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Steric effect on photochemistry of benzyl ester derivatives 1. Photolysis of 1-(naphthyl)ethyl alkanoates in methanol

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Abstract

The photochemistry of naphthylmethyl (NpM) and 1-(naphthyl)ethyl (NpE) alkanoates, **1a–d** and **2a–d**, has been examined in methanol (MeOH). Measurements of quantum yields for fluorescence and intersystem crossing and lifetimes for excited singlet and triplet states established similar photophysical behavior for all the esters studied here. The irradiation produced methyl NpM (or NpE) ether **3** and in-cage coupled product **4** as the major ionic and radical products, respectively. The conversion was found to be substituent-dependent, varying from 95% for **1c** (2-NpMA) to 52% for **2b** (1-NpEP). In contrast, a poorer correlation between the product distribution and ester structure was observed. The results indicate an important contribution of steric hindrance around the ester bond to the photocleavage. Steric effect on the stabilization of ionic and radical intermediates **I–III** in Scheme 1 also perturbed the product distribution. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Benzyl ester derivatives; Photolysis; Naphthylmethyl

1. Introduction

Photochemistry of arylmethyl–heteroatom compounds in polar solvents has been a continued interest to photochemists because of the diversity of photoreactivity [1,2]. Much of the work is based on a mechanism for substituted benzyl acetates originally proposed by Zimmerman and Sandel [3,4] that the competition between homolytic versus heterolytic cleavage of the arylmethyl–heteroatom bond is responsible for formation of radical-derived and ion-derived products and that the ease of photoheterolysis follows the reverse of ground-state reactivity; i.e., *meta*-substituted benzyl derivatives give higher yields of ionic products than *para*-substituted ones. On the other hand, Pincock et al. [5] have recently published an extensive study on the photolysis of a series of substituted 1-naphthylmethyl (1-NpM) and benzyl esters in methanol (MeOH). They proposed a mechanistic extreme of homolytic cleavage followed by ground-state electron transfer as the dominant pathway for formation of ion pair intermediates and thus ion-derived products. At the present stage, as for photocleavage of arylmethyl esters ($ArCH_2OCOR$), there is still room for improvement on a mechanistic conclusion: whether photoheterolysis does preferentially occur or not. A general mechanism for the esters is shown in Scheme 1, where for simplicity multiplicity is omitted.

We have been investigating photophysics and photochemistry of various types of polymers containing aromatic chromophores [6], which serve as 'photon-harvesting' polymers [7] and 'photozymes' [8]. Recently, we accidentally found that polymers containing 1-(2-naphthyl)ethyl (2-NpE) ester residues underwent facile photocleavage in MeOH and water [9] and that their photoreactivity was much different from those for the corresponding monomer model compound, 2-NpE pivalate [9] and 1-NpM ester derivatives [10–12]. We speculate some contribution of steric hindrance of the substituent groups and polymer chains to the photocleavage.

Steric effect on photochemistry has already received notice, e.g., Wagner et al. [13] have succeeded sterical control of ground-state conformation and photoreactivity for methyl-substituted α-arylacetophenones. The importance of conformational populations in benzyl ester photo-

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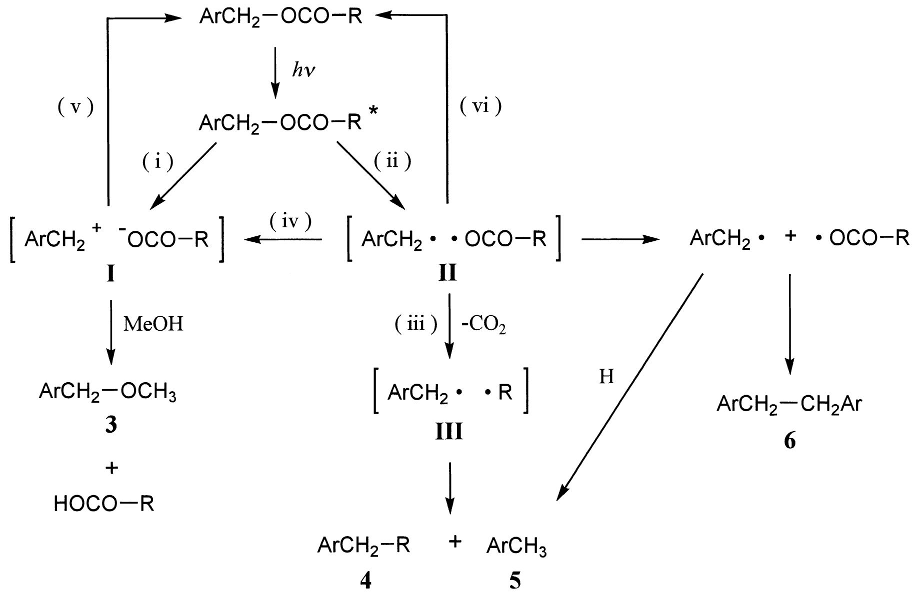
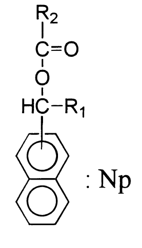


