ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 127 (1999) 75–81

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Steric effect on photochemistry of benzyl ester derivatives

2. Effects of substituents and oxygen on photolysis of α-methyl-substituted benzyl alkanoates

Toshiyuki Goshima [a], Yoshihiro Itoh [a,*], Masanobu Kojima [b], Takashi Karatsu [c]

[a] *Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386-8567, Japan*
[b] *Faculty of Agriculture, Shinshu University, Matsumoto, Nagano 390-8621, Japan*
[c] *Faculty of Engineering, Chiba University, Chiba 263-8522, Japan*

Received 26 April 1999; received in revised form 11 June 1999; accepted 14 June 1999

Abstract

The photochemistry of α-methyl-substituted benzyl acetates and pivalates, **1a–c** and **2a–c**, respectively, has been examined in methanol (MeOH). Sensitization and quenching experiments confirmed the predominance of the singlet-state photolysis of these esters. The product distribution depended on methyl groups, on the methylene carbon, and/or alkyl groups attached to the carbonyl group. Ester conversion decreased with methyl substitution. These results are explicable on the basis of steric hindrance, or conformational restriction, around the ester bond. We also found that the photolysis was markedly affected by oxygen, particularly for the most hindered ester **2c**. It is likely that the effect of oxygen is attributed to the formation of an excited charge-transfer complex between the esters and an oxygen molecule.

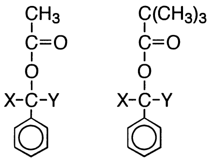
Keywords: Photolysis; Benzyl ester; Substituent effect; Steric hindrance

---

1. Introduction

Substituent effect on photochemical reactions of arylmethyl heteroatom compounds has been paid continuous attention for mechanistic reasons [1,2]. In most cases, the photoreactivity relies on whether electron-donating or electron-accepting nature of substituents on the aromatic ring affects their excited states or not. Several mechanistic extremes have been outlined [2], but a comprehensive understanding of experimental results has not been achieved yet.

Ground state control of photoreactivity is another fascinating subject. Pincock and co-workers [3,4] have noted the influence of conformational mobility on the photolysis of indanyl and α-substituted 1-naphthylmethyl esters. In the related field, Wagner et al. [5] have demonstrated for α-substituted arylacetophenones that the reactivity in the excited triplet state can be controlled by their ground state conformational preferences.



1 **2**

a: X = H Y = H
b: X = H Y = CH_3
c: X = CH_3 Y = CH_3

Scheme 1.

In our preceding paper [6], we studied the photochemistry of a series of naphthylmethyl esters, and suggested that steric hindrance, or conformational restriction, around the ester bond is responsible for photocleavage efficiency. To test that this effect is general in arylmethyl esters, the photochemistry of benzyl acetates and pivalates with α-methyl substituents, **1a–c** and **2a–c**, respectively, has been studied (Scheme 1). We found a distinctive effect of the steric hindrance on both ester conversions and product yields.

---

[*] Corresponding author. Tel./fax: +81-268-21-5489
E-mail address: yositoh@giptc.shinshu-u.ac.jp (Y. Itoh)

1010-6030/99/$ – see front matter ©1999 Elsevier Science S.A. All rights reserved.
PII: S1010-6030(99)00136-7

In addition, we unexpectedly found a large effect of oxygen on the photolysis. Such oxygen-sensitive photolyses of benzyl-type compounds have already been reported [7,8], but no clear reason has been shown. Here, possible mechanisms, including formation of excited charge-transfer (CT) complexes, are discussed.

2. Experimental details

2.1. Materials

Benzyl acetate (**1a**) (Wako) and 1-phenylethyl acetate (**1b**) (Aldrich) were distilled under reduced pressure. 2-Phenyl-2-propyl acetate (**1c**) was prepared according to the method of Detilleux and Jadot [9]: bp 102°C at 4 mm Hg (lit. [9], 124–125°C at 15 mm Hg);^{1}H NMR ($CDCl_3$) δ 1.76 (s, 6H), 2.02 (s, 3H), 7.32 ppm (br s, 5H).

Pivalates (**2a–c**) were synthesized by the reaction of the corresponding alcohols with pivaloyl chloride, as reported previously [6], and purified by distillation under reduced pressure.

- **2a**: bp 100°C at 3 mm Hg (lit. [10], 63–65°C at 1.5 mm Hg); ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 9H), 5.09 (s, 2H), 7.30 ppm (br s, 5H).
- **2b**: bp 63°C at 1 mm Hg (lit. [11], 115°C at 4 mm Hg); ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 9H), 1.46 (d, 3H, $J = 6.6$ Hz), 5.84 (q, 1H, $J = 6.6$ Hz), 7.27 ppm (br s, 5H).
- **2c**: bp 80–82°C at 1–2 mm Hg; ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 9H), 1.74 (s, 6H), 7.30 ppm (br s, 5H).

