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1-Oxoindan-2-yl and 1,3-dioxoindan-2-yl esters as photoremovable protecting groups

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Abstract

1-Oxoindan-2-yl and 1,3-dioxoindan-2-yl carboxylic acid esters react with an excess of hydrogen atom or electron donors to release the corresponding acids, in addition to indan-1-one and indan-1,3-dione, respectively, as by-products. The maximum degradation quantum yields of 1-oxoindan-2-yl esters in H-donating propan-2-ol were found to approach 10, indicating that a chain reaction process, involving hydrogen transfer from the ketyl radical intermediates formed from an excited ester by hydrogen abstraction from an alcohol, participates. Such a cleavage mechanism parallels that observed earlier in photolysis of phenacyl esters. The corresponding 4,7-dimethyl substituted derivatives showed no contribution of the photoenolization mechanism apparently because of electronic and geometric reasons. Both 1-oxoindan-2-yl and 1,3-dioxoindan-2-yl chromophores are proposed to be utilized as photoremovable protecting groups in applications when higher concentrations of the hydrogen/electron donors are experimentally feasible.

Keywords: Photochemistry; Hydrogen abstraction; Electron transfer; Indanone; Indandione; Carboxylic acid esters

1. Introduction

Photoremovable protecting groups (PPGs) have found applications in various fields including organic synthesis, biochemical and biological studies, photolithography, or combinatorial chemistry [1–4]. α-Substituted alkylaryl ketone chromophores, including 4-hydroxyphenacyl [5–8], 4-methoxyphenacyl [9], 2-alkylphenacyl [10–14], pyridacyl [15], phenacyl [16,17], or benzoin [18,19], have already been successfully utilized as PPGs. These compounds undergo different cleavage mechanisms and give various reaction side-products. Simple α-substituted phenacyl derivatives are, for example, reductively cleaved to yield acetophenone and the corresponding deprotected functionality (HX) upon irradiation in the presence of H-atom (Scheme 1) [16] or electron (Scheme 2) [17,20] donors. In contrast, α-substituted 2-alkylphenacyl compounds can release molecules thanks to a photoenolization reaction via the singlet or triplet excited states and the corresponding photoenol intermediates (Scheme 3) [13,21].

In this work, 1-oxoindan-2-yl (**1**) and 1,3-dioxoindan-2-yl (**2**) chromophores were studied as potential photoremovable protecting groups for carboxylic acids. Their unsubstituted (**1a**,**b**; **2a**) or 4,7-dimethyl (**1c**,**d**; **2b**) derivatives (Scheme 4) can be considered as phenacyl or *o*-alkylphenacyl moiety analogues, possessing a rigid cyclopentane(di)one rings. The synthesis of these compounds, their photochemical reactivity, and mechanistic considerations are reported here.

2. Results and discussion

This research was initiated by our effort to improve spectral characteristics of a phenacyl photoremovable protecting group by constraining the phenylcarbonyl moiety geometry and by introducing an additional carbonyl group being in conjugation with the phenyl ring. The UV spectra of selected oxoindanyl and dioxoindanyl esters, compared to phenacyl benzoate, in propan-2-ol are portrayed in Fig. 1. In general, all derivatives absorb over 350 nm. It has been shown earlier that both S_{n,π^*} (the lowest singlet excited state) and S_{π,π^*} energy levels decrease in simple indan-1,3-dione compared to indan-1-one [22]. Indeed, the corresponding absorption bands in compounds **2a**,**b** are bathochromically shifted and tail toward the visible part of the

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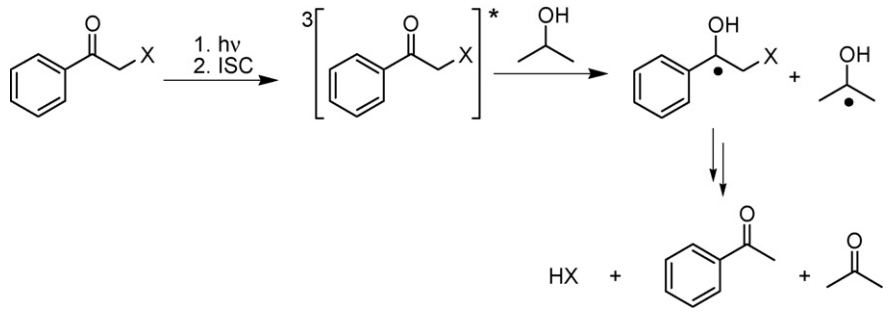
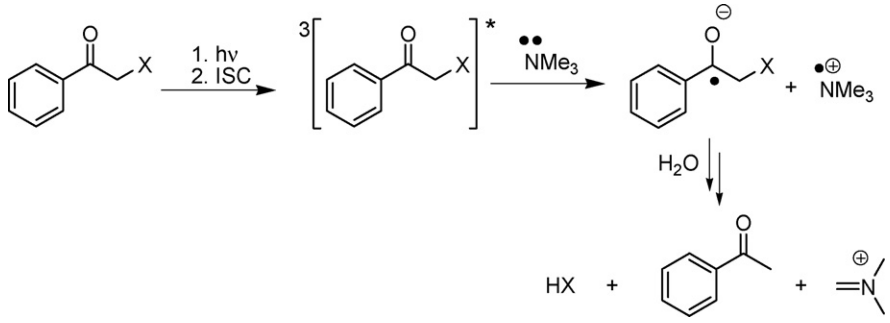
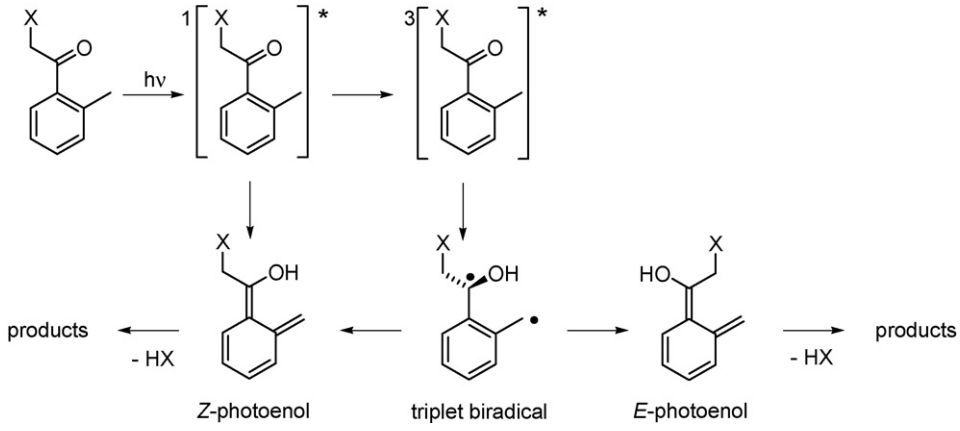


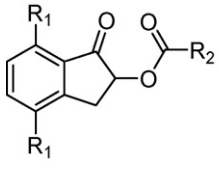
Scheme 1. Photocleavage of the phenacyl compounds in the presence of hydrogen donors (e.g., propan-2-ol).



