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A convenient route to 1,4-monoprotected dialdehydes, 1,4-ketoaldehydes, γ-lactols and γ-lactones through radical alkylation of α,β-unsaturated aldehydes in organic and organic-aqueous media

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Abstract—α,β-Unsaturated aldehydes were smoothly alkylated by radicals generated through photosensitised hydrogen abstraction of benzophenone. In this way, and by using 1,3-dioxolane as radical precursor, monoprotected 1,4-dialdehydes were obtained from crotonaldehyde, 2-hexenal, 4-methyl-2-pentenal and cyclohexencarboxyaldehyde in a moderate yield, and in a low yield from β-aryl-α,β-unsaturated aldehydes. With 2-alkyl-1,3-dioxolanes, monoprotected 1,4-ketoaldehydes were analogously prepared. By using methanol, ethanol and isopropanol as radical precursors γ-lactols were likewise obtained from the above aliphatic aldehydes. These single-step syntheses compared favorably with multi-step approaches previously proposed for some of these compounds. The lactols were conveniently oxidized to the corresponding γ-lactones. An alternative to the photosensitisation in organic medium was the use of mixed aqueous-organic solvent and a hydrosoluble photosensitiser (benzophenone disodium disulfonate was prepared for this purpose and successfully used), which allowed a more convenient work up.

1. Introduction

The use of radicals in organic synthesis has increased dramatically during the last two decades and many methods for the formation of C–C bonds via carbon-centred radicals have been developed, which, among other ones, have the advantage of tolerating the presence of water. For more than a century, C–C bond formation in aqueous media has been virtually limited to electrochemical processes and aldol condensation reactions. Using radicals in water or a water-containing mixed solvent reduces the use of toxic or dangerous solvents, simplifies the work-up (often a simple extraction), and takes advantage of the specific effects occurring in water, such as hydrogen-bonding. However, except for the pioneering work by Luche[1] on the alkylation of α,β-unsaturated carbonyl compounds under sonication, only very recently were radicals employed in the formation of C–C bonds in aqueous media.[2,3] Such reactions were usually carried out through some modification of the usual methods of generation of radicals e.g. through hydrosoluble initiators,[5] the Et_3B/O_2 method[6] and H_3PO_2 as the reducing agent.[7] In some of the latter experiments the chemical yields in water were better than in an organic medium and the yield was still satisfactory in HCl (1 M) and NaOH (1 M).

An appealing target for the approach via radicals is the conjugate alkylation of α,β-unsaturated aldehydes, in view of the shortcomings of other methods due to the high susceptibility of such substrates to 1,2 rather than 1,4 attack[8a] and to their easy polymerization. In fact, alkylation by organometallic species such as magnesium,[9a] cadmium,[9b] lithium,[9c,d] manganese[9e] and zirconium[9f] derivatives gave good yields of the 1,4 adducts only in some cases and under copper catalysis,[10] and an improvement in the regioselectivity was achieved only by complexation of the carbonyl group[8b] or through a derivatization/protection procedure (e.g. via imines or acetals). As for radical alkylation, application to α,β-unsaturated aldehydes is limited to a few examples including early work on borane radical induced alkylations[11a,b] as well as radical generation via decomposition of α-hydroxydiazenes[11c] and via photolysis of alkylmercury halides.[11d]

In this paper, we report photochemical alkylations of α,β-unsaturated aldehydes by α-oxy and α,α-dioxy substituted radicals produced by means of photosensitised hydrogen transfer from alcohols and 1,3-dioxolanes. Such reactions were carried out both in organic media (benzophenone as

Keywords: alkylation; reactions in water; radical and radical reactions; photochemistry; aldehydes.

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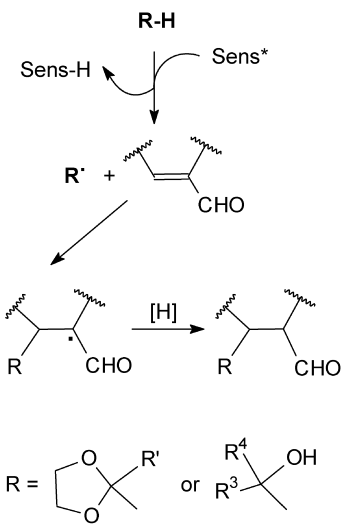
the sensitiser) and in mixed aqueous media (sensitised by benzophenone disodium disulfonate).

2. Results

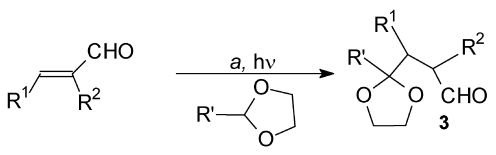
In the last years our group has exploited the photochemical hydrogen transfer method for the functionalization of various α,β-unsaturated ketones,[12a,b] amides,[12c] nitriles[12d] as well as captodative olefins.[12e] The same approach (see Scheme 1) has now been applied for the synthesis of products useful as synthetic intermediates starting from α,β-unsaturated aldehydes. In our approach, alkyl radicals are generated from precursors RH through hydrogen abstraction by an excited sensitiser (Sens*). The radical thus formed attacks the electrophilic olefin in the β position and finally yields the alkylated aldehydes. As radical sources we chose 1,3-dioxolane derivatives and alcohols. The former ones have been developed for this use in our laboratory and shown to be useful for the introduction of a masked aldehyde or ketone moiety,[12a,b] and the latter ones have been employed in photoinitiated syntheses to some extent. As shown in Scheme 1, in this way a synthesis of γ-dioxolanylaldehydes and, respectively, of γ-(hydroxyalkyl)aldehydes (which may ring-close to lactols) is envisaged.

2.1. Synthesis of monoprotected 1,4-dialdehydes (ketoaldehydes)

These compounds were prepared by photosensitised addition of 1,3-dioxolane (used neat), or respectively, 2-substituted-1,3-dioxolanes (as 1 M solution). Irradiation of aldehydes **1** with phosphor-coated lamps (center of emission 315 nm) in solution containing an excess of dioxolanes **2** in the absence of the sensitiser did not lead to alkylated products **3**. Sensitisation under the same conditions afforded in most cases the expected 3-[2-(1,3-dioxolanyl)]aldehydes **3** (Scheme 2). Yields and reaction times were dependent on the substrate employed and conditions and the results are shown in Table 1. Acrolein **1a** was the only substrate studied which readily (3 h)



Scheme 1.



1a R^1 = H, R^2 = H
b R^1 = Me, R^2 = H
c R^1 = *n*-Propyl, R^2 = H
d R^1 = 2-Methylethyl, R^2 = H
e R^1 = R^2 = -$(CH_2)_4$-
f R^1 = Ph, R^2 = H
g R^1 = *p*-$MeOC_6H_4$, R^2 = H
h R^1 = 1-Propenyl, R^2 = H

2 k R' = H
l R' = Methyl
m R' = Ethyl
n R' = *n*-Hexyl

Scheme 2. *Reagents and conditions*: (a) Procedure A: Ph_2CO in neat **2** or in **2**/MeCN mixtures. Procedure B: BPSS in a **2**/H_2O/MeCN or **2**/H_2O mixtures.

polymerized under irradiation in the presence of **2k** and this precluded alkylation. However, crotonaldehyde **1b** gave the desired dioxolanyl derivatives in a significant yield (30–40%, entries 2–7).[13] Changing the conditions from the organic to the mixed aqueous medium and using a water-soluble sensitiser little affected the product yield and only in the synthesis of **3bk** the reaction time was lengthend.

Reactions with **1c** proceeded satisfactory and the alkylation occurred with all the dioxolanes considered (entries 8–15). Noteworthy, neither using the dioxolane 1 M (as it is the case for **2n**) rather than neat (as with **2k**), nor increasing steric hindrance (using 2-substituted dioxolanes rather than parent **2k**) lowered the product yield, although such changes prolonged the required reaction time (compare entry 14 and entry 8, 16 h rather than 3). The reaction took place in the same way with **1d**, showing that branching in the β position did not hinder radical addition.

