Tetrahedron xxx (xxxx) xxx

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Photochemical addition of cyclic ethers/acetals to olefins using ^{t}BuOO^{t}Bu: Synthesis of masked ketones/aldehydes and diols

Mamiko Hayakawa [a], Rina Shimizu [a], Hajime Omori [a], Hisashi Shirota [a], Kou Uchida [a], Hiroshi Mashimo [a], Han Xu [a], Ryuusei Yamada [a], Seiya Niino [a], Yoshiki Wakame [a], Chuanxiang Liu [b, 1], Tadashi Aoyama [a], Akihiko Ouchi [a, *]

[a] Department of Materials and Applied Chemistry, College of Science and Technology, Nihon University, Kanda-Surugadai, Chiyoda-ku, Tokyo, 101-8308, Japan

[b] National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, 305-8565, Japan

ARTICLE INFO

Article history:
Received 5 August 2020
Received in revised form
22 August 2020
Accepted 27 August 2020
Available online xxx

Keywords:
Photochemical reaction
C–C bond formation
Radical
Ether
Acetal
Olefin

ABSTRACT

A fast photochemical C–C bond formation between cyclic ethers/acetals and olefins using di-*tert*-butyl peroxide (DTBP) was developed. This method provides easy access to 2-substituted cyclic ethers, and 2- or 4-substituted cyclic acetals. Acyl/formyl groups or diols can be obtained by the hydrolysis of the 2- or 4-substituted cyclic acetals, respectively. The reactions proceeded at room temperature and gave the expected products in good to excellent yields; efficient reactions were completed within 0.5 h at room temperature in >95% yield.

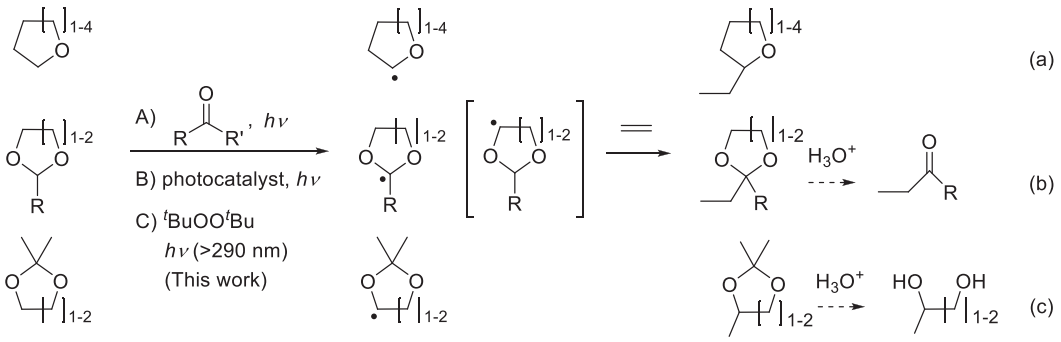
1. Introduction

C–C bond formation is one of the most important reactions in organic synthesis and has been extensively and intensively studied. In contrast to ionic reactions, radical reactions are less studied probably due to the necessity of severe conditions, such as high temperature, for the generation of radicals, which often induce undesirable side reactions. However, many functional groups that need protection under ionic reaction conditions are tolerated in radical reactions, which is a significant advantage toward the synthesis of organic compounds. Therefore, the development of simple and efficient radical reactions for the construction of new C–C bonds is still a challenge in synthetic chemistry. The addition of carbon radicals to olefins is one of the fundamental radical C–C bond forming reactions that has been widely studied [1]. In particular, the addition of cyclic ethers and acetals to C=C bonds (Scheme 1) is of synthetic importance because the introduction of side chains at the carbon next to oxygen in cyclic ethers (Scheme 1a) can be used toward the synthesis of various bioactive natural compounds [2] and acetals can be used as synthons for ketones and aldehydes (Scheme 1b), and for diols (Scheme 1c). Thus, the reactions shown in Scheme 1b and c imply that the reaction involves not only C–C bond formation but also the introduction of synthetically useful functional groups.

For the generation of carbon radicals, C-heteroatom and C–H bond cleavage reactions have been widely used, in which the latter has advantage over the former because it needs additional reactions to introduce the requisite C-heteroatom bond, which often require toxic reagents and harsh conditions [1]. Indeed, C–C bond formation using the direct activation of C–H bonds is now considered as one of the most challenging reactions. Conventional studies on the generation of carbon radicals via the abstraction of the hydrogen atom of a C–H bond can be briefly classified into three types: (i) Thermal reactions using radical initiators, (ii) photochemical reactions using ketones, and (iii) reactions using photoredox catalysts.

* Corresponding author.
E-mail address: ouchi.akihiko@nihon-u.ac.jp (A. Ouchi).
[1] Present address: Pharmaceutical Engineering Group, School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 100 Haiquan Rd, Shanghai 201418, China.

https://doi.org/10.1016/j.tet.2020.131557
0040-4020/



Scheme 1. Three different methods (A, B, and C) for the generation of radicals from cyclic ethers/acetals and their addition to olefins.

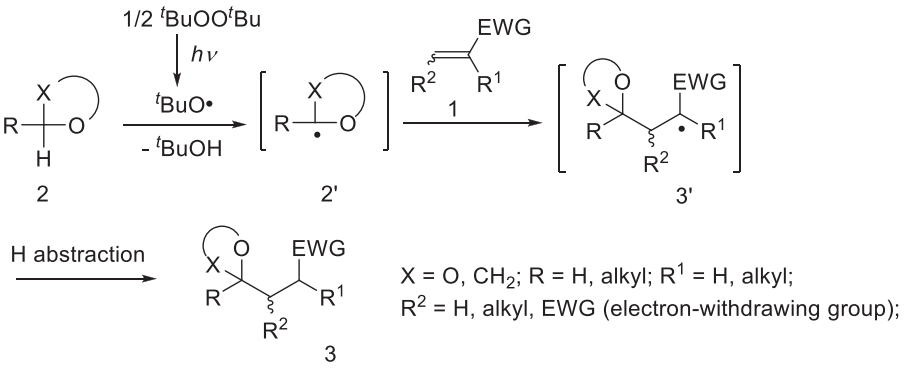
The first method (type i) has already been studied for the reactions shown in Scheme 1 using various radical initiators, mostly peroxides [3]. However, in these early studies, high temperature and long reaction times were generally used so that the yields of the desired products were generally low. Although every effort has been made toward the improvement of these thermal reactions using di-*tert*-butyl peroxide (DTBP) [4] and other peroxides [5], peracids [6], AIBN [7], and other methods [8], they still cannot avoid the disadvantages of using high temperatures and/or long reaction times.

The generation of carbon radicals via the photochemical excitation of ketones and successive abstraction of α-hydrogen of heteroatoms (type ii) has also been studied for a long time [3b,9,10]. Electronically excited ketones induce significant radical nature at their oxygen and carbon atoms, which enables the abstraction of a hydrogen atom from the C–H bond by the oxygen atom (Scheme 1, method A). This reaction has also been used for asymmetric reactions [11] and aqueous phase reactions [10o,p], as well as in additions to C=N bonds [12]. Recently, in the context of green chemistry, various photocatalysts using visible light irradiation have been studied for the generation of carbon radicals (type iii) and successive addition to olefins (Scheme 1, method B). Tetrabutylammonium decatungstate [3b,9c,13,14] uranyl cation [15], eosin Y [16], and cyclopropenium ion [17] have been used for hydrogen abstraction from ethers/acetals. Organic [18] and metal complex [19] photoredox catalysts are also used for the generation of hydrogen abstracting species via SET processes. However, type ii and iii photochemical reactions generally require prolonged irradiation times, and most of the photocatalysts are very expensive and/or not commercially available. In addition, the use of ketones, aromatic ketones in most cases, in the reaction makes the purification of products difficult in many cases.

To overcome the disadvantages of conventional radical additions to olefins, we report a photochemical reaction using >290 nm light and DTBP, a commercially available inexpensive reagent (Scheme 1, method C). This method was applied to the reactions shown in Scheme 1, which proceeded efficiently at room temperature to give the desired products in good to excellent yield over a short reaction time; efficient reactions were completed within 0.5 h at room temperature in >95% yield. Scheme 2 shows a plausible mechanism for the reaction. The reaction was initiated by the photochemical cleavage of DTBP to form *t*-BuO• radicals [20]. The resulting *t*-BuO• radicals abstract an α-hydrogen in cyclic ethers/acetals **2** [21] to generate its corresponding carbon radical (**2′**), which successively adds to olefin **1** to give the desired products **3** via radical **3′** and its H abstraction [22]. The *t*-BuOH formed during the reaction can be easily removed by evaporation. The use of >290 nm light has the advantage of avoiding any undesirable photochemical side reactions of various functional groups because this wavelength of light is not absorbed by most functional groups.

2. Results and discussion

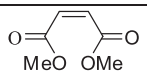
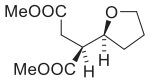
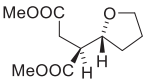
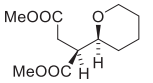
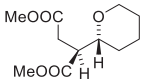
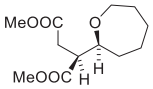
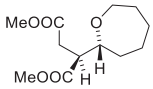
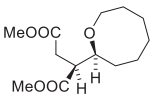
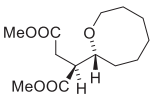
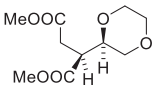
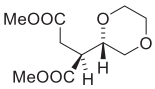
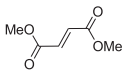
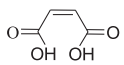
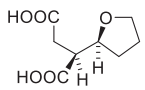
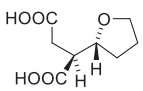
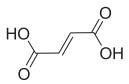
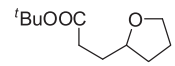
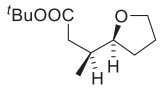
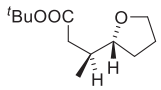
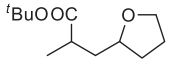
Addition of cyclic ethers to olefins. The reaction between dimethyl maleate (**1a-*cis***) and various cyclic ethers was studied, and the results are shown in Table 1. The irradiation was conducted with degassed solutions in the presence of 0.5 eq of DTBP under a nitrogen atmosphere at room temperature using >290 nm light [22]. The effect of the irradiation time was investigated using the reaction between **1a-*cis*** and THF (**2A**) (Entries 1 – 5). The reaction was completed within 0.5 h in 98% yield, which was comprised of two diastereomers **3aA-*syn*** (more polar) and **3aA-*anti*** (less polar) (*ca.* 3:2) (Entry 2). To determine the *syn* and *anti* configurations of the diastereomers, NOESY and ROESY measurements of **3aA-*syn***



Scheme 2. Plausible reaction mechanism.

Please cite this article as: M. Hayakawa et al., Photochemical addition of cyclic ethers/acetals to olefins using ^{t}BuOO^{t}Bu: Synthesis of masked ketones/aldehydes and diols, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131557

Table 1
Addition of cyclic ethers to olefins[a].

Entry	Olefin (**1**)	Ether (**2**)	Irradiation time (h)	Conversion of (**1**) (%)	Yield[b] (%)	
1	 **1a-*cis***	 **2A**	0.25	81	 **3aA-*syn*** 54	 **3aA-*anti*** 33
2			0.5	100	60 (52)	38 (30)
3			1	100	59	38
4			2	100	60	39
5			3	100	58	38
6		 **2B**	1	78	 **3aB-*syn*** 36	 **3aB-*anti*** 23
7			2	100	45 (38)	29 (22)
8			3	100	44	28
9		 **2C**	2	100	 **3aC-*syn*** 36 (29)	 **3aC-*anti*** 35 (32)
10		 **2D**	2	100	 **3aD-*syn*** 29 (27)	 **3aD-*anti*** 27 (26)
11		 **2E**	2	100	 **3aE-*syn*** 38 (31)	 **3aE-*anti*** 28 (21)
12			3	100	38	28
13	 **1a-*trans***	**2A**	0.25	92	**3aA-*syn*** 38	**3aA-*anti*** 47
14			0.5	100	45	50
15	 **1b-*cis***	**2A**	0.5	>99	 **3bA-*syn*** 45	 **3bA-*anti*** 51
16	 **1b-*trans***	**2A**	0.5	100	**3bA-*syn*** 45	**3bA-*anti*** 55
17	 **1d**	**2A**	1	100		**3dA** 41 (33)
18	 **1e**	**2A**	0.5	94	 **3eA-*syn*** 12	 **3eA-*anti*** 11
19			1	91	26, 25	(30, *syn/anti* = 1/1)[c]
20			2	99	36, 34	
21			3	100	35, 35	
22	 **1f**	**2A**	1	100		**3fA** 0

[a] Photolysis condition, substrates: olefin (0.2 mmol) and DTBP (0.1 mmol) in ether (10 mL), light source: 500-W xenon short-arc lamp fitted with an 18-cm water filter and a UV-29 cutoff filter (20 mW·cm^{-2}), N_2 atm, room temp. [b] Yields are based on the consumed starting material and determined by NMR spectroscopy. The yields are the average of two (Entries 1 – 16, 21, 22), three (Entries 18, 20), five (Entry 17), and seven (Entry 19) independent runs. The yields in parentheses are those of isolated yields. [c] Isolated as a mixture of *syn* and *anti* isomers. The *syn*/*anti* ratio was determined by NMR spectra.

