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Photochemical C–C Bond Formation between Alcohols and Olefins by an Environmentally Benign Radical Reaction

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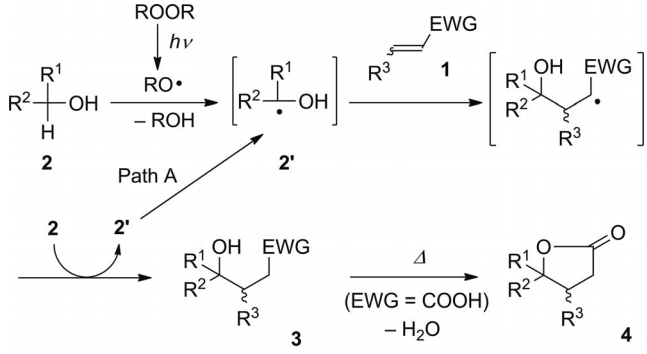
A radical C–C bond formation between olefins and alcohols proceeded efficiently by simple light irradiation at room temperature. The reaction proceeded in the presence of commercially available *t*BuOO*t*Bu without using the harmful elements and/or compounds that have an unpleasant smell that are often used in conventional radical reactions. In addition, the reaction did not require photosensitizers or photocatalysts, which eliminated the time-consuming separation of sensitizers after the reaction, or the synthesis of photocatalysts as reported in previous procedures.

Introduction

The addition of carbon radicals to olefins is one of the important reactions in organic synthesis for the construction of C–C bonds.[1] Recently, carbon radicals have mostly been generated by the cleavage of carbon–heteroatom bonds. The advantage of this type of reaction is that radicals can be generated efficiently on the carbon atom where the heteroatom was located. However, there are significant disadvantages: (i) carbon–heteroatom bonds must be introduced in advance, which requires additional synthetic steps, and (ii) harmful elements and/or compounds that have an unpleasant smell, such as tin, mercury, boron, halogens, or chalcogenides are generally used, and this is not good for the environment.

Carbon radicals are also generated by C–H bond cleavage. Alcohols have been frequently used as radical precursors,[2] because the radicals can be selectively generated at their α-carbons.[3] Both thermal and photochemical processes have been reported for the generation of radicals and their addition to olefins. The most common thermal reactions are those using peroxides,[3b,4] but the reactions are conducted at high temperature, so they suffer from the occurrence of various unfavorable side-reactions. In contrast, photochemical reactions[5] are generally conducted at room temperature or below, so side-reactions that occur at high temperatures are avoided. Two main types of photochemical reaction have been developed, using either excited-state ketones[2,6,7] or photocatalysts.[8,9] However, these ketone- and photocatalyst-induced reactions generally require long irradiation times, and the separation of these additives after the reactions is often time-consuming.

In this paper, we report a fast and efficient C–C bond formation between alcohols and olefins, in a procedure that is improved over those reported previously.[3–9] We have used only commercially available stable peroxides and light irradiation, without using harmful elements and/or compounds that have an unpleasant smell. In addition, the reaction did not require photosensitizers or photocatalysts, which eliminates the time-consuming separation of the sensitizers after the reaction, or the synthesis of the photocatalysts that were necessary in conventional procedures. The reaction was expected to proceed following the mechanism shown in Scheme 1. The key step of the reaction was the photochemical generation of oxy-radicals[10] at room temperature.



Scheme 1. Photochemical addition of alcohols to olefins.

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Results and Discussion

Effect of Oxygen

The reaction was investigated using maleic acid (**1a**; 20 mM) and di-*tert*-butyl peroxide (DTBP; 10 mM) in 2-propanol (**2a**; Scheme 1: $R^1 = R^2 = Me$, R = *t*Bu, R^3 = EWG = COOH) using a long-necked quartz cell (optical path: 10 mm) and a xenon lamp (500 W Xe short-arc lamp fitted with an 18 cm water filter and a UV-29 cut-off filter, 15 mW cm^{-2}, 1 h, room temp.). Terebic acid (**4a**), which was formed by the lactonization of the adduct (i.e., **3a**) during the evaporation of excess **2a** after the photolysis, was obtained as the major product.

The photolysis was conducted using various degassing procedures. The yield of **4a** was 56% without degassing, 70 and 80% after bubbling Ar for 3 and 10 min, respectively, and 91% after degassing with four freeze–pump–thaw cycles.[11] Although freeze–pump–thaw cycles were most effective, this procedure required long treatment times, and only a small amount of solution could be degassed each time. Therefore, the following simple procedure was developed for synthetic purposes: sonication under vacuum (50 Torr) for 5 s, followed by purging with Ar or N_2, which was repeated 10 times at ice-water temperature. The yield of **4a** using these vacuum–sonication–purging cycles was 93%, which was the same as that using the most effective freeze–pump–thaw cycles. This result indicated that this degassing method was very efficient and able to treat a large amount of solution in a short time.

Effect of Photochemical Radical Initiator

Three peroxides, DTBP, H_2O_2, and benzoyl peroxide (BPO), were tested (Table 1). 2,2′-Azobis(isobutyronitrile) (AIBN) was also tested for comparison with the peroxides. The results in Table 1 indicate that the yield of **4a** increased with the increase in reactivity of the radicals that were generated from the radical initiators (DTBP ≈ H_2O_2 > BPO > AIBN).[3b] Of the four initiators, DTBP was found to be most effective, and the *t*BuOH generated from the DTBP in the photolysis was removed during the work-up procedure.

Table 1. Effect of radical initiators.[a]

Entry	Radical initiator	Conversion of **1a** [%]	Yield of **4a** [%][b]
1	DTBP	100	93
2	H_2O_2[c]	> 99	79
3	BPO	> 99	40
4	AIBN[d]	56	10

[a] Photolysis condition, substrates: **1a** (20 mM) and radical initiator (10 mM) in **2a**, light source: 500 W xenon short-arc lamp fitted with an 18 cm water filter and a UV-29 cut-off filter (15 mW cm^{-2}), irradiation time: 1 h, optical path: 10 mm, Ar atmosphere; room temp. [b] The yield is based on the consumed starting material. [c] 30% aqueous H_2O_2 was used. [d] N_2 atmosphere.

Effect of the Wavelength of the Light

The photolysis was conducted using different wavelengths of light, and the results are shown in Figure 1 (a). The photolyses were conducted with a xenon lamp fitted with different cut-off filters whose emission spectra are shown in Figure 1 (b). The consumption of **1a** decreased when the wavelength of light was > 330 nm (UV-33 filter); this is rationalized by the low absorptivity by DTBP of light in this wavelength range.[11] Figure 1 shows that irradiation using a UV-29 filter was found to be optimal for the photolysis because the yield of **4a** showed a maximum when a UV-29 filter was used. In this wavelength range, both DTBP and **1a** absorb light, and **4a** was also obtained by the direct absorption of light by **1a** (vide infra). However, the efficiency of this reaction path was very low, so that it is rational to conclude that the reaction proceeded preferentially by the process shown in Scheme 1.

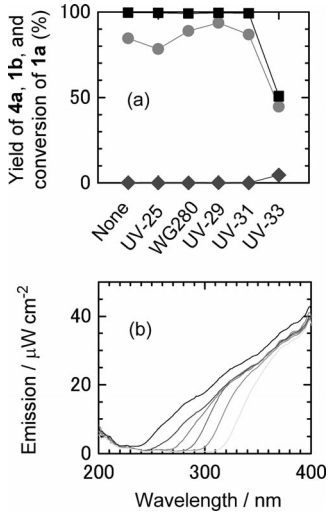


Figure 1. (a) The effect of cut-off filters on the yields[12] of terebic (**4a**) and fumaric (**1b**) acids, and remaining maleic acid (**1a**).[13b] Symbols: **1a** (■), **4a** (●), and **1b** (◆). Substrates: **1a** (20 mM) and DTBP (10 mM) in **2a**, light source: 500 W xenon short-arc lamp fitted with an 18 cm water filter and a cut-off filter, light intensity: 16.50 mW cm^{-2} without cut-off filter, irradiation time: 1 h, optical path: 10 mm, N_2 atmosphere, room temp. (b) Emission spectra of the xenon lamp fitted with different cut-off filters. Filter (from left to right): none (–), UV-25 (–), WG280 (–), UV-29 (–), UV-31 (–), UV-33 (–); the light source was the same as that for (a).

