Synthesis of γ-lactols, γ-lactones and 1,4-monoprotected succinaldehydes under moderately concentrated sunlight†

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The usefulness of solar light for carrying out photocatalytic reactions involving the formation of a carbon–carbon bond has been explored. Thus, some radical alkylations of α,β-unsaturated acids or aldehydes have been carried out in a mixed aqueous solution. Under these conditions, alkyl radicals are generated from *i*-PrOH and 1,3-dioxolane by photocatalyzed hydrogen abstraction. A water soluble photocatalyst (disodium benzophenondisulfonate, BPSS) was used, which greatly simplifies work up. With reasonably efficient radical traps (*e.g.* maleic acid), the syntheses could be carried out up to completion on a 10 gram scale within 10–15 hours exposure to sunlight in a solar concentrator (SOLFIN apparatus) in November in Almeria (Spain). The alkylation of some α,β-unsaturated aldehydes have been likewise performed under the same conditions.

Introduction

Over the last fifty years organic photochemistry has become a rich and multiform discipline. A large variety of photochemical reactions have been established and most of them have found application as key steps in organic synthesis.[1] The increasing interest for 'clean' processes in view of growing environmental concern and the resulting trend towards 'green' or 'sustainable' chemistry allows the prediction that photochemistry, being based on the 'green' reagent par excellence, light, will have a more significant role in the future,[2] in particular if solar light is exploited. In the early years of synthetic organic photochemistry,[3] the sun was the obvious and indeed the most reliable light source. The application of solar-driven chemistry, however, has been strongly limited by two factors, both related to the characteristics of solar emission, that is the low density and the poor matching with the absorption by the reagents.

We thought that if conditions were found that make photochemical syntheses more versatile and widen their scope, the chances of an extensive application may increase. An appealing approach is using photocatalyzed reactions,[4] since it should be easier to optimise the match between source emission and absorption spectra of a single species used as photocatalyst than for the large variety of photoreactive molecules. This is one of the motivations that led us to focus our attention on the potential of photocatalyzed reactions (*via* hydrogen atom transfer) for chemical synthesis and for carbon–carbon bond formation in particular.[5–7] Previous work aimed at the assessment of solar photochemistry as a synthetic method has been recently carried out and promising results by using concentrated solar light have been obtained.[8,9]

Sunlight photoreactors equipped with a parabolic mirror such as SOLFIN (SOLar synthesis of FINe chemicals, Fig. 1), represent the most convenient method available for carrying out photochemical reactions under concentrated sunlight.

In the SOLFIN reactor the solar radiation is collected by a cylindrical parabolic mirror (concentration factor ~ 4) having a tilting angle of about 35° directed towards the sun (south), and concentrated onto a coaxial tube placed on the focus line through which the solution (total volume of 1.2 L) is circulated (by means of a magnetic-coupled centrifugal pump) through an external reservoir of *ca.* 300 mL. The coaxial tube is cooled by water running in the inner tube (see Fig. 1).

The SOLFIN apparatus is characterized by the simplicity of use and has been employed for the gram scale synthesis of organic compounds.[7,10] Under such conditions, optimized yields in terms of time and space required have been obtained and the process appears appealing for industrial application.

In a collaborative effort with the Plataforma Solar de Almeria we previously demonstrated that by using a very simple apparatus, such as that available at SOLFIN, some photocatalyzed benzylations were conveniently carried out in multigram scale in a short time.[7] It was deemed appropriate to extend the scope of the solar induced alkylation and to explore the dependence on the reagent structures and conditions.

The reactions examined were alkylations based on hydrogen abstraction by a photocatalyst and subsequent conjugate addition of the resulting radical (Scheme 1) to electron deficient alkenes and alkynes. This method has been successfully applied to the alkylation of several electron-poor olefins (α,β-unsaturated aldehydes, acids, ketones, amides, nitriles and captodative olefins) by radicals generated by the benzophenone triplet state and using a wide range of starting materials.[4] The

