Homolytic Reactions of Ligated Boranes. Part 17.[1] Amine–Boranes as Polarity Reversal Catalysts for Radical Chain Reactions of Esters with Vinylic Epoxides and with Allylic *tert*-Butyl Peroxides

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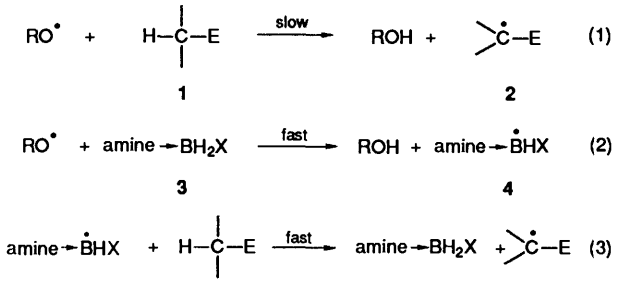
In the presence of an amine–borane catalyst, methyl acetate, dimethyl malonate and dimethyl methylmalonate (HZ) each react with 1-methylene-2,3-epoxycyclohexanes or -pentanes at a C–H group α to the ester function to give allylic alcohols. The reaction proceeds by a radical chain mechanism and is initiated by UV photolysis of added di-*tert*-butyl peroxide at 30 °C; isolated yields are generally 50–70%. The amine–borane, usually quinuclidine–borane (QNB), acts as a polarity reversal catalyst to facilitate regioselective overall transfer of hydrogen from an α-C–H group of the ester to an allyloxyl radical to give the allylic alcohol. The α-alkoxycarbonylalkyl radical (Z•) also formed in this reaction adds to the vinyl epoxide to give an oxiranylcarbinyl radical, subsequent ring opening of which regenerates the allyloxyl radical. In the presence of QNB, methyl acetate, dimethyl malonate, triethyl methanetricarboxylate and ethyl cyanoacetate each react at an α-C–H group with an allylic *tert*-butyl peroxide $H_2C{=}C(R)CMe_2OOBu^t$ (R = H or Me) to give the 2,3-epoxypropanation products $ZCH_2\overset{\frown}{C(R)CMe_2O}$ in 50–80% yield. Again, a radical chain mechanism is followed and the amine–borane catalyses α-hydrogen-atom transfer from the ester to $Bu^tO^•$, which is generated by an S_Hi reaction of the β-*tert*-butylperoxyalkyl radical formed by addition of Z• to the allylic peroxide.

Alkoxyl radicals, being electrophilic,[2] abstract hydrogen relatively slowly from an electron-deficient α-C–H group in an ester, ketone or nitrile **1** [E = CO_2R, C(O)R, CN], because of adverse polar effects which operate in the transition state. We have shown previously that these sluggish abstractions can be promoted by amine–borane complexes **3** (X = H or alkyl), which act as donor polarity reversal catalysts.[3–5] The single-step reaction (1) is then replaced by the catalytic cycle of reactions (2) and (3), both of which benefit from favourable

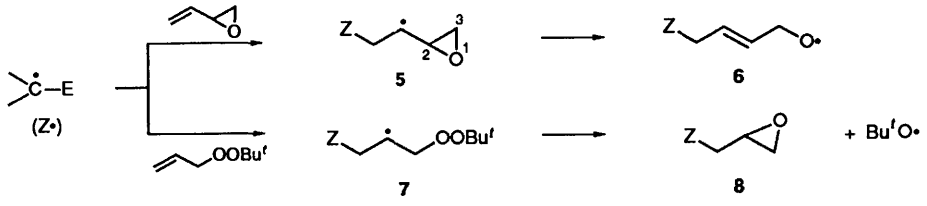


charge-transfer interactions in the transition state, because the amine-boryl radical **4** is highly nucleophilic.[3c] Amine–boryl radicals react with very high regioselectivity at such electron-deficient α-C–H groups, while alkoxyl radicals are much less discriminating abstractors of hydrogen.

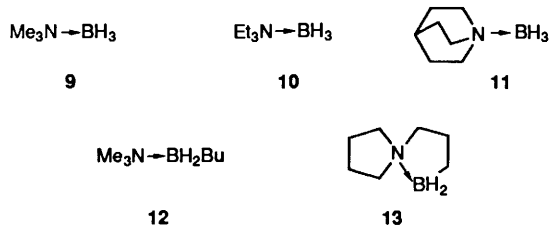
Most of our previous work on polarity reversal catalysis (PRC) by amine–boranes has been concerned with non-chain processes in which the radical **2** goes on to dimerise and/or disproportionate. The aim of the present research was to devise radical chain processes which incorporate PRC of reaction (1) into the propagation stage, such that the overall chain reaction is catalysed and its regiochemistry is controlled by the amine–borane. In order to establish a viable chain process, the radical **2** must be efficiently scavenged in a reaction which generates an alkoxyl radical as one of the products. We considered that vinyl epoxides and allylic *tert*-butyl peroxides might accomplish this transformation, while not reacting rapidly with either the amine-boryl radical **4** or with its parent **3**. For both types of reagent, addition of **2** (Z•) to the C=C group would be followed by rapid bond cleavage to form an alkoxyl radical, as shown in Scheme 1 for the unsubstituted acceptors. Addition to the vinyl epoxide gives an oxiranylcarbinyl radical **5** which undergoes ring opening with C–O bond fission to form an allyloxyl radical **6**.[6,†] The β-peroxyalkyl radical adduct **7**, formed by addition to the allylic peroxide, undergoes O–O bond cleavage in an intramolecular homolytic substitution (S_Hi) process to produce the epoxide **8** and the *tert*-butoxyl radical.[8,9]

Here we describe the radical chain reactions of esters which possess α-C–H groups with vinyl epoxides and with allylic *tert*-butyl peroxides, under the influence of catalysis by one of the amine–boranes **9–13**. Part of this work has been published in preliminary form.[10,11]

† This mode of cleavage occurs when hydrogen atoms or alkyl groups are attached to C-3 of the oxirane ring in **5**. However, when a vinyl, aryl or acyl group is attached to C-3, cleavage of the C(2)–C(3) bond competes or is seen exclusively.[7]



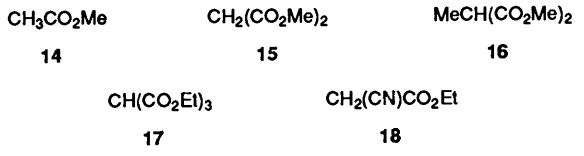
Scheme 1



9 10 11 12 13

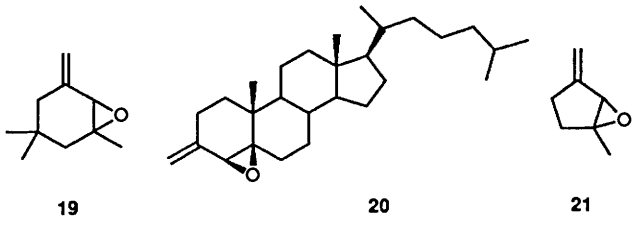
Results and Discussion

Preliminary work[10,11] showed that triethylamine–borane **10** was ineffective as a catalyst, probably on account of the low thermal stability and high heterolytic reactivity of this complex, which contains a relatively weak N→B bond. Of the remaining amine–boranes, quinuclidine–borane **11** (QNB) was generally the most effective and convenient catalyst, although **9**, **12** and **13** were also successful. However, it must be borne in mind that radicals of the type amine→$\dot{B}H_2$ have a greater tendency than amine→$\dot{B}HR$ to add to unsaturated functions (*e.g.* C≡N) in competition with hydrogen-atom abstraction from an α-C–H group.[3b] If this property were to be an important consideration, then **12** or **13** could become the catalyst of choice. Most of the work reported in this paper, which involved the esters **14**–**18**,* was carried out using QNB as polarity reversal catalyst.

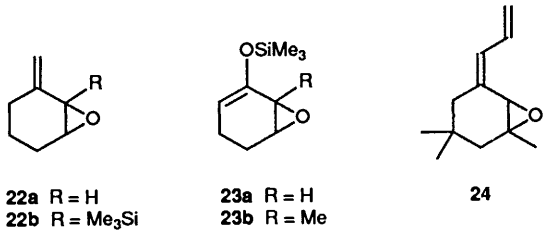


14 15 16 17 18

Reactions of Vinylic Epoxides.—The unsaturated epoxides **19**–**22** and **24** were synthesised by Wittig reactions of the corresponding α,β-epoxy ketones and compounds **23a** and **23b** were prepared by *O*-silylation of the enolates derived from the appropriate epoxy ketones.



