

Selective C8-O Bond Cleavage of Chalcone Epoxides Induced by
Pyrilium Salt Sensitized Photoreactions and Dark Reactions with Cerium(IV) Salts

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Summary The C8-O bonds of chalcone epoxides (1a, 1b) were selectively cleaved by pyrylium salt sensitized photoreactions, affording β -ketoaldehydes (2a, 2b) in CH_2Cl_2 and MeOH-adducts (3a, 3b) in MeOH. Similarly, cerium(IV) salts catalyzed the MeOH-adduct formations of 1a and 1b in the dark. On the other hand, nitrate ester (4b) was obtained on treatment of 1b with a cerium(IV) salt in MeCN.

Single electron transfer (SET) induced ring opening reactions of epoxides have demonstrated both C-C and C-O bond cleavages. In former cases, the intermediacy of C-C bond cleaved epoxide cation radicals was proved by molecular oxygen trapping to give trioxolane derivatives.¹ In latter cases, isolation of rearranged carbonyl compounds was considered to be evidence of regioselective C-O bond cleavage of epoxide cation radicals.² Although, addition of nucleophiles to reaction system is known to be an effective tool for trapping of cation radical intermediates,³ so far few attempts to apply this method to SET reactions of epoxides have been reported.⁴ In the course of our studies concerning ion radical and free radical selective ring opening reactions of α,β -epoxy carbonyl compounds,⁵ our attention was focused on the cation radical reactivities of these substances. We planned to generate cation radicals of chalcone epoxides (1a, 1b) and to capture them by certain nucleophiles. Herein, we wish to report that regioselective ring opening of 1a and 1b occurred to give rearranged products (2a, 2b) and nucleophile adducts (3a, 3b, and 4b) on treatment with pyrylium salts (TPPX) and cerium(IV) salts (Ce(IV)) as electron acceptors.

Exploratory study began with conducting photosensitized reactions of chalcone epoxide (1a) with 2,4,6-triphenylpyrylium tetrafluoroborate (TPPBF₄) in CH_2Cl_2 (entries 1-6 in Table 1). Irradiation of TPPBF₄ with 1a afforded β -ketoaldehyde (2a)⁶ (entry 1). Upon

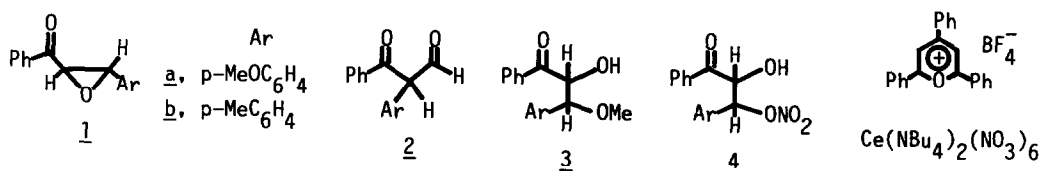


Table 1 TPPBF₄ Sensitized Photoreactions of 1a in CH₂Cl₂ and in MeOH.^a

entry	quencher ^b	$\frac{E^{\text{ox}}}{V}$ vs SCE	in CH ₂ Cl ₂			entry	quencher ^b	in MeOH		
			irrad time min	conv ^c %	yield ^c of <u>2a</u> %			irrad time min	conv ^c %	yield ^c of <u>3a</u> %
1			0.5	100	80 ^d	7		30	100	97
2 ^e			1	1	0					
3 ^f			5	5	0	8 ^f		30	11	7
4	TMB	0.77	1	5	0	9	TMB	30	11	9
5	DMB	1.28	0.5	55	21	10	DMB	30	13	12
6	TRMB	1.51	0.5	91	56	11	TRMB	30	54	51

^a) Irradiation through Toshiba L-42 glass filter ($\lambda > 390\text{nm}$) with 500W Hg-Xe lamp in CH₂Cl₂ (distilled over CaH₂) or MeOH (dried with molecular sieves 3A) at [1a] = 50 mM, [TPPBF₄] = 3.9 mM. ^b) [quencher] = 50 mM, TMB: 1,2,4,5-tetramethoxybenzene, DMB: 1,4-dimethoxybenzene, TRMB: 1,3,5-trimethoxybenzene. ^c) Determined by ¹H NMR. ^d) Isolated yield. ^e) [TPPBF₄] = 0 mM. ^f) Stirred in the dark.

