Photochemical [2+2] Cycloadditions.
II. Photochemical Addition of 3-Butyl-2-cyclopentenone to Some ω-Bromo-1-alkenes

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Irradiation (λ > 295 nm) of the title ketone in the presence of ω-bromo-1-alkenes (ω = 4,5,6) gave mixtures of head-to-head and head-to-tail [2 + 2] cycloadducts and cyclobutanes formed by secondary reactions. The reaction rates and the product distribution are highly influenced by the distance between the bromine atom and the reacting double bonds. These influences are most likely due to heavy-atom effects and dipole-dipole interactions.

A significant problem in synthetic application of intermolecular enone photocycloaddition is the lack of control of the regiochemistry in reactions involving asymmetrically substituted alkenes. The selectivity in such reactions is often low; typically, cycloadducts are formed as 1:1 to 3.5:1.5 mixtures of the head-to-head (HH) and head-to-tail (HT) regioisomers.[1-3] Corey[4] and others[2,5,6] have shown that the direction of cycloaddition is controlled to a considerable extent by the electron distribution of the reacting double bonds, which of course is an intrinsic property of the reacting system under consideration. Another factor influencing the regioselectivity is the interaction between the overall dipoles of the excited enone and the ground state alkene.[6] Since dipole interactions are strongly affected by the dielectric constant of the reaction medium, it has been possible to control the regiochemistry to a large degree by solvent variation.[3,6,7] As pointed out by de Mayo,[6] this suggests that regiochemical control of photocycloaddition may be achieved by appropriate polar substitution of a molecule at positions other than on the reacting double bond. Such substituents can then be removed after having fulfilled their function.

Among the substituents expected to exert such a directing effect are the halogens,[6] which can be fairly easily introduced and removed by a number of methods. However, halogen atoms, particularly bromine and iodine, affect excited molecules by heavy-atom effects,[8] and this could influence both the efficiency and the course of photocycloaddition reactions, rendering halogen substitution less attractive than might have been anticipated. We therefore became interested in studying photochemical addition of cyclic enones to haloalkenes; the present paper describes the results of our work concerning photocycloaddition of 3-butyl-2-cyclopentenone (1) to some ω-bromo-1-alkenes (2).

Results

All the reactions were carried out by illuminating degassed solutions of the reactants at approximately 5 °C for 5 h with light from a medium-pressure mercury lamp. Most of the photolyses were performed with light filtered through Pyrex (cut-off 295 nm). A variety of different solvents was tried, but due to secondary reactions and subsequent formation of very intractable mixtures of high-boiling products in aprotic solvents, all the preparative reactions were carried out in ethanol. The ethanol solutions were 0.016–0.031 M in 3-butyl-2-cyclopentenone and 0.13–0.25 M
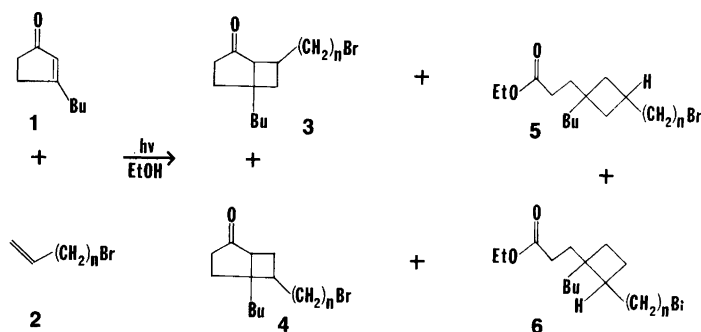
Scheme 1.   **a**: $n = 4$; **b**: $n = 3$; **c**: $n = 2$

in bromoalkene. The alkenes were used in excess to avoid dimerization of the enone[9] and, indeed, analysis of the crude reaction mixtures using an authentic sample of the isomeric dimers[9] showed that no dimer was formed in any of the reactions. The composition of product mixtures was determined from GC analyses on the basis of non-calibrated peak areas.

