Regioselective Photocycloaddition of 2-Cyclopentenone to Some Allenes

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Irradiation ($\lambda > 295$ nm) of 2-cyclopentenone in the presence of 3-methyl-1,2-bu-tadiene, 2-methyl-2,3-pentadiene, and 1,2-cyclononadiene gave mixtures of cy-cloadducts in good yields (>78 %). The mixtures contained head-to-head and head-to-tail isomers in an approximate ratio of 80:20. The additions to the acyclic allenes occurred across the less highly substituted double bond. The mechanism of the reactions is discussed.

Photochemical [2 + 2] cycloaddition of 2-cycloal-kenones to C−C double bonds has emerged as a valuable reaction in organic synthesis.[1-9] The re-action has been used to synthesize cyclobutanes per se[3,4,9-15] and to prepare reactive synthetic in-termediates;[9,16-19] it has also played the key role in the synthesis of a number of natural products, such as atisine,[20] α- and β- bourbonene,[21] gran-disol,[22] lineatin,[23,24] and stemarin.[25] But in spite of these and other useful applications, lack of re-gioselectivity in reactions involving unsymmetri-cally substituted olefins generally represents a problem, although it has been partly solved in some cases by solvent variation[13] and by perform-ing the reaction with the reactants solubilized in aqueous micelle solutions.[26] However, exceptions are known and several notable examples involve photoaddition of various cyclic α-, β-unsaturated ketones to 1,2-propadiene (allene). In some of these reactions, the head-to-head (HH) regio-isomer is formed exclusively;[25,27-29] in many other cases, the HH cycloadduct is obtained in consid-erably higher yield than the corresponding head-to-tail (HT) isomer.[15,24,30] We, therefore, became interested in studying the regioselectivity of en-one photocycloadditions to substituted allenes which had not been investigated at all when this work was initiated, and we report here our re-sults on addition of 2-cyclopentenone (1) to three alkylated allenes (2).
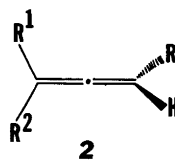

a R=H, R^1=R^2=Me; b R=R^1=R^2=Me; c R, R^1=(CH$_2$)$_6$, R^2=H.

Results

The reactions were carried out by irradiating de-gassed ethanol solutions of the reactants at 0 °C with pyrex-filtered light ($\lambda > 295$ nm) from a me-dium pressure mercury lamp until all the ketone was consumed. The solutions were 0.0333 M in 2-cyclopentenone and 0.133 M in allene. The al-lenes were used in excess to suppress photodi-merization of 1[31] and indeed, analysis of the crude reaction mixtures using authentic samples

HH   **HT**
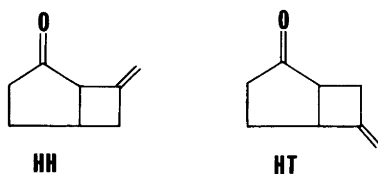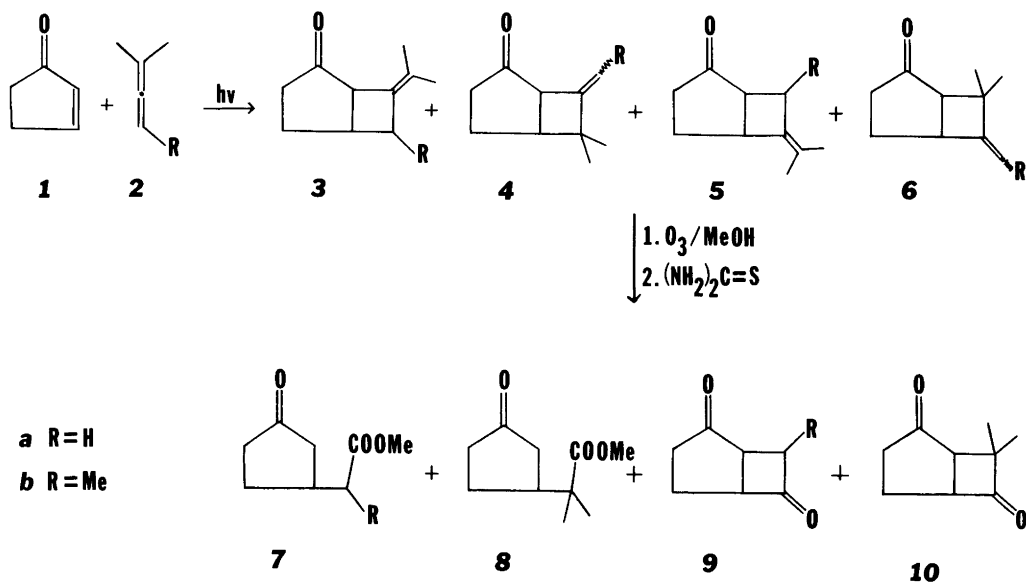
Scheme 1.

