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Photochemical [2+2] Cycloadditions. IV.† Cycloaddition of 2-Cyclopentenone to Some (ω–1)-Alken-1-ols; Evidence for Regioselectivity due to Hydrogen Bonding

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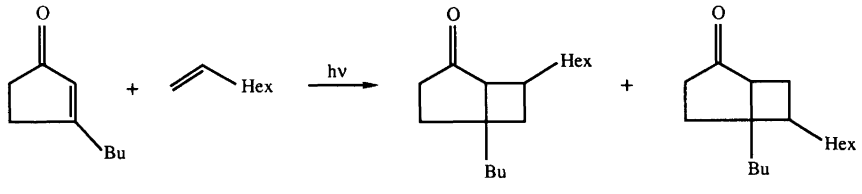
Irradiation ($\lambda > 295$ nm) of the title ketone in the presence of an (ω–1)-alken-1-ol (ω = 3,4,5) gave mixtures of the head-to-head and head-to-tail [2 + 2] cycloadducts in good yields. Both the regioisomer composition and the reaction efficiency were very sensitive to the solvent employed and to the alkenol concentration used. In hexane the head-to-head regioisomer was the major product at low alkenol concentration while in methanol and in hexane at high alkenol concentration the head-to-tail adduct predominated. It is proposed that this change in regioselectivity may be due to hydrogen-bonding effects either between the enone and the alkenol prior to reaction, or in the intermediate biradicals formed in the reaction.

Intermolecular photocycloaddition of conjugated cyclic enones to alkenes to form bicyclo[*n*.2.0]alkanes has proved to be a useful reaction in organic synthesis.[1–4] The reaction has been used to synthesize cyclobutanes *per se*[1,2,5–7] and to prepare compounds that have been of value in the synthesis of a number of natural products.[8–11] But in spite of these successes the lack of regioselectivity in reactions with unsymmetrically substituted alkenes remains a problem. For example, with simple alkyl-substituted alkenes close to 1 : 1 mixtures of the head-to-head (HH) and head-to-tail (HT) adducts are formed (Scheme 1), while with alkenes bearing a more electron-rich substituent such as an alkoxy group the HT regioisomer is favoured to some extent.[1–4,12–14] From the literature it is apparent that the regioselectivity is controlled by a number of factors, of which the influence of substituents on the electronic distribution of the reacting double bonds, i.e., an intrinsic property of the reactants, is of considerable importance.[15–19] It has also been shown that the fates of the isomeric biradical intermediates involved in the reaction can play a major role in controlling product regiochemistry since for each biradical intermediate reversion to ground-state starting materials can compete with closure to products (Scheme 2).[20] In addition, it has been demonstrated that the regiochemistry may be influenced by interactions between the overall dipole of the excited enone and that of the ground-state alkene.[16] This suggests that it might be possible to achieve some regiochemical control of photocycloaddition reactions by introducing one or several polar substituents at



47% (HH) 53% (HT)

Scheme 1.

† Part III, see Ref. 33.
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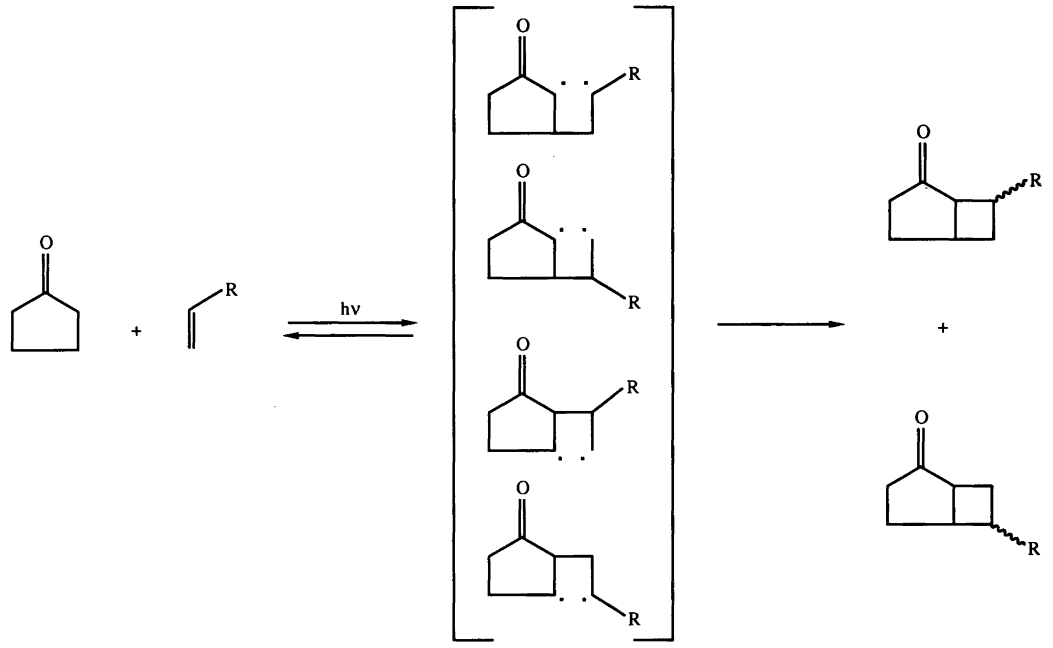


Scheme 2.

remote positions rather than directly on the reacting double bonds.

