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Photocatalytic Ring Opening of α-Epoxyketones: 1,3-Dioxolane Formation[a]

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Summary. Photocatalytic ring opening of α-epoxyketones by 2,4,6-triphenylpyrylium tetrafluoroborate in acetone resulted in the formation of 1,3-dioxolanes as major products through C–O bond cleavage and the formation of alcoholic by-products through C–C bond cleavage. The type and nature of the substituent affects the rate of ring opening.

Keywords. Dioxolanes; Electron transfer; α-Epoxyketones; Photochemistry; Ring opening.

Introduction

Single electron transfer (SET) induced ring opening of epoxides and α-epoxyketones has been of great interest for several years and is still under intensive investigation [1–9]. Such reactions have been recognized as important processes not only in thermal but also in photochemical transformations. Two types of ring openings (C–C and C–O bond cleavages) have been observed from epoxide radical cation intermediates. In the former case, intermediates have been trapped by molecular oxygen or tetracyanoethylene to give trioxolane or oxacyclopentane derivatives [4, 5]. In the case of C–O bond cleavage, proof has been obtained either by rearrangement to carbonyl compounds [1, 2, 6] or by nucleophilic attack of appropriate reagents [3, 8, 9].

In recent studies we have investigated the effect of substituents on the photocatalytic ring opening of various α-epoxyketones by 2,4,6-triphenylpyrylium tetrafluoroborate as a photocatalyst, followed by nucleophilic attack of methanol to form methyl ether derivatives [10]. The results indicated that electron donating groups increase the rate of ring opening; however, the stereoselectivity decreased depending on type and stability of the reaction intermediates. The aim of this work was to study the effect of substituents on the photocatalytic ring opening of α-epoxyketones **1a**–**f** in acetone and to explain the nature of the reaction intermediate responsible for the formation of the isomeric products.

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[b] Taken in part from the planned doctoral thesis of *F. Nikpour*, University of Isfahan

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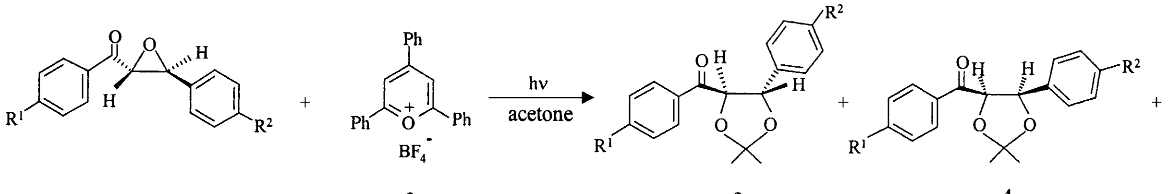
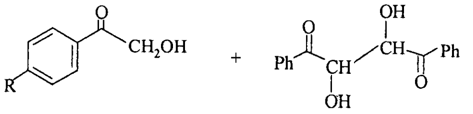
Results and Discussion

Irradiation of α-epoxyketones **1a**–**f** and the photocatalyst 2,4,6-triphenylpyrylium tetrafluroborate (**2**) in a molar ratio of 10:1 in acetone at 400 nm resulted in an opening of the epoxide ring and formation of 1,3-dioxolanes **3a**–**e** and **4a**–**f** as major products besides alcoholic products **5a**,**b** and **6**.



1 **2** **3** **4**

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	OCH_3	OCH_3



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a: $R = CH_3$; **b**: $R = OCH_3$

6

IR and ^{1}H NMR data gave useful information for the structural assignment of the photoproducts. The IR spectra of 1,3-dioxolanes **3a**–**e** and **4a**–**f** showed an increase of aliphatic CH-stretching due to addition of acetone. A shift of the carbonyl group to higher frequency due to loss of epoxide ring strain after ring opening is also observed (Table 1).

