An Efficient Photoinduced Deprotection of Aromatic Acetals and Ketals

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A novel type of photodeprotection reaction of simple aromatic acetals and ketals is described. The deprotection is highly efficient under optimized conditions. The aromatic ring confers the photoreactivity to the compounds. The efficiency of the process depends on the structure of the acetal moiety. The common minor side reaction, the photooxidation, becomes the major reaction pathway in the cases of cyclic acetals. The use of photon as only reagent makes this procedure especially attractive for acetal deprotection.

Introduction. – Using laser beams to trigger photochemical reactions allows controlling the timing and the localization of the photochemically induced transformations with high precision. This is a major asset when photochemical reactions are applied in life sciences and material sciences. Broadening the scope of a photochemical deprotection reaction widens the toolbox developed by chemists for those two fields. We have discovered a novel and efficient photochemical deprotection of aromatic dialkyl acetals and ketals. This reaction can be applied to normal dialkyl acetals without having to introduce a specially designed chromophore.

Photochemical transformations have attracted the attention of chemists from the beginning of systematic organic synthesis [1]. The scientific interest concentrated on the challenging mechanisms, the complex and synthetically attractive product structures, and the selectivity of the processes as a function of the chromophore involved. In recent years, the emphasis of the research in photochemistry focused on applications in live sciences and in material sciences. The *in vitro* detection of biological processes in living cells, even in whole living organisms, has given new insights into vital biochemical processes [2]. Caged compounds have become valuable tools of chemical biology [3]. Significant applications of caged compounds in neurochemistry have been reported [4]. The recent growing understanding of the photophysics and photochemistry of polymeric materials [5] have led to the creation of micro- and nanopatterned structures on surfaces and functional assemblies with unprecedented precision. Photodeprotection reactions have gained in importance as the chemical, biological, and material properties of a compound can be changed on purpose [6].

Protection and deprotection reactions are an important, often inevitable part of modern natural-product syntheses. One of the key issues in protecting-group procedures is orthogonality [7]. Orthogonal protecting groups allow the selective removal of one of them without affecting the others. Photochemical liberation of functional groups occurs without adding a chemical reagent, and the deprotection is

often fast and neat. The cleavage of a photolabile protecting group (PPG) is, therefore, most of the times orthogonal to the conditions needed for the thermal deprotections; the inverse is often not true. Acetals are widely used protecting groups in organic synthesis [8]. The use of PPGs for carbonyl compounds has attracted considerable attention recently [9].

Different classes of photochemical deprotection reactions for the release of carbonyl and dihydroxy groups have been described. A common feature of all these photochemical reactions is the need of a specific chromophore or of a allocated functional group to generate the activated intermediate during the photochemical process. The position of the chromophore can be used as criterium to classify PPGs. Photolabile acetals can be employed for protecting either carbonyl or dihydroxy groups, depending on the position of the photoreactive moiety.

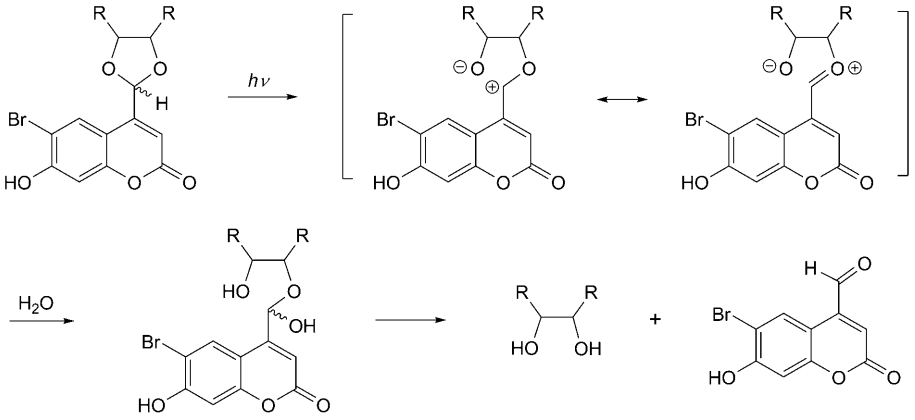
Several different photoremovable protecting groups for aldehydes and ketones have been reported. The 2-nitrobenzyl function has been used since its discovery in 1901 [10] to protect carbonyl functions [11][12]. Carbonyl groups protected with 3,5-dimethoxy-α,α-diphenylsalicylic alcohol (= 3,5-dimethoxy-α,α-diphenylbenzenemethanol) derivatives can be released upon UV irradiation [13]. The so-called 'meta' effect [14][15] has been invoked to rationalize this photodeprotection reaction. Acetals derived from (2,5-dihydroxyphenyl)ethylene glycol take advantage of a photochemically induced hydrogen shift [16]. Caged carbonyl groups derived from 6-bromo-4-(1,2-dihydroxyethyl)-7-hydroxycoumarin (Bhc-diol = 6-bromo-4-(1,2-dihydroxyethyl)-7-hydroxy-2*H*-1-benzopyran-2-one) [17] and 2-anthraquinonylethyl-1′,2′-diols (Aqe-diol = 2-(1,2-dihydroethyl)anthracene-9,10-dione) [18] have been successfully used as PPGs.

Alternatively, the chromophore can be attached to the carbonyl part and will, thereby, release 1,2- or 1,3-diols after the photodeprotection. The same type of chromophores are used than in the cases described above. The heterolysis of the benzylic C–O bond can be triggered, *e.g.*, by the photoexcitation of (6-bromo-7-hydroxycoumarin-4-yl)methylene acetals (= 6-bromo-7-hydroxy-4-(1,3-dioxolan-2-yl)-2*H*-1-benzopyran-2-ones) [19]. The change of the electronic distribution in the excited state of the acetals leads to the cleavage of the benzylic C–O bond followed by chemical hydrolysis of the intermediate created by the photoexcitation (*Scheme 1*). The acetals of 5-methoxy- and 5-hydroxysalicylaldehyde (= 5-methoxy-2-hydroxy- and 2,5-dihydroxybenzaldehyde) photodecompose with good to excellent yields [20]. The release of the protecting group is induced by a photochemical proton shift. The photorelease of 1,2 and 1,3-diols from 2-nitrobenzylidene acetals has been described as well [21].

In our research program aiming at the synthesis of triphenylene-based dimers for the application in material sciences, we synthesized the triphenylene-biased acetal **3**. During UV irradiation (TLC lamp, 366 nm) of **3** dissolved in CH_2Cl_2, the unexpected photochemical deprotection of acetal **3** occurred with high efficiency. The light-induced process was identified by means of a color change in the fluorescence emission (from blue to yellow).

Based on this observation, we decided to study the scope of this transformation. We could demonstrate that the photodeprotection is not limited to the 2-(prop-1-yn-1-yl)triphenylene chromophore of compound **3**. We describe a new and efficient

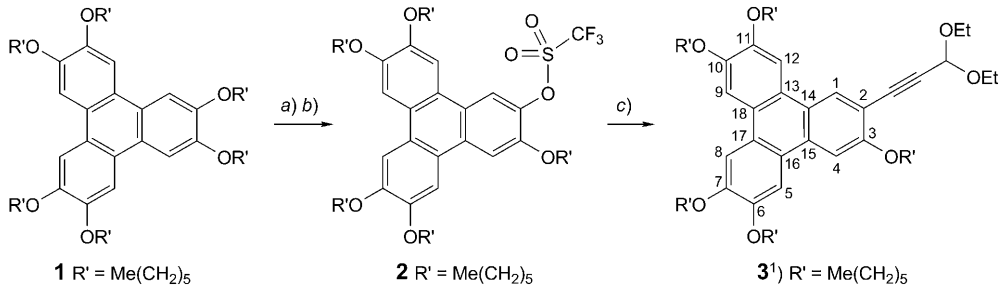
Scheme 1. *Plausible Mechanism of Light-Mediated Uncaging of Coumarin-Derived Acetals Proposed by* Lin *and* Lawrence [19]



procedure to deprotect simple benzene- and naphthalene-based acetals and ketals photochemically. We report our studies of the reaction conditions of the photolysis and of the identification of the by-products formed in some cases.

