Photoreactions of 4-(Tribromomethyl)-4-methyl-2,5-cyclohexadienone and Its Derivatives with Amines: Radical Cyclization and Ring Expansion Reactions Promoted through Photoinduced Electron Transfer Processes

Eietsu Hasegawa,*,† Yukinobu Tamura,† Kimiko Suzuki,† Akira Yoneoka,† and Toshio Suzuki‡

Department of Chemistry, Faculty of Science, and Graduate School of Science and Technology, Niigata University, Ikarashi, Niigata 950-2181, Japan

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Photoreactions of 4-(tribromomethyl)-4-methyl-2,5-cyclohexadienone (**1**) and its derivatives with amines were studied. Irradiation of **1** with amine produced 4-bromo-5-methyltropone (**2**) along with 4-(dibromomethyl)-4-methyl-2,5-cyclohexadienone (**3**). The effects of solvent, added water, and the structural variation in amine on the product ratio were explored. Isolation of the amine-derived products revealed that oxidative dealkylation of amine proceeded during the photoreaction. On the basis of the results obtained, a reaction mechanism involving fragmentation of the dienone anion-radical and amine cation-radical pair is proposed. Photoreactions of dienone **4** with amine produced the tropones **6** and **7**, whereas tropone **9** was produced from **8**. Trialkyltin radical-induced reductions of dienones **1** and **4** with tri-*n*-butyltin hydride demonstrated common features with the photoreactions. It was also found that irradiation of dienone **3** with amine produced 4-methyltropone (**10**).

Introduction

Ketyl radicals are among the best known anion radical species which undergo various chemical transformation.[1] Their reactivities are governed by not only the inherent nature of these species but also the conditions under which they are generated. Normally, photoinduced electron transfer (PET) between carbonyl compounds and electron donors such as amines can produce ketyl radicals.[2] The reactions involving ketyl radicals generated through PET processes are influenced by the nature of the associated donor cation radicals. In our earlier study, we noticed that the PET reaction of 4-(trihalomethyl)-4-methyl-2,5-cyclohexadienones would be interesting for the reasons described below. On one hand, single electron transfer (SET) to compounds possessing electron-deficient σ-bonds such as carbon−halogen bonds results in dissociative electron transfer to cleave these bonds.[3] Therefore, the presence of a carbonyl group and a carbon−halogen bond in the same molecule could irreversibly reduce the distant carbon−halogen bond through intramolecular electron transfer upon generation of a ketyl radical.[4] Since such a process should finally generate a carbon radical, the PET reaction of the substrates possessing both an α,β-unsaturated enone structure and a carbon−halogen bond would lead to the carbon−carbon bond formation at the β-position of enone (formal intramolecular 1,4-radical addition).[5,6] On the other hand, SET to 4,4-disubstituted-2,5-cyclohexadienones in some cases leads to the facile cleavage of carbon−carbon as well as carbon−heteroatom bonds at the C_4 position, thus gaining resonance stabilization through aromatization, which yields substituted phenols as isolable products.[7,8] Interestingly, no information was available about the behavior of 4-(trihalomethyl)-4-methyl-2,5-cyclohexadienones under PET conditions before our study,[9] although the photochemistry of 2,5-cyclohexadienones has been extensively studied earlier by Schuster and co-workers.[10] Our preliminary observation revealed that irradiation of 4-(tribromomethyl)-4-methyl-2,5-cyclohexadienone with certain amines produced 4-bromo-5-methyltropone in moderate yield.[9] The present paper describes in detail our results on the PET reactions of 4-(tribromomethyl)-

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† Department of Chemistry, Faculty of Science.

‡ Graduate School of Science and Technology.

[1] Comprehensive review: Berger, D. J.; Tanko, J. M. In *The Chemistry of Double- Bonded Functional Groups;* Patai, S., Ed.; Wiley: New York, 1997; pp 1281−1354.

[2] (a) *Photoinduced Electron Transfer, Part C;* Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988. (b) Yoon, U. C.; Mariano, P. S.; Givens, R. S.; Atwater, B. W., III. In *Advances in Electron-Transfer Chemistry;* Mariano, P. S., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 4; pp 117−205.

[3] (a) Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987. (b) Savéant, J. M. In *Advances in Electron-Transfer Chemistry;* Mariano, P. S., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 4; pp 53−116.

[4] Kimura, N.; Takamuku, S. *J. Am. Chem. Soc.* **1994**, *116*, 4087.

[5] So far, only one related example has been reported: Givens, R. S.; Atwater, B. W. *J. Am. Chem. Soc.* **1986**, *108*, 5028.

[6] (a) Intramolecular displacements of nucleofuges by ketyl radical species have been accomplished by nonphotochemical methods.[6b−d] (b) Stork, G.; Rosen, P.; Goldman, N.; Coombs, R. V.; Tsuji, J. *J. Am. Chem. Soc.* **1965**, *87*, 275. (c) Scheffold, R.; Doke, M.; Dike, S.; Herld, T.; Walder, L. *J. Am. Chem. Soc.* **1980**, *102*, 3642. (d) Gassman, P. G.; Rasmy, O. M.; Murdock, T. O.; Saito, K. *J. Org. Chem.* **1981**, *46*, 5455.