19 20 21



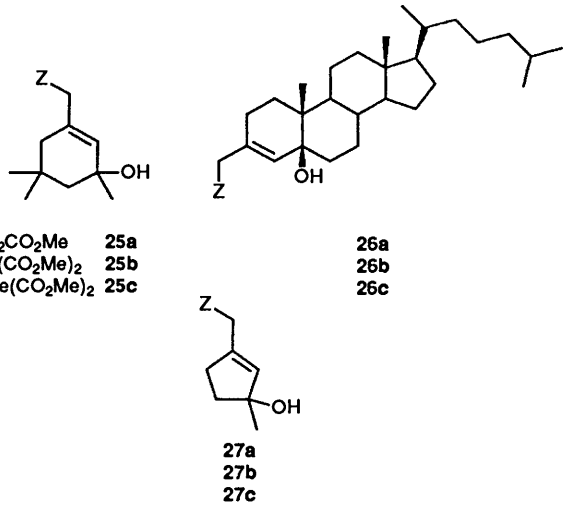
22a R = H
22b R = Me_3Si

23a R = H
23b R = Me

24

A solution of the vinylic epoxide **19** (1.5 mmol), QNB **11** (0.75 mmol), methyl acetate **14** (0.5 cm^3) and di-*tert*-butyl peroxide (DTBP) (1.5 mmol) in benzene (1.0 cm^3) was irradiated through quartz with light from a 125 W medium-pressure mercury discharge lamp for 3 h at 30 °C. The DTBP acts as an initiator

* Similar results were obtained with the diethyl ester analogues of **15** and **16**.

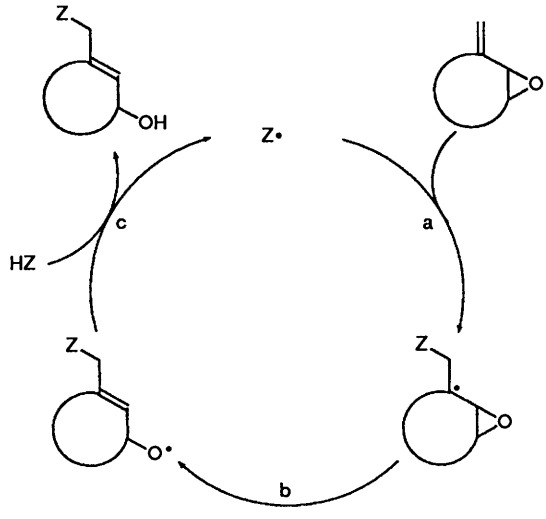


Z = CH_2CO_2Me **25a**
Z = $CH(CO_2Me)_2$ **25b**
Z = $CMe(CO_2Me)_2$ **25c**

26a
26b
26c

27a
27b
27c

and undergoes photolysis to form *tert*-butoxyl radicals. A smooth reaction took place to form the allylic alcohol **25a** in 65% yield, as judged by ^1H NMR spectroscopy in the presence of 1,3,5-tri-*tert*-butylbenzene as internal standard. The alcohol **25a** was isolated in 61% yield by column chromatography. No significant reaction took place in the absence of the amine–borane, or without UV irradiation, or in the presence of the radical scavenger 3,5-di-*tert*-butyl-4-hydroxyanisole (5 mol% based on **19**).



Scheme 2

We conclude that the radical chain mechanism shown in Scheme 2 is followed and that hydrogen abstraction from the α-C–H group of the ester (HZ) (step c) is catalysed by the QNB. The optimum amount of catalyst was found to be 50 mol% based on the vinyl epoxide; this gave the best compromise between yield of product and ease of its isolation by column chromatography.

Corresponding reactions of methyl acetate with the vinyl epoxides **20** and **21** gave the allylic alcohols **26a** (62%) and **27a** (45%), respectively; the isolated yields are given in Table 1. Dimethyl malonate **15** (1.5 mmol) or dimethyl methylmalonate **16** (1.5 mmol) reacted in a similar way with each of the vinylic epoxides **19**–**21** (1.3 mmol), together with QNB (0.65 mmol) and DTBP (1.5 mmol) in benzene (1.5 cm^3), to give the appropriate allylic alcohol **25**–**27** in the yields shown in Table 1. The orientation of the oxirane ring relative to the radical centre in the intermediate oxiranylcarbinyl radicals derived from the

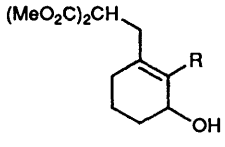
Table 1 Allylic alcohols from reactions of esters with vinylic epoxides catalysed by quinuclidine–borane[a]

Vinyl epoxide[b] (mmol)	Ester[c]	Reaction time[d] (h)	Allylic alcohol product	Isolated yield[e] (%)
19 (1.5)	$MeCO_2Me$[f]	3	**25a**	61
19 (1.5)	$H_2C(CO_2Me)_2$	3	**25b**	75
19 (1.5)	$H(Me)C(CO_2Me)_2$	3	**25c**	65
20 (1.3)	$MeCO_2Me$[f]	2.5	**26a**	56
20 (1.3)	$H_2C(CO_2Me)_2$	2.5	**26b**	76
20 (1.3)	$H(Me)C(CO_2Me)_2$	2.5	**26c**	64
21 (1.3)	$MeCO_2Me$[f]	3.5	**27a**	36
21 (1.3)	$H_2C(CO_2Me)_2$	3.5	**27b**	54
21 (1.3)	$H(Me)C(CO_2Me)_2$	3.5	**27c**	66
22a (2.0)	$H_2C(CO_2Me)_2$	4	**28a**	55
22b (2.0)	$H_2C(CO_2Me)_2$	3	**28b**	62
23b (1.5)	$H_2C(CO_2Me)_2$	3	**29b**	15

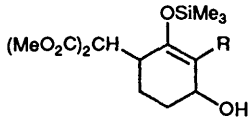
[a] 0.50 Molar equiv. based on vinyl epoxide. [b] The solvent was benzene (1.5 cm^3). [c] 1.15 Molar equiv. based on vinyl epoxide, unless stated otherwise. [d] The reaction mixture was irradiated at 30 °C with light from a 125 W medium-pressure mercury lamp *ca.* 7 cm away from the sample. [e] Based on vinyl epoxide. [f] Methyl acetate (0.5 cm^3) was present along with benzene (1.0 cm^3) co-solvent.

cyclic vinyl epoxides **19**–**24** is such that ring opening with C–O cleavage will be strongly favoured for stereoelectronic reasons. Ring-opening of the oxiranylcarbinyl radical derived from the steroidal β-epoxide **20** must lead stereospecifically to the β-alcohols **26a–c**.

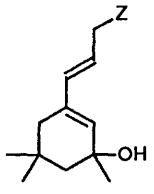
We have shown previously[4] that electrophilic 1,1-bis(alkoxycarbonyl)methyl radicals $HC(CO_2R)_2$, formed by α-hydrogen abstraction from malonates, add much more rapidly to allyltrimethylsilane than to propene. This result was attributed to the predominance of polar effects in controlling the rate of addition, the silane having the more electron-rich double bond. The vinyl epoxide **22b** was synthesised in the hope that it would provide a much more effective trap for electrophilic α-carbonylalkyl radicals, in comparison with its protic parent **22a**. However, for reactions with dimethyl malonate under the same conditions, the yields (by NMR) of **28a** (65%) amd **28b** (70%) were very similar.*



28a R = H
28b R = Me_3Si



29a R = H
29b R = Me



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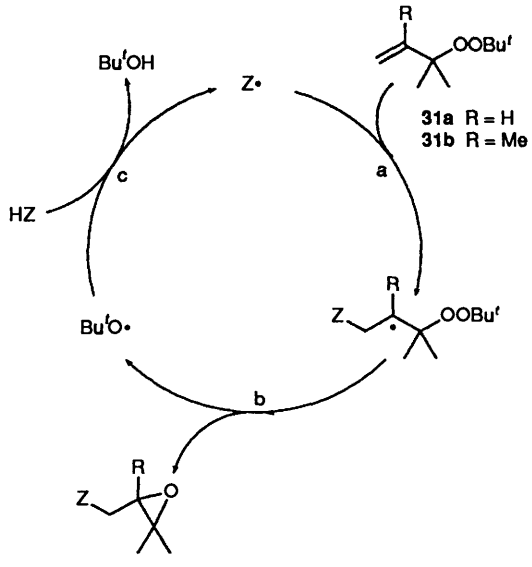
Electrophilic α-carbonylalkyl radicals also add relatively rapidly to the electron-rich double bond in a vinyl ether[4] and vinyl epoxides of the type **23** are readily available from α,β-epoxy ketones. However, none of the product **29a** was obtained from reactions of dimethyl malonate with **23a** in the presence of QNB, although all the vinyl epoxide was consumed. We considered that the problem could be that **29a** is also an enol ether in which the double bond is similarly substituted, and therefore similarly reactive, to that in the starting material. In support of this hypothesis, corresponding treatment of the methylated vinyl epoxide **23b** did give **29b**, but in only 20% yield.