Scheme 1. General mechanism for the photolysis of arylmethyl esters ($ArCH_2OCOR$) in MeOH.



Np	R_1	R_2: $-CH_3$	R_2: $-C(CH_3)_3$
1-Np	-H	**1a** (1-NpMA)	**2a** (1-NpMP)
1-Np	$-CH_3$	**1b** (1-NpEA)	**2b** (1-NpEP)
2-Np	-H	**1c** (2-NpMA)	**2c** (2-NpMP)
2-Np	$-CH_3$	**1d** (2-NpEA)	**2d** (2-NpEP)

Fig. 1. Structural formulae and abbreviations of esters **1a–d** and **2a–d**.

chemistry has also been indicated for indanyl derivatives by Pincock and Wedge [14]. In the present work, the photocleavage reactions of NpM and NpE acetates **1a–d** and pivalates **2a–d** in MeOH have been studied (Fig. 1). Here, the results will be discussed using a general mechanism including two possible pathways for formation of ion-derived products, photoheterolysis and ground-state electron transfer paths, as shown in Scheme 1.

2. Experimental details

2.1. Materials

1-Naphthylmethanol and 2-naphthylmethanol were purchased from Aldrich. 1-(1-Naphthyl)ethanol and 1-(2-naphthyl)ethanol were prepared from ketones by reduction with lithium aluminum hydride in tetrahydrofuran (THF). Acetates and pivalates were prepared by reacting the corresponding alcohols with acetyl chloride and pivaloyl chloride, respectively, in triethylamine-THF mixtures [9]. The crude products were purified by recrystallization from *n*-hexane or by silica-gel column chromatography with benzene as an eluent. The products were characterized by ^{1}H-NMR and GC–MS spectroscopy: the data for **1a**, **2a**, and **2d** were identical with those reported previously [15,16,9].

1b (1-NpEA): colorless oil; ^{1}H-NMR ($CDCl_3$) δ 1.68 (d, 3H, J=6.6 Hz), 2.08 (s, 3H), 6.65 (q, 1H, J=6.5 Hz), 7.3–8.1 (m, 7H).

1c (2-NpMA): m.p. 55–56°C [lit., 49.5–51.5°C] [17]; ^{1}H-NMR ($CDCl_3$) δ 2.00 (s, 3H), 5.14 (s, 2H), 7.1–7.9 (m, 7H).

1d (2-NpEA): colorless oil; ^{1}H-NMR ($CDCl_3$) δ 1.50 (d, 3H, J=6.4 Hz), 1.92 (s, 3H), 6.11 (q, 1H, J=6.4 Hz), 7.0–7.9 (m, 7H).

2b (1-NpEP): colorless oil; ^{1}H-NMR ($CDCl_3$) δ 1.20 (s, 9H), 1.63 (d, 3H, J=6.6 Hz), 6.61 (q, 1H, J=6.5 Hz), 7.2–8.2 (m, 7H).

2c (2-NpMP): m.p. 30–31°C; ^{1}H-NMR ($CDCl_3$) δ 1.15 (s, 9H), 5.08 (s, 2H), 7.1–7.8 (m, 7H).

Ethers **3a–d** were prepared by reacting the corresponding alcohols with NaH followed by CH_3I. The crude products were purified by silica-gel column chromatography with benzene as an eluent. The NMR data for **3a** and **3b** were identical with those reported previously [12,18].

3c ($2\text{-}NpCH_2OCH_3$): yellowish oil; ^{1}H-NMR ($CDCl_3$) δ 3.31 (s, 3H), 4.48 (s, 2H), 7.3–8.0 (m, 7H).