We have previously tried to influence the regiochemistry in photocycloaddition reactions by means of a bromine atom remotely attached to the alkene, i.e., by irradiating 3-butyl-2-cyclopentenone in the presence of various (ω–1)-bromo-substituted alkenes.[21] However, regiochemical control of any significance was not achieved owing to both inefficient primary reactions and considerable secondary reactions, which are attributable in part to heavy-atom effects from the halogen atom. In order to improve this situation we, therefore, wanted to replace the bromine atom by a hydroxy group, which is polar, but does not give rise to heavy-atom effects. In addition, it was also thought that alkenols, in the proper solvents, will be involved in hydrogen bonding to the enone, and that this might conceivably influence the regiochemical outcome of the cycloaddition reaction.

From the literature little is known about the behaviour of alkenols with excited conjugated cyclic enones. For example, some reactions have been carried out in methanol,[11,22] but this solvent prevents assessment of the effect of hydrogen bonding. Similarly, when an acetonitrile solution of 2-propenol and 3-methyl-5,6-diaza-2,4-cyclohexadienone or 4-methyl-5,6-diaza-2,4-cyclohexadienone is irradiated, the corresponding HT adducts are formed exclusively;[23–25] however, in this case the regioselectivity is probably a result of nitrogen influence. We have found that photochemical addition of 2-cyclopentenone to some (ω–1)-alken-1-ols gives the corresponding cycloadducts in good yields with a regioisomeric preference which is sensitive to the solvents as well as the alkenol concentration. Full details of this study are reported here.

Results and discussion

Preparative photocycloadditions were performed by irradiating deoxygenated solutions of the reactants at room temperature with Pyrex-filtered light from a medium-pressure mercury lamp. In all cases the solutions were 0.020–0.031 M in 2-cyclopentenone (**1**) and ten times higher in (ω–1)-alken-1-ol (**2**). The alkenols were used in

Table 1. The amount of enone consumed after irradiation of solutions (20 ml) containing 2-cyclopentenone (0.40 mmol) and (ω–1)-alken-1-ol (4.0 mmol) for 25 min with light from a medium-pressure mercury lamp.

Solvent	Viscosity/cP[a]	Relative permittivity[a]	2-Cyclopentenone consumed (%)[b]			
			2-Propenol	3-Butenol	4-Pentenol	5-Hexenol
Diethyl ether	0.24	4.34	84	84	77	82
Hexane	0.31	1.88	78	72	74	70
Acetonitrile	0.32	37.5	50	34	39	40
Methanol	0.55	32.70	43	46	41	39
Ethanol	1.20	24.58	41	42	40	64

[a] Measured at 20°C; taken from Ref. 32. [b] Determined by GC analysis using *p*-dichlorobenzene as an internal standard.

Table 2. Product distribution and total yield of **3** and **4** in the photocycloaddition of **1** to **2**.

(ω–1)-Alken-1-ol	Solvent	Isolated yield(%)	Product distribution[a]				3/4 (HH : FH)
			endo-**3**	*exo*-**3**	*endo*-**4**	*exo*-**4**	
2a	Hexane	84	—	71	5	24	2.45
	Diethyl ether	—	—	42	22	36	0.72
	Ethanol	—	—	33	18	49	0.49
	Acetonitrile	—	—	38	17	45	0.61
2b	Hexane	86	—	65	9	26	1.86
	Diethyl ether	—	—	40	18	42	0.67
	Ethanol	—	—	34	19	47	0.52
	Acetonitrile	—	—	37	22	41	0.59
2c	Hexane	79	7	53	11	29	1.50
	Diethyl ether	—	5	34	18	43	0.64
	Ethanol	—	3	32	17	48	0.54
	Acetonitrile	—	4	34	16	46	0.61

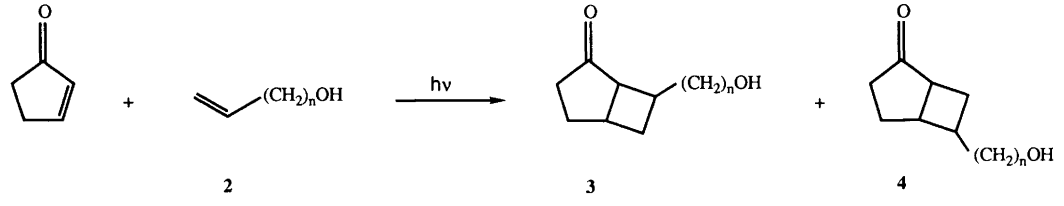
[a] Determined by GC analysis before isolation assuming identical response ratios for all isomers from the same alkenol.

a large excess to suppress dimerization of the enone[26] and this was in fact achieved; dimer formation was hardly observed. The progress of the reactions was monitored by GC analysis to avoid over-irradiation and formation of secondary products.

The outcome and efficiency of intermolecular photocycloaddition reactions are known to be influenced by solvent effects and small-scale exploratory experiments were therefore carried out to find the most suitable solvent. On the basis of the rate of enone consumption the most efficient reactions took place in non-polar solvents like hexane and diethyl ether (Table 1). The regioselectivity was the highest when the reactions were carried out in hexane and ethanol, but the HH isomers predominated as much in hexane as the HT isomers predominated in ethanol (Table 2). Consequently, the large-scale preparative experiments were performed in hexane.