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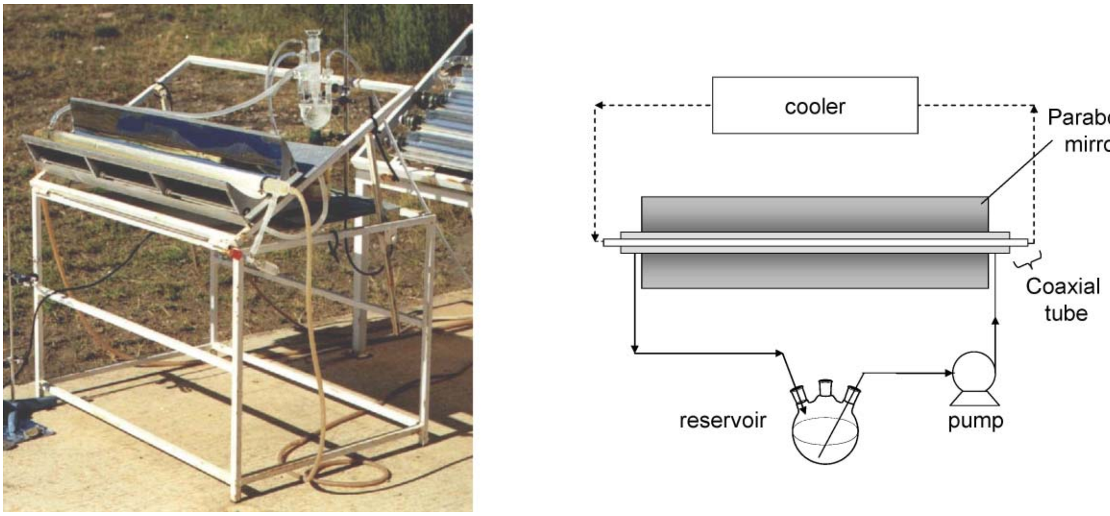
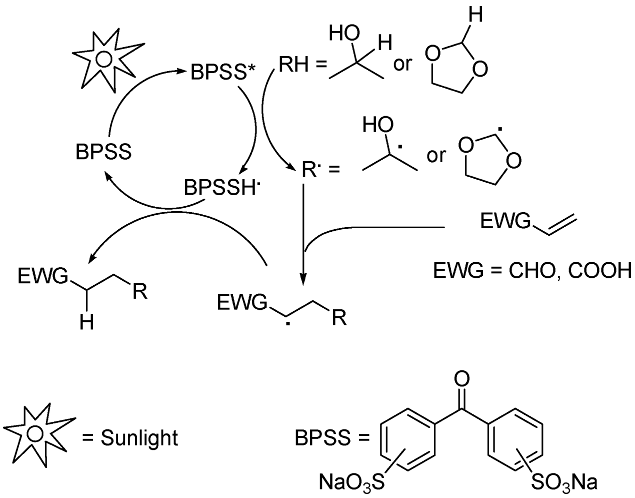


Fig. 1 The SOLFIN reactor and its schematic representation (see text for description).



Scheme 1 BPSS photocatalyzed alkylation of electron-poor olefins.

method has been demonstrated to operate with a variety of non-conventional radical precursors, such as alcohols,[11] acetals[12] and even alkanes,[5,13] thereby much broadening the scope of radical alkylation which is usually restricted to atom transfer from precursors containing weak C–X bonds such as bromides, or, more commonly, iodides. The feasibility of a sunlight promoted alkylation of electron-poor alkynes by using an aromatic ketone (benzophenone or supported aromatic ketones) as photocatalyst has been reported by Geraghty and Doohan. In that case, a cycloalkane was used both as the reactant and the solvent.[14]

Results and discussion

In order to make the method really significant for application, the isolation of the end products must be as simple as possible. In this sense, a problem when using a soluble photocatalyst is its separation from the products at the end of the reaction. Thus, we carried out the reaction in organic solvents admixed with water and used a water soluble photocatalyst such as disodium benzophenondisulfonate (BPSS, Scheme 1). This is obtained as a mixture of the 3,3′ and 4,4′ isomers from the sulfonation of benzophenone[11] and has the advantage that it is removed from the irradiated mixture by simple partitioning between an organic solvent (*e.g.* diethyl ether) and water after evaporation of the excess reagents. In addition, contamination of the end products by possible byproducts arising from BPSS[15] is avoided since these remain in the aqueous phase.

