Characteristic Reactivities of Some Rearrangeable Ketyl Radicals Generated through Photoinduced Electron Transfer Processes

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Mechanistic as well as synthetic aspects of the photoinduced electron transfer reactions of epoxy ketones, bromomethyl-substituted benzocyclic ketones, and tribromomethyl-substituted cyclohexadienones with amines are described.

INTRODUCTION

Over the past several decades, the photoinduced electron transfer (PET) chemistry of organic molecules has been a central topic in the area of organic photochemistry. Considerable advances have been made in the understanding of the PET reaction mechanisms as well as their synthetic application [1-3]. Radical cations generated through PET processes between electron-donor-substrates and electron-acceptor-sensitizers, such as aromatic nitriles, quinones, and cationic salts, have been extensively investigated [4]. On the other hand, the reactivity of organic radical anions in PET reactions have been less explored. This might be partly due to the absence of practical electron-donor-sensitizers as compared to electron-acceptor-counterparts described above. About ten years ago, the author decided to start a long-range research program to explore the reactivity and synthetic application of carbonyl radical anions (ketyl radicals) in PET reactions. In this program, in which amines were chosen as electron donors to produce ketyl radicals, reaction mechanisms as well as the selective transformation of certain ketyl precursors were investigated. In this account, the author will describe some characteristic aspects on the reactivity of rearrangeable ketyl radicals generated through PET processes with amines. The carbonyl substrates as well as the amines which were investigated are presented in Figure 1.

Since a large enhancement of electron-donating and electron-accepting ability of a molecule is expected on irradiation, the photoexcited molecule more readily undergoes single electron transfer (SET) with other molecules compared to its ground state counterpart. In their seminal paper, Rehm and Weller demonstrated that the feasibility of a SET process can be estimated by using equation (1) [5]. The free energy change (ΔG) for the SET process between the donor molecule and the acceptor molecule, one of which is electronically excited, is

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Received & Accepted; October 23, 2002

calculated by using their reduction and oxidation (redox) potentials ($E_{1/2}^{red}$, $E_{1/2}^{ox}$), the excitation energy (E_{00}), and the coulomb term (C). The term C is known to depend on the polarity of the solvent used; the value for a typical polar solvent, MeCN was proposed to be -0.06 eV [5,6]. Thus, SET between the triplet excited states of the ketones **1**, **4**, and **8** (E^{red} = -1.39 to -2.00 V vs SCE, measured; E_{00} = 67 to 76 kcal/mol, estimated from the data for the related compounds) and the ground states of amines (E^{ox} = +0.31 to +1.17 V vs SCE, measured) in Figure 1 are exothermic processes; ΔG could be estimated to be around the range within -10 and -25 kcal/mol.

$$\Delta G \text{ (kcal/mol)} = 23.06[E_{1/2}^{ox} - E_{1/2}^{red} + C] - E_{00} \qquad (1)$$

Ketyl radicals are known to undergo three different modes of reaction, including 1) bond formation either with electrophiles or with radicals, 2) C_α- and C_β-bond cleavages, 3) single electron capture and release [7,8]. In a general sense, the ketyl radicals
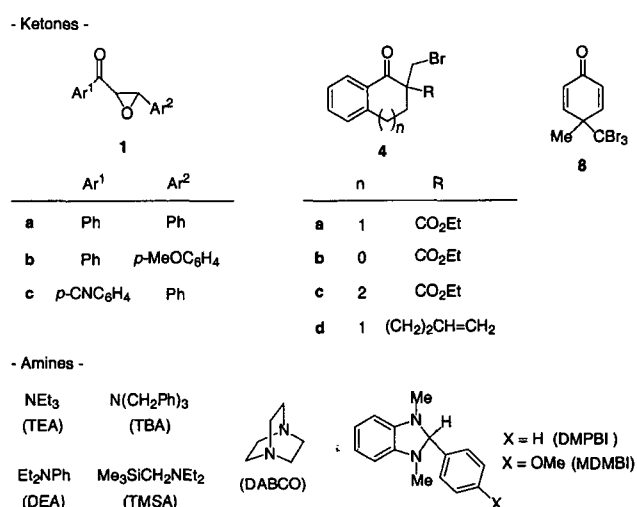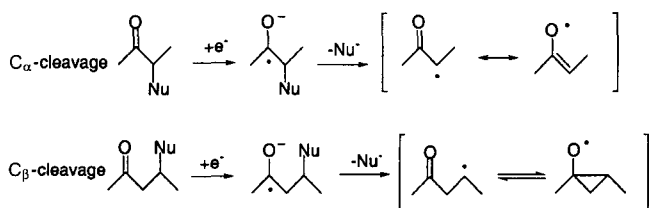