Incorporating the double bond in a ring as with cyclohexencarboxylaldehyde **1e** did not inhibit the alkylation, which however in this case gave a poor yield in acetonitrile, while the result was much better in mixed aqueous solvent. A mixture of the *cis* and *trans* diastereoisomers was formed (4:1). Due to the superimposition of NMR signals, the assignment was mainly based on the close analogy with the previously studied reaction of **2k** with 1-acetylcyclohexene, where the *cis* was the only isomer obtained.[12a]

Aromatic α,β- unsaturated aldehydes were less suited for the reaction under the above conditions, due to their high absorption at 315 nm. Unsensitised irradiation at this wavelength caused very little alkylation. Using the sensitiser and shifting to lamps with the emission centered at 366 nm gave better, though not satisfactory, yields of products **3fk** and **3gk**. With doubly unsaturated **1h** no significant amount of product **3hk** was obtained, although the aldehyde was consumed during the irradiation.

2.2. Synthesis of γ-butyrolactols or lactones

These compounds were prepared by using alcohols as radical precursors and the results are presented in Scheme 3 and Table 2. Acrolein (**1a**) polymerized by photosensitisation in the presence of alcohols (Table 2, entry 1). However, alkylation was satisfactory with the other aliphatic

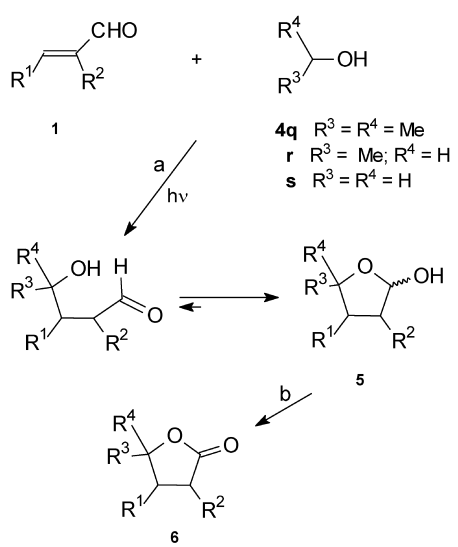
Table 1. Alkylation yields from α,β-unsaturated aldehydes and dioxolanes **2**

Entry	Aldehydes	Dioxolane	Products	Procedure	Reactions time (h)	Product yield (%)[a]
1	**1a**	**2k**	**3ak**	A[b]/B[c]	3	[d]
2	**1b**	**2k**	**3bk**	A[b]	3	40
3	**1b**	**2k**	**3bk**	B[c]	16	43
4	**1b**	**2m**	**3bm**	A[e]	16	38
5	**1b**	**2m**	**3bm**	B[f]	16	42
6	**1b**	**2n**	**3bn**	A[e]	16	30
7	**1b**	**2n**	**3bn**	B[f]	16	36
8	**1c**	**2k**	**3ck**	A[b]	3	39
9	**1c**	**2k**	**3ck**	B[c]	16	32
10	**1c**	**2l**	**3cl**	A[e]	16	49
11	**1c**	**2l**	**3cl**	B[f]	16	44
12	**1c**	**2m**	**3cm**	A[e]	16	28
13	**1c**	**2m**	**3cm**	B[g]	16	24
14	**1c**	**2n**	**3cn**	A[e]	16	40
15	**1c**	**2n**	**3cn**	B[g]	16	38
16	**1d**	**2k**	**3dk**	A[b]	3	38
17	**1d**	**2k**	**3dk**	B[b]	16	36
18	**1e**	**2k**	**3ek** (*cis*+*trans*)	A[b]	16	10
19	**1e**	**2k**	**3ek** (*cis*+*trans*)	B[b]	16	49
20	**1f**	**2k**	**3fk**	A[b]	6	25
21	**1g**	**2k**	**3gk**	A[b]	6	18
22	**1h**	**2k**	**3hk**	A[b]/B[c]	3	[h]

[a] Isolated yield.
[b] Irradiation in neat dioxolane.
[c] Irradiation in 1:1 **2k**–water mixture.
[d] Polymerization occurred during the irradiation.
[e] Irradiation in 1 M **2** in MeCN.
[f] Irradiation in 1 M **2** in 1:1 MeCN–water.
[g] Irradiation in 1 M **2** in 7:10 MeCN–water.
[h] No alkylation occurred while **1** was completely consumed. See Section 5.

aldehydes. In the case of crotonaldehyde (**1b**) alkylation with 2-propanol (**4q**) occurred smoothly leading to the desired lactol **5bq** as a 2:1 mixture of the two diastereomers.[14] The residue obtained from the irradiated solution could be directly oxidized to lactone **6bq** without isolating **5bq** by using $Br_2/BaCO_3$, with an overall yield of 31% for the two steps (entry 3, Table 2). Lactol **5bq** was likewise synthesised in water–alcohol mixture (procedure B) in a similar yield (48%, entry 4).

Alkylated products **5** were obtained in a reasonable yield



Scheme 3. *Reagents and conditions*: (a) Procedure A: Ph_2CO in neat **4**. Procedure B: BPSS in a **4**/H_2O mixtures. (b) Br_2, $BaCO_3$.

also by using ethanol (**4r**) and methanol (**4s**). As an example, lactol **5br** was obtained as a mixture of the four possible diastereoisomers. When the above oxidation procedure was applied, the *cis* and *trans* isomers of lactones **6br** (in about 1:1 ratio) were obtained and characterized after careful chromatographic separation. Better yields were reached in the alkylation of **1c** (entries 9–13), probably owing to the lower volatility of the final products. As an example, lactone **6cs** was prepared from **1c** by direct oxidation of the non-purified lactol intermediate. The same procedure was applied to carbocyclic aldehyde **1e**, with similar results in the formation of lactones 6 eq. (*cis*+*trans* isomers).

On the other hand, the alkylation by alcohols was unsuccessful not only, as in the case of dioxolanes, with doubly unsaturated aldehyde **1h**, but also with aromatic aldehydes **1f**, **g**.

2.3. Assessment of the efficiency of different water-soluble sensitisers

We prepared a water-soluble sensitiser, benzophenone disodium disulfonate (BPSS), for the experiments in mixed aqueous media. This salt is prepared in one-step (see Section 5) and we were curious to examine how it compared with other hydrosoluble sensitisers. We therefore tested three further sensitisers in the reaction of **1c** with **4q**, viz. the sodium salts of antraquinone 2-sodium sulfonic acid (AQSS, commercially available) and of 2- or 4-benzoyl-benzoic acid (2-BBSC and 4-BBSC, the corresponding acids are both commercialized). Irradiation for 8 h gave the results shown in Table 3. It is apparent that only 4-BBSC

Table 2. Yield of alkylated lactols (or lactones) from α,β-unsaturated aldehydes and alcohol **4**

Entry	Aldehydes	Alcohols	Lactols	Lactones[a]	Procedure	Irradiation time (h)	Product yield (%)[b]
1	**1a**	**4q**	**5aq**		A[c]/B[d]	3	[e]
2	**1b**	**4q**	**5bq**		A[c]	7	44
3	**1b**	**4q**		**6bq**	A[c]	7	31
4	**1b**	**4q**	**5bq**		B[d]	7	48
5	**1b**	**4r**	**5br**		A[c]	15	41
6	**1b**	**4r**		**6br** (*cis*+*trans*)	B[d]	15	14 (*cis*) +12 (*trans*)
7	**1b**	**4s**	**5bs**		B	15	58[f]
8	**1b**	**4s**		**6bs**	B	15	39
9	**1c**	**4q**	**5cq**		A[c]	7	63
10	**1c**	**4q**	**5cq**		B[d]	7	50
11	**1c**	**4q**	**5cq**		B[d]	7	57[f,g]
12	**1c**	**4q**		**6cq**	B[d]	7	35
13	**1c**	**4s**		**6cs**	A[c]	15	42
14	**1e**	**4q**		**6eq** (*cis*+*trans*)	A[c]	16	32
15	**1e**	**4q**		**6eq** (*cis*+*trans*)	B[d]	16	37
16	**1f**	**4q**	**5fq**		A[c]	16	[h]
17	**1g**	**4q**	**5gq**		A[c]	16	[h]
18	**1h**	**4q**	**5hq**		A[c]/B[d]	16	[h]

[a] Lactones were obtained by direct oxidation of the raw photolisates. See text.
[b] Isolated yield.
[c] Irradiation in neat alcohol.
[d] Irradiation in 1:1 alcohol **4**–water mixture.
[e] Polymerization occurred during the irradiation.
[f] Reactions carried out in an immersion reactor.
[g] Product **5cq** isolated by bulb to bulb distillation.
[h] No alkylation occurred while starting aldehyde **1** was wholly consumed. See text.

gives results comparable with BPSS, with essentially the same yield of **5cq**, even though the reaction was slightly slower. On the contrary, aldehyde **1c** was photostable in the presence of AQSS and 2-BBSC, just as it happened in the absence of the sensitisers. One may notice that the only alternative to BPSS is the most expensive one of the commercial photosensitisers tested.

