Solar and Visible-Light Photooxygenations of Furfural – An Example for the Manufacturing of Commodity Chemicals from Renewable Materials

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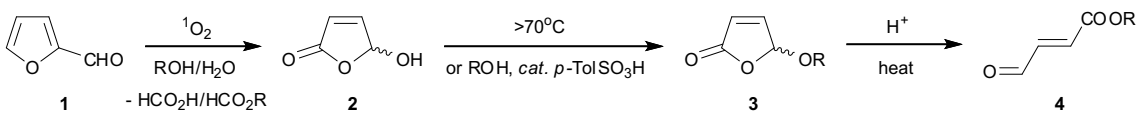
Abstract: This study investigated the photooxygenation of furfural as a bagasse-derived material to the important platform chemical 5-hydroxy-2(5H)-furanone. The reaction was successfully transferred from small laboratory-scales with artificial light to large solar demonstration scales in direct, natural sunlight. Due to the challenging isolation of pure hydroxyfuranone caused by thermal follow-up reactions, pseudo-esterifications and -transesterifications to the corresponding alkoxy-derivatives were furthermore conducted. The results from this investigation offer new opportunities for sugarcane bagasse waste utilization and product diversification of renewable biomass materials.

Keywords: furfural, furanones, photooxygenations, solar chemistry, renewable materials.

1 INTRODUCTION

Due to the growing interest in green and sustainable chemistry, many environmentally conscious methodologies for the synthesis of commodity chemicals from renewable feedstocks have been developed [1-4]. Commodity, fine or platform chemicals can be extracted directly from biomass or can alternatively be derived through chemical conversions of first-generation biomass substrates. Furfural (**1**), for example, is predominantly synthesized from pentose biomass, in particular sugarcane bagasse, via acid-catalysed dehydration [5, 6]. Sugarcane bagasse comprises mainly of cellulose, hemicellulose (pentosan), lignin and ash [7, 8], respectively. This makes bagasse an interesting and readily available resource for value adding and product diversification through chemical modification. While the majority of furfural is further transformed by reduction, its oxidation to 5-hydroxy-2(5H)-furanone (**2**) has recently emerged as an interesting alterative process [9]. Hydroxyfuranone itself represents a versatile C_4-building block in organic synthesis and is accessible through various oxygenation processes from furfural (**1**) [9, 10]. Most of the reported processes and procedures employ inorganic oxidizing agents and solid supported catalysts. These approaches are often challenging to upscale due to hazardous chemicals and wastes. The photooxygenation of furfural (**1**) to hydroxyfuranone (**2**) offers an alternative access instead (**Scheme 1**) [11]. This procedure utilizes short-lived singlet oxygen ($^1O_2$) as an oxidant, which is generated using catalytic amounts of an organic dye and visible light [12].



Scheme 1. Photooxygenation of furfural (**1**) to 5-hydroxyfuranone (**2**) and subsequent conversion to 5-alkoxyfuranones (**3**) and (*E*)-alkyl 4-oxobut-2-enoates (**4**).

Numerous protocols for the photooxygenative transformation of **1** have been described [13-17], and the reaction has also been realized in direct or concentrated sunlight on semi-technical scales [18, 19]. One of the most common follow-up reactions of hydroxyfuranone (**2**) is the conversion to its corresponding alkoxy-derivatives **3** [20-22]. These compounds are commonly found as side-products of the photooxygenation in alcohols or are readily available via pseudo-esterification from hydroxyfuranone (**2**). These alkoxy derivatives have also proven useful as (photo)chemical building blocks, especially for (cyclo)addition reactions [23, 24]. Under acidic conditions, thermal ring-opening and isomerization furthermore generates the corresponding (*E*)-alkyl 4-oxobut-2-enoates (**4**) [25]. Due to the chemical and synthetic versatility of both, hydroxy (**2**) and alkoxyfuranones (**3**), this study further investigated the photooxygenation of furfural (**1**) and subsequent pseudo-(trans)esterification as efficient and sustainable pathways to these important building blocks. The photochemical approach utilized different experimental setups and light sources, while the thermal conversions evaluated various sources of starting materials.

2 MATERIALS AND METHODS

2.1 General Information

Technical grade furan-2-carbaldehyde (furfural, **1**) was purified by fractional distillation at normal pressure. The pale-yellow fraction formed at 161°C was collected and its purity confirmed by GC-analysis. All other reagents and solvents were purchased from Merck Life Science Pty Ltd. (Bayswater, VIC, Australia) or Thermo Fisher Scientific Australia Pty Ltd. (Scoresby, VIC, Australia) and were used as supplied.

Melting points were measured in open capillaries using a Tathastu or Gallenkamp melting point apparatus and are uncorrected.

NMR spectra were recorded on a Bruker 400 AscendTM (^{1}H: 400 MHz and ^{13}C: 100 MHz) equipped with an auto-sampler. Data and spectra were processed using the MestReNova software (Version 6.0.2-5475, Mestrelab Research S.L., Santiago de Compostela, Spain). Samples were prepared in $CDCl_3$ (δ = 7.26/77.3 ppm), and the residual solvent peak was used as a reference [26].

Mass spectra were obtained on a Shimadzu LCMS-2020 equipped with a DUIS ion source. Samples were directly injected, and the ions generated were detected in positive, negative or both modes (mass range: 100-500 m/z). The mobile phase consisted of an aqueous solution of 0.1% formic acid in HPLC grade methanol. Experimentation and data processing were done using the LabSolutions for LCMS-2020 software.

Infrared analysis was conducted on an IR-ATR iD5 (Thermo Scientific) spectrometer. Signals were scanned over a range of 500-4000 cm^{-1}.

UV-Vis spectra were recorded on a Cary 60 UV-Vis Spectrometer (Agilent Technologies). Signals were scanned within the 200-800 nm range. Spectra and λ_{max} of characteristic peaks were processed using the CaryWin UV60 software (Varian).

TLC chromatography was performed on 20 cm × 20 cm × 0.2 mm plastic sheets coated with silica gel 60 F_{254} (0.2 mm thickness; Merck, Germany). Mixtures of ethyl acetate and *n*-hexane were used as mobile phases. Visualization was achieved by UV-analysis or by dipping into a potassium permanganate solution.

Flash chromatography was performed using the CombiFlash Lumen (Teledyn ISCO, USA) instrument with an adjustable 32-65 g or 15-25 g solid load cartridge. The cartridges were packed with 50-60 g or 15-21 g of silica gel 60 depending on their sizes. Elutions were carried out using gradients of ethyl acetate in *n*-hexane at a flow rate of 35 $ml.min^{-1}$. Peaks were detected by UV-Vis analysis at 254 nm and 280 nm, respectively, or evaporative light scattering (ELS) at 30°C. Active fractions were auto collected, evaporated and dried.

Small-scale batch reactions were conducted in a Rayonet RPR-200 photochemical chamber reactor (Southern New England Ultraviolet Company, USA) equipped with 16 × 8 W cool-white fluorescent tubes (TL Mini 8W/33-640 1PP/10, Phillips-Signify, The Netherlands) (**Figure 1a**). Reactions were carried out in Pyrex Schlenk vessels of 75pprox.. 100-150 ml capacity. Oxygen was fed through a narrow side arm attached to a sintered glass frit on the bottom of the flask. A cold finger with circulating chilled water was inserted into the vessel to cool the reacting solution during irradiation.