of the dimers revealed that no dimer was formed in any of the reactions. By using pyrex-filtered light, photochemical transformations of the al- lenes[32-34] were also avoided. However, a large number of other by-products, amounting to 14– 22 % of the product mixture, were always formed and these compounds made the purification and, thus, the subsequent structure elucidation of the cycloadducts very difficult. The crude reaction mixtures were, therefore, ozonolyzed in meth- anol.[24] This converted the cycloadducts from 2a and 2b to mixtures of ketoesters and diketones (Scheme 1) which could be distinguished by spec- troscopic and spectrometric means after purifica- tion.

When a mixture of 1 and 3-methyl-1,2-buta- diene (2a) was photolyzed, cycloadducts 3a–6a (Scheme 1) were formed in 78 % yield and iso- lated in 57 % yield. The adducts gave rise to three peaks in a ratio of 2:16:5 when analyzed by gas chromatography (GC) prior to isolation. The presence of several isomers was also substan- tiated by ^{1}H NMR spectroscopy. Thus, the pro- ton spectrum of the crude product showed a number of absorptions due to olefin protons (5.2–4.8 ppm), two broad singlets at 1.61 and 1.50 ppm due to isopropylidene methyl groups, and essentially two singlets at 1.26 and 1.15 ppm caused by methyl groups attached to cyclobutane

rings. These results were confirmed by analysis and work-up of the reaction mixture obtained by ozonolysis of the photolyzate. Four products re- sulting from oxidation of 3a–6a, amounting to 72 % of the mixture, were formed in an approxi- mate ratio of 24:3:5:4. The main product was as- signed the structure methyl (3-oxocyclopentyl)- ethanoate (7a)[35] on the basis of IR, MS, and ^{1}H and ^{13}C NMR data, proving that 7-isopropyli- dene-2-bicyclo[3.2.0]heptanone (3a), one of the HH isomers, was the main cycloadduct formed. The other HH isomer, 6,6-dimethyl-7-methyli- dene-2-bicyclo[3.2.0]heptanone (4a), was also obtained because one of the other ozonolysis products, comprising 8 % of the ozonolyzate, was identified as methyl 2-methyl-2-(3-oxocyclopen- tyl)propanoate (8a) based on spectroscopic and spectrometric evidence. Finally, the formation of 6-isobutylidene-2-bicyclo[3.2.0]heptanone (5a) and 7,7-dimethyl-6-methylidene-2-bicyclo[3.2.0]- heptanone (6a), resulting from head-to-tail addi- tion of 1 to 2a, was substantiated by isolation of a mixture of 2,6-bicyclo[3.2.0]heptanedione (9a)[26,36] and 7,7-dimethyl-2,6-bicyclo[3.2.0]hep- tanedione (10).[37] Since the ketone absorptions due to 10[37] were considerably stronger than those of 9a,[36] adduct 6a was conceivably formed in higher yield than 5a.

