Titanium Silicalite 1 (TS-1) Catalyzed Oxidative Transformations of Furan Derivatives with Hydrogen Peroxide

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Abstract: The oxidation of furan derivatives with titanium silicalite 1 (TS-1) and hydrogen peroxide is described. Oxidation products are identified and possible reaction pathways are discussed. It is shown that the oxidation of these compounds occurs *via* epoxidation of one of the furan double bonds. The initially formed epoxides immediately undergo rearrangement, furans yielding unsaturated 1,4-dicarbonyl compounds and furfuryl alcohols yielding 6-hydroxy-2*H*-pyran-3(6*H*)-ones. The latter compounds originate from cyclization of intermediate enedione alcohols. The presented method is particularly useful for the oxidation of 2,5-dimethylfuran to 3-hexene-2,5-dione and the conversion of furfuryl alcohol to 6-hydroxy-2*H*-pyran-3(6*H*)-one, a versatile synthon in organic synthesis.

Keywords: epoxidation; furan; furfuryl alcohol; hydrogen peroxide; titanium; zeolites

Introduction

Carbohydrates and their unsaturated derivatives, i.e., furan, pyran and dihydropyran compounds, are currently of interest as alternative, renewable raw materials for the synthesis of fine chemicals.[1] Since furan compounds are readily available and can be employed in a wide range of transformations, they are useful for the synthesis of many structurally diverse molecules. However, due to their high reactivity, these oxygen heterocycles are susceptible to side reactions such as cleavage and polymerisation. Therefore considerable care has to be taken in the selection of reagents, catalysts and reaction conditions in order to obtain desired products in reasonable yields. As already proven for hydrocarbon-derived molecules, liquid-phase catalytic oxidation might be a useful tool for the selective conversion of furan derivatives. On the other hand, performing the reaction using a heterogeneous catalyst and an inexpensive and environmentally benign oxidant such as hydrogen peroxide (H_2O_2) could lead to an even more attractive process. In this context, the confinement of redox-active metal centres onto the surface of an inorganic support is a recognised route to heterogeneous catalysis for liquid-phase oxidations.[2] A prominent example is the discovery of titanium(IV) silicalite 1 (TS-1).[3] TS-1 catalyses a variety of synthetically useful oxidation reactions under very mild conditions using aqueous H_2O_2 as the oxidant. Well-known applications include olefin epoxidation,[4] alkane[5] and arene[6] hydroxylation, and alcohol oxidation.[7] Its remarkable activity in these reactions is due to site isolation of Ti(IV) centres in the hydrophobic pores of silicalite which allows simultaneous adsorption of the hydrophobic substrate and the oxidant. Although TS-1 has been applied to most oxidisable functional groups, there are several unsaturated ring systems for which its efficacy has yet to be explored. One such system is furan and its derivatives. Since furan is a cyclic, dienic ether stabilised by resonance, different reaction pathways are possible in its oxidation with TS-1/H_2O_2. Hydroxylation of the heteroaromatic furan ring is a reasonable reaction pathway, as TS-1 is known as an efficient catalyst for ring hydroxylation of, e.g., phenol.[6] The primary product of furan hydroxylation would be 2-hydroxyfuran. On the other hand, epoxidation of one of the furan double bonds, similar to monoepoxidation of a conjugated diene such as 1,3-butadiene,[8] would yield an epoxide as the primary product. Furfuryl alcohol, another important furanic compound, may also undergo ring oxidation. On the other hand, oxidation of the hydroxymethyl group and consecutive oxidation of the formed furfural to furoic acid is another possible route. In this respect it is interesting to note that benzyl alcohol, a molecule which can undergo both alcohol oxidation and ring hydroxylation, is selectively converted to benzaldehyde on TS-1.[7a] To distinguish between the different possible reaction modes, a detailed study was undertaken on the oxidation of furan derivatives with TS-1 and H_2O_2.

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Results and Discussion

Oxidation of Furan and Alkyl-Substituted Furans

Oxidation of furan (10 mmol) with TS-1 (0.1 g) and H_2O_2 (15 mmol) in acetonitrile (10 mL) at 20 °C gave quantitative conversion after 5 h reaction. Gas chromatography showed the formation of mainly two products with 80% combined selectivity. According to GC-MS and ^{1}H NMR, these compounds are *cis*-2-butene-1,4-dial (maleic dialdehyde) and the corresponding *trans*-isomer (fumaric dialdehyde). The *cis*/*trans* ratio was 95/5 (Scheme 1, $R^1 = R^2 = H$). Although gas chromatography showed that the main products are the dialdehydes, NMR detected rather small amounts of these compounds. On the other hand, ^{1}H and ^{13}C NMR showed several signals which are characteristic for the hydrates of 2-butene-1,4-dial. The existence of *cis*-2-butene-1,4-dial as its cyclic hydrate (2,5-dihydrofuran-2,5-diol) in aqueous conditions has been well documented.[9] Presumably, during GC analysis the equilibrium between the dialdehydes and the corresponding hydrates is shifted towards the dialdehydes due to the high temperature in the GC injection port. Since NMR analysis more closely reflects the situation in the liquid phase, it is most likely that in solution, the dialdehyde hydrates are the predominant products. Moreover, polymers of these hydrates may be formed by intermolecular condensation.

