Heterocycles, Vol. 68, No. 9, 2006, pp. 1861 - 1874. © The Japan Institute of Heterocyclic Chemistry
Received, 18th April, 2006, Accepted, 27th June, 2006, Published online, 29th June, 2006. COM-06-10767

HIGHLY STEREOSELECTIVE FORMATION OF 1,3-DIOXOLANES BY PHOTOCATALYTIC RING OPENING REACRIONS OF α-EPOXYKETONES IN ACETONE SOLUTION USING 1-BENZYL-2,4,6-TRIPHENYLPYRIDINIUM TETRAFLUOROBORATE (NBTPT)

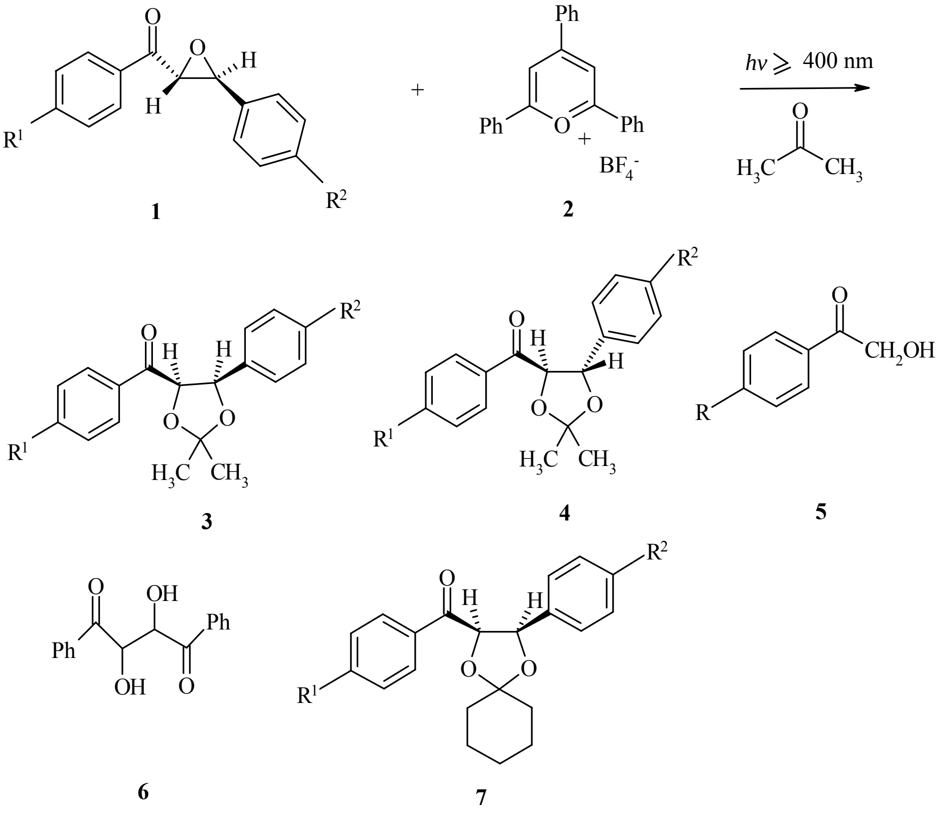
Hamid Reza Memarian,* Ali Saffar-Teluri, and Mohammad Kazem Amini

Department of Chemistry, Faculty of Science, University of Isfahan,
81746-73441, Isfahan, Iran. E-mail:memarian@sci.ui.ac.ir

Abstract - Highly stereoselective formation of 1,3-dioxolanes has been observed on photoinduced electron transfer ring opening of α-epoxyketones by 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (NBTPT) in acetone solution. The presence of various substituents on the donor molecule has not affected the rate of the ring opening and also stereoselectivity of the reaction too much. Stepwise addition of the photocatalyst leads to decreasing of irradiation time and increasing of the yield of products. Photoinduced electron transfer deoxygenation and isomerization of some α-epoxyketones has also been observed. Cyclic voltammetric study of the photocatalyst shows a greater tendency of NBTPT for accepting an electron in the excited state.

Photoinduced single electron transfer (SET) ring opening reactions of epoxides and α-epoxyketones have attracted considerable interest from both synthetic and mechanistic standpoints.[1-33] Such reactions have been recognized as important processes not only in thermal but also in photochemical transformations. Single electron transfer induced ring opening reactions of epoxides and α-epoxyketones have demonstrated C-C, and C-O bond cleavages through photoinduced electron transfer by various electron donors such as 1,4-dihydropyridines,[2] triethylamine (TEA),[3] tribenzylamine (TBA),[3] 1,3-dimethyl-2-phenylbenzimidazoline (DMPBI)[4-6] and 2-hydroxyphenyl-1,3-dimethylbenzimidazoline[7] or thermally induced single electron transfer by electron donating compounds such as samarium diiodide,[8] tributyltinhydride[9] and bis(cyclopentadienyl)titanium(III) chloride.[10] Ring opening of these compounds have also occurred thermally or photochemically by the presence of various electron acceptors. These reactions have been observed thermally by ceric ammonium nitrate,[11,12] 2,3-dichloro-5,6-dicyano-*p*-benzoquinone[13] and iron(III) chloride[14] or photoinduced electron transfer reactions by dicyanoanthracene,[15,16] tetracyanoethylene[17,18] and 2,4,6-triphenylpyrilium tetrafluoroborate.[19-23] In the case of C-C bond cleavage, the generated carbonyl ylides from epoxide radical cations have been trapped by molecular oxygen to form trioxolane derivatives[15-17] or by dipolarophiles to form various tetrahydrofurans and dihydrofurans.[24] In the absence of appropriate dipolarophiles, *cis*/*trans* isomerization of the epoxide ring has been observed. The cleavage of C_α-O and C_β-O bonds has been confirmed either by rearrangement to carbonyl compounds[25-32] or by nucleophilic attack of appropriate reagents.[19, 30, 33]

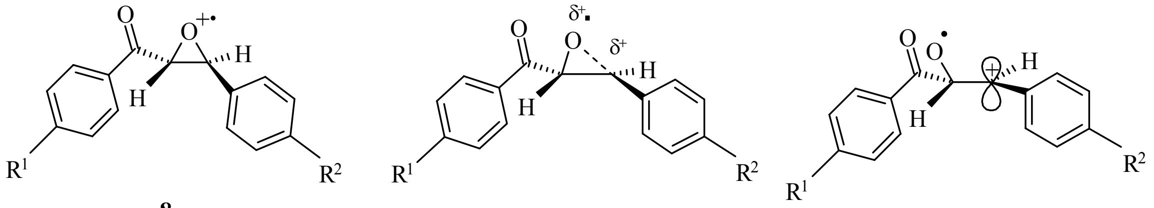
The use of the 2,4,6-triphenylpyridinium salt as intermediate for replacing amine by other functional groups in the nucleophilic substitution reactions has been studied.[34,35] Garcia and his co-workers have recently used *N*-alkyl-2,4,6-triphenylpyridinium tetrafluoroborate as photosensitizer in the photochemical cyclization of 5-methyl-4-hexenoic acid to the corresponding γ-lactone.[36]