Effect of the Concentration of 1a and DTBP

The concentrations of **1a** and DTBP in the photolysis reaction were varied, and the results are summarized in Table 2. Table 2, entries 1–6 show the effect of varying the DTBP concentration; the conversion of **1a** was almost quantitative when the number of equivalents of DTBP with respect to **1a** was ≥0.5 but decreased when the number of equivalents was <0.5, and the yield of **4a** showed a maximum when the number of equivalents was 0.5. These results indicate that the reaction proceeds most effectively when the concentrations of the photochemically generated *tert*-butoxy radicals and **4a** were the same. It should be noted that the reaction proceeded to some extent even in the absence of DTBP (Table 2, entry 6). This can be explained by

the generation of carbon radical **2′** by the abstraction of a hydrogen atom by the excited carbonyl oxygen[14] of maleic acid (**1a**).

Table 2. Effect of maleic acid (**1a**) and DTBP concentrations.[a]

Entry	Concentration [mM] **1a**	DTBP	Irradiation time [h]	Conversion of **1a** [%]	Yield of **4a** [%][b]
1	20	200	1	99	48
2	20	100	1	99	48
3	20	20	1	99	71
4	20	10	1	100	93
5	20	5	1	63	57 (5.9[c])
6	20	0	1	28	30 (19[c])
7	15	7.5	1	99	82
8	10	5	1	99	71
9	50	25	1	91	84 (0.7[c])
10	50	25	3	97	85 (0.2[c])
11	100	50	1	64	78 (6.3[c])
12	100	50	3	98	81 (0.1[c])

[a] Photolysis conditions, in 2-propanol (**2a**), light source: 500 W xenon short-arc lamp fitted with an 18 cm water filter and a UV-29 cut-off filter (15 mW cm^{-2}), optical path: 10 mm, N_2 atmosphere; room temp. [b] The yield is based on the consumed starting material; average of three independent runs. [c] Yield of fumaric acid (**1b**).

Table 2, entries 4, 7–9, and 11 showed the effect of the concentration of **1a** and DTBP when the ratio of the concentrations of **1a**/DTBP was fixed at 0.5. Conversion of **1a** was quantitative when the concentration of **1a** was below 20 mM, but it started to decrease when the concentration exceeded 50 mM. At the same time, the yield of **4a** showed a maximum when the concentration of **1a** was 20 mM. Table 2, entries 10 and 12 show that the conversion of **1a** and the yield of **4a** at high concentrations could be increased by prolonged irradiation, but the yield was less than the best yield obtained in Table 2, entry 4. In those cases with low conversion, the formation of fumaric acid (**1b**) was observed, which is explained by a photochemical *cis–trans* isomerization of **1a**.

The reaction mechanism shown in Scheme 1 implies that the reaction proceeds by a chain reaction, so that only a catalytic amount of DTBP is required. However, our results clearly show that 0.5 equiv. of DTBP with respect to **1a** was necessary, which indicates that Path A in Scheme 1 is very ineffective, if it operates at all. In the reaction between **1a** and EtOH, the formation of 2,3-dihydroxybutane was observed. This result indicates the presence of a coupling reaction of radicals **2′** generated from EtOH, which suppressed the chain process. At the same time, direct photolysis of **1a** and **2a** was also found to be ineffective (Table 2, entry 6). Although detailed mechanism of the reaction is still not clear, our results indicate that main pathway is most probably a stoichiometric process. However, a minor contribution of direct and/or chain reactions cannot be excluded.

Effect of Reaction Temperature

The photolysis of **1a** in **2a** was conducted at different temperatures (Figure 2). A drastic increase in the consumption of **1a** and the yield of **4a** was observed when the temperature was increased to around 0 °C, the consumption leveled off at temperatures above 20 °C, and the yield showed a maximum at 30–40 °C (yield: 98%), which indicated that room temperature was optimal for the photolysis.

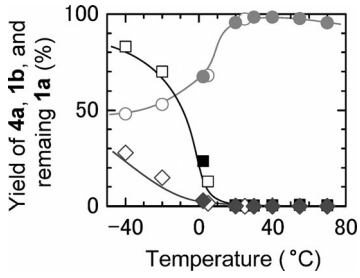


Figure 2. Yields[12] of terebic (**4a**) and fumaric (**1b**) acids, and remaining maleic acid (**1a**) as a function of reaction temperature.[13b] Symbols: **1a** (□, ■), **4a** (○, ●), and **1b** (◇, ◆). Substrates: **1a** (20 mM) and DTBP (10 mM) in **2a**, light source: 500 W xenon short-arc lamp fitted with an 18 cm water filter and a UV-29 cut-off filter (15 mW cm^{-2}), irradiation time: 1 h, optical path: 10 mm, N_2 atmosphere. Reaction temperature was controlled by a variable-temperature liquid-nitrogen cryostat (–40–25 °C, open symbols), or by a constant-temperature water bath (5–70 °C, filled symbols).

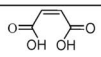
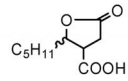
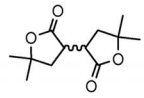
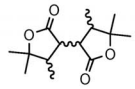
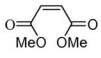
Reaction between Various Olefins and Alcohols

The scope of the reaction was investigated using various olefins and alcohols (Table 3). Table 3, entries 1–5 show the results of the reactions of **1a** with different alcohols **2a**–**d**. The reactions proceeded faster with secondary than with primary alcohols (Table 3, entries 1 vs. 2–5), which is consistent with frontier orbital theory.[15] In addition, the yields of adduct **4** were higher with secondary alcohol **2a** than with primary alcohols **2b**–**d** (Table 3, entries 1 vs. 2, 4, 5). When alcohols **2c** and **2d** were used, almost equal amounts of two isomers of **4**, with the carboxylic and alkyl substituents on the lactone ring in *cis* and *trans* relationships, were formed.

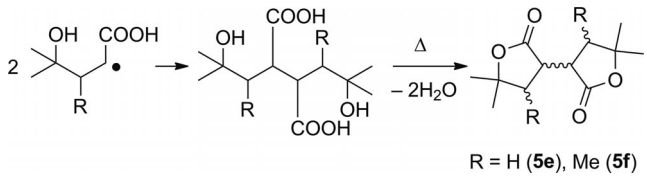
Table 3, entries 6–16 show the results with different olefins **1b**–**h**. Olefins having two electron-withdrawing groups, **1b** and **1g**, showed comparable behavior to **1a**, giving excellent yields of **4** (Table 3, entries 6 and 12). The reactions with **1e** and **1f** were slower, and the yields of **4e** and **4f** were lower than those obtained with **1a** (Table 3, entries 7 and 9). The decrease in the yield of **4f** was due to the formation of dimers **5f** (Table 3, entries 9–11, cf. Scheme 2). On the other hand, the decrease in the yield of **4e** was most probably due to the formation of polyacrylic acid, rather than the formation of dimers **5e** (Table 3, entries 7 and 8). The yields of **4e** and **4f** were increased by decreasing the concentration of olefins and DTBP (Table 3, entries 7–8 and 9–11).

The reaction of dimethyl maleate (**1h**) was slower than that of **1a** (Table 3, entries 13–16), which can be explained by the fact that esters are more weakly electron-withdrawing than carboxylic acids.[15] At the same time, lactonization of **3** to **4** did not proceeded during the standard work-up procedure at 50 °C, but rather two linear adducts,

Table 3. Reaction between various olefins and alcohols.