3d ($2\text{-}NpCH(CH_3)OCH_3$): yellowish oil; ^{1}H-NMR ($CDCl_3$) δ 1.46 (d, 3H, J=6.4 Hz), 3.23 (s, 3H), 4.41 (q, 1H, J=6.4 Hz), 7.3–8.0 (m, 7H).

The radical coupling product **4d′**, 2,2-dimethyl-3-(2-naphthyl)butane, was isolated from the products of preparative photolysis of 2-NpEA in MeOH by silica-gel column chromatography: colorless oil; ^{1}H-NMR($CDCl_3$) δ 1.13 (s, 9H), 1.48 (d, 3H, J=7.3 Hz), 2.85 (q, 1H, J=7.3 Hz), 7.4–8.0 (m, 7H).

For other photoproducts, neither isolation nor preparation was attempted. They were identified by GC–MS and determined by GC using authentically analogous compounds, many of which were commercially available.

2.2. Measurements

^{1}H-NMR spectra were recorded on a JEOL FX-90Q spectrometer. Mass spectra were obtained on a Shimadzu GCMS-QP1000 spectrometer. GC analysis was performed on a Hitachi 263–70 gas chromatograph equipped with a flame-ionization detector on either a 2% silicon OV-17 or 5% PEG 20M-P column. Phenanthrene was used as an internal standard.

Fluorescence spectra were obtained on a Shimadzu RF-5000 spectrofluorometer. All samples were degassed by bubbling with argon gas for 15 min. Fluorescence quantum yields were determined by a comparison with that of 0.16 for 2-methylnaphthalene in MeOH [19]. Fluorescence lifetime measurements were performed on a single-photon-counting instrument using an excitation of 280 nm. Details of instrumentation and data analysis have been described elsewhere [20]. Transient absorption spectra were measured by a conventional laser–flash photolysis system (fourth harmonics of Nd–YAG laser; 266 nm, 10 nm fwhm, 7 mJ/pulse) [21]. Quantum yields for the intersystem crossing (Φ_{ISC}) of **1a** and **2c** were determined by a comparison with that of naphthalene (Φ_{ISC}=0.80) [22] in the manner similar to that previously reported [23].

Irradiations were carried out with a 500 W high-pressure mercury lamp (EIKOSHA, EHB-W-500) in a merry-go-round apparatus. A 0.01 M solution (8 ml) of the ester in MeOH was placed in a quartz tube, purged with argon for 15 min prior to photolysis, and irradiated for 1 h at 25°C. The photolysis samples were analyzed by GC as described above.

3. Results and discussion

3.1. Emission properties

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

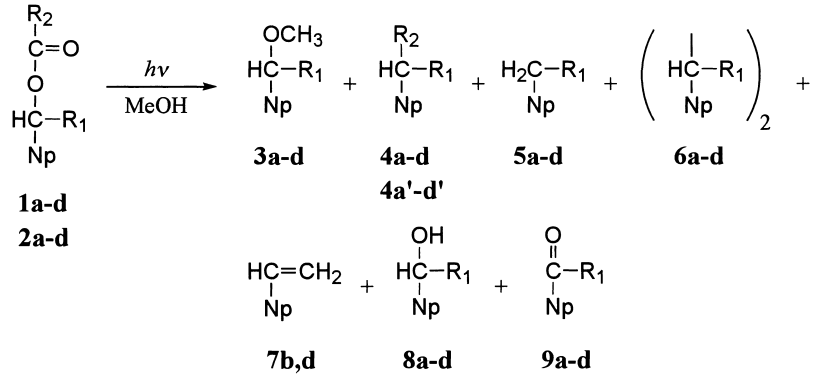
Ester	Φ_f[a]	τ_f (ns)[b]	Φ_{ISC}[c]	τ_T (μs)[d]
1a (1-NpMA)	0.12	39	0.74[e]	10 (11)[e]
1b (1-NpEA)	0.13	38		
1c (2-NpMA)	0.12	37		
1d (2-NpEA)	0.14	35		
2a (1-NpMP)	0.13	35		
2b (1-NpEP)	0.13	36		
2c (2-NpMP)	0.12	36	0.75[e]	12 (16)[e]
2d (2-NpEP)	0.13	38		

[a] Fluorescence quantum yield relative to 2-methylnaphthalene of 0.16 [19].
[b] Fluorescence lifetime.
[c] Quantum yield of intersystem crossing.
[d] Triplet-state lifetime.
[e] Measured in acetonitrile.