Please cite this article as: M. Hayakawa et al., Photochemical addition of cyclic ethers/acetals to olefins using ^{t}BuOO^{t}Bu: Synthesis of masked ketones/aldehydes and diols, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131557

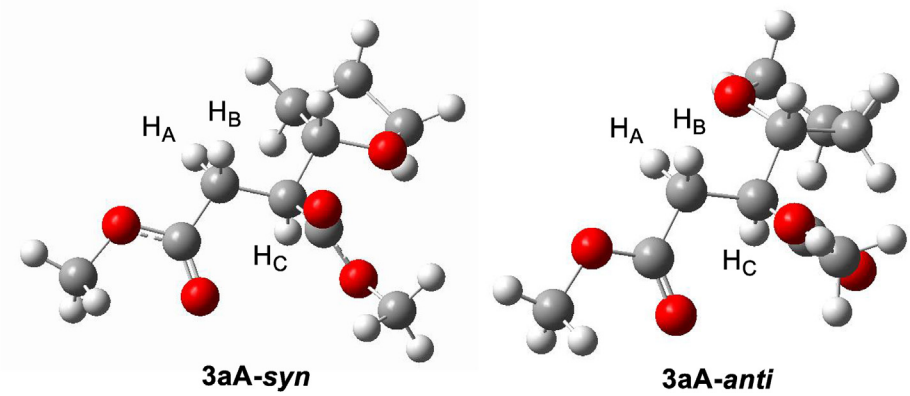
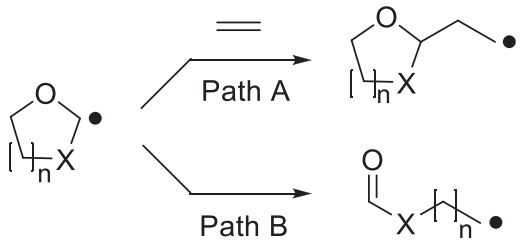


Fig. 1. The stable conformation of **3 aA-*syn*** and **-*anti*** calculated by DFT using B3LYP functional.



Scheme 3. The addition of cyclic ether radicals to olefins (Path A) and decyclization of the radical (Path B) [26, 28].

and **-*anti*** were conducted but NOE between H_C and H_A/H_B was not observed (Fig. 1). Therefore, the *syn* and *anti* configurations were *tentatively* determined upon comparison of the observed and calculated chemical shifts in ^{1}H NMR spectroscopy. The calculated chemical shift of H_A in their stable conformations showed a considerable high field shift in **3aA-*syn*** when compared with **3aA-*anti*** [23], whereas those of H_B and H_C were similar between the two diastereomers (Fig. 1). The more polar diastereomer showed a larger high field shift of H_A in the observed chemical shift [24] and was assigned as the *syn* isomer. The products, **3aA-*syn*** and **3aA-*anti***, were photochemically stable and did not decompose upon prolonged irradiation (Entries 2 – 5).

When tetrahydropyran (**2B**) was used (Entries 6 – 8), a similar reaction proceeded to give a diastereomeric mixture of **3aB-*syn*** and **3aB-*anti***, which required a longer irradiation time (2 h) and with a slight decrease in the yield. The reactions using oxepane (**2C**), oxocane (**2D**), and 1, 4-dioxane (**2E**) gave similar results to **2B** (Entries 9 – 12). The slow reaction of **2B** when compared to **2A** can be explained by (a) the slower abstraction of the α-hydrogen in **2B** by *t*-BuO• radicals compared to **2A** [21a] and/or (b) the slower addition of the 6-membered **2B** radical to the olefin compared to the 5-membered **2A** radical [25]. The decrease in the yield observed for the product obtained from **2B** when compared to that from **2A** was attributed to the competition between Path A and B in Scheme 3. Cyclic ether radicals are reported to decyclize into linear radicals (Scheme 3, Path B, X = CH_2) [26] and the slower addition of the 6-membered compared to 5-membered radicals to olefins (Scheme 3, Path A, X = CH_2) should cause a decrease in the yield of the desired addition products for 6-membered **2B**.

To confirm the absence of any dark reactions, the reactions of **1a-*cis*** and **2B**/**2C** were conducted in the dark at room temperature for 72 h; for both **2B** and **2C**, the adducts **3aB-*syn*/*anti*** and **3aC-*syn*/*anti*** were not detected. These results indicate that light irradiation is indispensable for the reactions.

The effect of various olefins was investigated using **2A**. Olefins bearing two electron-withdrawing groups, dimethyl fumarate (**1a-*trans***) (Entries 13, 14), maleic acid (**1b-*cis***) (Entry 15), and fumaric acid (**1b-*trans***) (Entry 16) showed almost the same results as **1a-*cis***. The isolation of **3bA-*syn*** and **-*anti*** was attempted using silica gel column chromatography, but it was unsuccessful due to the overlapping of the two isomers. The structure of the two isomers were confirmed by the hydrolysis of the **3aA-*syn*** and **-*anti*** isomers into their corresponding acids, **3bA-*syn*** and **-*anti***, respectively.

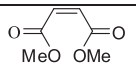
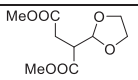
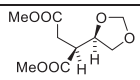
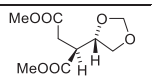
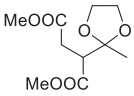
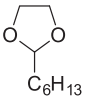
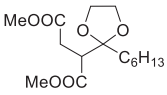
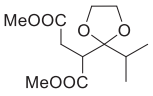
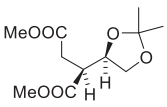
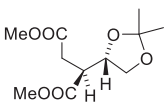
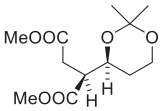
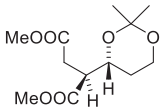
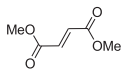
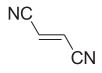
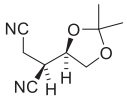
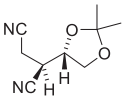
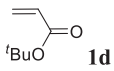
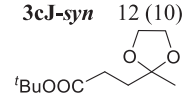
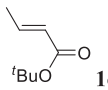
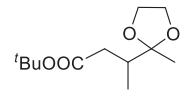
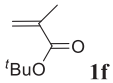
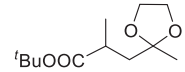
For olefins bearing a single electron-withdrawing group, the reactions of *tert*-butyl acrylate (**1d**) (Entry 17) and *tert*-butyl crotonate (**1e**) were completed within a short time and gave their corresponding products in moderate yield (Entries 18 – 21), but the expected product **3fA** was not obtained from *tert*-butyl methacrylate (**1f**) (Entry 22). TLC analysis of these reaction mixtures after the complete consumption of the olefins showed a significant amount of products at the origin, which indicates the formation of polymers and oligomers of the starting olefins [27].

Addition of cyclic acetals to olefins. The reactions of various cyclic acetals and olefins were carried out (Table 2). The reaction of 1,3-dioxolane (**2F**) and **1a-*cis*** was completed within 0.5 h with the quantitative formation of three products **3aF-*major***, **3aF-*syn***, and **3aF-*anti***, in which **3aF-*major*** was the predominant product (Entry 1). In addition, the products did not decompose upon prolonged irradiation (Entry 2). In the case of 2-methyl-1,3-dioxolane (**2G**) (Entry 3), **3aG** was obtained in an almost quantitative yield upon 0.5 h of irradiation. When the 2-methyl substituent of **2G** was changed to *n*-hexyl (**2H**) or *iso*-propyl (**2I**), the expected products **3aH** and **3aI** were obtained in good yield, but with some decrease when compared with **3aG** (Entries 4 – 6). The higher regioselectivity of **2G**–**I** at the 2-position compared to unsubstituted **2F** can be explained by the faster α-hydrogen abstraction by *t*-BuO• radicals in the presence of the 2-alkyl substituent [21a]. The steric effect of the 2-alkyl substituent has a significant effect on the yield of the products; larger substituents probably suppress the addition reaction (Scheme 3, Path A, X = O) and increase the ratio of the decyclization pathway [28] (Scheme 3, Path B, X = O).

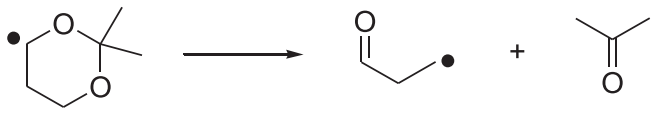
C–C bond formation between the 4-position of 1,3-dioxolane/1,3-dioxane and **1a-*cis*** was attempted by blocking the 2-position with two methyl substituents in 2,2-dimethyl-1,3-dioxolane (**2J**) (Entries 7 – 9) and 2,2-dimethyl-1,3-dioxane (**2K**) (Entries 10, 11). Similar to that observed for cyclic ethers, a longer irradiation time was required for 6-membered **2K** when compared to 5-membered **2J**. Two sets of diastereomeric products, **3aJ-*syn*** and **-*anti***, and **3aK-*syn*** and **-*anti***, were obtained from **2J** and **2K**, respectively, in moderate yield. For these acetals, the expulsion of acetone has been reported via a decyclization of their corresponding cyclic radicals

Please cite this article as: M. Hayakawa et al., Photochemical addition of cyclic ethers/acetals to olefins using ^{t}BuOO^{t}Bu: Synthesis of masked ketones/aldehydes and diols, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131557

Table 2
Addition of cyclic acetals to olefins[a].

Entry	Olefin (**1**)	Acetal (**2**)	Irradiation time (h)	Conversion of (**1**) (%)	Yield [b] (%)		
1	 **1a-*cis***	 **2F**	0.5	100	 **3aF-*major*** 87	 **3aF-*syn*** 9	 **3aF-*anti*** 4
2			1	100	88	8	4 (95) [c]
3		 **2G**	0.5	100		**3aG**	100 (95)
4		 **2H**	0.5	100		**3aH**	78 (75)
5			0.75	100			69 (70)
6		 **2I**	0.5	100		**3aI**	50 (48)
7		 **2J**	0.5	83	 **3aJ-*syn*** 16	 **3aJ-*anti*** 7	
8			0.75	100	19 (15)		8 (8)
9			1	100	10		0
10		 **2K**	2	92	 **3aK-*syn*** 18	 **3aK-*anti*** 12	
11			3	100	21 (10)		13 (4)
12	 **1a-*trans***	**2G**	0.5	100	**3aG**	91	
13	 **1c**	**2G**	0.5	100		**3cG**	71 (70)
14	**1c**	**2J**	2	100	 **3cJ-*syn*** 12 (10)	 **3cJ-*anti*** 10 (9)	
15	 **1d**	**2G**	0.5	100		**3dG**	37 (31)
16	 **1e**	**2G**	0.5	100		**3eG**	52 (47)
17	 **1f**	**2G**	0.5	100		**3fG**	0

[a] Photolysis condition, substrates: olefin (0.2 mmol) and DTBP (0.1 mmol) in acetals (10 mL), light source: 500-W xenon short-arc lamp fitted with an 18-cm water filter and a UV-29 cutoff filter (20 $mW \cdot cm^{-2}$), N_2 atm, room temp. [b] Yields are based on the consumed starting material and determined by NMR spectroscopy. The yields are the average of two (Entries 1 – 4, 6, 8, 12, 15, 17) and four (Entry 16) independent runs, and the others are of single runs. The yields in parentheses are those of isolated yields. [c] Isolated yield of the three isomers.



Scheme 4. Decyclization of 2,2-dimethyl−1,3-dioxane [28b].

(Scheme 4) [28b], which must have an effect on the yields of the desired products.

The effect of various olefins was investigated using **2G** and **2J**. The trend was similar to that observed with cyclic ethers. Dimethyl fumarate (**1a-*trans***) bearing two electron-withdrawing groups showed almost the same results to those observed for **1a-*cis*** (Entry 12). Fumaronitrile (**1c**) gave a good yield with **2G** upon 0.5 h of irradiation (Entry 13), but a moderate yield with **2J** (Entry 12). The isolation of the **3cJ-*syn*** and -***anti*** isomers using column chromatography was also unsuccessful; only some of **3cJ-*anti*** was isolated and the other isomers were obtained as a *syn* and *anti* mixture. The reactions of *tert*-butyl acrylate (**1d**) (Entry 15) and *tert*-butyl crotonate (**1e**) (Entry 16) bearing a single electron-withdrawing group with **2G** were completed within 0.5 h, but showed some decrease in the product yield. In contrast, the addition of **2G** to *tert*-butyl methacrylate (**1f**) (Entry 17) did not proceed at all though **1f** was completely consumed within 0.5 h. Similar to the results with cyclic ethers, TLC analysis of the reaction mixtures showed a significant amount of products at the origin, which was also attributed to polymers and oligomers of the starting olefins [27].