Entry	Olefin (**1**)	Alcohol (**2**)	Irr. time (h)	Photolysis condition[a]	Conv. of **1** (%)	Yield[b] (%)
1	 (**1a**)	*i*PrOH (**2a**)	1	A	100[c]	 (**4a**): 96
2		MeOH (**2b**)	2	A	>99[d]	 (**4b**): 61 (65[d])
3		EtOH (**2c**)	1	A	73[c]	 (**4c**): 79 (*cis*:*trans* = 1:1.2[d])
4			2	A	100[c] (>99[d])	**4c**: 77 (*cis*:*trans* = 1:1.1[d]) (74)[d]
5		*n*-$C_6H_{13}OH$ (**2d**)	2	A	100[c]	 (**4d**): 59 (*cis*-*trans* mixture[d])
6	 (**1b**)	**2a**	1	A	99[c]	**4a**: 82 (96[c])
7	 (**1e**)	**2a**	3	A	>99[d]	 (**4e**): 28 (30[d])  dimer (**5e**): 4[d]
8			3	A ;10/5 mM[e]	>99[d]	**4e**: 41[d]; dimer **5e**: 4[d]
9	 (**1f**)	**2a**	3	A	98[d]	 (**4f**): 44 (49[d])  dimer(**5f**): 43 (46[d])
10			3	A ;10/5 mM[e]	>99[d]	**4f**: 57[d]; dimer **5f**: 37[d]
11			3	A ;5/2.5 mM[e]	>99[d]	**4f**: 56[d]; dimer **5f**: 22[d]
12	 (**1g**)	**2a**	1	A	>99[d]	 (**3g**): 86 (91[d])
13	 (**1h**)	**2c**	3	A	>99[d]	 (**3h**): 74[d] (*syn*:*anti* = 1.37:1[d])
14			3	B	>99[d]	 (**4h**): 32, 32 (*cis*, *trans*) [36, 34 (*cis*, *trans*)[d]]
15		**2d**	3	A	>99[d]	 (**3i**): 69[d] (*syn*-*anti* mixture)[d]
16			3	B	>99[d]	 (**4i**):28, 29 (*cis*, *trans*) [29, 31 (*cis*, *trans*)[d]]

[a] Photolysis conditions. Conditions A: substrates: olefin (20 mM) and DTBP (10 mM) in alcohols, light source: 500 W xenon short-arc lamp fitted with an 18 cm water filter and a UV-29 cut-off filter (15 mW cm^{-2}), Ar (entries 1–5) or N_2 (entries 6–16) atmosphere, room temp. Reactions were conducted with 10 mL of solution using a quartz cylindrical cell (diameter: 3 cm), and excess alcohol was evaporated at 50 °C after irradiation; Conditions B: After photolysis conditions A, the residue was heated at 200 °C under a N_2 atmosphere for 1.5 h. [b] Isolated yield based on the consumed starting material. [c] Determined by HPLC analysis. [d] Determined by NMR spectroscopy. [e] 10:5 mM: 10 mM olefin and 5 mM DTBP; 5:2.5 mM: 5 mM olefin and 2.5 mM DTBP.



Scheme 2. Possible mechanism for the formation of dimers.

syn- and *anti*-**3** were formed (Table 3, entries 13 and 15). The isolation of *syn*- and *anti*-**3h** and **3i** was attempted by silica gel column chromatography, but it was unsuccessful due to the partial lactonization of **3** to give **4** during chromatography. When **3h** and **3i** were heated at 200 °C for 1.5 h under a N_2 atmosphere, they lactonized to give **4h** and **4i**, respectively, whose yields were similar to those of **4c** and **4d** (Table 3, entries 4 vs. 14, and entries 5 vs. 16). The *cis* and *trans* isomers of **4h** and **4i** were isolated by silica gel column chromatography, and each isomer was hydrolyzed into the corresponding acid, i.e. *cis*- and *trans*-**4c** and **4d**.[11]

Conclusions

A radical C–C bond formation between olefins and alcohols proceeded efficiently by simple light irradiation at room temperature. The reaction was conducted in the presence of commercially available peroxides or AIBN, and *t*BuOO*t*Bu was found to be most effective. The reaction proceeded without using harmful elements and/or compounds that have an unpleasant smell, which are often used in conventional radical reactions. In addition, the reaction did not require photosensitizers or photocatalysts, which eliminated the time-consuming separation of sensitizers after the reaction, or the synthesis of photocatalysts used in conventional procedures.

Experimental Section

General Remarks: ^{1}H (500 or 400 MHz) and ^{13}C (150, 125, or 100 MHz) NMR spectra were recorded with $CDCl_3$ or CD_3CN as solvent. As internal standards, TMS (δ = 0.0 ppm) was used for ^{1}H, and $CDCl_3$ (δ = 77.0 ppm) or CD_3CN (δ = 118.20 ppm) for ^{13}C NMR analyses. Olefins **1a**,**b**,**f**–**h**, di-*tert*-butyl peroxide (DTBP), H_2O_2, benzoyl peroxide (BPO), 2,2′-azobis(isobutyronitrile) (AIBN), and terebic acid (**5a**) were purchased and used as supplied. Acrylic acid (**1e**) was purchased and distilled before use. The alcohols used for the photolyses were spectral grade 2-propanol (**2a**) and ethanol (**2c**), and guaranteed reagent grade methanol (**2b**) and hexanol (**2d**).

General Procedure for the Photolysis Using a Quartz Cell: A 2-propanol (**2a**; 1 mL) solution of maleic acid (**1a**) and a radical initiator (DTBP, H_2O_2, BPO, or AIBN; see text for the concentrations of **1a** and radical initiators) was introduced into a synthetic quartz cell (10 mm width, 10 mm optical path) fitted with a three-way stopcock. The three-way stopcock was connected to the cell, to a nitrogen or an argon source, and to a small vacuum pump. The solution was evacuated to 50 Torr under sonication for 5 s, and then nitrogen or argon was introduced into the cell; this cycle was repeated 10 times. The photolysis was conducted with a 500 W xenon lamp (USHIO Optical Modulex SX-UI500XQ) fitted with an 18 cm water filter and a cut-off filter (Toshiba UV-25, UV-29, UV-31, UV-33, or Shibuya Kogaku WG280) under a nitrogen or an argon atmosphere. The light intensity of the xenon lamp was measured using an Ushio UIT-150-A Ultraviolet Radiometer equipped with a UVD-S365 photodetector. The emission spectra were measured using an Ushio USR-40D Spectroradiometer. In the experiments on the temperature effect, the temperature was controlled by a variable-temperature liquid nitrogen cryostat (–40 to 25 C; OptistatDN, Oxford Instruments plc) or by a constant-temperature water bath fitted with a recirculating chiller (5 to 70 °C; NCB-2500, Tokyo Rikakikai, co. Ltd.).

Determination of the Consumption of 1a and Yields of 4a and 1b

By HPLC Analysis: After photolysis, the solution was transferred to a round-bottomed flask (10 mL), and the alcohol was removed in vacuo at 50 °C. Pure water (2 mL) was added to the residual crude product using a pipette (2 mL). The consumption of **1a** and the yield of the products (i.e., **4a** and **1b**) were obtained by analysis of this solution by HPLC [Superspher 100, RP-8e column (250 mm, 4 mmID), Merck] with a UV detector (detected at 220 nm) using aqueous phosphoric acid (10 mL H_3PO_4 in 3 L H_2O) as eluent, and comparison with authentic samples. For all HPLC analyses, the absolute yields of the products were determined using standard solutions of authentic samples, and the yields of each product were calculated based on the consumption of starting material **1a**.

By NMR Analysis: After photolysis, the solution was transferred to a round-bottomed flask (10 mL), and the alcohol was removed in vacuo at 50 °C. Precisely weighed naphthalene (2–3 mg, depending on the samples) was added to the residual crude product. The mixture of the crude products and naphthalene was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. The consumption of **1a**, and the absolute yield of **4a**, were determined from the area of proton signals relative to those of the added naphthalene in the NMR spectra, and the yields of each product were calculated based on the consumption of starting material **1a**.

