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Benzophenone-photosensitized alkylation of arylalkenes with acetone, dimethyl sulfoxide, and their related compounds in the presence of *tert*-butylamine

Toshiaki Yamashita[a,*], Motonori Watanabe[b], Ryuji Kojima[b], Tsutomu Shiragami[b], Kensuke Shima[b], Masahide Yasuda[c]

[a] *Department of Chemical Science and Engineering, Miyakonojo National College of Technology, Miyakonojo, Miyazaki 885-8567, Japan*
[b] *Department of Materials Science, Faculty of Engineering, Miyazaki University, Gakuen-Kibanadai, Miyazaki 889-2192, Japan*
[c] *Cooperative Research Center, Miyazaki University, Gakuen-Kibanadai, Miyazaki 889-2192, Japan*

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Abstract

Diarylketones (Ar_2CO)-photosensitization in the presence of *tert*-butylamine (*t*-$BuNH_2$) caused the alkylation of 1,1-diphenylethene (**1a**) and 10,11-dihydro-5-methylene-5*H*-dibenzo[*a*,*d*]cycloheptene (**1b**) with alkylating reagents (R-H) such as MeCOR, dimethyl sulfoxide (DMSO), and $RCONR_2$. The photosensitized alkylation with DMSO was applied to stilbene (**1c**), 1-methyl-1,2-diphenylethene (**1d**), and anethole (**1e**). Since the presence of *t*-$BuNH_2$ was essential in the cases of the alkylation with MeCOR (R = Me, Et, OEt) and DMSO, it is reasonable to assume that *t*-BuN(H)· generated through the H-atom abstraction from *t*-$BuNH_2$ by $^3Ar_2CO^*$ abstracts H-atom from R-H. However, the direct H-atom abstraction from R-H by $^3Ar_2CO^*$ occurred to some extents in the cases of the alkylation with $HCONR_2$ and $MeCONR_2$ (R = Me and Et).

Keywords: Hydrogen abstraction; Alkylation; Benzophenone-photosensitization; *tert*-Butylamine

1. Introduction

Benzophenone (BP) in the triplet state ($^3BP^*$) is potentially capable of abstracting a hydrogen atom from hydrogen–carbon linkage of various reactants (R-H). Especially $^3BP^*$ can cause the efficient H-atom abstraction from R-H possessing electron-donating groups (e.g. alcohols, amines, ethers, and hydrocarbons), being thus applied to BP-photosensitized carbon–carbon bond formation by the addition of alkyl radicals (·R) to olefins [1]. However, the H-atom abstraction by $^3BP^*$ from the alkyl groups attached with electron-withdrawing groups such as cyano and chloro groups is very slow. In those cases, therefore, the BP-photosensitized addition of R-H to olefins does not occur at all or is very inefficient. Recently we have found that the novel BP-photosensitized cyanomethylation of diphenylethenes with acetonitrile where the presence of *t*-$BuNH_2$ is essential (Scheme 1) [2]. In this paper, we applied the BP-photosensitized reaction in the presence of *t*-$BuNH_2$ to the alkylation of diphenylethene derivatives (**1a**,**b**), stilbene derivatives (**1c**,**d**), and anethole (**1e**) with MeCOR, Me_2SO, and $RCONR_2$.

2. Experimental details

2.1. Instruments

Melting points were measured using an open capillary tube and are uncorrected. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on a Bruker AC 250P at 250 MHz and 62.9 MHz, respectively. Chemical shifts are reported in ppm relative to TMS (0 ppm, ^1H) or $CDCl_3$ (77.0 ppm, ^{13}C) as internal standards. Mass spectra were determined at an ionization voltage 70 eV on a Hitachi M-2000A. GLC analysis was performed with a 25 m fused-silica capillary column on a Hitachi G-5000A and Shimadzu GC-14A gas chromatography.

2.2. Materials

Commercially available **1a** and **1e** were distilled from sodium under reduced pressure before use. Commercially available **1c**, **1d**, *t*-$BuNH_2$ and Ar_2CO (4,4′-dichlorobenzo-

*Corresponding author. Tel.: +81-986-38-1010; fax: +81-986-38-7217; e-mail: photoya@cc.miyakonojo-nct.ac.jp

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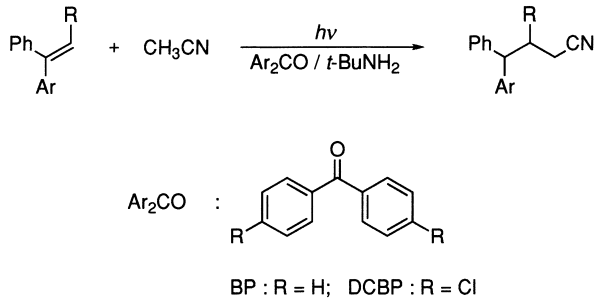


Scheme 1.

phenone and benzophenone) were used as received. The preparation of **1b** was performed according to literature method [3]. As the alkylating reagent (R-H), Me_2CO, MeCOEt, $MeCO_2Et$, DMSO, $HCONMe_2$, $MeCONMe_2$, $HCONEt_2$, and $MeCONEt_2$ were employed after distillation.