Mechanistically, it is proposed that the oxidation of furan with TS-1/H_2O_2 proceeds *via* direct epoxidation of one double bond of the furan ring (Scheme 1).[10] An unstable epoxide is formed, which immediately rearranges to *cis*-2-butene-1,4-dial. The epoxide intermediate itself was not observed. Isomerisation of *cis*-2-butene-1,4-dial yields the corresponding *trans*-isomer. A similar mechanism has been proposed for the oxidation of furan and alkyl-substituted furans with other oxidising agents such as peracids[11] and dioxiranes.[12] Since water is present in the TS-1/H_2O_2 system, the initially formed dialdehydes are converted to the corresponding hydrates.

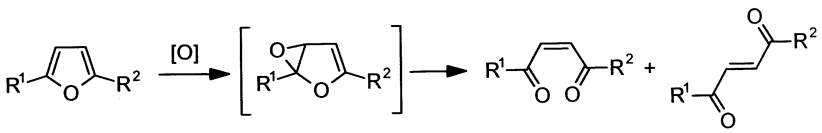
The behaviour of alkyl-substituted furans in the oxidation with TS-1/H_2O_2 confirms the proposed mechanism for furan. Thus, 2-methylfuran and 2,5-dimethylfuran were oxidised to the corresponding unsaturated 1,4-dicarbonyl compounds (Table 1). Standard reactions with *m*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 showed the formation of identical oxidation products from these furans.

2-Methylfuran furnished the unstable unsaturated ketoaldehyde, 4-oxo-2-pentenal (*cis*/*trans* ratio = 97/3), while 2,5-dimethylfuran yielded a mixture of *cis*- and *trans*-3-hexene-2,5-diones (*cis*/*trans* ratio = 68/32). These 3-hexene-2,5-diones are more stable under the reaction conditions, which is in line with the known lower tendency of ketones to form hydrates as compared to aldehydes. Because of their intrinsic instability, the dialdehydes or ketoaldehydes derived from furans cannot be isolated in a pure state. However, they can be used in further transformations by reaction with suitable trapping agents.[12b]

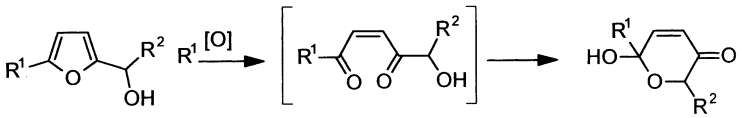
Oxidation of Furfuryl Alcohol and Alkyl-Substituted Furfuryl Alcohols

Oxidation of furfuryl alcohol (10 mmol) with TS-1 (0.1 g) and H_2O_2 (12.5 mmol) in acetonitrile (10 mL) at 20 °C gave quantitative conversion after 24 h reaction. GC-MS and NMR both showed the formation of 6-hydroxy-2*H*-pyran-3(6*H*)-one in 90% yield (Scheme 2, $R^1 = R^2 = H$). Selectivity to furfural or furoic acid was lower than 5%. The formation of 6-hydroxy-2*H*-pyran-3(6*H*)-one can be explained by assuming a similar mechanism as that proposed for the oxidation of furan. Thus, rearrangement of the initially formed epoxide yields an enedione alcohol. This compound undergoes cyclization by intramolecular attack of the hydroxy group on the aldehyde (Scheme 2). A stable cyclic hemiacetal, 6-hydroxy-2*H*-pyran-3(6*H*)-one, is formed.

In acetonitrile, no acyclic enedione alcohol was detected. Increasing the reaction temperature to 40 °C was possible without a decrease in selectivity (Figure 1).

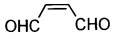
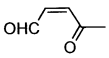
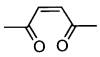


Scheme 1. Oxidation of furans with TS-1/H_2O_2.



Scheme 2. Oxidation of furfuryl alcohols with TS-1/H_2O_2.

Table 1. TS-1 catalyzed oxidation of furans with H_2O_2.[a]

Substrate	Time [h]	Conv.[b] [%]	Product	Select.[c] [%]	*cis*/*trans*
	3	94		77	96/4
	3	93		83	97/3
	3	94		85	68/32

[a] Reaction conditions: substrate (10 mmol), TS-1 (0.1 g), H_2O_2 (35 wt %, 12.5 mmol), CH_3CN (10 mL), 25 °C.
[b] GC analysis on the crude reaction mixture.
[c] Selectivity to unsaturated 1,4-dicarbonyl compounds.