We expected that the conjugated diene function in **24** would be more reactive towards radical addition than the alkene function in **19** and, hopefully, the allylic adduct radical derived from **24** would still undergo rapid opening of the oxirane ring. However, no unsaturated tertiary alcohols of the type **30** were obtained from amine–borane-catalysed reactions of **24** with the esters **14**–**16**, although 30–45% of the epoxide was consumed.

Reactions of Allylic tert-*Butyl Peroxides.*—Maillard, Montaudon and their co-workers have reported that 2,3-epoxypropanation of a hydrogen-atom donor HZ may be brought about by heating an allylic *tert*-butyl peroxide in the presence of HZ, usually as the solvent.[9] The reaction proceeds by a radical chain mechanism, the propagation steps of which are illustrated in Scheme 3, with initiation provided by thermal decomposition of the peroxide itself (at 110 °C) or of an added initiator (*e.g.*

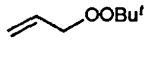


32 R = H
33 R = Me

a Z = CH_2CO_2Me
b Z = $CH(CO_2Me)_2$
c Z = $CMe(CO_2Me)_2$
d Z = $C(CO_2Et)_3$
e Z = $CH(CN)CO_2Et$

Scheme 3

tert-butyl peracetate at 110 °C). For example,[9a] when a dilute solution of allyl *tert*-butyl peroxide **34** in methyl acetate (50 molar equivalents) was heated in an autoclave at 140 °C for 10 h, the epoxypropanated product (31% total yield) consisted of **35** (70%) and **36** (30%), reflecting the low selectivity with which the *tert*-butoxyl radical abstracts hydrogen from the two types of the C–H group in the ester (Scheme 3, step c).



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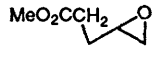

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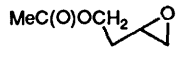

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* Of course, the overall yield from the chain reaction is dependent on factors other than the rate of radical addition to the vinylic epoxide.

Table 2 2,3-Epoxypropanation of esters with allylic *tert*-butyl peroxides catalysed by quinuclidine–borane[a]

Allylic peroxide[b]	Ester[c]	Reaction time[d] (h)	Epoxypropanated product	Isolated yield[e] (%)
31a	$MeCO_2Me$[f]	5	**32a**	54
	$H_2C(CO_2Me)_2$	4	**32b**	75
	$HC(CO_2Et)_3$	4	**32d**	50
	$H_2C(CN)CO_2Et$	4	**32e**	50
31b	$MeCO_2Me$[f]	5	**33a**	60
	$H_2C(CO_2Me)_2$	4	**33b**	80
	$HC(CO_2Et)_3$	4	**33d**	58
	$H_2C(CN)CO_2Et$	4	**33e**	56

[a] 0.20 Molar equiv. based on allylic peroxide. [b] Allylic peroxide (1.0 mmol) and DTBP (1.0 mmol) in benzene (1.0 cm^3). [c] 1.2 Molar equiv. based on allylic peroxide, unless stated otherwise. [d] The reaction mixture was irradiated at 30 °C with light from a 125 W medium-pressure mercury lamp *ca.* 7 cm away from the sample. [e] Based on allylic peroxide. [f] Methyl acetate (1.0 cm^3) was present along with benzene (1.0 cm^3) co-solvent.

In the presence of an amine–borane, abstraction from an electron-deficient α-C–H group in the ester should be selectively catalysed, so that the radical $MeO_2C\dot{C}H_2$ will now be the exclusive product of step c, and 2,3-epoxypropanation at the α-carbon atom should also proceed at lower temperatures than without polarity reversal catalysis.

The tertiary allylic peroxides **31a** and **31b**, both of which are readily prepared from *tert*-butyl hydroperoxide and the appropriate allylic alcohol in the presence of concentrated sulfuric acid, were chosen for study. A solution of the allylic peroxide **31a** (1.0 mmol), DTBP (1.0 mmol), methyl acetate (1 cm^3) and QNB (0.2 mmol) in benzene (1 cm^3) was irradiated at 30 °C through quartz with light from a medium-pressure mercury lamp for 5 h, as before. After removal of the solvents, the residue was examined by ^1H NMR spectroscopy (3,5-di-*tert*-butylbenzene standard) and found to contain the epoxide **32a** in 60% yield; this was isolated by column chromatography in 54% yield. The DTBP functions as a photochemical source of initiating alkoxyl radicals and serves to reduce corresponding unwanted photolysis of the allylic peroxide. No epoxypropanation at the methoxy–carbon atom, to give a product analogous to **36**, was detected, confirming that the regiochemistry is controlled by the selectivity of amine–boryl radical attack on the ester. No epoxide was formed in the absence of amine–borane or without photolysis. Relatively electrophilic radicals, such as $MeO_2C\dot{C}H_2$, would be expected to add more rapidly to the allylic peroxide **31b** than to **31a**, and the yield of **33a** was 70% (NMR) under the same conditions.

High yields of the epoxides **32b** or **33b** were obtained from similar reactions (4 h irradiation at 30 °C) of **31a** or **31b** (1.0 mmol) with dimethyl malonate (1.2 mmol), in the presence of DTBP (1.0 mmol) and QNB catalyst (0.2 mmol), in benzene (1 cm^3). The yield of **32b** was 85–87% (NMR) using either QNB or $Me_3N{\rightarrow}BH_2Bu$ **12** as catalyst, but none was detected in the absence of amine–borane. With **31b** and QNB or **12** as catalyst, the yield of **33b** was 85–90% (NMR). Similar photochemically-induced reactions of **31a** or **31b** with triethyl methanetricarboxylate **17** or ethyl cyanoacetate **18** in benzene gave reasonable yields of **32d** or **e** and **33d** or **e**, respectively; the results are presented in Table 2. However, with dimethyl methylmalonate **16**, only very low yields (*ca.* 10%) of **32c** or **33c** were obtained. Yields were not improved significantly at higher temperature (40–50 °C), or when the concentration of the allylic peroxide was increased, or when the amount of QNB was increased from 20 to 50 mol% based on the peroxide. These low yields can probably be ascribed to the relatively slow addition of $MeC(CO_2Me)_2$ to the allylic peroxides, since this radical is more sterically demanding and less electrophilic than $HC(CO_2Me)_2$;[4] the large bulk of $(EtO_2C)_3C^{\cdot}$ is offset by its high electrophilicity.

Thermal Initiation.—Attempted thermal initiation of these amine–borane catalysed reactions of vinylic epoxides and allylic peroxides was unsuccessful. Reactions of the vinyl epoxide **19** and the peroxide **31a** with dimethyl malonate and QNB catalyst were carried out in the presence of 5–20 mol% of azo(isobutyronitrile), dibenzoyl peroxide, or di-*tert*-butyl peroxyoxalate[12,*] by heating for 1–2 h at 80, 90 and 45 °C, respectively. Extremely poor yields, typically < 10%, of the expected products were observed in all cases. It is possible that amine–boryl radicals react preferentially at the azo or peroxide functions of the initiators rather than by abstracting hydrogen from the α-carbon atom of the malonate. Certainly QNB reacted vigorously with di-*tert*-butyl peroxyoxalate on mixing in benzene at room temperature in the absence of other reagents.

