

# Photochemical [2+2] Cycloadditions. III. Addition of 4-Substituted 2-Cyclopentenones to Allene; Configuration Determination by Lanthanide-Induced Shift Studies

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Photoaddition of 4-substituted 2-cyclopentenones to 1,2-propadiene gave mixtures of the head-to-head and head-to-tail cycloadducts in a ratio of ca. 90:10. The stereoisomeric composition was sensitive to solvent changes, as was the chemical yield of the cycloadducts. Under otherwise identical conditions the highest yields were obtained in non-polar solvents. The configurations of the cycloadducts were determined by LIS and <sup>13</sup>C NMR studies.

Light-induced cycloadditions of 2-cycloalkenones to 1,2-propadiene (allene) often take place with a high degree of regioselectivity. Generally, the head-to-head (HH) regioisomers are formed in considerably higher yields than the head-to-tail (HT) isomers,<sup>1-3</sup> and in some cases the HH adduct is in fact the only product.<sup>4-7</sup> However, the stereochemical outcome of enone–allene photoadditions has barely been looked into; the only contribution of any significance is that of de Mayo *et al.*,<sup>8</sup> who mainly studied the addition of allene to some steroidal enones and discovered that the reaction occurred predominantly (~9:1) from the less hindered  $\alpha$  side in solution. We therefore became interested in studying stereochemical aspects of the photocycloaddition of smaller, conjugated enones to allene; our results involving 2-cyclopentenones with an oxygen-containing substituent attached to C-4 are reported here.

## Results

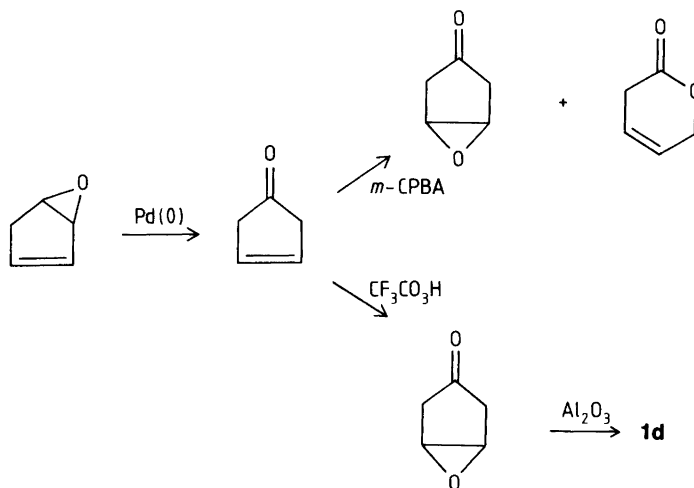
*Photochemical studies.* The conjugated enones employed (**1**) were synthesized from cyclopenta-

diene according to literature procedures. All the enones, but particularly 4-cumyloxy-2-cyclopentenone (**1b**), had to undergo thorough chromatographic purification to achieve a degree of purity (>97%) sufficient for our purpose. It should also be mentioned that the chemoselectivity of the oxidation step in Noyori's synthesis of 4-hydroxy-2-cyclopentenone (**1d**)<sup>9</sup> turned out to be sensitive to the peracid used. Using *m*-chloroperbenzoic acid instead of CF<sub>3</sub>COOOH, 3,6-dihydro-2*H*-pyran-2-one is formed in 38% yield in addition to 6-oxabicyclo[3.1.0]hexan-3-one (Scheme 1).

All the photolyses were carried out by irradiating degassed solutions, kept under nitrogen at –40 to –50 °C, with Pyrex-filtered light ( $\lambda > 300$  nm) from a medium-pressure mercury lamp. The solutions were 0.033 M in **1** and approximately 0.30 M in allene. The large excess of allene suppressed completely the dimerization of the enone,<sup>10</sup> and by employing Pyrex-filtered light photochemical transformations of allene were avoided.<sup>11</sup>

When hexane solutions of **1a** and allene were photolyzed, three products were obtained in a 5:57:38 ratio (Table 1). On the basis of spectroscopic evidence as well as elemental composition,

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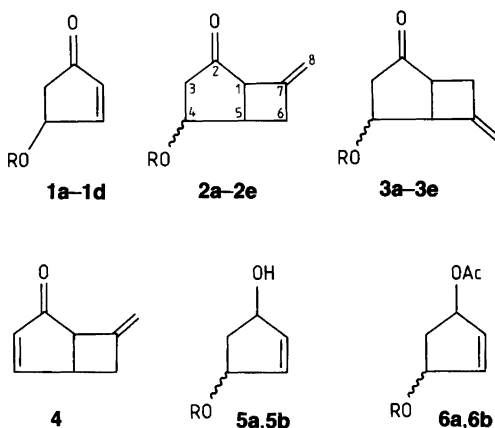


all products were determined to be [2+2] cycloadducts of **1a**. The two major products were the *endo* and *exo* isomers of 4-*tert*-butoxy-7-methylenebicyclo[3.2.0]heptan-2-one (**2a**), demonstrated by (among several pieces of evidence) the presence of multiplets at 3.38 and 3.48 ppm in the  $^1\text{H}$  NMR spectrum.<sup>8</sup> The configuration of the more abundant isomer could not be deduced with certainty from the physical data for **2a** alone. However, by comparing the  $^{13}\text{C}$  NMR spectra of the isomers with those of *endo*- and *exo*-**2d** (Table 2) it is safe to conclude that **2a** is formed predominantly in the *endo* configuration when the photolysis is carried out in hexane. The

third product was assigned the structure 4-*tert*-butoxy-6-methylenebicyclo[3.2.0]heptan-2-one (**3a**), mainly on the basis of its mass spectrum which exhibited the same major peaks as the mass spectra of *exo*- and *endo*-**2a**.