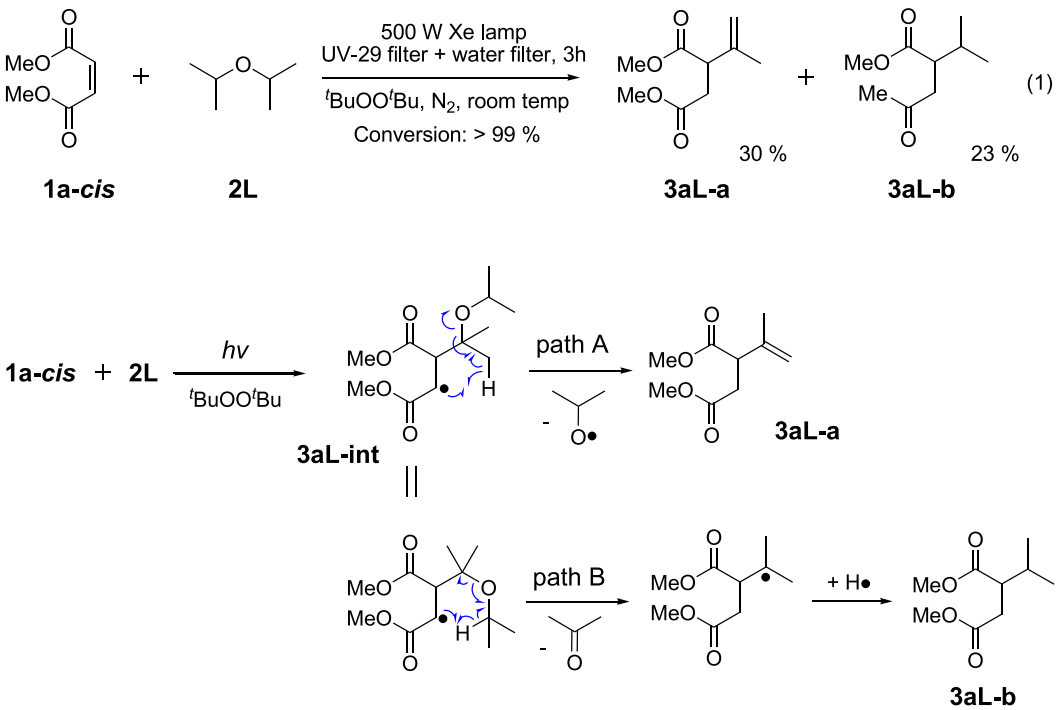
Reaction of an acyclic ether and olefin. Although some conventional photochemical C—C bond forming reactions have been reported between olefins and *cyclic* ethers and acetals, to the best of our knowledge, only one reaction has been reported with an *acyclic* ether, i.e., with ethyl *tert*-butyl ether [27], an ether that does not have hydrogen atoms at one α-carbon of the ether. Therefore, the reaction of **1a-*cis*** and diisopropyl ether (**2L**) was conducted to investigate the scope of this reaction in *acyclic* ethers. The result showed the formation of two unexpected compounds **3aL-a** and **3aL-b** (Equation (1)). The most probable pathways for the formation of these products are two types of intramolecular H abstractions of intermediate radical **3aL-int**, which are shown as paths A and B in Scheme 5. A similar intramolecular H abstraction as path A has been reported during the addition of acyclic ethers to hexafluoropropene, in which the ether radicals were generated by γ-ray irradiation [29].

3. Conclusion

A fast photochemical C—C bond forming reaction between cyclic ethers/acetals and olefins proceeds at room temperature using >290 nm light and DTBP, which gave the expected products in good to excellent yield; efficient reactions were completed within 0.5 h at room temperature in >95% yield. The acetals were used as acyl/formyl (reactions at their 2-position) and diol (reactions at their 4-position) synthons. The yields and irradiation times significantly depended on the size of the ring, in which 5-membered rings were found to be the best. The yields were also affected by the size of the 2-alkyl substituent on the cyclic acetal, which was attributed to their steric effect. The reaction with an acyclic ether, di-*iso*-propyl ether, gave two unexpected products and their plausible reaction mechanism was discussed. The reaction showed a considerable improvement to conventional carbon radical addition reactions to olefins, particularly reducing the reaction time and the use of commercially available and inexpensive DTBP.

4. Experimental section

General Remarks. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AVANCE 400 or a JEOL JNM-ECX400 spectrometer with $CDCl_3$ or acetone-d_6 as solvent. As internal standards, TMS (δ 0.0 ppm) in $CDCl_3$ or acetone-d_6 (δ



Scheme 5. Plausible reaction mechanisms for the formation of **3aL-a** and **3aL-b**.

Please cite this article as: M. Hayakawa et al., Photochemical addition of cyclic ethers/acetals to olefins using ^{t}BuOO^{t}Bu: Synthesis of masked ketones/aldehydes and diols, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131557

2.04 ppm) was used for ^{1}H NMR, and $CDCl_3$ (δ 77.0 ppm) or acetone-d_6 (δ 29.8 ppm) for ^{13}C NMR analyses. HRMS spectra were recorded on an Agilent G1969 LC/MDS TOF mass spectrometer. Olefins **1a-*cis***, **1a-*trans***, **1b-*cis***, **1b-*trans***, **1c**, ethers **2A**, **2B**, **2E**, acetals **2F**, **2G**, **2J**, and DTBP were purchased and used as bought. Olefins **1d**, **1e**, **1f**, ethers **2A**, **2B**, **2E**, and acetals **2F**, **2G**, **2J** were purchased and distilled before use. Oxepane (**2C**) [30], oxocane (**2D**) [31], 2-*n*-hexyl-1,3-dioxolane (**2H**) [10n], 2-*iso*-propyl-1,3-dioxolane (**2I**) [10n], and 2,2-dimethyl-1,3-dioxane (2**K**) [32] were synthesized according to the reported procedures.

General procedure for the photolysis. An ether or acetal (**2A**-**L**) (10 mL) solution of olefin (**1a**-**f**) (0.2 mmol) and DTBP (0.1 mmol) was introduced into a quartz cylindrical cell (diameter: 3 cm) equipped with a three-way stopcock. The three-way stopcock was connected to the cell, a nitrogen source, and small vacuum pump. The solution was evacuated to about 50 mmHg under sonication for 5s and nitrogen was then introduced into the cell; this cycle was repeated 10 times. The photolysis was conducted using a 500-W xenon lamp (USHIO Optical Modulex SX-UI500XQ) fitted with an 18-cm water filter and a cut-off filter (Toshiba UV-29) under a nitrogen atmosphere. The irradiated light intensity was 20 mW/cm^2, which was measured by an Ushio UIT-150-A Ultraviolet Radiometer equipped with a UVD-S365 photo detector. After photolysis, the ether or acetal was removed in vacuo at 40–50 °C/< 150 Torr (most of the products were volatile under reduced pressure) and the consumption of the olefin and the products yield were determined by NMR spectroscopy using a precise amount of naphthalene as an internal standard; the yields of each product were calculated based on the consumed starting material. The isolation of the products was conducted using silica gel column chromatography.

4.1. 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-dimethyl ester (3aA-syn, anti) [5d,7c,19b,33]

Dimethyl maleate (**1a-*cis***, 28.56 mg, 0.20 mmol) and DTBP (14.36 mg, 0.10 mmol) in THF (**2A**, 10 mL). Irradiation time: 0.5 h. NMR yield ($CDCl_3$), 98% (*syn*/*anti* = 60/38) (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (14/1 → 1/1).

3aA-*syn*: 22.17 mg (52%); colorless oil; ^{1}H-NMR ($CDCl_3$): δ = 1.59–1.70 (m, 1 H), 1.83–1.99 (m, 3 H), 2.48 (dd, J = 4.5, 16.6 Hz, 1 H), 2.78 (dd, J = 10.2, 16.6 Hz, 1 H), 3.09 (ddd, J = 4.5, 6.6, 10.2 Hz, 1 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 3.74 (ddd, J = 7.0, 7.0, 14.9 Hz, 1 H), 3.87 (ddd, J = 6.7, 8.3, 14.9 Hz, 1 H), 4.06 (ddd, J = 6.0, 6.0, 6.6 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 25.6, 28.6, 32.5, 46.0, 51.9, 52.0, 68.4, 78.9, 172.2, 173.3 ppm. IR (KBr disk): 2953, 2876, 1740, 1730, 1460, 1439, 1414, 1360, 1346, 1317, 1263, 1196, 1165, 1069, 1020, 1005, 926, 849 cm^{-1}. MS, *m*/*z* (relative intensity): 45 (7), 55 (41), 59 (27), 70 (14), 71 (100), 72 (13), 97 (11), 111 (30), 114 (14), 143 (55), 153 (13), 185 (20), 216 (M^+, 3), 217 (M^++1, 8).

3aA-*anti*: 12.83 mg (30%); colorless oil; ^{1}H-NMR ($CDCl_3$): δ = 1.67–1.78 (m, 1H), 1.82–1.94 (m, 2 H), 1.94–2.04 (m, 1 H), 2.70 (dd, J = 4.7, 16.7 Hz, 1 H), 2.80 (dd, J = 9.3, 16.7 Hz, 1 H), 2.92 (ddd, J = 4.7, 7.6, 9.3 Hz, 1 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 3.73 (ddd, J = 7.0, 7.0, 14.9 Hz, 1 H), 3.81 (ddd, J = 6.8, 8.3, 14.9 Hz, 1 H), 4.01 (ddd, J = 1.0, 6.9, 7.6 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 25.6, 29.6, 33.2, 46.6, 51.8, 52.0, 68.1, 78.7, 172.6, 173.3 ppm. IR (KBr disk): 2953, 2876, 1738, 1732, 1460, 1439, 1414, 1360, 1348, 1319, 1263, 1200, 1165, 1067, 1028, 1007, 968, 924, 891, 849 cm^{-1}. MS, *m*/*z* (relative intensity): 45 (3), 55 (16), 59 (13), 71 (100), 72 (5), 97 (4), 111 (10), 114 (3), 143 (15), 185 (6), 217 (M^++1, 2).

4.2. 2-(Tetrahydro-2H-pyran-2-yl)butanedioic acid 1,4-dimethyl ester (3aB-syn, anti) [19b]

Dimethyl maleate (**1a-*cis***, 28.83 mg, 0.20 mmol) and DTBP (14.81 mg, 0.10 mmol) in tetrahydropyran (**2B**, 10 mL). Irradiation time: 2 h. NMR yield ($CDCl_3$), 74% (*syn*/*anti* = 45/29) (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (14/1 → 1/1).

3aB-*syn*: 17.40 mg (38%); colorless oil; ^{1}H-NMR ($CDCl_3$): δ = 1.29–1.43 (m, 1 H), 1.43–1.61 (m, 4 H), 1.81–1.90 (m, 1 H), 2.55 (dd, J = 4.3, 16.8 Hz, 1 H), 2.78 (dd, J = 10.3, 16.8 Hz, 1 H), 3.03 (ddd, J = 4.3, 6.0, 10.3 Hz, 1 H), 3.67 (s, 3 H), 3.72 (s, 3 H), 3.41 (ddd, J = 2.6, 11.5, 11.5 Hz, 1 H), 3.52 (ddd, J = 1.9, 6.0, 10.9 Hz, 1 H), 3.98 (ddd, J = 2.0, 4.0, 11.5 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 23.3, 25.7, 28.4, 32.1, 46.9, 51.8, 51.9, 68.9, 77.7, 172.5, 173.3 ppm. IR (KBr disk): 2951, 2849, 1738, 1437, 1414, 1368, 1356, 1333, 1258, 1209, 1194, 1165, 1138, 1088, 1051, 1009, 997, 903, 891, 843 cm^{-1}. MS (*m*/*z*, relative intensity): 41 (70), 42 (20), 43 (57), 53 (25), 55 (75), 56 (39), 57 (56), 59 (51), 67 (57), 69 (40), 83 (42), 84 (20), 85 (97), 86 (35), 87 (27), 97 (20), 111 (44), 114 (47), 115 (40), 125 (83), 138 (20), 157 (100), 158 (28), 170 (22), 199 (42), 230 (M^+, 0.02).

3aB-*anti*: 10.10 mg (22%); colorless oil; ^{1}H-NMR ($CDCl_3$): δ = 1.29–1.42 (m, 1 H), 1.42–1.60 (m, 4 H), 1.78–1.91 (m, 1 H), 2.69 (dd, J = 4.8, 16.9 Hz, 1 H), 2.78 (dd, J = 9.4, 16.9 Hz, 1 H), 2.91 (ddd, J = 4.8, 6.4, 9.4 Hz, 1 H), 3.67 (s, 3 H), 3.71 (s, 3 H), 3.39 (ddd, J = 3.0, 11.3, 11.3 Hz, 1 H), 3.52 (ddd, J = 1.9, 6.4, 10.8 Hz, 1 H), 3.95 (ddd, J = 2.0, 2.0, 11.3 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 23.2, 25.7, 29.5, 32.2, 47.3, 51.7, 52.0, 68.8, 77.5, 172.9, 173.5 ppm. IR (KBr disk): 2995, 2953, 2851, 1738, 1437, 1416, 1368, 1358, 1341, 1285, 1265, 1209, 1200, 1163, 1088, 1045, 1011, 997, 899, 887, 851 cm^{-1}. MS (*m*/*z*, relative intensity): 41 (69), 42 (15), 43 (53), 44 (20), 53 (18), 55 (75), 56 (29), 57 (51), 59 (44), 67 (52), 69 (29), 83 (32), 85 (99), 86 (25), 87 (19), 111 (34), 114 (38), 115 (30), 125 (81), 157 (100), 158 (19), 170 (15), 199 (31), 230 (M^+, 0.02). HRMS: *m*/*z* calcd. for $C_{11}H_{18}O_5$: 230.1154; found: 230.1144.