Figure 1. Representative ketones and amines for photoinduced electron transfer reactions.
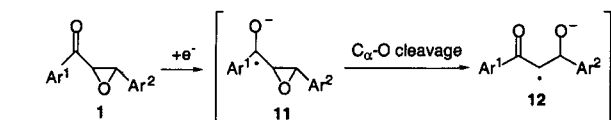
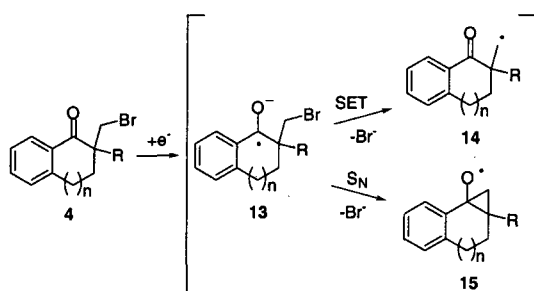Scheme 1.

Scheme 2.
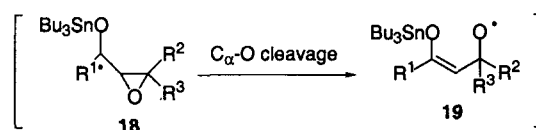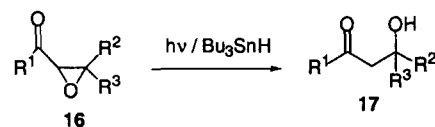

Scheme 3.

Scheme 4.

Scheme 5.

derived from carbonyl compounds that possess nucleofugal groups (Nu) at positions either C_α or C_β to the carbonyl undergo regioselective bond cleavages to give radical intermediates (Scheme 1). Equilibrium between the resulting intermediates may or may not exist depending on their structures as well as the conditions employed.

Therefore, in the reactions of the ketones 1, 4, and 8 (Figure 1), the following pathways were expected to proceed. On one hand, ketyl radicals 11, derived from aromatic epoxy ketones 1, should undergo selective C_α-O bond cleavage to give ring-opened distonic radical anions 12 (Scheme 2). On the other hand, ketyl radicals 13 of bromomethyl substituted benzocyclic ketones 4 are expected to undergo intramolecular reaction with distant carbon-halogen bonds. SET or nucleophilic substitution (S_N) gives the corresponding radical intermediates 14 or 15 respectively (Scheme 3). In the case of 8, similar reaction pathway occurring between the enone radical anion part and carbon bromine bond is considered. In the following section, the details of the PET reactions of these substrates are described.
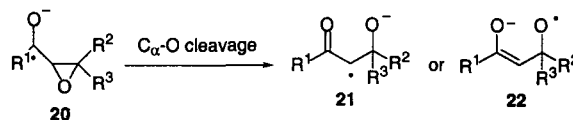
reactions of epoxy ketones 16 with tributyltin hydride since the expected intermediates in these reactions were the metal coordinated ketyl radicals 18 while the non-metal coordinated analogs were expected to be generated in PET reaction (Scheme 4) [9,10]. We found that hydroxy ketones 17 were produced in high yields. This observation was rationalized by the intermediacy of oxiranyl methyl radicals 18 possessing an electron-donating tributylstanyloxy substituent at the radical center, which undergo selective C_α-O bond cleavage to give the oxy radicals 19.

This result suggests that the ketyl radicals 20 of epoxy ketones 16, in which more negative charge is generated at the position adjacent to the epoxy ring, should undergo selective C_α-O bond cleavage to give either the α-keto radicals 21 or the enolate 22 (Scheme 5). As expected, irradiation of selected aromatic epoxy ketones 1 (trans-form) in the presence of triethylamine (TEA) produced diketones 2 and hydroxy ketones 3 (Amine = TEA in Scheme 6), the ratio of which depends on the reaction conditions (Table 1) [11]. While both 2 and 3 were obtained in MeCN and MeOH (entries 1, 2, 4, and 5), addition of LiClO₄ completely suppressed the formation of 2 (entries 3 and 6). In the latter cases, considerable amounts of acetophenone and benzaldehydes were detected.

