Stereoselectivity in the Ene Reaction of *syn*- and *anti*-1-(4-*tert*-Butylcyclohexylidene)-4-*tert*-butylcyclohexane with Singlet Oxygen, Nitrosyl Hydride, Nitrosoformaldehyde, 4-Phenyl-1,2,4-triazol-3,5-dione, Diethyl Azodicarboxylate and Methyl Propiolate

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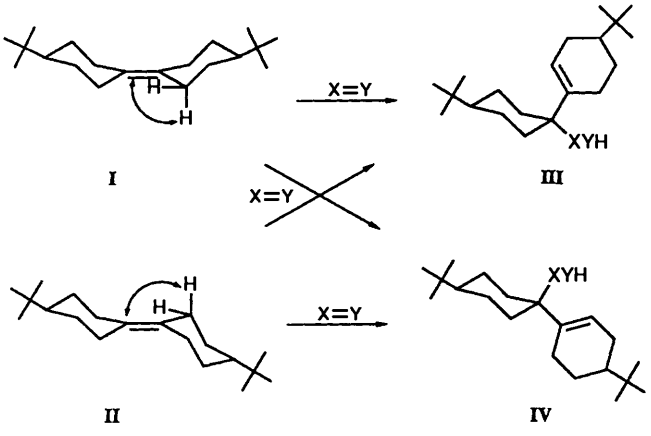
The stereochemistries of the ene reactions of *syn*- and *anti*-1-(4-*tert*-butylcyclohexylidene)-4-*tert*-butylcyclohexane (**I** and **II**) with a series of enophiles X=Y (singlet oxygen, nitrosyl hydride, nitrosoformaldehyde, 4-phenyl-1,2,4-triazol-3,5-dione, diethyl azodicarboxylate and methyl propiolate) to give, by axial or equatorial attack as shown, the allylic adducts **III** and **IV**, have been investigated.



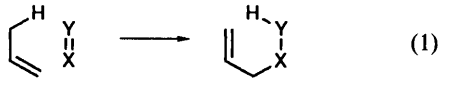
I **III** **II** **IV**

None of the reactions is stereospecific, the products being as follows (ene, enophile, **III**:**IV**): **I**, $^1O_2$, 60–68:40–32; **II**, $^1O_2$, 33–50:67–50; **I**, HN=O, 10:90; **II**, HN=O, 11:89; **I**, HCON=O, 25:75; **II**, HCON=O, 50:50; **I**, N=NCONPhCO, 17:83; **II**, N=NCONPhCO, 20:80; **I**, EtOCON=NCO$_2$Et, 77:23; **II**, EtOCON=NCO$_2$Et, 27:73; **I**, HC≡CCO$_2$Me, 53:47; **II**, HC≡CCO$_2$Me, 67:33.

The allylic hydroperoxides which are formed by the reaction of singlet oxygen react further with triplet oxygen to give allylic dihydroperoxides. The ene reactions of methyl propiolate are accompanied by the formation of cyclobutenes *via* cycloaddition.

The stereoselectivities of the ene reactions preclude a concerted suprafacial attack of the enophiles, but they support the model of the formation of an intermediate C=C/X=Y adduct which can undergo conformational change before the allylic hydrogen atom is transferred.

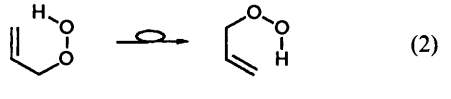
The ene reaction [eqn. (1)], in which an alkene (X=Y = $R_2C{=}CR_2$) undergoes hydroallylation by an ene, with rearrangement of the allylic moiety, was identified by Alder, Pascher and Schmitz in 1943,[1] and a similar reaction has subsequently been established with a variety of heteroenophiles.[2]



(1)

(X=Y = $R_2C{=}CR_2$, RC≡CR, O=O, RN=NR, RN=O, $R_2C{=}O$ *etc.*)

Many preparative and mechanistic studies have been carried out on reactions where the enophile is singlet oxygen;[3] the initial allylic hydroperoxide may undergo subsequent allylic rearrangement [eqn. (2)],[4] and epimerisation if the hydroperoxide is chiral.[5]

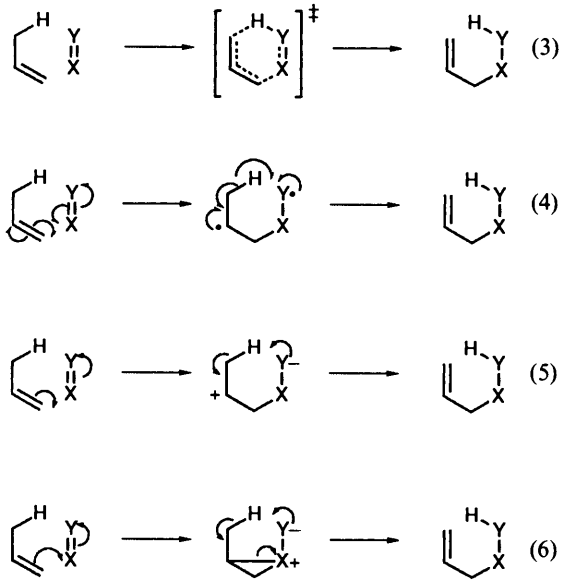


(2)

Relatively little work has been carried out on the ene reactions of nitroso compounds (X=Y = RN=O),[6] but it has been established that the products result from allylation at nitrogen. *N*-Phenyltriazolinedione (X=Y = N=NCONPhCO) has been used extensively for the activation of allylic hydrogen,[6b,7] and the close analogy with the reaction of singlet oxyen has been recognised.[3h,7e,f] Diethyl azodicarboxylate (X=Y = EtOCON=NCO$_2$Et) provides a less reactive equivalent reagent.[8] Comparatively little work has been carried out on ene reactions on which the enophile is an alkene or alkyne, but the reactivity can be usefully enhanced if the enophiles are activated by the same factors as are the dienophiles in Diels–Alder reactions, that is by the presence of electron attracting substituents, and by Lewis acids.[9]

No single mechanism appears to be capable of explaining all the features of ene reactions even with one particular enophile X=Y. The principal models which have been considered are shown in eqns. (3)–(6).

The suprafacial pericyclic mechanism [eqn. (3)] can accommodate the stereochemistry which is usually observed, and an



(3) (4) (5) (6)

antarafacial pericyclic variant[3b] has occasionally been proposed for some processes which show an unusual stereochemistry.

However, the stereochemical dependence of the deuterium isotope effects which are observed in the reaction of singlet oxygen,[3e,f,g,j] *N*-phenyltriazolinedione,[7b] pentafluoronitrosobenzene,[6b] formaldehyde,[9d] methyl chloroacrylate,[9d] or methyl propiolate[9d] with deuteriated 2-methylpropene, (*Z*)- and (*E*)-but-2-enes, (*Z*)- and (*E*)-stilbenes, and 2,3-dimethylbut-2-ene appears to indicate the formation of an intermediate. For example, singlet oxygen reacts with *cis*-, *trans*-, and *gem*-[$^2H_6$]2,3-dimethylbut-2-ene to show product isotope effects (k_H/k_D) of 1.05, 1.4 and 1.4, respectively.[3e] It is concluded that the first step of the reaction does not involve cleavage of a bond to hydrogen, but gives an intermediate in which hydrogen transfer in the second step can only occur at one particular pair of *cis* methyl groups. This argument has been widely accepted, and recent discussion has tended to focus on the precise nature of this intermediate. The diradical or zwitterionic representations [eqns. (4) and (5)] are usually rejected because there is little evidence for the incursion of reactions (*e.g.* rearrangements) characteristic of carbocations or carbon radicals, and a cyclic (perepoxide) structure as shown in eqn. (6) is preferred. A charge-transfer complex between the ene and enophile, of similar stereochemistry, might also be acceptable.

Many of these reactions under appropriate structural conditions can also give the products of [2 + 2] cycloaddition [eqn. (7)].

(7)

Against this rather confusing background, our attention was drawn to the work of Asveld and Kellogg[10] who studied the reaction of singlet oxygen with *syn*- and *anti*-1-(4-*tert*-butylcyclohexylidene)-4-*tert*-butylcyclohexane (**1** and **2**) (Scheme 1).

By the pericyclic mechanism [eqn. (3)], only equatorial attack on the *syn* alkene (**1**) should lead to reaction, because only this arrangement of reagents has a suitably orientated (axial) allylic hydrogen atom; alkene **1** should therefore give only the hydroperoxide **3**. By a similar reasoning, only axial attack on the *anti* alkene (**2**) should be profitable, and should give only the hydroperoxide **4**.

The reactions were in fact found not to be stereospecific. Alkene **1** gave the hydroperoxides **3** and **4** in a ratio of 3:2, and alkene **2** gave the same products in a ratio of 1:2. These results are incompatible with the pericyclic mechanism of eqn. (3), and suggest the formation of an intermediate (*e.g.* a perepoxide, eqn. (6), X=Y = O=O) with a lifetime sufficient to allow conformational change.

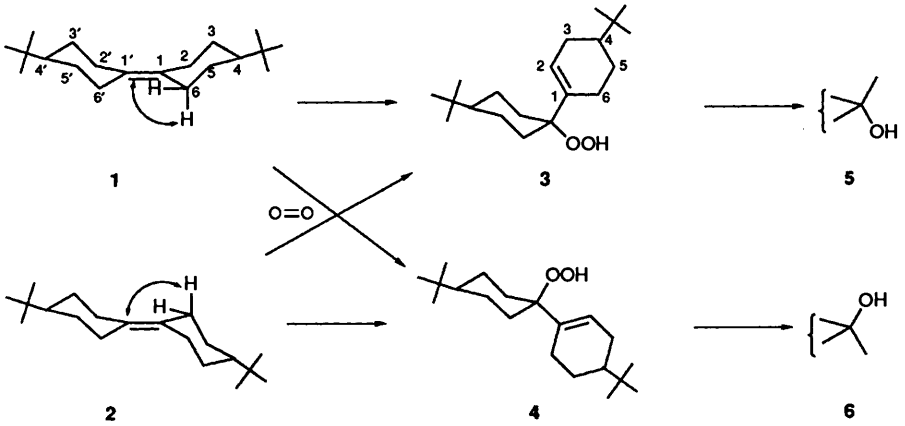
We report here an extension of Asveld and Kellogg's work in a study of the ene reactions of the alkenes **1** and **2** with singlet oxygen (which confirms their results), nitrosyl hydride (HN=O) and nitrosoformaldehyde (HCON=O), 4-phenyl-1,2,4-triazol-3,5-dione (PTAD, N=NCONPhCO), diethyl azodicarboxylate (DEAD, EtOCON=NCO$_2$Et) and methyl propiolate (MPP, HC≡CCO$_2$Me). Some work has also been carried out on the related alkenes, cyclohexylidenecyclohexane (**7**) and cyclopentylidenecyclopentane (**8**).

7 **8**

Results

$^1O_2$ *as the Enophile*.—We thought it worthwhile to extend Asveld and Kellogg's work on the singlet oxygenation for two reasons. Firstly, they deduced the structure of the alcohols **5** and **6**, corresponding to the hydroperoxides **3** and **4**, on the principle that axial alcohols elute more rapidly than equatorial alcohols on chromatography on aluminium oxide. Although this is not crucial to their broad conclusion that the reaction lacks regioselectivity, we felt more compelling evidence for the structure would be desirable.

Secondly, at the time their work was carried out it was not widely appreciated that chiral allylic hydroperoxides (*e.g.* 3-β-hydroxy-7α-hydroperoxycholest-5-ene[5]) are susceptible to epi-



Scheme 1

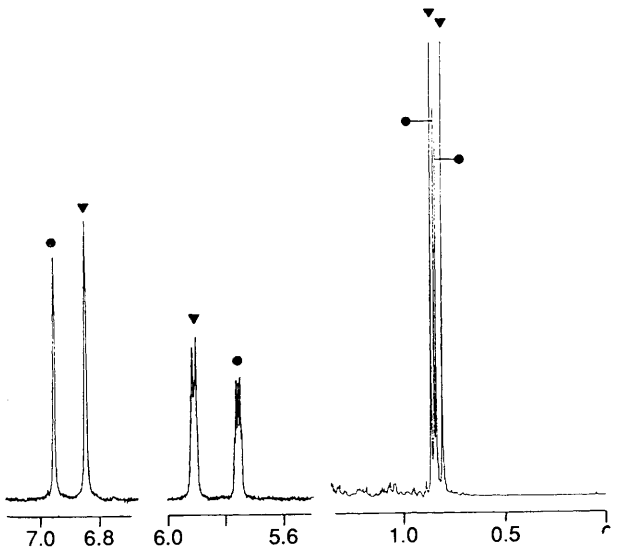


Fig. 1 400 MHz NMR spectra of the hydroperoxides 3 (▼) and 4 (●)

Table 1 The relative yields of 3 and 4 in the photooxygenation of 1 and 2 in different solvents and at different temperatures

Reactant	Solvent	Sensitizer[a]	T/°C	% 3	% 4
1	C_6H_6	TPP	20	60	40[b]
1	CH_2Cl_2	TPP	−85	>60	<40[b]
1	C_5H_5N	RB	20	68	32
1	$MeOH/C_6H_6$	RB	20	59	41
2	C_6H_6	TPP	20	33	67[b]
2	CH_2Cl_2	TPP	−75	*ca.* 50	*ca.* 50[b]
2	C_5H_5N	RB	20	44	56
2	$MeOH/C_6H_6$	RB	20	42	58

[a] TPP = tetraphenylporphine, RB = Rose Bengal. [b] See ref. 10.

merisation in solution. They were not able to separate and purify the hydroperoxides 3 and 4, and thus could not check that they did not interconvert in solution, which would invalidate their argument.