2. Results. – 2.1. *Synthesis and Photodeprotection of Triphenylene-Based Acetal* **3**[1]). For the synthesis of the triphenylene-based acetal **3** (*Scheme 2*), we started from 2,3,6,7,10,11-hexakis(hexyloxy)triphenylene (**1**), which was synthesized by oxidative coupling of 1,2-bis(hexyloxy)benzene with $MoCl_5$, following a procedure described by *Kumar* and *Manickam.* [22]. Selective ether cleavage [23] was achieved with '*B*-bromocatecholborane' (=2-bromo-1,3,2-benzodioxaborole) in CH_2Cl_2 to give the pentakis(hexyloxy)triphenylen-monool in a complex mixture of tetrakis(hexyloxy)-triphenylene-diol and tris(hexyloxy)triphenylene-triol regioisomers which could not be

Scheme 2



a) '*B*-Bromocatecholborane', CH_2Cl_2, r.t., 24 h. *b*) Trifluoromethanesulfonic anhydride, pyridine, CH_2Cl_2, r.t., 1 h; 40% (2 steps). *c*) 3,3-Diethoxyprop-1-yne, [$Pd(Ph_3P)_4$], Ph_3P, CuI, $(i\text{-}Pr)_2NH$, toluene, 60°, 24 h; 79%.

[1]) Arbitrary atom numbering (see ^{13}C-NMR spectra in the *Exper. Part*).

separated efficiently. The crude mixture was filtered through a pad of silica gel to remove the catechol (= benzene-1,2-diol) generated after quenching with cold H_2O. The mixture of triphenylene-monool, -diol, and -triol was directly treated with triflic anhydride (= trifluoromethanesulfonic anhydride) and pyridine in CH_2Cl_2 to give the corresponding mono-, bis-, and tris-trifluoromethanesulfonate derivatives. In contrast to the partially deprotected triphenylenols, compound **2** could be isolated by chromatography on silica gel. The crude **2** was purified by recrystallization in EtOH to give a moderate yield of 40% after two steps. The introduction of the propargylaldehyde diethyl acetal (= 3,3-diethoxyprop-1-yn-1-yl) moiety at the 2-position of **2** was achieved under *Sonogashira* coupling conditions [24], *i.e.*, 3,3-diethoxyprop-1-yne, $[Pd(Ph_3P)_4]$, and CuI were used in catalytic amount in toluene containing 5% of $(i\text{-}Pr)_2NH$. A higher amount of base in toluene led to degradation of the triflate function of **2**. The 2-(3,3-diethoxyprop-1-yn-1-yl)-3,6,7,10,11-pentakis(hexyloxy)triphenylene (**3**) could be chromatographed on silica gel and was isolated pure in 79% yield.

Following the unexpected fast color change of fluorescence emission of triphenylene-based acetal **3**, we identified the product formed as the 3-(triphenylen-2-yl)prop-2-ynal **4**. Fluorescence measurement for **3** and **4** ($3.0 \cdot 10^{-6}$ M in $CHCl_3$) with an excitation wavelength of 366 nm, showed emission bands at 413 nm for **3** and a broader band at 531 nm for **4**, respectively (*Fig.*).

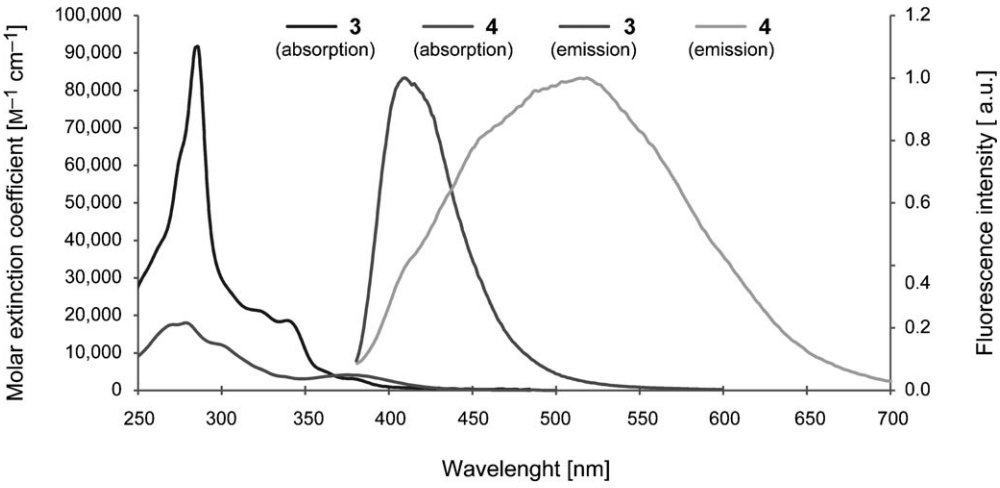
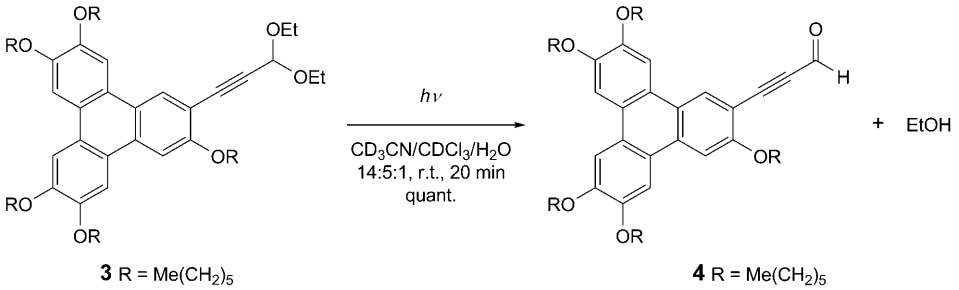


Figure. *Absorption and fluorescence spectra of* **3** *and* **4**. The fluorescence spectra are normalized to the same maximum intensity.

We tested the photodeprotection of **3** first, using a 125 W medium-pressure mercury lamp equipped with a *Pyrex* filter. Under these conditions, the substrate was essentially irradiated with the 366 nm Hg-line. Under optimized conditions, a 0.005M solution of **3** in $CD_3CN/CDCl_3/H_2O$ 70 : 25 : 5, without degassing the solvents, was irradiated at room temp. for 20 min converting thus acetal **3** quantitatively into aldehyde **4**. No traces of the starting material **3** could be detected by ^{1}H-NMR analysis of the reaction mixture (*Scheme 3*).

Scheme 3



3 R = $Me(CH_2)_5$ **4** R = $Me(CH_2)_5$

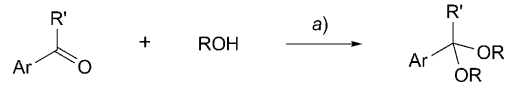
The ease and efficiency of the photodeprotection of acetal **3** containing none of the functional groups known to facilitate the photoactivation, came as a surprise. We asked therefore the question if the success of this photoreaction depends on the π-extended structure of the (alkyloxy)-substituted 2-(prop-1-yn-1-yl)triphenylene chromophore. We decided to study the scope of this photodeprotection with simpler aromatic compounds lacking the propynyl unit, such as benzene- and naphthalene-based acetals and ketals.

