% yield, showing that the adducts were stereo- and not regio-isomers. Because the adducts (83) are specific enol derivatives, the site of bromination is assured. With the ketones (84), however, bromination might take place on either side of the ketone. Nevertheless, bromination of the ketone (84) followed by desilylbromination in DMSO was a clean and almost as high-yielding a method of getting the ketoester (85). This observation conforms with our earlier experience [56] that a silyl group β to a ketone assists bromination at the intervening α position.

1-*Trimethylsilyl*-3-*trimethylsilyloxybutadiene* (20) *and methyl propiolate.* The diene (20) and methyl propiolate gave a single adduct (86), which was hydrolysed to the ketone (87) in 61% overall yield. The ¹H n.m.r. spectrum was definitive for this structure: the signal for H_a was a double doublet and that for H_f a triplet.

In each of the Diels–Alder reactions of the diene (20), the product was hydrolysed to a β-silylketone. We have shown elsewhere [56,57] that β-silylketones are masked enones. The diene (20), therefore, serves the same overall purpose as Danishefsky's diene, 1-methoxy-3-trimethylsilyloxybutadiene,[58] as indeed the series of reactions (20) ⟶ (83) ⟶ (85) demonstrates. For

most purposes, Danishefsky's diene is the reagent of choice, both because it is at least as readily available and because it is more reactive, but with his diene the elimination step leading to the enone is more or less unavoidable. Our diene has the potential advantage that the intermediates, such as (83) and (84), are not subject to elimination of the β-substituent, and the double bond does not therefore have to be introduced at this stage. The intermediates are therefore available for further manipulation before the double bond is introduced by bromination and desilylbromination.

The regioselectivity shown by the diene (3) may have been disappointing, but the sum of the results with the substituted 1-silyldienes shown in Schemes 12—14 is more encouraging. It is clear that the presence of a silyl group on the diene can be expected to make little difference to regioselectivity and to have little effect on intramolecular Diels–Alder reactions.[59] This makes such reactions highly predictable, which augurs well for their usefulness in synthesis.

The Synthetic Potential of 1,4-*Bis(trimethylsilyl)butadiene* (6).—The last diene we studied, (6), presented no problems with regioselectivity; we made it in order to solve a different problem. The transformation of a cyclohexene, made by a Diels–Alder reaction, into a cyclohexadiene has often been used in the synthesis of annulenes and propelladienes, but it has not always been possible to control the position of the two double bonds in the product relative to the position of the original double bond of the adduct. We thought that the doubly silylated diene (6) would be a reagent which would solve these difficulties.

The diene (6) gave the adduct (23), as described above, and this adduct could be reduced with lithium aluminium hydride and the resultant diol cyclised to give the allylsilane (88). We hoped that bromination, or an equivalent reaction, would give an allyl bromide, which would then undergo easy desilylbromination. Provided that it was always the silyl group which was the electrofugal group, the net result ought to be the formation of the diene (90), in which the double bonds are placed specifically one on each side of the position occupied by the double bond in the original allylsilane (88).

However, in practice (Scheme 15), the allylsilane function in the ether (88) was not well-behaved in the sense of Scheme 1. First, recrystallisation of this compound without taking any precaution against atmospheric oxygen gave a hydroperoxide formulated as (89), in which the silyl group had been retained. Epoxidation gave the epoxide of (88) cleanly, but treatment of this epoxide with acid gave a poor yield of products, which we formulated as the dienes (91) and (92), in which one or both of the silyl groups had been retained. Finally, bromination gave, as the only identifiable products, two dibromides which we formulated as (93) and (94), the former indicating that we had had some success in our venture. We ascribe our failures to the fact that the silyl groups are almost certainly in the *endo* face of the bicyclic system. There they may be both inaccessible

and unable easily to achieve favourable overlap preceding their elimination. Steric constraints, limiting the usually reliable aptitude for a silyl group to be displaced from carbon, have been noted before.[60] We did not pursue this line exhaustively; it still remains a possible but obviously not an easy solution to the problem.
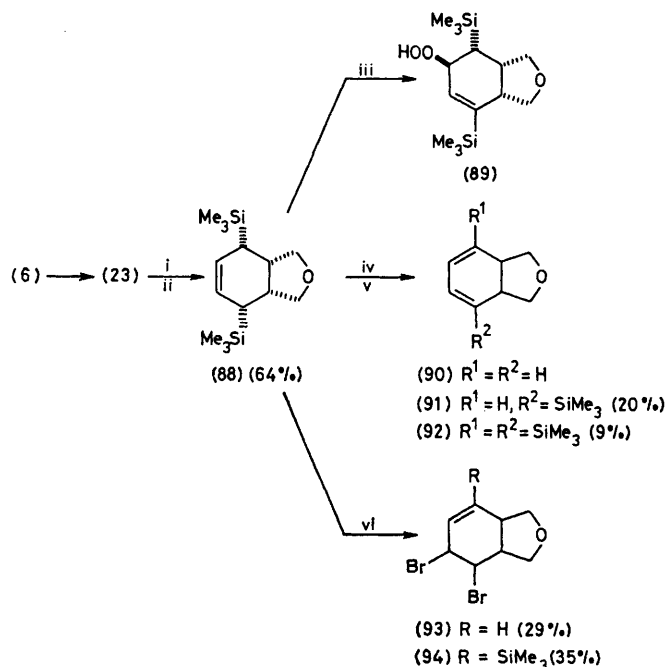
SCHEME 15 *Reagents:* i, LiAlH₄; ii, MeSO₂Cl, Py; iii, O₂; iv, MCPBA; v, TsOH, C₆D₆; vi, Br₂

Conclusion.—The Diels–Alder reaction of 1-silyldienes is a good route to allylsilanes, especially when the dienophile is symmetrical or when the diene has other substituents on it to control the regioselectivity. The allylsilanes in turn provide an excellent opportunity either for introducing further functional groups or for moving the double bond one place round the ring.

EXPERIMENTAL

Except where otherwise stated, reaction mixtures were worked up by washing with water, sodium hydrogencarbonate solution, or brine, drying (MgSO₄), and evaporation on a rotary evaporator. Preparative t.l.c. was carried out on Merck Kieselgel 60 PF254 (1 mm thickness). R_F Values refer to Merck plates precoated with Kieselgel F254 (0.25 mm).

(EE)-1-*Trimethylsilylpenta*-1,3-*diene* (4) —n-Butyllithium (12.3 ml of a 1.54M-solution in hexane) was added dropwise to a stirred solution of bis(trimethylsilyl)methane [61] (3.0 g) in dry tetramethylethylenediamine (TMEDA) under nitrogen at 0 °C, and the mixture was kept at room temperature for 7 days. Crotonaldehyde (1.7 ml) in dry ether (2 ml) was then added dropwise with stirring, and the mixture was kept at room temperature for 0.5 h. Dilution with ether, work-up, and column chromatography on silica gel eluting with light petroleum (b.p. 30—40 °C) gave a 2 : 1 mixture of the *diene* (4) and bis(trimethylsilyl)-

methane (2.1 g, 51%), $\delta(\text{CDCl}_3)$ 6.46 (1 H, dd, J 18 and 9 Hz, CH=CHSi), 5.5—6.3 (2 H, m, CH=CHMe), 5.68 (1 H, d, J 18 Hz, CH=CHSi), 1.74 (3 H, d, J 6 Hz, Me), and 0.05 (9 H, s, SiMe$_3$), $\nu_{\text{max.}}$ (film) 2 960 (=CH), 1 648 and 1 575 (C=C), and 845 cm^{-1} (*trans*-CH=CH), m/z 140 (41%, M^+), 125 (92, M — Me), and 73 (100, SiMe$_3$). The diene was further characterised as its Diels–Alder adducts (see below). A closely similar preparation of the diene (5) from cinnamaldehyde gave an oil (32%), $\delta(\text{CCl}_4)$ 7.3br (5 H, Ar), 5.6—6.9 (4 H, m, 4 × =CH), and 0.2 (9 H, s, SiMe$_3$), $\lambda_{\text{max.}}$ (EtOH) 291 (ε 31 500), 228 (11 900), and 223 (12 400), m/z 202 (M^+). This was not characterised further. Another similar preparation with acrolein (work-up by distillation) gave the diene (3), contaminated with hexamethyldisiloxane [5% (n.m.r.)].

(EE)-1,4-*Bis(trimethylsilyl)buta-1,3-diene* (6).—The anion (1), prepared from bis(trimethylsilyl)methane (5.0 g) as above, and (*E*)-3-trimethylsilylprop-2-enal (11) (4.0 g) were combined as described above. Work-up and distillation gave the *diene* (6) (3.8 g, 62%), b.p. 84—88 °C at 23 mmHg, $\delta(\text{CCl}_4)$ 6.28—6.60 (2 H, m, CH=CHSi), 5.62—5.96 (2 H, m, CH=CHSi), and 0.04 (18 H, s, SiMe$_3$), $\nu_{\text{max.}}$ (film) 2 960 (=CH), 1 560 (C=C), 1 255 (SiMe$_3$), and 845 cm^{-1} (*trans*-CH=CH), $\lambda_{\text{max.}}$ (EtOH) 246 nm (ε 12 600) (Found: M^+, 198.1259. $\text{C}_{10}\text{H}_{22}\text{Si}_2$ requires M, 198.1256).

1,3-*Bis(trimethylsilyl)allyl-lithium* (2).—1,3-Bistrimethylsilylpropene was prepared by the method of Corriu and his co-workers in 46% yield.[62] Although they did not actually prepare this compound this way, it is known.[63] 1,3-Bistrimethylsilylpropene (1 mmol), TMEDA (1 mol), and n-butyl-lithium (1 mmol of a 1.4м solution in hexane) were mixed at room temperature; the anion (2) formed almost immediately, as verified by the appearance of a triplet (J 15 Hz) at δ 6.7 in the n.m.r. spectrum.

Reaction of the Lithium Reagent (2) *with Formaldehyde and Benzaldehyde.*—The anion (2) (16.1 mmol) was added to a suspension of paraformaldehyde (0.5 g) in dry tetrahydrofuran (THF) (30 ml) under nitrogen at —70 °C. The mixture was brought to room temperature and kept there for 1 h. Work-up and distillation, with hydroquinone (100 mg) added, gave 1-trimethylsilylbutadiene (3), b.p. 110—115 °C, contaminated with hexamethyldisiloxane. The n.m.r. spectrum indicated a yield of 10%. A similar preparation using benzaldehyde gave 1-trimethylsilyl-4-phenylbutadiene (5) (53%), spectroscopically identical to the sample prepared above.

(*E*)-3-*Trimethylsilylprop-2-enal* (11).—(i) *Method used in this work.* 3-Trimethylsilylprop-2-enol[12] (9) (26.1 g) and manganese dioxide[64] (160 g) were stirred in light petroleum (800 ml) at room temperature for 12 h. The mixture was filtered, evaporated, and distilled to give the aldehyde (11) (18.9 g, 78%), b.p. 144—148 °C (lit.,[8] 53—54 °C at 30 mmHg), $\delta(\text{CCl}_4)$ 9.41 (1 H, d, J 7 Hz, CHO), 7.12 (1 H, d, J 19 Hz, SiCH=), 6.36 (1 H, dd, J 19 and 7 Hz, CHCHO), and 0.17 (9 H, s, SiMe$_3$), $\nu_{\text{max.}}$ (film) 1 695 cm^{-1} (CHO).

(ii) *A better method* (*experiment by* D. A. PERRY). Pyridinium dichromate[13] (56.5 g) was added with stirring to the alcohol (9) (13 g) in dichloromethane (180 ml) under nitrogen. After having been kept for 24 h at room temperature, the mixture was filtered through Celite, and the thick black residue was washed with more dichloromethane. The solvent was evaporated off, the residue was taken up in ether and filtered through Celite again, and the ether was evaporated off. The residue was purified by chromatography on silica gel (300 g) eluting with dichloromethane to

give the aldehyde pure enough for subsequent reactions (11.5 g, 90%).

(*E*)-1,4-*Bis(trimethylsilyl)but-3-en-2-ol* (13).—Chloromethyltrimethylsilane[65] (19 g) and magnesium turnings (3.77 g) were refluxed in dry ether (80 ml) for 1 h. The aldehyde (11) (18.9 g) was then added with cooling and the mixture was refluxed for 4 h. Ammonium chloride solution was added, the mixture was worked up, and the residue was distilled to give the *alcohol* (13) (28.9 g, 91%), b.p. 74—76 °C at 1.5 mmHg, $\delta(\text{CCl}_4)$ 5.98 (1 H, dd, J 5 and 19 Hz, SiCH= CH), 5.70 (1 H, d, J 19 Hz, SiCH=CH), 4.15 (1 H, dt, J 5 and 7 Hz, CHOH), 1.96br (1 H, s, OH), 0.85 (2 H, d, J 7 Hz, CH$_2$Si), 0.04 (9 H, s, SiMe$_3$), and 0.0 (9 H, s, SiMe$_3$), $\nu_{\text{max.}}$ (film) 3 350 (OH), 1 640 (C=C), 1 255 (SiMe$_3$), and 870 and 845 cm^{-1} (*trans*-CH=CH), m/z 216 (M^+).