When a hexane solution of **1** and 2-propenol (**2a**) was irradiated until most of the enone had been consumed three main and several minor products were formed (Scheme 3). The main products were isolated as a 64 : 27 : 9 mixture by short-path distillation in 84% yield. Attempts to isolate pure samples of the individual products were unsuccessful, and their structures were therefore elucidated from the results of spectroscopic and spectrometric examination of product mixtures containing the compounds in different proportions. The products were found to be one isomer of the HH [2 + 2] adduct 7-(hydroxymethyl)bicyclo[3.2.0]heptan-2-one (**3a**) (major) and a mixture of the *endo* and *exo* isomers of the corresponding HT adduct 6-(hydroxymethyl)bicyclo-[3.2.0]heptan-2-one (**4a**) (minor). The elemental composition of the isomers was confirmed by combustion and GC–MS analyses, and their structures were supported by high resolution mass spectra, which exhibited fragmentation patterns similar to those observed in the spectra of various other derivatives of bicyclo[3.2.0]heptan-2-one.[12,19,21] The conclusions were furthermore substantiated by converting a 70 : 24 : 6 mixture of **3a**, *exo*-**4a** and *endo*-**4a**, respectively, to an approximately 6 : 3 : 1 mixture of the known[19] cycloadducts 7-methylbicyclo[3.2.0]heptan-2-one (**5**), 6-*exo*-methylbicyclo[3.2.0]heptan-2-one (*exo*-**6**) and 6-*endo*-methylbicyclo[3.2.0]heptan-2-one (*endo*-**6**), respectively. Interestingly, this transformation also allowed us to conclude that **3a** was formed in the *exo* configuration; thus, C-1 in our **5** isomer gave rise to a ^{13}C NMR signal at δ 52.7, which is identical with that observed for *exo*-**5**, but significantly different from that exhibited by *endo*-**5** (49.6 ppm).[19] It therefore appears that addition of 2-cyclopentenone to **2a** affords the cycloadducts with a HH : HT ratio of 2.45, which is considerably higher than that achieved by addition of conjugated cyclic enones to other alkyl-substituted alkenes.[1–4]

Previously ^{13}C NMR spectroscopy has emerged as a



2 3 4

a: n = 1; **b**: n = 2; **c**: n = 3

Scheme 3.

Table 3. The ^{13}C NMR chemical shift for C-1 in some cycloadducts formed by photocycloaddition of 2-cyclopentenone to various alkenes.

Regioisomer	Stereoisomer	Chemical shift[a]	Reference
7-MHBO[b]	*endo*	49.6	19
	exo	52.7	19
6-MHBO[b]	*endo*	42.4	19
	exo	43.9	19
3a	Only one	47.8	This work
4a	Minor	41.9	This work
	Major	41.8	This work
3b	Only one	51.0	This work
4b	Minor	37.0	This work
	Major	42.4	This work
3c	Only one	51.2	This work
4c	Minor	36.9	This work
	Major	42.4	This work

[a]The shifts are reported in ppm downfield from internal tetramethylsilane. [b]MBHO = methylbicyclo[3.2.0]heptan-2-one.

Table 4. The quantum yields of cycloadduct formation and the regioisomer ratio for the photochemical cycloaddition of (ω–1)-alken-1-ols to 2-cyclopentenone (0.08 M) in methanol solution.

(ω–1)-Alken-1-ol	[Alkenol]/M	HH : HT[a]	Φ[b]
2-Propenol	2.009	0.26	0.116
	0.866	0.28	0.139
	0.489	0.26	0.127
	0.180	0.30	0.105
	0.086	0.23	0.069
3-Butenol	1.964	0.57	0.115
	0.841	0.55	0.097
	0.422	0.60	0.105
	0.148	0.59	0.075
	0.079	0.60	0.057
4-Pentenol	1.984	0.47	0.096
	0.836	0.45	0.103
	0.423	0.46	0.098
	0.154	0.43	0.073
	0.059	0.48	0.044

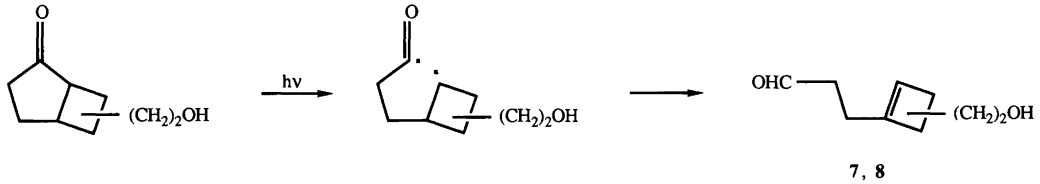
[a]Ratio of head-to-head adducts (*exo*-**3** and *endo*-**3**) to head-to-tail adducts (*exo*-**4** and *endo*-**4**). [b]The total quantum yield of formation of the *exo* and *endo* isomers of **3** and **4** using 313 nm light.

useful tool for the determination of the regiochemistry of [2 + 2] photocycloadducts mainly because the signal due to C-1 (α to the carbonyl group) appears at significantly lower field for the HH isomers than for the corresponding HT isomers.[12,19,21] Comparison of the data compiled in Table 3 reveals that this is also the case for **3a** and **4a**, and this supports the proposed regiochemical assignments.

The amounts of the minor products could be increased at the expense of the three major products by increasing the time of irradiation, and this indicates that these compounds result from cleavage of cycloadducts **3a** and **4a**. This interpretation of the origin of the by-product formation was supported by the fact that several impure samples of the products gave rise to spectra, which showed the presence of aldehyde functions (IR absorptions around 2700 and 1720 cm^{-1}; ^1H NMR signals around 9.7 ppm; ^{13}C NMR absorptions around 202 ppm) and carbon–carbon double bonds (IR absorption around 1630 cm^{-1}; ^1H NMR signals around 5.7 ppm; ^{13}C NMR peaks in the 120–150 ppm region). It is also noteworthy that a cleavage product containing these functions was isolated and identified when a mixture of **1** and 3-butenol (**2b**) was excessively irradiated (*vide infra*).