Larger scale irradiations were conducted in an immersion well reactor from an unknown manufacturer (**Figure 1b**). The reactor had a capacity of 250 ml and was made from Pyrex glass. A 150 W medium-pressure mercury lamp (TQ-150, Heraeus Nobelelight, Germany) was inserted into the reactor. Through the narrow glass tube alongside the flask, an FEP tube was passed with a porous metal filter attached at its end for oxygen supply. The reaction mixture was magnetically stirred during operation. Chilled water was circulated through the immersion well to cool the reacting solution and lamp. The entire setup was placed in a wooden box to protect from UV-rays. Solar illuminations were performed in a custom-made flatbed reactor by Wexford Viking Glass Ltd in Ireland (**Figure 1c**). The reactor consisted of a rectangular box (35 × 98 cm or 3430 cm^2 exposed aperture) with an outer thickness of 3 cm and a 10 L capacity. It was fabricated from thick Pyrex glass in an aluminium frame and was covered with a reflective aluminium film on its back. The flatbed reactor was placed on a tilted steel frame angled at 76pprox.. 17°. Teflon tubing was used to connect the reactor to the adjacent colling loop. The lower outlet was linked to a rotary pump (Type 2-MD-SC, Little Giant, USA), which pumped the reaction mixture against gravity through a large intensive-condenser cooled with tap water. The solution was fed back into the flatbed through an opening at its top. Air was supplied at 15 LPM via a stainless-steel gas inlet tube at the bottom of the reactor. An air pump with a flow meter was connected to the gas inlet valve via PVC tubing. The temperature of the flatbed chamber was monitored with a mercury thermometer, which was inserted through an opening at the top of the flatbed and kept submerged throughout operation. The reactor loop was kept in a stainless-steel tray, which was also used to roughly orient the entire solar loop towards the sun. All solar experiments were carried out in either December 2019, May 2020 or November 2020 outside the Molecular Genetics Building on the James Cook University campus (latitude 19°19’50” S and longitude 146°45’33” E) in Townsville, Australia. UV radiation indices were collected from the Australian Radiation Protection and Nuclear Safety Agency (ARPANSA).

(a) (b) ©

Figures 1. (a) Schlenk flask inside a Rayonet chamber reactor. (b) Immersion well reactor. (c) Solar flatbed reactor.

2.2 Experimental Procedures

2.2.1 Small-scale Irradiations in the Rayonet Reactor

A solution of 3.2-9.7 g (2.8-8.4 ml, 33-101 mmol) of distilled furfural, 100 ml of technical ethanol (96%) and 55-147 mg of rose bengal was transferred to a Schlenk flask. A cold finger was inserted, and the gas feeding tube was connected to the oxygen supply. Once a gentle and stable gas supply was achieved, the Rayonet reactor was turned on. During the reaction, any evaporated solvent was refilled regularly. At the end of the irradiation, the gas supply was stopped and disconnected, the reaction mixture was poured into a round bottom flask, and the reactor was rinsed with approx. 50 ml of technical ethanol. The combined ethanolic solutions were subsequently evaporated at <30°C and ≤100 mbar. The crude oily residue obtained was dissolved in little dichloromethane. To this dark red solution, liquid nitrogen was added in small portions until crystals started to form. The crystals were collected by filtration on a Büchner funnel, washed with cold dichloromethane and air dried. Alternatively, crystallization was facilitated by seeding with small amounts of pure hydroxyfuranone crystals followed by refrigeration overnight.

2.2.2 Laboratory-scale Irradiations in the Immersion-well Reactor

28.6-29.9 g (24.7-25.8 ml, 298-311 mmol) of distilled furfural and 650-786 mg of rose bengal were dissolved in 250 ml of methanol and transferred to an immersion well reactor. The gas feeding was adjusted to a gentle purging, magnetic stirring was started, and the lamp was ignited. During operation, any evaporated methanol was refilled and of bleached rose bengal (0.5 g portions) was refed in regular intervals. At the end of the irradiation, the oxygen supply was stopped, the reaction mixture was transferred to a round bottom flask, and the reactor vessel was thoroughly rinsed with approx. 50 ml of methanol. The combined methanolic phases were subsequently evaporated at <30°C and ≤100 mbar. The product was isolated from the oily residue as described above under 2.2.1.

2.2.3 Demonstration-scale Illuminations in the Flatbed Reactor

A 500 ml flask wrapped with aluminium foil was filled with 247-282 g (213-243 ml, 2.57-2.94 mol) of distilled furfural and 100 ml of technical or absolute ethanol. To this solution, 5.3-10.4 g of rose bengal were added in portions upon swirling until a homogeneous solution was obtained. The solar flatbed was directed towards the sun and the cooling water to the external condenser was started. Then 6.8-7.9 l of technical or absolute ethanol were filled into the reactor through the top opening, and the reactor was covered with light-tight black cloth. The furfural-rose bengal stock solution was subsequently added through the top opening, followed by 100 ml of wash ethanol used for rinsing of the stock vessel. The air pump was switched on, the gas feeding valve was opened, a gentle air stream through the solution was adjusted, and the circulation pump was switched on. Once a stable flow was achieved, the black cloth was removed, and the system was exposed to sunlight. Approximately every 30 minutes, the reactor was repositioned towards the direction of the sun. Additional portions of rose bengal (1 g) and ethanol (100-200 ml) were occasionally added to compensate for photobleaching and evaporation losses, respectively. During interruptions overnight, the gas feeding line was closed, the air and circulation pumps were stopped, the cooling water was turned off, and the reactor was covered with dark cloth. Reactions were restarted the following day as described above. At the end of the illumination, the reactor was covered again with the light-tight cloth, and the reaction mixture and additional ca. 250 ml of wash ethanol were emptied into three amber 2.5 L Winchester bottles. Approximately 500 ml portions of the crude reaction mixture were successively evaporated at <30°C and ≤100 mbar. The product was subsequently isolated as described above under 2.2.1.

2.2.4 Synthesis of Alkoxyfuranones by Pseudo-Esterification

A mixture of 2.02-9.35 g (20.2-93.4 mmol) of hydroxyfuranone, 0.5 g (2.63 mmol) of *para*-toluenesulfonic acid monohydrate, alcohol (ca. 1.1 mol-equivalent) and 150 ml of chloroform was refluxed on a Dean-Stark setup. Once no more water was formed (after approx. 5-6 hours), the reaction mixture was cooled to room temperature, carefully washed with aqueous $NaHCO_3$-solution and brine, dried over anhydrous Na_2SO_4, and concentrated to dryness at <50°C and ≤100 mbar. The desired alkoxyfuranones were subsequent isolated by vacuum distillation or flash chromatography.

2.2.5 Synthesis of Alkoxyfuranones by Pseudo-Transesterification

A solution of 10.2-25.6 g (79.6-200.2 mmol) of ethoxyfuranone, 0.5 g (2.63 mmol) of *para*-toluenesulfonic acid monohydrate, alcohol (ca. 1.1 mol-equivalent) and 150 ml of chloroform was refluxed on a Dean-Stark setup for 15 hours. The reaction mixture was treated as described above under 2.2.4. The desired alkoxyfuranones were subsequent isolated by flash chromatography.

2.3 Spectroscopic details

All compounds isolated were identified by NMR-spectroscopy, and their spectroscopic details matched previously described data [14, 17, 20, 27-30].

5-Hydroxyfuran-2(5H)-one (**2**) [14, 17]. Colourless solid. M.p.: 54-56°C (Lit.: 52°C [14]). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29 (dd, *J* = 5.6, 1.2 Hz, 1H, =CH), 6.23 (dd, *J* = 5.6, 1.1 Hz, 1H, =CH), 6.21 (dd, *J* = 1.2, 1.1 Hz, 1H, C<u>H</u>OH), 4.21 (br. s, 1H, OH). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 171.6 (s, 1C, C=O), 152.2 (d,

1C, CHOH), 124.8 (d, 1C, =CH), 99.0 (d, 1C, =CH). ESI-MS: *m/z* = 99 ([M-H]$^-$, 96%), 100 ([M+H]$^+$, 4%), 199 ([2M-H]$^-$, 92%), 200 ([2M]$^+$, 8%). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3250, 1719, 1911, 1275, 1127, 704.