1-Phenylethyl methyl ether (**3b**) was prepared according to the method of Inoue et al. [12]: bp 60–62°C at 26 mm Hg (lit. [12], 74–75°C at 30–32 mm Hg); ^{1}H NMR ($CDCl_3$) δ 1.39 (d, 3H, $J = 6.4$ Hz), 3.15 (s, 3H), 4.21 (q, 1H, $J = 6.4$ Hz), 7.26 ppm (br s, 5H).

2-Phenyl-2-propyl methyl ether (**3c**) was prepared by the reaction of 2-phenyl-2-propanol with NaH followed by CH_3I [6] and distilled under reduced pressure: bp 59°C at 3 mm Hg (lit. [12], 77–78°C at 12–13 mm Hg); ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 6H), 3.01 (s, 3H), 7.1–7.4 ppm (m, 5H).

4-*tert*-Butylcumene (**7c**) was prepared by treating cumene with *tert*-butanol in concentrated sulfuric acid [13] and distilled under reduced pressure: bp 71–75°C at 4 mm Hg (lit. [13], 125.5°C at 44 mm Hg); ^{1}H NMR ($CDCl_3$) δ 1.23 (d, 6H, $J = 7.7$ Hz), 1.29 (s, 9H), 2.7–3.0 (m, 1H), 7.1–7.4 ppm (m, 4H).

2,2-Dimethyl-3-phenylbutane (**5b**), 4-*tert*-butyl-1-ethylbenzene (**7b**), and *meso*- and *dl*-2,3-diphenylbutane (**9b**) were isolated from the products of preparative photolysis of **2b** in MeOH by silica-gel column chromatography with benzene or *n*-hexane as an eluent.

- **5b**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 9H), 1.23 (d, 3H, $J = 7.2$ Hz), 2.50 (q, 1H, $J = 7.2$ Hz), 7.02 ppm (br s, 5H).
- **7b**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.23 (t, 3H, $J = 7.5$ Hz), 1.31 (s, 9H), 2.67 (q, 2H, $J = 7.5$ Hz), 7.1–7.4 ppm (m, 4H).
- **9b** (*meso*-isomer): mp 124–126°C (lit. [14], mp 126–127°C); ^{1}H NMR ($CDCl_3$) δ 1.02 (d, 6H, $J = 6.6$ Hz), 2.4–2.9 (m, 2H), 7.0–7.4 ppm (m, 10H).
- **9b** (*dl*-isomer): colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.27 (d, 6H, $J = 6.6$ Hz), 2.7–3.1 (m, 2H), 6.9–7.3 ppm (m, 10H).

Most of the other photoproducts were commercially available. Some products, neither isolation nor preparation of which was attempted, were identified by GC-MS and GC.

2.2. Measurements

Instrumentations for ^{1}H NMR and mass spectra were described previously [6]. GC analysis was also performed according to the previous method [6], except that 2-ethylnaphthalene was used as a standard.

Fluorescence spectra were recorded at room temperature on a Shimadzu RF-5000 spectrofluorometer. All samples were degassed by bubbling with nitrogen for 15 min. Fluorescence quantum yields (Φ_f) were determined by comparison with that of 0.13 for toluene in MeOH [15]. Fluorescence lifetime measurements (τ_f) were performed on a Horiba NAES 1100 single photon counting instrument using an excitation of 254 nm and an emission of 280 nm [16]. Samples were degassed by three freeze–pump–thaw cycles. Phosphorescence spectra were obtained in degassed methylcyclohexane at 77 K on the spectrofluorometer, equipped with a home-made phosphorescence attachment [17].

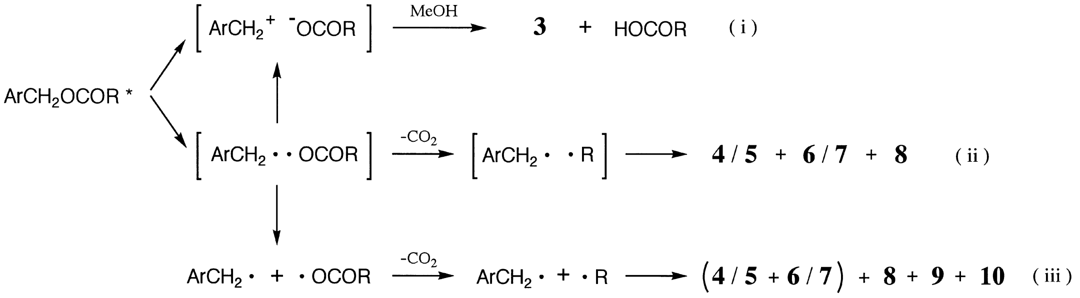
For quantitative photolyses, irradiations were carried out with a 500-W high-pressure mercury lamp (EIKOSHA, EHB-W-500) in a merry-go-round apparatus. A 0.02M solution (4 ml) of the ester in MeOH was placed in a quartz tube, degassed by bubbling argon for 10 min, and irradiated for 1 h at 25°C. Three separate photolyses on each ester were analyzed by GC, as described above. Sensitization experiments with acetone were performed by irradiation through a Pyrex filter. The quantum yields for ester conversion (Φ_r) were determined at low conversions (<10%) using the apparatus equipped with a 60-W low-pressure mercury lamp (EIKOSHA, EL-J-60). Chlorobenzene in MeOH ($\Phi_r = 0.14$) [18] was used as a standard.