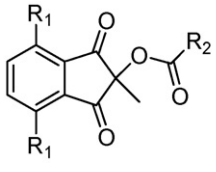
Scheme 2. Photocleavage of the phenacyl compounds in the presence of electron donors (e.g., trimethylamine).



Scheme 3. Photoenolization as a tool to release protected moieties HX (a general scheme).



1a: R_1 = H; R_2 = CH_3
1b: R_1 = H; R_2 = Ph
1c: R_1 = CH_3; R_2 = CH_3
1d: R_1 = CH_3; R_2 = Ph



2a: R_1 = H; R_2 = Ph
2b: R_1 = CH_3; R_2 = CH_3

Scheme 4.

spectrum. While the n,π* bands in both compounds have the same shape and intensity ($\lambda_{max}^{\mathbf{2a,b}} \sim 370$ nm), the π,π* band is bathochromically shifted in case of the 4,7-dimethyl derivative ($\lambda_{max}^{\mathbf{2a}} = 302$ nm; $\lambda_{max}^{\mathbf{2b}} = 321$ nm), in the same way as observed in indan-1,3-dione compared to indan-1-one [23]. The steric effect of an *ortho* alkyl group is opposed by a more dominant electronic effect caused by increased polarizability in a direction transverse to the ring-carbonyl axis [23]. According to the NMR data, there is no apparent enolization in **1c**,**d** or **2b** in propan-2-ol.

Exhaustive (preparative) irradiation of **1b**,**d** and **2a**,**b** derivatives was performed in order to determine the extent of carboxylic acid release under different reaction conditions. The compounds were photostable in acetonitrile, the solvent which is incapable of efficient H-atom or electron donation. In contrast,

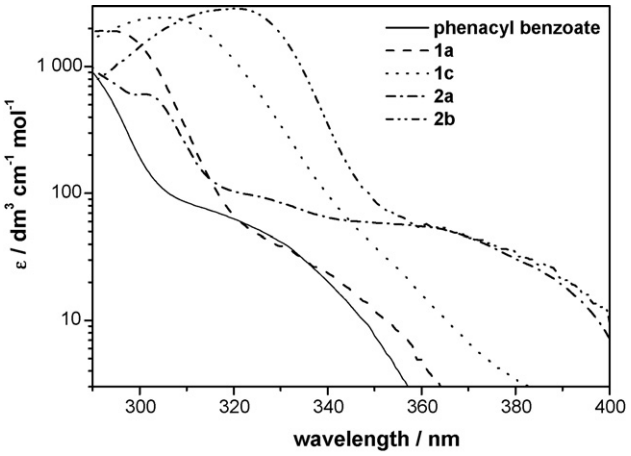
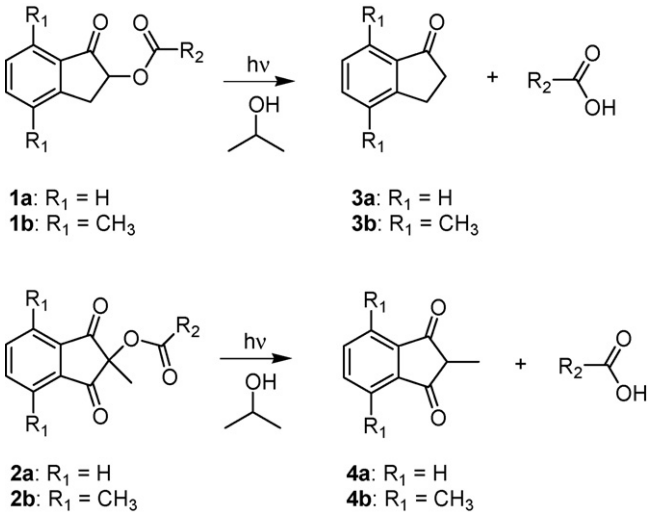


Fig. 1. Absorption spectra of phenacyl benzoate and the starting compounds (**1a**,**b** and **2a**,**b**). The *Y*-axis is shown in the logarithmic scale.



Scheme 5.

they released the acid in high chemical yields when irradiated in the presence of propan-2-ol or an amine (Table 1), while the corresponding indanones **3a**,**b** or indandiones **4a**,**b** were obtained as the major side-products (Scheme 5). However, **3** and **4** were produced exclusively only at very low conversions; additional (secondary) unidentified side-products appeared upon exhaustive irradiation (*vide infra*).

The quantum yields of the ester **1a**–**d** and **2a**,**b** consumption ($\Phi_{consumption}$) and the corresponding indanone/indandione or acid formation (Φ_{ketone}; Φ_{RCOOH}) in neat propan-2-ol or acetonitrile are shown in Table 2. While the $\Phi_{consumption}$ values are very high for **1a** and **1b**, almost approaching 20 in the presence of pyridine, photodegradation of other compounds (**1c**,**d** and **2a**,**b**) was considerably less efficient ($\Phi_{consumption}$ = 0.6–2.1). As expected, photolysis of both **1d** and **2b** in acetonitrile was completely inefficient. There is an apparent discrepancy between the quantum yield values, $\Phi_{consumption}$ and Φ_{ketone}, in most cases, while those of the ester depletion efficiency and benzoic acid formation are in agreement. The same material imbalance was, nevertheless, observed for phenacyl and pyridacyl esters in alcohols [15], suggesting that secondary photochemical processes must be responsible for the primary products degradation.

