

## Exploratory Study on Photoinduced Single Electron Transfer Reactions of $\alpha,\beta$ -Epoxy Ketones with Amines

Eietsu Hasegawa,\* Kenyuki Ishiyama, Takaaki Horaguchi, and Takahachi Shimizu

Department of Chemistry, Faculty of Science, Niigata University, Ikarashi, Niigata 950-21, Japan

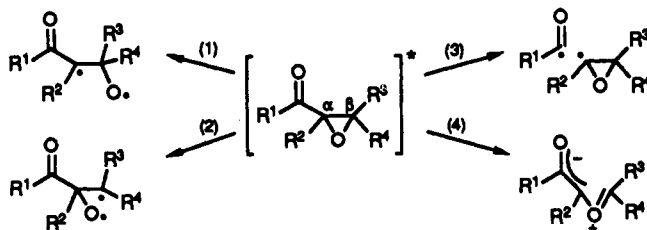
Received June 25, 1990

Photoinduced single electron transfer (SET) reactions of  $\alpha,\beta$ -epoxy ketones have been studied using alkylamine electron donors. Irradiation of chalcone epoxide **1** with triethylamine (TEA) afforded  $\beta$ -diketone **2** and  $\beta$ -hydroxy ketone **3**. Photoreaction of **1** with TEA in MeOH resulted in a slightly increased product ratio (**3**/**2**) compared with that in MeCN. When 1,4-diazabicyclo[2.2.2]octane (DABCO) was used instead of TEA, a decrease in the yield of **3** was observed. Only **2** was obtained on irradiation of a solution of **1** in TEA and MeCN containing  $\text{LiClO}_4$ . Studies of photoreactions of dypnone epoxide **9**, benzoylisopropylethylene epoxide **12**, and acrylophenone epoxide **15** indicate that the nature of  $\beta$ -substituent also influences the product distribution. It was also found that 1,6-bis(dimethylamino)pyrene (BDMAP) sensitizes the photoreaction of **1** in the presence of TEA to produce **2**. Based on the results obtained, a reaction mechanism involving selective  $\text{C}\alpha\text{-O}$  bond cleavage of intermediate  $\alpha,\beta$ -epoxy ketone anion radicals is proposed.

### Introduction

Much attention has been focused on the reactivity of organic ion radicals since these species are important intermediates in electron-transfer reactions.<sup>1,2</sup> Irradiation of electron donor-acceptor systems is known to be a useful method to generate cation radical and anion radical pairs.<sup>2</sup>

Photochemical studies on  $\alpha,\beta$ -epoxy ketones have demonstrated that several types of photochemical processes are open to these substances, and these depend on substitution and the nature of reactive excited states.<sup>3</sup> These include (1)  $\text{C}\alpha\text{-O}$  bond cleavage followed by  $\beta$ -substituent migration to afford  $\beta$ -diketones,<sup>4</sup> (2)  $\text{C}\beta\text{-O}$  bond cleavage when aryl substituents are at the  $\beta$ -position to generate  $\alpha$ -diketone formation via  $\alpha$ -substituent migration,<sup>5</sup> (3) cleavage  $\alpha$  to the carbonyl to produce epoxy and acyl radicals,<sup>6</sup> and (4)  $\text{C}\alpha\text{-C}\beta$  bond cleavage to give ylide intermediates.<sup>7</sup>



(1) (a) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* 1984, 20, 55. (b) Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987.

(2) (a) Mattes, S. L.; Farid, S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233. (b) Davidson, R. S. *Ad. Phys. Org. Chem.* 1983, 19, 1. (c) Julliard, M.; Chanon, M. *Chem. Rev.* 1983, 83, 425. (d) Mariano, P. S. *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: London, 1984; p 145. (e) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* 1986, 86, 401. (f) Fox, M. A. *Adv. Photochem.* 1986, 13, 295. (g) *Photoinduced Electron Transfer, Parts A-D*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988.

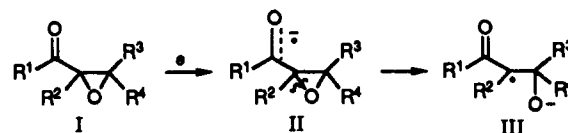
(3) (a) Nastashi, M.; Streith, J. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 445. (b) Padwa, A. *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1967; Vol. 1, p 91. (c) Bertoniere, N. R.; Griffin, G. W. *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1973; Vol. 3, p 115.

(4) (a) Bodforss, S. *Chem. Ber.* 1918, 51, 214. (b) Johnson, C. K.; Domony, B.; Reusch, W. J. *Am. Chem. Soc.* 1963, 85, 3984. (c) Markos, C. S.; Reusch, W. *Ibid.* 1967, 89, 3363. (d) Dewar, D. J.; Sutherland, R. G. *J. Chem. Soc., Perkin Trans 2* 1977, 1522. (e) Paquette, L. A.; Nitz, T. J.; Ross, R. J.; Springer, J. P. *J. Am. Chem. Soc.* 1984, 106, 1446.

(5) (a) Pappas, S. P.; Gresham, R. M.; Miller, M. J. *J. Am. Chem. Soc.* 1970, 92, 5797. (b) Pappas, S. P.; Bao, L. O. *Ibid.* 1973, 95, 7906. (c) Hallett, P.; Muzart, J.; Pete, J. P. *J. Org. Chem.* 1981, 46, 4275.

(6) (a) Dunston, J. M.; Yates, P. *Tetrahedron Lett.* 1964, 505. (b) Padwa, A. *Ibid.* 1964, 813. (c) Simikin, R. D.; Zimmerman, H. E. *Ibid.* 1964, 1847.

It is interesting that  $\alpha,\beta$ -epoxy ketones have not received much attention as anion radical precursors in photoinduced SET chemistry.<sup>8</sup> In connection with our studies of ion-radical and free-radical ring-opening reactions of epoxy carbonyl compounds,<sup>9</sup> we became interested in the chemistry of  $\alpha,\beta$ -epoxy ketone anion radicals which are generated by irradiation of the precursor ketones in the presence of electron donors. Recent efforts focusing on the SET photochemistry of carbonyl compounds and amines have demonstrated that carbonyl anion radicals are formed under several different reaction conditions.<sup>10</sup> The presence of negative charge at the carbonyl carbon of  $\alpha,\beta$ -epoxy ketone anion radicals should cause selective  $\text{C}\alpha\text{-O}$  bond cleavage ( $\text{I} \rightarrow \text{II} \rightarrow \text{III}$ ).<sup>11</sup> If efficient proton



(7) (a) Muzart, J.; Pete, J. P. *Tetrahedron Lett.* 1979, 2797. (b) Lee, G. A. *J. Org. Chem.* 1978, 43, 4256. (c) Kumar, C. V.; Das, P. K.; O'Sullivan, W. I.; Ege, S. N.; Griffin, G. W. *J. Chem. Soc., Perkin Trans 2* 1984, 1745. (d) Kumar, C. V.; Ramaiah, D.; Das, P. K.; George, M. V. *J. Org. Chem.* 1985, 50, 2818.

