Diastereoselective 1,3-Dioxolane Formation by Photocatalytic Ring Opening of α-Epoxyketones

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Photocatalytic ring opening of α-epoxyketones by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in acetone resulted in the diastereoselective formation of 1,3-dioxolanes through C_α–O bond cleavage. The facility of the ring opening is influenced by the nature and the location of the additional substituent on the α-epoxyketones.

Key words: DDQ, Electron Transfer, α-Epoxyketones, Photocatalyst, Ring Opening

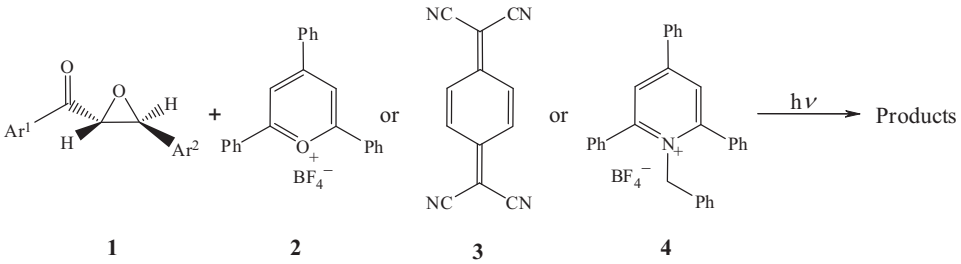
Introduction

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is a versatile reagent in organic synthesis. Owing to its oxidizing ability and also its relative stability under various reaction conditions cause it to be one of the most used reagents to perform several organic transformations such as oxidation of benzhydrols [1], dehydrogenation [2, 3], deprotection of benzyl ethers [4], anodic oxidation of naphthalenes [5], thiocyanation of aromatic and heteroaromatic compounds [6, 7], and aromatization of 1,4-dihydropyridines [8]. DDQ is also a well-known electron acceptor, and its interaction with a variety of electron donors *via* the formation of charge transfer (CT) complexes has been the subject of several investigations [9 – 11].

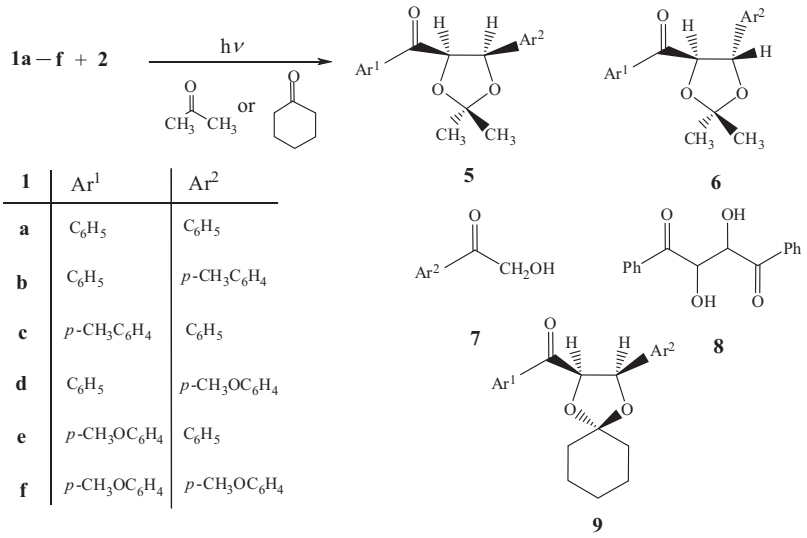
Epoxides, as oxygen-containing three-membered heterocyclic rings, are among the most versatile building blocks in organic synthesis due to their facile formation and higher reactivity toward nucleophiles. Ring opening reactions of epoxides and α-epoxyketones, thermally or photochemically, have attracted considerable interest from both synthetic and mechanistic standpoints. Single electron transfer (SET) induced ring opening of these compounds in the presence of a suitable catalyst or photocatalyst leads to the formation of radical cation intermediates. Nucleophilic attack of suitable species to these intermediates results in the formation of 1,3-dioxolane, trioxolane or ether derivatives [12, 13].

Previously, we have reported the light-induced ring opening of α-epoxyketones **1** in the presence of various photocatalysts such as 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) **2** [14 – 18], 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) **3** [19] and *N*-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate (NBTPT) **4** [20] in methanol, acetic acid, acetone and cyclohexanone solutions (Scheme 1).