2.2. *Synthesis and Photodeprotection of Simple Aromatic Ketals and Acetals* **5**–**16**. For the studies of the photochemical deprotection reaction, we needed simpler aromatic acetals and ketals as substrates. We chose to replace the 2-(prop-1-yn-1-yl)triphenylene aromatic part by the simpler benzene and naphthalene moieties. These simpler substrates lacking the triple bond should facilitate the study of their photohydrolysis. These simpler chromophores could be excited with medium-pressure Hg-lamps, equipped with a *Pyrex* filter in the case of naphthalene derivatives. The aromatic rings we used were unsubstituted, so any special effect of the substituent could be excluded. If photodeprotection was observed with these simple model compounds, this could confidently be attributed to the change of electron distribution in the excited state, and no other effect would have to be invoked.

Trialkyl orthoformates (=tris(alkyloxy)methanes) in the presence of acid catalysts have been reported to convert carbonyl groups efficiently into their corresponding acetals [25]. Many of the reported procedures require a large excess of reagents, long reaction times or harsh reaction conditions, and moisture-sensitive and expensive reagents. Some of these acetal-forming reaction conditions were not giving satisfactory results for the acetalization of aromatic ketones.

The starting materials **5**–**16** needed for our studies were synthesized adapting the procedure described by *Patel* and co-workers [26] (*Scheme 4* and *Table 1*). At room temperature, tetrabutylammonium tribromide (0.04 equiv.) functioned as promoter in the presence of trimethyl orthoformate (2.2 equiv.) and the corresponding alcohol (8.0 equiv.) in an adequate solvent. The *in situ* generation of HBr from tetrabutylammonium tribromide [27] is supposed to catalyze the reaction. The acetalization of naphthalene-2-carboxaldehyde gave 80% of acetal **8** in dry MeOH and 96% in dry $MeNO_2$. In our hands, MeCN was the best solvent for the synthesis of benzene-based ketals and acetals **13**–**16** (*Table 2*, *Entries 9* and *10*). $MeNO_2$ led to the best yield in the

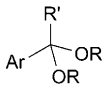
Scheme 4[a])



a) Trimethyl orthoformate, tetrabutylammonium tribromide (Bu_4NBr_3), solvent (*Method A:* MeCN; *Method B:* $MeNO_2$).

[a]) For Ar, R, and R′, see *Table 1*.

Table 1. *Starting Ketals and Acetals* **5**–**16**



5 – 16

	Ar	R′	RO or OR–RO		Ar	R′	RO or OR–RO
5	naphthalen-2-yl	Me	MeO	**11**	Ph	Me	MeO
6	naphthalen-2-yl	Me	OCH_2CH_2O	**12**	Ph	Me	OCH_2CH_2O
7	naphthalen-2-yl	Me	$OCH_2CH_2CH_2O$	**13**	Ph	Me	$OCH_2CH_2CH_2O$
8	naphthalen-2-yl	H	MeO	**14**	Ph	H	MeO
9	naphthalen-2-yl	H	OCH_2CH_2O	**15**	Ph	H	OCH_2CH_2O
10	naphthalen-2-yl	H	$OCH_2CH_2CH_2O$	**16**	Ph	H	$OCH_2CH_2CH_2O$

Table 2. *Synthesis of Starting Ketals and Acetals* **5**–**13** *and* **16**

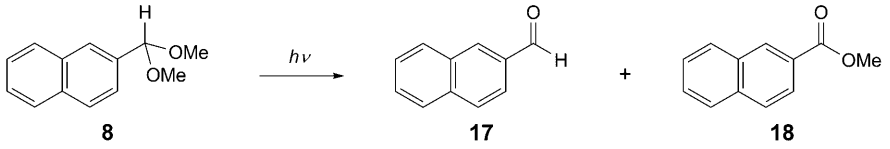
Entry	Ar	R′	ROH or HOR–ROH	Method	Product (yield [%])
1	naphthalen-2-yl	Me	MeOH	*B*	**5** (90)
2	naphthalen-2-yl	Me	$HO(CH_2)_2OH$	*B*	**6** (81)
3	naphthalen-2-yl	Me	$HO(CH_2)_3OH$	*B*	**7** (75)
4	naphthalen-2-yl	H	MeOH	*B*	**8** (96)
5	naphthalen-2-yl	H	$HO(CH_2)_2OH$	*B*	**9** (79)
6	naphthalen-2-yl	H	$HO(CH_2)_3OH$	*B*	**10** (85)
7	Ph	Me	MeOH	*A*	**11** (95)
8	Ph	Me	$HO(CH_2)_2OH$	*A*	**12** (80)
9	Ph	Me	$HO(CH_2)_3OH$	*A*	**13** (74)
10	Ph	H	$HO(CH_2)_3OH$	*A*	**16** (90)

naphthalene series **5**–**10** (*Entries 1*–*6*). The acetals and ketals could be isolated under these conditions in 74–96% yield (*Table 2*).

Our preliminary photodeprotection tests were conducted with 2-(dimethoxymethyl)naphthalene (**8**) in a quartz NMR tube in $CDCl_3$ as solvent and were monitored by ^{1}H-NMR measurements. To avoid photochemical heating of the solutions and thereby creating a thermal activation, we used a water-cooling system to maintain the temperature at 26°. Thus, 75% of **8** was consumed after 60 min of irradiation to form 65% of aldehyde **17** and 10% of the photooxidation product **18** (*Scheme 5*). Simultaneously, a control experiment without UV irradiation showed no sign of hydrolysis. A purely thermal deprotection of the acetal could be excluded by this result.

It is known that treating $CHCl_3$ solutions by intensive UV irradiation leads to the formation of HCl [28]. The photochemically induced formation of small amounts of HCl in $CHCl_3$ could be possibly explain the hydrolysis of acetal **8**. We, therefore, replaced $CHCl_3$ by MeCN. MeCN possesses no end absorption extending towards the emission lines of a medium-pressure Hg-lamp. Thus, the solvent is not activated directly upon UV irradiation, and we could find no report showing the formation of protons under UV irradiation with the Hg-lines 254 or 366 nm for short times.

Scheme 5



8 **17** **18**

To compare the photolability of the various benzene- and naphthalene-based acetals and ketals, we developed standardized conditions for the photolysis experiments. The reactions were conducted on a 10 mg scale (0.50 mmol) of the acetal or ketal. The latter was dissolved in CD_3CN (0.6 ml), and H_2O (32 µl) was added, to give a 0.08M solution of CD_3CN/H_2O 95:5. The solution was transferred to an NMR quartz tube (diameter 5 mm) and irradiated with a 125 W Hg-lamp by using the 254 nm and/or the 365 nm bands depending on the filter used (quartz or *Pyrex*). The reaction was monitored by ^{1}H-NMR measurements observing the decreasing starting-material concentration and increasing formation of products. At the end of the reaction, an aliquot (150 µl) of the sample was analyzed by GC (see *Exper. Part*) identifying the peaks by comparison with samples of known structure.

We tested the influence of the presence of H_2O in the reaction media on the photodeprotection of **8** by using a *Pyrex* filter (*Table 3*). At least 5% of H_2O were needed to obtain a good conversion. Increasing the amount of H_2O from 5 to 50% did not significantly change the outcome of the reaction. The limit of solubility of **8** at a concentration of 10^{-2} M was reached in 65% of H_2O/MeCN.

