to bulb distillation (bp 126 °C (760 mm)): GC purity = 99.9%; IR (neat) 3020 (m), cm^{-1}; IR (CHCl$_3$) 3060 (br, w), 1600 (m), 1460–1400 (m) cm^{-1}; ^{1}H NMR (400 MHz) 5.49–5.42 (pseudo ABX[43] t, J = 2.9 Hz, 2 H, vinyl). The first order coupling constants for the magnetically equivalent vinyl H's (elucidated by the ^{13}C method of Laszlo and Schleyer[47]) were as follows: $J_{2,3}$ = 9.25 Hz,[45] $J_{2,1}$ = 5.4 Hz, $J_{2,4}$ = 1.5 Hz. Other assignments are as follows: δ 2.23–2.17 (m, 2 H, bridgehead homoallylic[9]), 2.17–2.07 (m, 2 H, allylic), 1.82–1.73 (m, 4 H), 1.65–1.56 (m, 6 H), 1.55 (s, H$_2$O in CDCl$_3$); broad band decoupled ^{13}C NMR (100 MHz) δ 128.82 (vinyl), 45.51, 44.38, 33.51, 24.05; coupled ^{13}C NMR (100 MHz) δ 128.82 (d, J = 158.2 Hz), 45.51 (d, J = 134.9 Hz), 44.38 (d, J = 134.9 Hz), 33.51 (t, J = 125.1 Hz), 24.05 (t, J = 125.8 Hz); low-resolution GC (SE-54)/MS (70 eV) m/e (relative intensity) 135.1 (M + 1, 9.2), 134.1 (M$^+$, 47.5), 133.1 (M − 1, 8.57), 91.1 (100); UV λ (pentane) 196 nm. Anal. Calcd for C$_{10}$H$_{14}$: C, 89.49; H, 10.51. Found: C, 89.66; H, 10.77.

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Photochemically and Thermally Induced Free-Radical Reactions of α,β-Epoxy Ketones with Tributyltin Hydride: Selective C$_\alpha$–O Bond Cleavage of Oxiranylmethyl Radicals Derived from α,β-Epoxy Ketones

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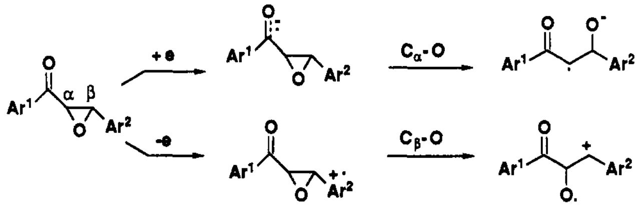
Free-radical reactions of α,β-epoxy ketones with tributyltin hydride have been studied. These substances were selectively converted to β-hydroxy ketones under both photochemical and thermal conditions. The photoreaction is initiated by hydrogen abstraction of an epoxy ketone triplet from tributyltin hydride, while azoisobutyronitrile is used as an initiator for the thermal reaction. In general, the photoreaction conditions are particularly useful for aroyl-substituted epoxy ketones while the thermal conditions are applicable to a variety of epoxy ketones. It was also found that the epoxy esters and epoxy alcohols did not undergo the ring-opening reaction under the similar conditions. Tributyltin radical attack on the carbonyl of epoxy ketones is a key process for both the photoreaction and the thermal reaction. Regioselective ring opening of the resulting oxiranylmethyl radical finally produces β-hydroxy ketones. In order to capture the free-radical intermediates, the reaction of epoxy ketones with allyltributyltin was conducted. The isolation of α-allylated β-hydroxy ketones is interpreted by the involvement of a novel 1,5-tributyltin transfer.

Introduction

Free radicals play important roles in many chemical and biological processes.[1] Intensive studies on organic free radicals conducted in the area of physical organic chemistry have provided substantial information about fundamental properties of these species.[2] Such efforts have also stimulated synthetic organic chemists to apply free-radical processes to organic synthesis.[3]

Our program on *selective organic reactions induced by ion radicals or free radicals* has started by studying the ring-opening reactions of epoxy carbonyl compounds.[4] We expected that anion radical generation from α,β-epoxy carbonyl compounds would cause selective C$_\alpha$–O bond cleavage while cation radicals from these substances would undergo selective C$_\beta$–O bond cleavage. These expectations

Scheme I



Scheme II

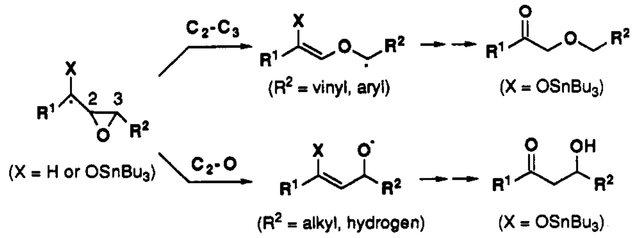


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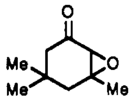
Table I. Photoreactions of α,β-Epoxy Ketones (EK) with Tributyltin Hydride (TBTH) in Benzene

entry	EK[a]	R^1	R^2	R^3	time (min)	TBTH (equiv)	conv (%)	HK	yield (%)
1	**t-1a**	Ph	H	Ph	30	2.1	100	**2a**	93
2	**t-1a**				30	1.1	100	**2a**	96
3	**t-1a**				30	0.51	57	**2a**	54
4	**c-1a**	Ph	Ph	H	120	2.1	100	**2a**	78
5	**1b**	Ph	H	p-MeOC$_6$H$_4$	30	2.1	100	**2b**	84
6	**4**	Ph	H	i-Pr	30	2.1	100	**5**	81
7	**6**	Ph	H	H	30	2.1	100	**7**	84
8	**8**	Ph	Me	Ph	30	2.1	100	**9**	87
9	**10**	Me	H	Ph	120	2.1	17	**11**	5
10[b]	**10**				120	2.1	30	**11**	24
11	**12**	Me	H	n-Pen	120	2.1	11	**13**	2
12[b]	**12**				120	2.1	54	**13**	40
13	**14**				120	2.1	24	**15**	0
14[c]	**14**				120	3.2	55	**15**	44

[a] [EK] = 49 mM. [b] [AIBN] = 10 mM. [c] [AIBN] = 25 mM.