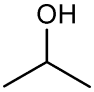
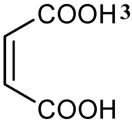
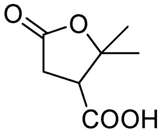
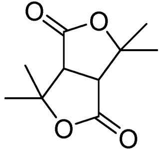
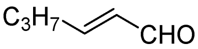
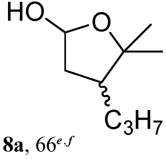
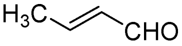
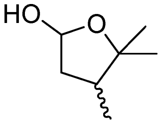
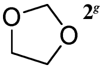
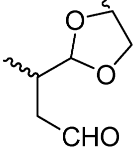
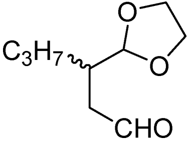
BPSS absorbs sufficiently in the near UV and visible light of the solar spectrum (see ESI†) to make the use of solar light appealing. Experiments with UV lamps[11] showed that BPSS acts as photocatalyst and abstracts a hydrogen from a radical precursor RH (*e.g.* an alcohol or a 1,3-dioxolane as shown in Scheme 1) and the resulting alkyl radical ($R^\bullet$) is trapped by an electrophilic alkene. Back hydrogen transfer from the radical adduct to the persistent ketyl radical ($BPSSH^\bullet$) arising from the aromatic ketone regenerates the photocatalyst and completes the sequence.[4]

The illuminations were carried out in two different periods. The first one (for the reactions reported in entries 1,2, Table 1) ranged from mid October to mid November and was characterized by a relatively low average solar flux (19.3 W/m^2). The latter one from the end of June to mid July (for the other reactions) was carried out under sunny weather conditions (27.7 W/m^2).

We used *i*-PrOH (**1**) and 1,3-dioxolane (**2**) as the radical precursors and unsaturated acids or aldehydes (**3–6**) as radical traps. The choice of these reactants are based on the synthetic interest of the products obtained, the low toxicity of the chemicals involved, and the solubility in water, the most promising medium for "green" applications (Table 1). In our experiments we found that a 20% molar concentration of the photocatalyst (BPSS) with respect to the olefin was sufficient for obtaining a satisfactory reaction. A further decrease to 10% concentration gave a similar chemical yield of the photoproducts, but a longer irradiation time was required in that case.

The work consisted in two parts. In the first one a model reaction was investigated with the isolation of the product; in the latter one, the scope was explored with the use of HPLC analyses. Thus, optimization of the synthetic process was performed focussing on the synthesis of lactone **7a** by conjugate addition

Table 1 BPSS (0.01 M) photocatalyzed alkylation of unsaturated aldehydes or acids under solar light

Entry	Hydrogen donor	Alkene/Alkyne, (conc., M)	t_{irr} (h)	Alkene/Alkyne conv. (%)	Product, yield (%)[a]
1	 **1**[b]	 **3**, (0.1 M)	14	90	 **7a**, 83[c], 75[d]
2	**1**[b]	 **4**, (0.07 M)	4.5	35	 **7b**, 43
3	**1**[b]	 **5**, (0.1 M)	12	76	 **8a**, 46[e]
4	**1**[b]	**5**, (0.1 M)	6	83	**8a**, 66[e,f]
5	**1**[b]	 **6**, (0.1 M)	11	55	 **8b**, 55[e]
6	 **2**[g]	**6**, (0.1 M)	9	80	 **9a**, 31
7	**2**[g]	**5**, (0.1 M)	6	88	 **9b**, 40[f]

[a] Yield based on the consumed alkene/alkyne. [b] Reaction carried out in a 1:1 **1**/water mixture. [c] The same yield was obtained by using *i*-PrOH/water 4:1 mixture as the solvent. [d] Isolated yields. [e] 2:1 Mixture of the two diastereomers. [f] BPPS 0.02 M. [g] Reaction carried out in a 5:7 mixture of **2**/water.