Photoxygenation of 1 in pyridine with Rose Bengal as a sensitizer gave the two isomeric hydroperoxides in a ratio of 68:32, as determined by 400 MHz NMR spectroscopy (Fig. 1).

Table 2 The rate of formation of 9 and 10 from 4 at room temperature

t/h	% 9	% 10
18	4	3
47	8	6
72	11	9
94	11.5	10
192	27	25
242	32	28

One shows two singlets at δ 0.81 and 0.86 for two *tert*-butyl groups, a multiplet at 5.91 for the vinyl proton, and a singlet at 6.82 for the OOH group. The other has singlets at 0.84 and 0.85 (Bu^t), a quintet at 5.76 (=CH–) and a singlet at 6.95 (OOH).

Under the same conditions, photooxygenation of 2 gave the two hydroperoxides in the ratio of 44:56.

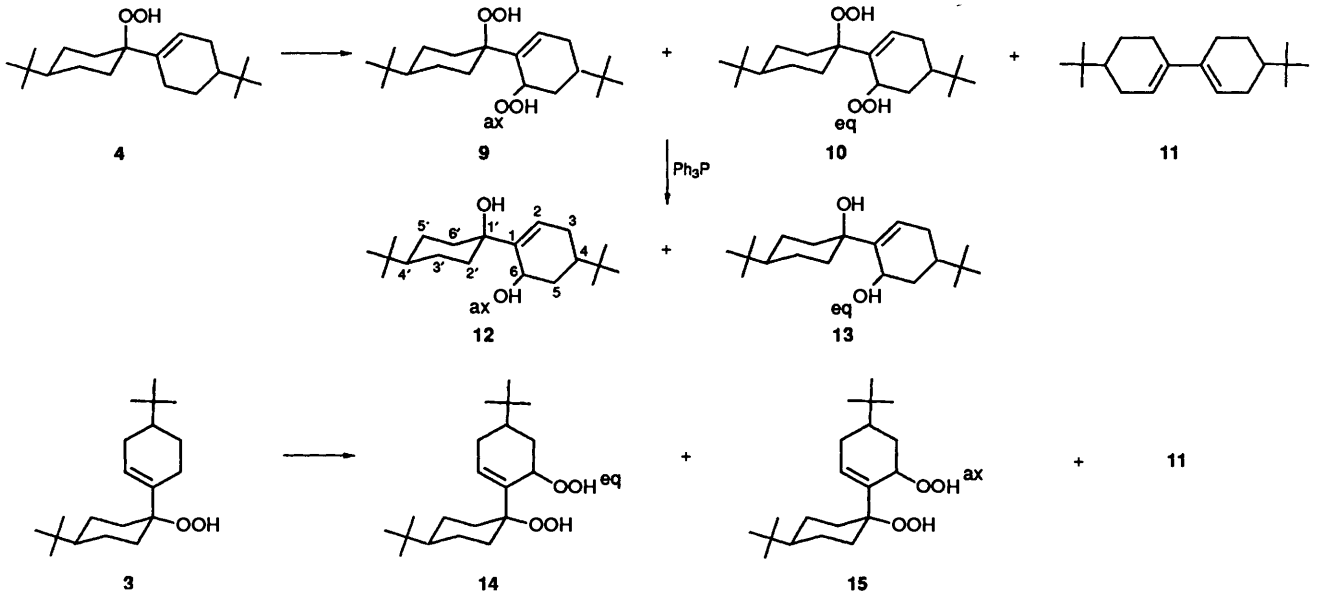
The hydroperoxides 3 and 4 were separated and purified by careful chromatography on silica gel, and characterised by ^1H (Fig. 1) and ^{13}C NMR, MS and IR spectroscopy; the chemical shifts of the ring protons in the former compounds were analysed by a 2D H–H COSY experiment.

The hydroperoxides 3 and 4 were reduced to the corresponding alcohols 5 and 6 and the structure of the 4-nitrobenzoate of 6 was determined by single crystal X-ray diffraction.[11] This confirmed Asveld and Kellogg's assignment of the two structures as shown in Scheme 1 and Fig. 1, and in Table 1 and subsequent Tables.

With the hydroperoxides separated, it was a simple matter to determine whether they were interconvertible under the conditions of the singlet oxygenation. No such exchange was found. Asveld and Kellogg showed, and we confirmed, that the alkenes themselves (1 and 2) did not isomerise under the reaction conditions. We have therefore removed any possible doubt about the stereospecificity of the oxygenation.

Table 1 shows that the effect of solvent and temperature on the oxidation of the two alkenes is negligible. When methanol is used as the solvent, there is no interception of a dipolar zwitterionic or perepoxide intermediate.

When the hydroperoxide 4 was kept in $CDCl_3$ for 72 h under air, the NMR spectrum showed that the dihydroperoxides 9 and 10 were formed, as shown in Scheme 2. The rate of the reaction is illustrated in Table 2, which shows that there is no stereoselectivity for the introduction of the second OOH group.



Scheme 2

Table 3 The rate of formation of **14** and **15** from **3** at room temperature

t/h	% **14**	% **15**
18	5	—
43	28	7
66	39	9
95	50	10
120	63	15
140	65	16

We have previously observed a similar reaction with the hydroperoxide derived from cyclohexylidenecyclohexane (**7**)[12c] and have identified the mechanism as involving a 3-step homolytic propagation cycle, in which the allylperoxyl radical abstracts allylic hydrogen intramolecularly to give an allyl radical; this reacts with oxygen to give a second allylperoxyl radical, and then the third propagation step intervenes intermolecularly, when this second allylperoxyl radical abstracts the hydrogen of the OOH group of the initial hydroperoxide to regenerate the first allylperoxyl radical.

The reaction was catalysed by azoisobutyronitrile (AIBN) and inhibited by 2,6-di-*tert*-butyl-4-methylphenol (DBMP). It was repeated with AIBN on a preparative scale, and the dihydroperoxides **9** and **10** were reduced to the diols **12** and **13**, together with a small amount of the diene **11**.

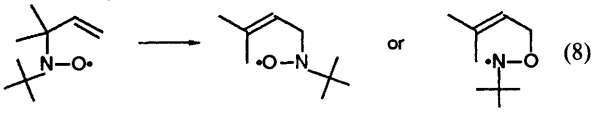
Similarly, the corresponding dihydroperoxides **14** and **15** were formed when **3** was allowed to stand in chloroform under air. The relative rates of formation of **14** and **15** are shown in Table 3, but the reaction was not carried out on a preparative scale because **3** is unstable on silica gel, and is difficult to isolate in large enough quantities.

It will be seen from Tables 2 and 3 that **3** is more reactive than **4**, and that in **4** the entry of the second hydroperoxyl group is selective in favour of the equatorial position. This can be rationalised in terms of the greater steric constraints which exist when the cyclohexenyl ring of **3** is axially oriented.

HN=O *and* HCON=O *as Enophiles.*—We[12] and Porter[13] have produced evidence that the rearrangement of an allylic hydroperoxide involves a pericyclic reaction of the corresponding peroxyl radical, *via* the transition state **16**, but the alternative transition state **17** cannot be excluded. To choose between these and other possible mechanisms it would be desirable to differentiate the two oxygen atoms by ^{18}O labelling, but there appears to be no established method for doing this.

16 **17**

We were therefore interested in some results of Craig and Roberts[14] which might be interpreted as implying that a similar rearrangement is possible with nitroxyl radicals [eqn. (8)]. A transition state analogous to **16** would give an *N*-allylhydroxylamine, whereas one analogous to **17** would give an *O*-allylhydroxylamine.



(8)

Nitrosyl hydride (HN=O) and nitrosoformaldehyde (HCON=O) have recently become readily available in solution through the work of Ensley and Mahadevan,[6c] who showed that

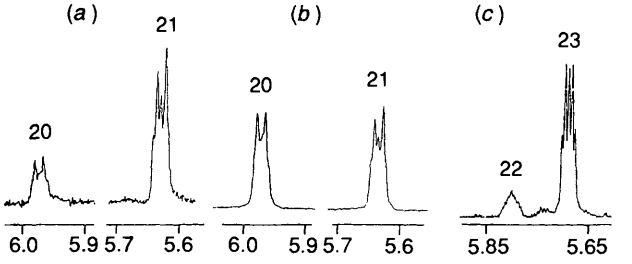
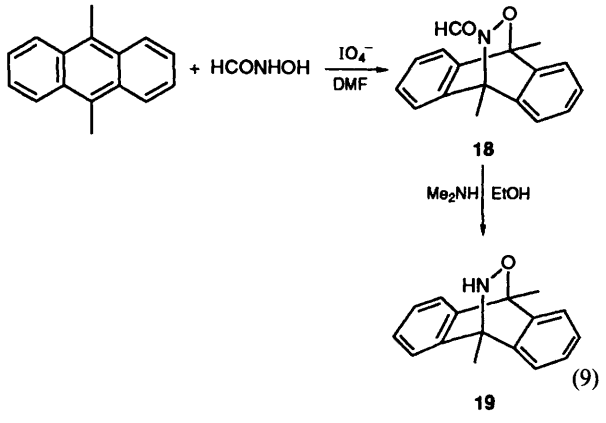


Fig. 2 Vinyl region of the 400 MHz NMR spectra of the products from the reactions (*a*) **1** with HCON=O, (*b*) **2** with HCON=O and (*c*) **1** with HN=O

HN=O would give an ene reaction with 2,3-dimethylbut-2-ene, and HN=O and HCON=O would give a similar reaction with 2-cyclopentylidenecyclopentanone.

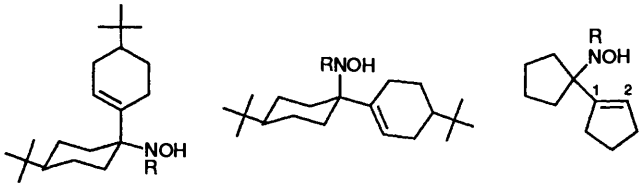
We have therefore compared the stereoselectivity of the reaction of the alkenes **1** and **2** with singlet oxygen and with HN=O and HCON=O, and looked for the occurrence of a rearrangement similar to that shown in eqn. (8).

We use the modification of Ensley's procedure shown in eqn. (9) to prepare the 9,10-adducts of nitrosyl hydride and nitrosoformaldehyde with 9,10-dimethylanthracene, (**18** and **19**).



(9)

Treatment of the *syn* alkene (**1**) with **18** in toluene at 110 °C gave the adducts **20** and **21** (yield 62%) in a ratio of 1:3; the vinyl region of the NMR spectrum is shown in Fig. 2. Treatment of the *anti* alkene (**2**) under similar conditions gave the same two isomers (65%) in a ratio of 1:1 (see Fig. 2). The isomers **20** and **21** were separated by chromatography, and the structures assigned on the basis of NMR spectroscopy as described below.



20 R = HCO
22 R = H

21 R = HCO
23 R = H

24 R = HCO
25 R = H

Treatment of **1** and **2** with the HN=O precursor **19** in benzene at 65 °C gave the two isomers **22** and **23**, in a yield of 72% in a ratio of 1:9 in the first case, and a yield of 60% in a ratio of 1:10 in the second. The major isomer was isolated, but not the minor isomer.