The results obtained in these studies have shown that the diastereoselectivity observed in this reaction depends on the type of photocatalyst and on the nucleophilic power and the steric hindrance of the attacking species. Whereas irradiation of **1a – f** in the presence of pyrylium salt **2** in dry acetone resulted in the formation of diastereomeric *cis*- and *trans*-1,3-dioxolanes **5a – f** and **6a – f** besides the formation of alcoholic by-products **7** and **8** [16], diastereospecific formation of *cis*-spirodioxolanes **9a – f** is observed by carrying out the irradiation in cyclohexanone solution (Scheme 2) [15]. An interesting point is that the irradiation of **1a – f** in the presence of TCNQ (**3**) in acetone resulted in the formation of *cis*-1,3-dioxolanes **5a – f** besides the formation of alcoholic by-products **7** and **8** [19], while by using the photocatalyst **4**, the formation of *cis*-1,3-dioxolanes **5a – f** accompanied by the formation of a trace amount of *trans*-1,3-dioxolanes



Scheme 1.



1	Ar^1	Ar^2
a	C_6H_5	C_6H_5
b	C_6H_5	p-$CH_3C_6H_4$
c	p-$CH_3C_6H_4$	C_6H_5
d	C_6H_5	p-$CH_3OC_6H_4$
e	p-$CH_3OC_6H_4$	C_6H_5
f	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$

Scheme 2.

6a – f is observed [20]. In continuation of these studies, we used DDQ as catalyst and also as photocatalyst for the ring opening reaction of α-epoxyketones in methanol under thermal conditions [21] and under microwave and UV irradiations [22]. The results of these studies indicate the formation of distereomeric methoxyalcohols. The observed different behavior of the excited photocatalyst toward α-epoxyketones, especially the diastereoselectivity of the reaction depending on the electronic nature of α-epoxyketones and also the nucleophilicity of the solvent, led us to extend our study to the photocatalytic ring opening of certain α-epoxyketones using DDQ in dry acetone solution under UV irradiation. The aims of the present study are to elucidate the effect of the electronic nature of α-epoxyketones on the rate of reaction, and to compare the diastereoselectivity of the reaction with that observed using another photocatalysts.

Results and Discussion

Irradiation ($\lambda \geq 350$ nm) of α-epoxyketones **1a – i** and DDQ (**10**) in a molar ratio of 10 : 1 in dry acetone resulted in the opening of the epoxide ring and formation of diastereomeric 1,3-dioxolanes **5a – h** and **6a – g**, and chalcones **11h** and **11i** (Scheme 3). The results are summarized in Table 1.

The data presented in Table 1 show that the rate of ring opening of α-epoxyketones **1a – i** by DDQ is dependent on the nature and location of the additional substituent on the parent molecule **1a**. Since we have earlier observed catalytic ring opening of α-epoxyketones by DDQ in methanol at room temperature and under reflux conditions [21], we have also carried out the same reaction with **1a** as a test substrate, but in acetone. In contrast to the failure of the reaction at room temperature, a fast reaction

Table 1. Photocatalytic ring opening reaction of **1a–i** by **10** in dry acetone.

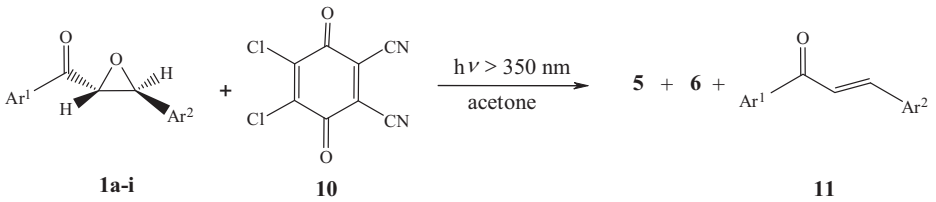
1	Ar^1	Ar^2	Irrad. time (h)[a]	Yield (%)[b]			
				Recov. **1**	**5**	**6**	**11**
a	C_6H_5	C_6H_5	6	10	38 (40)	31 (32)	–
b	C_6H_5	*p*-$CH_3C_6H_4$	1.5	–	40	34	–
c	*p*-$CH_3C_6H_4$	C_6H_5	6	42	25 (43)	10(17)	–
d	C_6H_5	*p*-$CH_3OC_6H_4$	2	–	42	38	–
e	*p*-$CH_3OC_6H_4$	C_6H_5	6	68	15 (44)	10 (30)	–
f	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	2.5	–	40	37	–
g	*p*-ClC_6H_4	C_6H_5	6	62	21 (42)	9 (17)	–
h	C_6H_5	*p*-ClC_6H_4	6	35	12 (20)	–	31 (71)
i	*p*-BrC_6H_4	C_6H_5	6	67	–	–	31 (91)

