Photoinduced Electron-transfer Reaction of α-Bromomethyl-substituted Benzocyclic β-Keto Esters with Amines: Selective Reaction Pathways Depending on the Nature of Amine Radical Cations

Eietsu Hasegawa,[1]* Emi Tosaka,[1] Akira Yoneoka,[1] Yukinobu Tamura,[1] Shin-ya Takizawa,[1] Masaaki Tomura,[2] Yoshiro Yamashita[3]

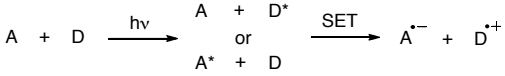
[1]*Department of Chemistry, Faculty of Science, Niigata University, Ikarashi-2, 8050, Niigata 950-2181, Japan*
[2]*Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*
[3]*Department of Electronic Chemistry, Interdiciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan*
Phone: +81-25-262-6159
Fax: +81-25-262-6159
E-mail: ehase@chem.sc.niigata-u.ac.jp

Abstract Photoinduced electron-transfer (PET) reaction of α-bromomethyl-substituted benzocyclic β-keto esters with tertiary amines was investigated. Debrominated β-keto esters as well as ring-expanded γ-keto esters were obtained as major products. On the basis of mechanistic experiments performed, it is concluded that these products are formed through a reaction sequence of selective carbon–bromine bond cleavage and following competitive hydrogen abstraction and Dowd–Beckwith ring-expansion of the resulting primary alkyl radicals. A characteristic product distribution observed for the type of amine used is rationalized by a selective reaction pathway of generated radical intermediates that depends on the nature of amine radical cations.

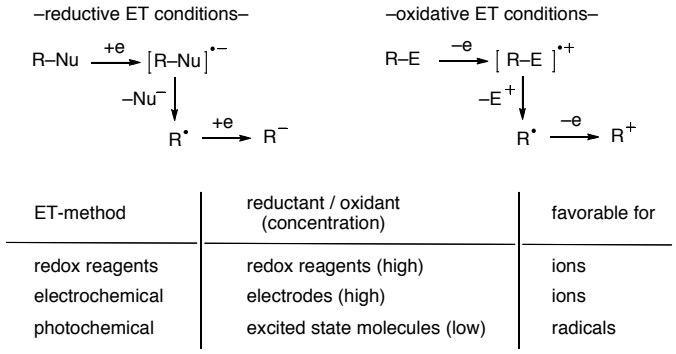
Key words Photoinduced electron-transfer • α-Bromomethyl-substituted benzocyclic β-keto esters • Tertiary amines • Radical ions • Dowd–Beckwith ring-expansion

Introduction

Electron-transfer (ET) is a fundamental reaction process operating in various reduction and oxidation (redox) reactions [1–5], and single electron-transfer (SET) of neutral organic molecules generates their radical ions [6–10]. Among methods to promote ET reactions are, redox reagent ET, electrochemical ET, and photoinduced electron-transfer (PET). PET reaction has unique features that are not usually associated with other ground state ET reactions [11–24]. Firstly, PET between electron-acceptor (A) and -donor (D) molecules produces a pair of radical anions and radical cations (Scheme 1). Therefore, radical ions generated under the PET conditions suffer various reaction pathways depending on their inherent nature as well as co-existing counter radical ions. Secondly, radical intermediates formed through fragmentation of radical ions become more persistent under the PET conditions compared to other ground state ET conditions because steady state concentrations of PET-generated redox reagents, such as short lived excited molecules, are low (Scheme 2). Therefore, PET provides a unique opportunity to investigate how radical intermediates react under the ET conditions.



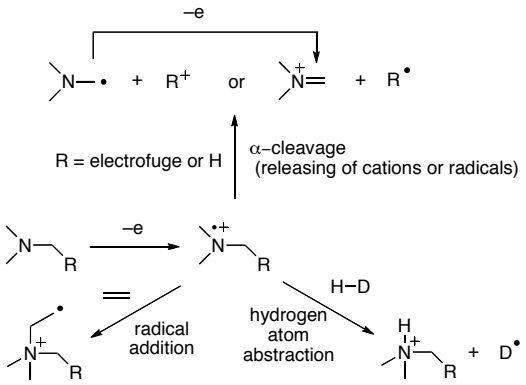
Scheme 1 Photoinduced electron-transfer of electron acceptor (A) and donor (D) molecules



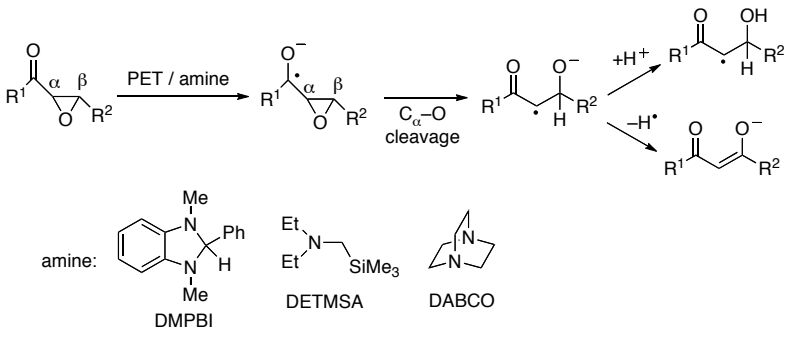
ET-method	reductant / oxidant (concentration)	favorable for
redox reagents	redox reagents (high)	ions
electrochemical	electrodes (high)	ions
photochemical	excited state molecules (low)	radicals

Scheme 2 Comparison of fragmentation reaction pathways of organic radical ions generated by three representative ET-methods in solutions

We have investigated PET reactions of various carbonyl and halogenated compounds [25–39]. Tertiary amines are recognized as effective electron donors [40–45], and frequently used to photochemically reduce these substrates. The radical cations of tertiary amines have various chemical reactivities, and among them are deprotonation, releasing electrofuges, and hydrogen atom abstraction (Scheme 3). We have demonstrated that 1,3-dimethy-2-phenylbenzimidazoline (DMPBI), *N,N*-diethyltrimethylsilylmethylamine (DETMSA), and 1,4-diazabicyclo[2.2.2]octane (DABCO) show such behaviors in PET reaction of epoxy ketones (Scheme 4) [28, 29, 31].



Scheme 3 Representative reaction pathways of tertiary amine radical cations



Scheme 4 Reaction patterns of epoxy ketone radical anions under PET conditions

During our early efforts, we have discovered that PET with amines is a useful means to promote a ring-expansion reaction of α-halomethyl-substituted cyclic β-keto esters [30, 31]. Dowd and Beckwith originally investigated this type of rearrangement employing tributyltin-based free radical conditions [46–51]. Since then, related free radical reactions as well as mechanistic investigations have been reported [52–58]. Miscellaneous ET conditions were also applied to promote similar transformations [59–62]. However, until recently [63,64], no example of PET-promoted Dowd−Beckwith ring-expansion has been published except for our previous

publications [30, 31].

In this full paper, we report details of PET-promoted Dowd–Beckwith ring-expansion reaction of α-bromomethyl-substituted benzocyclic β-keto esters with tertiary amines. Characteristic product distributions were observed depending on the kind of amine used. The factors to control the reaction pathway of generated radical intermediates are discussed. The substrates, amines and products that were investigated are shown in Chart 1.

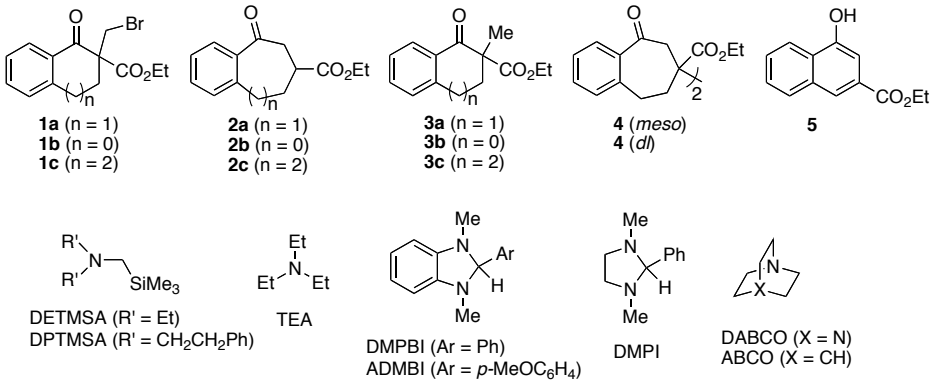


Chart 1 Substrates **1**, products **2**, **3**, **4**, and **5**, amine donors

Experimental

General procedures

NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (Me_4Si) as an internal standard at 200 MHz and 500 MHz for ^{1}H-NMR, and 50 MHz for ^{13}C-NMR. Photoreactions were conducted in a Pyrex test tube (1.5 cm diameter) immersed in a water bath at room temperature with a 500 W Xe–Hg lamp as a light source. Column chromatography was performed with silica gel (Wakogel C-200). Preparative thin layer chromatography (TLC) was performed on 20 cm × 20 cm plates coated with silica gel (Wakogel B-5F). Acetonitrile (MeCN) was distilled over P_2O_5 and subsequently with K_2CO_3. *N,N*-dimethylformamide (DMF) was dried with molecular sieves 4A and distilled under reduced pressure. Benzene (PhH) was treated with H_2SO_4, water, 5% NaOH, water, $CaCl_2$, and then distilled with CaH_2. Tetrahydrofuran (THF) was distilled over sodium–benzophenone under N_2. Other reagents and solvents were purchased and used without further purification.