2.3. Photoreactions

Into a Pyrex vessel a R-H solution (60 ml) or a benzene/H_2O/R-H solution (60 ml, 7:1:2, v/v/v) containing **1** (2 mmol) and Ar_2CO (1.0 mmol) was introduced, and then *t*-$BuNH_2$ (30 mmol) was added to the solution after argon bubbling for 30 min. The solutions were irradiated for 18 h with an Eikosha PIH-300 high-pressure mercury lamp. The progress of photoreactions was followed by GLC analysis. After the photoreaction mixture was evaporated under reduced pressure, the resulting residue was chromatographed on silica gel to isolate products (**2**–**7**) and unreacted **1**. Column chromatography was carried out using silica gel (BW-300, Fuji Silicia) with hexane, hexane–ethyl acetate (4:1, v/v), and ethyl acetate as eluent. The structures of 5,5-diphenyl-2-pentanone (**2a**) and 1-(*tert*-butylamino)-2,2-diphenylethane (**4**) were determined by comparisons of their spectroscopic properties with authentic samples [2,4].

6,6-Diphenyl-3-hexanone (**2b**): Oil. ^{1}H NMR δ 0.91 (3H, t, $J = 7.3$ Hz), 2.19–2.28 (6H, m), 3.81 (1H, t, $J = 6.0$ Hz), 7.09–7.66 (10 H, m); ^{13}C NMR δ 7.73, 29.22, 35.95, 40.56, 50.37, 126.23, 127.76, 128.70, 144.30, 211.17. Exact mass calc. for $C_{18}H_{20}O$ 252.1514, found *m/z* 252.1488.

3-Methyl-5,5-diphenyl-2-pentanone (**2b′**): Oil.^{1}H NMR δ 1.11 (3H, d, $J = 6.8$ Hz), 2.01 (3H, s), 2.29–2.55 (3H, m), 3.94 (1H, t, $J = 7.6$ Hz), 7.16–7.30 (10H, m); ^{13}CNMR δ 16.71, 28.36, 38.31, 44.72, 48.66, 126.28, 127.75, 128.47, 144.09, 124.24, 212.29. Exact mass calc. for $C_{18}H_{20}O$ 252.1514, found *m/z* 252.1519.

Ethyl 4,4-diphenylbutanoate (**2c**): ^{1}H NMR δ 1.18 (3H, t, J =7.3 Hz), 2.23 (2H, t, $J = 7.0$ Hz), 2.32–2.41 (2H, m), 3.90 (1H, t, $J = 7.7$ Hz), 4.05 (2H, q, $J = 7.1$ Hz), 7.12–7.32 (10H, m); ^{13}C NMR δ 14.16, 30.49, 32.74, 50.43, 60.25, 126.24, 126.28, 127.67, 127.77, 128.45, 128.58, 144.06, 144.20, 173.37. Exact mass calc. for $C_{18}H_{20}O_2$ 268.1463, found *m/z* 268.1434.

1-Methyl-3,3-diphenylpropyl acetate (**2c′**): ^{1}H NMR δ 1.20 (3H, d, $J = 6.2$ Hz), 1.89 (3H, s), 2.16 (1H, ddd, $J = 13.8$, 8.7, 5.0 Hz), 2.41 (1H, ddd, $J = 14.5$, 8.5, 7.3 Hz), 4.01 (1H, dd, $J = 9.0$, 7.0 Hz), 4.70–4.83 (1H, m), 7.10–7.30 (10H, m); ^{13}C NMR δ 20.26, 21.11, 41.56, 47.74, 69.51, 126.15, 126.25, 127.59, 127.63, 128.38, 128.46, 144.03, 144.09, 170.37. Exact mass calc. for $C_{18}H_{20}O_2$ 268.1463, found *m/z* 268.1415.

3,3-Diphenylpropyl methyl sulfoxide (**2d**): ^{1}H NMR δ 2.31 (3H, s), 2.43–2.56 (1H, t, $J = 6.9$ Hz), 7.12–7.32 (10H, m); ^{13}C NMR δ 27.59, 37.70, 49.51, 51.92, 126.04, 127.10, 128.11, 142.68, 142.92. Exact mass calc. for $C_{16}H_{18}OS$ 258.1078, found *m/z* 258.1085.

4-[5-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptyl)]-2-butanone (**3a**): ^{1}H NMR δ 2.02 (3H, s), 2.34–2.35 (4H, m), 2.98–3.02 (2H, m), 3.30–3.40 (2H, m), 3.98 (1H, br t), 7.10–7.27 (8H, m); ^{13}C NMR δ 29.99, 31.00, 33.26, 42.09, 52.50, 126.06, 126.65, 129.78, 130.39, 139.55, 141.01, 208.41. Exact mass calc. for $C_{19}H_{20}O$ 264.1514, found *m/z* 264.1549.

1-[5-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptyl)]-3-pentanone (**3b**): ^{1}H NMR δ 0.97 (3H, t, $J = 7.3$ Hz), 2.26 (2H, q, $J = 7.3$ Hz), 2.30–2.40 (4H, m), 2.90–3.10 (2H, m), 3.25–3.35 (2H, m), 3.99 (1H, br t), 7.15–7.20 (8H, m); ^{13}C NMR δ 7.74, 31.00, 33.20, 35.93, 40.69, 52.00, 126.00, 126.57, 130.00, 130.32, 139.53, 140.98. Exact mass calc. for $C_{20}H_{22}O$ 278.1671, found *m/z* 278.1690.

