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Short communication

Formation of cyclooctatriene and bicyclooctadiene through regioselective intermolecular (2+2) photocycloaddition of benzoic acids to allyl alcohol in water

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1. Introduction

The photocycloaddition of benzene derivatives to alkenes is a convenient and useful method for the preparation of polycyclic compounds in a single step under mild conditions, whose preparation is difficult by other methods [1-5]. This photoreaction can mainly yield either (3+2) or (2+2) adducts, depending on the nature of benzene and alkene [6]. Although the intermolecular and intramolecular (3+2) additions have been extensively investigated from mechanistic and synthetic viewpoints [7-9], (2+2) addition, which is believed to be the preferred process when there is significant donor-acceptor interaction between the two molecules, is relatively less known [10-15].

With the current emphasis on performing a molecular transformation under an environmentally friendly condition, an organic photoreaction in water has received considerable attention as an environmentally friendly synthetic process since light is a clean and powerful reagent. Furthermore, during our investigation of the organic photoreaction using the photosensitive surfactant in water, we found that water as an organic reaction medium could offer many advantages such as higher reactivity and selectivity than an organic solvent [16,17]. This result encouraged us to investigate the photocycloaddition of benzene derivatives to alkenes in water.

ABSTRACT

The regioselective intermolecular (2+2) photocycloaddition of the sodium salt of benzoic acids **1** to allyl alcohol **2** proceeded in water to afford cyclooctatrienes **3** and bicyclooctadienes **4**. The efficiency and product distribution of this photoreaction were strongly influenced by the substituent of benzoic acid and solvent polarity. The photocycloaddition of benzoic acids in water is an environmentally friendly method for the preparation of cyclooctatriene and bicyclooctadiene.

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We herein report that the regioselective intermolecular (2+2)photocycloaddition of the sodium salt of benzoic acids 1 to allyl alcohol **2** proceeded in water, and subsequently the (2+2)cycloadducts underwent electrocyclic rearrangement and photocyclization to form cyclooctatrienes 3 and bicyclooctadienes 4. To the best of our knowledge, this is the first example of the formation of cyclooctatrienes and bicyclooctadienes through the intermolecular (2+2) photocycloaddition and subsequent electrocyclic rearrangement and photocyclization in such a manner, although the intramolecular photocycloaddition of (3-alken-1oxy)alkanophenones has already been reported [18-27]. Since benzoic acids and allyl alcohol are usually inexpensive and commercially available, this photoreaction can be useful to produce cyclooctatrienes and bicyclooctadienes in a single step under mild conditions. Cyclooctatrienes and bicyclooctadienes are an important moiety in naturally occurring compounds such as Ophibolins and Aleurodiscal [28-32], and used as a reactant for the construction of medium-sized ring compounds and more complex polycyclic compounds [33-36].

2. Experimental

2.1. General

Melting points were taken on a hot stage and were uncorrected. IR spectra were recorded on JASCO FT/IR-620, and GC–MS spectra were obtained using Shimadzu GCMS-QP5000. ¹H and ¹³C NMR

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were recorded on JEOL JNM-AL500 (500 and 125 MHz) spectrometer and for solutions in CDCl₃ containing tetramethylsilane as an internal standard. The light source was Eiko-sha 120 W lowpressure mercury arc. Benzoic acids **5** were recrystallized from hexane and EtOAc. Allyl alcohol **2**, acetonitrile, and water were freshly distilled before use.

2.2. Preparation of the sodium salt of benzoic acids 1

Benzoic acids **5** (10 mmol) were added to a solution of NaOH (10 mmol) in methanol (50 ml), and the mixture was refluxed for 2 h. After cooling to room temperature, ether (25 ml) was added to the solution and filtered. The filtrate was dried in vacuo to afford the sodium salt of benzoic acids **1** in quantitative yields.

2.3. General procedure for the photoreaction of 1 with 2

An aqueous solution (150 ml) containing the sodium salt of benzoic acids **1** (0.75 mmol, 5 mM) and allyl alcohol **2** (7.5 mmol, 50 mM) in quartz vessels under an argon atmosphere was irradiated with a 120 W low-pressure mercury lamp. The solution was neutralized by 1 M HCl, extracted with ethyl acetate, dried over Na₂SO₄, and concentrated under reduced pressure to afford the cycloadducts. These products were isolated by silica gel column chromatography using hexane and EtOAc as eluents and then by preparative HPLC using a GPC column.