Experimental

NMR spectra were recorded using a Varian VXR-400 instrument (400 MHz for ^1H). The solvent was $CDCl_3$ and chemical shifts are reported relative to Me_4Si present as internal standard; *J* values are quoted in Hz. Electron impact mass spectra (70 eV) were obtained using a VG 7070H instrument. IR spectra (of liquid films, unless stated otherwise) were taken on a Perkin-Elmer PE 983 instrument; the units of $\tilde{\nu}$ are cm^{-1}.

Column chromatography and TLC were carried out using Merck Kieselgel 60 (230–400 mesh) and Kieselgel 60 F_{254} coated aluminium plates, respectively. Benzene was dried over calcium hydride and methyl acetate was dried over magnesium sulfate; both were distilled before use and stored under argon. The other esters were obtained commercially and used without purification, after being purged with argon. DTBP (Aldrich, 98%) was purified as described previously[4] and stored under argon. All reactions were carried out under an atmosphere of dry argon.

Trimethylamine–borane **9** (Aldrich) was purified by sublimation under reduced pressure and triethylamine–borane **10** (Aldrich) was distilled before use. Quinuclidine–borane[13] **11** was prepared from the amine (Fluka) and dimethyl sulfide–borane (BMS; Aldrich) and was purified by sublimation under reduced pressure. Trimethylamine–butylborane **12** was prepared by the method of Hawthorne.[14]

5-Azonia-1-borataspiro[4.4]*nonane* **13**.—This compound was prepared by a modification of the literature procedure.[15] BMS (10.0 mol dm^{-3} solution in an excess of dimethyl sulfide; 11.0 cm^3, 0.11 mol) was added dropwise with vigorous stirring to *N*-allylpyrrolidine[16] (11.75 g, 0.10 mol) in hexane (40 cm^3) cooled in an ice–water bath. The mixture was warmed to room temperature, stirred for 30 min and then heated under reflux for 30 min. The solvent was removed by evaporation under reduced pressure and triethylamine (0.3 cm^3) was added to the mixture which was then stirred and heated in an oil-bath at 90 °C for 2 h. Distillation of the mixture gave **13** (5.5 g, 44%), b.p. 68 °C at 1 Torr (lit.,[15] b.p. 106–110 °C at 12 Torr); δ_H 0.81 (2 H, m), 1.80 (2 H, m), 1.92 (2 H, m), 1.95 (2 H, br q, J_{BH} 92, BH_2), 2.11 (2 H, m), 2.70 (2 H, m), 2.82 (2 H, t, *J* 7.20) and 3.20 (2 H, m).

3,5,5-Trimethyl-1-methylene-2,3-epoxycyclohexane **19**.—This compound was prepared by a Wittig reaction of the corre-

* For reasons of safety, this compound was handled as a 1.2 mol dm^{-3} solution in benzene.

sponding 2,3-epoxy ketone with methylenetriphenylphosphorane according to a literature procedure.[17] Final purification was carried out by trap (25 °C)-to-trap (liq. N_2) distillation at 0.3–0.5 Torr; δ_H 0.78 (3 H, s, Me), 0.91 (3 H, s, Me), 1.34 (3 H, s, Me), 1.51 (1 H, dd, *J* 14.76 and 2.31), 1.67 (1 H, dd, *J* 13.54 and 2.24), 1.78 (1 H, br d, *J* 14.76), 2.10 (1 H, br d, *J* 13.54), 3.25 (1 H, s), 5.02 (1 H, t, *J* 1.84) and 5.21 (1 H, t, *J* 1.84); δ_C 24.82, 26.92, 30.72, 31.45, 41.23, 43.41, 62.84, 67.89, 115.06 and 143.13.

3-*Methylene*-4β,5β-*epoxycholestane* **20**.—This compound was prepared as a viscous oil in 65% yield following the literature procedure,[17] from 4β,5β-epoxycholestan-3-one[18] and $Ph_3P{=}CH_2$; δ_H 0.63 (3 H, s, 18-Me), 0.859 (3 H, d, *J* 6.55, 26- or 27-Me), 0.864 (3 H, d, *J* 6.68, 27- or 26-Me), 0.90 (3 H, d, *J* 6.61, 21-Me), 1.04 (3 H, s, 19-Me), 3.12 (1 H, s, 4α-H), 5.10 (1 H, d, *J* 1.76, CH=) and 5.24 (1 H, d, *J* 1.76, CH=); δ_C 11.96, 18.63, 18.86, 21.38, 22.55, 22.80, 23.84, 24.26, 28.00, 28.17 (2C), 30.51, 30.81, 35.04, 35.75, 36.14, 36.66, 39.49, 39.71, 42.59, 45.87, 56.08, 56.21, 63.52 (C-4), 66.94 (C-5), 117.49 and 141.83 (C-3); $\tilde{\nu}_{max}$ 2932, 2858, 1461, 1445, 1378, 894 and 677; *m*/*z* (%) 398 (M^+, 30), 383 (8), 369 (10), 328 (11) and 43 (100) (Found: M^+, 398. 3532. $C_{28}H_{46}O$ requires *M*, 398.3549).

3-*Methyl*-1-*methylene*-2,3-*epoxycyclopentane* **21**.—This compound was prepared by the reaction[17] of $Ph_3P{=}CH_2$ with 3-methyl-2,3-epoxycyclopentanone[19] at 0 °C for 1 h. After work-up, the product was separated from $Ph_3P{=}O$ by the trap (25 °C)-to-trap (liq. N_2) distillation at 0.3 Torr. Normal distillation then gave pure **21** (62%), b.p. 82 °C at 260 Torr; δ_H 1.50 (3 H, s, Me), 1.70 (1 H, dt, *J* 13.47 and 9.24), 1.98 (1 H, ddd, *J* 13.47, 6.68 and 3.34), 2.17 (2 H, m), 3.40 (1 H, s), 4.99 (1 H, s) and 5.21 (1 H, s); δ_C 18.03, 27.61, 31.14, 65.45, 67.12, 109.96 and 149.33; $\tilde{\nu}_{max}$ 2952, 2924, 1662, 1445, 1404, 1214, 1071, 897 and 827; *m*/*z* (%) 110 (M^+, 50), 95 (50), 79 (27), 67 (57) and 43 (100) (Found: M^+, 110.0730. $C_7H_{10}O$ requires *M*, 110.0732).

1-*Methylene*-2,3-*epoxycyclohexane* **22a**.—2,3-Epoxycyclohexanone[20] was obtained by epoxidation of cyclohex-2-enone at 5–10 °C for 3 h, according to the literature method.[21] The epoxy ketone (1.9 g, 17 mmol) in dry diethyl ether was added dropwise to a solution of $Ph_3P{=}CH_2$, which had been prepared from Ph_3PCH_3Br (7.14 g, 20 mmol) and lithium diisopropylamide (LDA) (itself prepared from 20 mmol of isopropylamine and 20 mmol of 2.5 mol dm^{-3} BuLi solution in hexanes) at 0 °C. The mixture was stirred at 0 °C for 2 h and then hydrolysed with aqueous NH_4Cl (10% w/v, 50 cm^3). The organic layer was separated and the aqueous layer was extracted with ether (3 × 20 cm^3). The combined ethereal extracts were dried ($MgSO_4$) and the solvent was removed by distillation at atmospheric pressure. The crude product was separated from $Ph_3P{=}O$ by trap-to-trap distillation and redistillation at atmospheric pressure gave **22a** (1.5 g, 80%), b.p. 92–94 °C; δ_H 1.39 (1 H, m), 1.57 (1 H, m), 1.82 (1 H, m), 2.02 (2 H, m), 2.24 (1 H, m), 3.36 (1 H, dt, *J* 3.93 and 1.53), 3.40 (1 H, d, *J* 3.93), 5.09 (1 H, q, *J* 1.56) and 5.21 (1 H, d, *J* 1.56); δ_C 19.74, 24.03, 28.60, 54.20, 55.10, 116.12 and 142.61; $\tilde{\nu}_{max}$ 2932, 1638, 1435, 1241, 897 and 750; *m*/*z* (%) 110 (M^+, 42), 95 (43) 81 (65) and 39 (100) (Found: M^+, 110.0736. $C_7H_{10}O$ requires *M*, 110.0732).