(*E*)-1-*Trimethylsilylbuta-1,3-diene* (3).—The alcohol (13) (6 g) was stirred in dry ether (30 ml) with toluene-*p*-sulphonic acid (25 mg) at room temperature for 1 h. Work-up gave a mixture of hexamethyldisiloxane and the diene (3) in 1 : 2 ratio (n.m.r.) (5.7 g, 99%). Distillation in the presence of hydroquinone gave a similar mixture with a yield of 91%. In general the undistilled diene was used in the Diels–Alder reactions; $\delta(\text{CDCl}_3)$ 6.6—4.9 (5 H, m, 5 × =CH) and 0.02 (9 H, s, SiMe$_3$), $\nu_{\text{max.}}$ (film) 1 580 (C=C), 1 255 (SiMe$_3$), 1 060 (hexamethyldisiloxane), and 870 or 845 cm^{-1} (*trans*-CH=CH), $\lambda_{\text{max.}}$ (EtOH) 227 nm.

3-*Pentamethyldisilylprop-2-ynol* (8).—Propargyl alcohol (7.76 g) in dry THF (30 ml) was added to a solution of ethylmagnesium bromide [from ethyl bromide (31.76 g) in THF (200 ml) at 0 °C] dropwise at room temperature and the mixture was kept at room temperature for a further 1 h. Chloropentamethyldisilane[66] (23.1 g) in dry THF (40 ml) was then added dropwise with stirring and the mixture was refluxed for 4 h. The mixture was cooled to 0 °C and saturated ammonium chloride solution was added. Work-up and distillation gave the *alcohol* (8) (9.2 g, 36%), b.p. 111—115 °C at 17 mmHg (Found: C, 51.5; H, 9.95. $\text{C}_8\text{H}_{18}\text{OSi}_2$ requires C, 51.6; H, 9.75%), $\delta(\text{CCl}_4)$ 4.18 (2 H, s, CH$_2$), 2.55 (1 H, s, OH), 0.16 (6 H, s, SiMe$_2$), and 0.08 (9 H, s, SiMe$_3$), $\nu_{\text{max.}}$ (film) 3 330 (OH), 2 180 (C≡C), and 1 251 cm^{-1} (SiMe$_3$).

(*E*)-3-*Pentamethyldisilylprop-2-enol* (10).—The alcohol (8) (8.6 g) in dry THF (40 ml) was added dropwise with stirring to a suspension of lithium aluminium hydride (2.7 g) in dry THF (60 ml) and the mixture was refluxed for 4 h. Work-up and distillation gave the *alcohol* (10) (7.4 g, 85%), b.p. 106—108 °C at 17 mmHg (Found: C, 51.5; H, 10.45. $\text{C}_8\text{H}_{20}\text{OSi}_2$ requires C, 51.0; H, 10.7%), $\delta(\text{CDCl}_3)$ 6.03 (1 H, dt, J 19 and 4 Hz, CH=CHCH$_2$), 5.82 (1 H, d, J 19 Hz, CH=CHCH$_2$), 4.06 (2 H, d, J 4 Hz, CH$_2$), 0.01 (6 H, s, SiMe$_2$), and —0.05 (9 H, s, SiMe$_3$), $\nu_{\text{max.}}$ (film) 3 330 (OH), 1 620 (C=C), and 1 250 cm^{-1} (SiMe$_3$), m/z 173 (33% M — Me), 157 (35, M — CH$_2$OH), 115 (42, M — Me$_3$Si), 98 (83, M — Me$_3$Si — CH$_2$OH), and 73 (100, Me$_3$Si).

(*E*)-3-*Pentamethyldisilylprop-2-enal* (12).—The alcohol (10) (7.0 g) and manganese dioxide (32.4 g) were stirred in light petroleum (130 ml) (b.p. 30—40 °C) at room temperature for 8 h. The mixture was filtered, evaporated, and distilled to give the *aldehyde* (12) (5.1 g, 74%), b.p. 88—90 °C at 17 mmHg, $\delta(\text{CCl}_4)$ 9.38 (1 H, d, J 7 Hz, CHO), 7.18 (1 H, d, J 19 Hz, CH=CHCHO), 6.41 (1 H, dd, J 19 and 7 Hz, CH=CHCHO), 0.22 (6 H, s, SiMe$_2$), and 0.10 (9 H, s, SiMe$_3$). This compound was further characterised in the next step.

(*E*)-4-*Pentamethyldisilyl-1-trimethylsilylbut-3-en-2-ol* (14).—Chloromethyltrimethylsilane[65] (3.33 g) in dry ether

(5 ml) was added to magnesium turnings (0.66 g) in dry ether (20 ml) and the mixture was refluxed for 1 h. The aldehyde (12) (4.6 g) in dry ether (5 ml) was added dropwise with cooling and then the mixture refluxed for 4 h. After cooling the mixture, saturated ammonium chloride solution was added. Work-up gave the pure *alcohol* (14) (6.7 g, 99%) (Found: C, 52.3; H, 10.85. $C_{12}H_{30}OSi_3$ requires C, 52.5; H, 11.0%), $\delta(CDCl_3)$ 6.00 (1 H, dd, J 19 and 5 Hz, CH=C*H*CHOH), 5.80 (1 H, d, J 9 Hz, C*H*=CHCHOH), 4.24 (1 H, m, C*H*OH), 1.8 (1 H, s, OH), 0.94 (2 H, dd, J 7 and 2 Hz, CH_2), 0.10 (6 H, s, $SiMe_2$), and 0.04 (9 H, s, $SiMe_3$), $\nu_{max.}$ (film) 3 350 (OH), 1 615 (C=C), and 1 253 cm^{-1} ($SiMe_3$).

(E)-1-*Pentamethyldisilylbuta*-1,3-*diene* (15).—The alcohol (14) (1.8 g) was stirred in dry ether (5 ml) with a crystal of toluene-*p*-sulphonic acid at room temperature for 0.5 h. Work-up and column chromatography on silica gel (25 g) eluting with light petroleum (b.p. 30—40 °C) gave the *diene* (15) (0.89 g, 73%), $\delta(CDCl_3)$ 6.6—4.9 (5 H, m, 5 × =CH), 0.03 (6 H, s, $SiMe_2$), and −0.04 (9 H, s, $SiMe_3$), $\nu_{max.}$ (film) 2 960 (CH), 1 575 (C=C), 1 251 ($SiMe_3$), and 840 cm^{-1} (*trans*-CH=CH), $\lambda_{max.}$ (EtOH) 227 nm. This compound was further characterised as its Diels–Alder adduct (24) with maleic anhydride.

Methyl (E)-3-*Trimethylsilylpropenoate* (16).—The alcohol (9) (6 g) and manganese dioxide (40 g) were stirred in light petroleum (200 ml) (b.p. 30—40 °C) at room temperature for 3 h. The mixture was then filtered and the solvent was removed *in vacuo*. The residue in methanol (10 ml) was added dropwise to a vigorously stirred mixture of methanol (10 ml), acetic acid (4 ml), and sodium cyanide[67] (11.5 g) at 0 °C. The mixture was then stirred for 12 h at room temperature, filtered, and worked up using dichloromethane as organic solvent, to give the ester[68] (5.3 g, 72%), $\delta(CDCl_3)$ 7.25 (1 H, d, J 19 Hz, C*H*=CHCO), 6.25 (1 H, d, J 19 Hz, CH=C*H*CO), 3.73 (3 H, s, OMe), and 0.10 (9 H, s, $SiMe_3$), $\nu_{max.}$ (film) 2 960 (CH), 1 730 (CO), 1 600 (C=C), 1 230 ($SiMe_3$), and 846 cm^{-1} (*trans*-CH=CH). On one occasion, when half the amount of manganese dioxide was used and the reagents were mixed at room temperature, the product was heavily contaminated with the corresponding saturated ester. This can be accounted for by 'enolisation' of the intermediate cyanohydrin, reprotonation α to the silicon, ketonisation of the intermediate enol thus produced, and methanolysis of the acyl cyanide.

(E)-3-*Methyl*-1-*trimethylsilylbuta*-1,3-*diene* (17).—The ester (16) (6.1 g) was added slowly with stirring to a solution of methylmagnesium iodide [from methyl iodide (11 g) and magnesium (1.88 g) in dry ether (50 ml)], at 0 °C, and the mixture was stirred for 2 h. Ammonium chloride solution was added and work-up gave 3-methyl-1-trimethylsilylbut-1-en-3-ol[18] (5.33 g, 87%), $\delta(CCl_4)$ 6.05 (1 H, d, J 19 Hz, SiCH=C*H*), 5.71 (1 H, d, J 19 Hz, SiC*H*=CH), 1.77 (1 H, s, OH), 1.22 (6 H, s, Me), and 0.04 (9 H, s, $SiMe_3$), $\nu_{max.}$ (film) 3 360 (OH), 1 620 (C=O), 1 253 ($SiMe_3$), and 845 cm^{-1} (*trans*-CH=CH), m/z 143 (30%, M − Me), 140 (35, M − H_2O), 125 (100, M − Me − H_2O), and 73 (78, $SiMe_3$). Methanesulphonyl chloride (0.6 ml) was added dropwise with stirring to the alcohol (1.0 g, without further purific-ation) and triethylamine (2.2 ml) in ether (10 ml) at 0 °C. Stirring was continued for 0.5 h, and the mixture was allowed to come to room temperature. Work-up and column chromatography (SiO_2), eluting with light petroleum (b.p. 30—40 °C), gave the diene[18] (17) (0.71 g, 80%), $\delta(CDCl_3)$ 6.59 (1 H, d, J 19 Hz, SiCH=C*H*), 5.82 (1 H, d, J 19 Hz, SiC*H*=CH), 4.99 (2 H, m, =CH_2), 1.84 (3 H, d, J 1

Hz, CMe), and 0.12 (9 H, s, $SiMe_3$), $\nu_{max.}$ (film) 1 580 (C=C), 1 254 ($SiMe_3$), and 846 cm^{-1} (*trans*-CH=CH). The diene was further characterised as its Diels–Alder adduct (25) with maleic anhydride.

(E)-4-*Trimethylsilylbut*-3-*en*-2-*ol* (18).—The aldehyde (11) (28.8 g) in ether (15 ml) was added dropwise at 0 °C to methylmagnesium iodide [from methyl iodide (15.4 ml) and magnesium (6.01 g) in ether (100 ml)], and the mixture was refluxed for 1 h. Ammonium chloride solution was added and work-up followed by distillation gave the *alcohol* (18) (28.4 g, 88%), b.p. 70—71 °C at 16 mmHg (Found: C, 58.4; H, 11.15. $C_7H_{16}OSi$ requires C, 58.3; H, 11.2%), $\delta(CCl_4)$ 5.98 (1 H, dd, J 19 and 4 Hz, SiCH=C*H*), 5.72 (1 H, d, J 19 Hz, SiC*H*=CH), 4.13 (1 H, dq, J 4 and 7 Hz, C*H*Me), 2.66 (1 H, s, OH), 1.15 (3 H, d, J 7 Hz, *Me*CH), and 0.00 (9 H, s, $SiMe_3$), $\nu_{max.}$ (film) 3 340 (OH), 1 625 (C=C), 1 255 ($SiMe_3$), and 845 cm^{-1} (*trans*-CH=CH), m/z 144 (15%, M^+), 129 (87, M − Me), and 73 (100, $SiMe_3$).

(E)-4-*Trimethylsilylbut*-3-*en*-2-*one* (19).—The alcohol (18) (8.6 g) and manganese dioxide[64] (52 g) were stirred in light petroleum (b.p. 30—40 °C) (220 ml) at room temperature for 12 h. The mixture was filtered and evaporated and the residue was distilled to give the ketone[18] (6.4 g, 76%), b.p. 67—68 °C at 19 mmHg, $\delta(CCl_4)$ 6.94 (1 H, d, J 19 Hz, C*H*=CHCO), 6.37 (1 H, d, J 19 Hz, CH=C*H*CO), 2.24 (3 H, s, MeCO), and 0.18 (9 H, s, $SiMe_3$), $\nu_{max.}$ (film) 1 683 (CO), 1 590 (C=C), 1 258 ($SiMe_3$), and 846 cm^{-1} (*trans*-CH=CH).

(E)-1-*Trimethylsilyl*-3-*trimethylsilyloxybuta*-1,3-*diene* (20).—n-Butyl-lithium (14.4 ml of a 1.54M-solution in hexane) was added to a stirred solution of di-isopropylamine (3.1 ml) in dry THF (10 ml) under nitrogen at −78 °C. After 15 min, the ketone (19) (3 g) in dry THF (5 ml) was added dropwise, and the mixture was kept for 1 h. Chloro-trimethylsilane (2.81 ml) in dry THF (4 ml) was then added and the mixture was allowed to come to room temperature over 4 h. The mixture was diluted with light petroleum (b.p. 40—60 °C) and washed with sodium carbonate solu-tion, dried (Na_2SO_4), concentrated *in vacuo* and distilled to give the *diene* (20) (3.8 g, 84%), b.p. 82—84 °C at 19 mmHg (Found: C, 56.3; H, 10.55. $C_{10}H_{22}OSi_2$ requires C, 56.0; H, 10.35%), $\delta(CCl_4)$ 6.23 (1 H, d, J 18 Hz, SiC*H*=CH), 6.02 (1 H, d, J 18 Hz, SiCH=C*H*), 4.28 (2 H, s, =CH_2), 0.20 (9 H, s, $OSiMe_3$), and 0.08 (9 H, s, $SiMe_3$), $\nu_{max.}$ (film) 1 620 (C=C), 1 580 (C=C), 1 255 ($SiMe_3$), 1 028 (C–O), and 847 cm^{-1} (*trans*-CH=CH), m/z 214 (24%, M^+), 199 (29, M − Me), 141 (100, M − Me_3Si), and 73 (84, Me_3Si).