Falvey and Banerjee [16] have proposed a mechanism of phenacyl esters cleavage in the presence of H-atom donors. It was suggested that two distinct ketyl radicals are initially formed and that an intermediate (not shown) is produced by their mutual recombination. We have recently reported that the reductive cleavage of phenacyl esters in the presence of H-atom donors proceeds via a radical chain mechanism to some extent, because the quantum yields exceed the unity [15]. According to this research, a radical coupling between ketyl radicals, both formed from the excited ester by hydrogen abstraction from an

Table 1
Irradiation of oxoindan-2-yl and dioxoindan-2-yl esters[a]

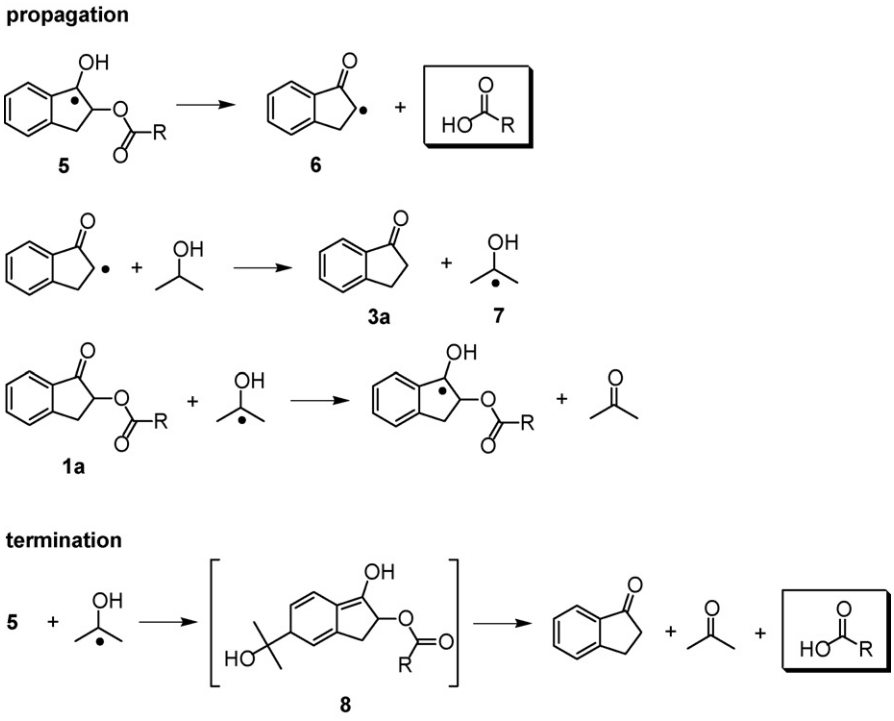
Ester	Solvent (conditions)	Yield of acid release[b]
1b	Acetonitrile	No reaction
	Propan-2-ol	93%[c]
1d	Acetonitrile	No reaction
	Propan-2-ol	91% [c]
2a	Propan-2-ol	83%[c]
	Acetonitrile (2×10^{-2} M aniline)	90%[c]
	Acetonitrile (2×10^{-2} M triethyl amine)	92%[c]
2b	Acetonitrile	Traces only[d]

[a] Esters ($c = 6 \times 10^{-3}$ M) were irradiated by multi-wavelength radiation through a Pyrex filter (>80 nm) for 20–60 min; the samples were degassed prior irradiation by purging with Ar.
[b] Determined by GC.
[c] Benzoic acid formation.
[d] Acetic acid formation.

Table 2
Photochemistry of **1a**–**d** and **2a**,**b**[a]

Ester	Solvent (conditions)	$\Phi_{consumption}$[b]	Φ_{ketone}[c]	Φ_{RCOOH}[d]
1a	Propan-2-ol	6.8	4.7	n.e.[e]
	Propan-2-ol (0.2 M pyridine)	19.1	13.4	n.e.[e]
1b	Propan-2-ol	12.5	10.0	11.5
	Propan-2-ol (0.2 M pyridine)	15.2	14.1	14.3
1c	Propan-2-ol	1.4	0.62	n.e.[e]
	Propan-2-ol (0.2 M pyridine)	2.1	0.82	n.e.[e]
1d	Acetonitrile	n.d.[f]	n.d.[f]	n.d.[f]
	Propan-2-ol	1.1	0.65	1.1
	Propan-2-ol (0.2 M pyridine)	1.6	1.1	1.4
2a	Propan-2-ol	0.58	n.d.[f]	0.45
2b	Acetonitrile	<0.05	n.d.[f]	n.e.[e]
	Propan-2-ol	0.93	n.d.[f]	n.e.[e]

[a] Esters ($c = 6 \times 10^{-3}$ M) were irradiated at 313 nm and 20 °C; the samples were degassed prior irradiation by purging with Ar. The conversion was kept below 10% in order to avoid the photoproduct interference. The values were obtained from at least three measurements; the relative standard deviation was always below 6%.
[b] The quantum yields of the ester consumption.
[c] The quantum yield of the corresponding indanone or indandione formation.
[d] The quantum yield of the carboxylic acid formation.
[e] Not evaluated.
[f] Not detected.



Scheme 6. Radical propagation and termination steps in the photolysis of **1a**.

alcohol (a H-atom donor), is accompanied by the elimination of benzoic acid from the ester ketyl radical itself. The magnitude of a radical chain process is then dependent on the efficiency of consecutive steps that produce free radicals capable of a subsequent ester reduction. Correspondingly, 1-oxoindan-2-yl and 1,3-dioxoindan-2-yl esters (e.g., **1a** in Scheme 6) can be degraded in propan-2-ol via a similar free radical chain cleavage mechanism, in which the propagation sequence is triggered by elimination of a carboxylic acid from the ketyl radical **5** before collapsing into a putative [16] recombination intermediate **8**, terminating the chain process. In the key step, the resulting radical **6** removes hydrogen atom from alcohol to give rise indan-1-one (**3a**) and the ketyl radical **7**. The transfer of hydrogen atom from **7** (a chain carrier) to the ground state ester **1a** then represents the last step of propagation.

We have already noted that addition of some basic substances, such as pyridine, increases the efficiency of the photocleavage of the phenacyl and pyridacyl esters in alcohols [15]. This effect is attributed to an interaction of a base with the OH group of the ketyl radical (e.g., **5** in Scheme 6), which consequently enhances the rate of carboxylate elimination. Table 2 shows that the presence of pyridine had an augmentative effect on the quantum yields in all experiments, notably in the case of **1a**. An observation that photocleavage of the esters is only moderately sensitive to the basic additives may indicate that the elimination efficiency of an acid from the corresponding ketyl radicals is already high. Steric hindrance of the *ortho* methyl group in ketyl radicals formed from **1c** and **1d**, somewhat better leaving group ability of benzoic acid (**1b**) compared to acetic acid (**1a**), and electron donating effects of the 4,7-dimethyl substitution may be responsible for the differences in a relative enhancement of the $\Phi_{consumption}$ values in the presence of pyridine.