For preparative photolyses, a 0.05M solution (550 ml) of the ester in MeOH was irradiated for 24 h under argon atmosphere with the 500-W high-pressure lamp in a quartz vessel. Photoproducts were isolated by silica-gel column chromatography.

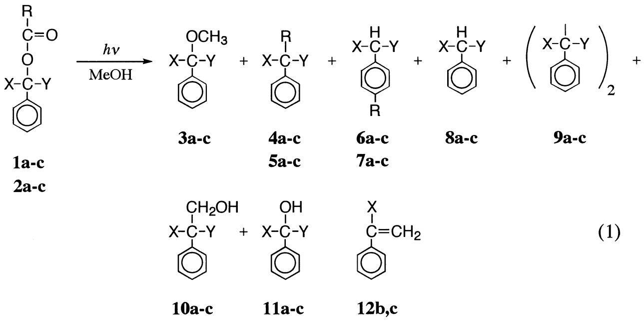
3. Results and discussion

3.1. Products on irradiation of esters **1** and **2**

When esters **1** and **2** were photolyzed in MeOH, eight benzylic products were identified by GC and GC/MS:



Scheme 2. General mechanism for the photolysis of benzyl esters ($ArCH_2OCOR$) in MeOH: formation of products **3–10**.



(1)

The formation of products **3–10** is explicable by the most likely mechanism that has been considered for benzyl-heteroatom compounds [1,2] and naphthylmethyl esters [6], as shown in Scheme 2. Ether **3** is derived from benzyl cation (path (i)). The products **4–10** are all derived from benzyl radicals: **4** and **5** are formed by coupling of benzyl radical with alkyl radical, **6** and **7** are their *para*-isomers (the formation mechanism of which will be discussed later), **8** is formed by hydrogen abstraction of benzyl radical, **9** by coupling of benzyl radicals, and **10** by the reaction of benzyl radical with MeOH. Among these radical products, **4–8** are formed mainly in cage and partly out of cage (paths (ii) and (iii)), and **9** and **10** are all out of cage (path (iii)). Benzyl alcohol derivatives **11** are also radical products, the formation mechanism of which will be discussed below. Styrene derivatives **12** obtained for methyl-substituted esters seem to be formed in the Norrish Type II reaction [6].

The yields of products, determined by GC, are given in Table 1. As in our previous case [6], the present experiments showed a poor mass balance of photoproducts: the total yields for **3–12** were only 35–70% of the esters consumed. Some of the rest were estimated to be high-boiling benzylic oligomers by GPC and GC measurements, the yields of which were determined to be always less than 10% by GC, and most of the others might be assigned to be oxygen-related compounds, as will be discussed later. Substituent effect on the photolysis will be described in the latter section.

3.2. Photophysical properties and multiplicity

Photophysical data for esters **1a–c** and **2a–c** are listed in Table 2. There is no essential difference in the photophysical properties of acetates **1** and pivalates **2**, as reported previously [6,10]. Introduction of methyl groups into the methylene carbon (α-position) of esters remarkably decreased the quantum yield (Φ_f) and lifetime (τ_f) of fluorescence. This observation is in contrast with our previous result that the corresponding naphthylmethyl esters show no substituent effect on the excited-state behavior [6]. It has been reported for alkylbenzenes that Φ_f, τ_f, and the quantum yield of intersystem crossing decrease in the order, toluene, ethylbenzene, cumene, and *tert*-butylbenzene, whereas that of internal conversion increases in that order [19]. Therefore, the enhanced non-radiative decay of methyl-substituted benzyl esters will be the consequence of the increased internal conversion.

Dissociation energies (BDE) for the methylene carbon–oxygen bond of the esters were calculated using the heats of formation (H_f) for the esters and the corresponding benzyl and acyloxy radicals, evaluated with a semiempirical MO method (PM3) incorporated into the MOPAC package of programs (Table 2) [20]. The excitation energies of esters were estimated from the wavelengths of the 0–0 band in the fluorescence and phosphorescence spectra to be 107 kcal/mol for the singlet state (E_S) and 82 kcal/mol for the triplet state (E_T), respectively. Apparently, the E_S and E_T values are higher than BDE for all esters so that the bond cleavage occurs possibly in both the excited singlet and triplet states.

