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Novel Photoreaction of 4-Tribromomethyl-4-methyl-2,5-cyclohexadienone with Amine

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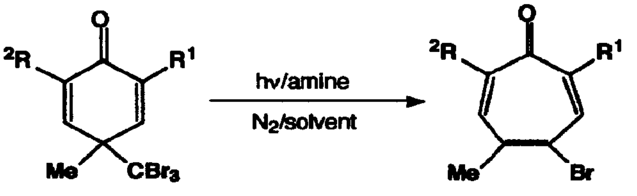
Abstract: Irradiation of 4-tribromomethyl-4-methyl-2,5-cyclohexadienone in the presence of amines gave 4-bromo-5-methyltropone as a major product. On the basis of the results obtained, the mechanism involving single electron transfer from the amine ground state to the dienone excited state was proposed.

Photoinduced single electron transfer (SET) between the carbonyl excited states and the ground state electron donors produce the ketyl anion radicals.[2] If there are both carbonyl group and nucleofugal group in a single molecule, SET reduction of such compound may undergo intramolecular S_N2 type displacement of nucleofuge by ketyl anion part.[3] Application of this method to α, β–unsaturated carbonyl compounds tethering nucleofuge would lead the carbon-carbon bond formation at the β-position.[4,5] In this context, the SET photoreaction of 4-methyl-4-trihalomethyl-2,5-cyclohexadienone is interesting. So far no information about how such dienones behave under the photoinduced SET conditions is available,[6] although photochemistry of the dienones has been extensively studied by Schuster and coworkers.[7] We first studied the photoreaction of 4-tribromomethyl-4-methyl-2,5-cyclohexadienone **1** in the presence of amines and found the unprecedented photorearrangement giving 4-bromo-5-methyl tropone **2**.



1 (R^1=R^2=H)
6 (R^1=Me, R^2=H)
8 (R^1=R^2=Me)

2 (R^1=R^2=H)
7a (R^1=Me, R^2=H)
7b (R^1=H, R^2=Me)
9 (R^1=R^2=Me)

Irradiation of **1** in the presence of amines in various solvents gave 4-bromo-5-methyltropone **2** in moderate to good yields (Table 1).[8] First, we paid attention to the amine structure effect on the reactivity of **1** and found that photoreaction with trimethylsilylmethyldiethylamine (TMSA)[9] is more efficient than those with other amines. This observation could not be simply rationalized by the order of electron donating ability of amine (see entries 1-4). Actually, the yield of **2** and the conversion of **1** for photoreaction with tribenzylamine (TBA) is significantly higher than those with triethylamine (TEA) and 1,4-diazabicyclo[2.2.2]octane (DABCO) whose oxidation potentials are lower than that of TBA. The cation radical of TBA undergoes deprotonation to give a stable benzyl radical while the cation radical of DABCO is known to be relatively stable and a poor proton donor.[10] The cation radical of TMSA is known to undergo desilylation as well as deprotonation.[9]

Table 1. Photoreactions of 4-Tribromomethyl-4-methyl-2,5-cyclohexadienones (1) with amines.a)

entry	amine	b)E_p^{ox}	solvent	c)E_T	time/min	conv/%	d)2/%
1	TMSA	0.57	CH_2Cl_2	41.1	30	58	31(54)
2	DABCO	0.71	CH_2Cl_2	41.1	90	18	7(40)
3	TEA	0.89	CH_2Cl_2	41.1	90	31	19(61)
4	TBA	1.17	CH_2Cl_2	41.1	90	75	65(87)
5	TMSA	0.57	C_6H_6	34.5	30	46	30(64)
6	TMSA	0.57	MeCN	46.0	30	80	33(41)
7	TMSA	0.57	*aq*MeCNe)	---	30	62	42(68)
8	TMSA	0.57	MeOH	55.5	30	47	36(76)