3-Methyl-4-[5-(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptyl)]-2-butanone (**3b′**): ^{1}H NMR δ 1.08 (3H, t, $J =$ 7.0 Hz), 1.96 (3H, s), 2.30–2.45 (2H, m), 2.50–2.70 (1H, m), 2.90–3.10 (2H, m), 3.30–3.50 (2H, m), 3.99 (1H, br t), 7.06–7.23 (8H, m); ^{13}C NMR δ 17.32, 28.28, 30.64, 33.16, 45.07, 52.00, 126.02, 126.65, 139.22, 130.31, 139.39, 140.97, 212.20.

2-[5-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptyl)]ethyl methyl sulfoxide (**3c**): Oil. ^{1}H NMR δ 2.44 (3H, s), 2.51–2.62 (4H, m), 3.01 (2H, m), 3.30 (2H, m), 4.11 (1H, t, $J =$ 7.3 Hz), 7.00–7.24 (8H, m); ^{13}C NMR δ 30.04, 33.19, 33.24, 38.56, 126.22, 126.93, 129.64, 130.52, 139.48, 140.19.

2,3-Diphenylpropyl methyl sulfoxide (**5a**): ^{1}H NMR δ 2.37 (3H, s) and 2.44 (3H, s), 2.82–3.22 (8H, m), 6.98–7.34 (20H, m), ^{13}C NMR δ 39.02 and 38.44, 42.03 and 41.65, 42.83 and 41.76, 61.25 and 60.22, 126.20 and 126.15, 127.03 and 126.87, 127.63 and 127.40, 128.14 and 128.03, 128.50 and 128.43, 128.92 and 129.07, 138.30 and 138.28, 141.23 and 141.71. Exact mass calc. for $C_{16}H_{18}OS$ 258.1079, found *m/z* 258.1053.

2,3-Diphenyl-3-methylpropyl methyl sulfoxide (**5b**): ^{1}H NMR δ 1.05 (3H, d, $J = 6.3$ Hz) and 1.07 (3H, d, $J = 6.8$ Hz), 2.25 (3H, s) and 2.29 (3H, s), 2.68–2.84 (3H, m), 2.99–3.09 (4H, m), 3.37 (1H, dt, $J = 4.2$, 11.2 Hz), 7.20–7.41 (20H, m), ^{13}C NMR δ 20.04 and 21.16, 37.85 and 39.04, 46.08, 47.62 and 47.04, 60.03 and 61.10, 126.91, 127.30, 127.51, 127.99, 128.33, 128.77, 141.15 and 141.10, 144.33 and 144.34. Exact mass calc. for $C_{17}H_{20}OS$ 272.1236, found *m/z* 272.1196.

Methyl 2-methyl-3-(*p*-methoxyphenyl)propyl sulfoxide (**5c**): ^{1}H NMR δ 1.01 (3H, d, $J = 8.8$ Hz) and 1.04 (3H,

d, $J = 7.3$ Hz), 2.18–2.81 (10H, m), 2.46 (6H, s), 3.71 (6H, s), 6.80 (4H, d, $J = 8.5$ Hz), 7.05 (4H, d, $J = 8.2$ Hz); ^{13}C NMR δ 17.87 and 18.81, 29.42 and 30.22, 37.92 and 37.90, 41.19 and 40.33, 54.20, 60.58, 112.92, 129.23 and 129.31, 130.29 and 130.35, 157.16. Exact mass calc. for $C_{12}H_{18}O_2S$ 226.1027, found *m/z* 226.1006.

N,N-Dimethyl-3,3-diphenylpropanamide (**7a**): M.p. 101–103 °C; ^{1}H NMR δ 2.83 (3H, s), 2.84 (3H, s), 3.03 (2H, d, $J = 7.4$ Hz), 4.68 (1H, t, $J = 7.4$ Hz), 7.16–7.29 (10H, m); ^{13}C NMR δ 35.38, 37.08, 39.14, 47.01, 126.21, 127.65, 128.34, 144.22, 171.00. Exact mass calc. for $C_{17}H_{19}NO$ 253.1467, found *m/z* 253.1449.

N-(3,3-Diphenylpropyl)-*N*-methylformamide (**7a′**): M.p. 162–164°C; ^{1}H NMR δ 2.29 and 2.32 (2H, q, $J = 7.3$ and 7.5 Hz), 2.87 (3H, s), 3.19 and 3.28 (2H, t, $J = 6.9$ Hz), 3.86 and 3.94 (1H, t, $J = 8.0$ and 7.8 Hz), 7.27–7.38 (10H, m), 7.80 and 7.79 (1H, s); ^{13}C NMR δ 29.36 and 32.22, 33.43 and 37.45, 47.80 and 47.93, 126.20 and 126.40, 126.67 and 127.22, 127.61 and 128.17, 128.57 and 128.79, 143.42 and 143.92, 162.45 and 162.83. Exact mass calc. for $C_{17}H_{19}NO$ 253.1467, found *m/z* 253.1504.