(8) Photochemical reaction of epoxy quinone with amines has been reported, which is only an example related to photoinduced SET reaction of epoxy carbonyl compounds. Maruyama, K.; Otsuki, T.; Osuka, A.; Suzuki, H. *Chem. Lett.* 1982, 1.

(9) (a) Hasegawa, E.; Ishiyama, K.; Horaguchi, T.; Shimizu, T. *J. Chem. Soc., Chem. Commun.* 1990, 550. (b) Hasegawa, E.; Ishiyama, K.; Kashiwazaki, H.; Horaguchi, T.; Shimizu, T. *Tetrahedron Lett.* 1990, 31, 4045.

(10) (a) Davidson, R. S.; Steiner, P. R. *J. Chem. Soc., Perkin Trans 1* 1972, 1375. (b) Davidson, R. S.; Orotin, S. P. *J. Chem. Soc., Chem. Commun.* 1974, 209. (c) Guttenplane, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* 1972, 94, 4040. (d) Inbar, S.; Linschitz, H.; Cohen, S. G. *Ibid.* 1981, 103, 1048. (e) Wagner, P. J.; Kamppainen, A. E.; Jellinek, T. *Ibid.* 1972, 94, 7512. (f) Wagner, P. J.; Ersfeld, D. A. *Ibid.* 1976, 98, 4515. (g) Shaefer, L. G.; Peters, K. S. *Ibid.* 1980, 102, 7566. (h) Simon, J. D.; Peters, K. S. *Ibid.* 1981, 103, 6403. (i) Manring, L. E.; Peters, K. S. *Ibid.* 1983, 105, 5708. (j) Manring, L. E.; Peters, K. S. *Ibid.* 1985, 107, 187. (k) Cookson, R. C.; Hudec, J.; Mirza, N. A. *J. Chem. Soc., Chem. Commun.* 1968, 180. (l) Pienta, N. J.; Mckimmey, J. E. *J. Am. Chem. Soc.* 1982, 104, 5501. (m) Pienta, N. J. *Ibid.* 1984, 106, 2706. (n) Smith, D.; Pienta, N. J. *Tetrahedron Lett.* 1984, 25, 915. (o) Schuster, D. I.; Bonneau, R.; Dunn, D. A.; Rao, J. M.; Dubien, J. J. *J. Am. Chem. Soc.* 1984, 106, 2706. (p) Dunn, D. A.; Schuster, D. I.; Bonneau, R. *Ibid.* 1985, 107, 2802. (q) Givens, R. S.; Atwater, B. W. *Ibid.* 1986, 108, 5028. (r) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *Ibid.* 1988, 110, 8099. (s) Xu, W.; Jeon, Y. T.; Hasegawa, E.; Yoon, U. C.; Mariano, P. S. *Ibid.* 1989, 111, 406. (t) Ci, X.; da Silva, R. S.; Nicodem, D.; Whitten, D. G., *Ibid.* 1989, 111, 1337.

Table I. Photoreactions of Epoxy Ketones with TEA<sup>a</sup>

EK	solv	irrad time, min	conv, %	product yields, <sup>b</sup> %	
				DK	HK
1a	MeCN	5	39	60	22
	MeOH	10	31	49	28
1b	MeCN	5	36	26	15
	MeOH	10	37	11	8
1c	MeCN	5	30	58	25
	MeOH	10	37	46	26
1d	MeCN	5	41	67	17
	MeOH	10	37	41	22
9	MeCN	5	60	0	44
	MeOH	5	74	0	45
12	MeCN	10	52	16	36
	MeOH	20	47	14	38
15	MeCN	20	63	0	30
	MeOH	20	44	0	35

<sup>a</sup>[EK] = 8.5–8.6 mM, [TEA] = 0.98 M. <sup>b</sup>Isolated yields based on conversion of EK.

and hydrogen atom abstraction processes follow, this pathway via ring-opened anion radical III would lead to formation of  $\beta$ -hydroxy ketones. To test this, we have conducted photoinduced SET reactions of several aryl substituted  $\alpha,\beta$ -epoxy ketones (EK) using triethylamine (TEA) as an electron donor. We have found that  $\beta$ -hydroxy ketone (HK) formation does indeed occur but that unexpected  $\beta$ -diketones (DK) are obtained as major products in some cases.

### Results and Discussion

Preparative irradiations of the *trans*-chalcone epoxides (1), *trans*-dypnone epoxide (9), *trans*-benzoylisopropyl-ethylene epoxide (12), and acrylophenone epoxide (15) were conducted in MeCN and MeOH solutions containing TEA. The results of these reactions are summarized in

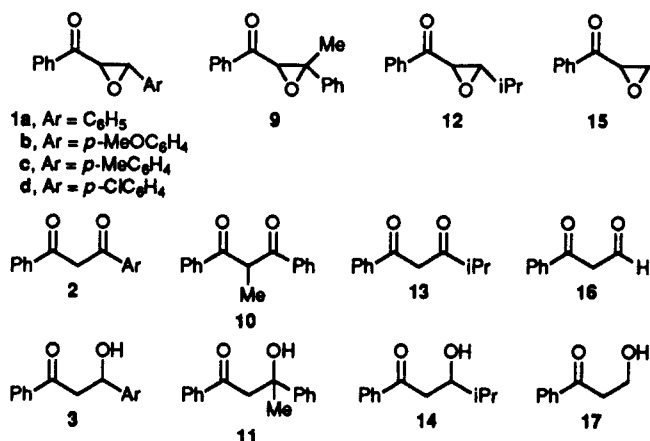
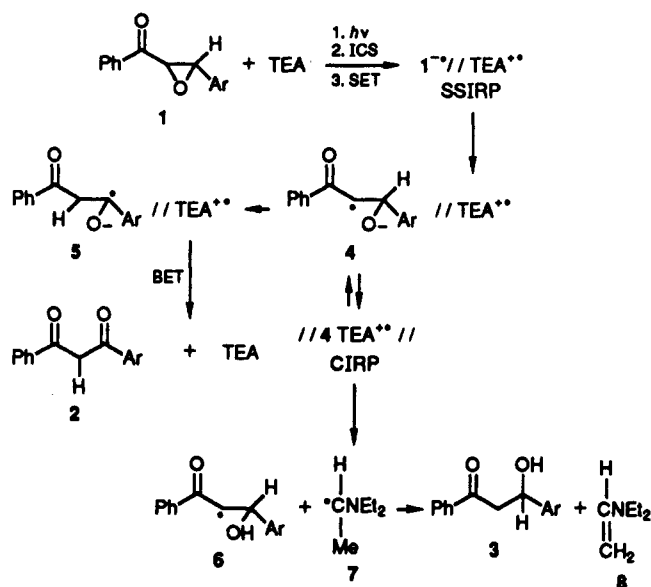