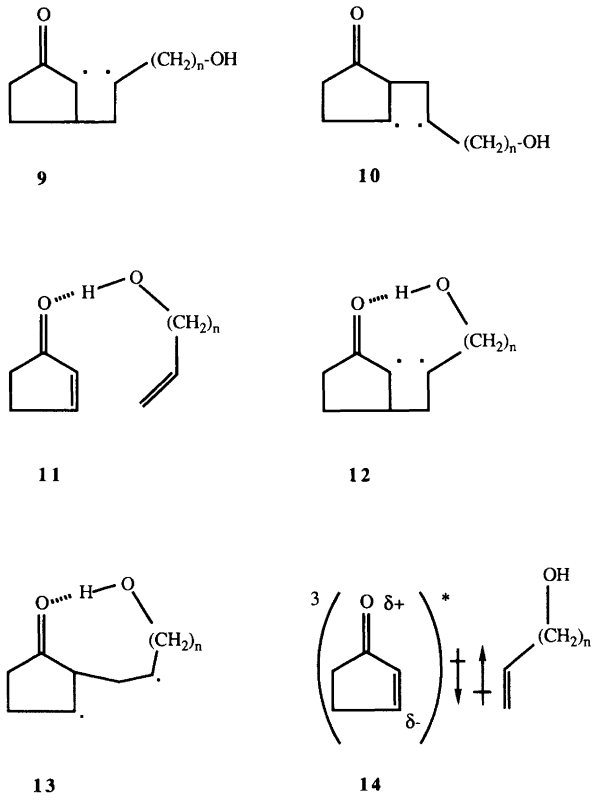
When **1** was irradiated in the presence of 3-butenol (**2b**) and 4-pentenol (**2c**) cycloaddition occurred essentially as in the case of **2a**. In hexane the corresponding cycloadducts **3** and **4** were obtained as regioisomeric mixtures in approximately 80% yield. By comparing their ^{13}C NMR spectra and particularly the chemical shift for C-1 with the corresponding data for **3a** and **4a** (Table 3) the regiochemistry could be deduced. In both cases the HH isomers predominated, but the longer the carbon chain the higher the abundance of the HT isomers (Table 2). When polar solvents were used, however, the HH : HT ratio dropped to 0.5–0.6 for all alcohols (Table 2).

As in the case of **2a**, photocycloaddition of **1** to **2b** and **2c** gave minor amounts of several by-products, which exhibited IR and NMR absorptions indicative of aldehyde and carbon–carbon double bond functions. In order to elucidate their structures a mixture of **1** and 3-butenol was irradiated for a considerable length of time (~25 h) after all the enone had been consumed. This yielded much larger quantities of the same by-products which, however, could not be separated. The structures of the main by-products were therefore assigned on the basis of IR, MS, and NMR spectra of several mixtures containing the compounds in different proportions. From these data (see the Experimental) it is apparent that the by-product mixture mainly consists of 3-[3-(2-hydroxyethyl)-1-cyclobutenyl]propanal (**7**) and 3-[4-(2-hydroxyethyl)-1-cyclobutenyl]propanal (**8**) which may conceivably have been formed as outlined in Scheme 4.



7, 8

Scheme 4.



Scheme 5.

Table 5. The quantum yields of cycloadduct formation and the regioisomer ratio for the photochemical cycloaddition of (ω–1)-alken-1-ols to 2-cyclopentenone (0.08 M) in hexane solution.

(ω–1)-Alken-1-ol	[Alkenol]/M	HH : HT[a]	Φ[b]
2-Propenol	2.039	0.87	0.178
	1.004	1.31	0.164
	0.509	1.49	0.195
	0.244	2.42	0.165
	0.182	2.08	0.171
	0.092	2.35	0.111
3-Butenol	1.955	0.84	0.194
	0.833	1.17	0.218
	0.406	1.67	0.207
	0.152	2.03	0.158
	0.068	2.30	0.132
	0.035	2.53	0.093
4-Pentenol	1.982	0.71	0.288
	0.832	1.05	0.303
	0.418	1.13	0.256
	0.160	1.29	0.287
	0.062	1.41	0.162
	0.030	1.56	0.101

[a] Ratio of head-to-head adducts (*exo*-**3** and *endo*-**3**) to head-to-tail adducts (*exo*-**4** and *endo*-**4**). [b] The total quantum yield of formation of the *exo* and *endo* isomers of **3** and **4** using 313 nm light.

In order to quantify the solvent effect as well as to define more accurately the influence of alkenol structure on the reaction, the quantum yields of cycloaddition were determined for each alkenol in both methanol and hexane. The quantum yield of cycloaddition was expected to increase with increasing alkenol concentration up to a limit corresponding to interception of all triplet-excited 2-cyclopentenone molecules by the alkenol; below this limit some of the excited states decay to the ground state before collision and reaction with alkenol can occur. Consequently, the quantum yield of cycloaddition was measured as a function of alkenol concentration so that the limiting quantum yield at infinite alkenol concentration could be estimated. The results are shown in Tables 4 and 5 and Figs. 1 and 2.