Mixtures of **1a** and allene were also irradiated in acetonitrile and on silica gel. Under both conditions, but particularly in the absence of solvent, the total rate of cycloaddition dropped, as did the **2a/3a** and the *endo*-**2a/exo**-**2a** ratios (Table 1).

The photoaddition of the other cyclopentenones (**1b–1d**) to allene proceeded in much the same manner as the addition of **1a**. All the IR, NMR and MS data were compatible with the cycloadduct structures *endo*-**2**, *exo*-**2** and **3**, but from the data it was impossible to determine the configuration of the HH isomers. This ambiguity was removed by a combination of lanthanide-induced shift (LIS) studies (*vide infra*) and  $^{13}\text{C}$  NMR spectroscopy. The LIS studies were carried out with the predominant isomer of **2d**, which was most conveniently obtained by selective desilylation of the isomer of **2c** formed in lower yield in acetonitrile. The studies revealed that this isomer of **2d** had the *endo* configuration and, consequently, that *exo*-**2c** predominated when **1c** underwent photochemical addition to allene. With these results available it was clear that the parts of the  $^{13}\text{C}$  NMR spectra due to the ring structures of *endo*-**2c** and *endo*-**2d** were almost identical, and likewise, that the same was the case for the  $^{13}\text{C}$  spectra of the corresponding *exo* isomers (Table 2). This is of course not surpris-



**a** R = *t*-Bu; **b** R = PhMe<sub>2</sub>C; **c** R = *t*-BuMe<sub>2</sub>Si;  
**d** R = H; **e** R = Me<sub>3</sub>Si

Table 1. Yields of cycloadducts, formed by irradiating enone **1** and allene for 0.5 h, according to uncalibrated GC analysis.

Enone	Solvent	2:3	endo-2:exo-2	Yield %
<b>1a</b>	Hexane	95: 5	59:41	76
	Acetonitrile	89:11	38:62	58
	Silica gel	80:20	34:66	3 <sup>a</sup>
<b>1b</b>	Hexane	96: 4	56:44	65
	Acetonitrile	90:10	47:53	33
<b>1c</b>	Hexane	95: 5	50:50	77
	Ether	92: 8	43:57	85
	Ethyl acetate	90:10	39:61	60
	Ethanol	90:10	44:56	33
<b>1d</b>	Acetonitrile	87:13	35:65	31
	Hexane	87:13	63:37	27
	Ethanol	92: 8	57:43	54
	Acetonitrile	90:10	62:38	45

<sup>a</sup>Irradiation time: 2 h.

ing, since the bicyclic moiety is identical for each isomer pair. The very close similarity observed in the chemical shifts provides strong evidence that conclusions can be reached with respect to isomer configuration by comparing <sup>13</sup>C NMR spectra.

Many unsuccessful experiments, including preparative TLC, column chromatography and circular thin-layer chromatography, were carried out in an attempt to obtain pure samples of the individual cycloadducts. In all cases the separation was inadequate. Particularly discouraging results were experienced when reaction mixtures from **1b** and **1d** were used. Mixtures of **2b** and **3b** suffered significant deprotection which resulted

in formation of **2d** and **3d**; this might be expected considering the lability of the cumyloxy moiety. When mixtures of **2d** and **3d** were employed, extensive loss of material took place. Some of the material is conceivably attached strongly to the stationary phase and lost as such; however, most of the loss is probably due to decomposition, since **2d** and **3d** turned out to be fairly unstable when stored.

The silylation/desilylation experiments performed also deserve some comments. Trimethylsilylation of **2d**, which was carried out to determine the *endo/exo* ratio of the alcohol, took place smoothly, whereas *tert*-butyldimethylsilylation of

Table 2. <sup>13</sup>C NMR chemical shifts of the carbon atoms in *endo-2* and *exo-2*.<sup>a</sup>

Isomer	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	R
<i>endo-2a</i>	58.1	212.2	43.2	69.0	36.5	29.6	142.6	109.3	28.4, 73.7
<i>exo-2a</i>	56.1	214.6	45.5	73.2	40.5	33.9	141.7	110.1	28.5, 74.1
<i>endo-2b</i>	57.6	211.3	42.5	70.2	35.9	29.5	142.2	109.0	28.6, 28.8, 77.5, 125.5, 126.9, 127.9, 143.3
<i>exo-2b</i>	55.7	213.8	44.9	74.6	39.6	33.6	141.4	109.7	28.5, 28.7, 77.5, 125.6, 126.9, 127.9, 146.3
<i>endo-2c</i>	58.5	212.1	43.9	69.4	36.7	29.2	142.4	109.5	-4.8, 25.8
<i>exo-2c</i>	55.7	214.3	45.2	74.1	41.1	33.0	141.4	110.3	-4.8, 25.8
<i>endo-2d</i>	58.9	212.2	43.2	69.3	36.2	28.9	141.8	109.8	
<i>exo-2d</i>	55.5	214.9	44.8	73.4	40.3	33.1	141.0	110.6	

<sup>a</sup>Relative to internal TMS in CDCl<sub>3</sub>.

the same compound failed irrespective of the experimental procedure adopted. This difference must be caused by more extensive steric interactions in the latter case. Such interactions apparently influence the desilylation of adduct **2c** as well; this reaction proceeded slowly for both stereoisomers, but particularly so for *endo-2c*. Steric interactions may also explain why 7-methylene-3-bicyclo[3.2.0]hepten-2-one (**4**) is formed as a by-product in the latter case.