Diels–Alder Reactions of the Dienes (3), (4), (6), (15), (17), *and* (20) *with Maleic Anhydride.*—Typically, the diene and maleic anhydride were mixed in equimolar amounts, allow-ing for any co-distillate with which the diene was con-taminated, a crystal of hydroquinone was added, and the mixture stirred at 95—100 °C for 0.5 h under nitrogen. The diene (20) needed only 10 min at 80 °C. The adducts obtained were: 3-trimethylsilylcyclohex-4-ene-1,2-dicarb-oxylic anhydride (21) (74%), plates, m.p. 125—126 °C (from cyclohexane) (lit.,[9] 124.5 °C); 3-*methyl*-6-*trimethyl-cyclohex*-4-*ene*-1,2-*dicarboxylic anhydride* (22) (69%), b.p. (short-path distillation) 112 °C at 0.15 mmHg (Found: C, 60.8; H, 7.6. $C_{12}H_{18}O_3Si$ requires C, 60.5; H, 7.6%), $\delta(CDCl_3)$ 5.88 (2 H, m, 2 × =CH), 3.47 (1 H, dd, J 9 and 6 Hz, CHCO), 3.30 (1 H, dd, J 9 and 7 Hz, CHCO), 2.44 (1 H, m, C*H*Me), 1.55 (1 H, m, C*H*SiMe$_3$), 1.38 (3 H, d, J 7 Hz, CH*Me*), and 0.16 (9 H, s, $SiMe_3$), $\nu_{max.}$ (film) 1 850 and 1 775 (anhydride) and 1 252 cm^{-1} ($SiMe_3$), m/z 238 (5%, M^+), 223 (60, M − Me), 195 (12, M − Me − CO), 166 (16, M −

$CO - CO_2$), 151 (65, $M - Me - CO - CO_2$), 93, (91, $M - SiMe_3 - CO - CO_2$), and 73 (100, Me_3Si); 3,6-*bis(trimethylsilyl)cyclohex-4-ene-1,2-dicarboxylic anhydride* (23) (63%), needles, m.p. 174—175 °C (from cyclohexane) (Found: C, 56.4; H, 8.15. $C_{14}H_{24}O_3Si_2$ requires C, 56.7; H, 8.1%), $\delta(CDCl_3)$ 6.08 (2 H, d, J 2 Hz, 2 × =CH), 3.49 (2 H, dd, J 4 and 2 Hz, CHCO), 1.55 (2 H, m, CHSiMe$_3$), and 0.19 (18 H, s, SiMe$_3$), $\nu_{max.}$ (Nujol mull) 1 852 and 1 780 (anhydride), 1 645 (C=C), and 1 250 cm^{-1} (SiMe$_3$), m/z 296 (M^+), 281 ($M - Me$), 253 ($M - Me - CO$), and 73 (Me$_3$Si); 3-*(pentamethyldisilyl)cyclohex-4-ene-1,2-dicarboxylic anhydride* (24) (82%), b.p. (short path distillation) 120 °C at 0.1 mmHg (Found: C, 55.0; H, 8.1. $C_{13}H_{22}O_3Si_2$ requires C, 55.3; H, 7.85%), $\delta(CDCl_3)$ 5.93 (2 H, m, 2 × =CH), 3.40 (2 H, m, 2 × CHCO), 2.74—2.04 (2 H, =CHCH_2), 1.78 (1 H, m, CHSiMe$_2$), 0.17 (3 H, s, SiMeMe), 0.16 (3 H, s, SiMeMe), and 0.08 (9 H, s, SiMe$_3$), $\nu_{max.}$ (film) 1 850 and 1 782 (anhydride) and 1 245 cm^{-1} (SiMe$_3$), m/z 267 (82%, $M - Me$), 239 (50, $M - Me - CO$), 210 (82, $M - CO - CO_2$), 209 (100, $M - SiMe_3$), 181 (100, $M - SiMe_3 - CO$), 131 (100, SiMe$_2$SiMe$_3$), and 73 (100, SiMe$_3$); 5-*methyl-3-trimethylsilylcyclohex-4-ene-1,2-dicarboxylic anhydride* (25) (60%), needles, m.p. 67—68 °C [from light petroleum (b.p. 60—80 °C)] (Found: C, 60.5; H, 7.8. $C_{12}H_{18}O_3Si$ requires C, 60.5; H, 7.6%), $\delta(CDCl_3)$ 5.56 (1 H, m, =CH), 3.40 (2 H, m, 2 × CHCO), 2.68—2.04 (2 H, m, =CHCH_2), 1.78 (3 H, d, J 1 Hz, Me), 1.56 (1 H, m, CHSiMe$_3$), and 0.12 (9 H, s, SiMe$_3$), $\nu_{max.}$ (Nujol mull) 1 857 and 1 780 (anhydride) and 1 255 cm^{-1} (SiMe$_3$), m/z 223 (100%, $M - Me$), 210 (31, $M - CO$), 195 (18, $M - Me - CO$), 166 (82, $M - CO - CO_2$), 151 (50, $M - Me - CO - CO_2$), and 73 (52, SiMe$_3$); the adduct (26) showed the expected spectroscopic properties and was hydrolysed in THF with dilute hydrochloric acid for 10 min at room temperature; work-up gave 4-*oxo-6-trimethylsilylcyclohexane-1,2-dicarboxylic anhydride* (30) (73% overall), m.p. 145—146 °C [from benzene–light petroleum (b.p. 60—80 °C)] (Found: C, 54.5; H, 6.65. $C_{11}H_{16}$-SiO_4 requires C, 55.0; H, 6.70%), $\delta(CDCl_3)$ 3.62 (2 H, m, 2 × CHCO), 2.85 (2 H, m, CH_2CHCO), 2.44 (1 H, dd, J 18 and 2 Hz, CH_AH$_B$CHSi), 1.97 (1 H, dd, J 18 and 14 Hz, CH$_A$H$_B$CHSi), 1.52 (1 H, ddd, J 14, 4, and 2 Hz, CHSi), and 0.14 (9 H, s, SiMe$_3$), $\nu_{max.}$ (Nujol mull) 1 856 and 1 786 (anhydride), 1 709 (CO), and 1 254 cm^{-1} (SiMe$_3$), m/z 240 (15%, M^+), 225 (35, $M - Me$), 196 (15, $M - CO_2$), 168 (40, $M - CO - CO_2$), 153 (70, $M - Me - CO - CO_2$), and 73 (100, SiMe$_3$).

Protodesilylation of the Adducts (21), (22), (24), *and* (25) *with Toluene-p-sulphonic Acid.*—Typically, the adduct (1 mmol) and anhydrous toluene-p-sulphonic acid (1 mmol) were refluxed in benzene for 1—2 h. The reaction could be followed easily by ^{1}H n.m.r., since the signal from the Me$_3$Si group moved downfield in each case as it was detached from carbon. Work-up gave the anydrides: (27), $\delta(CDCl_3)$ 5.6—6.2 (2 H, m, 2 × =CH), 3.1—3.8 (2 H, m, 2 × CHCO), and 2.4—1.9 (4 H, m, 2 × CH$_2$), characterised by hydrolysis in warm dilute sodium hydroxide solution and acidification to give cyclohex-3-ene-1,2-dicarboxylic acid (76% overall), m.p. 182—183 °C (lit.,^{19} 174 °C) identical (mixed m.p., i.r.) with an authentic sample,^{19} for which we found a m.p. of 179—181 °C; 6-*methylcyclohex-3-ene-1,2-dicar-boxylic anhydride* (28) (84%), b.p. (short-path distillation) 85 °C at 0.1 mmHg, $\delta(CCl_4)$ 6.2—5.6 (2 H, m, 2 × =CH), 3.58 (1 H, m, =CHCHCO), 3.25 (1 H, m, CMeCHCO), 2.08 (3 H, m, CH_2CHMe), and 1.30 (3 H, d, J 6 Hz, CHMe), $\nu_{max.}$ (CCl$_4$) 1 867 and 1 785 cm^{-1} (anhydride), m/z 166

(16%, M^+), 151 (75, $M - Me$), 128 (17, $M - CO$), 122 (13, $M - CO_2$), 94 (97, $M - CO - CO_2$), and 79 (100, $M - Me - CO - CO_2$), this anhydride was further characterised as the corresponding dicarboxylic acid, 6-*methylcyclohex-3-ene-1,2-dicarboxylic acid*, prisms, m.p. 167—168 °C (from water) (Found: C, 58.7; H, 6.6. $C_9H_{12}O_4$ requires C, 58.7; H, 6.55%); 5-*methylcyclohex-3-ene-1,2-dicarboxylic anhydride* (29) (65%) an oil $\delta(CCl_4)$ 5.85 (2 H, m, 2 × =CH), 3.55 (1 H, br d, J 9 Hz, =CHCHCO), 3.20 (1 H, ddd, J 11, 9, and 5 Hz, CH$_2$CHCO), 2.22 (2 H, m, CHMe-CH_AH$_B$CHCO), 1.22 (1 H, ddd, J 21, 11, and 3 Hz, CHMe-CH$_A$H$_B$CHCO), and 1.09 (3 H, d, J 6 Hz, CHMe), $\nu_{max.}$ (film) 1 865 and 1 785 cm^{-1} (anhydride), m/z 166 (35%, M^+), 138 (100, $M - CO$), and 94 (85, $M - CO - CO_2$); this anhydride was further characterised as the corresponding dimethyl ester (KOH, CH$_2$N$_2$) *dimethyl 5-methylcyclohex-3-ene-1,2-dicarboxylate* (Found: m/z, 152.0831. $C_9H_{12}O_2$ requires $M - CO_2Me - H$, 152.0836). The anhydride (27) was also prepared from the allylsilane (24) in 90% yield.

cis,cis-3-*Methylcyclohexane-1,2-dicarboxylic Acid* (31).—The anhydride (28), prepared from the anhydride (22) (0.467 g) as described above, was hydrogenated without purification in THF (20 ml) over palladium–charcoal (10%, 0.06 g). The mixture was filtered, evaporated, and the residue boiled in water for 15 min. Work-up gave the acid (31) (0.245 g, 67%) as needles, m.p. 166—167 °C (from water) (lit.,^{69} 169—170 °C), identical (i.r., n.m.r.) with an authentic sample prepared by hydrogenation of the adduct of *trans*-piperylene with maleic anhydride.^{70}

Competitive Diels–Alder Reaction between the Dienes (3) *and* (15) *and* N-*Phenylmaleimide.*—The diene (3) (0.35 g of a 2 : 1 mixture of the diene and hexamethyldisiloxane, 1.7 mmol), the diene (15) (0.31 g, 1.7 mmol), and N-phenyl-maleimide (0.292 g, 1.7 mmol) were stirred and heated at 60 °C for 24 h under nitrogen in the presence of a crystal of hydroquinone in benzene (5 ml). Work-up and t.l.c., eluting three times with 20% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C) gave 3a,4,7,7a-*tetrahydro-2-phenyl-4-trimethylsilylisoindole-1,3(2H)-dione* (0.309 g, 61%), $\delta(CDCl_3)$ 7.6—7.1 (5 H, m, aromatic), 5.99 (2 H, m, 2 × =CH), 3.33 (2 H, m, CHCO), 2.75 (1 H, m, CH_AH$_B$), 2.25 (1 H, m, CH$_A$H$_B$), 1.71 (1 H, m, CHSi), and 0.17 (9 H, SiMe$_3$), $\nu_{max.}$ (film) 1 775 and 1 710 (COs), 1 602 and 1 503 (Ar), and 1 251 cm^{-1} (SiMe$_3$) (Found: M^+, 299.1364. $C_{17}H_{21}NO_2Si$ requires M, 299.1341), m/z 299 (77%, M^+), 284 (38, $M - Me$), 179 (19, $M - H - PhNCO$), 119 (7, PhNCO), and 73 (100, Me$_3$Si), and 3a,4,7,7a-*tetrahydro-2-phenyl-4-penta-methyldisilylisoindole-1,3(2H)-dione* (0.237 g, 39%), $\delta(CDCl_3)$ 7.6—7.1 (5 H, m, aromatic), 5.94 (2 H, m, 2 × =CH), 3.29 (2 H, m, CHCO), 2.75 (1 H, m, CH_AH$_B$), 2.25 (1 H, m, CH$_A$H$_B$), 1.77 (1 H, m, CHSi), 0.19 (3 H, s, SiMe$_A$Me$_B$), 0.17 (3 H, s, SiMe$_A$Me$_B$), and 0.06 (9 H, s, SiMe$_3$), m/z 357 (11%, M^+), 342 (36, $M - Me$), 284 (100, $M - SiMe_3$), 223 (21, $M - Me - PhNCO$), 221 (68, $M - Ph - 3Me$), 207 (68, $M - SiMe_3 - Ph$), 131 (29, Me$_3$SiSiMe$_2$), and 73 (35, Me$_3$Si).

