Tetrahedron Letters, Vol.32, No.18, pp 2029-2032, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

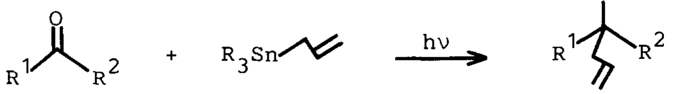
FREE RADICAL TRAPPING OF α-KETO RADICALS DERIVED FROM α,β-EPOXY KETONES VIA PHOTOINDUCED SINGLE ELECTRON TRANSFER PROCESS

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

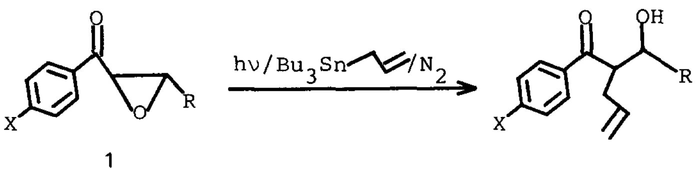
Department of Chemistry, Faculty of Science, Niigata University,
Ikarashi, Niigata 950-21, Japan

Summary: Irradiation of aromatic α,β-epoxy ketones in the presence of allyltributyltin afforded α-allyl-β-hydroxy ketones by a single electron transfer mechanism.

Photoinduced single electron transfer (SET) processes provide reasonably efficient carbon-carbon bond formations through ion radical fragmentations.[1] Allyltrialkyltins are considered to be good candidates as electron donors for this purpose since the cation radicals of these compounds undergo facile fragmentation to give allyl radical and trialkyltin cations.[2] Irradiations of aromatic ketones and allyltrialkyltins are reported to afford coupling products which are usually allylated at carbonyl carbon via SET mechanism (equation (1)).[2e,f] We now report that selective allylation occurred at α-carbon to carbonyl instead of carbonyl carbon upon irradiation of aromatic epoxy ketones 1, trans-chalcone epoxides 1a-e; acrylophenone epoxide 1f, with allyltributyltin (equation (2)).



(1)



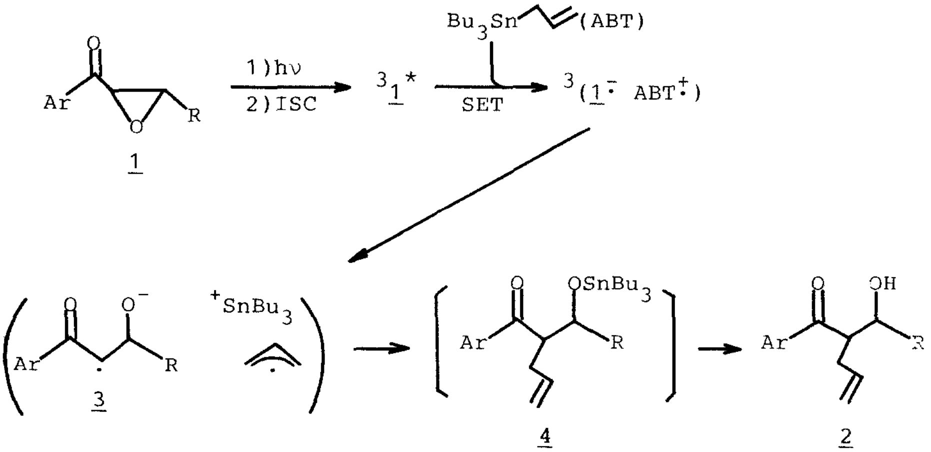
(2)

1

2

When the epoxy ketone 1a (individual compound numbers refer to Table) was irradiated with allyltributyltin (ABT) in acetonitrile ([1a] = 21 mM; [ABT] = 43 mM; $\lambda > 340$ nm; 30 min), 44 % of the α-allyl-β-hydroxy ketone 2a[3] was isolated at 70 % conversion of 1a. Prolonged irradiation (2 h) of the solution did not cause serious decomposition of 2a (59

%). On the other hand, when the solution was stirred in the dark for 2h, 1a was quantitatively recovered. Addition of LiClO$_4$ (42 mM) into the photoreaction solution resulted in apparent increase in the recovery of 1a (77 %) and decrease in the yield of 2a (8 %), which is inconsistent with free ion radical mechanism.[4] These results would indicate that the reaction proceeds through a contact ion radical pair or an exciplex. This is also consistent with observations made upon irradiation of 1a with ABT in nonpolar solvents, such as benzene and methylene chloride. Conversions of 1a in these solvents were lower than that in acetonitrile, but 2a was obtained in good yields after 30 min irradiation (26 % at 38 % conversion of 1a in benzene; 23 % at 34 % conversion in methylene chloride).