General Procedure for the Preparative Photolysis: An alcohol (10 mL) solution of an olefin (**1a**,**b**,**f**–**h**) and DTBP was introduced into a quartz cylindrical cell (diameter: 3 cm) fitted with a three-way stopcock. The three-way stopcock was connected to the cell, to a nitrogen or argon source, and to a small vacuum pump. The solution was evacuated to 50 Torr under sonication for 5 s, and then nitrogen was introduced into the cell; this cycle was repeated 10 times. The photolysis was conducted with a 500 W xenon lamp (USHIO Optical Modulex SX-UI500XQ) fitted with an 18 cm water filter and a Toshiba UV-29 cut-off filter (15 mW cm^{-2}) under a nitrogen atmosphere. The light intensity of the xenon lamp was measured by an Ushio UIT-150-A Ultraviolet Radiometer equipped with a UVD-S365 photodetector. After photolysis, the alcohol was removed in vacuo at 50 °C, and the consumption of olefins and the yield of products were determined by NMR spectroscopic measurements using precise amounts of naphthalene (8–13 mg), as internal standards; the yields of each product were calculated based on the consumption of starting material. Isolation of the products was conducted by silica gel column chromatography.

2,2-Dimethyl-5-oxo-tetrahydrofuran-3-carboxylic Acid (Terebic Acid, 4a):[16] Maleic acid (**1a**; 23.35 mg, 0.20 mmol) and DTBP (14.75 mg, 0.10 mmol) in 2-propanol (**2a**; 10 mL). Irradiation time: 1 h. Conversion: 100% (determined by HPLC analysis). Eluent for chromatography: ethyl acetate/acetic acid (20:1). Isolated yield: 30.62 mg (96%). White solid. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.33 (s, 3 H), 1.54 (s, 3 H), 2.67 (dd, J = 17.8, 8.7 Hz, 1 H), 2.90

(dd, J = 17.8, 8.7 Hz, 1 H), 3.23 (dd, J = 8.7, 8.7 Hz, 1 H), 6.2 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 23.5, 28.2, 32.5, 50.6, 84.9, 172.0, 175.3 ppm. IR (KBr): $\tilde{\nu}$ = 3167, 3129, 3059, 2990, 2955, 2940, 2720, 2644, 2565, 2525, 2494, 1746, 1738, 1454, 1425, 1406, 1393, 1375, 1325, 1288, 1233, 1196, 1165, 1142, 1119, 1084, 1016, 982, 953, 937, 918, 856, 835, 789, 718, 660, 602, 552, 529, 449, 432 cm^{-1}. MS (EI): m/z (%) = 40 (39), 41 (43), 42 (10), 43 (100), 44 (24), 45 (10), 55 (74), 56 (17), 59 (69), 69 (31), 72 (22), 100 (22), 114 (11), 115 (21), 143 (56), 158 (1) $[M]^+$, 159 (1) $[M + 1]^+$.

5-Oxo-tetrahydrofuran-3-carboxylic Acid (4b):[17] Maleic acid (**1a**; 23.24 mg, 0.20 mmol) and DTBP (15.16 mg, 0.10 mmol) in methanol (**2b**; 10 mL). Irradiation time: 2 h. Yield according to NMR: 65% (conversion: > 99%). Eluent for chromatography: ethyl acetate/acetic acid (20:1). Isolated yield: 15.94 mg (61%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.70 (d, J = 7.3 Hz, 1 H), 2.71 (d, J = 8.3 Hz, 1 H), 3.46 (dddd, J = 8.3, 8.0, 7.3, 5.5 Hz, 1 H), 4.0 (br. s, 1 H), 4.39 (dd, J = 9.2, 5.5 Hz, 1 H), 4.45 (dd, J = 9.2, 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4, 40.3, 70.1, 173.4, 176.6 ppm. IR (KBr): $\tilde{\nu}$ = 3445, 3009, 2988, 2957, 2930, 1771, 1732, 1717, 1653, 1645, 1636, 1575, 1558, 1539, 1521, 1506, 1437, 1418, 1387, 1192, 1078, 1032, 1001, 910, 862, 821, 673 cm^{-1}. MS (EI): m/z (%) = 32 (26), 39 (38), 40 (16), 41 (73), 42 (39), 43 (47), 44 (30), 45 (46), 55 (100), 56 (12), 57 (32), 58 (22), 68 (25), 69 (30), 70 (17), 71 (69), 72 (40), 73 (32), 83 (14), 84 (20), 85 (25), 86 (15), 88 (17), 99 (16), 100 (17), 102 (29), 113 (8), 130 (3) $[M]^+$, 131 (9) $[M + 1]^+$.

***cis*- and *trans*-5-Oxo-2-methyl-tetrahydrofuran-3-carboxylic Acid (*cis*-and *trans*-4c)**

Method A: Maleic acid (**1a**; 23.19 mg, 0.20 mmol) and DTBP (14.81 mg, 0.10 mmol) in ethanol (**2c**; 10 mL). Irradiation time: 1 h. Conversion: 73% (determined by HPLC analysis). Eluent for chromatography: ethyl acetate/acetic acid (20:1). Isolated yield: 13.43 mg (79%; *cis* and *trans* mixture, *cis*/*trans* = 1:1.2: determined by NMR spectroscopy). White powder. Spectroscopic data were the same as the authentic *cis* and *trans* isomers (vide infra).

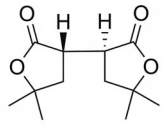
Method B: Maleic acid (**1a**; 23.22 mg, 0.20 mmol) and DTBP (15.07 mg, 0.10 mmol) in ethanol (**2c**; 10 mL). Irradiation time: 2 h. Yield according to NMR: 74% (conversion: > 99%). Eluent for chromatography: ethyl acetate/acetic acid (20:1). Isolated yield: 22.36 mg (77%; *cis* and *trans* mixture, *cis*/*trans* = 1:1.1: determined by NMR spectroscopy). White powder. Spectroscopic data were the same as the authentic *cis* and *trans* isomers (vide infra).

***cis*- and *trans*-5-Oxo-2-pentyl-tetrahydrofuran-3-carboxylic Acid (*cis*- and *trans*-4d):** Maleic acid (**1a**; 23.34 mg, 0.20 mmol) and DTBP (14.92 mg, 0.10 mmol) in hexanol (**2d**; 10 mL). Irradiation time: 2 h. Conversion: 100% (determined by HPLC analysis). Eluent for chromatography: ethyl acetate/acetic acid (20:1). Isolated yield: 23.75 mg (59%; *cis* and *trans* mixture). White powder. Spectroscopic data were the same as the authentic *cis* and *trans* isomers (vide infra).

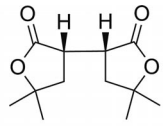
2,2-Dimethyl-5-oxo-tetrahydrofuran-3-carboxylic Acid (Terebic Acid, 4a): Fumaric acid (**1b**; 23.29 mg, 0.20 mmol) and DTBP (14.41 mg, 0.99 mmol) in 2-propanol (**2a**; 10 mL). Irradiation time: 1 h. HPLC yield: 96% (conversion: 99%). Eluent for chromatography: ethyl acetate/acetic acid (20:1). Isolated yield: 25.9 mg (82%). White powder. Spectroscopic data and melting point of the isolated sample were identical to **4a** obtained from **1a** (vide supra).

5,5-Dimethyl-tetrahydrofuran-2-one (4e), 3*S*,3′*S*- and 3*R*,3′*R*-5,5,5′,5′-Tetramethyltetrahydro-[3,3′]bifuranyl-2,2′-dione (Dimer 5e-1), and 3*S*,3′*R*- and 3*R*,3′*S*-5,5,5′,5′-Tetramethyltetrahydro-[3,3′]bifuranyl-2,2′-dione (Dimer 5e-2)[18]

Method A: Acrylic acid (**1c**; 40.11 mg, 0.56 mmol) and DTBP (40.34 mg, 0.28 mmol) in 2-propanol (**2a**; 25 mL) was prepared. Photolysis was conducted twice using 10 mL of the solution each time. Irradiation time: 3 h. Yield according to NMR, run 1: 30% (conversion: > 99%, dimers **5e-1** and **5e-2**: 4%), run 2: 29% (conversion: > 99%, dimers **5e-1** and **5e-2**: 4%). The crude products from runs 1 and 2 were combined and purified. Eluent for chromatography: hexane/ethyl acetate (99:1 → 3:1). Isolated yield of **4e**: 14.0 mg (28%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 6 H), 2.06 (t, J = 8.2 Hz, 2 H), 2.62 (t, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 27.7 (×2), 29.3, 34.7, 84.5, 176.6 ppm. IR (liquid film): $\tilde{\nu}$ = 2963, 2928, 2872, 2855, 1765, 1462, 1452, 1443, 1422, 1389, 1375, 1366, 1277, 1261, 1223, 1171, 1136, 1107, 1024, 957, 908, 800, 733, 650 cm^{-1}. MS (EI): m/z = 55 (63), 56 (48), 59 (35), 70 (39), 71 (24), 84 (15), 86 (10), 99 (100), 114 (8) $[M]^+$.