5-*Hydroxycyclohex-3-ene-1,2-dicarboxylic Acid* (33).—The anhydride (21) (3.4 g) was warmed with aqueous potassium hydroxide solution (1.5 g in 20 ml) until clear. Acidification gave the dicarboxylic acid ^{9} (32) (3.4 g, 95%) as needles, m.p. 190—192 °C. This acid (0.84 g) and un-buffered commercial ' 40% peracetic acid ' (0.9 ml) in ether (40 ml) were kept at room temperature for 24 h, when a fine precipitate of the *hydroxy-diacid* (33) (0.42 g, 66%) was formed, m.p. 185—186.5 °C (from MeOH) [The crude

material was essentially pure (^{1}H n.m.r.) and recrystallisation from methanol was wasteful]; δ(CD$_3$OD) 5.95 (2 H, br m, 2 × =CH), 4.20br (1 H, m, CHOH), 3.48br (1 H, m, H-2), 3.03 (1 H, dt, J 10 and 5 Hz, H-1), 2.35 (1 H, ddd, J 14, 10 and 5 Hz, CH$_A$H$_B$), and 2.07 (1 H, dt, J 14 and 5 Hz, CH$_A$H$_B$), $\nu_{max.}$ (KBr) 3 380 (OH), 3 325—2 300 (CO$_2$H), and 1 695 cm^{-1} (CO); the bis-p-bromophenacyl ester had m.p. 172.5—173 °C (Found: C, 49.4; H, 3.55. C$_{24}$H$_{20}$O$_7$-Br$_2$ requires C, 49.5; H, 3.45%).

Dimethyl 5-Phenylthiocyclohex-3-ene-1,2-dicarboxylate (37).—The acid (32) prepared from the anhydride (21) (0.7 g) was treated with diazomethane in ether, the solvent was removed, and the residue was purified by column chromatography on silica gel eluting with ethyl acetate–light petroleum (b.p. 40—60 °C) to give *dimethyl 3-trimethylsilylcyclohex-4-ene-1,2-dicarboxylate* (36) (0.67 g, 80%), δ(CCl$_4$) 5.58 (2 H, m, 2 × =CH), 3.65 (3 H, s, OMe), 3.58 (3 H, s, OMe), 3.23 (1 H, dd, J 6 and 3 Hz, CHCO), 2.8—2.0 (3 H, m, C=CHCH$_2$ and CHCO), 1.78 (1 H, m, CHSi), and 0.02 (3 H, s, SiMe$_3$), $\nu_{max.}$ (film) 1 740 (CO) and 1 253 cm^{-1} (SiMe$_3$), (Found: M^+, 270.1286. C$_{13}$H$_{22}$O$_4$Si requires M, 270.1284). The ester (36) (0.114 g) in dry nitromethane (1.5 ml) was added to a solution phenylsulphenyl tetrafluoroborate [prepared[25] from phenylsulphenyl chloride (0.066 ml) and silver tetrafluoroborate (0.084 g)] in dry nitromethane (3 ml) at −23 °C, and the mixture was allowed to warm to room temperature. It was then diluted with chloroform (10 ml), filtered, the solvent was removed and the residue was purified by t.l.c., eluting with ethyl acetate–light petroleum (b.p. 40—60 °C) (1 : 4 v/v), to give an oil (125 mg) consisting of the *ester* (37), the dimethyl ester corresponding to the anhydride (27), and probably a stereoisomer of (37) in the ratio (n.m.r.) of 8 : 1 : 1. The effective yield of (37) is therefore 78%; δ(CCl$_4$) 7.3 (5 H, m, aromatic), 5.88 (2 H, m, 2 × =CH), 3.85 (1 H, m, CHS), 3.62 (6 H, s, OMe), 3.47 (1 H, m, =CHCHCO), 3.05 (1 H, m, CH$_2$CHCO), and 2.54—2.0 (2 H, m, CH$_2$), $\nu_{max.}$ (film) 1 735 (CO) and 1 585 cm^{-1} (Ph) (Found: M^+, 306.0925. C$_{16}$H$_{18}$O$_4$S requires M, 306.0930), m/z 306 (48%, M^+), 246 (100, M − CO$_2$Me), 197 (34, M − PhS), and 109 (96, PhS). The impurities showed up most distinctively in the olefinic region of the ^{1}H n.m.r. spectrum, the protodesilylation product having a narrow multiplet at δ 5.75, coincident with the signal from an authentic sample, and the stereoisomer of (37) having a similarly shaped multiplet to that from (37) but appearing just upfield from it at δ 5.80.

The Stereochemistry of the Hydroxy-acid (33).—The hydroxy-acid (33) (300 mg) was hydrogenated in ethanol (15 ml) over Adams catalyst (20 mg), consuming hydrogen (38 ml) over 1 h. Work-up and treatment with diazomethane gave the ester (34), R_F [EtOAc–light petroleum (b.p. 40—60 °C) 2 : 1 v/v] 0.3, δ(CCl$_4$) 3.60 (6 H, s, OMe), 3.2—2.6 (3 H, m, 3 × CH), and 2.5—1.2 (6 H, m, 3 × CH$_2$), $\nu_{max.}$ (CCl$_4$) 3 400br (OH) and 1 735 cm^{-1} (CO). The same hydroxy-ester was prepared following McQuillin,[26] except that (i) methyl esters were used, (ii) m-chloroperbenzoic acid gave a mixture of the two possible epoxides, which were separated by t.l.c. [EtOAc–light petroleum (b.p. 40—60 °C)], the faster-running anti-epoxide was used for the next step, and (iii) tributyltin hydride was superior to Raney nickel for the removal of the bromine from the bromohydrin. The isomeric alcohol (35) was prepared from the syn-epoxide above, which gave a known[27] lactone on treatment with hydrobromic acid. Debromination and methanolysis by the method of Klein, Dunkelblum, and Avrahami,[27] gave the

alcohol (35), R_F 0.27, δ(CCl$_4$) 3.70 (6 H, s, OMe), 3.2—2.6 (3 H, m, 3 × CH), and 2.5—1.2 (6 H, m, 3 × CH$_2$), $\nu_{max.}$ (CCl$_4$) 3 420 (OH) and 1 730 cm^{-1} (CO), clearly different from the two samples of the other alcohol.

The Stereochemistry of the Sulphide (37).—The sulphide (97 mg) and sodium metaperiodate (70 mg) were kept in methanol (7.5 ml) and water (7.5 ml) for 10 h at room temperature. The solvent was evaporated off at room temperature *in vacuo* and the residue was purified by t.l.c. [EtOAc–light petroleum (b.p. 40—60 °C), 2 : 1 v/v] to give a mixture of sulphoxides (100 mg, 98%). This was used directly in methanol (10 ml) containing trimethyl phosphite (115 mg) and refluxed under nitrogen for 40 h. The solvent was evaporated *in vacuo* and the residue was purified by t.l.c. [EtOAc–light petroleum (b.p. 40—60 °C)] to give *dimethyl trans-3-hydroxycyclohex-4-ene-cis-1,2-dicarboxylate* (38) (40 mg, 50%), R_F 0.5, δ(CCl$_4$) 5.60 (2 H, m, 2 × =CH), 4.55 (1 H, m, CHOH), 3.67 (3 H, s, OMe), 3.65 (3 H, s, OMe), 3.4—2.7 (2 H, m, 2 × CHCO), and 2.5—2.3 (2 H, m, CH$_2$), $\nu_{max.}$ (CCl$_4$) 3.400br (OH), 1 735 (CO), and 1 655 cm^{-1} (C=C) (Found: M^+, 214.0842. C$_{10}$H$_{14}$O$_5$ requires M, 214.0841). *cis-3-Acetoxycyclohex-4-ene-cis-1,2-dicarboxylic* anhydride[29] (100 mg) was heated gently in water (5 ml) containing potassium hydroxide (40 mg). The solution was cooled, shaken with Amberlite IR 120(H), separated, and evaporated *in vacuo* to give the hydroxy-diacid. This was immediately esterified with diazomethane to give *dimethyl cis-3-hydroxycyclohex-4-ene-cis-1,2-dicarboxylate* (39) (60 mg, 60%), δ(CCl$_4$) 5.6 (2 H, m, 2 × =CH), 4.0—4.5 (2 H, m, CHOH), 3.61 (3 H, s, OMe), 3.59 (3 H, s, OMe), 3.1—2.8 (2 H, m, 2 × CHCO), and 2.5—2.2 (2 H, m, CH$_2$), $\nu_{max.}$ (CCl$_4$) 3 450br (OH) and 1 740 cm^{-1} (CO) (Found: M^+, 214.0843. C$_{10}$H$_{14}$O$_5$ requires M, 214.0841). The hydroxy-diacid showed a considerable aptitude for lactonisation, hence the use of Amberlite and the speedy esterification. Hydrogenation of (38) gave the corresponding saturated ester R_F [EtOAc–light petroleum (b.p. 40—60 °C) 2 : 1 v/v] 0.47, δ(CCl$_4$) 3.70 and 3.65 (OMe's), clearly different from the esters (34) and (35).

Reaction of 1-Trimethylsilylbutadiene with Methyl Acrylate.—The mixture of the diene (3) and hexamethyldisiloxane (2.4 g, 2 : 1 by n.m.r.), methyl acrylate (0.86 g) and a few crystals of hydroquinone were heated at 150 °C in a sealed tube for 24 h. Column chromatography on silica gel eluting with benzene gave the mixture of adducts (40) and (41) (0.88 g, 42%) as an oil (Found: C, 62.1; H, 9.95. C$_{11}$H$_{20}$SiO$_2$ requires C, 62.2; H, 9.5%); δ(CDCl$_3$) 5.61 (2 H, m, 2 × =CH), 3.66 (3 H, s, OMe), 2.55 (1 H, m, CHCO), 2.4—1.4 (5 H, m, CH and 2 × CH$_2$), and 0.02 and 0.00 (9 H, s, 2 × SiMe$_3$), $\nu_{max.}$ (film) 1 740 (CO), 1 644 (C=C), and 1 255 cm^{-1} (SiMe$_3$), m/z 212 (29%, M^+), 211 (65, M − H), 181 (22, M − MeO), and 73 (100, SiMe$_3$).

Protodesilylation of the Mixture of Adducts (40) *and* (41).—The mixture of adducts (0.212 g) was refluxed with toluene-p-sulphonic acid (0.172 g) in benzene (3 ml) for 1 h. Work up and t.l.c. gave a mixture of methyl cyclohex-2-ene-carboxylate (49) and methyl cyclohex-3-enecarboxylate (50) in the ratio 3 : 1 [as determined by integration of the olefinic n.m.r. signals]. A well resolved multiplet at δ 2.98 was the allylic hydrogen α to the methoxycarbonyl group in (49); this integrated in agreement with the ratio 3 : 1.

Authentic Samples of the Protodesilylation Products (49) *and* (50).—The ester (49), prepared by treating the known[71] acid with diazomethane, had δ(CDCl$_3$) 5.68 (2 H, m, 2 × =CH), 3.60 (3 H, s, OMe), 2.98 (1 H, m, CHCO), and 2.2—1.5

(6 H, m, 3 × CH$_2$), $\nu_{max.}$ (film) 1 740 cm^{-1}. The ester (50), prepared by Diels–Alder reaction of butadiene with methyl acrylate,[2] had δ(CCl$_4$) 5.58 (2 H, m, 2 × =CH), 3.60 (3 H, s, OMe), and 2.7—1.5 (7 H, m, CH and 3 × CH$_2$), $\nu_{max.}$ (film) 1 740 cm^{-1} (CO).

Reaction of 1-Trimethylsilylbutadiene with Methyl Propiolate.—The mixture of the diene (3) and hexamethyldisiloxane (4.1 g, 2 : 1 by n.m.r.), methyl propiolate[72] (1.2 g), and a few crystals of hydroquinone were heated at 150 °C in a sealed tube for 40 h. Column chromatography on silica gel eluting with benzene gave first methyl 6-trimethylsilylcyclohexa-1,4-dienecarboxylate (42) (1.2 g, 40%), δ(CCl$_4$) 6.66 (1 H, m, H$_a$), 5.76 (1 H, m, H$_e$), 5.44 (1 H, m, H$_d$), 3.66 (3 H, s, OMe), 2.81 (3 H, m, H$_b$, H$_c$, and H$_f$), and 0.02 (9 H, s, SiMe$_3$), $\nu_{max.}$ (film) 1 720 (CO), 1 667 (C=C), and 1 255 cm^{-1} (SiMe$_3$), m/z 210 (36%, M^+), 209 (45, M − H), 208 (45, M − H$_2$), 195 (45, M − Me), 194 (73, M − H − Me), 193 (100, M − H$_2$ − Me), 177 (45, M − H$_2$ − OMe), and 73 (100, SiMe$_3$), and secondly methyl 3-trimethylsilylcyclohexa-1,4-dienecarboxylate (43) (1.1 g, 37%), δ(CCl$_4$) 6.99 (1 H, m, H$_a$), 5.62 (2 H, m, H$_c$ and H$_d$), 3.66 (3 H, s, OMe), 3.1—2.75 (2 H, m, H$_e$ and H$_f$), 2.51 (1 H, m, H$_b$), and 0.02 (9 H, s, SiMe$_3$), $\nu_{max.}$ (film) 1 722 (CO), 1 670 (C=C), and 1 265 cm^{-1} (SiMe$_3$), m/z 210 (8, M^+), 194 (37, M − H − Me), and 193 (100, M − H$_2$ − Me).