of *i*-PrOH (**1**) onto maleic acid (**3**) as the model reaction. In a first run, a solution of **3** in a mixture **1**-water 4:1 was exposed in the SOLFIN apparatus for five hours (from 11 am to 4 pm), in a sunny day. The consumption of maleic acid reached 59%. In a second run a higher percentage of water was used in the solvent mixture and the reaction was carried out around noon during three consecutive days (total time of sunlight exposure: 14 hours). The progress of the reaction was monitored by HPLC measuring the consumption of **3**, as shown in Fig. 2. Obviously, the performance was affected by the weather conditions, and the reaction progressed slowly during the second day of irradiation, characterized by cloudy weather. The irradiated solution was extracted with diethyl ether, the organic phase evaporated and the solid residue was crystallized affording the expected product, terebic acid **7a**, in 75% isolated yield. Under these conditions, an increase in *i*-PrOH concentration did not significantly affect either the alkylation yield or the irradiation time required. In contrast, a previous benzophenone photomediated synthesis of **7a** in neat *i*-PrOH under artificial light gave terebic acid in a markedly lower yield (50%).[16] In a blank experiment under the same conditions omitting BPSS almost no reaction occurred (4% consumption of maleic acid after 5 hours).

The second synthesis involved the addition to a triple rather than a double bond, the radical trap being in this case acetylendicarboxylic acid (**4**, 0.07 M). Electrophilic alkynes are poorer traps than the corresponding alkenes, thus it is expected that after the first alkylation a second attack would be faster. In fact, the product isolated incorporated two alkyl groups (bislactone **7b**) *via* the α,β-unsaturated lactone **4′** intermediate (Scheme 2). Illumination for 4.5 hours resulted in a conversion of **4** of 35% (with a 43% yield of **7b** based on the consumption of **4**).

Lactols **8a** and **8b** were obtained in moderate yields (> 50%) from the corresponding unsaturated aldehydes in the reaction with **1** (Scheme 3, Table 1 entries 3–5).

In the synthesis of **8a** a linear behaviour for the formation of both the lactol and the consumption of **5** was observed (Fig. 3). When increasing the concentration of BPPS up to 0.02 M the olefin consumption was markedly accelerated as shown in Fig. 4 and the alkylation yield increased (compare entry 3 and 4 in Table 1). In a typical reaction 1.2 L of a 1 to 1 *i*-PrOH-water mixture containing 14 mL of *trans*-2-hexenal (**5**, 0.1 M) and 7.4 g (0.02 M) of BPSS was deaerated by flushing with nitrogen for 30 min in the SOLFIN reactor. The solution was then exposed to solar light for 12 hours (over two days) while the temperature of the reacting mixture was maintained at 15–20 °C by cooling with a slow flow of water.[17] The course of the reaction was followed by HPLC by withdrawing samples at regular intervals.

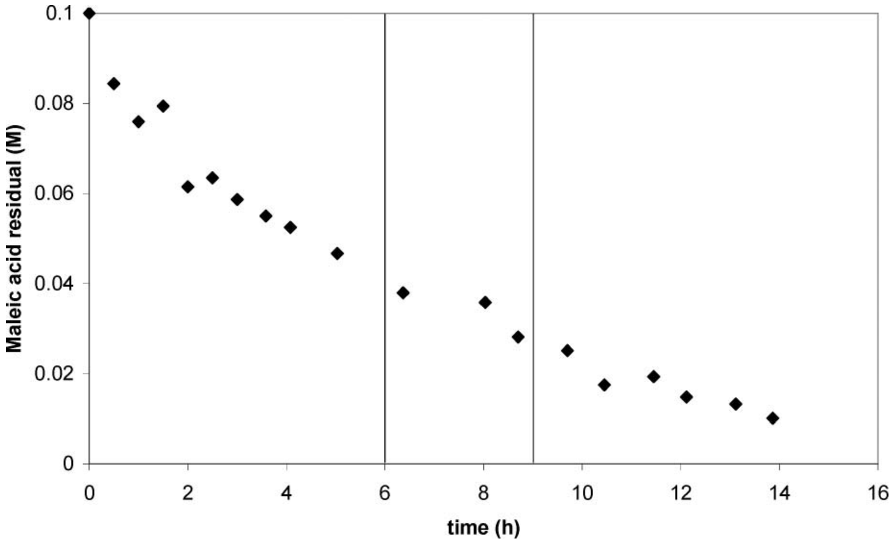
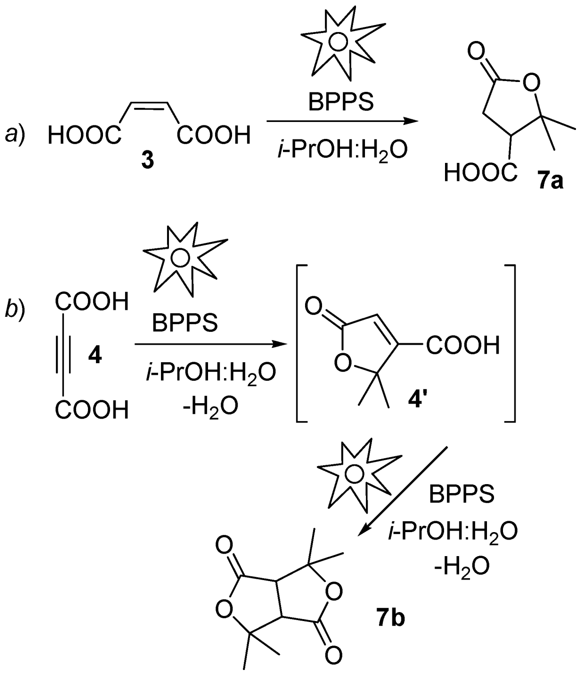