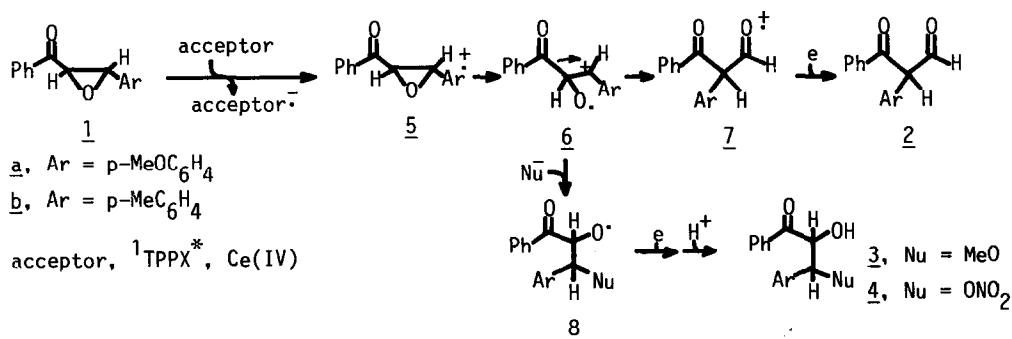
similar irradiation of 1a and TPPClO₄, 2a was obtained in 44% yield. Two control experiments (entries 2 and 3) clearly demonstrated that photoexcitation of TPPBF₄ is necessary for the formation of 2a. Reaction quenching experiments were carried out to obtain insights into a reaction mechanism (entries 4–6). The yield of 2a increases as an oxidation potential (E^{ox}) of quencher increases, supporting a single electron transfer mechanism. Chalcone epoxide (1b) was similarly converted to β -ketoaldehyde (2b)⁶ (51%) on irradiation of TPPBF₄ with 1b in CH₂Cl₂ for 25 min. When TPPBF₄ sensitized photoreactions of 1a were conducted in MeOH, MeOH-adduct (3a)⁷ was obtained instead of 2a (entry 7). TPPClO₄ was also an effective sensitizer producing 95% of 3a under similar photochemical conditions. Photoexcitation of TPPBF₄ is required for efficient conversion of 1a to 3a (entries 7 and 8). Better electron donors quenched the reaction more efficiently (entries 9, 10, and 11). Likewise, MeOH-adduct (3b)⁷ (75%) was obtained when 1b and TPPBF₄ were irradiated for 1 h in MeOH.

Since cerium(IV) salts are known as efficient SET oxidants,⁸ we decided to apply this method to SET oxidation reactions of 1a and 1b. Stirring of 1a with Ce(NBu₄)₂(NO₃)₆ (CBN)⁹ (1eq) in MeCN in the dark afforded complex mixtures which did not contain 2a. On the other hand, upon similar treatment of 1b with CBN (1eq) for 30 h, 58% of nitrate ester (4b)¹⁰ was isolated. Similarly, 4b was obtained when the reaction was conducted in CH₂Cl₂. Dark reaction of 1b with CBN (1eq) for 1.5 h in MeOH afforded 3b (67%) along with 6% of 4b. Likewise, 58% of 3b and 4% of 4b were obtained when 1b and Ce(NH₄)₂(NO₃)₆ (CAN) (1eq) were stirred for 1.5 h in MeOH. However, similar treatment of 1b with Ce(NH₄)₂(NO₃)₅·4H₂O in MeOH resulted in more than 90% recovery of 1b, which clearly indicates that cerium(III) is not responsible for the formation of 3b.¹¹ Varying the amount of CBN (1eq, 0.5eq, 0.1eq)

giving **3b** (67%, 81%, 91%) suggest that catalytic amounts of CBN is enough for complete conversion of **1b** in MeOH. It turned out that CBN (1eq) was also effective for the formation of **3a** (60%) from **1a** on stirring for 0.5 h in MeOH.

Consequently, the reactions described above would follow a reaction mechanism depicted in Scheme 1. SET processes between **1** ($E_{\text{ox}}^{\text{Ph}} = 1.59 \text{ V vs SCE for } \mathbf{1a}, > 2.1 \text{ V for } \mathbf{1b}$) and acceptors ($E^{\text{red}} = 2.5 \text{ V for } {}^1\text{TPPBF}_4^*$, $E_{\text{red}}^{\text{red}} = 0.75 \text{ V for CBN}$) initiate generations of chalcone epoxide cation radicals (**5**). Selective C8-O bond cleavage of **5** results in the formation of ring opened cation radicals (**6**). Subsequently, **6** undergo 1,2-benzoyl shift to give β -ketoaldehyde cation radicals (**7**) which are finally converted to **2**. When nucleophiles, such as MeOH and NO_3^- , exist around **6**, **6** are captured by nucleophiles to give oxiradicals (**8**) which are ultimately transformed to nucleophile adducts (**3**, **4**).¹²