Scheme 1

Recently, we have reported on the photocatalytic ring opening of some α-epoxyketones (**1**) of our interest with 2,4,6-triphenylpyrilium tetrafluoroborate (TPT) (**2**) as photocatalyst in methanol,[20] cyclohexanone,[21] acetone[22] and acetic acid solutions.[23] The interesting point in our studies was especially to compare the results obtained in acetone solution with those obtained in cyclohexanone solution. Whereas irradiation of various α-epoxyketones in the presence of **2** in dry acetone resulted in the formation of *cis*- and *trans*-1,3-dioxolanes (**3**) and (**4**) and also in the formation of alcoholic by-products (**5**) and (**6**), only the formation of *cis*-1,3-dioxolane (**7**) has been observed on irradiation in cyclohexanone solution (Scheme 1).

As noted therein, the rate of the ring opening was affected by the nature of substituents and their location on the α-epoxyketones, but the steric hindrance of the nucleophile (cyclohexanone compared with acetone) has also a great effect on the formation of the stereoisomeric 1,3-dioxolanes. On the basis of the observed stereoselectivity of the reaction and also the influence of the nature of the substituent on the rate of the ring opening, we have proposed the involvement of the intermediates (**8-10**) for the nucleophilic attack in these reactions (Scheme 2).[21, 22]



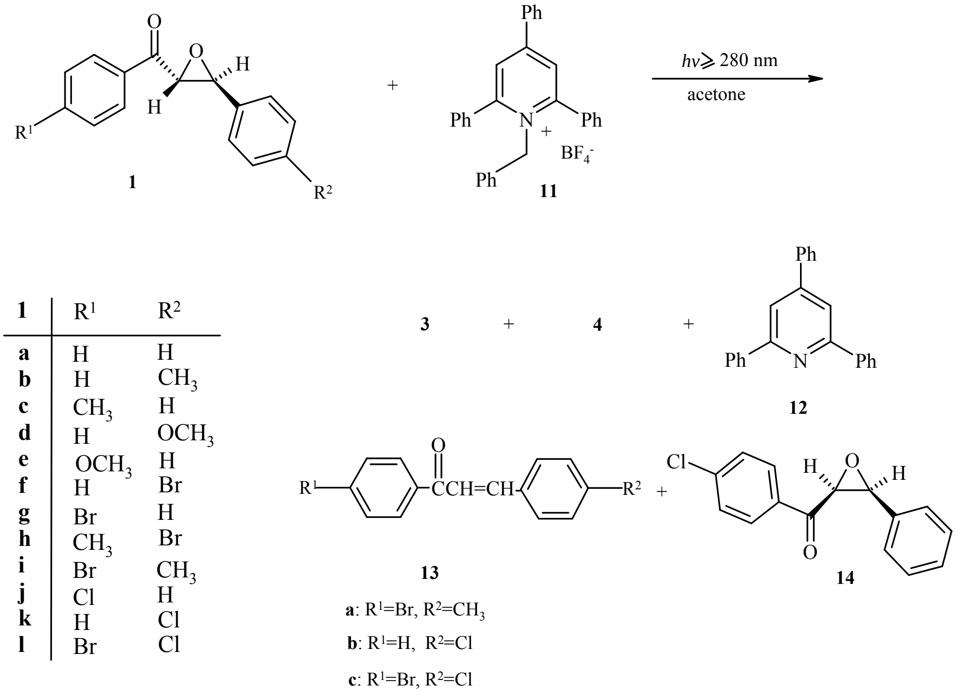
8 **9** **10**

Scheme 2

Since the extent of electron transfer from α-epoxyketones to the excited photocatalyst is the key step in these reactions, we decided to use the photocatalyst 1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (NBTPT) (**11**) which we thought to be a weaker electron acceptor (nitrogen *vs.* oxygen), and therefore, higher stereoselectivity of reactions should be expected. Now we wish to report on the photocatalytic ring opening of α-epoxyketones (**1a-1l**) by using of **11** in acetone solution.

RESULTS AND DISCUSSION

Irradiation (λ ≥ 280 nm) of α-epoxyketones (**1a-1l**) with **11** in a 10:1 molar ratio in dry acetone solution by bubbling of argon through the solution under irradiation resulted in the formation of different products (**3**, **4**, **13**, **14**) besides 2,4,6-triphenylpyridine (**12**) (Scheme 3).



1	R^1	R^2
a	H	H
b	H	CH_3
c	CH_3	H
d	H	OCH_3
e	OCH_3	H
f	H	Br
g	Br	H
h	CH_3	Br
i	Br	CH_3
j	Cl	H
k	H	Cl
l	Br	Cl

Scheme 3

The results obtained in the present work show that substituted α-epoxyketones (**1a-1l**) behave totally different in this reaction. Whereas ring opening of α-epoxyketones (**1a-1h**) resulted in the formation of *cis*-1,3-dioxolanes (**3a-3h**) as major products besides smaller amount of *trans*-1,3-dioxolanes (**4a-4h**) (according to TLC observation) as minor products, α-epoxyketones (**1i**), (**1k**) and (**1l**) were converted to their corresponding precursor, namely, chalcones (**13a-13c**). The compound (**1j**) was isomerized to its *cis*-isomer (**14**). The results are summarized in Table 1.

Table1. Photochemical reactions of **1a-1l** catalyzed by **11** in acetone solution

1	Conversion(%)^{a,b}	**12** (mg)	Product (%)^{c}			
			Dioxolanes		Chalcones	*Cis*
			3	**4**		
a	90	23	**a** (68)	**a** (trace)	-	-
b	92	22	**b** (70)	**b** (trace)	-	-
c	88	23	**c** (69)	**c** (trace)	-	-
d	85	23	**d** (72)	**d** (trace)	-	-
e	89	23	**e** (68)	**e** (trace)	-	-
f	79	21	**f** (67)	**f** (trace)	-	-
g	81	23	**g** (66)	**g** (trace)	-	-
h	80	23	**h** (68)	**h** (trace)	-	-
i	82	22	-	-	**13a** (76)	-
j	89	23	-	-	-	**14** (81)
k	83	23	-	-	**13b** (71)	-
l	81	23	-	-	**13c** (67)	-

[a]Irradiation time for all compounds was **9** hours. [b][**1a-1l**] = 0.04 M, [**11**] = 0.004 M, corresponding to molar ratio of 10:1, [c]Isolated yield, the amounts of unconsumed **1a-1l** are determined and given in the experimental part.