Substrates, amine donors, and sensitizers

Substrates **1a** and **1c** are known compounds [52]. Preparation of **1b** is described below. To a mixture of NaH (ca. 60% in oil, 1.19 g, 29.7 mmol) and hexamethylphosphoric triamide (HMPA) (5.0 mL, 28.7 mmol) in THF (20 mL) was slowly added a THF solution (10 mL) of ethyl 1-indanone-2-carboxylate (4.88 g, 23.9 mmol) that was obtained by NaH-promoted reaction of 1-indanone with diethyl carbonate. After stirred for 1 h under N_2, CH_2Br_2 (8.4 mL, 120 mmol) was added, and the resulting mixture was heated at 75 °C for 22 h. Then, extraction with Et_2O was performed after addition of H_2O. The extract was treated with sat. aqueous $Na_2S_2O_3$, sat. aqueous $NaHCO_3$, sat. aqueous NaCl, and dried over anhydrous $MgSO_4$ and then concentrated. Column chromatography with dichloromethane (CH_2Cl_2) gave **1b** (5.28 g, 17.8 mmol, 74%). Further purification was performed by distillation: pale yellow oil; bp 149–150 °C (0.60 mmHg). IR (Neat) 1736, 1712 cm^{-1}. ^{1}H-NMR (200 MHz) δ 1.23 (t, J = 7.0 Hz, 3H), 3.39 (d, J = 18.0 Hz, 1H), 3.79 (d, J = 18.0 Hz, 1H), 3.80 (d, J = 10.4 Hz, 1H), 4.01 (d, J = 10.4 Hz, 1H), 4.19 (q, J = 7.0 Hz, 2H), 7.42–7.67 (m, 3H), 7.79 (d, J = 7.7 Hz, 1H). ^{13}C-NMR (50 MHz) δ 14.0 (q), 34.4 (t), 36.7 (t), 61.4 (s), 62.3 (t), 125.0 (d), 126.4 (d), 127.9 (d), 134.8 (s), 135.8 (d), 153.2 (s), 168.5 (s), 199.0 (s). Anal. calcd for $C_{13}H_{13}O_3Br$ C, 52.55; H, 4.41, found C, 52.55; H, 4.19.

DETMSA [65], DMPBI [33, 37], 2-anisyl-1,3-dimethylbenzimidazoline (ADMBI) [37], and 1,3-dimethy-2-phenylimidazoline (DMPI) [31], depicted in Chart 1, were prepared by the literature procedures. *N,N*-diphenethyltrimethylsilylmethylamine (DPTMSA) (see Chart 1) was prepared similarly to DETMSA as described below. To a mixture of diphenethylamine (588 mg, 2.61 mmol), that was obtained by a reaction of phenethylamine with phenethylbromide, and triethylamine (TEA) (0.75 mL, 5.38 mmol) in MeCN (3 mL) was slowly added a MeCN solution (1 mL) of iodotrimethylsilane (838 mg, 3.92 mmol). The resulting mixture was heated at 88 °C for 17 h. After addition of 0.5 M NaOH, extraction with Et_2O was performed. The extract was treated with water, sat. aqueous NaCl, and dried over anhydrous $MgSO_4$ and then concentrated. Column chromatography [ethylacetate (EtOAc) / n-C_6H_{14} = 1 / 3] gave DPTMSA (668 mg, 2.14 mmol, 82%). Further

purification was performed by distillation: pale yellow oil; bp ~100 °C (0.25 mmHg). IR (Neat) 1030, 856 cm^{-1}. ^{1}H-NMR (200 MHz) δ 0.05 (s, 9H), 2.12 (s, 2H), 2.74 (s, 8H), 7.16–7.32 (m, 10H). ^{13}C-NMR (50 MHz) δ 1.2 (q, 3C), 33.4 (t), 45.7 (t, 2C), 59.4 (t, 2C), 125.9 (d, 2C), 128.3 (d, 4C), 128.8 (d, 4C), 140.8 (s, 2C). Anal. calcd for $C_{20}H_{29}NSi$ C, 77.10; H, 9.38; N, 4.50, found C, 77.10; H, 9.00; N, 4.49. HRMS (EI) calcd for $C_{20}H_{29}NSi$ 311.2069, found 311.2089; calcd for $C_{17}H_{20}N$ (M^+-$SiMe_3$) 238.1596, found 238.1564.

Sensitizers, 9,10-bis(dimethylamino)anthracene (BDMAA), 9,10-dimethoxyanthracene (DMA), 1,6-bis(dimethylamino)pyrene (BDMAP), 1,6-dimethoxypyrene (DMP), depicted in Scheme 11, are all known, and their preparations were reported [38].

*General procedure for photoreaction of **1** with amine donors*

A solution of **1** (0.50–0.64 mmol) and an appropriate quantity of amine donor in a solvent [MeCN, DMF, PhH, THF or methanol (MeOH)] with or without additives was purged with N_2 for 5 min prior to irradiation. This solution was irradiated with light, $\lambda > 280$ nm for the direct irradiation of **1** and $\lambda > 360$ nm using a cut-off glass-filter for sensitization reactions using a sensitizer (0.025–0.032 mmol) for an appropriate irradiation time. A photolysate obtained from the reaction in MeCN, DMF, PhH, THF or MeOH was usually concentrated, and extraction was performed if necessary. A photolysate for the reaction in DMF was extracted with EtOAc. The extract was treated with water, sat. aqueous NaCl, and dried over anhydrous $MgSO_4$ and then concentrated. The residue was subjected to column chromatography and/or TLC separations using appropriate solvents (EtOAc / *n*-C_6H_{14}, EtOAc / PhH, CH_2Cl_2, etc.) to give the recovered **1** and the products. Photoproducts were identified by their NMR and IR spectra.

Photoproducts **2a**, **2c**, **3a**, and **3c** are known [52]. Ring-expansion product **2b**: IR (Neat) 1726, 1684, 1182 cm^{-1}. ^{1}H-NMR (200 MHz) δ 1.25 (t, *J* = 7.2 Hz, 3H), 2.74–3.21 (m, 5H), 4.17 (q, *J* = 7.2 Hz, 2H), 7.26–7.37 (m, 2H), 7.51 (td, *J* = 7.4, 1.5 Hz, 1H), 8.00–8.04 (m, 1H). ^{13}C-NMR (50 MHz) δ 14.1 (q), 32.0 (t), 40.2 (d), 40.7 (t), 61.0 (t), 127.1 (d, 2C), 128.8 (d), 131.8 (s), 133.8 (d), 141.5 (s), 173.0 (s), 195.9 (s). Anal. calcd for $C_{13}H_{14}O_3$ C, 71.54; H, 6.47, found C, 71.56; H, 6.18.

Reduced product **3b**: IR (Neat) 1740, 1712 cm^{-1}. ^{1}H-NMR (200 MHz) δ 1.19 (t, *J* = 7.1 Hz, 3H), 1.52 (s, 3H), 3.00 (d, *J* = 17.5 Hz, 1H), 3.71 (d, *J* = 17.5 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 7.37–7.50 (m, 2H), 7.60–7.68 (m, 1H), 7.80 (d, *J* = 7.5 Hz, 1H). ^{13}C-NMR (50 MHz) δ 14.0 (q), 21.0 (q), 40.0 (t), 56.0 (s), 61.5 (t), 124.9 (d), 126.4 (d), 127.8 (d), 134.7 (s), 135.3 (d), 152.6 (s), 172.0 (s), 203.5 (s). Anal. calcd for $C_{13}H_{14}O_3$ C, 71.54; H, 6.47, found C, 72.05; H, 6.32. HRMS (EI) calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0936.

Ring-expanded dimers **4**: *meso*-form, mp 217–218 °C, recrystallized from CH_2Cl_2 / ethanol (EtOH). IR (Neat) 1712, 1672 cm^{-1}. ^{1}H-NMR (200 MHz) δ 1.05 (t, *J* = 7.2 Hz, 6H), 2.18–2.30 (m, 2H), 2.65–2.96 (m, 8H), 3.39–3.78 (m, 6H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.23–7.44 (m, 4H), 7.68 (dd, *J* = 7.7, 1.7 Hz, 2H). ^{13}C-NMR (50 MHz) δ 13.5 (q, 2C), 31.0 (t, 2C), 31.2 (t, 2C), 45.6 (t, 2C), 52.4 (s, 2C), 61.6 (t, 2C), 127.0 (d, 2C), 128.6 (d, 2C), 129.5 (d, 2C), 132.8 (d, 2C), 137.2 (s, 2C), 140.4 (s, 2C), 172.5 (s, 2C), 200.8 (s, 2C). Anal. calcd for $C_{28}H_{30}O_6$ C, 72.71; H, 6.54, found C, 72.85; H, 6.49. *dl*-form, mp 175–176 °C, recrystallized from EtOH. IR (Neat) 1726, 1676 cm^{-1}. ^{1}H-NMR (200 MHz) δ 0.99 (t, *J* = 7.2 Hz, 6H), 2.16–2.28 (m, 2H), 2.64–2.97 (m, 8H), 3.35–3.66 (m, 6H), 7.15 (d, *J* = 7.4 Hz, 2H), 7.22–7.43 (m, 4H), 7.62 (dd, *J* = 7.6, 1.5 Hz, 2H). ^{13}C-NMR (50 MHz) δ 13.4 (q, 2C), 30.3 (t, 2C), 31.0 (t, 2C), 45.3 (t, 2C), 52.3 (s, 2C), 61.5 (t, 2C), 127.1 (d, 2C), 128.5 (d, 2C), 129.5 (d, 2C), 132.8 (d, 2C), 137.4 (s, 2C), 139.4 (s, 2C), 172.4 (s, 2C), 201.1 (s, 2C). Anal. calcd for $C_{28}H_{30}O_6$ C, 72.71; H, 6.54, found C, 72.76; H, 6.39.