Table 3. *Influence of Solvent and Time on the Photodeprotection* (*Pyrex* filter) *of Acetal* **8** (*Scheme 5*)

Solvent	Time [min]	Yield [%]		
		8	**17**	**18**
CD_3CN	200	84	n.d.[a])	16
CD_3CN/H_2O 99.5:0.5	20	38	56	6
CD_3CN/H_2O 95:5	20	n.d.[a])	97	3
CD_3CN/H_2O 50:50	20	n.d.[a])	100	n.d.[a])
CD_3CN/H_2O 36:64	20	n.d.[a])	100	n.d.[a])

[a]) n.d. = not detected.

Irradiating the naphthalene-based ketals **5**–**7**, dissolved in CD_3CN/H_2O 95:5, in a quartz vessel, total transformation to 2-acetonaphthone (=1-(naphthalen-2-yl)ethanone; **19**) could be achieved within 20 min (*Scheme 6* and *Table 4*, *Entries 1*, *3*, and *5*).

Irradiating selectively at 365 nm by using a *Pyrex* filter led to very good conversions (93 to 100%) to the ketone **19** within 30 to 60 min (*Table 4*, *Entries 2*, *4*, and *6*). Longer irradiation time did not lead to higher conversions. Despite the low molar extinction of compounds **5**–**10** at 366 nm, their photodeprotection was still very efficient when a *Pyrex* filter was used (irradiation at 365 nm, see *Entries 2*, *4*, and *6* in *Table 4*). The photodeprotection could be successfully done on a 1-g scale with **5** as substrate. A 4 times higher concentration of the starting material **5** than that described above still allowed an efficient photodeprotection. After 20 min of irradiation, evaporation of the solvent, followed by a recrystallization in MeOH, the product **19** could be isolated in 96% yield with high purity.

Scheme 6

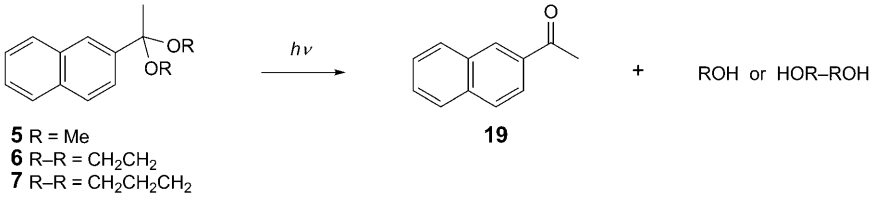


Table 4. *Photodeprotection of Naphthalene-Based Ketals* **5**–**7** *under Different Conditions* (*Scheme 6*)

Entry	Ketal	$\lambda_{irradiation}$ (filter) [nm]	Time [min]	Yield of **19** [%]	ROH or HOR–ROH (product)
1	**5**	254, 365 (quartz)	20	100	MeOH
2	**5**	365 (*Pyrex*)	30	100	MeOH
3	**6**	254, 365 (quartz)	20	100	$HO(CH_2)_2OH$
4	**6**	365 (*Pyrex*)	40	93	$HO(CH_2)_2OH$
5	**7**	254, 365 (quartz)	20	100	$HO(CH_2)_3OH$
6	**7**	365 (*Pyrex*)	60	94	$HO(CH_2)_3OH$

Irradiating the naphthalene-based acetals **8**–**10** dissolved in CD_3CN/H_2O 95:5 through a *Pyrex* filter, slightly different results were obtained compared to experiments reported for the naphthalene-based ketals **5**–**7** (*Scheme 7* and *Table 5*). The acyclic acetal **8** was completely deprotected to aldehyde **17** after 20 min irradiation with the formation of 3% of by-product **18** formed by photooxidation (*Table 5*, *Entry 1*); whereas the cyclic acetals **9** and **10** formed no or a very low amount (4%) of aldehyde **17**, even when we irradiated for 200 min (*Entries 2* and *3*). The major products in those cases were the corresponding ring-opened esters **20** and **21** formed in 20 and 9% yield, respectively. Irradiation of **8**–**10** in a quartz vessel led to a similar product distribution. Degassing the solvent by bubbling N_2 for 20 min prior to irradiation did not diminish the importance of the ester formation significantly. A control experiment with the naphthalene-2-carboxaldehyde (**17**) under the photodeprotection conditions showed that the product is photostable even after 200 min of irradiation. The photodeprotection could be applied successfully on a synthetic scale to 1 g of **8**. Under the conditions described above but with a 4 times higher concentration of the starting material **8**, **17** could be isolated in pure form in a 98% yield after evaporation of the solvent and recrystallization in MeOH.

Scheme 7

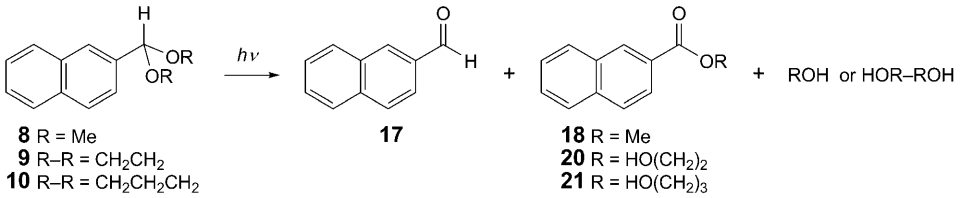


Table 5. *Photodecomposition* (*Pyrex* filter) *of Naphthalene-Based Acetals* **8**–**10** (*Scheme 7*)

Entry	Acetal	Time [min]	Yield [%]			ROH or HOR–ROH (product)
			acetal	**17**	ester	
1	**8**	20	n.d.[a]) (**8**)	97	3 (**18**)	MeOH
2	**9**	200	76 (**9**)	4	20 (**20**)	$HO(CH_2)_2OH$
3	**10**	200	91 (**10**)	n.d.[a])	9 (**21**)	$HO(CH_2)_3OH$

[a]) n.d. = not detected.

The benzene-based ketals **11**–**13** absorbed exclusively below 300 nm. Therefore, we irradiated all the samples in a quartz vessel. Photodeprotection of the ketals to acetophenone (=1-phenylethanone; **22**) occurred but the desired products were accompanied by the products of detrimental side reactions (*Scheme 8* and *Table 6*). It is well documented that H-abstraction may occur from the triplet excited state of acetophenone [29]. Several reactions starting from the ketyl radical have been reported in the literature. The generated transient ketyl radical may dimerize to give pinacols, it may undergo further H-abstraction or it may combine with the donor radical yielding

Scheme 8

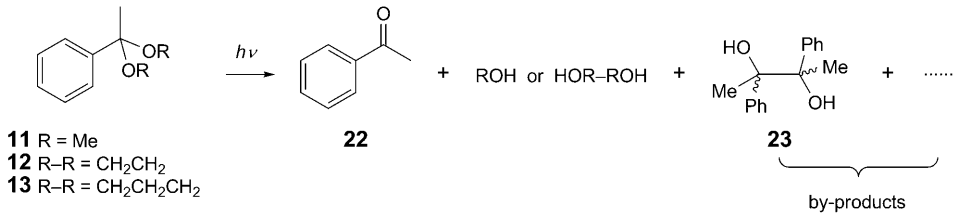


Table 6. *Photodecomposition* (Quartz vessel) *of Benzene-Based Ketals* **11**–**13** (*Scheme 8*)

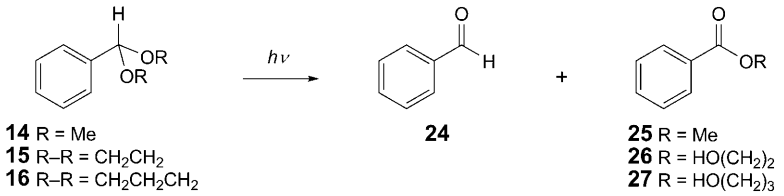
Ketal	Time [min]	Yield [%]		
		ketal	**22**	by-products
11	20	8 (**11**)	69	23
12	20	n.d.[a]) (**12**)	97	3
13	20	1 (**13**)	73	22

[a]) n.d. = not detected.

adducts. In the cases of the photodeprotection of **11**–**13**, we identified by GC/MS analysis three different by-products. The pinacol adduct **23** was the only by-product characterized. In a control experiment, acetophenone (**22**) was irradiated under the same conditions for 20 min and formed the same mixture of three products with a conversion of 65%.