N-(3,3-Diphenylpropyl)-*N*-methylacetamide (**7b**): M.p. 91–93 °C; ^{1}H NMR δ 1.82 and 1.99 (3H, s), 2.28 and 2.32 (2H, q, $J = 7.7$ Hz), 2.86 and 2.90 (3H, s), 3.21 and 3.32 (2H, t, $J = 7.6$ Hz), 3.87 and 3.94 (1H, t, $J = 7.7$ and 7.8 Hz), 7.13–7.33 (10H, m); ^{13}C NMR δ 20.87 and 21.82, 32.83 and 32.95, 33.88 and 36.30, 46.91 and 48.44, 49.13 and 49.20, 126.19 and 126.59, 127.47 and 127.61, 128.43 and 128.70, 143.62 and 144.33, 170.33. Exact mass calc. for $C_{18}H_{21}NO$ 267.1623, found *m/z* 267.1618.

N,N-Diethyl-3,3-diphenylpropanamide (**7c**): ^{1}H NMR δ 0.98 (3H, t, $J = 7.1$ Hz), 1.04 (3H, t, $J = 7.1$ Hz), 3.00 (2H, d, $J = 7.6$ Hz), 3.14 (2H, q, $J = 7.1$ Hz), 3.28 (2H, q, $J = 7.1$ Hz), 4.73 (2H, t, $J = 7.1$ Hz), 7.14–7.37 (10H, m); ^{13}C NMR δ 12.78, 14.22, 38.88, 40.20, 41.77, 47.04, 126.16, 127.80, 128.28, 144.14, 170.05. Exact mass calc. for $C_{19}H_{23}NO$: 281.1780, found *m/z* 281.1764.

N-Ethyl-*N*-(1-methyl-3,3-diphenylpropyl)acetamide (**7d**): ^{1}H NMR δ 1.25–1.59 (6H, m), 1.52 (3H, s), 2.20–2.31 (2H, m), 3.14–3.47 (2H, m), 3.59–3.72 (1H, m), 3.83–3.92 (1H, m), 7.16–7.31 (10H, m); ^{13}C NMR δ 14.72 and 15.98, 19.06 and 19.95, 21.56 and 22.31, 29.16 and 35.45, 40.16 and 40.63, 47.88 and 48.73, 51.51 and 53.71, 126.07 and 126.40, 127.26 and 127.72, 128.34 and 128.60, 143.03 and 144.33, 170.35 and 170.48. Exact mass calc. for $C_{20}H_{25}NO$ 295.1936, found *m/z* 295.1980.

2.4. Calculation by PM3

The calculation was performed on a Silicon Graphics Indigo 2 IRIS work station using a Daikin MOL-MOLIS/CRY version 2.0 and MOPAC version 6 [5,6]. The SCF calculations of the heat of formation of R-H and the radical species (·R) were performed by PM3-RHF and PM3-UHF methods, respectively. The calculation data were shown in Table 1.

Table 1
Calculation of the heat of formation (*H*) for hydrogen donors (R-H) and their radicals (·R) (kJ mol^{-1})

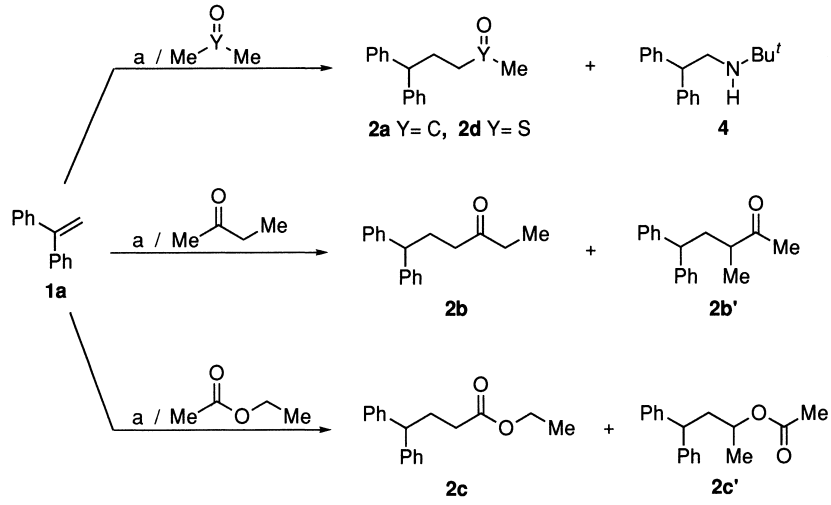
R-H	*H* (R-H)[a]	·R	H (·R)[b]	ΔH[c]
t-BuNH$_2$	−106	·N(H)Bu^t	37	143
MeCN	97	·CH$_2$CN	238	141
Me$_2$CO	−223	·CH$_2$COMe	−79	144
Me$_2$SO	−161	·CH$_2$SOMe	−28	133
MeCOEt	−239	·CH$_2$COEt	−96	143
		·CH(Me)COMe	−128	111
		·CH$_2$CH$_2$COMe	−99	140
MeCO$_2$Et	−416	·CH$_2$CO$_2$Et	−268	148
		·CH(Me)OCOMe	−313	103
		·CH$_2$CH$_2$OCOMe	−277	139
Me$_2$NCHO	−182	·CONMe$_2$	−79	103
		·CH$_2$N(Me)CHO	−77	105
Me$_2$NC(O)Me	−212	·CH$_2$CONMe$_2$	−71	141
		·CH$_2$N(Me)C(O)Me	−104	107
Et$_2$NCHO	−238	·CONEt$_2$	−128	105
		·CH(Me)N(Et)CHO	−137	101
		·CH$_2$CH$_2$N(Et)CHO	−91	142
MeCONEt$_2$	−271	·CH$_2$CONEt$_2$	−124	147
		·CH(Me)N(Et)C(O)Me	−167	104
		·CH$_2$C233H$_2$N(Et)C(O)Me	−130	141