Falvey and co-workers have studied the effect of various ring substituents on the rate in terms of both the redox potential and the rate of carboxylate elimination from phenacyl esters [17,20]. They argued that the electron withdrawing substituents decreased the rate of the carboxylate elimination, whereas enhanced the ease of the ester reduction. In our work, the esters **2a**,**b** were photolyzed with considerably lower quantum efficiencies compared to **1**. An additional electron accepting carbonyl group must slow down the benzoate release from **2** and, as a result, it diminishes the quantum yield.

The quantum yield values of the **1c**,**d** photodegradation ($\Phi_{degradation}$ = 1.1–2.1; Table 2) in propan-2-ol, albeit considerably lower than in the case of **1a**,**b**, may still indicate a limited participation of a free radical chain mechanism on the photocleavage. The methyl groups adjacent to the carbonyl group in these compounds, but also in **2b**, present a steric obstacle that may slow down the rate of propagation and/or initial H-atom abstraction reaction. It is well known that alkyl phenyl ketones have the lowest n,π* and π,π triplet excited states close in energy (i.e., in thermal equilibrium) and that an electron-releasing substituent such as the 4-methyl group in the aromatic ring of the phenacyl group stabilizes the π,π* triplet, which is far less reactive towards the hydrogen abstraction than the n,π* state [24]. Additionally, n,π* (the lowest state) and π,π* triplet gaps are smaller in both **3a** and **4a** compared to acetophenone [22]. Therefore, if two methyl groups present in **1c**,**d** and **2b** slow down the bimolecular hydrogen abstraction step, the steady-state ketyl **7** concentration will be lower, diminishing, in consequence, the probability of the chain propagation step.

Several research groups have recognized that photoinduced electron transfer reaction may be an important mechanistic approach to PPG release. A reductive cleavage of phenacyl esters can proceed through sensitized reaction, in which the chromophore accepts an electron from an excited-state donor, or through direct reductive cleavage, in which an excited PPG abstracts an electron from an electron donor (such as amine) [20]. Pyrex-filtered irradiation ($\lambda > 280$ nm) of **2a** in the presence of triethyl amine (Table 1), which is transparent in this wavelength range, must release an acid via the latter mechanism. Both mechanistic variations are anticipated when partially absorbing aniline was used [17] (Table 1).

Garcia-Garibay and co-workers have studied intramolecular H-atom abstraction in 4,7-dimethylindan-1-one **3b** at cryogenic conditions or ambient temperature [25]. They found that the indanone does not undergo photoenolization reaction due to large contribution from less reactive π,π* state to the triplet state and large C=O···H–C distance, unfavorable for the transfer. Nevertheless, we have synthesized and studied 4,7-dimethyl-1-oxoindan-2-yl esters **1c**,**d** and 2,4,7-trimethyl-1,3-dioxoindan-2-yl acetate **2b** in order to find whether a structural change in the position **2** or electronic aspects – an additional carbonyl group in indan-1,3-dione causing that the T_{n,π^*}–T_{π,π^*} gap increases again [22] – could trigger the photoenolization process after all. Only involvement of the *Z*-photoenol intermediate (Scheme 3) in the elimination should be possible here because its configuration is locked in the five-membered ring (*E*-photoenol formation from the triplet biradical requires the C–C bond rotation [26]; Scheme 3). Reversible photoenolization of the *o*-methyl ketones can be investigated simply by incorporation of deuterium to the *o*-methyl group while the ketone is irradiated in protic deuterated solvents (e.g., [26,27]). Thus, **3b** as a model compound for **1c** or **1d** was irradiated in CD_3OD and the course of the reaction was followed by ^{1}H NMR. The CH_3 signals in the ^{1}H NMR spectrum were assigned using the HSQC-TOCSY NMR correlations. The irradiation induced intensity decrease and broadening of one of the methyl signals (Fig. 2). Interestingly, the disappearing singlet at $\delta = 2.31$ ppm corresponded to the methyl group in the position **4** (Scheme 7). Neither intensity nor shape of the other signal at $\delta = 2.54$ ppm, assigned to the methyl group in position **7** (*ortho* to the carbonyl), changed during irradiation time that was required for almost complete disappearing of the singlet at $\delta = 2.31$ ppm. It has been shown earlier that photochemical excitation of 3-methylphenyl ketones can induce relatively efficient deuterium exchange ($\Phi \sim 0.1$) of hydrogens in the CH_3 group in the meta position to the carbonyl group [28]. However, the authors claim that reaction took place only in acidic aqueous solutions and that it was not observed in neutral aqueous solutions or in deuterated organic solvents such as CD_3CN. It is possible that similar photochemical activation of *m*-methyl hydrogen atoms for deuterium exchange occurs during irradiation of **3b** in protic solvents in the absence of a strong acid, albeit with much lower efficiency than in its presence. Intermolecular cycloaddition of photoenols with dienophiles can be another experimental evidence that photoenolization occurs [29]. For this work, solutions of 4,7-dimethylindanone or 2-methylacetophenone in acetonitrile, irradiated in the presence of a dienophile (maleic acid anhydride), showed that the former compound exhibited no product formation, while 2-methylacetophenone underwent the expected cycloaddition (apparently with the longer lived *E*-photoenol). Since none of the *o*-methyl derivatives (**1c**,**d**; **2b**) released the corresponding acids upon photolysis in acetonitrile and based on the results observed earlier [25] and in this work, we believe that photoenolization reaction does not occur