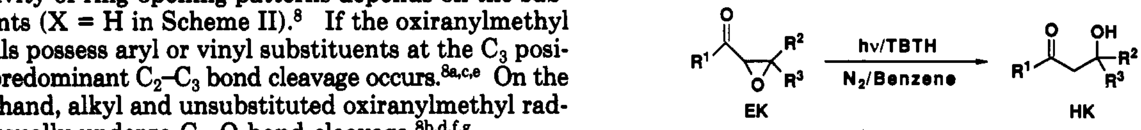
were examined by conducting single electron-transfer reactions of several aromatic α,β-epoxy ketones with electron donors[4c,d] or electron acceptors (Scheme I).[4b]

We have been also interested in free-radical reactions of epoxy carbonyl compounds.[4a] Photochemically excited carbonyls are known to undergo hydrogen abstraction from hydrogen donors to produce ketyl radicals.[5] On the other hand, group 14 metal-centered radicals, $^{\bullet}SiR_3$, $^{\bullet}GeR_3$, and $^{\bullet}SnR_3$, efficiently add to carbonyl oxygen to generate metaloxymethyl radicals.[6] Among such compounds is tributyltin hydride.[5-7] Thus, reactions of α,β-epoxy ketones with tributyltin hydride are expected to give oxiranylmethyl radicals under both photochemical and thermal reaction conditions. Recent investigations on the reactions of oxiranylmethyl radicals have demonstrated that the selectivity of ring-opening patterns depends on the substituents (X = H in Scheme II).[8] If the oxiranylmethyl radicals possess aryl or vinyl substituents at the C_3 position, predominant C_2–C_3 bond cleavage occurs.[8a,c,e] On the other hand, alkyl and unsubstituted oxiranylmethyl radicals usually undergo C_2–O bond cleavage.[8b,d,f,g]

Based on the literature observations, we anticipated that the oxiranylmethyl radicals (X = OSnBu$_3$ in Scheme II) derived from α,β-epoxy ketones upon treatment with tributyltin hydride could follow two reaction pathways depending on the β-substituents to give β-keto ethers and β-hydroxy ketones. Our preliminary results[4a] and continuing studies demonstrate that photoreactions as well as thermal reactions of several epoxy ketones with tributyltin hydride produce β-hydroxy ketones predominantly.[9] No β-keto ethers were isolated in these studies. Detailed results and mechanistic considerations concerning this selective conversion of α,β-epoxy ketones to β-hydroxy ketones are presented below.

Results

Photoreactions of α,β-Epoxy Ketones with Tributyltin Hydride. Photoreactions of several α,β-epoxy ketones (EK) with tributyltin hydride (TBTH) were carried out with a high-pressure Hg lamp filtered through Pyrex as a light source (eq 1). The results are summarized



(1)

in Table I. Irradiation of a N_2 prepurged benzene solution of *trans*-chalcone epoxide **t-1a** (49 mM) and TBTH (101 mM) produced β-hydroxy ketone **2a** in 93% yield. One equivalent of TBTH is needed for the complete conversion of **t-1a** as was shown by varying the amount of TBTH (2.1, 1.1, or 0.5 equiv with respect to **t-1a**). Similarly, *cis*-chalcone epoxide **c-1a** was converted to **2a** although a longer irradiation time was needed than that for **t-1a**. In both cases, small amounts of dibenzoylmethane **3a**[4c] (1–3%) were also isolated. Since photoreaction of **3a** with TBTH to give **2a** is possible, a similar irradiation of **3a** and TBTH was conducted. However, no **2a** was obtained, and **3a** was mostly recovered. This experiment suggests that **2a** is a direct product from **1a**. Other α,β-epoxy ketones (**1b**, **4**, **6**, **8**, **10**, **12**, and **14**) were similarly subjected to the photoreactions with TBTH in benzene. In the cases of epoxy ketones possessing aroyl chromophores (**1b**, **4**, **6**, and **8**), the yields of the corresponding hydroxy ketones were relatively high as shown in Table I. On the other hand, similar photoreactions of acyl-substituted epoxides (**10**, **12**, and **14**) were ineffective (11–24% conversion, 0–5% yield). Upon addition of azoisobutyronitrile (AIBN) to these

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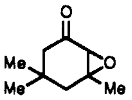
(9) (a) Although there have been some examples of photochemical[9b] and thermal[9c] reactions of α,β-epoxy ketones with tributyltin hydride, a little mechanistic information for the β-hydroxy ketone formation is available from these studies. (b) Pete, J. P.; Viriot-Villaum, M. L. *Bull. Soc. Soc. Chim. Fr.* **1971**, 3699. (c) Dequeil-Castiang, M.; Raham, A.; Daham, N. *J. Org. Chem.* **1986**, *51*, 1672.

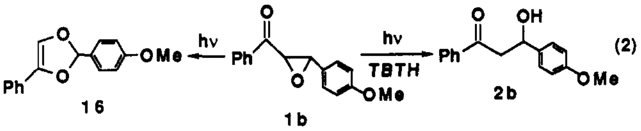
Table II. Reactions of α,β-Epoxy Ketones (EK) with Tributyltin Hydride Induced by Thermal Decomposition of Azoisobutyronitrile in Benzene[a]

entry	EK	R^1	R^2	R^3	TBTH (equiv)	AIBN (equiv)	conv (%)	HK	yield (%)
1	**t-1a**	Ph	H	Ph	1.2	0.12	100	**2a**	83
2	**t-1a**				1.2	0	5	**2a**	4
3	**c-1a**	Ph	Ph	H	1.2	0.12	99	**2a**	88
4	**1b**	Ph	H	p-MeOC$_6$H$_4$	1.2	0.12	100	**2b**	71
5	**4**	Ph	H	*i*-Pr	1.5	0.15	97	**5**	75
6	**6**	Ph	H	H	1.5	0.15	100	**7**	89
7	**8**	Ph	Me	Ph	1.2	0.12	80	**9**	20
8[b]	**10**	Me	H	Ph	1.2	0.12	93	**11**	74
9	**10**				2.2	0.22	98	**11**	91
10	**12**	Me	H	*n*-Pen	2.3	0.23	94	**13**	80
11	**14**				3.0	0.50	83	**15**	23

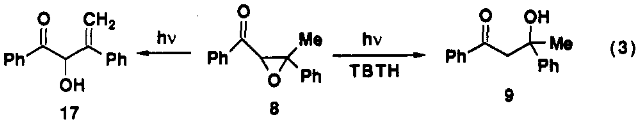
[a] Reaction time: 60 min; [EK] = 40 mM. [b] Reaction time: 90 min.

photoreaction solutions, however, the yields of hydroxy ketones **11**, **13**, and **15** as well as the conversions of **10**, **12**, and **14** increased (30–55% conv, 24–44% yield).

The results in Table I reveal several other interesting aspects of these reactions. Since generation of a catalytic amount of tributyltin radical seems to be enough for the initiation of the reaction, this method could be applicable to epoxy ketones which undergo other competing photochemical reactions. While photoreaction of *trans*-4-methoxychalcone epoxide (**1b**) produces 2-(4-methoxyphenyl)-4-phenyl-1,3-dioxole (**16**) through C_α–C_β bond cleavage,[10] irradiation of **1b** with TBTH afforded hydroxy ketone **2b** in 84% yield (eq 2). Photoreaction of *trans*-dypnone epoxide **8** is known to afford 1,3-diphenyl-2-hydroxy-3-buten-1-one (**17**) which is derived via intramolecular hydrogen abstraction from the β-methyl by the $n\pi^*$ triplet of the benzoyl group.[11] In contrast, when **8** was irradiated with TBTH, hydroxy ketone **9** was obtained in 87% yield without formation of **17** (eq 3).