1-*Methylene*-2-*trimethylsilyl*-2,3-*epoxycyclohexane* **22b**.—2-Trimethylsilylcyclohex-2-enone (b.p. 105–108 °C at 20 Torr) was prepared according to the literature method;[22] δ_H 0.08 (9 H, s, $SiMe_3$), 1.94 (2 H, m), 2.34 (4 H, m) and 7.14 (1 H, t, *J* 3.90, 3-H); δ_C −1.48, 22.77, 27.20, 38.61, 141.80, 158.16 and 202.47.

Hydrogen peroxide (30% w/v aqueous solution, 20 cm^3, 0.18 mol) was added to 2-trimethylsilylcyclohex-2-enone (10.0 g, 0.06 mol) in methanol (100 cm^3) cooled in an ice–water bath. A solution of sodium hydroxide (1.0 g) in water (10 cm^3) was added dropwise with stirring so as to maintain the temperature of the reaction mixture < 10 °C. After the addition was complete, the mixture was stirred at 5–10 °C for 3 h and then poured into water (100 cm^3) and extracted with diethyl ether (3 × 30 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure and the residual oil was distilled to give 2-trimethylsilyl-2,3-epoxycyclohexanone (7.5 g, 68%), b.p. 54–56 °C at 0.5 Torr; δ_H 0.10 (9 H, s), 1.63 (1 H, m), 1.96 (3 H, m), 2.25 (1 H, m), 2.56 (1 H, m) and 3.42 (1 H, t, *J* 2.71); δ_C −3.36, 17.74, 23.32, 36.90, 56.99, 59.84 and 210.39; $\tilde{\nu}_{max}$ 2945, 1688, 1248, 840 and 747; *m*/*z* (%) 184 (M^+, 3), 169 (88), 153 (7) and 73 (100) (Found: M^+, 184.0912. $C_9H_{16}O_2Si$ requires *M*, 184.0920). The Wittig reaction of 2-trimethylsilyl-2,3-epoxycyclohexanone (15 mmol) with $Ph_3P{=}CH_2$ (prepared from 20 mmol of Ph_3PCH_3Br and LDA), as described for the preparation of **22a**, gave **22b** as a clear oil (1.6 g, 57%) after column chromatography (pentane eluent); δ_H 0.12 (9 H, s), 1.46 (2 H, m), 1.82 (2 H, m), 2.20 (2 H, m), 3.19 (1 H, t, *J* 2.21), 5.13 (1 H, m) and 5.23 (1 H, s); δ_C −2.35, 19.68, 24.96, 31.62, 54.71, 57.26, 117.21 and 145.28; $\tilde{\nu}_{max}$ 2939, 1631, 1434, 1248, 897 and 733; *m*/*z* (%) 182 (M^+, 8), 167 (27), 93 (14) and 73 (100) (Found: M^+, 182.1105. $C_{10}H_{18}OSi$ requires *M*, 182.1127).

2-*Trimethylsiloxy*-3,4-*epoxycyclohex*-1-*ene* **23a** *and* 2-*Trimethylsiloxy*-3-*methyl*-3,4-*epoxycyclohex*-1-*ene* **23b**.—These were prepared according to the literature procedures.[23] Compound **23a**: b.p. 58–60 °C at 1 Torr (lit.,[23] b.p. 50–60 °C at 0.6–1 Torr); compound **23b**: b.p. 61–63 °C at 1.5 Torr (lit.,[23] b.p. 51–59 °C at 0.5–1.2 Torr).

1-*Allylidene*-3,5,5-*trimethyl*-2,3-*epoxycyclohexane* **24**.—BuLi in hexanes (2.5 mol dm^{-3}; 10 cm^3, 25 mmol) was added to a stirred solution of diisopropylamine (2.5 g, 25 mmol) in dry tetrahydrofuran (THF) (30 cm^3) cooled in an ice–water bath. After the addition, stirring was continued for 20 min before the LDA solution was transferred *via* a cannula to a suspension of allyltriphenylphosphonium bromide (9.6 g, 25 mmol) in THF (50 cm^3). The orange–red mixture was then stirred at room temperature for 1 h before 3,5,5-trimethyl-2,3-epoxycyclohexanone (3.1 g, 20 mmol) in THF (5 cm^3) was added and stirring was continued at room temperature for 36 h. The mixture was hydrolysed with 10% aqueous NH_4Cl (50 cm^3) after which the organic layer was separated and the THF was removed by rotary evaporation. The residue was combined with the diethyl ether extracts (3 × 25 cm^3) of the aqueous layer, the solution was dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography (pentane–diethyl ether, 50:1 v/v, eluent) to give **24** as a viscous oil (2.2 g, 62%); δ_H 0.79 (3 H, s, Me), 0.91 (3 H, s, Me), 1.37 (3 H, s), 1.54 (1 H, dd, *J* 14.82 and 2.12), 1.61 (1 H, dd, *J* 14.82 and 2.18), 1.82 (1 H, d, *J* 14.80), 2.19 (1 H, d, *J* 14.80), 3.68 (1 H, s), 5.14 (1 H, dm, *J* 10.11), 5.23 (1 H, dm, *J* 16.92), 6.15 (1 H, dm, *J* 11.24) and 6.82 (1 H, ddd, *J* 16.90, 11.25 and 10.15); δ_C 25.05, 27.34, 30.50, 42.96, 43.59, 57.75, 60.17, 64.51, 117.71, 131.35, 131.72 and 135.68; $\tilde{\nu}_{max}$ 2945, 2912, 1638, 1461, 984 and 900; *m*/*z* (%) 178 (M^+, 17), 163 (3), 147 (4), 120 (25), 79 (40) and 43 (100) (Found: M^+, 178.1364. $C_{12}H_{18}O$ requires *M*, 178.1358).

tert-*Butyl* 1,1-*Dimethylallyl Peroxide* **31a**.—This compound was prepared by a modification of the method described by Ordway.[24] *tert*-Butyl hydroperoxide (70% in solution in water, Aldrich; 50 cm^3) was shaken with dichloromethane (50 cm^3) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 20 cm^3) and the combined extracts were dried ($MgSO_4$). The solvent was removed by rotary evaporation (bath 20 °C) to leave hydroperoxide of sufficient purity (≥95%) to be used for preparation of the allylic

peroxides. Concentrated sulfuric acid (5.0 cm^3) was added dropwise to a vigorously stirred mixture of 2-methylbut-3-en-2-ol (15.0 g, 0.17 mol) and *tert*-butyl hydroperoxide (16.5 g, 0.18 mol) cooled in an ice–water bath, at a rate such that the internal temperature did not exceed 20 °C. After the addition was complete, the mixture was stirred for a further 30 min at 0–10 °C; the upper layer was then separated and the lower layer was extracted with diethyl ether (3 × 30 cm^3). The combined upper layer and extracts were washed successively with water (30 cm^3), saturated aqueous $NaHCO_3$ (30 cm^3) and water (30 cm^3) and then dried ($MgSO_4$). The solvent was removed by rotary evaporation at 15 °C and the residue was distilled to give **31a** (10.3 g, 38%), b.p. 45–48 °C at 10 Torr; δ_H 1.22 (9 H, s, 3 Me), 1.30 (6 H, s, 2 Me), 5.06 (1 H, dd, *J* 10.90 and 1.20), 5.14 (1 H, dd, *J* 17.65 and 1.20) and 6.00 (1 H, dd, *J* 17.65 and 10.90); δ_C 24.56 (3-C), 26.63 (2-C), 78.66, 80.02, 113.00 and 143.40.

tert-*Butyl* 1,1,2-*Trimethylallyl Peroxide* **31b**.—A mixture of 2,3-dimethylbut-3-en-2-ol[25] (15.0 g, 0.15 mol) and *tert*-butyl hydroperoxide (14.0 g, 0.16 mol) was cooled to *ca.* −20 °C and vigorously stirred while concentrated sulfuric acid (3.0 cm^3) was added dropwise at a rate such that the temperature of the reaction mixture did not exceed −10 °C. After the addition was complete, the mixture was warmed to room temperature and stirred for 30 min. The upper layer was separated and the lower layer was extracted with ether (3 × 50 cm^3). The combined upper layer and extracts were washed successively with water, saturated aqueous $NaHCO_3$ and brine and then dried ($MgSO_4$). The solvent was removed by rotary evaporation at room temperature and the residue was distilled to give **31b** (11.5 g, 45%), b.p. 42–45 °C at 8 Torr; δ_H 1.22 (9 H, s, 3 Me), 1.32 (6 H, s, 2 Me), 1.80 (3 H, dd, *J* 1.47 and 0.78), 4.82 (1 H, dq, *J* 1.52 and 1.47) and 4.90 (1 H, dq, *J* 1.52 and 0.78); δ_C 24.58 (2C), 26.64 (4C), 78.37, 81.48, 110.25 and 149.85; $\tilde{\nu}_{max}$ 2970, 2945, 1449, 1359, 1193, 1151 and 895; *m/z* (%) 172 (M^+, 5), 99 (6), 83 (77) and 43 (100) (Found: M^+, 172.1449. $C_{10}H_{20}O_2$ requires *M*, 172.1463).