4.3. 2-(2-Oxepanyl)butanedioic acid 1,4-dimethyl ester (3aC-syn, anti)

Dimethyl maleate (**1a-*cis***, 28.82 mg, 0.20 mmol) and DTBP (14.85 mg, 0.10 mmol) in oxepane (**2C**, 10 mL). Irradiation time: 2 h. NMR yield ($CDCl_3$), 67% (*syn*/*anti* = 33/34) (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (40/1 → 0/1).

3aC-*syn*: 13.95 mg (29%); colorless oil; ^{1}H-NMR ($CDCl_3$): δ = 1.40–1.81 (m, 8H), 2.52 (dd, J = 16.8, 4.4 Hz, 1H), 2.78 (dd, J = 16.8, 10.8 Hz, 1H), 3.01 (ddd, J = 10.8, 6.6, 4.4 Hz, 1H), 3.53 (ddd, J = 4.8, 6.8, 11.9 Hz, 1H), 3.67 (s, 3H), 3.64–3.71 (m, 1H), 3.72 (s, 3H), 3.85 (ddd, J = 4.8, 6.6, 11.9 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 26.1, 26.3, 30.6, 32.7, 32.8, 47.6, 51.8, 51.9, 69.5, 79.4, 172.5, 173.5 ppm. IR (KBr disk): 3633, 3562, 3459, 2932, 2857, 1738, 1437, 1414, 1362, 1334, 1262, 1198, 1168, 1118, 1003, 971, 900, 873, 846, 686, 591, 534, 488, 405 cm^{-1}. MS, *m*/*z* (relative intensity): 41 (44), 42 (42), 43 (33), 55 (100), 57 (14), 59 (26), 69 (11), 71 (11), 81 (65), 83 (15), 87 (10), 99 (80), 114 (23), 115 (39), 139 (29), 171 (30). HRMS: *m*/*z* calcd. for $C_{12}H_{20}O_5$ + Na: 267.1208; found: 267.12028.

3aC-*anti*: 15.76 mg (32%); colorless oil; ^{1}H-NMR ($CDCl_3$): δ = 1.40–1.80 (m, 8H), 2.71 (dd, J = 5.6, 16.8 Hz, 1H), 2.77 (dd, J = 8.4, 16.8 Hz, 1H), 2.92 (ddd, J = 5.6, 7.2, 8.4 Hz, 1H), 3.50 (ddd, J = 6.2, 6.8, 10.4 Hz, 1H), 3.68 (s, 3H), 3.71 (s, 3H), 3.65–3.74 (m, 1H), 3.80 (ddd, J = 7.2, 7.2, 10.4 Hz, 1H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 26.16, 26.24, 30.7, 32.7, 33.7, 47.8, 51.8, 52.0, 69.0, 79.1, 172.9, 173.8 ppm. IR (KBr disk): 2932, 2857, 1738, 1437, 1367, 1343, 1261, 1200, 1163, 1114, 1027, 1003, 971, 850, 537, 474, 411 cm^{-1}. MS, *m*/*z* (relative intensity): 41 (48), 42 (42), 43 (35), 55 (100), 57 (14), 59 (27), 69 (12), 71 (12), 81 (69), 83 (16), 87 (11), 99 (83), 114 (24), 115 (41), 139 (28), 171 (32). HRMS: *m*/*z* calcd. for $C_{12}H_{20}O_5$ + Na: 267.1208; found: 267.1209.

Please cite this article as: M. Hayakawa et al., Photochemical addition of cyclic ethers/acetals to olefins using ^{t}BuOO^{t}Bu: Synthesis of masked ketones/aldehydes and diols, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131557

4.4. 2-(2-Oxocanyl)butanedioic acid 1,4-dimethyl ester (3aD-syn, anti)

Dimethyl maleate (**1a-*cis***, 29.00 mg, 0.20 mmol) and DTBP (14.70 mg, 0.10 mmol) in oxocane (**2D**, 10 mL). Irradiation time: 2 h. NMR yield ($CDCl_3$), 56% (*syn*/*anti* = 29/27) (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (40/1 → 0/1).

3aD-*syn*: 14.03 mg (27%); colorless oil; ^{1}H-NMR ($CDCl_3$): δ = 1.38–1.83 (m, 10 H), 2.51 (dd, J = 4.4, 16.8 Hz, 1 H), 2.75 (dd, J = 10.6, 16.8 Hz, 1 H), 2.99 (ddd, J = 4.4, 6.4, 10.6 Hz, 1 H), 3.51 (ddd, J = 3.4, 6.2, 12.0 Hz, 1 H), 3.67 (s, 3 H), 3.62–3.75 (m, 1 H), 3.72 (s, 3 H), 3.83 (ddd, J = 3.4, 8.4, 12.0 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 24.6, 26.5, 26.9, 27.7, 32.0, 32.4, 47.8, 51.8, 51.9, 71.5, 78.8, 172.6, 173.7 ppm. IR (KBr disk): 2925, 2853, 1738, 1437, 1362, 1332, 1261, 1196, 1165, 1098, 1012, 971, 894, 848, 800, 564, 440 cm^{-1}. MS, *m*/*z* (relative intensity): 41 (100), 42 (24), 43 (48), 44 (10), 45 (21), 53 (13), 54 (10), 55 (65), 56 (22), 57 (19), 59 (30), 67 (23), 68 (11), 69 (39), 71 (16), 79 (11), 83 (15), 95 (66), 113 (51), 114 (20), 115 (37), 143 (11), 260 (M^++1 0.04). HRMS: *m*/*z* calcd. for $C_{13}H_{22}O_5$: 259.1545; found: 259.1563.

3aD-*anti*: 13.51 mg (26%); colorless oil; ^{1}H-NMR ($CDCl_3$): δ = 1.38–1.85 (m, 10 H), 2.68 (dd, J = 4.8, 16.4 Hz, 1 H), 2.77 (dd, J = 9.6, 16.4 Hz, 1 H), 2.87 (ddd, J = 4.8, 6.4, 9.6 Hz, 1 H), 3.46 (ddd, J = 3.4, 6.8, 12.0 Hz, 1 H), 3.67 (s, 3 H), 3.68–3.75 (m, 1 H), 3.71 (s, 3 H), 3.83 (ddd, J = 3.2, 8.0, 12.0 Hz, 1 H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 24.6, 26.4, 26.9, 28.0, 32.5, 33.1, 48.3, 51.8, 51.9, 71.6, 79.1, 172.9, 174.0 ppm. IR (KBr disk): 2959, 2923, 2852, 1731, 1455, 1260, 1096, 1020, 799 cm^{-1}. MS, *m*/*z* (relative intensity): 41 (100), 42 (25), 43 (48), 45 (21), 53 (12), 54 (10), 55 (69), 56 (26), 57 (18), 59 (30), 67 (21), 68 (10), 69 (38), 71 (16), 79 (11), 83 (17), 87 (10), 95 (66), 113 (51), 114 (20), 115 (43), 142 (10), 143 (14), 259 (M^+, 0.07). HRMS: *m*/*z* calcd. for $C_{13}H_{22}O_5$: 259.1545; found: 259.1534.

4.5. 2-(1, 4-Dioxan-2-yl)butanedioic acid dimethyl ester (3aE-syn, anti) [14b,19b,34]

Dimethyl maleate (**1a-*cis***, 28.60 mg, 0.20 mmol) and DTBP (14.54 mg, 0.10 mmol) in 1,4-dioxane (**2E**, 10 mL). Irradiation time: 2 h. NMR yield ($CDCl_3$), 66% (*syn*/*anti* = 38/28) (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (14/1 → 1/1).

3aE-*syn*: 14.24 mg (31%); colorless oil; ^{1}H-NMR ($CDCl_3$): δ = 2.53 (dd, J = 4.6, 16.9 Hz, 1 H), 2.84 (dd, J = 10.0, 16.9 Hz, 1 H), 3.03 (ddd, J = 4.6, 5.4, 10.0 Hz, 1 H), 3.46 (dd, J = 10.1, 11.5 Hz, 1 H), 3.57 (ddd, J = 2.9, 11.5, 11.5 Hz, 1 H), 3.66–3.72 (m, 2H), 3.68 (s, 3 H), 3.74 (s, 3 H), 3.73–3.83 (m, 3H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 32.3, 43.5, 52.0, 52.2, 66.3, 67.2, 68.7, 75.3, 172.0, 172.3 ppm. IR (KBr disk): 2957, 2914, 2859, 1738, 1439, 1414, 1366, 1337, 1302, 1277, 1258, 1234, 1200, 1169, 1119, 1043, 1005, 970, 941, 920, 905, 880, 849, 619 cm^{-1}. MS, *m*/*z* (relative intensity): 41 (52), 42 (26), 43 (65), 44 (30), 45 (49), 53 (21), 55 (83), 58 (26), 59 (75), 69 (22), 71 (28), 83 (30), 86 (50), 87 (100), 96 (46), 97 (61), 99 (26), 113 (26), 114 (90), 115 (61), 125 (29), 129(70), 146 (36), 157 (67), 172 (87), 200 (52), 201 (37), 232 (M^+, 0.1).

3aE-*anti*: 9.79 mg (21%); colorless oil; ^{1}H-NMR ($CDCl_3$): δ = 2.71 (dd, J = 4.7, 17.0 Hz, 1 H), 2.80 (dd, J = 9.2, 17.0 Hz, 1 H), 2.93 (ddd, J = 4.7, 7.1, 9.2 Hz, 1 H), 3.39 (dd, J = 10.3, 11.9 Hz, 1 H), 3.57 (ddd, J = 2.9, 11.7, 11.7 Hz, 1 H), 3.66–3.71 (m, 2H), 3.68 (s, 3 H), 3.72 (s, 3 H), 3.74–3.81 (m, 3H) ppm. ^{13}C-NMR ($CDCl_3$): δ = 31.9, 43.6, 51.9, 52.3, 66.3, 67.0, 69.5, 74.6, 172.47, 172.52 ppm. IR (KBr disk): 2957, 2914, 2857, 1738, 1439, 1416, 1364, 1344, 1300, 1277, 1258, 1198, 1167, 1119, 1063, 1026, 1009, 957, 916, 905, 878, 847, 617 cm^{-1}. MS, *m*/*z* (relative intensity): 41 (44), 42 (21), 43 (60), 44 (30), 45 (39), 55 (84), 59 (72), 71 (22), 83 (23), 86 (39), 87 (100), 96 (36), 97 (52), 114 (90), 115 (52), 125 (37), 129(60), 146 (24), 157 (54), 172 (84), 200 (48), 201 (32), 232 (M^+, 0.1).

4.6. 2-(Tetrahydro-2-furanyl)butanedioic acid 1,4-dimethyl ester (3aA-syn, anti) [5d,7c,19b,33]

Dimethyl fumarate (**1a-*trans***, 28.86 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in THF (**2A**, 10 mL). Irradiation time: 0.5 h. NMR yield ($CDCl_3$), 95% (*syn*/*anti* = 45/50) (conversion: 100%).

4.7. 2-(2-Tetrahydro-2-furanyl)butanedioic acid (3bA-syn, anti) [33a,35]

Maleic acid (**1b-*cis***, 23.20 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in THF (**2A**, 10 mL). Irradiation time: 0.5 h. NMR yield (acetone-d_6), 96% (*syn*/*anti* = 45/51) (conversion: 99.9%).

4.8. 2-(2-Tetrahydro-2-furanyl)butanedioic acid (3bA-syn, anti) [33a,35]

Fumaric acid (**1b-*trans***, 23.11 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in THF (**2A**, 10 mL). Irradiation time: 0.5 h. NMR yield (acetone-d_6), 100% (*syn*/*anti* = 45/55) (conversion: 100%).

4.9. Tetrahydro-2-furan propanoic acid tert-butyl ester (3dA)

tert-Butyl acrylate (**1d**, 25.60 mg, 0.20 mmol) and DTBP (14.67 mg, 0.10 mmol) in THF (**2A**, 10 mL). Irradiation time: 1 h. NMR yield ($CDCl_3$), 40% (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (80/1 → 0/1).

3dA: 13.23 mg (33%); colorless oil; ^{1}H-NMR (δ, $CDCl_3$): 1.44 (s, 9 H), 1.39–1.52 (m, 1 H), 1.79 (ddd, J = 6.4, 7.6, 7.6 Hz, 2 H), 1.82–1.93 (m, 2 H), 1.93–2.03 (m, 1 H), 2.28 (dt, J = 7.6, 15.2 Hz, 1 H), 2.36 (dt, J = 7.6, 15.2 Hz, 1 H), 3.72 (ddd, J = 6.4, 7.9, 7.9 Hz, 1 H), 3.78–3.88 (m, 2 H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 25.7, 28.1, 30.8, 31.1, 32.4, 67.6, 78.3, 80.1, 172.9 ppm. IR (KBr disk): 2974, 2870, 1726, 1457, 1391, 1365, 1256, 1148, 1113, 1070, 1020, 958, 917, 849, 756, 462, 431 cm^{-1}. MS (*m*/*z*, relative intensity): 41 (42), 42 (11), 43 (35), 44 (4), 55 (12), 56 (10), 57 (55), 70 (4), 71 (100), 72 (4), 73 (8), 81 (7), 84 (7), 85 (23), 97 (10), 98 (6), 101 (4), 116 (15), 125 (7), 127 (38), 143 (6), 144 (9), 145 (9). HRMS: *m*/*z* calcd. for $C_{11}H_{20}O_3$: 201.1472; found: 201.1490.

