Intramolecular Photoaddition of Alkenes to Chiral 1,3-Dioxin-4-ones: Evidence for Effect of Pyramidalization on the Facial Selectivity†,‡

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Intramolecular photoaddition of alkenes to chiral 1,3-dioxin-4-ones **5** present, for the first time, examples with high facial selectivity in which the addition proceeds *preferentially* from the *less exposed side* (b-side) under kinetic control conditions. This unprecedented facial selectivity cannot be explained only on the basis of steric effects; however, it is consistent with the direction of pyramidalization in structure **3**. It can be concluded that the geometry of the pyramidalized C_β in the triplet excited dioxinones plays an important role in defining the facial selectivity in this reaction. However, steric effect cannot be neglected in rationalizing the facial selectivity as found by comparing the facial selectivity obtained in the irradiation of the studied compounds.

Introduction

The high facial selectivity found in the thermal and photochemical reactions of chiral 1,3-dioxin-4-ones have triggered increasing interest in both their mechanistic aspects and synthetic applications.[1-8] Seebach et al.[9] have found that conjugated addition of dialkyl cuprates and catalytic hydrogenation to chiral dioxinone **1a** take place with complete stereoselectivity from the opposite side of the equatorial *tert*-butyl substituent at the acetal center (b-side). However, poor facial selectivity was obtained[7,8] in the intermolecular photoaddition of this dioxinone to different cyclic alkenes. Lange et al.[7,8] have succeeded in achieving high facial selectivity of this reaction in dioxinone **1b**, with preferred approach from the equatorial *tert*-butyl side (a-side). This selectivity is consistent with other examples of intermolecular[4-6] and the few examples of *intramolecular*[3] photocycloadditions of alkenes to chiral dioxinones and follows *but does not prove*, the reasonable explanation of preferred approach from the more exposed side.

The conformation of the dioxinone at the triplet excited state and the order of first bond formation were expected to affect the facial selectivity of the photoaddition reaction. Sato[3] has investigated the intramolecular photoaddition of chiral dioxinones of type **2** and came to the conclusion that dioxinones "exist as the sofa-conformation even in the excited state, just as in the ground state". On the other hand, Seebach et al.[9] have shown pyramidalization at the C_β position in a large number of different

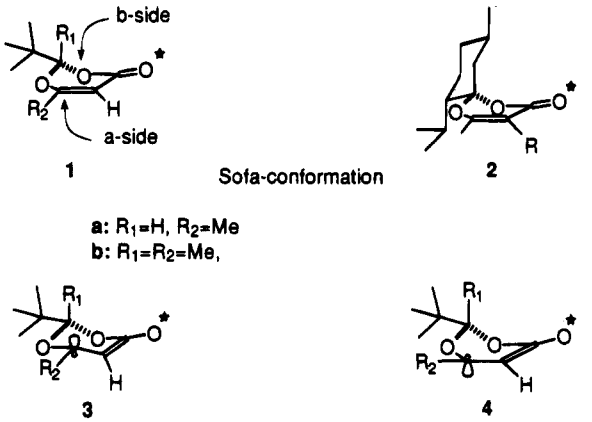

Figure 1. Possible triplet conformations of chiral dioxinones.

1,3-dioxin-4-ones in their ground state and stronger pyramidalization in the excited triplet state as calculated for a parent system. They proposed, in accordance to the Wiesner's model,[10] that "pyramidalization of C_β in triplet-excited state of chiral dioxinones of type **1** is strong and could be the origin of the observed stereoselectivity in these systems". Structures **3** and **4** in Figure 1 present the respective lowest triplet states calculated by Seebachl;[9] the structures differ by having opposite directions of pyramidalization.

Winkler et al.,[11] have shown that the first bond-forming step in the intramolecular photoaddition of alkenes to dioxinones takes place at position C_β. Preferred pyramidalization in the direction of the less exposed side (the axial methyl at the acetal center) described in structure **3b** and first bond formation at this position are essential features for obtaining selective photocycloadditions of alkenes to chiral dioxinones from this side, leading to the kinetically favored products. In such cases the preferred approach is not necessarily from the more exposed side.

As a part of our interest in applying the intramolecular photoaddition of chiral dioxinones and dihydropyrones[12]

† Dedicated to the memory of Professor Dan Becker, a teacher and friend whose enthusiasm and curiosity about science have enlightened our lives.