When a solution containing **1** and 6-bromo-1-hexene (**2a**) was irradiated a complex reaction mixture was obtained. The composition of the mixture appeared to be essentially independent of the irradiation time as long as at least half of the enone was consumed. The volatile products were isolated by short-path distillation, which afforded (in 56% yield) a 9:33:7:51 mixture of four compounds that were assigned the structures **3a–6a**, respectively (Scheme 1, Table 1). Several attempts to obtain pure samples of the individual cyclobutanes were unsuccessful, and the structure elucidation was therefore carried out on the basis of spectroscopic and spectrometric examination of different mixtures of the products. Two of the products were apparently the HH [2 + 2] cycloadduct 7-(4-bromobu-

tyl)-5-butyl-2-bicyclo[3.2.0]heptanone (**3a**) and the corresponding HT adduct 6-(4-bromobutyl)-5-butyl-2-bicyclo[3.2.0]heptanone (**4a**). The elemental composition of both compounds was confirmed by high resolution GC/MS, which also showed that the mass spectrum of each regioisomer was very similar to that of an authentic sample of the corresponding dibutylbicyclo[3.2.0]heptanone.[3] The most striking difference between the mass spectra of **3a** and **4a** is the presence of two intense peaks due to ions with compositions C_7H_{10} ^{81}BrO (m/z 191) and C_7H_{10} ^{79}BrO (m/z 189) in that of the former. On the basis of characteristic fragmentation processes for the cyclopentanone and cyclobutane moieties[3,10] these fragments are conceivably formed by fission of the C-2, C-3 bond, followed by a splitting of the four-membered ring. A corollary of this interpretation is that the mass spectra of the analogous cycloadducts formed from the homologous alkenes **2b** and **2c** should exhibit similar peaks at m/z 177/175 and m/z 163/161, respectively. This was, in fact, the case (*vide infra*), and these findings confirm that the least abundant cycloadduct is the HH isomer **3a**. This conclusion

Table 1. Yields and product distributions in photocycloaddition of **1** to **2**.

Alkene	Conversion of 1/%	Yield of 3–6/%[a]	Distribution				HH/HT[b]	Ester/ketone[c]	
			3	**4**	**5**	**6**		HH	HT
2a	100	56	9	33	7	51	16/84	0.8	1.6
2b	80	52	15	31	24	30	39/61	1.6	1.0
2c	40	86	32	29	39	0	71/29	1.2	0

[a]Based on consumed cycloalkenone. [b]HH = **3+5**, HT = **4+6**. [c]HH = **5/3**, HT = **6/4**.

Table 2. ^{13}C NMR chemical shifts[a] of C–1 and C–5 in some cycloadducts formed by photoaddition of 3-butyl-2-cyclopentenone to some 1-alkenes.

Regioisomer	Stereoisomer[b]	C–1	C–5	Ref.
3a	One	56.1	42.2	This work
4a	Major	47.0	48.9	This work
	Minor	47.5	47.9	This work
3b	Major (72 %)	56.0	42.2	This work
	Minor (28 %)	52.8	39.7	This work
4b	Major (62 %)	47.0	48.9	This work
	Minor (38 %)	47.5	47.8	This work
7[c] (HH)	Major	56.2	42.2	3
	Minor	53.0	39.8	3
8[c] (HT)	One	47.1	48.9	3
9[c]	Major	56.2	42.2	3
	Minor	53.1	39.8	3
10[c]	One	47.1	48.9	3

[a]The shifts are reported in ppm downfield from internal TMS. [b]The stereoisomeric ratios are determined on the basis of the intensities of the C–1/C–5 signals in the completely decoupled ^{13}C NMR spectra of the distilled product mixtures. [c]7: 5,7-dibutyl-2-bicyclo[3.2.0]heptanone; 8: 5,6-dibutyl-2-bicyclo[3.2.0]heptanone; 9: 5-butyl-7-hexyl-2-bicyclo[3.2.0]heptanone; 10: 5-butyl-6-hexyl-2-bicyclo[3.2.0]heptanone.