On the basis of these results, the reaction mechanism for production of hydroxy ketones 3 shown in Scheme 7 was proposed. The intermediacy of the ring opened radical anions 12 was confirmed by use of time resolved EPR spectroscopy (K. Akiyama, S. Tero-Kubota, Y. Ikegami, and E. Hasegawa,

DISCUSSION

PET Reactions of Epoxy Ketones with Amines. Mechanistic Aspects

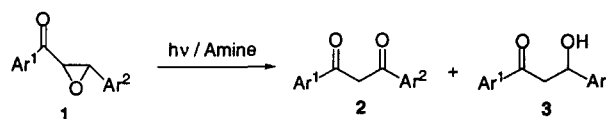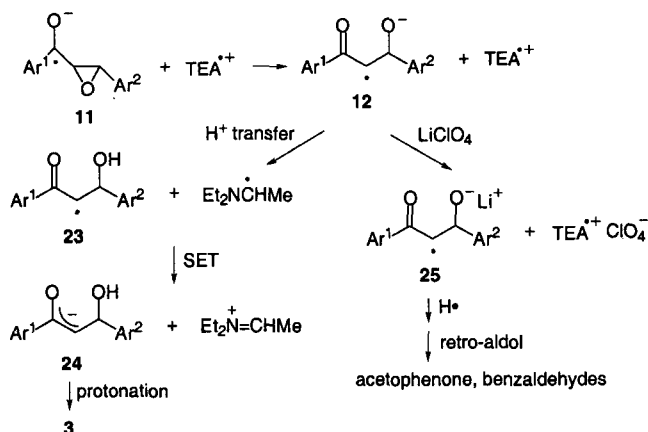At the beginning of our studies, we probed the free radical

Scheme 6.

Table 1. Photoreaction of epoxy ketones **1a** and **1b** with triethylamine

Entry	1	Solvent	LiClO$_4$	Yield of 2(%)	Yield of 3(%)
1	1a	MeCN	0	60	22
2	1a	MeOH	0	49	28
3	1a	MeCN	added	70	0
4	1b	MeCN	0	26	15
5	1b	MeOH	0	11	8
6	1b	MeCN	added	68	0

Yields of **2** and **3** are reported on the basis of the conversion of **1**.

Scheme 7.

Scheme 8.

Table 2. Photoreaction of epoxy ketone **1c** with various amines

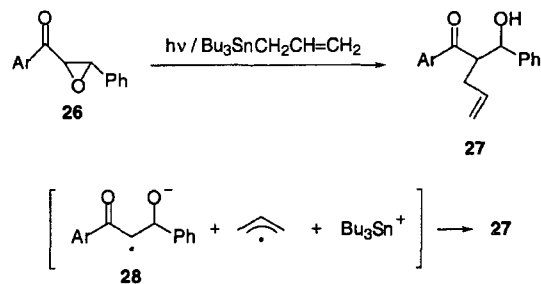| Entry	Amine	E_p^{ox} (V vs SCE)	Solvent	Yield of 2c (%)	Yield of 3c (%)
1	TEA	+0.89	MeCN	40	7
2	TEA	+0.89	PhH	77	8
3	DABCO	+0.71	PhH	71	0
4	DEA	+0.76	PhH	7	42
5	TBA	+1.17	PhH	12	50

Yields of **2c** and **3c** are reported on the basis of the conversion of **1c**.

unpublished). Proton transfer from the radical cation of TEA to **12** gives α-keto radicals **23** followed by SET from α-amino radical to produce the enolate **24** which is protonated to give **3**. However, in the presence of LiClO$_4$, ion-pair exchange between the formed radical ion pair and LiClO$_4$ occurs, and this interrupts proton transfer from the radical cation of TEA to **12**. Complexation of lithium cation to **12** giving **25** causes retro-aldol type decomposition to occur to finally produce the observed fragmentation products. Further studies were required to elucidate the reaction mechanism for formation of diketones **2** (see below). Subsequently, other related PET reactions of epoxy ketones were briefly explored. Irradiation of **26** in the presence of allyltributyltin as an electron donor produced α-allyl-β-hydroxy ketones **27** which were presumably formed by coupling of the ring-opened radical anions **28** and allyl radical (Scheme 8) [12].