Photophysical data for esters **1a–d** and **2a–d** in the excited singlet and triplet states in MeOH are listed in Table 1. Although the fluorescence quantum yields (Φ_f) and fluorescence lifetimes (τ_f) for **1a** and **2a** are somewhat smaller than those reported in the literature [11], the similarity in the values for all esters clearly indicates that the presence of the methyl group at the methylene position, the substituent position of the naphthyl (Np) ring, and the alkyl acid groups have little effect on the intrinsic excited-state properties of the Np residues. From these results and the lower triplet energies for Np compounds (ca. 250 kJ mol^{-1}) [12,24], it can be assumed that the bond cleavage (C–O: ca. 270 kJ mol^{-1} [25]) occurs solely in their excited singlet state [26] and that the change in the photoreactivity does not reflect their intrinsic deactivation processes such as fluorescence and intersystem crossing. In photochemistry of ring-substituted naphthylmethyl and benzyl esters [12,27], by contrast, one would have to take into account their different excited-state properties to probe the mechanism, as pointed out previously [4,28].

3.2. Product analysis

Irradiation of each ester in MeOH resulted in the formation of two major products, ether **3** and coupling product **4**, and other products **5–9**:



(1)

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

Ester	Conv. (%)[c]	Ether	Coupling	Alkyl	Dimer[b]	Vinyl	Alcohol+ketone
		3	**4**	**5**	**6**	**7**	**8**+**9**
1a (1-NpMA)	94	52 (55)	<1	<1	<1		≈1
1b (1-NpEA)	65	51 (78)	<1	<1	–[d]	<1	≈1
1c (2-NpMA)	95	60 (64)	4	<1	<1		≈2
1d (2-NpEA)	94	53 (57)	4	<1	–[d]	2	≈4
2a (1-NpMP)	82	40 (49)	3	1	<1		≈2
2b (1-NpEP)	52	21 (40)	3	1	–[d]	<1	≈2
2c (2-NpMP)	91	18 (20)	20 (22)	7	5		≈4
2d (2-NpEP)	86	10 (12)	16 (19)	7	9	2	≈6

[a] [ester]=1.0×10^{-2} M; irradiation time, 1 h; numbers in parentheses are yields of products based on the ester consumed.
[b] Twice the molar yield.
[c] Yields for ester conversion.
[d] Not determined.

The yields for disappearance of the esters and for appearance of the photoproducts were determined by GC analysis (Table 2). Pincock et al. reported an excellent mass balance of photoproducts for 1-NpM esters [10–12]. In the present experiments, by contrast, the total yields of products **3–9** were only 50–80% of the esters consumed and the rest were not still identified (see below), although the yield ratios of **3** and **4** for **1a** and **2a** were close to those they reported [11]. Similar results were obtained by irradiation with a 60 W low-pressure mercury lamp (effective excitation wavelength, λ=254 nm) and a 500 W high-pressure mercury lamp through Pyrex (λ>300 nm), indicating little wavelength effect on their photoreactivity. In addition, we confirmed that the product distribution does not change essentially except for **7** during the course of the irradiation, while the results reported here were obtained at high conversion runs. Thus, we have no reason for the above difference at this stage.

For pivalates **2a–d**, moderate amounts of alkylnaphthalene **5** and out-of-cage dimer **6** were obtained. The former would be mainly produced by disproportionation between the NpM (or NpE) and *tert*-butyl radicals in cage because of a higher degree of disproportionation of *tert*-butyl radicals [29]:

$$[\mathrm{NpCHR_1}^{\bullet}\ {}^{\bullet}\mathrm{C(CH_3)_3}] \rightarrow \mathrm{NpCH_2R_1} + \mathrm{H_2C} = \mathrm{C(CH_3)_2} \qquad (2)$$

The dominance of the in-cage reaction was confirmed by the fact that the photolysis of **2c** (2-NpMP) in CD_3OD resulted in no deuterium incorporation into **5c**; i.e., no D-abstraction of the 2-NpM radical from CD_3OD occurred. In contrast, the irradiation of **1c** (2-NpMA) in CD_3OD lead to the formation of 2-$NpCH_2D$, though the yield was very low (<1%).