The ^{1}H NMR spectra showed two singlets for the methyl groups and an AB system for the hydrogens on the dioxolane ring. The stereochemical assignment of the isomeric dioxolanes was achieved on the following basis:

i) The anisotropic effects of both aromatic rings on one of the methyl groups in the *cis*-products **4a**–**f** causes a shielding of its protons which therefore appear at higher fields in comparison to the other methyl group [11]. The consequence of this phenomenon is that the difference between the chemical shifts of the methyl groups in the *cis*-products **4a**–**f** is greater than that in the *trans*-products **3a**–**e**.

Table 1. Comparison of the IR data of **1a**–**f** with those of **3a**–**e** and **4a**–**f** (ν(C=O)/cm^{-1})

	1	**2**	**3**
a	1670	1690	1695
b	1660	1684	1685
c	1665	1678	1685
d	1660	1688	1688
e	1665	1680	1685
f	1645	–	1656

ii) The chemical shifts for 4-H and 5-H of **4a**–**f** (*cis*-products) are closer to each other in comparison to those of **3a**–**e** (*trans*-products). Semiempirical PM3 calculations on both isomers showed that 5-H is located in the plane of the phenyl ring, whereas 4-H lies parallel to the phenyl ring of the benzoyl moiety (Fig. 1). This causes a deshielding of 5-H and shielding of 4-H, respectively.

iii) According to the *Karplus-Conroy* equation [12, 13] and using the *Karplus* diagram [14], a larger coupling constant is expected for 4-H and 5-H in the *cis*-products **4a**–**f**. The results are summarized in Table 2.

Formations of the alcoholic products **5a**,**b** and **6** has not been observed upon photocatalytic ring opening of **1a**–**f** in methanol [10] or by BF_3 catalyzed ring opening of **1a**,**b**,**d** in acetone so far [15]. IR data, ^{1}H NMR spectra, and a

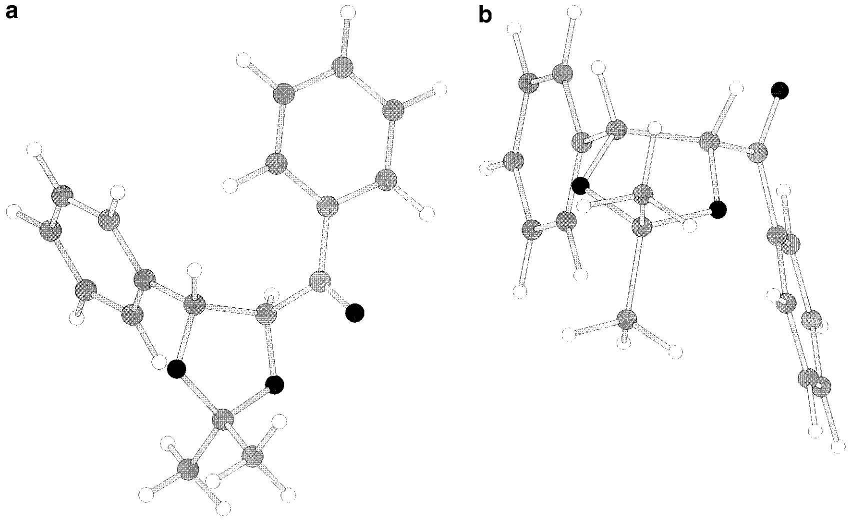


Fig. 1. Optimized structures of **3a** (a) and **4a** (b) from PM3 calculations

Table 2. Structurally relevant ^{1}H NMR chemical shifts (δ/ppm) and ^{1}H–^{1}H couplings J/Hz of **3a**–**e** and **4a**–**f**

	δ_A 4-H	δ_B 5-H	J_{AB}	CH_3	
3a	4.93	5.51	7.3	1.42	1.61
4a	5.48	5.75	8.2	1.57	1.81
3b	4.91	5.39	7.3	1.40	1.59
4b	5.45	5.80	7.6	1.49	1.79
3c	4.90	5.42	7.3	1.42	1.60
4c	5.48	5.74	7.6	1.52	1.80
3d	5.20	5.51	7.2	1.43	1.60
4d	5.47	5.73	7.6	1.52	1.79
3e	5.18	5.47	7.1	1.42	1.59
4e	5.49	5.72	7.4	1.53	1.82
4f	4.89	5.35	7.6	1.44	1.60