IR, ^{1}H NMR and MS spectral data gave useful information for the structural assignment of the photoproducts. The IR spectra of the new 1,3-dioxolanes (**3f-3h**) compared with the IR spectra of α-epoxyketones (**1f-1h**) showed an increase of aliphatic CH-stretching due to addition of acetone. Owing to the ring opening and the loss of the epoxide ring strain, a shift of CO-stretching to higher frequency has been observed. A comparison of the CO-stretching in the IR spectra of (**1a-1h**) and (**3a-3h**) is shown in Table 2.

Table 2. Comparison of the CO-stretching in the IR-spectra of **1a-1h** with those of **3a-3h**

1	CO / cm^{-1}	**3**	CO / cm^{-1}	ref.
a	1670	**a**	1695	22
b	1660	**b**	1685	22
c	1665	**c**	1685	22
d	1660	**d**	1688	22
e	1665	**e**	1685	22
f	1661	**f**	1693	this work
g	1677	**g**	1695	this work
h	1674	**h**	1686	this work

The ^{1}H NMR spectra of **3a-3h** showed two singlets for the methyl groups and also an AB-system for the 4-H and 5-H of the dioxolane ring. *Cis*-orientation of the hydrogens of the dioxolane ring was confirmed by comparison of their chemical shifts, coupling constants and upfield shift of one methyl group compared to the other one due to anisotropy effect of both aryl and aroyl groups. A comparison of these data with those of the known dioxolanes[22] supports this suggestion (Table 3).

Regarding the results obtained from the control experiment and the results presented in Table 1 we found that:

1. 1. The presence of photocatalyst NBTPT is necessary for the reaction, because irradiation of **1a-1l** without NBTPT resulted only in the conversion of smaller amounts of some of these compounds to their corresponding precursors chalcones and we did not observe the formation of any 1,3-dioxolanes (**3**) and (**4**), and also the *cis*-isomer (**14**).
2. Stepwise addition of **11** to the solution of α-epoxyketones resulted in the complete conversion of them, shortening of the irradiation time and also increasing the yield of all products (Table 4).
3. Whereas irradiation of **11** alone in acetone solution resulted in the formation of only 10 % of **12**, complete consumption of **11** has been observed on its irradiation in the presence of **1a-1l**.
4. Two types of reactions, photo-degradation of **11** to **12** and photoelectron transfer from α-epoxyketones to excited **11,** were occurred simultaneously.

Table 3. Structurally relevant ^{1}HNMR chemical shift (δ/ppm) and ^{1}H-^{1}H couplings (*J*/Hz) of **3a-3h**.

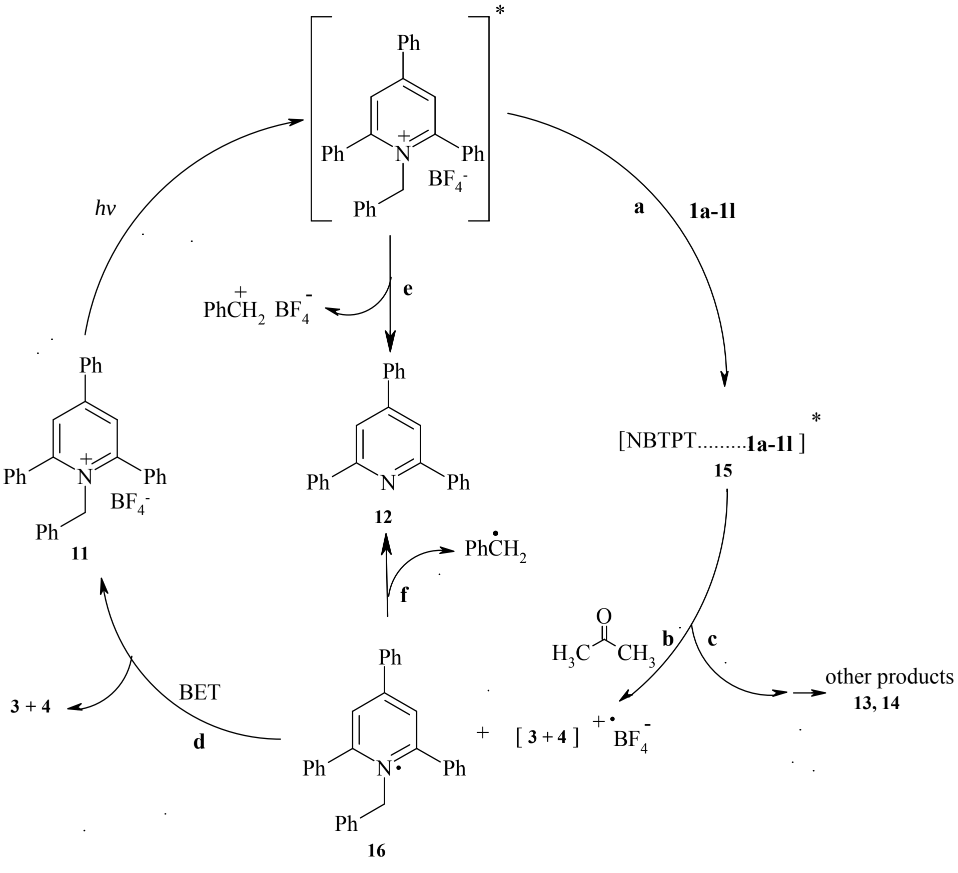
3	δ_A 4-H	δ_B 5-H	J_{AB}	CH_3		ref.
a	5.48	5.75	8.2	1.57	1.81	22
b	5.45	5.80	7.6	1.49	1.79	22
c	5.48	5.74	7.6	1.52	1.80	22
d	5.47	5.73	7.6	1.52	1.79	22
e	5.49	5.72	7.4	1.53	1.82	22
f	5.52	5.84	8.0	1.60	1.86	this work
g	5.59	5.80	8.0	1.62	1.90	this work
h	5.53	5.83	7.9	1.61	1.86	this work

Table 4. Photochemical reactions of **1a-1l** in acetone catalyzed by stepwise addition of **11**[a]

			Product (%)[b]			
1	Irradiation time (h)[a]	**12** (mg)	Dioxolanes		Chalcones	*Cis*
			3	**4**		
a	7	23	**a** (82)	**a** (trace)	-	-
b	5	22	**b** (84)	**b** (trace)	-	-
c	6.5	22	**c** (81)	**c** (trace)	-	-
d	5	21	**d** (83)	**d** (trace)	-	-
e	6	22	**e** (80)	**e** (trace)	-	-
f	7	22	**f** (79)	**f** (trace)	-	-
g	7	23	**g** (80)	**g** (trace)	-	-
h	7	23	**h** (78)	**h** (trace)	-	-
i	7	21	-	-	**13a** (81)	-
j	7.5	22	-	-	-	**14** (90)
k	7	23	-	-	**13b** (79)	-
l	7	22	-	-	**13c** (74)	-

[a] 0.0039g of photocatalyst [**11**] = 0.004 M was added in three times. [**1a-l**] = 0.04 M, [b] Isolated yield.