Table I.<sup>12</sup> When a MeCN solution of 1a and TEA was irradiated,<sup>13</sup> the diketone 2a was obtained as a major

(11) There are several approaches for the investigation of reductive cleavage reactions of  $\alpha,\beta$ -epoxy ketones from the viewpoint of synthetic organic chemistry. Little attention, however, has been focused on the reactivity of  $\alpha,\beta$ -epoxy ketone anion radical itself. (a) Smith, J. G. *Synthesis* 1984, 629 and references cited therein. (b) Shapiro, E. L.; Gentles, M. J.; Kabasakiam, P.; Maggati, A. *J. Org. Chem.* 1981, 46, 5017. (c) Osuka, A.; Takaoka, K.; Suzuki, H. *Chem. Lett.* 1984, 271. (d) McChesney, J. D.; Thompson, T. N. *J. Org. Chem.* 1985, 50, 3473. (e) Custiang, M. D.; Rahm, A.; Dahan, N. *Ibid.* 1986, 51, 1672. (f) Molander, G. A.; Hahn, G. *Ibid.* 1986, 51, 2596. (g) Torii, S.; Okumoto, H.; Nakayasu, S.; Kotani, T. *Chem. Lett.* 1989, 1975.

(12) While spectroscopic data obtained for photoproducts, diketones and hydroxy ketones, were consistent with proposed structures, their independent preparations were also performed (see the Experimental Section).

Scheme I



product along with the hydroxy ketone 3a. Since prolonged irradiation of the solution resulted in decomposition of photoproducts, irradiation had to be terminated at low conversion of 1a. Indeed, irradiation of 2a with TEA in MeCN afforded complex mixtures which contained pinacol type dimers<sup>14</sup> and none of the hydroxy ketone 3a. Similar results were obtained for photoreactions of 1b, 1c, and 1d with TEA in MeCN. Irradiation of epoxy ketones 1 in MeCN and in the absence of TEA for 1–2 h also produced diketones 2. However, the yields of 2 in these reactions were poor (36% for 2a, <1% for 2b,<sup>15</sup> 5% for 2c, 3% for 2d).

Based on above results and the observations made in studies of ketone–amine photoreactions,<sup>10</sup> a mechanism involving C $\alpha$ –O bond cleavage of the anion radical of 1 (1<sup>-</sup>) is proposed to explain these transformations (Scheme I). The processes are initiated by SET from TEA to the excited triplet of epoxy ketones 1 (31\*). The efficiency of this step is supported by calculations which show that the free energy changes for the SET processes between 31\* and TEA are negative.<sup>16</sup> It should be noted that photoexcitation of 1 gives 31\* via an expectedly efficient intersystem crossing (ISC).<sup>7d</sup> Ground-state TEA quenches 31\* to afford

(13) Absorption spectrum of the mixture of 1a (8.50 mM) and TEA (0.98 M) in MeCN did not show any new absorption bands, which indicates that no significant interaction exists between 1a and TEA at their ground states. Although TEA apparently absorbs the Pyrex-filtered light which was used for preparative photoreactions of epoxy ketones, the absorption spectrum of this system indicated that most of the incident light (>91%) would be absorbed by 1a under the conditions employed.

(14) Evans, D. H.; Woodbury, E. C. *J. Org. Chem.* 1967, 32, 2158.

(15) It was reported that irradiation of 1b afforded 2-(4-methoxyphenyl)-4-phenyl-1,3-dioxole which is presumably formed via C $\alpha$ –C $\beta$  bond fission.<sup>7b</sup>

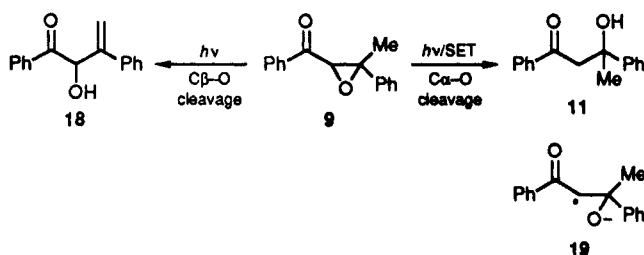
(16) (a) The free energy changes ( $\Delta G$ ) for the SET processes between 31\* and TEA was calculated to be -10 to -11 kcal/mol from the equation,<sup>16b</sup>  $\Delta G$  (kcal/mol) = 23.06( $E_{1/2}^{ox} - E_{1/2}^{red} + C$ ) -  $E_{0,0}$  in which  $E_{1/2}^{ox}$  and  $E_{1/2}^{red}$  represent redox potentials of electron donor and acceptor,<sup>17</sup>  $E_{0,0}$  and  $C$  represent excitation energy of those substrates and Coulomb term, respectively. Excitation energy of the triplet state of 1a was estimated to be about 71 kcal/mol from its phosphorescence.<sup>4d</sup> The Coulomb term in MeCN is known to be -0.06 eV.<sup>16b</sup> (b) Rehm, D.; Weller, A. *Isr. J. Chem.* 1970, 8, 259.

(17) Redox potentials ( $E_{1/2}^{ox}$ ,  $E_{1/2}^{red}$ , V vs SCE) were estimated from peak potentials obtained by cyclic voltammetry (Pt electrode, scan rate 20 mV/s or 100 mV/s) in MeCN containing tetraethyl ammonium perchlorate (0.1 M).  $E_p^{red}$  = -1.70 for 1a; -1.73 for 1b; -1.75 for 1c; -1.73 for 1d; -1.83 for 9; -1.76 for 12; -1.77 for 15.  $E_p^{ox}$  = +0.89 for TEA; +0.71 for DABCO; +0.42 for BDMAP.