For NpE esters, minor amounts of vinylnaphthalene **7** ($\leq$2%) were identified. Since abstractable hydrogens are available on the carbon γ to the carbonyl group, then Norrish type II process should occur. Hydrogen elimination of the NpE radicals in and out of cages must be also considered. However, little effect of oxygen, a radical scavenger, on the relative yield of **7** excludes the possibility of an out-of-cage radical reaction path (Table 3). Furthermore, the fact that *tert*-butyl radical abstracts hydrogen from alkyl radicals much less efficiently than methyl radical [29] would not explain the formation of **7** for the pivalates via an in-cage radical path. The formation of **7** in the photolysis of the above esters in non-polar solvents such as benzene and hexane would also rule out an ionic pathway [24].

We note that the photolysis is accompanied by formation of certain amounts of unusual products, alcohol **8** and naphthaldehyde or acetonaphthone **9**, the yields of which fluctuated slightly. This trend becomes important for the 2-NpE esters. The fact that oxygen markedly increases the relative amounts of **8** and **9** along with the disappearance of **6** is suggestive of their origin in the reaction of NpM (or NpE) radicals with the dissolved oxygen (Table 3). Here,

Table 3
Product yields (%) for photolysis of **2d** (2-NpEP) in MeOH under O_2 atmosphere[a]

Condition	Conv. (%)[c]	Ether	Coupling	Alkyl	Dimer[b]	Vinyl	Alcohol	Ketone
		3	**4**	**5**	**6**	**7**	**8**	**9**
Ar	86	10	16	7	9	2	2	4
O_2	38	10	16	5	–0	3	8	28

[a] [ester]=1.0×10^{-2} M; irradiation time 1 h; numbers are yields of products based on the ester consumed.
[b] Twice the molar yield.
[c] Yields for ester conversion.

the decreased conversion of the ester is due to the quenching of the excited singlet-state by oxygen. Under argon atmosphere, however, the total yields of **8** and **9** ($>10^{-4}$ M) seem to be beyond the oxygen concentration in the MeOH solution: for reference, air-saturated MeOH solutions contain as high as 2×10^{-3} M of oxygen [30]. In this connection, we have found that under argon atmosphere photolysis of 0.02 M of 2-phenyl-2-propyl pivalate, analogous to the present esters, yielded 2×10^{-3} M of the corresponding alcohol [24]. Thus the dissolved oxygen may not be the main origin of the oxygen atoms in **8** and **9**. We and others have also observed for photolysis of some NpM ester derivatives that the yields of oxidized products analogous to **8** and **9** respond to very low concentration of oxygen [24,31]. This fact must lead not to exclude a possibility of some specific interaction of the esters and dissolved oxygen such as formation of a charge-transfer complex [32]. An alternative explanation may involve a homolytic cleavage of the acyl-oxygen bond followed by hydrogen addition or abstraction:

$$\mathrm{NpCHR_1-OCO-R_2} \xrightarrow{h\nu} [\mathrm{NpCHR_1-O^{\bullet}\ {}^{\bullet}CO-R_2}] \xrightarrow{+\mathrm{H}\ \mathrm{or}\ -\mathrm{H}} \underset{\mathbf{8}}{\mathrm{NpCHR_1}-\mathrm{OH}} + \underset{\mathbf{9}}{\mathrm{Np(C=O)R_1}} + \mathrm{CO} + {}^{\bullet}\mathrm{R_2} \tag{3}$$

In fact, formation of products like **8** and **9** and/or liberation of CO gas have been reported for some arylmethyl esters [31,33,34]. They commonly have a branched structure in the alcohol moiety. This implies that steric hindrance around the ester bond permits the cleavage of the acyl–oxygen bond to some extent.

Besides the products **3–9**, various but small amounts of high-boiling products, not enough to allow isolation and characterization, were detected by GC. However, it can be safely said that most of these products are formed by coupling of more than three radical components because of the followings: (1) For some esters, *tert*-butyl- or methyl-substituted dimers were characterized by GC–MS. (2) In the presence of oxygen, no high-boiling products were formed. (3) GPC analysis indicated the formation of polymeric compounds containing Np groups (molecular weight $<10^3$). The amounts of these products for pivalates tended to increase with decreasing those of in-cage products **3–5**. However, strange to say was that their total yields were estimated to be at most 15%, which was far less than the estimated yields for undefined products other than **3–9** (20–50%). The cause of this apparent difference needs to be investigated further.