*LIS studies of endo-2c and endo-2d.* A prerequisite for observing lanthanide-induced NMR shifts is that complexation between a paramagnetic lanthanide ion and a basic functional group, e.g. a hydroxy group, takes place.<sup>12,13</sup> When this occurs the dipolar magnetic field of the Ln(III) ion induces resonance shifts ( $\Delta_i$ ) that follow the simple geometrical dependence given by the McConnell–Robertson equation:<sup>14</sup>

$$\Delta_i = K \frac{3 \cos^2 \varphi_i - 1}{r_i^3}$$

where  $K$  is a constant,  $r_i$  is the distance between the lanthanide ion and nucleus  $i$ , and  $\varphi_i$  is the angle between the lanthanide ion–nucleus  $i$  vector and the lanthanide ion–functional group bond. This relationship connects molecular geometry and induced NMR shifts, and allows computational analysis of the LIS data and thus, an evaluation of the molecular structure of the complex.

The first substrate employed, i.e. one isomer of **2d**, contains two potential coordinating sites, viz. the hydroxy and the carbonyl moieties. Special attention in the selection of the shift reagent is therefore required. The reagent normally encountered, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium, Eu(fod)<sub>3</sub>, is a relatively hard Lewis acid and, hence, is

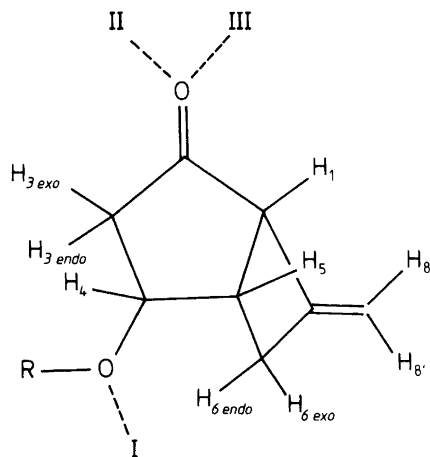


Fig. 1. Potential sites, denoted I, II and III, for coordination of LIS reagents to cycloadduct **2**.

considered to exhibit lower selectivity than the softer analogue tris(dipivalomethanato)europium, Eu(dpm)<sub>3</sub>. The latter reagent is, indeed, reported to coordinate preferentially to hydroxy groups in the presence of other weaker complexing groups,<sup>12,15,16</sup> e.g. carbonyl and ether oxygen, and Eu(dpm)<sub>3</sub> was therefore used in this case.

Stepwise addition of Eu(dpm)<sub>3</sub> to the substrate induced the changes in the proton chemical shifts compiled in Table 3 when extrapolated to a 1:1 substrate/shift reagent ratio. The large induced shifts observed for H-3, H-5 and one of the hydrogen atoms attached to C-6 clearly revealed that europium coordination took place at the hydroxy group (position I, Fig. 1 with R=H). The LIS value was even larger for H-4, but due to a substantial Fermi contact contribution so close to the lanthanide ion<sup>13</sup> this hydrogen was omitted from the LIS calculations.

The computational analysis of the LIS effects was carried out by combined application of the

Table 3. Observed and calculated proton LIS values for *endo-2d* with Eu(dpm)<sub>3</sub> as reagent.<sup>a</sup>

	$\Delta\delta/10^{-2}$ ppm							
	H-1	H-3 <sub>exo</sub>	H-3 <sub>endo</sub>	H-5	H-6 <sub>exo</sub>	H-6 <sub>endo</sub>	H-8	H-8'
Observed	27	57	72	46	28	70	14	13
Calculated <sup>b</sup>	24	52	73	49	27	72	15	14

<sup>a</sup>The shift for H-4 is omitted (see text). <sup>b</sup>Eu–O = 2.8 Å,  $\alpha = 43^\circ$ ,  $\varphi = -80^\circ$ ; R = 5.4 %.

COORD<sup>17</sup> and the PARADIGM<sup>18,19</sup> programs. On the basis of the X-ray structure of tricyclo[5.3.0.0<sup>2,6</sup>]decan-3,8-dione<sup>20</sup> and standard bond-length and bond-angle values<sup>21</sup> the former program was used to obtain an atomic coordinate description of the geometries of *endo-2d* and *exo-2d*. With the geometry fixed, the other program was used to vary the position of the Eu(III) ion systematically over a spherical surface (radius = the Eu–O distance) and to calculate the resulting LIS values and the corresponding *R* factor. The first simulation was carried out on the assumption that the isolated hydroxyketone was *endo-2d* and gave an *R* factor of 12.4 %, which is rather poor. However, careful investigation of the calculated LIS values revealed that the discrepancy between the calculated and the observed shifts was mainly attributable to the protons attached to C-5 and C-6. The predicted values for H-6 were smaller than observed, whereas the value for H-5 was too high. These results indicated that the model was roughly correct but that the Eu–H-5 distance was too short and the Eu–H-6 distances were too large. However, systematic changes of the fixed geometry of *endo-2d* by variation of the C-1–C-5–C-4–C-3 torsion angle improved the results of the LIS calculations considerably. The best set of calculated LIS values, compiled in Table 3, was obtained for an envelope conformation of the 5-membered ring with a torsion angle of 10°; the corresponding normalized standard deviation was 5.47 %.

When similar calculations were carried out assuming that the isolated hydroxyketone was *exo-2d*, the best *R* factor obtained was 48 %, which represents a nearly random correlation. At a confidence level of better than 99.5 % we therefore conclude that the isomer of **2d** in question has the *endo* configuration.