Scheme 1



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- 6) Identifications of 2a and 2b were achieved by direct comparisons of their spectroscopic data with those of β -ketoaldehydes independently prepared by treatments of 1a and 1b with BF_3OEt_2 in CH_2Cl_2 (H. O. House, J. Am. Chem. Soc., 1956, 78, 2298; 1961, 83, 979).
- 7) Spectroscopic data (^1H NMR, ^{13}C NMR, IR) for 3a (1:1 mixture of two diastereomers): ^1H NMR (90 MHz, CDCl_3) δ 3.07 (s, 3H), 3.76 (s, 3H), 3.84 (d, 1H, $J = 7.3$ Hz), 4.51 (d, 1H, $J = 3.3$ Hz), 5.14 (dd, 1H, $J = 7.3, 3.3$ Hz), 6.85 (br d, 2H, $J = 8.7$ Hz), 7.26 (br d, 2H, $J = 8.7$ Hz), 7.30–7.65 (m, 3H), 7.80–8.00 (m, 2H); ^{13}C NMR (22.49 MHz, CDCl_3) δ 55.21 (q), 57.05 (q), 76.88 (d), 84.03 (d), 113.83 (d), 128.68 (d), 128.79 (d), 129.33 (s), 133.50 (d), 135.13 (s), 159.67 (s), 199.44 (s); IR (CCl_4) 3480, 1692, 1248 cm^{-1} . ^1H NMR (90 MHz, CDCl_3) δ 3.20 (s, 3H), 3.61 (d, 1H, $J = 7.9$ Hz), 3.74 (s, 3H), 4.47 (d, 1H, $J = 4.2$ Hz), 5.36 (dd, 1H, $J = 7.9, 4.2$ Hz), 6.78 (br d, 2H, $J = 8.8$ Hz), 7.06 (br d, 2H, $J = 8.8$ Hz), 7.30–7.60 (m, 3H), 7.75–7.95 (m, 2H); ^{13}C NMR (22.49 MHz, CDCl_3) δ 55.21 (q), 57.00 (q), 76.23 (d), 85.22 (d), 113.67 (d), 128.46 (s), 128.63 (d), 128.79 (d), 133.61 (d), 135.40 (s), 159.67 (s), 199.82 (s); IR (CCl_4) 3488, 1684, 1248 cm^{-1} . Similar spectroscopic data were obtained for 3b.
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- 10) Spectroscopic data (^1H NMR, ^{13}C NMR, IR) for 4b (1:9 mixture of two diastereomers): ^1H NMR (90 MHz, CDCl_3) δ 2.30 (s, 3H), 3.73 (br d, 1H, $J = 7.0$ Hz), 5.64 (br dd, 1H, $J = 7.0, 3.3$ Hz), 6.13 (d, 1H, $J = 3.3$ Hz), 6.80–8.00 (m, 9H); ^{13}C NMR (22.49 MHz, CDCl_3) δ 21.18 (q), 73.74 (d), 84.85 (d), 127.49 (d), 128.35 (s), 128.73 (d), 129.17 (d), 129.28 (d), 133.94 (s), 134.64 (d), 139.51 (s), 196.84 (s); IR (CCl_4) 3468, 1690, 1642, 1278 cm^{-1} . ^1H NMR (90 MHz, CDCl_3) δ 2.28 (s, 3H), 4.00 (br d, 1H, $J = 7.3$ Hz), 5.35 (br dd, 1H, $J = 7.3, 4.0$ Hz), 6.06 (d, 1H, $J = 4.0$ Hz), 6.90–7.90 (m, 9H); ^{13}C NMR (22.49 MHz, CDCl_3) δ 21.08 (q), 74.39 (d), 84.47 (d), 127.22 (d), 128.63 (d), 128.95 (d), 129.38 (d), 131.01 (s), 134.04 (s), 134.26 (d), 139.41 (s), 197.65 (s); IR (CCl_4) 3468, 1690, 1644, 1274 cm^{-1} .
- 11) Certain cerium(III) salts are known to catalyze ring opening reactions of epoxides (A. E. Vougiouka, H. B. Kagan, Tetrahedron Lett., 1987, 28, 6065).
- 12) Mechanistically complex but interesting observations were obtained for TPPBF_4 photo-sensitized reactions, for example, i) the rearrangement of 1a to 2a quite slowly occurred in MeCN (1 h, 17% of 2a at 40% conversion of 1a); ii) pyridine quenched the reactions although pyridine ($E_{\text{P}}^{\text{R}^{\text{x}}} > 2.5$ V) must be much weaker electron donor than TRMB ($E_{\text{P}}^{\text{R}^{\text{x}}} = 1.51$ V) which is inefficient as a quencher. Apparently, a reaction mechanism proposed in Scheme 1 is a tentative one at present time. Thus, more detailed mechanistic studies will be awaited to uncover reactions of chalcone epoxides (1) with acceptors.

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