4.10. Tetrahydro-β-methyl-2-furanpropanoic acid tert-butyl ester (3eA-syn, anti)

tert-Butyl crotonate (**1e**, 28.37 mg, 0.20 mmol) and DTBP (14.57 mg, 0.10 mmol) in THF (**2A**, 10 mL). Irradiation time: 1 h. NMR yield ($CDCl_3$), 48% (*syn*/*anti* = 24/24) (conversion: 93%). Eluent for chromatography: hexane/ethyl acetate (80/1 → 0/1). **3eA-*syn*** + **3eA-*anti***: 10.60 mg (30%; *syn*/*anti* = 1/1); colorless oil. The obtained two products were further separated by column chromatography: hexane/ethyl acetate (80/1 → 20/1). Only a part of **3eA-*anti*** was isolated by the second chromatographic separations and the rest of **3eA-*anti*** and **3eA-*syn*** were obtained as a mixture.

3eA-*anti*: ^{1}H-NMR (δ, $CDCl_3$): 0.91 (d, J = 6.4 Hz, 3 H), 1.45 (s, 9 H), 1.46–1.64 (m, 1 H), 1.80–1.96 (m, 3 H), 1.95–2.08 (m, 1 H), 2.00 (dd, J = 8.8, 10.0 Hz, 1 H), 2.52 (dd, J = 8.8, 10.0 Hz, 1 H), 3.56 (ddd, J = 7.1, 7.1, 7.1 Hz, 1 H), 3.72 (ddd, J = 6.1, 7.7, 8.4 Hz, 1 H), 3.81 (ddd, J = 6.8, 6.8, 8.4 Hz, 1 H) ppm.

3eA-*syn* + **3eA-*anti***: ^{1}H-NMR (δ, $CDCl_3$): 0.99 (d, J = 6.4 Hz, 3 H), 1.45 (s, 9 H), 1.78–2.06 (m, 5 H), 2.06–2.18 (m, 1 H), 2.33 (dd, J = 4.8, 14.4 Hz, 1 H), 3.64–3.76 (m, 2 H), 3.79–3.87 (m, 1 H) ppm.

Please cite this article as: M. Hayakawa et al., Photochemical addition of cyclic ethers/acetals to olefins using ^{t}BuOO^{t}Bu: Synthesis of masked ketones/aldehydes and diols, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131557

4.11. 2-(1,3-dioxolan-4-yl)butanedioic acid 1,4-dimethyl ester (3aF-syn, anti) [19b] and 2-(1,3-dioxolan-2-yl)butanedioic acid 1,4-dimethyl ester (3aF-major) [5d,h,19b,36]

Dimethyl maleate (**1a-*cis***, 28.99 mg, 0.20 mmol) and DTBP (14.63 mg, 0.10 mmol) in 1,3-dioxolane (**2F**, 10 mL). Irradiation time: 1 h. NMR yield ($CDCl_3$), 100% (*syn*/*anti*/major = 8/4/88) (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (14/1 → 2/1). **3aF-*major*** + **3aF-*syn*** + **3aF-*anti***: 41.64 mg (95%). The obtained three products were further separated by column chromatography: hexane/ethyl acetate (8/1 → 1/1). Only a part of **3aF-*major*** was isolated by the second chromatographic separations and **3aF-*syn*** and −***anti***, and the rest of **3aF-*major*** were obtained as a mixture.

3aF-*major*: 19.77 mg (45%); colorless oil; ^{1}H-NMR (δ, $CDCl_3$): 2.63 (dd, J = 4.8, 16.9 Hz, 1 H), 2.81 (dd, J = 9.2, 16.9 Hz, 1 H), 3.25 (ddd, J = 4.2, 4.8, 9.2 Hz, 1 H), 3.69 (s, 3 H), 3.75 (s, 3H), 3.85−3.92 (m, 2H), 3.92−4.02 (m, 2H), 5.20 (d, J = 4.2 Hz, 1H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 30.0, 45.6, 51.8, 52.2, 65.3, 102.7, 171.3, 172.3 ppm. IR (KBr disk): 2994, 2955, 2893, 1738, 1439, 1395, 1364, 1327, 1267, 1227, 1194, 1165, 1148, 1105, 1036, 999, 984, 945, 897, 853, 756, 667, 554, 480 cm^{-1}. MS (*m*/*z*, relative intensity): 40 (14), 41 (28), 42 (28), 43 (41), 44 (29), 45 (67), 46 (13), 53 (11), 54 (10), 55 (48), 56 (10), 59 (38), 69 (11), 71 (13), 73 (100), 74 (32), 75 (11), 83 (14), 87 (26), 99 (31), 103 (18), 113 (37), 114 (18), 115 (18), 127 (10), 145 (27), 157 (11), 187 (21), 219 (0.14, M^+).

3aF-*major* + **3aF-*syn*** +**3aF-*anti*:** 19.77 mg (45%, *major*/*syn*/*anti* = 71/10/19); colorless oil

3aF-*syn*: ^{1}H-NMR (δ, $CDCl_3$): 2.52 (dd, J = 4.8, 16.8 Hz, 1 H), 2.65 (dd, J = 4.3, 16.8 Hz, 1 H), 3.17−3.22 (m, 1H), 3.69 (s, 3H), 3.74 (s, 3H), 3.8−3.84 (m, 1H), 3.87−4.02 (m, 1H), 4.27−4.32 (m, 1H), 4.81 (s, 1H), 5.05 (s, 1H).

3aF-*major* + **3aF-*syn*** +**3aF-*anti***: MS (*m*/*z*, relative intensity): 40 (13), 41 (30), 42 (19), 43 (59), 44 (96), 45 (100), 55 (39), 59 (31), 71 (10), 73 (45), 87 (12), 97 (20), 99 (15), 113 (24), 114 (34), 125 (16), 129 (10), 146 (10), 156 (19), 219 (0.07, M^+).

Pure **3aF-*anti*** was isolated from other experiment.

3aF-*anti*: ^{1}H-NMR (δ, $CDCl_3$): 2.76 (dd, J = 5.0, 16.9 Hz, 1 H), 2.85 (dd, J = 7.8, 16.9 Hz, 1 H), 2.98 (ddd, J = 5.0, 7.8, 8.2 Hz, 1 H), 3.69 (s, 3H), 3.72 (s, 3H), 3.79 (dd, J = 5.5, 8.7 Hz, 1 H), 4.03 (dd, J = 6.4, 8.7 Hz, 1 H), 4.25 (ddd, J = 5.5, 6.4, 8.2 Hz, 1 H), 4.83 (s, 1H), 5.00 (s, 1H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 32.5, 45.0, 51.9, 52.3, 69.0, 74.8, 95.1, 172.2, 172.3 ppm. IR (KBr disk): 2999, 2955, 2876, 2860, 1738, 1730, 1462, 1438, 1414, 1368, 1265, 1202, 1167, 1088, 1024, 941, 851, 735 cm^{-1}. MS (*m*/*z*, relative intensity): 45 (100), 55 (43), 59 (41), 69 (13), 71 (14), 73 (61), 87 (18), 97 (20), 99 (16), 113 (32), 114 (31), 125 (18), 128 (11), 129(14), 145 (11), 146 (15), 156 (32), 187 (13), 219 (0.6, M^+).

4.12. 2-(2-Methyl-1, 3-dioxolan-2-yl)butanedioic acid 1,4-dimethyl ester (3aG) [5h,37]

Dimethyl maleate (**1a-*cis***, 28.56 mg, 0.20 mmol) and DTBP (14.51 mg, 0.10 mmol) in 2-methyl-1,3-dioxolane (**2G**, 10 mL). Irradiation time: 0.5 h. NMR yield ($CDCl_3$), 97% (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (14/1 → 2/1).

3aG: 43.72 mg (95%); colorless oil. ^{1}H-NMR (δ, $CDCl_3$): 1.39 (s, 3H), 2.65 (dd, J = 4.4, 16.9 Hz, 1 H), 2.85 (dd, J = 10.4, 16.9 Hz, 1 H), 3.19 (dd, J = 4.4, 10.4 Hz, 1 H), 3.67 (s, 3 H), 3.74 (s, 3 H), 3.91−4.05 (m, 4 H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 22.0, 32.4, 49.6, 51.8, 52.1, 64.85, 64.90, 108.7, 172.1, 172.5 ppm. IR (KBr): 2992, 2955, 2893, 2851, 1740, 1437, 1416, 1383, 1352, 1294, 1271, 1211, 1165, 1093, 1043, 1009, 951, 880, 853, 818, 766, 694, 650, 559, 513, 405 cm^{-1}. MS (*m*/*z*, relative intensity): 41 (17), 42 (12), 43 (81), 44 (23), 45 (29), 53 (18), 54 (8), 55 (43), 59 (35), 69 (9), 81 (6), 83 (12), 85 (16), 87 (100), 88 (44), 89 (11), 97 (13), 99 (22), 103 (15), 110 (5), 111 (12), 113 (23), 114 (7), 129 (23), 142 (5), 143 (10), 157 (56), 158 (11), 170 (15), 185 (39), 217 (5), 233 (M^++1, 0.08).

4.13. 2-(2-Hexyl-1, 3-dioxolan-2-yl)butanedioic acid 1,4-dimethyl ester (3aH)

Dimethyl maleate (**1a-*cis***, 28.91 mg, 0.20 mmol) and DTBP (14.77 mg, 0.10 mmol) in 2-hexyl-1,3-dioxolane (**2H**, 10 mL). Irradiation time: 0.5 h. NMR yield ($CDCl_3$), 77% (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (20/1 → 0/1).

3aH: 45.75 mg (75%); colorless oil. ^{1}H-NMR (δ, $CDCl_3$): 0.88 (t, J = 6.9 Hz, 3H), 1.18−1.49 (m, 8H), 1.58−1.77 (m, 2H), 2.61 (dd, J = 4.6, 16.9 Hz, 1H), 2.86 (dd, J = 10.5, 16.9 Hz, 1H), 3.25 (dd, J = 4.6, 10.5 Hz, 1H), 3.67 (s, 3H), 3.74 (s, 3H) 3.90−4.07 (m, 4H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 14.0, 22.5, 22.7, 29.3, 31.7, 32.2, 35.4, 48.6, 51.8, 52.1, 65.4, 65.5, 110.4, 172.3, 172.7 ppm. IR (KBr): 2954, 2932, 2872, 2858, 1741, 1459, 1438, 1415, 1350, 1301, 1266, 1206, 1166, 1096, 1039, 1004, 950, 898, 870, 852, 822, 775, 730, 569, 422 cm^{-1}. MS (*m*/*z*, relative intensity): 55 (23), 99 (16), 113 (10), 157 (100), 185 (24), 217 (7), 303 (0.05, M^++1). HRMS: *m*/*z* calcd. for $C_{15}H_{26}O_6$ + Na: 325.1627; found: 325.1642.

4.14. 2-(2-Isopropyl-1, 3-dioxolan-2-yl)butanedioic acid 1,4-dimethyl ester (3aI)

Dimethyl maleate (**1a-*cis***, 28.83 mg, 0.20 mmol) and DTBP (14.95 mg, 0.10 mmol) in 2-isopropyl-1,3-dioxolane (**2I**, 10 mL). Irradiation time: 0.5 h. NMR yield ($CDCl_3$), 52% (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (10/1 → 0/1).

3aI: 25.09 mg (48%); colorless oil. ^{1}H-NMR (δ, $CDCl_3$): 0.94 (d, J = 6.9, 3H), 0.99 (d, J = 6.4, 3H), 2.05 (dq, J = 6.4, 6.9 Hz, 1H), 2.58 (dd, J = 4.1, 17.1 Hz, 1H), 2.90 (dd, J = 10.6, 17.1 Hz, 1H), 3.42 (dd, J = 4.1, 10.6 Hz, 1H), 3.67 (s, 3H) 3.73 (s, 3H), 3.94−4.09 (m, 4H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 16.9, 17.1, 32.2, 35.9, 47.8, 51.8, 52.1, 66.4, 66.6, 112.7, 172.6, 172.7 ppm. IR (KBr): 3636, 3552, 3458, 2954, 2898, 2850, 1739, 1471, 1437, 1415, 1384, 1359, 1266, 1207, 1161, 1087, 1033, 991, 956, 900, 881, 848, 762, 686, 597, 570, 502, 469, 444 cm^{-1}. MS (*m*/*z*, relative intensity): 43 (81), 55 (28), 71 (15), 99 (14), 115 (100), 185 (25), 259 (0.17, M^+). HRMS: *m*/*z* calcd. for $C_{12}H_{20}O_6$ + H: 261.1338; found: 261.1333.

4.15. 2-(2, 2-Dimethyl-1, 3-dioxolan-4-yl)butanedioic acid 1,4-dimethyl ester (3aJ-syn, anti)

Dimethyl maleate (**1a-*cis***, 28.69 mg, 0.20 mmol) and DTBP (14.77 mg, 0.10 mmol) in 2, 2-dimethyl-1, 3-dioxolane (**2J**, 10 mL). Irradiation time: 0.75 h. NMR yield ($CDCl_3$), 26% (*syn*/*anti* = 18/8) (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (20/1 → 0/1).

