Pergamon

Tetrahedron 57 (2001) 10319–10328

TETRAHEDRON

Synthesis of monoprotected 1,4-diketones by photoinduced alkylation of enones with 2-substituted-1,3-dioxolanes

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Received 24 July 2001; revised 26 September 2001; accepted 18 October 2001

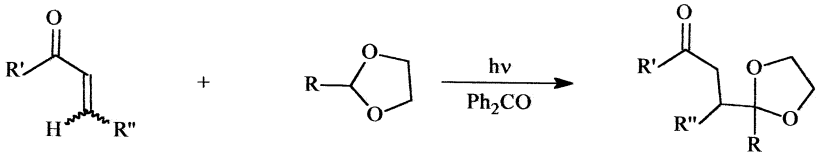
Abstract—Photosensitized hydrogen abstraction from 2-alkyl-1,3-dioxolanes by triplet benzophenone gives the corresponding 1,3-dioxolan-2-yl radicals and these are trapped by α,β-unsatured ketones yielding monoprotected 1,4-diketones. With open chain ketones (3-buten-2-one and 4-penten-3-one) the yields are low and competitive pathways in part consume the radicals. With cyclic enones however, yields are good as tested with cyclopentenone, cyclohexenone and 4-hydroxy-cyclopentenone. More generally, this is a viable alternative for the synthesis of 1,4-diketones via radicals while the thermal initiation gives only low yield. The reaction cannot be extended to strongly stabilized radicals, such as the 2-phenyl-1,3-dioxolanyl radical.

1. Introduction

Recently we reported a mild procedure for the synthesis of monoprotected 1,4-ketoaldehydes by introducing a 1,3-dioxolanyl group onto α,β-unsatured ketones.[1] In view of the versatility of the 1,3-dioxolanyl moiety, which not only is a removable protecting group but is also directly convertible into other functionalities,[2] it appeared worthwhile to test the scope of the method. The synthesis of more heavily functionalized 4-ketoaldehydes, as well as of several monoprotected 1,4-diketones starting from 2-alkyl-1,3-dioxolanes is reported. Apart from partial protection of diketones, which usually gives a mixture,[3a] monoprotected 1,4-diketones have been previously obtained through multistep syntheses, viz. via γ-oxosulfones ketals,[3b] by acylation of organonickel complexes,[3c] from γ-nitroketal derivatives[3d] or by oxidation of γ-hydroxyketals.[3e] This fact and the major role 1,4-diketones have for the synthesis of natural compounds with a cyclopentan(en)one structure such as prostaglandins, jasmonoids, pentenomycins and cyclopentanoid antibiotics as well as of various heterocycles (e.g. furans, pyrroles, thiophenes and pyridazines)[4] gave impetus to this study, aimed to explore whether a photoinduced radical alkylation based upon non-toxic and inexpensive reagents could afford a viable alternative.

2. Results

The radical precursors considered in the present study were 1,3-dioxolanes bearing different alkyl substituents in position 2, methyl (compound **2k**), ethyl (**2l**), branched (2-methylpropyl, **2m**) and a long chain (*n*-hexyl, **2n**). An aromatic 1,3-dioxolane (2-phenyl-1,3-dioxolane, **2o**) was also considered (see Scheme 1).



1a R' = Me, R" = H
b R' = Et, R" = H
c R',R" = -(CH2)2-
d R',R" = -(CH2)3-
e R',R" = -(CH2)4-

2 k R=Methyl
l R=Ethyl
m R=2-Methylpropyl
n R = *n*-Hexyl
o R = Phenyl

3

Scheme 1.

Keywords: alkylation; radicals and radical reactions; 1,4-diketones; photochemistry; prostanoids.
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0040–4020/01/$ - see front matter
PII: S0040-4020(01)01058-4

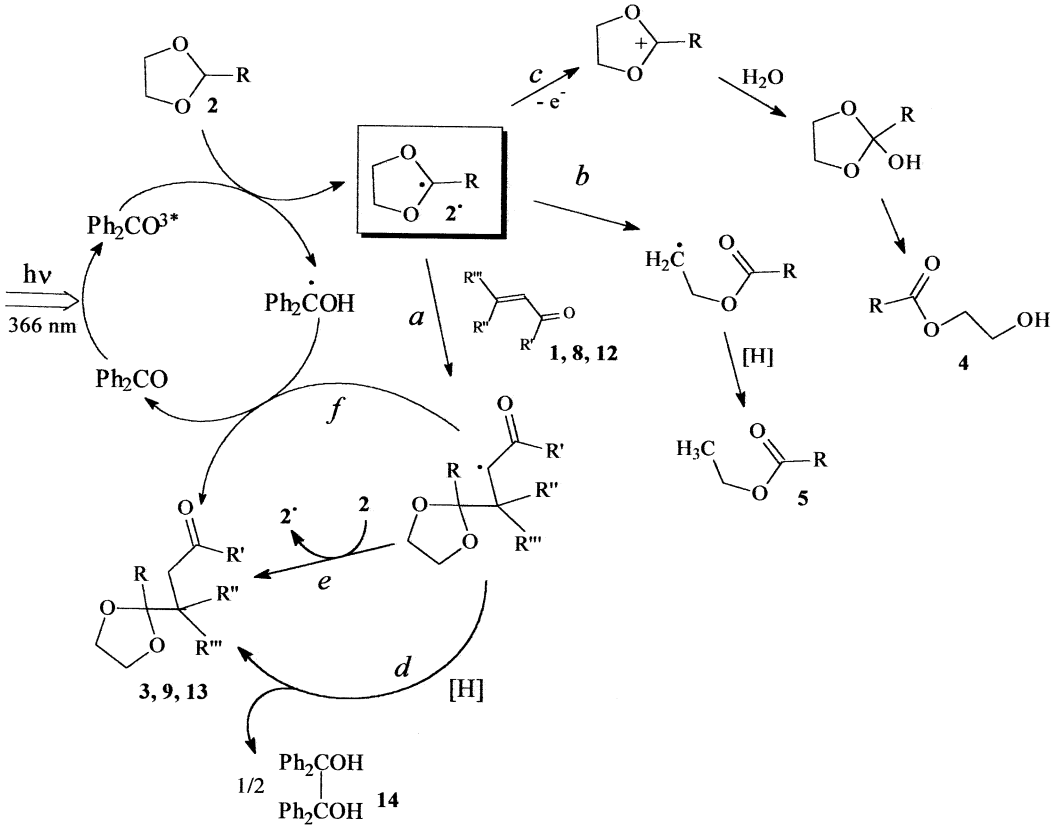
Table 1. Alkylation yields from α,β-unsatured ketones and dioxolanes **2**