We were unable to prepare single crystals of the major isomer or its hydrochloride which were suitable for X-ray diffraction, and the structures of the adducts had to be inferred from the NMR spectra. Relevant ^1H and ^{13}C chemical shifts are collected in Table 4. It can be seen that the separation of the proton chemical shifts for the *tert*-butyl groups is generally smaller

Table 4 ^1H and ^{13}C NMR data for 4-*tert*-butylcyclohex-1-enyl-4-*tert*-butylcyclohexanes

Compound	$\Delta(\delta_H$-Bu$^t)$/Hz	δ_H 1-H	δ_C C-1	C-2	C-3
XYH = OOH (**3**)	21.6	5.91	133.6	129.1	86.2
OH (**5**)	20.8	5.78	138.0	124.0	73.8
HCONHOH (**20**)	18.0	5.97	131.4	130.4	66.6
NNHCONPhCO (**26**)	5.68	5.94	132.42	129.99	67.17
XYH = OOH (**4**)	4.0	5.76	140.1	123.1	84.2
OH (**6**)	2.4	5.73	144.3	119.4	72.8
HCONOH (**21**)	2.8	5.63	139.4	122.7	66.1
NHOH (**23**)	3.2	5.68	134.6	127.4	66.5
$O_2CC_6H_4NO_2$	0	5.73	137.1	121.9	85.9
NNHCONPhCO (**27**)	7.51	5.61	139.3	123.0	67.18

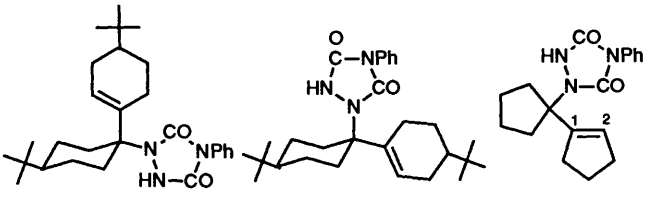
when X is in an axial position (with the exception of the PTAD adduct: see below), and the vinylic protons appear further downfield when X is axial. Meanwhile the ^{13}C signals for C-3 are shifted upfield, and C-1 downfield, when X is axial rather than equatorial. This tendency is general in substituted *tert*-butylcyclohexanes.[15] On the basis of this evidence, we assigned the structure of the major product of the reaction of **1** and **2** with HN=O as that shown in **23**, and of the minor product (if present) as that shown in **22**. The structues of **20** and **21** were assigned in a similar way. The nature of compounds **22** and **23** as *N*-alkyl- rather than *O*-alkyl-hydroxylamines was confirmed by the ^1H NMR spectrum of **23** which, in $CDCl_3$, shows two broad signals at δ 4.15 and 5.10, and in dimethyl sulphoxide showed two sharp signals at δ 5.12 and 6.15 for the NH and OH groups, respectively. The rate of formation of **23** was unchanged when DBMP was added as a potential radical trap.

The alkenes **1** and **2** do not interconvert under the conditions of their ene reactions with HN=O and HCON=O; indeed they are stable at the higher temperature (145 °C for 4 h) at which they are prepared. Similarly, the reaction products showed no tendency to undergo epimerization or allylic rearrangement [*cf.* eqn. (8)] in solution.

In an attempt to observe the allylic rearrangement in *N*-allylhydroxylamines, we therefore investigated the ene reactions of other alkenes which, with singlet oxygen, give hydroperoxides which rearrange particularly readily. Cholesterol, cholest-5-en-3-one and 1,2,3,4,5,6,7,8-octahydronaphthalene could not be induced to form adducts with HN=O or HCON=O. Cyclopentylidenecyclopentane (**8**), however, formed the adducts **24** and **25**. Whereas the hydroperoxide formed from the reaction with singlet oxygen rearranges even at low temperature, the hydroxylamine **25** was unchanged when a solution was kept at room temperature for one week, or when a solution containing 10 mol% of AIBN was heated to 55 °C for 1 h.

4-Phenyl-1,2,4-triazol-3,5-dione and Diethyl Azodicarboxylate as the Enophiles.—The alkenes **1** and **2** reacted with PTAD in *ca.* 2 h at room temperature to give the adducts **26** and **27** in quantitative yields in a ratio of 1:5 from **1** and 1:4 from **2**. Again the assignment of structures is based on ^{13}C chemical shifts (Table 4).

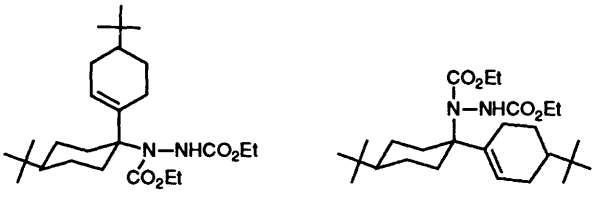
Cyclopentylidenecyclopentane (**8**) is more reactive than **1** or **2**, and immediately bleached the red colour of PTAD at room temperature to give **28** in quantitative yield. All three products (**26**–**28**) were stable in solution, and showed no evidence of undergoing rearrangements of the types which are characteristic of some hydroperoxides.



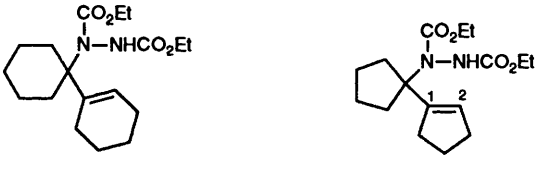
26 **27** **28**

DEAD was less reactive than PTAD as an enophile. It reacted with **1** in refluxing dichloromethane in 8 h to give **29** and **30** in 89% yield in a ratio of 3.5:1, while it reacted with **2** under the same conditions over two days to give **29** and **30** in a ratio of 1:2.7.

Again, the configuration of **29** and **30** can be assigned on the basis that the NMR signal of the vinyl proton in the equatorial



29 **30**



31 **32**

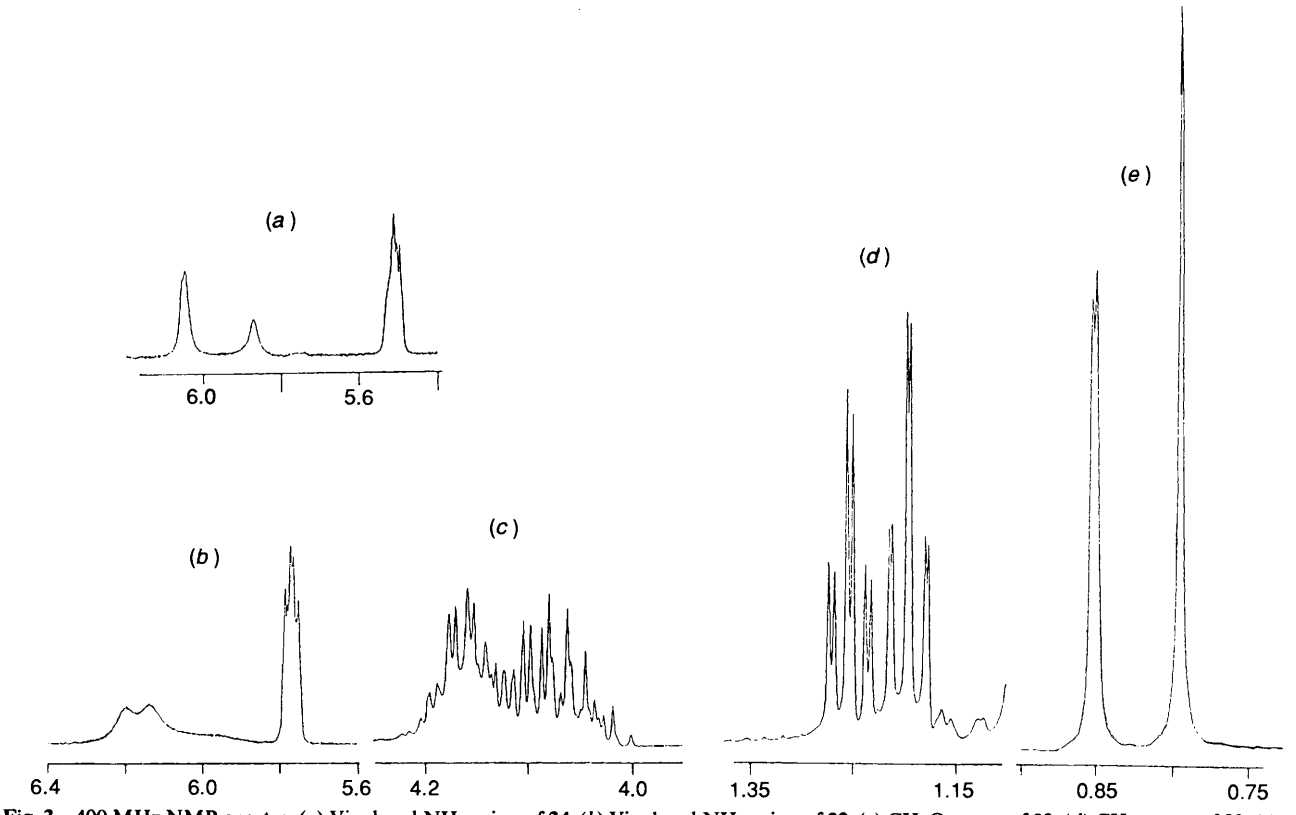


Fig. 3 400 MHz NMR spectra. (*a*) Vinyl and NH region of **34**. (*b*) Vinyl and NH region of **32**. (*c*) CH_2O group of **32**. (*d*) CH_3 group of **32**. (*e*) *tert*-Butyl group of **32**.

Table 5 ^1H and ^{13}C NMR data for the compounds **34–39**

	34	**35**	**36**	**37**	**38**	**39**
Bu^t	0.78	0.81	0.79	0.819	0.79	0.81
Bu^t	0.85	0.82	0.84	0.821	0.87	0.82
MeO	3.71	3.68	3.68	3.66	3.72	3.67
1-H	5.52	5.62[a]				
3-H	5.72[b]	5.60[c]	7.18	6.60	7.10	6.68
4-H	6.72[d]	6.72[e]				
C-1	116.71	120.07				
C-2	135.19	141.76				
C-3	158.60	155.22	153.07	154.04	150.70	155.39
C-4	125.30	121.46	145.77	142.15	143.64	141.64
C-5	167.90	167.45	164.01	162.40	163.04	164.02

[a] m. [b] d, *J* 16.10. [c] d, *J* 15.90. [d] d, *J* 15.85. [e] d, *J* 16.23.

Table 6 Products of ene reactions of *syn*- and *anti*-4-*tert*-butylcyclohexylidene-4-*tert*-butylcyclohexane (**1** and **2**) with enophiles

Ene	Enophile	% III	% IV
1	O=O	60–68	32–40
2	O=O	33–50	50–67
1	HN=O	10	90
2	HN=O	11	89
1	HCON=O	25	75
2	HCON=O	50	50
1	PTAD[a]	17	83
2	PTAD[a]	20	80
1	DEAD[b]	77	23
2	DEAD[b]	27	73
1	MPP[c]	53	47
2	MPP[c]	67	33

[a] PTAD = $\overline{N{=}NCONPhCO}$. [b] DEAD = $EtO_2CN{=}NCO_2Et$. [c] MPP = $HC{\equiv}CCO_2Me$.

substituent in **30** is downfield of that in the axial substitutent in **29**, as shown in Figs. (3*a*) and (*b*).

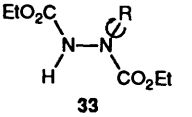
The ^1H and ^{13}C NMR spectra showed a further interesting feature. The ^1H signals of the *tert*-butyl groups in **29** appear as a singlet at δ 0.78 and a doublet at 0.84 as shown in Fig. 3(*e*), and there are 4 sets of methyl groups and 4 sets of methylene groups as shown in Figs. 3(*c*) and 3(*d*). The NH group in **29** appears as two broad singlets of equal intensity at δ 6.18 and 6.25; at 50 °C these signals become closer together [Fig. 3(*b*)], but otherwise the spectrum does not change.

Similarly the ^{13}C NMR spectrum of **29** shows two sets of olefinic carbon atoms at δ 126.66 and 133.45, and at 127.00 and 134.43, and there are 4 signals for the carbonyl carbon atoms at δ 155.73, 155.93, 156.82 and 156.94.

The spectrum of **30** showed a similar phenomenon, but the intensities of the two NH signals were in the ratio 2.6:1 as shown in Fig. 3(*a*), and this was in accord with the relevant intensities of the signals for the *tert*-butyl groups at δ 0.825 and 0.828.

To avoid any complications resulting from the complexity of the *tert*-butylcyclohexanyl rings, the adducts **31** and **32** were prepared from **7** and **8**. Again the products showed two sets of signals for the methyl groups, in a ratio of 3:1 for **31** and 4:1 for **32**. Similarly **31** shows the presence of four carbonyl carbon atoms at δ 156.33 and 156.65 (major), and 156.26 and 157.29 (minor). The spectra of **31** and **32** did not change over the range 25–50 °C, except that the NH signals became closer.