3aJ-*syn*: 7.30 mg (15%); colorless oil; ^{1}H-NMR (δ, $CDCl_3$): 1.33 (s, 3H), 1.41 (s, 3H), 2.52 (dd, J = 4.4, 16.8 Hz, 1H), 2.79 (dd, J = 9.8, 16.8 Hz, 1H), 3.20 (ddd, J = 4.4, 5.8, 9.8 Hz, 1H), 3.69 (s, 3H), 3.73 (s, 3H) 3.80 (dd, J = 6.0, 8.8 Hz, 1H), 4.01 (dd, J = 6.4, 8.8 Hz, 1H), 4.36 (ddd, J = 5.8, 6.0, 6.4 Hz, 1H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 24.9, 26.2, 31.8, 44.2, 52.0, 52.2, 66.3, 75.1, 109.5, 172.1, 172.5 ppm. IR (KBr disk): 3855, 3630, 3457, 2988, 2954, 2359, 1737, 1438, 1372, 1257, 1210, 1164, 1063, 1007, 915, 853, 797, 642, 595, 548, 457, 431, 416 cm^{-1}. MS (*m*/*z*, relative intensity): 43 (100), 55 (11), 59 (18), 72 (17), 97 (15), 101 (13), 129 (11), 157 (33), 171 (22), 231 (13), 245 (0.2, M^+ − H). HRMS: *m*/*z* calcd. for $C_{11}H_{18}O_6$: 246.1103; found: 246.1118.

3aJ-*anti*: 3.67 mg (8%); colorless oil; ^{1}H-NMR (δ, $CDCl_3$): 1.33 (s, 3H), 1.40 (s, 3H), 2.74 (dd, J = 4.4, 17.0 Hz, 1H), 2.83 (dd, J = 8.2, 17.0 Hz, 1H), 2.97 (ddd, J = 4.4, 8.2, 8.2 Hz, 1H), 3.69 (s, 3H), 3.72 (s, 3H), 3.82 (dd, J = 6.0, 8.8 Hz, 1H), 4.12 (dd, J = 6.4, 8.8 Hz, 1H), 4.28

Please cite this article as: M. Hayakawa et al., Photochemical addition of cyclic ethers/acetals to olefins using ^{t}BuOO^{t}Bu: Synthesis of masked ketones/aldehydes and diols, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131557

(ddd, J = 6.0, 6.4, 8.2 Hz, 1H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 25.2, 26.5, 32.5, 45.4, 51.8, 52.2, 66.2, 75.0, 109.4, 172.4, 172.5 ppm. IR (KBr disk): 3630, 3461, 2988, 2954, 1738, 1439, 1414, 1372, 1258, 1211, 1167, 1064, 1007, 916, 854, 795, 758, 681, 644, 514, 430 cm^{-1}. MS (m/z, relative intensity): 43 (100), 55 (12), 59 (20), 72 (18), 97 (15), 101 (13), 111 (10), 129 (16), 157 (11), 171 (39), 246 (0.14, M^+). HRMS: m/z calcd. for $C_{11}H_{18}O_6$: 246.1103; found: 246.1080.

4.16. 2-(2, 2-Dimethyi-1, 3-dioxan-4-yl)butanedioic acid 1,4-dimethyl ester (3aK-syn, anti)

Dimethyl maleate (**1a-*cis***, 28.61 mg, 0.20 mmol) and DTBP (14.93 mg, 0.10 mmol) in 2, 2-dimethyl-1,3-dioxane (**2K**, 10 mL). Irradiation time: 3 h. NMR yield ($CDCl_3$), 34% (*syn*/*anti* = 21/13) (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (20/1 → 0/1).

3aK-*syn*: 4.91 mg (10%); colorless oil; ^{1}H-NMR (δ, $CDCl_3$): 1.2−1.48 (m, 1 H), 1.35 (s, 3 H), 1.44 (s, 3 H), 1.70 (dddd, J = 5.6, 12.0, 12.4, 12.4 Hz, 1 H), 2.60 (dd, J = 4.8, 17.2 Hz, 1 H), 2.75 (dd, J = 10.0, 17.2 Hz, 1 H), 3.08 (ddd, J = 4.8, 5.6, 10.0 Hz, 1 H), 3.68 (s, 3 H), 3.72 (s, 3 H), 3.84 (ddd, J = 2.0, 5.6, 12.0 Hz, 1 H), 3.94 (ddd, J = 2.8, 12.0, 12.0 Hz, 1 H), 4.20 (ddd, J = 2.4, 5.6, 12.0 Hz, 1 H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 19.1, 27.2, 29.7, 31.1, 46.4, 51.8, 52.0, 59.6, 68.8, 98.7, 172.5, 172.6 ppm. IR (KBr disk): 2992, 2949, 2925, 2854, 1737, 1464, 1438, 1371, 1328, 1270, 1244, 1225, 1197, 1162, 1120, 1101, 1050, 1002, 970, 862, 847, 767, 524 cm^{-1}. MS (m/z, relative intensity): 41 (17), 43 (100), 55 (26), 57 (27), 58 (20), 59 (52), 67 (13), 71 (21), 93 (14), 115 (14), 125 (10), 139 (16), 153 (43), 171 (26), 245 (23), 260 (0.62, M^+). HRMS: m/z calcd. for $C_{12}H_{20}O_6$ + H: 261.1338; found: 261.1344.

3aK-*anti*: 2.03 mg (4%); colorless oil; ^{1}H-NMR (δ, $CDCl_3$): 1.34 (s, 3 H), 1.37−1.46 (m, 1 H), 1.42 (s, 3 H), 1.69 (dddd, J = 5.2, 11.6, 12.4, 12.4 Hz, 1 H), 2.73 (d, J = 7.2 Hz, 2 H), 2.90 (dt, J = 7.2, 7.2 Hz, 1 H), 3.67 (s, 3 H), 3.72 (s, 3 H), 3.83 (ddd, J = 1.6, 5.2, 12.0 Hz, 1 H), 3.94 (ddd, J = 3.0, 12.0, 12.4 Hz, 1 H), 4.08 (ddd, J = 2.8, 7.2, 11.6 Hz, 1 H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 19.1, 29.3, 29.7, 32.1, 47.3, 51.8, 52.0, 59.6, 69.0, 98.7, 172.7, 173.1 ppm. IR (KBr disk): 2993, 2953, 2925, 2871, 1737, 1438, 1381, 1338, 1267, 1245, 1199, 1165, 1131, 1092, 1049, 1025, 1009, 969, 843 cm^{-1}. MS (m/z, relative intensity): 41 (18), 43 (100), 44 (24), 55 (27), 57 (29), 58 (19), 59 (57), 67 (12), 71 (22), 73 (11), 93 (14), 115 (14), 125 (12), 139 (17), 153 (47), 171 (29), 245 (25). HRMS: m/z calcd. for $C_{12}H_{20}O_6$ + H: 261.1338; found: 261.1311.

4.17. 2-(2-Methyl-1, 3-dioxolan-2-yl)butanedinitrile (3cG)

Fumaronitrile (**1c-*cis***, 15.62 mg, 0.20 mmol) and DTBP (14.77 mg, 0.10 mmol) in 2-methyl-1,3-dioxolane (**2G**, 10 mL). Irradiation time: 0.5 h. NMR yield ($CDCl_3$), 71% (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (80/1 → 0/1).

3cG: 23.40 mg (70%); colorless oil. ^{1}H-NMR (δ, $CDCl_3$): 1.51 (s, 3H), 2.79 (dd, J = 8.0, 17.7 Hz, 1 H), 2.83 (dd, J = 6.0, 17.7 Hz, 1 H), 3.21 (dd, J = 6.0, 8.0 Hz, 1 H), 4.03−4.15 (m, 4 H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 16.5, 22.3, 38.1, 65.61, 65.63, 107.2, 116.1, 116.9 ppm. IR (KBr): 3001, 2979, 2950, 2898, 2247, 1440, 1390, 1268, 1237, 1211, 1170, 1106, 1062, 1027, 950, 891, 793, 719, 652, 559 cm^{-1}. MS (m/z, relative intensity): 40 (3), 41 (4), 42 (6), 43 (100), 44 (3), 45 (16), 51 (3), 52 (10), 53 (4), 54 (4), 66 (4), 79 (6), 80 (5), 87 (62), 88 (3), 93 (4), 07 (12), 151 (10). HRMS: m/z calcd. for $C_8H_{10}O_2N_2$ + Na: 189.0640; found: 189.0639.

4.18. 2-(2, 2-Dimethyl-1, 3-dioxolan-4-yl)butanedinitrile (3cJ-syn, anti)

Fumaronitrile (**1c-*cis***, 15.61 mg, 0.20 mmol) and DTBP (14.76 mg, 0.10 mmol) in 2, 2-dimethyl-1, 3-dioxolane (**2J**, 10 mL). Irradiation time: 2 h. NMR yield ($CDCl_3$), 22% (*syn*/*anti* = 12/10) (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (1/0 → 0/1).

3cJ-*syn*: 3.9 mg (10%); colorless oil; ^{1}H-NMR (δ, $CDCl_3$): 1.39 (s, 3H), 1.53 (s, 3H), 2.88 (d, J = 7.2 Hz, 2 H), 3.09 (dt, J = 3.2, 7.2 Hz, 1 H), 3.96 (dd, J = 5.6, 9.3 Hz, 1 H), 4.23 (dd, J = 6.4, 9.3 Hz, 1 H), 4.35 (ddd, J = 3.2, 5.6, 6.4 Hz, 1 H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 18.3, 25.0, 26.1, 33.0, 66.9, 73.1, 111.3, 115.5, 116.2 ppm. IR (KBr disk): 2989, 2939, 2251, 1458, 1423, 1375, 1260, 1220, 1152, 1111, 1062, 972, 933, 844, 511 cm^{-1}. MS (m/z, relative intensity): 40 (49), 41 (9), 42 (11), 43 (100), 44 (5), 52 (2), 59 (3), 72 (7), 73 (3), 101 (2), 110 (4), 165 (17, M^+-Me).

3cJ-*anti*: 3.4 mg (9%); colorless oil; ^{1}H-NMR (δ, $CDCl_3$): 1.36 (s, 3H), 1.46 (s, 3H), 2.81 (dd, J = 7.2, 17.2 Hz, 1 H), 2.87 (dd, J = 5.2, 17.2 Hz, 1 H), 2.96 (ddd, J = 5.2, 7.2, 7.8 Hz, 1 H), 4.03 (dd, J = 3.6, 9.2 Hz, 1 H), 4.23−4.33 (m, 2 H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 18.0, 24.8, 26.9, 33.2, 67.4, 74.0, 111.5, 115.2, 116.4 ppm. IR (KBr disk): 2988, 2937, 2250, 1456, 1423, 1375, 1259, 1215, 1151, 1059, 981, 840, 514 cm^{-1}. MS (m/z, relative intensity): 40 (4), 41 (10), 42 (12), 43 (100), 44 (6), 52 (2), 59 (3), 61 (3), 72 (7), 101 (3), 110 (4), 165 (16, M^+-Me).

4.19. 3-(2-Methyl-1, 3-dioxolan-2-yl)propionic acid tert-butyl ester (3dG)

tert-Butyl acrylate (**1d**, 25.43 mg, 0.20 mmol) and DTBP (14.63 mg, 0.10 mmol) in 2-methyl-1, 3-dioxolane (**2G**, 10 mL). Irradiation time: 0.5 h. NMR yield ($CDCl_3$), 36% (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (20/1 → 0/1).

3dG: 13.45 mg (31%); colorless oil; ^{1}H-NMR (δ, $CDCl_3$): 1.32 (s, 3 H), 1.44 (s, 9 H), 1.97 (t, J = 7.8 Hz, 2 H), 2.31 (t, J = 7.8, 2 H), 3.89−3.98 (m, 4 H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 24.0, 28.0, 30.3, 34.0, 64.7, 80.1, 109.3, 172.9 ppm. IR (KBr disk): 3440, 2979, 2932, 2883, 2678, 2370, 2321, 1731, 1478, 1455, 1391, 1368, 1311, 1282, 1255, 1157, 1099, 1056, 977, 948, 866, 852, 805, 756, 650, 559, 526, 491, 439 cm^{-1}. MS (m/z, relative intensity): 41 (53), 43 (67), 57 (31), 87 (100), 99 (24), 143 (18), 145 (15), 216 (0.05, M^+). HRMS: m/z calcd. for $C_{11}H_{20}O_4$ + H: 217.1440; found: 217.1498.

4.20. 3-Methyl-3-(2-methyl-1, 3-dioxolan-2-yl)propanoic acid tert-butyl ester (3eG)

tert-Butyl crotonate (**1e**, 28.76 mg, 0.20 mmol) and DTBP (14.97 mg, 0.10 mmol) 2-methyl-1,3-dioxolane (**2G**, 10 mL). Irradiation time: 0.5 h. NMR yield ($CDCl_3$), 49% (conversion: 100%). Eluent for chromatography: hexane/ethyl acetate (20/1 → 0/1).