[a] Irradiation times are given after maximum progression of reaction (not necessarily 100 % conversion);
[b] based on used (consumed) **1a–i**.

was observed under reflux conditions, even faster than under UV irradiation. According to this finding, we propose the same reaction mechanism, as was proposed earlier [21, 22] (Scheme 4):

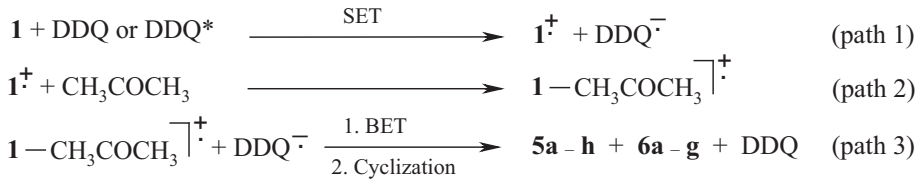
I. Single electron transfer (SET) either from **1a – i** to DDQ in the excited state (DDQ*) or possibly to DDQ in the ground state (electron affinity of DDQ ~ 3 eV) [23] leads to the formation of **1a – i**$^{\bullet+}$ and DDQ$^{\bullet-}$ (path 1).
II. Nucleophilic attack of acetone at **1a – i**$^{\bullet+}$ forms **1a – i**–$(CH_3)_2CO^{\bullet+}$ adducts (path 2).
III. Back electron transfer (BET) from DDQ$^{\bullet-}$ to **1a – i**–$(CH_3)_2CO^{\bullet+}$ adducts followed the cyclization accomplishes the reaction (path 3).

Regarding the proposed mechanism, due to electron transfer from **1a – i** as electron donor molecules to DDQ as an electron acceptor molecule, the radical cation species **1a – i**$^{\bullet+}$ are formed. These species could produce three different intermediates (**12 – 14**), which are trapped by nucleophilic attack of acetone (Scheme 5). The preferred participation of one of these intermediates in the reaction should depend on the electron-donating ability of the additional substituent and its location. Whereas the presence of electron donor groups such as *p*-methyl- or *p*-methoxyphenyl directly attached to the epoxide ring (**1b**, **1d**, and **1f**) causes a facile ring opening, the *p*-chlorophenyl substituent as an electron acceptor group on the same position (**1h**) reduces the rate of the reaction. It should be noted that the same substituents on the phenyl ring of the benzoyl group (**1c**, **1e**, **1g**, and **1i**) have a less remarkable effect. This indicates the influence of the substituent on the electron-donating ability of α-epoxyketones toward photoexcited DDQ.

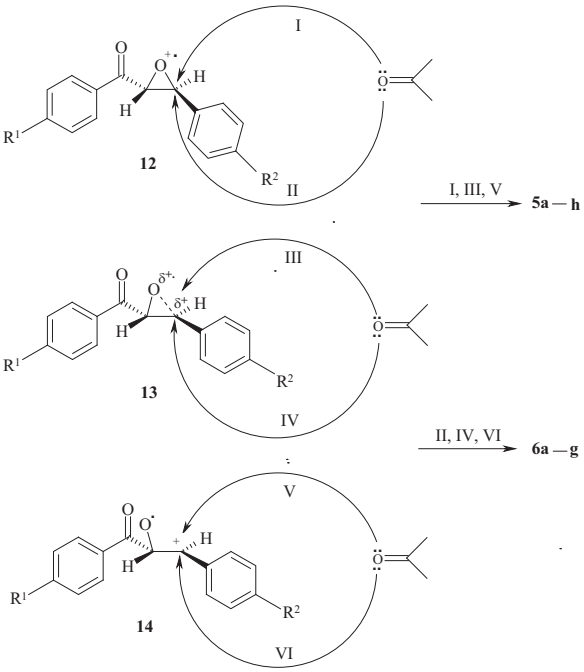


1a-i **10** **11**

Scheme 3.