$1^-$  and  $\text{TEA}^{++}$ . Selective  $\text{C}\alpha\text{-O}$  bond cleavage of  $1^-$  would occur to form the ring-opened anion radical **4**,<sup>18</sup> a process which is driven by the relief of ring strain. Formal 1,2-hydrogen migration in **4** results in the formation of the anion radical **5**, and subsequent back electron transfer (BET) from **5** to  $\text{TEA}^{++}$  produces **2**.

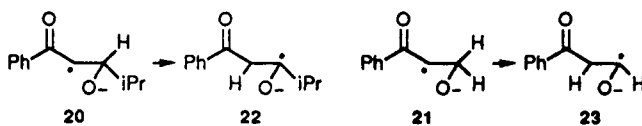
In these reactions, solvent-separated ion radical pair (SSIRP) between **4** and  $\text{TEA}^{++}$  should be in equilibrium with the contact ion radical pair (CIRP). In the CIRP, **4** can abstract a proton from  $\text{TEA}^{++}$  to give  $\alpha$ -keto radical **6** and  $\alpha$ -amino radical **7**. Ultimately, **6** would abstract a hydrogen atom from **7** to give hydroxy ketone **3** and enamine **8**. Alternatively, sequential SET from **7** to **6** and proton transfer in an enolate iminium ion pair could occur to produce same products.<sup>19</sup>

In order to determine how the nature of  $\beta$ -substituents would influence this SET photoprocess, photoreactions of **9**, **12**, and **15** with TEA in MeCN were probed. Interestingly, diketones were no longer the major photoproducts in reactions of these systems. Instead hydroxy ketones are produced predominantly, although the yields were low. It should be noted that irradiation of **9** is known to produce 1,3-diphenyl-2-hydroxy-3-butene-1-one (**18**) via intramo-



lecular hydrogen atom abstraction by the benzoyl  $n\pi^*$  triplet.<sup>20</sup> However, we could not observe formation of **18** on irradiation of **9** with TEA in MeCN. This indicates that the excited triplet state of **9** is efficiently quenched by SET from TEA. That diketone **10** is not formed in a reaction of **9** in the presence of TEA is presumably due to the different migration aptitude between methyl and hydrogen (compare **19** with **4**). This migration tendency (hydrogen > methyl) is quite similar to that observed in the photochemistry of  $\alpha,\beta$ -epoxy ketones.<sup>1,4c</sup>

In comparison, irradiation of **12** with TEA in MeCN afforded hydroxy ketone **14** as the major product along with lesser quantities of **13**. The hydroxy ketone vs diketone product ratio from **12** (2.3) is obviously greater than that observed from reactions of **1** (0.3–0.6). Irradiation of epoxy ketone **15** under similar conditions gave only hydroxy ketone **17**. These results indicate that the remaining substituent at  $\beta$ -position in anion radical related to **4** also affects the efficiency of hydrogen migration. In the cases of **20** and **21**,  $\beta$ -hydrogen migration would form anion radicals **22** and **23**, respectively, which would be less stable than **5** which is derived from anion radical **4**.<sup>21</sup>

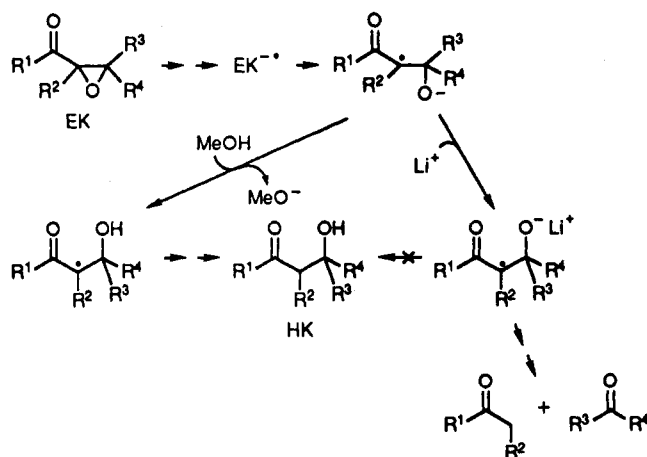


(18) Akiyama, K.; Tero-Kubota, S.; Ikegami, Y.; Hasegawa, E.; Ishiyama, K.; Horaguchi, T.; Shimizu, T., unpublished results.

(19) We have looked for coupling products derived from **6** and **7** since processes giving such products would provide a potential method for interesting carbon-carbon bond formation. However, we have not succeeded in isolation of coupling products yet.

(20) Zimmerman, H. E.; Cowley, B. R.; Tseng, C. Y.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 947.

Scheme II

Table II. Photoreactions of Epoxy Ketones with TEA in the Presence of  $\text{LiClO}_4$  in MeCN<sup>a</sup>

EK	irrad time, min	conv, %	product yields, <sup>b</sup> %	
			DK	HK
<b>1a</b>	20	97	70	0
<b>1b</b>	20	100	68	0
<b>1c</b>	20	93	65	0
<b>1d</b>	20	65	68	0
<b>9</b>	5	81	0	0
<b>12</b>	20	57	6	16
<b>15</b>	20	60	0	10

<sup>a</sup>  $[\text{EK}] = 8.5\text{--}8.6$  mM,  $[\text{TEA}] = 0.98$  M,  $[\text{LiClO}_4] = 0.13$  M.

<sup>b</sup> Isolated yields based on conversion of EK.