2.4. Characterization Data

2.4.1. 1-carboxy-7-hydroxymethyl-1,3,5-cyclooctatriene 3a

White solid; mp 107–108 °C; IR (KBr, cm⁻¹) 3324, 2907, 1676; ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, *J* = 4.3 Hz, 1H), 6.05 (dd, *J* = 5.5, 12.8 Hz, 1H), 5.98 (dd, *J* = 4.9, 12.8 Hz, 1H), 5.92–5.88 (m, 1H), 5.74 (dd, *J* = 4.0, 13.4 Hz, 1H), 3.68 (dd, *J* = 4.3, 11.3 Hz, 1H), 3.46 (dd, *J* = 8.2, 11.3 Hz, 1H), 2.81–2.72 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.3, 141.6, 134.9, 133.8, 130.5, 125.9, 125.2, 66.8, 43.0, 27.0; MS *m/z* 180 (M⁺).

2.4.2. 1-carboxy-7-hydroxymethyl-4-methyl-1,3,5cyclooctatriene **3b**

White solid; mp 154–155 °C; IR (KBr, cm⁻¹) 3312, 2912, 1683; ¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, *J* = 4.0 Hz, 1H), 5.78 (d, *J* = 12.6 Hz, 1H), 5.61 (dd, *J* = 4.3, 12.6 Hz, 1H), 3.65 (dd, *J* = 4.6, 11.3 Hz, 1H), 3.45 (dd, *J* = 8.0, 11.3 Hz, 1H), 2.84 (m, 1H), 2.68 (d, *J* = 7.0 Hz, 2H), 1.97 (s,3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.4, 142.4, 139.7, 132.5, 132.2, 130.0, 122.0, 66.5, 42.6, 27.0, 25.9; MS *m/z* 194 (M⁺); anal. calcd for C₁₁H₁₄O₃: C 68.02, H 7.27, O 24.71. Found: C 68.17, H 7.29, O 24.54.

2.4.3. 1-carboxy-7-hydroxymethyl-4-methoxy-1,3,5cyclooctatriene **3c**

White solid; mp 141–142 °C; IR (KBr, cm⁻¹) 3309, 2937, 1676; ¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, *J* = 5.5 Hz, 1H), 5.84–5.81 (m, 1H), 5.74 (dd, *J* = 4.0, 8.9 Hz, 1H), 5.20 (d, *J* = 5.5 Hz, 1H), 3.72–3.66 (m, 4H), 3.46 (dd, *J* = 7.9, 9.7 Hz, 1H), 2.85 (m, 1H), 2.74–2.68 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 172.9, 157.2, 142.0, 135.1, 129.8, 124.6, 97.6, 66.3, 55.3, 43.5, 26.5; MS *m/z* 210 (M⁺); anal. calcd for C₁₁H₁₄O₄: C, 62.85 H, 6.71. Found: C, 62.72 H, 6.64.

2.4.4. 1-carboxy-7-hydroxymethyl-bicyclo[4.2.0]octa-2,5-diene 4a

Colorless oil; IR (neat, cm⁻¹) 3398, 2928, 1700; ¹H NMR (500 MHz, CDCl₃) δ 6.17 (d, *J*=2.7 Hz, 1H), 6.06 (d, *J*=2.7 Hz, 1H), 5.92–5.89 (m, 1H), 5.85 (dd, *J*=1.8, 10.1 Hz, 1H), 3.68 (d, *J*=6.4 Hz, 2H), 3.56 (d, *J*=5.5 Hz, 1H), 2.27 (m, 1H), 2.12 (dd, *J*=4.6, 13.1 Hz, 1H),

1.60 (t, *J* = 12.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 180.5, 138.7, 135.7, 130.9, 127.4, 66.3, 54.3, 45.4, 34.6, 31.3; MS *m/z* 180 (M⁺).