16 1b 2b



17 8 9

Another interesting aspect is obtained by photoreactions of **t-1a** and **c-1a** with TBTH (compare entry 1 with 4 in Table I). In order to obtain more detailed information, photoreactions of these stereoisomers with TBTH in benzene were conducted for different time intervals. A Xe–Hg lamp was used as a light source through the glass filter to cut the light below 320 nm to prevent photodecomposition of the products. The conversion of **1a** and the yield of **2a** were determined by ^{1}H NMR. The results in Figure 1 show that there is a remarkable difference in photoreaction efficiency between **t-1a** and **c-1a**. On the other hand, when a N_2 prepurged benzene solution containing **t-1a** (20 mM), **c-1a** (20 mM), TBTH (25 mM), and AIBN (2.5 mM) was refluxed under N_2 for 60 min, 32% recovery of **t-1a** and 44% recovery of **c-1a** together with 44% of **2a** were observed. While absorption spectra of **t-1a** and **c-1a** in benzene are almost same at the concentrations of the photoreactions, it is known that the photoreactivity of **t-1a** is greater than that of **c-1a**.[12] Therefore, the difference in the reactivity between **t-1a** and **c-1a** toward TBTH is probably due to the photoinitiation rate rather than the rate of the propagation step. This rationalization is also consistent with the following observation. When a benzene solution of the mixture of **t-1a** (49 mM) and **c-1a** (49 mM) with TBTH (60 mM) was irradiated for 10 min, 25% of **c-1a** as well as 56% of **t-1a** reacted to produce 40% of **2a**. Under the similar conditions, while **t-1a** was completely consumed to give 95% of **2a** in the absence of **c-1a**, 96% of **c-1a** was recovered in the absence of **t-1a**.

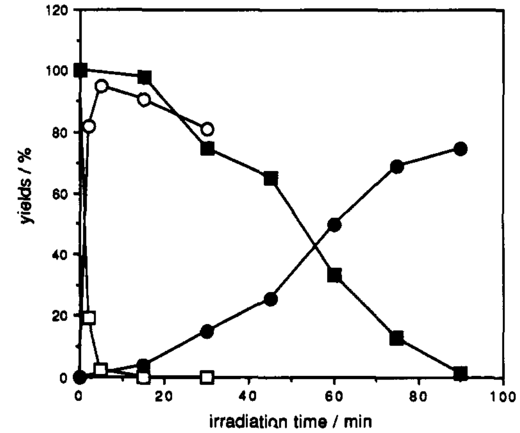
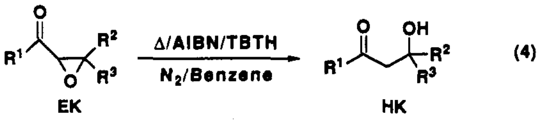


Figure 1. Time dependencies of photoconversions of **t-1a** (□) to **2a** (○) and of **c-1a** (■) to **2a** (●) by TBTH in benzene ([**t-1a**] = [**c-1a**] = 49 mM; [TBTH] = 59 mM).

Reactions of α,β-Epoxy Ketones with Tributyltin Hydride Induced by Thermal Decomposition of Azoisobutyronitrile. Another general method for the generation of tributyltin radical is the thermal decomposition of AIBN in the presence of TBTH.[3,7] Degassed benzene solutions containing epoxy ketones and TBTH with AIBN were refluxed under N_2 (eq 4 and Table II).



For example, **t-1a** was converted to **2a** in 83% while 95% of **t-1a** was recovered in the absence of AIBN. Similar reactions of other epoxy ketones produced the corresponding hydroxy ketones in good yields. Acyl epoxides

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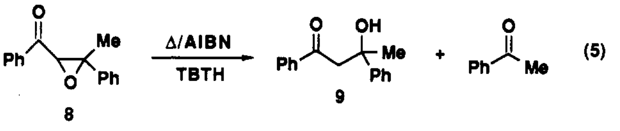
Table III. Reactions of Epoxides 22–24 with Tributyltin Hydride Induced by Thermal Decomposition of Azoisobutyronitrile in Benzene[a]

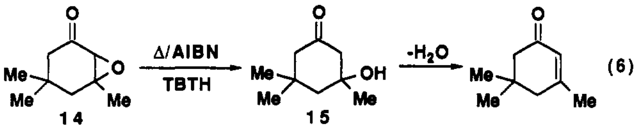
entry	EP	R^1	R^2	TBTH (equiv)	AIBN (equiv)	conv (%)	AL (%)
1	**22**	MeOCO	Ph	2.4	0.24	26	0
2	**23**	PhCO(OH)	Ph	1.2	0.12	8	0
3	**24**	Ph	Ph	1.2	0.12	3	0

[a] Reaction time: 60 min; [EP] = 40–41 mM.

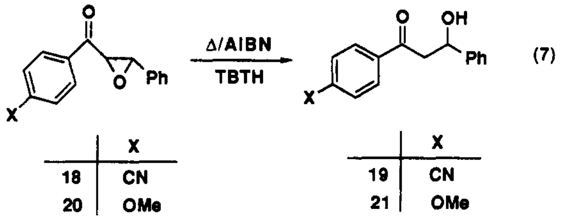
10 and 12, which were relatively unreactive under the photoreaction conditions, were converted to hydroxy ketones 11 and 13 in 91% and 80% yields respectively.

Furthermore, Table II shows several interesting aspects. In the reactions of β-disubstituted epoxy ketones 8 and 14, the yields of hydroxy ketones 9 and 15 were quite low. In the former case, 61% of acetophenone was obtained as a major product (eq 5). Probably, retroaldol reaction of the product occurred. In the latter case, 30% of isophorone was obtained (eq 6). Isophorone was probably produced from dehydration of 15. For the preparations of the compounds which are thermally labile, the photoreaction seems more useful than the thermal reaction.

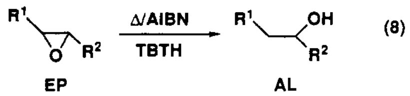




Because the reactions seem to involve tributyltin attack on the carbonyl, substituents in the benzoyl group should influence the epoxy ketone reactivity toward tributyltin radical. In fact, when a benzene solution of *trans*-4′-cyanochalcone epoxide (18) (21 mM) and *trans*-4′-methoxychalcone epoxide (20) (21 mM) in the presence of TBTH (25 mM) and AIBN (2.5 mM) was refluxed for 60 min, the corresponding hydroxy ketones 19 (58%) and 21 (16%) were obtained with conversions of epoxy ketones of 64% for 18 and 18% for 20 respectively (eq 7). The electron-withdrawing group on benzoyl is a better substituent to promote the reaction than the electron-donating one (this point will be discussed later).



Several epoxides lacking ketone carbonyls were also subjected to the similar reaction conditions (eq 8 and Table III). Reflux of a benzene solution containing methyl



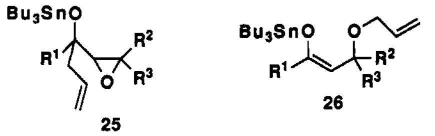
cinnamate epoxide (22) and TBTH in the presence of AIBN did not produce the expected hydroxy ester. Similarly, neither *trans*-1,3-diphenyl-2-propen-1-ol epoxide (23) nor *trans*-stilbene oxide 24 gave the corresponding hydroxy compounds. These results indicate that either aroyl- or acyl-substituted epoxides are necessary for the reaction.