General Procedure for Reactions of Vinylic Epoxides with Esters.—A solution of the vinyl epoxide (1.3–2.0 mmol, see Table 1), the ester (1.15 mol equiv.), DTBP (1 mol equiv.) and the amine–borane (0.5 mol equiv.) in benzene (1.5 cm^3) was placed in a stoppered quartz tube (10 mm o.d., 1 mm wall) under argon. For reactions of methyl acetate, this ester (0.5 cm^3) was used as co-solvent with benzene (1.0 cm^3). The sample was positioned 7 cm away from the discharge tube and was irradiated for 3 h. 1,3,5-Tri-*tert*-butylbenzene was added as a concentration standard and, after removal of the solvent, the residue was examined by ^1H NMR spectroscopy to determine the yield. The products were isolated by column chromatography [pentane–diethyl ether, 3:2 (v/v) eluent] and the isolated yields are shown in Table 1. The characteristics of the products are given below; with the exception of **26c**, all were oils.

3-(2-*Methoxycarbonylethyl*)-1,5,5-*trimethylcyclohex*-2-*enol* **25a**. δ_H 0.93 (3 H, s, Me), 0.99 (3 H, s, Me), 1.21 (3 H, s, Me), 1.35 (1 H, br s, OH), 1.47 (1 H, d, *J* 13.60), 1.60 (1 H, d, *J* 13.60), 1.70 (2 H, m), 2.25 (2 H, m), 2.40 (2 H, m), 3.64 (3 H, s, OMe) and 5.33 (1 H, s); δ_C 27.68, 30.22, 30.82, 31.23, 32.28, 32.57, 42.44, 50.10, 51.69, 69.30, 127.20, 136.67 and 173.59; $\tilde{\nu}_{max}$ 3432, 2945, 2918, 1735, 1434, 1361, 1184, 1094 and 904 (Found: C, 68.7; H, 9.95. $C_{13}H_{22}O_3$ requires C, 68.98; H, 9.80%).

3-(2,2-*Dimethoxycarbonylethyl*)-1,5,5-*trimethylcyclohex*-2-*enol* **25b**. δ_H 0.95 (3 H, s, Me), 1.00 (3 H, s, Me), 1.22 (3 H, s, Me), 1.43 (1 H, br s, OH), 1.47 (1 H, d, *J* 14.15), 1.61 (1 H, d, *J* 14.15), 1.70 (1 H, d, *J* 16.90), 1.76 (1 H, d, *J* 16.90), 2.56 (2 H, d, *J* 7.87), 3.57 (1 H, t, *J* 7.87), 3.72 (6 H, s, 2-MeO) and 5.38 (1 H, br s); δ_C 27.59, 30.22, 30.80, 31.15, 36.49, 42.18, 49.91, 50.19, 52.47, 69.13, 129.41, 134.13 and 169.30; $\tilde{\nu}_{max}$ 3519, 3446, 2945, 1752, 1434, 1364, 1281, 1154, 1057 and 904 (Found: C, 63.5; H, 8.55. $C_{15}H_{24}O_5$ requires C, 63.34; H, 8.51%).

3-(2,2-*Dimethoxycarbonyl*-2-*methylethyl*)-1,5,5-*trimethylcyclohex*-2-*enol* **25c**. δ_H 0.92 (3 H, s, Me), 1.00 (3 H, s, Me), 1.23 (3 H, s, Me), 1.39 (3 H, s, Me), 1.48 (1 H, d, *J* 14.32), 1.53 (1 H, br s, OH), 1.63 (1 H, d, *J* 14.32), 1.68 (2 H, m), 3.71 (6 H, s, 2-MeO) and 5.43 (1 H, s); δ_C 20.17, 27.53, 30.41, 30.94, 31.26, 43.41, 43.59, 49.89, 52.48, 53.61, 69.25, 132.39, 133.31 and 172.55; $\tilde{\nu}_{max}$ 3456, 2951, 2922, 2870, 1730, 1452, 1433, 1244, 1109 and 908 (Found: C, 64.25; H, 8.9. $C_{16}H_{26}O_5$ requires C, 64.39; H, 8.79%).

3-(2-*Methoxycarbonylethyl*)*cholest*-3-*en*-5β-*ol* **26a**. δ_H 0.62 (3 H, s, 18-Me), 0.83 (3 H, d, *J* 6.55, 26- or 27-Me), 0.834 (3 H, d, *J* 6.59, 27- or 26-Me), 0.87 (3 H, d, *J* 6.49, 21-Me), 0.92 (3 H, s, 19-Me), 2.27 (2 H, m, $CH_2CH_2C{=}O$), 2.44 (2 H, m, CH_2CH_2-C=O), 3.65 (3 H, s, MeO) and 5.23 (1 H, s, 4-H); δ_C 11.92, 16.20, 18.30, 22.48, 22.54, 22.79, 23.75, 24.16, 25.45, 27.99 (2 C), 28.19, 28.96, 32.09, 32.42, 34.75, 35.40, 35.72, 36.12, 38.72, 39.47, 39.95, 42.45, 43.22, 51.77, 56.13, 56.29, 72.18 (C-5), 128.49 (C-4), 140.07 (C-3) and 173.56 (C=O); $\tilde{\nu}_{max}$ 3453, 2932, 2865, 1732, 1461, 1438, 1374 and 910 (Found: C, 78.95; H, 11.2. $C_{31}H_{52}O_3$ requires C, 78.75; H, 11.09%).

3-(2,2-*Dimethoxycarbonylethyl*)*cholest*-3-*en*-5β-*ol* **26b**. δ_H 0.62 (3 H, s, 18-Me), 0.830 (3 H, d, *J* 6.61, 26- or 27-Me), 0.835 (3 H, d, *J* 6.59, 27- or 26-Me), 0.87 (3 H, d, *J* 6.61, 21-Me), 0.92 (3 H, s, 19-Me), 2.56 [2 H, m, $CH_2CH(C{=}O)_2$], 3.58 [1 H, t, *J* 7.79, $CH_2CH(C{=}O)_2$], 3.71 (6 H, s, MeO) and 5.27 (1 H, s, 4-H); δ_C 11.90, 16.14, 18.62, 22.46, 22.54, 22.80, 23.84, 24.16, 25.24, 28.00, 28.21, 28.90, 34.73, 35.24, 35.76, 36.13, 38.62, 39.46, 39.92, 42.46, 43.10, 50.30, 52.61, 52.69 (MeO), 56.20, 56.24, 72.10 (C-5), 130.64 (C-4), 137.59 (C-3) and 169.33 (C=O); $\tilde{\nu}_{max}$ 3465, 2932, 2858, 1732, 1435, 1238, 1151 and 910 (Found: C, 74.9; H, 10.55. $C_{33}H_{54}O_5$ requires C, 74.66; H, 10.26%).