On the basis of conventional <sup>1</sup>H and <sup>13</sup>C NMR spectra and the LIS experiments outlined above it was impossible to separate the signals due to the individual olefinic protons (H-8 and H-8', see Fig. 1). In order to remove this ambiguity LIS experiments were performed with *endo-2c*, the *tert*-butyldimethylsilylated analog of *endo-2d*. By replacing the hydroxy group with a very weakly coordinating silyloxy moiety and by using Eu(fod)<sub>3</sub> instead of Eu(dpm)<sub>3</sub>, we hoped to achieve europium coordination to the carbonyl oxygen and thus be able to solve the problem. Addition of Eu(fod)<sub>3</sub> to *endo-2c* induced shifts with the LIS value compiled in Table 4. The large shifts observed for H-1 and both hydrogens at C-3 clearly demonstrate that carbonyl group coordination occurs. Furthermore, there is a significant difference in the induced shift for the olefinic hydrogen. LIS simulation, based on the optimum geometry of *endo-2d*, was therefore carried out and these calculations showed convincingly (*R* = 10 %) that H-8 experiences a much larger induced shift than H-8'. This completes the assignment of the proton spectrum.

The calculations involving *endo-2c* were based on a "one-site model" which assumes that all the coordination sites of the oxygen atom are equivalent. This is not the case for an unsymmetrical ketone like **2c**. Another calculation based on the presence of two different oxygen binding sites, II and III (Fig. 1 with R = *t*-BuMe<sub>2</sub>Si), was therefore carried out. This improved the results slightly (see Table 4). Interestingly, the two-site model predicted a 86:14 distribution between the europium positions II and III, which seems reasonable considering the steric repulsion in position III.

Table 4. Observed and calculated proton LIS values for *endo-2c* with Eu(fod)<sub>3</sub> as reagent.

	$\Delta\delta/10^{-2}$ ppm								
	H-1	H-3 <sub>exo</sub>	H-3 <sub>endo</sub>	H-4	H-5	H-6 <sub>exo</sub>	H-6 <sub>endo</sub>	H-8	H-8'
Observed	239	239	229	92	84	66	82	105	59
Calculated <sup>a</sup>	220	233	222	112	113	77	98	103	61
Calculated <sup>b</sup>	223	237	217	109	114	76	94	104	64

<sup>a</sup>Based on a one-site model with Eu–O = 2.4 Å,  $\varrho = 15^\circ$ ,  $\varphi = 25^\circ$ ; *R* = 10 %. <sup>b</sup>Based on a two-site model with Eu–O = 2.8 Å,  $\varrho_1 = \varrho_2 = 35^\circ$ ,  $\varphi_1 = 0^\circ$ ,  $\varphi_2 = 180^\circ$ , population<sub>II</sub>: population<sub>III</sub> = 86:14; *R* = 9.5 %.

## Discussion

The photoaddition of the 4-substituted 2-cyclopentenones **1a–1d** to allene gave the corresponding cycloadducts as mixtures of the HH and HT isomers in ratios close to 90:10 (Table 1). This isomeric composition is almost identical to that obtained when allene reacts with 2-cyclopentenone itself under comparable conditions.<sup>22</sup> It is therefore apparent that the regioselectivity is barely influenced even by fairly large substituents attached to C-4. A corollary from this is that the ability of C<sub>α</sub> and C<sub>β</sub> of the enone system to attack a terminal carbon atom of allene<sup>2,4-6,23,24</sup> is by and large insensitive to the same groups. As a consequence it seems to be difficult to use the steric bulk of substituents at C-4 as a means of influencing the regioselectivity of the photocycloaddition of conjugated enones to allene.

Mechanistically, the present [2+2] cycloaddition is believed to proceed through several excited species<sup>25-27</sup> to a mixture of 1,4-diradicals which collapse to cycloadducts **2** and **3**.<sup>24</sup> The excited species are fairly polar and the course of reaction, which is determined by the steps preceding diradical formation, should therefore to some extent be affected by solvent changes. Inspection of Table 1 reveals that this is indeed the case, albeit considerably less so than in other cases.<sup>28-30</sup> Among the parameters compiled in Table 1 the reaction efficiency is evidently most sensitive to solvent variations. This is particularly the case when enone **1c** is used; thus, cycloadducts **2c** and **3c** are formed in 77% total yield when the cycloaddition is carried out in hexane but only in 31% yield when performed in acetonitrile under otherwise identical conditions. The same trend is also observed when enones **1a** and **1b** are employed. For intermolecular cycloaddition reactions this difference might be anticipated since the diffusion rate generally is smaller in acetonitrile than in hexane, due to viscosity differences.<sup>31,32</sup> However, the viscosity cannot be the only parameter affecting the yield; if it were, the behaviour of hydroxyenone **1d** should resemble that of the other enones. That is not the case, the total yield of **2d** and **3d** being much higher in acetonitrile than in hexane, which proves that other factors such as hydrogen bonding and association effects also have to be considered.

Another general trend which emerges from Table 1 is the solvent-dependent variation in the

*endo-2/exo-2* ratio; the more polar the solvent, the larger the relative amount of the *exo* isomer except in the case of adduct **2d**. This variation might be due to solvation, which supposedly is more extensive in polar than in unpolar solvents and more pronounced in the vicinity of the RO group than on the molecular face away from this group. Consequently, the more polar the solvent the more probable will a *trans* attack of the enone become, rendering the *exo* stereoisomer relatively more predominant. Again, hydroxyenone **1d** exhibits irregular behaviour. The reason for this is far from clear, but the similar *endolexo* ratio observed when hexane and ethanol were used as solvents may indicate that self-association of **1d** takes place in hexane.