Scheme 4.



Scheme 5.

An important result of the present study is obtained from a comparison of the observed diastereoselectivity of the reaction with that obtained in the presence of the photocatalysts **2**, **3**, and **4**. The light absorptivities of the photocatalysts **2**, **3**, **4**, and **10** are not the same, which definitely influences the time of reaction. The observed diastereoselectivity, which is presented in Table 2, may be explained by the steric hindrance of the photocatalysts during the nucleophilic attack of acetone to the proposed intermediates **12** – **14**.

Density functional theory at the B3LYP/6-31++G(d,p) level was applied to explain the observed diastereoselectivity of the nucleophilic attack of acetone in the presence of various photocatalysts.

Table 2. The diastereoselectivity in the photocatalytic ring opening reaction of **1a–f** by **2**, **3** and **4** in dry acetone.

1	**2**		**3**		**4**	
	5 (%)	**6** (%)	**5** (%)	**6** (%)	**5** (%)	**6** (%)
a	23	14	41	–	68	trace
b	28	10	60	–	70	trace
c	24	11	35	–	69	trace
d	29	11	54	–	72	trace
e	27	8	38	–	68	trace
f	23	–	42	–	67	trace

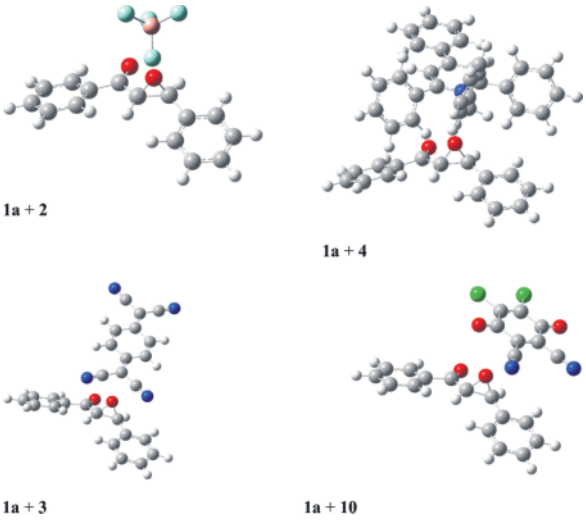


Fig. 1 (color online). Orientation of the counterions to $\mathbf{1a}^{+\bullet}$ obtained by electron transfer of **1a** to **2**, **3**, **4**, and **10**, respectively, showing the steric hindrance for nucleophilic attack.

After electron transfer from **1a** – **i** to the photocatalysts **2**, **3**, **4** or **10**, complexes between ionic species of both molecules are formed. This is shown in Fig. 1 with the intermediate **12** as an example. Cyclic voltammetric studies of both photocatalysts **2** (TPT) and **4** (NBTPT) showed [20] that **2** with the reduction potential of -0.58 V (*vs.* SCE) is a stronger electron acceptor compared to **4** with the reduction potential of -1.4 V. These results explain that after the electron transfer process to **2**, BF_4^- should be a counterion of the intermediate **12**, while in the case of the weaker electron acceptor species **4**, the whole molecule **4** with the partial positive charge on its nitrogen atom orientated towards the oxygen of the epoxide ring (as a charge transfer complex formed in the excited state, exciplex) should be the counterion of this intermediate. This explains the possibility of a nucleophilic attack of acetone from both sides in the former case, whereas in the latter case the presence of the voluminous **4** adjacent to the epoxide ring causes a steric hindrance on the upper side. This proposal is supported by the highly stereoselective formation of 1,3-dioxolanes **6** using the photocatalyst **4** [20], whereas in the case of **2** the formation of both diastereomers, types **5** and **6** has been observed [16]. Irradiation of α-epoxyketones **1a** – **f** in the presence of TCNQ (**3**) in acetone resulted also in the highly stereoselective formation of 1,3-dioxolanes **6**. This explains the alignment of the

large $TCNQ^-$ species at the epoxy oxygen atom of **12**, which hinders the nucleophilic attack of acetone from the upper side [19]. In the present study, using the photocatalyst DDQ (**10**), the DDQ^- radical anion is formed after electron transfer. Due to the favorable formation of the aromatic ring in this species, the negative charge is more localized on the oxygen atom. The ring is far enough from the heterocycle, which again explains the possibility for a nucleophilic attack of acetone from both sides. This argument supports the formation of both diastereomers, types **5** and **6**, in the present study.