Entry	Ketone	Dioxolane	Products	Reactions conditions (time, h)	Product yield (%)[a]
1	**1a**	**2k**	**3ak**	*hν* (2.5)	28
2	**1a**	**2k**[b]	**3ak**	*hν* (2.5)	49[c]
3	**1a**	**2k**	**3ak**	Δ[d]	<3[c,d]
4	**1a**	**2l**	**3al**	*hν* (2.5)	28
5	**1a**	**2m**	**3am**	*hν* (2.5)	32
6	**1a**	**2n**	**3an**	*hν* (15)	<5[c]
7	**1a**	**2o**	**4o**, **5o**, **6**, **7**	*hν* (4)	[e]
8	**1b**	**2l**	**3bl**	*hν* (2.5)	21
9	**1c**	**2k**	**3ck**	*hν* (2.5)	78
10	**1c**	**2l**	**3cl**	*hν* (2.5)	70
11	**1c**	**2n**	**3cn**	*hν* (2.5)	68
12	**1c**	**2o**	**4o**, **5o**, **6**, **7**	*hν* (4)	[e]
13	**1d**	**2k**	**3dk**	*hν* (7)	48
14	**1d**	**2k**	**3dk**	Δ[d]	21[c,d]
15	**1d**	**2n**	**3dn**	*hν* (7)	57
16	**8**	**2k**	**9k/9k′** (11/1)[f], **10**	*hν* (2)	75, 7.2
17	**8**	**2p**	**9p/9p′** (2.2/1)[f]	*hν* (2)	74
18	**8**	**2p**	**9p/9p′** (6/1)[f]	*hν* (4)	60[g]
19	**12**	**2p**	**13**, **13′**	*hν* (2)	46, 22

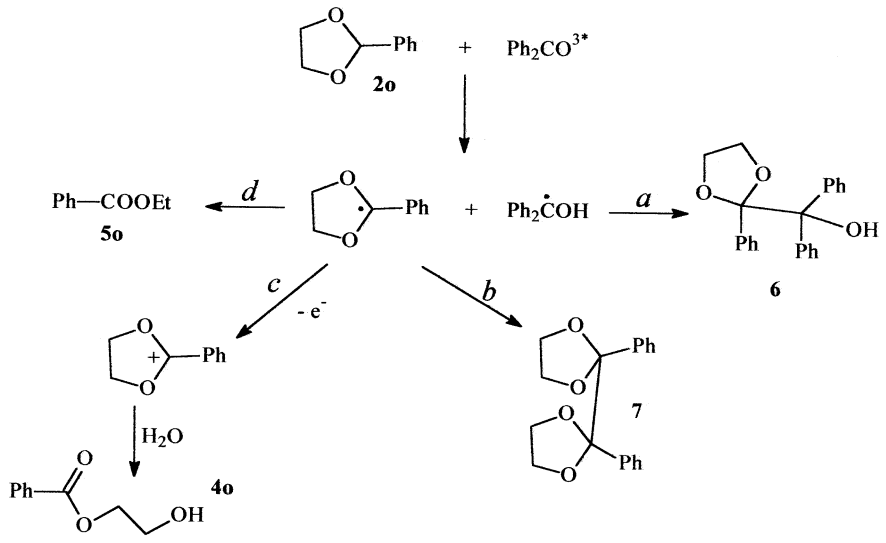
[a] Isolated yield.
[b] Neat dioxolane **2k** as the solvent.
[c] GC yield.
[d] Thermal reaction. See Text.
[e] No alkylation occurred. See Text.
[f] Mixture of diastereoisomer (*trans* as the main isomer).
[g] Reaction in aqueous medium.

2.1. Alkylation of open chain α,β-unsatured ketones

The photochemical alkylation was first tested on two representative open chain unsatured ketones, 3-buten-2-one (**1a**) and 1-penten-3-one (**1b**). Irradiations were carried out on a solution of the starting ketone (0.05 M) in a 1 M solution of the dioxolane **2** in acetonitrile in the presence of benzophenone as the sensitizer (0.02 M). Preliminary experiments have shown that no alkylation occurred in the absence of the sensitizer.



Scheme 2.



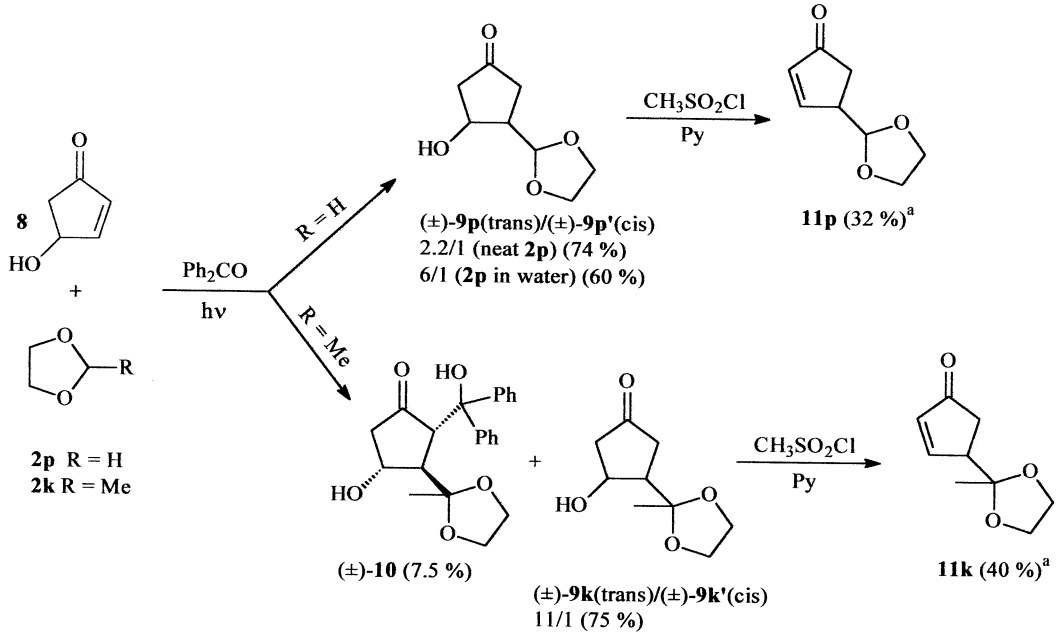
Scheme 3.

Under these conditions, on using 1,3-dioxolanes **2k**, **2l** and **2m** as radical precursors enone **1a** was alkylated and saturated ketones **3** were obtained, but the isolated yields were low (21–28%, see Table 1, entries 1, 4, 5). A higher yield of **3ak** resulted when the alkylation of **1a** was carried out in neat **2k** (49%, entry 2) accompanied by a relevant amount of **4a**. With 2-hexyl-1,3-dioxolane **2n**, the formation of only a small amount of alkylated **3an** was demonstrated by GC/MS. Some byproducts arising from alternative decomposition pathways of dioxolane **2n** were detected in this case, viz. β-hydroxyethyl heptanoate **4n** and ethyl heptanoate **5n** (Scheme 2). The results with enone **1b** were analogous and alkylated ketone **3bl** was formed from **2l** in a somewhat lower yield than **3al** (21%).