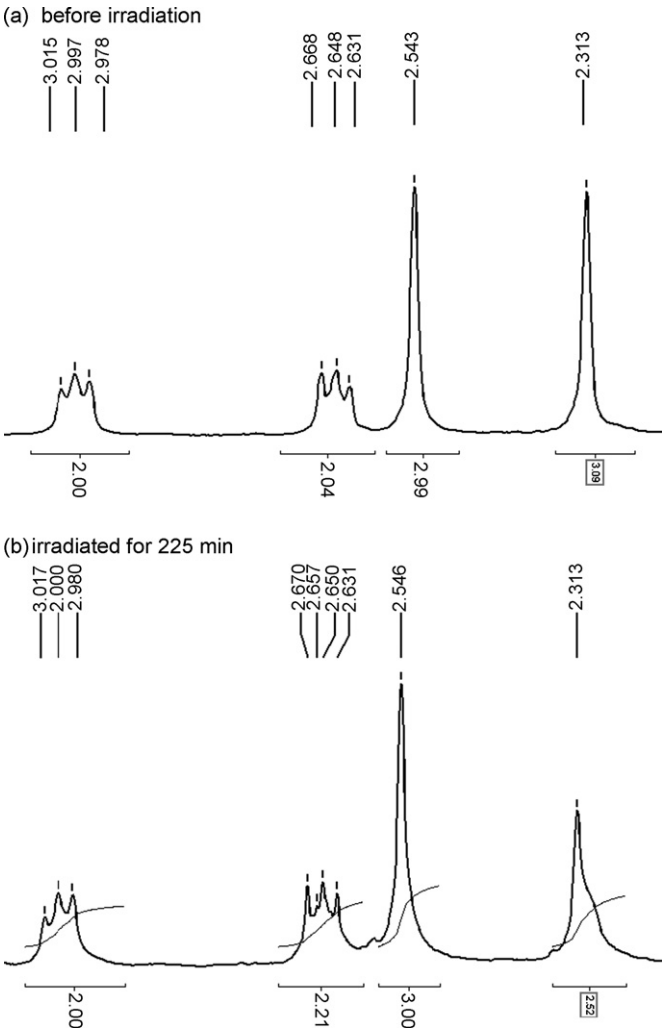
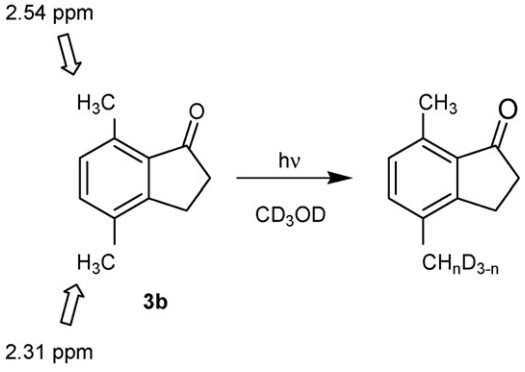


Fig. 2. Irradiation of **3b** in CD_3OD before (a) and after (b) irradiation.



Scheme 7. Photolysis of **3b** in deuterated proton donors.

or that the *Z*-photoenol reketonizes so rapidly that the deuterium exchange or cycloaddition cannot compete. As a result, simple 1-oxoindan-2-yl (**1a**,**b**) and 1,3-dioxoindan-2-yl (**2a**) esters, synthetically more accessible than the corresponding 4,7-dimethyl derivatives, are more rational alternatives in the PPG applications.

In conclusion, this work showed that both 1-oxoindan-2-yl and 1,3-dioxoindan-2-yl chromophores can be utilized as photoremovable protecting groups for carboxylic acids in applications when higher concentrations of the hydrogen (or electron) donors are experimentally feasible. In the presence of an H-atom donor, the cleavage reaction is based on intermolecular hydrogen transfer from the ketyl radical intermediates formed from an excited ester by hydrogen abstraction. The corresponding 4,7-dimethyl substituted derivatives showed no contribution of the photoenolization mechanism because of electronic and geometric reasons. Improved absorption properties of the indan-1,3-dione derivatives compared to indan-1-one derivatives can be beneficial, especially when the presence of other photolabile groups or compounds in the sample is anticipated. When a radical chain mechanism of the photorelease dominates, the carboxylic acid should, however, not contain any potentially chemically interfering groups. Simple conventional or even photochemical [27] synthesis of the starting indan(di)ones is another apparent advantage.

3. Experimental part

3.1. Methods

NMR spectra were recorded on a Bruker 300 MHz spectrometer. ^{1}H and ^{13}C NMR data were measured in $CDCl_3$ with tetramethylsilane as an internal standard or in CD_3OD. Gas chromatography was performed on a Shimadzu GC-2010 gas chromatograph equipped with a SPIRA KI 8 column (15 m, 5% diphenyldimethylsiloxane). UV spectra were obtained on a Shimadzu UV-1601 instrument with matched 1.0-cm quartz cells.

3.2. Materials

Acetonitrile (99.5%), ethyl acetate (99.7%), hexane (99%), propan-2-ol (99.8%) were purchased from Penta and purified by distillation. Acetic acid (99.5%; Penta), indan-1-one (98%; Fluka), 3-chloropropionyl chloride (98%; Fluka), bromine (98%; Fluka), benzoic acid (98%; Lachema), sodium formate (98%; Lachema), lead tetraacetate (95%; Aldrich), 1,3-dicyclohexylcarbodiimide (DCC; 99%; Aldrich); 4-(dimethylamino)pyridine (DMAP; 99%; Aldrich), ninhydrin (97%; Aldrich), ethylene glycol (98%; Fluka), *p*-toluenesulfonic acid (99%; Merck), valerophenone (99%; Aldrich), maleic acid anhydride (98%; Aldrich), and hexadecane (98%; Merck) were used as received.

Malonyl dichloride was prepared from malonic acid and thionyl chloride [30] and purified by distillation under reduced pressure, bp 45–47 °C at 11–15 Torr.

4,7-Dimethylindan-1-one was prepared from *p*-xylene and 3-chloropropionyl chloride according to literature [31].

4,7-Dimethylindan-1,3-dione was prepared from *p*-xylene and malonyl dichloride. Malonyl dichloride (10.5 g, 74.5 mmol) was slowly added to a vigorously stirred mixture of *p*-xylene (9.5 g, 91.3 mmol), 35 ml of cyclohexane, and $AlCl_3$ (30 g, 225 mmol) at 0 °C. The resulting brown solid was carefully triturated and heated to 50 °C for 3 h. Water (100 ml) and ice (100 g) were then added and the aqueous layer was extracted three times with dichloromethane. The organic solution was dried with $MgSO_4$ and evaporated under reduced pressure. The crude product was recrystallized from benzene to afford 7.0 g (54%) of pure product. ^{1}H NMR (δ, ppm): 1.30 (d, J = 7.6 Hz, 3H), 2.61 (s, 6H), 2.91 (q, J = 7.6 Hz, 1H), 7.36 (s, 2H). ^{13}C NMR (δ, ppm): 10.5 (CH_3), 18.5 (CH_3), 49.5 (CH), 136.0 (C_q), 137.2 (CH), 139.5 (C_q), 202.5 (C_q).

2,4,7-Trimethylindan-1,3-dione was synthesized by methylation of 4,7-dimethylindan-1,3-dione with methyl iodide in the presence of potassium *t*-butoxide [32]. The mixture of the starting compound and methylated ketones was separated by column chromatography on silica using CH_2Cl_2 as a mobile phase. The yield of 2,4,7-trimethylindan-1,3-dione was 230 mg starting from 1 g of 4,7-dimethylindan-1,3-dione. ^{1}H NMR (δ, ppm): 1.30 (d, J = 7.6 Hz, 3H), 2.61 (s, 6H), 2.91 (q, J = 7.6 Hz, 1H), 7.36 (s, 2H). ^{13}C NMR (δ, ppm): 10.5 (CH_3), 18.5 (CH_3), 49.5 (CH), 136.0 (C_q), 137.2 (CH), 139.5 (C_q), 202.5 (C_q).

