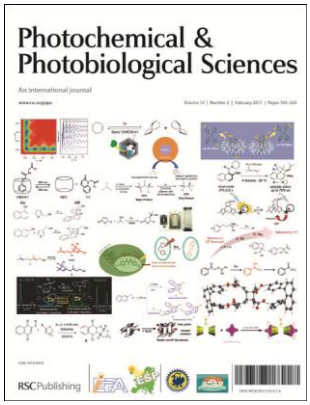

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PAPER

Hydroxy-group effect on the regioselectivity in a photochemical oxetane formation reaction (the Paternò-Büchi Reaction) of geraniol derivatives†‡

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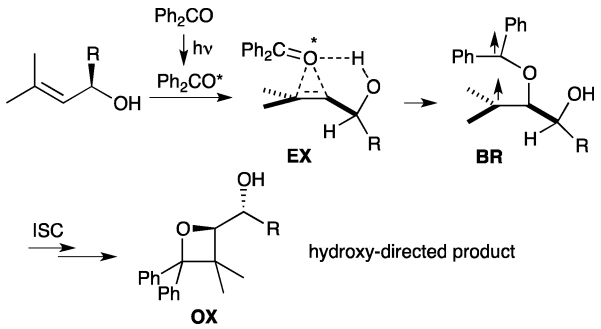
The Paternò–Büchi (PB) reaction of geraniol derivatives **1**, which contain allylic alcohol functionality and unfunctionalized double bonds, with benzophenone was investigated to see the effect of the hydroxyl group on the regioselectivity of the oxetane formation, *i.e.*, **2/3**. At low concentration of geraniol (**1a**), oxetanes **2a** and **3a** were formed in a ratio of **2a/3a** = *ca.* 50/50. The oxetane **2a** is derived from the PB reaction at the allylic alcohol moiety, whereas the PB reaction at the unfunctionalized double bond produces the oxetane **3a**. The PB reaction of the hydroxy-protected methyl ether **1b** and acetate **1c** gave selectively oxetanes **3b,c** derived from the reaction at the more nucleophilic double bond, **2/3** ~ 15/85. The hydroxyl-group effect was found to be small, but apparently increased the formation of **2a** in the PB reaction with geraniol (**1a**).

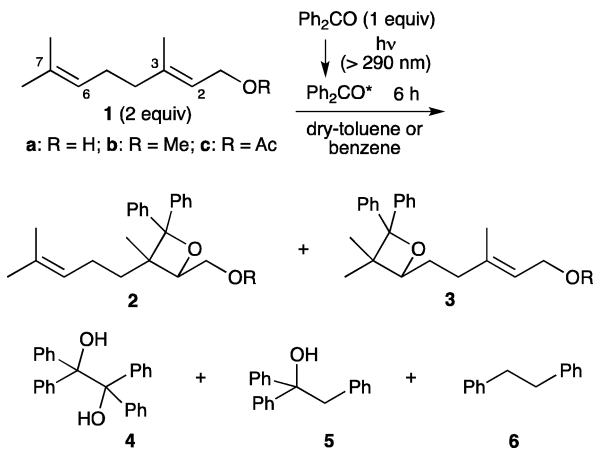
Introduction

Oxetanes, four-membered heterocycles, are key structural units not only in biologically[1] and synthetically[2] important compounds, but also in industrial curing agents.[3] Thus, the regio- and stereoselective preparation of oxetanes is an active area in organic synthesis. The photochemical [2 + 2] cycloaddition of carbonyls with alkenes, so-called Paternò–Büchi (PB) reaction,[4] is a useful method for synthesizing the strained structure. Since the reaction involves the carbonyl in the electronically excited state, which possesses a high energy (~70 kcal mol^{-1}), the regio- and stereoselective synthesis of oxetanes is still challenging subject. In recent decades, however, several examples of the selective formation of oxetanes have been reported.[5] Among them, the hydroxy-directed regio- and diastereoselectivity in the PB reaction of allylic alcohols has attracted considerable attention from both the synthetic and mechanistic point of view.[6] The origin of the hydroxy-directed formation of oxetanes **OX** was recently concluded to be hydrogen-bonding stabilization not in the biradical intermediate **BR**, but in the exciplex intermediate **EX** (Scheme 1).[7]

In the present study, geraniol (**1a**) and its derivatives **1b,c** were chosen to see how the hydroxyl group affect the regioselectivity in the formation of oxetane (Scheme 2). They contain the allylic alcohol functionality as well as the unfunctionalized double bond.