A third solvent-dependent factor which usually influences the regioselectivity of intermolecular [2+2] photocycloadditions very significantly is the interaction between the overall dipoles of the excited enone and the ground state olefin.<sup>28-30</sup> In the reactions studied here, however, the ground state reactant, allene, has no dipole moment, thereby eliminating this interaction completely. The insignificant variation of the HH/HT ratio with solvent variation is in accordance with expectations.

## Experimental

**General.** IR spectra (liquid film unless otherwise stated) were recorded on a Shimadzu IR-420 spectrophotometer. <sup>1</sup>H NMR spectra were obtained on Jeol PMX 60 SI (60 MHz), Jeol FX 90Q (90 MHz) and Varian XL 300 (300 MHz) spectrometers, and <sup>13</sup>C NMR spectra on a Jeol FX 90Q (22.50 MHz) instrument. CDCl<sub>3</sub> was used as solvent and tetramethylsilane (TMS) was added as internal standard. Chemical shifts are reported in ppm downfield from TMS. The DEPT pulse sequence<sup>33</sup> was used to determine the multiplicity of partly overlapping <sup>13</sup>C signals. Mass spectra were obtained on a VG Micromass 7070H spectrometer. CI mass spectra were recorded at low and high resolution using isobutane as reagent gas. EI mass spectra were acquired by GC/MS analysis at 70 eV; the gas chromatograph connected to the mass spectrometer was a Hewlett-Packard 5710 equipped with a Chrompack CPSil 5CB silica column (26 m × 0.32 mm i.d.). Otherwise, GC analyses were performed on a Carlo Erba Fractovap 4160 gas chromatograph

equipped with FID and a Chrompack CPSil 5CB fused silica column (26 m × 0.32 mm i.d.) and connected to an LDC/Milton Roy CC-10B integrator. No corrections were made for response ratios. Circular thin-layer chromatography (CTLC) was carried out on a Chromatotron equipped with a thin-layer rotor coated with silica PF-254 containing CaSO<sub>4</sub> · 0.5 H<sub>2</sub>O. The photo-lyses were performed with a 400 W medium-pressure mercury lamp (Applied Photophysics 3040).

**Solvents.** Spectroscopic grade hexane and anhydrous ethanol were used without further purification. Acetonitrile was heated under reflux over P<sub>2</sub>O<sub>5</sub> and purified by distillation. Ethyl acetate was dried over CaCl<sub>2</sub>, heated under reflux over P<sub>2</sub>O<sub>5</sub> and distilled. Ether was dried over CaCl<sub>2</sub>, heated under reflux over LiAlH<sub>4</sub> and distilled.

**Starting materials.** Allene was commercially available. 4-*tert*-Butyldimethylsilyloxy-2-cyclopentenone (**1c**) was prepared from cyclopentadiene as described by Davis and Untch.<sup>34</sup>

4-*tert*-Butyloxy-2-cyclopentenone (**1a**) was synthesized by Jones oxidation of a 2/3 *cis/trans* mixture of 4-*tert*-butyloxy-2-cyclopenten-1-ol (**5a**),<sup>35</sup> which was obtained from the corresponding acetate **6a**. The product was isolated in 80% yield by column chromatography [SiO<sub>2</sub>, chloroform/hexane (1:1)] and purified to a purity of >97% (GC) by CTLC [chloroform/hexane (1:2)]. IR: 1710 (s), 1650 (w), 1380 (m), 1360 (m), 1170 (m), 1095 (m), 780 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (60 MHz): δ 1.20 (9H, s), 2.35 (1H, dd, *J* 3 Hz and 18 Hz, H-5), 2.70 (1H, dd, *J* 6 Hz and 18 Hz, H-5'), 4.85 (1H, m, H-4), 6.10 (1H, dd, *J* 1.5 Hz and 6 Hz, H-2), 7.40 (1H, dd, *J* 2.5 Hz and 6 Hz, H-3); <sup>13</sup>C NMR: δ 28.3 (3×CH<sub>3</sub>), 44.8 (CH<sub>2</sub>, C-5), 70.1 (CH, C-4), 74.7 (C), 134.6 (CH, C-2), 163.5 (CH, C-3), 206.6 (C=O); MS [EI, *m/z* (% rel. int.)]: 154 (*M*<sup>+</sup>, 7), 139 (22), 98 (31), 97 (10), 82 (8), 81 (100), 70 (8).

4-Cumyloxy-2-cyclopentenone (**1b**) was prepared according to the synthetic scheme outlined by Stork and Isobe.<sup>36</sup> Oxidation of cyclopentadiene with cumyl hydroperoxide (80% solution in cumene) gave 4-cumyloxy-2-cyclopentenyl acetate (**6b**) as a 54:46 isomeric mixture (GC); IR: 1740 (s), 1690 (w), 1610 (w), 1505 (m), 1458 (m), 1390