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(1) Demuth, M.; Palomer, A.; Sluma, H. D.; Dey, A. K.; Kruger, C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1117.
(2) Ernest, I.; Fritz, H.; Rihs, G. *Helv. Chim. Acta* **1987**, *70*, 203.
(3) Sato, M.; Abe, Y.; Kaneko, C. *Heterocycles* **1990**, *30*, 217.
(4) Sato, M.; Abe, Y.; Ohuchi, H.; Kaneko, C. *Heterocycles* **1990**, *31*, 2115.
(5) Sato, M.; Ohuchi, H.; Abe, Y.; Kaneko, C. *Tetrahedron Asymmetry* **1992**, *3*, 313.
(6) Sato, M.; Abe, Y.; Kaneko, C. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1779.
(7) Lange, G. L.; Organ, M. G. *Tetrahedron Lett.* **1993**, *34*, 1425.
(8) Organ, M. G.; Froese, R. D. J.; Goddard, J. D.; Taylor, N. J.; Lange, G. L. *J. Am. Chem. Soc.* **1994**, *116*, 3312.
(9) Seebach, D.; Zimmermann, J.; Gysel, U.; Ziegler, R.; Ha, T. K. *J. Am. Chem. Soc.* **1988**, *110*, 4763.
(10) (a) Marini-Bettolo, G.; Sahoo, S. P.; Poulton, G. A.; Tsai, T. Y. R.; Wiesner, K. *Tetrahedron* **1980**, *36*, 719. (b) Wiesner, K. *Tetrahedron* **1975**, *31*, 1655. (c) Cargill, R. L.; Morton, G. H.; Bordner, J. *J. Org. Chem.* **1980**, *45*, 3930. (d) Moens, L.; Baizer, M. M.; Little R. D. *J. Org. Chem.* **1986**, *51*, 4497.
(11) Winkler, J. D.; Shao, B. *Tetrahedron Lett.* **1993**, *34*, 3355.
(12) Haddad, N.; Kuzmenkov, I. *Tetrahedron Lett.* **1993**, *34*, 6127.

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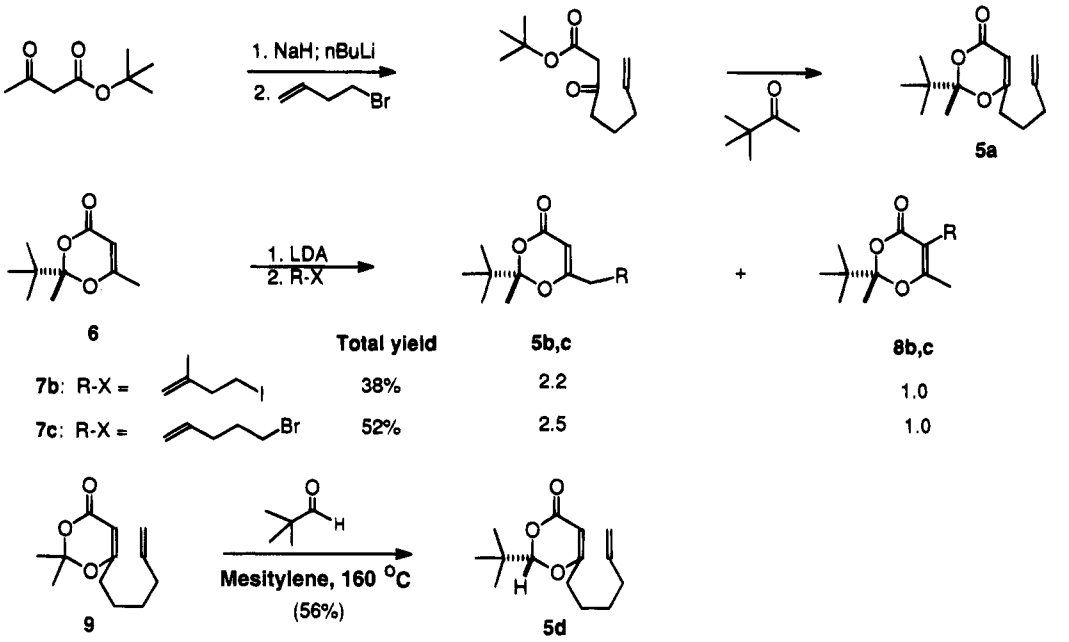
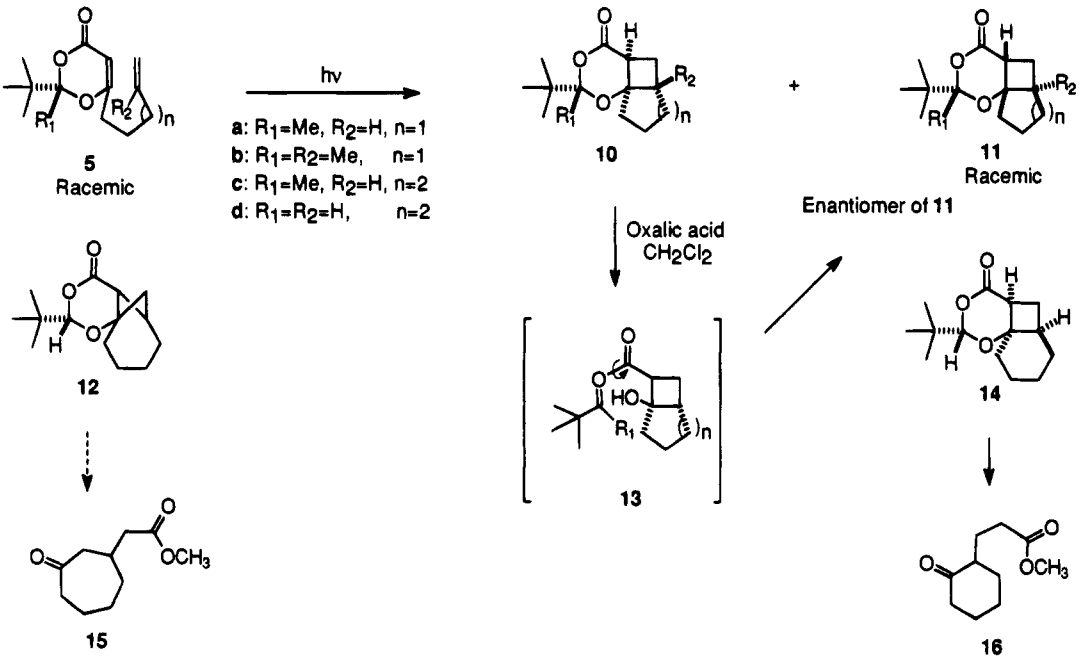
Scheme 1