3. Discussion

3.1. General course of the reaction

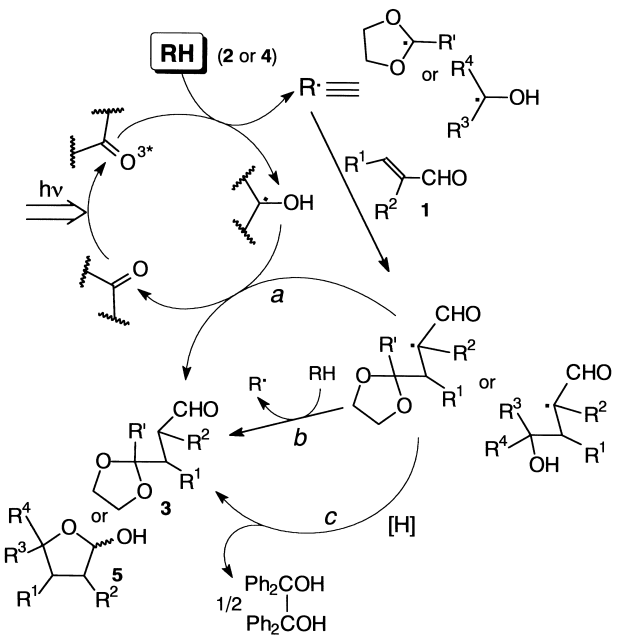
The mild conditions of photosensitisation appear well suited for the radical alkylation of such sensitive substrates as unsaturated aldehydes. The mechanism leading to alkylated aldehydes **3** and **5** is depicted in Scheme 4. Promotion of the sensitiser to the triplet state leads to hydrogen abstraction from the donors (RH) and radical R· is trapped by the unsaturated aldehydes leading to an adduct radical.[15] The sequence is completed by hydrogen abstraction from either the ketyl radical (path *a*) or a reagent, such as RH, (**1**, path *b*) or the solvent (path *c*). The first two paths do not consume the sentisitizer stoichiometrically, as path *a* regenerates it and path *b* leads to a chain alkylation. The present reaction is efficient by using the sensitiser at a substoichiometric concentration (20–40%), and the relative independence of the results on the structure of R–H suggests that path *a* is the most important one. Path *c*, on the contrary, leads to stoichiometrical consumption of the sensitiser and produces pinacols.[16]

Under our conditions, where [RH] (in any case a better hydrogen donor than aldehydes)[17] exceeds by a factor ≥10 the concentration of the unsaturated aldehyde, no competing hydrogen abstraction occurs neither from the formyl group,

Table 3. Comparison of different water soluble sensitisers in the reaction of **1c** and **4q** after 8 h of irradiation

Sensitiser	Conversion of **1c** (%)	Relative yield of **5cq**
None	<5	–
BPSS	100	1
AQSS	<5	[a]
4-BBSC	90	0.88
2-BBSC	<5	[a]

[a] Product **5cq** not detected by GC analysis.



Scheme 4.

although such abstraction by excited benzophenone has been reported,[18] nor from the γ-position.

3.2. Scope of the method

Yields are mostly moderate, but this does not deprive the method of interest in view of the mild conditions, the simplicity and directness of the method, leading through a single photochemical reaction to products that are otherwise obtained in several steps, and avoiding the use of heavy metals. Both dioxolanes and alcohols are suitable radical precursors. The irradiation time depends on the concentration of these hydrogen donor (e.g. compare entry 2 in Table 1 with **2k** used neat and entry 4 with **2m** used 1 M) and on their structure (e.g. alkylations with isopropanol are in every case about twice as fast as with ethanol and methanol, see Table 2), but the yield reached after the appropriate irradiation time are not much different.

α,β-Unsaturated aldehydes proved to be efficient radical traps. Indeed, in the alkylation with 2-alkyl-dioxolanes **2l**–**n** yields are better than with structurally similar ketones.[12b] Exceptions are acrolein **1a**, which undergoes a fast polymerization under this conditions and doubly unsaturated aldehyde **1h** that likewise is consumed efficiently thus precluding alkylation. Aromatic aldehydes have a triplet energy close to that of the sensitiser (cinnamaldehyde, **1f**, 300 kJ mol^{-1}, benzophenone, 287)[19] and thus energy transfer and geometric isomerization greatly hinders hydrogen abstraction from the radical precursors R–H. Nevertheless, some alkylation takes place with dioxolanes, if not with the alcohols.

In the alkylation with alcohols, γ-butyrolactols are obtained often as a diastereoisomeric mixture. Such products can be further transformed without purification, however; in particular we oxidized them directly to the corresponding lactones. This simple preparation of β-alkyl-γ-lactones is of interest also because the alternative approach from α,β-unsaturated acids through the same photosensitised radical method was previously found to give poor yields.[20,21] In the present case, the preparation of the lactones was cleaner when the photoalkylation had been carried out in mixed aqueous solution (procedure B), since the oxidation step was facilitated by the elimination of most byproducts by extraction (see further below).

With cyclohexencaboxylaldeyde (**1e**) in mixed aqueous solvent the addition is somewhat diastereoselective, both when using isopropanol (*cis*/*trans* 2:1 for lactone **6eq**) and, to a larger degree, with dioxolane (4.6:1 for the *cis* isomer in the formation of compound **3ek**). Addition of ethanol to crotonaldehyde is unselective (see entry 6 in Table 2).

3.3. Water-containing solvent and hydrophylic sensitisers

As can be seen from Tables 1 and 2, the presence of water did not influence the alkylation processes (except for the irradiation time in some cases) and the overall yields in the formation of either dioxolanyl aldehydes **3** or lactols **5** were about the same both by procedure A and B, the latter involving a mixed solvent containing up to 50% water and using a water soluble sensitiser. The fact that procedure B is feasible is significant for different reasons: (a) the amount of toxic organic solvents such as MeCN is reduced (b) the final products are obtained by simple extraction of the irradiated mixtures often with a satisfactory degree of purity, either for isolation requiring a less elaborated chromatography than after irradiation in organic medium or for simplified further elaboration, (c) during the extraction procedure all of the byproducts arising from the sensitiser remain in the aqueous phase. A water-soluble sensitiser, BPSS, was obtained by sulfonation of the inexpensive benzophenone; of the commercial sensitisers tested, only 4-BBSC comes near to the results with BPSS (see Table 3). Previously, both 4-BBSC[22a,b] and *p*-sulfonated benzophenones[22c,d] have been reported to abstract hydrogen in alcohol–water mixtures with efficiency similarly to non-sulfonated benzophenone through laser flash photolysis studies.[22a,d] On the contrary, sensitisers with slightly different structures, such 2-BBSC and AQSS were much less effective. This peculiarity is presently under investigation.