On the basis of the foregoing results, the following mechanism is proposed for the reactions (Scheme 4). According to the proposed mechanism, irradiation of a mixture of **11** and α-epoxyketone leads to excitation of **11**. The excited **11** then interacts with the present α-epoxyketone to form a charge transfer complex (**15**). The nucleophilic attack of acetone to this complex leads to the intermediates $\mathbf{[3+4]^{+\cdot}\,BF_4^-}$ and the radical (**16**) (path b). Back electron transfer (BET) gives the product (**3**) and (**4**)**,** and recovery of **11** (path d). Triphenylpyridine (**12**) can be formed either by photo-degradation of **11** according to a heterolytic cleavage of excited NBTPT (path e) or the homolytic cleavage of the intermediate (**16**) (path f). This argument can be supported according to the obtained results mentioned in point 3. It should be noted that we did not obtain any product derived from benzyl cation or radical intermediates.

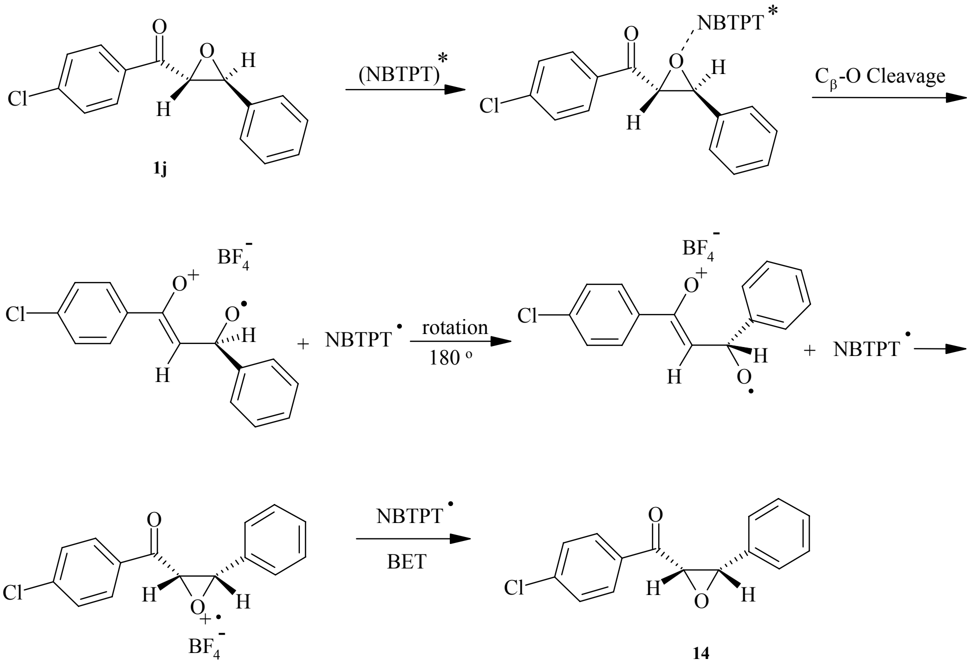


Scheme 4

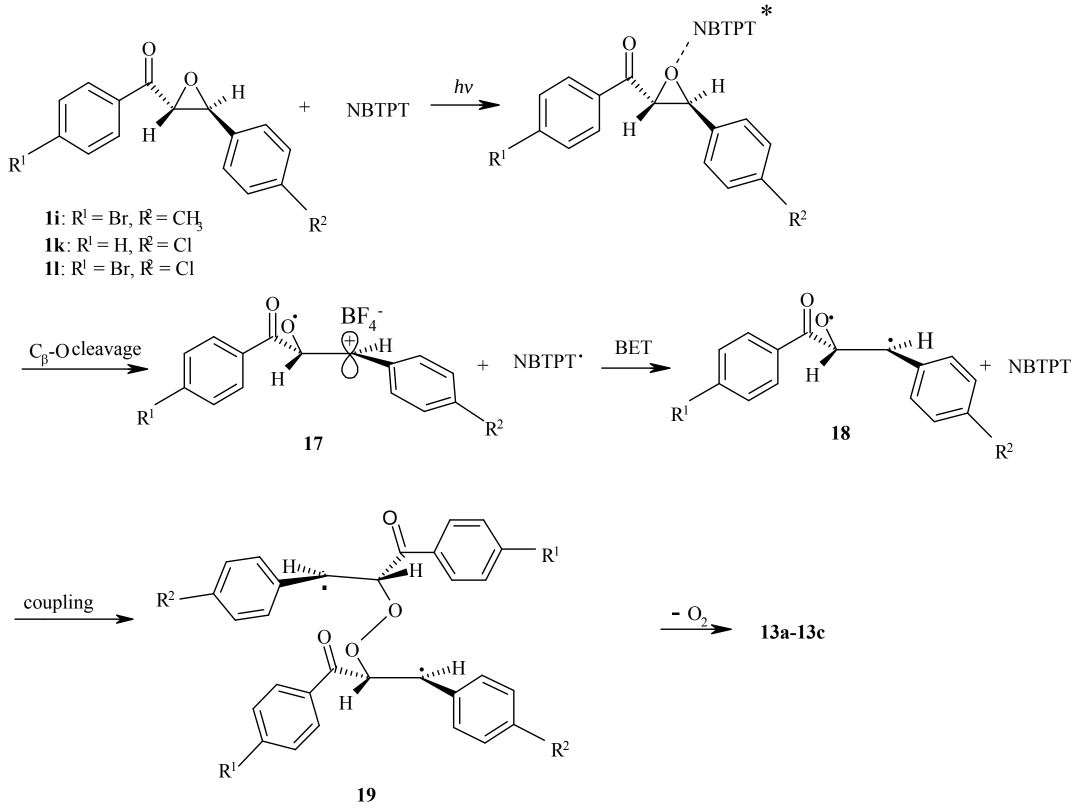
The photoisomerization of α-epoxyketones through heterolytic C_α-O bond cleavage has been reported.[37] Since the presence of the photocatalyst (NBTPT) is involved in the isomerization of **1j**, according to the reported mechanism,[37] we will present the same mechanism but with the involvement of NBTPT as a first example of photoinduced electron transfer isomerization of an α-epoxyketone as follows (Scheme 5).

The interesting point in our reaction is also deoxygenation of some α-epoxyketones. Our results indicated that the presence of NBTPT increased especially the yield of chalcones (**13a-13c**) during the deoxygenation of α-epoxyketones (**1i**), (**ik**), and (**1l**), respectively. Therefore, the following mechanism can be presented for this conversion (Scheme 6).