was supported by ^{13}C NMR spectra of several mixtures of the products. Particularly informative were the signals due to C-1 and C-5 (Table 2), because their relative intensities are connected with the composition of the mixtures and the systematic variation in their chemical shifts reflects the α-shielding and γ-deshielding effects of the 4-bromobutyl substituent.[3] Comparison of the data compiled in Table 2 clearly reveals that the major [2 + 2] cycloadduct formed by photoaddition of 1 to 2a is the HT regioisomer, i.e.
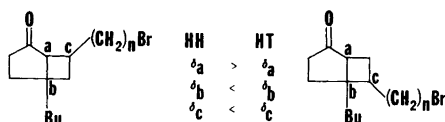
4a. The data also show that 4a is formed as an approximately 3:2 mixture of stereoisomers, whereas 3a is obtained as a single isomer. By comparing the chemical shifts of C-1 and C-5 for 3a with those for the two isomers of 3b (*vide infra*) it is reasonable to conclude that 3a has the *cis* configuration. Finally, it should be mentioned that IR and ^{1}H NMR spectra of impure samples of mixtures of 3a and 4a display absorptions compatible with the proposed structures.

For a number of reasons the two remaining main products formed by addition of 1 to 2a were assigned the structures ethyl 3-[3-(4-bromobutyl)-1-butylcyclobutyl]propanoate (5a) and ethyl 3-[2-(4-bromobutyl)-1-butylcyclobutyl]propanoate (6a), although the elemental composition could not be determined by either combustion analysis, due to the presence of impurities, or by high-resolution mass spectrometry, because no molecular ion was obtained. The presence of an ethyl ester moiety was apparent from the ^{1}H and ^{13}C NMR spectra; the proton spectrum exhibited a quartet at 4.12 ppm coupled to a triplet at 1.26 ppm, whereas the carbon spectrum contained signals due to a carboxylate group (174.2 ppm) and a methylene group next to an ester oxygen atom (60.2 ppm). By comparing approximate integrated intensities the ketone:ester ratio was determined to be 2:3 which is almost identical to the ratio determined by GC analysis. Furthermore, the IR spectrum of a mixture of 5a and 6a displays absorptions due to the ester moiety (1740 and 1180 cm⁻¹), in addition to alkyl and C-Br absorptions. The proposed structures are also supported by the mass spectra of the compounds. In both spectra the peaks with the highest m/z values (303/301) are attributed to the ions formed by loss of the ethoxy group from the molecular

ion, a predominant fragmentation process for ethyl esters. These ions can subsequently undergo a number of cleavage reactions, some of which depend on the substitution pattern of the cyclobutane ring. Thus, 6a can undergo ring splitting in two ways, leading to expulsion of ethylene and 6-bromo-1-hexene, whereas 5a, due to symmetry, can only expel 2a. Ethylene extrusion from the ions with m/z 303/301 is only observed in the case of the more abundant regioisomer and we therefore believe that the predominant ester is 6a. This conclusion is supported by the occurrence of a significant peak (m/z 184) caused by loss of 6-bromo-1-hexene from the molecular ion of the other regioisomer 5a. Subsequent decomposition of the m/z 184 ion conceivably yields m/z 142 by ketene expulsion, m/z 139 by loss of an ethoxy radical, and m/z 138 by ethanol elimination. Loss of ketene from m/z 138 then furnishes m/z 96, the base peak of the spectrum. If this interpretation is correct, the fragment ions mentioned above should be present in the mass spectra of 5, irrespective of the number of methylene groups in the ω-bromoalkyl substituent attached to C-3; this was indeed the case (see Experimental).

The photoaddition of 1 to 5-bromo-1-pentene (2b) proceeded essentially as the addition to 2a under the same conditions, albeit less efficiently (Table 1). Bulb-to-bulb distillation of the complex photolyzate afforded 20 % of unreacted ketone and 52 % of a 15:31:24:30 mixture of adducts 3b–6b, respectively (Table 1). Although none of the products could be obtained as single, pure compounds their structures could be determined on the basis of spectra of impure samples. It was also most helpful to compare their spectroscopic properties with those of the corresponding cycloadducts 3a–6a. The adduct formed in lowest yield was assigned the structure 7-(3-bromopropyl)-5-butyl-2-bicyclo[3.2.0]heptanone (3b). This conclusion was substantiated mainly by the following: The correct elemental composition of the molecular ion of the compound, the resemblance between its mass spectrum and that of 3a, the occurrence in the mass spectrum of strong peaks at m/z 177/175 (vide supra) and, finally, the similarity in the chemical shifts of C-1 and C-5 for 3b and for other HH cycloadducts (Table 2). Unlike 3a, which was a single isomer, 3b appears to consist of two stereoisomers in a 72:28 ratio, as revealed by the intensities of the C-1 and C-5