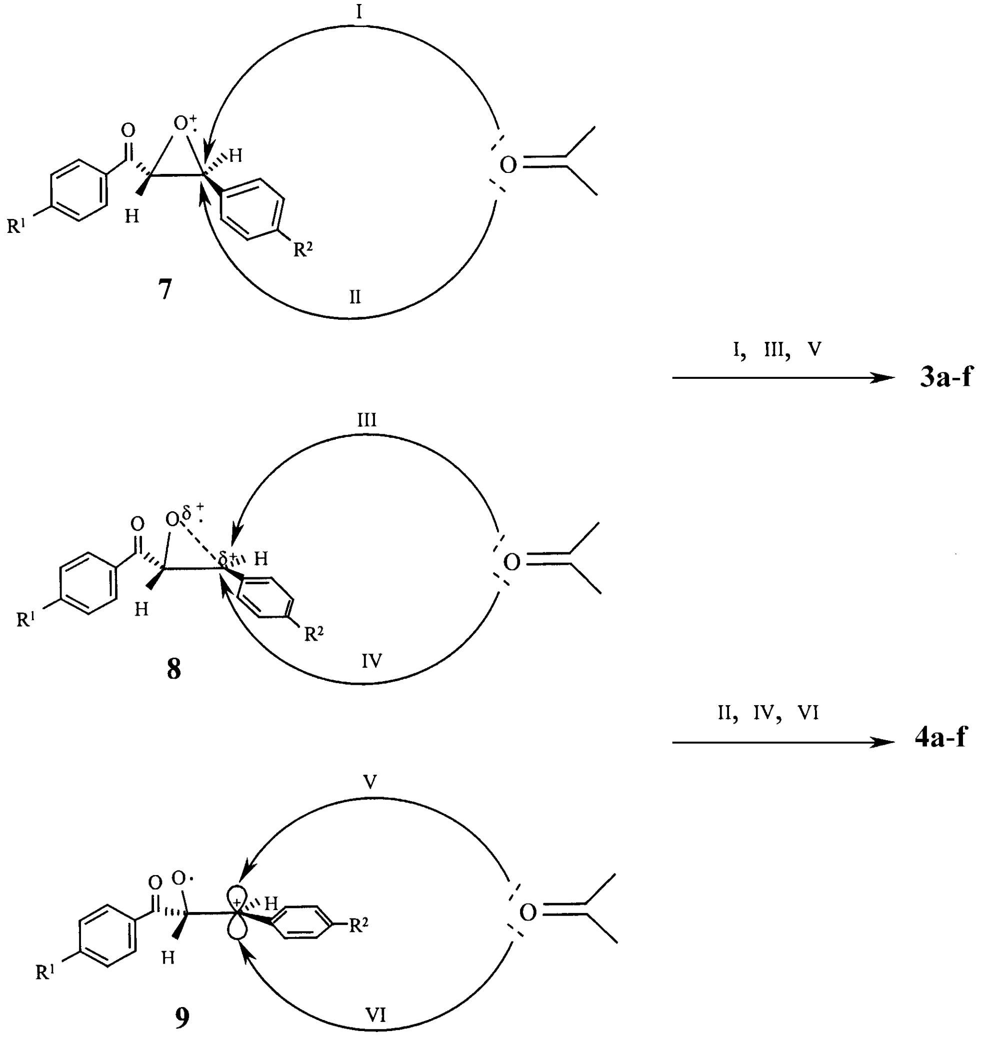
Table 3. Photochemical reactions of **1a–f** in acetone catalyzed by **2**[a]