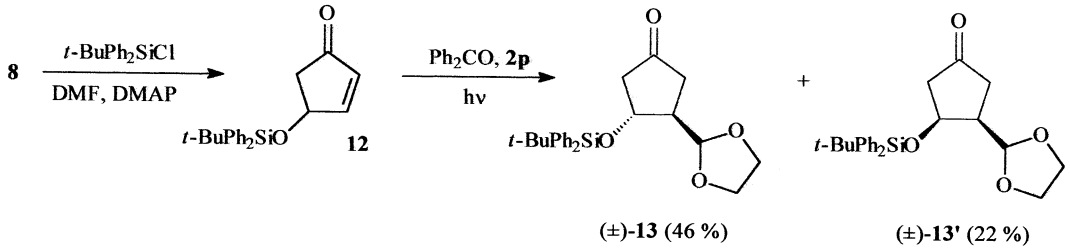
Alkylation was unsuccessful with dioxolane **2o**. In this case, several dioxolane derived products were identified, viz. 2-hydroxyethyl benzoate (**4o**), ethyl benzoate (**5o**), 1,1-diphenyl-(2-phenyl-1,3-dioxolan-2-yl)-methanol (**6**) and 2,2′-diphenyl-[2,2′]bis-1,3-dioxolanyl (**7**) (see Scheme 3).

2.2. Cyclic α,β-unsatured ketones

More satisfactory results were obtained with five- and six-membered enones. In particularly, 3-alkylcyclopentanones **3ck**, **l**, **n** were obtained in a high yield (>70%) in a short irradiation time (2.5 h) from cyclopentenone and the corresponding 2-substituted-1,3-dioxolanes. The reaction could not be extended to dioxolane **2o**, however. Similar to the reaction of **1a**, in the last case only products resulting from alternative reactions of dioxolane were obtained. The alkylation of cyclohexenone (**1d**) was also successful, with a reasonable yield of products **3dk** and **3dn** (48 and 57%,



Scheme 4. a. Overall yields based on starting cyclopentenone **8**.



Scheme 5.

respectively). Cycloheptenone (**1e**) on the other hand, was consumed but was not alkylated under these conditions.

In view of the success with five- and six-membered ring enones, the reaction was extended to 4-hydroxy-cyclopentenone **8**. The reaction with **2k** yielded **9k** (*trans* isomer) as the main product besides a minor amount of the *cis* isomer (**9k′**) (74.2%, overall alkylation yield; *trans*/*cis* 11/1, Scheme 4) as well as a small amount of a doubly alkylated product, all *trans* 4-hydroxy-2-(hydroxy-diphenyl-methyl)-3-(2-methyl-1,3-dioxolan-2-yl)-cyclopentanone **10** (7%). The crude **9k**/**9k′** mixture was easily transformed into cyclopentenone **11k** (40%, one pot synthesis from **8**) through the intermediacy of the corresponding methansulfonate.

The same alkylation–elimination procedure was applied to the reaction with **8** and 1,3-dioxolane (**2p**) as the radical precursor. Again, a mixture of *trans* (**9p**) and *cis* (**9p′**) isomers was obtained, although attack was less stereoselective (*trans*/*cis* 2.2/1). As in the previous case, the isomer mixture was easily transformed into enone **11p**.

It was explored whether the selectivity in the formation of the *trans* isomer **9p** with respect to **9p′** was improved when the OH group was substituted by a bulky *t*-butyldiphenylsilyloxy group. However, there were no appreciable advantages in this direction, except for the fact that both of the isomers (**13**, *trans* and **13′**, *cis*) were easily isolated by silica gel chromatography (overall yield 68%, Scheme 5). A marked improvement of the selectivity (from 2.2/1 to 6/1) was achieved carrying out the reaction on enone **8** in mixed dioxolane–water solution. In this case a water-soluble sensitizer such as benzophenone sodium sulfonate was used (see Section 5 and entry 18 in Table 1).

2.3. Alkylation by thermal radical chain method

It was obviously important to compare the above photochemical alkylations of enones with thermal initiated reactions. Therefore we also tested the synthesis of compound **3** by generating 1,3-dioxolanyl radicals by thermal radical initiators, viz. AIBN and benzoyl peroxide. No detectable alkylated ketone **3ak** was obtained from **1a** and **2k** with AIBN and only a small amount (<3%) with benzoyl peroxide. (Table 1, entry 3). The last initiator gave a better yield with **1d** as the starting ketone (21%, **3dk**, see Section 5 and Table 1 entry 14). We could not improve the thermal alkylation beyond these limits.

3. Discussion

The present synthesis involves the alkylation of electrophilic alkenes by dioxolanyl radicals. Previous attempts to generate such radicals by thermal hydrogen abstraction have met only a limited success. Decomposition of peroxides in the presence of 1,3-dioxolanes and olefins led to some alkylation, in particular with electron-withdrawing substituted alkenes but side-reactions such as cleavage to ethyl esters (see later) or, in some cases, polymerization consumed most of the radicals.[5,6] Better results were reported employing di-*t*-butyl-hyponitrite (DBH) as a radical initiator which has the advantage of an easier work up (the initiator gives rise to volatile byproducts) but its application is limited due to the non-trivial synthesis of the initiator.[7] Indeed attempts to use dioxolanes in thermally initiated radical alkylation were also carried out during present work (Table 1, entries 3, 14) and the yields were low.

Photochemical initiation was generally more effective.[8] The mechanism is reported in Scheme 2. Excitation of benzophenone to the triplet state is followed by hydrogen abstraction from dioxolanes **2** yielding the corresponding dioxolan-2-yl radicals **2**. Substitution in position 2 does not hinder this step. Stereoelectronic factors remain favorable, and Ingold has shown that the rate of hydrogen abstraction from such derivatives is only slightly lower than with the parent 1,3-dioxolanes.[9a] A practical limitation for the extension of the method is that the elimination of excess reagent is cumbersome with high boiling dioxolanes; this limits the concentration of dioxolanes used. Yields are somewhat lower in dilute solutions of dioxolanes **2** rather than in the neat reagent (compare entries 1 and 2). Nevertheless a lower concentration of alkyldioxolanes as the hydrogen donors led to a simpler products mixture (see Section 5).

The radicals are trapped by the olefins present in solution (**1**, **8**, **12**, path *a*) and the resulting adduct radicals give rise to the final 1,4-monoprotected dioxolanyl derivatives (**3**, **9**, **13**) through hydrogen abstraction. The latter process involves hydrogen transfer from the solvent (path *d*), the dioxolane (path *e*)[9b] or the ketyl radical intermediate (path *f*). The first path (path *d*) yields benzopinacol (**14**) as a sideproduct, but the last two allow the use of benzophenone in a less than stoichiometric amount (we used 40%, see Section 5).