Scheme 1 The hydroxy-directed diastereoselectivity in the PB reaction of allylic alcohols with benzophenone.



Scheme 2 The PB reaction of geraniol derivatives **1** with benzophenone.

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‡ Electronic supplementary information (ESI) available: ^{1}H and ^{13}C-NMR spectra of compounds **2a–c** and **3a–c**. See DOI: 10.1039/c1pp05056g

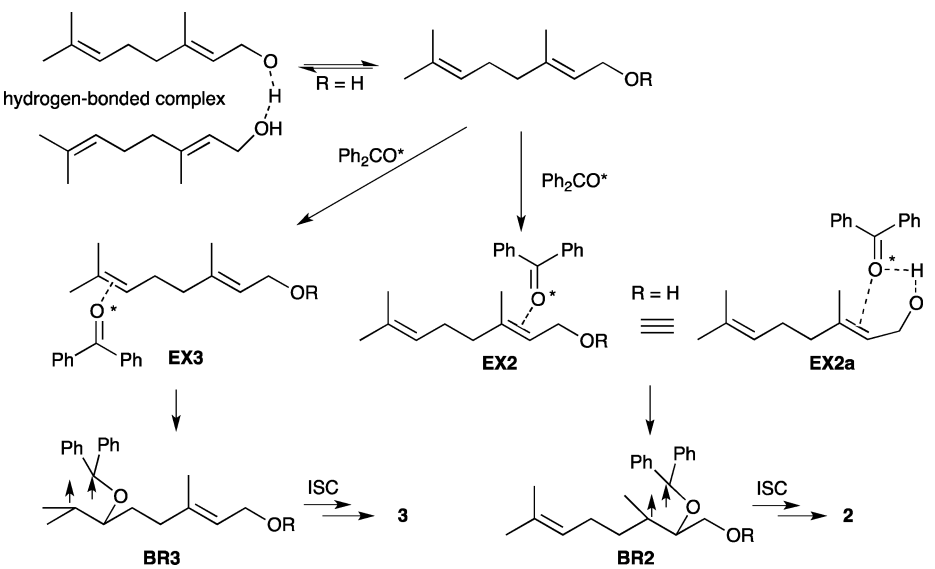
Table 1 The PB reaction of **1a** with benzophenone[a]

Entry	Solvent[b]	Conc. (mM)	Temp. (°C)	**2a** (%)[c]	**3a** (%)[c]	**2a**/**3a**	**4**, **5**, **6** (%)
1	tol.	340	–75	13[d]	44	23/77	12, 1, 1
2	tol.	340	–40	14[d]	38	27/73	14, 1, 1
3	tol.	340	20	16[e]	26	38/62	22, 2, 1
4[g]	ben.	340	20	15[e]	29	35/65	18, 0, 0
5	tol.	6.8	–75	27[d]	28	49/51	13, 9, 2
6	tol.	6.8	–40	18[d]	20	47/53	26, 14, 5
7	tol.	6.8	20	10[f]	12	46/54	43, 29, 16
8[h]	ben.	6.8	20	20[f]	26	44/56	14, 0, 0

[a] Irradiation was carried our under nitrogen atmosphere. [b] tol. = toluene; ben. = benzene. [c] Yields were determined by ^{1}H NMR analysis (500 MHz), Ph_3CH as an internal standard; error ± 3%. Ph_3CH was added after the photolysis. [d] *trans*/*cis* = >97/3. [e] *trans*/*cis* = 76/24. [f] *trans*/*cis* = 77/23. [g] The quantum yield (Φ) of compounds **2a** and **3a** was determined to be 0.32. [h] The quantum yield (Φ) of compounds **2a** and **3a** was determined to be 0.15.