Scheme 2



in the synthesis of spiro systems, we have investigated the intramolecular photocycloaddition of systems **1** bearing an alkenyl side chain at the C_β position. Our results present, for the first time, examples with high preferential approach of the C=C double bond from the less exposed side (b-side) of dioxinones **1**.

Results and Discussion

Compounds **5a–5c** were prepared in racemic form following either one of the two known procedures,[13a] with the corresponding modifications: (a) dianion alkylation of *tert*-butyl acetoacetate with the corresponding alkenyl halide[13b] followed by dioxinone formation upon treatment with pinacolon[14] under acidic conditions or (b) alkylation of dioxinone **6**[8,14] with the corresponding alkenyl halide[15] **7**; the yields of the desired photosubstrates in both methods were in the range of 30–52%. Dioxinone **5d** was prepared by refluxing dioxinone **9**[13a,15] with pivaldehyde in mesitylene (Scheme 1).[6]

Irradiations of compounds **5a–5d** were carried out in acetonitrile/acetone 1:1 solution (ca. 0.05 M), using a Hanau mercury lamp, through a Pyrex glass filter. A high regioselective photocycloaddition was found in all cases as could be expected.[12,13a] The results are summarized in Scheme 2 and Table 1.

(13) (a) Winkler, J. D.; Hey, P. J.; Hannon, F. J. *Heterocycles* **1987**, *25*, 55. (b) Huckin, S.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082.

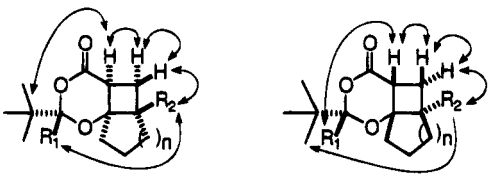
(14) Sato, M.; Ogasawara, H.; Oi, K.; Kato, T. *Chem. Pharm. Bull.* **1983**, *31*, 1896.

(15) (a) Smith, A. B., III; Levenberg, P. A.; Jerris, P. J.; Scarborough, R. M.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 1501. (b) Millar, J. G.; Underhill, E. W. *J. Org. Chem.* **1986**, *51*, 4726.

Table 1. Intramolecular Photoaddition[a] of Dioxinones 5a–5d

entry	compd	products[b] (ratio[c])	T (°C)
1	**5a**	**10a** (1.0), **11a** (2.0)	0
2	**5b**	**10b** (1.0), **11b** (2.4)	0 or −70
3	**5c**	**10c** (1.0), **11c** (1.0)	0
4	**5c**	**10c** (1.8), **11c** (1.0)	−70
6	**5d**	**10d** (3.3), **11d** (1.5), **14** (1.0)	0
7	**5d**	**10d** (17.1), **11d** (3.7), **14** (1.0)	−70

[a] Irradiations were carried out through a Pyrex glass filter, in 50% acetone (triplet sensitizer)/acetonitrile solution, using a Hanau (Q-81) mercury lamp; the progress of the reaction was followed by TLC. [b] Isolated yields are over 85%. [c] The ratio of the products was determined by NMR.