A similar phenomenon has been reported by Lee and Taylor[8d] in the product formed from the reaction of DEAD with 2,3-dimethylbut-2-ene, and they ascribed it to restriction of rotation about the R–N bond in **33**. This effect was also noticed



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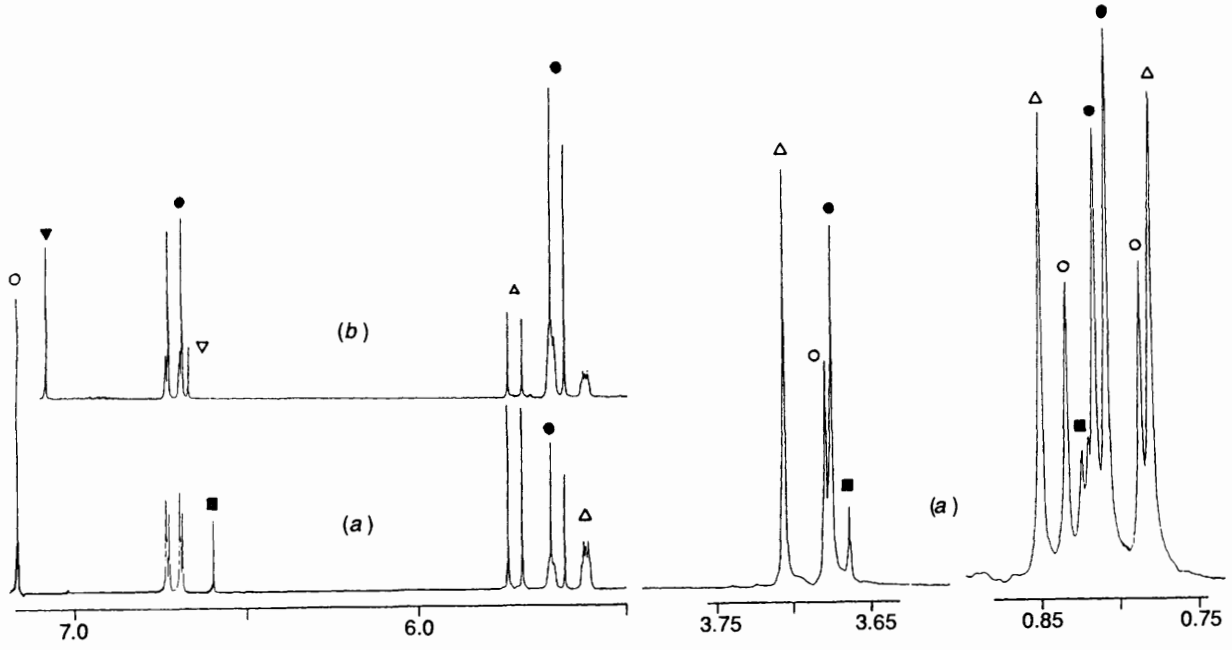


Fig. 4 400 MHz ^{1}H NMR spectra of the products of the reaction of MPP (*a*) with **1**, and (*b*) with **2**. The signals for the various compounds are labelled as follows; **34** (△), **35** (●), **36** (○), **37** (■), **38** (▼) and **39** (▽).

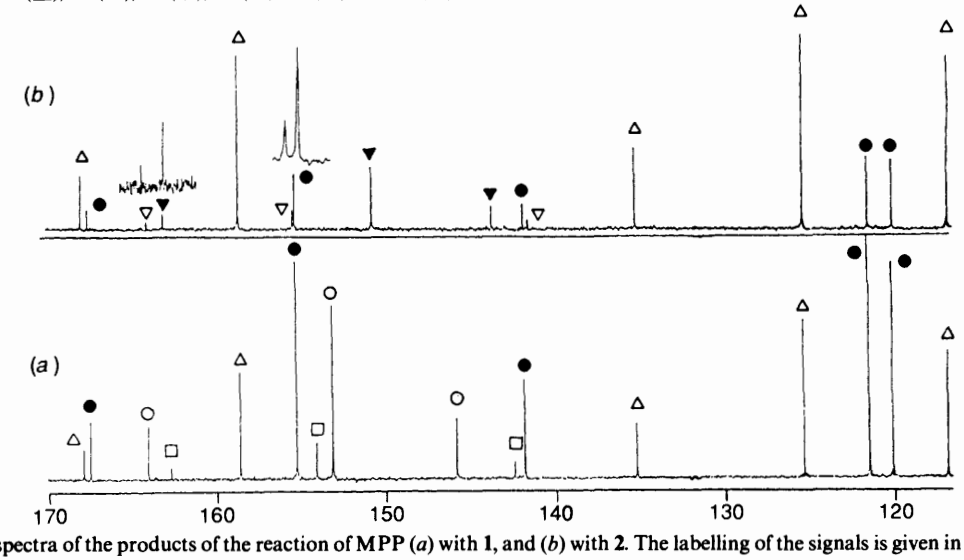


Fig. 5 ^{13}C NMR spectra of the products of the reaction of MPP (*a*) with **1**, and (*b*) with **2**. The labelling of the signals is given in the caption to Fig. 4.

in the product from *p*-cymene, but not in the product **31** which was reported in the same paper.

Methyl Propiolate as the Enophile.—The Lewis-acid-catalysed reactions of methyl propiolate with allylic enes have been widely studied because of their synthetic utility and mechanistic interest. It was found that ethylaluminium dichloride is the best catalyst as it also reacts as a proton scavenger, preventing acid-catalysed side reactions.[9a,b] Tetrasubstituted alkenes give exclusively ene products, whereas disubstituted alkenes give exclusively the products of stereospecific cycloaddition.

We have carried out the ethylaluminium dichloride catalysed reactions of the alkenes **1**, **2**, **7** and **8** with methyl propiolate according to Snider's procedure: **1**, **2** and **7** gave the products of both the ene reaction and of cycloaddition, but **8** showed only the ene reaction as illustrated in Scheme 3.

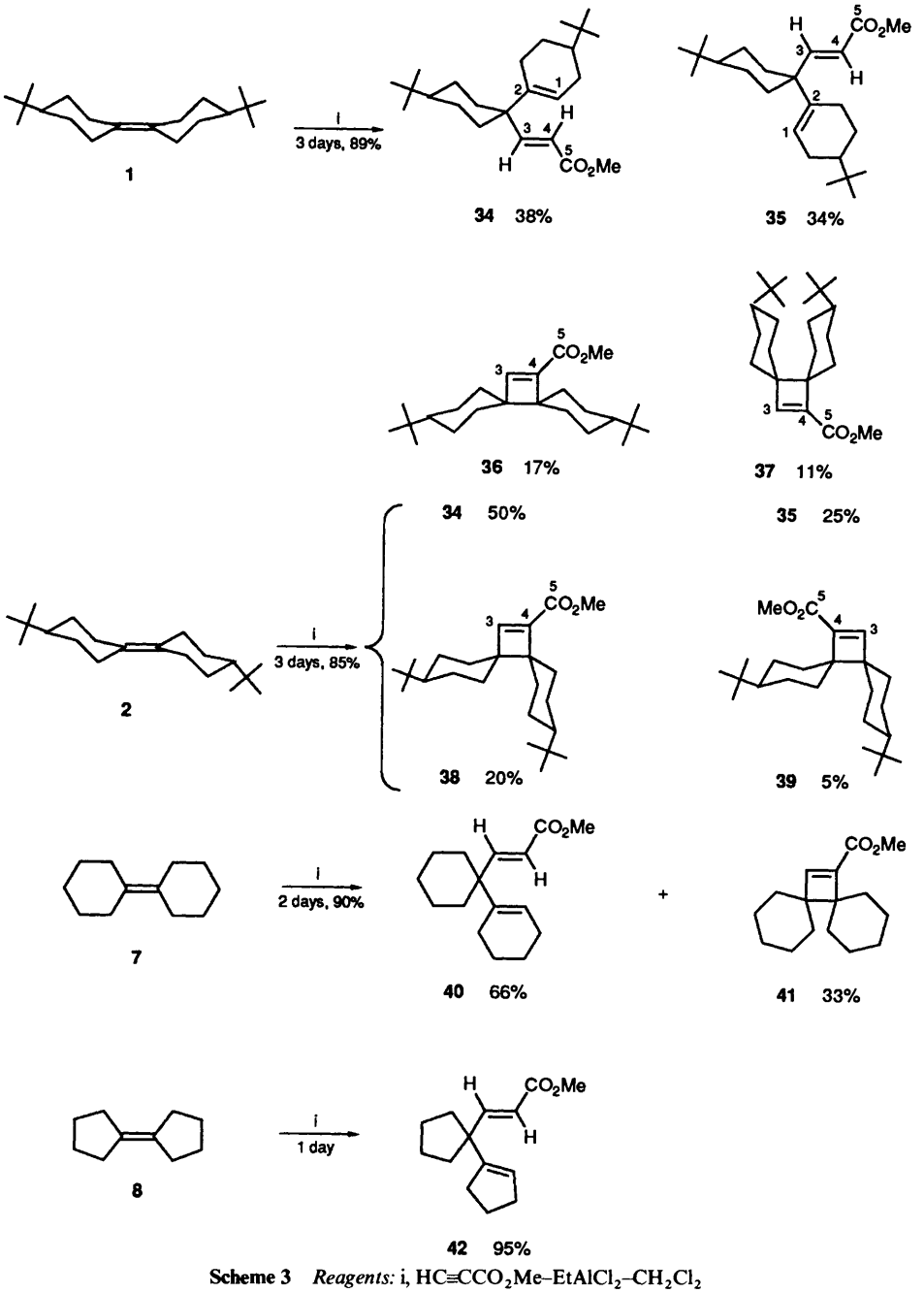
The ^{1}H and ^{13}C NMR spectra of the products from **1** and **2** are shown in Figs. 4 and 5, and the assignments of the signals are given in Table 5.

Discussion

The stereoselectivities of all the ene reactions are summarised in Table 6. For each reaction we have established that there is no isomerisation of the reactants (**1** ⇌ **2**) or of the products under the reaction conditions, hence the distribution of products is kinetically controlled.

It is immediately apparent that none of the reactions is stereospecific. The ratio of *cis* and *trans* products must represent the ratio of axial and equatorial attack on the double bond, and none of the reactions can occur by a single-step concerted process [eqn. (3)] with the enes **1** or **2** in their ground-state conformations, because these reactions would be stereospecific. The second major point to emerge is that none of the products undergoes a homolytic allylic rearrangement: the allylic hydroperoxides appear to be unique in this respect.

In order to determine whether the ene reactions might take place by a concerted process involving some conformation other than the ground state ones illustrated in **1** and **2**, it is important to establish the relative magnitudes of the activation energies for positional exchange (E_{ex}) of axial and equatorial allylic hydrogen atoms in **1** and **2**, and for the reactions of the various enophiles (E_r) [eqn. (1)]. If $E_r < E_{ex}$, we can assume, on the basis of the Curtin–Hammett principle,[16] that the reactions occur on the enes (**1**, **2** and **7**) in their original



Scheme 3 *Reagents:* i, $HC{\equiv}CCO_2Me$–$EtAlCl_2$–CH_2Cl_2

conformations. On the other hand, if $E_{ex} < E_r$, conformational change in **1** or **2** can occur before the transition state, and the ground state structures of **1** or **2** may tell us little about the geometry of the transition states of the ene reactions.

The activation energy for the axial–equatorial exhange of the allylic protons in cyclohexylidenecyclohexane (**7**) has been measured by Dr. J. E. Anderson using dynamic NMR spectroscopy.[17] In $CHFCl_2/CHF_2Cl/CD_2Cl_2$ at -150 °C these protons give two signals ($\Delta\nu_{\frac{1}{2}}$ 40 Hz) at δ 1.6 and 2.8. These signals coalesce at δ 2.2 at -130 °C, whence $\Delta G^{\ddagger}$ for the exchange process is *ca.* 6.2 kcal mol^{-1}.* This is to be compared with a value of 10.3 kcal mol^{-1} which has been obtained for cyclohexane, 8.4 kcal mol^{-1} for methylenecyclohexane, and 5.8 kcal mol^{-1} for 2-propylidenecyclohexane.[18] Similar measurements cannot be carried out on the *tert*-butyl substituted homologues, because the ring-inverted conformers are present in concentrations which are too low to detect by NMR spectroscopy, but the *tert*-butyl groups would not be expected to have any large effect on the barrier.[19] Ring inversion would procede through the boat (or twist boat) conformation,[19] and we may assume that the activation energy for exchanging axial and equatorial hydrogens by either the chair ⟶ boat, or chair ⟶ boat ⟶ boat, or chair ⟶ boat ⟶ boat ⟶ chair processes in **1** and **2** would be $\geqslant$6.2 kcal mol^{-1}.

$^1O_2$.—The activation energy for oxidation by singlet oxygen is usually 1–2 kcal mol^{-1}. By the Curtin–Hammett principle we are therefore justified in assuming, as Asveld and Kellogg did,[10] that singlet oxygen attacks the alkenes **1** and **2** when they are in their low-energy chair conformations.