Compound	Irradiation time/h[b]	Product (yield/%)[c]			
		Dioxolanes			Alcohol
		trans	*cis*	ratio **4**/**3**	
1a	10	**3a** (14)	**4a** (23)	1.64	**6** (30)
1b	4	**3b** (10)	**4b** (28)	2.80	**6** (28)
1c	9	**3c** (11)	**4c** (24)	2.18	**5a** (41)
1d	4	**3d** (11)	**4d** (29)	2.64	**6** (21)
1e	10	**3e** (8)	**4e** (27)	3.37	**5b** (42)
1f	4	–	**4f** (23)	–	**5b** (38)

[a] Molar ratio of **1a–f**:**2** = 10:1, [**1a–f**] = 0.04 *M*, [**2**] = 0.004 *M*; [b] the times refer to total disappearance of starting **1a–f**; [c] isolated yield

comparison of their melting points with reported data supported the formation of these products. It should be mentioned that the formation of **3f** has not been observed, but the conversion of small amount of **1f** to its precursor (corresponding chalcone) was noticed during the reaction.

We have proposed earlier a complete mechanism for the ring opening of **1a**–**f** in methanol [10]. Selective excitation of the photocatalyst **2** in the presence of **1a**–**f** ($\lambda \geq 400$ nm) followed by electron transfer from the latter to photoexcited **2** leads probably to the formation of three different radical cations **7**–**9** which should be considered for the nucleophilic attack of acetone and the formation of dioxolanes. It should be mentioned that irradiation of **1a**–**f** in the absence of **2** at $\lambda \geq 400$ nm in acetone does not result in the formation of any products. The results presented in Table 3 indicate that the irradiation time for total consumption of **1a**–**f** is directly related to the extent of electron donating ability of **1a**–**f** towards photoexcited **2**. Furthermore, the electron donating character of **1a**–**f** affects not only the rate of the ring opening; the ratio of diastereomeric dioxolanes is also dependent on the location of the additional substituent on the parent molecule **1a**. Whereas the methyl or methoxy groups in the *para* position of the phenyl ring (**1b** or **1d**) increase the rate of the ring opening (shortening of the irradiation time); the same substituent on the benzoyl group (**1c** or **1d**) has a smaller effect. The formation of the *cis*-1,3-dioxolanes **4a**–**f** is explained either by nucleophilic attack of acetone to the intermediates **7** or **8** from the opposite side to the leaving group (oxygen atom of the epoxide ring; S_N2 mechanism, paths II and IV) or to the intermediate **9** from the bottom side (path VI). The observed high diastereoselectivity in this reaction indicates the participation of the intermediate **8** rather than **9**, since the intermediate **8** should be formed better in a aprotic solvent such as acetone. In contrast to these results, we have proposed earlier the involvement of the intermediate **9** in methanol solution because of the non-diastereoselectivity of the reaction [10]. The formation of alcoholic products **5a**,**b** and **6** is explained by C–C bond cleavage. The important point is that when the phenyl group attached to the oxirane ring carries the additional substituent, the formation of diol **6** has been observed; when this substituent is located on the benzoyl group, the formation of the keto-alcohol **5a**,**b** is observed.



Experimental

Melting points were determined with a Stuart Scientific SMP2-apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-435 spectrometer. ^{1}H NMR spectra were measured in $CDCl_3$ solutions containing *TMS* as an internal standard on a Bruker AW 80 spectrometer (80 MHz). Mass spectra were obtained on a MAT 8200 spectrometer. Elemental analyses were performed with a CHN–O-Rapid analyzer; the results agreed favourably with the calculated values. Preparative layer chromatography (PLC) was carried out on $20 \times 20\,\mathrm{cm}^2$ plates coated with a 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 vapour lamp from Narva with cooling of samples in Duran glass by running cold water. The light was passed through a filter solution ($75\,\mathrm{g} \cdot \mathrm{dm}^{-3}$ of $NaNO_2$ and $4.4\,\mathrm{g} \cdot \mathrm{dm}^{-3}$ of $CuSO_4$ in 2.7 *M* NH_4OH) [16] to obtain $\lambda \geq 400\,\mathrm{nm}$ for the selective excitation of **2** and also to prevent the absorption of light by **1a**–**f**.