Double Irradiation and Europium–shifted Spectra of the Adducts (42) *and* (43).—Addition of 5% Eu(fod)$_3$ to the solution of (42) caused the signals of the MeO group, H$_a$ and H$_f$ to shift downfield. Irradiation at H$_e$ caused H$_f$ to appear as a broadened triplet (J 6 Hz) from coupling to H$_b$ and H$_c$.[73] Irradiation at H$_{b,c}$ collapsed the signal of H$_a$ to a singlet, H$_e$ to a double doublet (J 10 and 5 Hz), and H$_d$ to a doublet (J 10 Hz) broadened slightly by allylic coupling to H$_f$. Irradiation at H$_f$ resulted in H$_e$ collapsing to a doublet (J 10 Hz). Addition of 5% Eu(fod)$_3$ to the solution of (43) caused the signals of the MeO group, H$_a$ and H$_{e,f}$ to shift downfield. Irradiation at H$_a$ caused H$_b$ to collapse to a broadened triplet (J 7 Hz) from coupling to H$_e$ and H$_f$.[73] Irradiation at H$_{e,f}$ collapsed the signal of H$_a$ to a doublet (J 4 Hz). Irradiation at H$_b$ collapsed the signal of H$_a$ to a singlet. In the shifted spectrum, H$_e$ and H$_f$ both appear as double double doublets (J 21, 6, and 3 for H$_e$ and 21, 7, and 2 for H$_f$).

Reaction of the Adduct (42) *with DDQ.*—The adduct (42) (0.112 g) and dichlorodicyanobenzoquinone (DDQ) (0.121 g) were stirred in benzene (2 ml) at room temperature for 2 h. T.l.c., eluting with 5% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C), gave methyl 3-trimethylsilylbenzoate[74] (53) (0.104 g, 94%), δ(CCl$_4$) 8.07 (1 H, s, H-2), 7.90 (1 H, dt, J 1 and 8 Hz, H-6), 7.62 (1 H, dt, J 1 and 8 Hz, H-4), 7.34 (1 H, t, J 8 Hz, H-5), 3.85 (3 H, s, OMe), and 0.28 (9 H, s, SiMe$_3$), $\nu_{max.}$ (film) 1 730 (CO), 1 595 (Ar), and 1 285 cm^{-1} (SiMe$_3$).

Reaction of Adduct (43) *with DDQ.*—The adduct (43) (0.1 g) and DDQ (0.108 g) were stirred in a mixture of methanol (1.5 ml) and ether (1.5 ml) at room temperature for 1 h. T.l.c. eluting with benzene gave methyl 3-trimethylsilylbenzoate (53) (0.088 g, 89%), identical with the sample described above.

Reaction of 1-Trimethylsilylbutadiene with Citraconic Anhydride.—Citraconic anhydride (1.2 g) and a few crystals of hydroquinone were heated to 100 °C and the mixture of the diene (3) and hexamethyldisiloxane were added (0.5 g at a time) in portions over 72 h, following the reaction by ^{1}H n.m.r. When the reaction had gone to *ca.* 66% conversion,

the rate was markedly reduced. The mixture was stirred with potassium hydroxide solution (1.2 g in 10 ml) for 0.5 h, washed with ether, and the aqueous layer was acidified and worked up to give a brown gum of acids (2.7 g). These (0.5 g) were separated by preparative t.l.c. (SiO$_2$; di-isopropyl ether–methanol–acetic acid, 94 : 5 : 1 v/v/v) to give acid A (0.117 g, 24%), R_F 0.4, and acid B (0.135 g, 28%), R_F 0.3. Oxalyl chloride (0.1 ml) was added dropwise with stirring to acid B (46 mg) in ether (3 ml) and the mixture was kept at room temperature for 15 min. Work-up gave 2-*methyl-3-trimethylsilylcyclohex-4-ene-1,2-dicarboxylic anhydride* (44) (31 mg, 72%) as needles, m.p. 65—66 °C [from light petroleum (b.p. 30—40 °C)] (Found: C, 60.5; H, 7.65. C$_{12}$H$_{18}$O$_3$Si requires C, 60.5; H, 7.6%), δ(CCl$_4$) 5.89 (2 H, m, 2 × =CH), 2.91 (1 H, dd, J 8 and 4 Hz, CHCO), 2.8—2.3 (2 H, m, CH$_2$), 1.68 (1 H, m, CHSi), 1.52 (3 H, s, Me), and 0.11 (9 H, s, SiMe$_3$), m/z 238 (M^+), 223 (M − Me), 210 (M − CO), 195 (M − CO − Me), 166 (M − CO − CO$_2$), 151 (M − CO − CO$_2$ − Me), and 73 (Me$_3$Si). Similarly the acid A (41 mg) gave 1-*methyl-3-trimethylsilylcyclohex-4-ene-1,2-dicarboxylic anhydride* (45) as needles, m.p. 89—90 °C [from light petroleum (b.p. 30—40 °C)] (Found: C, 60.5; H, 7.55. C$_{12}$H$_{18}$O$_3$Si requires C, 60.5; H, 7.6%), δ(CCl$_4$) 5.89 (2 H, m, 2 × =CH), 2.97 (1 H, d, J 7 Hz, CHCO), 2.50 (1 H, dt, J 2 and 16 Hz, CH_AH$_B$), 1.98 (1 H, dt, J 2 and 16 Hz, CH$_A$H$_B$), 1.63 (1 H, m, CHSi), 1.41 (3 H, s, Me), and 0.17 (9 H, s, SiMe$_3$), m/z 238, 223, 195, 166, 151, and 73.

Reaction of 1-Trimethylsilylbutadiene with 2,6-Dimethylbenzoquinone.—The mixture of the diene (3) and hexamethyldisiloxane (0.79 g, 2 : 1 by n.m.r.), 2,6-dimethylbenzoquinone[75] (0.34 g), and a few crystals of hydroquinone were heated at 140 °C in a sealed tube for 24 h and the products were purified by column chromatography on silica gel eluting with benzene to give the mixture of adducts (46) and (47) (0.205 g, 32%) in the ratio of 1 : 1 [as determined by integration of the C-Me signals at δ 1.08 (46) and 1.28 (47)]. The two adducts were prepared separately by the methods described below.

2,8a-*Dimethyl-8-trimethylsilyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione* (46).—The mixture of the diene (3) and hexamethyldisiloxane (2.5 g, 2 : 1 by ^{1}H n.m.r.), 2,6-dimethylbenzoquinone (0.68 g), and a few crystals of hydroquinone were heated at 140 °C in a sealed tube for 43 h, and the products were purified by column chromatography as before. The first fractions appeared to be adducts with two equivalents of diene to one of dienophile. The second fraction was the pure *adduct* (46) (0.451 g, 37%), a pale yellow oil (Found: C, 68.5; H, 8.4. C$_{15}$H$_{22}$O$_2$Si requires C, 68.65; H, 8.45%), δ(CCl$_4$) 6.49 (1 H, q, J 1 Hz, =CHCO), 5.53 (2 H, m, 2 × =CH), 2.85 (1 H, dd, J 7 and 9 Hz, CH$_2$CHCO), 2.36—2.04 (2 H, m, CH$_2$), 1.98 (1 H, m, CHSi), 1.94 (3 H, d, J 1 Hz, =CMe), 1.08 (3 H, s, Me), and −0.03 (9 H, s, SiMe$_3$), $\nu_{max.}$ (film) 1 685 (CO), 1 630 (C=C), and 1 255 cm^{-1} (SiMe$_3$), m/z 262 (45%, M^+), 247 (45, M − Me), 219 (17, M − Me − CO), and 73 (SiMe$_3$).

2,8a-*Dimethyl-5-trimethylsilyl-4a,5,8,8a-tetrahydronaphthalene-1,4-dione* (47).—The mixture of the diene (3) and hexamethyldisiloxane (2.1 g, 2 : 1 by ^{1}H n.m.r.), 2,6-dimethylbenzoquinone (0.68 g), boron trifluoride–ether (0.63 ml), and a few crystals of hydroquinone were refluxed in ether (5 ml) under nitrogen for 40 h. Work-up and column chromatography as before gave the *adduct* (47) (0.554 g, 43%), pale yellow prisms, m.p. 65—66 °C (from isopentane) (Found: C, 68.6; H, 8.45. C$_{15}$H$_{22}$O$_2$Si requires C, 68.65; H, 8.45%), δ(CCl$_4$) 6.44 (1 H, q, J 1 Hz, =CHCO), 5.8—5.3

(2 H, m, 2 × =CH), 2.84 (1 H, d, J 5 Hz, CHSiCHCO), 2.4—2.1 (1 H, m, CH_AH_B), 1.94 (3 H, d, J 1 Hz, =CMe), 1.82—1.5 (2 H, m, CHSi and CH$_A$H$_B$), 1.28 (3 H, s, Me), and 0.07 (9 H, s, SiMe$_3$), $\nu_{max.}$ (Nujol mull) 1 694 (CO), 1 638 (C=C), and 1 255 cm^{-1} (SiMe$_3$), m/z 262 (6%), 247 (39), 234 (73, M — CO), 219 (100), and 73 (100).

Reaction of 1-Trimethylsilylbutadiene with Diethyl Oxomalonate.—The mixture of the diene (3) and hexamethyldisiloxane (1.5 g, 2 : 1 by ^{1}H n.m.r.), diethyl oxomalonate (0.87 g), and a few crystals of hydroquinone were heated in a sealed tube at 150 °C for 40 h. Column chromatography on silica gel eluting with benzene gave *diethyl 6-trimethylsilyl-3,6-dihydro-2H-pyran-2,2-dicarboxylate* (48) (0.723 g, 48%) as an oil, δ(CCl$_4$) 5.63 (2 H, m, 2 × =CH), 4.20 (1 H, s, CHSi), 4.13 (2 H, q, J 7 Hz, OCH$_2$CH$_3$), 4.11 (2 H, q, J 7 Hz, OCH$_2$CH$_3$), 2.76—2.25 (2 H, m, CH$_2$), 1.21 (3 H, t, J 7 Hz, OCH$_2$CH$_3$), 1.19 (3 H, t, J 7 Hz, OCH$_2$CH$_3$), and 0.01 (9 H, s, SiMe$_3$), $\nu_{max.}$ (film) 1 746 (CO) and 1 252 cm^{-1} (SiMe$_3$) (Found: M^+, 300.1391. C$_{14}$H$_{24}$O$_5$Si requires M, 300.1392) m/z 300 (14%, M^+), 285 (7, M — Me), and 73 (SiMe$_3$).

Lewis-acid-catalysed Reactions of 1-Trimethylsilylbutadiene.—The dienophile, the mixture of the diene and hexamethyldisiloxane (2 : 1), and boron trifluoride–ether, in the proportions given below, were heated with a few crystals of hydroquinone at the temperatures and for the times given below. (*a*) Methyl acrylate (0.86 g, 3.0 g, 1.13 g, 80 °C, 18 h) gave a mixture of the adducts (40) and (41) (0.4 g, 19%), protodesilylation of which gave the esters (49) and (50) in the ratio 1 : 1 (*b*) Methyl propiolate (0.42 g, 1.8 g, 0.63 ml, 100 °C, 23 h) gave only the adduct (42) (0.212 g, 20%). (*c*) Citraconic anhydride (0.506 g, 1.6 g, 0.57 ml, 100 °C, 24 h) gave the anhydrides (44) and (45), which were separated by hydrolysis and chromatography, as before. The corresponding dicarboxylic acids (0.203 g, 34% and 0.187 g, 31%) were identical with those obtained above, as were the anhydrides obtained from them by treatment with oxalyl chloride. (*d*) The experiment with 2,6-dimethylbenzoquinone was described above.