Photocycloaddition of 1 to 2-methyl-2,3-pen-

tadiene (*2b*) produced a 17:3:1:5 mixture of cycloadducts which comprised 85 % of the crude product, but was isolated in only 48 % yield. Their structures were supported by the proton NMR spectrum of a mixture of cycloadducts which contained several absorptions due to methyl groups attached to cyclobutane rings (1.0–1.4 ppm), methyl groups bonded to sp^2 hybridized carbon atoms (1.5–1.7 ppm), and olefinic hydrogen atoms (4.6–5.4 ppm), but the structure elucidation had to be based on analysis and work-up of the products obtained by ozone treatment of the crude photolyzate. As borne out by GC analysis, such treatment gave a 2:24:6:5 mixture of products derived from cycloadducts *3b–6b* in 79 % total yield. The main product was isolated by column chromatography and assigned the structure methyl 2-(3-oxocyclopentyl)propanoate (*7b*) on the basis of spectroscopic and spectrometric evidence. This assignment was supported by the similarity between the proton NMR spectrum of *7b* and that of the corresponding carboxylic acid.[38] Consequently, 7-isopropylidene-6-methyl-2-bicyclo[3.2.0]heptanone (*3b*) was the major cycloadduct formed. Separation of the three remaining degradation products was, however, unsuccessful; but by performing IR, NMR, and GC/MS analyses of various mixtures of the compounds and using samples of ketoester *8* and diketone *10* obtained from adducts *4a* and *6a* and an authentic sample of 7-methyl-2,6-bicyclo[3.2.0]heptanedione (*9b*),[39] it was concluded that the *8:9b:10* ratio was 6:2:5. It was, therefore, reasonable to believe that cycloadducts *4b*, *5b*, and *6b* (Scheme 1) were obtained in a ratio of 5:1:3.

Irradiation of 2-cyclopentenone in the presence of 1,2-cyclononadiene (*2c*) gave a 5:16 mixture of two major products in 86 % yield. The products were isolated in 75 % yield by Kugelrohr distillation. The spectroscopic properties were compatible with the structures tricyclo-[7.5.0.0^{10,14}]tetradec-8-en-11-one (*3c*) and tricyclo[7.5.0.0^{10,14}]tetradec-1-en-11-one (*5c*) and these assignments were confirmed by the structures of the compounds obtained by subjecting the photolyzate consecutively to ozone in methanol, thiourea, Jones reagent, and diazomethane (Scheme 2). Thus, the main product, comprising 63 % of the reaction mixture after esterification, was identified as dimethyl 2-(3-oxocyclopentyl)-nonanedioate (*11*), proving that ketone *3c* was the predominant cycloadduct. (Whether this ketone is a single compound or a mixture of stereoisomers is uncertain). In addition to ketodiester *11*, oxidation of the photolyzate gave rise to two minor products which amounted to 5 and 8 % of the total reaction mixture after esterification. Neither of the compounds could be isolated pure, but since both gave rise to IR absorptions at 1780 and 1740 cm^{-1} and peaks in the ^{13}C NMR spectrum at 178 and 216 ppm we felt confident that the compounds were the *cis* and *trans* isomers of 7-(6-methoxycarbonylhexyl)-2,6-bicyclo-[3.2.0]heptanedione (*12*). This confirmed that the HT regioisomer *5c* was the less abundant cycloadduct and, furthermore, that *5c* was formed as a 5:8 stereoisomeric mixture.