Dimer **5e-1**



Dimer **5e-2**

Isolated yield of **5e-1**: 1.4 mg (2.7%). White powder, m.p. 155–156 °C (ref.[18] m.p. 164–165 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 6 H), 1.50 (s, 6 H), 1.91 (dd, J = 12.4, 12.4 Hz, 2 H), 2.23 (dd, J = 12.4, 8.7 Hz, 2 H), 3.47 (ddd, J = 12.4, 8.7, 3.7 Hz, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 27.0, 28.8, 36.2, 40.0, 82.8, 176.2 ppm. IR (KBr): $\tilde{\nu}$ = 2978, 2968, 2922, 2872, 2853, 1749, 1468, 1454, 1387, 1375, 1368, 1319, 1298, 1277, 1260, 1186, 1134, 1107, 1045, 1022, 980, 959, 949, 928, 866, 824, 802, 735, 691, 650, 604, 596, 577, 548, 405 cm^{-1}. MS (EI): m/z = 53 (19), 55 (42), 56 (20), 57 (24), 59 (11), 67 (24), 69 (27), 71 (11), 79 (17), 81 (100), 82 (33), 95 (50), 96 (25), 97 (10), 111 (42), 114 (18), 123 (28), 126 (55), 127 (10), 165 (31), 182 (12), 211 (23), 226 (0.3) $[M]^+$, 227 (2) $[M + 1]^+$.

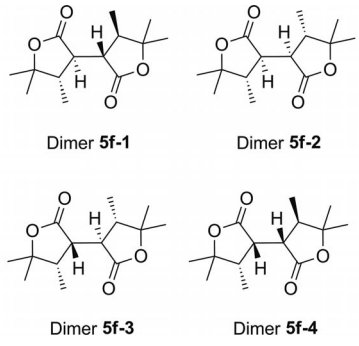
Isolated yield of **5e-2**: 1.4 mg (2.7%). White powder, m.p. 145–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 6 H), 1.50 (s, 6 H), 1.93 (dd, J = 13.7, 12.8 Hz, 2 H), 2.47 (dd, J = 12.8, 8.7 Hz, 2 H), 3.12 (ddd, J = 13.7, 8.7, 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.0, 28.8, 39.5, 41.6, 82.8, 175.7 ppm. IR (KBr): $\tilde{\nu}$ = 3431, 2980, 2932, 2886, 2851, 1753, 1460, 1389, 1377, 1356, 1321, 1310, 1281, 1265, 1192, 1173, 1144, 1111, 1099, 1026, 972, 953, 934, 926, 917, 862, 804, 773, 736, 689, 642, 604, 571, 469, 434 cm^{-1}. MS (EI): m/z = 45 (10), 53 (27), 54 (13), 55 (55), 56 (22), 57 (19), 59 (27), 67 (27), 69 (27), 77 (13), 79 (23), 80 (11), 81 (100), 82 (26), 83 (11), 93 (10), 95 (41), 96 (18), 111 (42), 114 (31), 123 (22), 126 (40), 165 (23), 211 (15), 226 (2) $[M]^+$, 227 (3) $[M + 1]^+$.

Method B: A solution of acrylic acid (**1c**; 40.11 mg, 0.56 mmol) and DTBP (40.34 mg, 0.28 mmol) in 2-propanol (**2a**; 25 mL) was prepared. A portion (5 mL) of this solution was diluted to 10 mL with **2a**, and the resulting solution was then subjected to photolysis. Irradiation time: 3 h. Yield according to NMR: 41% (conversion: > 99%, dimers **5e-1** and **5e-2**: 4%).

4,5,5-Trimethyltetrahydrofuran-2-one (4f), 3*R*,4*S*,3′*S*,4′*R*- and 3*S*,4*R*,3′*R*,4′*S*-4,5,5,4′,5′,5′-Hexamethyltetrahydro-[3,3′]bifuranyl-2,2′-dione (Dimer 5f-1), 3*R*,4*S*,3′*R*,4′*S*- and 3*S*,4*R*,3′*S*,4′*R*-4,5,5,4′,5′,5′-Hexamethyltetrahydro-[3,3′]bifuranyl-2,2′-dione (Dimer 5f-2), 3*S*,4*S*,3′*R*,4′*S*- and 3*R*,4*R*,3′*S*,4′*R*-4,5,5,4′,5′,5′-Hexa-

methyltetrahydro-[3,3′]bifuranyl-2,2′-dione (Dimer 5f-3), and 3*S*,4*S*,3′*S*,4′*R*- and 3*R*,4*R*,3′*R*,4′*S*-4,5,5,4′,5′,5′-Hexamethyltetrahydro-[3,3′]bifuranyl-2,2′-dione (Dimer 5f-4)[14a]

Method A: A solution of crotonic acid (**1f**; 85.94 mg, 0.10 mmol) and DTBP (73.55 mg, 0.50 mmol) in 2-propanol (**2a**; 50 mL) was prepared. Photolysis was conducted three times using 10 mL of the solution each time. Irradiation time: 3 h. Yield according to NMR, run 1: 51% (conversion: > 99%, dimers **5f-1** + **5f-2**: 24%, dimer **5f-3**: 9%, dimer **5f-4**: 6%), run 2: 49% (conversion: > 99%, dimers **5f-1** + **5f-2**: 31%, dimer **5f-3**: 11%, dimer **5f-4**: 10%), run 3: 46% (conversion: > 99%, dimers **5f-1** + **5f-2**: 24%, dimer **5f-3**: 11%, dimer **5f-4**: 12%). The crude products of runs 1–3 were combined and purified. Eluent for chromatography: hexane/ethyl acetate (99:1 → 3:1). Isolated yield of **4f**: 33.4 mg (44%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (d, J = 6.9 Hz, 3 H), 1.26 (s, 3 H), 1.43 (s, 3 H), 2.27 (dd, J = 16.3, 10.3 Hz, 1 H), 2.36 (ddq, J = 10.3, 7.3, 6.9 Hz, 1 H), 2.64 (dd, J = 16.3, 7.3 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 21.5, 27.0, 36.7, 39.8, 86.9, 175.7 ppm. IR (liquid film): $\tilde{\nu}$ = 2976, 2936, 2882, 1771, 1456, 1423, 1391, 1375, 1273, 1260, 1231, 1175, 1132, 1113, 1084, 1040, 1018, 962, 934, 918, 833, 727, 667, 637, 598, 544, 525, 500 cm^{-1}. MS (EI): m/z = 55 (13), 59 (100), 69 (60), 70 (24), 84 (22), 85 (11), 95 (13), 113 (59), 128 (11) $[M + 1]^+$. The mixture of the four dimers **5f-1–5f-4**[14a] was also isolated, 33 mg (43%). The four dimers were further purified and isolated.



Data for **5f-1**: White powder, m.p. 179.5–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (d, J = 6.8 Hz, 6 H), 1.28 (s, 6 H), 1.48 (s, 6 H), 2.41 (dd, J = 12.8, 6.8 Hz, 2 H), 2.82 (d, J = 12.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.6, 21.4, 27.0, 41.9, 44.2, 85.4, 175.7 ppm. IR (KBr): $\tilde{\nu}$ = 2986, 2976, 2928, 2884, 2853, 1767, 1474, 1385, 1371, 1329, 1308, 1263, 1236, 1221, 1177, 1136, 1121, 1074, 1042, 961, 947, 934, 908, 889, 725, 669, 638, 588, 577, 501, 405 cm^{-1}. MS (EI): m/z = 53 (27), 55 (49), 57 (19), 59 (13), 67 (44), 69 (34), 70 (33), 77 (14), 79 (21), 81 (27), 82 (11), 83 (23), 91 (12), 95 (30), 109 (100), 110 (11), 123 (28), 124 (38), 125 (18), 127 (32), 128 (28), 140 (14), 151 (14), 254 (0.7) $[M]^+$, 255 (1) $[M + 1]^+$.