The overall yield of the alkylation process depends primarily on the efficient trapping of radical **2**$^{\cdot}$ with respect to competitive paths. Among these, the first one is the above mentioned[5] rearrangement to ethylesters **5** via the

open chain 2-oxycarbonyl radicals (path *b*), while the second involves oxidation of **2**˙ to the corresponding cation followed by water assisted opening to give 2-hydroxyethyl-esters **4** (path *c*). The oxidizing agent is probably benzophenone ground state.[10]

The efficiency of the key trapping step depends primarily on the structure of the enone. With open chain enones yields are low, particularly with the hexyldioxolanyl radical from **2n**. On the other hand, satisfactory results are obtained with five- and six- (but not seven-) membered enones with isolated yields in the range 65–78%. The rigid structure of these compounds make them better radical traps for both electronic and steric reasons and causes a more favorable competition with the dioxolanyl radical rearrangement.

No alkylation takes place with 2-phenyl-1,3-dioxolane (**2o**). In this case a strongly stabilized radical (**2o** is both a tertiary and a benzylic radical, see Scheme 3) is formed and trapping by **1** is slow. As one may expect with such persistent radicals, termination by coupling predominates and yields product **6** (from heterocoupling with the persistent ketyl radical, path *a*) and **7** (homocoupling, path *b*). This is accompanied by oxidation to hydroxyethyl esters **4o**, a process which completely supersedes rearrangement to ethyl benzoate **5o** (of which only traces are formed), an indication of the high stabilization of radical **2o**.[10] A little amount of hydroxy ester is also formed from **2n**. Notice however that under thermal conditions benzoate esters have been previously reported to be formed in high yield from 2-phenyl-1,3-diox(ol)ane derivatives,[13] evidencing the temperature dependence of the fate of the radical.

The overall comparison (both this work and literature) between photochemical and thermal generation of 2-alkyl-1,3-dioxolanyl radicals makes it apparent that the mild conditions of the former method minimize competitive reactions and allow more efficient trapping by electrophilic alkenes, except when phenyl substitution makes addition too slow.

3.1. Synthetic utility of the method

1,4-Diketones[14] and their monoprotected derivatives are highly versatile intermediates,[15a] for which a mild synthetic entry is a desirable alternative to available methods. In particular 1,4-diketones corresponding to the dioxolanes prepared in the present work have been employed in the pinacolization process for the stereoselective synthesis of monocyclic *cis*-cyclobutane-1,2-diols,[15b] as a source for chiral diols[15c,d] and as intermediates for the synthesis of molecules of biological interest.[16] Furthermore, these 1,4-diketones could easily transformed into cyclopentenone derivatives used in the synthesis of antibiotics (type A streptogramins),[17a] unstable cyclopentenoid antibiotic (methylenomicyn B)[17b] or compounds with antifungal activity (e.g. pinguisanes).[17c]

The photoinduced alkylation of 4-hydroxycyclopenten-2-one (**8**) was tested in view of the possible application of the process to prostaglandins synthesis. The yield of alkylation is high with both dioxolanes **2p** and **2k** and in the latter case a marked preference for the desired *trans* stereochemistry is observed (Table 1, entries 16–18).[18] The thus obtained masked ketoaldehyde **9p** is a suitable precursor for PGE, as well as, through an elimination reaction of PGA (via alkylation in 2). Differently from the case of **2k**, diastereoselectivity is modest with parent dioxolane **2p** and is unchanged when the bulky silyloxyketone **12** is used as the trap (entry 19). Noteworthy, photochemical hydrogen abstraction in aqueous medium using a water-soluble sensitizer such as benzophenone sodium sulfonate[19] markedly improves the diastereoselectivity in the synthesis of **9p** (from 38 to 72% d.e., see Section 5) probably due to the establishment of hydrogen bonds. This is promising in view of the fact that related masked aldehydes have been already employed in the synthesis of both chiral carbocyclic nucleosides[20a] or brefeldin.[20b] Furthermore, the good chemical yield in the formation of **9p/9p′** (or **9k/9k′**) and the easy conversion of the mixture into compound **11p** (**11k**, see Scheme 4) enhances the versatility of these products.

4. Conclusions

Hydrogen abstraction is usually not regarded as a viable method for the generation of alkyl radicals and their use in the nucleophilic alkylation of enones.[21] Even with 1,3-dioxolanes, when stereoselective factors greatly facilitate hydrogen transfer, the thermal process requires a relatively high temperature and under such conditions rearrangement of the radical makes trapping by electrophilic alkenes ineffective. Under the mild conditions of photochemical initiation this limitation is overcome and the synthesis of useful intermediates is practicable, at least with cyclic enones.

5. Experimental

5.1. General

NMR spectra were recorded on a 300 MHz spectrometer. The assignments were made on the basis of ^{1}H and ^{13}C NMR; chemical shifts are reported in ppm downfield from TMS. IR spectra were in accordance for the structure with all the new compounds and are reported in selected cases. 2-Methyl-1,3-dioxolane, 2-cyclohexen-1-one and 2-cyclopenten-1-one were commercial samples and were used without purification. 2-Ethyl-1,3-dioxolane,[22] 2-(2-methylpropyl)-1,3-dioxolane, 2-phenyl-1,3-dioxolane and 2-hexyl-1,3-dioxolane were synthesized from the corresponding aldehydes (see later). 4-Hydroxy-cyclopentenone was obtained from furfuryl alcohol.[23] The photochemical reactions were performed in quartz tubes by using nitrogen-purged solution and a multilamp reactor fitted with six 15 W phosphor-coated lamps (maximum of emission 366 nm) for the irradiation.

5.2. Synthesis of dioxolanes 2, general procedure

A solution of the suitable aldehyde, ethylene glycol and PTSA in benzene was refluxed with a water separator until the total consumption of the starting aldehyde. Usual work-up and distillation yielded the final dioxolanes.[24]

Compound **2m**: 2-(2-methylpropyl)-1,3-dioxolane (80% yield) ^{1}H ($CDCl_3$) δ 1.0 (d, 6H, J=7 Hz), 1.5 (dd, 2H, J=5 and 7 Hz), 1.8 (m, 1H), 3.8 (m, 2H), 3.95 (m, 2H), 4.85 (t, 1H, J=5 Hz).

Compound **2n**: 2-hexyl-1,3-dioxolane (82% yield).[25a]

Compound **2o**: 2-phenyl-1,3-dioxolane (67% yield).[25b]

5.3. Synthesis of 4-(*tert*-butyldiphenyl-silyloxy)-cyclopent-2-enone (12)

A solution of **8** (295 mg, 3 mmol), DMAP (735 mg, 6 mmol), *t*-$BuPh_2SiCl$ (935 μL, 3.6 mmol) in DMF (3.8 mL) was stirred for 2 h and then poured in water and extracted with Et_2O (3 times). Crude silyl ether **12** was purified on silica gel (cyclohexane/ethyl acetate 6/4) and isolated as an oil in an almost quantitative yield.[25c]

5.4. Alkylation of ketones 1 by thermal radical chain method

AIBN as radical initiator. A solution of **1a** (37 μL, 0.45 mmol, 0.05 M), **2k** (810 μL, 6 mmol, 1 M), AIBN (30 mg, 0.18 mmol, 0.02 M) in 9 mL of MeCN was heated at 40–45°C for 1 h and then refluxed for 10 min. GC analysis showed no formation of compound **3ak**.