5-Methoxyfuran-2(5H)-one (**3a**) [27]. Yellowish liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.21 (dd, *J* = 5.7, 1.2 Hz, 1H, =CH), 6.25 (dd, *J* = 5.7, 1.2 Hz, 1H, =CH), 5.86 (dd, *J* = 1.2 Hz, 1H, CHO), 3.58 (s, 3H, OCH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 170.5, (s, 1C, C=O), 150.1 (d, 1C, =CH), 125.4 (d, 1C, =CH), 104.2 (d, 1C, CHOMe), 57.2 (q, 1C, OCH_3). ESI-MS: *m/z* = 115 ([M+H]$^+$, 100%). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2939, 1761, 1472, 1128, 990.

5-Ethoxyfuran-2(5H)-one (**3b**) [28]. Yellowish liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.20 (dd, *J* = 5.7, 1.2 Hz, 1H, =CH), 6.21 (dd, *J* = 5.7, 1.3 Hz, 1H, =CH), 5.92 (dd, *J* = 1.3, 1.2 Hz, 1H, CHOEt), 3.92 (dq, *J* = 9.4, 7.1 Hz, 1H, OCH_2), 3.75 (dq, *J* = 9.4, 7.1 Hz, 1H, OCH_2), 1.27 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 170.6 (s, 1C, C=O), 150.5 (d, 1C, =CH), 125.1 (d, 1C, =CH), 103.3 (d, 1C, CHOEt), 66.3 (t, 1C, OCH_2), 15.1 (q, 1C, CH_3). ESI-MS: *m/z* = 129 ([M+H]$^+$, 100%). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2981, 1756, 1349, 1116, 1007, 890, 699.

5-Isopropoxyfuran-2(5H)-one (**3c**) [29]. Yellowish liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.17 (dd, *J* = 5.7, 1.0 Hz, 1H, =CH), 6.19 (dd, *J* = 5.7, 1.1 Hz, 1H, =CH), 5.99 (dd, *J* = 1.2, 1.1 Hz, 1H, CHO^{i}Pr), 4.09 (m, 1H, OCH), 1.26 (t, *J* = 7.1 Hz, 6H, 2 × CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 170.9 (s, 1C, C=O), 150.9 (d, 1C, =CH), 124.8 (d, 1C, =CH), 102.2 (d, 1C, CHO^{i}Pr), 73.7 (d, 1C, OCH), 23.3 (q, 1C, CH_3), 22.1 (q, 1C, CH_3). ESI-MS: *m/z* = 157 ([M+CH_3]$^+$, 100%), 159 ([M+OH]$^-$, 31%). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2976, 1755, 1383, 1112, 1009, 891, 684.

5-Butoxyfuran-2(5H)-one (**3e**) [20]. Yellowish liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.20 (dd, *J* = 5.7, 1.2 Hz, 1H, =CH), 6.22 (dd, *J* = 5.7, 1.3 Hz, 1H, =CH), 5.92 (dd, *J* = 1.3, 1.2 Hz, 1H, CHO^{n}Bu), 3.87 (dt, *J* = 9.3, 6.6 Hz, 1H, OCH_2), 3.68 (dt, *J* = 9.3, 6.6 Hz, 1H$_g$), 1.61 (m, 2H, CH_2), 1.39 (m, 2H, CH_2), 0.92 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 170.7 (s, 1C, C=O), 150.5 (d, 1C, =CH), 125.2 (d, 1C, =CH), 103.5 (d, 1C, CHO^{n}Bu), 70.5 (t, 1C, OCH_2), 31.6 (t, 1C, CH_2), 19.2 (t, 1C, CH_2), 13.9 (q, 1C, CH_3). ESI-MS: *m/z* = 157 ([M+H]$^+$, 100%). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955, 1757, 1463, 1123, 1016, 890, 685.

5-Hexyloxyfuran-2(5H)-one (**3f**) [30]. Yellowish liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.20 (dd, *J* = 5.7, 1.2 Hz, 1H, =CH), 6.22 (dd, *J* = 5.7, 1.3 Hz, 1H, =CH), 5.91 (dd, *J* = 1.3, 1.2 Hz, 1H, CHO^{n}Hex), 3.85 (dt, *J* = 9.3, 6.7 Hz, 1H, OCH_2), 3.76 (m, 1H, OCH_2), 1.70-1.53 (m, 4H, 2 × CH_2), 1.37-1.20 (m, 4H, 2 × CH_2), 0.88 (t, *J* = 6.9 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 170.7 (s, 1C, C=O), 150.5 (d, 1C, =CH), 125.1 (d, 1C, =CH), 103.5 (d, 1C, CHO^{n}Hex), 70.8 (t, 1C, OCH_2), 31.6 (t, 1C, CH_2), 29.6 (t, 1C, CH_2), 25.7 (t, 1C, CH_2), 22.7 (t, 1C, CH_2), 14.1 (q, 1C, CH_3). ESI-MS: *m/z* = 185 ([M+H]$^+$, 100%). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2930, 1759, 1467, 1125, 1079, 890, 686.

5-Cyclohexyloxyfuran-2(5H)-one (**3g**) [29]. Yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.18 (dd, *J* = 5.7, 1.2 Hz, 1H, =CH), 6.20 (dd, *J* = 5.7, 1.3 Hz, 1H, =CH), 6.04 (dd, *J* = 1.3, 1.2 Hz, 1H, CHO^{c}Hex), 3.78 (ddd, *J* = 13.3, 8.6, 3.9 Hz, 1H, OCH),1.99-1.93 (m, 2H, CH_2), 1.76-1.72 (m, 2H, CH_2), 1.58-1.53 (m, 2H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 170.9 (s, 1C, C=O), 150.9 (d, 1C, =CH), 124.9 (d, 1C, =CH), 102.1 (d, 1H, CHO^{c}Hex), 79.3 (d, 1C, OCH), 33.3 (t, 1C, CH_2), 32.1 (t, 1C, CH_2), 25.5 (d, 2C, 2 × CH_2), 24.1 (d, 1C, CH_2). ESI-MS: *m/z* = 183 ([M+H]$^+$, 100%). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2955, 1757, 1437, 1133, 1076, 991, 684.

5-Dodecyloxyfuran-2(5H)-one (**3h**) [30]. Colourless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.44 (dd, *J* = 5.7, 1.2 Hz, 1H, =CH), 6.27 (dd, *J* = 5.7, 1.3 Hz, 1H, =CH), 6.07 (dd, *J* = 1.3, 1.2 Hz, 1H, CHODodec), 3.81 (dt, *J* = 9.5, 6.6 Hz, 1H, OCH_2), 3.71 (dt, *J* = 9.5, 6.6 Hz, 1H, OCH_2), 1.62 (m, 2H, CH_2), 1.40-1.23 (m, 18H, 9 × CH_2), 0.88 (t, *J* = 6.9 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 165.1 (s, 1C, C=O), 140.4 (d, 1C, =CH), 125.2 (d, 1C, =CH), 103.5 (d, 1C, CHODodec), 70.8 (t, 1C, OCH_2), 66.1 (t, 1C, CH_2), 32.1 (t, 1C, CH_2), 29.8 (t, 2C, 2 × CH_2), 29.5 (t, 2C, 2 × CH_2), 28.6 (t, 1C, CH_2), 26.0 (t, 1C, CH_2), 22.8 (t, 1C, CH_2), 14.3 (q, 1C, CH_3). ESI-MS: *m/z* = 269 ([M+H]$^+$, 100%), 267 ([M-H]$^-$, 5%).