Data for **5f-2**: White powder, m.p. 150–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (d, J = 6.8 Hz, 6 H), 1.27 (s, 6 H), 1.46 (s, 6 H), 2.29 (ddd, J = 14.2, 6.8, 1.8 Hz, 2 H), 2.81 (dd, J = 14.2, 1.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7, 21.7, 27.1, 42.5, 45.6, 85.2, 175.0 ppm. IR (KBr): $\tilde{\nu}$ = 2976, 2941, 2884, 2851, 1765, 1476, 1460, 1393, 1375, 1317, 1306, 1265, 1254, 1240, 1227, 1196, 1180, 1132, 1125, 1080, 1069, 1043, 964, 951, 908, 897, 880, 725, 664, 638, 610, 588, 571, 503, 467 cm^{-1}. MS (EI): m/z = 53 (20), 55 (49), 57 (20), 59 (15), 67 (34), 69 (32), 70 (59), 77 (10), 79 (16), 81 (24), 82 (15), 83 (65), 95 (38), 109 (100), 110 (12), 111 (12), 113 (14), 123 (28), 124 (47), 125 (28), 127 (32), 128 (81), 140 (45), 141 (16), 151 (17), 193 (12), 221 (12), 239 (13), 254 (0.2) $[M]^+$, 255 (5) $[M + 1]^+$.

Data for **5f-3**: White powder, m.p. 160.5–161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (d, J = 7.3 Hz, 3 H), 1.18 (d, J = 6.9 Hz, 3 H), 1.28 (s, 3 H), 1.38 (s, 3 H), 1.43 (s, 3 H), 1.47 (s, 3 H), 2.47 (dd, J = 11.5, 7.3 Hz, 1 H), 2.60 (dd, J = 7.5, 6.9 Hz, 1 H), 2.78 (dd, J = 11.5, 7.3 Hz, 1 H), 3.13 (dd, J = 7.5, 7.3 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.8, 14.1, 22.2, 23.8, 27.5, 27.6, 41.5, 43.2, 43.8, 43.9, 85.1, 85.4, 175.0, 175.7 ppm. IR (KBr): $\tilde{\nu}$ = 2974, 2934, 2876, 1769, 1468, 1452, 1441, 1393, 1385, 1373, 1356, 1342, 1325, 1287, 1267, 1231, 1219, 1196, 1179, 1136, 1121, 1067, 1051, 1026, 953, 934, 908, 881, 868, 824, 737, 679, 633, 606, 598, 588, 529, 501, 461, 439, 405 cm^{-1}. MS (EI): m/z = 53 (20), 55 (44), 57 (18), 59 (16), 67 (35), 69 (31), 70 (52), 77 (11), 79 (16), 81 (24), 82 (11), 83 (30), 95 (33), 109 (100), 110 (16), 111 (12), 113 (13), 123 (26), 124 (36), 125 (24), 127 (52), 128 (57), 140 (38), 141 (10), 151 (17), 193 (12), 221 (12), 239 (19), 254 (2) $[M]^+$, 255 (4) $[M + 1]^+$.

Data for **5f-4**: White powder, m.p. 165.5–166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, J = 6.8 Hz, 3 H), 1.16 (d, J = 7.7 Hz, 3 H), 1.26 (s, 3 H), 1.43 (s, 3 H), 1.44 (s, 3 H), 1.48 (s, 3 H), 2.47 (dd, J = 9.6, 7.7 Hz, 1 H), 2.56 (dd, J = 12.9, 1.4 Hz, 1 H), 2.66 (dd, J = 12.9, 6.8 Hz, 1 H), 3.08 (dd, J = 9.6, 1.4 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.7, 12.7, 21.5, 23.6, 27.1, 28.7, 41.9, 42.1, 44.8, 44.8, 85.0, 85.7, 174.9, 175.8 ppm. IR (KBr): $\tilde{\nu}$ = 2982, 2936, 2897, 1749, 1470, 1387, 1377, 1358, 1335, 1314, 1265, 1229, 1211, 1196, 1179, 1148, 1132, 1096, 1072, 1109, 1030, 961, 947, 932, 908, 889, 804, 785, 752, 733, 679, 650, 606, 592, 571, 532, 503, 480, 432 cm^{-1}. MS (EI): m/z = 53 (25), 55 (54), 57 (21), 59 (15), 67 (41), 69 (39), 70 (75), 77 (12), 79 (19), 81 (26), 82 (14), 83 (33), 91 (10), 95 (38), 109 (100), 110 (11), 123 (27), 124 (39), 125 (25), 127 (22), 128 (31), 140 (33), 141 (11), 151 (19), 193 (9), 239 (9), 254 (1) $[M]^+$, 255 (1) $[M + 1]^+$. HRMS (EI): calcd. for $C_{14}H_{22}O_4$ 254.1518; found 254.1467.

Method B: Crotonic acid (**1f**; 22.46 mg, 0.26 mmol) and DTBP (18.29 mg, 0.13 mmol) in 2-propanol (**2a**; 25 mL) was prepared. Photolysis was conducted using 10 mL of the solution. Irradiation time: 3 h. Yield according to NMR: 57% (conversion: > 99%, dimers **5f-1** + **5f-2**: 22%, dimer **5f-3**: 10%, dimer **5f-4**: 5%).

Method C: Crotonic acid (**1f**; 22.46 mg, 0.26 mmol) and DTBP (18.29 mg, 0.13 mmol) in 2-propanol (**2a**; 25 mL) was prepared. A portion (5 mL) of the solution was diluted to 10 mL with 2-propanol, and the resulting solution was subjected to photolysis. Irradiation time: 3 h. Yield according to NMR: 56% (conversion: > 99%, dimers **5f-1** + **5f-2**: 13%, dimer **5f-3**: 5%, dimer **5f-4**: 4%).

2-(1-Hydroxy-1-methylethyl)succinonitrile (3g): (i) A solution of fumaronitrile (**1e**; 37.65 mg, 0.48 mmol) and DTBP (37.71 mg, 0.26 mmol) in 2-propanol (**2a**; 25 mL) was prepared. Photolysis was conducted using 10 mL of the solution. Irradiation time: 1 h. Yield according to NMR, run 1: 91% (conversion: > 99%). (ii) A solution of fumaronitrile (**1e**; 37.01 mg, 0.47 mmol) and DTBP (37.11 mg, 0.25 mmol) in 2-propanol (**2a**; 25 mL) was prepared. Photolysis was conducted twice using 10 mL of the solution each time. Irradiation time: 1 h. Yield according to NMR, run 2: 90% (conversion: > 99%), run 3: 91% (conversion: > 99%). (iii) The crude products of runs 1–3 were combined and purified. Eluent for chromatography: hexane/ethyl acetate (7:1 → 5:1). Isolated yield: 68 mg (86%). Pale brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.44 (s, 6 H), 2.39 (br. s, 1 H), 2.79 (dd, J = 17.0, 9.1 Hz, 1 H), 2.90 (dd, J = 17.0, 5.1 Hz, 1 H), 2.98 (dd, J = 9.1, 5.1 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.4, 26.5, 28.1, 40.8, 70.8, 116.8, 117.9 ppm. IR (liquid film): $\tilde{\nu}$ = 3465, 2982, 2943, 2884, 2249, 1634, 1470, 1423, 1383, 1273, 1196, 1146, 1055, 1013, 966, 935, 907, 881, 864, 822, 781, 685, 596, 503 cm^{-1}. MS (EI): m/z =

31 (74), 39 (37), 40 (17), 41 (64), 42 (20), 43 (94), 44 (14), 51 (13), 52 (28), 53 (20), 54 (39), 59 (100), 60 (14), 68 (15), 80 (14), 81 (41), 94 (11), 123 (44), 138 (0.4) $[M]^+$, 139 (2) $[M + 1]^+$. $C_7H_{10}N_2O$ (138.17): calcd. C 60.85, H 7.30, N 20.27; found C 60.83, H 7.32, N 19.85.