signals in the completely decoupled ^{13}C NMR spectrum. If the ^{13}C substituent parameters reported by Eliel and Pietrusiewicz[11] for methylated cyclobutanes are approximately applicable in our case, the fact that the major isomer exhibits the C-1 signal at a significantly lower field than the minor stereoisomer (Table 2) indicates that 3b consists mainly of the cis isomer. The product isolated in highest yield was identified as 6-(3-bromopropyl)-5-butyl-2-bicyclo[3.2.0]heptanone (4b), i.e. the other [2 + 2] cycloadduct, on the basis of IR, MS, and ^1H and ^{13}C NMR data. The ^{13}C NMR spectrum clearly showed that the adduct was a 62:38 mixture of stereoisomers, but because of the substitution pattern the spectrum does not allow us to establish their stereochemistry.

The other two major products were ethyl 3-[3-(3-bromopropyl)-1-butylcyclobutyl]propanoate (5b) and ethyl 3-[2-(3-bromopropyl)-1-butylcyclobutyl]propanoate (6b), according to spectroscopic and spectrometric evidence. The presence of the ethoxy carbonyl moiety was substantiated by the ^1H and ^{13}C NMR spectra and by the absence of a molecular ion in the mass spectra. Furthermore, the mass spectra of 5b and 5a were very similar, as were those of 6b and 6a; e.g. ethylene elimination from the M^+ $-CH_3CH_2O$ fragment is observed only for 5b, whereas significant formation of the m/z 184, 142, 139 and 138 ions (vide supra) appears to occur for 6b exclusively.

Irradiation of an ethanol solution of 1 and 4-bromo-1-butene (2c) gave a mixture of three main products and some unreacted enone. After illumination for 5 h, i.e. the reaction time needed to consume all the ketone during addition to 2a under identical conditions, 60 % of 1 had still not reacted. Column chromatography afforded 86 % (based on consumed ketone) of a mixture of the main products, which were identified as 7-(2-bromoethyl)-5-butyl-2-bicyclo[3.2.0]heptanone (3c), 6-(2-bromoethyl)-5-butyl-2-bicyclo[3.2.0]heptanone (4c), and ethyl 3-[3-(2-bromoethyl)-1-butylcyclobutyl]propanoate (5c) (Table 1). The structures were elucidated using spectroscopic and spectrometric methods and by comparing the spectra of 3c–5c with those of 3a–6a and 3b–6b.

Photolysis of an ethanol solution of 1 (0.20 M) and 2c (1.30 M) with filtered light (λ > 310 nm) from a medium-pressure mercury lamp progressed slower, but more cleanly. After 5 h of

irradiation only 25 % of the ketone had reacted and been converted to a mixture that contained 75 % of **3c** and **4c** in a ratio of approximately 2:1, and six other products whose structures remain unknown; **5c** was not detected. Subsequent illumination of this reaction mixture with Pyrex-filtered light ($\lambda > 295$ nm) gave some ester **5c** at the expense of **3c**, which proves that **5c** is a secondary reaction product.

Finally, it should be mentioned that attempts to perform photoaddition of 3-acetoxy-2-cyclohexenone to **2** in ethanol according to the general procedure were unsuccessful. Even **2a**, which was the most reactive alkene toward excited **1**, did not undergo addition during 90 h of irradiation.

Discussion

The results of the photocycloadditions of 3-butyl-2-cyclopentenone to ω-bromo-1-alkenes, summarized in Table 1, show several notable features. Under essentially identical conditions the addition of **1** to 6-bromo-1-hexene is approximately 50 % more efficient than the addition to 4-bromo-1-butene. The reaction, therefore, seems to be less effective the closer the bromine atom is to the reacting double bonds. Secondly, it is also evident that the bromine atom-double bond distance is of importance for the regioselectivity of the addition; thus, taking into account that esters **5** and **6** result from cleavage of **3** and **4**, respectively, the head-to-head mode of addition increases from 16 % to 71 % when the distance is made shorter by replacing **2a** with **2c**. Finally, it is noteworthy that bicycloheptanones **3** and **4** are transformed, in most cases to a considerable extent, to esters **5** and **6**, since the corresponding butyl- and hexyl-substituted 5-butyl-2-bicyclo[3.2.0]heptanones are photochemically inert under the same conditions. It is, therefore, clear that the cycloaddition of **1** to **2** is influenced profoundly by the bromine atom attached to the alkenes.