Naphthol **5**: mp 141–143 °C, recrystallized from CH_2Cl_2/*n*-C_6H_{14}. IR (Neat) 3416, 1684, 1250 cm^{-1}. ^{1}H-NMR (200 MHz) δ 1.45 (t, *J* = 7.1 Hz, 3H), 4.46 (q, *J* = 7.1 Hz, 2H), 6.68 (broad s, 1H), 7.50–7.66 (m, 3H), 7.88–7.93 (m, 1H), 8.20–8.29 (m, 2H). ^{13}C-NMR (50 MHz) δ 14.4 (q), 61.5 (t), 107.7 (d), 122.1 (d), 123.4 (d), 126.9 (s), 127.1 (d), 127.5 (d), 127.6 (s), 129.1 (s), 133.8 (s), 152.1 (s), 167.4 (s). Anal. calcd for $C_{13}H_{12}O_3$ C, 72.21; H, 5.59, found C, 72.50; H, 5.67.

Determination of the percentage of deuterium incorporation into photoproducts

DMPBI-D [66, 67] was synthesized in the same manner as DMPBI [37], in which deuterated benzaldehyde (PhCDO) obtained by deprotection of 2-deuterio-2-phenyl-1,3-dithiane was protected with *N,N*-dimethyl-*o*-phenylenediamine. ^{1}H-NMR analysis revealed no H peak at C_2 of DMPBI. D_2O (Aldrich, 99.96 D%) was purchased and used for photoreactions. Percent of deuterium incorporated (D%) into photoproducts was determined by the following equations. For **2a**, D% = 100 × [1 – (H intensity at C_3) / (H intensity at C_4)]. In the case of **2b**, D% = 100 × {[1 – (H intensities at C_3 and C_4) – (H intensity of methylene protons of $CO_2CH_2CH_3$)] / (H intensity at C_4)}. For **3a**, H intensity of CH_3 was compared to CH_2D of **3a**-D using H intensity at C_3 as a standard peak.

*Triethylborane (Et_3B) and air promoted reaction of **1a** with DMPBI*

To a mixture of DMPBI (173.1 mg, 0.772 mmol) and **1a** (200.1 mg, 0.643 mmol) in PhH (20 mL) was added 1.0 M THF solution of Et_3B (0.16 mL, 0.16 mmol). The resulting mixture was stirred for 5 min under N_2 followed by introduction of air (2 mL) by syringe. After stirring for additional 4 h, the reaction mixture was concentrated. The residue was subjected to column chromatography (EtOAc / *n*-C_6H_{14}) and subsequent TLC separation (EtOAc / PhH) gave **2a** (11.6 mg, 0.0499 mmol, 8%), **3a** (21.3 mg, 0.0917 mmol, 14%), and recovered **1a** (134.8 mg, 0.433 mmol, 67%).

Results and Discussion

*Photoreaction of **1a** with silyl-substituted amines (DETMSA, DBTMSA) and TEA*

Irradiation of **1a** with DETMSA produced **2a**, **3a** and **4**. Compounds **4** were obtained as a mixture of two diastereomers, *meso* and *dl* isomers. The individual stereoisomers of **4** were characterized by their spectral data, and finally determined by X-ray crystallographic analysis (Figure 1). Results of reactions in various solvents are summarized in Table 1. Both irradiation and DETMSA are necessary to obtain the observed products, which were confirmed by the facts that stirring of same solution in the dark for 2 h resulted in quantitative recovery of **1a**, and none of **2a**, **3a** and **4** were obtained on irradiation of **1a** in the absence of DETMSA for 2 h while about 8% of **1a** was consumed. Several interesting observations can be pointed out from Table 1. Yields of ring-expanded products **2a** and **4** in MeCN and MeOH were greater than that in PhH (entries 1, 8 and 9). As the quantity of water increased, the yield of **2a** significantly increased while both **3a** and **4** gradually decreased (entries 1, 3, 4 and 5). The product ratio did not depend significantly on the irradiation time (entries 2, 4, 6 and 7), which suggests that the products do not interconvert, and that there is no significant degradation occurring during the course of the experiment. We therefore decided to conduct further mechanistic experiments mainly in MeCN.

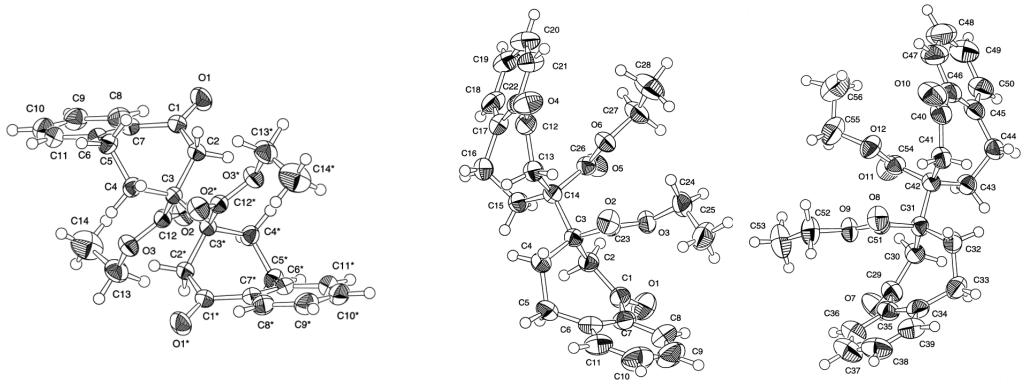


Figure 1. ORTEP plots of X-ray crystallographic data of **4** (*meso*- and *dl*-forms)[68]

Table 1 Photoreaction of **1a** with DETMSA in various solvents[a]

entry	solvent	H_2O (%)	irrad. time (h)	conv. of **1a** (%)	yields (%)[b] **2a**	**3a**	**4**
1	MeCN		1	65	55	10	21
2	MeCN	10	0.5	54	71	9	13
3	MeCN	5	1	76	61	10	20
4	MeCN	10	1	75	68	7	16
5	MeCN	30	1	75	75	6	10
6	MeCN	10	1.5	87	69	6	18
7[c]	MeCN	10	2	88	68	6	17
8	MeOH		1	83	53	7	28
9	PhH		1	87	44	9	13
10	PhH	10	1	93	33	13	19

[a]**1a** (0.64 mmol), DETMSA (5 equiv. *vs* **1a**). Total volume of the mixed solvent was kept to 10 mL. [b]Isolated yields based on the conversion of **1a**. The yield of **3a** was determined by ^{1}H-NMR analysis of the mixture of **1a** and **3a**. [c]Average of two independent experiments.

We next investigated the effects of amines (Table 2). Product distributions are comparable between DETMSA and TEA while longer irradiation was requisite for TEA than for DETMSA (compare entry 6 with 9). As the quantity of DETMSA increased, the yield of **2a** increased and that of **4** decreased (compare entry 1 with 2,

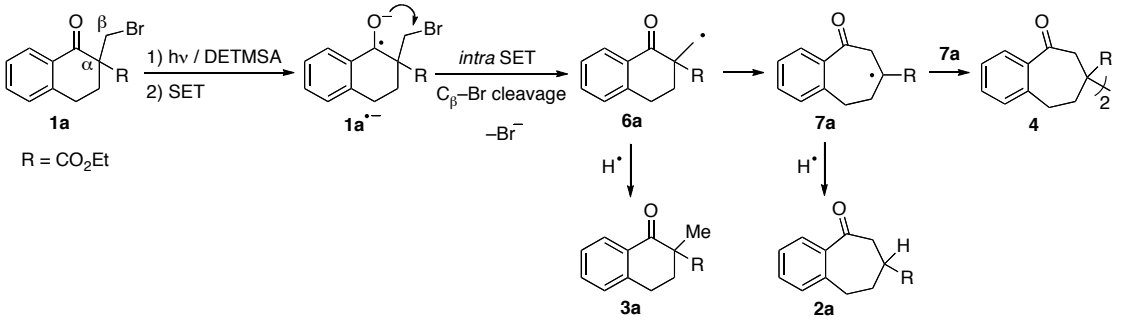
also see entries 3, 4, and 5). It should be also noted that irradiation of **1a** with DABCO in MeCN gave complicated mixture in which no **2a**, **3a** and **4** were detected regardless of the presence or absence of water (not shown in Table 2).