Table IV. Photoreaction and Thermal Reaction of Diepoxy Ketone 29 with Tributyltin Hydride in Benzene

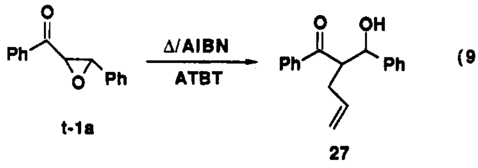
					yields (%)	
entry	method[a]	TBTH (equiv)	AIBN (equiv)	conv (%)	**30**	**31**
1	photo	1.2	0	81	75	0
2	photo	5.0	0	100	85	0
3	thermal	1.2	0.12	91	79	0
4	thermal	2.4	0.24	100	40	46
5	thermal	5.0	0.50	100	5	68

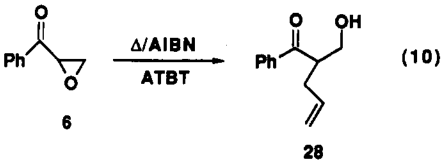
[a] Photo: photoreaction, Hg lamp (Pyrex); reaction time, 60 min; [29] = 49 mM. Thermal: thermal reaction, reflux; reaction time, 60 min; [29] = 40 mM.

Reactions of Epoxy Ketones with Allyltributyltin. Our next interest was to learn if radical intermediates involved in this reaction could be captured by other traps. We chose a reaction system of allyltributyltin (ATBT) and AIBN for this purpose. Our anticipation was that the radicals generated from epoxy ketones would be captured by allyl radical to give C-allylated product 25 or O-allylated product 26. However, α-allyl β-hydroxy ketone 27 was



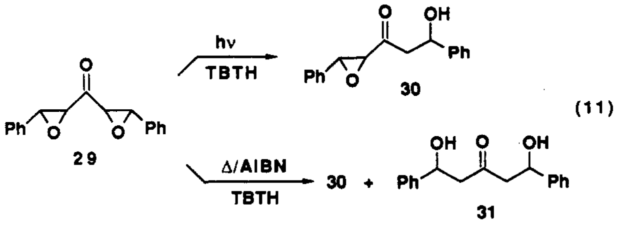
isolated in 69% yield as a diastereomeric mixture when a benzene solution of t-1a (177 mM) and ATBT (711 mM) with AIBN (89 mM) was refluxed for 120 min under N_2 (eq 9). Similarly, α-allyl adduct 28 was isolated in 81%





yield upon treatment of 6 (177 mM) with ATBT (360 mM) and AIBN (89 mM) (eq 10). Once again, both epoxide 23 and epoxide 24 (cf. Table III) were recovered (96–97%) when these compounds were subjected to the reactions with ATBT and AIBN.

Reactions of Diepoxy Ketone with Tributyltin Hydride. To investigate the scope of this free-radical reaction, some experiments were conducted using diepoxy ketone 29 (eq 11). The photoreaction and thermal reaction of 29 and TBTH were conducted, and the results are summarized in Table IV. Irradiation of 29 and TBTH



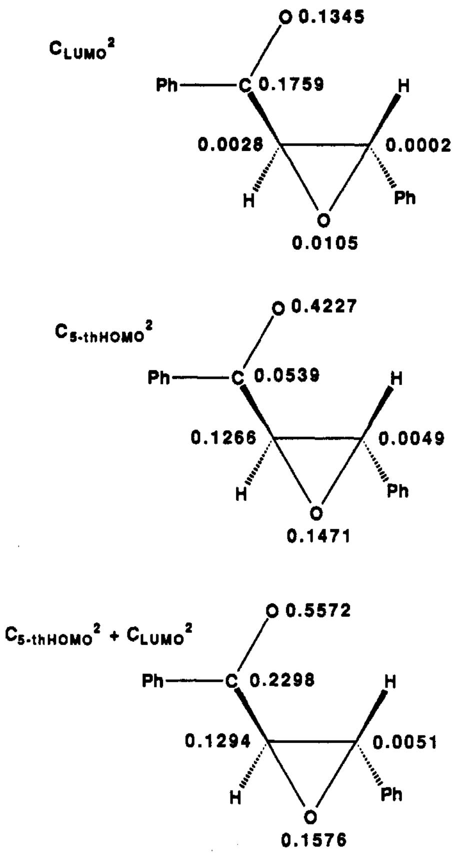


Figure 2. Frontier electron densities at each atom of the epoxy ketone ring of **t-1a**.

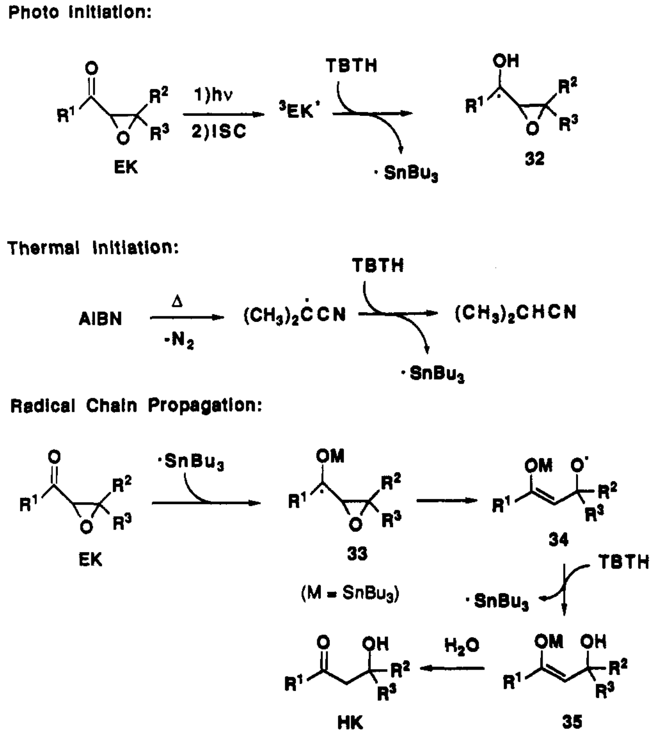
(1.2 equiv vs **29**) in benzene afforded monohydroxy ketone **30** in which one epoxy ring still remains. Interestingly, even when an excess amount (5.0 equiv) of TBTH was used, only **30** was obtained in 85% with no isolation of dihydroxy ketone **31**. On the contrary to the photoreaction, when benzene solutions of **31** containing various amounts of TBTH (1.2, 2.4, and 5.0 equiv) were refluxed in the presence of AIBN, the mixtures of **30** and **31** were obtained at different ratios.

Calculations. To find the most reactive site of **t-1a** toward tributyl radical, we performed a semiempirical molecular orbital calculation, AM1.[13] According to the frontier orbital theory, radicals (SOMO) can interact with both HOMO and LUMO of neutral molecules.[14] While the highest four occupied molecular orbitals of **t-1a** are localized on the phenyl substituents, the 5th HOMO level is characterized by substantial contributions from the epoxy ketone moiety. Thus, the squares of the 5th HOMO orbital coefficients as well as those of LUMO orbital coefficients at each atom of **t-1a** were obtained and shown in Figure 2. Also, summation of these values was obtained to show the general indication for the radical reactivity of **t-1a**.