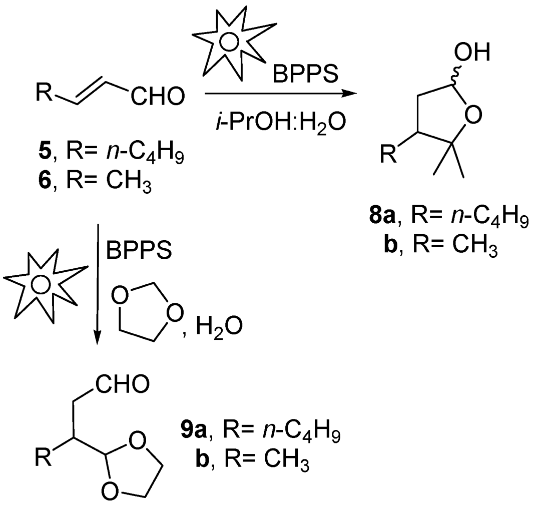
Fig. 2 Consumption of maleic acid (**3**) *vs* t in the photocatalyzed reaction with *i*-PrOH. Vertical bars are day intervals.



Scheme 2 BPSS photocatalyzed synthesis of (bis)lactones.

When using 1,3-dioxolane (**2**) in place of **1**, a lower concentration of the radical precursor was used (**2**/water = 5/7 v/v) and monoprotected dicarbonyls **9a** and **9b** were obtained in moderate yield (30–40%); a few hours of sunlight exposure were sufficient in this case (Table 1, Fig. 5–6).

In the reaction with 1,3-dioxolane, lowering the amount of BPSS (0.01 M) was detrimental, especially when using low-boiling radical traps such as crotonaldehyde (**6**). In fact, in this case the concentration of the alkylated olefin reached a plateau after 8 h illumination (Fig. 5), reasonably due to a loss of the volatile unsaturated aldehyde during the irradiation and during the nitrogen flushing process.



Scheme 3 Sunlight mediated preparation of γ-lactols and 1,4-monoprotected succinaldehydes.

In order to increase both the yield of monoprotected dialdehydes and the rate of the reaction, a 0.02 M BPSS concentration and a less volatile unsaturated aldehyde (2-hexenal) were tested (Table 1, entry 7). In this case, a significant consumption of **5** (*ca.* 88%) was reached after only 6h sun exposure with the concomitant formation of the dioxolane derivative **9b** (Fig. 6).

The above data support that photocatalyzed reactions are conveniently carried out 1) in water containing solution 2) even when using a photocatalyst not absorbing in the visible.