An ensuing mechanistic study led to several important observations [13]. In order to determine if amine donors are essential for the rearrangement of epoxy ketone to diketone, PET reaction of the epoxy ketone **1c** with the strong electron-donor, 1,2,4,5-tetramethoxy benzene (TMB), E_p^{ox} (V vs SCE) =+0.77, was probed. Immediately we noticed that the reaction progressed quite slowly, and the diketone **2c** was not formed at all while it was obtained as the major product in the reaction of **1c** with less electron-donating TEA (see below).

These results suggest that the electron-donating ability of the donor is not sufficient factor to promote the rearrangement.

Subsequently, photoreactions of **1c** with various amines were investigated (Scheme 6) (Table 2). Unexpectedly, the yields of **2c** were found to be greater in benzene than in acetonitrile (entries 1 and 2). This suggests that the rearrangement of **1c** to **2c** does not occur after diffusion of the initially formed radical ion pair into free radical ions. Rather, it occurs within the radical ion pair in the presence of an amine radical cation. Another noteworthy observation is that the product ratio of **2c** and **3c** was significantly influenced by the amine used. For example, **3c** was the major product from reaction with tribenzylamine (TBA), whose radical cation efficiently donates a proton to the anionic intermediate derived from **1c** (entry 5). In the opposite sense, the absence of **3c** in the product mixture from reaction with 1,4-diazabicyclo[2.2.2]octane (DABCO) is also understood because the radical cation of DABCO is both exceptionally stable and a poor proton donor (entry 3).

On the basis of these results, a reaction mechanism, in which interaction between the radical anion derived from epoxy ketone **1c** and an amine radical cation governs the selective pathway to the observed products **2c** and **3c**, was proposed (Scheme 9).

The pathway for formation of **3c** is essentially the same as the one presented in Scheme 7. In the pathway to **2c**, an amine radical cation abstracts a β-hydrogen from **29** to give the ammonium cation and enolate anion **30**. This process should be more favorable in a less polar solvents because these solvents shift the equilibrium of free radical ions to radical ion pairs. The striking contrast in the ratio (**2c/3c**) observed in the reaction with TEA compared to that with diethylaniline (DEA)

Scheme 9.

Scheme 10.

dry THF: **32** (major)
aqueous THF: **3a** (88%)
aqueous PhH: **3a** (85%)
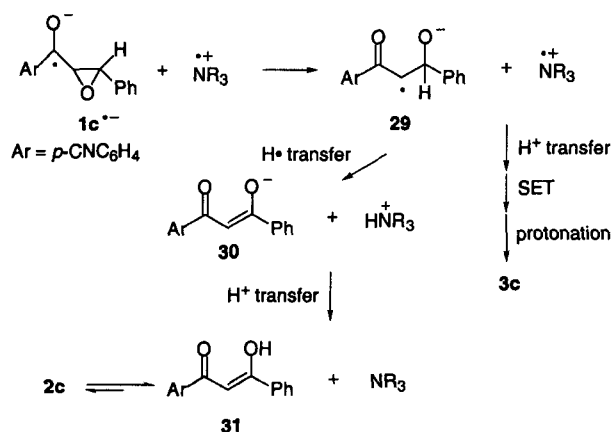
Scheme 11.

needs to be addressed. Although the proton-donating ability of the radical cation of DEA is lower than that of TEA, the yield of **3c** from DEA was greater than that for TEA. On the other hand, the yield of **2c** for TEA was greater than that for DEA. This is consistent with the mechanism shown in Scheme 9 since the efficiency of the hydrogen abstraction by the amine radical cation would be qualitatively correlated with the N-H bond strength of the corresponding ammonium salt.

Synthetic Aspects

The transformation of epoxy ketones to hydroxy ketones is recognized as a synthetically important chemical process [14]. Cossy reported photoreactions of several aliphatic and aromatic epoxy ketones in the presence of TEA [15,16]. This method was successfully applied to the synthesis of the bioactive compound, ptaquilosin [17]. Mattay also examined photoreaction of an epoxy ketone possessing a tethered alkenyl substituent with TEA in expectation of the radical cyclization onto the alkene. The desired cyclized product was not obtained in this case and the enone was isolated in low yield [18].