The influence of the halogen substituent is intimately related to the mechanism for the cycloaddition reaction. The generalized scheme outlined below (Scheme 2) accommodates the steps relevant to cycloadduct formation. Subsequent to initial excitation of the enone (E) to the singlet state, intersystem crossing to ^{3}E occurs, conceivably with an efficiency equal to or close to 100 %.[1,2,8,12] The triplet enone may either decay

to ^{1}E (in an unimolecular process which is affected by bromine atoms on the basis of the concentration and not the length of the olefin carbon chain) or undergo irreversible association to ground state alkene (A) molecules to give a mixture of regioisomeric excited complexes (exciplexes) ([^{3}EA]*).[2,8,12] The excited enone is fairly polar in nature and will tend to align relative to the alkene in such a way that their dipole moments are antiparallel. The composition of the exciplex mixture is certainly affected by these directing forces, but only partially since exciplex formation is a kinetically controlled process that proceeds almost at diffusion rate. However, dipole-dipole interactions are weaker the farther apart the dipoles are and the directing forces between ^{3}E and A are therefore weakest when A = **2a** and strongest when A = **2c**. Consequently, the HH mode of cycloaddition of **1** to **2** should be more pronounced in the case of **2c** than in the case of **2a** provided the regiochemical outcome of the photoaddition is determined to a significant extent by the exciplex structure; this is exactly what is observed (Table 1).

The lifetimes of the exciplexes are short as a result of two processes, viz. formation of 1,4-diradical intermediates [·EA·], and decomposition to ground state enone and alkene with rate constants k_1 and k_2, respectively. The latter is purely an energy-wasting process, so the more effective it is the less efficient is the cycloadduct formation. Usually, this non-productive reaction is assumed to be negligible, i.e. $k_1 >> k_2$,[2,12] which presumably is correct when the alkene is essentially non-polar and does not contain atoms that are capable of facilitating spin inversion. However, when bromoalkenes are involved the situation is somewhat different: some of the exciplex structures, generated by head-to-tail association of ^{3}E to A due to the kinetic control of the exciplex
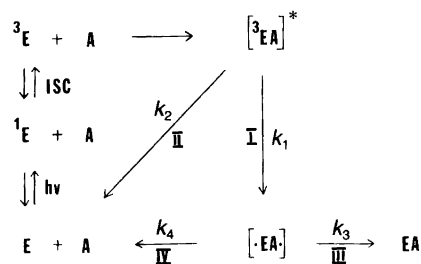
Scheme 2.

formation, are likely to be fairly unstable as the result of significant dipole-dipole interactions; secondly, the bromine atom present is capable of increasing the rates of spin-forbidden $T_1 \rightarrow S_o$ processes.[8] Both these effects contribute to increase the non-productive consumption of $[^3EA]^*$. How considerable the effect is depends, once again, on the distance from the bromine atom to the site where the bond-breaking processes take place: the shorter it is the more profound the effect is expected to be. This is indeed observed: the photoaddition is much more efficient for 6-bromo-1-hexene (2a) than for 4-bromo-1-butene (2c), and, furthermore, products resulting from head-to-head addition are much more abundant in the latter case than in the former (Table 1).

Although it is likely that the exciplex mixture undergoes to some extent direct decomposition to E and A in the present cases (pathway II, Scheme 2), the majority of the excited complexes probably proceed to give a mixture of triplet 1,4-diradicals. These radicals can either undergo spin inversion and product formation (rate constant k_3) or disproportionate and afford ground state enone and alkene after relaxation (rate constant k_4). Which one of the two pathways predominates is of decisive importance for the efficiency of the cycloaddition reaction; the larger k_4 is relative to k_3 the less efficient is the reaction. The relative rate of product formation from $[\cdot EA\cdot]$, k_3/k_4, is unknown for the systems under consideration, but considering the large variation in k_3/k_4 reported for photoadditions of 2-cyclo-

pentenone to a number of symmetrical olefins[12] it is very unlikely, due to differences in dipolar interactions and heavy-atom effects, that the rate ratio for A = 2a is equal to that for A = 2c.