[a] The heat of formation (*H* (kJ mol^{-1})) calculated by PM3-RHF method.
[b] The heat of formation (*H* (kJ mol^{-1})) calculated by PM3-UHF method.
[c] Difference (ΔH (kJ mol^{-1})) in the heat of formation between R-H and ·R; $\Delta H = H$(·R)−H(R-H).

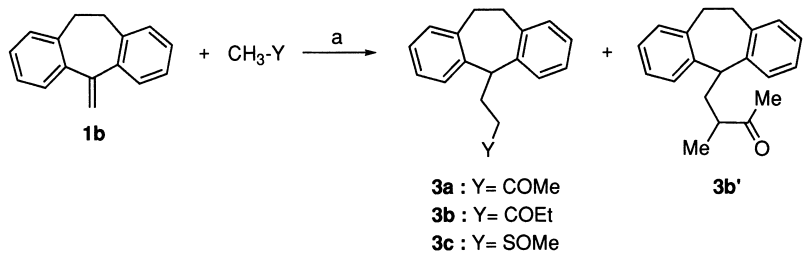
3. Results and discussion

3.1. Photoalkylations

4,4′-Dichlorobenzophenone (DCBP) and benzophenone (BP) were employed as the triplet sensitizer (Ar_2CO), since these were effective for photosensitized cyanomethylation [2]. The Ar_2CO- photosensitized alkylations were performed by irradiation of a solution of the alkylating reagent (R-H) containing **1a–e**, *t*-BuNH$_2$, and Ar_2CO by a high-pressure mercury lamp through a Pyrex filter. Irradiation of an acetone solution containing **1a**, DCBP, and *t*-BuNH$_2$ gave 5,5-diphenyl-2-pentanone (**2a**) in 87% yield (Scheme 2). Also, the photoalkylation of **1b** with acetone gave 4-[5-(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptyl)]-2-butanone (**3a**) in 79% yield (Scheme 3). The results were summarized in Table 2. When 2-butanone and ethyl acetate were used as R-H, two alkylated products were obtained, respectively. The photoalkylation of **1a** with 2-butanone gave 6,6-diphenyl-3-hexanone (**2b**) and 3-methyl-5,5-diphenyl-2-pentanone (**2b**) (entry 6), and the photoalkylation of **1b** with 2-butanone gave 1-[5-(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptyl)]-3-pentanone (**3b**) and 3-methyl-4-[5-(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptyl)]-2-butanone (**3b′**) (entry 7). The photoalkylation of **1a** with ethyl acetate gave a mixture of ethyl 4,4-diphenylbutanoate (**2c**) and 1-methyl-3,3-diphenylpropyl acetate (**2c′**) (entry 8). In the absence of *t*-BuNH$_2$, the Ar_2CO-photosensitized alkylation did not occur, i.e. **2a** was not formed from irradiation of DCBP with **1a** in acetone to recover the starting materials (entry 3).



Scheme 2. [a] Reagents : $h\nu$/Ar_2CO/t-$BuNH_2$.



Scheme 3. [a] Reagents : $h\nu$/Ar_2CO/t-$BuNH_2$.

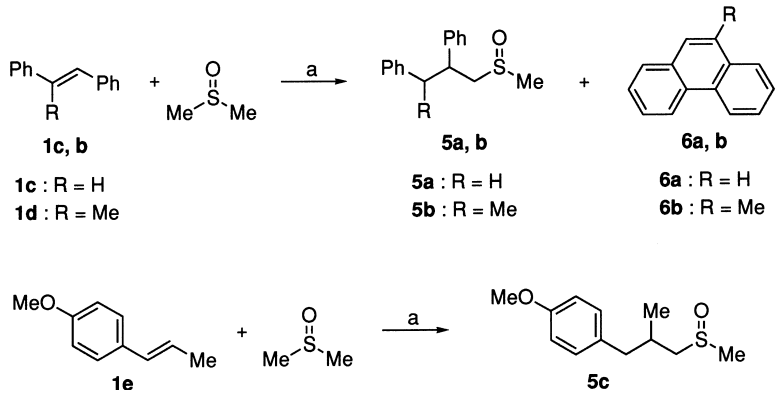
Moreover, the photoalkylations of **1b** with acetone and 2-butanone proceeded in a benzene / H_2O / R-H (7:1:2, v/v/v) solution (entries 5 and 7).