10 11

a: R_1=Me, R_2=H, n=1; **b**: R_1=R_2=Me, n=1;
c: R_1=Me, R_2=H, n=2; **d**:R_1=R_2=H, n=2;

Figure 2. Arrows on structures **10** and **11** summarize selected NOE interactions, in the range of 0.8%–12%, found to be common to all of the corresponding photoproducts. The arrows present NOE enhancement in both directions. In compounds **10a** and **10d** no enhancement of the *tert*-butyl signal was detected on irradiating the proton at the C_α stereogenic center.

Table 2. Chemical Shifts of the *tert*-Butyl and R_1 (Me, H) Substituents in Photoproducts 10a–14

δ (ppm)	10a	11a	10b	11b	10c	11c	10d	11d	14
tert-butyl	0.99	1.01	0.97	1.04	0.93	1.01	0.97	0.96	1.01
R_1	1.66	1.39	1.58	1.42	1.56	1.42	5.26	4.86	5.56

The photoproducts were easily separated by flash chromatography and their structures determined by NMR.[16] The relative configurations of the stereogenic centers in the photoproducts were easily defined by nuclear Overhouser effect (NOE) experiments; the key NOE enhancements are summarized in Figure 2. In addition, the chemical shift of the substituents (*tert*-butyl, methyl, or H) at the acetal center could indicate the face of the photoaddition (Table 2) as previously concluded for related structures.[6,8]

Irradiation of **5a** at 0 °C afforded the corresponding parallel products **10a** and **11a** in a 1:2 ratio, respectively. The major product **11a** was formed by approaching the dioxinone from the more exposed side (equatorial *tert*-butyl group) while the minor product **10a** formed by approaching the dioxinone from the less exposed side. A slight increase in the steric effect at the alkenyl side chain, examined by irradiating compound **5b**, afforded a small increase in the facial selectivity from the more exposed side.

Based on the assumption of a sofa-conformation in the excited state and of planar geometry at position C_β (**1**), it would be reasonable to assume that the decrease of geometrical constrain achieved by homologation of the alkenyl side chain could be expected to increase the stereoselectivity of the photoaddition by preferential approach of the C=C double bond from the more exposed side.[3] However, irradiation of **5c** at 0 °C afforded the corresponding parallel products **10c** and **11c** in a 1:1 ratio. This result of decrease in the stereoselectivity, which is opposite to that expected from the assumption above, prompted us to examine the facial selectivity at lower temperature and on decreasing the steric effect at the dioxinone.

Irradiation of **5c** at −70 °C in the presence of 4-*tert*-butylcyclohexanone as internal standard (IS) clearly resulted in preferential cycloaddition from the less exposed side, leading to the kinetically controlled photoproduct **10c** as the major product in a mixture with the more thermodynamically stable epimer **11c** (6 kcal/mol[17]) in a 1.8:1 ratio, respectively. Treatment of the photoproducts mixture, in the presence of IS, with oxalic acid in methylene chloride afforded, after 1.5 h at room temperature, clean isomerization of **10c** at the acetal center, presumably *via* intermediate **13**, to the more thermodynamically stable epimer **11c** (the corresponding enantiomer) in a 1:4.7 ratio, respectively, with small deviation in the IS (2.6%). However, the expected complete isomerization of **10c** to **11c** was obtained after 5 h. This unprecedented example of preferred facial selectivity from the less exposed side cannot be explained only on the basis of the suggested planar geometry at the excited dioxinone **1** and preferential approach from the more exposed side. However, this result is consistent with the direction of the pyramidalization with the preferred conformation corresponding to structure **3**, and supports the assumption[9] that the pyramidalization affects the facial selectivity in the photoaddition reactions of dioxinones. The inversion in the preferred pyramidalization in these systems over the intermolecular photoadditions might be attributed to the increase in the steric effect at position C_β which prefers **3** over **4**, possessing a larger dihedral angle with the substituent at position C_α. This point is still under investigation.