From the discussion above it is evident that the bromine atom attached to the alkenes introduces interactions that are likely to make the non-productive reaction pathways (II and IV) (relative to product-forming steps I and III) (see Scheme 2) more favourable when the alkene is a hydrocarbon. However, no conclusion can be drawn as to whether II or IV is the primary energy-wasting step in the process.

Compared to the photocycloaddition of 1 to various terminal alkenes the additions to 2 are very complex. The complexity results from secondary reactions of ketones 3 and 4, which are essentially the only primary products as borne out by the composition of the reaction mixture obtained when light with $\lambda > 310$ nm was used. Major secondary products were cyclobutane derivatives 5 and 6, the formation of which involves Norrish type I reactions.[8] Thus, cleavage of 3 and 4 yields biradical 7 which gives ketene 8 by 1,4 hydrogen abstraction[13,14] (Scheme 3). When the reaction is carried out in ethanol the ketene is immediately trapped and converted to esters 5 and 6.[15] If the reaction is carried out in aprotic solvents the ketene will give other products,[16] which partly explains why intractable mixtures are produced in such solvents. However, more important in that respect is perhaps that type I cleavage reactions can give a number of products other than ketene 8.[8] At any rate, whatever the by-products are it is evident that from a synthetic point of view, bromine substitution of the alkenes does not improve the course of the photoaddition of 1 to terminal alkenes.

One puzzling point concerning the results in Table 1 is the different reactivity exhibited by adducts 3 and 4. Particularly striking is the observation that 4c does not give any of the corresponding ester 6c whatsoever. However, the data available at present do not allow speculation about the causes of these differences, and we hope that further studies of the photochemical and photophysical properties of pure samples of 3 and 4 will be illuminating in that respect.

$$3 + 4 \xrightarrow{h\nu} 7$$

$$5 + 6 \xleftarrow{EtOH} 8$$
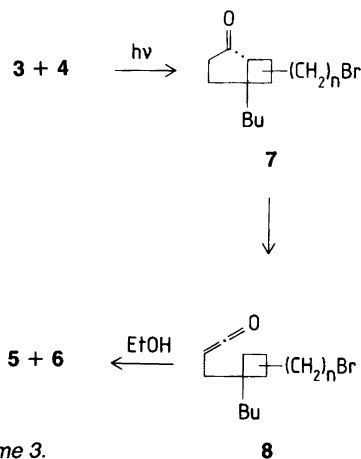
Scheme 3.

Experimental

The equipment employed has been described elsewhere.[17] IR spectra were recorded for samples in the form of thin films. ^{1}H NMR spectra were obtained at 89.55 MHz and ^{13}C NMR spectra at 22.50 MHz using CDCl$_3$ as solvent. Chemical shifts are reported in ppm downfield from internal tetramethylsilane (TMS). Electron ionization mass spectra were recorded at 70 eV and are reported as m/z (% relative intensity).

Materials. 3-Butyl-2-cyclopentenone (**1**) was prepared according to Büchi's procedure.[3,18] All other chemicals were commercially available.

Photolysis; general procedure. An oxygen-free solution of ketone and alkene in ethanol (300 ml) was kept at 5 °C under nitrogen and irradiated for 5 h with light from a 400 W medium-pressure mercury arc lamp. The lamp was kept in a water-cooled Pyrex well (cut-off 295 nm) which was immersed in the solution. Solvent and unreacted starting material were removed under vacuum and the products were isolated by column chromatography or distillation.