If hydroxy ketone formation occurs via the pathway shown in Scheme I, the efficiency of proton transfer in the CIRP should govern the yield of hydroxy ketone. To test this, we conducted a photoreaction of **1a** using 1,4-diazabicyclo[2.2.2]octane (DABCO) as the electron donor instead of TEA. Importantly, the cation radical of DABCO is known to be relatively stable and a poor proton donor unlike other aliphatic amine cation radicals.<sup>23</sup> Irradiation of **1a** (8.7 mM) with DABCO (0.29 M) for 5 min in MeCN resulted in products having significantly lower hydroxy ketone ratio (**2a**, 59%; **3a**, 3%; **3a/2a** = 0.05 at 22% conversion) compared to photoreaction in the presence of TEA (**3a/2a** = 0.37). This result is fully consistent with the proposed mechanism and the dramatically different acidities of  $\text{DABCO}^{++}$  and  $\text{TEA}^{++}$ .<sup>24</sup>

Polar protic solvents, such as alcohols, are known to shift the equilibrium from CIRP to SSIRP in ketone-amine SET photochemical processes.<sup>25</sup> As a result, we have studied photoreactions of the epoxy ketones with TEA in

(21) There might be at least two alternative mechanisms for diketone formation. One possibility is that 1,3-biradical formed via BET from **4** to  $\text{TEA}^{++}$  would react in a similar way to known photoreactions of  $\alpha,\beta$ -epoxy ketones.<sup>3,4</sup> Intramolecular proton transfer to oxianion in **4** to give the anion radical of enol form of diketone could be also possible since  $\beta$ -proton of **4** is considered to be somewhat acidic.<sup>22</sup>

(22) (a) Hayon, E.; Ibata, J.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072. (b) Lilie, J.; Henglein, A. *Ber Bunsenges, Phys. Chem.* **1969**, *73*, 170. (c) Russel, G. A.; Kim, B. H.; Kulkarni, S. V. *J. Org. Chem.* **1989**, *54*, 3768.

(23) (a) Mann, C. K.; Barns, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1973; p 283. (b) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243.

(24) (a) Reference 23. (b) Das, S.; von Sonntag, C. *Z. Naturforsch.* **1986**, *41a*, 505. (c) Nelsen, S. F.; Ippoliti, J. T. *J. Am. Chem. Soc.* **1986**, *108*, 4879. (d) Bordwell, F. G.; Cheng, J. P.; Seyedrezai, S. E.; Wilson, C. A. *Ibid.* **1988**, *110*, 8178. (e) Dinincenzo, J. P.; Banach, T. E. *Ibid.* **1989**, *111*, 8646.

(25) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6542.

MeOH (Table I). We anticipated that the hydroxy ketone yields would decrease under these conditions because proton transfer between 4 and TEA<sup>+</sup> would be slower (Scheme I). However, in the reactions of 1 and 12, slight increases in product ratios of hydroxy ketone to diketone (3/2 = 0.5–0.7; 14/13 = 2.7) were observed, and no significant decrease in the hydroxy ketone yields were seen in reactions of 9 and 15. Our interpretation of these results is that protonation of ring-opened anion radicals (4, 19, 20, 21) by MeOH must be occurring since these anion radicals have aliphatic alkoxide structures. This should compensate for the decrease in the rate of proton transfer between the anion radicals and TEA<sup>+</sup> pairs (Scheme II).

Peters and co-workers demonstrated that addition of certain salts, such as LiClO<sub>4</sub> and NaClO<sub>4</sub>, to irradiated solutions of ketones and amines favors SSIRP formation as a result of ion-pair exchange (special salt effect).<sup>26</sup> An obvious decrease in the yield of hydroxy ketone was observed when LiClO<sub>4</sub> was added to the epoxy ketone and TEA mixtures (Table II). Appreciable amounts of acetophenone (5–20%) and benzaldehydes (6–24%) were detected in crude photoproduct mixtures from photo-reactions of 1 with TEA in MeCN containing LiClO<sub>4</sub>. Irradiation of 9 with TEA in the presence of LiClO<sub>4</sub> resulted in a significant formation of acetophenone (61%) while no formation of 10 was observed. These results indicate that ion-pair exchange does occur in above systems, and that this interrupts proton transfer from TEA<sup>+</sup> to anion radicals derived from epoxy ketone. Complexation of lithium cation to these anion radicals apparently causes retro-aldol type decomposition to produce acetophenone and benzaldehydes (Scheme II).

SET photosensitization can provide another useful method to selectively generate epoxy ketone anion radicals without direct excitation of epoxy ketones. Recently, Okada and co-workers demonstrated that 1,6-bis(dimethylamino)pyrene (BDMAP) acts as an efficient electron-donor-type sensitizer.<sup>27</sup> Since the oxidation potential ( $E^{\text{ox}}$ ) of the singlet excited state of BDMAP (<sup>1</sup>BDMAP\*) is estimated to be about -2.4 V (SCE),<sup>17,27</sup> the epoxy ketones can be efficiently reduced to their anion radicals by <sup>1</sup>BDMAP\*. When a MeCN solution of 1a (17 mM) and BDMAP (1.8 mM) was irradiated with a light above 390 nm, none of 2a and trace amounts of 3a were obtained, and 92% of 1a was recovered. Finally, it was found that addition of TEA (1.1 M) to the same solution resulted in formation of 2a (68%) and 3a (9%).<sup>28</sup> When BDMAP was not present in the solution, more than 98% of 1a was recovered in a control irradiation ( $\lambda > 390$  nm).

In summary, we have found that aryl-substituted  $\alpha,\beta$ -epoxy ketone anion radicals are generated on irradiation in the presence of tertiary amines. The anion radicals formed in this way undergo selective C $\alpha$ -O bond cleavage.  $\beta$ -Diketones as well as  $\beta$ -hydroxy ketones were obtained in varying ratios, which are governed by the medium (solvent proticity and salt effect), amine cation radical acidity, and the nature of  $\beta$ -substituents.

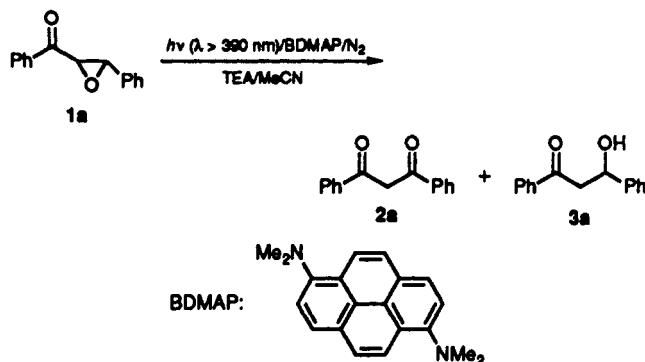
### Experimental Section

**General.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at

(26) (a) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *104*, 6142. (b) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 4875.

(27) Okada, K.; Okamoto, K.; Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8736.

(28) This particular TEA effect has not been thoroughly explored yet. It is probable that decomposition of BDMAP\* occurs, and this results in interrupting processes to produce observed products in BDMAP photosensitized reaction. When TEA is present in the reaction solution, BDMAP\* can be efficiently reduced to BDMAP by SET from TEA since this must be an exothermic process ( $\Delta G \approx -11$  kcal/mol).