Reaction of 1-Pentamethyldisilylbutadiene (15) with Methyl Acrylate.—The diene (15) (0.6 g), methyl acrylate (0.35 g), and a few crystals of hydroquinone were heated at 150 °C for 24 h in a sealed tube. Column chromatography on silica gel eluting with ethyl acetate–light petroleum (b.p. 60—80 °C) (3%) gave a mixture of *methyl 2-pentamethyldisilylcyclohex-3-enecarboxylate* (59) and *methyl 3-pentamethyldisilylcyclohex-4-enecarboxylate* (60) (0.312 g, 35%) as an oil (Found: C, 57.5; 9.45. C$_{13}$H$_{26}$O$_2$Si$_2$ requires C, 57.7; H, 9.7%), δ(CDCl$_3$) 5.66 (2 H, m, 2 × =CH), 3.72 and 3.70 (3 H, 2 × s, OMe), 2.60 (1 H, m, CHCO), 2.4—1.5 (5 H, m, CH and 2 × CH$_2$), and 0.12 (15 H, s, SiMe$_2$SiMe$_3$), $\nu_{max.}$ (film) 1 740 (CO), 1 644 (C=C), and 1 250 cm^{-1} (SiMe$_3$), m/z 270 (6%, M^+), 269 (10, M — H), 255 (38, M — Me), 197 (100, M — SiMe$_3$), 131, (74, Me$_3$SiMe$_2$Si), and 73 (42, Me$_3$Si). The mixture of adducts (0.26 g) was refluxed in benzene (2 ml) with toluene-p-sulphonic acid (0.165 g) for 0.5 h. Work-up and t.l.c. gave the mixture of esters (49) and (50) (0.134 g, 99%) in the ratio 3 : 1 (^{1}H n.m.r.).

Reaction of 3-Methyl-1-trimethylsilylbutadiene (17) with Methyl Acrylate.—The diene (17) (0.65 g), methyl acrylate (0.43 g), and a few crystals of hydroquinone were heated in a sealed tube at 150 °C for 24 h. Column chromatography on silica gel eluting with 5% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C) gave a mixture of the *cis-* and *trans-*isomers of *methyl 4-methyl-2-trimethylsilylcyclohex-3-enecarboxylate* (61) (0.527 g, 51%) as an oil, δ(CCl$_4$) 5.27 (1 H, m, =CH),

3.60 (3 H, s, OMe), 2.8—1.7 (6 H, m, CH and CH$_2$), 1.64br (3 H, s, CMe), and —0.06 (9 H, s, SiMe$_3$), $\nu_{max.}$ (film) 1 741 (CO) and 1 255 cm^{-1} (SiMe$_3$), (Found: M^+, 226.1368. C$_{12}$H$_{22}$O$_2$Si requires M, 226.1388; m/z, 195.0849. C$_{11}$H$_{19}$-OSi requires M — OMe, 195.0841); m/z 226 (44%, M^+), 211 (38, M — Me), 195 (19, M — OMe), 167 (19, M — CO$_2$Me), 94 (100, M — SiMe$_3$), and 73 (100, SiMe$_3$).

Protodesilylation of the Adducts (61).—The mixture of adducts (61) (0.121 g) was refluxed in benzene (3 ml) with toluene-p-sulphonic acid (0.092 g) for 3 h. Work-up and t.l.c., eluting with benzene, gave the mixture of esters (62) as an oil (0.071 g, 86%), δ(CCl$_4$) 5.63 (2 H, m, 2 × =CH), 3.63 (3 H, s, OMe), 2.96 (1 H, m, CHCO), 2.5—1.1 (5 H, CH and 2 × CH$_2$), and 0.98 (3 H, 2 × d, J 7 Hz, CHMe), $\nu_{max.}$ (film) 1 740 (CO) and 1 655 cm^{-1} (C=C), m/z 154 (24%, M^+), 122 (29, M — MeOH), 95 (85, M — CO$_2$Me), and 94 (M — HCO$_2$Me). This mixture was kept in methanol (2 ml) with sodium methoxide (0.032 g) at room temperature for 144 h. Work-up gave *methyl 4-methylcyclohex-1-enecarboxylate* (63) (0.066 g, 95%), δ(CDCl$_3$) 6.85 (1 H, m, =CH), 3.66 (3 H, s, OMe), 2.6—1.2 (7 H, m, CH and 3 × CH$_2$), and 0.98 (3 H, d, J 5 Hz, CHMe), $\nu_{max.}$ (film) 1 720 (CO) and 1 652 cm^{-1} (C=C) (Found: M^+, 154.0994. C$_9$H$_{14}$O$_2$ requires 154.0993); m/z 154 (62%, M^+), 139 (38, M — Me), 123 (23, M — MeO), 122 (23, M — MeOH), 95 (93, M — CO$_2$Me), and 94 (100, M — HCO$_2$Me).

Reaction of 3-Methyl-1-trimethylsilylbutadiene (17) *with Methyl Propiolate.*—The diene (17) (0.6 g), methyl propiolate (0.42 g), and a few crystals of hydroquinone were heated at 150 °C for 22 h in a sealed tube. Preparative t.l.c. on silica gel eluting with 5% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C) gave *methyl 4-methyl-6-trimethylsilylcyclohexa-1,4-dienecarboxylate* (0.396 g, 42%), δ(CCl$_4$) 6.67 (1 H, t, J 4 Hz, CH=CHCO), 5.46 (1 H, m, CH=CMe), 3.68 (3 H, s, OMe), 2.76 (3 H, m, CHSi and CH$_2$), 1.70 (3 H, s, =CMe), and —0.05 (9 H, s, SiMe$_3$), $\nu_{max.}$ (film) 1 730 (CO), 1 685 and 1 640 (C=C), and 1 255 cm^{-1} (SiMe$_3$), m/z 224 (29%, M^+), 223 (30, M — H), 222 (30, M — H$_2$), 209 (31, M — Me), 208 (29, M — H — Me) 207, (98, M — H$_2$ — Me), 193 (12, M — MeO), 191 (12, M — H$_2$ — MeO), 119 (95, M — H — MeO — Me$_3$Si), and 73 (100, Me$_3$Si), *methyl 5-methyl-3-trimethylsilylcyclohexa-1,4-dienecarboxylate* (65) (0.111 g, 12%), δ(CDCl$_3$) 7.02 (1 H, m, CH=CCO), 5.32 (1 H, m, CH=CMe), 3.74 (3 H, s, OMe), 2.83 (3 H, m, CHSi and CH$_2$), 1.72 (3 H, d, J 1 Hz, =CMe), and 0.04 (9 H, s, SiMe$_3$), $\nu_{max.}$ (film) 1 728 (CO), 1 685 and 1 638 (C=C), and 1 255 cm^{-1} SiMe$_3$), m/z 224 (18%, M^+), 223 (18), 222 (18), 209 (18), 208 (18), 207 (55), 191 (9), 119 (59), and 73 (100), and methyl 4-methylbenzoate (67) (0.019 g, 3%) δ(CCl$_4$) 7.84 (2 H, d, J 8 Hz, H-2), 7.14 (2 H, d, J 8 Hz, H-3), 3.83 (3 H, s, OMe), and 2.38 (3 H, s, C-Me), $\nu_{max.}$ 1 725 (CO), 1 619, 1 580 and 1 515 cm^{-1} (Ar), identical with an authentic sample.

Protodesilylation of the Adduct (64).—The adduct (64) (0.047 g) was refluxed in benzene (1.5 ml) with toluene-p-sulphonic acid (0.04 g) for 3 h. Work-up and preparative t.l.c., eluting with 10% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C), gave *methyl 4-methylcyclohexa-1,5-dienecarboxylate* (66) δ(CCl$_4$) 6.78 (1 H, m, CH=CCO), 6.25 (1 H, dt, J 9 and 1 Hz, =CH-CCO), 5.66 (1 H, dd, J 9 and 3 Hz, CH=CH-CCO), 3.68 (3 H, s, OMe), 2.6—2.1 (3 H, m, CHMe and CH$_2$), and 1.03 (3 H, d, J 6 Hz, CHMe), $\nu_{max.}$ (film) 1 725 (CO), 1 648 and 1 595 cm^{-1} (C=C), m/z 152 (49%, M^+), 151 (31, M — H), 150 (54, M — H$_2$), 137 (56, M — Me), 121 (38, M — MeO), 119 (68, M — H$_2$ — MeO), 93 (68, M — CO$_2$Me), and 91 (100, M — H$_2$ — CO$_2$Me).

Protodesilylation and Dehydrogenation of the Adduct (64).—The adduct (64) (0.134 g) was refluxed in dry benzene (3 ml) with toluene-*p*-sulphonic acid (0.103 g) for 14 h. The mixture was worked up and the product kept in benzene (3 ml) with DDQ (0.136 g) for 1 h. Work-up and preparative t.l.c., eluting with ethyl acetate (5%) in light petroleum (b.p. 40—60 °C), gave methyl 4-methylbenzoate (67) (0.059 g, 65%), identical (¹H n.m.r., i.r.) with an authentic sample.

Protodesilylation and Dehydrogenation of the Adduct (65).—The adduct (65) (0.08 g) was refluxed in dry benzene (1.5 ml) with toluene-*p*-sulphonic acid (0.062 g) for 1 h. The solution was worked up and the product kept in benzene (3.5 ml) with DDQ (0.078 g) for 1 h. Work-up and preparative t.l.c., eluting with the same solvent as above, gave methyl 3-methylbenzoate (68) (0.042 g, 79%), identical (¹H n.m.r., i.r.) with an authentic sample.

Reaction of the Adduct (64) *with DDQ.*—The adduct (64) (0.63 g) was kept in benzene (2 ml) with DDQ (0.07 g) at room temperature for 0.5 h. Work-up and preparative t.l.c., eluting with the same solvent mixture as above, gave a mixture of methyl 4-methyl-3-trimethylsilylbenzoate and methyl 4-methyl-2-trimethylsilylbenzoate in the ratio (¹H n.m.r.) 3 : 1, $v_{max.}$ (film) 1 725 (CO), 1 605 (Ar), and 1 260 cm⁻¹ (SiMe₃). The major isomer showed δ(CCl₄) 8.10 (1 H, d, *J* 2 Hz, H-2), 7.90 (1 H, dd, *J* 8 and 2 Hz, H-6), 7.22 (1 H, d, *J* 8 Hz, H-5), 3.92 (3 H, s, OMe), 2.56 (3 H, s, CMe), and 0.42 (9 H, s, SiMe₃); the minor isomer showed δ(CCl₄) 7.88 (1 H, d, *J* 8 Hz, H-6), 7.50 (1 H, s, H-3), 7.23 (1 H, d, *J* 8 Hz, H-4), 3.92 (3 H, s, OMe), 2.47 (3 H, s, CMe), and 0.35 (9 H, s, SiMe₃).

Reaction of 1-*Trimethylsilylpentadiene* (4) *with Methyl Acrylate.*—The diene (0.63 g), methyl acrylate (0.5 g), and a few crystals of hydroquinone were heated at 140 °C for 48 h in a sealed tube. Column chromatography on silica gel (50 g), eluting with ethyl acetate (5%) in light petroleum (b.p. 60—80 °C), gave a mixture (0.674 g, 66%) of *methyl 2-methyl-5-trimethylsilylcyclohex-3-enecarboxylate* (69) and *methyl 5-methyl-2-trimethylsilylcyclohex-3-enecarboxylate* (70) (Found: C, 63.5; H, 9.8. C₁₂H₂₂O₂Si requires C, 63.7; H, 9.8%), δ(CCl₄) 5.5 (2 H, m, 2 × =CH), 3.65 (3 H, s, OMe), 2.8—1.4 (5 H, m, 3 × CH and CH₂), 1.15—0.85 (3 H, 4 × d, *J* 7 Hz, CHMe), and 0.03, 0, and −0.01 (9 H, 3 × s, SiMe₃), $v_{max.}$ (film) 1 738 (CO), 1 640 (C=C), and 1 250 cm⁻¹ (SiMe₃), *m/z* 226 (60%, M^+), 211 (44, *M* − Me), 195 (19, *M* − MeO), 122 (93, *M* − MeO − SiMe₃), and 73 (100, SiMe₃). The mixture of adducts (0.17 g) was refluxed in benzene (2 ml) with toluene-*p*-sulphonic acid (0.129 g) for 2 h. Work-up and t.l.c., eluting with 10% v/v ethyl acetate–light petroleum (b.p. 60—80 °C), gave a mixture (0.112 g, 97%) of methyl 6-methylcyclohex-3-enecarboxylate (71) [76] and *methyl 5-methylcyclohex-2-enecarboxylate* (72) (Found: C, 70.4; H, 9.35. C₉H₁₄O₂ requires C, 70.1; H, 9.15%), δ(CDCl₃) 5.77 [m, =CHs of (72)], 5.64 [m, =CHs of (71)], 3.69 (3 H, s, OMe), 3.14 [m, CHCO of (72)], 2.8—1.2 (m, remaining CHs and CH₂s), and 1.06—0.82 (3 H, 4 × d, *J* 7 Hz, CHMe), $v_{max.}$ (film) 1 740 (CO) and 1 660 cm⁻¹ (C=C), *m/z* 154 (54%, M^+), 123 (34, *M* − MeO), 122, (94, *M* − MeOH), 95 (100, *M* − CO₂Me), and 94 (100, *M* − HCO₂Me). This mixture (0.07 g) was kept in methanol (2 ml) containing sodium methoxide (0.024 g) at room temperature for 24 h. Work-up gave a mixture of the ester (71) and methyl 5-methylcyclohex-1-enecarboxylate (73) (0.068 g, 97%), δ(CDCl₃) 6.97 [m, =CH of (73)], 5.66 [m, =CHs of (71)], 3.75 [s, OMe of (73)], 3.72 [s, OMe of (71)], 2.8—1.6 (remain-

ing CHs and CH₂s), and 1.04, 0.98, and 0.95 (3 × d, *J* 7 Hz, CHMe), $v_{max.}$ (film) 1 740 (sat. CO), 1 720 (C=CCO), and 1 655 cm⁻¹ (C=C). The integration of the olefinic signals before and after treatment with base indicated that the esters (71) and (72) were present in the ratio of 2 : 1, and the integration of the other distinctive signals identified above were in agreement with this approximate value.