Photocycloaddition of **1** *to 6-bromo-1-hexene* *(***2a***).* Irradiation of a solution of **1** (0.72 g, 5.2 mmol) and **2a** (6.92 g, 42.4 mmol) according to the general procedure gave a crude product (1.8 g) which contained no unreacted ketone according to GLC analysis. Bulb-to-bulb distillation afforded 0.95 g (56 %) of a mixture of volatile products (**3a–6a**), b.p. 108 °C/1.0 mmHg. IR: 2960 (s), 2925 (s), 2860 (m), 1740 (s), 1470 (m), 1180 (m), 720 (m) cm^{-1}; ^{1}H NMR: δ 0.90–2.75 (m), 1.26 (t, J 7 Hz), 3.40 (t, J 6 Hz), 4.12 (q, J 7Hz); ^{13}C NMR: δ 14.0 (CH$_3$), 14.2 (CH$_3$), 22.5–41.5 (47 distinguishable peaks of varying intensity in the decoupled spectrum), 42.2 (C), 43.0 (C), 43.3 (CH$_2$), 47.0 (CH), 47.5 (CH), 47.9 (C), 48.9 (C), 56.1 (CH), 60.2 (CH$_2$), 174.2 (C=O), 221.0 (C=O). GC analysis revealed that the product mixture consisted mainly (95 %) of four photoadducts in a non-calibrated ratio of 9:51:33:7 (in order of retention). The mass spectra were obtained by GC/MS analysis. **3a**: 302/300 (M^+,6), 274/272 (0.6), 273/271 (2), 245/243 (4), 221 (5), 191/189 (68), 165 (12), 140 (5), 139 (55), 138 (7), 110 (12), 109 (22), 97 (21), 96 (100), 95 (23); mol. wt.: calc. for C$_{15}$H$_{25}$^{81}BrO 302.1068, found

302.1074. **4a**: 273/271 (0.3), 221 (0.6), 140 (6), 139 (75), 138 (10), 110 (11), 109 (14), 97 (21), 96 (100), 95 (26). **5a**: 303/301 (2), 285/283 (1), 277/275 (1), 260/258 (1), 245 (2), 197/195 (2), 184 (0.1), 170 (19), 165 (3), 141 (6), 139 (5), 138 (27), 128 (90), 115 (9), 110 (30), 109 (13), 99 (6), 96 (100). **6a**: 247/245 (3), 185 (2), 184 (20), 165 (5), 155 (7), 142 (69), 139 (15), 138 (33), 123 (7), 110 (45), 109 (15), 97 (51), 96 (100), 95 (30).

Photocycloaddition of **1** *to 5-bromo-1-pentene* *(***2b***).* Illumination of a solution of **1** (0.68 g, 4.9 mmol) and **2b** (5.85 g, 39.3 mmol) as described in the general procedure gave a crude product (1.6 g) which contained 20 % unreacted starting material according to GC analysis. Short-path distillation furnished 0.63 g of a mixture of photoaddition products, b.p. 100 °C/0.9 mmHg. IR: 2965 (s), 2940 (s), 2870 (m), 1740 (s), 1470 (m), 1185 (m), 710 (s) cm^{-1}; ^{1}H NMR: δ 0.90–2.75 (m), 1.26 (t, J 7 Hz), 3.40 (2t, J 6 Hz), 4.12 (q, J 7 Hz); ^{13}C NMR: δ 14.0 (CH$_3$), 14.2 (CH$_3$), 20.0–40.0 (44 distinguishable peaks in the decoupled spectrum), 40.1 (CH$_2$), 40.7, 40.8, 41.3 (CH), 42.2 (C), 42.7 (CH), 43.0 (C), 47.0 (CH), 47.5 (CH$_2$), 47.8 (C), 48.9 (C), 51.5 (CH), 52.8 (CH), 56.0 (CH), 60.3 (CH$_2$), 60.5 (CH$_2$), 174.2 (C=O), 174.6 (C=O), 221.1 (C=O), 222.6 (C=O). GC analyses showed, on the basis of non-calibrated peak areas, that a 15:30:31:24 (in order of elution) mixture of adducts **3b–6b** amounted to 97 % of the isolated product; a fifth product was present in too small a quantity to allow identification. The mass spectra of the photoadducts were obtained by GC/MS analyses. **3b**: 288/286 (M^+,6), 259/257 (2), 245/243 (2), 232/230 (3), 207 (5), 190 (4), 177 (75), 175 (77), 165 (10), 152 (10), 139 (37), 138 (8), 123 (5), 110 (10), 109 (17), 97 (18), 96 (100), 95 (25); mol. wt.: calc. for C$_{14}$H$_{23}$^{81}BrO 288.0912, found 288.0916. **4b**: 288 (M^+,0.1), 259/257 (0.3), 245/243 (0.2), 231 (1), 207 (0.5), 177/175 (1), 165 (2), 152 (1), 140 (4), 139 (59), 138 (12), 123 (2), 110 (10), 109 (9), 97 (10), 96 (100), 95 (12); mol. wt.: calc. for C$_{14}$H$_{23}$^{81}BrO 288.0912, found 288.0909. **5b**: 289/287 (1), 271/269 (1), 263 (1), 261/259 (1), 239 (1), 231 (2), 218/216 (1), 211 (1), 197 (3), 170 (15), 165 (4), 141 (8), 138 (25), 129 (7), 128 (86), 127 (9), 123 (5), 115 (11), 110 (30), 109 (13), 97 (40), 96 (100), 95 (18). **6b**: 289/287 (3), 277/275 (1), 271/269 (1), 260/258 (1), 253 (2), 231 (3), 218/216 (1), 211 (3), 195 (2), 184 (17), 183 (3), 170 (1),