1-Oxoindan-2-yl acetate (**1a**), *4,7-dimethyl-1-oxoindan-2-yl acetate* (**1c**), *and 2,4,7-trimethyl-1,3-dioxoindan-2-yl acetate* (**2a**) were prepared by oxidation of the corresponding ketones by lead tetraacetate according to literature [33–35]. **1a**: Yield = 0.79 g starting from 1.04 g of indan-1-one (53%). ^{1}H NMR (δ, ppm): 1.93 (s, 3H), 2.79 (dd, J_1 = 4.8 Hz, J_2 = 16.9 Hz, 1H), 3.38 (dd, J_1 = 8.0 Hz, J_2 = 16.9 Hz, 1H), 5.17 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 7.17 (dd, J = 7.6 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.41 (dd, J = 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H). ^{13}C NMR (δ, ppm): 20.8 (CH_3), 33.4 (CH_2), 74.2 (CH), 124.4 (CH), 127.0 (CH), 128.3 (CH), 134.7 (C_q), 136.0 (CH), 150.7 (C_q), 170.3 (C_q), 200.6 (C_q). MS: 191 (M + 1), 149, 148, 147, 131, 120, 119, 102, 103, 91, 65, 43. **1c**: Yield = 0.82 g starting from 0.89 g of indan-1-one (67%). ^{1}H NMR (δ, ppm): 2.08 (s, 3H), 2.16 (s, 3H), 2.45 (s, 3H), 2.70 (dd, J_1 = 4.6 Hz, J_2 = 6.9 Hz, 1H), 3.36 (dd, J_1 = 16.9 Hz, J_2 = 7.9 Hz, 1H), 5.24 (dd, J_1 = 7.9 Hz, J_2 = 4.6 Hz, 1 H), 6.92 (d, J = 7.6 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H). ^{13}C NMR (δ, ppm): 17.12 (CH_3), 17.58 (CH_3), 20.52 (CH_3), 31.53 (CH_2), 73.88 (CH), 29.61 (CH), 131.51(C_q), 132.53 (C_q), 135.40 (CH), 136.23 (C_q), 149.56 (C_q), 170.14, 201.30. MS: 219 (M + 1), 159, 158, 147, 129, 130, 119, 115, 103, 91, 43. **2a**: Yield = 0.25 g starting from 0.28 g of 2,4,7-trimethylindan-1,3-dione (68%). ^{1}H NMR (δ, ppm): 1.47 (s, 3H), 2.08 (s, 3H), 2.64 (s, 6H), 7.43 (s, 2H). ^{13}C NMR (δ, ppm): 18.4 (CH_3), 19.2 (CH_3), 19.8 (CH_3), 79.1 (C_q), 136.1 (C_q), 136.7 (C_q), 137.8 (CH), 169.7 (C_q), 198.2 (C_q). MS: 247, 246 (M +), 205, 204, 161, 133, 132, 104, 103, 43.

1-Oxoindan-2-yl benzoate (**1b**) *and 4,7-dimethyl-1-oxoindan-2-yl benzoate* (**1d**) were prepared from the parent indanones in three steps. The corresponding indanone

(39.6 mmol) was brominated with bromine (6.34 g, 39.7 mmol) in glacial acetic acid (50 ml) at room temperature. After 2 h, the solution in acetic acid was poured on ice, and extracted three times with Et_2O (20 ml). The organic solution was washed with aqueous solution of Na_2CO_3. The extract was dried with $MgSO_4$ and evaporated to give the corresponding brominated indanone in ~90%. 2-Bromoindan-1-one: ^{1}H NMR (δ, ppm): 3.34 (dd, $J_1 = 3.1$ Hz, $J_2 = 18.2$ Hz, 1H), 3.79 (dd, $J_1 = 7.6$ Hz, $J_2 = 18.2$ Hz, 1H), 4.60 (dd, $J_1 = 7.6$ Hz, $J_2 = 3.1$ Hz, 1H), 7.37 (dd, $J_1 = 7.6$ Hz, 1H), 7.40 (d, $J = 7.0$ Hz, 1H), 7.61 (dd, $J_1 = 7.0$ Hz, 1 H), 7.74 (d, $J = 7.6$ Hz, 1 H). ^{13}C NMR (δ, ppm): 37.9 (CH_2), 44.2 (CH), 124.9 (CH), 126.5 (CH), 128.2 (CH), 133.4 (C_q), 136.0 (CH), 151.1 (C_q), 199.6 (C_q). 2-Bromo-4,7-dimethylindan-1-one: ^{1}H NMR (δ, ppm): 2.27 (s, 3H), 2.59 (s, 3H), 3.23 (dd, $J_1 = 3.0$ Hz, $J_2 = 18.2$ Hz, 1H), 3.66 (dd, $J_1 = 7.6$ Hz, $J_2 = 18.2$ Hz, 1H), 4.61 (dd, $J_1 = 7.6$ Hz, $J_2 = 3.0$ Hz, 1H), 7.07 (d, $J = 7.4$ Hz, 1 H), 7.30 (d, $J = 7.4$ Hz, 1 H). ^{13}C NMR (δ, ppm): 17.3 (CH_3), 18.0 (CH_3), 36.4 (CH_2), 44.9 (CH), 130.0 (CH), 130.7 (C_q), 132.6 (C_q), 135.8 (CH), 137.2 (C_q), 150.5 (C_q), 200.5 (C_q).