(*E*)-Ethyl 4-oxobut-2-enoate (**4b**). In mixture with **3b**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.76 (d, *J* = 7.6 Hz, 1H, CHO), 6.97 (dd, *J* = 15.9, 7.6 Hz, 1H, =CH), 6.72 (d, *J* = 15.9 Hz, 1H, =CH), 4.30 (q, *J* = 7.1 Hz, 2H, OCH_2), 1.34 (t, *J* = 7.1 Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 192.6 (d, 1C, CHO), 165.0 (s, 1C, C=O), 140.5 (d, 1C, =CH), 139.5 (d, 1C, =CH), 61.9 (t, 1C, OCH_2), 14.2 (q, 1C, CH_3).

3 RESULTS AND DISCUSSIONS

3.1 Photooxygenation Experiments

Several protocols for the photooxygenation of furfural (**1**) have been reported [13-17, 19]. The initial irradiation procedure patented by Schenck used ethanol as a solvent and solely produced ethoxyfuranone (**3b**) [31]. A later study revealed that hydroxyfuranone (**2**) can be isolated if the temperature is kept below 70°C during the reaction and subsequent isolation [32]. Hydroxyfuranone (**2**) is known to crystallize at low temperatures (<0°C), but only when in a sufficient purity to achieve supersaturation. Due to this difficult and demanding crystallization, crude **2** is typically used for further transformations without purification [14].

3.1.1 Small-scale Irradiations in the Rayonet Reactor

A series of photooxygenation experiments was initially conducted in the Rayonet laboratory reactor (**Figure 1a**) using modified procedures reported by Hui and co-workers [16], Esser et al. [19] and Schenck [31], respectively. Rose bengal disodium salt was chosen as common sensitizer due to its favourable singlet oxygen generation efficiency [33]. Likewise, ethanol (technical grade, 96%) was selected as solvent due to its low toxicity and excellent solvation ability [34]. Solutions of freshly distilled furfural (**1**) were irradiated at 21°C using different loadings of reagent and sensitizer (**Scheme 1**). During each reaction, the distinctive bright red colour of rose bengal notably faded to reddish orange, especially for lower sensitizer and higher furfural concentrations. At the end of each photooxygenation experiment, the solution was carefully evaporated at <30°C to minimize undesired thermal conversions, and the crude reaction mixture was analysed by ^{1}H-NMR spectroscopy to determine its composition (**Table 1**). Pure hydroxyfuranone (**2**) was subsequently isolated by freeze crystallization. A common issue was the persistence of residual rose bengal or coloured impurities in the crystal lattice of the isolated product, thus demanding repeated decolourization treatments.

Table 1. Experimental parameters and results for irradiations in the Rayonet reactor (100 ml of 96% EtOH, 21°C).

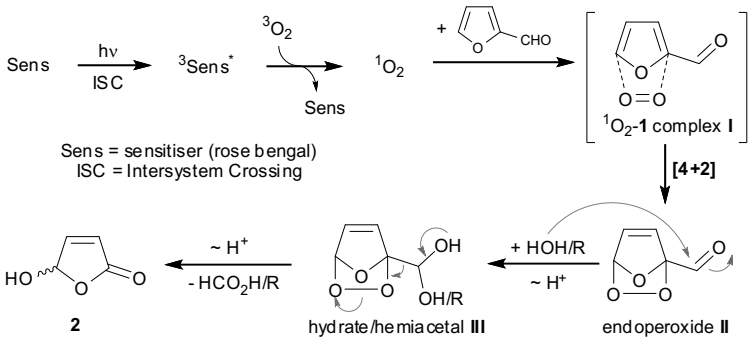
Entry	Loadings		Time	Composition of crude product[a]				Yield of 2
	1 (g/mM)	RB[b] (mg/mol%)	(hrs)	1 (%)	2 (%)	3b (%)	4b (%)	(%)[c]
1	5.8/575	55/0.09	9	1	94	4	1	36
2	9.7/929	147/0.14	20	4	87	8	1	47
3	5.5/546	78/0.13	20	—	73	22	5	30
4	3.2/325	84/0.25	20	—	98	1	1	33
5[d]	3.2/325	85/0.25	1	—	98	1	1	33
6	3.2/325	86/0.26	7	—	99	1	—	46
7	9.7/929	142/0.14	2	—	100	—	—	52

[a] Determined by ^{1}H-NMR (±2%). [b] RB = rose bengal disodium salt. [c] Isolated yield after crystallization. [d] Samples (ca. 1 ml) taken every 10 minutes.

Under all irradiation conditions, excellent to complete consumptions of **1** were observed, although irradiation times varied widely from 1-20 hours. The desired hydroxyfuranone (**2**) was detected as the main to sole component with 73-100% in the crude reaction mixture. However, significant material losses and hence reduced recovery rates of **2** were caused by repeated recrystallization [35]. As a result, the desired product **2** was isolated in varying yields of 30-52%. Exhaustive reaction times somewhat favoured the formation of the ethoxy-derivative **3b** (**Table 1**, Entries 2 and 3), while the amounts of (*E*)-ethyl 4-oxobut-2-enoate (**4b**) remained generally low. Naturally, the best isolated yield of 52% was achieved when hydroxyfuranone (**2**) was formed as the sole product (**Table 1**, Entry 7).

According to the generally accepted reaction mechanism (**Scheme 2**) [25], singlet oxygen initially forms a complex with furfural (**I**), which completes the [4+2]-cycloaddition to the endoperoxide intermediate **II**.

Nucleophilic attack by either water or alcohol at the exposed carbonyl group generates an unstable hydrate or hemiacetal intermediate (**III**), which subsequently collapse to hydroxyfuranone (**2**). Formic acid or its alkyl-ester are formed as additional decomposition products. As water is significantly more nucleophilic than alcohol, the presence of water is beneficial for the formation of **1**. Consecutive photooxidation of formic acid to carbon dioxide and water has also been suggested, hence explaining the formation of **2** under anhydrous conditions [36].



Scheme 2. Mechanism of the photooxygenation of furfural (**1**) to 5-hydroxyfuranone (**2**).

The generation and accumulation of formic acid likely catalysed pseudo-esterification of hydroxyfuranone (**2**) to its ethoxy-derivative **3b** during prolonged reaction and elevated temperatures [31, 32]. To investigate this, a solution of **2** (30 mg) in 9 ml of methanol and 0.5 ml of formic acid was heated to 70°C for 4 hours. After careful neutralisation and extraction, NMR analysis of the crude product confirmed complete conversion into methoxyfuranone (**3a**). Subsequent micro-vacuum distillation furnished pure **3a** in a yield of 60%. This experiment thus unambiguously confirms that pseudo-esterification can unintentionally occur during the photooxygenation process or its isolation and purification stages. Heat management is thus crucial to obtain hydroxyfuranone (**2**) in sufficient quantities and purity.

To monitor the progress of the irradiation, samples from Entry 5 with the lowest concentration of **1** were taken every 10 minutes and were subsequently analysed by ^{1}H-NMR (**Figure 2**). The conversion of furfural (**1**) quickly reached approx. 80% within the first 10 minutes and near completion after just 40 minutes, respectively. The amounts of the ethoxylated side-products **3b** and **4b** fluctuated slightly during the experiment, possibly due to their unintended formation during evaporation and storage. Bleaching of the sensitizer was noticeable and may have retarded the reaction at higher conversions.