Using DMSO as R-H, the photoalkylation of **1a** gave 3,3-diphenylpropyl methyl sulfoxide (**2d**) in 77% yield along with the formation of 1-(*tert*-butylamino)-2,2-diphenylethane (**4**, 13%) (entry 9). The photoalkylation of **1b** with DMSO gave 2-[5-(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptyl)]ethyl methyl sulfoxide (**3c**, 62%) (entry 11). Moreover, these Ar_2CO-photosensitized alkylation with DMSO were applied to stilbene (**1c**), 1-methyl-1,2-diphenylethene (**1d**), and anethole (**1e**): the photoalkylation of **1c–e** with

Table 2
Ar_2CO-photosensitized alkylation of **1a–e** with R-H in the presence of t-$BuNH_2$[a]

Entry	R-H	1	Ar_2CO	Solvent	Product yield (%)		Conversion of **1** (%)
1	Me_2CO	**1a**	DCBP	Neat	**2a** 87		100
2[b]	Me_2CO	**1a**	BP	Neat	**2a** 48		89
3[c]	Me_2CO	**1a**	DCBP	Neat	**2a** 0		0
4	Me_2CO	**1b**	DCBP	Neat	**3a** 79		80
5	Me2CO	**1b**	DCBP	C_6H_6/H_2O	**3a** 43		51
6	MeCOEt	**1a**	DCBP	Neat	**2b** 23	**2b′** 44	100
7	MeCOEt	**1b**	DCBP	C_6H_6/H_2O	**3b** 25	**3b′** 36	94
8	$MeCO_2Et$	**1a**	BP	Neat	**2c** 15	**2c′** 25	93
9	Me_2SO	**1a**	DCBP	Neat	**2d** 77	**4** 13	95
10[c]	Me_2SO	**1a**	DCBP	Neat	**2d** 0	**4** 0	0
11	Me_2SO	**1b**	DCBP	Neat	**3c** 62		90
12	Me_2SO	**1c**	BP	Neat	**5a** 45	**6a** 23	96
13	Me_2SO	**1d**	BP	Neat	**5b** 23	**6b** 23	70
14	Me_2SO	**1e**	BP	Neat	**5c** 44		100

[a] Irradiation was performed for a solution (60 ml) containing **1a–e** (2 mmol), Ar_2CO (1 mmol), and t-$BuNH_2$ (30 mmol) for 18 h. The terms of neat and C_6H_6/H_2O refer to a solution of R-H (60 ml) and C_6H_6/H_2O/R-H (60 ml, 7:1:2, v/v/v) solution.
[b] Data from [2].
[c] In the absence of t-$BuNH_2$.



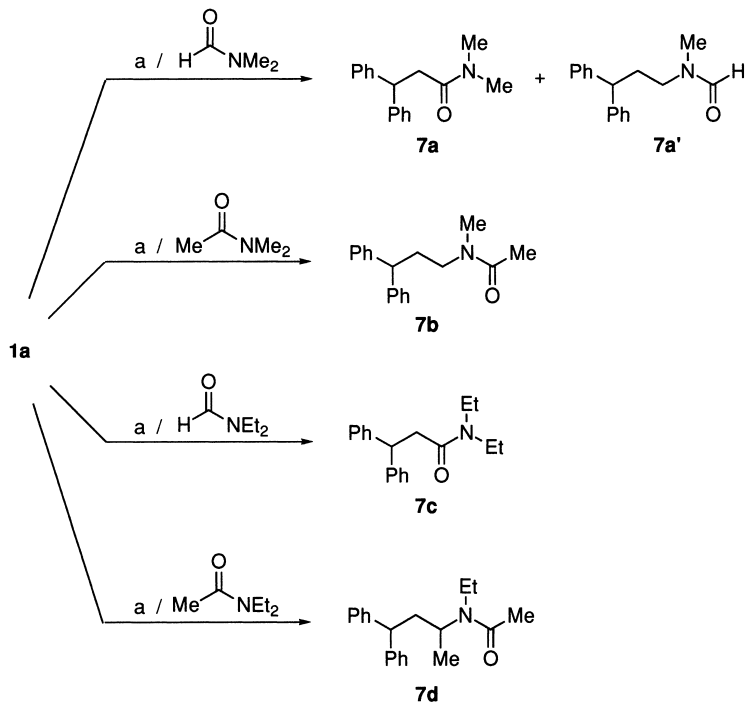
Scheme 4. [a] Reagents : $h\upsilon$/Ar_2CO/t-$BuNH_2$.

DMSO gave arylpropyl methyl sulfoxide derivatives (**5a–c**) accompanied with the formation of phenathrene derivatives (**6a**,**b**) in the case of **1c**,**d** (entries 12–14, Scheme 4). The **1c–e** were not photoalkylated with acetonitrile and acetone in similar conditions.

The photoalkylations with $HCONR_2$ and $MeCONR_2$ (R = Me and Et) in the absence of t-$BuNH_2$ occurred to some extent (Scheme 5 and Table 3), as has been reported for the acetone-photosensitized alkylations of olefines with $HCONH_2$ [7]. However, the photoalkylation with the amides in the presence of t-$BuNH_2$ proceeded more efficiently. The regioselectivity of alkylated products depended upon the amides used. In the photoalkylation of **1a** with $HCONMe_2$, H-atom abstraction from both the formyl and the *N*-methyl groups resulted in the formation of *N,N*-dimethyl-3,3-diphenylpropanamide (**7a**) and *N*-(3,3-diphenylpropyl)-*N*-methylformamide (**7a′**) in 45% and 46% yields (entry 15). In the case of $MeCONMe_2$, only H-atom abstraction from the *N*-methyl group occurred to give *N*-(3,3-diphenylpropyl)-*N*-methylacetamide (**7b**) (entry 19). In the case of $HCONEt_2$, H-atom abstraction occurred at the formyl group to give *N,N*-diethyl-3,3-diphenylpropanamide (**7c**) (entry 21). The photoalkylation of **1a** with $MeCONEt_2$ proceeded very inefficiently to give *N*-ethyl-*N*-(1-methyl-3,3-diphenylpropyl)acetamide (**7d**) (entry 23).