Table 2 Photoreaction of **1a** with various amine donors in dry or aqueous MeCN[a]

entry	donor (equiv. *vs* **1a**)	H_2O (%)	irrad. time (h)	conv. of **1a** (%)	yields (%)[b] **2a**	**3a**	**4**
1	DETMSA (1.5)		1	56	42	8	30
2	DETMSA (5)		1	65	55	10	21
3	DETMSA (1.5)	10	1	61	56	7	24
4	DETMSA (5)	10	1	75	68	7	16
5	DETMSA (10)	10	1	73	73	10	12
6[c]	DETMSA (5)	10	2	88	68	6	17
7	DPTMSA (5)	10	2	40	61	10	28
8	TEA (5)		5	87	34	8	16
9	TEA (5)	10	5	91	33	10	16

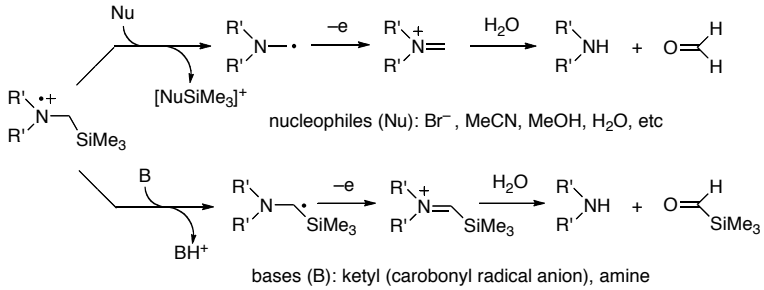
[a]**1a** (0.64 mmol), solvent (10 mL). Total volume of MeCN and water was kept to 10 mL. [b]Isolated yields based on the conversion of **1a**. The yield of **3a** was determined by ^{1}H-NMR analysis of the mixture of **1a** and **3a**. [c]Average of two independent experiments.

On the basis of the above results, plausible reaction pathways to give the observed products are presented in Scheme 5. PET produces a radical anion of **1a** (**1a**$^{\bullet-}$, ketyl form) and following intramolecular SET (dissociative) to Cβ–Br bond gives a primary alkyl radical **6a**, as discussed in the previous communications on PET reactions of β-bromo substituted benzocycloalkanones including **1a** [30, 34]. This primary alkyl radical undergoes competitive hydrogen atom abstraction and Dowd–Beckwith ring-expansion to give respective **3a** and **7a**. While the ring-expanded radical **7a** abstracts hydrogen atom to become **2a**, **7a** also undergoes dimerization to give **4**. Under the ordinary free radical conditions using trialkyltin hydrides, formation of dimeric product like **4** was never reported [46–58]. This would suggest that a trapping of **6a** by hydrogen atom is slow under these conditions compared to when an effective hydrogen-atom donor such as an alkyltin hydride is present.



Scheme 5 Radical pathways in PET reaction of **1a** with DETMSA

α-Silyl-substituted amines such as DETMSA and DPTMSA are recognized as silicone activated amines that become more effective electron donors than non-silyl-substituted amines such as TEA [43, 65, 69, 70]. As shown in Scheme 6, their radical cations undergo efficient desilylation assisted by nucleophiles such as certain anions and solvents. On the other hand, basic species abstract proton at the position adjacent to silyl-substituted carbons, that generates another α-amino alkyl radicals [65]. Therefore, increase of the quantity of H_2O and that of DETMSA assist the desilylation and deprotonation processes of the radical cation of DETMSA (DETMSA$^{\bullet+}$), respectively. Consequently, these effects should assist the progress of PET reaction of **1a**, which are indeed observed in Table 1 and Table 2. Notably, such a water effect was not observed for reactions with TEA (entries 8 and 9 in Table 2). In the reaction with DPTMSA, oxidative dealkylation product, diphenethylamine, was indeed obtained (entry 7 in Table 2).



Scheme 6 Desilylation and deprotonation of α-siylylamine radical cations

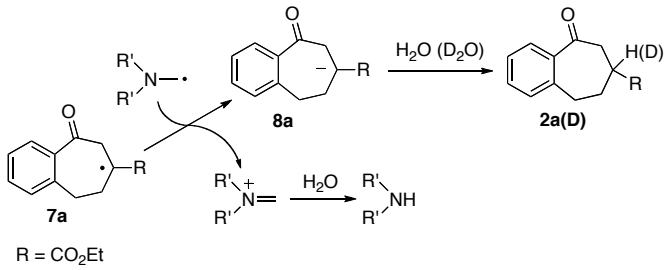
To gain more information of the involving intermediates, we conducted deuterium labeling experiments using D_2O expecting that anionic species, if generated, should be deuterated (Table 3). Then, significant amount of deuterium was introduced to the β-carbon of **2a** while deuterium incorporation at the methyl of **3a** was negligible. (entries 1, 2 and 4).

Table 3 Deuterium labeling experiment by D_2O in photoreaction of **1a** with DETMSA[a]

entry	solvent	additive	irrad. time (h)	conv. of **1a** (%)	yields (%)[b] **2a** (D% at C_3)[c]	**3a** (D% at CH_3)[c]	**4**
1	MeCN	D_2O	1	70	64 (81)	11 (~0)	obsd[d]
2	MeCN	D_2O	2	90	60 (82)	7 (~0)	obsd[d]
3	MeCN	H_2O	2	90	59	7	obsd[d]
4	DMF	D_2O	2	46	42 (87)	13 ([d])	25

[a]**1a** (0.64 mmol), DETMSA (5 equiv. *vs* **1a**). Total volume of organic solvent and water (5%) was kept to 10 mL. [b]Isolated yields based on the conversion of **1a**. The yield of **3a** was determined by ^{1}H-NMR analysis of the mixture of **1a** and **3a**. [c]Determined by ^{1}H-NMR analysis (see Experimental). [d]Not determined.

These observations could be rationalized by the assumption that **7a** is reduced to become anion **8a** that is protonated (deuterated) by H_2O (D_2O) (Scheme 7), in which most plausible reductants are α-amino alkyl radicals due to their strong electron-donating ability [71]. On the other hand, primary alkyl radical **6a** in Scheme 5 is not deuterated by D_2O.



Scheme 7 Ionic pathway in PET reaction of **1a** with α-silylamines

*Photoreaction of **1a** with imidazolines (DMPBI, DMPI)*

We next conducted photoreaction of **1a** with imidazolines, DMPBI and DMPI (Table 4). By contrast to silylamines, formation of **3a** became significant while the yield of **4** dramatically dropped to become negligible in the reactions with DMPBI. While a sizeable solvent effect on the product yields was not observed in the case of DMPBI (entries 1, 3, and 4), addition of water significantly decreased the yield of **2a** and increased that of **3a** (entry 2). This tendency is opposite to the case of DETMSA (see Table 1). The yield of **3a** for DMPBI was greater than that with DMPI (compare entry 5 with entries 1, 3, and 4). The absence of a significant solvent effect suggests that solvents do not act as effective hydrogen atom donors. In these reactions, plausible hydrogen-atom donors are radical cations and neutral forms of imidazolines. As the quantity of DMPI increased, the yield of **3a** increased and that of **2a** decreased although not significant. This suggests that DMPI is a less effective hydrogen donor than DMPBI to convert the primary alkyl radical **6a** to **3a** (entries 5–7).

Table 4 Photoreaction of **1a** with DMPBI or DMPI in various solvents[a]

entry	donor (equiv. *vs* **1a**)	solvent	conv. of **1a** (%)	yields (%)[b] **2a**	**3a**	**4**
1	DMPBI (1.2)	MeCN	93	31	19	4
2	DMPBI (1.2)	aqMeCN[c]	62	11	33	0
3	DMPBI (1.2)	DMF	85	35	22	6
4	DMPBI (1.2)	PhH	89	36	24	6
5	DMPI (1.2)	PhH	70	46	6	14
6	DMPI (5)	PhH	82	45	11	11
7	DMPI (15)	PhH	67	32	34	14

[a]**1a** (0.64 mmol), irradiation time: 2 h. Total volume of the mixed solvent was kept to 10 mL. [b]Isolated yields based on the conversion of **1a**. The yield of **3a** was determined by ^{1}H-NMR analysis of the mixture of **1a** and **3a**. [c]Aqueous condition: 10% volume of H_2O was added.

Deuterium labeling experiment by the use of D_2O further uncovered the difference of the electron and hydrogen-donating property between DMPBI and DMPI (Table 5). Namely, significant deuterium incorporation at β-carbon of **2a** was observed in the case of DMPI and it was minimal in the case of DMPBI. Increase of DMPI quantity decreased the yield of **2a** and increased that of **3a**, which is same as the tendency reported in Table 4, and the percentage of deuterium incorporated significantly increased (entries 3 and 4). The latter observation could be rationalized by the assumption that more generation of α-aminoalkyl radical from the deprotonation of the DMPI radical cation by excess DMPI. It should be also noted that the yield of **2a** was again low and that of **3a** was high in aqueous MeCN (compare entry 1 of Table 5 with entry 2 of Table 4). On the other hand, such an unexpected water effect was not observed in aqueous DMF (compare entry 2 of Table 5 with entry 3 of Table 4).