Another result of this study is the deoxygenation of some α-epoxyketones **1h** and **1i** to the corresponding chalcones **11h** and **11i**. The same reaction also occurs by irradiation of these compounds in the presence of **4** [20].

Conclusion

In the present study, photocatalytic ring opening of α-epoxyketones by DDQ in acetone resulted in the formation of diastereomeric 1,3-dioxolanes. These results and those of our previous investigations explain that besides steric hindrance for the nucleophile, the type of the photocatalyst determines the diastereoselectivity of the reaction.

Experimental Section

Melting points were determined with a Stuart Scientific SMP2 apparatus and are uncorrected. IR spectra were recorded using KBr pellets on a Jasco FT/IR-6300 spectrometer. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. Mass spectra were measured by electron impact at 70 eV on a Micromass Platform II instrument. Preparative thin layer chromatography (PTLC) was carried out on 20×20 cm^2 plates, coated with a 1 mm layer of Merck silica gel PF_{254}, prepared by applying the silica as slurry and drying in air. All irradiations were carried out in a 20 mL Duran cell with a 5×25 Watt lamp ($\lambda = 350$ nm) in a Rayonet reactor, Model PRP-100. A solution of 0.8 mmol of **1a**–**i** in 20 mL of acetone ($c = 0.04$ M) and 0.08 mmol of DDQ ($c = 0.004$ M) was irradiated for the time given in Table 1. Some of the photoproducts are known, and their spectroscopic data have already been reported [16].

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

PTLC, *n*-hexane-ethyl acetate = 5 : 1, two times; zone 1 ($R_f = 0.7$), 35 mg (32 % based on consumed **1a** and 31 % based on used **1a**) of **6a**, recrystallized from *n*-hexane-ethyl acetate, m. p.: 85 °C, lit. [16] 87 – 89 °C. Zone 2: $R_f = 0.56$, recovered **1a** (19 mg, 10 % based on used **1a**); zone 3 ($R_f = 0.5$), 42 mg (40 % based on consumed **1a** and 38 % based on used **1a**) of **5a**, recrystallized from *n*-hexane-ethyl acetate; m. p.: 120 °C, lit. [16] 116 – 118 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.61$ (s, 3H, CH_3), 1.88 (s, 3H, CH_3), AB system ($\delta_A = 5.56$, $\delta_B = 5.84$, $^3J_{AB} = 8.0$ Hz, 2H, 4-H, 5-H), 7.05 – 7.12 (m, 5H, phenyl), 7.22 – 7.28 (m, 2H, *m*-H of PhCO), 7.38 – 7.42 (m, 1H, *p*-H of PhCO), 7.47 (d, $J = 8.0$ Hz, 2H, *o*-H of PhCO) ppm.

*trans-4-Benzoyl-2,2-dimethyl-5-phenyl-1,3-dioxolane (**6a**)*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.53$ (s, 3H, CH_3), 1.70 (s, 3H, CH_3), AB system ($\delta_A = 5.02$, $\delta_B = 5.49$, $^3J_{AB} = 7.6$ Hz, 2H, 4-H, 5-H), 7.28 – 7.47 (m, 7H, phenyl H and *m*-H of PhCO), 7.54 – 7.58 (m, 1H, *p*-H of PhCO), 7.90 (d, $J = 8.0$ Hz, 2H, *o*-H of PhCO) ppm.