Reaction of 1-*Trimethylsilylpentadiene* (4) *with Methyl Propiolate.*—The diene (0.7 g), methyl propiolate (0.5 g), and a few crystals of hydroquinone were heated at 130 °C for 48 h in a sealed tube. Column chromatography on silica gel (40 g) eluting with ethyl acetate (3%) in light petroleum (b.p. 40—60 °C) gave a mixture (0.76 g, 68%) of *methyl 6-methyl-3-trimethylsilylcyclohexa-1,4-dienecarboxylate* (74) and *methyl 3-methyl-6-trimethylsilylcyclohexa-1,4-dienecarboxylate* (75) (Found: C, 64.3; H, 9.05. C₁₂H₂₀O₂Si requires C, 64.2; H, 9.0%), δ(CDCl₃) 6.95 (1 H, d, *J* 4 Hz, CH=CCO), 5.53 (2 H, m, other =CHs), 3.71 (3 H, s, OMe), 3.37—2.37 (2 H, m, =CHC*H*CH=), 1.10 (3 H, d, *J* 6 Hz, CHMe), and 0.07 (9 H, s, SiMe₃), $v_{max.}$ (film) 1 715 (CO), 1 665 and 1 624 (C=C), and 1 255 cm⁻¹ (SiMe₃), *m/z* 224 (5%, M^+), 222 (9, *M* − H₂), 209 (52, *M* − Me), 207 (49, *M* − H₂ − Me), 193 (11, *M* − MeO), and 73 (100, SiMe₃). This mixture (0.224 g) was refluxed in benzene (2 ml) containing toluene-*p*-sulphonic acid (0.172 g) for 1.5 h. The mixture was worked up, redissolved in benzene (3 ml) and refluxed with DDQ (0.227 g) for 2 h. Work-up and t.l.c., eluting with 20% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C) gave a mixture of methyl 2-methylbenzoate (77) and methyl 3-methylbenzoate (68) (0.141 g, 94%). The ¹H n.m.r. spectrum was identical to that of the authentic esters. Integration of the well-separated *O*-Me signals indicated that the two esters were present in the ratio 3 : 1.

Methyl 6-*Methylcyclohexa-1,3-dienecarboxylate* (76).—In one case, chromatography of the crude mixture of adducts (74) and (75) gave a fraction rich (9 : 1 by ¹H n.m.r.) in the isomer (74). This mixture (0.224 g) was refluxed in benzene (2 ml) with toluene-*p*-sulphonic acid for 1 h. Work-up and preparative t.l.c., eluting with 20% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C) gave the *ester* (76) 0.144 g, 95%), δ(CDCl₃) 6.99 (1 H, dd, *J* 4 and 2 Hz, CH=CCO), 6.06 (2 H, m, CH=CH), 5.80 (3 H, s, OMe), 2.86 (1 H, dq, *J* 8 and 7 Hz, C*H*Me), 2.58 (1 H, dd, *J* 18 and 8 Hz, C*H*_AH_B), 2.34—2.06 (1 H, m, CH_A*H*_B), and 1.04 (3 H, d, *J* 7 Hz, CHMe), $v_{max.}$ (film) 1 713 (CO), and 1 644 and 1 580 cm⁻¹ (C=C) (Found: M^+, 152.0838. C₉H₁₂O₂ requires *M*, 152.0836), *m/z* 152 (70%, M^+), 151 (13, *M* − H), 150 (30, *M* − H₂), 137 (27, *M* − Me), 121 (47, *M* − MeO), 119 (66, *M* − H₂ − MeO), 93, (100, *M* − CO₂Me), and 91 (100, *M* − H₂ − CO₂Me).

Reaction of 1-*Trimethylsilyl-3-trimethylsilyloxybutadiene* (20) *with Methyl Acrylate.*—The diene (20) (3.1 g), methyl acrylate (1.3 g), and a few crystals of hydroquinone were heated at 120 °C for 40 h, and the mixture was distilled to give a mixture of the *cis-* and *trans-*isomers of *methyl 2-trimethylsilyl-4-trimethylsilyloxycyclohex-3-enecarboxylate* (78) (2.72 g, 63%), b.p. 95—98 °C at 0.4 mmHg (Found: C, 56.2; H, 9.35. C₁₄H₂₈O₃Si₂ requires C, 56.0; H, 9.4%), δ(CCl₄) 4.68 (1 H, m, =CH), 3.56 (3 H, s, OMe), 2.7 and 2.3 (1 H, CHCO of each isomer), 2.1—1.7 (5 H, m, CHSi and 2 × CH₂), 0.09 (9 H, s, OSiMe₃), and −0.08 (9 H, s, CSiMe₃), $v_{max.}$ (film) 1 740 (CO), 1 663 (C=C), and 1 255 cm⁻¹ (SiMe₃), *m/z* 300 (54%, M^+), 285 (97, *M* − Me), 269 (72, *M* − MeO), 241 (23, *M* − CO₂Me), 226 (100, *M* − Me − CO₂Me), 168 (82, *M* − CO₂Me − SiMe₃), and 73 (70, SiMe₃). This

mixture (0.3 g) was kept in THF (2 ml) with hydrochloric acid (2 ml; 0.1M) for 10 min. Work-up and preparative t.l.c., eluting with 10% (v/v) ethyl acetate–light petroleum (b.p. 60—80 °C), gave a mixture of the *cis*- and *trans*-isomers of *methyl 4-oxo-2-trimethylsilylcyclohexanecarboxylate* (79) (0.206 g, 91%) (Found: C, 58.4; H, 8.95. $C_{11}H_{20}O_3Si$ requires C, 57.9; H, 8.85%), δ(CCl₄) 3.58 and 3.55 (3 H, 2 × s, OMe), 2.8—1.7 (7 H, m, CHCO and 3 × CH₂), 1.45 and 1.20 (1 H, ddd, *J* 11, 10, and 5 Hz, and dt, *J* 14 and 4 Hz, respectively, CHSi), and −0.11 and −0.12 (9 H, 2 × s, SiMe₃), ν_max. (film) 1 735 (ester), 1 715 (ketone), and 1 250 cm⁻¹ (SiMe₃), *m/z* 228 (35%, *M*⁺), 213 (59, *M* − Me) 169 (41, *M* − CO₂Me), and 73 (100, SiMe₃).

Methyl 4-Hydroxybenzoate (80).—The mixture of adducts (78) (0.3 g) and *N*-bromosuccinimide (NBS) (0.18 g, 1 mol equiv.) were stirred in dry THF (3 ml) initially at 0 °C and then allowed to come to room temperature over 15 min. Work-up gave the α-bromoketones which were immediately dissolved in DMSO (3 ml) and kept for 15 h with a few crystals of sodium iodide. Work-up gave the phenol (80) (0.132 g, 87%) as prisms, m.p. 127—128 °C (from CHCl₃–CCl₄) (lit.,[77] 127—129 °C), δ(CDCl₃) 7.94 (2 H, d, *J* 8 Hz, H-2 and H-6), 6.86 (2 H, d, *J* 8 Hz, H-3 and H-5), and 3.89 (3 H, s, OMe), ν_max. (Nujol mull) 3 300 (OH), 1 684 (CO), 1 612, 1 594, and 1 519 cm⁻¹ (Ar), *m/z* 152 (50%, *M*⁺), 121 (100, *M* − MeO), and 93 (20, *M* − CO₂Me).

Methyl 3-Bromo-4-hydroxybenzoate (81).—The mixture of adducts (78) (0.3 g) and NBS (0.36 g, 2 mol equiv.) were stirred in dry THF (4 ml) as described above and then DMSO (2 ml) was added, and the mixture was refluxed for 0.5 h. Work-up and preparative t.l.c. gave the bromophenol (81) (0.226 g, 98%) as prisms, m.p. 106—107 °C (from CCl₄) (lit.,[77] 107 °C), δ(CCl₄) 8.17 (1 H, d, *J* 2 Hz, H-2), 7.91 (1 H, dd, *J* 8 and 2 Hz, H-6), 7.03 (1 H, d, *J* 8 Hz, H-5), 6.0br (1 H, s, OH), and 3.89 (3 H, s, OMe), *m/z* 232/230 (50%, *M*⁺).

Methyl 4-Oxocyclohex-1- and 4-Oxocyclohex-2-enecarboxylate (82).—The mixture of adducts (78) (0.3 g) was treated with NBS (0.18 g, 1 mol equiv.) as before; caesium fluoride (0.152 g) and dry dimethylformamide (3 ml) were then added to the THF and the mixture was stirred at room temperature for 3 h. Work-up and preparative t.l.c. eluting with 40% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C) gave a mixture of the *esters* (82) (0.121 g, 78%) in the proportion of 5 parts of the 1-ene to 2 parts of the 2-ene. The 1-ene had δ(CDCl₃) 7.0 (1 H, m, =CH), 3.78 (3 H, s, OMe), 3.04 (2 H, m, COCH₂CH=), 2.9—2.4 (4 H, m, CH₂CH₂), ν_max. (film) 1 720 (ester and ketone), 1 660 cm⁻¹ (C=C); the 2-ene had δ(CDCl₃) 7.06 (1 H, dd, *J* 10 and 3 Hz, COCH=CH), 6.08 (1 H, dd, *J* 10 and 2 Hz, COCH=CH), 3.78 (3 H, s, OMe), 3.45 (1 H, m, CHCO₂Me), and 2.6—2.2 (4 H, m, CH₂CH₂), ν_max. (film) 1 742 (ester), 1 690 (ketone), and 1 615 cm⁻¹ (C=C); both isomers had *m/z* 154 (100%, *M*⁺), 126 (92, *M* − 28), 123 (49, *M* − OMe), and 95 (40, *M* − CO₂Me).

Reaction of 1-Trimethylsilyl-3-trimethylsilyloxybutadiene (20) with Methyl Methacrylate.—The diene (20) (5.0 g), methyl methacrylate (2.8 g), and a few crystals of hydroquinone were heated at 130 °C for 64 h in a sealed tube. Distillation gave a mixture of *cis*- and *trans*-isomers of *methyl 1-methyl-2-trimethylsilyl-4-trimethylsilyloxycyclohex-3-enecarboxylate* (83) (3.37 g, 46%), b.p. 107—110 °C at 0.5 mmHg (Found: C, 57.1; H, 9.8. $C_{15}H_{30}O_3Si_2$ requires C, 57.3; H, 9.6%), δ(CCl₄) 4.73 (1 H, m, =CH), 3.62 (3 H, s, OMe), 2.4—1.5 (5 H, m, CH and 2 × CH₂), 1.26 and 1.16

(3 H, 2 × s, CMe), 0.16 and 0.14 (9 H, 2 × s, OSiMe₃), and 0.01 and −0.02 (9 H, 2 × s, CSiMe₃), ν_max. (film) 1 730 (CO), 1 660 (C=C), and 1 253 cm⁻¹ (SiMe₃), *m/z* 314 (33% *M*⁺), 299 (73, *M* − Me), 283 (33, *M* − MeO), 241 (53, *M* − SiMe₃), 195 (35, *M* − Me − MeO − SiMe₃), 182 (100, *M* − SiMe₃ − CO₂Me), and 73 (SiMe₃). The mixture of adducts (0.5 g) was kept in THF (3 ml) with hydrochloric acid (2 ml, 0.1M) at room temperature for 0.5 h. Work-up and preparative t.l.c., eluting with 10% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C), gave the *cis*- and *trans*-isomers of *methyl 1-methyl-4-oxo-2-trimethylsilylcyclohexanecarboxylate* (84) (0.364 g, 95%) (Found: C, 59.5; H, 8.9. $C_{12}H_{22}O_3Si$ requires C, 59.5; H, 9.15%), δ(CCl₄) 3.68 and 3.62 (3 H, 2 × s, OMe), 2.5—1.6 (7 H, CH and 3 × CH₂), 1.35 and 1.27 (3 H, 2 × s, CMe), and 0.0 and −0.05 (9 H, 2 × s, SiMe₃), ν_max. (film) 1 720 (CO) and 1 255 cm⁻¹ (SiMe₃), *m/z* 242 (29%, *M*⁺), 227 (82, *M* − Me), 183 (63, *M* − CO₂Me), and 73 (100, SiMe₃).

Methyl 1-Methyl-4-oxocyclohex-2-enecarboxylate (85).—(a) The mixture of adducts (83) (0.314 g) was stirred in THF (2 ml) with NBS (0.178 g) at room temperature for 15 min. The solvent was evaporated off and the residue was kept in DMSO (1 ml) for 5 min. Work-up and preparative t.l.c., eluting with 40% (v/v) ethyl acetate–light petroleum (b.p. 60—80 °C) gave the ketoester [58] (85) (0.138 g, 82%), δ(CCl₄) 6.74 (1 H, d, *J* 10 Hz, CH=CHCO), 5.86 (1 H, d, *J* 10 Hz, CH=CHCO), 3.72 (3 H, s, OMe), 2.6—1.8 (4 H, m, 2 × CH₂), and 1.42 (3 H, s, CMe), ν_max. (film) 1 728 (ester), 1 680 (ketone), and 1 620 cm⁻¹ C=C), (Found: *M*⁺, 168.0780. $C_9H_{12}O_3$ requires *M*, 168.0786), *m/z* 168 (55%, *M*⁺), 140 (91, *M* − 28), and 109 (100, *M* − CO₂Me).