3.3. Substituent effect on ester conversion

In most of photocleavage reactions where either ionic or radical products are formed exclusively, quantum yields for disappearance of starting compounds are parallel with those for appearance of photoproducts mainly because the stabilities of ionic or radical intermediates dominate the reaction. In the former photoheterolysis reaction, substituent effect can often be correlated with Hammet σ values [35]. Such tendency was not observed for the present case: neither the yields of the ionic product **3** and the radical products **4–6** nor the ratios of those were correlated with the yields for the ester conversion (Table 2).

Interestingly, the ester conversion was found to be structure dependent: the yields were in the order: (1) 2-Np derivatives>1-Np derivatives; (2) NpM esters>NpE esters; (3) acetates>pivalates. This result will be discussed in detail from several viewpoints: stability of intermediates, internal return, steric hindrance, etc.

If the cleavage efficiencies of the esters are governed by the stabilities of intermediates **I–III** in Scheme 1 and the stabilities are related closely to those of the free radicals and ions corresponding to the intermediate components, the above orders seem to be opposite. To probe into this problem, heats of formation (H_f) and ionization potentials (IP) for the free radicals and ions were evaluated with a semiempirical MO method (PM3) incorporated into the MOPAC package of programs (Table 4) [36]. Although the calculated values were not necessarily in agreement with experimental ones [37–39], a rough comparison for the interested pairs would be satisfactory: the values for the

Table 4
Calculated heats of formation (H_f) and ionization potentials (IP) for radicals and ions[a]

Radical	H_f (kcal mol^{-1})	IP (eV)	Ion	H_f (kcal mol^{-1})	IP (eV)
1-NpM •	69.7	7.53	1-NpM$^+$	235.8	
1-NpE •	58.8	7.44	1-NpE$^+$	220.9	
2-NpM •	70.3	7.64	2-NpM$^+$	238.0	
2-NpE •	60.1	7.65	2-NpE$^+$	222.6	
CH_3COO •	−45.2	12.3	CH_3COO^-	−119.6	3.93
$(CH_3)_3COO$ •	−59.8	12.2	$(CH_3)_3COO^-$	−135.1	4.07
CH_3 •	29.8	9.84			
$(CH_3)_3C$ •	−6.0	8.39			

[a] MOPAC Ver. 6: parameters; PM3, DOUBLET (radical), charge=1 or −1 (ion).

2-Np, NpM, and acetate derivatives were nearly equal to or larger than those for the 1-Np, NpE, and pivalate ones, respectively. Therefore, it may be said that the stabilities of the 'free-type' radical and ion intermediates do not dominate the photocleavage reactions. Using the H_f values given in Table 4, those for the starting ester compounds, and the singlet electronic excitation energies, calculated from the 0–0 band for the ester fluorescence, the heats of the photoheterolysis (i) and photohomolysis (ii) reaction paths in Scheme 1 were roughly estimated (data not shown). The values increased in the order: 1-NpEP<1-NpEA<2-NpEP<2-NpEA<1-NpMP<1-NpMA<2-NpMP<2-NpMA. The order for the heat of the electron transfer path (iv), calculated in the same way, also showed a similar trend. Interestingly, these qualitatively follow the opposite order in the yield for the ester conversion in Table 2. This clearly indicates that the photocleavage of the present esters does not respond to the reaction energies.

Givens et al. [26] reported that the yield of photocleavage for 2-NpM phenylacetate in benzene, where a homolysis process only occurred, was 10-fold larger than that for 1-NpM phenylacetate. This reversal of ground-state reactivity has been interpreted in terms of the change in charge distribution of the excited state from the ground state, which basically parallels with the 'meta effect' originally proposed by Zimmerman and Sandel [3]. This proposal can explain the increased yields for ester disappearance and product appearance for the present 2-Np derivatives (Table 2). On the other hand, negligible difference in the excited-state reactivity is expected for the NpM and NpE esters and the acetates and pivalates because the methyl substituents and the acid groups do not attach directly to the Np rings. Thus extending the above concept to the latter two cases may not be valid.