3-(2,2-*Dimethoxycarbonyl*-2-*methylethyl*)*cholest*-3-*en*-5β-*ol* **26c**. M.p. 110–112 °C (from pentane); δ_H 0.61 (3 H, s, 18-Me), 0.83 (3 H, d, *J* 6.64, 26- or 27-Me), 0.834 (3 H, d, *J* 6.64, 27- or 26-Me), 0.87 (3 H, d, *J* 6.52, 21-Me), 0.91 (3 H, s, 19-Me), 1.38 [3 H, s, $MeC(C{=}O)_2$], 2.63, 2.66 [2 H, AB quartet, *J* 14.04, $CH_2CMe(C{=}O)_2$], 3.70 (6 H, s, 2-MeO) and 5.25 (1 H, s, 4-H); δ_C 11.91, 16.10, 18.60, 20.25, 22.45, 22.53, 22.81, 23.80, 24.22, 26.48, 27.99, 28.20, 28.32, 28.96, 34.76, 35.21, 35.75, 36.11, 38.44, 39.48, 39.91, 42.44, 43.08, 43.17, 52.55, 53.38, 56.01, 56.26, 58.87, 72.33 (C-5), 133.57 (C-4), 136.77 (C-3) and 172.61 (C=O); $\tilde{\nu}_{max}$ 3546, 2939, 2852, 1735, 1456, 1374, 1284, 1097 and 977 (Found: C, 74.8; H, 10.5. $C_{34}H_{56}O_5$ requires C, 74.94; H, 10.37%).

3-(2-*Methoxycarbonylethyl*)-1-*methylcyclopent*-2-*enol* **27a**. δ_H 1.35 (3 H, s, Me), 1.54 (1 H, br s, OH), 1.97 (2 H, m), 2.40 (4 H, m), 2.48 (2 H, m), 3.67 (3 H, s, MeO) and 5.31 (1 H, t, *J* 1.68); δ_C 26.30, 27.64, 32.21, 33.65, 40.15, 51.62, 83.43, 131.44, 145.48 and 173.51; $\tilde{\nu}_{max}$ 3456, 2950, 1730, 1431, 1150 and 730; *m/z* (%) 184 (M^+, 7), 169 (10), 151 (9) and 92 (100) (Found: M^+, 184.1088. $C_{10}H_{16}O_3$ requires *M*, 184.1099).

3-(2,2-*Dimethoxycarbonylethyl*)-1-*methylcyclopent*-2-*enol* **27b**. δ_H 1.33 (3 H, s, Me), 1.52 (1 H, br s, OH), 1.96 (2 H, m), 2.25 (1 H, m), 2.42 (1 H, m), 2.68 (2 H, dd, *J* 7.24 and 5.96), 3.60 (1 H, t, *J* 7.74) and 5.39 (1 H, t, *J* 1.62); δ_C 27.49, 30.29, 33.52, 40.15, 50.34, 52.70, 83.36, 133.30, 142.90 and 169.35; $\tilde{\nu}_{max}$ 3466, 2952, 1732, 1435, 1154 and 733; *m/z* (%) 242 (M^+, 5), 227 (51), 164 (41), 132 (53) and 92 (100) (Found: M^+, 242.1149. $C_{12}H_{18}O_5$ requires *M*, 242.1154).

3-(2,2-*Dimethoxycarbonyl*-2-*methylethyl*)-1-*methylcyclopent*-2-*enol* **27c**. δ_H 1.32 (3 H, s, Me), 1.40 (3 H, s, Me), 1.60 (1 H, br s, OH), 1.93 (2 H, m), 2.15 (1 H, m), 2.32 (1 H, m), 2.72 (2 H, s), 3.72 (6 H, s, OMe) and 5.42 (1 H, br s); δ_C 20.23, 27.39, 34.22, 36.90, 40.40, 52.54, 53.18, 83.02, 136.45, 141.26 and 172.47; $\tilde{\nu}_{max}$ 3432, 2952, 1732, 1451, 1431, 1244, 1114 and 910; *m/z* (%) 256 (M^+, 8), 241 (100), 181 (96), 146 (71) and 93 (71) (Found: M^+, 256.1312. $C_{13}H_{20}O_5$ requires *M*, 256.1311).

3-(2,2-*Dimethoxycarbonylethyl*)*cyclohex*-2-*enol* **28a**. δ_H 1.55 (2 H, m), 1.67 (2 H, m), 1.94 (2 H, m), 2.58 (2 H, d, *J* 7.87), 3.59 (1 H, t, *J* 7.87), 3.73 (6 H, s, MeO), 4.17 (1 H, m) and 5.23 (1 H, m); δ_C 18.99, 28.19, 31.54, 36.28, 50.17, 52.55, 65.57, 126.42, 137.97 and 169.38; $\tilde{\nu}_{max}$ 3515, 3442, 2941, 1750, 1436, 1368, 1281 and 733; *m*/*z* (%) 242 (M^+, 9), 224 (8), 179 (10) and 110 (100) (Found: M^+, 242.1145. $C_{12}H_{18}O_5$ requires *M*, 242.1154).

3-(2,2-*Dimethoxycarbonylethyl*)-2-*trimethylsilylcyclohex*-2-*enol* **28b**. δ_H 0.22 (9 H, s, Me_3Si), 1.89 (1 H, m), 2.08 (1 H, m), 2.28 (4 H, m), 2.99 (2 H, d, *J* 8.00), 3.62 (1 H, t, *J* 8.00), 3.73 (6 H, s, MeO) and 4.20 (1 H, m); δ_C 0.76, 17.34, 30.06, 31.44, 36.66, 50.49, 52.52, 67.01, 136.38, 147.45 and 167.26; $\tilde{\nu}_{max}$ 3530, 3448, 2947, 1752, 1431, 1360 and 930; *m*/*z* (%) 314 (M^+, 5), 297 (20) and 124 (100) (Found: M^+, 314.1548. $C_{15}H_{26}O_5Si$ requires *M*, 314.1550).

4-(*Dimethoxycarbonylmethyl*)-2-*methyl*-3-*trimethylsiloxycyclohex*-2-*enol* **29b**. δ_H 0.18 (9 H, s, Me_3Si), 1.10–1.95 (5 H, m), 1.68 (3 H, s), 2.87 (1 H, br s, OH), 3.63 (1 H, d, *J* 7.64), 3.70 (6 H, s, OMe), and 4.12 (1 H, m); δ_C 0.52, 21.82, 28.82, 30.15, 39.68, 52.36, 52.62, 69.86, 117.55, 146.11 and 168.50; $\tilde{\nu}_{max}$ 3466, 2952, 1732, 1435, 1254, 910 and 733; *m*/*z* (%) 330 (M^+, 8), 313 (5), 253 (8) and 198 (100) (Found: M^+, 330.1492. $C_{15}H_{26}O_6Si$ requires *M*, 330.1499).

General Procedure for Reactions of Allylic Peroxides with Esters.—The method was similar to that described for the reactions of vinyl epoxides. Samples consisted of the allylic peroxide (1.0 mmol), the ester (1.0 mmol), DTBP (1.0 mmol), amine–borane (0.2 mmol) and benzene (1.0 cm^3). With methyl acetate, the ester (1.0 cm^3) was used as co-solvent with benzene (1.0 cm^3). The irradiation time was 3–5 h and the eluent for column chromatography was pentane–diethyl ether (5:1, v/v).

Methyl 5-*methyl*-4,5-*epoxyhexanoate* **32a**. δ_H 1.27 (3 H, s, Me), 1.31 (3 H, s, Me), 1.77 (1 H, ddt, *J* 14.15, 7.40 and 7.60), 1.92 (1 H, ddt, *J* 14.15, 5.27 and 7.33), 2.47 (2 H, q, *J* 7.33), 2.76 (1 H, dd, *J* 7.33 and 5.27), 2.76 (1 H, dd, *J* 7.41 and 5.27) and 3.69 (3 H, s, MeO); δ_C 18.65, 24.37, 24.74, 30.93, 51.65, 58.64, 63.13 and 173.32; $\tilde{\nu}_{max}$ 2951, 1736, 1436, 1375, 1250, 1170 and 873; *m*/*z* (%) 158 (M^+, 6), 115 (37), 101 (74) and 85 (100) (Found: M^+, 158.0932. $C_8H_{14}O_3$ requires *M*, 158.0943).