Results and discussion

First of all, the regioselectivity of the PB reaction of **1a** (R = H) with benzophenone was investigated using a high-pressure Hg lamp (150 W) through a Pyrex filter ($h\nu$ > 290 nm) in a dried and oxygen-free toluene or benzene solution (Scheme 2, Table 1). Toluene is a useful solvent to see the effect in a wide range of temperatures. In accordance with the hydroxy-group directivity, the oxetane formation at the 2,3 double bond should be preferred over the 6,7 one to afford oxetane **2a** selectively. As shown in entries 1–4, however, the regioselective formation of oxetane **3a** derived from the reaction at the 6,7 double bond was observed at the concentration of [**1a**] = 340 mM; **2a**/**3a** = *ca.* 30/70. Compounds **4**–**6**[8] were also isolated in the photochemical reaction. The structure of compounds **2a** and **3a** was determined by measuring the 2D-NMR spectra. Thus, the methine (C*H*) proton of the oxetane ring in **2a** was found to be coupled with the methylene protons (–CH_2OH) of **2a**. Alternatively, the methylene protons (CH_2OH) in **3a** was found to be coupled with the vinyl proton of **3a**. The formation of **2a** slightly increased with increasing the reaction temperature, *e.g.* **2a**/**3a** = 23/77 at –75 °C and **2a**/**3a** = 38/62 at 20 °C (entries 1–4). At the lower concentration [**1a**] = 6.8 mM, the formation of **2a** increased to give nearly the 1 : 1 mixture of oxetanes **2a** and **3a**, and also the increase of the formation of compounds **4**–**6** was observed (entries 5–8). Thus, the regioselectivity (**2a**/**3a**) was found to be dependent on the concentration of the alcohol. The concentration effect on the selectivity suggests that the intermolecular association of **1a** plays a role in determining the regioselectivity (Scheme 3). In fact, the ^{1}H NMR resonance of the hydroxyl proton (OH) of **1a** was temperature and concentration sensitive (Fig. 1a,b). Thus, a downfield shift of the proton resonance was observed from δ 1.82 (20 °C) to 5.62 (–60 °C) with a decrease in temperature when geraniol **1a** (340 mM) and benzophenone (170 mM) were dissolved in dried toluene-d_8 (Fig. 1a). No change was observed in the resonance of the *ortho*-protons of benzophenone (δ 7.88). A similar shift in the hydroxyl proton resonance was also observed in the absence of benzophenone, *i.e.* δ 1.68 (20 °C) to 5.64 (–60 °C). As shown in Fig. 1a, however, significant downfield shifts were observed for the vinylic proton H_b and the allylic protons H_c, H_b; δ 5.41 (20 °C) to 5.65 (–60 °C), H_c; δ 4.02 (20 °C) to 4.29 (–60 °C). The shift in the resonance for H_a was quite small, δ 5.14 (20 °C) to 5.19 (–60 °C). At lower concentration of **1a** (Fig. 1b), a small shift in the resonance of the OH proton was observed, δ 0.45 (20 °C) to 0.63 (–60 °C). Thus, the hydrogen-bonded association of **1a** was revealed at lower temperature and higher concentration



Scheme 3 Mechanism of the PB reaction of **1** with benzophenone.

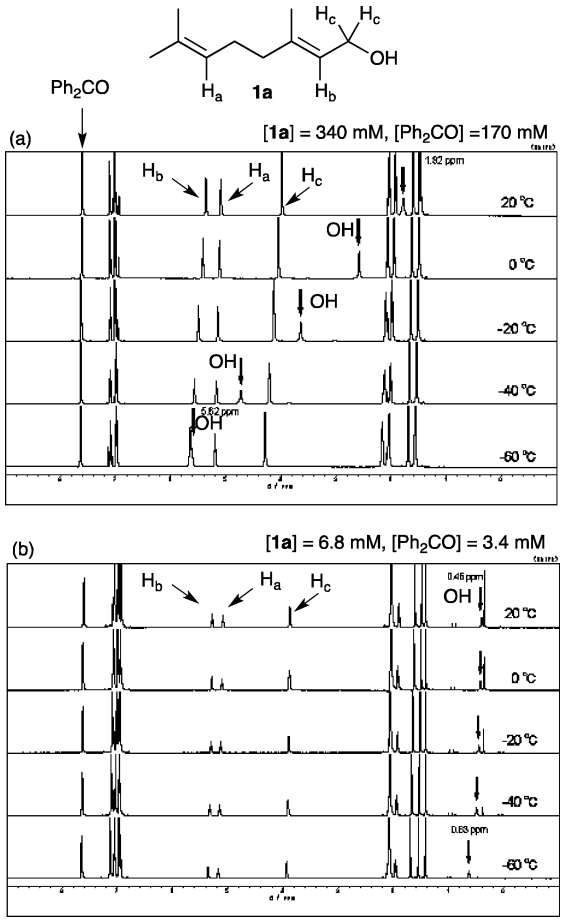


Fig. 1 Valuable temperature ^{1}H NMR spectra of **1a** (500 MHz, C_7D_8) at (a) higher concentration of [**1a**] = 340 mM and [Ph_2CO] = 170 mM, and (b) lower concentration of [**1a**] = 6.8 mM and [Ph_2CO] = 3.4 mM.