On the basis of these results, it could be concluded that the steric effect (examined in **5b**) and the pyramidalization affect the facial selectivity in this reaction. Accepting this argument, one would be able to predict that replacing the methyl substituent at the acetal center in **5c** with hydorgen would increase the facial selectivity from the opposite side of the *tert*-butyl substituent. Irradiation of the less hindered dioxinone **5d** at 0 °C afforded a three-component mixture of **10d**, **11d**, and **14** in a 3.3:1.5:1 ratio, respectively. Photoproducts **10d** and **11d** were separated by flash chromatography and their structure determined by NMR.[16] The major product **10d** was formed by approaching the dioxinone from the opposite side of the equatorial *tert*-butyl group, while product **11d** was formed by approaching the dioxinone from the *tert*-butyl side. The structure of the minor product **14** was determined as follows: Treatment of the photoproduct mixture with *p*-TsOH/MeOH afforded a single product[13a] **16**. This result excludes the alternative cross product **12**, since no detectable amount (GC) of **15** was produced upon hydrolysis, and suggests a parallel cycloadduct of type **14**, produced *via* the "twisted" approach[12,18] of the alkenyl side chain. The resonance of the acetal proton

(16) The relative stereochemical relationship of the stereogenic protons was determined by NOE difference. The location of these protons was determined by combination of COSY-45, XH-CORR, and JMOD-XH methods and was supported by NOE experiments. For determination of similar structures by NMR, cf. Becker, D.; Haddad, N. *Tetrahedron* **1993**, *49*, 947. Becker, D.; Haddad, N. *Isr. J. Chem.* **1989**, *29*, 303.

(17) Calculated using the Macromodel V-3.5X of Allinger MM2 program.

(18) Becker, D.; Morlender, N.; Haddad, N. *Tetrahedron Lett.*, in press.

at 5.56 ppm indicates addition from the hydrogen side (b-side).[6,8] However, irradiation of **5d** at −70 °C afforded **10d**, **11d**, and **14** in the ratio of 17.1:3.7:1, respectively, indicating a greater tendency of approach from the hydrogen side of the acetal center.

In summary, we have shown for the first time a high facial selectivity in the photoaddition of alkenes to chiral dioxinones, in which the addition proceeds *preferentially* from the *less exposed* side under kinetic control conditions. This unprecedented facial selectivity cannot be explained only on the basis of steric effect; however, it is consistent with the direction of pyramidalization in structure **3**. It can be concluded that the geometry of the pyramidalized C_β in the triplet excited dioxinones plays an important role in defining the facial selectivity in their intramolecular photoaddition to alkenes. However, steric effect cannot be neglected in rationalizing the facial selectivity in this reaction as found in comparing the facial selectivity found in the photoaddition of the studied compounds.

Experimental Section

THF was distilled from the potassium benzophenone ketyl, and HMPA was distilled over CaH_2. Silica gel 60 (230−400 mesh ASTM) for column chromatography was used. Nuclear magnetic resonance spectra were obtained on Bruker AM-400 MHz and AM-200 MHz NMR instruments. 4-Bromo-1-butene and 5-bromo-1-pentene obtained from Aldrich and used without further purification.

2-*tert*-Butyl-2-methyl-6-(4′-pentenyl)-1,3-dioxin-4-one (5a). A solution of *tert*-butyl acetoacetate (3.0 g, 19.0 mmol) in 4 mL of THF was added dropwise to a precooled (0 °C) suspension of sodium hydride (0.9 g, 28.5 mmol) in THF (30 mL) and HMPA (5.0 mL). The mixture was stirred for an additional 15 min, and then *n*-BuLi (9.0 mL, 22.5 mmol, 2.5 M solution in cyclohexane) was added over a 10 min period. The orange solution was stirred for additional 10 min at the same temperature followed by dropwise addition of 4-bromo-1-butene (1.5 mL, 15.0 mmol) in THF (5 mL). The resulting mixture was stirred for 10 min at 0 °C and then 1.5 h at room temperature and quenched by addition of 30 mL of ethyl ether and cold 10% HCl to pH = 2. The aqueous fraction was further extracted with ethyl ether (2 × 10 mL), and the organic extracts were combined and then washed with brine solution, dried over $MgSO_4$, and concentrated under reduced pressure. Purifcation by flash chromatography (2% ethyl acetate in hexane) afforded 1.75 g of *tert*-butyl-3-oxooct-7-enoate in 70% yield: NMR ($CDCl_3$) δ 5.75 (m, 1H), 4.91 (m, 2H), 3.32 (s, 2H), 2.50 (t, 2H), 2.02 (m, 2H), 1.58 (m, 2H), 1.43 (s, 9H).