3.4. Synthetic significance

The present method offers an easy entry to different succinaldehyde monoacetals[23] and γ-(monoprotected) ketoaldehydes. As for the latter compounds, the photochemical procedure gives selectively masked dicarbonyls that can not be obtained in a single step from the corresponding γ-ketoaldehydes because the protection involves the less electrophilic ketone function. Noteworthy, compounds **3dk**, **3bm** and **3gk** have been previously reported in the literature as intermediates for the synthesis of molecules having biological activity but have been obtained through several steps. For example, aldehyde **3dk** has been obtained in five steps and employed in the synthesis of ryanodol.[24a] Likewise, the dioxolanyl derivatives **3bm** is a building block for the synthesis of sordinin (a male pheromone compound emitted by *Cosmopolites sordidus*)[24b] and *O*-methyljoubertiamine (a *seco*-mesembrane alkaloid) has been obtained from **3gk**.[24c]

γ-Lactols are another important class of compounds in organic synthesis; this importance is especially due to their easy transformation to tetrahydrofuran derivatives or lactones.[25] We will not deal with this point in detail, but γ-butyrolactones are ubiquitous in nature and many of them are biologically significant (alkaloids, macrocyclic antibiotics and pheromones).[26,27] Thus a new mild access to this class of compounds is of interest.

4. Conclusions

In this work, radicals generated by photosensitised hydrogen abstraction were successfully used for the synthesis of 1,4-monoprotected dialdehydes and ketoaldehydes as well of γ-lactols and lactones starting from α,β-unsaturated aldehydes, a class of substrates to which radical addition processes had been only rarely applied up to now. The reactions could be performed both in organic media and in mixed aqueous media; in the last case water-soluble sensitisers were used and work up was simplified. 1,3-Dioxolane and its 2-substituted derivatives or respectively

alcohols were used as radical precursors, obtaining moderate yields from aliphatic unsaturated aldehydes, though less positive results were obtained with the arylated derivatives.

5. Experimental

5.1. General

Unsaturated aldehydes **1** were of commercial origin except for **1d**[28] **1e**,[29] which were prepared according to literature procedures, and were freshly distilled (or purified) just before use. Dioxolanes **2k** and **2l** were commercial samples and used as received whereas **2m** and **2n** were prepared from the corresponding aldehydes.[12b] 2-BBSC and 4-BBSC were obtained from the commercial acids. The photochemical reactions were performed in quartz tubes by using nitrogen-purged solution and external illumination by means of a multilamp reactor fitted with six 15 W phosphor-coated lamps (maximum of emission 315 or 366 nm). Workup of the photolytes involved concentration in vacuo followed by chromatographic separation (cyclohexane/ethyl acetate mixtures as eluants) using Millipore 60 Å 35–70 μm silica gel (otherwise indicated). The structural attribution of new products was made mainly on the basis of ^{1}H and ^{13}C NMR, recorded on a 300 MHz spectrometer; chemical shifts are reported in ppm downfield from TMS.

5.1.1. Synthesis of benzophenone disodium disulfonate (BPSS). Benzophenone (50 g, 274 mmol) was heated at 60°C under mechanical stirring until melting. Oleum (90 mL, 20% SO_3 content) was then slowly added and the resulting mixture was heated to 160°C for 4 h. The solution was then allowed to cool down to room temperature and poured into 150 g of crushed ice under vigorous stirring. A white solid (unreacted benzophenone) separated out and was filtered off. The filtrate was cautiously neutralized under stirring with 40% NaOH aqueous solution. The milky solid thus formed was again eliminated and the filtrate was evaporated in vacuo. The resulting solid was dissolved in water and MeOH was added in order to precipitate most of the Na_2SO_4 present. The last procedure (dissolution in water and precipitation of Na_2SO_4 with MeOH) was repeated a few times until the resulting solid showed a satisfactory degree of purity (>90%).[30] The resulting BPSS (after reaching constant weight in vacuum essicator, 12.7 g, 12% yield) was a mixture of 3,3′- and 4,4′-benzophenone disodium disulfonate (bis-*meta*/bis-*para* ratio ca. 2:1) as shown by NMR analysis. Ionic chromatographic sulfate determination revealed the presence of 5% Na_2SO_4. These data, coupled with elemental analysis, were consistent with a BPSS monohydrate structure.

^{1}H (D_2O, from the mixture) δ 7.65 (2H, t, J=6.0 Hz, meta), 7.85–7.95 (8H, m, 4H meta and 4H para), 8.05 (4H, d, J=6.0 Hz, para), 8.15 (2H, bs, meta). ^{13}C (D_2O, from the mixture) δ 125.6 (CH), 126.7 (CH), 129.4 (CH), 130.0 (CH), 130.7 (CH), 136.8 (meta), 138.6 (para), 142.9 (meta), 146.3 (para), 197.8 (CO, meta), 198.1 (CO, para). IR (KBr) ν, (cm^{-1}) 2950, 1642, 1100. Anal. Found: C, 36.30; H, 2.32. Calcd for $C_{13}H_8Na_2O_4S_2{\cdot}H_2O$ containing 5% Na_2SO_4: C, 36.77; H, 2.37.

5.2. Photochemical synthesis of substituted aldehydes 3. General procedure

Procedure A: A solution of the aldehyde **1** (0.05–0.1 M), dioxolane **2** (used as the solvent in the case of **2k** or 1 M in the other cases) and the sensitiser (benzophenone, 0.02 M) in acetonitrile was irradiated until **1** was consumed. Workup of the photolytes involved concentration in vacuo and chromatographic separation.

Procedure B: A solution of the aldehyde **1** (0.1 M), dioxolane **2** (1 M) and the sensitiser (BPSS 0.02 M) in acetonitrile/water (a 1:1 mixture of **2**-water in the case of **2k**) was irradiated until **1** was consumed. Workup of the photolytes involved elimination of the organic solvents in vacuo, extraction with CH_2Cl_2 (4 times) of the resulting aqueous phase and, when appropriate, chromatographic purification of the residue.

5.2.1. 3-(1,3-Dioxolan-2-yl)-butyraldehyde (3bk). Proc. A: From 205 μL of **1b** (2.5 mmol, 0.05 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 50 mL of 1,3-dioxolane irradiated for 3 h at 315 nm. After column chromatography (C_6H_{12}/EtAc 9:1 containing 0.2% Et_3N) 144 mg of the title compound **3bk** (oil) were isolated (40% yield).

Proc. B: From 500 μL of **1b** (6 mmol, 0.1 M) and 485 mg of BPSS (1.2 mmol, 0.02 M) in 60 mL of a 1:1 mixture of 1,3-dioxolane/water irradiated for 16 h at 315 nm. Purification by column chromatography yielded 372 mg of **3bk** (43% yield).

3bk: Spectroscopic data in accord with the literature.[31]

Chromatography in the absence of Et_3N yielded the *trans*-acetalized product *1,2-bis-[(1,3-dioxolan-2-yl)propane* as the only isolated product. ^{1}H NMR ($CDCl_3$): δ 1.05 (3H, d, J=7.0 Hz, CH_3CH_x), 1.40–1.60 (1H, m, CH_aH_b-$CH(OCH_2)_2$, A part of an ABX system), 1.80–1.90 (1H, m, $CH_aH_bCH(OCH_2)_2$, B part of an ABX system), 1.90–2.05 (1H, m, CH_3CH_x, X part of an ABX system), 3.70–3.85 (4H, m, OCH_2CH_2O), 3.90–4.10 (4H, m, OCH_2CH_2-O), 4.70 (1H, d, J=4.0 Hz, OC*H*O), 4.90 (1H, t, J=5.0 Hz, OC*H*O). ^{13}C NMR: δ 14.3 (CH_3), 32.9 (CH), 35.0 (CH_2), 64.6 (CH_2), 64.7 (CH_2), 64.8 (CH_2), 64.9 (CH_2), 103.3 (CH), 108.9 (CH). IR (neat) ν, (cm^{-1}) 2945, 1101. Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.70; H, 8.31.