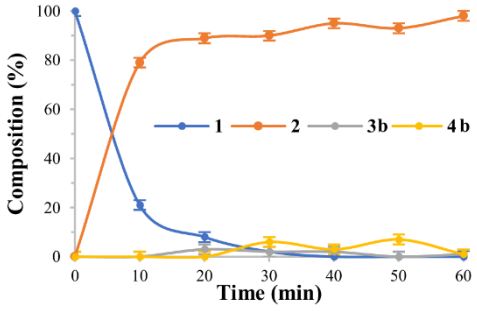


Figure 2. Composition over time profile (Entry 5).

Sensitizer bleaching is commonly observed during photooxygenations [37], especially for large scale operations that demand extended irradiation times. Thus, a solution of rose bengal (57 mg) in technical ethanol (100 ml) was irradiated for 5 hours in the Rayonet reactor while being purged with oxygen. At the end of the reaction, the λ_{max} absorbance of the solution at 558 nm had dropped by almost 50%, clearly demonstrating the extend of bleaching. Photooxygenations of furfural are mainly conducted in either methanol or ethanol [13-17, 19]. Although photoreactions in these alcohols generally proceed fast and efficiently, they easily produce larger amounts of the methoxylated or ethoxylated compounds **3a,b** and **4a,b** through thermal follow-up reactions. Hence, additional photooxygenation experiments were conducted with diluted solutions of **1** in ethanol, isopropanol and *tert*-amyl alcohol, respectively. The later alcohols were investigated as potentially less reactive solvents for consecutive

pseudo-esterifications. To assist with the solvation of rose bengal and breakdown of the endoperoxide intermediate **II** (**Scheme 2**), 4 vol-% of water were added and the solutions were extensively sonicated prior to light exposure. Despite this treatment, the *tert*-amyl alcohol solution remained partially turbid. After irradiation for 10 hours, the compositions of the carefully evaporated and dried reaction mixtures were analysed by ^{1}H-NMR (**Table 2**). An isolation of **2** was not attempted for these reactions.

Table 2. Experimental parameters and results for solvent screening (100 ml, 10 hrs, 21°C).

Entry	Loadings		ROH[a]	Composition of crude product[b]			
	1 (g/mM)	RB[c] (mg/mol%)		1 (%)	2 (%)	3 (%)	4b (%)
8	2.1/215	22.3/0.10	EtOH	—	74	24 (**3b**)	2 (**4b**)
9	2.1/215	22.1/0.10	^{i}PrOH	8	86	3 (**3c**)	3 (**4c**)
10	2.0/205	21.0/0.10	^{t}AmOH	21	69	— (**3d**)	10 (**4d**)

[a] 4 Vol-% of water. [b] Determined by ^{1}H-NMR (±2%). [c] RB = rose bengal disodium salt.

Under almost identical irradiation conditions, the selection of alcoholic solvent impacted significantly on the conversion rates and hence product compositions. As with previous experiments, irradiation in ethanolic solution achieved complete consumption, but produced a mixture of the desired hydroxyfuranone (**2**) and its thermal follow-up products **3b** and **4b** (Entry 8). The photooxygenation conducted in isopropanol showed a near complete conversion of 92% with a favourable selectivity towards **2** and only minor amounts of the corresponding alkoxy-derivatives **3b** and **4b** of 3% each (Entry 9). In contrast, 21% of unreacted **1** remained in *tert*-amyl alcohol as the solvent, with 10% of (*E*)-*tert*-pentyl 4-oxobut-2-enoate (**4d**) as the only detectable side-product (Entry 10).

The choice of solvent significantly changes the optical and physicochemical properties of the solution. In particular, polarities, light transmittances and oxygen solubilities decrease in the order of EtOH > ^{i}PrOH > ^{t}AmOH [38], thus effecting the efficiency of the photooxygenation. The decreasing polarity also reduces the solubility of rose bengal and produces less transparent solutions with hindered light penetration. Similarly, the decrease in nucleophilicity of the alcohols due to increasing steric hinderance of their alkyl groups minimizes pseudo-esterifications [39, 40], hence improving selectivity. In contrast, rising boiling points necessitate harsher evaporation conditions, especially for *tert*-amyl alcohol (B.p.: 101°C), thus favouring further thermal transformations. The results from the solvent study generally align with these interpretations as the reaction conducted in ethanol gave the highest conversion but showed the lowest selectivity (Entry 8). In contrast, the usage of *tert*-amyl alcohol furnished the lowest conversion and solely produced **4d** as a side-product instead (Entry 10). Similarly, incomplete reactions and large amounts of thermal by-products have also been described for photooxygenations of **1** in *n*-butanol at 60°C [41].

3.1.2 Laboratory-scale Irradiations in the Immersion-well Reactor

To obtain multigram quantities of the desired hydroxyfuranone (**2**), the photooxygenation was furthermore conducted in a larger laboratory-scale immersion well reactor equipped with a more powerful 150 W medium-pressure mercury lamp (**Figure 1b**) [38, 42]. Adapting the reaction protocol developed by Moradai et al. [14], solutions of **1** and rose bengal in methanol were irradiated while being purged with a gentle stream of oxygen gas (**Scheme 1**). Despite the more powerful light source, the reaction temperature remained constant at 21°C during irradiation. However, the harsher UV-conditions caused severe bleaching of the photosensitiser rose bengal for all reactions [33, 43, 44], and the colour of the reaction mixtures generally changed from bright, transparent and red to fluorescent, turbid and orange. Additional feeding of fresh sensitizer material was thus required to improve subsequent conversions. After careful evaporation, the composition of each crude product was analysed by ^{1}H-NMR and product **2** was then isolated by crystallization (**Table 3**). Initially, all photooxygenation experiments readily consumed furfural (**1**) as notifiable from TLC monitoring. However, increasing sensitizer bleaching significantly retarded the progress of the reaction and hence demanded exhaustive irradiation times of 19-36 hours to reach near or complete consumptions.

Table 3. Experimental parameters and results for irradiations in the Immersion-well reactor (250 ml of MeOH, 21°C).

Entry	Loadings		Time	Composition of crude product[a]				Yield of 2
	1 (g/mM)	RB[b] (mg/mol%)	(hrs)	1 (%)	2 (%)	3a (%)	4a (%)	(%)[c]
11	29.0/1098	657/0.22	35	—	95	5	—	35
12	28.6/1084	650/0.21	22	—	96	4	—	60
13	29.6/1118	648/0.21	21	—	85	5	10	24
14	29.6/1118	744/0.24	36	6	83	7	4	23
15[d]	29.9/1131	786/0.25	19	—	81	6	13	24

[a] Determined by ^{1}H-NMR (±2%). [b] RB = rose bengal disodium salt. [c] Isolated yield after crystallization. [d] Samples (ca. 1 ml) taken every hour during the first 9 hours.

As mixing is mainly provided through gas purging and magnetic stirring, mass transfer and oxygen saturation may differ between experiments, which naturally impacts process efficiencies. The large quantities of photodegradants also complicated the crystallization process and thus, the isolated yields of hydroxyfuranone (**2**) ranged widely from 23-60% [35]. Although all experiments were conducted under similar conditions, the highest yield of **2** of 60% was obtained after 21 hours of irradiation (**Table 2**, Entry 12). The methoxy-derivative **3a** was detected in all transformations, but its amounts remained low with ≤7%. In contrast, the open (*E*)-methyl 4-oxobut-2-enoate (**4a**) was only observed in three cases, but in lower quantities ≤13% (Entries 13-15). Despite the fluctuating yields, the immersion-well setup readily produces multi-gram amounts of pure **2** due to its larger size and more powerful lamp. Advanced models with dedicated gas feeding or mixing elements may further improve performances [38, 42].