90 and 22.49 MHz, respectively, on a JEOL FX-90Q spectrometer. Chemical shifts are reported in parts per million downfield from Me<sub>4</sub>Si as the internal standard. IR spectra were obtained on a Hitachi 270-30 infrared spectrophotometer. UV spectra were measured on a JASCO U best-30 UV/vis UV spectrophotometer. Redox potentials were recorded on a BAS CV-1B voltammetric analyzer. Column chromatography was performed with Wakogel C-200 silica gel. Preparative TLC was conducted on 20 cm × 20 cm plates coated with Wakogel B-5F silica gel. Melting points are reported uncorrected.

Acetonitrile (Wako) was distilled over phosphorus pentoxide and subsequently with calcium hydride. Methanol (Wako) was distilled and dried with 3A molecular sieves. Triethylamine (Wako) was distilled over calcium hydride. Diazabicyclooctane (Tokyo Kasei) and anhydrous lithium perchlorate (Wako) were used without purification.

Preparative photochemical reactions were performed using Riko 400-W high-pressure mercury lamp (UVL-400P) within a Pyrex, water-cooled well immersed in the photolysis solution. The solution was purged with N<sub>2</sub> before and during irradiation.

**Preparations of Epoxy Ketones.** Epoxy ketones (1, 9, 12, 15) were prepared from corresponding unsaturated ketones using alkaline hydrogen peroxide. The typical experiment is described below. To a well-stirred MeOH (120 mL) solution of 10.0 g (0.048 mol) of 1,3-diphenyl-2-propene-1-one (chalcone) cooled with ice-water was slowly added a mixture of 12 mL (0.12 mol) of 31% H<sub>2</sub>O<sub>2</sub> and 12 mL (0.024 mol) of 2 N NaOH. The mixture was stirred for 1 h and filtered to collect colorless solid (10.4 g, 97%), which was then washed with water and cold MeOH. This solid was recrystallized from MeOH. 1a, mp 88 °C (89–90)<sup>29</sup>. Melting points (lit. mp, °C) and yields for other epoxy ketones were as follows: 1b: 84 °C (85–86);<sup>29</sup> 83%. 1c: 77–78 °C (77–78);<sup>29</sup> 83%. 1d: 78–80 °C (79–80);<sup>29</sup> 89%. 9: 91–92 °C (93–95);<sup>30</sup> 47%. 12: bp 82–83 °C (0.25 mmHg); 83%. 15: 49–50 °C; 46%. Physical data for 12 and 15. 12: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.07 (d, 3 H,  $J = 6.8$  Hz), 1.10 (d, 3 H,  $J = 6.6$  Hz), 1.52–2.00 (m, 1 H), 2.96 (dd, 1 H,  $J = 6.5, 2.1$  Hz), 4.08 (d, 1 H,  $J = 2.1$  Hz), 7.28–7.69 (m, 3 H), 7.81–8.08 (m, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  18.2 (q), 18.9 (q), 30.5 (d), 56.5 (d), 64.9 (d), 128.2 (d), 128.8 (d), 133.7 (d), 135.6 (s), 194.6 (s); IR (neat) 2960, 1690, 1230, 694 cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>: C, 75.76; H, 7.42. Found: C, 75.64; H, 7.41. 15: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.97 (dd, 1 H,  $J = 5.9, 2.6$  Hz), 3.13 (dd, 1 H,  $J = 5.9, 4.4$  Hz), 4.25 (dd, 1 H,  $J = 4.4, 2.6$  Hz), 7.30–7.72 (m, 3 H), 7.80–8.12 (m, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  47.5 (t), 51.0 (d), 128.3 (d), 128.8 (d), 133.9 (d), 135.5 (s), 194.7 (s); IR (KBr) 1686, 1230, 708 cm<sup>-1</sup>. Anal. Calcd for C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>: C, 72.96; H, 5.44. Found: C, 72.69; H, 5.52.

**Photoreactions of Epoxy Ketones with Amines.** MeCN or MeOH solutions of an appropriate epoxy ketone and TEA with or without LiClO<sub>4</sub> were irradiated with Pyrex-filtered light. The progress of the photoreaction was checked by TLC. The photolysates were concentrated in vacuo to afford the residues. When DABCO was used instead of TEA, the residue was extracted with CHCl<sub>3</sub>. The CHCl<sub>3</sub> solution was washed with 2 N HCl, aqueous NaHCO<sub>3</sub>, and aqueous NaCl and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. When LiClO<sub>4</sub> was added to the photochemical solutions, the residues were extracted with CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> solutions were washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude

(29) House, H. O.; Ryerson, G. D. *J. Am. Chem. Soc.* **1961**, *83*, 979.

(30) Wasserman, H. H.; Aubrey, N. E.; Zimmerman, H. E. *J. Am. Chem. Soc.* **1953**, *75*, 96.

product mixtures were subjected to column or TLC separations using the following solvent systems:  $C_6H_6/CH_2Cl_2$  (1/1) for 1;  $CH_2Cl_2$  for 9;  $C_6H_6/CH_2Cl_2$  (1/1) or  $CH_2Cl_2$  for 12;  $CH_2Cl_2/CH_3COCH_3$  (79/1) for 15, which afforded diketones, hydroxy ketones, and unreacted epoxy ketones. Yields of benzaldehydes and acetophenone were determined by  $^1H$  NMR spectroscopy of photoproduct mixtures before column or TLC separations. The conversion of 1b was necessarily determined by  $^1H$  NMR analysis before separation since 1b was found to be rather labile on silica gel.