[7] (a) C−O bond cleavage: Liotta, D.; Saindane, M.; Wykole, L. *J. Am. Chem. Soc.* **1983**, *105*, 2922. (b) C−Br bond cleavage: Lopez, L.; Calò, V. *J. Chem. Soc., Chem. Commun.* **1984**, 1266. (c) Recent examples of C−C bond cleavage: Tanko, J. M.; Brammer, L. E., Jr. *J. Chem. Soc., Chem. Commun.* **1994**, 1165. Philips, J. P.; Gillmore, J. G.; Schwartz, P.; Brammer, L. E., Jr.; Berger, D. J.; Tanko, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 195. Gillmore, J. G.; Tanko, J. M. *Tetrahedron Lett.* **1998**, *39*, 8795.

[8] (a) Electrochemical reduction of 4-(trichloromethyl)-4-methyl-2,5-cyclohexadienone in the presence of a proton source is known to produce *p*-cresol as a major product.[8b] (b) Mazzenga, A.; Lomnitz, D.; Villgas, J.; Polowczyc, C. J. *Tetrahedon Lett.* **1969**, *10*, 1665.

[9] Hasegawa, E.; Tamura, Y.; Horaguchi, T.; Suzuki, T.; Isogai, K. *Tetrahedron Lett.* **1994**, *35*, 8643.

10.1021/jo990215v CCC: $18.00

Chart 1

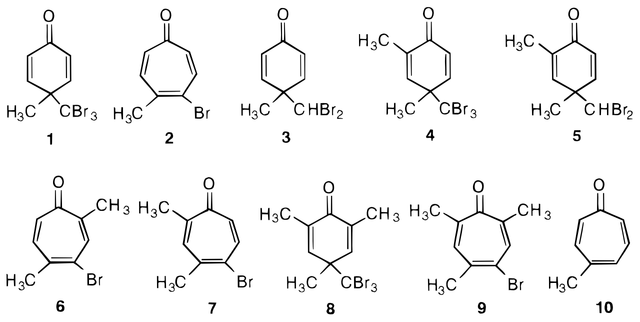
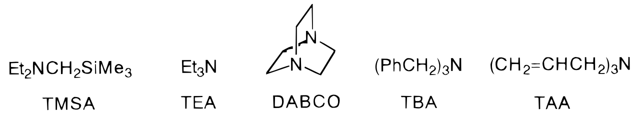


Chart 2



4-methyl-2,5-cyclohexadienone and its derivatives with various amines (Charts 1 and 2).

Results and Discussion

When a N_2-prepurged methylene chloride solution of 4-(tribromomethyl)-4-methyl-2,5-cyclohexadienone (**1**)[11] and *N*,*N*-diethyl((trimethylsilyl)methyl)amine (Et_2NCH_2-TMS, TMSA)[12] was irradiated for 5 min, 48% of 4-bromo-5-methyltropone (**2**) was isolated along with 6% of 4-(dibromomethyl)-4-methyl-2,5-cyclohexadienone (**3**) based on the consumption of **1**. The structure of **2** was determined by its spectral data, and that of **3**, by comparing it with an authentic sample prepared independently. Although **1** was consumed to some extent in the absence of TMSA by irradiation for 30 min, neither **2** nor **3** was produced. On the other hand, treatment of **1** with TMSA in the dark for 60 min resulted in complete recovery of **1**. Interestingly, the reaction of **1** with TMSA in acetonitrile led to the formation of a small amount of **2** indicating that **1** slowly reacts with TMSA in a polar solvent without irradiation.[13] The above preliminary observations would suggest that **2** and **3** are produced through the interaction between the photoexcited **1** and TMSA, most probably the SET interaction between them.

To gain more insight into the reaction mechanism, we carried out the photoreactions of **1** with TMSA in various solvents and observed that **2** was generally the major product in these experiments (Table 1). While there is no pronounced correlation between the reaction efficiency and the solvent polarity, some notable information can be derived from Table 1.

Table 1. Photoreactions of 1 with TMSA in Various Solvents[a]

entry	solvent	$E_T(30)$[b] (kcal/mol)	conv of **1** (%)	yields[c] (%)	
				2	**3**[d]
1	C_6H_6	34.5	61	50	6
2	THF	37.4	85	30	33[c]
3	CH_2Cl_2	41.1	64	48	6
4	MeCN	46.0	83	34	2
5[e]	aq MeCN		73	48	3
6	MeOH	55.5	59	56	2

[a] **1** (0.56 mmol), TMSA (5 equiv), solvent (15 mL), >280 nm (Pyrex), 5 min. [b] Polarity parameter.[14] [c] Isolated yields on the basis of the conversion of **1**. [d] Determined by ^{1}H NMR analysis of the mixture of **1** and **3**. [e] MeCN/H_2O = 14/1.

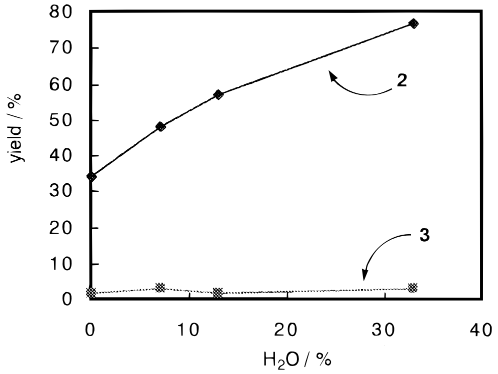


Figure 1. Effect of H_2O quantity on the photoreaction of **1** with TMSA in MeCN.