Discussion

Photochemically and thermally induced ring-opening reactions of α,β-epoxy ketones with tributyltin hydride have been described above. Hydrogen abstraction from tributyltin hydride by photoexcited epoxy ketones appears to initiate the photoreaction while decomposition of azoisobutyronitrile in the presence of tributyltin hydride induces the thermal reaction. In both cases, a subsequent free-radical chain process involving a tributyltin radical attack on epoxy ketone is probable.

Scheme III



A plausible reaction mechanism is proposed in Scheme III. Photoexcitation of epoxy ketones leads to excited triplets states of these compounds via efficient intersystem crossing (ISC).[15] Since triplet carbonyls are known to abstract hydrogen from TBTH to give ketyl radicals and tributyltin radical,[16] the ketyl radicals **32**[17] and tributyltin radical are formed in a similar manner via triplet states of EK. The tributyltin radical generated in situ adds to the ground-state epoxy ketones to form [(tributylstannyl)oxy]methyl radicals **33**, which undergo C_α–O bond cleavage to give the oxy radicals **34**. Subsequent hydrogen abstraction of **34** from TBTH gives β-hydroxy tributylstannyl enol ethers **35** which may be hydrolyzed to hydroxy ketones during workup. These interpretations are consistent with the fact that tributyltin radical generated by the photodecomposition of AIBN indeed accelerated photoreactions of acyl epoxides which less efficiently absorb the Pyrex filtered light than aroyl epoxides (entries 9–14 in Table I). In the thermal reaction, a catalytic amount of tributyltin radical is generated from the hydrogen abstraction of TBTH by a carbon radical derived from AIBN.[3,7] Tributyltin attack on the carbonyl of epoxy ketone is also confirmed by the following consideration. In general, the SOMO of nucleophilic radicals tend to interact with the LUMO of reactants.[14] Thus, nucleophilic tributyltin radical[3a] adds to **t-1a** through the interaction between the SOMO of tributyltin radical and the LUMO of **t-1a**. In fact, the reaction of 4′-cyanochalcone epoxide

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(13) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3092.

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(15) Kumar, C. V.; Ramaiah, D.; Das, P. K.; George, M. V. *J. Org. Chem.* **1985**, *50*, 2818.

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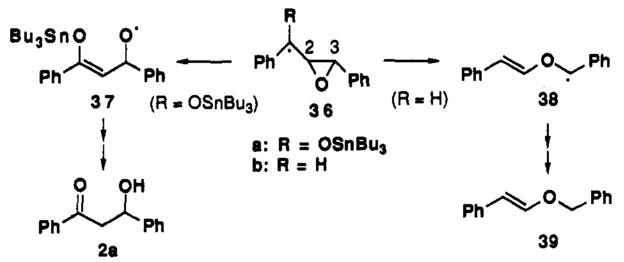
(17) The ketyl radicals **37** may undergo Cα–O bond cleavage. Subsequent hydrogen abstraction by the resulting alkoxy radicals also produces hydroxy ketones. However, this process requires 2 equiv of TBTH, which is inconsistent with the results obtained (see entries 1–3 in Table I).

Scheme IV



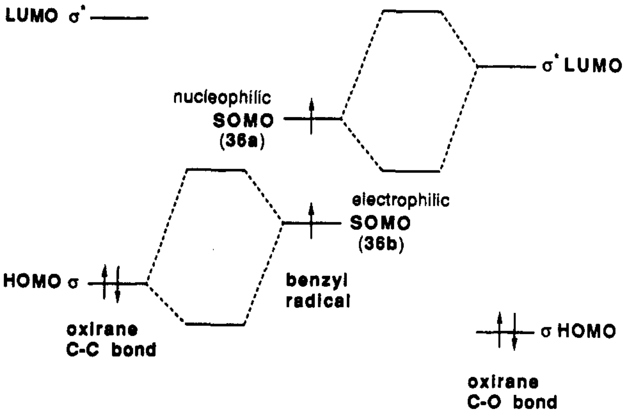


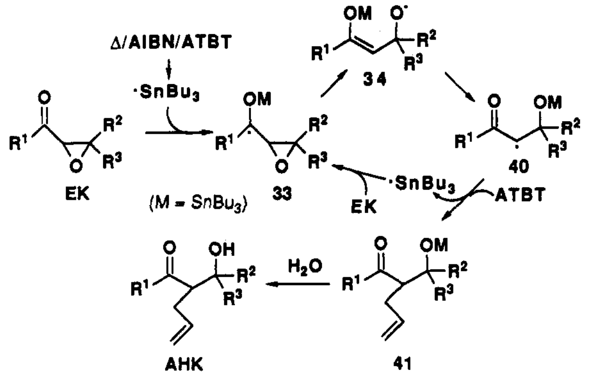
Figure 3. Interaction diagram of the frontier orbitals in the oxiranylmethyl radicals **36** (left for **36b** and right for **36a**).

(**18**) was more efficient than that of 4′-methoxychalcone epoxide (**20**) because cyano group lowers the LUMO energy of **t-1a** so that frontier orbital interaction becomes more efficient while methoxy group acts in an opposite manner.[14a] AM1 calculation also indicates that electron densities at the carbonyl are much higher than those of the epoxy ring in the LUMO of **t-1a** (Figure 2).

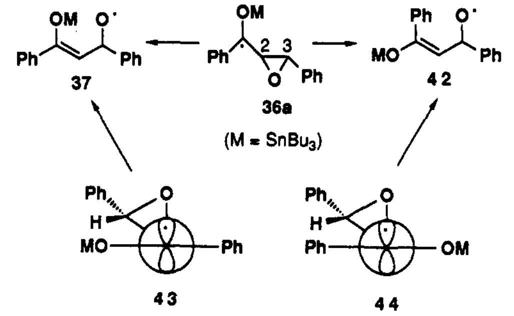
In this study, the most noteworthy observation is that the reactions of epoxy ketones possessing β-aryl substituents produced hydroxy ketones rather than keto ethers (**36a** in Scheme IV). In contrast, Murphy and co-workers reported that regioselective C_2–C_3 bond cleavage predominantly occurred in the reaction of *trans*-1-chloro-1,3-diphenylpropene epoxide with TBTH (**36b** in Scheme IV). Since ring-opening reactions of oxiranylmethyl radicals appear to be highly exothermic reactions, the transition states for the reactions resemble reactants in structure and energy. Thus, the frontier orbitals for these reactions are the SOMO of the radicals and the LUMO or HOMO of the carbon–carbon and carbon–oxygen bonds of the oxirane ring. The energies of LUMO and HOMO for the carbon–oxygen bond are lower than those for the carbon–carbon bond.[14a] Highly electron-donating substituents at the radical site raise the SOMO of the radical while hydrogen does not. Thus, a plausible interaction diagram of the frontier orbitals is shown in Figure 3. In the case of **36b**, the SOMO of the radical electrophilicly interacts with the HOMO of the carbon–carbon bond to give **38**. On the other hand, in the case of **36a**, the SOMO of the radical nucleophilicly interacts with the LUMO of the carbon–oxygen bond to give **37**.[18]