Our results on the oxygenation of **1** and **2** confirm Asveld and Kellogg's results. Neither reaction is stereoselective, but both give *ca.* 60% of the product expected from a concerted process, and 40% of the other isomer; these ratios are not very sensitive

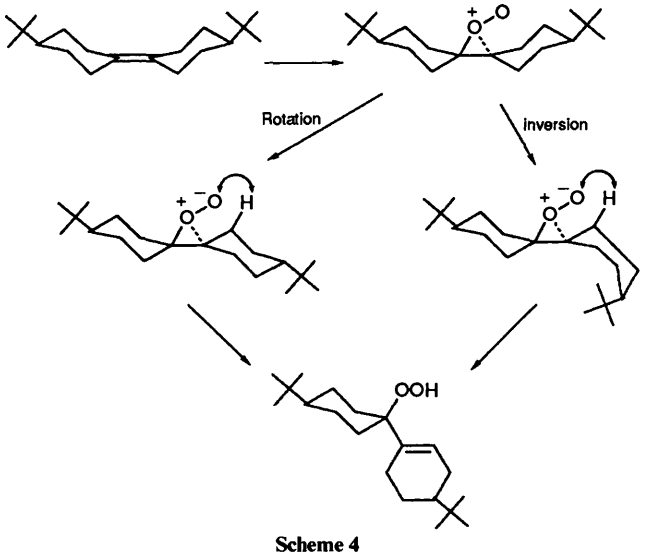
* 1 cal = 4.184 J.

to change of solvent, and a polar solvent (methanol) does not affect the nature of the products.

These results could be accommodated by competing concerted suprafacial and antarafacial reactions of oxygen, but on steric grounds, it seems unlikely that these two reactions would proceed at similar rates. Further, if the results of experiments on the kinetic deuterium isotope effects are also relevant to the alkenes **1** and **2**, we have to accept that attack by oxygen occurs in both the axial and equatorial senses to give a complex. If there is a suitably oriented axial allylic hydrogen, this is then transferred to give the product. If there is no suitably oriented hydrogen, either chair–boat inversion, or rotation about the erstwhile double bond has to occur before the reaction can be completed. (We note, however, that the stereospecificity of reactions with olefins carrying chiral substituents require that no rotation occurs in the intermediate about the original double bond [3h]). These processes are illustrated in Scheme 4 for axial attack on the *syn* ene to give the *cis* adduct; the exact nature of the adduct (diradical, zwitterion, perepoxide or charge-transfer complex) is deliberately not specified.

An alternative route to these singlet adducts between alkenes and oxygen might be provided by the trialkylsilyl hydrotrioxides, $R_3SiOOOH$, which are generated from silanes, R_3SiH and ozone at low temperature. These react with alkenes *via* intermediates which are usually represented as zwitterions or perepoxides, but the ultimate products are usually carbonyl compounds formed by cleavage of the double bond.[20]

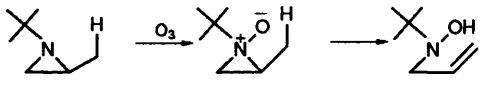
It is interesting that a similar structural problem is presented by the species R_2CO_2 which can be represented as diradicals $R_2\dot{C}OO^{\bullet}$, zwitterions $R_2\overset{+}{C}O\,\bar{O}$, carbonyl oxides, $R_2C{=}\overset{+}{O}{-}\bar{O}$ or dioxiranes $R_2\overset{\frown}{COO}$.



Scheme 4

HN=O *and* HCON=O.—Very little appears to have been published previously on the ene reactions of HN=O and HCON=O, and there are no reports of measurements of the activation energies of these reactions. However, these species exist only as short-lived reactive intermediates which rapidly self-react to give N_2O and water; in aqueous solution the rate constant is 2–8 × 10^9 dm^3 mol^{-1} s^{-1}.[21] As the yields from our ene reactions are high, it seems likely that E_r is low, so that we may, with caution, proceed on the assumption that the reactions occur with the enes **1** and **2** in their ground state conformations.

HN=O reacts with the alkenes **1** and **2** to give from each a similar mixture of products (Table 6), containing predominantly the isomer which would be expected from equatorial attack. This precludes a concerted reaction with the alkene in its ground state conformation, and, if E_r is indeed less than E_{ex}, it precludes any concerted mechanism, but would permit a diradical, zwitterionic or aziridine *N*-oxide-like intermediate. In fact, Baldwin has shown[22] that (*E*)-*N*-*tert*-butyl-2-methylaziridine can be oxidised at −75 °C to the *N*-oxide, which does then rearrange at −30 °C to give the allylhydroxylamine [eqn. (10)].


(10)

The reaction of HCON=O with the *syn* ene (**1**) similarly proceeds predominantly by equatorial attack, and the reaction with the *anti* ene (**2**) is not stereoselective: again, neither of the two reagents shows the stereoselectivity that would be expected from a concerted suprafacial mechanism.

The failure of either reagent to react with cholesterol, cholest-5-en-3-one and 1,2,3,4,5,6,7,8-octahydronaphthalene was rather surprising, but does not appear to shed any further light on the reaction mechanism.

If the allylic hydroxylamines were to rearrange in a manner similar to the allylic hydroperoxides, the various steps would be as in eqns. (11)–(13), where R and R′ represent unrearranged and rearranged allylic groups, respectively.

$$R\text{–}NH\text{–}OH \longrightarrow R\text{–}NH\text{–}O^{\bullet} \quad (11)$$

$$R\text{–}NH\text{–}O^{\bullet} \longrightarrow R'\text{–}NH\text{–}O^{\bullet} \text{ or } R'\text{–}ONH^{\bullet} \quad (12)$$

$$R'\text{–}NH\text{–}O^{\bullet} \text{ or } R'\text{–}ONH^{\bullet} + RNHOH \longrightarrow R'\text{–}NH\text{–}OH \text{ or } R'\text{–}ONH_2 + R\text{–}NH\text{–}O^{\bullet} \quad (13)$$

With AIBN as the initiator, the initial nitroxyl radical should be formed readily, and the final transfer of hydrogen would be thermally neutral for the nitroxyl radical, or mildly exothermic for the aminyl radical. The rate-limiting factor would therefore appear to be the rearrangement of the allylnitroxyl radical itself; if it gave a nitrogen-centred radical, the reaction might be expected to be exothermic by a few kcal mol^{-1}.

PTAD and DEAD.—Some kinetic measurements have been made on the reactions of PTAD. Green [7b] showed that its ene reaction with 2,3-dimethylbut-2-ene at 23.5 °C had a rate constant of 3 × 10^6 dm^3 mol^{-1} s^{-1}, and if we assume that the reaction has the same *A* factor as that of hex-3-ene, this indicates an activation energy of 4.9 kcal mol^{-1}. It thus appears likely that the reactions of **1** and **2** with PTAD have an activation energy less than that for ring inversion, and that the reactions occur on the ground state conformations.

The reaction of PTAD with the enes **1** and **2** showed a very similar stereoselectivity to the reactions of HN=O, giving from both enes a preponderance of the product of axial attack. This rules out a concerted process, but leaves open the options listed above for the reactions of HN=O.

We can find no relevant measurements on the kinetics of the reactions of DEAD, but it is much less reactive than PTAD, and E_{ex} is probably less than E_r. The stereochemistries of the reaction of DEAD with the alkenes **1** and **2** (see Table 6) are rather similar to those of the reactions of singlet oxygen. Again a concerted reaction with the alkenes is ruled out because it would be stereospecific, but now a concerted reaction involving the alkenes with, for example, one ring in a chair conformation is in principle permitted as are the mechanisms involving diradical, ionic or aziridinyl-like intermediates.

MPP.—MPP is still less reactive, and the same condition applies: conformational change may precede reaction.

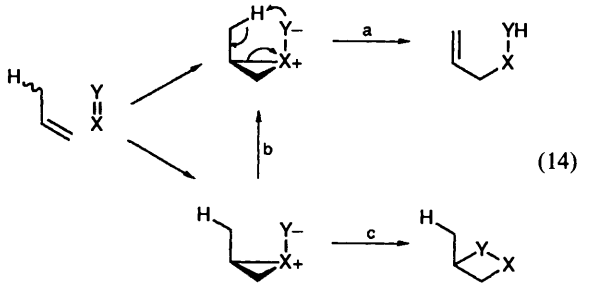
Reactions of MPP with tetraalkylethenes have previously been reported to give only the ene adducts, but we find that **1** and **2** also give substantial amounts of the corresponding cyclobutenes (25–28%); the configuration of the alkenes is preserved in these cycloadducts, confirming that no interconversion of **1** and **2** occurs during the reaction. The possibility that these reactions occur by an antarafacial cycloaddition cannot be ruled out, but the steric argument against this seems very strong.

The ene reactions of **1** and **2** are sterically rather unselective, with some preference for the isomer formed by equatorial attack of the enophile. In view of the deuterium isotope effect which argues powerfully for the formation of an intermediate, the results would appear to suggest again the formation of an intermediate with a lifetime long enough for conformational change to occur, with exchange of axial and equatorial hydrogen atoms before the intramolecular transfer of hydrogen; an alternative mode of reaction of the same intermediate might be ring-closure to give the cyclobutene products.

Cyclohexylidenecyclohexane (**7**) partitions between the ene reaction and cycloaddition in a similar way to **1** and **2**, but cyclopentylidenecyclopentane (**8**) reacted like a conventional tetraalkylethene and gave only the ene adduct.

Conclusion

Our results reported here, where we have used Kellogg's method to investigate the reactions of the enophiles $^1O_2$, HN=O, HCON=O, PTAD, DEAD and MPP, provide evidence consistent with that obtained by others using Sanderson's isotope effect technique with the enophiles $^1O_2$, $C_6H_5N{=}O$, PTAD, MPP, $CH_2{=}O$ and $O{=}C(CO_2Et)_2$. In every case, they require that the reactions cannot occur by a concerted mechanism on the molecules in their ground state conformations. Our results do not exclude the possibility that some of the reactions might occur with the enes in less stable conformations, but the model which seems to be consistent with all the evidence is that all the reactions proceed through an intermediate complex between the ene and the enophile. Intramolecular transfer then occurs of a suitably oriented hydrogen atom [eqn. (14a)], preceded if necessary by conformational change to reorient the hydrogen atom [eqn. (14b)]. With some combinations of ene and enophile, and particularly when the ene cannot present a hydrogen atom in the preferred orientation (*e.g.* in adamantylideneadamantane[23]) the same intermediate may collapse to give a 4-membered ring [eqn. (14c)].



(14)

The precise nature of these intermediates remains in question, but the best representation appears to be as the perepoxides, aziridine *N*-oxides, aziridinium imides, *etc.* as illustrated in eqn. (14).

Experimental

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian VXR400 spectrometer and the chemical shifts have been measured relative to the solvent by using δ_H = 7.24 and δ_C = 77.00 ppm unless specified otherwise. Coupling constants are in Hz. Mass spectra were recorded on a VG 7070H spectrometer. IR spectra were taken on a Perkin-Elmer PE983 instrument. TLC was carried out using Merck aluminium sheet silica gel 60 F_{254} and visualised with 8% of vanillin in concentrated sulphuric acid. Column chromatography was carried out on Merck silica gel 60 (70–230 mesh).

syn- *and* anti-1-(4-tert-*Butylcyclohexylidene*)-4-tert-*butylcyclohexane* (**1** *and* **2**), *Cyclohexylidenecyclohexane* (**7**) *and Cyclopentylidenecyclopentane* (**8**).—Compounds **1** and **2** were prepared by Kellogg's method[24] and showed the following characteristics.

1. M.p. 131–133 °C (lit.,[24] 137–138.5 °C). δ_H 0.86 (18 H, s, 6 Me), 0.92 (4 H, dddd, *J* 13.14, 13.14, 13.14 and 3.15, 3,3′,5,5′-H_{eq}), 1.158 (2 H, tt, *J* 11.94, 3.15, 4,4′-H), 1.60 (4 H, t, *J* 13.74, 3,3′, 5,5′-H_{ax}), 1.81 (4 H, d, *J* 11.57, 2,2′,6,6′-H_{eq}), 2.74 (4 H, d, *J* 13.33, 2,2′,6,6′-H_{ax}); δ_C 27.65 (Me), 29.25, 29.77, 32.42 (quaternary C), 48.72, 128.98.

2. M.p. 174–176 °C (lit.,[24] 183–183.5 °C). δ_H 0.81 (18 H, s, 6 Me), 0.91 (4 H, dddd, *J* 12.36, 12.36, 12.36, 3.37, 3,3′,5,5′-H_{eq}), 1.15 (2 H, tt, *J* 11.86, 3.15, 4,4′-H), 1.62 (4 H, td, *J* 13.54, 2.47, 3,3′,5,5′-H_{ax}), 1.79 (4 H, d, *J* 11.86, 2,2′,6,6′-H_{eq}), 2.75 (4 H, d, *J* 13.42, 2,2′,6,6′-H_{ax}); δ_C 27.64 (Me), 28.91, 29.75, 32.46 (quaternary C), 48.59, 128.79.