It has been reported that only the singlet state contributes to photolysis of benzyl carboxylates [10] and phosphates [21]. To check the multiplicity for the present esters, sensitization and quenching experiments were done for pivalates **2a–c** (Table 3).

In acetone sensitization, the ester conversion increased in the order **2a** < **2b** < **2c**, reflecting their BDE values (Table 2). Only a minor amount of ether **3** was formed for all esters in the sensitization, while the direct irradiation provided a certain quantity of **3** (3–6%) (Table 1). This implies only a modest reactivity in the triplet state.

It should be noted that oxygen, working as a triplet quencher and a radical scavenger, scarcely decreased the ester conversion and did not inhibit the formation of radical products **4–10**, especially for the products **4–8** formed mainly in cage (Table 3). These results clearly indicate the neglected contribution of the triplet state in the present case.

Table 1
Product yields (%) for photolysis of **1a–c** and **2a–c** in MeOH[a]

Ester	Conversion[c]	Ether	Coupling	Coupling	Alkyl	Dimer[b]	Solvent-additive	Alcohol	Vinyl
		3	**4/5**	**6/7**	**8**	**9**	**10**	**11**	**12**
1a	78	18	13	–	trace	13	12	1	–
1b	59	12	9	trace	trace	5[d]	6	2	1
1c	30	8	5	trace	trace	6	3	6	19
2a	68	6	23	trace	8	12	4	trace	–
2b	52	3	15	3	5	8[d]	4	trace	1
2c	47	3	3	20	4	4	2	17	15

[a] [ester] = 0.02 M; irradiation time, 1 h; $\lambda_{ex} > 250$ nm; numbers are yields of products based on the ester consumed.
[b] Twice the molar yield.
[c] Yields for ester conversion.
[d] Total yield for *meso-* and *dl-* forms of 2,3-diphenylbutane.

Table 2
Photophysical properties of esters **1a–c** and **2a–c** in MeOH

Ester	E_s (kcal mol^{-1})[a]	Φ_f [b]	τ_f (ns)[c]	E_T (kcal mol^{-1})[d]	BDE (kcal mol^{-1})[e]
1a	107	0.05	[g]	[g]	73 (67)[f]
1b	107	0.03	[g]	[g]	65
1c	107	0.007	[g]	[g]	56
2a	107	0.05	10.4	82	70
2b	107	0.03	6.4	[g]	63
2c	107	0.007	0.5	82	52

[a] Singlet energy determined from the 0–0 band in the fluorescence spectrum in MeOH.
[b] Fluorescence quantum yield based on a value of 0.13 for toluene in MeOH [15].
[c] Fluorescence lifetime determined by single-photon counting [16].
[d] Triplet energy determined from the 0–0 band in the phosphorescence spectrum in methylcyclohexane at 77 K.
[e] Dissociation energy for methylene carbon–oxygen calculated by the PM3 method [6,20].
[f] See [36].
[g] Not determined.

Table 3
Conversion yields (%) for quenched and sensitized photolysis of **2a–c**[a]

					Ion	Radical	Radical	Alcohol
Ester	Additive	Conversion[b]	Relative conversion[c]	I_{rel}[d]	**3**	**4–8**	**9,10**	**11**
2a	acetone[e]	4	–	–	1	–	–	trace
	O_2[f]	62	0.91	0.35	4	12	9	3
	PP[g]	28 (48)	0.57	0.52	trace (trace)	11 (30)	9 (17)	trace (trace)
2b	acetone[e]	8	–	–	1	–	–	trace
	O_2[f]	56	1.08	0.48	2	17	4	4
2c	acetone[e]	23	–	–	2	13	46	4
	O_2[f]	42	0.89	0.57	3	21	trace	40

[a] [ester] = 0.02M; irradiation time, 1 h; $\lambda_{ex} > 250$ nm; numbers are yields of products based on the ester consumed.
[b] Yields for ester conversion.
[c] Yields for ester conversion normalized to those in the absence of additive.
[d] Ratio of the fluorescence intensities in the presence and absence of the additive.
[e] Irradiated in 2 : 8 acetone-MeOH; $\lambda_{ex} > 300$ nm: irradiation in MeOH at $\lambda_{ex} > 300$ nm caused no reaction.
[f] Irradiated in O_2-saturated MeOH.
[g] PP, *trans*-piperylene; [PP] = 0.013 M; irradiated in *tert*-butanol; numbers in parentheses are yields of products in the absence of additive.