A solution of 0.8 mmol of **1a**–**f** in $20\,\mathrm{cm}^3$ acetone ($c = 0.04\,M$) and 0.08 mmol of **2** ($c = 0.004\,M$) was irradiated for the time given in Table 3.

Irradiation of 1,3-diphenyl-2,3-epoxy-1-propanone (**1a**; $C_{15}H_{12}O_2$)

PLC, petroleum ether:ethyl acetate = 12:1, two times; zone 1: 31 mg (14%) of **3a**, washed with *n*-pentane, m.p.: 87–89°C (Ref. [15]: 90–91°C).

trans-4-Benzoyl-2,2-dimethyl-5-phenyl-1,3-dioxolane (**3a**; $C_{18}H_{18}O_3$)

IR (KBr): $\nu = 3025–3055, 2890–2990, 1690, 1590\,cm^{-1}$; ^{1}H NMR: $\delta = 1.42$ (s, 3H, CH_3), 1.61 (s, 3H, CH_3), AB-system ($\delta_A = 4.93$, $\delta_B = 5.51$, $|^3J_{AB}| = 7.3$ Hz, 2H, 4-H, 5-H), 7.10–8.00 (m, 10H, aromatic H) ppm; zone 2: 51 mg (23%) of **4a**, recrystallized from *n*-hexane, m.p.: 116–118°C (Ref. [15]: 117–118°C).

cis-4-Benzoyl-2,2-dimethyl-5-phenyl-1,3-dioxolane (**4a**; $C_{18}H_{18}O_3$)

IR (KBr): $\nu = 3030–3060, 2910–2995, 1695, 1595\,cm^{-1}$; ^{1}H NMR: $\delta = 1,57$ (s, 3H, CH_3), 1.81 (s, 3H, CH_3), AB-system ($\delta_A = 5.48$, $\delta_B = 5.75$, $|^3J_{AB}| = 8.2$ Hz, 2H, 4-H, 5-H), 7.02 (s, 5H, phenyl ring), 7.15–7.55 (m, 5H, benzoyl group) ppm; zone 3: 64 mg (30%) of **6**, recrystallized from ethanol/ether, m.p.: 71–73°C (Ref. [17]: 73–74°C).

1,2-Dibenzoyl-1,2-ethanediol (**6**; $C_{16}H_{14}O_4$)

IR (KBr): $\nu = 3360–3420, 3050, 2850–2930, 1690, 1680, 1595\,cm^{-1}$; ^{1}H NMR: $\delta = 3.50$ (br s, 2H, OH), 4.80 (s, 2H, CH), 6.90–8.10 (m, 10H, aromatic H) ppm.

Irradiation of 3-p-methylphenyl-1-phenyl-2,3-epoxy-1,3-propanone (**1b**; $C_{16}H_{14}O_2$)

PLC, petroleum ether:ethyl acetate = 12:1, two times; zone 1: 23 mg (10%) of **3b**, washed with ether, m.p.: 45–48°C (Ref. [15]: 47–48°C).

trans-4-Benzoyl-2,2-dimethyl-5-p-methylphenyl-1,3-dioxolane (**3b**; $C_{19}H_{20}O_3$)

IR (KBr): $\nu = 3040, 2860–2995, 1684, 1595\,cm^{-1}$; ^{1}H NMR: $\delta = 1.40$ (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), AB-system ($\delta_A = 4.91$, $\delta_B = 5.39$, $|^3J_{AB}| = 7.3$ Hz, 2H, 4-H, 5-H), 7.00–7.98 (m, 9H, aromatic H) ppm; zone 2: 66 mg (28%) of **4b**, recrystallized from *n*-pentane, m.p.: 147–149°C (Ref. [15]: 148–149°C).