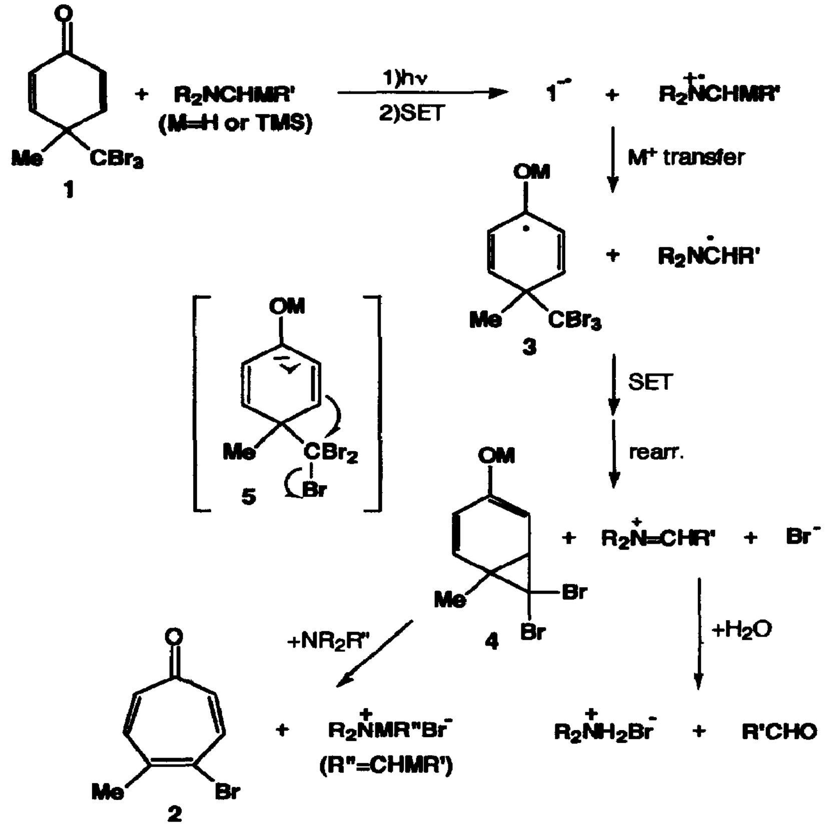
a)Conditions: 500W Xe-Hg lamp (Pyrex); N_2; 1 (0.56 mmol), amine (5equiv), solvent (15 ml).
b)Peak potentials (V vs SCE). c)Solvent polarity parameter ($E_T(30)$, kcal/mol): Reichardt, C. *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 29. d)Isolated yields by column chromatography (based on the conversion of 1). e)$MeCN/H_2O$=14/1.

Thus, the reaction efficiency would be governed by the ease of cation release from amine cation radical[9b,c] as well as the electron donating ability of amine. Secondly, we conducted the photoreactions of **1** with TMSA in various solvents and found no pronounced correlation between the reaction efficiency and the solvent polarity (entries 1, 5, 6, 7, and 8). However, the presence of protic species in the solution increased the yields of **2** (entries 6, 7 and 8). Neither irradiation without amine (30min) nor treatment with TMSA in the dark (60 min) caused any conversion of **1** in methylene chloride. In order to know the fate of amine cation radical, we decided to search for the amine derived products. We chose TBA since the reaction is clean and the products from TBA must be less volatile compared to other aliphatic amines. Dibenzyl amine and benzaldehyde were obtained in good yields by irradiation of **1** and TBA in methylene chloride.[11] These products are diagnostic compounds for oxidative dealkylation of TBA.[2]

In order to determine the generality of the reaction, we conducted the photoreactions of other methyl substituted dienones **6**, **8** with TMSA in methylene chloride. Irradiation of **6** and TMSA for 90 min produced the tropone in 45% mixture of regioisomers (**7a**:**7b** = 78:22) at 70% conversion of **6**. Similarly, the tropone **9** was isolated in 51 % at 66% conversion of **8**.