The proton NMR spectrum of the reaction mixture obtained by ozonolysis/thiourea reduction of the crude mixture of *3c* and *5c* showed four distinct singlets in the 3.26–3.36 ppm region. Since these signals were absent in the ^{1}H spectrum of the product mixture furnished by Jones oxidation of the reduced ozonolyzate, the peaks are conceivably due to methoxy groups of iso-

1 + 2c
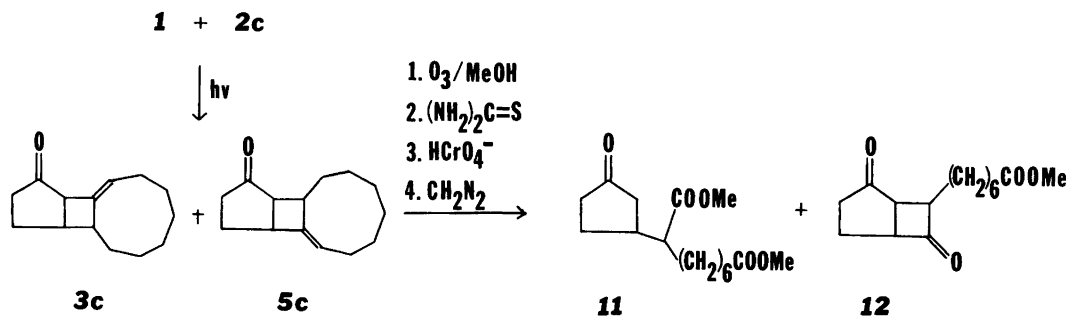
Scheme 2.

Table 1. Cycloadducts formed by photocycloaddition of 2-cyclopentenone to 2.

Allene	Adduct Yield/%[a]	Adduct distribution/%[a]				HH:HT Ratio	a:b[a] Ratio
		3	4	5	6		
2a	78	67	11	8	14	78:22	75:25
2b	85	65	19	4	12	84:16	69:31
2c	86	76		24		76:24	–

[a]Determined by a combination of ¹H NMR spectroscopy and GC analysis.
[b]The less substituted allene double bond is denoted a and the more substituted one is denoted b.

meric dimethyl acetals. Such compounds are known to be formed when methoxyhydroperoxides, obtained during ozonolysis of olefins in methanol, are reduced by thiourea.[40]

Discussion

The photoaddition of 2-cyclopentenone to the allenes employed gave cycloadducts as approximately 80:20 mixtures of the HH and HT regioisomers (Table 1). The regioselectivity was, therefore, significantly lower than that achieved when allene itself reacts with 2-cyclopentenone and 2-cyclohexenone,[14,30,41] essentially the same as that obtained when the latter ketone cycloadds photolytically to 3-methyl-1,2-butadiene,[42] but considerably better than the selectivity observed when 2-cyclohexenone photoadds to 1,2-hexadiene.[42] Obviously, this type of cycloaddition is sensitive to alkyl groups attached to the propadiene moiety.

Mechanistically, a [2 + 2] photocycloaddition is believed to involve an initial oriented π complex between a ground state alkene and an excited enone which then proceeds through a 1,4-diradical on the way to the cycloadducts.[14] According to Wiesner,[27-29] the configuration of the major cycloadduct is determined by the geometry of the excited enone which features essentially a trigonal, slightly positive[43-46] α-carbon and a pyramidal, slightly negative [43-46] β-carbon. As a result of this, head-to-head adducts, formed during photocycloaddition of α-,β- unsaturated enones to 1,2-propadiene, conceivably result from a radical-like attack of the β-carbon on one of the terminal carbon atoms of allene.[30]

How HT regioisomeric adducts are formed is less evident. It is known that methyl, ethyl, and isopropyl radicals add exclusively to a terminal

carbon atom of propadiene[47,48] and that a number of other radicals add predominantly in the same manner[47-55] (Table 2). Furthermore, a recent molecular orbital calculation (MINDO/3) predicted that terminal addition of the methyl radical to allene is favored.[56] It is also clear that excited α,β unsaturated ketones bind initially to olefins at both C_a and C_b.[3,4,30,57,58] We therefore believe that photolytic addition of conjugated enones to 1,2-propadiene to give HT cycloadducts takes place by initial bonding between C_α and a terminal carbon atom of allene. Consequently, the HH:HT ratio reflects the relative ability of C_α and C_β of an α-,β-unsaturated ketone to undergo bond formation to a terminal allene carbon. When 2-cyclopentenone cycloadds photochemically to alkyl-substituted allenes, however, central attack is much more likely to take place. Thus, extensive investigations involving different types of radicals have shown that central attack becomes progressively more important as the number of alkyl substituents increases.[49,50,59,60] Representative examples involve the tosyl radical which predomi-

Table 2. Selectivity in radical attack on 1,2-propadiene.