In these experiments and those conducted in our laboratory (see above), the yields of hydroxy ketone photoproducts were modest to good. However, several problems were encountered. For example, other compounds, such as diketones, were the major products formed in some photoreactions and the reactions could not be conducted to completion since prolonged irradiation caused decomposition of hydroxy ketones. Therefore, it was desired to discover the optimal PET conditions to produce hydroxy ketones in better yields. On the basis of the above discussion, the key properties of the amine donors, required for optimal yields of hydroxy ketones, are 1) good electron donating ability and 2) efficient proton-donating abilities of their radical cations. 1,3-Dimethy-2-phenylbenzimidazoline (DMPBI) [19,20] seemed to be an ideal candidate since it has been reported that it is first oxidized to become its radical cation (DMPBI⁺•) followed by deprotonation to give an α-amino radical (DMPBI•) which is converted to imidazolium
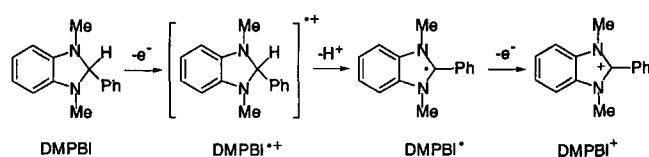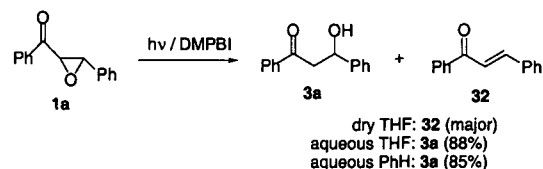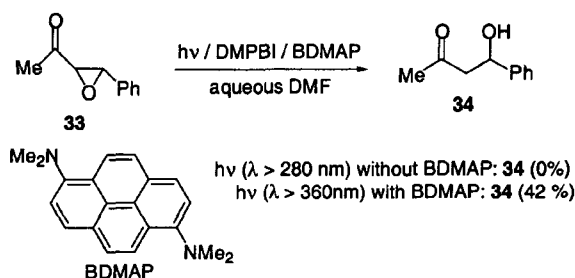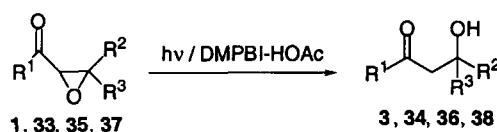
(DMPBI⁺) (Scheme 10) [21-24].

Thus, DMPBI was first applied to the PET reduction of epoxy ketone **1a** (Scheme 11) [25,26]. While the reaction in dry THF gave enone **32** as a major product, under the same irradiation conditions in wet (*ca* 1% aqueous) solvents such as THF and PhH produced **3a** in good yields. When the water contents of the solvents exceeded 2%, the yield of **2a** gradually decreased and those of the fragmentation products such as acetophenone and benzaldehyde increased. On the other hand, photoreduction of acetyl substituted epoxide **33** to **34** required the use of light of λ > 360 nm, DMF as solvent and 1,6-bisdimethylaminopyrene (BDMAP) as sensitizer (Scheme 12). A related investigations finally demonstrated that DMPBI-acetic acid is an effective reagent system for promoting photoinduced reductive transformation of epoxy ketones to hydroxy ketones (Scheme 13) (Table 3) [27]. Irradiation of benzoyl substituted epoxides **1**, **35** and **37** in THF, by using Pyrex filtered-light, led to production of the corresponding hydroxy ketones **3**, **36**

hv (λ > 280 nm) without BDMAP: **34** (0%)
hv (λ > 360nm) with BDMAP: **34** (42 %)

Scheme 12.

1, 33, 35, 37   **3, 34, 36, 38**

Scheme 13.

Table 3. Photoreaction of Epoxy Ketones (EK) 1, 33, 35 and 37 with DMPBI and AcOH

Entry	EK	R^1	R^2	R^3	Conversion of EK (%)	Yield of HK (%)
1	trans-1a	Ph	H	Ph	100	96
2	cis-1a	Ph	Ph	H	100	94
3	1b	Ph	H	p-MeOC$_6$H$_4$	100	88
4	35	Ph	H	i-Pr	100	72
5	37	Ph	H	H	100	69
6	33	Me	H	Ph	70	93

Yields of hydroxy ketones (HK) are reported on the basis of the conversion of epoxy ketones (EK)

and 38, respectively, in good to excellent yields (entry 1-5). BDMAP-photosensitized condition ($\lambda > 360$ nm) in DMF was used for the reduction of 33 to 34 (entry 6).