Irradiating the benzene-based acetals **14**–**16** dissolved in CD_3CN/H_2O 95:5 in a quartz vessel did not show any formation of benzaldehyde **24** even when we irradiated for 200 min (*Scheme 9* and *Table 7*). The only products formed were the corresponding esters **25**–**27** in 8, 11, and 7%, respectively. Degassing the solvent by bubbling N_2 before irradiation did not lead to significant changes in the amount of ester formed.

Scheme 9



14 R = Me
15 R–R = CH_2CH_2
16 R–R = $CH_2CH_2CH_2$

24

25 R = Me
26 R = $HO(CH_2)_2$
27 R = $HO(CH_2)_3$

Table 7. *Photodecomposition* (Quartz vessel) *of Benzene-Based Acetals* **14**–**16** (*Scheme 9*)

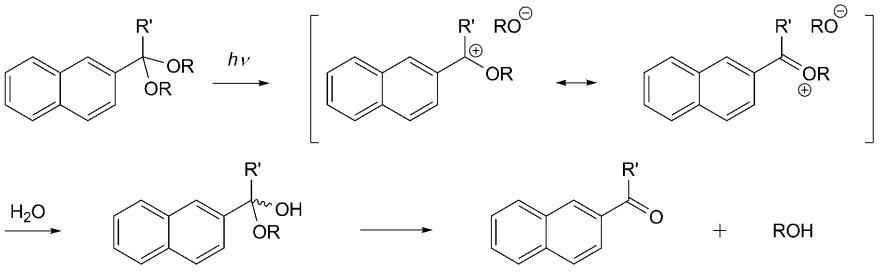
Acetal	Time [min]	Yield [%]		
		acetal	**24**	ester
14	50	92 (**14**)	n.d.[a])	8 (**25**)
15	200	89 (**15**)	n.d.[a])	11 (**26**)
16	200	93 (**16**)	n.d.[a])	7 (**27**)

[a]) n.d. = not detected.

3. Discussion. – The photohydrolysis can be successfully applied to a series of simple aromatic acetals and ketals. Adding at least 5% of H_2O to the polar solvent MeCN is necessary to perform the reaction efficiently. The acyclic and cyclic naphthalene-based ketals **5**–**7** could be deprotected cleanly and efficiently by UV irradiation, whereas the cyclic naphthalene-based acetals **9** and **10** could not be transformed into the corresponding aldehyde. Comparing the results from the six different ketals **5**–**7** and **11**–**13** showed that the photodeprotection can be achieved efficiently. The reactions with the benzene-based ketals **11**–**13** as starting material suffered from a subsequent photodegradation of the released acetophenone (**22**). In the case of the cyclic acetals **9**, **10**, **15**, and **16**, a photooxidation process became the major pathway forming the corresponding ring-opened ester **20**, **21**, **26**, and **27** in moderate yields.

The mechanism of this novel photoinduced hydrolysis of aromatic acetals and ketals remains to be studied in depth. A hypothetical mechanism (*Scheme 10*) can be proposed, based on the mechanism suggested by *Lin* and *Lawrence* [19] for the photouncaging of coumarin acetal derivatives. Excitation of the chromophore should induce a heterolytic-bond photodissociation [30] to generate a resonance-stabilized

Scheme 10



carbocation as transient species. The intermediate created after the heterolytic-bond-breaking process is supposed to be captured by H_2O. The hemiacetal obtained by this process is then thermally transformed into the carbonyl compound. At this point of our studies, it cannot be excluded that the reaction might proceed *via* a radical-cation species. *Miranda* and co-workers [31] have reported the triphenylpyrylium tetrafluoroborate sensitized photolysis of acetals occurring *via* radical-cation species.

Summarizing the experimental evidence collected, the difference of reactivity observed in the photodeprotection between the naphthalene-based ketals **5**–**7** and the acetals **8**–**10** is consistent with the difference in reactivity in the thermal hydrolysis. The 2-methyl-2-(naphthalen-2-yl)-1,3-dioxane derivatives have been shown to hydrolyze *ca.* 7–8 times faster than their corresponding 2-(naphthalen-2-yl)-1,3-dioxane [32]. The authors proposed that the presence of the axial Me group in cyclic ketals may accelerate the hydrolysis. The release of strain when ring opening occurs is cited as reason for the rate difference.

In the cases of benzene- and naphthalene-based acetals, the major side reaction is a competing photooxydation to the ester. The side reaction is probably due to the formation and the reaction of singlet oxygen or of a photocreated reactive species with triplet oxygen. Direct oxidation of acetals to the corresponding esters involving molecular oxygen and a radical generator has been previously described [33].

4. Conclusion. – We detected a novel, efficient photodeprotection reaction independent on the presence of specific substituents at the aromatic ring. We showed that naphthalene-based ketals **5**–**7** and 2-(prop-1-yn-1-yl)triphenylene-based acetal **3** cleanly release simple alcohols upon exposure to UV light in an excellent yield. The 2-acetonaphthone moiety (see **19**) represents an interesting platform for further application as a PPGs of 1,2- and 1,3-diols derivatives such as carbohydrates.

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Experimental Part

General. Purchased chemicals were used without further purification. The solvents CH_2Cl_2, toluene, and MeCN were purchased from *Sigma–Aldrich* with the grade *puriss.*, absolute, on molecular sieve ($H_2O \leq 0.005\%$), $\geq 99.5\%$ (GC). Compounds **14** (benzaldehyde dimethyl acetal) was purchased from *Acros* in *puriss.* grade. Compounds **15** (2-phenyl-1,3-dioxolane), **17** (2-naphthaldehyde), **19** (2-acetonaphthone) were bought from *Sigma–Aldrich* in *puriss.* grade. All photolyses were conducted in a quartz NMR tube or a quartz vessel at 20° with water circulation in a photochemical reactor equipped with a medium-pressure Hg-lamp (*HPK125 Philips*; 125 W; emission lines: 253.7, 296.7, 365.4, 404.7, and 435.8 nm) and a *Pyrex* (>280 nm) or quartz filter (>190 nm). TLC: *Merck 60 F_{254}* acidic silica-gel-coated (SiO_2) or neutral Al_2O_3-coated Al plates, 0.2 mm; detection under UV light (254 nm) or with $KMnO_4$ soln. Column chromatography (CC): SiO_2 60 Å, 32–63 μm (*Brunschwig*). M.p.: *Gallenkamp* melting-point apparatus; uncorrected. GC: *Agilent-6850A* (column *HP-1*, length 3 m, i.d. 0.32 mm, film 0.25 μm); temp. gradient: initial temp. 100° for 3 min, then heating 15°/min up to 280°, further 8 min at 280°. UV/VIS: *Varian-Cary300-1E* UV/VIS spectrophotometer; λ_{max} (ε[l mol^{-1} cm^{-1}]) in nm. Fluorescence spectra: *Perkin-Elmer-LS-50-B* luminescence spectrometer. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-Avance-400* instrument; at 298 K; δ in ppm rel. to the used solvent, *J* in Hz; NMR solvents from *Cambridge Isotope Laboratories, Inc.* ESI-MS: *Finnigan-LCQ* mass spectrometer at the University of Neuchâtel; in *m*/*z*. HR-MS: *Bruker-BioAPEX-II-Daltonics* apparatus at the University of Fribourg; performed by Mr. *F. Nydegger*; in *m*/*z*.