7 was prepared by Turro's method.[25] M.p. 52 °C (lit.,[25] 53–54 °C). δ_H 1.51 (12 H, m), 2.20 (8 H, t, *J* 6.18); δ_C 28.31, 29.72, 30.10, 130.42.

8 was prepared by pyrolysis[26] of the orthoformate ester of (1-hydroxycyclopentyl)cyclopentan-1-ol[27] which showed δ_H 1.45–1.88 (16 H, complex) 1.94 (2 H, br, OH); δ_C 24.85, 36.41, 87.15. **8** showed b.p. 98 °C/28 mmHg (lit.,[26] 87 °C/23 mmHg); δ_H 1.64 (8 H, m), 2.11 (8 H, m); δ_C 26.97, 31.25, 132.33.

Photooxygenation of **1** *and* **2**.—A solution of **1** (200 mg, 0.72 mmol) and Rose Bengal (*ca.* 5–10 mg) in the appropriate solvent was stirred under an atmosphere of oxygen, with cooling, while being irradiated with a 400 W sodium lamp at a distance of 5 cm until 16 cm^3 of oxygen had been taken up (*ca.* 1 h). The solvent was evaporated at reduced pressure without heating. The ^1H NMR spectrum showed that the crude product consisted of 68% of the equatorial hydroperoxide (**3**) and 32% of the axial hydroperoxide (**4**) when pyridine was the solvent, and 59% of **3** and 41% of **4** when 1:1 methanol–benzene was the solvent. The mixture was separated chromatographically on silica gel using pentane–CH_2Cl_2 (1:1 v/v) as eluent to give, in sequence of elution, the following products.

4 (50 mg). M.p. 148–150 °C; δ_H 0.84 (9 H, s, 3 Me), 0.85 (9 H, s, 3 Me), 0.90–2.26 (16 H, complex, ring protons), 5.76 (1 H, quint, *J* 2.52, 2-H), 6.94 (1 H, s, OOH); δ_C 22.35, 22.46, 24.39, 25.43, 26.89, 27.16 (3C), 27.58 (3C), 31.44, 32.19, 32.42, 32.84, 44.00, 47.75, 84.15, 123.08, 140.10; *m/z* (70 eV) (rel. intensity) 309 (M^+ + 1), 275 (30), 57 (100); IR (Nujol) ν_{max}/cm^{-1} 3343 (OH str) (Found: C, 77.9; H, 11.7. $C_{20}H_{36}O_2$ requires C, 77.87; H, 11.76%).

3 (15 mg). M.p. 121–124 °C; δ_H (assigned by a 2D COSY experiment) 0.81 (9 H, s, 3 Me), 0.86 (9 H, s, 3 Me), 0.90–1.14 (4 H, complex, 3′,5′-H), 1.22 (1 H, m, 2′-H_{ax}), 1.32 (1 H, tt, *J* 13.48, 13.40, 4′-H), 1.44 (1 H, tt, *J* 13.19, 13.10, 4-H), 1.66 (2 H, m, 2′,6′-H_{eq}), 1.88 (3 H, m, 5,6′-H), 2.03 (1 H, dq, *J* 12.85, 3.65, 6-H_{eq}), 2.19 (2 H, m, 3-H), 2.38 (1 H, dq, *J* 13.16 and 3.15, 6-H_{ax}), 5.91 (1 H, dm *J* 5.33, 2-H), 6.83 1 H, s, OOH); δ_C 24.04, 24.45, 24.51, 25.20, 27.17 (3C), 27.28, 27.62 (3C), 31.56, 31.79, 32.22, 32.27, 43.93, 47.90, 86.23, 129.07, 133.57; *m/z* (70 eV) (rel. intensity) 308 ($M^{\cdot+}$), 275 (31), 57 (100); (Found: M^+, 308.1717. $C_{20}H_{36}O_2$ requires *M*, 308.2715). ν_{max}(Nujol)/cm^{-1} 3345 (OH str). Elution of the rest of the mixture gave impure **3** con-

taminated mainly with 4-*tert*-butyl-cyclohexanone, which may result from decomposition of **3** on silica gel.

The NMR spectra showed that **3** did not isomerize to **4**, or *vice versa*, when **3** or **4** along with the sensitizer in $CDCl_3$ were irradiated with light from the 400 W sodium lamp for 3 h.

The photoxygenation of **2** was carried out in the same way as described above. The product consisted of 44% of **3** and 56% of **4** when 1:1 methanol–benzene was the solvent.

The crude mixture was reduced with an excess (3 equivalents) of triphenylphosphine in ether. The solvent was removed and the residue was chromatographed using CH_2Cl_2–pentane (1:1 v/v) as eluent giving the following products.

6 (55 mg). M.p. 177–179 °C (lit.,[10] 180–183.5 °C). δ_H 0.84 (9 H, s, 3 Me), 0.85 (9 H, s, 3 Me), 0.92 (1 H, tt, *J* 11.85, 3.09), 1.09 (2 H, m), 1.20 (1 H, ddd, *J* 13.15, 5.12, 2.05), 1.32–1.66 (8 H, complex), 1.74–1.88 (2 H, m), 1.92–2.10 (2 H, m), 2.20 (1 H, dm, *J* 16.85, 2.55), 5.73 (1 H, m, *J* 2.59); δ_C 22.55, 22.68, 24.51, 25.74, 26.80, 27.19 (3C), 27.59 (3C), 32.18, 32.42, 36.29, 36.37, 44.07, 47.71, 72.76, 119.42, 144.28.

5 (20 mg). M.p. 159–161 °C (lit.,[10] 154–155 °C). δ_H 0.80 (9 H, s, 3 Me), 0.85 (9 H, s, 3 Me), 0.99–1.21 (4 H, m), 1.25 (1 H, s, OH), 1.32 (1 H, td, *J* 13.25, 3.16), 1.42 (1 H, td, *J* 13.20, 3.80), 1.63 (2 H, m), 1.76–1.95 (3 H, complex), 2.11 (2 H, dm, *J* 16.72, 3.65), 2.20 (1 H, dm, *J* 13.13, 3.02), 2.28 (1 H, dm, *J* 16.50, 2.03), 5.78 (1 H, m, *J* 2.81); δ_C 24.10, 24.59, 25.04, 25.17, 27.17 (3C), 27.55, 27.66 (3C), 32.20, 32.24, 36.39, 37.12, 43.90, 47.76, 73.79, 124.04, 138.24.

4-*Nitrobenzoate of* **6**.—A solution of **6** (0.15 g, 0.5 mmol) and of *p*-nitrobenzoyl chloride (0.25 g, 1.3 mmol) in pyridine (3 cm^3) was kept at *ca.* 40 °C overnight. The product was precipitated with saturated sodium hydrogen carbonate solution, then recrystallized from CH_2Cl_2–ethanol (1:5 v/v) to give C-4-tert-*butyl*-1-(4-tert-*butylcyclohex*-1-*enyl*)*cyclohexyl* 4-*nitrobenzoate* (150 mg, 68%). It melted at 145 °C and then solidified and remelted at 230 °C. δ_H 0.84 (18 H, s, 6 Me), 1.11 (2 H, m), 1.21–1.39 (3 H, complex), 1.55 (2 H, m), 1.72 (2 H, br d, *J* 12.93), 1.78–1.98 (3 H, m), 2.12 (2 H, dm, *J* 16.18, 1.80), 2.57 (2 H, tm, *J* 16.06, 2.32), 5.73 (1 H, m), 8.19 (2 H, d, *J* 9.04), 8.29 (2 H, d, *J* 9.04); δ_C 22.72, 22.75, 24.22 (2C), 25.48, 26.84, 27.12 (3C), 27.44 (3C), 32.17, 32.37, 34.40, 43.71, 47.11, 85.89, 121.91, 123.54, 130.42, 137.08, 139.36, 150.29, 162.77. ν_{max}(Nujol)/cm^{-1} 3030, 1712, 1673, 1607, 1527; *m/z* (70 eV) (rel. intensity) 274 (47, $M^{\cdot+}$ – $O_2NC_6H_4COOH$), 259 (10), 217 (55), 167 (35), 57 (100) (Found: C, 73.5; H, 8.9; N, 3.1. $C_{27}H_{39}NO_4$ requires C, 73.44; H, 8.90; N, 3.17%). When the compound was dissolved in CH_2Cl_2–ethanol (2:3 v/v) and the solution was allowed to stand at room temperature to evaporate the solvent at a slow rate, the desired single crystals for X-ray diffraction were obtained.

Autooxidation of **3** *and* **4**.—When **4** was kept in $CDCl_3$ for 72 h under air, ^1H NMR spectroscopy showed that the dihydroperoxides **9** (11%) and **10** (9%) were formed with the following characteristics: δ_H 4.76 (t, *J* 3.18, 6-H_{eq} of **10**), 4.84 (br m, 6-H_{ax} of **9**), 6.04 (d, *J* 4.75, 2-H of **9**), 6.08 (dm, *J* 6.12, 2-H of **10**). The process was inhibited by DBMP and accelerated by AIBN. When a solution of **4** and 10 mmol% of AIBN in $CDCl_3$ was kept at 45 °C for 2 days, the yields of **9** and **10** increased to 45 and 40%, respectively.

A preparative reaction was as follows. A tube containing **4** (100 mg, 0.32 mmol), and AIBN (5 mg) in 7 cm^3 of chloroform (dried over silica gel), and fitted with a balloon of oxygen, was kept at 40 °C for 2 days. Triphenylphosphine (250 mg, 0.95 mmol) was added and the mixture was shaken for 5 min. The solvent was removed by evaporation. The residue was chromatographed at first with CH_2Cl_2–pentane (1:1 v/v) as eluent giving (±)- and *meso*-bi-4-*tert*-butylcyclohexenyl (**11**) (8 mg, 9%), m.p. 149–154 °C (lit., 153 °C[28a] and 140–148 °C[28b]). δ_H 0.85 (18 H, s, 6 Me), 1.12–1.23 (4 H, complex), 1.86 (4 H, m), 2.11 (4 H, m), 2.34 (2 H, tm, *J* 16.50, 2.75), 5.75 (2 H, br t, *J* 5.50); δ_C 24.34, 24.41, 26.90, 27.13 (3C), 27.19 (3C), 32.15, 44.10, 121.50, 121.87, 136.23 and 136.43.

The column was then eluted with CH_2Cl_2–pentane–diethyl ether (1:1:1 v/v) until no spot could be detected by TLC. The resulting fractions were combined and the solvent was removed. The residue was separated on a column with CH_2Cl_2–pentane–diethyl ether (5:5:1 v/v) as eluent giving the diol c-5-tert-*butyl*-2(t-4-tert-*butyl*-1-*hydroxycyclohexan*-r-1-*yl*)*cyclohex*-2-*en*-r-1-*ol* (**12**) (35 mg), which was recrystallized from CH_2Cl_2; m.p. 192–195 °C, δ_H 0.846 (9 H, s, 3 Me), 0.851 (9 H, s, 3 Me), 0.95 (1 H, m), 1.26 (2 H, m), 1.39 (3 H, m), 1.50–1.63 (4 H, complex), 1.89 (2 H, m), 1.893–2.15 (3 H, complex), 2.66 (1 H, br, OH), 3.63 (1 H, br, OH), 4.61 (1 H, m, 6-H_a), 5.68 (1 H, dt, *J* 5.83, 1.62, 2-H); δ_C 22.35, 22.50, 27.00 (3C), 27.57 (3C), 32.01, 32.42, 35.12, 37.19, 37.62, 42.75, 47.73, 70.50, 74.05, 123.58, 144.16; ν_{max}(Nujol)/cm^{-1} 3232 (OH str) (Found: C, 77.8; H, 12.0. $C_{20}H_{36}O_2$ requires C, 77.87; H, 11.74%).

A second fraction (25 mg) was collected which consisted of a mixture of **12** and t-5-tert-*butyl*-2(t-4-tert-*butyl*-1-*hydroxycyclohexan*-r-1-*yl*)*cyclohex*-2-*en*-r-1-*ol* (**13**) in a ratio of 2:3. **13** showed the following characteristics: δ_H 2.32 (1 H, br, OH), 2.70 (1 H, br, OH) 4.53 (1 H, m, 6-H_{eq}), 5.79 (1 H, dd, *J* 5.62, 2.25, 2-H); δ_C 64.52 (1′-C), 73.82 (6-C), 124.75 (2-C), 143.76 (1-C). For this mixture: Found: C, 77.75, H, 11.96. $C_{20}H_{36}O_2$ requires C, 77.87; H, 11.74%.

The corresponding dihydroperoxides **14** and **15** showed δ_H 4.62 (m, 6-H_{ax} of **14**), 4.67 (t, *J* 2.60, 6-H_{eq} of **15**), 623 (d, *J* 5.05, 2-H of **15**), 6.24 (d, *J* 5.27, 2-H of **14**).