165 (4), 155 (7), 143 (6), 142 (78), 139 (9), 138 (34), 129 (6), 128 (2), 127 (6), 123 (8), 110 (42), 109 (18), 101 (15), 97 (56), 96 (100), 95 (25).

Photoaddition of **1** *to 4-bromo-1-butene (**2c**).* Photolysis of a solution of **1** (0.70 g, 5.1 mmol) and **2c** (5.55 g, 40.9 mmol) according to the general procedure gave 1.4 g of crude product. Unreacted ketone (60 % according to GC analysis) and excess alkene were removed by vacuum distillation. Due to thermal decomposition the products were isolated by column chromatography (silica gel; acetone/chloroform, 1:19). This gave 0.83 g of a product mixture that consisted essentially of **3c**, **4c** and **5c** in a ratio of 32:29:39, respectively, according to GC analysis. IR: 2965 (s), 2940 (m), 2870 (m), 1740 (m), 1470 (m), 1180 (s), 705 (s) cm^{-1}; ^{1}H NMR: δ 0.90–2.71 (m), 1.26 (t, J 7 Hz), 3.29 (m), 4.13 (q, J 7 Hz); ^{13}C NMR: δ 14.0 (CH$_3$), 14.2 (CH$_3$), 21.0–61.0 (42 distinguishable peaks in the decoupled spectrum), 60.3 (CH$_2$), 173.9 (C=O), 174.1 (C=O), 220.0 (C=O). The mass spectra of the products were obtained by GC/MS analysis. **3c**: 274/272, (M^+, 4), 259/257 (2), 245/243 (2), 235/233 (2), 229 (2), 217/215 (4), 203/201 (1), 193 (7), 189 (4), 175 (5), 165 (10), 163/161 (63), 139 (14), 123 (14), 110 (13), 109 (22), 107 (11), 97 (30), 96 (100), 95 (37); mol. wt., calc. for C$_{13}$H$_{21}$^{81}BrO 274.0755, found 274.0743. **4c**: 274/272 (M^+ ,0.5), 245/243 (0.5), 215 (2), 193 (2), 139 (43), 138 (48), 123 (8), 110 (8), 109 (32), 108 (22), 97 (25), 96 (100), 95 (35); mol. wt.: calc. for C$_{13}$H$_{21}$^{81}BrO 274.0755, found 274.0756. **5c**: 275/273 (3), 257/255 (2), 239 (1), 210 (4), 209 (4), 208 (3), 184 (10), 142 (70), 139 (5), 138 (27), 110 (9), 109 (35), 101 (8), 97 (60), 96 (100), 95 (25).

A nitrogen-purged solution of enone **1** (0.56 g, 4.1 mmol) and alkene **2c** (3.5 g, 26 mmol) in ethanol (15 ml) was also irradiated at room temperature with light passed through a filter with cut-off at 310 nm and 50 % transmission at 335 nm. GC analysis after 5 h of photolysis showed that the reaction mixture contained **1** (75 %), as well as **3c** and **4c** (18 %) in a ratio of 1:2.

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