Concentrated sulfuric acid (0.1 mL, 1.4 mmol) was added dropwise to a cold solution (−10 °C) of *tert*-butyl-3-oxooct-7-enoate (300 mg, 1.4 mmol) and pinacolone (300 mg, 2.8 mmol) in acetic anhydride (0.8 mL), and the temperature was kept below −5 °C during the addition of the acid then at 0 °C for 18 h. The reaction mixture was then poured into a cold (0 °C) solution of 10% Na_2CO_3 (ca. 8 mL), extracted with chloroform (3 × 5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash chromatography (5% ethyl acetate in hexane) afforded 99 mg of the desired product in 31% yield: IR ($CHCl_3$) 1710, 1630 cm^{-1}; NMR ($CDCl_3$) δ 5.71 (m, 1H), 5.18 (s, 1H), 5.0 (m, 2H), 2.15 (m, 4H), 1.63 (m, 2H), 1.53 (s, 3H), 1.08 (s, 9H); HRMS calcd for $C_{14}H_{22}O_3$ *m/z* 238.1569, found *m/z* 238.1552.

2*tert*-Butyl-2-methyl-6-(4′-methyl-4′-pentenyl)-1,3-dioxin-4-one (5b) (General Procedure). 4-Iodo-2-methyl-1-butene was prepared from 3-methyl-3-buten-1-ol (commercially available) following Millar's procedure[15b] in 60% yield: NMR ($CDCl_3$) δ 4.74 (d, 2H), 3.25 (t, 2H), 2.55 (t, 2H), 1.72 (s, 3H).

LDA in THF solution was prepared by dropwise addition of n-BuLi (0.9 mL, 2.2 mmol, 2.4 M solution in cyclohexane) to a cold (−70 °C) solution of diisopropylamine (0.3 mL, 2.2 mmol) and HMPA (0.4 mL) in THF (10 mL). The mixture was stirred for 30 min at the same temperature to ensure complete formation of LDA. Dioxinone[8,14] **6** (357 mg, 1.94 mmol) was dissolved in THF (5 mL) and added dropwise to the LDA mixture over a 20 min period. After the mixture was stirred for an additional 45 min at this temperature, 4-iodo-2-methyl-1-butene (418 mg, 2.13 mmol) in THF (2 mL) was added dropwise, the temperature was allowed to warm slowly to room temperature (1 h), and the mixture was stired for an additional 30 min. The reaction quenched by addition of 10% HCl (5 mL) and then extraction with ethyl ether (3 × 10 mL), and the organic extracts were combined and washed with brine solution, dried over $MgSO_4$, and then concentrated under reduced pressure to afford a mixture of the desired product (**5b**) and the corresponding C_α isomer (**8b**).

Separation by flash chromatography (16% ethyl acetate in hexane) afforded 128 mg of **5b** and 58 mg of **8b** in 38% total yield.

Dioxinone **5b**: IR ($CHCl_3$) 1710, 1630 cm^{-1}; NMR ($CDCl_3$) δ 5.19 (s, 1H), 4.71 (s, 1H), 4.65 (s, 1H), 2.22 (t, 2H), 2.05 (t, 2H), 1.71 (t, 2H), 1.70 (s, 3H), 1.48 (s, 3H), 1.10 (s, 9H); HR-MS calcd for $C_{15}H_{24}O_3$ *m/z* 252.1726, found *m/z* 252.1801.

Dioxinone **8b**: IR ($CHCl_3$) 1710, 1630 cm^{-1}; NMR ($CDCl_3$) δ 4.71 (d, 2H), 2.22 (m, 4H), 1.95 (s, 3H), 1.75 (s, 3H), 1.56 (s, 3H), 1.08 (s, 9H); HR-MS calcd for $C_{15}H_{24}O_3$ *m/z* 252.1726, found *m/z* 252.1737.

2-*tert*-Butyl-6-(5′-hexenyl)-2-methyl-1,3-dioxin-4-one (5c). Prepared from dioxinone **6** (400 mg, 2.17 mmol) and 5-bromo-1-pentene (356 mg, 2.39 mmol) following the general procedure described for **5b**. Similar workup afforded 203 mg of the desired product **5c** and 81 mg of the corresponding C_α isomer **8c** in 52% total yield.

Dioxinone **5c**: IR ($CHCl_3$) 1710, 1630 cm^{-1}; NMR ($CDCl_3$) δ 5.76 (m, 1H), 5.19 (s, 1H), 4.98 (m, 2H), 2.21 (t, 2H), 2.05 (m, 2H), 1.56 (s, 3H), 1.44 (m, 4H), 1.08 (s, 9H); CI-MS [MH^+] 253.2, [$M - H]^-$ 251.2; HR-MS calcd for [$M - C_4H_9]^+C_{11}H_{15}O_3$ *m/z* 195.1021, found *m/z* 195.1028.