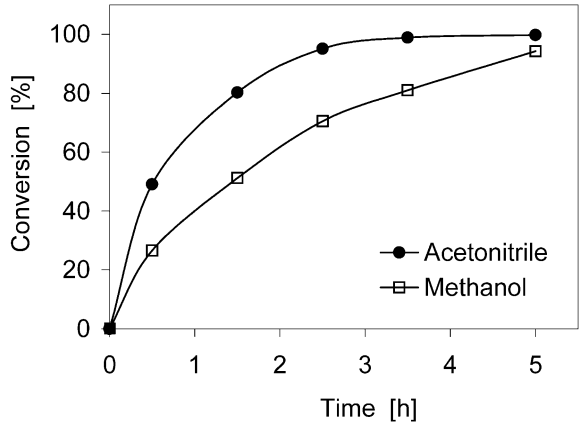
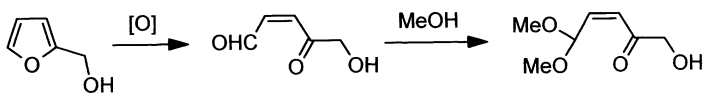


Figure 1. Conversion of furfuryl alcohol as a function of time in acetonitrile and in methanol. Reaction conditions: furfuryl alcohol (10 mmol), TS-1 (0.1 g), H_2O_2 (12.5 mmol), CH_3CN or CH_3OH (10 mL), 40 °C.

In methanol as the solvent, the oxidation of furfuryl alcohol was slower and the selectivity to 6-hydroxy-2*H*-pyran-3(6*H*)-one was lower due to the addition of methanol to the intermediate 5-hydroxy-4-oxo-2-pentenal (Figure 1, Scheme 3). At full conversion (7 h), the selectivity towards the acyclic dimethyl acetal was 20%, while the selectivity to 6-hydroxy-2*H*-pyran-3(6*H*)-one was 65%. Therefore, further reactions were carried out in CH_3CN.

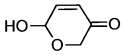
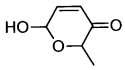
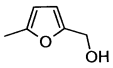
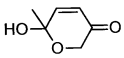
Next, oxidation of 1-(2-furyl)ethanol and 5-methylfurfuryl alcohol was attempted (Table 2). Oxidation of 1-(2-furyl)ethanol afforded 6-hydroxy-2-methyl-2*H*-pyran-3(6*H*)-one as a diastereomeric mixture (*cis*/*trans* ratio = 60/40). Oxidation of 5-methylfurfuryl alcohol proceeded more sluggishly. Selectivity to the cyclic hemiketal 6-hydroxy-6-methyl-2*H*-pyran-3(6*H*)-one was only 20%; the acyclic enedione, 1-hydroxy-3-hexene-2,5-dione, was also present. This is probably due to the higher stability of the diketone intermediate towards intramolecular attack of the hydroxy group on the ketone. Further oxidation of the open-chain enedione lowers the selectivity. In contrast, in the oxidation of furfuryl alcohol and 1-(2-furyl)ethanol, the products are smoothly cyclised to hydroxypyranones.



Scheme 3. Formation of the dimethyl acetal of 5-hydroxy-4-oxo-2-pentenal.

The rate of oxidation of the three studied furfuryl alcohols decreased in the order furfuryl alcohol > 1-(2-furyl)ethanol > 5-methylfurfuryl alcohol. This order (furfuryl alcohol > 5-methylfurfuryl alcohol) disagrees with the one that would be expected for peracids and other electrophilic epoxidising agents; for these, inductive effects of the substituent groups predominate over steric constraints. Therefore, it is apparent that steric effects due to methyl-substitution at the double bond play a major role in the observed trend. Similar behaviour has been observed for the oxidation of butenes with TS-1/H_2O_2.[4d] Although both restricted transition state shape selectivity and hindered diffusion of reagents and products within the zeolite pores may influence the rate of oxidation, the much lower reactivity of 5-methylfurfuryl alcohol compared to that of 1-(2-furyl)ethanol shows that even for molecules with equal access to the zeolite pores, the degree of substitution at the double bond influences the reactivity. Compared to the oxidation of furans, the oxidation of furfuryl alcohols occurred at a much lower rate. This means that the electron-withdrawing effect of the hydroxy moiety is dominant over any other factors in determining the reactivity of the furan double bonds. No rate-enhancing effect of the alcohol in the allylic position, e.g., by coordination to framework Ti species as an alcoholate, was observed. Based on both electronic and steric factors, it is proposed that the epoxidation occurs at the double bond which is not substituted with the hydroxymethyl group. The importance of the electron density at the double bond in determining the reactivity of furan compounds is further illustrated by the oxidation of furfural and furoic acid. In the reaction of furfural with TS-1/H_2O_2 at 40 °C in CH_3CN, small amounts of various oxidation products were observed after 24 h. Total conversion was 40%. Next to ring