cis-4-Benzoyl-2,2-dimethyl-5-p-methylphenyl-1,3-dioxolane (**4b**; $C_{19}H_{20}O_3$)

IR (KBr): $\nu = 3040, 2860–2990, 1685, 1590\,cm^{-1}$; ^{1}H NMR: $\delta = 1.49$ (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), AB-system ($\delta_A = 5.45$, $\delta_B = 5.80$, $|^3J_{AB}| = 7.6$ Hz, 2H, 4-H, 5-H), 6.65–7.55 (m, 9H, aromatic H) ppm; zone 3: 60 mg (28%) of **6**, recrystallized from ethanol/ether, m.p.: 71–73°C (Ref. [17]: 73–74°C).

Irradiation of 1-p-methylphenyl-3-phenyl-2,3-epoxy-1-propanone (**1c**; $C_{16}H_{14}O_2$)

PLC, petroleum ether:ethyl acetate = 12:1, two times; zone 1: 26 mg (11%) of **3c**, washed with *n*-pentane/ether, m.p.: 82–83°C.

trans-2,2-Dimethyl-4-p-methylbenzoyl-5-phenyl-1,3-dioxolane (**3c**; $C_{19}H_{20}O_3$)

IR (KBr): $\nu = 3040, 2850–2995, 1678, 1610\,cm^{-1}$; ^{1}H NMR: $\delta = 1.42$ (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), AB-system ($\delta_A = 4.90$, $\delta_B = 5.42$, $|^3J_{AB}| = 7.3$ Hz, 2H, 4-H, 5-H), AB-system

($\delta_A = 7.10$, $\delta_B = 7.85$, $|^3J_{AB}| = 7.7$ Hz, 4H, aromatic H), 7.30 (bs, 5H, aromatic H) ppm; EI-MS (70 eV, 50°C): m/z (%) = 238 [M^+–CH_3COCH_3] (21), 190 [M^+–C_6H_5CHO] (32), 177 [M^+–$CH_3C_6H_4CO$] (49), 119 [$CH_3C_6H_4CO^+$] (100), 91 [$C_7H_7^+$] (86), 77 [$C_6H_5^+$] (32); zone 2: 56 mg (24%) of **4c**, washed with *n*-pentane/ether, m.p.: 132–133°C.

cis-2,2-Dimethyl-4-p-methylbenzoyl-5-phenyl-1,3-dioxolane (**4c**; $C_{19}H_{20}O_3$)

IR (KBr): $\nu = 3045$, 2900–2995, 1685, 1610 cm^{-1}; ^{1}H NMR: $\delta = 1.52$ (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), AB-system ($\delta_A = 5.48$, $\delta_B = 5.74$, $|^3J_{AB}| = 7.6$ Hz, 2H, 4-H, 5-H), AB-system ($\delta_A = 6.90$, $\delta_B = 7.35$, $|^3J_{AB}| = 7.7$ Hz, 4H, aromatic H), 6.98 (s, 5H, aromatic H) ppm; EI-MS (70 eV, 50°C): m/z (%) = 281 [M^+–CH_3] (0.3), 238 [M^+–CH_3COCH_3] (21), 190 [M^+–C_6H_5CHO] (8), 177 [M^+–$CH_3C_6H_4CO$] (12), 119 [$CH_3C_6H_4CO^+$] (100), 91 [$C_7H_7^+$] (37), 77 [$C_6H_5^+$] (3); zone 3: 64 mg (41%) of **5a**, recrystallized from ethanol/ether, m.p.: 87–89°C (Ref. [18]: 90°C).

p-Methylbenzoylmethanol (**5a**; $C_9H_{10}O_2$)

IR (KBr): $\nu = 3350$–3410, 3050, 2990, 1679, 1610 cm^{-1}; ^{1}H NMR: $\delta = 2.39$ (s, 3H, CH_3), 3.26 (br s, 1H, OH), 4.79 (s, 2H, CH_2), AB-system ($\delta_A = 7.22$, $\delta_B = 7.77$, $|^3J_{AB}| = 7.5$ Hz) ppm.