According to the proposed mechanism, C_β-O cleavage of the complex leads to formation of the intermediate (**17**). Back electron transfer (BET) to **17** gives the 1,3-carbo-oxy diradical (**18**). Coupling of the diradical (**18**) leads to the formation of peroxy diradical intermediate (**19**). This intermediate accomplished the reaction by formation of the chalcones (**13a-13c**) by elimination of molecular oxygen.



Scheme 5



Scheme 6

Cyclic voltammetric studies of the photocatalysts

One-electron reduced species of an acceptor molecule plays an important role especially in reactions in which the electron transfer step is the key step to the reaction. Since the observed ring opening of α-epoxyketones does not occur either in the absence of light and NBTPT or TPT as photocatalysts, we were interested to compare the cyclic voltammograms of NBTPT and TPT in the absence and in the presence of light in order to elucidate their reactivity towards incoming electron in both ground and excited states. The cyclic voltammograms (CVs) of NBTPT and TPT in Ar-saturated dichloromethane solutions containing 0.05 M tetrabutylammonium perchlorate are shown in Figure1.

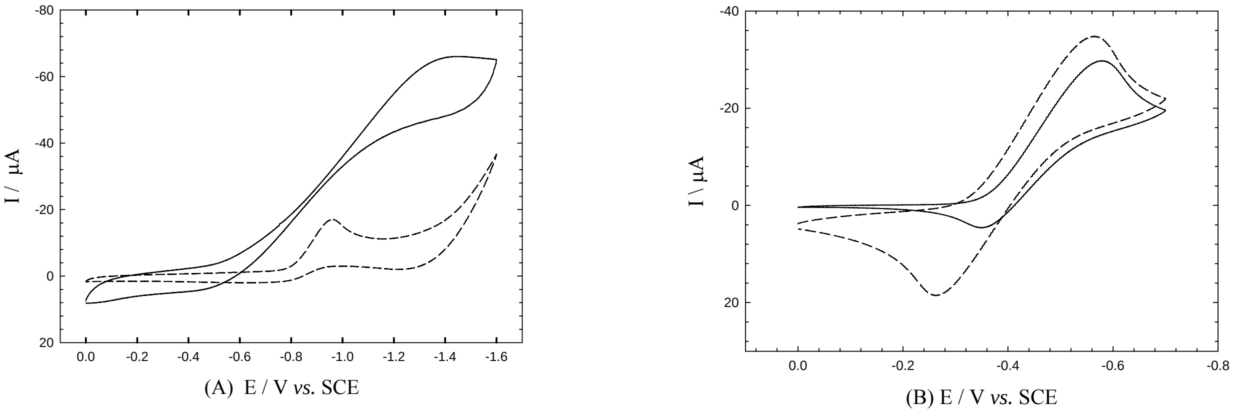
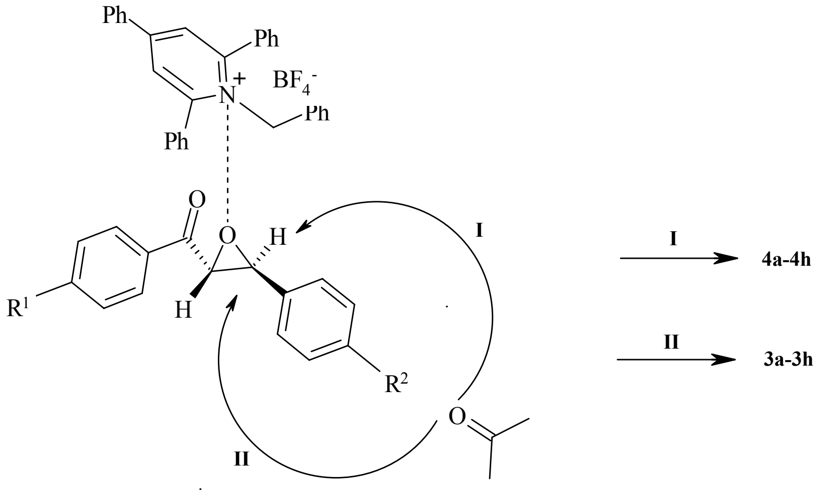


Figure 1. Cyclic voltammograms of (A) NBTPT (1×10^{-3} M) (B) TPT (1×10^{-3} M) in the absence of light (—) and in the presence of light (----) in argon saturated dichloromethane solutions containing tetrabutylammonium perchlorate (0.05 M) as the supporting electrolyte at a scan rate of 200 mV s^{-1}. (SCE = standard calomel electrode)

As can be seen, TPT is more readily reduced compared to NBTPT, both in presence and absence of light; the reduction peak potential for TPT occurs at - 0.58 V (*vs.* SCE) in comparison to - 1.4 V for NBTPT. Although reduction of NBTPT is more sensitive to light, i.e., it shows an approximately 440 mV positive shift in the reduction peak potential in the presence of light, but even in the presence of light TPT is still a better electron acceptor.

The results of cyclic voltammetric studies of photocatalyst TPT and NBTPT explain the observed highly stereoselective ring opening of **1a-1h** in the presence of NBTPT compared with TPT in acetone solution. Owing to efficient electron transfer from α-epoxyketones to TPT, as stronger electron acceptor compared with NBTPT, one of the proposed intermediates (**8-10**) should be formed, in which BF_4^- is the counter ion of these intermediates. The presence of electron donor groups on the phenyl ring attached to the epoxide ring (R^2 in Scheme 2), facilitates the electron transfer to the excited TPT and decreasing stereoselectivity of the reaction. Cyclic voltammetric studies support our suggestion that NBTPT is a weaker electron acceptor compared with TPT. Therefore, we should not expect complete electron transfer from donor molecule (α-epoxyketone) to NBTPT and formation of one of the intermediates (**8-10**). Indeed, we need to propose a complex between excited NBTPT and α-epoxyketones. This complex leads to the preferred attack of acetone as a nucleophilic reagent to the carbon atom in the rear of the bond comprising the oxygen leaving group due to the steric hindrance of NBTPT. This suggestion also supports the observation that the effect of the additional substituents on the parent molecules (**1a-1h**) does not affect the extent of stereoselectivity of the reactions (Scheme 7).



Scheme 7

It is interesting to compare the results obtained on reaction of **1a-1h** compared with those obtained with **1i-1l**. We measured the oxidation potential of these α-epoxyketones by means of cyclic voltammetry to calculate the free energy. The ΔG values for the reaction (in kJ/mol) can be calculated from the simplified Rehm-Weller Equation.[38]

$$\Delta G = 96.5\,(E_{ox} - E_{red}) - E_s$$

Where E_s is the singlet energy of NBTPT obtained from intersection of the normalized absorption and emission spectra ($\lambda_{0.0}$ = 375 nm), 319 kJ/mol. E_{red} the redox potential of NBTPT -1.4 V versus SCE and E_{ox} the oxidation potential of **1a-1l**. Thus, the ΔG were obtained (Table 5). These data show that the electron-transfer process is exothermic for **1a-1h** but not for **1i-1l**. Therefore, better formation of charge transfer complex (**15**) (Scheme 4) for **1a-1h** should be expected. On the other hand, formation of a very weaker complex shown in Scheme 5 and 6 should be involved by reaction with **1i-1l**.