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

PLC, *n*-hexane-ethyl acetate = 5 : 1; zone 1 ($R_f = 0.6$), 40 mg (34 % based on consumed **1b**) of **6b**, recrystallized from *n*-hexane-ethyl acetate; m. p.: 50 °C, lit. [16] 45 – 48 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.59$ (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), AB system ($\delta_A = 5.54$, $\delta_B = 5.81$, $^3J_{AB} = 8.0$ Hz, 2H, 4-H, 5-H), 6.83 (d, $J = 8.0$ Hz, 2H, *m*-H of aryl), 6.99 (d, $J = 8.0$ Hz, 2H, *o*-H of aryl), 7.23 – 7.28 (m, 2H, *m*-H of PhCO), 7.39 – 7.42 (m, 1H, *p*-H of PhCO), 7.48 (d, $J = 7.6$ Hz, 2H, *o*-H of PhCO) ppm.

*trans-4-Benzoyl-2,2-dimethyl-5-(p-methylphenyl)-1,3-dioxolane (**6b**)*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.52$ (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), AB system ($\delta_A = 5.01$, $\delta_B = 5.44$, $^3J_{AB} = 7.6$ Hz, 2H, 4-H, 5-H), 7.17 (d, $J = 7.6$ Hz, 2H, *m*-H of aryl), 7.29 – 7.35 (m, 4H, *m*-H and *o*-H of PhCO), 7.61 – 7.66 (m, 1H, *p*-H of PhCO), 7.91 (d, $J = 7.6$ Hz, *o*-H of aryl) ppm; zone 2: $R_f = 0.33$, **5b** (45 mg, 40 % based on used **1b**), washed with *n*-hexane-ethyl acetate; m. p.: 150 – 152 °C, lit. [16] 147 – 149 °C.

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

PLC, *n*-hexane-ethyl acetate = 5 : 1; zone 1 ($R_f = 0.83$), 12 mg (17 % based on consumed **1c** and 10 % based on used **1c**) of **6c**, washed with *n*-hexane-ethyl acetate; m. p.: 81 °C, lit. [16] 82 – 83 °C.

*cis-4-(p-Methylbenzoyl)-2,2-dimethyl-5-phenyl-1,3-dioxolane (**5c**)*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.60$ (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), AB system ($\delta_A = 5.56$, $\delta_B = 5.81$, $^3J_{AB} = 8$ Hz, 2H, 4-H, 5-H), 7.03 – 7.11 (m, 7H, phenyl and *m*-H of ArCO), 7.40 (d, $J = 8.0$ Hz, 2H, *o*-H of ArCO) ppm.

*trans-4-(p-Methylbenzoyl)-2,2-dimethyl-5-phenyl-1,3-dioxolane (**6c**)*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.50$ (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), AB system ($\delta_A = 5.00$, $\delta_B = 5.47$, $^3J_{AB} = 7.6$ Hz, 2H, 4-H, 5-H), 7.20 (d, $J = 8.0$ Hz, 2H, *o*-H of phenyl), 7.28 – 7.37 (m, 3H, *m*-H and *o*-H of phenyl), 7.44 (d, $J = 7.6$ Hz, 2H, *m*-H of ArCO), 7.80 (d, $J = 8.0$ Hz, 2H, *o*-H of ArCO) ppm; zone 2: $R_f = 0.61$, recovered **1c** (40 mg, 42 % based on used **1c**); zone 3 ($R_f = 0.5$), 30 mg (43 % based on consumed **1c** and 25 % based on used **1c**) of **5c**, washed with *n*-hexane-ethyl acetate; m. p.: 131 °C, lit. [16] 132 – 133 °C.

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

PLC, *n*-hexane-ethyl acetate = 5 : 1; zone 1 ($R_f = 0.42$), 45 mg (38 % based on used **1d**) of **6d**, washed with *n*-hexane-ethyl acetate; m. p.: 45 – 48 °C, lit. [16] 43 – 47 °C.

*cis-4-(p-Benzoyl)-5-methoxyphenyl-2,2-dimethyl-1,3-dioxolane (**5d**)*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.59$ (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), AB system ($\delta_A = 5.53$, $\delta_B = 5.80$, $^3J_{AB} = 7.6$ Hz, 2H, 4-H, 5-H), 6.58 (d, $J = 8.0$ Hz, 2H, *o*-H of aryl), 7.02 (m, 2H, *m*-H of aryl), 7.24 – 7.28 (m, 2H, *m*-H of PhCO), 7.39 – 7.43 (m, 1H, *p*-H of PhCO), 7.50 (d, $J = 7.2$ Hz, 2H, *o*-H of PhCO) ppm.