Compound **3bk** was very sensitive to oxidation in solution forming the corresponding acid [*3-(1,3-dioxolan-2-yl)-butyric acid*]. This was detected in mixture with **3bk** after some time in solution. ^{1}H NMR ($CDCl_3$, from the mixture): δ 1.00 (3H, d, J=7.0 Hz, CH_3CH_x), 2.15–2.25 (1H, m, CH_aH_bCOOH, A part of an ABX system), 2.45–2.50 (1H, m, CH_3CH_x, X part of an ABX system), 2.55–2.60 (1H, m, CH_aH_bCOOH, B part of an ABX system), 4.00 (4H, m, OCH_2CH_2O), 4.90–5.00 (1H, m, OC*H*O). ^{13}C NMR ($CDCl_3$): δ 15.1 (CH_3), 34.3 (CH), 35.8 (CH_2), 65.5 (CH_2), 65.6 (CH_2), 106.7 (CH), 177.8 (COOH).

5.2.2. 3-(2-Ethyl-1,3-dioxolan-2-yl)-butyraldehyde (3bm). Proc. A: From 205 μL of **1b** (2.5 mmol, 0.05 M), 5.2 mL of **2m** (50 mmol, 1 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 45 mL of acetonitrile irradiated for 16 h at 315 nm. After column chromatography (C_6H_{12}/EtAc 95:5) 164 mg of the title compound **3bm** (oil) were isolated (38% yield).

Proc. B: From 500 μL of **1b** (6 mmol, 0.1 M), 6.2 mL of **2m** (60 mmol, 1 M) and 485 mg of BPSS (1.2 mmol, 0.02 M) in 54 mL of a 1:1 mixture of acetonitrile/water irradiated for 16 h at 315 nm. Purification on column yielded 435 mg of **3bm** (42% yield).

3bm: Spectroscopic data in accord with the literature.[32]

5.2.3. 3-(2-Hexyl-1,3-dioxolan-2-yl)-butyraldehyde (3bn). Proc. A: From 205 μL of **1b** (2.5 mmol, 0.05 M), 8.5 mL of **2n** (50 mmol, 1 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 41.5 mL of acetonitrile irradiated for 16 h at 315 nm. Most of compound **2n** was then eliminated by distillation in vacuo and after column chromatography (C_6H_{12}/EtAc 95:5) of the resulting raw material, 170 mg of the title compound **3bn** (oil) were isolated (30% yield).

Proc. B: From 250 μL of **1b** (3 mmol, 0.06 M), 1.5 mL of **2n** (9 mmol, 0.2 M) and 243 mg of BPSS (0.6 mmol, 0.012 M) in 50 mL of a 7:3 mixture of acetonitrile/water irradiated for 16 h at 315 nm. Purification on column yielded 245 mg of **3bn** (36% yield).

3bn: colourless oil, ^{1}H NMR ($CDCl_3$): δ 0.85 (3H, t, J=7.0 Hz, CH_3CH$_2$), 1.00 (3H, d, J=7.0 Hz, CH_3CH), 1.15–1.40 (8H, m, CH_2CH_2CH_2CH_2), 1.50–1.70 (2H, m, CH_2CH(OCH$_2$)$_2$), 2.15–2.25 (1H, m, CH$_3$CH_x, X part of an ABX system), 2.45–2.55 (2H, m, C$H_a$$H_b$CHO, AB part of an ABX system), 3.90 (4H, m, OCH_2CH_2O), 9.60 (1H, bs, CH$_a$H$_b$CHO). IR (neat) ν, (cm^{-1}) 2955, 2877, 1708, 1103. Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.24; H, 10.51.

5.2.4. 3-[1,3]Dioxolan-2-yl-hexanal (3ck). Proc. A: From 290 μL of **1c** (2.5 mmol, 0.05 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 50 mL of 1,3-dioxolane irradiated for 3 h at 315 nm. After column chromatography (C_6H_{12}/EtAc 9:1) 168 mg of the title compound **3ck** (oil) were isolated (39% yield).

Proc. B: From 700 μL of **1c** (6 mmol, 0.1 M) and 485 mg of BPSS (1.2 mmol, 0.02 M) in 60 mL of a 1:1 mixture of 1,3-dioxolane/water irradiated for 16 h at 315 nm. Purification by column chromatography yielded 330 mg of **3ck** (32% yield).

3ck: colourless oil, ^{1}H NMR ($CDCl_3$): δ 0.95 (3H, t, J=7.0 Hz, CH_3CH$_2$), 1.10–1.60 (4H, m, CH$_3$CH_2CH_2), 2.25 (1H, ddd, J=2.0, 4.0, 15.0 Hz, CH_aH$_b$CHO, A part of an ABX system), 2.35–2.40 (1H, m, CH$_3$CH_x, X part of an ABX system), 2.45 (1H, ddd, J=3.0, 7.0, 15.0 Hz, CH$_a$$H_b$-CHO, B part of an ABX system), 3.80–4.00 (4H, m, OCH_2CH_2O), 4.90 (1H, d, J=3.0 Hz, OCHO), 9.60 (1H, dd, J=2.0, 3.0 Hz, CH$_a$H$_b$CHO). ^{13}C NMR: δ 13.8 (CH$_3$), 20.1 (CH$_2$), 32.3 (CH$_2$), 37.1 (CH), 42.7 (CH$_2$), 54.6 (CH$_2$), 54.8 (CH$_2$), 105 (CH), 202 (CHO). IR (neat) ν, (cm^{-1}) 2968, 2882, 1707, 1101. Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.79; H, 9.33.

5.2.5. 3-(2-Methyl-1,3-dioxolan-2-yl)-hexanal (3cl). Proc. A: From 580 μL of **1c** (5 mmol, 0.1 M), 4.5 mL of **2l** (50 mmol, 1 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 45.5 mL of acetonitrile irradiated for 16 h at 315 nm. After column chromatography (Cy/EtAc 92:8) 455 mg of the title compound **3cl** (oil) were isolated (49% yield).

Proc. B: From 700 μL of **1c** (6 mmol, 0.1 M), 5.4 mL of **2l** (60 mmol, 1 M) and 485 mg of BPSS (1.2 mmol, 0.02 M) in 54.5 mL of a 1:1 mixture of acetonitrile/water irradiated for 16 h at 315 nm. Purification on column yielded 492 mg of **3cl** (44% yield).

3cl: colourless oil, ^{1}H NMR ($CDCl_3$): δ 0.95 (3H, t, J=7.0 Hz, CH_3CH$_2$), 1.10–1.60 (4H, m, CH$_3$CH_2CH_2), 1.30 (3H, s, CH_3C(OCH$_2$)$_2$), 2.20–2.50 (3H, m, CH_xCH_a-H_b), 3.80–3.90 (4H, m, OCH_2CH_2O), 9.65 (1H, d, J=3.0 Hz, CH$_a$H$_b$CHO). ^{13}C NMR: δ 14.0 (CH$_3$), 20.7 (CH$_2$), 20.9 (CH$_3$), 32.4 (CH), 42.3 (CH$_2$), 43.8 (CH$_2$), 63.9 (CH$_2$), 64.5 (CH$_2$), 201.8 (CO). IR (neat) ν, (cm^{-1}) 2958, 2872, 1708, 1037. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.55; H, 9.66.

5.2.6. 3-(2-Ethyl-1,3-dioxolan-2-yl)-hexanal (3cm). Proc. A: From 290 μL of **1c** (2.5 mmol, 0.05 M), 5.2 mL of **2m** (50 mmol, 1 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 45.5 mL of acetonitrile irradiated for 16 h at 315 nm. After column chromatography (C_6H_{12}/EtAc 95:5) 140 mg of the title compound **3cl** (oil) were isolated (28% yield).

Proc. B: From 170 μL of **1c** (1.5 mmol, 0.03 M) 1 mL of **2m** (10 mmol, 0.2 M) and 242 mg of BPSS (0.6 mmol, 0.012 M) in 50 mL of a 7:10 mixture of MeCN/water irradiated for 16 h at 315 nm. Purification on column yielded 72 mg of **3cm** (24% yield).

3cm: colourless oil, ^{1}H NMR ($CDCl_3$): δ 0.85 (3H, t, J=7.0 Hz, *Me*), 0.90 (3H, t, J=7.0 Hz, *Me*), 1.15–1.80 (6H, m, 3CH_2), 2.15–2.50 (3H, m, CH_xCH_aH$_b$), 3.80–4.00 (4H, m, OCH_2CH_2O), 9.60 (1H, dd, J=2.0, 3.0 Hz, CH$_a$H$_b$CHO). IR (neat) ν, (cm^{-1}) 2952, 2868, 1708, 1098. Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 66.01; H, 10.01.