***syn*- and *anti*-Dimethyl 2-(1-Hydroxy-1-ethyl)succinate (*syn*- and *anti*-3h):**[19] Dimethyl maleate (1h, 28.9 mg, 0.20 mmol) and DTBP (16.00 mg, 0.11 mmol) in ethanol (2c, 10 mL). Irradiation time: 3 h. Yield according to NMR: 74% (*syn*/*anti* or *anti*/*syn* ratio = 1:1.37; conversion: > 99%). Isolation of the products was not possible due to gradual transformation of **3h** into lactone **4h** during silica gel chromatography.

***cis*- and *trans*-Methyl 2-methyl-5-oxo-tetrahydro-3-furancarboxylate (*cis*- and *trans*-4h):**[20] A solution of dimethyl maleate (**1h**; 143.87 mg, 0.10 mmol) and DTBP (78.29 mg, 0.54 mmol) in ethanol (**2c**; 50 mL) was prepared. Photolysis was conducted using 10 mL of the solution. Irradiation time: 3 h. After removal of **2c** from the reaction mixture in vacuo, the residue was heated at 200 °C for 1.5 h under a nitrogen atmosphere. Yield according to NMR: 70% (*cis*/*trans* = 36:34; conversion: > 99%). The products were purified by silica gel preparative TLC (hexane/ethyl acetate = 10:1; **4h** was volatile under high vacuum).

Isolated yield of ***cis*-4h**: 10.0 mg (32%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (d, J = 6.4 Hz, 3 H), 2.67 (dd, J = 17.7, 8.7 Hz, 1 H), 2.94 (dd, J = 17.7, 6.4 Hz, 1 H), 3.47 (ddd, J = 8.7, 7.8, 6.4 Hz, 1 H), 3.76 (s, 3 H), 4.85 (dq, J = 7.8, 6.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.7, 31.2, 44.4, 52.2, 76.2, 170.6, 174.7 ppm. IR (liquid film): $\tilde{\nu}$ = 2986, 2955, 2853, 1784, 1736, 1439, 1416, 1391, 1373, 1323, 1267, 1252, 1215, 1192, 1175, 1134, 1098, 1053, 995, 978, 941, 910, 891, 854, 837, 785, 770, 721, 658, 609, 538, 517, 484, 440 cm^{-1}. MS (EI): m/z = 39 (33), 41 (20), 42 (30), 43 (70), 45 (12), 53 (17), 54 (23), 55 (100), 56 (14), 58 (11), 59 (56), 82 (37), 83 (66), 85 (19), 86 (22), 87 (13), 99 (73), 113 (17), 114 (85), 115 (54), 127 (28), 143 (13), 158 (2) $[M]^+$, 159 (6) $[M + 1]^+$.

Isolated yield of ***trans*-4h**: 10.0 mg (32%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52 (d, J = 6.4 Hz, 3 H), 2.80 (dd, J = 17.2, 9.2 Hz, 1 H), 2.94 (dd, J = 17.2, 9.6 Hz, 1 H), 3.02 (ddd, J = 9.6, 9.2, 7.3 Hz, 1 H), 3.77 (s, 3 H), 4.68 (dq, J = 7.3, 6.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7, 32.3, 47.4, 52.7, 78.1, 171.1, 174.2 ppm. IR (liquid film): $\tilde{\nu}$ = 2984, 2957, 2849, 1786, 1737, 1439, 1422, 1385, 1375, 1354, 1323, 1261, 1206, 1184, 1119, 1090, 1053, 1030, 961, 945, 899, 847, 833, 766, 718, 687, 667, 540, 447 cm^{-1}. MS (EI): m/z = 39 (36), 41 (22), 42 (29), 43 (74), 45 (12), 53 (18), 54 (23), 55 (100), 56 (16), 58 (11), 59 (64), 69 (11), 71 (14), 82 (22), 83 (50), 84 (13), 85 (23), 86 (22), 87 (71), 98 (28), 99 (42), 101 (14), 114 (52), 115 (42), 116 (71), 127 (27), 130 (33), 158 (0.5) $[M]^+$, 159 (8) $[M + 1]^+$.

***syn*- and *anti*-Dimethyl 2-(1-hydroxy-1-hexyl)succinate (*syn*-and *anti*-3i):** Dimethyl maleate (**1h**; 33.46 mg, 0.23 mmol) and DTBP (14.82 mg, 0.10 mmol) in hexanol (**2d**; 10 mL). Irradiation time: 3 h. Yield according to NMR: 69% (conversion: > 99%). Isolation of the products was not possible due to the gradual transformation of **3i** into lactone **4i** during silica gel chromatography.

***cis*- and *trans*-Methyl 2-pentyl-5-oxo-tetrahydro-3-furancarboxylate (*cis*-and *trans*-4i):** A solution of dimethyl maleate (**1h**; 83.76 mg, 0.58 mmol) and DTBP (35.67 mg, 0.24 mmol) in hexanol (**2d**; 25 mL) was prepared. Photolysis was conducted using 10 mL of the solution. Irradiation time: 3 h. After removal of **2d** from reaction mixture in vacuo, the residue was heated at 200 °C for 1.5 h under a nitrogen atmosphere. Yield according to NMR: 60% (*cis*/*trans* = 29:31; conversion: > 99%). Eluent for chromatography: hexane/ethyl acetate (7:1; **4i** was volatile under high vacuum).

Isolated yield of ***cis*-4i**: 14 mg (28%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.2 Hz, 3 H), 1.2–1.7 (m, 8 H), 2.67 (dd, J = 17.7, 8.7 Hz, 1 H), 2.90 (dd, J = 17.7, 5.5 Hz, 1 H), 3.44 (ddd, J = 8.7, 7.3, 5.5 Hz, 1 H), 3.75 (s, 3 H), 4.63 (ddd, J = 9.9, 7.3, 3.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.4, 25.5, 31.3, 31.4, 31.8, 44.3, 52.3, 80.4, 170.7, 174.8 ppm. IR (liquid film): $\tilde{\nu}$ = 2955, 2936, 2872, 2860, 1784, 1738, 1460, 1439, 1416, 1393, 1371, 1331, 1288, 1256, 1213, 1173, 1038, 1003, 949, 910, 894, 878, 812, 847, 829, 770, 727, 679, 658, 635, 538 cm^{-1}. MS (EI): m/z = 55 (96), 59 (18), 83 (26), 87 (19), 95 (12), 111 (11), 114 (54), 115 (100), 143 (47), 154 (26), 155 (10), 182 (14), 214 (0.3) $[M]^+$, 215 (21) $[M + 1]^+$.

Isolated yield of ***trans*-4i**:[21] 14.2 mg (29%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 6.8 Hz, 3 H), 1.25–1.6 (m, 6 H), 1.65–1.82 (m, 2 H), 2.77 (dd, J = 17.7, 9.6 Hz, 1 H), 2.92 (dd, J = 17.7, 9.2 Hz, 1 H), 3.04 (ddd, J = 9.6, 9.2, 7.3 Hz, 1 H), 3.76 (s, 3 H), 4.57 (dt, J = 7.3, 5.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 22.4, 24.8, 31.3, 32.2, 35.3, 45.7, 52.7, 81.9, 171.6, 174.4 ppm. IR (liquid film): $\tilde{\nu}$ = 2955, 2934, 2860, 1784, 1738, 1460, 1437, 1368, 1341, 1261, 1204, 1177, 1119, 1067, 999, 949, 858, 822, 768, 727, 665, 538 cm^{-1}. MS (EI): m/z = 39 (23), 41 (51), 42 (18), 43 (47), 54 (12), 55 (89), 56 (14), 59 (32), 69 (12), 71 (13), 83 (41), 85 (11), 87 (58), 99 (18), 111 (12), 113 (20), 114 (41), 115 (100), 116 (38), 127 (13), 130 (47), 143 (67), 154 (18), 214 (0.2) $[M]^+$, 215 (2) $[M + 1]^+$.

General Procedure for the Hydrolysis of Esters 4: 4, AcOH, and HCl (6 N) were added to a 20 mL round-bottomed flask fitted with a reflux condenser and a magnetic stirrer. The reaction mixture was heated at 100 °C for 3 h under a nitrogen atmosphere. After evaporation of the solvent in vacuo, the crude white solid was purified by silica gel column chromatography.