There is, however, an unexpected fact that the quenching of the excited singlet states of **2a–c** by oxygen was efficient, but little photolysis quenching occurred: from the fluorescence lifetimes (τ_f) and the relative fluorescence intensities (I_{rel}), listed in Tables 2 and 3, respectively, the quenching rate constants (k_q) were determined to be $\sim 2 \times 10^{10}$ M^{-1} s^{-1} for **2a** and **2b** and $\sim 2 \times 10^{11}$ M^{-1} s^{-1} for **2c**. Therefore, the photolysis might involve an oxygen-assisted cleavage pathway (see below). The predominance of the singlet-state photolysis was further confirmed by the fact that *trans*-piperylene (PP), used as a triplet quencher, decreased the ester conversion and the fluorescence intensity to the same extent, but not perfectly. Thus, PP seems to work as a singlet quencher in this case.

Table 4
Charge densities of carbon atoms in benzyl-type radicals calculated by PM3

Radical	α-carbon	*para*-
Benzyl	−0.140	−0.103
1-Phenylethyl	−0.136	−0.111
Cumyl	−0.118	−0.116

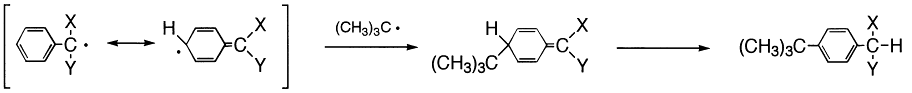
Table 5
Heats of formation (H_f) for products **5** and **7** calculated by PM3

	H_f (kcal mol^{-1})		
Ester	**5**	**7**	ΔH_f (kcal/mol^{-1})
2a	−4.6	−9.0	−4.4
2b	−8.1	−12.5	−4.4
2c	−8.8	−17.3	−8.5

3.3. Substituent effect on product yields

In agreement with Pincock's observation [10] and our previous result [6], the photolysis of pivalates **2** provided radical products preferentially and acetates **1** gave both ionic and radical products (Table 1), which may be ascribed to rapid decarboxylation of pivaloyloxy radical [10].

An interesting observation is that introducing methyl substituents into benzyl pivalates decreased the yield of coupling product **5** and increased that of the *para*-isomer **7**. Since most of alkylbenzenes **5**, **7**, and **8** are formed in cage (path (ii) in Scheme 2) for pivalates [6], we deduce that steric hindrance of α-substituted methyl groups suppresses the in-cage coupling of *tert*-butyl and substituted benzyl radicals in themselves, leading to the increase in the yield of **7**. In fact, Nelsen and Bartlett indicated that such *para* attack is significant in the reaction of *tert*-butyl and cumyl radicals. They assigned the product, which had not been isolated, to a quinoid structure [22]. Considering the fact that such quinoids are not very stable [23], it is speculated that the quinoid intermediates are transformed to the more stable *para*-isomers by the 1,5-hydrogen shift:



(2)

The preferred formation of the *para*-isomer **7c** for **2c** may be further supported by the results of the above-mentioned semiempirical MO calculations (PM3) [20]:

1. The charge densities of the carbon atom in the *para*-position of benzyl and 1-phenylethyl radicals are lower than those of the methylene and methine carbons, respectively, while the density in the *para*-position of cumyl radical is as high as that of the tertiary carbon (Table 4). Thus, cumyl radical has the increased reactivity in the *para*-position.
2. Comparison of the difference in the calculated H_f values (ΔH_f) for **5** and **7** shows that **7c** (ΔH_f ~ -9 kcal/mol) is more stabilized energetically than **7a** and **7b** (ΔH_f ~ -4 kcal/mol) (Table 5).

In contrast, acetates **1b** and **1c** yielded only a trace amount of *para*-isomers **6b** and **6c**, respectively, probably because of the less steric repulsion between methyl and substituted benzyl radicals formed in cage and the dominance of out-of-cage reaction paths (path (iii) in Scheme 2) [6].

The yields of out-of-cage products **3**, **9**, and **10** were also substituent dependent. The decreased yields of **3** for substituted esters are consistent with the expectation that benzyl cation would be the most reactive for nucleophilic reagents in the series of the α-substituted benzyl cations, which is probably a reflection of combined steric and electronic effects at the cation center [24]. At a glance, this situation seems to be the same for the formation of radical products **9** and **10**. However, we should note that cumyl radical is extremely susceptible to dimerization, or formation of **9c** [25]. Judging from a little difference in the total yields of products **5**, **7**, and **8** for **2a–c**, formed mainly in cage, the efficiencies of escape of geminate radicals from the cage seem to be not much different. Therefore, the decreased yields of **9** and **10** imply that the formation of **11**, **12**, or other unidentified products would compete with that of **9** and **10**.