(3)

A plausible reaction mechanism for the photoreaction of 1a and ABT is proposed as in equation (3). Triplet excited state[5] of 1a (E^{red} ≃ +1.7 V)[6] could efficiently oxidize ABT (E_p^{ox} = +1.48 V vs. SCE) to give a triplet ion radical pair via SET mechanism. Cation radical of ABT undergoes facile C-Sn bond cleavage as previously demonstrated in photoreactions with electron acceptors.[2] On the other hand, the anion radical of 1a undergoes Cα-O bond cleavage to give the ring opened anion radical 3a.[7] This α-keto radical would be coupled with allyl radical and tributyltin cation formed by fragmentation of ABT cation radical. This process should produce the tin containing adduct 4a which is probably hydrolyzed to the hydroxy ketone 2a during the work-up.[8]

Importance of SET interaction of epoxy ketone triplets and ABT is further supported by the results obtained from photoreactions of epoxy ketones 1 with ABT shown in Table. Although both quantum yields and lifetimes of triplet states are similar between 1a and 1d, the conversion of the former is much higher than that of the latter (entries 1 and 4). This can be explained by the obvious difference of reduction potentials between 1a and 1d (ΔE_p^{red} = 0.47 V). Interestingly, no allyl adduct was formed for 1e although the

Table. Photoreaction of epoxy ketones 1 with allyltributyltin in benzene.[a]

Entry	1			Φ_T[b]	τ_T[b] / ns	E_p^{red}[c] / V vs. SCE	Conv. / %	2[d] / %
		X	R					
1	a	CN	Ph	0.98	85	-1.39	98	80(81)
2	b	H	Ph	0.88	3.3	-1.70	37	28(74)
3	c	Me	Ph	0.96	11	-1.80	40	35(89)
4	d	MeO	Ph	1.00	94	-1.86	15	11(76)
5	e	H	p-An[e]	0.60	0.8	-1.73	22	0
6	f	H	H	-	-	-1.77	9	7(80)

[a] 500 W Xe-Hg lamp ($\lambda > 340$ nm); 3 h; [1] = 131 mM and [ABT] = 265 mM. [b] Ref. 5. [c] Pt electrode; Et_4NClO_4 in MeCN (0.1 M); scan rate, 200 mV/s. [d] Isolated yields (silica gel TLC). Values in parenthesis are based on the conversion of 1. [e] $p\text{-}MeOC_6H_4$.

reduction potential of 1e is similar to that of 1b (entries 2 and 5). Even longer irradiation (Pyrex, 5 h) of 1e with ABT did not produce 2e. This would be due to relatively short lifetime of triplet excited state of 1e and the presence of other competing photochemical processes, for example, facile Cα-Cβ bond cleavage.[9] It was also found that the presence of β-aryl substituent is not essential for this adduct formation (entry 6).

In summary, we found that the irradiation of some aromatic α,β-epoxy ketones with allyltributyltin afforded α-allyl-β-hydroxy ketones. Contact ion radical pair or exciplex rather than free ion radicals is proposed as a key intermediate for the reaction. Isolation of α-allylated products is noteworthy since this is a first observation to support the involvement of ring opened anion radical intermediate possessing α-keto radical structure in SET photoreaction of epoxy ketones.[10]

Acknowledgement We are grateful to Professor Masaki Kamata (Niigata University) for his assistance to measure redox potentials.

References

1) a) Photoinduced Electron Transfer, Part C, M. A. Fox and M. Chanon, Eds., Elsevier, Amsterdam, 1988. b) J. Mattey, Synthesis, 1989, 233.

2) a) D. F. Eaton, J. Am. Chem. Soc., 1981, 103, 7235. b) R. M. Borg and P. S. Mariano, Tetrahedron Lett., 1986, 27, 2818. c) K. Maruyama, H. Imahori, A. Osuka, A. Takuwa, and H. Tagawa, Chem Lett., 1986, 1719. d) K. Mizuno, S. Toda, and Y. Ohtsuji, Ibid., 1987, 203./ e) A. Takuwa, H. Tagawa, H. Iwamoto, O. Soga, and K. Maruyama, Ibid., 1987, 1019. f) A.