Radical	Attack/%		Reference
	Terminal	Central	
Me₃Sn•	55	45	49
PhSO₂•	62	38	50
Br•	67	33	51
PhS•	75	25	52
MeCOS•	90	10	53,54
CF₃•	100	0	47,48
CCl₃•	100	0	52,55
CH₃•	100	0	47,48

Scheme 3.

$$13 \qquad 14$$

$$\downarrow \qquad \qquad \downarrow$$

$$3 + 4 \qquad \qquad 5 + 6$$
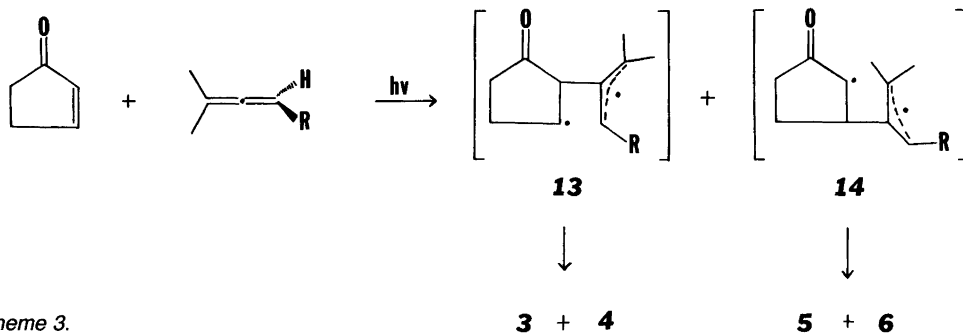
nantly attacks 1,2-propadiene terminally (Table 2) but adds exclusively to the central carbon atom of allenes *2a, 2b,* and *2c,*[61] and the trichloromethyl radical which adds terminally to 1,2-propadiene (Table 2) but centrally to the allene moiety in 1,2-cyclononadiene.[60] This implies that the selectivity of radical additions to allene derivatives is determined to a considerable extent by steric and electronic effects of the substituents and not very much by the nature of the attacking radical. Consequently, we believe that the four regioisomers obtained from *2a* and *2b* were formed via the resonance-stabilized allyl diradicals *13* and *14* (Scheme 3) which resulted from irreversible[61] central addition of C_α and C_β, respectively, to the allene moiety. The predominant formation of *3* and *6* relative to *4* and *5,* respectively, probably reflects larger steric interactions in the latter group of compounds as does the predominant addition of *1* to the less substituted double bond of the allenes (Table 1). Similarly, we suggest that ketone *1* underwent α- and β-bond formation to *2c* to generate diradicals *15* and *16* (Scheme 4). These transients are probably less stable than diradicals *13* and *14* since rotation to form a planar allyl radical in a 9-membered carbocycle introduces a significant amount of strain, and they would, therefore, react quickly

to adducts *3c* and *5c,* respectively. This may partly explain why no products involving transannular hydrogen transfer were observed.[62]

If it is correct, as suggested above, that the cycloadduct HH:HT ratio reflects the ability of C_α and C_β to attack the same carbon atom in the allene moiety, it is reasonable to believe that the ratio is sensitive to changes in the electronic distribution around C_α and C_β. Consequently, the different electronic distribution in α-,β-unsaturated ketones compared to α-,β-unsaturated esters[24,63-65] ought to result in different HH:HT ratios when such compounds cycloadd photochemically to the same allenes. This is indeed true in all comparable reactions involving 1,2-propadiene[24] and monoalkylated allenes[42,66,67] and it was also the case when *1* (Scheme 1, Table 1) and anhydromevalonolactone *(17)*[24] (Scheme 5) were added to allene *2b*. These observations lend support to the notion that photocycloaddition of α,β unsaturated ketones to C−C double bonds can involve bond formation at both C_α and C_β.[3,4,30]