Table 5 Deuterium labeling experiment by D_2O in photoreaction of **1a** with DMPBI or DMPI[a]

entry	donor (equiv. *vs* **1a**)	solvent	conv. of **1a** (%)	yields (%)[b] **2a** (D% at C_3)[c]	**3a**[d]	**4**
1	DMPBI (1.2)	MeCN	64	11 (1)	29	0
2	DMPBI (1.2)	DMF	62	37 (2)	21	4
3	DMPI (1.2)	MeCN	60	41 (63)	5	30
4	DMPI (15)	MeCN	47	27 (80)	19	23

[a]**1a** (0.64 mmol), irradiation time: 2 h. Total volume of organic solvent and D_2O (5%) was kept to 10 mL. [b]Isolated yields based on the conversion of **1a**. The yield of **3a** was determined by ^{1}H-NMR analysis of the mixture of **1a** and **3a**. [c]Determined by ^{1}H-NMR analysis (see Experimental). [d]D% at CH_3 of **3a** was not determined.

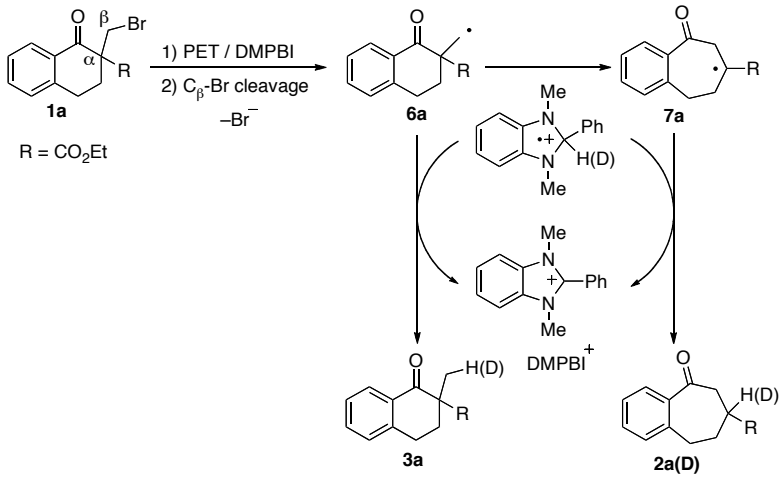
The above results suggest that DMPBI directly donates hydrogen atom to the radical intermediates **6a** and **7a**. We then conducted photoreactions of **1a** with 2-deuterated DMPBI (DMPBI-D) (Table 6). Conversion and product yields were considerably lower than those of reactions using DMPBI (Table 4), which would be consistent with the difference of bond dissociation energy between C–D for DMPBI-D and C–H for DMPBI. As expected, significant deuterium incorporations into both β-carbon of **2a** and methyl carbon of **3a** were observed. Particularly noteworthy is that the percentage of deuterium incorporation was not influenced by addition of D_2O (compare entry 4 with 5).

Table 6 Deuterium labeling experiment by DMPBI-D in photoreaction of **1a**[a]

entry	solvent	additive	irrad. time (h)	conv. of **1a** (%)	yields (%)[b] **2a** (D% at C_3)[c]	**3a** (D% at CH_3)[c]	**4**
1	MeCN		1	53	4 (57)	10 (71)	0
2	MeCN	H_2O	4	49	trace ([d])	8 (71)	0
3	DMF		2	34	11 (63)	14 (36)	trace
4	DMF	H_2O	6	44	16 (75)	12 (41)	3
5	DMF	D_2O	6	41	11 (74)	14 (40)	trace
6	PhH		2	51	39 (25)	6 (60)	7

[a]**1a** (0.64 mmol), DMPBI-D (1.2 equiv. *vs* **1a**). Total volume of organic solvent and water (5%) was kept to 10 mL. [b]Isolated yields based on the conversion of **1a**. The yield of **3a** was determined by ^{1}H-NMR analysis of the mixture of **1a** and **3a**. [c]Determined by ^{1}H-NMR analysis (see Experimental). [d]Not determined.

On the basis of the above results, plausible reaction pathways are proposed in Scheme 8. Both alkyl radicals **6a** and **7a** abstract hydrogen atom from the radical cation of DMPBI (DMPBI$^{\bullet+}$). It has been recently reported that DMPBI$^{\bullet+}$ is more effective hydrogen atom donor than its neutral form because the former gives a stable imidazolium cation and the latter gives imidazoline radical [72]. Therefore, DMPBI-D significantly deters these steps to reduce the yields of **2a** and **3a**. Indeed, marked deuterium incorporation into these products was observed. As described above, addition of water (H_2O and D_2O) significantly changed the product ratio in MeCN while such a water effect was not observed in DMF. At present, it seems difficult to rationalize these unexpected observations. On the other hand, water decelerated the reactions to some extent in both solvents (see Table 4 and 5). Water solvation to the initially formed radical anion of **1a** (see Scheme 5) may interfere intramolecular SET between the ketyl part and Cβ–Br bond of **1a**$^{\bullet-}$. As discussed earlier, water accelerates desilylation of DETMSA$^{\bullet+}$, which assists the overall reaction progress, while deprotonation of DMPBI$^{\bullet+}$ may not be assisted by water.



Scheme 8 PET reaction pathways of **1a** with DMPBI

As suggested in Scheme 6, deprotonation of amine radical cations could be achieved by co-existing amines because acidity of the amine radical cations are known to be comparable to those of alkyl ammoniums [73–75]. We then conducted deuterium labeling experiments of **1a** by using D_2O in the presence of various amine bases (Table 7). When *tert*-butylamine (*t*BuNH$_2$), *n*-butylamine (*n*BuNH$_2$), and diethylamine (Et$_2$NH) were used, deuterium incorporation into **2a** was significant. On the other hand, when less basic pyridine and 2,6-di-*tert*-butylpyridine were used, the percentage of deuterium incorporation into **2a** was low. Since competitive PET reaction between DMPBI and the amine bases added was considered, photoreaction of **1a** with Et$_2$NH was performed to find that Et$_2$NH indeed promoted the reaction (entries 8 and 12). Interestingly, sizable amount of **4** were obtained, which is similar to the reactions with TEA and DMPI (see Table 2, 4 and 5). On the other hand, inspection of remained quantity of DMPBI in the presence of amine bases (entries 5, 6, 10, 13 and 14) revealed that more quantity of DMPBI was consumed against reacted **1a** (base: *t*BuNH$_2$, *n*BuNH$_2$, Et$_2$NH, pyridine, and 2,6-di-*tert*-butylpyridine; reacted **1a**: 0.243, 0.285, 0.332, 0.431, and 0.266 mmol; consumed DMPBI: 0.326, 0.381, 0.424, 0.560, and 0.482 mmol). Therefore, we concluded that DMPBI more efficiently reacts with **1a** than co-existing amine bases.

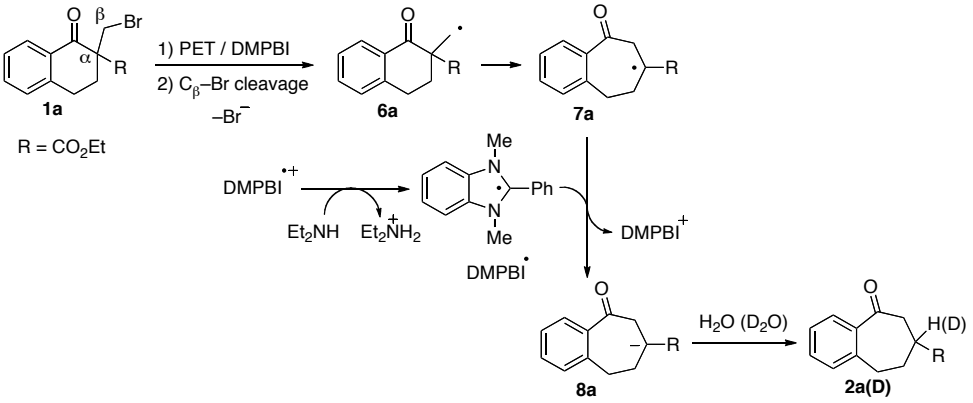
Table 7 Deuterium labeling experiment by D_2O in photoreaction of **1a** with DMPBI[a]

entry	base (equiv. *vs* **1a**)	solvent	conv. of **1a** (%)	yields (%)[b] **2a** (D% at C_3)[c]	**3a**[d]	**4**
1[e]		MeCN	64	11 (1)	29	0
2	Et$_2$NH (12)	MeCN	99	18 (58)	1	0
3	pyridine (12)	MeCN	91	47 (5)	29	0
4[f]		DMF	62	37 (2)	21	4
5	*t*BuNH$_2$ (12)	DMF	40	35 (39)	23	4
6	*n*BuNH$_2$ (12)	DMF	44	32 (39)	24	4
7	Et$_2$NH (1.8)	DMF	45	33 (80)	23	0
8[g]	Et$_2$NH (1.8)	DMF	29	37 (88)	13	12
9	Et$_2$NH (6)	DMF	47	32 (68)	23	0
10	Et$_2$NH (12)	DMF	50	28 (65)	22	4

11	Et_2NH (24)	DMF	48	35 (48)	25	0
12[g]	Et_2NH (24)	DMF	34	29 (54)	17	7
13	pyridine (12)	DMF	70	51 (5)	19	2
14	2,6-di-*tert*-butylpyridine (12)	DMF	41	46 (2)	22	0

[a]**1a** (0.64 mmol), DMPBI (1.2 equiv *vs* **1a**), irradiation time: 2 h. Total volume of organic solvent and D_2O (5%) was kept to 10 mL. [b]Isolated yields based on the conversion of **1a**. The yield of **3a** was determined by ^{1}H-NMR analysis of the mixture of **1a** and **3a**. [c]Determined by ^{1}H-NMR analysis (see Experimental). [d]D% at CH_3 of **3a** was not determined. [e]Same as entry 1 of Table 5. [f]Same as entry 3 of Table 5. [g]No DMPBI was added .