For example, the yield of **2** in a polar protic solvent is greater than in a polar aprotic solvent (compare entry 6 with 4). Addition of water also increased the yield of **2** (entry 5). On the other hand, **3** was obtained in yield identical to that of **2** in tetrahydrofuran, which is significantly higher than yields obtained in other solvents (entry 2). The observation that a protic species influenced the product ratio prompted us to conduct a detailed study on the effect of added water on the reaction in acetonitrile. As seen in Figure 1, the addition of water to the reaction mixture significantly increased the yield of **2**. Similar phenomena were observed when the reactions were carried out in aqueous methanol and aqueous tetrahydrofuran (**2**/**3**: 56/2 in MeOH, 68/2 in 13% aqueous MeOH; 30/33 in THF, 43/24 in 13% aqueous THF). The yield of **3** was so low in acetonitrile as well as in methanol that the effect of water could not be followed in detail. On the other hand, added water indeed changed the yield of **3** in tetrahydrofuran.

Next, we investigated the effect of various amines on the reactivity of **1**. As seen in Table 2, the reaction efficiency could not be simply controlled by the electron-donating ability of amine (see the oxidation potential of amine and the conversion of **1** versus the irradiation time). Since the overall reaction efficiency in some cases is governed by the subsequent chemical processes competing with unproductive back electron transfer of the geminate ion radical pair, the reactivity of amine cation radicals formed should influence the reaction of the anion radical of **1**. The cation radical of α-silylamine such as TMSA is known to undergo more efficient fragmentation

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(10) (a) Patel, D. J.; Schuster, D. I. *J. Am. Chem. Soc.* **1968**, *90*, 5137. (b) Schuster, D. I.; Patel, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 5145. (c) Schuster, D. I.; Prabhu, K. V. *J. Am. Chem. Soc.* **1974**, *96*, 3511. (d) Brisimitzakis, A. C.; Schuster, D. I.; van der Veen, J. M. *Can. J. Chem.* **1985**, *63*, 685. (e) Also see the recent review: Schultz, A. G. In *Handbook of Organic Photochemistry and Photobiology;* Horspool, W. M., Song, P. S., Eds.; CRC Press: Boca Raton, FL, 1994; Chapter 55, pp 685–700.

(11) Absorption spectrum of dienone **1** [λ_{max}, nm (ϵ)]: 230 (14 477), 348 (17) in MeCN; 233 (14 894), 348 (18) in CH_2Cl_2. Also see the data for 4-(trichloromethyl)-4-methyl-2,5-cyclohexadienone [λ_{max}, nm (ϵ)]: 230 (15 000), 339 (16), 350 (15) in MeOH.[10a]

(12) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.* **1988**, *110*, 8099.

(13) We could not rule out the possibility of photopromotion for the observed reaction since it was difficult to completely prevent the accidental exposure of the reaction solution to room light.

(14) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29.

(15) Measured by cyclic voltammetry (CV) at a platinum electrode in MeCN with 0.1 M Et_4NClO_4 as a supporting electrolyte; scan rate 100 mV/s or 200 mV/s. All CV's of dienones and amines gave irreversible waves. Peak potentials of the reduction wave for the dienone (E_p^{red}) and oxidation wave for the amine (E_p^{ox}) are reported versus SCE.

Table 2. Photoreactions of 1 with Various Amines[a]

entry	amine	E_p^{ox} [b] (V vs SCE)	time (min)	conv of **1** (%)	yields[c] (%) **2**	yields[c] (%) **3**[d]
1	TMSA	0.55	5	64	48	6
2	DABCO	0.72	30	34	8	0
3	TEA	0.88	5	24	50	5
4	TAA	1.12	30	27	66	0
5	TBA	1.17	10	58	79	0

[a] **1** (0.56 mmol), amine (5 equiv), CH_2Cl_2 (15 mL), >280 nm (Pyrex). [b] See ref 15. [c] Isolated yields on the basis of the conversion of **1**. [d] Determined by ^1H NMR analysis of the mixture of **1** and **3**.

through desilylation as well as deprotonation than nonsilyl-substituted amines.[12,16] Thus, while the yield of **2** for the reaction with TMSA is essentially the same as that with triethylamine (TEA), the conversion of **1** in the former case appears to be greater than that in the latter. The cation radicals of tribenzylamine (TBA) and triallylamine (TAA) would undergo deprotonation to give benzyl and allyl radicals respectively, while that of 1,4-diazabicyclo[2.2.2]octane (DABCO) is known to be relatively stable and also a poor proton donor.[17] As expected, the conversion of **1** and the yield of **2** with TBA are significantly greater than that attained with DABCO which has an oxidation potential lower than TBA. The yield of **2** with TAA is also greater than with DABCO. Therefore, the effective formation of **2** could be attributed to the ease of fragmentation of amine cation radicals as well as the electron-donating ability of the amine.

Since the nature of the amine cation radical is responsible for the subsequent reaction of the anion radical of **1**, it may be mechanistically informative to explore the amine-derived products. Toward this objective, we chose TBA since the reaction involving this amine was relatively clean and the expected products from it may be less volatile compared with other aliphatic amines so that their isolation and characterization could be easier. Thus, photoreaction of **1** and TBA (5 equiv) for 20 min was carried out. The ether soluble part of the crude reaction mixture contained a mixture of benzaldehyde (76%), **2** (76%), and unreacted **1** (15%). By treatment with a base, the ether insoluble fraction was eventually identified as a mixture of dibenzylamine (70%) and TBA. Thus, it would be reasonable to conclude that both dibenzylamine and some TBA exist as ammonium salts in the reaction mixture before the treatment with the base. Since dibenzylamine and benzaldehyde are diagnostic compounds for oxidative dealkylation of TBA,[2b] electron transfer from TBA indeed occurs during the reaction, which would also be likely for other amines.