*trans-4-(p-Benzoyl)-5-methoxyphenyl-2,2-dimethyl-1,3-dioxolane (**6d**)*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.52$ (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), AB system ($\delta_A = 5.00$, $\delta_B = 5.39$, $^3J_{AB} = 7.6$ Hz, 2H, 4-H, 5-H), 6.89 (d, $J = 8.0$ Hz, 2H, *o*-H of aryl), 7.28 – 7.43 (m, 4H, *m*-H of aryl and PhCO), 7.54 – 7.55 (m, 1H, *p*-H of PhCO), 7.89 (d, $J = 6.8$ Hz, 2H, *o*-H of PhCO) ppm; zone 2 ($R_f = 0.17$), 50 mg (42 % based on used **1d**) of **5d**, washed with *n*-hexane-ethyl acetate; m. p.: 130 – 133 °C, lit. [16] 127 – 129 °C.

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

PLC, *n*-hexane-ethyl acetate = 5 : 1; zone 1 ($R_f = 0.46$), 12 mg (30 % based on consumed **1e** and 10 % based on used **1c**) of **6e** as a viscous oil; zone 2: $R_f = 0.4$, recovered **1e** (69 mg, 68 % based on used **1e**); zone 3 ($R_f = 0.24$), 18 mg (44 % based on consumed **1e** and 15 % based on used **1e**) of **5e**, recrystallized from *n*-hexane-ethyl acetate; m. p.: 120 °C, lit. [16] 121 – 123 °C.

*Irradiation of trans-1,3-di(p-methoxyphenyl)-2,3-epoxy-1-propanone (**1f**)*

PLC, *n*-hexane-ethyl acetate = 5 : 1; zone 1 ($R_f = 0.57$), 50 mg (37 % based on used **1e**) of **6f** as a viscous oil.

*trans-4-(p-Methoxybenzoyl)-5-methoxyphenyl-2,2-dimethyl-1,3-dioxolane (**6f**)*

IR: ν = 2987 (aromatic CH), 2838 – 2935 (aliphatic CH), 1678 (C=O), 1599 (C=C) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), AB system (δ_A = 4.97, δ_B = 5.39, $^3J_{AB}$ = 8.0 Hz, 2H, 4-H, 5-H), 6.86 – 6.90 (m, 4H, *m*-H of aryl and ArCO), 7.38 (d, J = 7.6 Hz, 2H, *o*-H of aryl), 7.89 (d, J = 8.4 Hz, 2H, *o*-H of ArCO) ppm. – MS (EI, 70 eV, 50 °C): m/z (%) = 284 $[M - CH_3COCH_3]^+$ (100), 269 $[M - CH_3COCH_3 - CH_3]^+$ (22), 177 $[M - CH_3COCH_3 - CH_3OC_6H_4]^+$ (84), 149 $[M - CH_3COCH_3 - CH_3OC_6H_4CO]^+$ (95), 135 $[CH_3OC_6H_4CO]^+$ (100), 121 $[CH_3OC_6H_4CH_2]^+$ (100), 107 $[CH_3OC_6H_4]^+$ (94), 92 $[C_6H_4O]^+$ (93); zone 2: R_f = 0.31, (54 mg, 40 % based on used **1f**).

*Irradiation of trans-1-(p-chlorophenyl)-3-phenyl-2,3-epoxy-1-propanone (**1g**)*

PLC, *n*-hexane-ethyl acetate = 5 : 1; zone 1 ($R_f = 0.61$), 22 mg (17 % based on consumed **1g** and 9 % based on used **1g**) of **6g** as a viscous oil.

*cis-4-(p-Chlorobenzoyl)-2,2-dimethyl-5-phenyl-1,3-dioxolane (**5g**)*

IR: ν = 3372 (aromatic CH), 2933 – –2983 (aliphatic CH), 1695 (C=O), 1588 (C=C) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), AB system (δ_A = 5.56, δ_B = 5.74, $^3J_{AB}$ = 7.6 Hz, 2H, 4-H, 5-H), 7.08–7.11 (m, 4H, *o*-H and *m*-H of phenyl), 7.20 (m, 2H, *m*-H of ArCO), 7.27 (brd s, 1H, *p*-H of phenyl), 7.42 (d, J = 7.2 Hz, 2H, *o*-H of ArCO) ppm.