The results obtained in *methanol* indicate that the limiting quantum yield for all three alkenols is similar and lies between 0.10 and 0.14. This implies that on an average 90–86% of the biradical intermediates revert to starting materials and that only 10–14% close to yield products. It has been shown[20,27,28] for the photocycloaddition reactions of 2-cyclopentenone with mono-substituted

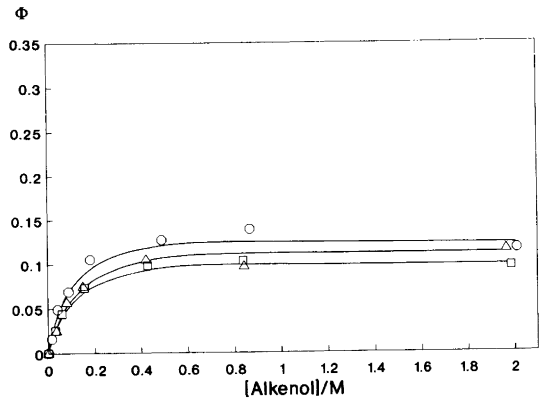


Fig. 1. Quantum yield of cycloadduct formation (Φ) for the photochemical cycloaddition of (ω–1)-alken-1-ols to 2-cyclopentenone (0.08 M) in methanol solution: ○, 2-propenol; △, 3-butenol; □, 4-pentenol.

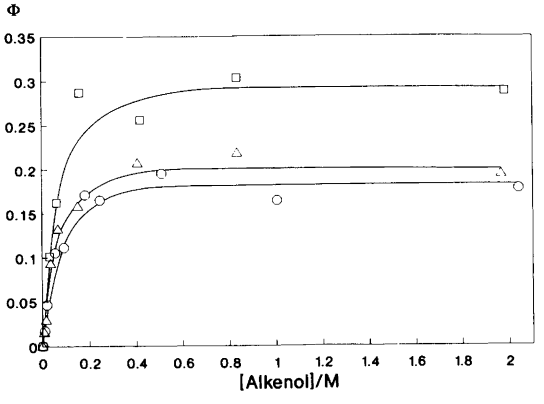


Fig. 2. Quantum yield of cycloadduct formation (Φ) for the photochemical cycloaddition of (ω–1)-alken-1-ols to 2-cyclopentenone (0.08 M) in hexane solution: ○, 2-propenol; △, 3-butenol; □, 4-pentenol.

alkenes that the triplet 1,4-biradical intermediates are predominantly formed by bonding of the less substituted end of the alkene to both the 2-position and the 3-position of the cyclopentenone. Thus, for the alkenols examined in this work, the structure of the biradical intermediates would be **9** and **10**. The regiochemistry observed for the products obtained in methanol indicates that for all three alkenols the HT isomer is favoured. This implies that biradical **10** is formed faster and therefore to a greater extent, or alternatively, that biradical **10** closes to products more efficiently than does biradical **9**, even if **10** is formed more slowly than **9** and hence to a lesser extent.

The results obtained when the solvent was changed to *hexane* are substantially different in several respects. Firstly, the limiting quantum yields of product formation at infinite alkenol concentration are higher. This is in accordance with the qualitative observations made in the preparative experiments and suggests that, in hexane, the biradicals **9** and **10** are more prone to close to products than they are in methanol. Secondly, the HH : HT ratio was found to vary with the alkenol concentration; thus, at lower concentrations the HH isomer predominated while the HT isomer became the major product regioisomer at high alkenol concentrations (Table 5). Several arguments can be offered to explain this dependence of product regiochemistry on alkenol concentration. One possibility is that hydrogen bonding between the enone and the alkenol (i.e., structure **11**) could promote formation of biradical **9** and hence the head-to-head product in a quasi-intramolecular process. In the presence of high alkenol concentrations intermolecular reactions between the alkenol and the excited state of structure **11** may compete with 'intramolecular' cycloaddition and so increase the proportion of head-to-tail product. A second possibility is that at low alkenol concentration intramolecular hydrogen bonding in the biradical **9** (i.e., structure **12**) may facilitate closure to product. This effect would increase the proportion of the HH regioisomer because if the HT cycloadduct precursor, biradical **10**, were to form an intramolecular hydrogen bond (as in structure **13**) the probability of closure to adduct and formation of HT product would decrease because the biradical is held in a conformation unsuitable for closure to product. At high alkenol concentrations the extent of intramolecular hydrogen bonding in **9** and **10** would be reduced by intermolecular hydrogen bonding so that the product regioisomeric ratio would ressemble that obtained in methanol. A third explanation of the greater proportion of HH isomer in hexane at low alkenol concentrations is that, in non-polar media, the overall dipole of the alkenols aligns antiparallel to the presumed[1-4,12] dipole of the enone excited state (i.e., structure **14**); this would favour formation of biradical **9**. The effect would be felt less when methanol is the solvent since solvation of the dipoles would reduce the interaction. However, the dipole interactions could be important when hexane is the solvent until the alkenol concentration reaches a level that increases the polarity of the medium. This argument is the same as that developed by de Mayo to explain the solvent effect on the regiochemistry of photocycloaddition of 2-cyclohexenone ketal to a substituted 2-cyclopentenone.[16]

Our results demonstrate that a remote hydroxy substituent can have a profound effect on the regioselectivity of the photocycloaddition reaction of an alkene with a cyclic conjugated enone and can cause reversal of the normally preferred orientation of addition. This finding could be of importance for synthetic applications where control of regiochemistry is required.