Benzyltrimethylammonium Periodate.—Periodic acid (11.4 g, 0.05 mol) in 20 cm^3 of water was added in portions to cold 40% benzyltrimethylammonium hydroxide (21 cm^3, 0.05 mol). The mixture was then allowed to stand in ice for 1 h. The precipitate which formed was filtered off and washed with a small amount of cold methanol and dried to give benzyltrimethylammonium periodate (16 g, 94%), m.p. 131–133 °C, δ_H (DMSO, TMS), 3.02 (9 H, s, 3 Me), 4.51 (2 H, s, CH_2), 7.53 (5 H, br, Ph); δ_C (DMSO, TMS), 51.76 (CH_3), 67.87 (CH_2), 128.34, 128.88 (2C), 130.26, 132.72 (2C).

9,10-(N-*Formylnitroso*)-9,10-*dimethylanthracene* (**18**).[6c]—A solution of formohydroxamic acid[29] (0.65 g, 10 mmol) in DMF (5 cm^3) was added dropwise at room temperature to a solution of dimethylanthracene[30] (1 g, 4.8 mmol) and of benzyltrimethylammonium periodate (3.45 g, 10 mmol) in a mixture of CH_2Cl_2 (10 cm^3) and DMF (10 cm^3). During the addition, an increase in temperature was observed, which was moderated by water cooling. After the addition the solution was stirred for 30 min, then poured onto ice (10 g), when the solution developed a dark brown colour. CH_2Cl_2 (10 cm^3) was added, followed by sufficient aqueous sodium metabisulphite (20%) dropwise at 0 °C until the solution became clear. The oily phase was separated and the aqueous phase was extracted 5 or 6 times with CH_2Cl_2, then washed with saturated sodium hydrogen carbonate solution and with water. The resulting solution was concentrated down to 5–10 cm^3 at room temperature, then ether (15 cm^3) was added. The precipitate which formed was filtered off and washed with cold ether to give **18** (0.8–0.9 g, 63–79% based on DMA) as slightly yellow needles, m.p. 193 °C (decomp.). The ^1H and ^{13}C NMR spectra were the same as reported in the literature.[6c]

In our hands, this method gave a better yield than Ensley's method, where only DMF is used in the first stage of the reaction, and ammonia rather than dimethylamine is used in the second.

9,10-*Nitroso*-9,10-*dimethylanthracene* (**19**).[6b]—A 33% solution of dimethylamine in ethanol (10 cm^3) was added dropwise in the dark to a suspension of **18** (1 g) in CH_2Cl_2 (10 cm^3) and ethanol (10 cm^3) under argon at room temperature. The mixture was stirred until all the suspension had dissolved (3–5 h). The solvent was removed at room temperature to give **19** in almost quantitative yield; it contained a small amount of DMF which can be removed under reduced pressure, but the crude product was used directly for generating HNO.

The crude material was dissolved in CH_2Cl_2 (3 cm^3), precipitated with methanol (5 cm^3), and washed with cold methanol. It melted at 120–130 °C (decomp.) then resolidified and remelted at 175–180 °C. The ^1H and ^{13}C NMR spectra were consistent with those in the literature.[6b] The compound is sensitive to air and light, and it decomposed when a solution in $CDCl_3$ at room temperature was kept in the light of the laboratory for 3 h, or in the dark for 3 days.

Reactions of **18** *with Alkenes.*—The general procedure was as follows. A mixture of the alkene and **18** (1.5:1 mol) in toluene (15 cm^3) was kept at 110–120 °C until all the suspended material dissolved. The solvent was removed at room temperature and the residue was examined by NMR, then the crude products were separated chromatographically on silica gel at first with pentane–CH_2Cl_2 (1:1 v/v) to remove dimethylanthracene and unreacted alkenes, then using pentane–CH_2Cl_2–diethyl ether (4:1:1 v/v) to collect the products.

The reaction of **18** with **1** gave 62% of t-N-[4-tert-*butyl*-1-(4-tert-*butylcyclohex*-1-*enyl*)*cyclohexyl*]-N-*formylhydroxylamine* (**20**) and c-N-[4-tert-*butyl*-1-(4-tert-*butylcyclohex*-1-*enyl*)*cyclohexyl*]-N-*formylhydroxylamine* (**21**) in a ratio of 1:3, while the reaction of **18** with **2** gave 65% of **20** and **21** in a ratio of 1:1. The reaction of **18** and **8** gave N-(1-*cyclopent*-1-*enylcyclopentyl*)-N-*formylhydroxylamine* (**24**) in 82% yield.

These compounds had the following characteristics.

20: M.p. 182–185 °C. δ_H 0.81 (9 H, s, 3 Me), 0.86 (9 H, s, 3 Me), 0.98–1.28 (6 H, complex), 1.64 (2 H, m), 1.87 (4 H, m), 2.02 (1 H, m), 2.10–2.30 (3 H, complex), 5.97 (1 H, m, 2-H), 8.01 (1 H, s, HC=O), 8.20 (1 H, br, OH); δ_C 23.03, 23.44, 24.02, 24.33, 25.55, 27.10 (3C), 27.48 (3C), 31.07, 32.18, 32.27, 32.29, 43.69, 47.31, 66.61, 130.46, 131.44, 153.84; ν_{max}(Nujol) 3412, 1651, 1194, 1054, 863; *m/z* (FAB, NaI) (rel. intensity) 358 (50, M + Na^{+}) 275 (12), 84 (100).

21: M.p. 174–176 °C. δ_H 0.82 (9 H, s, 3 Me), 0.83 (9 H, s, 3 Me), 1.00–1.25 (5 H, complex), 1.52–1.71 (4 H, complex), 1.72–1.90 (3 H, m), 2.03 (2 H, m), 2.28 (1 H, dm, *J* 14.82, 3.09), 2.35 (1 H, dm, *J* 14.82, 2.87), 5.63 (1 H, m, 2-H), 8.5 (1 H, br, OH), 8.16 (1 H, s, HC=O); δ_C 22.47, 22.60, 24.29, 25.45, 26.89, 27.12 (3C), 27.45 (3C), 32.13 (quaternary C), 32.38, 32.44, 43.71, 47.52, 66.10, 122.68, 139.38, 155.46. IR similar to **20** (Found: C, 75.2; H, 11.4; N, 3.9. $C_{21}H_{37}NO_2$ requires C, 75.17; H, 11.11; N, 4.17%). Single crystals were obtained by recrystallization from CH_2Cl_2–pentane (1:5 v/v).

24: M.p. 77–79 °C. δ_H 1.72 (4 H, m), 1.83–1.99 (4 H, complex) 2.16 (2 H, m), 2.24 (2 H, m), 2.34 (2 H, m), 5.67 (1 H, quart, *J* 2.31, 2-H), 8.06 (1 H, s, HC=O), 8.23 (1 H, br, OH); δ_C 22.48 (2C), 23.39, 31.68, 32.49, 34.52 (2C), 71.67, 127.95 (C-2), 143.77 (C-1), 154.64 (C=O); ν_{max}(Nujol) 3380, 2954, 1627, 1515 (Found: C, 67.6; H, 8.7; N, 7.1).

Reaction of **19** *with Alkenes.*—The procedure was the same as described above except that benzene was used as solvent and the temperature was below 65 °C. Reactions of both **1** and **2** with **19** gave the two isomers t-N-[4-tert-*butyl*-1-(4-tert-*butylcyclohex*-1-*enyl*)*cyclohexyl*]*hydroxylamine* (**22**) and c-N-[4-tert-*butyl*-1-(4-tert-*butylcyclohex*-1-*enyl*)*cyclohexyl*]*hydroxylamine* (**23**), in a yield of 72% in a ratio of 1:9 in the first case, and a yield of 60% in a ratio of 1:10 in the second.

The major isomer (**23**) was isolated with the following characteristics: m.p. 159–160 °C. δ_H 0.84 (9 H, s, 3 Me), 0.845 (9 H, s), 0.94 (1 H, m), 1.11 (1 H, tt, *J* 12.29, 12.13), 1.19–1.40 (5 H, complex), 1.57 (2 H, m), 1.80–2.07 (5 H, complex), 2.09 (1 H, dm, *J* 14.50), 2.18 (1 H, dm, *J* 14.50), 4.15 (1 H, br, OH), 5.10 (1 H, br, NH), 5.68 (1 H, quint, *J* 2.53, 2-H); two sharp signals at δ 5.12 and 6.15 for the NH and OH groups can be seen with a solution in DMSO. δ_C 22.52, 22.54, 24.59, 25.20, 27.07 (3C), 27.17 (3C), 27.58, 31.46, 32.06, 32.19, 32.39, 44.06, 48.05, 60.94, 122.44, 140.81; *m/z* (70 eV) (rel. intensity) 289 (4, $M^{\cdot+}$ − 18), 274 (19), 192 (90.8), 57 (100); ν_{max}(Nujol) 3359, 3279 (NH and OH str) (Found: C, 78.2; H, 12.25; N, 4.5. $C_{20}H_{37}NO$ requires C, 78.14; H, 12.13; N, 4.50%). Both reactions were monitored by NMR spectroscopy in C_6D_6 at 65 °C. No epimerization was observed during the course of the reaction.

The reaction of **19** with **8** gave N-(1-*cyclopent*-1′-*enylcyclopentyl*)*hydroxylamine* (**25**) in 85% yield, m.p. 58–60 °C. δ_H 1.55–1.58 (10 H, m), 1.86 (2 H, quint, *J* 7.16), 2.31 (4 H, m), 5.56 (1 H, m, 2-H), 5.58 (2 H, br, OH + NH). Two broad peaks at δ 6.58 and 6.83 for OH and NH groups could be observed when the spectrum was recorded in DMSO solvent. δ_C 23.51, 24.35, 32.01, 32.46, 34.18 (2C), 70.24, 125.30, 147.37; *m/z* (70 eV) (rel. intensity), 167 (7, $M^{\cdot+}$), 135 (100); (Found: M^+, 167.1309. $C_{10}H_{17}NO$ requires *M*, 167.1305). ν_{max}(Nujol)/cm^{-1} 3253, 3132 (NH and OH str). The compound was unchanged when a solution in $CDCl_3$ was kept at room temperature for one week, or when a solution containing 10 mol% of AIBN was kept at 55 °C for 1 h.

Cholesterol, cholest-5-en-3-one, and 1,2,3,4,5,6,7,8-octahydronaphthalene could not be induced to form adducts with **18** and **19**.

Reactions of 4-*Phenyl*-1,2,4-*triazoline*-2,5-*dione with Alkenes.*—A solution of **1** (0.46 g, 1.7 mmol) and PTAD (0.30 g, 1.7 mmol) in CH_2Cl_2 (15 cm^3) was refluxed under argon for 30 min. The solvent was removed giving the adducts t-1-[4-tert-*butyl*-1-(4-tert-*butylcyclohex*-1-*enyl*)*cyclohexyl*]-4-*phenyl*-1,2-*dihydro*-1,2,4-*triazole*-3,5-*dione* (**26**) and c-1-[4--tert-*butyl*-1-(4-tert-*butylcyclohex*-1-*enyl*)*cyclohexyl*]-4-*phenyl*-1,2-*dihydro*-1,2,4-*triazole*-3,5-*dione* (**27**) in quantitative yield in a ratio of 1:5 (NMR spectroscopy). The products were separated on silica gel using CH_2Cl_2–pentane–diethyl ether (3:6:1 v/v) to give **26** and **27** with the following characteristics.

27: M.p. 194–196 °C. δ_H 0.82 (9 H, s, 3 Me), 0.84 (9 H, 3 Me), 1.00–1.95 (12 H, complex), 2.06 (1 H, dm, *J* 17.63, 2.53), 2.18 (1 H, dm, *J* 17.53, 2.31), 2.60 (1 H, d, *J* 13.69), 2.74 (1 H, d, *J* 13.70), 5.61 (1 H, m, *J* 2.60), 7.34 (1 H, tt, *J* 8.33, 1.85), 7.44 (2 H, td, *J* 8.25, 7.34), 7.52 (2 H, dt, *J* 8.20, 1.80), 8.67 (1 H, br, NH); δ_C 23.37, 23.44, 24.28, 25.94, 26.91, 27.11 (3C), 27.51 (3C), 32.12, 32.40, 33.68, 33.92, 43.64, 47.65, 67.18, 123.00, 125.56 (2C), 127.93, 128.89 (2C), 131.46, 139,33, 151.53, 153.41; ν_{max}(Nujol)/cm^{-1} 3388, 3158, 1762, 1696 (Found: C, 74.8; H, 9.4; N, 9.3. $C_{28}H_{41}N_3O$ requires C, 74.46; H, 9.15; N, 9.30%).