5.5. Benzoyl peroxide as initiator[26]

Alkylation of **1a**. To a refluxed solution of **2k** (1.4 mL, 16 mmol, 1 M) in 5 mL of MeCN a solution of **1a** (64 μL, 0.8 mmol, 0.05 M) and benzoyl peroxide (145 mg, 0.6 mmol, 0.037 M) in 3 mL of MeCN was dropwise added in 2 h under nitrogen. After 3 h of refluxing only a small amount (<3%) of **3ak** was detected by GC analysis.

5.6. Alkylation of 1d

The experiment was carried out as in the case of **1a** starting from a 0.05 M solution of **1d**. After 3 h of reaction **3dk** was formed in 21% yield.

5.7. Photochemical synthesis of ketones 3, general procedure

A solution of the enone (0.05 M), 2-alkyl-1,3-dioxolane (1 M) and benzophenone (0.02 M) in acetonitrile was irradiated until the enone was consumed. The reaction course was followed by TLC (cyclohexane/ethyl acetate) and GC. Workup of the photolytes involved concentration in vacuo and bulb to bulb distillation or chromatographic separation using Millipore 60 Å, 35–70 μm silica gel.

5.7.1. 4-(2-Methyl-1,3-dioxolan-2-yl)-butan-2-one (3ak). From 210 μL (2.5 mmol, 0.05 M) of 3-buten-2-one (**1a**), 180 mg (1 mmol, 0.02 M) of benzophenone, 4.5 mL (45 mmol, 1 M) of 2-methyl-1,3-dioxolane (**2k**) in 45 mL of acetonitrile. After distillation of the resulting residue, 4-(2-methyl-[1,3]-dioxolan-2-yl)-butan-2-one (**3ak**, 115 mg, 28%) was isolated as a colorless liquid.

The same reaction carried out in neat **2k** (3 mL). Product **3ak** was formed in 49% yield (GC/MS) and was accompanied by a large amount (about 0.3 M) of hydroxyester **4a**.

Compound **3ak**: ^{1}H ($CDCl_3$) δ 1.3 (s, 3H), 2.0 (t, 2H, J=7 Hz), 2.15 (s, 3H), 2.5 (t, 2H, J=7 Hz), 3.95 (m, 4H).[27] IR (neat) ν/cm^{-1} 1717, 1052. Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.70; H, 8.97.

Compound **4a**: MS (*m*/*z*) 103 (M−1, 2), 88 (82), 73 (100), 72 (93).

5.7.2. 4-(2-Ethyl-1,3-dioxolan-2-yl)-butan-2-one (3al). From 250 μL (3 mmol, 0.05 M) of **1a**, 220 mg (1.2 mmol, 0.02 M) of benzophenone, 7 mL (60 mmol, 1 M) of 2-ethyl-1,3-dioxolane (**2l**) in 60 mL of acetonitrile. After distillation of the resulting residue, the title compound (**3al**, 120 mg, 28%) was isolated as a colorless liquid.

Compound **3al**: ^{1}H ($CDCl_3$) δ 0.95 (t, 3H, J=7 Hz), 1.6 (q, 2H, J=7 Hz), 1.95 (t, 2H, J=7 Hz), 2.1 (s, 3H), 2.5 (t, 2H, J=7 Hz), 3.9 (s, 4H). ^{13}C ($CDCl_3$) δ 8.0 (CH_3), 29.7 (CH_3), 30.0 (CH_2), 30.3 (CH_2), 38.0 (CH_2), 64.7 (CH_2), 111.2, 208.6 (CO). IR (neat) ν/cm^{-1} 1720, 1049. Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.70; H, 9.30.

5.7.3. 4-[2(2-Methylpropyl)-1,3-dioxolan-2-yl)]-butan-2-one (3am). From 210 μL (2.5 mmol, 0.05 M) of **1a**, 180 mg (1 mmol, 0.02 M) of benzophenone, 6.8 mL (50 mmol, 1 M) of 2-(2-methylpropyl)-1,3-dioxolane (**2m**) in 50 mL of acetonitrile. Column cromatography (cyclohexane/ethyl acetate 8/2) separation afforded 4-[2(2-methylpropyl)-1,3-dioxolan-2-yl)]-butan-2-one (**3am**, 98 mg, 32%) as a colorless liquid.

Compound **3am**: ^{1}H ($CDCl_3$) δ 0.95 (d, 6H, J=7 Hz), 1.5 (d, 2H, J=7 Hz), 1.75 (m, 1H), 1.95 (t, 2H, J=7 Hz), 2.15 (s, 3H), 2.5 (t, 2H, J=7 Hz), 3.9 (s, 4H). ^{13}C ($CDCl_3$) δ 23.8 (CH_3), 24.0 (CH_3), 29.7 (CH), 31.0 (CH_2), 38.0 (CH_2), 45.3 (CH_2), 64.5 (CH_2), 111.0, 208.4 (CO). IR (neat) ν/cm^{-1} 1716, 1054. Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 66.08; H, 9.98.

5.7.4. Attempted synthesis of 4-(2-hexyl-1,3-dioxolan-2-yl)-butan-2-one (3an). 11 μL (0.15 mmol, 0.05 M) of **1a**, 11 mg (0.06 mmol, 0.02 M) of benzophenone, 0.51 mL (3 mmol, 1 M) of **2n** in 3 mL of acetonitrile were irradiated for 15 h. GC/MS analysis showed a little consumption of **2n** (ca. 10%) with the formation of heptanoic acid 2-hydroxyethyl ester (**4n**, ca. 5%) and heptanoic acid ethyl ester (**5n**, <2%, both based on starting dioxolane **2n**). A small amount of adduct **3an** (<5%, based on alkene **1a**) was also formed.

Compound **3an**: MS (*m*/*z*) 229 (12, M+1), 157 (75), 143 (100), 43 (53).

Compound **4n**: MS (*m*/*z*) 175 (66, M+1), 157 (67), 113 (94), 43 (100).[28]

Compound **5n**: MS (*m*/*z*) 158 (100, M), 113 (20), 43 (21), 41 (23).[28]

5.7.5. 4-(2-Ethyl-1,3-dioxolan-2-yl)-pentan-3-one (3bl). From 240 μL (2.4 mmol, 0.05 M) of **1b**, 175 mg

(0.96 mmol, 0.02 M) of benzophenone, 6 mL (48 mmol, 1 M) **2l** in 48 mL of acetonitrile. After distillation of the resulting residue, the title compound (**3bl**, 67 mg, 21%) was isolated as a colorless liquid.