Table 5. Free energy change for electron transfer from **1a-1l** to singlet NBTPT

compound	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**	**1k**	**1l**
E_{ox} (V)	1.110	1.107	1.108	1.322	1.180	1.203	1.172	1.214	2.229	2.072	2.110	2.064
ΔG (kJ/mol)	-76.79	-77.07	-76.98	-56.33	-70.03	-67.81	-70.80	-66.75	+31.20	+16.05	+19.72	+15.28

EXPERIMENTAL

Melting points were determined with a Stuart Scientific SMP2-apparatus and are uncorrected. NBTPT has been prepared according to the reported procedure.[39] IR spectra were recorded on a Philips PU-9716. ^1H NMR spectra were measured in $CDCl_3$ solutions containing tetramethylsilane (TMS) as internal standard on a Bruker drx-500 (500 MHz). MS were obtained on a Plattform II from Micromass. The cyclic voltammetric experiments were performed on AUTOLAB 30, Potentiostat Galvanostat. The electrochemical studies were conducted by using dichloromethane solution containing tetrabutylammonium perchlorate under argon. A three electrode with a saturated calomel electrode (SCE) as the reference, a platinium foil as the counter electrode and a platinium disk as the working electrode was used. Preparative layer chromatography (PLC) was carried out on 20 × 20 cm^2 plates coated with 1 mm layer of Merck silica gel PF_{254} prepared by applying the silica as a slurry and drying in air. All irradiations were carried out using a 400 W high-pressure Hg vapor lamp from Narva. The samples were placed in Duran glass, which were cooled by running cold water.

A solution of 0.8 mmol of **1a-1l** in 20 mL of acetone (c = 0.04 M) and 0.08 mmol of **11** (c = 0.004 M) was irradiated for the time given in Table 1.

Irradiation of 1,3-diphenyl-2,3-epoxy-1-propanone (**1a**)

PLC, petroleum ether:AcOEt = 12:1, two times; zone 1, 23 mg of **12**, recrystallized from EtOH, mp: 134-135 °C (lit.,[40]: 135 °C); zone 2, 18 mg of **1a**; zone 3, trace of **4a**; zone 4, 138 mg (68 %) of **3a**, recrystallized from *n*-hexane, mp 116-118 ºC (lit.,[22]: 116-118 ºC).

cis-4-Benzoyl-2,2-dimethyl-5-phenyl-1,3-dioxolane (**3a**)

IR (KBr): 3050, 2920-2990, 1695, 1600 cm^{-1}.

Irradiation of 3-(*p*-methylphenyl)-2,3-epoxy-1-propanone (**1b**)

PLC, petroleum ether:AcOEt = 12:1, two times; zone 1, 22 mg of **12**; zone 2, trace of **4b**; zone 3, 15 mg of **1b**; zone 4, 153 mg (70 %) of **3b**, recrystallized from *n*-pentane, mp 148-150 ºC (lit.,[22]: 147-149 ºC).

cis-4-Benzoyl-2,2-dimethyl-5-(*p*-methylphenyl)-1,3-dioxolane (**3b**)

IR (KBr): 3030, 2870-2995, 1685, 1595 cm^{-1}.

Irradiation of 1-(*p*-methylphenyl)-3-phenyl-2,3-epoxy-1-propanone (**1c**)

PLC, petroleum ether:AcOEt = 12:1, two times; zone 1, 23 mg of **12**; zone 2, trace of **4c**; zone 3, 23 mg of **1c**; zone 4, 144 mg (69 %) of **3c**, washed with *n*-pentane:Et_2O, mp 131-132 ºC (lit.,[22]: 132-133 ºC).

cis-2,2-Dimethyl-4-(*p*-methylbenzoyl)-5-phenyl-1,3-dioxolane (**3c**)

IR (KBr): 3045, 2900-2995, 1685, 1610 cm^{-1}.

Irradiation of 3-(*p*-methoxyphenyl)-1-phenyl-2,3-epoxy-1-propanone (**1d**)

PLC, petroleum ether:AcOEt = 10:1, two times; zone 1, 23 mg of **12**; zone 2, trace of **4d**; zone 3, 30 mg of **1d**; zone 4, 153 mg (72 %) of **3d**, recrystallized from *n*-hexane, mp 128-129 ºC ((lit.,[22]: 127-129 ºC).

cis-4-Benzoyl-5-(*p*-methoxyphenyl)-2,2-dimethyl-1,3-dioxolane (**3d**)
IR (KBr): 3010, 2860-2950, 1688, 1620 cm^{-1}.

Irradiation of 1-(*p*-methylphenyl)-3-phenyl-2,3-epoxy-1-propanone (**1e**)
PLC, petroleum ether:AcOEt = 10:1, two times; zone 1, 23 mg of **12**; zone 2, trace of **4e**; zone 3, 22 mg of **1e**; zone 4, 151 mg (68 %) of **3e**, recrystallized from *n*-hexane, mp 120-122 ºC ((lit.,[22]: 121-123 ºC).

cis-4-(*p*-Methoxybenzoyl)-2,2-dimethyl-5-phenyl-1,3-dioxolane (**3e**)
IR (KBr): 3050, 2820-2980, 1685, 1600 cm^{-1}.

Irradiation of 3-(*p*-bromophenyl)-1-phenyl-2,3-epoxy-1-propanone (**1f**)
PLC, petroleum ether:AcOEt = 11:1, two times; zone 1, 21 mg of **12**; zone 2, trace of **4f**; zone 3, 51 mg of **1f**; zone 4, 153 mg (67 %) of **3f**, recrystallized from *n*-hexane:AcOEt, mp 164-165 ºC.

cis-4-Benzoyl-5-(*p*-bromophenyl)-2,2-dimethyl-1,3-dioxolane (**3f**)
IR (KBr): 3020, 2910-2990, 1693, 1595, 1397, 1250, 1100 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 1.60 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), AB-system ($\delta_A = 5.52$, $\delta_B = 5.84$, $^3J_{AB} = 8.0$ Hz, 2H, 4-H, 5-H), AB-system ($\delta_A = 6.69$, $\delta_B = 7.17$, $^3J_{AB} = 8.1$ Hz, 4H, aromatic H), 7.28-7.50 (m, 5H, aromatic H) ppm; EI-MS (70 eV, 50 ºC): *m/z* (%) = 361 [M^+] (2), 304 [M^+ ^{81}Br - CH_3COCH_3] (3), 303 [M^+ ^{81}Br - C_3H_7O] (3), 302 [M^+ ^{79}Br - CH_3COCH_3] (3), 301 [M^+ ^{79}Br - C3H7O] (3), 186 [$^{81}BrC_6H_4CHO^+$] (3), 185 [$^{81}BrC_6H_4CO^+$] (7), 184 [$^{79}BrC_6H_4CHO^+$] (3), 183 [$^{79}BrC_6H_4CO^+$] (7), 157 [$^{81}BrC_6H_4^+$] (4), 155 [$^{79}BrC_6H_4^+$] (4), 105 [$C_6H_5CO^+$] (47), 77 [$C_6H_5^+$] (98), 69 [$C_3H_5CO^+$] (100).