Scheme 1

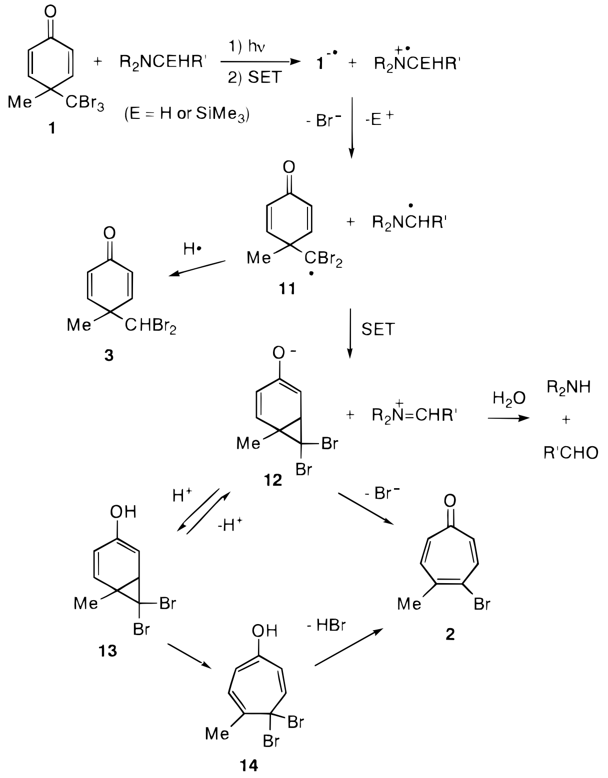

Table 3. Redox Potentials of Dienones and Amines and Free Energy Calculation for their PET Processes

dienone	E_p^{red} [a] (V vs SCE)	amine	E_p^{ox} [a] (V vs SCE)	ΔG[b] (kcal/mol)
1	−1.68	TMSA	0.55	−17
1	−1.68	DABCO	0.72	−13
1	−1.68	TEA	0.88	−9
1	−1.68	TAA	1.12	−4
1	−1.68	TBA	1.17	−3
3	−1.68	TMSA	0.55	−17
4	−1.87	TMSA	0.55	−13
8	−1.98	TMSA	0.55	−10

[a] See ref 15. [b] See refs 18 and 19.

On the basis of the above derived key observations, namely, that (i) no pronounced relationship existed between solvent polarity and the product ratio, (ii) addition of water increased the yield of **2**, and (iii) a hydrogen-atom-donating solvent such as tetrahydrofuran increased the yield of **3**, we propose the following reaction mechanism as shown in Scheme 1. The photoexcited state of **1** is reduced by ground-state amine through SET to give the anion radical of **1** and the cation radical of amine; see Table 3.[18,19] The anion radical of **1** undergoes debromination to give the carbon radical **11**.[20] If **11** abstracts a hydrogen atom, **3** is produced. This is consistent with the observation that the yield of **3** was significantly greater in tetrahydrofuran than in other solvents. Subsequent cyclization and reduction of **11** yields **12** while the order of each step could not be easily specified. One possibility is that the radical **11** rearranges followed by SET to give **12** and then undergoes debromination to give **2** since intramolecular conjugate addition of a similar carbon radical to dienone is known.[21] Even if **12** is protonated to yield **13** prior to rearrangement, **13** would

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(16) (a) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233. (b) Zhang, X.; Yeh, S.-R.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211. (c) Su, Z.; Mariano, P. S.; Falvey, D. E.; Yoon, U. C.; Oh, S. W. *J. Am. Chem. Soc.* **1998**, *120*, 10676.

(17) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 8, 243.

(18) Single electron transfer among the excited triplet of **1** and the amines is considered to be exothermic on the basis of the calculated free energy change[19] for this process employing the oxidation potential of the specific amine, reduction potential of **1**, and the triplet energy of **1**, which is assumed to be similar to that of trichloro derivative (67 kcal/mol, 2.91 eV).[10b] Calculated free energy changes (ΔG) for **1** and other dienones with amines are summarized in Table 3.

(19) (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Weller, A. *Z. Phys. Chem.* **1982**, *133*, 93.

(20) Either direct reduction of the C−Br bond or the formation of dienone ketyl followed by intramolecular single electron transfer to the C−Br bond could produce **11**.

(21) Barbier, M.; Barton, D. H. R.; Devys, M.; Topgi, R. S. *Tetrahedron* **1987**, *43*, 5031.

eventually undergo ring expansion, via the well-known norcaradiene−cycoheptatriene rearrangement,[22] to give **14**. Under basic conditions, **14** could be easily dehydrobrominated to give **2**.[23,24] In any case, SET reduction involving radical intermediates would occur, and the α-amino radical generated by either desilylation or deprotonation of the amine cation radicals must be a most plausible candidate as a reductant.[25] Oxidation of the α-amino radical gives an iminium intermediate which readily undergoes hydrolysis to give secondary amine and aldehyde. Such products were indeed isolated when photoreactions of **1** and TBA were performed. Therefore, effective generation of α-amino radical should accelerate the reduction of **11** to **12**. The observed effect of H_2O on the reaction of **1** with TMSA is consistent with this rationalization since the compounds such as water and methanol are known to accelerate the desilylation of cation radicals of α-silylamines.[16] Finally, the observation that the reaction proceeded in less polar solvents such as methylene chloride and benzene would be consistent with the postulate that **2** is produced through an ion-radical pair rather than in a free ion-radical.