The progress of the photooxygenation in Entry 15 was furthermore monitored for the first 9 hours. Samples were taken every hour of irradiation and were analysed by ^{1}H-NMR (**Figure 3**). In contrast to the reaction conducted in the Rayonet reactor and in ethanol, the amount of **1** decreased more slowly and irregularly due to the need to refeed bleached sensitizer. Noteworthy, no methoxylated byproducts **3a** or **4a** were detectable in the first 5 hours. A conversion of approx. 90% was reached after 6 hours. Subsequent analyses during the final 3 hours revealed irregular amounts of **3a** and **4a**, again suggesting their formation during sample evaporation and storage.

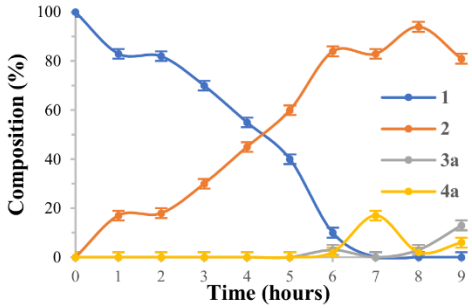


Figure 3. Composition over time profile (Entry 15).

3.1.3 Demonstration-scale Illuminations in the Flatbed Reactor

The large demonstration-scale solar photooxygenation experiments (**Scheme 1**) demanded a scale-up from 0.1-0.25 litres to up to 8 litres. Solutions of furfural (**1**), rose bengal and ethanol (technical or absolute) were prepared in the flatbed reactor and exposed to natural sunlight (**Figure 1c**) [18, 45, 46]. Atmospheric air was bubbled through the reaction mixture, which provided turbulent mixing and oxygen saturation. Cooling of the reaction mixture was achieved by circulation through an external cooling loop, although temperatures inside the flatbed readily reached 23-46°C. Since illumination conditions such as sunlight intensity, outdoor temperature and atmospheric oxygen content naturally vary depending on time and season, all four solar transformations were monitored. Samples of 2 ml volume were collected at designated reaction times, and their chemical compositions were subsequently determined by ^{1}H-NMR spectroscopy. After completed exposure, the final reaction mixture was carefully evaporated, dried and again analysed for its composition (**Table 4**). Due to the large volumes of solvent and significant amounts of formic acid (B.p.: 101°C) generated, complete evaporation and drying proved

time-consuming and challenging. The isolation of **2** was attempted by either seeding with pure crystals and refrigeration or freeze crystallization using liquid nitrogen.

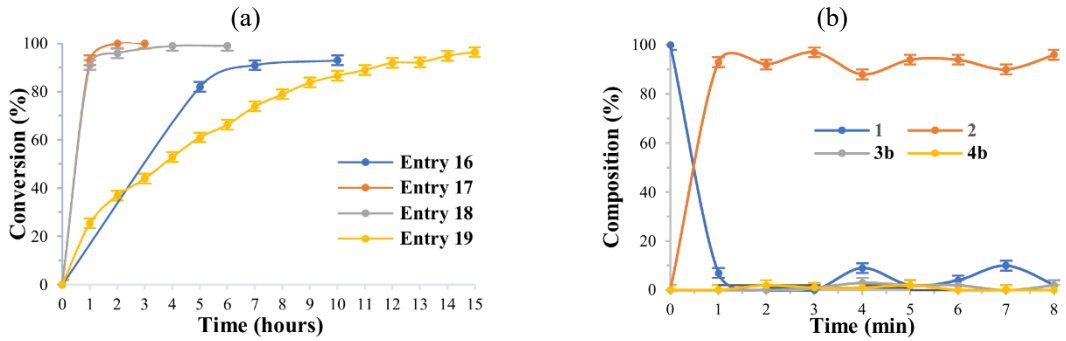
Table 4. Experimental parameters and results for solar illumination in the flatbed reactor.

Entry	Loadings			Time	Temp.	Composition of crude product[a]				Yield of
	1 (g)	RB[b] (g)	EtOH (l)	(hrs)	(°C)	1 (%)	2 (%)	3b (%)	4b (%)	2 (%)[c]
16[d]	274	5.3	7.0[e]	12	36-43	7/3	71/68	20/27	2/2	30
17[d]	247	6.1	7.5[e]	9	23-33	2/1	92/67	2/25	—/7	25
18[d]	260	6.5	7.9[f]	11	27-30	9/8	89/41	2/36	—/15	42 (**3b**)[g]
19[d]	282	10.4	7.5[e]	18	33-46	5/2	70/61	23/29	2/10	49

[a] Determined by ^{1}H-NMR (±2%) for final sample/dried crude product. [b] RB = rose bengal disodium salt. [c] Isolated yield after crystallization. [d] Samples (ca. 2 ml) taken in regular intervals. [e] Technical (96%). [f] absolute. [g] After subsequent pseudo-esterification of crude product (see section 3.2.1).

Entries 16-18 were each conducted over two days with 2-7 hours of exposure daily. In contrast, Entry 19 ran for three days with 6 hours of illumination each day. All solar photooxygenations achieved high conversions of furfural (**1**) of >90%. While the initial analyses of the product samples showed good to high selectivities for hydroxyfuranone (**2**) formation, these dropped notably for the final product batches after complete evaporation and drying. For Entry 18, for example, the amount of **2** decreased from 89% to 41% during workup and hence, all crystallization attempts of **2** failed due to the increased amounts of byproducts **3b** and **4b**. The crude product from this experiment was thus subjected to further pseudo-esterification to ethoxyfuranone **3b** (see chapter 3.2.1), which was then isolated in 42% yield. In all other cases, material losses were again unavoidable during the crystallization, filtration and washing processes [35]. The highest isolated yield was obtained for Entry 19 with 49% or 144 g of pure **2**, although this experiment experienced the highest temperatures of up to 46°C. The absence of water showed no significant impact on photooxygenation performances as seen from Entry 18, and conversion rates and selectivities were found similar to those of Entry 17. The slightly shorter illumination period of 9 vs. 11 hours in the latter experiment may result from the improved solubility of rose bengal in technical ethanol and hence the improved transparency of the solution.