Compound **3bl**: ^{1}H ($CDCl_3$) δ 0.95 (t, 3H, J=7 Hz), 1.05 (t, 3H, J=7 Hz), 1.65 (q, 2H, J=7 Hz), 1.95 (t, 2H, J=7 Hz), 2.5 (m, 4H), 3.95 (s, 4H). ^{13}C ($CDCl_3$) δ 7.8 (CH_3), 8.0 (CH_3), 30.0 (CH_2), 30.3 (CH_2), 35.7 (CH_2), 36.6 (CH_2), 64.9 (2 CH_2), 111.2, 211.1 (CO). IR (neat) ν/cm^{-1} 1717, 1050. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.40; H, 9.66.

5.7.6. 3-(2-Methyl-1,3-dioxolan-2-yl)-cyclopentanone (3ck). From 125 μL (1.5 mmol, 0.05 M) of 2-cyclopenten-1-one (**1c**), 110 mg (0.6 mmol, 0.02 M) of benzophenone, 2.7 mL (30 mmol, 1 M) of **2k** in 30 mL of acetonitrile. Separation by means of column chromatography (cyclohexane/ethyl acetate 8/2) afforded 3-(2-methyl-1,3-dioxolan-2-yl)-cyclopentanone (**3ck**, 200 mg, 78%) as a colorless liquid.

Compound **3ck**: ^{1}H ($CDCl_3$) δ 1.3 (s, 3H), 1.75–1.95 (m, 1H), 2.0–2.4 (m, 5H), 2.45–2.6 (m, 1H), 3.85–4.05 (m, 4H). ^{13}C ($CDCl_3$) δ 22.6 (CH_3), 24.0 (CH_2), 38.1 (CH_2), 40.0 (CH_2), 45.2 (CH), 64.7 (CH_2), 65.1 (CH_2), 110.1, 218.7 (CO). IR (neat) ν/cm^{-1} 1739, 1226, 1155. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.53; H, 8.32.

5.7.7. 3-(2-Ethyl-1,3-dioxolan-2-yl)-cyclopentanone (3cl). From 210 μL (2.5 mmol, 0.05 M) of 2-cyclopenten-1-one (**1c**), 180 mg (1 mmol, 0.02 M) of benzophenone, 6.3 mL (50 mmol, 1 M) of **2l** in 50 mL of acetonitrile. Separation by means of column chromatography (cyclohexane/ethyl acetate 9/1) afforded the title compound (**3cl**, 320 mg, 70%) as a colorless liquid.

Compound **3cl**: ^{1}H ($CDCl_3$) δ 0.85 (t, 3H, J=7 Hz), 1.65 (q, 2H, J=7 Hz), 1.8 (m, 1H), 1.95–2.35 (m, 5H), 2.6 (m, 1H), 3.9 (m, 4H). ^{13}C ($CDCl_3$) δ 8.5 (CH_3), 24.2 (CH_2), 29.5 (CH_2), 38.6 (CH_2), 40.4 (CH_2), 43.2 (CH), 65.8 (CH_2), 66.2 (CH_2), 112.6, 219.2 (CO). IR (neat) ν/cm^{-1} 1736, 1224, 1158. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.16; H, 8.77.

5.7.8. 3-(2-Hexyl-1,3-dioxolan-2-yl)-cyclopentanone (3cn). From 210 μL (2.5 mmol, 0.05 M) of **1c**, 180 mg (1 mmol, 0.02 M) of benzophenone, 8.5 mL (50 mmol, 1 M) of **2n** in 50 mL of acetonitrile. Separation by means of column chromatography (cyclohexane/ethyl acetate 9/1) afforded the title compound (**3cn**, 408 mg, 68%) as a colorless liquid.

Compound **3cn**: ^{1}H ($CDCl_3$) δ 0.9 (t, 3H, J=7 Hz), 1.15–1.45 (m, 8H), 1.5–1.75 (m, 2H), 1.75–1.95 (m, 1H), 1.95–2.45 (m, 5H), 2.55–2.7 (m, 1H), 3.8–4.1 (m, 4H). ^{13}C ($CDCl_3$) δ 14.0 (CH_3), 22.4 (CH_2), 23.7 (CH_2), 23.8 (CH_2), 29.5 (CH_2), 31.7 (CH_2), 36.3 (CH_2), 38.1 (CH_2), 40.0 (CH_2), 43.2 (CH), 65.2 (CH_2), 65.6 (CH_2), 112.0, 218.8 (CO). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.89; H, 10.11.

5.7.9. 3-(2-Methyl-1,3-dioxolan-2-yl)-cyclohexanone (3dk). From 240 μL (2.5 mmol, 0.05 M) of 2-cyclohexen-1-one (**1d**), 180 mg (1 mmol, 0.02 M) of benzophenone, 4.5 mL (50 mmol, 1 M) of **2k** in 50 mL of acetonitrile. Separation by column chromatography (cyclohexane/ethyl acetate 8/2) afforded 3-(2-methyl-1,3-dioxolan-2-yl)-cyclohexanone (**3dk**, 220 mg, 48%) as a colorless liquid.[29]

Compound **3dk**: ^{1}H ($CDCl_3$) δ 1.25 (s, 3H), 1.5–1.75 (m, 2H), 1.95–2.2 (m, 3H), 2.2–2.4 (m, 3H), 2.5 (m, 1H), 3.95 (m, 4H). ^{13}C ($CDCl_3$) δ 21.5 (CH_3), 24.6 (CH_2), 25.6 (CH_2), 41.1 (CH_2), 42.4 (CH_2), 46.8 (CH), 64.6 (CH_2), 64.9 (CH_2), 110.3, 211.5 (CO). IR (neat) ν/cm^{-1} 1710, 1224, 1146. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.14; H, 8.77.

5.7.10. 3-(2-Hexyl-1,3-dioxolan-2-yl)-cyclohexanone (3dn). From 240 μL (2.5 mmol, 0.05 M) of 2-cyclohexen-1-one (**1d**), 180 mg (1 mmol, 0.02 M) of benzophenone, 8.5 mL (50 mmol, 1 M) of **2n** in 50 mL of acetonitrile. Separation by column chromatography (cyclohexane/ethyl acetate 9/1) afforded the title compound (**3dn**, 362 mg, 57%) as a colorless liquid.