Experimental

General. UV spectra were obtained on a Shimadzu UV-160 spectrophotometer. IR spectra were recorded on Shimadzu IR-435 and Shimadzu IR-420 spectrophotometers with the compounds as liquid films unless stated otherwise. ^{1}H NMR spectra were obtained on Jeol PMX 60 SI (60 MHz) and Jeol FX 90Q (89.55 MHz) spectrometers and ^{13}C NMR spectra on a Jeol FX 90Q (22.50 MHz) instrument. $CDCl_3$ was used as the solvent unless stated otherwise and tetramethylsilane (TMS) was added as an internal reference. Chemical shifts are reported in ppm downfield from TMS. GC analyses were performed on a Carlo Erba HRGC 5300 Mega Series gas chromatograph, which was equipped with FID and a Supelco SPD-5 fused silica coloumn (30 m × 0.32 mm i.d.) and connected to an LDC/Milton Roy CI-10B integrator. No corrections were made for response ratios. Mass spectra were obtained on a VG 7070H Micromass spectrometer, operated in the EI mode at 70 eV, which was attached to a Hewlett Packard 5710A gas chromatograph with a Supelco SPB-5 fused silica coloumn (30 m × 0.32 mm i.e.). The spectra are reported as *m/z* (% rel. int.). Preparative photolyses were carried out with a 400 W medium-pressure mercury lamp from Applied Photophysics (model 3040). All starting materials were commercially available.

Preparative photocycloaddition: general procedure. A solution (25 ml), consisting of approximately 0.5 g (6 mmol) of 2-cyclopentenone (**1**), 58 mmol of (ω–1)-alken-1-ol and solvent, was transferred to a 30 ml vial, deoxygenated for 5 min with argon, and sealed tightly with a screw-cap. The vial was fastened outside a water-cooled Pyrex well (cut-off 295 nm, 50% transmission at 315 nm) which contained a 400 W mercury lamp. After irradiation for 1.5 h, solvent and unchanged starting material were removed under vacuum and the products were isolated by column chromatography or distillation.

Photocycloaddition of **1** *to 2-propenol* (**2a**). Irradiation of a hexane solution of **1** (0.53 g, 6.46 mmol) and **2a** (3.35 g, 57.7 mmol) according to the general procedure gave a crude product which contained no unchanged ketone (GC analysis) and mainly three products in a 73 : 22 : 5 ratio. Kugelrohr distillation at 45°/0.5 mbar gave 0.76 g (84%) of an almost pure mixture of cycloadducts *exo*-**3a**,

exo-**4a** and *endo*-**4a**, which were further purified by column chromatography (SiO_2, $CHCl_3$) to 99% purity. GC analysis revealed that the *exo*-**3a** : *exo*-**4a** : *endo*-**4a** ratio in the final product mixture was 64 : 27 : 9. IR (isomer mixture): 3400 (s), 2920 (s), 1730 (s), 1410 (m), 1110 (m), 1050 (m) cm^{-1}; ^1H NMR (isomer mixture): δ 1.9–2.3 (4 H, m), 2.3–3.0 (5 H, m), 3.5–3.7 (2 H, m), 3.81 (1 H, br s).

exo-**3a**: ^{13}C NMR: δ 27.7 (CH_2), 28.0 (CH_2), 32.6 (CH), 37.1 (CH_2), 38.1 (CH), 47.8 (CH), 65.7 (CH_2), 222.6 (C=O); MS: 140 (42, M^+), 138 (10), 122 (51), 109 (20), 107 (12), 96 (14), 91 (33), 85 (17), 83 (100), 82 (92).

exo-**4a**: ^{13}C NMR: δ 25.0 (CH_2), 27.1 (CH_2), 36.7 (CH_2), 38.7 (CH), 40.3 (CH), 41.8 (CH), 65.9 (CH_2), 223.3 (C=O); MS: 140 (51, M^+), 138 (3), 122 (31), 109 (7), 107 (6), 96 (10), 91 (13), 85 (3), 83 (100), 82 (74).

endo-**4a**: ^{13}C NMR: δ 21.1 (CH_2), 26.3 (CH_2), 29.6 (CH_2), 35.9 (CH), 36.0 (CH), 41.9 (CH), 62.8 (CH_2), 223 (C=O); MS: 140 (12, M^+), 138 (14), 122 (36), 109 (8), 107 (12), 96 (7), 91 (18), 83 (89), 82 (100).

Photocycloaddition of **1** *to 3-butenol* (**2b**). Irradiation of a hexane solution of **1** (0.50 g, 6.09 mmol) and **2b** (4.15 g, 57.6 mmol) as outlined in the general procedure afforded a crude product which contained some unchanged ketone (GC analysis) and four products in an 11 : 57 : 24 : 8 ratio. Kugelrohr distillation at 50°C/0.2 mbar gave 0.81 g (86%) of a clean mixture of three cycloadducts, *exo*-**3b**, *exo*-**4b** and *endo*-**4b**, which were further purified by column chromatography (SiO_2, $CHCl_3$). GC analysis revealed that the *exo*-**3b** : *exo*-**4b** : *endo*-**4b** ratio in the final product mixture was 69 : 25 : 6. IR (isomer mixture): 3400 (s), 2920 (s), 2850 (s), 1730 (s), 1410 (m), 1160 (m), 1050 (m) cm^{-1}; ^1H NMR (isomer mixture): δ 1.6–2.1 (6 H, m), 2.1–2.7 (6 H, m), 3.5–3.7 (2 H, m).