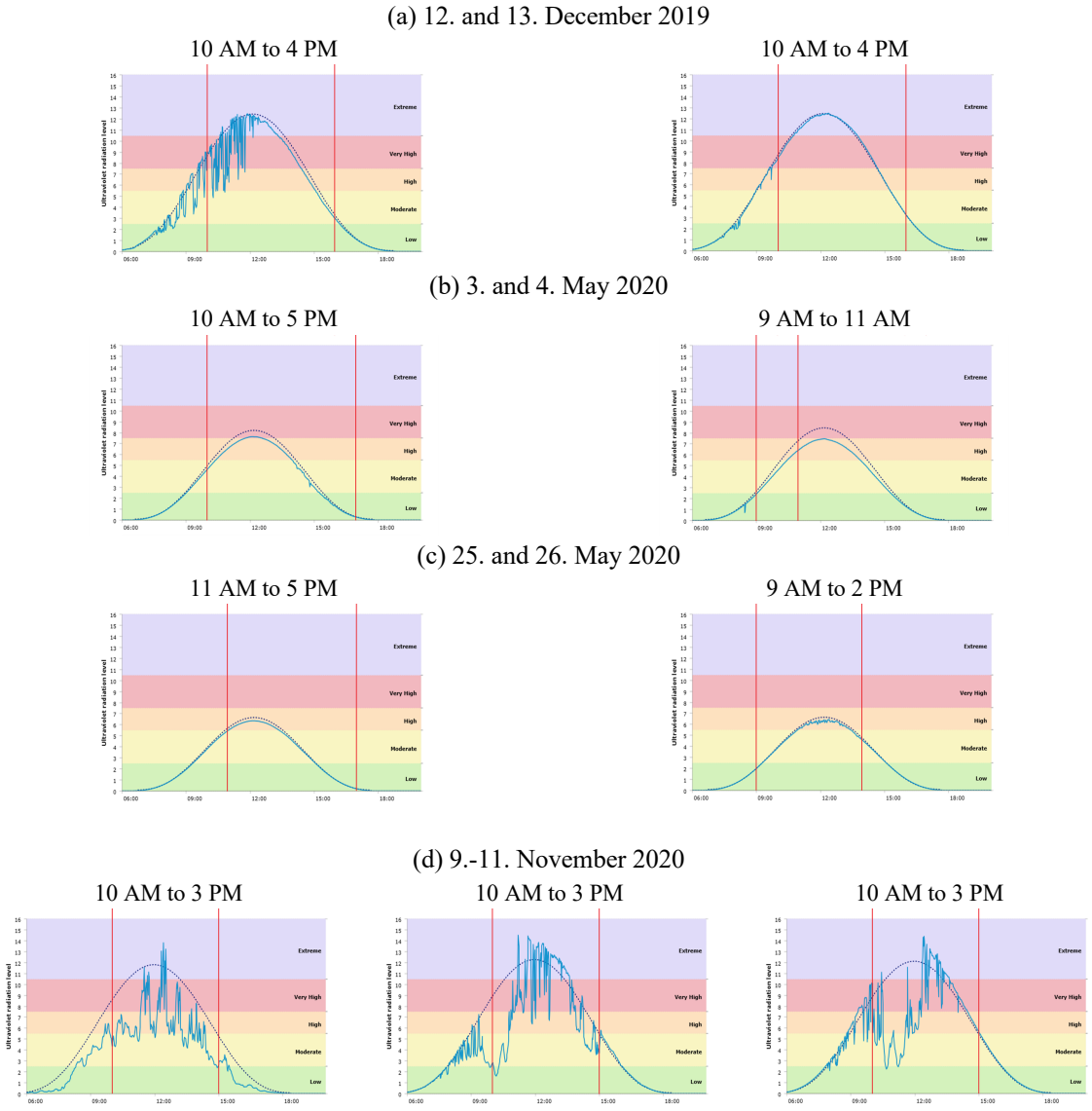
The four solar experiments were routinely sampled and analysed to determine their conversion over time profiles (**Figure 4a**). Entries 17 and 18 proceeded rapidly and showed near complete conversions of >90% already after one hour of exposure. In contrast, Entry 16 displayed a somewhat slower conversion, but reached a consumption of **1** of 82% after 5 hours in direct sunlight. A slow but steady conversion of furfural **1** over the first 15 hours was noted for Entry 19 instead. The composition profile of Entry 17 is furthermore exemplarily shown in **Figure 4b**. After the first hour, the composition of the reaction mixture remained relatively constant over the next 7 hours of exposure. After workup, however, the proportion of **2** had dropped from 92% to 67%, while the amount of ethoxyfuranone (**3b**) had increased from 2% to 25%. A similarly rapid conversion of **1** was observed for Entry 18, while Entries 16 and 17 proceeded more slowly (not shown).



Figures 4. (a) Conversion over time profiles. (b) Composition over time profile (Entry 17).

The different solar performances most likely resulted from the varying sunlight conditions during each experimental phase (**Figures 5**). Clearer and sunnier weather conditions naturally initiated better conversion rates as evident from solar Entries 17 (**Figure 5b**) and 18 (**Figure 5c**). In contrast, less favourable solar conditions

demanded prolonged illuminations as shown by solar Entries 16 (**Figure 5a**) and 19 (**Figure 5d**). Different sensitiser concentrations also impacted on the transparency and hence light penetration efficiency of the reaction mixture. Fluctuating oxygen saturation due to temperature differences may furthermore alter singlet oxygen generation. While the simple flatbed reactor operated satisfactory and produced large quantities of **2**, it would benefit from better cooling and improved gas-feeding inside the illuminated reaction chamber.

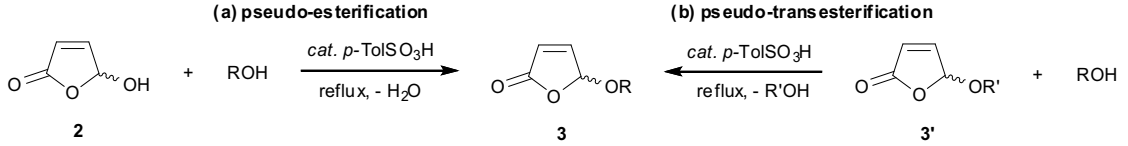


Figures 5. UV indices (ARPANSA) during solar exposures: (a) Entry 16. (b) Entry 17. (c) Entry 18. (d) Entry 19. Vertical red lines represent the experimental time frames.

3.2 Pseudo-Esterification and -Transesterification Experiments

Due to the somewhat unsatisfactory and unreliable yields of hydroxyfuranone (**2**) achieved through photooxygenation, its alkoxy-derivatives **3** may represent alternative commodity and platform chemicals. Alkoxyfuranones (**3**) are readily available from **2** through acid-catalysed pseudo-esterification (**Scheme 3a**) and consequently, a variety of reaction protocols have been described [20, 25, 30]. To complete these transformations, the water generated is commonly removed by azeotropic distillation using chloroform or toluene. In addition, pseudo-transesterification of methoxy- or ethoxyfuranone (**3a,b**) may serve as an access to more complex alkoxylated analogues (**Scheme 3b**) [22, 47, 48]. Both conversion processes also represent an interesting option for the organic waste streams of the photooxygenation protocol. In particular, the liquid filtrates collected mainly

contained residual hydroxyfuranone (**2**) and larger amounts of either methoxy- (**3a**) or ethoxyfuranone (**3b**), respectively.



Schemes 3. (a) Pseudo-esterification and (b) pseudo-transesterification to 5-alkoxyfuranones.

3.2.1 Pseudo-Esterification Reactions

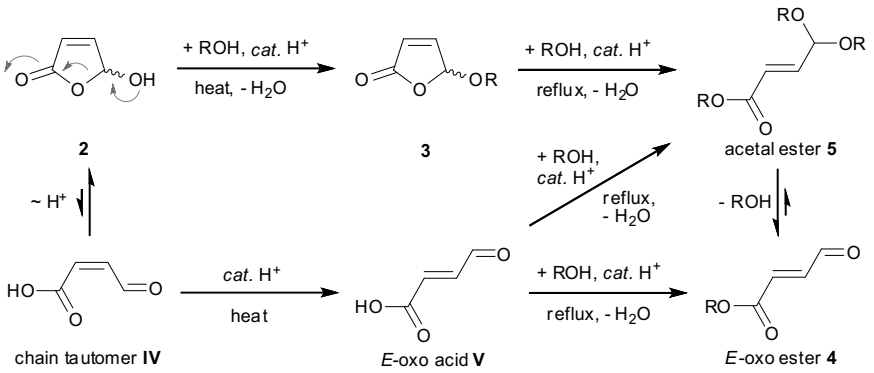
Heating of hydroxyfuranone (**2**) in chloroform with either methanol, ethanol or *n*-butanol and in the presence of catalytic amounts of *para*-toluenesulfonic acid monohydrate readily produced the desired alkoxyfuranones **3a,b** and **e** (**Scheme 3a**). After 5-6 hours of azeotropic distillations, the formation of water had generally ceased, the reaction mixtures were neutralized, and the solvent and residual alcohol were removed by careful evaporation. Analyses of the crude reaction mixtures confirmed complete conversions and minor amounts of ≤20% of the corresponding ring-opened (*E*)-alkyl 4-oxobut-2-enoates **4**. Subsequent vacuum distillation or flash chromatography furnished compounds **3a,b** and **e** in reduced isolated yields of 36-62% due to purification losses (**Table 5**) [35].