As for the first point, the sulfonate gave results that are fully comparable with those previously reported in an organic medium by using benzophenone as the photocatalyst. The choice of BPSS allows to use water as (co)solvent in the process. BPSS has been previously proved to be just as good a hydrogen abstractor as benzophenone is.[11] A 0.01 M concentration of BPSS was sufficient for alkylating almost completely 0.1 M maleic acid. Moreover, BPSS is advantageous with respect

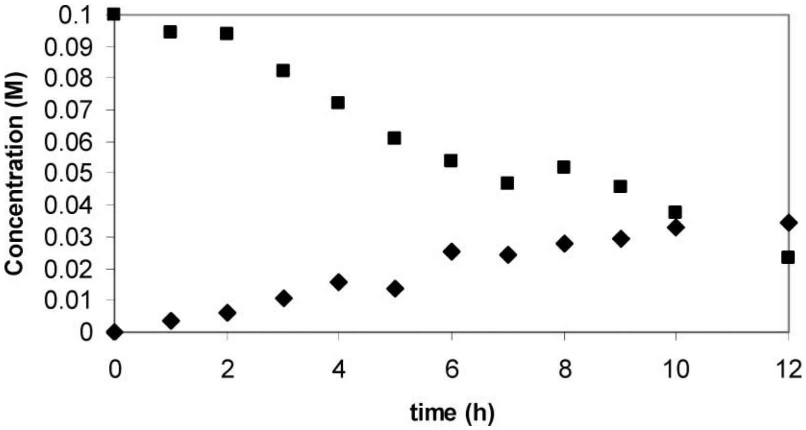


Fig. 3 Formation of **8a** (diamonds) and consumption of **5** (squares) in the 12 h insolation of an *i*-PrOH/water mixture of 2-hexenal (**7a**, 0.1 M) and BPSS (0.01 M).

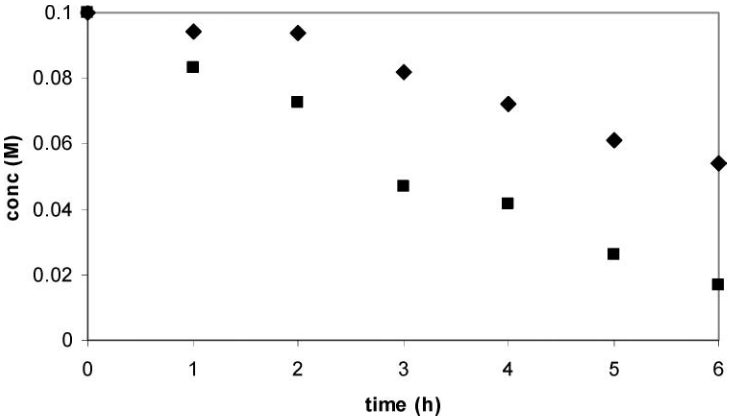


Fig. 4 Relative consumption rate of 2-hexenal (**5**) in the reaction with *i*-PrOH in the presence of 0.01 M BPSS (diamonds) and 0.02 M BPSS (squares), respectively.

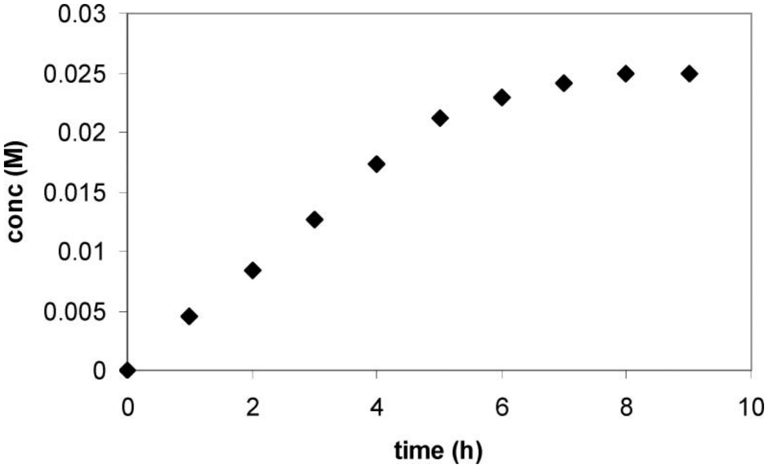


Fig. 5 Formation of **9b** during the 9 h illumination of a **2**/water mixture of crotonaldehyde (**6**, 0.1 M) and BPSS (0.01 M).

to benzophenone (BP) as the photocatalyst since it forms byproducts just as BP, but these are water-soluble and easily separated from the alkylated products.[15] Carrying out the same reaction in the laboratory on the same scale requires an only slightly shorter time (10 h) when using a 125 W mercury lamp[18] and in that case the cost of electrical energy has to be taken into account.[19] The rate of the reaction increased when using a 20% molar amount of BPSS and this was found useful in the reaction involving delicate or volatile radical traps.