of **1a** (Scheme 3). At higher concentration of alcohol **1a** (R = H) and low temperature, the hydrogen-bonding stabilization in the exciplex **EX2a** would be suppressed, since the association of **1a** such as dimerization masks the hydroxyl group (Scheme 3).

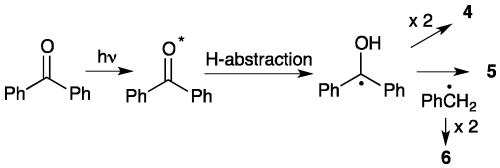
To obtain more information about the hydroxyl group effect on the regioselectivity, the PB reactions of the hydroxy-protected methyl ether **1b**[9] and acetate **1c**[10] with benzophenone were investigated in a dried and oxygen-free toluene solution (Table 2). As shown in entries 1–4, the regioselectivity, **2**/**3** = 15/85–11/89, was not dependent on the concentration of **1b,c**. Thus, the electrophilic oxygen of the benzophenone triplet state preferably approaches to the more nucleophilic 6,7 double-bond to afford the triplet biradical **BR3** *via* the exciplex **EX3** (Scheme 3). The

Table 2 The PB reaction of **1b,c** with benzophenone[a]

Entry	**1**	Conc. (mM)	Temp. (°C)	**2** (%)[b]	**3** (%)[b]	**2**/**3**	**4**, **5**, **6** (%)
1	**1b**	340	−75	**2b** (6)[c]	**3b** (33)	15/85	9, 1, 1
2	**1b**	6.8	−75	**2b** (5)[c]	**3b** (29)	15/85	17, 12, 3
3	**1c**	340	−75	**2c** (7)[c]	**3c** (56)	11/89	4, 2, 2
4	**1c**	6.8	−75	**2c** (5)[c]	**3c** (39)	11/89	18, 16, 3

[a] Irradiation was carried our under nitrogen atmosphere. [b] Yields were determined by ^{1}H NMR analysis (500 MHz), Ph_3CH as an internal standard; error ± 3%. [c] *trans*/*cis* = > 97/3.

trans-cis isomerization in the 2,3-double bond moiety, which was observed in the formation of oxetane **2a** at 20 °C (entries 3, 4, 7, 8 in Table 1), was rationalized by the conformational change in the triplet biradicals during the intersystem crossing (ISC) process to the singlet state. The formation of **4–6** is explained by the reaction initiated from the hydrogen-abstraction of the triplet state of benzophenone (Scheme 4).



Scheme 4 Mechanism for the formation of **4–6**.

Conclusions

In this study, we have examined the hydroxy-group directivity in the PB reaction of geraniol derivatives. In the reaction of **1a**, oxetanes **2a** and **3a** was obtained in a ratio of nearly the 1 : 1 mixture. The PB reaction of the hydroxy-protected **1b,c** produced regioselectively oxetanes **3b,c**, which are derived from the reaction at the unfunctionalized double bond. The inductive electron withdrawal by the hydroxy/alkoxy group will lower the nucleophilicity of the 2,3 double bond, if this electronic property is the decisive reactivity factor, the preferential oxetane-formation at the 6,7 double bond would be expected. Actually, the selective formation of **3b,c** was observed in the PB reaction of **1b,c**. However, the significant increase of the formation of **2a** was found in the reaction of **1a**. The experimental results clearly indicate that the hydroxy directivity plays an important role in increasing the formation of **2a**.