Experimental

IR spectra were recorded, unless stated otherwise, in CCl_4 on a Shimadzu IR-420 spectrophotometer. NMR spectra were obtained using Jeol
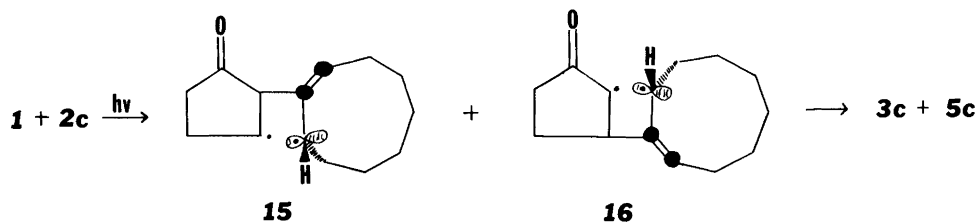
Scheme 4.
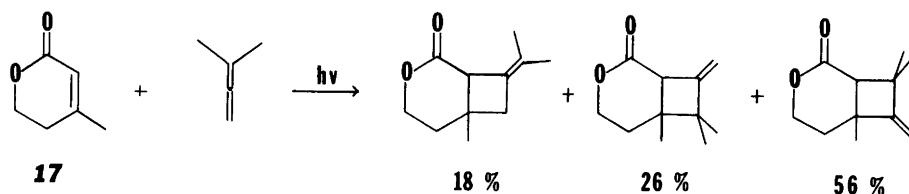
Scheme 5.

PMX60 SI and Jeol 90Q FT spectrometers. CDCl₃ was used as solvent unless stated otherwise and tetramethylsilane (TMS) was added as internal standard. Chemical shifts are reported in ppm downfield from TMS. Mass spectra were obtained on a VG Micromass 7070H spectrometer operated in the EI mode at 70 eV. A Hewlett-Packard 5710 gas chromatograph equipped with a Supelco SE 54 fused silica column (25 m, ID 0.25 mm) and connected to the spectrometer was employed when GC/MS analyses were carried out. Otherwise, GC analyses were performed on a Varian 3700 gas chromatograph equipped with FID and a Varian 3 % OV 17 column (3 m, ID 2 mm) or a Carlo Erba Fractovap 4160 equipped with FID and a Chrompack SE 54 fused silica column (25 m, ID 0.32 mm). Ozonolysis was carried out using a BOC-MIC II Ozonizer. The photolyses were performed with a 400 W medium pressure mercury lamp (Applied Photophysics 3040).

Materials. 2-Cyclopentenone (*1*) and 3-methyl-1,2-butadiene (*2a*) were commercially available, whereas 2-methyl-2,3-pentadiene (*2b*) and 1,2-cyclononadiene (*2c*) were synthesized as described in the literature.[68]

Photolysis, general procedure. An oxygen-free solution of *1* (0.820 g, 10.0 mmol) and *2* (40.0 mmol) in ethanol (300 ml), kept at 0 °C under nitrogen, was irradiated with light from a 400 W medium pressure mercury lamp. The lamp was kept in a water-cooled pyrex well (cut-off 295 nm) which was immersed in the solution. The irradiation was stoped when the enone was consumed (approximately 4.5 h) as indicated by GC analysis. The solvent was removed under vacuum and the residue subsequently analyzed prior to distillation.