Irradiation of 3-p-methoxyphenyl-1-phenyl-2,3-epoxy-1-propanone (**1d**; $C_{16}H_{14}O_3$)

PLC, petroleum ether:ethyl acetate = 10:1, two times; zone 1: 28 mg (11%) of **3d**, washed with *n*-pentane/ether, m.p.: 43–47°C (Ref. [15]: 47–48°C).

trans-4-Benzoyl-5-p-methoxyphenyl-2,2-dimethyl-1,3-dioxolane (**3d**; $C_{19}H_{20}O_4$)

IR (KBr): $\nu = 3060$, 2840–2990, 1688, 1616, 1595 cm^{-1}; ^{1}H NMR: $\delta = 1.43$ (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), AB-system ($\delta_A = 5.20$, $\delta_B = 5.51$, $|^3J_{AB}| = 7.2$ Hz, 2H, 4-H, 5-H), AB-system ($\delta_A = 6.94$, $\delta_B = 7.29$, $|^3J_{AB}| = 8.2$ Hz, 4H, aromatic H), 7.40–8.00 (m, 5H, aromatic H) ppm; zone 2: 74 mg (29%) of **4d**, recrystallized from *n*-hexane, m.p.: 127–129°C.

cis-4-Benzoyl-5-p-methoxyphenyl-2,2-dimethyl-1,3-dioxolane (**4d**; $C_{19}H_{20}O_4$)

IR (KBr): $\nu = 3010$, 2860–2950, 1688, 1620 cm^{-1}; ^{1}H NMR: $\delta = 1.52$ (s, 3H, CH_3), 1.79 (s, 3H, CH_3), 3.62 (s, 3H, OCH_3), AB-system ($\delta_A = 5.47$, $\delta_B = 5.73$, $|^3J_{AB}| = 7.6$ Hz, 2H, 4-H, 5-H), AB-system ($\delta_A = 6.49$, $\delta_B = 6.98$, $|^3J_{AB}| = 8.2$ Hz, 4H, aromatic H), 7.15–7.55 (m, 5H, aromatic H) ppm; EI-MS (70 eV, 60°C): m/z (%) = 312 [M^+] (3), 254 [M^+–CH_3COCH_3] (29), 176 [M^+–C_6H_5CO–OCH_3] (54), 161 [M^+–C_6H_5CO–OCH_3–CH_3] (47), 149 [M^+–CH_3COCH_3–C_6H_5CO] (23), 105 [$C_6H_5CO^+$] (100), 77 [$C_6H_5^+$] (35); zone 3: 45 mg (21%) of **6**.

Irradiation of 1-p-methylphenyl-3-phenyl-2,3-epoxy-1-propanone (**1e**; $C_{16}H_{14}O_3$)

PLC, petroleum ether:ethyl acetate = 10:1, two times; zone 1:20 mg (8%) of **3e**, viscose oil.

trans-4-p-Methoxybenzoyl-2,2-dimethyl-5-phenyl-1,3-dioxolane (**3e**; $C_{19}H_{20}O_4$)

IR (film): $\nu = 3045$, 2840–2920, 1680, 1598 cm^{-1}; ^{1}H NMR: $\delta = 1.42$ (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), AB-system ($\delta_A = 5.18$, $\delta_B = 5.47$, $|^3J_{AB}| = 7.1$ Hz, 2H, 4-H, 5-H), AB-system ($\delta_A = 6.81$, $\delta_B = 7.90$, $|^3J_{AB}| = 8.1$ Hz, 4H, aromatic H), 7.35 (s, 5H, aromatic H) ppm; EI-MS (70 eV, 150°C): m/z (%) = 254 [M^+–CH_3COCH_3] (92), 177 [M^+–$CH_3OC_6H_4CO$] (23), 135 [$CH_3OC_6H_4$