2.4.5. 1-carboxy-7-hydroxymethyl-4-methyl-bicyclo[4.2.0]octa-2,5-diene **4b**

White solid; mp 136–137 °C; IR (KBr, cm⁻¹) 3335, 2926, 1681; ¹H NMR (500 MHz, CDCl₃) δ 6.18 (d, J = 2.8 Hz, 1H), 5.99 (d, J = 2.8 Hz, 1H), 5.83–5.81 (m, 1H), 5.67 (dd, J = 2.8, 6.5 Hz, 1H), 3.69 (d, J = 6.1 Hz, 2H), 2.12 (m, 1H), 2.01 (dd, J = 4.6, 8.8 Hz, 1H), 1.68 (t, J = 12.8 Hz, 1H), 1.27 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 178.2, 141.5, 133.0, 132.5, 130.1, 66.3, 58.3, 49.1, 34.6, 31.9, 22.0; MS *m/z* 194 (M⁺); anal. calcd for C₁₁H₁₄O₃: C, 68.02 H, 7.27. Found: C, 68.29 H, 7.25.

3. Results and discussion

Irradiation of an aqueous solution containing the sodium salt of benzoic acid **1a** (5 mM) and allyl alcohol **2** (50 mM) for 6 h afforded cvclooctatriene **3a** (10%), bicvclooctadiene **4a** (9%), and the recovery of benzoic acid (62%) in isolated yields (Table 1, entry 1). Similar irradiation of the sodium salt of 4-methylbenzoic acid 1b mainly yielded the corresponding bicyclooctadiene 4b along with cyclooctatriene **3b** (entry 2). In contrast, the photoreaction of **1c** having a methoxy group exclusively produced cyclooctatriene **3c** (entry 3). When **1d** having a cyano group was subjected to a photoreaction, these cycloadducts were not obtained (entry 4). Thus, the product distribution was dependent on the substituent of **1**. The structures of cyclooctatriene **3** and bicyclooctadiene **4** were determined by their spectral data and confirmed by the X-ray crystallographic analysis of 3c and 4b (Figs. 1 and 2). It is noteworthy that the single regioisomers and stereoisomers were formed in the photocycloaddition. Prolonged irradiation (12h) increased the yield of all products with the exception of **1d** and decreased the recovery of benzoic acids (entries 5-8), since the photochemical Birch-type reduction of 1 in basic aqueous solution could occur, as reported earlier [37,38]. In fact, the addition of NaOH to this solution resulted in low product yields and recovery. In the case of **1a** (entries 1 and 5), a longer irradiation time caused a decrease in the vield of **3a** and increase in the yield of **4a**, indicating that **4** could be produced by the secondary photoreaction of 3.



Fig. 1. ORTEP drawing of **3c**. $C_{11}H_{14}O_4$, FW = 210.23, monoclinic, P2₁/c (#14), Z=4, a = 10.048 (2)Å, b = 4.5928 (9)Å, c = 23.419 (4)Å, $\beta = 88.624$ (9), V = 1080.5 (3)Å³, $D_{calc} = 1.292 \text{ g/cm}^3$, refl/para = 15.72, $R_1 = 0.080$, wR₂ = 0.176, goodness of fit = 1.00, $\mu = 0.98$.

Table 1

Photocycloaddition of sodium salt of benzoic acids **1** or benzoic acids **5** with allyl alcohol **2**.



Entry	1 or 5	Solvent	Irradn time (h)	Product yields (%)		Recovery of benzoic acids (%)
				3	4	
1	1 a	H ₂ O	6	10	9	62
2	1b			4	23	40
3	1 c			25	0	33
4	1d			0	0	62
5	1 a		12	4	20	37
6	1b			3	40	8
7	1c			28	0	3
8	1d			0	0	46
9	5a	CH ₃ CN	6	3	5	82
10	5b			2	21	71
11	5c			12	0	83
12	5d			0	0	72
13	5c	Et ₂ O		7	0	87
14	5c	CH_2Cl_2		0	0	82



Fig. 2. ORTEP drawing of **4b**. $C_{11}H_{14}O_3$, FW = 194.23, orthorhombic, P2₁2₁2₁ (#19), Z=4, *a*=8.768 (2)Å, *b*=10.077 (3)Å, *c*=11.469 (3)Å, *V*=1013.3 (4)Å³, D_{calc} = 1.273 g/cm³, refl/para = 9.48, R_1 = 0.045, wR₂ = 0.043, goodness of fit = 1.01, μ = 0.92.