Ozonolysis of cycloadduct mixtures, general procedure. A stream of ozone and oxygen was bubbled through a solution of cycloadducts in dry methanol (100 ml) at −78 °C until the solution

turned blue. Nitrogen was then flushed through the solution to remove excess ozone. The reaction mixture was worked up as described by Gupta *et al.*, using thiourea to reduce the ozonides.[40]

Photocycloaddition of 1 to 2a. Irradiation of *1* and allene *2a* (2.72 g) gave a crude product that contained 78 % of a 2:16:5 mixture (GC analysis) of cycloadducts. Separation of the individual adducts on a preparative scale was very difficult and they were therefore isolated as an isomeric mixture. Distillation afforded 0.86 g (57 %) of *3a–6a*, b.p. 80 °C/0.6 mmHg. IR: 1735, 950, 930, 890, 870 cm⁻¹; ¹H NMR (90 MHz): δ 1.0–3.4 (m), 1.15 and 1.26 (2s in a 1:1 ratio), 1.50 and 1.61 (2 broad s in a 1:1 ratio), 4.8–5.2 (m).

Ozonolysis of 3a–6a. The crude product from several photocycloadditions of *1* to *2a* (2.608 g) was ozonolyzed; 2.105 g of a complex product mixture formed. GC analyses showed that the mixture contained 72 % of four major products in a ratio of 24:3:5:4. IR: 1785 (w), 1740 (st), 1150 (m), 1040 (m) cm⁻¹. The main component was purified by column chromatography (SiO₂, chloroform:hexane = 3:2) and identified as methyl (3-oxocyclopentyl)ethanoate (*7a*).[35] ¹³C NMR (22.5 MHz): δ 29.1 (CH₂), 33.4 (CH), 37.9 (CH₂), 39.3 (CH₂), 44.3 (CH₂), 51.3 (OCH₃), 171.8 (COO), 216.4 (CO); MS (*m/e*, % rel. int.): 156 (*M*⁺, 14) 125 (24), 99 (30), 97 (11), 83 (100), 82 (49), 74 (32), 69 (26). A second product was partly purified by column chromatography (SiO₂, chloroform:hexane = 3:2) and assigned the structure methyl 2-methyl-2-(3-oxocyclopentyl)propanoate (*8*). ¹H NMR (90 MHz): δ 1.0–2.8 (7 H, m), 1.18 (6 H, s), 3.68 (3 H, s); MS (*m/e*, % rel. int.): 184 (*M*⁺, 19), 153 (11), 125 (9), 111 (86), 110 (55), 96 (13), 95 (17), 83 (89), 82 (100), 81 (13), 69 (8). Mol. wt.: calcd. for C₁₀H₁₆O₃ 184.1099, found 184.1113.

Photocycloaddition of 1 to 2b. Irradiation of *1* and *2b* (3.280 g) according to the general pro-

cedure gave a crude product (1.48 g) which contained 85 % of a 17:3:1:5 mixture of the isomeric cycloadducts *3b–6b*. Distillation afforded 0.79 g (48 %) of these products, b.p. 55 °C/0.4 mmHg. IR (film): 1735 (s), 990 (w), 940 (w), 900 (w), 790 (w) cm^{-1}; ^{1}H NMR (60 MHz, CCl$_4$): δ 1.0–3.0 (m), 1.23 and 1.29 (2d in a 1:2 ratio, J 7 Hz), 1.53–1.63 (several broad s), 4.6–5.4 (m).

Ozonolysis of 3b–6b. Ozone treatment of the crude product (4.477 g) from several photocycloadditions of *1* to *2b* gave 4.090 g of a complex product mixture which contained 79 % of a 2:24:6:5 mixture of compounds resulting from adducts *3b–6b*. IR: 1785 (w), 1750 (m), 1740 (s), 1150 (m) cm^{-1}. The main component, methyl 2-(3-oxocyclopentyl)propanoate (*7b*), was isolated by column chromatography (SiO$_2$, chloroform: hexane = 3:2). IR: 1750 (s), 1740 (s), 1150 (s) cm^{-1}; ^{1}H NMR (90 MHz): δ 0.9–2.6 (8 H, m), 1.23 (3 H, d, J 6.4 Hz), 3.68 (3H, s); ^{13}C NMR (22.5 MHz): δ 15.1 (CH$_3$), 27.1 (CH$_2$), 38.5 (CH$_2$), 40.0 (CH), 43.3 (CH$_2$), 44.4 (CH), 51.6 (OCH$_3$), 175.9 (COO), 217.3 (CO). MS (*m/e*, % rel. int.): 170 (*M$^+$*, 2), 139 (10), 113 (37), 111 (15), 97 (13), 88 (39), 83 (100), 82 (12), 69 (14). Mol. wt.: calcd. for C$_9$H$_{14}$O$_3$ 170.094; found 170.099.