It is interesting to compare this reagent system to other reducing reagents, which convert epoxy ketones to hydroxy ketones. For example, the yields of hydroxy ketones obtained under this condition are as good as those obtained in typical free radical reactions which, although quite effective, require the use of toxic tributyltin hydride [10].

PET Reactions of Bromomethyl Substituted Benzocyclic Ketones with Amines

Investigation of SET reactions of compounds possessing both carbonyls and carbon-halogen bonds (*eg.*, ketones 4 in Figure 1) provides an interesting opportunity to learn how ketyl radicals intramolecularly react with distant carbon-halogen bonds [28,29]. We first studied the photoreactivity of ethyl 2-bromomethyl-1-tetralone-2-carboxylate 4a with *N,N*-diethyl (trimethylsilyl)methylamine (TMSA) in MeCN. This reaction produced benzocycloheptanone 5a, the reduced product 6a and the dimeric compounds 39 (as a mixture of two diastereomers) (Scheme 14) [30]. Irradiation of a D$_2$O-MeCN solution of 4a, led to formation of 5a-D, which contains *ca* 82% of deuterium at C$_3$, while no deuterium was incorporated into 6a. Therefore, 5a is mainly formed through an ionic route in which its precursor is protonated. On the other hand, 6a is produced through hydrogen atom abstraction by a radical intermediate.

On the basis of the above results, the plausible reaction mechanism shown in Scheme 15 can be presented. SET to photoexcited 4a from TMSA produces radical anion of 4a
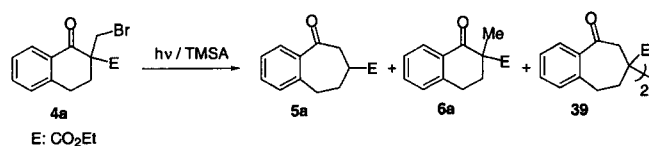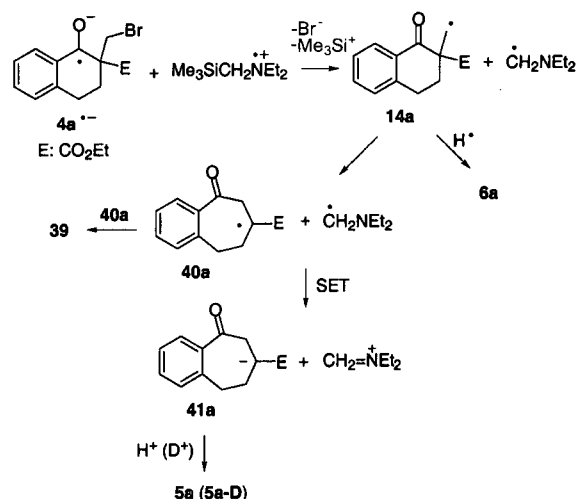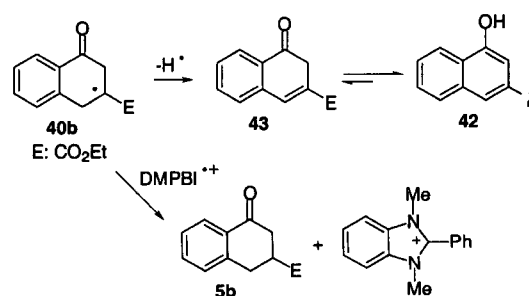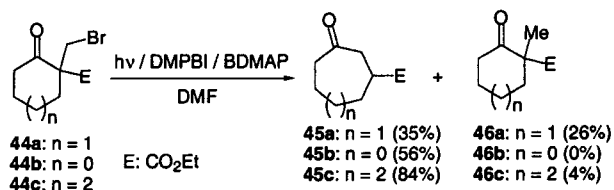

Scheme 15.

and radical cation of TMSA. The resulting radical anion of 4a undergoes carbon-bromine bond cleavage through intramolecular SET to give the carbon radical 14a, which abstracts a hydrogen atom to produce 6a. Radical cation of TMSA also undergoes rapid fragmentation assisted by appropriate silophiles such as MeCN, H$_2$O to become α-amino radical [31-33]. The carbon radical 14a, whose generation from radical anion of 4a was recently confirmed by the time resolved EPR spectroscopy (K. Yamamichi, K. Akiyama, E. Hasegawa and S. Tero-Kubota, unpublished), rearranges to the one-carbon homologated carbon radical 40a. Similar radical cyclization-ring expansion sequences are well documented [34,35]. SET within the radical pair of 40a and α-amino radical produces the carbanion 41a, which is protonated to give 5a, and an iminium cation. Formation of dimer 39 likely occurs by escape of 40a from the solvent cage.