Table 5. Experimental parameters and results for pseudo-esterifications (150 ml of $CHCl_3$, 0.5 g *p*-$TolSO_3H$).

Entry	2 (g/mmol)	ROH (ml/mmol)	Time (hrs)[a]	Yield of 3 (%)
20	18.8/187.9	MeOH, 8.4/207.1	6	57 (**3a**)[b]
21	10.3/102.9	EtOH, 6.6/113.2	6	62 (**3b**)[b]
22	2.02/20.2	^{n}BuOH, 2.1/22.9	5	36 (**3e**)[c]

[a] Time until formation of water had ceased. [b] After vacuum distillation. [c] After flash chromatography.

Several pathways for the formation of alkoxyfuranones and their derivatives have been proposed (**Scheme 4**) [25]. Hydroxyfuranone (**2**) partially exists in its chain tautomeric form **IV** [49], which can undergo acid-catalysed isomerisation to its corresponding *E*-oxo acid **V**. Subsequent esterification and acetalization furnishes the commonly observed (*E*)-alkyl 4-oxobut-2-enoates **4** and their analogue acetal esters **5** [50, 51]. Alternatively, direct pseudo-esterification of hydroxyfuranone (**2**) produces the analogue alkoxy derivatives **3**. Prolonged and extreme heating in the presence of excess alcohol generates the related acetal esters **5**, which subsequently transform into their equivalent *E*-oxo esters **4** [25]. Gassama and co-workers, for example, conducted azeotropic distillations of **2** with long-chain alcohols in two different solvents. Heating in toluene for 72 hours predominantly furnished the *E*-oxo esters **4**, while refluxing in chloroform for 1 hour favoured the generation of the alkoxyfuranones **3** instead [30]. To further minimize the formation of the acetal esters **5**, the respected alcohols for pseudo-esterification are used in equimolar or in slight excess amounts.



Scheme 4. Pseudo-esterification of 5-hydroxyfuranone (**2**) and subsequent pathways.

The pseudo-esterification protocol was furthermore applied to the reaction mixture obtained from solar Entry 18. Its crude product mass contained significant amounts of the desired **2** that could not be isolated by crystallization. Thus, the complete conversion of **2** into ethoxyfuranone **3b** by azeotropic distillation was attempted. The crude reaction mixture (345 g) containing 41% of **2** (approx. 1.4 mol) was dissolved in ethanol (85 ml, 1.48 mol) and 250 ml of chloroform. After addition of *para*-toluenesulfonic acid monohydrate (1.5 g), the solution was refluxed for 12 hours using a Dean-Stark apparatus. Subsequent neutralization, drying and evaporation yielded a refined product mass. ^{1}H-NMR analysis of the crude material confirmed that complete conversion of **2** had indeed occurred. However, besides small amounts of unreacted furfural (**1**) from the solar experiment, the mixture mainly consisted of ethoxyfuranone (**3b**) and its oxo ester **4b** in amounts of 53% and 39%. Hence, the amounts of **3b** and **4b** had increased by 17% and 24%, respectively, through this simple blending process. Careful successive vacuum distillation produced **3b** in a yield of 42% or 75 g and with a purity of 98%. This result clearly shows that further utilization of the waste streams from the photooxygenation process is feasible. However, the selectivity towards alkoxyfuranone (**3**) production remains challenging due to subsequent thermal rearrangement into the corresponding oxo esters **4** and acetal esters **5**. Heat management is thus crucial for both, the photooxygenation and pseudo-esterification process. However, as the open *E*-oxo esters **4** are versatile building blocks themselves [30, 51], exhaustive pseudo-esterification under more extreme conditions may provide a future access to these materials.

3.2.2 Pseudo-Transesterification Reactions

Since long-chain and branched alkoxyfuranones (**3**) represent important fragrance components [20] or starting materials for surfactants [25, 30], the pseudo-transesterification of methoxy or ethoxyfuranone **3a** and **b** represents an interesting pathway to these compounds. Thus far, only isolated examples for the synthesis of a versatile chiral menthoxyfuranone building block through pseudo-transesterification have been reported [22, 47, 48]. These methods utilize heating with equimolar amounts of menthol in the absence or presence of acid. For this study, a modified protocol of the pseudo-esterification described in chapter 3.2.1 was applied to the conversion of ethoxyfuranone (**3b**). Azeotropic distillation of **3b** in chloroform and either *n*-hexanol, cyclohexanol or dodecanol with catalytic amounts of *para*-toluenesulfonic acid monohydrate for 15 hours furnished the corresponding alkoxyfuranones **3f-h** (**Scheme 3b**). Inspection of the crude materials revealed complete conversion of **3b**. However, substantial amounts of the isomeric (*E*)-alkyl 4-oxobut-2-enoates **4f-h** of 25-53% were also noted, probably due to the nonoptimal prolonged heating times. For *n*-hexanol, small amounts of the acetal ester **5f** of 4% were furthermore detected (Entry 23). Purification by flash chromatography subsequently gave the alkoxy derivatives **3f-h** in reduced but moderate yields of 38-63% (**Table 6**) [35]. Thus, pseudo-transesterification from the more readily accessible ethoxyfuranone (**3b**) offers an alternative general access to more complex alkoxy analogues.

Table 6. Experimental parameters and results for pseudo-transesterifications (150 ml of $CHCl_3$, 0.5 g *p*-$TolSO_3H$).

Entry	3b	ROH	Time	Composition of crude product[a]			Yield of 3
	(g/mmol)	(ml/mmol)	(hrs)	3 (%)	4 (%)	5 (%)	(%)[b]
23	11.3/88.2	^{n}HexOH, 12.1/97.1	15	43	53	4	38 (**3f**)
24	10.2/79.6	^{c}HexOH, 9.2/88.2	15	75	25	—	63 (**3g**)
25	25.6/200.2	^{n}DodecOH, 49.4/220.0	15	70	30	—	60 (**3h**)

[a] Determined by ^{1}H-NMR (±2%). [b] After flash chromatography.

4 CONCLUSIONS AND OUTLOOK

The photooxygenation of sugarcane derived furfural (**1**) represents an interesting example for the sustainable manufacturing of important building block chemicals. Irradiations with artificial or natural sunlight furnish the versatile building block chemical hydroxyfuranone (**2**) in yields of 30-52%. The isolation and purification of **2** remained challenging due to rapid thermal follow-up reactions. Nevertheless, demonstration-scale solar reactions produced large multi-gram quantities of pure hydroxyfuranone (**2**). Successive pseudo-esterification of **2** by azeotropic distillation furnished the corresponding alkoxy derivatives **3a,b** and **e** in moderate isolated quantities of 36-62%. Likewise, a crude solar photooxygenation product served as a suitable resource for larger scale pseudo-

esterification to ethoxyfuranone (**3b**). A different approach successfully investigated pseudo-transesterifications of **3b** to the more complex alkoxyfuranones **3f-h** in yields of 38-63%. For all reactions studied, successive ring-openings and acetalizations were observed as dominant and difficult to control side-reactions. Despite this, the photochemical and thermal reactions investigated in this study add to the of growing number of transformations of renewable materials to versatile and valuable commodity chemicals [1-4, 18, 25].

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