3.4. Substituent effect on ester conversion

Note that the ester conversions for **1** and **2** also decreased with methyl substitution, as in the case of naphthylmethyl derivatives [6]: the quantum yields for ester conversion (Φ_r) were determined to be 0.091, 0.079, and 0.063 for **2a**, **2b**, and **2c**, respectively. We have demonstrated a large contribution of steric hindrance around the ester bond to the photocleavage. In the same way, as previously [6], calculated H_f values for pivalates **2** are plotted as a function of the rotational angle about the methylene carbon–oxygen bond in Fig. 1. Apparently, introduction of methyl substituents restricted the rotation. It can be further said that there are two stabilized conformations with angles of about 90° and 270° where the carbonyl and phenyl groups can interact spatially and may thus undergo the carbon–oxygen bond cleavage, and that substituted esters **2b** and **2c** would have a lower possibility of these 'reactive' conformations due to the increased barrier of rotation. Acetates **1** also showed the same tendency, though the absolute H_f values were lower. These results, consistent with those for naphthylmethyl esters [6], suggest the importance of conformational population in benzyl ester photochemistry.

There is another possible explanation for substituent dependence of the ester conversion: the enhanced deactivation processes in the excited singlet state for substituted esters (e.g., decrease in Φ_f and τ_f) may diminish the photocleav-

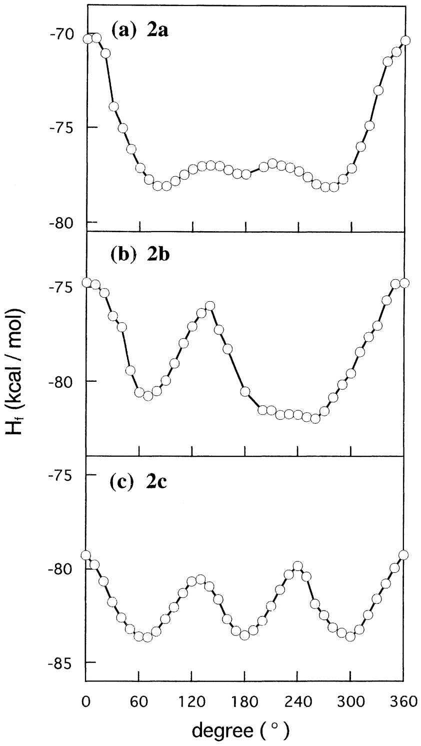


Fig. 1. Heats of formation (H_f) as a function of rotational angle about the methylene carbon–oxygen bond: (a) **2a**; (b) **2b**; (c) **2c**; the angle is taken as 0° when the carbonyl carbon eclipses the phenyl C_1 atom.

age (Table 2). However, we believe this effect to be minor because there is no close correlation between the excited state properties and the photoreactivities for naphthylmethyl derivatives [6] and ring-substituted benzyl esters [26].

3.5. Effect of oxygen on formation of alcohol **11**

The photolysis of substituted esters yielded a certain amount of alcohol **11**, the yield of which increased significantly with methyl substitution (Table 1). We have already encountered a similar phenomenon for naphthylmethyl esters and have considered mechanistic possibilities, including (i) homolytic cleavage of the acyl–oxygen bond (α-scission), (ii) oxidation with dissolved oxygen (O_2-oxidation), and (iii) formation of a charge-transfer complex (CT complex) [6]. We will inspect these possibilities in the present system.

The α-scission mechanism has been proposed for photolysis of several sterically hindered esters, which results in formation of oxidized products and/or liberation of CO gas [6,7,27,28]. As in the case of naphthylmethyl esters [6], the conformational analysis with the PM3 method assured that **2c** preferentially has a stabilized conformation with an angle of 180° about the acyl–oxygen bond where the carbonyl group always interacts spatially with the phenyl ring (data not shown), which might allow the acyl–oxygen bond cleavage and, thus, the formation of **11**. However, the oxygen concentration dependence cannot be explained by this mechanism, as will be discussed below.

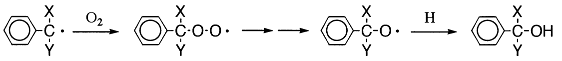
Table 6
Product yields (%) for photolysis of **2a** and **2c** in MeOH under argon atmosphere and in vacuum[a]

		Argon/Vacuum				
Ester	Conversion[b]	Ion **3**	Radical **5, 7–10**	Alcohol **11**	Vinyl **12**	SUM **3–12**
2a	68/67	6/9	47/64	trace/–	–/–	53/83
2c	47/31	3/4	34/59	17/trace	15/32	69/96

[a] [ester] = 0.02M; irradiation time, 1 h; $\lambda_{ex} > 250$ nm; numbers are yields of products based on the ester consumed.

[b] Yields for ester conversion.