Experimental

General procedure for the photoreactions of benzophenone with geraniol derivatives

A dried and degassed toluene solution of freshly prepared geraniol derivatives **1a–c** and benzophenone was irradiated for 6 h with a high-pressure Hg lamp through a Pyrex filter at various temperatures and concentrations. After the solvent was removed under reduced pressure using a vacuum pump (0.2 mmHg, < 10 °C), the photolysate was directly analyzed by ^{1}H NMR (500 MHz) spectroscopy. The product yields were determined on the basis of the ^{1}H NMR (500 MHz) peak areas; error ±3%. Triphenylmethane (Ph_3CH) was added after the photolysis, and used as an internal standard. The product ratios were determined by comparisons of the peak areas. The photoproducts were isolated using silica-gel column chromatography.

((2*S*,3*R*)-3-Methyl-3-(4-methylpent-3-en-1-yl)-4,4-diphenyloxetan-2-yl)methanol (2a). ^{1}H NMR (500 MHz, C_6D_6): δ 1.02 (s, 3H), 1.40–1.50 (m, 2H), 1.45 (s, 3H), 1.54 (s, 3H), 1.69–1.78 (m, 1H), 1.82–1.93 (m, 1H), 3.47–3.53 (m, 1H), 3.59–3.65 (m, 1H), 4.52 (dd, J = 5.56 and 6.19 Hz, 1H), 4.90–4.95 (m, 1H), 6.97–7.05 (m, 2H), 7.13–7.20 (m, 4H), 7.46–7.50 (m, 2H), 7.67–7.71 (m, 2H); ^{13}C NMR (125 MHz, C_6D_6): δ 17.57 (CH_3), 17.95 (CH_3),

23.73 (CH_2), 25.63 (CH_3), 39.54 (CH_2), 48.56 (C), 63.25 (CH_2), 84.37 (CH), 92.09 (C), 124.82 (CH), 125.56 (CH), 126.18 (CH), 126.60 (CH), 126.85 (CH), 128.05 (CH), 128.29 (CH), 131.24 (C), 144.20 (C), 145.47 (C); EI-MS (M^+): Calcd for $C_{23}H_{28}O_2$, 336.2089; Found, 336.2097; IR (neat, cm^{-1}): 3434, 3058, 2968, 2929, 2870, 1737, 1448, 990, 709.

(*E*)-5-(3,3-Dimethyl-4,4-diphenyloxetan-2-yl)-3-methylpent-2-en-1-ol (3a). ^1H NMR (500 MHz, C_6D_6): δ 0.95 (s, 3H), 0,99 (s, 3H), 1.43–1.53 (m, 1H), 1.49 (s, 3H), 1.73–1.85 (m, 1H), 1.88–1.98 (m, 1H), 2.15–2.25 (m, 1H), 3.99–4.05 (m, 2H), 4.29 (dd, J = 4.29 and 8.76 Hz, 1H), 5.42–5.49 (m, 1H), 6.98–7.08 (m, 2H), 7.12–7.25 (m, 4H), 7.53–7.58 (m, 2H), 7.68–7.73 (m, 2H); ^{13}C NMR (125 MHz, C_6D_6): δ 16.18 (CH_3), 21.28 (CH_3), 26.08 (CH_3), 30.28 (CH_2), 35.21 (CH_2), 45.59 (C), 59.29 (CH_2), 85.23 (CH), 90.73 (C), 125.06 (CH), 125.49 (CH), 126.06 (CH), 126.53 (CH), 126.70 (CH), 127.95 (CH), 128.26 (CH), 137.74 (C), 144.97 (C), 145.88 (C); EI-MS (M^+): Calcd for $C_{23}H_{28}O_2$, 336.2089; Found, 336.2084; IR (neat, cm^{-1}): 3400, 3057, 2959, 2934, 2870, 1669, 1447, 996, 709.

(*E*)-1-Methoxy-3,7-dimethylocta-2,6-diene (1b). NaH (0.35 g, 8.65 mmol) was washed with hexane. The washed NaH was dissolved in dry THF (10 ml). To this solution, geraniol **1a** (1.00 g, 6.50 mmol) in dry THF (10 ml) was added dropwise. The reaction mixture was stirred 1 h at 0 °C. After the addition, MeI (1.41 g, 9.90 mmol) in dry THF (10 ml) was added to the reaction mixture at rt. After the addition, the reaction mixture was stirred over night. The reaction mixture was quenched by the addition of water and extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (hexane–EtOAc = 9 : 1 v/v) to give yellow oil (0.95 g, 5.65 mmol, yield = 87%). ^1H NMR (500 MHz, $CDCl_3$): δ 1.60 (s, 3H), 1.68 (s, 6H), 2.02–2.07 (m, 2H), 2.08–2.14 (m, 2H), 3.32 (s, 3H), 3.93 (d, J = 6.78 Hz, 2H), 5.07–5.13 (m, 1H), 5.32–5.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.39 (CH_3), 17.63 (CH_3), 25.64 (CH_3), 26.38 (CH_2), 39.57 (CH_2), 57.70 (CH_3), 68.94 (CH_2), 120.72 (CH), 123.97 (CH), 131.60 (C), 140.31 (C); APCI-MS ($[M+H]^+$): Calcd for $C_{11}H_{21}O$, 169.1587; Found, 169.1586.