As described above, since the PET process involves free radical intermediates, we decided to study the reaction of dienone **1** with tri-*n*-butyltin hydride (TBTH).[21] When a benzene solution of **1**, TBTH (1 equiv), and azobis(isobutyronitrile) (AIBN, 0.1 equiv) was refluxed for 3 h, 57% of **2** as well as 8% of **3** along with a small amount of 4-methyltropone (**10**) was obtained at 67% conversion of **1**. Doubling the amount of TBTH resulted in the formation of **2** (32%), **3** (5%), and **10** (11%).

We next carried out photoreactions of dienones **4** or **8** with TMSA as well as thermal reaction of **4** with TBTH. Particularly, the reaction of **4** was interesting since the formation of the regioisomers of tropones was expected. In fact, irradiation of **4** and TMSA for 10 min produced the tropone in 40% yield as a mixture of regioisomers (**6**/**7** = 75/25) at 69% conversion of **4**. Tropone **9** was isolated in 72% yield at 60% conversion of **8** under similar irradiation conditions. In both cases, none of the mono-debrominated dienones was obtained. The isomers **6** and **7** were also formed in the reaction of **4** with TBTH (1 equiv) although the reaction was not very clean. Upon refluxing of the benzene solution of **4** and TBTH, the ratio **6**/**7** was found to be 61/39 (total yields were less than 10%) along with 10% of **5** at 74% conversion of **4**. On the other hand, when the reaction was performed at room temperature initiated by triethylborane−air,[26] the ratio of **6**/**7** varied slightly to 66/34 (total yields of two isomers: 17%) along with 14% of **5** at 84% conversion of **4**. These ratios of isomers are not significantly different from that observed in the PET reaction (**6**/**7** = 75/25), which would be consistent with the proposal that a carbon radical such as **11** is involved in the PET reaction (Scheme 1).[27]

Table 4. Photoreactions of 3 with Various Amines in Various Solvents[a]

entry	solvent	$E_T(30)$[b] kcal/mol	amine	E_p^{ox} [c] (V vs SCE)	time (min)	conv of **3** (%)	yield of **10**[d] (%)
1	C_6H_6	34.5	TMSA	0.55	30	45	63
2	THF	37.4	TMSA	0.55	30	42	59
3	CH_2Cl_2	41.1	TMSA	0.55	30	58	77
4	MeCN	46.0	TMSA	0.55	30	59	62
5[e]	aq MeCN		TMSA	0.55	30	55	60
6	MeOH	55.5	TMSA	0.55	30	25	28
7	CH_2Cl_2	41.1	DABCO	0.72	90	28	29
8	CH_2Cl_2	41.1	TEA	0.88	90	50	45
9	CH_2Cl_2	41.1	TBA	1.17	90	67	0

[a] **3** (0.71 mmol), amine (5 equiv), solvent (19 mL), >280 nm (Pyrex). [b] See ref 14. [c] See ref 15. [d] Isolated yields on the basis of the conversion of **3**. [e] MeCN/H_2O = 12.6 /6.4.

Since dienone **3** was considered to be also photoreactive, reaction of **3** with amine was studied (Table 4). Irradiation of **3** with TMSA for 30 min in methylene chloride produced tropone **10** in 77% yield at 58% conversion of **3** (entry 3). Photoreaction of **3** without amine for 90 min resulted in significant consumption of **3** (76%); however, no **10** was formed. Moreover, 98% of **3** was recovered after treatment with TMSA for 90 min in the dark. Similarly, photoreactions of **3** were carried out in other solvents to give **10** in variable yields (entries 1, 2, and 4−6). Photoreactions of **3** with various amines for 90 min in methylene chloride revealed that TMSA was more effective than other amines such as TEA, DABCO, and TBA (entries 7−9). Although the above observations are quite similar to the case of **1**, other aspects do differ when compared to the reaction between **1** and **3**. A longer irradiation time was required in the case of **3** as compared with **1**. This would suggest that fragmentation of the anion radical of **3** is less efficient than that of **1**, which renders the back electron transfer in the geminate ion-radical pair more competitive in the case of **3**. Because of this, photoreaction of **3** with TBA probably did not produce **10** at all (entry 9). No significant effect of added water on both the conversion of **3** and the yield of **10** was observed (compare entry 4 to 5). Moreover, photoreaction in MeOH was rather complicated in which the yield of **10** was significantly reduced (entry 6). It should also be noted that 4-(bromomethyl)-4-methyl-2,5-cyclohexadienone was not isolated in these experiments (even in photoreaction using THF as the solvent). Therefore, it would be difficult to rationalize these observations by simply employing the same mechanistic approach as in the reaction of **1**.

Conclusion

We have found that photoreactions of 4-(tribromomethyl)-4-methyl-2,5-cyclohexadienone and its derivatives with amines produced 4-bromo-5-methyltropones. The effects of solvent, added water, the structure of amine on the product ratio, and amine-derived products permit

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[22] Review: Maier, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 402.

[23] Banwell, M. G.; Onrust, R. *Tetrahedron Lett.* **1985**, *26*, 4543.

[24] One reviewer suggested other possible pathways such as (i) direct cyclization of the anion radical of **1** in an intramolecular S_N process followed by SET to give **12**[5,6] and (ii) reduction of **11** followed by α-debromination to give a carbene which undergoes a 1,2 shift to yield **2**. Although there are no direct experimental results to rule out these possibilities, we prefer the radical cyclization mechanism for the PET reaction since thermally initiated reactions of dienones with TBTH indeed gave the same products (see the text).

[25] (a) Oxidation potentials ($E_{1/2}^{ox}$ V vs SCE) of α-amino radicals derived from TEA and TBA are −1.12 and −0.92 V, respectively.[25b] (b) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

[26] Nozaki, K.; Ohshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 403.