Irradiation of 1-(*p*-bromophenyl)-3-phenyl-2,3-epoxy-1-propanone (**1g**)
PLC, petroleum ether:AcOEt = 10:1, two times; zone 1, 23 mg of **12**; zone 2, trace of **4g**; zone 3, 46 mg of **1g**; zone 4, 154 mg (66 %) of **3g**, recrystallized from *n*-hexane:AcOEt, mp 125-126 ºC.

cis-4-(*p*-Bromobenzoyl)-2,2-dimethyl-5-phenyl-1,3-dioxolane (**3g**)
IR (KBr): 3050, 2940-2980, 1695, 1585, 1476, 1210, 1090 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 1.62 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), AB-system (δ_A=5.59, δ_B=5.80, $^3J_{AB} = 8.0$ Hz, 2H, 4-H, 5-H), 7.10-7.15 (m, 5H, aromatic H), AB-system ($\delta_A = 7.36$, $\delta_B = 7.40$, $^3J_{AB} = 8.5$ Hz, 4H, aromatic H) ppm; EI-MS (70 eV, 50 ºC): *m/z* (%) 361 [M^+] (3), 304 [M^+ ^{81}Br - CH_3COCH_3] (9), 302 [M^+ ^{79}Br - CH_3COCH_3] (9), 185 [$^{81}BrC_6H_4CO^+$] (67), 183 [$^{79}BrC_6H_4CO^+$] (67), 157 [$^{81}BrC_6H_4^+$] (28), 155 [$^{79}BrC_6H_4^+$] (28), 105 [$C_6H_5CO^+$] (77), 91 [$C_7H_7^+$] (100), 77 [$C_6H_5^+$] (82).

Irradiation of 3-(*p*-bromophenyl)-1-(*p*-methylphenyl)-2,3-epoxy-1-propanone (**1h**)
PLC, petroleum ether:AcOEt = 11:1, two times; zone 1, 23 mg of **12**; zone 2, trace of **4h**; zone 3, 11 mg of **1h**; zone 4, 163 mg (68 %) of **3h**, recrystallized from *n*-hexane:AcOEt, mp 140-141 ºC.

cis-5-(*p*-Bromophenyl)-2,2-dimethyl-4-(*p*-methylbenzoyl)-1,3-dioxolane (**3h**)
IR (KBr): 3020, 2920-2980, 1686, 1610, 1397, 1205, 1096 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): 1.61 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), AB-system ($\delta_A = 5.53$, $\delta_B = 5.83$, $^3J_{AB} = 7.9$ Hz, 2H, 4-H,

5-H), AB-system ($\delta_A = 7.00$, $\delta_B = 7.21$, $^3J_{AB} = 8.3$ Hz, 4H, aromatic H), AB-system ($\delta_A = 7.11$, $\delta_B = 7.44$, $^3J_{AB} = 8.1$ Hz, 4H, aromatic H), ppm; EI-MS (70 eV, 50 ºC): *m/z* (%) 375 [M^+] (3), 318 [M^{+} ^{81}Br- CH_3COCH_3] (9), 316 [M^{+} ^{79}Br- CH_3COCH_3] (10), 285 [M^{+} ^{81}Br - C_7H_7] (2), 256 [M^+-C_7H_7CO] (4), 186 [$^{81}BrC_6H_4CHO^+$] (6), 185 [$^{81}BrC_6H_4CO^+$] (14), 184 [$^{79}BrC_6H_4CHO^+$] (7), 183 [$^{79}BrC_6H_4CO^+$] (13), 157 [$^{81}BrC_6H_4^+$] (9), 155 [$^{79}BrC_6H_4^+$] (9), 149 [$C_7H_7COCO^+$] (6), 119 [$C_7H_7CO^+$] (21), 91 [$C_7H_7^+$] (22), 69 [$C_3H_5CO^+$] (100).

Irradiation of 1-(*p*-bromophenyl)-3-(*p*-methylphenyl)-2,3-epoxy-1-propanone (**1i**)
PLC, petroleum ether:AcOEt = 10:1, two times; zone 1, 22 mg of **12**; zone 2, 149 mg (76%) of **13a**, mp 162-164 ºC ((lit.,[41]: 163-164 ºC); zone 3, 46 mg of **1i**.

Irradiation of 1-(*p*-chlorophenyl)-3-phenyl-2,3-epoxy-1-propanone (**1j**)
PLC, petroleum ether:AcOEt = 10:3, two times; zone 1, 23 mg of **12**; zone 2, 23 mg of **1j**; zone 3, 149 mg (81 %) of **14**, recrystallized from MeOH, mp 116-117 ºC.

cis-1-(*p*-Chlorophenyl)-3-phenyl-2,3-epoxy-1-propanone (**14**)
IR (KBr): 3040, 2900-2950, 1696, 1584, 1414, 1226, 1087 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): AB-system ($\delta_A = 4.12$, $\delta_B = 4.29$, $^3J_{AB} = 1.3$ Hz, 2H, 2-H, 3-H), 7.40-7.46 (m, 5H, aromatic H), AB-system ($\delta_A = 7.51$, $\delta_B = 8.01$, $^3J_{AB} = 8.4$ Hz, 4H, aromatic H), ppm; EI-MS (70 eV, 50 ºC): m/z (%) 258 [M^{+} ^{35}Cl] (3), 166 [$^{37}ClC_6H_4COCHO^+$] (6), 141 [$^{37}ClC_6H_4CO^+$] (27), 139 [$^{35}ClC_6H_4CO^+$] (88), 113 [$^{37}ClC_6H_4^+$] (14), 111 [$^{35}ClC_6H_4^+$] (42), 91 [$C_7H_7^+$] (38), 87 [$^{37}ClC_4H_2^+$] (31), 85 [$^{35}ClC_4H_2^+$] (100), 77 [$C_6H_5^+$] (22), 75 [$C_6H_3^+$] (43), 65 [$C_5H_5^+$] (24), 63 [$C_5H_3^+$] (25), 51 (95).