(m), 1375 (m), 1250 (s), 775 (m), 708 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (60 MHz): δ 1.50 (6H, s), 1.85 and 2.00 (3H, 2s in a ratio of 55:45), 2.4–3.0 (2H, m), 4.10 and 4.50 (2H, 2m in a 2:3 ratio), 5.7–6.0 (2H, m), 7.2–7.5 (5H, m); MS [EI, *m/z* (% rel. int.)] 141 (1), 119 (100). Subsequent saponification (KOH in H<sub>2</sub>O/MeOH) gave 4-cumyloxy-2-cyclopenten-1-ol (**5b**) which was isolated as a 39:61 isomeric mixture (GC) by dry column chromatography [SiO<sub>2</sub>, chloroform/hexane (1:1)]; IR: 3350 (s), 1680 (w), 1600 (w), 1500 (m), 1380 (m), 1360 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (60 MHz): δ 1.60 (6H, s), 1.9–2.8 (2H, m), 3.9–4.6 (2H, m), 4.90 (1H, broad s), 5.8 (2H, m), 7.2–7.5 (5H, m); MS [EI, *m/z* (% rel. int.)]: 203 (2), 121 (56), 119 (100). Jones oxidation of the alcohol gave ketone **1b**, which was isolated by column chromatography [SiO<sub>2</sub>, chloroform/hexane (1:1)] and purified to a purity of >97% by CTLC [chloroform/hexane (1:1)]; IR: 1720 (s), 1660 (m), 1600 (m), 1500 (m), 1385 (s), 1370 (m), 1360 (m), 885 (m), 835 (m), 790 (m), 770 (m), 705 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (60 MHz): δ 1.60 (6H, broad s), 2.2–2.8 (2H, m, H-5 and H-5'), 4.4 (1H, m, H-4), 6.10 (1H, dd, *J* 1.5 Hz and 7.0 Hz, H-2), 7.1–7.6 (6H, m, H-3 and phenyl); <sup>13</sup>C NMR: δ 28.0 (CH<sub>3</sub>), 29.6 (CH<sub>3</sub>), 44.3 (CH<sub>2</sub>, C-5), 71.7 (CH, C-4), 78.4 (C), 126.0 (CH), 127.4 (CH), 128.4 (CH), 134.6 (CH), 145.7 (C), 163.1 (CH, C-3), 206.1 (C=O); MS [EI, *m/z* (% rel. int.)]: 201 (22), 121 (22), 120 (22), 119 (100), 118 (6), 105 (7), 103 (7), 91 (53).

4-Hydroxy-2-cyclopentenone (**1d**) was prepared essentially as reported by Noyori *et al.*<sup>9,37</sup> However, peroxidation of 3-cyclopentenone (1.63 g, 0.020 mol), obtained by Pd(PPh<sub>3</sub>)<sub>4</sub>-catalyzed rearrangement of 3,4-epoxycyclopentene,<sup>9</sup> was carried out at ambient temperature with *m*-chloroperbenzoic acid (4.37 g, 0.020 mol) in dichloromethane (45 ml) containing sodium bicarbonate (5 g). The reaction was quenched after 4 h by adding Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O (3 g) in dichloromethane (10 ml). The precipitate was removed by suction filtration and washed well with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was washed with aqueous NaHCO<sub>3</sub> before drying (Na<sub>2</sub>SO<sub>4</sub>). Usual work-up gave 1.40 g (75%) of a 62:38 (<sup>1</sup>H NMR) mixture of 6-oxabicyclo[3.1.0]hexan-3-one [<sup>1</sup>H NMR (60 MHz): δ 2.50 (4H, m), 2.85 (2H, m); <sup>13</sup>C NMR: δ 39.7 (CH<sub>2</sub>), 53.0 (CH), 211.4 (C=O)] and 3,6-dihydro-2*H*-pyran-2-one [<sup>1</sup>H NMR (60 MHz): δ 3.10 (2H, m), 4.90 (2H, m), 5.90 (2H, m); <sup>13</sup>C NMR:

$\delta$  30.3 (CH<sub>2</sub>), 69.0 (CH<sub>2</sub>), 122.1 (CH), 122.6 (CH), 168.7 (C=O)]. The synthesis was completed as described by Noyori.<sup>9</sup>

*Photolysis under homogeneous conditions; general procedure.* An oxygen-free solution of **1** (0.035 M) was kept in a closed Pyrex tube which was immersed in a Pyrex beaker (cut-off 300 nm) containing ethanol at approximately  $-50^{\circ}\text{C}$ . Allene (3.5–3.7 g, 9 mmol) was introduced at 1 atm pressure, the tube was reclosed, and the resulting solution was irradiated with light from a 400 W medium-pressure mercury lamp. The solution was kept at  $-40$  to  $-50^{\circ}\text{C}$  during the irradiation. The photolyzate was analyzed by GC after 0.5 h; the results are compiled in Table 1. The irradiation was stopped when most of the enone was consumed (approximately 3 h) as indicated by GC analysis. The solvent was removed under vacuum and the residue was subsequently analyzed before work-up.

*Photocycloaddition of 1 to allene on silica gel; general procedure.* Silica gel (Merck Kieselgel 60, 70–230 mesh ASTM) was dried at  $220^{\circ}\text{C}$  and 10 mmHg for 24 h. The gel was allowed to reach room temperature and was then transferred to a Pyrex tube before adding a solution of enone in dry hexane (5 ml). The solvent was removed under vacuum and the resulting sample was cooled to  $-78^{\circ}\text{C}$  (EtOH/CO<sub>2</sub>) prior to condensation of allene. A slight overpressure developed when the temperature was increased to  $-30^{\circ}\text{C}$  and this pressure was maintained by a balloon fastened to the top of the tube. The tube was kept in a vertical position and was rotated around its long axis during the irradiation while the temperature was maintained at  $-30^{\circ}\text{C}$ . The irradiation was stopped after 2 h and the organic material was extracted with ethyl acetate and methanol. The reaction mixture was analyzed by GC.