The O_2-oxidation mechanism seems to involve an initial reaction of benzyl radical with dissolved oxygen to form benzylperoxide and then benzyloxy radicals. Hydrogen abstraction will finally give benzyl alcohol:



(3)

This mechanism practically promoted the photolysis of pivalates **2** in the O_2-saturated solution where the formation of out-of-cage radical products **9** and **10** decreased and the yield of alcohol 11 increased remarkably (Table 3). Thus, the participation of oxygen in the photolysis under argon atmosphere must be considered. We subsequently irradiated **2a** and **2c** after freeze–pump–thaw degassing (Table 6). Almost complete degassing for both esters actually inhibited the formation of alcohol **11** and facilitated the other pathways. This confirms a certain contribution of oxygen to the photolysis under argon atmosphere. A few workers have already noticed that the photoreactivity of benzyl-type compounds is very sensitive to low oxygen concentration, but have had no clear reason [7,8]. We further note a remarkable increase in the total yield of products **3–12** in vacuum. Thus, most of the unidentified products for the present esters under argon atmosphere may be oxygen-related compounds. It is, however, unexpected that the photolysis of 0.02M of **2c** under argon atmosphere yielded 2×10^{-3} M of **11c** (Table 1), which was as high as the oxygen concentration of air-saturated MeOH solution [29], i.e., far beyond an expected concentration of oxygen dissolved in MeOH under argon atmosphere. This fact may exclude such dynamic pathways via a collision of benzyl radical and dissolved oxygen for formation of **11** as in eq. (3).

A likely mechanism is the formation of a CT complex, since aromatic compounds and oxygen are known to form complexes [30]. Pasternak and Morduchowitz [31] reported that irradiation of cumene under oxygen atmosphere yielded cumyl alcohol exclusively and efficiently compared with those of toluene and ethylbenzene, which was not in conflict with the present result. They proposed a mechanism involving the formation of excited CT complexes formed between alkylbenzenes and oxygen, followed by dissociation to yield benzylperoxide and then benzyl alcohol. Kojima et al. [32–34] demonstrated that photoexcitation of CT complexes of styrene derivatives and oxygen induced electron transfer to afford styrene dimers and oxidized products.

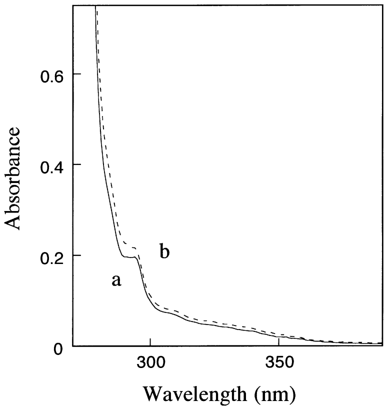


Fig. 2. Absorption spectra of ester **2a** in MeOH under argon (a) and oxygen (b) atmosphere: [ester] = 0.1 M; cell length, 10 cm.

Complex formation for all the present esters was evidenced by the observation of a slightly tailed absorption band in the O_2-saturated solution, which was reasonably assigned to the CT band. A typical spectrum for **2a** is shown in Fig. 2. It is thus likely that the effect of oxygen is attributed to the formation of an excited CT complex between the esters and an oxygen molecule. At this stage, however, we could not refer to mechanistic possibilities for the succeeding reaction paths.

More noticeable is a marked oxygen effect on the photolysis of cumyl esters. First, a significant amount of alcohol **11** was formed preferentially for cumyl esters **1c** and **2c** (Table 1). Second, the excited singlet-state quenching by oxygen was far more effective for **2c** than for **2a** and **2b**, as described above: the apparent k_q value for **2c** was still beyond the diffusion control limit ($1.2 \times 10^{10}\ M^{-1}\ s^{-1}$ at 25°C in MeOH [35]). Third, the ester conversion of **2c** decreased in vacuum, while that of **2a** did not (Table 6). These facts not only suggest a stronger interaction of cumyl esters and oxygen, but also may support the presence of an oxygen-assisted cleavage pathway.

It can thus be concluded that oxygen affects both product formation and photocleavage paths and that the formation of alcohol **11** under argon atmosphere, being concerned mostly in the latter one, favors a mechanism, including excited CT complex formation.

4. Conclusions

In this paper, we have shown for α-substituted benzyl esters that a distinct effect of α-substitutents on both ester conversions and products yields results from steric hindrance around the ester bond. This result, which is qualitatively consistent with our previous one for naphthylmethyl esters [6], confirms the generality of steric effect on the photochemistry of this type of arylmethyl esters. Furthermore, the fact that formation of alcohol **11** is very sensitive to oxygen in low concentration, suggests that an oxygen-assisted photolysis path via excited CT complex formation is still working under argon atmosphere.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 09650977) and a Grant-in-Aid for COE Research (No. 10CE2003) from the Ministry of Education, Science, Sports and Culture of Japan.