Dioxinone **8c**: IR ($CHCl_3$) 1710, 1630 cm^{-1}; NMR ($CDCl_3$) δ 5.78 (m, 1H), 4.96 (m, 2H), 2.29 (m, 2H), 2.08 (m, 2H), 1.95 (s, 3H), 1.52 (m, 2H), 1.51 (s, 3H), 1.03 (s, 9H); HR-MS calcd for $C_{15}H_{24}O_3$ *m/z* 252.1726, found *m/z* 252.1712.

2-*tert*-Butyl-6-(5′-hexenyl)-1,3-dioxin-4-one (5d). A solution of 2,2-dimethyl-6-(5′-hexenyl)-1,3-dioxin-4-one[13a,15] (**9**) (250 mg, 1.2 mmol) and pivaldehyde (900 mg, 3.6 mmol) in mesitylene (5 mL) was refluxed for 30 min, the excess of the aldehyde was removed under reduced pressure, and then the crude product was purified by flash chromatography (6% → 20% ethyl acetate in hexane) to afford 160 mg of the desired product in 56% yield: IR ($CHCl_3$) 1710, 1630 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 5.71 (m, 1H), 5.25 (s, 1H), 4.98 (s, 1H), 4.96 (m, 2H), 2.28 (t, 2H), 2.03 (m, 2H), 1.43 (m, 4H), 1.02 (s, 9H); HR-MS calcd for $C_{14}H_{22}O_3$ *m/z* 238.1569, found *m/z* 238.1574.

General Procedure for the Irradiations of Dioxinones 5a-5d. An 80-W Hanau mercury vapor lamp (Q-81) was used for irradiations *via* a Pyrex glass filter (λ > 295). All irradiations were carried out in 16 mL of 50% acetone/acetonitrile as solvent under nitrogen atmosphere. The concentrations were always kept below 0.05 M, and the reactions were followed by the UV absorption of the starting materials on TLC which usually was complete after 30 min at 0 °C and 3 h at −70 °C. The solvents were removed under reduced pressure, and the crude photoproducts were separated by flash chromatography to afford the corresponding products in 80−95% total yield.

3α-*tert*-Butyl-6α,8β-dihydro-3β-methyl-2,4-dioxa-5-oxotricyclo[5.4.0.0^{1,8}]undecane (10a): IR ($CHCl_3$) 1720 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.88 (m, 2H), 2.24 (m, 1H), 1.81 (m, 6H), 1.66 (s, 3H), 1.60 (m, 1H), 0.99 (s, 9H); HR-MS calcd for $C_{14}H_{22}O_3$ *m/z* 238.1569, found *m/z* 238.1562.

3α-*tert*-Butyl-6β,8α-dihydro-3β-methyl-2,4-dioxa-5-oxotricyclo[5.4.0.0^{1,8}]undecane (11a): IR ($CHCl_3$) 1720 cm^{-1}; ^{1}H-NMR (1:1 $C_6D_6/CDCl_3$) δ 2.86 (dd, *J* = 10.9, 5.1 Hz, 1H), 2.58 (m, 1H), 2.39 (m, 1H), 2.01 (dd, *J* = 12.3, 5.5 Hz, 1H), 1.94 (dd, *J* = 12.3, 5.9 Hz, 1H), 1.85 (m, 2H), 1.72 (m, 2H), 1.46 (q, 1H), 1.41 (s, 3H), 1.02 (s, 9H); HR-MS calcd for $C_{14}H_{22}O_3$ *m/z* 238.1569, found *m/z* 238.1571.

3α-*tert*-Butyl-6α-hydro-3β,8β-dimethyl-2,4-dioxa-5-oxotricyclo[5.4.0.0^{1,8}]undecane (10b): IR ($CHCl_3$) 1720 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.78 (dd, J = 10.8, 4.7 Hz, 1H), 2.08 (dd, J = 15.4, 6.2 Hz, 1H), 1.99 (t, 1H), 1.77 (m, 3H), 1.63 (m, 1H), 1.58 (s, 3H), 1.52 (m, 1H0, 1.43 (dd, J = 12.4, 6.1 Hz, 1H), 1.11 (s, 3H), 0.97 (s, 9H); HR-MS calcd for $C_{15}H_{24}O_3$ m/z 252.1726, found m/z 252.1725.

3α-*tert*-Butyl-6β-hydro-3β,8α-dimethyl-2,4-dioxa-5-oxotricyclo[5.4.0.0^{1,8}]undecane (11b): IR ($CHCl_3$) 1720 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.78 (dd, J = 10.7, 5.2 Hz, 1H), 2.04 (m, 2H), 1.95 (dd, J = 12.5, 4.9 Hz, 1H), 1.85 (m, 1H), 1.72 (m, 2H), 1.53 (m, 2H), 1.42 (s, 3H), 1.08 (s, 3H), 1.04 (s, 9H); HR-MS calcd for $C_{15}H_{24}O_3$ m/z 252.1726, found m/z 252.1725.