*Addition of 1a to allene.* Irradiation of a hexane (30 ml) solution of **1a** (0.160 g) and allene for 3 h gave a reaction mixture which consisted of unreacted **1a** (1%) and three adducts, viz. **3a**, *endo-2a* and *exo-2a* in sequence of elution, in a ratio of 5:57:38, respectively. IR: 1740 (s), 1665 (m), 1385 (m), 1365 (m), 1190 (m), 1145 (m), 890 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz):  $\delta$  1.15 and 1.17 (9H, 2s in a 41:59 ratio), 2.2–3.2 (5H, complex m), 3.38 and 3.48 (1H, 2m in a 58:42 ratio), 4.10

and 4.37 [1H, broad d (*J* 6.1 Hz) and dt (*J* 10.5 Hz and 7.2 Hz) in a 41:59 ratio], 4.83 (1H, m), 4.93 and 4.98 (1H, 2m in a 56:44 ratio), and in addition some peaks of very low intensity which might be due to the least abundant product; <sup>13</sup>C NMR spectra of *endo-* and *exo-2a*: see Table 2; MS [EI, *m/z* (% rel. int.)]: **3a**: 138 (43), 120 (34), 109 (8), 91 (100); *endo-2a*: 138 (43), 120 (34), 109 (8), 96 (23), 95 (54), 94 (16), 93 (43), 92 (44), 91 (100), 79 (63); *exo-2a*: 138 (11), 120 (41), 109 (2), 96 (7), 95 (10), 94 (4), 93 (21), 92 (30), 91 (100), 79 (34). Mol. wt. of **2a** by high resolution CI/MS: calc. for C<sub>12</sub>H<sub>19</sub>O<sub>2</sub> (MH<sup>+</sup>) 195.1385; found 195.1408.

Mixtures of **1a** and allene in acetonitrile and on silica gel were also irradiated; the results are compiled in Table 1.

*Addition of 1b to allene.* Irradiation of enone **1b** (0.214 g) and allene in hexane (30 ml) for 3 h gave 0.170 g of a reaction mixture which consisted of 3% of unreacted enone and three adducts, viz. **3b**, *exo-2b* and *endo-2b* in sequence of elution, in a ratio of 3:43:54 (GC), respectively. IR: 1740 (s), 1675 (m), 1605 (w), 1500 (m), 1450 (m), 1385 (m), 1370 (m), 1155 (s), 1015 (m), 770 (m), 740 (m), 705 (m) cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz):  $\delta$  1.530, 1.536, 1.541, 1.580, 1.600 and 1.620 (6H, 6s), 2.29–2.38 (2H, m), 2.71–3.52 (4H, complex m), 3.84 and 4.03 [1H, broad d (*J* 6.0 Hz) and dt (*J* 7.9 Hz and 10.6 Hz) in a 48:52 ratio], 4.78 and 4.85 (1H, 2 m in a 45:55 ratio), 4.93 and 4.97 (1H, 2m in a 54:46 ratio), 7.20–7.50 (5H, m), and in addition several signals of low intensity which are compatible with **3b**; <sup>13</sup>C NMR data for *endo-* and *exo-2b*: see Table 2; MS [EI, *m/z* (% rel. int.)] **3b**: 121 (16), 120 (11), 119 (100), 118 (7), 117 (6), 103 (6), 92 (10), 91 (46), 79 (11), 77 (12); *exo-2b*: 122 (2), 121 (20), 120 (18), 119 (100), 118 (6), 117 (5), 115 (2), 105 (2), 103 (5), 93 (2), 92 (7), 91 (50), 79 (11), 77 (13); *endo-2b*: 241 (0.3), 122 (1), 121 (14), 120 (24), 119 (100), 118 (6), 117 (5), 115 (2), 105 (2), 103 (6), 93 (4), 92 (7), 91 (65), 79 (17), 77 (15). No product pure enough for elemental analysis was obtained and mass spectrometry (EI and CI) failed to give molecular ions that allowed mol. wt. determination.

Mixtures of **1b** and allene in acetonitrile were also irradiated; the results are compiled in Table 1.

*Addition of 1c to allene.* A solution of enone **1c**



(0.230 g) and allene in hexane (30 ml) was irradiated according to the general procedure and a mixture of photoadducts was obtained. GC analysis revealed unreacted **1c** (1%) and four adducts, viz. *endo*- or *exo*-**3c**, *exo*- or *endo*-**3c**, *exo*-**2c** and *endo*-**2c** in sequence of elution, in a ratio of 3:2:47:47, respectively. IR: 1740 (s), 1665 (w), 1470 (m), 1360 (m), 1250 (m), 1105 (m), 1060 (m), 830 (m), 775 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz):  $\delta$  0.06 and 0.07 (6H, 2s in a 50:50 ratio), 0.86 and 0.89 (9H, 2s in a 50:50 ratio), 2.20–3.20 (5H, m), 3.4–3.5 (1H, m), 4.32 and 4.51 [1H, d ( $J$  4.4 Hz) and dt ( $J$  7.4 Hz and 11.5 Hz) in a 50:50 ratio], 4.86 (1H, m), 4.96 and 5.02 (1H, 2m in a 51:49 ratio);  $^{13}\text{C}$  NMR data for *endo*- and *exo*-**2c**: see Table 2; MS [EI,  $m/z$  (% rel. int.)]: **3c** (*endo* or *exo*): 196 (12), 195 (100), 180 (8), 165 (19), 153 (12), 101 (14), 81 (8), 77 (22), 75 (55), 73 (12); **3c** (*exo* or *endo*): 196 (11), 195 (84), 165 (13), 155 (9), 153 (7), 151 (6), 101 (14), 97 (7), 95 (4), 91 (16), 83 (4), 81 (10), 79 (4), 77 (22), 75 (100), 73 (17); *exo*-**2c**: 196 (3), 195 (26), 167 (5), 166 (4), 165 (35), 151 (11), 139 (7), 101 (7), 97 (6), 91 (12), 79 (20), 77 (9), 75 (100), 73 (25); *endo*-**2c**: 196 (3), 195 (28), 180 (2), 167 (6), 166 (6), 165 (43), 153 (3), 151 (9), 139 (9), 101 (7), 97 (7), 91 (10), 79 (23), 77 (10), 75 (100), 73 (29). Mol. wt. of the cycloadducts by high resolution CI/MS: calc. for  $\text{C}_{14}\text{H}_{26}\text{O}_2\text{Si}$  ( $\text{MH}^+$ ) 253.1624; found 253.1640.