Methyl 4,5-*dimethyl*-4,5-*epoxyhexanoate* **33a**. δ_H 1.27 (3 H, s, Me), 1.28 (3 H, s, Me), 1.29 (3 H, s, Me), 1.81 (1 H, ddd, *J* 13.95, 9.65 and 7.05), 1.93 (1 H, m), 2.40 (1 H, ddd, *J* 9.65, 7.05 and 2.35), 2.41 (1 H, ddd, *J* 9.65, 7.05 and 2.35) and 3.70 (3 H, s). The simulated ABCD spectrum agreed with that obtained experimentally; δ_C 18.32, 20.82, 21.23, 29.93, 30.24, 51.63, 62.44, 63.51 and 173.52; $\tilde{\nu}_{max}$ 2963, 1736, 1436, 1375, 1170 and 847; *m*/*z* (%) 172 (M^+, 4), 141 (5), 130 (14), 113 (18), 99 (64) and 43 (100) (Found: M^+, 172.1082. $C_9H_{16}O_3$ requires *M*, 172.1099).

Methyl 2-*methoxycarbonyl*-5-*methyl*-4,5-*epoxyhexanoate* **32b**. δ_H 1.28 (3 H, s, Me), 1.30 (3 H, s, Me), 2.01 (1 H, ddd, *J* 13.79, 7.62 and 6.04), 2.25 (1 H, ddd, *J* 13.80, 8.80 and 4.81), 2.79 (1 H, dd, *J* 7.62 and 4.81), 3.58 (1 H, dd, *J* 8.80 and 6.05), 3.75 (3 H, s, MeO) and 3.77 (3 H, s, MeO); δ_C 18.69, 24.64, 28.28, 49.07, 52.69, 58.90, 61.36 and 169.32; $\tilde{\nu}_{max}$ 2970, 1730, 1461, 1367, 1273, 1039 and 732; *m*/*z* (%) 216 (M^+, 8), 159 (45), 85 (62) and 57 (100) (Found: M^+, 216.1005. $C_{10}H_{16}O_5$ requires *M*, 216.0998).

Methyl 2-*methoxycarbonyl*-4,5-*dimethyl*-4,5-*epoxyhexanoate* **33b**. δ_H 1.29 (3 H, s, Me), 1.30 (3 H, s, Me), 1.31 (3 H, s, Me), 2.15 (1 H, dd, *J* 14.32 and 7.51), 2.30 (1 H, dd, *J* 14.32 and 7.51), 3.57 (1 H, t, *J* 7.51) and 3.74 (6 H, s, MeO); δ_C 18.90, 20.82, 21.52, 33.00, 48.52, 52.64, 62.45, 62.71 and 169.61; $\tilde{\nu}_{max}$ 2951, 1752, 1733, 1432, 1378, 1282, 1199, 1065 and 850; *m*/*z* (%) 230 (M^+, 5), 215 (18), 200 (62), 146 (70), 126 (76) and 43 (100) (Found: M^+, 230.1148. $C_{11}H_{18}O_5$ requires *M*, 230.1154).

Methyl 2-*methoxycarbonyl*-2,5-*dimethyl*-4,5-*epoxyhexanoate* **32c** *and methyl* 2-*methoxycarbonyl*-4,5-*epoxy*-2,4,5-*trimethylhexanoate* **33c**. These two compounds were formed in low yield and were identified only by NMR spectroscopy. **32c**: δ_H 1.26 (3 H, s, Me), 1.30 (3 H, s, Me), 1.53 (3 H, s, Me), 2.02 (1 H, dd, *J* 14.60 and 6.96), 2.20 (1 H, dd, *J* 14.60 and 4.95), 2.76 (1 H, dd, *J* 6.96 and 4.95) and 3.75 (6 H, s, MeO); δ_C 18.77, 20.35, 24.68, 35.06, 52.53, 52.68, 57.88, 60.22 and 172.24.

33c: δ_H 1.24 (3 H, s, Me), 1.28 (3 H, s, Me), 1.31 (3 H, s, Me), 1.52 (3 H, s, Me), 2.20 (1 H, d, *J* 4.88), 2.48 (1 H, d, *J* 4.88) and 3.72 (6 H, s, MeO); δ_C 18.68, 20.30, 21.08, 29.65, 38.83, 52.65, 52.78, 62.03, 62.26 and 172.60.

Ethyl 2,2-*bis*(*ethoxycarbonyl*)-4,5-*epoxy*-5-*methylhexanoate* **32d**. δ_H 1.25 (3 H, s, Me), 1.29 (3 H, s, Me), 1.28 (9 H, 3 sets of t, *J* 7.15, 3-Me), 2.37 (2 H, 2 sets of dd, *J* 14.88 and 5.65), 2.98 (1 H, br t, *J* 5.65) and 4.27 (6 H, 3 sets of q, *J* 7.15, 3 CH_2); δ_C 13.87 (3 C), 18.75, 24.59, 32.62, 58.58, 60.21, 62.33, 64.14 and 166.59; $\tilde{\nu}_{max}$ 2981, 2932, 1743, 1465, 1443, 1265 and 858; *m*/*z* (%) 316 (M^+, 5), 300 (8), 257 (16) and 59 (100) (Found: M^+, 316.1519. $C_{15}H_{24}O_7$ requires *M*, 316.1522).

Ethyl 2,2-*bis*(*ethoxycarbonyl*)-4,5-*dimethyl*-4,5-*epoxyhexanoate* **33d**. δ_H 1.25 (3 H, s, Me), 1.27 (9 H, t, *J* 7.05, 3 Me), 1.275 (3 H, s, Me), 1.30 (3 H, s, Me), 2.52 (1 H, d, *J* 15.10), 2.71 (1 H, d, *J* 15.10) and 4.26 (6 H, q, *J* 7.05, 3 CH_2); δ_C 13.82 (3 C), 18.68, 20.72, 21.30, 37.83, 62.31 (3 C), 62.56, 63.51, 64.07 and 166.66; $\tilde{\nu}_{max}$ 2976, 2932, 1740, 1461, 1445, 1365, 1269, 1218, 1138, 1046 and 857; *m*/*z* (%) 330 (M^+, 12), 315 (4), 272 (8), 243 (16), 169 (22), 125 (27) and 27 (100) (Found: M^+, 330.1677. $C_{16}H_{26}O_7$ requires *M*, 330.1679).

Ethyl 2-*cyano*-5-*methyl*-4,5-*epoxyhexanoate* **32e**. NMR spectroscopy showed that **32e** consisted of approximately equal amounts of the two possible diastereoisomers; δ_H 1.34 (9 H, m, 3 Me), 2.08–2.31 (2 H, m), 2.92 (1 H, two sets of dd, *J* 7.86 and 4.86; 7.64 and 5.21), 3.67 (1 H, two sets of dd, *J* 10.02 and 5.21; 7.49 and 5.43) and 4.29 (2 H, 2q, *J* 7.14, 7.08); δ_C isomer A: 13.75, 18.72, 24.51, 29.30, 34.74, 59.05, 60.13, 63.14, 116.02 and 165.40; isomer B: 13.92, 18.83, 24.55, 29.48, 35.10, 59.48, 60.29, 63.14, 115.96 and 165.45; *m*/*z* (%) 197 (M^+, 5), 180 (6), 152 (9), 110 (10), 85 (100) and 59 (85) (Found: M^+, 197.1054. $C_{10}H_{15}NO_3$ requires *M*, 197.1052).

Ethyl 2-*cyano*-4,5-*dimethyl*-4,5-*epoxyhexanoate* **33e**. Approximately equal amounts of the two diastereoisomers were present; δ_H 1.30–1.42 (12 H, m, 4 Me), 2.05–2.40 [2 H, four sets of dd, 2.09 (*J* 14.05 and 10.11), 2.23 (*J* 14.44 and 7.05), 2.32 (*J* 14.44 and 6.68), 2.36 (*J* 14.05 and 5.71)], 3.63 (1 H, two sets of dd, *J* 10.11 and 5.71; 6.68 and 5.71) and 4.27 (2 H, m); δ_C isomer A: 13.65, 18.85, 21.04, 21.25, 34.32, 34.41, 61.60, 63.11, 63.42, 116.35 and 165.71; isomer B: 13.77, 19.00, 20.91, 21.08, 34.21, 34.47, 61.79, 63.02, 63.11, 116.35 and 165.86; *m*/*z* (%) 211 (M^+, 8), 168 (15), 124 (26), 99 (30) and 59 (100) (Found: M^+, 211.1228. $C_{11}H_{17}NO_3$ requires *M*, 211.1208).

Acknowledgements

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