3α-*tert*-Butyl-6α,8β-dihydro-3β-methyl-2,4-dioxa-5-oxotricyclo[6.4.0.0^{1,8}]dodecane (10c): IR ($CHCl_3$) 1720 cm^{-1}; ^1H-NMR (C_6D_6) δ 2.61 (m, 1H), 2.35 (bd, 1H), 1.70 (m, 2H), 1.43 (m, 1H), 1.38 (m, 1H), 1.39 (s, 3H), 1.23 (m, 4H), 1.06 (m, 2H) 1.09 (s, 9H); CI-MS [MH^+] 253.2; HR-MS calcd for [M − C_4H_9]$^+$ $C_{11}H_{15}O_3$ m/z 195.1021, found m/z 195.1002.

3α-*tert*-Butyl-6β,8α-dihydro-3β-methyl-2,4-dioxa-5-oxotricyclo[6.4.0.0^{1,8}]dodecane (11c): IR ($CHCl_3$) 1720 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.81 (bd, 1H), 2.38 (m, 1H), 2.19 (dt, J = 9.85, 2.0 Hz, 1H), 2.00 (bd, 1H), 1.94 (q, 1H), 1.71 (dt, J = 12.9, 4.8 Hz, 1H), 1.57 (m, 4H), 1.42 (s, 3H), 1.36 (m, 2H), 1.01 (s, 9H); HR-MS calcd for $C_{15}H_{24}O_3$ m/z 252.1726, found m/z 252.1722.

3α-*tert*-Butyl-3β,6α,8β-trihydro-2,4-dioxa-5-oxotricyclo-[6.4.0.0^{1,8}]dodecane (10d): IR ($CHCl_3$) 1720 cm^{-1}; ^1H-NMR (C_6D_6) δ 4.98 (s, 1H), 2.59 (dd, J = 10.1, 4.1 Hz, 1H), 2.29 (m, 1H), 1.75 (dt, J = 12.2, 4.1 Hz, 1H), 1.57 (dt, J = 13.8, 2.7 Hz, 2H), 1.47 (m, 1H), 1.16 (m, 5H), 1.03 (m, 1H), 0.98 (s, 9H); HR-MS calcd for $C_{14}H_{22}O_3$ m/z 238.1569, found m/z 238.1568.

3α-*tert*-Butyl-3β,6β,8α-trihydro-2,4-dioxa-5-oxotricyclo-[5.4.0.0^{1,8}]dodecane (11d): IR ($CHCl_3$) 1720 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 4.86 (s, 1H), 2.81 (dd, J = 9.2, 3.2 Hz, 1H), 2.38 (m, 2H), 1.95 (q, 2H), 1.84 (m, 1H), 1.71 (m, 3H), 1.69 (m, 3H), 0.96 (s, 9H); HR-MS calcd for $C_{14}H_{22}O_3$ m/z 238.1569, found m/z 238.1567.

Fragmentation of Photoproducts Mixture 10d, 11d, and 14. A catalytic amount of *p*-toluenesulfonic acid (5 mg) was added to the photoproducts mixture **10d**, **11d**, and **14** (30.0 mg) in methanol solution (5 mL). The mixture was refluxed 12 h, and then the reaction was worked up by addition of H_2O (3 mL) and evaporation of the methanol under reduced pressure followed by extraction with chloroform (3 × 3 mL). The combined organics were dried over $MgSO_4$ and then concentrated to afford 16 mg of a single product[13a] **16** (70% yield) with no detectable amount of isomer **15** by GC−MS: ^1H-NMR ($CDCl_3$) δ 3.64 (s, 3H), 2.35 (m, 5H), 2.06 (m, 3H), 1.84 (m, 1H), 1.64 (m, 2H), 1.53 (m, 1H), 1.39 (m, 1H); ^{13}C-NMR (JMOD-XH) ($CDCl_3$) δ 212.5 (+), 174.0 (+), 51.5 (−), 49.8 (−), 42.2 (+), 34.2 (+), 31.7 (+), 28.1 (+), 25.1 (+), 24.9 (+).

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Supporting Information Available: Copies of ^1H-NMR spectra of **5a-d**, **8b-c**, **10a-d**, **11a-d**, **16** and the corresponding mixtures as obtained upon irradiation of **5a** and **5c**, and isomerization of the photoproducts of **5c** in the presence of IS (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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