**Physical Data for Diketones.** 2a: mp 76–77 °C (EtOH);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  6.84 (s, 1 H, enole CH), 7.26–7.65 (m, 6 H), 7.74–8.10 (m, 4 H), 16.87 (br s, 1 H, enole OH);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  93.0 (d), 127.1 (d), 128.5 (d), 132.3 (d), 135.4 (s), 185.6 (s); IR (KBr) 1596, 1548, 1482, 1228, 754  $cm^{-1}$ . Anal. Calcd for  $C_{15}H_{12}O_2$ : C, 80.34; H, 5.39. Found: C, 80.40; H, 5.71. 2b: mp 127–128 °C (EtOH);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.85 (s, 3 H), 6.77 (s, 1 H), 6.90–6.99 (m, 2 H), 7.43–7.50 (m, 3 H), 7.90–8.00 (m, 2 H), 16.99 (br s, 1 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  55.4 (q), 92.4 (d), 114.0 (d), 126.9 (d), 128.2 (s), 128.6 (d), 129.3 (d), 132.1 (d), 135.6 (s), 163.3 (s), 184.0 (s), 186.1 (s); IR (KBr) 1604, 1536, 1484, 1260, 1230, 770  $cm^{-1}$ . Anal. Calcd for  $C_{16}H_{14}O_2$ : C, 75.57; H, 5.55. Found: C, 75.46; H, 5.58. 2c: mp 80–81.5 °C (EtOH);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.41 (s, 3 H), 6.82 (s, 1 H), 7.21–7.52 (m, 5 H), 7.83–8.02 (m, 4 H), 16.90 (br s, 1 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  21.5 (q), 92.8 (d), 127.1 (d), 127.2 (d), 128.6 (d), 129.3 (d), 132.2 (d), 132.9 (s), 135.6 (s), 143.2 (s), 185.1 (s), 185.9 (s); IR (KBr) 1606, 1532, 1484, 1230, 1186, 768  $cm^{-1}$ . Anal. Calcd for  $C_{16}H_{14}O_2$ : C, 80.65; H, 5.92. Found: C, 80.48; H, 6.13. 2d: mp 82.5–84 °C (EtOH);  $^1H$  NMR ( $CDCl_3$ )  $\delta$  6.80 (s, 1 H), 7.37–7.59 (m, 5 H), 7.84–8.02 (m, 4 H), 16.79 (br s, 1 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  92.9 (d), 127.1 (d), 128.4 (d), 128.6 (d), 128.8 (d), 132.5 (d), 133.9 (s), 135.2 (s), 138.6 (s), 184.4 (s), 185.6 (s); IR (KBr) 1592, 1518, 1478, 1090, 758  $cm^{-1}$ . Anal. Calcd for  $C_{15}H_{11}ClO_2$ : C, 69.64; H, 4.29. Found: C, 69.40; H, 4.28. 13:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.21 (d, 6 H,  $J = 6.8$  Hz), 2.61 (q, 1 H,  $J = 6.8$  Hz), 6.17 (s, 1 H), 7.28–7.50 (m, 3 H), 7.68–7.94 (m, 2 H), 16.25 (br s, 1 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  19.4 (q), 37.5 (d), 94.2 (d), 127.0 (d), 128.6 (d), 132.1 (d), 135.3 (s), 183.9 (s), 201.1 (s); IR (neat) 2968, 2928, 2872, 1602, 1466, 768, 692  $cm^{-1}$ . Anal. Calcd for  $C_{12}H_{14}O_2$ : C, 75.76; H, 7.42. Found: C, 75.30; H, 7.44.

**Physical Data for Hydroxy Ketones.** 3a: mp 44–46 °C ( $CH_2Cl_2-n-C_6H_{14}$ );  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.31 (d, 1 H,  $J = 5.5$  Hz), 3.32 (d, 1 H,  $J = 6.8$  Hz), 3.73 (d, 1 H,  $J = 3.1$  Hz), 5.13–5.41 (m, 1 H), 7.05–7.64 (m, 8 H), 7.73–7.98 (m, 2 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  47.4 (t), 70.0 (d), 125.8 (d), 127.5 (d), 128.1 (d), 128.5 (d), 128.6 (d), 133.5 (d), 136.6 (s), 143.1 (s), 199.9 (s); IR (KBr) 3540, 1664, 1212, 754  $cm^{-1}$ . Anal. Calcd for  $C_{15}H_{14}O_2$ : C, 79.63; H, 6.24. Found: C, 79.42; H, 6.17. 3b:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.33 (d, 1 H,  $J = 5.3$  Hz), 3.34 (d, 1 H,  $J = 6.8$  Hz), 3.63 (br s, 1 H), 3.78 (s, 3 H), 5.27 (br t, 1 H), 6.69–6.95 (m, 2 H), 7.15–7.62 (m, 5 H), 7.72–7.99 (m, 2 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  47.4 (t), 55.3 (q), 69.7 (d), 113.9 (d), 127.0 (d), 128.1 (d), 128.6 (d), 133.4 (d), 135.3 (s), 136.8 (s), 159.1 (s), 200.0 (s); IR (neat) 3492, 1676, 1510, 1246  $cm^{-1}$ . Anal. Calcd for  $C_{16}H_{16}O_2$ : C, 74.98; H, 6.29. Found: C, 74.68; H, 6.35. 3c: mp 47–48 °C ( $CH_2Cl_2-n-C_6H_{14}$ );  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.32 (s, 3 H), 3.31 (d, 1 H,  $J = 5.3$  Hz), 3.32 (d, 1 H,  $J = 6.8$  Hz), 3.64 (br d, 1 H,  $J = 2.6$  Hz), 5.08–5.36 (m, 1 H), 6.92–7.61 (m, 7 H), 7.68–7.96 (m, 2 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  21.0 (q), 47.4 (t), 69.8 (d), 125.7 (d), 128.1 (d), 128.5 (d), 129.1 (d), 133.3 (d), 136.7 (s), 137.1 (s), 140.3 (s), 199.8 (s); IR (neat) 3476, 1678, 1448, 1212, 756, 688  $cm^{-1}$ . Anal. Calcd for  $C_{16}H_{16}O_2$ : C, 79.98; H, 6.71. Found: C, 79.53; H, 6.76. 3d: mp 96–96.5 °C ( $CH_2Cl_2-n-C_6H_{14}$ );  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.295 (d, 1 H,  $J = 5.7$  Hz), 3.299 (d, 1 H,  $J = 6.4$  Hz), 3.81 (br s, 1 H), 5.28 (br t, 1 H), 7.10–7.65 (m, 7 H), 7.72–7.96 (m, 2 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  42.2 (t), 69.4 (d), 127.2 (d), 128.2 (d), 128.7 (d), 133.3 (s), 133.7 (d), 136.5 (s), 141.6 (s), 199.7 (s); IR (KBr) 3472, 1664, 1264, 1214, 830, 752, 686  $cm^{-1}$ . Anal. Calcd for  $C_{15}H_{13}ClO_2$ : C, 69.10; H, 5.03. Found: C, 68.90; H, 5.13. 11: mp 52–54 °C ( $CH_2Cl_2-n-C_6H_{14}$ );  $^1H$  NMR ( $CDCl_3$ )  $\delta$  1.60 (s, 3 H), 3.29 (d, 1 H,  $J = 17.4$  Hz), 3.77 (d, 1 H,  $J = 17.4$  Hz), 4.88 (s, 1 H), 7.08–7.59 (m, 8 H), 7.64–7.92 (m, 2 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  30.8 (q), 48.9 (t), 73.5 (s), 124.3 (d), 126.6 (d), 128.0 (d), 128.2 (d), 128.6 (d), 133.6 (d), 137.0 (s), 147.6 (s), 201.2 (s); IR (KBr) 3488, 1656, 1384, 1218  $cm^{-1}$ . Anal. Calcd for  $C_{16}H_{16}O_2$ : C, 79.98; H, 6.71. Found: C, 79.72; H, 6.73. 14: mp 50–51 °C ( $CH_2Cl_2-n-C_6H_{14}$ );  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.98 (d, 3 H,  $J = 6.6$  Hz), 1.00 (d, 3 H,  $J =$