Scheme 1. Photoreaction of 3 or 4b and the thermal reaction of 4b in CH₃CN.



Scheme 2. Plausible mechanism of the photocycloaddition of 1 to 2.

Next, the photoreaction of benzoic acids **5** with **2** in an organic solvent was examined. The excitation of benzoic acids **5** (5 mM) with **2** (50 mM) in acetonitrile under the same condition provided lower product yields and higher recovery of **5** (Table 1, entries 9–12) [39]. In addition, the use of a less polar solvent such as ethyl ether or CH_2Cl_2 resulted in lower yields of **3** and **4** (entries 13 and 14). Thus, the efficiency of the photocycloaddition was strongly influenced by the solvent polarity. The use of ethyl vinyl ether, acrylonitrile, methyl acrylate, and acrylic acid instead of **2** did not give any adducts.

To gain insight into the mechanism of this photoreaction, we examined the photoreaction of **3** and the thermal reaction of **4b** (Scheme 1). The irradiation of **3b** (5 mM) for 6 h in acetonitrile yielded **4b** and **1b** in 46% and 15% yields, respectively; however, a similar irradiation of **3c** did not result in the formation of **4c**. Thus, the substituent of **3** affects the efficiency of the photocyclization of **3** to **4**. Considerably low yields of **1b** and **3b** were observed in the photoreaction of **4b**, while the heating of **4b** (reflux in acetonitrile for 12 h) provided a good yield of **3b**. Thus, the cyclorevision of **4** to **3** proceeded under thermal condition but not this photochemical condition.

The fluorescence of 1 was not quenched by 2 in water, and the formation of cycloadducts 3 and 4 was quenched by molecular oxygen and 2-methyl-1,3-butadiene ($E_T = 251 \text{ kJ} \text{ mol}^{-1}$) [40]. In addition, the intersystem crossing to the excited triplet state in benzoic acid occurred efficiently [41-44], and similar intramolecular photocycloaddition occurred via the excited triplet state of the benzene group, as reported earlier [27]. From these results, we show a plausible mechanism of this photoreaction in Scheme 2. The regioselective intermolecular (2+2) cycloaddition between the excited triplet state of **1** and **2** yields the cyclobutane **6**. The efficiency of the (2+2) photocycloaddition is dependent on the substituent of 1 and solvent polarity, and the use of water as a solvent accelerated the photocycloaddition. In the case of the photoreaction of 1 in water, the electron transfer from the hydroxide ion to the excited triplet state of 1 could proceed to suppress the cycloaddition and decrease the recovery of benzoic acids [37,38]. It is evident from these results that the highest yield of adducts is obtained when water is used as a solvent in the presence of the lowest concentration of the base. Subsequently, the (2+2) adduct **6** undergoes electrocyclic rearrangement to form cyclooctatrienes 3, which are stereoselectively photocyclized to produce 4. The higher yield of **4a**,**b** by irradiation for a longer time is attributed to the high efficiency of the photocyclization of **3a,b** to **4a,b** as compared to the photocycloreversion of 4a,b to 3a,b or 3a,b to 1a,b. In contrast, the photocyclization of **3c** to **4c** did not proceed at all to yield **3c** exclusively.

The molar extinction coefficients of **1b** and **3b** at 254 nm were 233 and 273, respectively, and the (2+2) photocycloaddition of **1b** with **2** was quenched by **3b** [45]. Thus, **3** acts as an internal filter as well as a triplet quencher, which causes the low conversion of **1** [46].

4. Conclusion

In conclusion, we found that the regioselective intermolecular (2+2) photocycloaddition of benzoic acids to allyl alcohol proceeded in a polar solvent to form cyclooctatrienes **3** and bicyclooctadienes **4**, and the efficiency and product distribution of this photoreaction depended on the substituent of benzoic acid. The photoreaction of **1** by the use of water as a solvent provided a higher yield of adducts and a clean process for the preparation of cyclooctatriene and bicyclooctadiene.

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