Photoreactions of other bromo ketones, 4b and 4c, with TMSA also produced same types of cyclization-ring expansion products, 5b and 5c, respectively. However, in the case of 4b, the major product was ethyl 1-hydroxynaphthalene-3-carboxylate 42 instead of 5b. As shown in Scheme 16, 42 presumably is formed *via* hydrogen atom abstraction from the carbon radical 40b. Formed enone 43 tautomerizes to 42. Interestingly, when

Scheme 16.

Scheme 14.

Scheme 17.

44a: n = 1
44b: n = 0   E: CO₂Et
44c: n = 2

45a: n = 1 (35%)   **46a:** n = 1 (26%)
**45b:** n = 0 (56%)   **46b:** n = 0 (0%)
45c: n = 2 (84%)   **46c:** n = 2 (4%)

TMSA was replaced by DMPBI, **5b** became the major product. This would be explained by the occurrence of hydrogen atom transfer from the radical cation of DMPBI to **40b**.

The BDMAP photosensitization method was found to be useful for the reaction of the aliphatic substrates **44a-c** with DMPBI (Scheme 17) [26]. The yields of the ring expansion products **45a-c** as well as the relative yields of **45a-c** to the reduced products **46a-c** were similar to those observed in the free radical reactions with tristrimethylsilylsilane (E. Hasegawa, unpublished).

Our next target molecule was 2-bromomethyl-2-(3-butenyl)-1-tetralone **4d** which was recently studied [36]. If intramolecular SET between the ketyl group and carbon-bromine bond in the radical anion of **4d** proceeds in a manner similar to the radical anions of **4a**, the formed carbon radical could undergo rapid 5-exo radical cyclization with the tethered butenyl substituent [37]. As expected, the spirocyclic product **7** was obtained on irradiation of **4d** with TMSA, DMPBI or 2-(4'-methoxyphenyl)-1,3-dimethylbenzimidazoline(MDMBI). Notably, the simple reduction product **47** was not isolated in these cases (Scheme 18).

In the plausible mechanism for the reaction presented in Scheme 19, rearrangement of **14d** to **48** should be much faster than the hydrogen atom transfer from the amine radical cations to **14d**, which is consistent with the observation that **47** was not formed. Hydrogen atom transfer from the amine radical cations to **48** gives **7**. This last step does indeed occur,
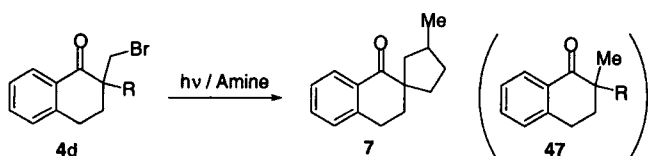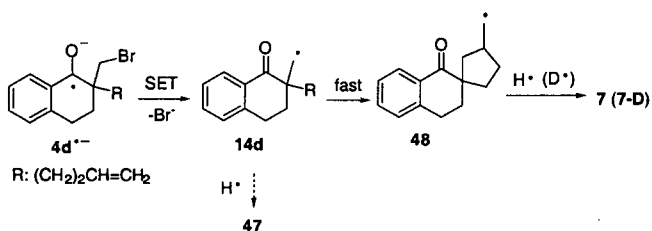
although not predominantly, since some deuterium incorporation at the methyl on the cyclopentane ring of **7** (**7-D**) was observed (40%-d in MeCN and 53%-d in PhH) when 2-deuterio DMPBI was used for the reaction.