The following hydrolysis of brominated indanones in boiling aqueous ethanol in the presence of sodium formate according to literature [36] afforded the corresponding 2-hydroxyindanones in ~50% chemical yields. The crude products were purified by column chromatography on silica using Et_2O as a mobile phase. 2-Hydroxyindan-1-one: ^{1}H NMR (δ, ppm): 2.98 (dd, $J_1 = 5.0$ Hz, $J_2 = 16.8$ Hz, 1H), 3.52 (dd, $J_1 = 7.8$ Hz, $J_2 = 16.8$ Hz, 1H), 3.97 (bb, 1H), 4.55 (dd, $J_1 = 7.8$ Hz, $J_2 = 5.0$ Hz, 1H), 7.33 (dd, $J = 7.6$ Hz, 1H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.57 (dd, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 7.6$ Hz, 1H). ^{13}C NMR (δ, ppm): 35.3 (CH_2), 74.1 (CH), 124.4 (CH), 126.8 (CH), 128.0 (CH), 134.2 (C_q), 135.9 (CH), 151.1 (C_q), 207.0 (C_q). 2-Hydroxy-4,7-dimethylindan-1-one: ^{1}H NMR (δ, ppm): 2.25 (s, 3H), 2.52 (s, 3H), 2.77 (dd, $J_1 = 4.6$ Hz, $J_2 = 16.5$ Hz, 1 H), 3.40 (dd, $J_1 = 7.9$ Hz, $J_2 = 16.5$ Hz, 1H), 4.22 (bb, 1H), 4.49 (dd, $J_1 = 7.9$ Hz, $J_2 = 4.6$ Hz, 1H), 6.98 (d, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 1H). ^{13}C NMR (δ, ppm): 17.4 (CH_3), 17.8 (CH_3), 33.5 (CH_2), 74.0 (CH), 129.5 (CH), 131.4 (C_q), 132.8 (C_q), 135.5 (CH), 136.3 (C_q), 150.4 (C_q), 208.2 (C_q).

The title 1-oxoindan-2-yl benzoate (**1b**) and 4,7-dimethyl-1-oxoindan-2-yl benzoate (**1d**) were prepared according to the following procedure. The corresponding 2-hydroxyindanone (2.63 g, 17.8 mmol) was dissolved in dry CH_2Cl_2 (100 ml), then benzoic acid (2.18 g, 17.9 mmol), 4-(dimethylamino)pyridine (DMAP; 0.54 g, 4.4 mmol) and 1,3-dicyclohexylcarbodiimide (DCC; 4.03 g, 19.5 mmol) were added and the mixture was stirred overnight. White precipitate was filtered off, and the solution was washed with aqueous solution of Na_2CO_3, dried with $MgSO_4$, and evaporated under reduced pressure. The ester was purified by column chromatography (silica; hexane-ethyl-acetate (1:1 v/v) mixture as a mobile phase). **1b**: Yield = 2.10 g (47%). ^{1}H NMR (δ, ppm): 3.01 (dd, $J_1 = 4.8$ Hz, $J_2 = 17.2$ Hz, 1H), 3.54 (dd, $J_1 = 7.9$ Hz, $J_2 = 17.2$ Hz, 1H), 5.49 (dd, $J_1 = 4.8$ Hz, $J_2 = 7.9$ Hz, 1H), 7.21–7.29 (m, 4H), 7.38–7.49 (m, 2H), 7.63 (d, $J = 7.6$ Hz, 1H), 7.94 (d, $J = 7.6$ Hz, 2H). ^{13}C NMR (δ, ppm): 33.0 (CH_2), 74.2 (CH), 123.8 (CH), 126.4 (CH), 127.7 (CH), 128.1 (CH), 129.0 (C_q), 129.5 (CH), 133.0 (CH), 134.2 (C_q), 135.5 (CH), 150.1 (C_q), 165.4 (C_q), 199.9 (C_q). MS: 253 ($M+1$), 147, 130, 119, 105, 91, 77. **1d**: Yield = 0.52 g (39%) starting from 0.62 g of the 2-hydroxy-4,7-dimethylindan-1-one. ^{1}H NMR (δ, ppm): 2.29 (s, 3H), 2.62 (s, 3H), 2.98 (dd, $J_1 = 4.6$ Hz, $J_2 = 16.9$ Hz, 1H), 3.62 (dd, $J_1 = 8.2$ Hz, $J_2 = 16.9$ Hz, 1H), 5.60 (dd, $J_1 = 4.6$ Hz, $J_2 = 8.2$ Hz, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.43 (dd, $J_1 = 7.3$ Hz, $J_2 = 7.3$ Hz, 2H), 7.56 (t, $J = 7.3$ Hz, 1 H), 8.10 (d, $J = 7.3$ Hz, 2 H). ^{13}C NMR (δ, ppm): 17.5 (CH_3), 17.9 (CH_3), 32.1 (CH_2), 74.6 (CH), 128.4 (CH), 129.6 (C_q), 130.0 (CH), 131.9 (C_q), 132.9 (C_q), 133.4 (CH), 135.9 (CH), 136.7 (C_q), 149.9 (C_q), 166.2 (C_q), 201.5 (C_q). MS: 281, 280 ($M+$), 159, 158, 147, 105, 91, 77.

Preparation of *2-methyl-1,3-dioxoindan-2-yl benzoate* (**2b**): ninhydrin (5.01 g, 28.1 mmol) was heated with ethylene glycol (4.00 g, 64.4 mmol) in the presence of catalytic amount of *p*-toluenesulfonic acid to yield 1,3-bis(ethylenedioxy)indan-2-one (4.5 g) according to literature [37]. This compound (2.59 g, 10.4 mmol) was dissolved in dry Et_2O (100 ml) and then treated with 2 M solution of CH_3MgI (5.2 ml; 10.4 mmol) in Et_2O. After 1 h water (30 ml) was added and the mixture was extracted three times with Et_2O. The collected extracts were dried with $MgSO_4$ and evaporated under reduced pressure. The crude 2-methyl-1,3-bis(ethylenedioxy)indan-2-ol was subsequently hydrolyzed by boiling in a mixture of water (4 ml), concentrated HCl (4 ml), and acetone (15 ml) for 2 h. The reaction mixture was then poured into saturated aqueous solution of Na_2CO_3 (30 ml) and extracted three times with CH_2Cl_2 (30 ml). The organic solution was evaporated to give 1.19 g (65%) yield of 2-hydroxy-2-methylindan-1,3-one. The title benzoate **2b** was prepared according to the procedure described above for 1-oxoindan-2-yl benzoate in 46% yield (0.87 g). **2b**: ^{1}H NMR (δ, ppm): 1.64 (s, 3H), 7.36 (dd, 2H), 7.51 (dd, 1H), 7.78–7.80 (m, 2H), 7.93–7.99 (m, 4H). ^{13}C NMR (δ, ppm): 18.6 (CH_3), 79.2 (C_q), 123.8 (CH), 127.4 (C_q), 128.5 (CH), 130.1 (CH), 134.0 (CH), 136.2 (CH), 138.3 (C_q), 165.2 (C_q), 196.7 (C_q). MS: 281, 280 ($M+$), 106, 105, 77.

Preparative photolyses were carried out in Pyrex vessels ($\lambda_{irr} > 290$ nm). The samples were purged with argon for 15 min before irradiation, and irradiated with a medium-pressure mercury lamp (400 W; Tesla Co.). The reaction mixtures containing hexadecane as an internal standard were analyzed by GC and the amount of free carboxylic acid was determined.