The above results let us propose a mechanism for PET reaction of **1a** and DMPBI in the presence of Et_2NH (Scheme 9). Et_2NH abstracts proton from DMPBI$^{\bullet+}$ to produce an imidazolyl radical (DMPBI$^{\bullet}$) that reduces radical **7a** to anion **8a**. In situ-generated ammonium $Et_2N^+H_2$ may protonate **8a** more efficiently than D_2O, which would be compatible with the fact that degree of deuterium incorporation into **2a** decreased as more quantity of Et_2NH was added (entries 7, 9–11).



Scheme 9 Diethylamine effect on PET reaction pathways of **1a** with DMPBI

One may consider the possibility of ET-initiated radical chain mechanism that is originally proposed by Tanner [76–80]. In this mechanism, initial ET between **1a** and DMPBI generates DMPBI$^{\bullet+}$, and then DMPBI$^{\bullet+}$ looses proton to become DMPBI$^{\bullet}$ that reduces **1a** to the radical anion of **1a**. Both **6a** and **7a** abstract DMPBI to give DMPBI$^{\bullet}$ that promotes the following chain process. Then, we applied Et_3B–air-initiated reaction, which is known to promote free radical reaction at room temperature [81, 82], to above system. Under free radical conditions, although DMPBI and Et_3B (0.2 equiv. *vs* DMPBI)–air in PhH at room temperature for 4 h promoted the reaction, conversion of **1a** (33%) and yields of **2a** (8%) and **3a** (14%) were significantly low, and no **4** was obtained (compare with entry 4 of Table 4). Further information comes from the comparison of electrochemical data. Oxidation potential of DMPBI$^{\bullet}$, which is same as the reduction potential of DMPBI$^+$ (–1.62 V vs SCE, estimated from the literature data, –2.06 V vs ferrocene /ferrocenium) [72] is lower than the reduction potential of **1a** (–1.85 V vs SCE) [30], which suggests that ET between **1a** and DMPBI$^{\bullet}$ would not be feasible. Thus, even if it is operating, its contribution to the reaction pathways should not be significant.

*Photoreactions of **1b** and **1c** with amines*

PET reactions of **1b** using silylamines, DMPBI and bicyclic amines were also investigated (Table 8). Contrasting product distributions can be seen between silylamines and DMPBI. While naphthol **5** was a major product in the reactions with silylamines (entries 1–7), the production of **2b** and **3b** were more significant in the reactions with DMPBI (entries 8–11). Another notable observation is that **5** was exclusively obtained in the reactions using DABCO and 1-azabicyclo[2.2.2]octane (ABCO) (entries 12–14). Finally, brief experiment revealed that DETMSA was effective and DMPBI was ineffective for PET-promoted Dowd–Beckwith ring-expansion reaction of **1c** (entries 15 and 16). We previously observed that **1c** is less effective substrate than **1a** and **1b** for free radical Dowd–Beckwith ring-expansion reactions using tributylstanane and tris(trimethylsilyl)silane [58].

Table 8 Photoreactions of **1b** and **1c** with amine donors in various solvents[a]

entry	substrate	donor	solvent	irrad. time	conv. of **1**	yields (%)[b]		
	1	(equiv. *vs* **1**)		(h)	(%)	**2**	**3**	**5**

1	**1b**	DETMSA (5)	MeCN	4	100	10	8	47
2	**1b**	DETMSA (5)	aqMeCN	2	55	16	6	44
3[c]	**1b**	DETMSA (5)	aqMeCN	4	80	13	2	52
4	**1b**	DETMSA (5)	PhH	4	98	5	6	54
5	**1b**	DETMSA (5)	THF	4	77	14	25	30
6	**1b**	DETMSA (5)	aqTHF	4	83	8	17	38
7	**1b**	DPTMSA (5)	PhH	4	69	7	6	39
8	**1b**	DMPBI (1.2)	PhH	2	98	49	22	4
9	**1b**	DMPBI (1)	aqMeCN	4	88	34	18	7
10	**1b**	DMPBI (1.5)	aqMeCN	4	97	43	17	8
11	**1b**	DMPBI (2)	aqMeCN	4	62	14	27	trace
12	**1b**	DABCO (5)	MeCN	4	47	0	0	51
13	**1b**	DABCO (5)	PhH	4	51	0	0	50
14[d]	**1b**	ABCO (5)	PhH	4	88	0	0	67
15[c]	**1c**	DETMSA (5)	aqMeCN	2	59	40	2	-
16	**1c**	DMPBI (1.2)	PhH	2	45	trace	5	-

[a]**1** (0.64 mmol). Total volume of organic solvent and H_2O (10%) was kept to 10 mL. [b]Isolated yields based on the conversion of **1**. The yield of **3** was determined by ^{1}H-NMR analysis of the mixture of **1** and **3**. [c]Average of two independent experiments. [d]Condition: **1b** (0.32 mmol), PhH (5 mL).

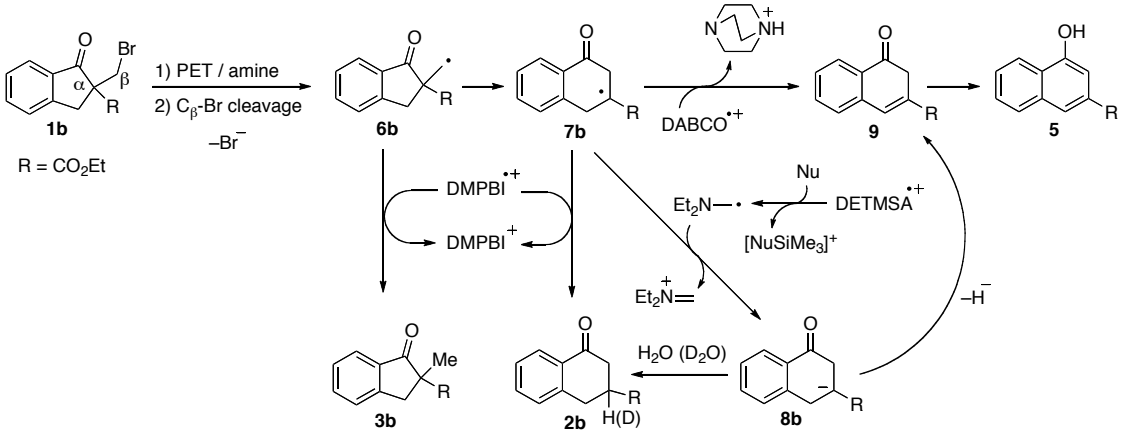
Deuterium labeling experiments using D_2O were conducted for the reactions of **1b**, and the essentially same results as those obtained in the reactions of **1a** were obtained (Table 9) (see above). Namely, significant deuterium incorporation to the ring-expansion product **2b** was observed in the case of DETMSA while no deuterium labeling to **2b** was observed in the case of DMPBI.

Table 9 Deuterium labeling experiment by D_2O in photoreaction of **1b** with DETMSA or DMPBI[a]

entry	donor (equiv. *vs* **1a**)	solvent	conv. of **1a** (%)	yields (%)[b] **2b** (D% at C_3)[c]	**3b**[d]	**5**
1	DETMSA (5)	MeCN	100	18 (80)	11	48
2	DMPBI (1.2)	DMF	94	32 (0)	23	3

[a]**1a** (0.64 mmol), irradiation time: 4 h. Total volume of organic solvent and D_2O (5%) was kept to 10 mL. [b]Isolated yields based on the conversion of **1b**. The yield of **3b** was determined by ^{1}H-NMR analysis of the mixture of **1a** and **3a**. [c]Determined by ^{1}H-NMR analysis (see Experimental). [d]D% at CH_3 of **3b** was not determined.