(b) The mixture of ketoesters (84) (0.35 g) was kept in carbon tetrachloride (3 ml) with bromine (77 µl) at 0 °C for 15 min. The solvent was removed and the residue was kept in DMSO (2 ml) for 20 min. Work-up and preparative t.l.c. as before gave the same ester (85) (0.178 g, 71%).

Reaction of 1-Trimethylsilyl-3-trimethylsilyloxybutadiene (20) with Methyl Propiolate.—The diene (20) (2.4 g), methyl propiolate (1.4 g), and a few crystals of hydroquinone were heated at 120 °C for 65 h in a sealed tube to give the crude adduct, methyl 6-trimethylsilyl-4-trimethylsilyloxycyclohexa-1,4-dienecarboxylate (86) (3.78 g), δ(CCl₄) 6.55 (1 H, m, CH=CCO), 4.75 (1 H, m, CH=COSi), 3.56 (3 H, s, OMe), 2.7 (3 H, m, CHSi and CH₂), 0.07 (9 H, s, OSiMe₃), and −0.13 (9 H, s, CSiMe₃), ν_max. (film) 1 720 (CO), 1 677 (C=C), and 1 255 cm⁻¹ (SiMe₃), *m/z* 298 (42%, *M*⁺), 297 (71, *M* − H), 283 (25, *M* − Me), 281 (64, *M* − H₂ − Me), 209 (73, *M* − OSiMe₃), 194 (68, *M* − Me − OSiMe₃), 193 (100, *M* − H − Me − OSiMe₃), and 73 (86, SiMe₃). The crude product (1.0 g) was stirred in THF (10 ml) with hydrochloric acid (3 ml, 0.1M) for 10 min at room temperature. Work-up and preparative t.l.c., eluting with 25% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C), gave *methyl 4-oxo-6-trimethylsilylcyclohex-1-enecarboxylate* (87) (0.44 g, 61% based on diene) (Found: C, 58.7; H, 8.0. $C_{11}H_{18}O_3Si$ requires C, 58.4; H, 8.0%), δ(CCl₄) 6.88 (1 H, dd, *J* 4 and 3 Hz, CH=CCO), 3.78 (3 H, s, OMe), 2.95 (2 H, m, =CHCH₂-CO), 2.76 (1 H, t, *J* 5 Hz, CHSi), 2.62 (2 H, d, *J* 5 Hz, CH₂CHSi), and 0.01 (9 H, s, SiMe₃), ν_max. (film) 1 720 (CO), 1 645 (C=C), and 1 255 cm⁻¹ (SiMe₃), *m/z* 226 (12%, *M*⁺), 225 (9, *M* − H), 211 (12, *M* − Me), 209 (30, *M* − H₂ − Me), 193 (47, *M* − H₂ − MeO), 152 (53, *M* − H − SiMe₃), 121 (100, M − H − MeO − SiMe₃), and 73 (100, SiMe₃).

1,3,3a,4,7,7a-*Hexahydro*-4,7-*bis*(*trimethylsilyl*)*isobenzo*-

furan (88).—3,6-Bistrimethylsilylcyclohex-4-ene-1,2-dicar-boxylic anhydride (23) (0.73 g) in ether (10 ml) was added dropwise with stirring to a suspension of lithium aluminium hydride (0.25 g) in ether (10 ml), and the mixture was refluxed for 10 h. Work-up gave 4,5-*bis(hydroxymethyl)*-3,6-*bis(trimethylsilyl)cyclohex-1-ene* (0.52 g, 74%) as needles, m.p. 134—135 °C (from CHCl$_3$) (Found: C, 58.5; H, 10.25. C$_{14}$H$_{30}$O$_2$Si$_2$ requires C, 58.7; H, 10.55%), δ(CDCl$_3$–CD$_3$OD) 5.44 (2 H, s, CH=CH), 3.77br (2 H, s, OH), 3.44 (4 H, m, CH$_2$O), 2.2 (2 H, m, CHCH$_2$), 1.65 (2 H, d, *J* 6 Hz, CHSi), and -0.06 (18 H, s, 2 × SiMe$_3$), $\nu_{max.}$ (Nujol mull) 3 300, 3 210 (OH), and 1 255 cm^{-1} (SiMe$_3$). The diol (1.0 g) was stirred in pyridine (15 ml) at 0 °C while methanesul-phonyl chloride (0.325 g) was added dropwise, and then at room temperature for 3 h. Work-up and column chromato-graphy on silica gel, eluting with 3% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C), gave the *ether* (88) (0.81 g, 87%) as plates, m.p. 85—86 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 62.6; H, 10.55. C$_{14}$H$_{28}$OSi$_2$ requires C, 62.6; H, 10.5%), δ(CCl$_4$) 5.91br (2 H, s, CH=CH), 3.80 (2 H, m, C*H*$_A$H$_B$O), 3.07 (2 H, m, CH$_A$*H*$_B$O), 2.74 (2 H, m, C*H*CH$_2$O), 1.46 (2 H, m, CHSi), and 0.04 (18 H, s, SiMe$_3$), $\nu_{max.}$ (Nujol mull) 1 260 cm^{-1} (SiMe$_3$). Re-crystallisation from light petroleum on one occasion gave instead 1,3,3a,6,7,7a-*hexahydro-6-hydroperoxy-4,7-bis*-*(trimethylsilyl)isobenzofuran* (89) as plates, m.p. 102—103 °C (Found: C, 55.4; H, 9.4. C$_{14}$H$_{28}$O$_3$Si$_2$ requires C, 55.9; H, 9.4%), δ(CDCl$_3$) 6.5 (1 H, m, =CH), 4.32 (1 H, dt, *J* 12 and 1 Hz, C*H*OOH), 3.96 (1 H, t, *J* 8 Hz, C*H*$_A$H$_B$O), 3.79 (1 H, t, *J* 8 Hz, CH$_A$'*H*$_B$'O), 3.30 (1 H, t, *J* 8 Hz, CH$_A$*H*$_B$O), 3.20 (1 H, dd, *J* 8 and 5 Hz, CH$_A$'*H*$_B$'O), 3.0—2.3 (2 H, m, 2 × C*H*CH$_2$), 1.10 (1 H, dd, *J* 12 and 4 Hz, CHSi), 0.08 (9 H, s, SiMe$_3$), and 0.06 (9 H, s, SiMe$_3$), $\nu_{max.}$ (Nujol mull) 3 280 (OH) and 1 250 cm^{-1} (SiMe$_3$), *m/z* 282 (13%, *M* − H$_2$O), 267 (26, *M* − OOH), 252 (73, *M* − OOH − Me), 179 (100, *M* − OOH − Me − SiMe$_3$), 164 (73, *M* − OOH − Me$_2$ − SiMe$_3$), and 73 (73, SiMe$_3$).

5,6-*Epoxy-4,7-bis(trimethylsilyl)perhydroisobenzofuran.*—*m*-Chloroperbenzoic acid (0.76 g), the allylsilane (88) (0.1 g), and sodium hydrogen carbonate (0.94 g) were stirred in dry carbon tetrachloride (1.5 ml) for 1 h at room temperature. Preparative t.l.c., eluting with benzene, gave the *epoxide* of (88) (0.84 g, 79%) as prisms, m.p. 122—124 °C (Found: C, 59.35; H, 10.05. C$_{14}$H$_{28}$O$_2$Si$_2$ requires C, 59.1; H, 9.9%), δ(CCl$_4$) 3.92 (2 H, m, C*H*$_A$H$_B$O), 2.98 (2 H, m, CH$_A$*H*$_B$O), 2.81 (2 H, m, CHOCH), 2.4 (2 H, m, 2 × C*H*CH$_2$), 0.6 (2 H, m, CHSi), and 0.04 (18 H, s, 2 × SiMe$_3$), $\nu_{max.}$ (Nujol mull) 1 255 cm^{-1} (SiMe$_3$), *m/z* 284 (7%, *M*$^+$), 269 (6, *M* − Me), 254 (9, *M* − Me$_2$), 237 (50, *M* − Me$_2$ − OH), 211 (12, *M* − SiMe$_3$), 181 (79, *M* − Me$_2$ − SiMe$_3$), and 73 (100, SiMe$_3$). This is only the second well-characterised allylsilane epoxide which does not have the silicon part of a ring.[4]

Reaction of 5,6-Epoxy-4,7-bis(trimethylsilyl)octahydro-isobenzofuran with Acid.—The epoxide (0.041 g) in deu-teriobenzene (1 ml) was kept at room temperature with toluene-*p*-sulphonic acid (0.05 g) for 5 h. Work-up and preparative t.l.c., eluting with benzene, gave two products: 1,3,3a,7a-*tetrahydro-4-trimethylsilylisobenzofuran* (91) (0.007 g, 25%) δ(CCl$_4$) 5.94 (2 H, m, 2 × =CH), 5.76 (1 H, m, =CH), 4.09 (2 H, m, C*H*$_A$H$_B$O), 3.51 (2 H, m, CH$_A$*H*$_B$O), 2.9 (2 H, m, 2 × CHCH$_2$), and 0.08 (9 H, s, SiMe$_3$), $\nu_{max.}$ (film) 1 255 cm^{-1} (Found: *M*$^+$, 194.1135. C$_{11}$H$_{18}$OSi requires *M*, 194.1126), *m/z* 194 (26%, *M*$^+$), 179 (32, *M* − Me), 149 (37, *M* − Me − CH$_2$O), 121 (16, *M* − SiMe$_3$),

and 73 (100, SiMe$_3$), and 1,3,3a,7a-*tetrahydro-4,7-bistri-methylsilylisobenzofuran* (92) (0.004 g, 11%), $\nu_{max.}$ (film) 1 255 cm^{-1} with no OH absorption (Found: *M*$^+$, 266.1526. C$_{14}$H$_{26}$OSi$_2$ requires *M*, 266.1521), *m/z* 266 (59%, *M*$^+$), 251 (54, *M* − Me), 221 (41, *M* − Me − CH$_2$O), 193 (14, *M* − SiMe$_3$), 163 (50, *M* − CH$_2$O − SiMe$_3$), 148 (100, *M* − Me − CH$_2$O − SiMe$_3$), and 73 (95, SiMe$_3$).

Reaction of 1,3,3a,4,7,7a-Hexahydro-4,7-bis(trimethyl-silyl)isobenzofuran (88) *with Bromine.*—Bromine (52 μl) was added to the allylsilane (88) (0.268 g) in carbon tetrachloride (10 ml) under nitrogen at 0 °C. T.l.c. showed that starting material was still present even though the bromine had been consumed instantly. A second mol equiv. of bromine was therefore added, and the mixture was worked up. Pre-parative t.l.c., eluting with 10% (v/v) ethyl acetate–light petroleum (b.p. 40—60 °C), gave two products: 4,5-*di-bromo-1,3,3a,4,5,7a-hexahydroisobenzofuran* (93) (0.08 g, 29%) (Found: C, 34.25; H, 3.65; Br, 56.55. C$_8$H$_{10}$-Br$_2$O requires C, 34.1; H, 3.55; Br, 56.7%), δ(CDCl$_3$) 6.2—5.7 (2 H, m, 2 × =CH), 5.0—3.4 (6 H, m, 2 × CH$_2$O and CHBr), and 3.25—2.25 (2 H, m, 2 × C*H*CH$_2$O), $\nu_{max.}$ (film) 1 650 cm^{-1} (C=C) (Found: *M*$^+$, 283.9059. C$_8$H$_{10}$-Br$_2$^{81}O requires *M*, 283.9059), *m/z* 284, 282, and 280 (3%, *M*$^+$), 283, 281, and 279 (5, *M* − H), 203 and 201 (73, *M* − Br), 122 (18, *M* − Br$_2$), 121 (17, *M* − H − Br$_2$), and 92 (100, *M* − Br$_2$ − CH$_2$O), and 4,5-*dibromo-1,3,3a,4,7,7a-hexahydro-4-trimethylsilylisobenzofuran* (94) (0.122 g, 35%) (Found: C, 37.2; H, 5.0; Br, 45.05. C$_{11}$H$_{18}$Br$_2$OSi requires C, 37.3; H, 5.1; Br, 45.1%), $\nu_{max.}$ (film) 1 645 and 1 608 (C=C), and 1 255 cm^{-1} (SiMe$_3$) (Found: *M*$^+$ − Br, 275.0285. C$_{11}$H$_{18}$BrOSi requires 275.0290), *m/z* 356, 354, 352 (*M*$^+$), 283, 281, 279 (*M* − SiMe$_3$), 275, 273 (*M* − Br), 194 (*M* − Br$_2$), 121 (*M* − SiMe$_3$ − Br$_2$), and 73 (SiMe$_3$).

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