Takuwa, Y. Nishigaichi, K. Yamashita, and H. Iwamoto, Ibid., 1990, 636.

3) Structures of allyl adducts 2 were determined by their spectroscopic data (IR, ^{1}H NMR, and ^{13}C NMR). Compounds 2a-d were obtained as the mixtures of two diasteromers in which the amount of one isomer is slightly greater than that of the other. Separations of those mixtures have not been completely achieved yet. For example, spectroscopic data of 2a, 2a-1 and 2a-2, are as follows. 2a-1, IR (neat) 3492, 2228, 1680 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.64 (t-like, J = 7.0, 6.6 Hz, 2H), 3.14 (broad s, 1H), 3.84 (q-like, J = 6.8, 6.6 Hz, 1H), 4.70-5.10 (m, 3H), 5.40-5.90 (m, 1H), 7.00-7.40 (m, 5H), 7.40-7.80 (m, 4H); ^{13}C NMR (22.49 MHz, $CDCl_3$) δ 33.00 (t), 54.34 (d), 74.44 (d), 116.06 (s), 117.41 (t), 117.79 (s), 126.35 (d), 127.92 (d), 128.41 (d), 132.25 (d), 134.96 (d), 140.65 (s), 141.68 (s), 202.26 (s). 2a-2, IR (neat) 3484, 2228, 1682 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.90-2.80 (m, 2H), 2.94 (broad s, 1H), 3.70-4.00 (m, 1H), 4.70-5.10 (m, 3H), 5.20-5.80 (m, 1H), 7.10-7.40 (m, 5H), 7.69 (broad d, J = 8.7 Hz, 2H), 7.97 (broad d, J = 8.7 Hz, 2H); ^{13}C NMR (22.49 MHz, $CDCl_3$) δ 34.50 (t), 53.75 (d), 76.23 (d), 116.16 (s), 117.73 (t), 117.90 (s), 126.57(d), 128.30(d), 128.68(d), 132.36(d), 134.10(d), 141.63(s), 142.06(s), 203.44(s).

4) a) J. D. Simon and K. S. Peters, J. Am. Chem. Soc., 1983, 105, 4875. b) E. Hasegawa, W. Xu, P. S. Mariano, U. C. Yoon, and J. U. Kim, Ibid., 1988, 110, 8099.

5) C. V. Kumar, D. Ramaiah, P. K. Das, and M. V. George, J. Org. Chem., 1985, 50, 2818.

6) The reduction potential of the triplet state of epoxy ketone 1a is estimated by its ground state reduction potential (E_p^{red}) and triplet energy (E_T). E_p^{red} of (1a) is -1.39 V vs. SCE as shown in Table. E_T of 1a must be about 70 kcal/mol which is assumed from the reported E_T of p-cyanoacetophenone (P. J. Wagner, R. J. Truman, A. E. Puchalski, and R. Wake, J. Am. Chem. Soc., 1986, 108, 7727).

7) Photoinduced SET reaction of aromatic α,β-epoxy ketones with amines has been conducted. While β-diketones as well as β-hydroxy ketones were obtained as major products, no formation of amine adducts was observed. E. Hasegawa, K. Ishiyama, T. Horaguchi, and T. Shimizu, J. Org. Chem., in press.

8) In photoinduced single electron transfer reaction of electron acceptors and allyltrialkyltins, no successful isolation of primary adducts containing tin has been so far reported.[2] Thus, it appears to be difficult to isolate the adduct 4a even if it is produced. Therefore, it is not unreasonable to propose the tin-oxygen bond formation in the ion radical pair.[2e,f] We also feel that, if such a bond formation does not occur, α-keto alkoxy anion would undergo retro aldol fragmentation. This would be supported by the observation that base treatment of the adduct 2a readily afforded 1-(p-cyanophenyl)-4-pentene-1-one (87 %, K_2CO_3 in aq MeCN, room temp, 30 min).

9) G. A. Lee, J. Org. Chem., 1978, 43, 4256.

10) Although homolytic Cα-O bond cleavage of 1 on irradiation may also produce α-keto radical, this route is probably a minor one for the formation of 2 since irradiation of 1a without ABT resulted in the quite lower conversion (< 8 %) of 1a than that (70 %) with ABT.

(Received in Japan 19 January 1991)