

Supplementary Information

Photoinduced ω -Bond Dissociation of *m*-Halomethylbenzophenones Studied by Laser Photolysis Techniques and DFT Calculations. Substituted Position Effects

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Transient absorption measurements of ortho-substituted benzophenones

To understand the substitution position effects to ω -cleavage, laser photolysis studies of ortho-HMBPs was carried out. *o*-Methylbenzophenone (*o*-MBP) was commercially purchased. *o*-Chloromethylbenzophenone (*o*-CMBP) was synthesized by a reaction of *o*-MBP with sulfuryl chloride in CCl₄ in the presence of benzoyl peroxide, and separated by passing through a silica-gel column with a mixture of hexane and benzene (5:1 v/v). *o*-Bromomethylbenzophenone (*o*-BMBP) was synthesized by a reaction of *o*-MBP with *N*-bromosuccinimide in benzene in the presence of benzoyl peroxide, but it seemed to decomposed upon separation on a silica-gel column. Therefore, we were unable to obtain *o*-BMBP. *o*-MBP and *o*-CMBP were purified by repeated recrystallizations from hexane.

Fig. S1 show the transient absorption spectra obtained upon 266 nm laser pulsing in *o*-MBP and *o*-CMBP in ACN at 295 K.

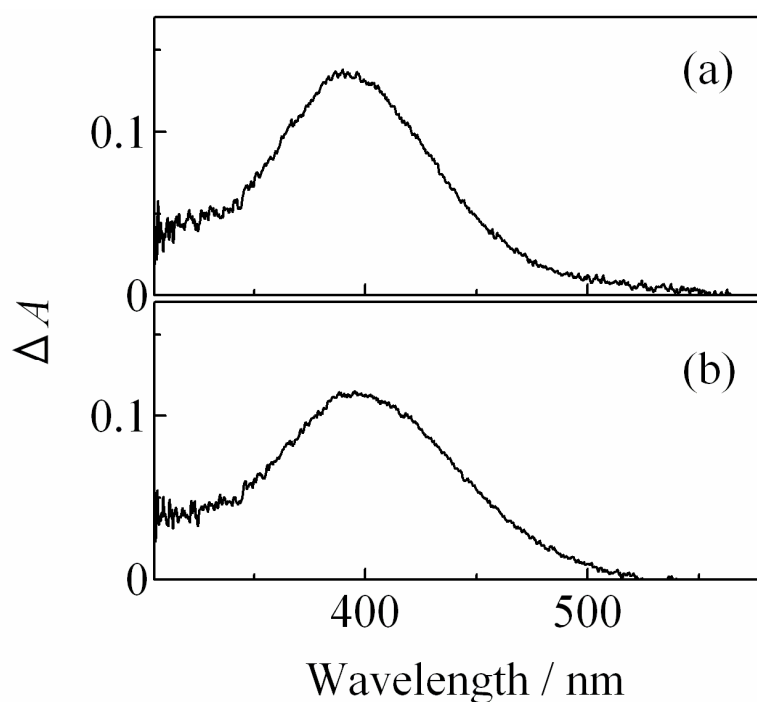
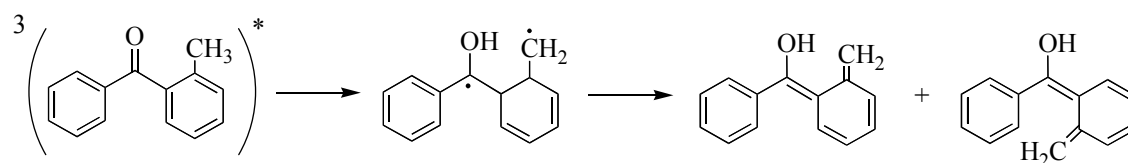


Fig. S1 Transient absorption spectra obtained at 500 ns upon 266 nm laser pulsing in *o*-MBP (a) and *o*-CMBP (b) in degassed acetonitrile at 295 K.

The obtained transient absorption spectra are similar to each other. It is well known that photoexcited *o*-MBP undergoes intramolecular H-atom abstraction in the triplet state to produce a biradical,¹ which forms the enol compounds within 26 ns.²



Therefore, the obtained transient absorption spectra are due to the corresponding enols. These observations indicate that ω -cleavage is absent in excited *o*-CMBP.

DFT calculation results

Potential energies plotted in Fig. 5 in the text are numerated in Tables S1 and 2.

Table S1 Potential energies, $E(S_1)$ and $E(T_1)$ of the S_1 and T_1 states of BMBPs at a distance, $d(\text{C-Br})$ between the benzylic carbon and Br atoms calculated at the B3LYP/6-311G(d) level.

$d(\text{C-Br}) / \text{nm}$	$E(S_1) / \text{kcal mol}^{-1}$		$E(T_1) / \text{kcal mol}^{-1}$	
	<i>m</i> -	<i>p</i> -	<i>m</i> -	<i>p</i> -
0.1900	78.09	76.92	66.57	-
0.1950	-	-	-	64.23
0.2000	-	74.01	-	-
0.2016	-	-	64.49	-
0.2020	76.00	-	-	-
0.2043	-	-	-	63.23
0.2100	76.73	-	65.25	-
0.2120	-	73.25	-	-
0.2150	-	-	-	64.10
0.2200	79.04	73.39	67.57	-
0.2250	80.52	-	69.09	65.79
0.2300	82.11	73.72	68.35	63.85
0.2350	82.48	73.91	65.92	62.27
0.2400	79.32	74.42	63.78	-
0.2450	-	74.39	-	-

0.2500	73.80	71.12	60.33	57.56
0.2600	-	-	57.81	-

Table S2 Potential energies, $E(S_1)$ and $E(T_1)$ of the S_1 and T_1 states of CMBPs at a distance, $d(\text{C-Cl})$ between the benzylic carbon and Cl atoms calculated at the B3LYP/6-311G(d) level.

$d(\text{C-Cl}) / \text{nm}$	$E(S_1) / \text{kcal mol}^{-1}$		$E(T_1) / \text{kcal mol}^{-1}$	
	<i>m</i> -	<i>p</i> -	<i>m</i> -	<i>p</i> -
0.1700	79.98	-	-	-
0.1740	-	77.01	66.40	-
0.1750	-	-	-	65.43
0.1800	-	-	-	64.02
0.1840	75.95	74.95	64.49	63.56
0.1900	-	-	-	63.79
0.2000	78.82	75.24	67.47	65.57
0.2100	82.36	76.43	71.09	68.21
0.2200	86.35	80.83	75.20	70.96
0.2250	88.36	-	-	69.32
0.2300	88.94	85.85	71.74	67.90
0.2350	-	-	70.18	-
0.2400	82.91	80.18	68.83	65.56
0.2500	-	-	66.82	63.87
0.2600	73.82	71.56	65.46	62.77

References

- 1 T. Suzuki, T. Omori, T. Ichimura, *J. Phys. Chem. A*, 2000, **104**, 11671, and references cited therein.
- 2 T. Nakayama, K. Hamanoue, T. Hidaka, M. Okamoto, H. Teranishi, *J. Photochem.*, 1984, **24**, 71.