3.2. Mechanism

The present Ar_2CO-photosensitized alkylation of **1** with MeCOR (R = Me, Et, OEt) and Me_2SO can not be inter-



Scheme 5. [a] Reagents : $h\upsilon$/Ar_2CO/t-$BuNH_2$.

Table 3
Ar_2CO-photosensitized alkylation of **1a** with $NCONR_2$ and $MeCONR_2$ in the presence of *t*-$BuNH_2$[a]

Entry	R-H	Ar_2CO	Solvent	Product yield (%)		Conversion of **1a** (%)
15	$HCONMe_2$	BP	neat	**7a** 45	**7a′** 46	100
16[b]	$HCONMe_2$	BP	neat	**7a** 11	**7a′** 22	89
17	$HCONMe_2$	DCBP	neat	**7a** 38	**7a′** 23	100
18[b]	$HCONMe_2$	DCBP	neat	**7a** 6	**7a′** 17	72
19	$MeCONMe_2$	DCBP	C_6H_6	**7b** 90		100
20[b]	$MeCONMe_2$	DCBP	C_6H_6	**7b** 72		100
21	$HCONEt_2$	DCBP	C_6H_6	**7c** 67		100
22[b]	$HCONEt_2$	DCBP	C_6H_6	**7c** 41		60
23	$MeCONEt_2$	DCBP	C_6H_6	**7d** 9		40

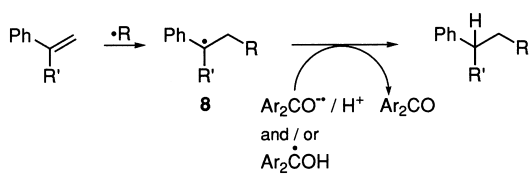
[a] Irradiation was performed for a solution (60 ml) containing **1a** (2 mmol), Ar_2CO (1 mmol), and *t*-$BuNH_2$ (30 mmol) for 19 h. The terms of neat and C_6H_6 refer to a solution of R-H (60 ml) and a benzene (60 ml) solution containing R-H (20 or 200 mmol), respectively.
[b] In the absence of *t*-$BuNH_2$.

preted by the direct H-atom abstraction from these hydrogen donors (R-H) by the excited triplet state of Ar_2CO ($^3Ar_2CO^*$), since no photoalkylation occurred at all in the absence of *t*-$BuNH_2$. The essential role of *t*-$BuNH_2$ is explained by the hydrogen atom transfer from the amino group of *t*-$BuNH_2$ to $^3Ar_2CO^*$ via a charge-transfer interaction to generate *t*-BuN(H)· and $Ar_2C(OH)$· (Eqs. (1) and (2)) [8,9], as have been previously reported in the Ar_2CO-photosensitized cyanomethylation of **1a**,**b** with acetonitrile in the presence of *t*-$BuNH_2$ [2]. Therefore, it is reasonable to assume that the H-atom abstraction by *t*-BuN(H)· from methyl and methylene groups attached to carbonyl and sulfonyl groups in R-H is a key step to generate the alkyl radicals (·R) (Eq. 3). The generation of *t*-BuN(H)· is suggested from the formation of 1-(*tert*-butylamino)-2,2-diphenylethane (**4**) which would be produced by the addition of *t*-BuN(H)· to **1a**. The photoalkylation of **1** might proceed through the addition of ·R to the double bond of **1** followed by the reduction of the adduct radicals (**8**) with Ar_2CO^{-}· and/or $Ar_2C(OH)$· to give the final products (Eq. 4). On the other hand, the photoalkylation of **1** with $HCONR_2$ (R = Me, Et) and $MeCONMe_2$ proceeded partially by the direct H-atom abstraction from these hydrogen donors by $^3Ar_2CO^*$, since the photoalkylation of **1** occurred in the absence of *t*-$BuNH_2$ [7].

$$^3Ar_2CO^* + t\text{-}BuNH_2 \longrightarrow [\,Ar_2CO^{\bullet-} / t\text{-}BuNH_2^{\bullet+}\,] \quad (1)$$

$$[\,Ar_2CO^{\bullet-} / t\text{-}BuNH_2^{\bullet+}\,] \longrightarrow Ar_2\dot{C}OH + t\text{-}Bu\dot{N}H \quad (2)$$

$$t\text{-}Bu\dot{N}H + R\text{-}H \rightleftharpoons t\text{-}BuNH_2 + \bullet R \quad (3)$$



(4)