Photocycloaddition of 1 to 2c. Irradiation of a solution of *1* and *2c* (4.880 g) as described in the general procedure gave two regioisomeric cycloadducts in a ratio of 5:16 in 86 % yield (GC analysis). Distillation furnished the adducts in 75 % yield (1.53 g), b.p. 180 °C/0.4 mmHg. IR (film): 1735 (s), 880 (3), 820 (w), 790 (w) cm^{-1}. ^{1}H NMR (90 MHz): δ 1.0–3.7 (19 H, m), 5.1–55 (1 H, m).

Degradation of 3c *and* 5c. Ozonolysis of the crude product from several photocycloadditions of *1* to *2c* (5.254 g) according to the general procedure gave 5.700 g of crude product. IR: 2720 (m), 1780 (m), 1745 (s), 1735 (s), 1150 (m), 1120 (m), 1050 (m) cm^{-1}. ^{1}H NMR (60 MHz): δ 1.0–3.8 (m), 3.26 (s), 3.28 (s), 3.33 (s), 3.36 (s), 3.70 (s), 3.72 (s), 9.7–9.9 (m).

Some of this product (1.345 g) was oxidized using Jones reagent[69] and 0.987 g of a complex reaction mixture was obtained. IR: 3600–2500 (s), 1780 (m), 1740 (s), 1710 (s), 1150 (m) cm^{-1}. ^{1}H NMR (60 MHz, CCl$_4$): δ 0.8–3.5 (m), 3.66 (s), 3.68 (s), 10.5 (broad s).

Some of the oxidized ozonolyzate (0.905 g) was dissolved in carbon tetrachloride (10 ml) and treated with a 0.1 M ether solution of diazomethane[70] until nitrogen evolution ceased. Evaporation of the solvent left 0.911 g of a residue which contained 76 % of three major compounds in a ratio of 25:2:3 (GC analysis). The main product, isolated by column chromatography (SiO$_2$, chloroform:hexane = 1:1), was dimethyl 2-(3-oxocyclopentyl)nonanedioate (*11*). IR: 1740 (s), 1150 (m) cm^{-1}. ^{1}H NMR (90 MHz): δ 1.0–1.8 (13 H, m), 2.0–2.5 (7 H, m), 3.67 (3 H, s), 3.69 (3 H, s). ^{13}C NMR (22.5 MHz): δ 24.8 (CH$_2$), 27.1 (CH$_2$), 27.6 (CH$_2$), 28.9 (CH$_2$), 29.1 (CH$_2$), 30.3 (CH$_2$), 33.9 (CH$_2$), 38.4 (CH$_2$), 39.3 (CH), 43.0 (CH$_2$), 50.6 (CH), 51.3 (2x OCH$_3$), 173.8 (COO), 175.2 (COO), 217.1 (CO). MS (*m/e*, % rel. int.): 281 (1), 241 (2), 239 (1), 216 (3), 207 (4), 171 (41), 138 (54), 129 (64), 111 (33), 97 (61), 87 (40), 83 (60), 74 (100). Anal. C$_{16}$H$_{26}$O$_5$:C, H. Impure samples of the two minor products gave rise to ^{13}C absorptions at 178.0 and 216.4 ppm and IR absorptions at 1780, 1740, and 1150 cm^{-1}.

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