Internal returns (IR) from the ion pair and radical pair intermediates (v and vi in Scheme 1) are important pathways for decreasing the ester conversion. However, no attempt was made to determine the IR efficiencies for the present esters. Kim and Pincock [18] estimated the efficiency to be ca. 30% for 1-NpE phenylacetate in MeOH by monitoring ^{18}O exchange between the alcohol and carbonyl oxygens, and proposed that IR occurs mainly through a contact radical pair corresponding to **II** in Scheme 1 in the present case. Here, if this 'radical-pair' path is dominant, IR for the present pivalates will occur more efficiently than that for the acetates because of the lower yields for the formers (Table 2). However, this is unlikely because extremely efficient decarboxylation (iii) for pivalates [11] should decrease the IR efficiency and thus increase the ester conversion. Furthermore, we note the result of Givens et al. [40] that the quantum yields of ^{18}O scrambling for NpM and benzyl phenylacetates in nonpolar solvents are parallel to the cleavage yields. These results lead to two possibilities that (1) IR is not a predominant factor for the decreased photoreactivity and (2) ^{18}O scrambling yields do not respond to the 'true' IR efficiencies. Anyhow, the present results could not be explained simply in terms of IR.

It should be noted that the most reactive compound is **1c** (2-NpMA) and the least dissociative one is **2b** (1-NpEP) (Table 2). This finding reminds us of a contribution of steric hindrance to the photocleavage reaction: the higher the steric hindrance around the ester bond is, the lower the ester conversion yield is. To estimate the extent of this steric factor, rotational energies for the esters were evaluated using the PM3 method. In Fig. 2, the calculated H_f values for the esters are plotted as a function of the rotational angle about the methylene carbon–oxygen bond. It appears that all the NpM esters rotate in a similar way and as freely as *n*-butane does about the center C–C bond (Fig. 2(a)) [41]. In the NpE esters, by contrast, repulsive forces between the methyl substituent and the neighboring hydrogen atoms on the Np ring restrict the rotation, i.e., the rotational angles

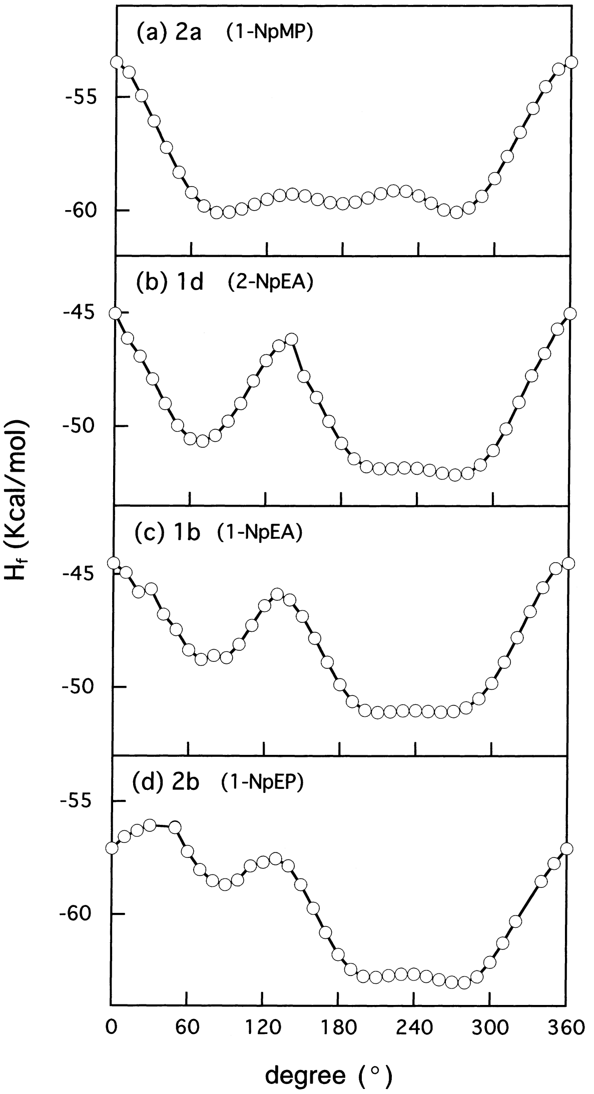


Fig. 2. Heats of formation (H_f) as a function of rotational angle about the methylene carbon–oxygen bond: (a) **2a** (1-NpMP) (b) **1d** (2-NpEA) (c) **1b** (1-NpEA) (d) **2b** (1-NpEP).