*trans-4-(p-Chlorobenzoyl)-2,2-dimethyl-5-phenyl-1,3-dioxolane (**6g**)*

IR: ν = 3432 (aromatic CH), 2849 – 2918 (aliphatic CH), 1687 (C=O), 1590 (C=C) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.50 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), AB system (δ_A = 4.94, δ_B = 5.48, $^3J_{AB}$ = 7.20 Hz, 2H, 4-H, 5-H), 7.33 – 7.40 (m, 5H, phenyl H), 7.46 (d, J = 6.4 Hz, 2H, *m*-H of ArCO), 7.87 (d, J = 7.6 Hz, 2H, *o*-H of ArCO)

ppm. – MS (EI, 70 eV, 60 °C): m/z (%) = 319 $[M^{37}Cl]^+$ (2), 317 $[M^{35}Cl]^+$ (6), 261 $[M^{37}Cl - CH_3COCH_3]^+$ (24), 259 $[M^{35}Cl - CH_3COCH_3]^+$ (83), 177 $[M - ClC_6H_5CO]^+$ (86), 119 $[M - CH_3COCH_3 - ClC_6H_4CO]^+$ (93); zone 2: R_f = 0.53, recovered **1f** (65 mg, 62 % based on used **1f**); zone 3 (R_f = 0.31), 20 mg (42 % based on consumed **1g** and 21 % based on used **1g**) of **5g**, washed with *n*-hexane-ethyl acetate; m. p.: 115 °C.

*Irradiation of trans-3-(p-chlorophenyl)-1-phenyl-2,3-epoxy-1-propanone (**1h**)*

PLC, *n*-hexane-ethyl acetate = 5 : 1, two times; zone 1 (R_f = 0.65), 40 mg (71 % based on consumed **1h** and 31 % based on used **1h**) of **11h**, recrystallized from *n*-hexane-ethyl acetate; m. p.: 108 – 110 °C, lit. [24] 111 – 113 °C; zone 2: R_f = 0.52, recovered **1h** (47 mg, 35 % based on used **1h**); zone 3 (R_f = 0.3), 15 mg (20 % based on consumed **1h** and 12 % based on used **1h**) of **5h**, washed with *n*-hexane-ethyl acetate, m. p.: 130 °C.

*cis-4-Benzoyl-5-(p-chlorophenyl)-2,2-dimethyl-1,3-dioxolane (**5h**)*

IR: ν = 3372 (aromatic CH), 2853 – 2924 (aliphatic CH), 1695 (C=O), 1597 (C=C) cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.60 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), AB system (δ_A = 5.53, δ_B = 5.82, $^3J_{AB}$ = 8 Hz, 2H, 4-H, 5-H), 7.02 – 7.03 (m, 4H, *m*-H of aryl and PhCO), 7.27 – 7.28 (m, 3H, *p*-H of PhCO and *o*-H of aryl), 7.44 – 7.49 (m, 2H, *o*-H of PhCO) ppm. – MS (EI, 70 eV, 60 °C): m/z (%) = 261 $[M^{37}Cl - CH_3COCH_3]^+$ (10), 259 $[M^{35}Cl - CH_3COCH_3]^+$ (32), 212 $[M^{35}Cl - C_6H_5CO]^+$ (16), 214 $[M^{37}Cl - C_6H_5CO]^+$ (5), 154 $[M - CH_3COCH_3 - C_6H_5CO]^+$ (50), 113 $[^{37}ClC_6H_4]^+$ (3), 111 $[^{35}ClC_6H_4]^+$ (9), 105 $[C_6H_5CO]^+$ (100).

*Irradiation of trans-3-(p-bromophenyl)-1-phenyl-2,3-epoxy-1-propanone (**1i**)*

PLC, *n*-hexane-ethyl acetate = 5 : 1, two times; zone 1 (R_f = 0.63), 45 mg (91 % based on consumed **1i** and 32 % based on used **1i**) of **11i**, recrystallized from *n*-hexane-ethyl acetate; m. p.: 121 °C, lit. [24] 127 – 128 °C; zone 2: R_f = 0.53, recovered **1i** (95 mg, 67 % based on used **1i**).

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