Another notable observation is that α-allylated β-hydroxy ketones (AHK), **27** and **28**, were produced in the reactions with allyltributyltin. These results strongly suggest the involvement of α-keto radical intermediates. A possible process to produce α-keto radicals is a direct attack of tributyltin radical on epoxy rings of **t-1a** and **6**. However, this possibility could be excluded since no C_β–O bond-cleaved products were obtained in the reactions of epoxy ketones in the presence of TBTH or ATBT. Also, such a process is inconsistent with the results obtained from AM1 calculation for **t-1a**. Thus, a reaction mechanism involving 1,5-tributyltin transfer[19] in **34** giving α-keto radicals **40** is tentatively proposed (Scheme V). In order to permit this rearrangement, **34** should have a cis configuration of (tributylstannyl)oxy (OM) and methyloxy radical ($R^2R^3CO^\bullet$) as shown in Scheme V. For example, in Scheme VI, the C_2–O bond cleavage of **36a** at the conformation **44** gives the oxy radical **42** that has a trans relationship between (tributylstannyl)oxy and (phenylmethyl)oxy radical while the bond cleavage at the conformation **43** produces cis isomer **37**. The relative stability in the **43**-like transition state leading to **37** is probably greater than the **44** like transition state leading to **42**. This interpretation would not be unreasonable by considering the A-strain effect of benzyl radicals.[20]

Scheme V



Scheme VI



Conclusion

All results and discussion presented above clearly demonstrate that α,β-epoxy ketones are efficiently and selectively converted to β-hydroxy ketones via free-radical processes utilizing tributyltin hydride and azoisobutyronitrile. The observations obtained here are noteworthy from the synthetic viewpoint as well as the mechanistic viewpoint. Indeed, several methods have been applied for the conversion of α,β-epoxy ketones to β-hydroxy ketones.[21]

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[18] (a) Similar arguments are offered in the ring-opening reactions of cyclopropylmethyl radicals.[18b,c] We are grateful to a reviewer for pointing out the importance of frontier orbital interaction to rationalize the observed regioselective ring opening of epoxy ketones. (b) Ratier, M.; Pereyre, M.; Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1907. (c) Mariano, P. S.; Bay, E. *J. Org. Chem.* **1980**, *45*, 1763.

[19] (a) Davies, A. G.; Tse, M. W. *J. Organomet. Chem.* **1978**, *155*, 25. (b) Recently, 1,5-tributyltin transfer from allyl carbon to oxy radical has been reported: Kim, S.; Lee, S.; Koh, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 5106.

[20] (a) Giese, B.; Bulliard, M.; Zeitz, H. G. *Synlett* **1991**, 425. (b) Curran, D. P.; Thoma, G. *Tetrahedron Lett.* **1991**, *32*, 6307.

Photoreaction is applicable for substances which can efficiently absorb the Pyrex-filtered light, and this is particularly useful for thermally labile compounds. On the other hand, thermal reaction can be used for the wide range of epoxy ketones, particularly useful for photochemically unreactive aliphatic epoxy ketones. Appropriate use of these two conditions provides the selective conversion of diepoxy ketones to monohydroxy and dihydroxy ketones. On the other hand, a little information about the reactivity of epoxy ketone derived oxiranylmethyl radicals has been available before this study.[9] It is now clear that the oxiranylmethyl radicals derived from epoxy ketones do not behave as those produced from halomethyl epoxides.[8c,e]

Experimental Section

General Procedures. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded at 90 and 22.49 MHz, respectively, on a JEOL FX-90Q spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane as the internal standard. IR spectra were obtained on a Hitachi 270-30 infrared spectrophotometer. UV spectra were recorded on a JASCO U best-30 UV/vis spectrophotometer. High-resolution mass spectra (HRMS) were recorded on a Shimadzu-Kratos Concept IS spectrometer at 70 eV. Elemental analyses were performed on a Yanako MT-3 CHN corder. All melting points are uncorrected.

Photolyses were carried out in Pyrex tubes that were placed in a water bath by using a Riko 400 W high-pressure Hg lamp (UVL-400P) or a 500-W Xe–Hg lamp as a light source. Column chromatography was performed with Wakogel C-200 silica gel. Preparative TLC was performed 20-cm × 20-cm plates coated with Wakogel B-5F silica gel. Reagent-grade solvents were used without further purification unless otherwise noted. Benzene for the photoreactions was spectroscopic grade and used without purification. Benzene for the thermal reactions was distilled over calcium hydride. Tributyltin hydride (TBTH, Aldrich), allyltributyltin (ATBT, Aldrich) and azoisobutyronitrile (AIBN, Wako) were used without further purification.

The AM1 calculations were performed on HITAC M-680H computer at the Computer Center of Institute for Molecular Science using the MOPAC 3.0 program developed by Stewart.[22] All calculations were performed using the restricted Hartree–Fock method with full optimization of all geometrical variables (bond lengths, bond angles and dihedral angles).

Preparation of Epoxy Ketones and Other Epoxides. Epoxy ketones **t-1a**, **1b**, **4**, **6**, and **8** were prepared from the corresponding unsaturated ketones using alkaline hydrogen peroxide, and the details have been already reported.[4c] Similarly, epoxy ketones **10**,[21g] **12**,[21d] **14**,[21d,g] and **20**[15] were obtained according to the literature procedures. Epoxy ketone **18** was prepared from *trans*-4′-cyanochalcone using sodium hypochlorite and pyridine.[15] Epoxy ester **22**[21g] and stilbene oxide **24** were prepared from methyl cinnamate and *trans*-stilbene by epoxidation with *m*-chloroperbenzoic acid. *cis*-Chalcone epoxide was prepared from *cis*-chalcone by the sequential reduction and oxidation steps according to the literature procedure.[23] Epoxy alcohol **23**[23] was prepared from **t-1a** on the treatment with sodium borohydride in ethanol. Diepoxy ketone **29** (31%) was prepared from *trans*-dibenzal acetone using alkaline hydrogen peroxide. **29** used for the reaction was obtained as a single diastereomer by recrystallization of the crude diastereomeric mixture from ethanol.

Physical and spectral data of **29**: mp 118–118.5 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 3.80 (d, 2 H, J = 1.9 Hz), 4.09 (d, 2 H, J = 1.9 Hz), 7.1–7.4 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 58.9 (d), 61.0 (d), 125.8 (d), 128.8 (d), 129.2 (s), 134.8 (s), 199.0 (s); IR (KBr) 3016, 1720, 1428, 1098, 890, 732, 698 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.70; H, 5.34.