References

[1] J.A. Pincock, Acc. Chem. Res. 30 (1997) 43.
[2] W.M. McGowan, E.F. Hilinski, J. Am. Chem. Soc. 117 (1995) 9019.
[3] J.A. Pincock, P.J. Wedge, J. Org. Chem. 60 (1995) 4067.
[4] S.M. Nevill, J.A. Pincock, Can. J. Chem. 75 (1997) 232.
[5] P.J. Wagner, B. Zhou, T. Hasegawa, D.L. Ward, J. Am. Chem. Soc. 113 (1991) 9640.
[6] Y. Itoh, M. Gouki, T. Goshima, A. Hachimori, M. Kojima, T. Karatsu, J. Photochem. Photobiol. A: Chem. 117 (1998) 91.
[7] M. Iwamura, T. Furuta, S. Fuchibe, A. Momotake. In: Abst. 15th IUPAC Symp. on Photochemistry, Prague, July 1994, p. 437.
[8] S.A. Fleming, A.W. Jensen, J. Org. Chem. 61 (1996) 7040.
[9] E. Detilleux, J. Jadot, Bull. Soc. Roy. Sci. Liege 24 (1955) 366.
[10] J.W. Hilborn, E. MacKnight, J.A. Pincock, P.J. Wedge, J. Am. Chem. Soc. 116 (1994) 3337.
[11] F. Hammerschmidt, A. Hanninger, Chem. Ber. 128 (1995) 1069.
[12] T. Inoue, K. Koyama, T. Matsuoka, K. Matsuoka, S. Tsutsumi, Kogyo Kagaku Zasshi 66 (1963) 1659.
[13] T. Yamamoto, Bull. Chem. Soc. Jpn. 40 (1967) 642.
[14] A.A. Khalaf, R.M. Roberts, J. Org. Chem. 31 (1966) 926.
[15] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, 2nd ed. Marcel Dekker, New York, 1993, p. 50.
[16] T. Karatsu, A. Kitamura, H. Zeng, T. Arai, H. Sakuragi, K. Tokumaru, Bull. Chem. Soc. Jpn. 68 (1995) 920.
[17] Y. Itoh, M. Inoue, A. Hachimori, K. Abe, Polym. Adv. Tech. 8 (1997) 35.
[18] T. Ichimura, M. Iwai, Y. Mori, J. Phys. Chem. 92 (1988) 4047.
[19] W.W. Schloman Jr., H. Morrison, J. Am. Chem. Soc. 99 (1977) 3342.
[20] MOPAC Ver. 6: J.J.P. Stewart, QCPE Bull. 9 (1989) 10.
[21] R.S. Givens, B. Matuszewski, P.S. Athey, M.R. Stoner, J. Am. Chem. Soc. 112 (1990) 6016.
[22] S.F. Nelsen, P.D. Bartlett, J. Am. Chem. Soc. 88 (1966) 137.
[23] M.J. Gibian, R.C. Corley, Chem. Rev. 73 (1973) 441.
[24] R.A. McClelland, C. Chan, F. Cozens, A. Modro, S. Steenken, Angew. Chem. Int. Ed. Engl. 30 (1991) 1337.
[25] S.A. Weiner, G.S. Hammond, J. Am. Chem. Soc. 91 (1969) 986.
[26] T. Goshima, Y. Itoh, M. Kojima, unpublished results, 1999.
[27] L.O. Ruzo, R.L. Holmstead, J.E. Casida, Tetrahedron Lett. 35 (1976) 3045.
[28] S.B. Simmers, S.S. Hobbs, D.J. Downs, T.J. Hutt, B.A. Degraff, J. Photochem. Photobiol. A: Chem. 41 (1988) 347.
[29] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, 2nd ed. Marcel Dekker, New York, 1993, p. 291.
[30] E.C. Lim, V.L. Kowalski, J. Chem. Phys. 36 (1962) 1729.
[31] M. Pasternak, A. Morduchowitz, Tetrahedron Lett. 24 (1983) 4275.
[32] M. Kojima, H. Sakuragi, K. Tokumaru, Bull. Chem. Soc. Jpn. 60 (1987) 3331.
[33] M. Kojima, H. Sakuragi, K. Tokumaru, Bull. Chem. Soc. Jpn. 62 (1989) 3863.
[34] M. Kojima, A. Ishida, S. Takamuku, Bull. Chem. Soc. Jpn. 71 (1998) 2211.
[35] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, 2nd ed. Marcel Dekker, New York, 1993, p. 208.
[36] D.F. McMillen, D.M. Golden, Ann. Rev. Phys. Chem. 33 (1982) 493.