[27] One reviewer pointed out that there is some difference in the ratio (**6**/**7**) between the photoreaction and the thermal reaction which may indicate that there are subtle differences in the routes to the two regioisomers. At present, we cannot answer this question. One possibility is that radical reduction followed by anion rearrangement may in part operate in the photoreaction with amine while only radical rearrangement occurs in the reaction with TBTH.

us to propose a reaction mechanism in which fragmentation of the dienone anion-radical and amine cation-radical pair is involved.[28] Trialkyltin radical-induced reductions of the same dienones with tri-*n*-butyltin hydride demonstrated common features with PET reactions. It was also found that irradiation of 4-(dibromomethyl)-4-methyl-2,5-cyclohexadienone with TMSA produced 4-methyltropone.

Experimental Section

General Procedures. Triethylamine and triallylamine were distilled with CaH_2. Tribenzylamine and diazabicyclooctane were purified by sublimation. *N,N*-Diethyl((trimethylsilyl)methyl)amine was prepared according to the literature procedure.[29] Acetonitrile was distilled over P_2O_5 and subsequently with CaH_2. Benzene was treated with H_2SO_4, 5% NaOH, and $CaCl_2$ and then distilled with CaH_2. Methanol (Wako) was distilled and dried with 3A molecular sieves. Tetrahydrofuran was distilled from sodium−benzophenone under N_2. Water for the reaction was obtained through an ion-exchange column. Other reagents and solvents were purchased and used without further purification.

NMR spectra were recorded in $CDCl_3$ with Me_4Si as the internal standard at 90 and 200 MHz for ^{1}H NMR and 22.49 and 49 MHz for ^{13}C NMR, respectively. Melting points that are uncorrected are reported. Photoreactions were conducted in a Pyrex tube (2.5 cm diameter) immersed in a water bath with a 500 W Xe−Hg lamp as a light source. Column chromatography was performed with Wakogel C-200 silica gel. Preparative TLC was performed on 20 cm × 20 cm plates coated with Wakogel B-5F silica gel.

Preparations of 4-(Tribromomethyl)-4-methyl-2,5-cyclohexadienones (1, 4, 8). To anhydrous $AlBr_3$ (15.0 mmol) and carbon disulfide (5 mL) was slowly added a carbon disulfide solution (4 mL) of *p*-cresol (10.0 mmol). This mixture was refluxed for 30 min followed by a carbon disulfide solution (3 mL) of tetrabromomethane (10.0 mmol) and continuously refluxed for an additional 3 h. To the residue obtained by concentration of the reaction solution were added ice water and concentrated HCl (20 mL). Then, it was allowed to stand for 30 min followed by extraction with methylene chloride. The organic layer was treated with 2 M NaOH and water and was dried over Na_2SO_4. The residue obtained by concentration was subjected to column chromatography (CH_2Cl_2) to give a solid, dienone **1** (6.0 mmol, 61%). This was recrystallized from $CH_2Cl_2/n\text{-}C_6H_{14}$. Dienones **4** and **8** were similarly synthesized although these yields were quite low: **4** (3%); **8** (8%).

1: mp 146−147 °C ($CH_2Cl_2/n\text{-}C_6H_{14}$) (lit.[30] mp 146−147 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.70 (d, 3H, $J = 1.2$ Hz), 6.46 (d, 2H, $J = 8.8$ Hz), 7.26 (d, 2H, $J = 8.8$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.8 (q), 49.8 (s), 55.9 (s), 130.7 (d, 2C), 148.2 (d, 2C), 184.5 (s); IR (KBr) 1658 cm^{-1}; HRMS *m*/*z* calcd for $C_8H_7OBr_3$ 355.8046, found 355.8010, calcd for $C_8H_7OBr_2{}^{81}Br$ 357.8026, found 357.8031, calcd for $C_8H_7OBr^{81}Br_2$ 359.8006, found 359.8026, calcd for $C_8H_7O^{81}Br_3$ 361.7986, found 361.8008.

4: mp 117−118 °C ($n\text{-}C_6H_{14}$) (lit.[30] mp 116−117 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.68 (s, 3H), 1.98 (d, 3H, $J = 1.4$ Hz), 6.45 (d, 2H, $J = 10.2$ Hz), 7.00−7.03 (m, 1H), 7.22 (dd, 1H, $J = 10.2$, 3.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.3 (q), 24.7 (q), 51.2 (s), 55.9 (s), 130.6 (d), 137.6 (s), 143.4 (d), 147.9 (d), 185.2 (s); IR (KBr) 1662, 1638 cm^{-1}; HRMS *m*/*z* calcd for $C_9H_9OBr_3$ 369.8202, found 369.8230, calcd for $C_9H_9OBr_2{}^{81}Br$ 371.8182, found 371.8171, calcd for $C_9H_9OBr^{81}Br_2$ 373.8162, found 373.8148, calcd for $C_9H_9O^{81}Br_3$ 375.8142, found 375.8117.

8: mp 98−99 °C ($n\text{-}C_6H_{14}$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.65 (s, 3H), 1.97 (s, 6H), 6.97 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.5 (q, 2C), 24.5(q), 52.7 (s), 55.2 (s), 137.2 (s, 2C), 143.1 (d, 2C), 185.8 (s); IR (KBr) 1666, 1640 cm^{-1}; *m*/*z* calcd for $C_{10}H_{11}OBr_3$ 383.8359, found 383.8373, calcd for $C_{10}H_{11}OBr_2{}^{81}Br$ 385.8339, found 385.8316, calcd for $C_{10}H_{11}OBr^{81}Br_2$ 387.8319, found 387.8334, calcd for $C_{10}H_{11}O^{81}Br_3$ 389.8299, found 389.8312.