exo-**3b**: ^{13}C NMR: δ 27.9 (CH_2), 31.9 (CH_2), 32.2 (CH), 34.5 (CH), 38.3 (CH_2), 39.3 (CH_2), 51.0 (CH), 60.6 (CH_2), 222.4 (C=O); MS: 154 (2, M^+), 136 (7), 124 (6), 109 (12), 99 (19), 91 (12), 83 (100), 82 (43).

exo-**4b**: ^{13}C NMR: δ 27.0 (CH_2), 28.6 (CH_2), 35.5 (CH), 36.8 (CH_2), 39.5 (CH_2), 42.1 (CH), 42.5 (CH), 60.2 (CH_2), 223.1 (C=O); MS: 154 (10, M^+), 136 (6), 124 (17), 109 (11), 99 (1), 91 (10), 83 (100), 82 (48).

endo-**4b**: ^{13}C NMR: δ 21.0 (CH_2), 29.3 (CH_2), 30.0 (CH_2), 30.1 (CH), 31.5 (CH), 32.8 (CH), 37.0 (CH), 60.9 (CH_2), 221.6 (C=O); MS: 154 (5, M^+), 136 (9), 124 (2), 109 (8), 99 (1), 91 (14), 83 (100), 82 (53).

Over-irradiation gave a mixture of **7** and **8**, whose spectroscopic properties were as follows: IR (film): 3400 (s), 2920 (s), 2850 (s), 2700 (w), 1720 (s), 1630 (w), 1110 (s), 730 (s) cm^{-1}; ^1H NMR: δ 1.1–2.8 (9 H, m), 3.3–3.9 (2 H, m), 4.55 (1 H, br s), 5.5–5.9 (1 H, m), 9.73 (1 H, br s); ^{13}C NMR: δ 21.9 (CH_2), 23.6 (CH_2), 33.0 (CH_2), 36.3 (CH), 37.0 (CH_2), 40.6 (CH_2), 40.8 (CH_2), 40.9 (CH), 61.1 (CH_2), 61.5 (CH_2), 126.3 (CH), 131.9 (CH), 146.8 (C), 151.7 (C), 201.9 (C=O); MS: 154 (1, M^+), 153 (1), 136 (16), 134 (12), 132 (16), 131 (16), 118 (25), 117 (37), 116 (26), 116 (34), 107 (23), 106 (18), 105 (35), 104 (28), 103 (40), 93 (23), 92 (28), 91 (91), 81 (27), 80 (29), 79 (100), 78 (47), 77 (78). Anal. $C_9H_{14}O_2$: C, H.

Photocycloaddition of **1** *to 4-pentenol* (**2c**). Irradiation of a hexane solution of **1** (0.53 g, 6.46 mmol) and **2c** (4.89 g, 57.8 mmol) was carried out as described. The crude product contained some unchanged ketone (GC analysis) and four cycloadducts in a 5 : 57 : 36 : 2 ratio. Kugelrohr distillation at 50°C/0.2 mbar gave 0.86 g (79%) of a slightly yellow and clean mixture of the cycloadducts, *exo*-**3c**, *endo*-**3c**, *exo*-**4c** and *endo*-**4c**, which were further purified by column chromatography (SiO_2, $CHCl_3$). IR (isomer mixture): 3400 (s), 2920 (s), 2850 (s), 1730 (s), 1470 (m), 1410 (m), 1160 (m), 1050 (m) cm^{-1}; ^1H NMR (isomer mixture): δ 1.4–1.8 (4 H, m), 1.8–2.2 (5 H, m), 3.08 (1 H, br s), 3.5–3.7 (2 H, m).

exo-**3c**: ^{13}C NMR: δ 28.0 (CH_2), 30.0 (CH_2), 31.6 (CH_2), 32.0 (CH), 33.1 (CH_2), 36.6 (CH), 37.5 (CH_2), 51.2 (CH), 62.4 (CH_2), 222.0 (C=O); MS: 168 (1, M^+), 150 (9), 113 (5), 109 (15), 95 (13), 91 (8), 83 (100), 82 (29).

endo-**3c**: MS: 168 (1, M^+), 150 (29), 113 (3), 109 (12), 95 (17), 91 (15), 83 (91), 82 (100).

exo-**4c**: ^{13}C NMR: δ 27.1 (CH_2), 28.7 (CH_2), 29.9 (CH_2), 32.9 (CH_2), 36.8 (CH_2), 38.6 (CH), 41.8 (CH), 42.4 (CH), 62.4 (CH_2), 223.4 (C=O); MS: 168 (1, M^+), 150 (3), 109 (7), 95 (8), 91 (6), 83 (100), 82 (23).

endo-**4c**: ^{13}C NMR: δ 20.7, 27.7, 27.9, 31.4, 34.6, 36.9, 38.3, 42.1, 62.3, 222.1; MS: 168 (1, M^+), 150 (4), 113 (1), 109 (2), 95 (10), 91 (13), 83 (100), 82 (31).

Synthesis of **5** *and* **6**. To a stirred, cold (0°C) solution of 0.93 g (6.6 mmol) of a 66 : 27 : 7 mixture of *exo*-**3a** : *exo*-**4a** : *endo*-**4a** in 50 ml of dry ether were successively added 3.35 g (33.1 mmol) of triethylamine dissolved in 5 ml of dry ether and 2.28 g (19.9 mmol) of methylsulfonyl chloride.[29] The mixture was stirred at room temperature for 3 h, 100 ml of ether were added, and the organic phase was washed with water (2 × 25 ml) and saturated sodium hydrogencarbonate (2 × 10 ml). After drying ($MgSO_4$) the solvent was evaporated off, to yield 1.22 g of a 70 : 24 : 6 mixture of the corresponding mesylates. ^1HNMR: δ 0.8–3.1 (12 H, m), 4.1–4.4 (2 H, m). The product was used in the next step without further purification.