26: M.p. 202–204 °C. δ_H 0.80 (9 H, s, 3 Me), 0.814 (9 H, s, 3 Me), 0.90–1.24 (5 H, complex), 1.65 (2 H, m), 1.87 (4 H, m), 2.16 (2 H, m), 2.32 (2 H, m), 2.415 (1 H, dd, *J* 13.19, 3.09), 2.57 (1 H, dd, *J* 13.20, 2.59), 5.94 (1 H, m, *J* 2.24), 7.33 (1 H, tt, *J* 7.33, 1.86), 7.44 (2 H, td, *J* 8.25, 7.35), 7.52 (2 H, dt, *J* 8.20, 1.80), 8.50 (1 H, br, NH); ^{13}C NMR as for **27** to δ 67.17, then 125.89 (2C), 128.04, 128.97 (2C), 129.99, 131.36, 132.42, 151.25, 152.50; IR similar to **27**; *m/z* (70 eV) (rel. intensity), 452 (5, $M^{\cdot+}$ + 1), 275 (24), 178 (23), 57 (100).

The reaction of **2** with PTAD was carried out in an NMR tube, and gave **26** and **27** in quantitative yield in a ratio of 1:4.

Cyclopentylidenecyclopentane (**8**) is more reactive than **1** and **2**, and immediately bleached the red colour of PTAD at room temperature when **8** (0.39 g, 2.85 mmol) in CH_2Cl_2

(10 cm^3) was added to a solution of PTAD (0.5 g, 2.85 mmol) in CH_2Cl_2 (10 cm^3), giving 1-(1-*cyclopent*-1-*enylcyclopentyl*)-4-*phenyl*-1,2-*dihydro*-1,2,4-*triazole*-3,5-*dione* **28** in quantitative yield. The product was recrystallized from pentane–CH_2Cl_2 (5:1 v/v), m.p. 147–149 °C. δ_H 1.68 (2 H, m), 1.80 (2 H, m), 1.85 (2 H, t, *J* 7.42), 2.05 (2 H, m), 2.31 (4 H, m), 2.40 (2 H, m), 5.62 (1 H, m), 7.34 (1 H, tt, *J* 7.18, 1.56), 7.45 (4 H, m), 8.90 (1 H, s, NH); δ_C 22.84 (2C), 23.40, 32.26, 32.31, 35.59 (2C), 72.00, 125.64 (2C), 127.82, 128.02 (C-2), 128.95 (2C), 131.37, 143.65 (C-1), 151.84 (C=O), 153.34 (C=O); *m/z* (70 eV) (rel. intensity) 312 (5, $M^{\cdot+}$ + 1), 178 (60), 135 (100). (Found: C, 69.4; H, 6.8; N, 13.6. $C_{18}H_{21}N_3O$ requires C, 69.43; H, 6.80; N, 13.55%).

Reactions of Diethyl Azodicarboxylate with Alkenes.—A mixture of **1** (0.4 g, 1.5 mmol) and DEAD (0.36 g, 2.0 mmol) in CH_2Cl_2 (10 cm^3) was refluxed under argon for 8 h. Then the solvent was removed by evaporation to give *diethyl* t-1-[4-tert-*butyl*-1-(4-tert-*butylcyclohex*-1-*enyl*)*cyclohexyl*]*hydrazine*-1,2-*dicarboxylate* (**29**) and *diethyl* c-1-[4-tert-*butyl*-1-(4-tert-*butyl*-*cyclohex*-1-*enyl*)*cyclohydrazine*-1,2-*dicarboxylate* (**30**) in 89% yield in a ratio of 3.5:1 (NMR spectroscopy). The products were separated on silica gel using pentane–CH_2Cl_2–diethyl ether (3:1:1 v/v) as follows.

29 (0.49 g, 75%) was recrystallized three times from methanol; m.p. 105–106 °C. δ_H 0.78 (9 H, s, 3 Me), 0.85 (9 H, d, *J* 1.20, 3 Me), 0.90–1.14 (9 H, complex), 1.19 (3 H, tt, *J* 7.12, 7.12, Me), 1.24 (3 H, tt, *J* 7.18, 7.18, Me), 1.48–2.28 (20 H, complex), 2.35 (1 H, dm, *J* 13.70, 2.87), 2.53 (1 H, d, *J* 12.30), 2.86 (1 H, dm, *J* 13.63, 2.40), 3.98–4.21 (4 H, complex, CH_2), 5.75 (1 H, m, 2-H), 6.18 and 6.25 (1 H, br, NH) (see Fig. 3). At 50 °C, the two signals at 6.18 and 6.25 became closer together [Fig. 3(*b*)], but otherwise the spectrum did not change. δ_C 23.53, 24.06, 24.33, 24.56, 24.64, 26.25, 26.32, 27.22 (3C), 27.29, 27.44, 27.54 (3C), 32.25, 32.27, 32.61, 32.72, 32.90, 33.12, 43.99, 44.06, 47.38, 47.42, 47.49, 61.70, 61.76, 67.85, 68,54, 126.66, 127.00, 133.45, 134.43, 155,73, 155.93, 156.82, 156.94; ν_{max}(Nujol)/cm^{-1} 3346 (NH str), 1742, 1701 (C=O) (Found: C, 69.6; H, 10.4; N, 6.3. $C_{26}H_{46}N_2O_4$ requires C, 69.29; H, 10.29; N, 6.22%).

30 (10 mg; contaminated with small quantity of DEAD). δ_H 0.825 (9 H, s, 3 Me), 0.828 (9 H, s, 3 Me), 1.20 (3 H, tt, *J* 7.02, 7.02, Me), 1.25 (3 H, tt, *J* 7.05, Me), 4.01–4.25 (4 H, complex, CH_2), 5.51 (1 H, m, 2-H), 5.87 and 6.04 (1 H, 2 br, NH) (see Fig. 3*a*).

The reaction of **2** with DEAD was carried out in $CDCl_3$ in an NMR tube for 2 days, and with the above data, the products were identified as **29** and **30** in a ratio of 1:2.7.

The reactions of **7** and **8** with DEAD were carried out in the same way as described above, giving the following products.

31 [8d,31] (viscous oil, 90% yield). δ_H 1.16 (3 H, two interlaced t, *J* 7.05, in a ratio of 3:1), 1.21 (3 H, two interlaced t, *J* 7.05, in a ratio of 3:1), 1.21 (3 H, two interlaced t, *J* 7.05, in a ratio of 3:1), 1.30–2.28 (18 H, complex), 3.99–4.21 (4 H, complex), 5.62 (1 H, m, vinyl) 6.01 and 6.21 (1 H, 2 br, NH, in a ratio of 3:1); δ_C 14.35 (Me), 14.47 (Me), 22.05, 22.56, 22.90, 23.09, 24.53, 25.44, 25.79, 33.10, 33.27, 61.57, 61.70, 68.39, 123.87, 137.32, 156.25 and 157.29 (lower intensity), 156.32 and 156.65 (higher intensity).

Diethyl 1-(1-*cyclopent*-1-*enylcyclopentyl*)*hydrazine*-1,2-*dicarboxylate* (**32**) (viscous oil, 95% yield). δ_H 1.20 (3 H, two interlaced t, *J* 7.05, in a ratio of 4:1), 1.25 (3 H, two interlaced t, *J* 7.05, in a ratio of 4:1), 1.60 (2 H, m), 1.82 (4 H, m), 1.95 (2 H, m), 2.25 (6 H, m), 4.05–4.25 (4 H, complex, CH_2), 5.45 (1 H, m, 2-H), 6.14 and 6.34 (1 H, 2 br, NH, in a ratio of 4:1); δ_C 14.41 (Me), 14.47 (Me), 22.23, 23.21, 23.63, 32.12, 32.33, 36.26, 36.82, 61.88, 61.97, 72.52, 120.10, 145.94, 156.00, 157.17; ν_{max}(neat)/cm^{-1} 3286, 2952, 2865, 2865, 1752, 1711; *m/z* (70 eV) (rel. intensity) 311 (4, $M^{\cdot+}$ + 1), 177 (25), 135 (100). (Found: M^+, 311.1956. $C_{16}H_{26}N_2O_4$ + 1 requires *M*, 311.1962).

The Ethylaluminium Dichloride Catalysed Reactions of Methyl Propiolate with Alkenes.—These reactions were carried out by Snider's method.[9a,b] A typical procedure is as follows. A 1 mol dm^{-3} solution of ethylaluminium dichloride in hexane (2.0 cm^3) was syringed dropwise under argon into a solution of MPP (0.17 g, 1.0 mmol) in CH_2Cl_2 (7 cm^3) at room temperature. The mixture was stirred for 30 min, then a solution of **1** (0.4 g, 1.5 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise at room temperature. After 3 days, no starting alkene could be deleted by TLC. The solvent was removed by evaporation and the residue was chromatographed on silica gel using pentane–diethyl ether (10:1 v/v) as eluent giving a mixture of isomers of **34**, **35**, **36** and **37** in 89% yield in a ratio of 38:34:17:11. Their ^1H NMR and ^{13}C NMR characteristics are shown in Figs. 4 and 5, and Table 5. The mixture of isomers melted at 90–105 °C. ν_{max}(Nujol)/cm^{-1} 1724, 1638 (Found: C, 79.6; H, 11.1. $C_{20}H_{40}O_2$ requires C, 79.94; H, 11.18%).

The reaction of MPP with **2** after 3 days gave **34**, **35**, **38** and **39** in a yield of 85% and in a ratio of 50:25:20:5. Their ^1H and ^{13}C NMR characteristics are shown in Figs. 4 and 5, and Table 5. The mixture of isomers melted largely at 85–90 °C and finally at 115 °C. The IR spectrum was similar to that of the mixed isomers from the reaction of MPP with **1**. (Found: C, 79.8; H, 11.2. $C_{20}H_{40}O_2$ requires C, 79.94; H, 11.18%).

The reaction of MPP with **7** after 2 days gave (E)-*methyl* 3-[1-(*cyclohex*-1-*enyl*)*cyclohexyl*]*propenoate* (**40**) and *methyl dispiro*-[5.0.5.2]*tetradec*-13-*ene*-13-*carboxylate* (**41**) in 90% yield in a ratio of 66:33 with the following characteristics.

40 (viscous oil). δ_H 1.40–1.55 (14 H, complex), 1.80 (2 H, m), 2.04 (2 H, m), 3.70 (3 H, s, OMe), 5.58 (1 H, septet, *J* 1.63, ring vinyl), 5.67 (1 H, d, *J* 16.00, CH=), 6.73 (1 H, d, *J* 16.00, CH=); δ_C 22.20 (2C), 22.32, 23.25, 24.60, 25.78, 26.11, 33.52 (2C), 45.57, 51.35 (OMe), 118.33, 123.17, 138,52, 157.02, 167.67; *m/z* (70 eV) (rel. intensity), 248 (30, $M^{\cdot+}$), 216 (32), 189 (100); ν_{max}(neat)/cm^{-1} 2925, 2852, 1722, 1638 (Found: M^+, 248.1775. $C_{16}H_{24}O_2$ requires *M*, 248.1770).

41 (viscous oil). δ_H 1.35 (12 H, m), 1.58 (8 H, m), 3.68 (3 H, s, OMe), 7.13 (1 H, s, vinyl); δ_C 24.00 (2C), 24.28 (2C), 25.92, 26.38, 30.77 (2C), 31.97 (2C), 50.86 (OMe), 52.50, 53.00, 144.30, 151.20, 163.32; *m/z* (70 eV) (rel. intensity) 248 (40, $M^{\cdot+}$), 216 (55), 189 (50), 41 (100); ν_{max}(neat)/cm^{-1} 2950, 2866, 1724, 1644 (Found: M^+, 248.1776. $C_{16}H_{24}O_2$ requires *M*, 248.1770.

The reaction of MPP with **8** after 1 day gave exclusively the ene product (E)-*methyl* 3-[1-(*cyclopent*-1-*enyl*)*cyclopentyl*]*propenoate* (**42**) (95%) as an oil. δ_H 1.58–1.71 (6 H, complex), 1.76 (2 H, m), 1.81 (2 H, quint, *J* 7.60), 2.19 (2 H, tq, *J* 7.60, 1.90), 2.29 (2 H, tq, *J* 7.60, 1.90), 3.70 (3 H, s, OMe), 5.44 (1 H, quint, *J* 1.90, ring vinyl), 5.70 (1 H, d, *J* 15.75), 6.92 (1 H, d, *J* 15.75, vinyl); δ_C 23.28 (2C), 23.60, 32.33, 32.45, 35.98 (2C), 51.39, 51.45, 117.93, 124.92, 146.78, 155.27, 167.51; *m/z* (70 eV) (rel. intensity) 220 (23, $M^{\cdot+}$), 205 (2), 189 (13), 161 (100); ν_{max}(neat)/cm^{-1} 2950, 2866, 1724, 1644, 1423, 1310 (Found: M^+, 220.1456. $C_{14}H_{20}O_2$ requires *M*, 220.1458.)

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