3eG: 21.75 mg (47%); colorless oil; ^{1}H-NMR (δ, $CDCl_3$): 1.00 (d, J = 6.9 Hz, 3 H), 1.26 (s, 3 H), 1.45 (s, 9 H), 1.98 (dd, J = 8.9, 14.9 Hz, 1 H), 2.19−2.33 (m, 1 H), 2.49 (dd, J = 5.3, 14.9 Hz 1 H), 3.88−3.99 (m, 4 H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 15.3, 20.6, 28.1, 38.2, 38.5, 64.6, 64.7, 80.0, 111.4, 172.6 ppm. IR (KBr disk): 2979, 1730, 1458, 1368, 1296, 1256, 1154, 959, 872, 847, 760 cm^{-1}. MS (m/z, relative intensity): 41 (24), 43 (43), 57 (14), 87 (100), 113 (12), 157 (10), 231 (0.01, M^+). HRMS: m/z calcd. for $C_{12}H_{22}O_4$: 230.1512; found: 230.1514.

4.21. 2-Isopropenylbutanedioic acid 1,4-dimethyl ester (3aL-a) [38] and 2-isopropylbutanedioic acid 1,4-dimethyl ester (3aL-b). [39]

Dimethyl maleate (**1a-*cis***, 30.02 mg, 0.21 mmol) and DTBP (16.21 mg, 0.11 mmol) in isopropyl ether (**2L**, 10 mL). Irradiation time: 3 h. NMR yield ($CDCl_3$), **3aL-a**: 30%, **3aL-b**: 23% (conversion: 100%). Eluent for chromatography: hexane/CH_2Cl_2 (1/0 → 1/25 and then 1/0 → 19/1). Only a part of **3aL-a** was isolated by two chromatographic separations and **3aL-b** was obtained as a mixture with **3aL-a**.

Please cite this article as: M. Hayakawa et al., Photochemical addition of cyclic ethers/acetals to olefins using ^{t}BuOO^{t}Bu: Synthesis of masked ketones/aldehydes and diols, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131557

3aL-a: 8.4 mg (22%); colorless oil; ^{1}H-NMR (δ, $CDCl_3$): 1.76 (s, 3 H), 2.52 (dd, J = 5.5, 16.5 Hz, 1 H), 2.95 (dd, J = 9.6, 16.5 Hz, 1 H), 3.55 (dd, J = 5.5, 9.6 Hz, 1 H), 3.68 (s, 3 H), 3.71 (s, 3H), 4.91 (d, J = 1.0 Hz, 1 H), 4.93 (dd, J = 1.0, 1.5, 1 H), ppm. ^{13}C-NMR (δ, $CDCl_3$): 20.6, 35.1, 48.5, 51.8, 52.2, 114.3, 141.3, 172.1, 173.0 ppm. IR (KBr disk): 3082, 2953, 2847, 1738, 1647, 1437, 1339, 1296, 1260, 1217, 1163, 1096, 1003, 964, 901, 847, 772, 559 cm^{-1}. MS (m/z, relative intensity): 53 (27), 55 (100), 59 (61), 67 (56), 68 (23), 69 (51), 81 (13), 83 (66), 84 (46), 85 (86), 94 (16), 95 (42), 96 (14), 109 (14), 113 (26), 114 (18), 122 (24), 123 (28), 124 (31), 125 (13), 126 (20), 127 (29), 146 (42), 154 (42), 155 (98), 186 (M^+, 6), 187 (M^++1, 11).

3aL-b: 13.8 mg (mixture with **3aL-a**); ^{1}H-NMR (δ, $CDCl_3$): 0.92 (d, J = 6.0 Hz, 3 H), 0.94 (d, J = 6.0 Hz, 3 H), 1.93–2.04 (m, 1 H), 2.42 (ddd, J = 8.7, 8.7, 12.8 Hz, 1 H), 2.68–2.78 (m, 2 H), 3.67 (s, 3 H), 3.70 (s, 3 H) ppm. ^{13}C-NMR (δ, $CDCl_3$): 19.6, 20.1, 30.1, 32.9, 47.4, 51.6, 51.8, 172.9, 174.9 ppm. IR (mixture with **3aL-a**) (KBr disk): 2953, 2916, 1738, 1437, 1373, 1348, 1260, 1194, 1163, 1115, 1020, 1005, 899, 849 cm^{-1}. MS (mixture with **3aL-a**) (m/z, relative intensity): 45 (12), 54 (16), 55 (50), 59 (100), 67 (28), 68 (13), 69 (26), 83 (18), 84 (10), 85 (38), 87 (11), 94 (11), 95 (15), 97 (13), 101 (26), 113 (25), 114 (37), 115 (16), 122 (16), 126 (13), 146 (17), 154 (26), 155 (31), 157 (19), 188 (M^+, 0.0), 189 (M^++1, 0.02).

4.22. Hydrolysis of esters 3aA-syn and 3aA-anti

4.22.1. General procedure

To a 20 mL round bottom flask fitted with a reflux condenser and a magnetic stirrer was added **3aA** (***syn*** or ***anti***), 5 mL of AcOH, and 5 mL of 6 N HCl. 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 (ethyl acetate/acetic acid = 1/0 → 30/1).

4.22.2. 2-(Tetrahydro-2-furanyl)butanedioic acid (syn) (3bA-syn) [33a,35]

3aA-*syn* (39.55 mg, 0.18 mmol) was hydrolyzed and purified to **3bA-*syn*** (8.7 mg, 25%), white solid; ^{1}H NMR (acetone-d_6): δ = 1.65–1.77 (1H, m), 1.80–1.99 (3H, m), 2.45 (1H, dd, J = 3.9, 16.8 Hz), 2.68 (1H, dd, J = 10.3, 16.8 Hz), 3.00 (1H, ddd, J = 3.9, 6.3, 10.3 Hz), 3.66 (1H, ddd, J = 6.5, 7.7, 7.7 Hz), 3.82 (1H, ddd, J = 6.5, 8.2, 8.2 Hz), 4.06 (1H, ddd, J = 6.3, 6.5, 7.6 Hz), 10.8 (2H, br s) ppm. ^{13}C NMR (acetone-d_6): δ = 26.3, 29.0, 32.6, 46.5, 68.6, 79.7, 173.4, 174.1 ppm. IR (KBr): 3437 (br), 3044 (br), 2984 (br), 2967 (br), 2930 (br), 2886 (br), 1773, 1699, 1437, 1408, 1314, 1275, 1254, 1219, 1192, 1138, 1114, 1070, 1020, 999, 941, 923, 841, 696, 667, 542, 444 cm^{-1}. MS, m/z (relative intensity): 40 (10), 41 (54), 42 (28), 43 (96), 44 (36), 45 (19), 53 (9), 55 (37), 57 (11), 67 (8), 69 (9), 71 (100), 97 (7), 111 (29), 114 (8), 125 (9), 129 (47), 143 (7), 188 (0.1, M^+).

4.22.3. 2-(Tetrahydro-2-furanyl)butanedioic acid (anti) (3bA-anti) [33a,35]

3aA-*anti* (23.20 mg, 0.11 mmol) was hydrolyzed and purified to **3bA-*anti*** (6.1 mg, 30%), white solid; ^{1}H NMR (acetone-d_6): δ = 1.72–1.82 (1H, m), 1.82–1.94 (2H, m), 1.94–2.20 (1H, m), 2.63 (1H, dd, J = 5.0, 16.9 Hz), 2.69 (1H, dd, J = 8.5, 16.9 Hz), 2.82 (1H, ddd, J = 5.0, 7.3, 8.5 Hz), 3.65 (1H, ddd, J = 6.5, 7.4, 8.0 Hz), 3.78 (1H, ddd, J = 6.5, 6.6, 6.6 Hz), 3.98 (1H, ddd, J = 7.0, 7.0, 7.3 Hz), 10.5 (2H, br s) ppm. ^{13}C NMR (acetone-d_6): δ = 26.2, 30.4, 33.4, 47.2, 68.3, 80.0, 173.6, 174.3 ppm. IR (KBr): 3435 (br), 2978 (br), 2957 (br), 2928 (br), 2882 (br), 1732, 1705, 1558, 1435, 1402, 1385, 1352, 1312, 1275, 1234, 1175, 1065, 1045, 1016, 991, 957, 928, 841, 698, 665, 642, 604, 567, 521, 440 cm^{-1}. MS, m/z (relative intensity): 40 (8), 41 (56), 42 (32), 43 (86), 44 (24), 45 (20), 53 (9), 55 (35), 57 (8), 67 (7), 69 (9), 71 (100), 72 (7), 97 (7), 100 (6), 111 (34), 114 (6), 129 (57), 188 (0.03, M^+).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number JP17K05953 and the Sasakawa Scientific Research Grant from The Japan Science Society (M. H.). We thank Professor Masako Takada for the use of her Gaussian system and Ms. Kaori Wada for NOESY and ROESY measurements.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2020.131557.

References

[1] (a) B. Giese, Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds, Pergamon Press, Oxford, 1986;
(b) D.P. Curran, In Organic Synthesis. Part 1. Synthesis, 1988, pp. 417–439;
(c) D.P. Curran, N.A. Porter, B. Giese, Stereochemistry of Radical Reactions, VCH, Weinheim, 1996.
[2] A.B. Smith III, R.J. Fox, T.M. Razler, Accounts Chem. Res. 41 (2008) 675–687.
[3] Review. (a) C. Walling, E.S. Huyser, in: A.C. Cope, R. Adams, A.H. Blatt, V. Boekelheide, T.L. Cairns, D.Y. Curtin, C. Niemann (Eds.), Organic Reactions, vol. 13, John Wiley & Sons, New York, 1963, pp. 91–149 (Chapter 3);
(b) N.W.A. Geraghty, M.T. Lohan, A. Griesbeck, in: third ed., in: M. Oelgemöller, F. Ghetti (Eds.), CRC Handbook of Organic Photochemistry and Photobiology, vol. 1, CRC Press, Boca Raton, 2012, pp. 452–455 (Chapter 19), Section 19.2.
[4] (a) S. Modena, A. Fontana, G. Moggi, J. Fluor. Chem. 30 (1985) 109–121;
(b) V. Gevorgyan, E. Priede, E. Liepiņš, M. Gavars, E. Lukevics, J. Organomet. Chem. 393 (1990) 333–338;
(c) J. Chen, Y.-F. Zhang, X. Zheng, A. Vij, D. Wingate, D. Meng, K. White, R.L. Kirchmeier, J.M. Shreeve, Inorg. Chem. 35 (1996) 1590–1601;
(d) J. Chen, R.L. Kirchmeier, J.M. Shreeve, Inorg. Chem. 35 (1996) 6676–6681;
(e) W. Zhou, P. Qian, J. Zhao, H. Fang, J. Han, Y. Pan, Org. Lett. 17 (2015), 1169–1163;
(f) Y. Lan, P. Fan, X.-W. Liu, F.-F. Meng, T. Ahmad, Y.-H. Xu, T.-P. Loh, Chem. Commun. 53 (2017) 12353–12356;
(g) Q. Wang, J. Lou, P. Wu, K. Wu, Z. Yu, Adv. Synth. Catal. 359 (2017) 2981–2998;
(h) R. Chen, J.-T. Yu, J. Cheng, Org. Biomol. Chem. 16 (2018) 1823–1827.
[5] (a) A. Citterio, A. Arnoldi, A. Griffini, Tetrahedron 38 (1982) 393–395;
(b) D.P. Matthews, J.R. McCarthy, J. Org. Chem. 55 (1990) 2973–2975;
(c) H.-S. Dang, B.P. Roberts, Tetrahedron Lett. 40 (1999) 8929–8933;
(d) T. Sueda, Y. Takeuchi, T. Saefuji, M. Ochiai, Molecules 10 (2005) 195–200;
(e) T. Okano, M. Hiraishi, T. Mizutani, Bull. Chem. Soc. Jpn. 80 (2007) 752–757;
(f) A. Hosoya, Y. Umino, T. Narita, H. Hamana, J. Fluor. Chem. 129 (2008) 91–96;
(g) R. Rinaldi, H.F.N. de Oliveira, H. Schumann, U. Schuchardt, J. Mol. Catal. Chem. 307 (2009) 1–8;
(h) J.C. Jung, T.H. Kim, K. Lee, Tetrahedron Lett. 52 (2011) 4662–4664.
[6] (a) M. Degueil-Castaing, K. Mohr, B. Maillard, Synth. Commun. 22 (1992) 1703–1712;
(b) X.-Q. Chu, H. Meng, Y. Zi, X.-P. Xu, S.-J. Ji, Chem. Commun. 50 (2014) 9718–9721.
[7] (a) A. Weichert, H.M.R. Hoffmann, J. Org. Chem. 56 (1991) 4098–4112;
(b) K. Tamamoto, S. Yamada, M. Higashi, T. Konno, T. Ishihara, J. Fluor. Chem. 190 (2016) 23–30;
(c) H. Zeng, D. Lu, Y. Gong, Eur. J. Org Chem. (2017) 7231–7237;
(d) H. Zeng, S. Yang, H. Li, D. Lu, Y. Gong, J.-T. Zhu, J. Org. Chem. 83 (2018) 5256–5266.
[8] (a) S. Tsujimoto, S. Sakaguchi, Y. Ishii, Tetrahedron Lett. 44 (2003) 5601–5604;
(b) T. Okano, M. Chokai, M. Hiraishi, M. Yoshizawa, T. Kusukawa, M. Fujita, Tetrahedron 60 (2004) 4031–4035;
(c) T. Akindele, Y. Yamamoto, M. Maekawa, H. Umeki, K. Yamada, K. Tomioka, Org. Lett. 8 (2006) 5729–5732;
(d) J. Shen, C.-H. Tan, Org. Biomol. Chem. 6 (2008) 4096–4098;
(e) K. Yamada, M. Maekawa, T. Akindele, M. Nakano, Y. Yamamoto, K. Tomioka, J. Org. Chem. 73 (2008) 9535–9538;
(f) Y. Jang, T. Lee, H. Kim, Bull. Kor. Chem. Soc. 30 (2009) 31–32.
[9] Review. (a) B. Giese, T. Göbel, B. Kopping, H. Zipse, G. Helmchen, in: fourth ed., in: R.W. Hoffmann, J. Mulzerm, E. Schaumann (Eds.), Methods of Organic Chemistry (Houben-Weyle), E21, Georg Thieme, Stuttgart, 1996,

pp. 2203–2249. Section 1.5.4;
(b) M. Fagnoni, D. Dondi, D. Ravelli, A. Albini, Chem. Rev. 107 (2007) 2725–2756;
(c) V. Dichiarante, M. Fagnoni, in: A. Albini, M. Fagnoni (Eds.), Handbook of Synthetic Photochemistry, Wiley-VCH, Weinheim, 2010, pp. 67–94 (Chapter 3).