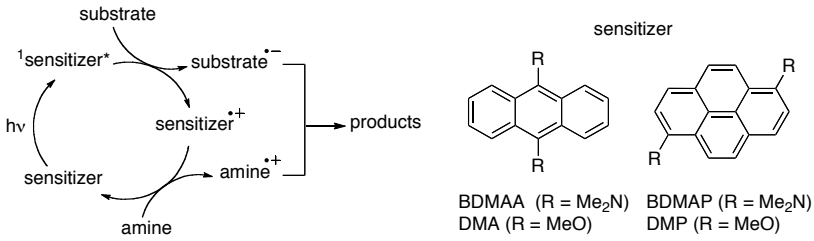
Selective PET reaction pathways of **1b** depending on three types of tertiary amines are presented in Scheme 10. In the case of DETMSA, **2b** and **3b** are formed through the sequence similar to the reaction of **1a**. On the other hand, major product **5**, a tautomer of **9**, must be formed via either hydrogen atom elimination of **7b** or hydride elimination of **8b** giving **9**, in which hydrogen atom and hydride acceptors could not be specified. When DMPBI is used as a donor, both **6b** and **7b** efficiently abstract hydrogen atom from DMPBI$^{\bullet+}$. In the case of DABCO, hydrogen atom abstraction from **7b** by DABCO$^{\bullet+}$ is mainly responsible for the formation of **5**. DABCO$^{\bullet+}$ is known to be stable [83], so that it does not undergo deprotonation but abstracts hydrogen atom from **7b** to give **9**.



Scheme 10 PET reaction pathways of **1b** with three types of tertiary amines

*Photosensitized reaction of **1a** with amines*

Photosensitization is an alternative means to promote PET reactions, and also attractive from the viewpoint of organic synthesis [11–13, 20, 23]. By using photosensitization, a sensitizer is selectively excited by the light that is not absorbed by substrates. As a result, undesired photoreactions arising from the excited states of the substrates do not take place. We have previously demonstrated that PET sensitization method using electron-donating arene sensitizers and amines are effective to promote reductive transformation of various organic substrates (Scheme 11) [25, 31, 33–39].



Scheme 11 Photosensitization pathways using arene sensitizers and amines

We then conducted deuterium labeling experiments for BDMAP photosensitized reaction of **1a** using DETMSA and DMPBI (Table 10). The results showed similar tendency of deuterium incorporation at the appropriate positions of **2a** and **3a** to the direct irradiation experiments of **1a** with amines. Namely, percentage of deuterium labeling of **2a** by D_2O added was high for the reaction with DETMSA (entry 1) and low for the reaction with DMPBI (entry 2). By contrast, addition of Et_2NH increased both of the conversion of **1a** and the deuterium labeling of **2a** (compare entry 3 with entry 2), which is rationalized by effective deprotonation from DMPBI radical cation by Et_2NH discussed above. When DMPBI was replaced by DMPBI-D, deuterium labeling of **2b** became significant and that of **3a** was observed while the reaction required longer irradiation time and the yields of **2a** and **3a** were relatively low in the presence or absence of water.

Table 10 Deuterium labeling experiment in BDMAP photosensitized reaction of **1a** in DMF[a]

entry	donor	additive	irrad. time	conv. of **1a**	yields (%)[b]		
			(h)	(%)	**2a** (D% at C_3)[c]	**3a** (D% at CH_3)[c]	**4**
1	DETMSA	D_2O	8	52	40 (89)	13 (~0)	16
2	DMPBI	D_2O	7	45	28 (3)	18 (~0)	trace
3	DMPBI	D_2O, Et_2NH	7	68	41 (83)	26 (~0)	trace
4	DMPBI-D		8	42	2 (75)	14 (39)	4
5	DMPBI-D	H_2O	12	56	7 (74)	10 (35)	12

[a]**1a** (0.64 mmol), BDMAP (0.05 equiv. *vs* **1a**), DETMSA (5 equiv. *vs* **1a**), DMPBI and DMPBI-D (1.2 equiv. *vs* **1a**), Et_2NH (1.8 equiv. *vs* **1a**). Total volume of DMF and water (5%) was kept to 10 mL. [b]Isolated yields based on the conversion of **1a**. The yield of **3a** was determined by ^{1}H-NMR analysis of the mixture of **1a** and **3a**. [c]Determined by ^{1}H-NMR analysis (see Experimental).

We next conducted photosensitization reaction of **1a** using ADMBI (see Chart 1), which was reported to be more effective reagent than DMPBI [38]. Dimethylamino or methoxy-substituted anthracenes and pyrenes were employed as sensitizers (Scheme 11). As shown in Table 11, although all sensitizers were effective to promote the reaction, the yields of desired **2a** were relatively low and less than those of **3a** while no **4** was obtained.

Table 11 Photosensitized reaction of **1a** using ADMBI in DMF[a]

entry	sensitizer	conv. of **1a**	yields (%)[b]	
		(%)	**2a**	**3a**
1	BDMAA	51	24	24
2	DMA	64	16[c]	25
3	BDMAP	77	19	31
4	DMP	74	14[c]	23

[a]**1a** (0.50 mmol), sensitizer (0.05 equiv. *vs* **1a**), ADMBI (1.2 equiv. *vs* **1a**), DMF (5 mL), irradiation time: 5 h.

[b]Isolated yields based on the conversion of **1a**. [c]Determined by ^{1}H-NMR.

Conclusion

We have investigated photoinduced electron-transfer (PET) reaction of α-bromomethyl-substituted benzocyclic β-keto esters with tertiary amines. In the reactions, primary alkyl radicals derived from selective carbon–bromine bond cleavage undergo competitive hydrogen atom abstraction and Dowd–Beckwith ring-expansion. On the basis of detailed mechanistic experiments including deuterium labeling by the use of D_2O and DMPBI-D, effects of external amine bases, factors to govern reaction pathway of generated radical intermediates were discussed from the viewpoint of the nature of amine radical cations. Then, three types of reaction patterns of amine radical cations are suggested. For example, DETMSA$^{\bullet+}$ undergoes desilylation to form an α-amino alkyl radical that act as a SET reductant. On the other hand, DMPBI$^{\bullet+}$ donates hydrogen atom to radical intermediates derived from substrate radical anions. When certain amine bases are added, deprotonation of DMPBI$^{\bullet+}$ occurs and formed DMPBI$^{\bullet}$ then acts as a SET reductant. Finally, DABCO$^{\bullet+}$ undergoes neither deprotonation nor hydrogen atom donation, but abstracts hydrogen atom from the radical intermediates to give unsaturated products. Such a reaction pattern of DABCO$^{\bullet+}$ was previously suggested in PET reaction of epoxy ketones [29]. Photosensitization reactions were also investigated, and essentially the same reaction patterns and product distributions as those of direct irradiation reactions were observed. Unfortunately, an effective photosensitization condition to promote Dowd–Beckwith rearrangement giving the desired ring-expansion products in high yields could not be developed yet, that is certainly a future challenge to investigate.

Acknowledgements

This work was partly supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank Dr. Yukiko Matsumura (Tokyo Institute of Technology) for her assistance to measure elemental analyses and high resolution mass spectra of some of the compounds reported. We thank Professor James M. Tanko (Virginia Polytechnic Institute and State University, USA) for his help to edit the manuscript. Assistance of Mr. Tsuneaki Hoshi to prepare manuscript is also acknowledged.

References

1. L. Eberson, *Electron Transfer Reactions in Organic Chemistry*; Springer–Verlag: Berlin (1987).
2. *Advances in Electron Transfer Chemistry*; P. S. Mariano, Ed.; JAI Press: Greenwich, Vols 1–6 (1991–1999).
3. *Electron Transfer in Chemistry*; V. Balzani, Ed.; Wiley–VCH: Weinheim, Vols 1–5 (2001).
4. *Organic Electrochemistry*, 4th ed; H. Lund, O. Hammerich, Eds.; Marcel Dekker: New York, (2001).
5. *Tetrahedron Symposium-in Print, Electron Transfer Reagents in Organic Synthesis,* D. J. Procter, R. A. Flowers, Ed.; Vol 65; Issue 52 (2009).
6. M. Schmittel, A. Burghart, *Angew. Chem. Int. Ed. Engl.* **36**, 2550 (1997).
7. D. J. Berger, J. M. Tanko, In *The Chemistry of Double–Bonded Functional Groups*; S. Patai, Ed.; John Wiley & Sons: New York, pp 1281–1354 (1997).
8. H. D. Roth, In *Reactive Intermediate Chmeistry*; R. A. Moss, M. S. Platz, M. Jones, Jr., Eds.; John Wiley & Sons: Hoboken, Chapter 6, pp 205–272 (2004).
9. *Tetrahedron Symposium-in Print, The Chemistry of Radical Ions,* P. E. Floreancig, Ed.; Vol 62; No. 21 (2006).
10. Z. V. Todres, *Ion-Radical Organic Chemistry Principles and Applications*, 2nd ed; CRC press: Boca Raton (2009).
11. *Photoinduced Electron Transfer,* M. A. Fox, M. Chanon, Eds.; Elsevier: Amsterdam, Parts A–D (1988).
12. G. J. Kavarnos, *Fundamental of Photoinduced Electron Transfer*; VCH Press: New York, (1993).
13. *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed; W. M. Horspool, F. Lenci, Eds.; CRC Press: Boca Raton, (2004).
14. K. Mizuno, T. Hayamizu, H. Maeda, *Pure Appl. Chem.* **75**, 1049 (2003).
15. J. Cossy, D. Belloti, *Tetrahedron* **62**, 6459 (2006).
16. A. G. Griesbeck, N. Hoffmann, K. D. Warzecha, *Acc. Chem. Res.* **40**, 128 (2007).
17. P. E. Floreancig, *Synlett* 191 (2007).
18. P. A. Waske, N. T. Tzvetkov, J. Mattay, *Synlett* 669 (2007).
19. N. Hoffmann, *Chem. Rev.* **108**, 1052 (2008).
20. N. Hoffmann, *J. Photochem. Photobio. C.* **9**, 43 (2008).
21. D. Ravelli, D. Dondi, M. Fagnonia, A. Albini, *Chem. Soc. Rev.* **38**, 1999 (2009).
22. R. E. Galian, J. P. Prieto, *Energy Environ. Sci.* **3**, 1488 (2010).