On the basis of the results described above, we propose the reaction mechanism as shown in Scheme 1. The excited state of **1** generated by irradiation is reduced by ground state amine through SET to give the anion radical of **1** and the cation radical of amine.[12] The transfer of the cation (proton or TMS^+) among the ion radical pairs gives the cyclohexadienyl radical and α-amino radical. Subsequent SET processes are thought to be fast since α-amino radical is known as a strong SET reductant.[13] Although the following rearrangement process is highly speculative (either stepwise process through **5** or concerted process), a compound such as **4** may be a reasonable candidate for a precursor of **2**.[14] Acid-base reaction among **4** and the excess amine gives ammonium while the hydrolysis of the iminium finally gives aldehyde and ammonium of the secondary amine.[15] The formations of all these compounds were confirmed when photoreactions of **1** and TBA were performed.[11]

Scheme 1



In conclusion, we have found that 4-tribromomethyl-4-methyl-2,5-cyclohexadienones were converted to 4-bromo-5-methyltropones on irradiation with the amines. Further study will hopefully provide a chance to obtain full understanding on the reaction mechanism and to determine the synthetic utility of this unique photoprocess.

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8. a) Dienone **1**[8b]: mp 146-147 °C (CH_2Cl_2-nC_6H_{14}), IR (CCl_4) 1670 cm^{-1}, ^1H-NMR (200MHz, $CDCl_3$) δ 1.69 (s, 3H), 6.46 (d, 2H, J=10.3Hz), 7.25 (d, 2H, J=10.3Hz). ^{13}C-NMR (50MHz, $CDCl_3$) δ 25.3 (q, Me-4), 50.3 (s), 56.4 (s), 131.3 (d, C-2,6), 148.8 (d, C-3,5), 184.5 (s, C-1). Tropone **2**: mp 80-81.5 °C (C_6H_6), IR (CCl_4) 1642, 1584 cm^{-1}, ^1H-NMR (200MHz, $CDCl_3$) δ 2.47 (s, 3H, Me-4), 6.70 (dd, J=12.5, 2.8 Hz, 1H, H-2), 6.88 (dd, J=12.5, 2.8 Hz, 1H, H-7), 7.07 (d, J=12.5, 1H, H-6), 7.48 (d, J=12.5, 1H, H-3). ^{13}C-NMR (50MHz, $CDCl_3$) δ 29.7 (q, Me-5), 131.1 (s, C-4), 137.6 (d), 138.8 (d), 138.9 (d), 141.9 (d), 144.3 (s, C-5), 186.1 (s, C-1). Similarly the structures of compounds **6**,[8b] **7a**, **7b**, **8** and **9** were determined by their spectral data. b) Merchant, J. R.; Desay, V. B. *J. Chem. Soc.* **1964**, 2258; **1968**, 499.
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11. A methylene chloride solution of **1** and TBA was irradiated for 3h. Ether soluble part was subjected to the column separation to give **1** (6%), **2** (81%), benzaldehyde (70%), and TBA. Ether insoluble part was treated with 2N NaOH and was identified as the mixture of dibenzylamine (88%) and TBA. Thus, it would be reasonable to conclude that both dibenzylamine and some of TBA exist as ammonium salts before base treatment.
12. Single electron transfer among the excited triplet of **1** and the amines would be an exothermic process since the reduction potential (E_p^{red}) of **1** is -1.73 V and the triplet energy of **1** is probably similar to that of trichloro derivative (67 kcal/mol, 2.91 eV).[7b]
13. 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.[13b] b) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.
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15. a) Since Scheme 1 is a tentative mechanism, one may suspect the possibility of the single electron transfer among tribromomethyl part and the amine followed by conjugate addition of dibromomethyl radical to dienone.[15b] However, this mechanism seems inconsistent with the observations, i) the relationship between the yield of **2** and the amine structure, ii) the increase of the yield of **2** by protic solvent.
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