3.3. Quantum yield measurements

The experiments were carried out on an optical bench consisting of a high-pressure 350 W Hg(Xe) lamp, an Oriel CornerStone 130 1/8 m monochromator with grating 200–1600 nm and a 1-cm quartz cell containing the sample solution (degassed by purging with argon for 15 min before irradiation). The light intensity was monitored by a Si photodiode detector (UV enhanced) with an Oriel OPM multifunction optical power meter controlled by TRACQ32 software. Valerophenone was used as an actinometer [38].

3.4. Irradiation of **3b** in CD_3OD

3b (~30 mg) was dissolved in CD_3OD (1 ml) and the ^1H NMR spectrum were recorded immediately. The solution was kept in dark for 2 h and then the NMR spectrum was taken again with no observable change. The solution was then irradiated with a medium-pressure UV lamp (400 W) through a Pyrex filter ($\lambda > 290$ nm) and the NMR spectra were measured in regular time intervals.

3.5. Irradiation of **3b** or 2-methylacetophenone in the presence of a dienophile

Solutions of 4,7-dimethylindanone or 2-methylacetophenone (0.01 M) in the presence of maleic acid anhydride as a dienophile (0.01 M) in acetonitrile were purged with argon for 15 min and irradiated at $\lambda > 280$ nm for several hours. The reactions were monitored by GC.

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References

[1] M. Goeldner, R.S. Givens, Dynamic Studies in Biology, Wiley-WCH Verlag GmbH & Co. KGaA, Weinheim, 2005.
[2] R.S. Givens, P.G. Conrad, A.L. Yousef, J.-I. Lee, Photoremovable protecting groups, CRC Handbook of Organic Photochemistry and Photobiology, In: W.M. Horspool, F. Lenci (Eds.), Chapter 69 Boca Raton, 2004,p. 1.
[3] C.G. Bochet, J. Chem. Soc., Perkin Trans. 1 (2002) 125.
[4] A.P. Pelliccioli, J. Wirz, Photochem. Photobiol. Sci. 1 (2002) 441.
[5] R.S. Givens, C.H. Park, Tetrahedron Lett. 37 (1996) 6259.
[6] C.H. Park, R.S. Givens, J. Am. Chem. Soc. 119 (1997) 2453.
[7] K. Zhang, J.E.T. Corrie, V.R.N. Munasinghe, P. Wan, J. Am. Chem. Soc. 121 (1999) 5625.
[8] R.S. Givens, J.F.W. Weber, P.G. Conrad, G. Orosz, S.L. Donahue, S.A. Thayer, J. Am. Chem. Soc. 122 (2000) 2687.
[9] W.W. Epstein, M. Garrossian, J. Chem. Soc., Chem. Commun. (1987) 532.
[10] P. Klan, M. Zabadal, D. Heger, Org. Lett. 2 (2000) 1569.
[11] P. Klan, A.P. Pelliccioli, T. Pospisil, J. Wirz, Photochem. Photobiol. Sci. 1 (2002) 920.
[12] J. Literak, J. Wirz, P. Klan, Photochem. Photobiol. Sci. 4 (2005) 43.
[13] M. Zabadal, A.P. Pelliccioli, P. Klan, J. Wirz, J. Phys. Chem. A 105 (2001) 10329.
[14] L. Kammari, L. Plistil, J. Wirz, P. Klan, Photochem. Photobiol. Sci. 6 (2007) 50.
[15] J. Literak, A. Dostalova, P. Klan, J. Org. Chem. 71 (2006) 713.
[16] A. Banerjee, D.E. Falvey, J. Am. Chem. Soc. 120 (1998) 2965.
[17] A. Banerjee, D.E. Falvey, J. Org. Chem. 62 (1997) 6245.
[18] J.E.T. Corrie, D.R. Trentham, J. Chem. Soc., Perkin Trans. 1 (1992) 2409.
[19] J.F. Cameron, C.G. Willson, J.M.J. Frechet, J. Chem. Soc. Chem. Commun. (1995) 923.
[20] D.E. Falvey, C. Sundararajan, Photochem. Photobiol. Sci. 3 (2004) 831.
[21] A.P. Pelliccioli, P.P. Klan, M. Zabadal, J. Wirz, J. Am. Chem. Soc. 123 (2001) 7931.
[22] I.L. Belaits, R.N. Nurmukhametov, Zh. Obshch. Khim. 44 (1970) 29.
[23] G.D. Hedden, W.G. Brown, J. Am. Chem. Soc. 75 (1953) 3744.
[24] P.J. Wagner, P. Klan, Norrish type II photoelimination of ketones: cleavage of 1,4-biradicals formed by g-hydrogen abstraction, in: W.M. Horspool, F. Lenci (Eds.), CRC Handbook of Organic Photochemistry and Photobiology, CRC Press, Boca Raton, 2003, p. 1 (Chapter 52).
[25] B.A. Johnson, M.H. Kleinman, N.J. Turro, M.A. Garcia-Garibay, J. Org. Chem. 67 (2002) 6944.
[26] R. Haag, J. Wirz, P.J. Wagner, Helv. Chim. Acta 60 (1977) 2595.
[27] L. Plistil, T. Solomek, J. Wirz, D. Heger, P. Klan, J. Org. Chem. 71 (2006) 8050.
[28] L.A. Huck, P. Wan, Org. Lett. 6 (2004) 1797.
[29] T.J. Connolly, T. Durst, Tetrahedron 53 (1997) 15969.
[30] L. McMaster, F.F. Ahmann, J. Am. Chem. Soc. 50 (1928) 145.
[31] R.T. Hart, R.F. Tebbe, J. Am. Chem. Soc. 72 (1950) 3286.
[32] C.J. Li, D.L. Chen, Y.Q. Lu, J.X. Haberman, J.T. Mague, Tetrahedron 54 (1998) 2347.
[33] S. Moon, H. Bohm, J. Org. Chem. 37 (1972) 4338.
[34] J. Literák, S. Relich, P. Kulhánek, P. Klán, Mol. Divers. 7 (2003) 265.
[35] T.A. Spencer, A.L. Hall, C.F. Vonreyn, J. Org. Chem. 33 (1968) 3369.
[36] A. Banerjee, K. Lee, D.E. Falvey, Tetrahedron 55 (1999) 12699.
[37] D. Leinweber, R. Wartchow, H. Butenschon, Eur. J. Org. Chem. (1999) 167.
[38] P.J. Wagner, I.E. Kochevar, A.E. Kemppainen, J. Am. Chem. Soc. 94 (1972) 7489.