1. *3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-yl 1,1,1-Trifluoromethanesulfonate* (**2**) [34]. To a soln. of **1** (1.05 g, 1.27 mmol) in anh. CH_2Cl_2 (15 ml) at 0°, a soln. of '*B*-bromocatecholborane' (3.18 mmol, 0.3M in CH_2Cl_2) was added. Then the mixture was stirred at r.t. for 24 h. The mixture was poured into ice-water and extracted with CH_2Cl_2, the combined org. layer dried (Na_2SO_4) and concentrated to 2 ml, and the concentrate filtered through a pad of SiO_2 with CH_2Cl_2 (to remove the catechol). The CH_2Cl_2 soln. was concentrated to 5 ml, and pyridine (315 μl, 3.91 mmol) was added. Then 1,1,1-trifluoromethanesulfonic anhydride (255 μl, 1.52 mmol) was added slowly, and the mixture was stirred at r.t. for 1 h under Ar. The reaction was quenched with H_2O (5 ml), the mixture extracted with CH_2Cl_2 (3 × 15 ml), the combined org. layer washed with 1M HCl (20 ml) and brine (20 ml), dried (Na_2SO_4), and concentrated, the residue purified by CC (SiO_2, CH_2Cl_2/petroleum ether 1:1), and then the product recrystallized from EtOH: **2** (444 mg, 40% over 2 steps). Purple solid. R_f (CH_2Cl_2/petroleum ether 1:1) 0.55. M.p. 172–175°. UV/VIS ($CHCl_3$): 280 (134000). ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.21 (*s*, H–C(1)); 7.89 (*s*, H–C(4)); 7.83 (*s*, H–C(5)); 7.81 (*s*, H–C(8), H–C(9)); 7.73 (*s*, H–C(12)); 4.28–4.22 (*m*, 5 CH_2O); 2.01–1.89 (*m*, 5 CH_2CH_2O); 1.67–1.53 (*m*, 5 $CH_2CH_2)_2O$); 1.49–1.35 (*m*, 5 $CH_2CH_2(CH_2)_3O$); 1.01–0.89 (*m*, 5 *Me*$(CH_2)_5O$). ^{13}C-NMR ($CDCl_3$, 100 MHz[1]): 150.6 (C(7)); 149.8, 149.7 (C(10,11)); 149.2 (C(3,6)); 138.6 (C(2)); 129.8 (C(15)); 125.4 (C(17)); 123.7 (C(18)); 123.1 (C(13,14)); 122.5 (C(16)); 119.1 (*q*, ^1J(C,F) = 320, CF_3); 116.9 (C(1)); 108.3 (C(4)); 107.5 (C(9)); 107.0, 106.8, 106.7 (C(5,8,12)); 70.2, 70.0, 69.70, 69.66, 69.6 (5 CH_2O); 31.9 ($CH_2(CH_2)_3O$); 29.7 (CH_2CH_2O); 26.1 ($CH_2(CH_2)_2O$); 22.9 ($CH_2(CH_2)_3O$); 14.3 (*Me*$(CH_2)_5O$). HR-MS: 899.4712 ([*M* + Na]$^+$, $C_{49}H_{71}F_3NaO_8S^+$; calc. 899.4719).

2. *2-(3,3-Diethoxyprop-1-yn-1-yl)-3,6,7,10,11-pentakis(hexyloxy)triphenylene* (**3**). To a soln. of **2** (220 mg, 0.250 mmol), 3,3-diethoxyprop-1-yne (55 μl, 0.37 mmol), CuI (10 mg, 0.050 mmol), Ph_3P (20 mg, 0.075 mmol), and (i-Pr)$_2$NH (0.15 ml) in degassed toluene (1.0 ml) was added [Pd($Ph_3P)_4$] (29 mg, 0.025 mmol dissolved in 1.0 ml of toluene) under Ar. The homogeneous mixture was stirred at 60° for 20 h (TLC monitoring). After completion of the reaction, the mixture was filtered through *Celite*, H_2O (20 ml) was added, and the mixture was extracted with Et_2O (3 × 20 ml). The org. layer was washed with brine (30 ml), dried (anh. Na_2SO_4), and concentrated. The yellow solid was purified by CC (SiO_2) followed by recrystallization from dioxane/MeOH: **3** (161 mg, 79%). Yellow solid. R_f (CH_2Cl_2/petroleum ether 2:3) 0.20. M.p. 133–136°. UV/VIS (MeCN): 284 (124000). ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.56 (*s*, H–C(1)); 7.86 (*s*, H–C(5), H–C(12)); 7.81 (*s*, H–C(8), H–C(9)); 7.75 (*s*, H–C(4)); 5.63 (*s*, C*H*(OEt)$_2$); 4.24 (*m*, 5 CH_2O); 3.94 (*dq*, *J* = 9.5, 7.1, *A* of *ABX*$_3$, 2 MeCH_2); 3.75 (*dq*, *J* = 9.5, 7.1, *B* of *ABX*$_3$, 2 MeCH_2); 1.94 (*m*, 5 CH_2CH_2O); 1.57 (*m*, 5 $CH_2(CH_2)_2O$); 1.41 (*m*, 5 $CH_2CH_2(CH_2)_3O$); 1.33 (*t*, *J* = 7.1, *X* of *ABX*$_3$, 2 *Me*CH_2); 1.01–0.89 (*m*, 5 *Me*$(CH_2)_5O$). NOESY ($CDCl_3$): irrad. H–C(1) (8.56) → enh. H–C(12) (7.86); irrad. H–C(4) (7.75) → enh. H–C(5) (7.86) and CH_2O (4.24); irrad. H–C(5) + H–C(12)

(7.86) → enh. H–C(1) (8.56), H–C(4) (7.75), and CH_2O (4.24); irrad. H–C(8) + H–C(9) (7.81) → enh. CH_2O (4.24). ^{13}C-NMR ($CDCl_3$, 100 MHz)[1]): 158.0 (C(3)); 150.4 (C(6)); 149.7 (C(10)); 149.1 (C(11)); 149.0 (C(7)); 130.9 (C(15)); 129.2 (C(1)); 125.6 (C(17)); 123.6 (C(13)); 123.1 (C(14)); 122.9 (C(18)); 122.7 (C(16)); 111.2 (C(2)); 108.3 (C(5)); 107.7 (C(9)); 107.0 (C(8)); 106.4 (C(12)); 104.4 (C(4)); 92.3 ($CH(OEt)_2$); 88.5 (C≡CCH(OEt)$_2$); 82.6 (C≡CCH(OEt)$_2$); 70.14, 70.09, 69.6, 69.5, 69.1 (5 CH_2O); 61.2 (MeCH_2O); 31.84, 31.83 (CH_2)(CH_2)$_3$O; 29.6, 29.5 (CH_2CH_2O); 26.00, 25.98 (CH_2(CH_2)$_2$O); 22.8 (CH_2(CH_2)$_4$O); 15.4 (*Me*CH_2O); 14.2 (*Me*(CH_2)$_5$O). HR-MS: 877.5963 ([M + Na]$^+$, $C_{55}H_{82}NaO_7^+$; calc. 877.5958).