5.2.7. 3-(2-Hexyl-1,3-dioxolan-2-yl)-hexanal (3cn). Proc. A: From 290 μL of **1c** (2.5 mmol, 0.05 M), 8.5 mL of **2n** (50 mmol, 1 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 41.5 mL of acetonitrile irradiated for 16 h at 315 nm. Compound **3cn** (255 mg, oil, 40% yield) was isolated by bulb to bulb distillation.

Proc. B: From 170 μL of **1c** (1.5 mmol, 0.03 M) 1.5 mL of **2n** (10 mmol, 0.2 M) and 242 mg of BPSS (0.6 mmol, 0.012 M) in 50 mL of a 7:10 mixture of MeCN/water irradiated for 16 h at 315 nm. Purification by column chromatograph yielded 146 mg of **3cn** (38% yield).

3cn: colourless oil, ^{1}H NMR ($CDCl_3$): δ 0.78 (3H, t, J=7.0 Hz, *Me*), 0.80 (3H, t, J=7.0 Hz, *Me*), 1.20–1.70

(14H, m, 7CH_2), 2.10–2.40 (3H, m, CH_xC$H_a$$H_b$), 3.85–4.00 (4H, m, OC$H_2CH_2$O), 9.6 (1H, dd, J=2.0, 3.0 Hz, C$H_a$$H_b$-C*H*O). IR (neat) ν, (cm^{-1}) 2956, 2871, 1710, 1090. Anal. Calcd for $C_{15}H_{28}O_3$: C, 70.27; H, 11.01. Found: C, 70.22; H, 10.98.

5.2.8. 3-(1,3-Dioxolan-2-yl)-4-methylpentanal (3dk). Proc. A: From 245 mg of **1d** (2.5 mmol, 0.05 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 50 mL of 1,3-dioxolane irradiated for 3 h at 315 nm. After column chromatography (C_6H_{12}/EtAc 85:15) 164 mg of the title compound **3dk** (oil) were isolated (38% yield).

Proc. B: From 590 mg of **1d** (6 mmol, 0.1 M) and 485 mg of BPSS (1.2 mmol, 0.02 M) in 60 mL of a 1:1 mixture of 1,3-dioxolane/water irradiated for 16 h at 315 nm. Purification by column chromatography yielded 372 mg of **3dk** (36% yield).

3dk: Spectroscopic data in accord with the literature.[33]

5.2.9. 3-(1,3-Dioxolan-2-yl)-cyclohexancarbaldehyde (3ek). Proc. A: From 285 mg of **1e** (2.5 mmol, 0.05 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 50 mL of 1,3-dioxolane irradiated for 3 h at 315 nm. Purification by column chromatography (C_6H_{12}/EtAc 80:20) was tedious owing to the interference of different byproducts and only 37 mg of slighty impure **3ek** (oil, *cis*+*trans*) were isolated (10% yield).

Proc. B: From 570 μL of **1e** (5 mmol, 0.1 M) and 405 mg of BPSS (1 mmol, 0.02 M) in 50 mL of a 1:1 mixture of 1,3-dioxolane/water irradiated for 16 h at 315 nm. Purification by column chromatography yielded 358 mg of **3ek** (49% yield) as a mixture of the two diastereoisomers in the ratio 4.6:1. The *cis* configuration was assigned to the major component on the basis of the comparison with the corresponding adduct with 1-acetylcyclohexene,[12a] for which double irradiation experiments, not carried out here due to the close superimposition of signals, had supplied evidence.

^{1}H NMR ($CDCl_3$, mixture of the two diastereoisomers): δ 1.00–2.50 (18H, m, 8CH_2 and 2C*H*), 2.50–2.65 (2H, m, 2C*H*CHO), 3.70–4.00 (8H, m, 2 OCH_2CH_2O), 4.7 (1H, d, J=3.0 Hz, OC*H*O, minor isomer), 4.95 (1H, d, J=5.5 Hz, OC*H*O, major isomer), 9.35 (1H, d, J=5.0 Hz, C*H*O, minor isomer), 9.80 (1H, bs, C*H*O, major isomer).

^{13}C NMR: ($CDCl_3$, major isomer from the mixture) δ 22.9 (CH_2), 24.3 (CH_2), 25.0 (CH_2), 25.1 (CH_2), 42.1 (CH), 48.2 (CH), 64.5 (CH_2), 64.6 (CH_2), 104.7 (CH), 204.2 (CHO). ^{13}C NMR: ($CDCl_3$, minor isomer from the mixture) δ 24.4 (CH_2), 24.7 (CH_2), 25.6 (CH_2), 25.8 (CH_2), 41.3 (CH), 49.7 (CH), 64.5 (CH_2), 64.6 (CH_2), 105.8 (CH), 203.0 (CHO). IR (neat, mixture) ν, (cm^{-1}) 1730, 1085. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.25; H, 8.80.

5.2.10. 3-(1,3-Dioxolan-2-yl)-3-phenylpropanal (3fk). Proc. A: From 315 μL of **1f** (2.5 mmol, 0.05 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 50 mL of 1,3-dioxolane irradiated for 6 h at 366 nm. After column chromatography (neutral alumina, C_6H_{12}/EtAc 8:2) 129 mg of the title compound **3fk** (oil) were isolated (25% yield).

3fk: colourless oil, ^{1}H NMR ($CDCl_3$): δ 2.70–2.80 (1H, m, C$H_a$$H_b$CHO, A part of an ABX system), 2.95–3.05 (1H, m, CH$_a$$H_b$CHO, B part of an ABX system), 3.55–3.65 (1H, m, PhCH_x, X part of an ABX system), 3.80–4.00 (4H, m, OCH_2CH_2O), 5.05–5.15 (1H, m, OC*H*O), 7.20–7.40 (5H, m, *Ph*), 9.75 (1H, bs, C*H*O). ^{13}C NMR: ($CDCl_3$) δ 43.7 (CH_2), 43.8 (CH), 65.1 (CH_2), 65.3 (CH_2), 105.6 (CH),138.8, 126.2 (CH), 127.8 (CH), 128.5 (CH), 201 (CHO). IR (neat) ν, (cm^{-1}) 2938, 2858, 1721, 1617, 1089, 840. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.78; H, 6.77.

5.2.11. 3-[1,3]Dioxolan-2-yl-3-(4-methoxyphenyl)propanal (3gk). Proc. A: From 425 mg of **1g** (2.5 mmol, 0.05 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 50 mL of 1,3-dioxolane irradiated for 6 h at 366 nm. After column chromatography (neutral alumina, C_6H_{12}/EtAc 8:2) 106 mg of the title compound **3gk** (oil) were isolated (18% yield).

3gk: ^{1}H NMR ($CDCl_3$):[34] δ 2.70 (1H, ddd, J=2.0, 7.0, 16.5 Hz, C$H_a$$H_b$CHO, A part of an ABX system), 2.95 (1H, ddd, J=2.5, 7.0, 16.5 Hz, CH$_a$$H_b$CHO, B part of an ABX system), 3.55 (1H, dt, J=3.6, 7.0 Hz, 4-MeOPhCH_x, X part of an ABX system), 3.80 (3H, s, *Me*), 3.90–4.00 (4H, m, OCH_2CH_2O), 5.00 (1H, d, J=3.6 Hz, OC*H*O), 6.80–6.90 (2H, m, AA′BB′ system), 7.20–7.30 (2H, m, AA′BB′ system), 9.70 (1H, dd, J=2.0, 2.5 Hz, C*H*O). ^{13}C NMR ($CDCl_3$): δ 42.9 (CH), 43.8 (CH_2), 55.1 (CH_3O), 64.8 (CH_2), 65.3 (CH_2), 105.7 (CH), 113.9 (CH), 129.4 (CH), 130.8, 158.6, 201 (CHO). IR (neat) ν, (cm^{-1}) 2941, 2862, 1720, 1618, 1093, 842. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.00; H, 6.85.