and preferred conformations are limited (Fig. 2(b)). This restriction is slightly greater for the 1-Np derivatives (Fig. 2(c)), and the bulkiness of *tert*-butyl groups in the pivalates has an additive effect (Fig. 2(d)); i.e., a conformation with an angle of about 90° is destabilized energetically in that order. As a result, the degree of rotational freedom for the NpE esters will decrease in the order: 2-NpEA>2-NpEP>1-NpEA>1-NpEP, which is in accord with the decrease in the yield for ester conversion (Table 2). Therefore, it can be concluded that steric effect is of importance in the photocleavage of the NpE esters. We further speculate that the conformation with an angle of about 90°, where the carbonyl group interacts spatially with the Np ring, is preferred for the photocleavage reaction. These facts may support the result of Nevill and Pincock [42] that an extremely hindered 1-NpE ester does not undergo the C–O bond cleavage. It should be also noted that, compared with the rotation about the methylene carbon–oxygen bond for the NpE esters, the rotation about the acyl–oxygen bond is not restricted remarkably (Fig. 3), and it shows little substituent dependence. These might allow the homolytic cleavage of the acyl–oxygen bond, in particular for the NpE esters, to yield oxidized products **8** and **9** (Eq. (3)).

It is reasonable to assume that the components of the intermediates **I** and **II** are geometrically analogous to the corresponding free ions and radicals, planar molecules, rather than to the component parts of the starting esters. In such case, the bond cleavage would accompany a large structural relaxation or change and then would necessarily be suppressed by steric hindrance. This may be the present case.

Recently, Peters et al. [43–45] have discussed the photocleavage dynamics for diphenylmethyl halides by introducing a potential energy surface diagram based on a valence-bond description, which accounts for the factors that determine the partitioning between geminate radical pair and contact ion pair. This model might be employed for interpreting the discrepancy of the substituent effect on the ester conversion and product formation for the present esters. However, the fact that nanosecond laser photolysis of the esters yields no radical and ionic species except for the $T \rightarrow T_n$ absorption around 400 nm, due to the low reactivities and high intersystem crossing yields for the Np compounds (Table 1), disappointed our kinetic study [24].

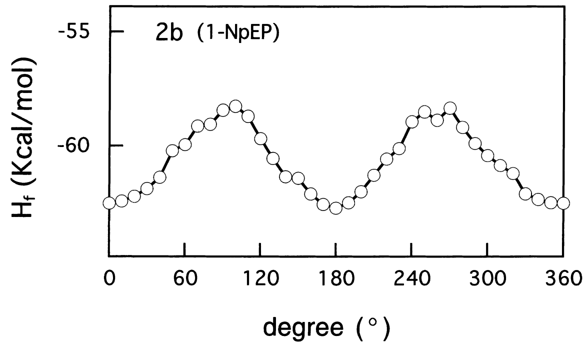


Fig. 3. Heats of formation (H_f) as a function of rotational angle about the acyl–oxygen bond for **2b** (1-NpEP).

3.4. Substituent effect on product distribution

As shown in Table 2, product yields, being not parallel to the yields for ester conversion, also showed a structure dependence. However, we will only have to survey the substituent effect on the product distribution because there are multiple pathways for formation of the intermediates and photoproducts (Scheme 1), which have not been always identified, and substituent groups would influence each pathway differently.

The preferential formation of **3** for the 1-Np derivatives and the acetates may be attributed to the larger stabilization of the 1-NpM and 1-NpE cations and the acetate anion (Table 4), and thus to facilitation of the electron transfer (iv) and photoheterolysis (i) paths in Scheme 1. On the other hand, the formation of the in-cage radical products **4** and **5** for the pivalates is accelerated by efficient decarboxylation (iii) [11]. These effects tend to be canceled out in the NpE esters probably because the steric hindrance destabilizes the intermediates **I** and **II**. The NpE esters are then liable to yield other products **6–9** in alternate pathways.

4. Conclusions

Steric hindrance around the ester bond for the naphthylmethyl derivatives is demonstrated to decrease the photocleavage yield, which may be due to restriction of preferred conformations. The product distribution is also affected by this effect. These results suggest that fixation of reactive conformers has a bright prospect of facilitating and controlling the photocleavage, as pointed out by Pincock and Wedge [14]. The present paper, however, could not refer to a key mechanism under controversy: Does the bond cleavage occur heterolytically or not? Detailed comparison of the present results with those for ring-substituted arylmethyl esters should be necessary.

5. List of symbols

alpha	α
delta	δ
degree	°
Phi	Φ
tau	τ
lambda	λ
dot	$\cdot$
long arrow	$\longrightarrow$
gamma	γ
equal to or less than	$\leq$

nu	ν
short arrow	→
micro	μ
about	≈

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