Irradiation of 3-(*p*-chlorophenyl)-1-phenyl-2,3-epoxy-1-propanone (**1k**)
PLC, petroleum ether:AcOEt = 10:1, two times; zone 1, 23 mg of **12**; zone 2, 114 mg (71 %) of **13b**, mp 112-114 ºC ((lit.,[41]: 111-113 ºC); zone 3, 35 mg of **1k**.

Irradiation of 1-(*p*-bromophenyl)-3-(*p*-chlorophenyl)-2,3-epoxy-1-propanone (**1l**)
PLC, petroleum ether:AcOEt = 10:1, two times; zone 1, 23 mg of **12**; zone 2, 139 mg (67 %) of **13c**, mp 165-166 ºC ((lit.,[41]: 166-167 ºC); zone 3, 51 mg of **1l**.

ACKNOWLEDGEMENTS

We are thankful to the Office of Graduate Studies of the University of Isfahan for their financial support.

REFERENCES

1 E. Hasegawa and M. Kamata in *CRC Handbook of Organic Photochemistry and Photobiology*, W. M. Horspool and F. Lenci Eds. CRC Press, Boca Raton, 2004, Chapter 53, pp. 1-17.
2 J. Zhang, M. Z. Jin, W. Zhang, L. Yang, and Z. L. Liu, *Tetrahedron Lett.*, 2002, **43**, 9687.
3 E. Hasegawa, K. Ishiyama, T. Fujita, T. Kato, and T. Abe, *J. Org. Chem.*, 1997, **62**, 2396.

4 E. Hasegawa, A. Yoneoka, K. Suzuki, T. Kato, T. Kitazume, and K. Yanagi, *Tetrahedron*, 1999, **55**, 12957.

5 E. Hasegawa, T. Kato, T. Kitazume, K. Yanagi, K. Hasegawa, and T. Horaguchi, *Tetrahedron Lett.*, 1996, **37**, 7079.

6 E. Hasewaga, N. Chiba, A. Nakajima, K. Suzuki, A. Yoneoka, and K. Iwaya, *Synthesis*, 2001, 1248.

7 E. Hasegawa, N. Chiba, T. Takahashi, S. Takizawa, T. Kiatayama, and T. Suzuki, *Chem. Lett.* 2004, **33**, 18.

8 G. A. Molander and G. Hahn, *J. Org. Chem.*, 1986, **51**, 2596.

9 E. Hasegawa, K. Ishiyama, T. Kato, T. Horaguchi, T. Shimizu, S. Tanaka, and Y. Yamashita, *J. Org. Chem.*, 1992, **57**, 5352.

10 C. Hardouin, F. Chevallier, B. Rousseau, and E. Doris, *J. Org. Chem.*, 2001, **66**, 1046.

11 N. Iranpoor and I. Mohammadpour Baltork, *Synth. Commun.*, 1990, **20,** 2789.

12 N. Iranpoor and I. Mohammadpour Baltork, F. Shiriny Zardaloo, *Tetrahedron*, 1991, **47,** 9861.

13 N. Iranpoor and I. Mohammadpour Baltork, *Tetrahedron Lett.*, 1990, **31,** 735.

14 N. Iranpoor and P. Salehi, *Synthesis*, 1994, 1152.

15 A. P. Schaap, S. Siddiqui, G. Prasad, A. F. M. Maqsudur Rahman, and J. P. Oliver, *J. Am. Chem. Soc.*, 1984, **106**, 6087.

16 S. Futamura, S. Kusunose, H. Ohta, and Y. Kamiya, *J. Chem. Soc., Perkin Trans. 1*, 1984, 15.

17 T. Miyashi, M. Kamata, and T. Mukai, *J. Am. Chem. Soc.*, 1987, **109,** 2780.

18 Y. Masaki, T. Miura, and M. Ochiai, *Bull. Chem. Soc. Jpn.*, 1996, **69,** 195.

19 E. Hasegawa, K. Ishiyama, H. Kashiwazaki, T. Horaguchi, and T. Shimizu, *Tetrahedron Lett.*, 1990, **31,** 4045.

20 H. R. Memarian, A. Hesami, F. Nikpour, and D. Döpp, *Indian J. Chem.*, 2001, **40B,** 662.

21 H. R. Memarian and F. Nikpour, *Molecules*, 2001, **6**, 63.

22 H. R. Memarian and F. Nikpour, *Monatsh. Chem.*, 2002, **133**, 1045.

23 H. R. Memarian and F. Nikpour, *J. Chin. Chem. Soc.*, 2002, **49,** 401.

24 P. Clawson, P. M. Lunn, and A. Whiting, *J. Chem. Soc., Chem. Commun.*, 1984, 134.

25 H. E. Zimmerman, B. R. Cowley, C. Y. Tseng, and J. W. Wilson, *J. Am. Chem. Soc.*, 1964, **86**, 947.

26 C. S. Markos and W. Reusch, *J. Am. Chem. Soc.*, 1967, **89,** 3363.

27 S. P. Pappas, R. M. Giesham, and M. J. Miller, *J. Am. Chem. Soc.*, 1970, **92,** 5797.

28 J. R. Williams, G. M. Sarkisian, J. Quigley, A. Hasiuk, and R. VanderVenen, *J. Org. Chem.*, 1974, **39,** 1028.

29 G. A. Lee, *J. Org. Chem.*, 1978, **43,** 4256.

30 P. Hallet, J. Muzart, and J. P. Pete, *Tetrahedron Lett.*, 1979, **29,** 2723.

31 P. Hallet, J. Muzart, and J. P. Pete, *Tetrahedron Lett.*, 1979, **29,** 2727.

32 A. Osuka, *J. Org. Chem.*, 1983, **48,** 1712.

33 J. Kagan, P. Y. Juang, B. E. Firth, J. T. Przybytek, and S. P. Singh, *Tetrahedron Lett.*, 1977, 4289.

34 A. R. Katritzky, M. F. Abdel-Megeed, G. Lhommet, and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, 1979, 426.

35 A. R. Katritzky, G. Musumarra, K. Sakizadeh, and M. Misic-Vukovic, *J. Org. Chem.*, 1981, **46**, 3820.

36 M. Alvaro, P. Formentin, H. Garcia, E. Palomares, and M. J. Sabater, *J. Org. Chem.*, 2002, **67,** 5184.

37 C. K. Johnson, B. Doming, and W. Reusch, *J. Am. Chem. Soc.*, 1963, **65,** 3895.

38 D. Rehm and A. Weller. *Isr. J. Chem.*, 1970, **8**, 259.

39 *Vogel's Textbook of Practical Organic Chemistry*, 5th. Ed., Longmann Scientific & Technical, Essex, 1989; p. 1170.

40 G. Reddelien, *Ber.*, 1920, **53,** 334.

41 D. R. Palleros, *J. Chem. Edu.*, 2004, **81,** 1345.