As for the second point, the spectral distribution and intensity of solar light has been compared with typical mercury lamps used in the laboratory. The portion of the solar emission absorbed by the photocatalyst amounts to few percent. Nevertheless, the present experiments show that triplet ketone

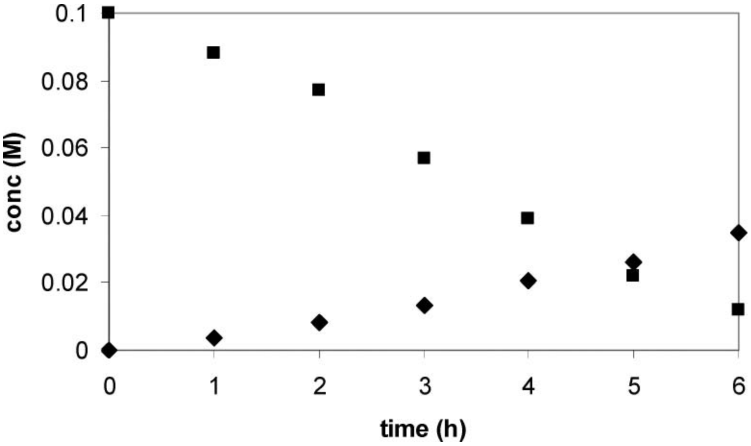


Fig. 6 Formation of **9b** (diamonds) and consumption of **5** (squares) in the 6 h illumination of a **2**/water mixture of 2-hexenal (**5**, 0.1 M) and BPSS (0.02 M).

photocatalyzed reactions can be carried out in 10 g scale in the very simple SOLFIN set up in a few hours, even under non-optimal conditions (late November, partially cloudy sky). The reactions occurred in a relatively short time with a next to monotone course (zeroth order, see for example Fig. 1), indicating that the change in the light flux during the central hours of the day was moderate and did not greatly affect the rate of the reaction. It is also important to notice that the amount of light harvested is relatively small and the exposed surface is 0.2 m^2.

In the case of aldehydes, the yield of alkylated products is moderate and this can be ascribed both to the volatility of the reagents and to the partial oxidation of the starting aldehydes to the corresponding acids. On the other hand, no other photoproducts arising from the starting olefins have been detected by HPLC analysis.

The yields of formation of lactols and of 1,4-monoprotected dialdehydes (see Table 1, entries 3–7) are in general comparable or even higher than those obtained when the same reaction mixtures were irradiated in a multilamp apparatus by using phosphor coated lamps.[11] Notice that using **1** as the precursor, lactonization and acetalization spontaneously occurred after alkylation, giving lactones **7** (starting from an unsaturated acid), and lactols **8** (from an unsaturated aldehyde) respectively. Both of the products obtained are useful synthetic targets. Lactols are versatile building blocks for the synthesis of furan derivatives,[20] while lactones are present in several biologically active natural occurring compounds.[21] The present method offers a facile access to these derivatives through the tandem formation of C–C and C–O bonds in a one pot procedure. On the other hand, starting from 1,3-dioxolane and an unsaturated aldehyde, monoprotected succinaldehydes **9a** and **9b**[22] were easily obtained.