***cis*-5-Oxo-2-methyl-tetrahydrofuran-3-carboxylic Acid (*cis*-4c):**[20] *cis*-**4h**: 50 mg (0.32 mmol); AcOH: 5 mL; HCl (10 N): 5 mL. Eluent for chromatography: hexane/ethyl acetate (99:1 → 1:2), yield of *cis*-**4c**: 34 mg (75%). White powder, m.p. 103–104 °C (ref.[20] m.p. 104–106 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (d, J = 6.4 Hz, 3 H), 2.71 (dd, J = 17.8, 8.7 Hz, 1 H), 2.96 (dd, J = 17.8, 6.4 Hz, 1 H), 3.51 (ddd, J = 8.7, 7.8, 6.4 Hz, 1 H), 3.8 (br. s, 1 H), 4.89 (dq, J = 7.8, 6.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.8, 31.2, 44.3, 76.1, 174.4, 174.6 ppm. IR (KBr): $\tilde{\nu}$ = 3207, 2995, 2965, 2943, 1749, 1740, 1422, 1406, 1387, 1350, 1317, 1254, 1186, 1159, 1138, 1067, 1030, 978, 961, 926, 839, 662, 540, 459 cm^{-1}. MS (EI): m/z = 32 (34), 39 (17), 41 (15), 43 (39), 44 (14), 45 (36), 54 (15), 55 (100), 56 (18), 57 (11), 72 (36), 73 (16), 82 (29), 83 (26), 85 (24), 100 (61), 101 (30), 129 (13), 144 (1) $[M]^+$, 145 (2) $[M + 1]^+$.

***trans*-5-Oxo-2-Methyl-tetrahydrofuran-3-carboxylic Acid (*trans*-4c):**[20] *trans*-**4h**: 91 mg (0.58 mmol); AcOH: 2 mL; HCl (6 N): 2 mL. Eluent for chromatography: hexane/ethyl acetate (4:1 → 1:2), yield of *trans*-**4c**: 30 mg (36%). White powder, m.p. 84–85 °C (ref.[20] m.p. 86 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.55 (d, J = 6.4 Hz, 3 H), 2.85 (dd, J = 17.8, 9.4 Hz, 1 H), 2.96 (dd, J = 17.8, 9.2 Hz, 1 H), 3.07 (ddd, J = 9.4, 9.2, 7.3 Hz, 1 H), 4.73 (dq, J = 7.3, 6.4 Hz, 1 H), 8.4 (br. s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.8, 32.0, 47.2, 78.0, 174.2, 175.8 ppm. IR (KBr): $\tilde{\nu}$ = 3416, 3179, 3082, 2997, 2930, 2855, 1749, 1736, 1630, 1427, 1406, 1387, 1358, 1348, 1321, 1285, 1261, 1223, 1179, 1123, 1084, 1045, 961, 943, 839, 671, 660 cm^{-1}. MS (EI): m/z = 45 (30), 54 (11), 55 (100), 56 (14), 72 (21), 73 (19), 83 (13), 84 (11), 85 (12), 98 (16), 100 (28), 101 (15), 102 (27), 116 (13), 144 (0.2) $[M]^+$, 145 (2) $[M + 1]^+$.

***cis*-5-Oxo-2-pentyl-tetrahydrofuran-3-carboxylic Acid (*cis*-4d):**[22] *cis*-**4i**: 54 mg (0.25 mmol); AcOH: 5 mL; HCl (6 N): 5 mL. Eluent for chromatography: hexane/ethyl acetate (3:1 → 1:2), yield of *cis*-**4d**: 28 mg (55%). White powder, m.p. 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.1 Hz, 3 H), 1.25–1.37 (m, 2 H), 1.37–1.50 (m, 2 H), 1.50–1.63 (m, 2 H), 1.63–1.71 (m, 2 H), 2.70 (dd, J = 17.7, 8.7 Hz, 1 H), 2.90 (dd, J = 17.7, 5.5 Hz, 1 H), 3.47 (ddd, J = 8.7, 7.3, 5.5 Hz, 1 H), 4.66 (dt, J = 7.3, 6.4 Hz, 1 H) ppm. ^{1}H NMR (400 MHz, CD_3CN): δ = 0.89 (t, J = 7.1 Hz, 3 H), 1.27–1.37 (m, 4 H), 1.37–1.53 (m, 2 H), 1.61 (dd, J = 7.3, 7.3 Hz, 2 H), 2.64 (dd, J = 17.4, 5.0 Hz, 1 H), 2.70 (dd, J = 17.4, 7.3 Hz, 1 H), 3.37 (ddd, J = 7.3, 6.9, 5.0 Hz, 1 H), 4.61 (dt, J = 6.9, 6.9 Hz, 1 H), 9.4 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.4, 25.5, 31.2, 31.3, 31.9, 44.2, 80.3, 174.9, 175.7 ppm. IR (KBr): $\tilde{\nu}$ = 3180, 2957, 2932, 2860, 1753, 1740, 1464, 1454, 1423, 1410, 1383, 1356, 1342, 1325, 1306, 1279, 1260, 1200, 1180, 1134, 1105, 1047, 1003, 976, 928, 849, 770, 735, 691, 662, 544, 511, 453, 415 cm^{-1}. MS (EI): m/z = 32 (21), 39 (45), 41 (78), 42 (24), 43 (64), 44 (14), 45 (28), 53 (13), 54 (14), 55 (97), 56 (24), 57 (33), 67 (14), 69 (11), 70 (11), 71 (18), 72 (17), 73 (42), 81 (12), 82 (17), 83 (59), 84 (13), 94 (11), 95 (15), 99 (22), 100 (54), 101 (100), 109 (12), 111 (16), 129 (88), 140 (16), 154 (32), 164 (10), 182 (12), 200 (0.1) $[M]^+$, 201 (6) $[M + 1]^+$.

***trans*-5-Oxo-2-pentyl-tetrahydrofuran-3-carboxylic Acid (*trans*-4d):**[21] *trans*-**4i**: 40 mg (0.19 mmol); AcOH: 5 mL; HCl (6 N): 5 mL. Eluent for chromatography: hexane/ethyl acetate (3:1), yield of *trans*-**4d**: 9 mg (24%). White powder, m.p. 86–87 °C (ref.[21,23] m.p. 84–85 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.1 Hz, 3 H), 1.2–1.37 (m, 2 H), 1.37–1.47 (m, 2 H), 1.47–1.60 (m, 2 H), 1.65–1.86 (m, 2 H), 2.82 (dd, J = 17.8, 9.6 Hz, 1 H), 2.94 (dd, J = 17.8, 8.2 Hz, 1 H), 3.09 (ddd, J = 9.6, 8.2, 7.1 Hz, 1 H), 4.62 (dt, J = 7.1, 5.0 Hz, 1 H), 6.8 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.4, 24.8, 31.3, 31.9, 35.3, 45.4, 81.8, 174.4, 176.0 ppm. IR (KBr): $\tilde{\nu}$ = 3110, 2955, 2930, 2860, 1780, 1748, 1466, 1431, 1393, 1358, 1317, 1238, 1207, 1194, 1163, 1111, 1080, 1069, 999, 955, 854, 735, 669, 604, 571, 434 cm^{-1}. MS (EI): m/z = 32 (19), 39 (35), 41 (67), 42 (21), 43 (64), 45 (22), 53 (11), 54 (13), 55 (96), 56 (23), 57 (26), 67 (10), 69 (13), 71 (15), 72 (12), 73 (43), 81 (10), 83 (49), 84 (14), 85 (10), 98 (11), 99 (25), 100 (40), 101 (100), 102 (25), 111 (14), 116 (33), 128 (10), 129 (76), 140 (10), 154 (11), 200 (0.5) $[M]^+$, 201 (4) $[M + 1]^+$.

Supporting Information (see footnote on the first page of this article): Experimental details and spectroscopic data. UV absorption spectra of **1a**,**b**,**e**–**h** and radical initiators. Effect of degassing method. ^{1}H and ^{13}C NMR spectra of **3g**, **4a**–**f**,**h**,**i**, and **5e**,**f**.

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