CO^+] (100), 119 [M^+–$CH_3OC_6H_4CO$–CH_3COCH_3] (14), 107 [$CH_3OC_6H_4^+$] (9), 105 ($C_6H_5CO^+$, 24), 77 ($C_6H_5^+$, 84); zone 2: 68 mg (27%) of **4e**, recrystallized from *n*-hexane, m.p.: 121–123°C.

cis-4-p-Methoxybenzoyl-2,2-dimethyl-5-phenyl-1,3-dioxolane (**4e**; $C_{19}H_{20}O_4$)

IR (KBr): $\nu = 3050$, 2820–2980, 1685, 1600 cm^{-1}; ^{1}H NMR: $\delta = 1.53$ (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 3.74 (s, 3H, OCH_3), AB-system ($\delta_A = 5.49$, $\delta_B = 5.72$, $|^3J_{AB}| = 7.4$ Hz, 2H, 4-H, 5-H), AB-system ($\delta_A = 6.05$, $\delta_B = 7.54$, $|^3J_{AB}| = 8.0$ Hz, 4H, aromatic H), 7.00 (s, 5H, aromatic H) ppm; EI-MS (70 eV, 50°C): m/z (%) = 312 [M^+] (1), 254 [M^+–CH_3COCH_3] (27), 206 [M^+–C_6H_5CHO] (7), 177 [M^+–$CH_3OC_6H_4CO$] (12), 135 [$CH_3OC_6H_4CO^+$] (100), 119 [M^+–$CH_3OC_6H_4CO$–CH_3COCH_3] (50), 107 [$CH_3OC_6H_4^+$] (8), 77 [$C_6H_5^+$] (14); zone 3: 69 mg (42%) of **5b**, recrystallized from ether/ethanol, m.p.: 98–100°C (Ref. [19]: 100°C).

p-Methoxybenzoylmethanol (**5b**; $C_9H_{10}O_3$)

IR (KBr): $\nu = 3380$, 1675, 1600 cm^{-1}; ^{1}H NMR: $\delta = 3.57$ (br s, 1H, OH), 3.80 (s, 3H, OCH_3), 4.74 (s, 2H, CH_2), AB-system ($\delta_A = 6.91$, $\delta_B = 7.87$, $|^3J_{AB}| = 8.2$ Hz, 4H, aromatic H) ppm.

Irradiation of 1,3-di-(p-methoxyphenyl)-2,3-epoxy-1-propanone (**1f**; $C_{17}H_{16}O_4$)

PLC, petroleum ether:ethyl acetate = 10:1, two times; zone 1: 57 mg (23%) of **4f**, yellowish viscose oil.

cis-4-(p-Methoxybenzoyl)-5-methoxyphenyl-2,2-dimethyl-1,3-dioxolane (**4f**; $C_{20}H_{22}O_5$)

IR (film): $\nu = 3050$, 2830–2920, 1656, 1594 cm^{-1}; ^{1}H NMR: $\delta = 1.44$ (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 3.74 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), AB-system ($\delta_A = 4.89$, $\delta_B = 5.35$, $|^3J_{AB}| = 7.6$ Hz, 2H, 4-H, 5-H), 6.68–7.98 (m, 8H, aromatic H) ppm; EI-MS (70 eV, 50°C): m/z (%) = 284 [M^+–CH_3COCH_3] (94), 269 [M^+–CH_3COCH_3–CH_3] (5), 177 [M^+–CH_3COCH_3–$CH_3OC_6H_4$] (23), 149 [M^+–CH_3COCH_3–$CH_3OC_6H_4CO$] (81), 135 [$CH_3OC_6H_4CO^+$] (100), 121 [$CH_3OC_6H_4CH_2^+$] (71), 107 [$CH_3OC_6H_4^+$] (47), 92 [$C_6H_5O^+$] (51); zone 2: 63 mg (38%) of **5b**.

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