(3*R*,4*S*)-4-(Methoxymethyl)-3-methyl-3-(4-methylpent-3-en-1-yl)-2,2-diphenyloxetane (2b). ^1H NMR (500 MHz, $CDCl_3$): δ 1.09 (s, 3H), 1.34–1.48 (m, 2H), 1.53 (s, 3H), 1.62 (s, 3H), 1.71–1.81 (m, 1H), 1.87–1.97 (m, 1H), 3.41 (s, 3H), 3.45–3.49 (m, 1H), 3.58–3.63 (m, 1H), 4.63 (dd, J = 4.26 and 7.39 Hz, 1H), 4.90–4.95 (m, 1H), 7.15–7.21 (m, 2H), 7.27–7.34 (m, 4H), 7.42–7.47 (m, 2H), 7.57–7.62 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.58 (CH_3), 17.75 (CH_3), 23.32 (CH_2), 25.63 (CH_3), 38.86 (CH_2), 48.51 (C), 59.34 (CH_3), 73.77 (CH_2), 82.46 (CH), 92.06 (C), 124.12 (CH), 125.23 (CH), 125.84 (CH), 126.35 (CH), 126.54 (CH), 127.66 (CH), 127.99 (CH), 131.57 (C), 143.46 (C), 144.80 (C); ESI-MS ($[M+Na]^+$): Calcd for $C_{24}H_{30}O_2Na$, 373.2138; Found, 373.2140; IR (neat, cm^{-1}): 3058, 2957, 2932, 2871, 1673, 1448, 1103, 996, 709.

(*E*)-4-(5-Methoxy-3-methylpent-3-en-1-yl)-3,3-dimethyl-2,2-diphenyloxetane (3b). ^1H NMR (500 MHz, $CDCl_3$): δ 1.05 (s, 3H), 1.06 (s, 3H), 1.58–1.68 (m, 1H), 1.70 (s, 3H), 1.75–1.85 (m, 1H), 1.98–2.06 (m, 1H), 2.19–2.28 (m, 1H), 3.32 (s, 3H), 3.94 (d, J 6.70 Hz, 2H), 4.31 (dd, J = 5.41 and 8.38 Hz, 1H), 5.37–5.41 (m, 1H), 7.13–7.20 (m, 2H), 7.25–7.34 (m, 4H), 7.43–7.48 (m, 2H), 7.56–7.61 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.50 (CH_3), 21.19 (CH_3), 26.12 (CH_3), 29.95 (CH_2), 34.91 (CH_2), 45.51 (C), 57.84 (CH_3), 68.94 (CH_2), 85.11 (CH), 90.44 (C), 120.98 (CH), 125.06 (CH), 125.61 (CH), 126.22 (CH), 126.36 (CH), 127.62 (CH), 127.90 (CH), 139.82 (C), 144.34 (C), 145.22 (C); ESI-MS ($[M+Na]^+$): Calcd for $C_{24}H_{30}O_2Na$, 373.2138; Found, 373.2144; IR (neat, cm^{-1}): 3058, 2957, 2932, 2871, 1673, 1448, 1103, 996, 709.