Preparations of 4-(Dibromomethyl)-4-methyl-2,5-cyclohexadienones (3, 5). A mixture of *p*-cresol (20.0 mmol), bromoform (66.0 mmol), and cetyltrimethylammonium bromide (0.20 mmol) was heated at 54 °C followed by slow addition of 10 M NaOH and was then heated for an additional 4 h. To this was added ice water followed by extraction with ether. The ether solution was treated with water and saturated NaCl and was dried over Na_2SO_4. The residue obtained by concentration was subjected to column chromatography (CH_2Cl_2) to give a solid, dienone **3** (3.6 mmol, 18%). This was recrystallized from $CH_2Cl_2/n\text{-}C_6H_{14}$. Dienone **5** was similarly synthesized: **5** (30%).

3: mp 60−61 °C ($CH_2Cl_2/n\text{-}C_6H_{14}$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.50 (d, 3H, $J = 2.3$ Hz), 5.67 (s, 1H), 6.39 (d, 2H, $J = 10.6$ Hz), 6.95 (d, 2H, $J = 10.6$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.6 (q), 47.5 (s), 50.0 (d), 130.6 (d, 2C), 149.4 (d, 2C), 184.8 (s); IR (KBr) 1680 cm^{-1}; HRMS *m*/*z* calcd for $C_8H_8OBr_2$ 277.8941, found 277.8938, calcd for $C_8H_8OBr^{81}Br$ 279.8921, found 279.8909, calcd for $C_8H_8O^{81}Br_2$ 281.8901, found 281.8896.

5: mp 65−67 °C ($CH_2Cl_2/n\text{-}C_6H_{14}$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.48 (s, 3H), 1.96 (d, 3H, $J = 1.4$ Hz), 5.64 (s, 1H), 6.39 (d, 1H, $J = 10.1$ Hz), 6.69−6.71 (m, 1H), 6.69 (dd, 1H, $J = 10.1$, 3.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.1 (q), 24.5 (q), 47.4 (s), 51.0 (d), 130.3 (d), 137.2 (s), 144.7 (d), 149.1 (d), 185.6 (s); IR (KBr) 1666, 1632 cm^{-1}; HRMS *m*/*z* calcd for $C_9H_{10}OBr_2$ 291.9098, found 291.9073, calcd for $C_9H_{10}OBr^{81}Br$ 293.9078, found 293.9088, calcd for $C_9H_{10}O^{81}Br_2$ 295.9058, found 295.9083.

Photoreactions of Dienones (1, 3, 4, 8) with Amines.[31] Dienone (0.56 mmol) and amine (2.80 mmol) were dissolved in an appropriate solvent (15 mL). This solution was purged with dry N_2 for 5 min and then irradiated for an appropriate time. Concentration of the photolyzed solution at ambient temperature gave a residue which was subsequently separated by column chromatography. While the eluent was usually a 1 to 1 mixture of EtOAc and $n\text{-}C_6H_{14}$, in some cases CH_2Cl_2 was used. For example, in the cases of **4** and **8**, CH_2Cl_2 was better for column chromatography. Usually, unreacted dienone and monodebrominated dienone were obtained as an inseparable mixture; therefore, those yields were determined by ^{1}H NMR. Since the mixture of regioisomers **6** and **7** could not be separated, the ratio (**6**/**7**) was determined by ^{1}H NMR analysis of their mixture in the reaction of **4**.

2: mp 80−81.5 °C (C_6H_6); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.63 (d, 3H, $J = 2.1$ Hz), 6.68 (d, 1H, $J = 13.0$ Hz), 6.85 (d, 1H, $J = 12.6$ Hz), 7.06 (dd, 1H, $J = 12.6$, 2.1 Hz), 7.46 (dd, 1H, $J = 13.0$, 2.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 29.7 (q), 131.0 (s), 137.5 (d), 138.7 (d), 138.8 (d), 141.8 (d), 144.3 (s), 186.0 (s); IR (KBr) 1636, 1572 cm^{-1}; HRMS *m*/*z* calcd for C_8H_7OBr 197.9680, found 197.9657, calcd for $C_8H_7O^{81}Br$ 199.9660, found 199.9660.

9: mp 79−80 °C (C_6H_6); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.27 (s, 3H), 2.47 (s, 3H), 7.29 (s, 1H), 7.72 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.1 (q), 23.7 (q), 29.8 (q), 128.1 (s), 137.0 (d), 139.7 (d), 140.6 (s), 144.9 (s), 146.0 (s), 184.8 (s); IR (KBr) 1608, 1572 cm^{-1}; HRMS *m*/*z* calcd for $C_{10}H_{11}OBr$ 225.9993, found 225.9990, calcd for $C_{10}H_{11}O^{81}Br$ 227.9973, found 227.9998.

10: oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.33 (s, 3H), 6.82−7.09 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.3 (q), 132.8 (d),

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[28] (a) We were also interested in the reactivity of **1** under other electron transfer conditions. Notably, the reaction of **1** with samarium diiodide, which is a well-known single electron reductant,[28b] gave neither **2** nor **3**. The only isolable product was *p*-cresol in low yields (11−23%) irrespective of the fact that MeOH was added or not as a proton source. Although rationalization of these observations seems to be difficult because of the relatively low mass balance, samarium-coordinated dienone ketyl derived from **1** may liberate either tribromomethyl radical or anion to yield the phenoxy intermediates. It should be noted here that *p*-cresol is another reasonable product in the reductive electron transfer reactions of 4,4-disubstituted-2,5-cyclohexadienones.[7,8] (b) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693. Molander, G. A. *Chem. Rev.* **1992**, *92*, 29. Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307.