Irradiations were also carried out in solvents other than hexane; the results are summarized in Table 1.

**Desilylation of photoadducts 2c and 3c.** The reaction mixture from the previous reaction was desilylated using two different procedures. When AcOH/THF/ $\text{H}_2\text{O}$  was employed as described by Corey,<sup>38</sup> a mixture containing *endo*-**2c** (61%), *exo*-**2c** (14%), **2d** (10%), **3c** (5%) and 7-methylenebicyclo[3.2.0]hept-3-en-2-one (**4**) (10%) was obtained. The elucidation of the structures of **2d** and **4** is based on the following data. **2d**: IR ( $\text{CCl}_4$ ): 3595 (w), 3430 (w), 1745 (s), 1668 (m), 1145 (m), 887 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (90 MHz):  $\delta$  2.0–3.8 (7H, complex m), 4.4–5.2 (3H, complex m);  $^{13}\text{C}$  NMR: see Table 2; MS [EI,  $m/z$  (% rel. int.)]: 138 ( $M^+$ , 3), 125 (3), 121 (4), 120 (50), 119 (9), 110 (2), 99 (3), 96 (5), 95 (20), 94 (3), 93 (9), 92 (23), 91 (100), 82 (10), 81 (10), 79 (10), 78 (9), 77 (10). Mol. wt. of **2d**: calc. for  $\text{C}_8\text{H}_{10}\text{O}_2$  138.0681; found 138.0676. **4**: IR ( $\text{CCl}_4$ ): 1710 (s),

1670 (m), 887 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (90 MHz):  $\delta$  2.1–3.8 (4H, complex m), 4.98 (1H, m), 5.25 (1H, m), 6.30 (1H, d,  $J$  5.6 Hz), 7.72 (1H, m.); MS [EI,  $m/z$  (% rel. int.)]: 120 ( $M^+$ , 50), 119 (9), 105 (1), 93 (1), 92 (21), 91 (100), 81 (2), 79 (4), 78 (3), 77 (6).

Desilylation of the same reaction mixture (0.41 g) in 40% aqueous HF (2 ml) in acetonitrile (40 ml)<sup>39</sup> gave a product mixture (0.35 g) which consisted of *endo*-**2c** (39%), *exo*-**2c** (11%), **2d** (45%), **3c** (3%) and **4** (2%). The products were partially separated by preparative TLC ( $\text{SiO}_2$ /chloroform). One of the mixtures obtained, 0.050 g, containing 91% of a 5:1 *endo*/*exo* mixture of **2c**, gave a mixture of **2d** (74%) and **4** (26%) in quantitative yield when deprotected in 6.5 ml of a 1:12 (w/w) mixture of 40% aq. HF and acetonitrile. Final purification by preparative TLC ( $\text{SiO}_2$ /chloroform) increased the purity of **2d** to 91%.

**Addition of 1d to allene.** Irradiation of **1d** (0.014 g) and allene (0.90 g) in hexane (4.0 ml) for 0.5 h gave a reaction mixture which contained unreacted starting material (73%) and a 87:13 mixture of **2d** and **3d**. Adduct **2d** was identical to that obtained by desilylation of **2c**.

Silylation of the adduct mixture employing *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide as described in the literature<sup>34</sup> was a failure. Trimethylsilylation<sup>40</sup> gave the corresponding ethers which were separable by gas-chromatographic methods. MS [EI,  $m/z$  (% rel. int.)]: *exo*-**2e**: 210 ( $M^+$ , 2), 195 (25), 167 (16), 165 (7), 153 (4), 151 (4), 116 (12), 101 (38), 92 (19), 91 (36), 83 (5), 81 (11), 77 (12), 75 (100), 73 (51); *endo*-**2e**: 195 (1), 168 (5), 167 (6), 165 (4), 153 (2), 151 (3), 120 (5), 117 (8), 101 (5), 92 (22), 91 (14), 79 (14), 78 (8), 77 (5), 75 (49), 73 (100). The ethers from **2d** were formed in an *endo*/*exo* ratio of 63:37 and they were identical with the two isomers obtained by trimethylsilylation of **2d** acquired by desilylation of a mixture of **2c** with known isomeric composition.

Irradiations were also carried out in acetonitrile and ethanol; the results are included in Table 1. Experiments involving mixtures of **1d** and allene on silica gel were unsuccessful, partly due to decomposition.

**Lanthanide-induced shift (LIS) experiments.** The  $^1\text{H}$  NMR spectra for these experiments were re-

corded on a Bruker WM-250 spectrometer. The LIS data were determined by stepwise addition of Eu(dpm)<sub>3</sub> or Eu(fod)<sub>3</sub> to 0.05 M solutions of substrate in CDCl<sub>3</sub>. The LIS values used for calculations were obtained by graphical extrapolation of the observed shifts to an equimolar ratio of europium reagent and substrate. For LIS calculations an Apple MacIntosh version of the computer program PARADIGM<sup>18,19</sup> was used. The atomic coordinates were calculated using the program COORD.<sup>17</sup>

The sample of **2d** (*endo/exo* = 5:1) which was used, was prepared by desilylation of **2c** employing HF in acetonitrile as described above. In addition, an analytical sample of **2c** (*endo/exo* = 12:1) was used; this was obtained by preparative TLC [SiO<sub>2</sub>, hexane/chloroform (1:4)].

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