(*E*)-3,7-Dimethylocta-2,6-dien-1-yl acetate (1c). In a flame-dried 50 mL two-neck round bottom flask, equipped with magnetic stir bar, were placed geraniol **1a** (3.0 mL, 17.29 mmol), triethylamine (2.7 mL, 19 mmol) and dry CH_2Cl_2 (15 mL) *via* syringe. The flask was cooled in an ice bath and acetic anhydride (1.8 mL, 19 mmol) was added dropwise *via* syringe. The resulting solution was stirred under a stream of nitrogen at room temperature overnight. The reaction mixture was washed with H_2O (20 mL), $NaHCO_3$ (2 × 20 mL) and H_2O (20 mL) and the aqueous extracts were back-extracted with CH_2Cl_2 (20 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (hexane–EtOAc = 9 : 1 v/v) to give colorless oil (2.96 g, 15.07 mmol, yield = 87%). ^1H NMR ($CDCl_3$, 500 MHz): δ1.60 (s, 3H), 1.68 (s, 3H), 1.70 (s, 3H), 2.01–2.14 (m, 7H), 4.58 (d, J = 7.08 Hz, 2H), 5.05–5.10 (m, 1H), 5.31–5.36 (m, 1H); APCI-MS ($[M+H]^+$): Calcd for $C_{12}H_{21}O_2$, 197.1536; Found, 197.1533.

((2*S*,3*R*)-3-Methyl-3-(4-methylpent-3-en-1-yl)-4,4-diphenyloxetan-2-yl)methyl acetate (2c). ^1H NMR (500 MHz, $CDCl_3$): ^1H NMR (500 MHz, $CDCl_3$): δ 1.11 (s, 3H), 1.36–1.49 (m, 2H), 1.53 (s, 3H), 1.62 (s, 3H), 1.71–1.81 (m, 1H), 1.88–1.98 (m, 1H), 2.10 (s, 3H), 4.20–4.24 (m, 2H), 4.64 (dd, J 5.27 and 6.42 Hz, 1H), 4.88–4.93 (m, 1H), 7.16–7.23 (m, 2H), 7.28–7.36 (m, 4H), 7.41–7.47 (m, 2H), 7.55–7.62 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.61 (CH_3), 17.89 (CH_3), 20.95 (CH_3), 23.26 (CH_2), 25.59 (CH_3), 38.84 (CH_2), 48.60 (C), 65.12 (CH_2), 81.28 (CH), 92.32 (C), 123.86 (CH), 125.16 (CH), 125.75 (CH), 126.51 (CH), 126.70 (CH), 127.76 (CH), 128.06 (CH), 131.83 (C), 143.20 (C), 144.35 (C), 170.85 (C); ESI-MS ($[M+Na]^+$): Calcd for $C_{25}H_{30}O_3Na$, 401.2087; Found, 401.2089; IR (neat, cm^{-1}): 3058, 2969, 2931, 2881, 1744, 1448, 1234, 995, 709.

(*E*)-5-(3,3-Dimethyl-4,4-diphenyloxetan-2-yl)-3-methylpent-2-en-1-yl acetate (3c). ^1H NMR (500 MHz, $CDCl_3$): δ 1.05 (s, 3H), 1.07 (s, 3H), 1.57–1.66 (m, 1H), 1.73 (s, 3H), 1.75–1.84 (m, 1H), 2.00–2.08 (m, 1H), 2.04 (s, 3H), 2.20–2.29 (m, 1H), 4.30 (dd, J = 4.87 and 8.53 Hz, 1H), 4.59 (d, J = 7.01 Hz, 2H), 5.37–5.42 (m, 1H), 7.14–7.20 (m, 2H), 7.26–7.33 (m, 4H), 7.43–7.47 (m, 2H), 7.56–7.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.49 (CH_3), 21.02 (CH_3), 21.22 (CH_3), 26.07 (CH_3), 29.78 (CH_2), 34.92 (CH_2), 45.52 (C), 61.30 (CH_2), 85.00 (CH), 90.47 (C), 1118.58 (CH), 125.05 (CH), 125.60 (CH), 126.25 (CH), 126.39 (CH), 127.62 (CH), 127.92 (CH), 141.72 (C), 144.30 (C), 145.21 (C), 171.05 (C); ESI-MS ($[M+Na]^+$): Calcd for $C_{25}H_{30}O_3Na$, 401.2087; Found, 401.2085; IR (neat, cm^{-1}): 3058, 2956, 2870, 1738, 1448, 1233, 996, 710.

Determination of quantum yields of oxetane formation

The quantum yields of the oxetane formations from the photoreaction of benzophenone with **1a** were measured by xenon

lamp (500 W) focused at 313 nm at room temperature. The photochemical transformation of valerophenone to acetophenone ($\Phi = 0.33$)[11] was used as a chemical actinometer.

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