3. *3-[3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-yl]prop-2-ynal* (**4**). A soln. of **3** (3.3 mg, 0.004 mmol) in $CD_3CN/CDCl_3/H_2O$ 70:25:5 (0.832 ml) was irradiated for 20 min in an NMR quartz tube. The solvent was evaporated, and the residue analyzed by ^{1}H-NMR: **4** (3.0 mg, quant.) Yellow solid. UV/VIS (MeCN): 278 (13100). ^{1}H-NMR ($CDCl_3$, 400 MHz): 9.53 (*s*, C≡CCHO); 8.64 (*s*, H–C(1)); 7.83–7.77 (*m*, H–C(5), H–C(8), H–C(9), H–C(12)); 7.75 (*s*, H–C(4)); 4.30–4.21 (*m*, 5 CH_2O); 1.95 (*m*, 5 CH_2CH_2O); 1.65–1.56 (*m*, 5 CH_2(CH_2)$_2$O); 1.41 (*m*, 5 CH_2CH_2(CH_2)$_2$O); 1.05–0.90 (*m*, 5 *Me*-(CH_2)$_5$O). ^{13}C-NMR ($CDCl_3$, 100 MHz)[1]): 177.0 (C≡CCHO); 158.7 (C(3)); 151.1, 149.9, 149.1, 149.0 (C(6,7,10,11)); 133.2 (C(2)); 131.4 (C(1)); 126.3, 123.8, 123.2, 123.1, 122.9, 122.4 (C(13,14,15,16,17,18)); 108.3, 107.6, 106.7, 106.0 (C(5,8,9,12)); 104.6 (C(4)); 94.0 (C≡CCHO); 93.1 (C≡CCHO); 70.1, 69.9, 69.5, 69.4, 69.3 (CH_2O); 31.8 (CH_2(CH_2)$_3$O); 29.6 (CH_2CH_2O); 26.0 (CH_2(CH_2)$_2$O); 22.8 (CH_2(CH_2)$_4$O); 14.2 (*Me*(CH_2)$_5$O). ESI-MS: 803.52 ([M + Na]$^+$).

4. *Aromatic Acetals and Ketals* **5**–**13** and **16**: *General Procedure* [26]. To a soln. of carbonyl compound (0.640 mmol), trimethyl orthoformate (155 µl, 1.410 mmol), and the corresponding alcohol (5.120 mmol) in dry MeCN (2.0 ml, *Method A*) or dry $MeNO_2$ (2.0 ml, *Method B*) was added tetrabutylammonium tribromide (12 mg, 0.025 mmol). The homogeneous mixture was stirred at r.t. (TLC and GC monitoring). After completion of the reaction, the mixture was poured into $NaHCO_3$ soln. (10 ml) and extracted with Et_2O (3 × 10 ml), and the org. layer dried (anh. Na_2SO_4) and concentrated. The crystalline compounds **6**, **7**, **8**, **10**, **12**, and **13** were purified by recrystallization from MeOH.

5. *2-(1,1-Dimethoxyethyl)naphthalene* (**5**). According to *Exper. 4* (*Method B*): 125 mg (90%). Clear oil. R_f (CH_2Cl_2/petroleum ether 1:1) 0.30. UV/VIS (MeCN): 224 (108000), 254 (3500), 366 (<200). ^{1}H-NMR (CD_3CN, 400 MHz): 8.01 (*s*, H–C(1)); 7.93–7.85 (*m*, 3 arom. H); 7.58 (*dd*, J = 8.6, 1.8, 1 arom. H); 7.52–7.49 (*m*, 2 arom. H); 3.18 (*s*, 2 MeO); 1.57 (*s*, Me). ^{13}C-NMR (CD_3CN, 100 MHz): 142.1 (C(2) (naph)); 134.4, 134.2 (*q*, arom. C); 129.6, 129.1, 128.8, 127.5, 127.4, 126.6, 125.8 (arom. CH); 102.9 (*q*, ketal C); 49.8 (MeO); 26.8 (Me). ESI-MS: 239.1 ([M + Na]$^+$).

6. *2-Methyl-2-(naphthalen-2-yl)-1,3-dioxolane* (**6**) [35]. According to *Exper. 4* (*Method B*): 111 mg (81%). White solid. M.p. 58.5–60.2°. R_f (CH_2Cl_2/petroleum ether 1:1) 0.20. UV/VIS (MeCN): 224 (93000), 254 (3500), 366 (<100). ^{1}H-NMR (CD_3CN, 400 MHz): 7.98 (*s*, 1 arom. H); 7.91–7.87 (*m*, 3 arom. H); 7.60 (*m*, 1 arom. H); 7.52 (*m*, 2 arom. H); 4.04 (*m*, *A* of *AA′BB′*, CH_2O); 3.78 (*m*, *B* of *AA′BB′*, CH_2O); 1.68 (*s*, Me). ^{13}C-NMR (CD_3CN, 100 MHz): 140.6 (C(2) (naph)); 133.0, 128.2, 128.1, 127.6, 126.4, 126.1, 126.0, 124.0, 123.7 (*q*, arom. C); 109.0 (*q*, ketal C); 64.5 (OCH_2CH_2O); 27.6 (Me). ESI-MS: 214.1 ([M + H]$^+$).

7. *2-Methyl-2-(naphthalen-2-yl)-1,3-dioxane* (**7**). According to *Exper. 4* (*Method B*): 124 mg (85%). White solid. M.p. 90.5–93.8°. R_f (CH_2Cl_2/petroleum ether 1:1) 0.20. UV/VIS (MeCN): 224 (92000), 254 (3500), 366 (1200). ^{1}H-NMR (CD_3CN, 400 MHz): 7.94–7.89 (*m*, 4 arom. H); 7.55–7.51 (*m*, 3 arom. H); 3.89–3.85 (*m*, 2 H_{eq} of CH_2CH_2); 3.82–3.75 (*m*, 2 H_{ax} of CH_2CH_2O); 2.06–1.92 (*m*, H_{ax} of CH_2CH_2O); 1.49 (*s*, Me); 1.25 (*dtt*, J = 13.5, 2.7, 1.5, H_{eq} of CH_2CH_2O). ^{13}C-NMR (CD_3CN, 100 MHz): 140.2 (C(2) (naph)); 134.4, 133.8 (*q*, arom. C); 129.3, 129.0, 128.5, 127.2, 127.1, 126.9, 125.7 (arom. CH); 101.2 (*q*, ketal C); 62.0 (CH_2CH_2O); 32.6 (CH_2CH_2O); 26.3 (Me). ESI-MS: 229.1 ([M + H]$^+$).

8. *2-(Dimethoxymethyl)naphthalene* (**8**) [36]. According to *Exper. 4* (*Method B*): 124 mg (96%). Clear oil. R_f (CH_2Cl_2/petroleum ether 1:1) 0.32. UV/VIS (MeCN): 224 (158000), 254 (5500), 366 (<300). ^{1}H-NMR (CD_3CN, 400 MHz): 7.91 (*m*, 4 arom. H); 7.53 (*m*, 3 arom. H); 5.51 (*s*, CH(OMe)$_2$); 3.34 (*s*, 2 MeO). ^{13}C-NMR (CD_3CN, 100 MHz): 137.2 (C(2) (naph)); 134.4, 133.9 (arom. C); 129.2, 128.9, 128.6, 127.3, 127.2, 126.7, 125.4 (arom. CH); 104.4 (acetal CH); 53.5 (MeO). HR-MS: 225.0888 ([M + Na]$^+$, $C_{13}H_{14}NaO_2^+$; calc. 225.0891).