23. J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* **40**, 102 (2011).
24. D. W. Cho, U. C. Yoon, P. S. Mariano, *Acc. Chem. Res.* **44**, 204 (2011).
25. E. Hasegawa, K. Ishiyama, T. Horaguchi, T. Shimizu, *J. Org. Chem.* **56**, 1631 (1991).
26. E. Hasegawa, Y. Tamura, T. Horaguchi, K. Isogai, T. Suzuki, *Tetrahedron Lett.* **35**, 8643 (1994).
27. E. Hasegawa, H. Katagi, D. Nakagawa, T. Horaguchi, S. Tanaka, Y. Yamashita, *Tetrahedron Lett.* **36**, 6915 (1995).
28. E. Hasegawa, T. Kato, T. Kitazume, K. Yanagi, K. Hasegawa, T. Horaguchi, *Tetrahedron Lett.* **37**, 7079 (1996).
29. E. Hasegawa, K. Ishiyama, T. Fujita, T. Kato, T. Abe, *J. Org. Chem.* **62**, 2396 (1997).
30. E. Hasegawa, Y. Tamura, E. Tosaka, *Chem. Commun.* 1895 (1997).
31. E. Hasegawa, A. Yoneoka, K. Suzuki, T. Kato, T. Kitazume, K. Yanagi, *Tetrahedron* **55**, 12957 (1999).
32. E. Hasegawa, Y. Tamura, K. Suzuki, A. Yoneoka, T. Suzuki, *J. Org. Chem.* **64**, 8780 (1999).
33. E. Hasegawa, N. Chiba, A. Nakajima, K. Suzuki, A. Yoneoka, K. Iwaya, *Synthesis* 1248 (2001).
34. E. Hasegawa, S. Takizawa, K. Iwaya, M. Kurokawa, N. Chiba, K. Yamamichi, *Chem. Commun.* 1966 (2002).
35. E. Hasegawa, *J. Photosci.* **10**, 61 (2003).
36. E. Hasegawa, N. Chiba, T. Takahashi, S. Takizawa, T. Kitayama, T. Suzuki, *Chem. Lett.* 18 (2004).
37. E. Hasegawa, T. Seida, N. Chiba, T. Takahashi, H. Ikeda, *J. Org. Chem.* **70**, 9632 (2005).
38. E. Hasegawa, S. Takizawa, T. Seida, A. Yamaguchi, N. Yamaguchi, N. Chiba, T. Takahashi, H. Ikeda, K. Akiyama, *Tetrahedron* **62**, 6581 (2006).
39. E. Hasegawa, H. Hirose, K. Sasaki, S. Takizawa, T. Seida, N. Chiba, *Heterocycles* **77**, 1147 (2009).
40. S. F. Nelsen, *J. Am. Chem. Soc.* **108**, 4879 (1988).
41. J. P. Dinnocenzo, T. E. Banach, *J. Am. Chem. Soc.* **111**, 8646 (1989).
42. V. D. Parker, M. Tilset, *J. Am. Chem. Soc.* **113**, 8778 (1991).
43. U. C. Yoon, P. S. Marinao, R. S. Givens, B. W. Atwater, In *Advances in Electron Transfer Chemistry*; P. S. Mariano, Ed.; JAI Press: Greenwich, Vol 4, pp 117–205 (1994).
44. F. D. Lewis, In *Advances in Electron Transfer Chemistry*; P. S. Mariano, Ed.; JAI Press: Greenwich, Vol 5, pp 1–39 (1996).
45. S. Das, V. Suresh, In *Electron Transfer in Chemistry*; V. Balzani, Ed.; Wiley-VCH: Weinheim, Vol. 2, pp 379–456 (2001).
46. P. Dowd, S. C. Choi, *J. Am. Chem. Soc*. **109**, 3493 (1987).
47. P. Dowd, S. C. Choi, *J. Am. Chem. Soc*. **109**, 6548 (1987).
48. A. L. J. Beckwith, D. M. O'Shea, S. W. Westwood, *J. Chem. Soc., Chem. Commun*. 666 (1987).
49. A. L. J. Beckwith, D. M. O'Shea, S. W. Westwood, *J. Am. Chem. Soc*. **110**, 2565 (1988).
50. P. Dowd, S. C. Choi, *Tetrahedron* **45**, 77 (1989).
51. P. Dowd, W. Zhang, *Chem. Rev.* **93**, 2091 (1993) and references cited therein.
52. W. R. Bowman, P. J. Westlake, *Tetrahedron* **48**, 4027 (1992).
53. I. Ryu, H. Fukushima, T. Okuda, K. Matsu, N. Kambe, N. Sonoda, M. Komatsu, *Synlett* 1265 (1997).
54. C. Chatgilialoglu, C. Ferreri, M. Lucarini, A. Ventrini, A. A. Zavitsas, *Chem. Eur. J.* **3**, 376 (1997).
55. C. Chatgilialoglu, V. I. Timokhin, M. Ballestri*, J. Org. Chem.* **63**, 1327 (1988).
56. M. Sugi, H. Togo, *Tetrahedron* **58**, 3171 (2002).
57. T. Yoshizumi, H. Miyazoe, Y. Sugimoto, H. Takahashi, O. Okamoto, *Synthesis* 1593 (2005).
58. E. Hasegawa, Y. Ogawa, K. Kakinuma, H. Tsuchida, E. Tosaka, S. Takizawa, H. Muraoka, T. Saikawa, *Tetrahedron* **64**, 7724 (2008).
59. T. Shono, N. Kse, N. Uematsu, S. Morimoto, E. Okazaki, *J. Org. Chem.* **55**, 5037 (1990).
60. E. Hasegawa, T. Kitazume, K. Suzuki, E. Tosaka, *Tetrahedron Lett.* **39**, 4059 (1998).
61. S. H. Chung, M. S. Cho, J. Y. Choi, D. W. Kwon, Y. H. Kim. *Synlett* 1266 (2001).
62. M. Sugi, D. Sakuma, H. Togo, *J. Org. Chem.* **68**, 7629 (2003).
63. H. Shimakoshi, M. Abiru, S. Izumi, Y. Hisaeda, *Chem. Commun*. 6427 (2009).
64. K. Tahara, Y. Hisaeda, *Green Chem*. **13**, 558 (2011).
65. E. Hasegawa, W. Xu, P. S. Mariano, U. C. Yoon, J. U. Kim, *J. Am. Chem. Soc.* **110**, 8099 (1988).
66. H. Chikashita, K. Itoh, *Bull. Chem. Soc. Jpn.* **59**, 1747(1986).
67. I-S. H. Lee, E. H. Jeoung, M. M. Kreevoy, *J. Am. Chem. Soc.* **123**, 7492 (2001).
68. CCDC 853453 and 853454 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033.
69. X. Zhang, S. R. Ye, S. Hong, M. Freccero, A. Albini, D. E. Falvey, P. S. Mariano, *J. Am. Chem. Soc.* **116**,

4211 (1994).
70. Z. Su, P. S. Mariano, D. E. Falvey, U. C. Yoon, S. W. Oh, *J. Am. Chem. Soc.* **120**, 10676 (1998).
71. D. D. M. Wayner, D. J. McPhee, D. Griller, *J. Am. Chem. Soc.* **110**, 132 (1988).
72. X-Q. Zhu, M-T. Zhang, A. Yu, C-H. Wang, J-P. Cheng, *J. Am. Chem. Soc.* **130**, 2501 (2008).
73. S. F. Nelsen, *J. Am. Chem. Soc.* **108**, 4879 (1988).
74. J. P. Dinnocenzo, T. E. Banach, *J. Am. Chem. Soc.* **111**, 8646 (1989).
75. V. D. Parker, M. Tilset, *J. Am. Chem. Soc.* **113**, 8778 (1991).
76. J. J. Chen, D. D. Tanner, *J. Org. Chem.* **53**, 3897 (1988).
77. D. D. Tanner, J. J. Chen, *J. Org. Chem.* **54**, 3842 (1989).
78. D. D. Tanner, J. J. Chen, L. Chen, C. Luelo, *J. Am. Chem. Soc.* **113**, 8074 (1991).
79. D. D. Tanner, J. J. Chen, *J. Org. Chem.* **57**, 662 (1992).
80. D. D. Tanner, J. J. Chen, C. Luelo, P. M. Peters, *J. Am. Chem. Soc.* **114**, 713 (1992).
81. K. Nozaki, K. Oshima, K. Utimoto, *J. Am. Chem. Soc.* **109**, 2547 (1987).
82. K. Nozaki, K. Oshima, K. Utimoto, *Bull. Chem. Soc. Jpn.* **64**, 403 (1991).
83. Y. L. Chow, W. C. Danen, S. F. Nelsen, D. H. Rosenblatt, *Chem. Rev.* **78**, 243 (1978).