5.3. Attempted synthesis of dioxolanes 3ak and 3hk

Application of the above procedures to aldehydes **1a** and **1h** both in organic and in aqueous media gave no detectable amount of the expected products **3ak** or **3hk**, while **1h** was consumed through undetermined paths and **1a** polymerized.

5.4. Photochemical synthesis of lactols 5. General procedure

Procedure A: A solution of the aldehyde **1** (0.05–0.1 M), the sensitiser (benzophenone, 0.02 M) in neat alcohol **4** was irradiated until **1** was consumed. Workup of the photolytes involved concentration in vacuo and chromatographic separation.

Procedure B: A solution of the aldehyde **1** (0.05–0.1 M), the sensitiser (BPSS 0.02 M) in a 1:1 mixture of **4**-water was irradiated until **1** was consumed. Workup of the photolytes involved elimination of the organic solvents in vacuo, extraction with CH_2Cl_2 (4 times) of the resulting aqueous phase and chromatographic purification of the residue.

5.5. Conversion to lactones 6. General procedure

Lactones **6** were obtained from crude lactols **5** by oxidation of the previous crude photolisates employing Br_2/$BaCO_3$ as an oxidant. The reaction was carried out dissolving the residue in H_2O/ dioxane 2:1 at room temperature in the dark

under stirring for 2 h.[35] The reaction was quenched with an aqueous saturated $Na_2S_2O_3$ solution until decoloration and then extracted with AcOEt (3 times). The crude lactone was purified on column chromatography.

5.5.1. 4,5,5-Trimethyltetrahydrofuran-2-ol (5bq). Proc. A: From 207 μL of **1b** (2.5 mmol, 0.05 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 50 mL of **4q** irradiated for 16 h at 315 nm. After column chromatography (C_6H_{12}/EtAc 8:2) 143 mg of the title compound **5bq** were obtained as a mixture of two diastereoisomer in a 2:1 ratio (44% yield).

Proc. B: From 500 μL of **1b** (6 mmol, 0.1 M) and 485 mg of BPSS (1.2 mmol, 0.02 M) in 60 mL of a 1:1 mixture of **4q**/water irradiated for 16 h at 315 nm. Purification by column chromatography yielded 372 mg of **5bq** (48% yield).

5bq: colourless oil, ^{1}H NMR ($CDCl_3$, major isomer, from the mixture) δ 0.95 (6H, s, 2 *Me*), 1.15 (3H, d, J=7.0 Hz, *Me*), 1.70 (1H, ddd, J=5.0, 7.0, 12.0 Hz, CH_aH$_b$CHOH), 1.95 (1H, dd, J=7.0, 12.0 Hz, CH$_a$$H_b$CHOH), 2.20–2.30 (1H, m, C*H*Me), 5.30 (1H, d, J=5.0 Hz, C*H*OH). ^{13}C NMR ($CDCl_3$, from the mixture): δ 13.8 (CH_3), 22.8 (CH_3), 28.8 (CH_3), 39.5 (CH), 41.0 (CH_2), 84.2, 95.9 (CH).

^{1}H NMR ($CDCl_3$, minor isomer, from the mixture) δ 0.90 (3H, d, J=7.0 Hz, *Me*), 1.30 (6H, s, 2 *Me*), 1.55–1.65 (1H, m, CH_aH$_b$CHOH), 1.85–1.95 (1H, m, CH$_a$$H_b$CHOH), 2.30–2.40 (1H, m, C*H*Me), 5.30 (1H, t, J=5.0 Hz, C*H*OH). ^{13}C NMR ($CDCl_3$, from the mixture): δ 14.0 (CH_3), 22.9 (CH_3), 27.4 (CH_3), 41.3 (CH_2), 42.7 (CH), 83.3, 95.8 (CH). IR (neat, mixture) ν, (cm^{-1}) 3425, 2978, 1450, 1360, 980. Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.63; H, 10.89.

5.5.2. 4,5,5-Trimethyltetrahydrofuran-2-one (6bq). The residue obtained from the procedure B irradiation was dissolved in 30 mL of H_2O/dioxane 2:1 mixture and oxidized by treatment with 1.3 g of $BaCO_3$ and 770 μL of Br_2. Chromatographic purification (C_6H_{12}/EtAc 8:2 as the eluant) afforded 238 mg of **6bq** (31% yield based on starting **1b**).

6bq: Spectroscopic data in accord with the literature.[36]

5.5.3. 4,5-Dimethyltetrahydrofuran-2-ol (5br). Proc. A: From 207 μL of **1b** (2.5 mmol, 0.05 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 50 mL of 4r irradiated for 16 h at 315 nm. After column chromatography (C_6H_{12}/EtAc 8:2) 119 mg of the title compound **5br** (oil) were obtained (41% yield). NMR analysis (^{1}H NMR and ^{13}C NMR) is consistent with a mixture of the four possible diastereoisomers of compound **5br** due to the presence of four emiacetalic hydrogens δ=4.35, 4.1, 3.8, 3.55 in a 3.2:1:1.5:1.5 ratio. The structure of this compound was also supported by the ensuing oxidation leading to compound **6br** (see below).

5.5.4. 4,5-Dimethyltetrahydrofuran-2-one (6br). Proc. B: From 500 μL of **1b** (6 mmol, 0.1 M) and 485 mg of BPSS (1.2 mmol, 0.02 M) in 60 mL of a 1:1 mixture of **4r**/water irradiated for 16 h at 315 nm. The residue obtained from the irradiation was dissolved in 30 mL of H_2O/dioxane 2:1 mixture and oxidized by treatment with 1.3 g of $BaCO_3$ and 770 μL of Br_2. Chromatographic purification (C_6H_{12}/EtAc 8:2 as the eluant) afforded 98 mg of the *cis*-4,5-dimethyl-tetrahydro-furan-2-one (14% yield) and 80 mg of *trans*-4,5-dimethyl-tetrahydro-furan-2-on (12% yield). Spectroscopic data were in accord with the literature.[37]

5.5.5. 4-Methyltetrahydrofuran-2-ol (5bs). Proc. B (in the immersion well photochemical reactor): The reaction was performed in an immersion well apparatus fitted with a Pyrex glass filtered 150 W medium-pressure mercury lamp starting from 2 mL of **1b** (24 mmol, 0.1 M) and 2.33 g of BPSS (4.8 mmol, 0.02 M) in 240 mL of a 1:1 mixture of **4s**/water (irradiation time=15 h). Purification by column chromatography (C_6H_{12}/EtAc 8:2) yielded 1.42 g of **5bs** (58% yield) as a mixture of two diastereoisomers in a 1.5:1 ratio.

5bs: The ^{1}H NMR spectra ($CDCl_3$) corresponded to those previously reported.[38]

^{13}C ($CDCl_3$, major isomer) δ 17.3 (CH_3), 30.8 (CH), 41.3 (CH_2), 73.7 (CH_2), 98.3 (CH).

^{13}C ($CDCl_3$, minor isomer) δ 16.7 (CH_3), 32.8 (CH), 41.2 (CH_2), 72.9 (CH_2), 98.8 (CH).

IR (neat, mixture) ν, (cm^{-1}) 3420, 2950, 2865, 1710 (traces), 1459, 1002. Anal. Calcd for $C_5H_{10}O_2$: C, 58.80; H, 9.87. Found: C, 58.71; H, 9.81.

5.5.6. 4-Methyltetrahydrofuran-2-one (6bs). 1.4 g (13.7 mmol) of lactol **5bs** (obtained as above) were dissolved in 70 mL of H_2O/dioxane 2:1 mixture and oxidized by treatment with 3 g of $BaCO_3$ and 1.7 mL of Br_2. The resulting mixture after quenching with $Na_2S_2O_3$ was extracted with Et_2O and the organic phase was distilled affording 937 mg of **6bs** (39% yield based on starting **1b**).