The crude product from the previous step (1.22 g, 5.6 mmol) and ethylene glycol (4.00 g, 64.5 mmol) were dissolved in 50 ml of benzene containing 2.5 g of Dowex 50 W × 8 and refluxed for 22 h in a Dean–Stark trap.[30] The mixture was cooled to room temperature and poured into 50 ml of a 5% sodium hydrogencarbonate solution, which was subsequently extracted with ether (2 × 50 ml). The combined extracts were washed with 2% sodium hydrogencarbonate and dried over sodium sulfate. Evaporation of the ether left 1.02 g of a 71 : 21 : 8 mixture of the corresponding ketalized mesylates. IR: 2950 (s), 2920 (s), 2850 (s), 1450 (m), 1350 (m), 1260 (m), 1170 (m), 1100 (m) cm^{-1}. The product was used in the next step without further purification.

The crude product from the previous step (1.02 g, 3.9 mmol) was dissolved in 5 ml of dry THF and stirred at room temperature under nitrogen atmosphere. A solution of lithium triethylborohydride (Super-Hydride®) in THF (10 ml, 1.0 M, 10 mmol) was then added with a syringe, and the resulting mixture was stirred, first at room temperature for 1 h and then at reflux for 2 h.[31] The reaction mixture was poured into ice–water (40 ml) and was then extracted with ether (3 × 30 ml). The combined extracts were washed with water (2 × 10 ml) and dried (sodium sulfate). Evaporation of the solvent left 0.65 g of a 58 : 28 : 14 mixture of reductively demesylated ketals. IR: 3600 (w), 3400 (w), 2950 (s), 2850 (s), 1460 (s), 1350 (s) cm^{-1}; ^1H NMR: δ 1.7–2.5 (m), 3.8–4.0 (m). The product was used in the next step without further purification.

The crude product from the previous step (0.20 g, 1.2 mmol) was dissolved in 12 ml of acetone containing 0.05 g of *p*-toluenesulfonic acid and stirred at room temperature for 3 h. Ether (75 ml) was added, the organic phase was washed with water (3 × 20 ml), the combined aqueous phases were extracted with ether (2 × 25 ml), and the combined ether fractions were washed with a 10% solution of sodium hydrogencarbonate (2 × 10 ml) and dried (Na_2SO_4). Work-up in the usual way gave 90 mg of a mixture of *exo*-7-methylbicyclo[3.2.0]heptane (*exo*-**5**), *exo*-6-methylbicyclo[3.2.0]heptane (*exo*-**6**), and *endo*-6-methylbicyclo[3.2.0]heptane (*endo*-**6**); IR (isomer mixture): 2950 (s), 2850 (s), 1730 (s), 1550 (m), 1450 (m), 1410 (w), 1370 (m), 1050 (m) cm^{-1}; ^1H NMR (isomer mixture): 0.8–2.8 (m).

(*exo*-**5**): ^{13}C NMR: δ 22.6 (CH_3), 27.9 (CH_2), 31.7 (CH), 32.0 (CH), 33.2 (CH_2), 37.3 (CH_2), 52.7 (CH), 221.7 (C=O); MS: 124 (39, M^+), 109 (8), 96 (17), 83 (54), 82 (100).

(*exo*-**6**): ^{13}C NMR: δ 21.7 (CH_3), 26.9 (CH_2), 30.3 (CH_2), 33.7 (CH), 36.8 (CH), 41.5 (CH_2), 43.9 (CH), 223.1 (C=O); MS: 124 (38, M^+), 109 (14), 96 (7), 83 (72), 82 (100).

(*endo*-**6**): ^{13}C NMR: δ 16.6, 20.9, 29.4, 31.7, 37.4, 38.1, 42.5, 222.1; MS: 124 (32, M^+), 109 (8), 96 (4), 83 (83), 82 (100).

General procedure for quantum yield determinations. Quantum yields were determined in spectroscopic grade methanol or hexane at low conversions of cyclopentenone (generally less than 5%) using a PTI Quantacount apparatus equipped with a high-pressure mercury lamp. The light from the lamp was passed through a monochromator to select the desired wavelength (313 nm); the estimated bandwidth was 5 nm. The intensity of the light was determined using an azoxybenzene and also a ferrioxalate actinometer. Appropriate corrections were made for transmitted light for those cases where the irradiated samples did not absorb all of the incident light. The irradiated samples were analysed by GC to determine the amount of cycloadducts for a given photon dose; a Hewlett Packard 5880 gas chromatograph equipped with a flame ionization detector and a DB-5 capillary column (30 m) was used. A minimum of five injections were carried out with each irradiated sample to establish limits of error. Decane was used as an internal standard and calibration curves were constructed using purified products so that absolute amounts of products formed in the irradiated samples could be estimated. The samples irradiated were 0.08 M in 2-cyclopentenone and 0–2.0 M in alkenol. The solutions were degassed three times by the freeze–pump–thaw method to a residual pressure of 10^{-4} mmHg prior to irradiation. The quantum yields are summarized in Tables 4 and 5 and in Figs. 1 and 2.

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