Conclusion

The solar light induced alkylation of α,β-unsaturated aldehydes and acids by isopropanol and 1,3-dioxolanes occurs on a reasonable scale and by using very simple reaction and work up procedures. Such photocatalyzed reactions appear to be a promising application of solar light for ‘green’ organic synthesis.[23–27] The low density of solar illumination is certainly a limit for the application, and particularly so when, as in several photochemical alkylations,[13,14] only the UV part of the spectrum is active. However, syntheses in the scale of some grams per day can be carried out by exposing a limited surface. The simple apparatus used could be easily implemented by using several reactors in parallel. The yields are mostly moderate, but a marked advantage is inherent in the mild conditions and the simplicity and directness of the method, leading through a single photochemical step to products that are otherwise obtained in several steps. As an example, terebic acid (**7a**) can be prepared *via* various photochemical[16] and thermal paths, but the latter often occur under metal mediated conditions.[28] The co-production of waste is minimal in these ‘direct’ syntheses and the only objection is the use of a large amount of solvent, which can be recovered, however, some energy consumption is required for cooling[29] in order to avoid losses due to evaporation (notice however that with higher boiling reactants cooling was not required[17]). The simple reactor described leads to the synthesis of 10–20 g of product in 1–2 days employing 0.2 m^2 of sun-exposed surface. This supports that for chemicals that are produced and commercialized in a kg scale per year, solar driven synthesis could be a reasonable alternative and this requires a 10 m^2 surface exposed to the sun.[30] The characteristic of the above syntheses (use of solar light, aqueous solution, no metal catalyst) seem to offer a convenient starting point toward a practical application.

Methods

The experiments were carried out at the SOLFIN facility at the Plataforma Solar de Almeria located in the desert of Tabernas (Spain) at 37°05′28″N, 2°21′19″W, 500 m above sea level. The facility receives a direct annual insolation of about 1900 kWh/m^2/year. The values of measured solar fluxes are available in the ESI.L† 1.2 L batches were used in each experiment and the reactor was exposed to solar light for 6 hours/days (exposed surface: 0.2 m^2). The course of the reaction was followed by HPLC (C18 column, MeCN/water mixtures as the eluant, flux 1 mL min^{-1} with UV detection at 254 nm) checking at half an hour or one hour intervals.

i-PrOH (**1**) and water of HPLC purity grade were used. Compounds **2–6** were commercially available and purified before use. Benzophenone disodium disulfonate (BPSS) was prepared as previously described.[11] ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. The attributions were made on the basis of ^{1}H and ^{13}C NMR, as well as DEPT-135 experiments and compared to those samples previously prepared;[11] chemical shifts are reported in ppm downfield from TMS.

General procedure for the synthesis of compounds 7-8

A degassed solution (by nitrogen bubbling) of olefin **3-6** (0.12 mol, 0.1 M, except where indicated) and BPSS (4.63 g, 12 mmol, 0.01 M, except where indicated) in 1.2 L of 1:1 *i*-PrOH/water mixture was exposed to moderately concentrated sunlight in the SOLFIN reactor. The progress of the reaction and the consumption of the substrates were monitored by HPLC analysis. The yields of **7b**,[31] **8a**,[11] **8b**[11] were determined by HPLC analysis by comparison with authentic samples.

Synthesis of 2,2-dimethyl-5-oxo-tetrahydrofuran-3-carboxylic acid (7a)

From maleic acid (**3**, 13.9 g, 0.12 mol, 0.1 M) and BPPS (4.63 g, 0.012 mol, 0.01 M) in a 1:1 *i*-PrOH/water mixture (1.2 L) irradiated for 14 hours. The photolyzed solution was extracted with diethyl ether (4 × 50 mL), the organic phases were collected, dried over MgSO$_4$ and the solvent eliminated *in vacuo*. Purification by crystallization (water) afforded 14.3 g of **7a** as a colorless solid (mp 176–177 °C, lit[32] 175–176 °C) in a 75% yield. Spectroscopic data of compound **7a** were in accordance with literature data.[33] Anal. Calcd for C$_7$H$_{10}$O$_4$: C 53.16, H 6.37. Found: C 53.2, H 6.4.

General procedure for the synthesis of compounds 9a,b

0.12 Mol of aldehyde **5**, **6** (0.1 M), and BPSS (4.63 g, 12 mmol, 0.01 M except where indicated) were dissolved in 1.2 L of a 5:7 mixture of 1,3-dioxolane/water. The solution was first degassed by nitrogen bubbling and then irradiated under the conditions described above. The progress of the reaction and the consumption of the substrates were monitored by HPLC analysis. The yields of **9a**,[11] and **9b**[11] were determined by HPLC analysis by comparison with authentic samples.

Acknowledgements

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Notes and references

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