Photoreactions of Epoxy Ketones with Tributyltin Hydride. A typical experiment is described below. A nitrogen-prepurged benzene (20 mL) solution containing **t-1a** (220.6 mg, 0.984 mmol) and TBTH (0.56 mL, 2.02 mmol) was irradiated in a Pyrex tube (diameter = 2.5 cm) for 30 min with a high-pressure Hg lamp. The photolysate was concentrated in vacuo to give the residue that was subjected to column chromatography. After unreacted TBTH was eluted with *n*-hexane, the acetone-eluted fraction was collected. This sequence was performed as the usual workup procedure for both photochemical and thermal reactions. Subsequently, crude products were separated by TLC (CH_2Cl_2/C_6H_6 = 1/1) to afford **2a** (207.2 mg, 0.916 mmol, 93.1%) and **3** (2.2 mg, 0.00981 mmol, 1.0%). Similarly, photoreactions of other epoxy ketones were conducted, and the results are summarized in Table I. Separation of the crude products was performed using column chromatography or TLC: **2b**, **9**, **11**, TLC (CH_2Cl_2/C_6H_6 = 1/1); **5**, **7**, TLC (CH_2Cl_2); **13**, column (CH_2Cl_2/Et_2O = 14/1); **15**, column (CH_2Cl_2/Et_2O = 4/1). Characterization of hydroxy ketones **2a**, **2b**, **5**, **7**, and **9** have been previously completed.[4c] Hydroxy ketones **11**, **13**, and **15** are known compounds.[21d,21g]

Time Dependencies of Photoreactions of *trans*-Chalcone Epoxide t-1a and *cis*-Chalcone Epoxide c-1a with Tributyltin Hydride. A stock solution of benzene (25 mL) containing **t-1a** (275.7 mg, 1.229 mmol) and TBTH (0.41 mL, 1.478 mmol) was prepared. An aliquot (5 mL) of this solution placed in a Pyrex tube (diameter = 1.3 cm) was purged with nitrogen and irradiated with a Xe–Hg lamp through a Toshiba UV-35 glass filter ($\lambda >$ 320 nm). The photolysate was subjected to the usual workup procedure. The reaction mixtures were analyzed by ^{1}H NMR using triphenylmethane as the internal standard to obtain the conversion of **t-1a** and the yield of **2a**. The following are results obtained, irradiation time (min), conversion (%), yield (%): 2, 80.8, 81.8; 5, 97.6, 94.7; 15, 100, 90.6; 30, 100, 80.8. Photoreactions of **c-1a** with TBTH were similarly performed and the results are described below: 15, 2.0, 3.8; 30, 25.5, 14.7; 45, 35.1, 25.5; 60, 66.6, 49.8; 75, 87.2, 69.1; 90, 98.4, 74.6. These results are summarized in Figure 1.

Photoreaction of the Mixture of t-1a and c-1a with Tributyltin Hydride. A nitrogen-prepurged benzene (5 mL) solution containing **t-1a** (55.1 mg, 0.249 mmol), **c-1a** (55.1 mg, 0.249 mmol), and TBTH (83 μL, 0.299 mmol) was irradiated with a Xe–Hg lamp ($\lambda >$ 320 nm) for 10 min. After the usual workup of the photolysate, ^{1}H NMR analysis was performed. As control experiments, **t-1a** and **c-1a** were independently irradiated (**t-1a** or **c-1a**, 55.1 mg, 0.249 mmol; TBTH, 83 μL; benzene, 5 mL; irradiation time, 10 min).

Thermal Reactions of Epoxy Ketones with Tributyltin Hydride in the Presence of Azoisobutyronitrile. A typical experiment is as follows. A nitrogen-prepurged benzene (22.5 mL) solution of **t-1a** (202.0 mg, 0.901 mmol), TBTH (0.3 mL, 1.082 mmol), and AIBN (17.9 mg, 0.109 mmol) was refluxed at 98 °C for 60 min under a nitrogen atmosphere. The reaction solution was worked up in the usual manner. TLC separation of crude products afforded **2a** (169.6 mg, 0.750 mmol, 83.2%). Reactions of other epoxy ketones were conducted similarly. The hydroxy ketones were isolated by TLC or column chromatography separations under the same conditions as those described in photoreactions. The results are presented in Table II.

Thermal Reaction of the Mixture of t-1a and c-1a with Tributyltin Hydride in the Presence of Azoisobutyronitrile. A nitrogen-prepurged benzene (11.25 mL) solution of **t-1a** (50.5 mg, 0.225 mmol), **c-1a** (50.5 mg, 0.225 mmol), TBTH (80 μL, 0.288 mmol), and AIBN (4.7 mg, 0.0286 mmol) was refluxed for 60 min. Subsequently, ^{1}H NMR analysis of the reaction mixture was performed after the usual workup.

Thermal Reaction of the Mixture of *trans*-4′-Cyanochalcone Epoxide (18) and *trans*-4′-Methoxychalcone Epoxide (20) with Tributyltin Hydride in the Presence of Azoisobutyronitrile. A nitrogen-prepurged benzene (29 mL) solution of **18** (149.6 mg, 0.600 mmol), **20** (143.0 mg, 0.600 mmol), TBTH (0.2 mL, 0.720 mmol), and AIBN (12.1 mg, 0.072 mmol)

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(22) Stewart, J. J. P. *QCPE Bull.* **1983**, *3*, 43.

(23) Wasserman, H. H.; Aubrey, N. E. *J. Am. Chem. Soc.* **1955**, *77*, 590.

was refluxed for 60 min. Then, the resulting solution was subjected to the usual workup and analyzed by ^{1}H NMR.

Physical and spectral data of **19** and **21** are described below. **19**: colorless oil; ^{1}H NMR (CDCl$_3$) δ 3.30 (d, 1 H, J = 4.1 Hz), 3.36 (d, 1 H, J = 7.9 Hz), 3.60 (broad s, 1 H), 5.31 (dd, 1 H, J = 4.1, 7.9 Hz), 7.15–7.45 (m, 5 H), 7.65–7.74 (m, 2 H), 7.94–8.03 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 47.8 (t), 69.9 (d), 116.6 (s), 117.8 (s), 125.7 (d), 127.8 (d), 128.6 (d), 132.5 (d), 139.6 (s), 142.9 (s), 198.3 (s); IR (neat) 3504, 2228, 1688, 1404, 1206, 700 cm^{-1}; HRMS *m/e* calcd for $C_{16}H_{13}NO_2$ 251.09463, found 251.09320. **21**: mp 46.5–47.5 °C (MeOC$_2$H$_4$OMe-*n*-C$_6$H$_{14}$); ^{1}H NMR (CDCl$_3$) δ 3.28 (d, 2 H, J = 6.2 Hz), 3.83 (s, 3 H), 3.83 (broad s, 1 H), 5.29 (dd, 1 H, J = 5.9, 6.2 Hz), 6.81–6.98 (m, 2 H), 7.23–7.44 (m, 5 H), 7.81–7.99 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 47.0 (t), 55.5 (q), 70.3 (d), 113.9 (d), 125.8 (d), 127.5 (d), 128.5 (d), 130.0 (s), 130.5 (d), 143.4 (s), 164.0 (s), 198.5 (s); IR (KBr) 3440, 2986, 1668, 1600, 1260, 1176, 698 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.13; H, 6.35.