[10] (a) I. Rosenthal, D. Elad, Tetrahedron 23 (1967) 3193–3204;
(b) I. Rosenthal, D.J. Elad, Org. Chem. 33 (1968) 805–811;
(c) J.S. Jewell, W.A. Szarek, Tetrahedron Lett. (1969) 43–46;
(d) K. Matsuura, K. Nishiyama, K. Yamada, Y. Araki, Y. Ishido, Bull. Chem. Soc. Jpn. 46 (1973) 2538–2542;
(e) B. Fraser-Reid, D.R. Hicks, D.L. Walker, D.E. Iley, M.B. Yunker, S.Y.-K. Tam, R.C. Anderson, Tetrahedron Lett. (1975) 297–300;
(f) B. Fraser-Reid, R.C. Anderson, D.R. Hicks, D.L. Walker, Can. J. Chem. 55 (1977) 3986–3995;
(g) B. Fraser-Reid, R. Underwood, M. Osterhout, J.A. Grossman, D. Liotta, J. Org. Chem. 51 (1986) 2152–2155;
(h) K. Inomata, H. Suhara, H. Kinoshita, H. Kotake, Chem. Lett. (1988) 813–816;
(i) K. Inomata, T. Hirata, H. Suhara, H. Kinoshita, H. Kotake, H. Senda, Chem. Lett. (1988) 2009–2012;
(j) K. Ogura, A. Yanagisawa, T. Fujino, K. Takahashi, Tetrahedron Lett. 29 (1988) 5387–5390;
(k) C. Manfrotto, M. Mella, M. Freccero, M. Fagnoni, A. Albini, J. Org. Chem. 64 (1999) 5024–5028;
(l) P.J. Parsons, J.K. Cowell, Synlett (2000) 107–109;
(m) V. Církva, S. Böhm, O. Paleta, J. Fluor. Chem. 102 (2000) 159–168;
(n) R. Mosca, M. Fagnoni, M. Mella, A. Albini, Tetrahedron 57 (2001) 10319–10328;
(o) D. Dondi, I. Caprioli, M. Fagnoni, M. Mella, A. Albini, Tetrahedron 59 (2003) 947–957;
(p) D. Dondi, S. Protti, A. Albini, S.M. Carpio, M. Fagnoni, Green Chem. 11 (2009) 1653–1659;
(q) Q. Glenadel, Y. Nassar, L. Raffier, S. Veys, O. Piva, Tetrahedron 74 (2018) 5367–5373.

[11] (a) N. Hoffmann, Tetrahedron: Asymmetry 5 (1994) 879–886;
(b) N. Mase, Y. Watanabe, T. Toru, Bull. Chem. Soc. Jpn. 71 (1998) 2957–2965;
(c) S.G. Pyne, K. Schafer, Tetrahedron 54 (1998) 5709–5720;
(d) H. Graalfs, R. Fröhlich, C. Wolff, J. Mattay, Eur. J. Org Chem. (1999) 1057–1073;
(e) G. Campari, M. Fagnoni, M. Mella, A. Albini, Tetrahedron: Asymmetry 11 (2000) 1891–1906;
(f) A.K. Ghosh, S. Leshchenko, M. Noetzel, J. Org. Chem. 69 (2004) 7822–7829.

[12] (a) M. Fernández, R. Alonso, Org. Lett. 5 (2003) 2461–2464;
(b) S. Kamijo, T. Hoshikawa, M. Inoue, Tetrahedron Lett. 52 (2011) 2885–2888;
(c) L. Zhang, Y. Deng, F. Shi, Tetrahedron Lett. 54 (2013) 5217–5219;
(d) S. Yang, S. Zhu, Y. Gong, Org. Lett. 21 (2019) 2019–2024.

[13] Review. (a) M.D. Tzirakis, I.N. Lykakis, M. Orfanopopoulos, Chem. Soc. Rev. 38 (2009) 2609–2621;
(b) D. Ravelli, D. Dondi, M. Fagnoni, A. Albini, Chem. Soc. Rev. 38 (2009) 1999–2011;
(c) D. Ravelli, S. Protti, M. Fagnoni, Acc. Chem. Res. 49 (2016) 2232–2242.

[14] (a) D. Dondi, M. Fagnoni, A. Albini, Chem. Eur J. 12 (2006) 4153–4163;
(b) S. Protti, D. Ravelli, M. Fagnoni, A. Albini, Chem. Commun. (2009) 7351–7353;
(c) M.D. Tzirakis, M. Orfanopoulos, Angew. Chem. Int. Ed. 49 (2010) 5891–5893;
(d) D. Ravelli, S. Montanaro, M. Zema, M. Fagnoni, A. Albini, Adv. Synth. Catal. 353 (2011) 3295–3300;
(e) D. Ravelli, A. Albini, M. Fagnoni, Chem. Eur J. 17 (2011) 572–579;
(f) D. Ravelli, M. Zoccolillo, M. Mella, M. Fagnoni, Adv. Synth. Catal. 356 (2014) 2781–2786;
(g) F. Bonassi, D. Ravelli, S. Protti, M. Fagnoni, Adv. Synth. Catal. 357 (2015) 3687–3695;
(h) J.J. Murphy, D. Bastida, S. Paria, M. Fagnoni, P. Melchiorre, Nature 532 (2016) 218–222;
(i) A. Bahamonde, J.J. Murphy, M. Savarese, É. Brémond, A. Cavalli, P. Melchiorre, J. Am. Chem. Soc. 139 (2017) 4559–4567;
(j) L. Capaldo, M. Fagnoni, D. Ravelli, Chem. Eur J. 23 (2017) 6527–6530;
(k) C. Raviola, D. Ravelli, Synlett 30 (2019) 803–808.

[15] L. Capaldo, D. Merli, M. Fagnoni, D. Ravelli, ACS Catal. 9 (2019) 3054–3058.

[16] (a) X.-Z. Fan, J.-W. Rong, H.-L. Wu, Q. Zhou, H.-P. Deng, J.D. Tan, C.-W. Xue, L.-Z. Wu, H.-R. Rao, J. Wu, Angew. Chem. Int. Ed. 57 (2018) 8514–8518;
(b) Y. Kuang, K. Wang, X. Shi, X. Huang, E. Meggers, J. Wu, Angew. Chem. Int. Ed. 58 (2019) 16859–16863.

[17] H. Huang, Z.M. Strater, T.H. Lambert, J. Am. Chem. Soc. 142 (2020) 1698–1703.

[18] (a) D. Xia, Y. Li, T. Miao, P. Li, L. Wang, Green Chem. 19 (2017) 1732–1739;
(b) J. Hou, A. Ee, H. Cao, H.-W. Ong, J.-H. Xu, J. Wu, Angew. Chem. Int. Ed. 57 (2018) 17220–17224.

[19] (a) J.L. Jeffrey, J.A. Terrett, D.W.C. MacMillan, Science 349 (2015) 1532–1536;
(b) S. Rohe, A.O. Morris, T. McCallum, L. Barriault, Angew. Chem. Int. Ed. 57 (2018) 15664–15669;
(c) C.M. Morton, Q. Zhu, H. Ripberger, L. Troian-Gautier, Z.S.D. Toa, R.R. Knowles, E.J. Alexanian, J. Am. Chem. Soc. 141 (2019) 13253–13260.

[20] (a) J. Fossey, D. Lefort, J. Sorba, Free Radicals in Organic Chemistry, John Wiley & Sons, Chichester, 1995, pp. 105–117 (Chapter 9);
(b) J.G. Calvert, J.N. Pitts Jr., Photochemistry, John Wiley & Sons, New York, 1966, p. 449. Section 5-4C Peroxides 6.

[21] (a) V. Malatesta, J.C. Scaiano, J. Org. Chem. 47 (1982) 1455–1459;
(b) J. Moriarty, H. Sidebottom, J. Wenger, A. Mellouki, G. Le Bras, J. Phys. Chem. 107 (2003) 1499–1505.

[22] Absorption spectra of various olefins and DTBP, and emission spectra of the light source are shown in the following literature. As shown in the spectra, dimethyl maleate (1a-cis) has weak absorption at >290 nm and a slight addition of isopropanol was observed in the absence of DTBP. However, a significant acceleration of the reaction was observed with the addition of DTBP. Although a radical chain is expected from the reaction, 0.5 eq of DTBP gave the best result, which is probably due to the consumption of the carbon radicals generated from isopropanol by other radical species in the reaction mixture, A. Ouchi, C. Liu, M. Kaneda, T. Hyugano, Eur. J. Org Chem. (2013) 3807–3816.

[23] Stable conformations (B3LYP/6-31++G) and chemical shifts were calculated by Gaussian 16; Gaussian 16, Revision A.03, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[24] Please see Supplementary data.

[25] R.L. Jacobs, G.G. Ecke, J. Org. Chem. 28 (1963) 3036–3038.

[26] T.J. Wallace, R.J. Gritter, J. Org. Chem. 27 (1962) 3067–3071.

[27] B. Abadie, D. Jardel, G. Pozzi, P. Toullec, J.-M. Vincent, Chem. Eur J. 25 (2019) 16120–16127.

[28] (a) D.L. Rakhmankulov, V.V. Zorin, E.V. Pastushenko, S.S. Zlotsky, Heterocycles 22 (1984) 817–839;
(b) B. Maillard, M. Gazaux, R. Lalande, Bull. Soc. Chim. Fr. (1975) 183–187.

[29] R.D. Chambers, B. Grievson, N.M. Kelly, J. Chem. Soc., Perkin Trans. 1 (1985) 2209–2213.

[30] G.A. Olah, A.P. Fung, R. Malhotra, Synthesis, 1981, pp. 474–476.

[31] W.L. Meyer, P.W. Taylor, S.A. Reed, M.C. Leister, H.-J. Schneider, G. Schmidt, F.E. Evans, R.A. Levine, J. Org. Chem. 57 (1992) 291–298.

[32] R.S. Musavirov, E.P. Nedogrei, V.I. Larionov, S.S. Zlot-skii, E.A. Kantor, D.L. Rakhmankulov, J. Gen. Chem. USSR 52 (1982) 1229–1236.

[33] (a) P. Singh, J. Org. Chem. 37 (1972) 836–841;
(b) G. Ahlgren, Acta Chem. Scand. B 29 (1975) 399.

[34] (a) C.S. Marvel, E.J. Prill, D.F. DeTar, J. Am. Chem. Soc. 69 (1947) 52–58;
(b) F. Bonassi, D. Ravelli, S. Protti, M. Fagnoni, Adv. Synth. Catal. 357 (2015) 3687–3695.

[35] A. Ledwith, M. Sambhi, J. Chem. Soc. B Phys. Org. (1966) 670–671.

[36] (a) O.G. Safiev, D.É. Kruglov, Y.N. Popov, S.S. Zlotskii, D.L. Rakhmankulov, Dokl. Chem. 272 (1983) 287–289;
(b) O.G. Safiev, D.É. Kruglov, Y.N. Popov, S.S. Zlot-skii, D.L. Rakhmankulov, J. Org. Chem. USSR 20 (1984) 997–1000;
(c) S. Yang, S. Zhu, D. Lu, Y. Gong, Org. Lett. 21 (2019) 2019–2024.

[37] K. Ramig, Y. Dong, S.D. Van Arnum, Tetrahedron Lett. 37 (1996) 443–446.

[38] H. Kanai, Y. Nishiguchi, H. Matsuda, Bull. Chem. Soc. Jpn. 56 (1983) 1592–1597.

[39] (a) F. Wada, T. Matsuda, Bull. Chem. Soc. Jpn. 46 (1973) 510–514;
(b) I.W. Lawston, T.D. Inch, J. Chem. Soc. Perkin Trans 1 (1983) 2629–2635;
(c) R. Kuwano, M. Sawamura, Y. Ito, Tetrahedron Asymmetry 6 (1995) 2521–2526;
(d) R. Ballini, G. Bosica, Liebigs Ann. (1996) 2087–2089.

Please cite this article as: M. Hayakawa et al., Photochemical addition of cyclic ethers/acetals to olefins using ^{t}BuOO^{t}Bu: Synthesis of masked ketones/aldehydes and diols, Tetrahedron, https://doi.org/10.1016/j.tet.2020.131557