6.8 Hz), 1.48–1.99 (m, 1 H), 3.07 (d, 1 H,  $J = 7.9$  Hz), 3.09 (d, 1 H,  $J = 4.2$  Hz), 3.36 (d, 1 H,  $J = 3.5$  Hz), 3.80–4.12 (m, 1 H), 7.20–7.63 (m, 3 H), 7.72–8.00 (m, 2 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  17.8 (q), 18.5 (q), 33.2 (d), 42.2 (t), 72.4 (d), 128.1 (d), 128.6 (d), 133.3 (d), 137.1 (s), 201.1 (s); IR (KBr) 3544, 2952, 2888, 1666, 1380, 1202, 1004, 750, 690  $cm^{-1}$ . Anal. Calcd for  $C_{12}H_{16}O_2$ : C, 74.97; H, 8.39. Found: C, 74.49; H, 8.36. 17:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  3.19 (t, 2 H,  $J = 5.6$  Hz), 3.49 (br s, 1 H), 3.75–4.15 (m, 2 H), 7.20–7.62 (m, 3 H), 7.70–7.98 (m, 2 H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  40.7 (t), 57.9 (t), 128.1 (d), 128.6 (d), 133.3 (d), 136.8 (s), 200.1 (s); IR (neat) 3424, 2884, 1678, 1596, 1448, 1214, 746, 688  $cm^{-1}$ . Anal. Calcd for  $C_9H_{10}O_2$ : C, 71.98; H, 6.71. Found: C, 71.70; H, 6.81.

**Photoreaction of Dibenzoylmethane (2a) with TEA in MeCN.** A MeCN (240 mL) solution of 486 mg (2.16 mmol) of 2a and 10 mL (72 mmol) of TEA was irradiated with Pyrex-filtered light for 20 min. The residue obtained by concentration of photolysate was subjected to column separation ( $CHCl_3$ ) to yield 150 mg (31%) of 2a and 146 mg (15%) of pinacol dimer which was identified by converting to 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene on the treatment with 2 N HCl in THF, mp 189–190 °C (MeOH) (191–192).<sup>31</sup>

**BDMAP-Sensitized Photoreactions of Chalcone Epoxide (1a) in MeCN.**  $N_2$ -purged MeCN solutions of 1a (154 mg, 0.69 mmol) and BDMAP<sup>32</sup> (20 mg, 0.07 mmol) with or without TEA (6 mL, 43 mmol) were irradiated with a 2-kW Xe lamp (Ushio UXL-2003D-0) through Toshiba L-42 glass filter ( $\lambda > 390$  nm) for 3 h. The residues obtained by concentration of photolysates were subjected to TLC separations. Similarly, a  $N_2$ -purged MeCN solution of 1a and TEA was irradiated and then worked up.

**Preparations of Diketones for Photoproduct Identifications.** To a suspension of NaH in THF was added a THF solution of substituted acetophenones and ethyl benzoate for 2, acetophenone and ethyl isobutyrate for 13. The mixture was refluxed for 0.5 h followed by addition of water containing AcOH. Then, the resulting mixture was extracted with  $CH_2Cl_2$  and dried over anhydrous  $Na_2SO_4$ . Melting points (°C) and yields for diketones. 2b: 127–128; 84%; 2c: 80–81.5; 69%. 2d: 82.5–84; 60%. 13: 37%. 2a was commercially available. Spectroscopic data obtained for these products were identical with those for photoproducted diketones.

**Preparations of Hydroxy Ketones for Photoproduct Identifications.** Hydroxy ketones were prepared from corresponding epoxy ketones according to Yoshikoshi's method.<sup>33</sup> The typical experiment is as follows. To a  $N_2$ -purged (10 min) mixture of 470 mg (1.46 mmol) of  $PH_2Se_2$  and 6 mL of EtOH was slowly added 110 mg (2.91 mmol) of  $NaBH_4$  followed by addition of 30  $\mu$ L of AcOH. The resulting solution was added at once to a EtOH (18 mL) solution of 220 mg (0.98 mmol) of 1a purged with  $N_2$  (5 min). The mixture was stirred for 10 min followed by extraction with AcOEt. Organic layer was washed with aqueous NaCl and water and dried over anhydrous  $MgSO_4$ . The residue obtained by concentration of the extract was subjected to column separation ( $CH_2Cl_2$ ) to give 210 mg (95%) of 3a. Yields for other hydroxy ketones are as follows: 3b, 75%; 3c, 94%; 3d, 91%; 11, 51%; 17, 66%. Hydroxy ketone (14) was prepared in 73% by condensation of acetophenone with isobutyraldehyde on treatment with  $K_2CO_3$ . Spectroscopic data obtained for these compounds were identical with those for photoproducted hydroxy ketones.

**Acknowledgment.** Professors Kimio Akiyama, Shozo Tero, and Yusaku Ikegami, Tohoku University, who are interested in our chemistry and conducting time resolved EPR study on related systems, are gratefully acknowledged for their invaluable information and discussion. The generous assistance of Professor Masaki Kamata, Niigata University, to measure redox potentials and to use 2-kW Xe lamp apparatus and UV spectrometer is appreciated. We are grateful to Professor Patrick S. Mariano, University of Maryland, for his helpful discussion.

(31) Bost, H. W.; Bailey, P. S. *J. Org. Chem.* 1956, 21, 803.

(32) Zweig, A.; Maurer, A. H.; Roberts, B. G. *J. Org. Chem.* 1967, 32, 1322.

(33) Miyashita, M.; Suzuki, T.; Yoshikoshi, A. *Tetrahedron Lett.* 1987, 28, 4293.