6bs: The ^{1}H NMR spectra ($CDCl_3$) corresponded to those previously reported.[39]

5.5.7. 5,5-Dimethyl-4-propyltetrahydrofuran-2-ol (5cq). Proc. A: From 290 μL of **1c** (2.5 mmol, 0.05 M) and 180 mg of benzophenone (1 mmol, 0.02 M) in 50 mL of **4q** irradiated for 16 h at 315 nm. After column chromatography (C_6H_{12}/EtAc 7:3) 249 mg of the title compound **5cq** (oil) were obtained as a mixture of two diastereoisomer in a 2:1 ratio (63% yield).

Proc. B: From 700 μL of **1c** (6 mmol, 0.1 M) and 485 mg of BPSS (1.2 mmol, 0.02 M) in 60 mL of a 1:1 mixture of **4q**/water irradiated for 6 h at 315 nm. Purification by column chromatography yielded 475 mg of **5cq** (50% yield).

Proc. B (in the immersion well photochemical reactor): The same reaction was repeated in a higher scale in an immersion well apparatus fitted with a Pyrex glass filtered 150 W medium-pressure mercury lamp starting from 3.5 mL of **1c** (30 mmol, 0.1 M) and 2.9 g of BPSS

(6 mmol, 0.02 M) in 300 mL of a 1:1 mixture of **4q**/water (irradiation time=6 h). The residue was bulb to bulb distilled affording 2.67 g of the title compound (57% yield).

5cq: colourless oil, ^{1}H NMR ($CDCl_3$, major isomer, from the mixture) δ 0.95 (3H, t, J=7.0 Hz, *Me*), 1.15 (3H, s, *Me*), 1.15–1.45 (4H, m, 2CH_2), 1.30 (3H, s, *Me*), 1.65 (1H, ddd, J=5.0, 7.0, 12.0 Hz, CH_aH$_b$CHOH), 1.95 (1H, dd, J=7.0, 12.0 Hz, CH$_a$$H_b$CHOH), 2.30–2.40 (1H, m, CH$_2$CHCH$_a$-H$_b$), 4.80 (1H, bd, J=5 Hz, OH), 5.30 (1H, t, J=5 Hz, CHOH). ^{13}C NMR ($CDCl_3$): δ 14.2 (CH_3), 22.4 (CH_2), 23.3 (CH_3), 29.8 (CH_3), 32.5 (CH_2), 45.6 (CH), 96.4 (CH).

^{1}H NMR ($CDCl_3$, minor isomer, from the mixture) δ 0.95 (3H, t, J=7.0 Hz, *Me*), 1.10 (3H, s, *Me*), 1.15–1.45 (4H, m, 2CH_2), 1.30 (3H, s, *Me*), 1.55 (1H, ddd, J=5.0, 11.0, 13.0 Hz, CH_aH$_b$CHOH), 1.75–1.85 (1H, m, CH$_a$$H_b$CHOH), 2.10–2.20 (1H, m, CHCH$_a$H$_b$), 5.00 (1H, bd, J=5 Hz, OH), 5.40 (1H, dq, J=5.0, 6.0 Hz, CHOH). ^{13}C NMR ($CDCl_3$): δ 14.2 (CH_3), 22.3 (CH_2), 23.6 (CH_3), 28.2 (CH_3), 32.7 (CH_2), 49.2 (CH), 97.3 (CH).

IR (neat, mixture) ν, (cm^{-1}) 3415, 2962, 2869, 1456, 1381, 1142. MS (*m*/*z*) 157 (1, M−1), 141 (19), 97 (13), 69 (15), 59 (18), 43 (100). Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.23; H, 11.43.

5.5.8. 5,5-Dimethyl-4-propyltetrahydrofuran-2-one (6cq). The residue obtained from the procedure B was dissolved in 30 mL of H_2O/dioxane 2:1 mixture and oxidized by means of 1.3 g of $BaCO_3$ and 770 μL of Br_2. Purification (C_6H_{12}/EtAc 8:2 as the eluant) afforded 330 mg of **6cq** (35% yield based on starting **1c**).

6cq: colourless oil, ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, J=7.0 Hz, *Me*), 1.20 (3H, s, *Me*), 1.2–1.5 (4H, m, 2CH_2), 1.4 (3H, s, *Me*), 2.1–2.3 (2H, m, CH_2COO), 2.55–2.65 (1H, m, CHCH$_2$COO). IR (neat) ν, (cm^{-1}) 2959, 2931, 2872, 1775, 1464, 1375, 1261, 1097. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.09; H, 10.24.

5.5.9. 4-Propyltetrahydrofuran-2-one (6cs). A solution of 700 μL of **1c** (6 mmol, 0.1 M) and 220 mg of benzophenone (1.2 mmol, 0.02 M) in 60 mL of **4s** was irradiated for 16 h at 315 nm. The residue obtained from the reaction was dissolved in 30 mL of H_2O/dioxane 2:1 mixture and oxidized by means of 1.3 g of $BaCO_3$ and 770 μL of Br_2. Purification by chromatography (C_6H_{12}/EtAc 9:1 as the eluant) afforded 300 mg of **6cs** (42% yield based on starting **1c**).

6cs: Spectroscopic data in accord with the literature.[40]

5.5.10. 3,3-Dimethyloctahydroisobenzofuran-1-one (6eq). A solution of 455 μL of **1e** (4 mmol, 0.1 M) and 323 mg of BPSS (0.8 mmol, 0.02 M) in 40 mL of a 1:1 mixture of **4q**/water was irradiated for 16 h at 315 nm. The residue obtained from the reaction was dissolved in 30 mL of H_2O/dioxane 2:1 mixture and oxidized by means of 1.3 g of $BaCO_3$ and 770 μL of Br_2. Purification by chromatography (C_6H_{12}/EtAc 8:2 as the eluant) afforded 230 mg of **6eq** (37% yield based on starting **1c**) as a *cis*/*trans* (2:1) mixture.[41] The same synthesis was performed analogously with procedure A with an overall yield of 32%.

6eq (*trans*+*cis*): ^{1}H NMR ($CDCl_3$) δ 1.1–1.2 (6H, m, *H* ring), 1.25 (3H, s, *Me*, *trans*), 1.30 (3H, s, *Me*, *cis*), 1.35 (3H, s, *Me*, *cis*), 1.40 (3H, s, *Me*, *trans*), 1.55–1.80 (8H, m, *H* ring), 2.10–2.25 (4H, m, *H* ring), 2.95–3.05 (2H, m, *H* ring).

cis isomer: ^{13}C ($CDCl_3$, from the mixture) δ 23.0 (CH_2), 23.3 (CH_3), 23.4 (CH_2), 24.1 (CH_2), 25.6 (CH_2), 26.6 (CH_3), 40.4 (CH), 43.9 (CH), 84.5, 178.2 (CO).

trans isomer: ^{13}C ($CDCl_3$, from the mixture) δ 21.1 (CH_3), 25.7 (CH_2), 25.8 (CH_2), 26.0 (CH_2), 26.5 (CH_2), 27.6 (CH_3), 44.3 (CH), 52.8 (CH), 86.1, 177.3 (CO).

IR (neat) ν, (cm^{-1}) 2929, 2857, 1765, 1449, 1376, 1268, 1124. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.33; H, 9.63.

5.6. Attempted synthesis of lactols 5aq, 5fq, 5gq and 5hq

Application of the above methods to aldehydes **1a** and **1f**–**h** (both procedure A and B) did not lead to expected alkylation. Aldehyde **1a** polymerized while the other aldehydes were consumed forming no detected products.

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14. NMR spectra of lactols **5** showed no signals attributable to open-chain γ-hydroxyaldehydes and the equilibrium in Scheme 3 was almost completely shifted to the hemiacetalic form.
15. 2-Alkyl-2-dioxolanyl radicals can also undergo ring opening, just as the corresponding cations formed by electron transfer to the sensitiser. As a result small amounts of the corresponding ethyl esters and, respectively, of the hydroxyethyl esters were observed, see Ref. 12b.
16. When hydrogen abstraction is inefficient, radical−radical coupling between the adduct radical and the ketyl radical from the sensitiser occurred to some extent (small amount of compounds of such structure were detected by NMR as impurities of the alkylated products in some fractions from column chromatography).
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