9. *2-(Naphthalen-2-yl)-1,3-dioxolane* (**9**) [37]. According to *Exper. 4* (*Method B*): 101 mg (79%). White solid. R_f (CH_2Cl_2/petroleum ether 1:1) 0.20. UV/VIS (MeCN): 224 (82000), 254 (4100), 366 (<100). ^{1}H-NMR (CD_3CN, 400 MHz): 7.93 (*m*, 4 arom. H); 7.56 (*m*, 3 arom. H); 5.90 (*s*, H–C(2) (diox)); 4.15 (*m*, *A* of *AA′BB′*, CH_2O); 4.04 (*m*, *B* of *AA′BB′*, CH_2O). ^{13}C-NMR (CD_3CN, 100 MHz): 135.3 (C(2) (naph)); 133.9, 133.0 (*q*, arom. C); 128.4, 128.3, 127.8 (arom. CH(4,5,8)); 126.4, 126.2 (arom. CH(6,7)); 126.1 (arom. CH(1)); 123.8 (arom. CH(3)); 104.0 (acetal CH); 65.4 (OCH_2CH_2O). HR-MS: 223.0730 ($[M+Na]^+$; $C_{13}H_{12}NaO_2^+$; calc. 223.0735).

10. *2-(Naphthalen-2-yl)-1,3-dioxane* (**10**) [38]. According to *Exper. 4* (*Method B*): 103 mg (75%). White solid. R_f (CH_2Cl_2/petroleum ether 1:1) 0.18. M.p. 82.1–83.9°. UV/VIS (MeCN): 222 (124000), 254 (4800), 366 (< 300). ^{1}H-NMR (CD_3CN, 400 MHz): 7.97 (br. *s*, arom. H–C(1)); 7.85 (*m*, arom. H–C(4), H–C(5), H–C(8)); 7.60 (*dd*, *J* = 8.5, 1.7, arom. H–C(3)); 7.48 (*m*, arom. H–C(6), H–C(7)); 5.68 (*s*, H–C(2) (dioxane)); 4.33 (*ddd*, *J* = 13.0, 5.0, 2.7, 2 H_{eq} of CH_2CH_2O); 4.06 (*ddd*, *J* = 13.0, 12.5, 1.5, 2 H_{ax} of CH_2CH_2O); 2.29 (*dtt*, *J* = 13.5, 12.4, 5.0, H_{ax} of CH_2CH_2O); 1.50 (*dtt*, *J* = 13.5, 2.7, 1.5, H_{eq} of CH_2CH_2O). ^{13}C-NMR (CD_3CN, 100 MHz): 136.1 (arom. C(2)); 133.6, 133.1 (*q*, arom. C); 128.4, 128.1, 127.7 (arom. CH(4,5,8)); 126.2, 126.0 (arom. CH(6,7)); 125.3 (arom. CH(1)); 123.8 (arom. CH(3)); 101.8 (*q*, acetal CH); 67.5 (CH_2CH_2O); 32.6 (CH_2CH_2O); 25.9 (Me). HR-MS: 237.0886 ($[M+Na]^+$; $C_{14}H_{14}NaO_2^+$; calc. 237.0891).

11. *(1,1-Dimethoxyethyl)benzene* (**11**) [26]. According to *Exper. 4* (*Method A*): 101 mg (95%). Yellow oil. R_f (CH_2Cl_2/petroleum ether 1:2) 0.85. ^{1}H-NMR (CD_3CN, 400 MHz): 7.46 (*m*, 2 arom. H); 7.37 (*m*, 2 arom. H); 7.30 (*tt*, *J* = 6.3, 1.4, H–C(4)); 3.12 (*s*, 2 MeO); 1.48 (*s*, Me). ^{13}C-NMR (CD_3CN, 100 MHz): 142.9 (arom. C(1)); 128.1, 127.5, 126.0 (arom. CH); 101.6 (*q*, ketal C); 49.0 (MeO); 26.0 (Me). ESI-MS: 189.2 ($[M+Na]^+$).

12. *2-Methyl-2-phenyl-1,3-dioxolane* (**12**) [35]. According to *Exper. 4* (*Method A*): 93 mg (88%). White solid. R_f (CH_2Cl_2/petroleum ether 1:2) 0.80. ^{1}H-NMR (CD_3CN, 400 MHz): 7.47 (*m*, 2 arom. H); 7.35 (*m*, 3 arom. H); 3.99 (*m*, *A* of *AA′BB′*, CH_2O); 3.73 (*m*, *B* of *AA′BB′*, CH_2O); 1.58 (*s*, Me). ^{13}C-NMR (CD_3CN, 100 MHz): 143.8 (arom. C(1)); 128.7, 128.2, 125.7 (arom. CH); 109.2 (*q*, ketal C); 64.8 (OCH_2CH_2O); 26.0 (Me). ESI-MS: 187.2 ($[M+Na]^+$).

13. *2-Methyl-2-phenyl-1,3-dioxane* (**13**) [39]. According to *Exper. 4* (*Method A*): 84 mg (74%). White solid. R_f (CH_2Cl_2/petroleum ether 1:2) 0.80. ^{1}H-NMR (CD_3CN, 400 MHz): 7.40 (*m*, 4 arom. H); 7.32 (*m*, 1 arom. H); 3.81 (*ddd*, *J* = 13.0, 5.0, 2.7, 2 H_{eq} of CH_2CH_2); 3.70 (*ddd*, *J* = 13.0, 12.5, 1.5, 2 H_{ax} of CH_2CH_2); 1.98 (*dtt*, *J* = 13.5, 12.4, 5.0, H_{ax} of CH_2CH_2O); 1.40 (*s*, Me); 1.27 (*dtt*, *J* = 13.5, 2.7, 1.5, H_{eq} of CH_2CH_2O). ^{13}C-NMR (CD_3CN, 100 MHz): 141.7 (arom. C(1)); 129.1, 129.0, 128.2 (arom. CH); 100.9 (*q*, ketal C); 61.6 (CH_2CH_2O); 32.8 (CH_2CH_2O); 26.0 (Me). ESI-MS: 201.1 ($[M+Na]^+$).

14. *2-Phenyl-1,3-dioxane* (**16**) [40][41]. According to *Exper. 4* (*Method A*): 94 mg (90%). Clear oil. R_f (CH_2Cl_2/petroleum ether 1:4) 0.60. ^{1}H-NMR (CD_3CN, 400 MHz): 7.45–7.35 (*m*, 5 arom. H); 5.51 (*s*, H–C(2) (dioxane)); 4.18 (*ddd*, *J* = 13.0, 5.0, 2.7, 2 H_{eq} of CH_2CH_2O); 3.98 (*ddd*, *J* = 13.0, 12.5, 1.5, 2 H_{ax} of CH_2CH_2O); 2.09 (*dtt*, *J* = 13.5, 12.4, 5.0, H_{ax} of CH_2CH_2O); 1.45 (*dtt*, *J* = 13.5, 2.7, 1.5, H_{eq} of CH_2CH_2O). ^{13}C-NMR (CD_3CN, 100 MHz): 138.5 (arom. C(1); 128.1, 127.6, 125.6 (arom. CH); 100.9 (acetal CH); 66.7 (CH_2O); 25.2 (CH_2CH_2O). ESI-MS: 187.2 ($[M+Na]^+$).

15. *Photoinduced Hydrolysis of Ketal* **5** *and* **8** *on a 1-g Scale in a Quartz Vessel: Procedure 1.* A soln. of ketal or acetal (5 mmol) in MeCN/H_2O 95:5 (15 ml) was irradiated for 20 min in a quartz vessel. The solvent was evaporated and the residue recrystallized from MeOH: **5** (1.081 g) gave **19** (817 mg, 96%), and **8** (1.011 g) gave **17** (765 mg, 98%).

16. *Photoinduced Hydrolysis of Ketals and Acetals* **5**–**16** *on a 10-mg Scale in an NMR Quartz Tube: Procedure 2.* A soln. of ketal or acetal (0.050 mmol) in CD_3CN/H_2O 95:5 (0.632 ml) was irradiated for 20 min in an NMR quartz tube, and the mixture was analyzed by GC and ^{1}H-NMR.

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