Compound **3dn**: ^{1}H ($CDCl_3$) δ 0.8 (t, 3H, J=7 Hz), 1.2–1.4 (m, 8H), 1.5–1.7 (m, 4H), 1.85–2.45 (m, 7H), 3.85 (m, 4H). ^{13}C ($CDCl_3$) δ 14.4 (CH_3), 23.0 (CH_2), 23.8 (CH_2), 25.1 (CH_2), 25.9 (CH_2), 30.0 (CH_2), 32.1 (CH_2), 35.5 (CH_2), 41.5 (CH_2), 42.7 (CH_2), 45.1 (CH), 65.6 (CH_2), 65.9 (CH_2), 112.1, 211.6 (CO). IR (neat) ν/cm^{-1} 1712, 1220, 1148. Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.85; H, 10.29.

5.7.11. Attempted alkylation with dioxolane 2o. 16.5 μL (0.2 mmol, 0.05 M) of **1a**, 14.5 mg (0.08 mmol, 0.02 M) of benzophenone, 590 μL (4 mmol, 1 M) of **2o** in 4 mL of acetonitrile were irradiated for 4 h. GC analysis of the final mixture showed a slight consumption of dioxolane **2o** with the formation of four new compounds (yield less than 2.5% each) viz. diphenyl-(2-phenyl-1,3-dioxolan-2-yl)-methanol as the main product (**6**), 2,2′-diphenyl-2,2′bis[1,3]dioxolanylethane (**7**), benzoic acid 2-hydroxyethyl ester (**4o**) and traces of ethyl benzoate (**5o**). These products were identified both by GC/MS analysis and by comparison with authentic samples;[30] the analysis ascertained that product **3ao** was not formed.

A similar reaction was carried out with olefin **1c** and again no alkylation product was detected.

Compound **4o**: MS (*m*/*z*) 167 (1, M+1), 123 (44), 105 (100), 77 (81), 51 (22).

Compound **6**: MS (*m*/*z*) 181 (5), 149 (100), 105 (93), 77 (63), 51 (11).

Compound **7**: MS (*m*/*z*) 149 (100, M/2), 105 (80), 77 (52), 51 (12).

5.7.12. 3-Hydroxy-4-(2-methyl-1,3-dioxolan-2-yl)-cyclopentanone (9k). From 265 mg of **8** (2.7 mmol, 0.06 M), 200 mg of benzophenone (1.1 mmol, 0.024 M), 4 mL of **2k** (45 mmol, 1 M) in 45 mL of acetonitrile. After the elimination of the solvent, water (45 mL) and then Et_2O (30 mL) was added to the raw photolisate. The aqueous phase was

then extracted with CH_2Cl_2 (30 mL×4) and the joined extracts were dried yielding 375 mg of 3-hydroxy-4-(2-methyl-1,3-dioxolan-2-yl)-cyclopentanone (**9k**, 75% yield, oil, *trans* isomer). The *cis* isomer (compound **9k′**) was detected by GC/MS technique from the photolisate mixture (*trans*/*cis* 11/1) Stereochemistry of **9k** was determined by 2D-NOESY experiment (no effect between H-3 and H-4)

The ether phase was purified on silica gel column (cyclohexane/ethyl acetate 55/45) yielding *(2S,3R,4R/2R,3S,4S) 4-hydroxy-2-(diphenylhydroxymethyl)-3-(2-methyl-1,3-dioxolan-2-yl)-cyclopentanone* **10** (25 mg, 7.5% yield). The all *trans* stereochemistry was assigned on the basis of the virtual *J* coupling constants between H-2 and H-3 and between H-3 and H-4.

Compound **9k**: ^{1}H (CD_3COCD_3) δ 1.35 (s, 3H), 2.1 (m, 1H), 2.15 (m, 1H), 2.4 (m, 1H), 2.5 (m, 1H), 2.55 (m, 1H), 3.9–4.0 (m, 4H), 4.5 (m, 1H). ^{13}C (CD_3COCD_3) δ 22.0 (CH_3), 38.0 (CH_2), 46.7 (CH_2), 52.6 (CH), 64.2 (CH_2), 64.7 (CH_2), 69.5 (CH), 109.7, 214.4 (CO). IR (neat) ν/cm^{-1} 3454, 1749, 1149, 1031. Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.09; H, 7.66. MS (*m*/*z*) 187 (1, M+1), 99 (16), 87 (100), 43 (37).

Compound **9k′**: MS (*m*/*z*) 187 (2, M+1), 99 (21), 87 (100), 43 (53).

Compound **10**: ^{1}H ($CDCl_3$) δ 1.3 (s, 3H), 2.35 (bd, 1H, *J*=19 Hz), 2.5 (bs, 1H), 2.7 (bdd, 1H, *J*=7 and 19 Hz), 3.6 (bs, 1H), 3.7 (m, 1H), 3.8–4.0 (m, 3H), 4.5 (bd, 1H, *J*=7 Hz), 7.2–7.6 (m, 10H). ^{13}C ($CDCl_3$) δ 22.0 (CH_3), 48.4 (CH_2), 56.1 (CH), 56.9 (CH), 64.4 (CH_2), 64.7 (CH_2), 69.4 (CH), 79.8, 109.8, 126.1 (CH), 126.3 (CH), 126.7 (CH), 126.8 (CH), 127.8 (CH), 128.1 (CH), 144.4, 146.2, 215.0 (CO). IR (neat) ν/cm^{-1} 3377, 1741, 1166, 1057. Anal. Calcd for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57. Found: C, 71.64; H, 6.46.

5.7.13. 4-(2-Methyl-1,3-dioxolan-2-yl)-cyclopent-2-enone (11k). The synthesis described above was repeated and the crude photolisate was dissolved in pyridine at −10°C and then methanesulfonyl chloride was added dropwise.[31] The mixture was stirred for 1 h and allowed to reach room temperature under stirring in 2 h. Et_2O was then added along with cold 5% HCl and the two phases poured in a separatory funnel with the help of further Et_2O. The organic phase was separated and washed with 5% $NaHCO_3$ and brine. The solution obtained was dried, the solvents evaporated and the residue purified on silica gel column (cyclohexane/ethyl acetate 6/4) affording the title compound (**11k**, 181 mg, oil) in 40% yield (based on cyclopentenone **8**).

Compound **11k**: ^{1}H ($CDCl_3$) δ 1.3 (s, 3H), 2.3 (dd, 1H, *J*=3 and 19 Hz, A part of an ABX system), 2.4 (dd, 1H, *J*=6.5 and 19 Hz, B part of an ABX system), 3.25 (m, 1H, X part of an ABX system), 3.85–4.05 (m, 4H), 6.25 (dd, 1H, *J*=2 and 6 Hz), 7.6 (dd, 1H, *J*=2.5 and 6 Hz). ^{13}C ($CDCl_3$) δ 22.2 (CH_3), 36.9 (CH_2), 50.2 (CH), 65.0 (CH_2), 65.1 (CH_2), 109.7, 135.6 (CH), 163.3 (CH), 209.2 (CO). IR (neat) ν/cm^{-1} 1708, 1587, 1055. Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.22; H, 7.24.