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136.6 (d), 139.8 (d), 139.9 (d), 141.1 (d), 145.9 (s), 187.8 (s); IR (neat) 1636, 1582 cm^{-1}; HRMS *m*/*z* calcd for C_8H_8O 120.0575, found 120.0554.

6:[32] mp 60−61 °C (not recrystallized); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.46 (s, 3H), 6.89 (d, 1H, $J = 12.5$ Hz), 7.05 (d, 1H, $J = 12.5$ Hz), 7.74 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.3 (q), 29.3 (q), 130.6 (s), 136.7 (d), 137.8 (d), 140.8 (d), 141.7 (s), 147.8 (s), 185.6 (s); IR (CCl_4) 1630, 1582 cm^1; HRMS *m*/*z* calcd for C_9H_9OBr 211.9836, found 211.9859, calcd for $C_9H_9O^{81}Br$ 213.9816, found 213.9831.

7:[32] mp 82−83 °C (not recrystallized); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.22 (d, 3H, $J = 1.0$ Hz), 2.48 (s, 3H), 6.71 (d, 1H, $J = 13.0$ Hz), 7.29 (d, 1H, $J = 1.0$ Hz), 7.44 (d, 1H, $J = 13.0$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.9 (q), 30.3 (q), 128.7 (s), 135.5 (d), 137.7 (d), 140.9 (d), 141.0 (s), 147.0 (s), 185.5 (s); IR (CCl_4) 1624, 1582 cm^1; HRMS *m*/*z* calcd for C_9H_9OBr 211.9836, found 211.9883, calcd for $C_9H_9O^{81}Br$ 213.9816, found 213.9808.

Photoreaction of Dienone (1) with Tribenzylamine: Identification of Amine-Derived Products. A N_2-prepurged methylene chloride solution (15 mL) of dienone **1** (0.56 mmol) and tribenzylamine (2.80 mmol) was irradiated for 20 min. Addition of ether (29 mL) to the residue obtained by concentration of the photolyzate gave an insoluble solid which was filtered out. The filtrate was concentrated and then separated by column chromatography (CH_2Cl_2 followed by 1/1 EtOAc/*n*-C_6H_{14}) to give **2** (0.43 mmol, 76%) and benzaldehyde (0.42 mmol, 76%) together with unreacted **1** (0.081 mmol, 15%) and tribenzylamine (1.66 mmol, 59%). The ether insoluble solid was dissolved in methylene chloride followed by 2 M NaOH and water and dried over Na_2SO_4. After concentration of the solution, the residue obtained was analyzed by ^{1}H NMR to reveal dibenzylamine (0.39 mmol, 70%) and tribenzylamine (0.69 mmol, 25%). The total amount of recovered TBA was 84%. Same workup procedure was also performed in the reaction for 10 min (entry 5 in Table 2): benzaldehyde, 57%; dibenzylamine, 43%; TBA, 89% at the conversion of **1** (58%).

Reactions of Dienones (1, 4) with Tributyltin Hydride. A N_2-prepurged benzene solution (100 mL) of dienone **1** (0.50 mmol), tributyltin hydride (TBTH, 0.48 mmol), and azobis(isobutyronitrile) (AIBN, 0.051 mmol) was heated at 85 °C for 3 h under N_2. The residue obtained by concentration of the benzene solution was treated with the DBU workup[33] and was subsequently subjected to column chromatography (1/1 and then 1/0 EtOAc/*n*-C_6H_{14}). Since complete separation was not achieved, the yields of the products and unreacted **1** were determined by ^{1}H NMR using *p*-dimethoxybenzene as the internal standard. Reactions of **1** with 2 equiv of TBTH and **4** with 1 equiv of TBTH were similarly conducted.

To a benzene solution (40 mL) of dienone **4** (0.20 mmol) and TBTH (0.20 mmol) was added a 1.0 M tetrahydrofuran solution of Et_3B (0.04 mL, 0.04 mmol) followed by introduction of air. The resulting solution was stirred at room temperature for 3 h. The residue obtained by concentration of the benzene solution was treated with the DBU workup[32] and was subsequently subjected to TLC separation (CH_2Cl_2) to give unreacted **4**, **5**, and the mixture of tropones **6** and **7**. The isomer ratio (**6**/**7**) was determined by ^{1}H NMR.

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Supporting Information Available: IR, ^{1}H NMR, and ^{13}C NMR spectra of the compounds dienones **1**, **3**, **4**, **5**, and **8** and tropones **2**, **6**, **7**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[31] All photochemical data described in this paper were obtained from the experiments in which the light sources are different from those previously reported.[9] We are fortunate to have found that the reproducibility for each new experiment was quite high except for the irradiation time required for the certain conversion of dienones. This is mainly due to the change of the lamp conditions; roughly estimated, the lamp intensity of this one is about 5−6 times greater than that of the previous one.

[32] One of the authors (T.S.) has found that a similar rearrangement of dienone **4** proceeded in the reaction with colloidal palladium dispersed in poly(vinyl alcohol) and diethylamine in MeOH under a hydrogen atmosphere to produce the mixture of tropones **6** and **7** in 91% yield (unpublished). In this case, the mixture was partly separated by silica gel column chromatography (EtOAc/*n*-C_6H_{14} = 1/2) to give pure **6** and **7** whose spectral data are presented in the Experimental Section. Their regiochemistries were determined by a NOE experiment with ^{1}H NMR.

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