Thermal Reactions of Epoxides 22–24 with Tributyltin Hydride in the Presence of Azoisobutyronitrile. In the reactions of epoxy ester **22**, epoxy alcohol **23**, and stilbene oxide **24** with TBTH and AIBN, the corresponding hydroxy compounds could not be obtained as shown in Table III. Most of starting epoxides were recovered. The methods to determine the recovery of epoxides are described below. For **22**, ^{1}H NMR analysis was conducted using triphenylmethane as the internal standard. Since **23** was found to be rather labile on silica gel, ^{1}H NMR analysis was performed using 1,2,4,5-tetramethoxybenzene as the internal standard before the usual workup. Unreacted **24** was isolated by the column separation (CH$_2$Cl$_2$/*n*-C$_6$H$_{14}$ = 1/3).

Thermal Reactions of t-1a and 6 with Allyltributyltin in the Presence of Azoisobutyronitrile. A nitrogen-prepurged benzene (2.6 mL) solution of **t-1a** (134.7 mg, 0.600 mmol), ATBT (0.77 mL, 2.41 mmol), and AIBN (49.3 mg, 0.300 mmol) was refluxed for 120 min under nitrogen atmosphere. The reaction solution was subsequently worked up in the usual manner. TLC separation (CH$_2$Cl$_2$/C$_6$H$_6$ = 1/1) of crude products afforded **27** (109.9 mg, 0.413 mmol, 68.8%) as a diastereomeric mixture (**27-A**/**27-B**) in which no pronounced diastereoselectivity was observed. Partial separation of the mixture has been achieved.

Reaction of **6** (88.9 mg, 0.600 mmol) with ATBT (0.39 mL, 1.22 mmol) and AIBN (49.3 mg, 0.300 mmol) was similarly conducted in benzene (3 mL). **28** (92.2 mg, 0.485 mmol, 80.8%) was isolated by TLC separation (CH$_2$Cl$_2$).

Physical and spectral data of **27** (**27-A** and **27-B**) and **28** are described below. **27-A**: ^{1}H NMR (CDCl$_3$) δ 2.40–2.70 (m, 2 H), 3.64 (broad s, 1 H), 3.70–3.95 (m, 1 H), 4.70–5.05 (m, 3 H), 5.30–5.85 (m, 1 H), 7.00–7.45 (m, 8 H), 7.55–7.90 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 32.3 (t), 53.2 (d), 74.0 (d), 116.8 (t), 126.3 (d), 127.5 (d), 128.3 (d), 128.5 (d), 133.1 (d), 135.5 (d), 137.3 (s), 142.0 (s), 203.8 (s); IR (neat) 3448, 3056, 1672, 1448, 1238, 918, 760, 700 cm^{-1}. **27-B**: ^{1}H NMR (CDCl$_3$) δ 2.10–2.50 (m, 2 H), 3.42 (broad s, 1 H), 3.70–4.00 (m, 1 H), 4.70–5.05 (m, 3 H), 5.30–5.80 (m, 1 H), 7.10–7.50 (m, 8 H), 7.70–7.90 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 34.7 (t), 52.8 (d), 75.6 (d), 117.4 (t), 126.3 (d), 126.5 (d), 127.8 (d), 128.4 (d), 133.1 (d), 134.5 (d), 138.1 (s), 142.5 (s), 204.6 (s); IR (neat) 3464, 3056, 1676, 1448, 1244, 1206, 700 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.96; H, 6.96. **28**: colorless oil; ^{1}H NMR (CDCl$_3$) δ 2.25–2.58 (m, 2 H), 2.91 (broad s, 1 H), 3.50–4.05 (m, 3 H), 4.85–5.15 (m, 2 H), 5.50–5.95 (m, 1 H), 7.25–7.65 (m, 3 H), 7.75–8.00 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 33.5 (t), 48.8 (d), 63.2 (t), 117.0 (t), 128.5 (d), 128.7 (d), 133.1 (d), 135.3 (d), 137.7 (s), 203.2 (s); IR (neat) 3428, 1678, 1446, 1242, 1208 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: 75.73; H, 7.54.

Reactions of Diepoxy Ketones 29 and Tributyltin Hydride. Photoreaction. A nitrogen-prepurged benzene (20 mL) solution of **29** (261.5 mg, 0.982 mmol) and TBTH (0.33 mL, 1.18 mmol, 1.2 equiv vs **29**) in a Pyrex tube was irradiated with a high-pressure Hg lamp for 60 min. Column chromatography (AcOEt/*n*-C$_6$H$_{14}$ = 1/2) separation of crude products yielded **30** (198.5 mg, 0.740 mmol, 75.3%) and **29** (50.2 mg, 0.189 mmol, 19.2%). Reaction of **29** and 5.0 equiv of TBTH was similarly conducted, and the result is shown in Table IV. **Thermal Reaction.** A nitrogen-prepurged benzene (22.5 mL) solution containing **29** (239.9 mg, 0.901 mmol), TBTH (0.6 mL, 2.16 mmol, 2.4 equiv vs **29**), and AIBN (36.2 mg, 0.216 mmol) was refluxed for 60 min under nitrogen atmosphere. Both **31** (113.5 mg, 0.417 mmol, 46.3%) and **30** (96.4 mg, 0.359 mmol, 39.8%) were obtained by the column chromatography (EtOAc/*n*-C$_6$H$_{14}$ = 1/2). Reactions of **29** with 1.2 equiv and 5.0 equiv of TBTH were similarly conducted, and the results are shown in Table IV.

Physical and spectral data of **30** and **31**. **30**: mp 85–86 °C (CH$_2$Cl$_2$-*n*-C$_6$H$_{14}$); ^{1}H NMR (CDCl$_3$) δ 2.84–3.10 (m, 2 H), 3.01 (broad s, 1 H), 3.51 (d, 1 H, J = 1.8 Hz), 3.86 (d, 1 H, J = 1.8 Hz), 5.17–5.31 (m, 1 H), 7.10–7.40 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 46.6 (t), 58.0 (d), 63.3 (d), 70.0 (d), 125.8 (d), 127.9 (d), 128.7 (d), 129.1 (d), 135.0 (s), 142.9 (s), 205.3 (s); IR (KBr) 3444, 3020, 1712, 1344, 1074, 762, 700, 548 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.07; H, 6.19. **31**: mp 58–59 °C (CH$_2$Cl$_2$-*n*-C$_6$H$_{14}$); ^{1}H NMR (CDCl$_3$) δ 2.79 (d, 2 H, J = 4.4 Hz), 2.83 (d, 2 H, J = 7.9 Hz), 3.07 (broad s, 2 H), 5.16 (dd, 2 H, J = 4.4, 7.9 Hz), 7.30 (broad s, 10 H); ^{13}C NMR (CDCl$_3$) δ 52.2 (t), 69.8 (d), 125.6 (d), 127.7 (d), 128.5 (d), 142.9 (s), 210.1 (s); IR (KBr) 3336, 3060, 1712, 1384, 1048, 896, 746, 698 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.82; H, 6.66.

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Supplementary Material Available: Results obtained in the reactions of an additional six epoxy ketones with tributyltin hydride including the experimental results (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.