5.7.14. 3-(1,3-Dioxolan-2-yl)-4-hydroxycyclopentanone (9p). From 265 mg of **8** (2.7 mmol, 0.06 M), 200 mg of benzophenone (1.1 mmol, 0.024 M) in 45 mL of neat 1,3-dioxolane **2p**. After elimination of the solvent, water (45 mL) and then Et_2O (30 mL) were added to the raw photolisate. The aqueous phase was then extracted with CH_2Cl_2 (30 mL×4) and the combined extracts were dried yielding 343 mg of 3-(1,3-dioxolan-2-yl)-4-hydroxycyclopentanone (mixture of isomer, **9p** *trans*/**9p′** *cis* 2.2/1) in 74% yield as an oil.

The same reaction was carried out in a 1/1 water/**2p** mixture of **8** in the presence of benzophenone sodium sulfonate as the sensitizer. Dioxolane was eliminated in vacuo and products **9p**/**9p′** (in a 6/1 ratio) were extracted with CH_2Cl_2 from the remaining aqueous mixture (278 mg, 60% yield).

Compounds **9p**+**9p′** (obtained as a mixture) ^{1}H (CD_3COCD_3) δ 2.0–2.6 (m, 10H), 3.8–4.0 (m, 8H), 4.45 (m, 1H, **9p**), 4.6 (m, 1H, **9p′**), 5.0 (d, 1H, *J*=3 Hz, **9p**), 5.1 (d, 1H, *J*=6 Hz, **9p′**). **9p**: (Major isomer) ^{13}C (CD_3COCD_3) δ 36.0 (CH_2), 46.4 (CH_2), 47.6 (CH), 64.7 (CH_2), 64.9 (CH_2), 69.4 (CH), 103.6 (CH), 214.5 (CO). MS (*m*/*z*) 171 (1, M−1), 99 (5), 73 (100), 45 (24). **9p′**: (Minor isomer) ^{13}C (CD_3COCD_3) δ 36.3 (CH_2), 45.2 (CH), 47.9 (CH_2), 64.3 (CH_2), 64.5 (CH_2), 68.9 (CH), 103.9 (CH), 214.6 (CO). MS (*m*/*z*) 171 (1, M−1), 99 (5), 73 (100), 45 (24). IR (neat) ν/cm^{-1} 3438, 1740, 1129.

5.7.15. 4-(1,3-Dioxolan-2-yl)-cyclopent-2-enone. (11p). The reaction was carried out on the raw photolisate under the same conditions used in the synthesis of **11k** starting from 264 mg (2.7 mmol) of **8**. Final purification by column chromatography (cyclohexane/ethyl acetate 65/35) yielded 133 mg (32% yield) of the title compound **11p**.

Compound **11p**: ^{1}H ($CDCl_3$) δ 2.25 (dd, 1H, *J*=2.5 and 19 Hz, A part of an ABX system), 2.4 (dd, 1H, *J*=6.5 and 19 Hz, B part of an ABX system), 3.2 (m, 1H, X part of an ABX system), 3.8–4.0 (m, 4H), 4.85 (d, 1H, *J*=4.5 Hz), 6.2 (dd, 1H, *J*=2 and 6 Hz), 7.6 (dd, 1H, *J*=2.5 and 6 Hz). ^{13}C ($CDCl_3$) δ 35.6 (CH_2), 45.5 (CH), 65.1 (CH_2), 65.2 (CH_2), 104.1 (CH), 135.8 (CH), 162.4 (CH), 208.7 (CO). IR (neat) ν/cm^{-1} 1707, 1588, 1065. Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.30; H, 6.55.

5.7.16. 3-(*tert*-Butyldiphenylsilyloxy)-4-[1,3]dioxolan-2-yl-cyclopentanone (13). From 900 mg of **12** (2.7 mmol, 0.06 M), benzophenone (1.05 mmol, 0.024 M) in 1,3-dioxolane (45 mL). Purification (silica gel column, cyclohexane/ethyl acetate 9/1) afforded 515 mg of 3-(*tert*-butyldiphenylsilyloxy)-4-[1,3]dioxolan-2-yl-cyclopentanone **13** (*trans* isomer, 46% yield) and 246 mg of 3-(*tert*-butyldiphenylsilyloxy)-4-[1,3]dioxolan-2-yl-cyclopentanone **13′** (*cis* isomer, 22% yield). The stereochemistry of both isomers was deduced from 2D-NOESY experiment on compound **13′**. In this case a correlation between H-3 and H-4 was observed and proved the *cis* configuration.

Compound **13**: ^{1}H (CD_3COCD_3) δ 1.1 (s, 9H), 2.05–2.2 (m, 2H), 2.35–2.5 (m, 2H), 2.7 (m, 1H), 3.7–3.85 (m, 4H), 4.6 (m, 1H), 4.75 (d, 1H, *J*=3 Hz), 7.5 (m, 6H), 7.75 (m, 4H).

^{13}C (CD_3COCD_3) δ 18.7, 26.3 (CH_3), 35.5 (CH_2), 46.8 (CH_2), 48.0 (CH), 64.7 (CH_2), 64.9 (CH_2), 72.1 (CH), 103.0 (CH), 128.0 (CH), 129.8 (CH), 133.4, 133.5, 135.6 (CH), 214.2 (CO). IR (neat) ν/cm^{-1} 3069, 1744, 1111, 1051. Anal. Calcd for $C_{24}H_{30}O_4Si$: C, 70.21; H, 7.36. Found: C, 70.13; H, 7.40.

Compound **13′**: ^1H (CD_3COCD_3) δ 1.1 (s, 9H), 2.1 (m, 2H), 2.15–2.4 (m, 2H), 2.5 (m, 1H), 3.8–4.0 (m, 4H), 4.8 (m, 1H), 5.3 (d, 1H, J=5.5 Hz), 7.5 (m, 6H), 7.75 (m, 4H). ^{13}C (CD_3COCD_3) δ 19.4, 26.8 (CH_3), 37.4 (CH_2), 46.0 (CH), 47.6 (CH_2), 64.9 (CH_2), 65.2 (CH_2), 72.4 (CH), 104.2 (CH), 128.1 (CH), 130.3 (CH), 133.5, 134.3, 136.1 (CH), 136.2 (CH), 214.0 (CO). IR (neat) ν/cm^{-1} 3069, 1744, 1111, 1041. Anal. Calcd for $C_{24}H_{30}O_4Si$: C, 70.21; H, 7.36. Found: C, 70.11; H, 7.44.

Acknowledgements

R. M. thanks Prochimica for a fellowship. We are greatly indebted to Millipore for the grant of silica gel. Partial support of this work by Murst (COFIN Program) Rome is gratefully acknowledged. We thank Dr P. P. Rossi (Prochimica) for his interest in this work.

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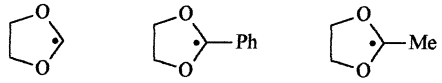

E_{ox} (vs SCE)	-0.94	-0.88	-1.19

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