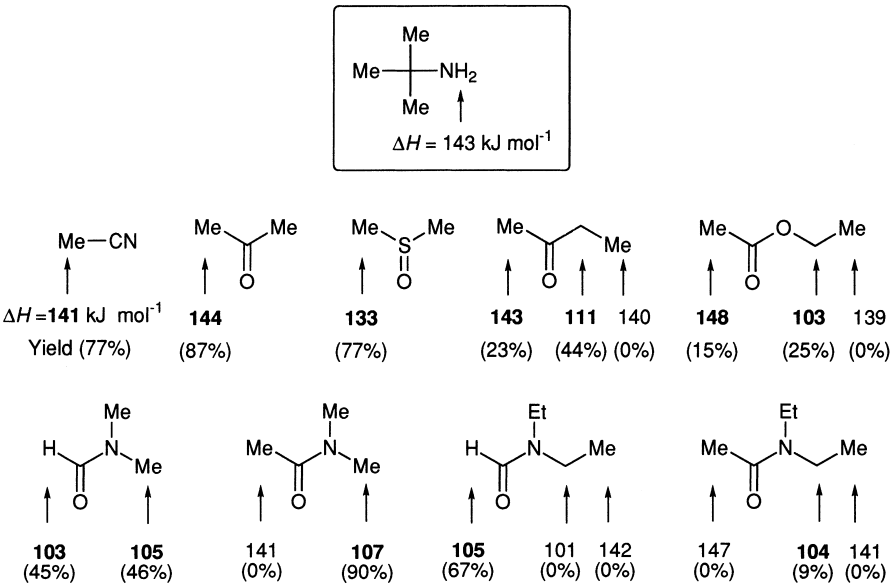
Thus, the H-atom abstraction from R-H by *t*-BuN(H)· is a key mechanistic pathway resulting in successful photoalkylations. The capability to abstract a hydrogen atom by *t*-BuN(H)· can be related to the bond-dissociation energy of the hydrogen atom from R-H. However, direct estimation of the bond-dissociation energy is not so easy. As a measure to estimate the C–H bond-dissociation energy, we used the difference (ΔH) in the heat of formation (H) between R-H and their radicals (R·); $\Delta H = H$ (R·) $- H$ (R-H) [10]. The values of H of R-H and R· were calculated by simple PM3-RHF and PM3-UHF methods, respectively.

$$R\text{-}H \rightarrow R\cdot \quad \Delta H\,(R\text{-}H)$$

$$t\text{-}BuNH\text{-}H \rightarrow t\text{-}BuN\,(H)\cdot \quad \Delta H\,(t\text{-}BuNH\text{-}H)$$

$$R\text{-}H + t\text{-}BuN(H)\cdot \rightarrow R\cdot + t\text{-}BuNH_2 \quad \Delta H\,(R\text{-}H) - \Delta H\,(t\text{-}BuNH\text{-}H)$$

The hydrogen atom of MeCN, Me_2CO, and Me_2SO ($\Delta H = 133$–144 kJ mol^{-1}) can be abstracted with *t*-BuN(H)· ($\Delta H = 143$ kJ mol^{-1}) (Scheme 6). In the cases of MeCOEt and $MeCO_2Et$, the H-atom abstraction from the methylene group ($\Delta H < 110$ kJ mol^{-1}) occurred more efficiently than those from $C\underline{H}_3CO$- and $C\underline{H}_3CH_2$- groups ($\Delta H > 140$ kJ mol^{-1}). Although the C–H bonds of $C\,\underline{H}_3CO$- and $C\underline{H}_3CH_2$- groups have almost same ΔH values, the H-atom abstraction occurred at $C\underline{H}_3CO$- group but not at $C\underline{H}_3CH_2$- group. Probably the hydrogen-bond interactions between carbonyl groups and *t*-$BuNH_2$ would accelerate the H-atom abstraction from the C–H bonds neighboring with the carbonyl groups [11,12]. The H-atom abstraction from $HCONR_2$ and $MeCONR_2$ (R = Me, Et) occurred at $\underline{H}CO$- and $\underline{Me}N$- which ΔH values were less than 110 kJ mol^{-1}, but did not occur at $C\underline{H}_3CO$- and $\underline{H}_3CCH_2$- groups having greater ΔH values than 130 kJ mol^{-1}. The H-atom abstraction from the *N*-methylene group ($\Delta H = 101$ and 104 kJ mol^{-1}) were very inefficient due to the steric hindrance around the methylene group. Moreover, it is found that $^3Ar_2CO^*$ can abstract directly the hydrogen atoms having ΔH values of <110 kJ mol^{-1} (e.g. $\underline{H}CONR_2$ and $\underline{1e}CON\underline{Me}_2$), but can not abstract those having ΔH values of > 130 kJ mol^{-1} (e.g. Me_2CO and Me_2SO).



Scheme 6.

In photochemical reaction system, aliphatic ketones in the excited states are well known to undergo H-atom abstraction [13–15] as well as cycloaddition [16–18]. However, aliphatic ketones in the ground states scarecely play as an alkylating reagent in photochemical reaction except for a few examples, i.e., the addition of $\cdot CH_2COMe$ generated by the H-atom abstraction of acetone to norbornene [19–21]. The present photosensitization using Ar_2CO/*t*-$BuNH_2$ pair are applied to alkylation by acetone, dimethyl sulfoxide, and their related compounds which were inert for usual Ar_2CO-photosensitizations. It is of mechanistic interest to note that *t*-BuN(H)· plays as a radical mediator abstracting a hydrogen atom from the alkylating reagents.

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