PET Reactions of Tribromomethyl Substituted Cyclohexadienone with Amines

PET reactions of the substrates possessing both an α,β-unsaturated enone structure and a carbon-halogen bond could lead to carbon-carbon bond formation at the β-position of enone (formal intramolecular 1,4-radical addition). To test this proposal, photoreaction of dienone **8** with amines was conducted in various solvents (Scheme 20) (Table 4). The ring expansion product, tropone **9**, was the major product except for the reaction in THF (entry 4). The yield of **9** was significantly increased by using 33% aqueous conditions (compare entry 3 to entry 2). While the yield of **9** for the reaction with TMSA was essentially the same as that with TEA, the conversion of **8** in the former case (entry 1) was about three times greater than
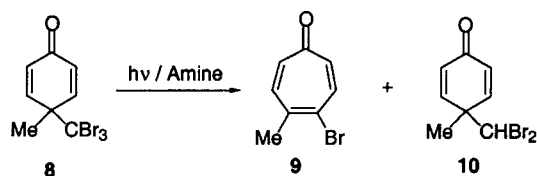
Scheme 20.

Table 4. Photoreaction of dienone **8** with amines

Entry	Amine	Solvent	Yield of 9(%)	Yield of 10(%)
1	TMSA	CH₂Cl₂	48	6
2	TMSA	MeCN	34	2
3	TMSA	aqueous MeCN	77	3
4	TMSA	THF	30	33
5	TEA	CH₂Cl₂	50	5
6	TBA	CH₂Cl₂	79	0

Yields of **9** and **10** are reported on the basis of the conversion of **8**.

4d
R: (CH₂)₂CH=CH₂

hv / Amine

7   (**47**)

Scheme 18.

4d⁻   **14d**   **48**
R: (CH₂)₂CH=CH₂

SET
-Br⁻

fast   H· (D·)
                → **7 (7-D)**

H·
47
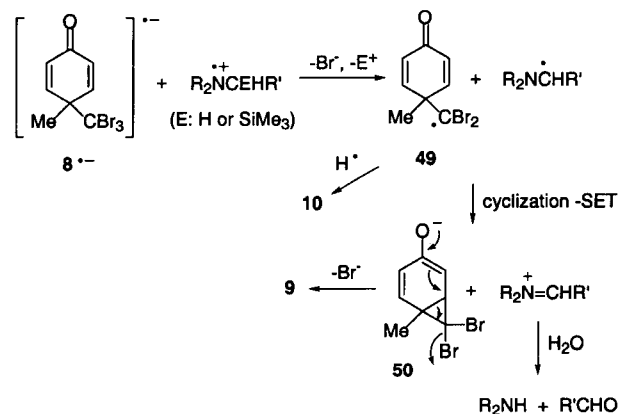
Scheme 19.

Scheme 21.

that in the latter (entry 5). The best yield of **9** was observed for reaction with TBA (entry 6) where both dibenzylamine and benzaldehyde were also produced. These products are diagnostic of the oxidative dealkylation of TBA.

On the basis of the observations made, the reaction mechanism presented in Scheme 21 was proposed. The radical anion of **8** undergoes debromination to give the carbon radical **49**. If **49** abstracts hydrogen atom, **10** is formed, which is consistent with the observation that the yield of **10** was significantly greater in THF than in other solvents. Subsequent cyclization and reduction of **49** yields **50** while the order of each step could not be easily specified. The anion **50** undergoes debromination to give **9**. Oxidation of the α-amino radical gives an iminium cation which readily undergoes hydrolysis to give secondary amine and aldehyde. Such products were indeed isolated in the reaction of **8** with TBA (see above). Therefore, effective generation of α-amino radical should accelerate the reduction of **49** to **50**. The observed effect of H_2O on the reaction of **8** with TMSA is consistent with this rationalization since H_2O is known to accelerate the desilylation of radical cations of α-silylamine [32,33].

SUMMARY

In this study, we demonstrated that PET processes of certain carbonyl compounds with amines produce ketyl radicals which undergo various chemical reactions depending on their structures and the conditions employed. We have addressed the issue of the chemistry of radical ion pairs in which specific interactions of ketyl radicals or rearranged intermediates with amine radical cations take place. Therefore, besides the nature of the ketyl radicals, other key factors governing the reaction pathways are the property of amine radical cations, and the surrounding medium including solvents and additives. From a synthetic viewpoint, PET processes provide unique, useful methods to generate radical species which are traditionally obtained by classical ground state methodologies promoted by redox reagents or electrochemical processes. We hope that further investigation on PET reactions of ketones or other related compounds with amines will lead to a deeper understanding of reaction mechanisms, to the development of new types of rearrangeable radical anion probes [23,24,28,29, 40-47], and to the discovery of new sythetically useful methods.

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