Table 2. TS-1 catalyzed oxidation of furfuryl alcohols with H_2O_2.[a]

Substrate	Time [h]	Conv.[b] [%]	Product	Select.[c] [%]
	3.5	99		93
	6.5	93		80[d]
	9.5	79		20

[a] Reaction conditions: substrate (10 mmol), TS-1 (0.1 g), H_2O_2 (35 wt %, 12.5 mmol), CH_3CN (10 mL), 40 °C.
[b] GC analysis on the crude reaction mixture.
[c] Selectivity to cyclic 6-hydroxy-2*H*-pyran-3(6*H*)-ones.
[d] *Cis*/*trans* ratio = 60/40.

oxidation, oxidation of the aldehyde group was an important reaction pathway. Both furoic acid and products derived from a Baeyer–Villiger type oxidation of furfural were observed. Also at higher temperatures or in other solvents, no reasonable yields to one of the products could be obtained. In accordance with the low reactivity of furfural, furoic acid was virtually inert under these conditions. Thus, the reactivity of furan compounds towards TS-1/H_2O_2 decreases in the order furan > furfuryl alcohol > furfural > furoic acid.

The TS-1 catalyst was reused three times in the oxidation of furfuryl alcohol (Figure 2). The activity significantly decreased upon consecutive reuse. This deactivation may be due to the drying treatment of TS-1 which was carried out at 60 °C between each run. Decomposition of the adsorbed products may block the pores and prevent diffusion of reactants and products. However, calcination of the used TS-1 fully restored its catalytic activity.

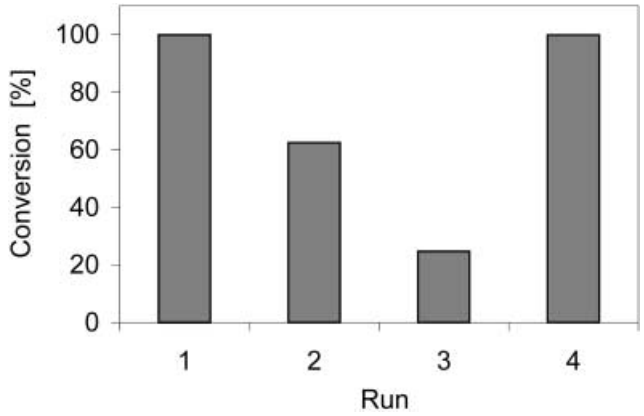


Figure 2. Influence of TS-1 reuse on the catalytic activity in the oxidation of furfuryl alcohol. Reaction conditions: furfuryl alcohol (20 mmol), TS-1 (0.2 g), H_2O_2 (25 mmol), CH_3CN (20 mL), 40 °C, 6 h. The catalyst was centrifuged, washed with CH_3CN (10 mL) and dried at 60 °C overnight. After 3 runs the catalyst was calcined at 550 °C for 10 h.

Using a reduced amount of TS-1, the oxidation of furfuryl alcohol was carried out on a larger scale. The amount of H_2O_2 was lowered to 1.1 equivalents relative to furfuryl alcohol. Furfuryl alcohol (60 mmol), TS-1 (0.15 g) and H_2O_2 (66 mmol) were stirred at 40 °C in CH_3CN (60 mL). After 24 h, GC analysis showed 99% conversion and a selectivity to 6-hydroxy-2*H*-pyran-3(6*H*)-one of 90%. Thus, 400 mmol furfuryl alcohol (40 g) were converted per g TS-1 within 24 h. This experiment illustrates the high productivity and high oxidant efficiency of the TS-1 catalyst for this reaction. In addition it shows that the deactivation of TS-1 observed during the recycle experiment (Figure 2) mainly occurs during the intermediate drying treatment and only to a minor extent during the reaction itself.

The formed 6-hydroxy-2*H*-pyran-3(6*H*)-ones are interesting compounds as they contain an α,β-unsaturated ketone, a hemiacetal, and an allylic alcohol functionality. Owing to their multifunctional nature and the various possibilities for further elaboration with selected nucleophiles and electrophiles, 6-hydroxy-2*H*-pyran-3(6*H*)-ones and the corresponding alkoxy- and acyloxy-derivatives are attractive synthons for the preparation of sugar analogues and numerous compounds showing biological activity.[13] Not surprisingly, a variety of procedures has been reported for their preparation starting from furfuryl alcohols. The three most widely used stoichiometric methods include oxidation with *N*-bromosuccinimide (NBS),[14] peroxy acids[15] and Br_2 in methanol.[16] Only few catalytic procedures are known. For example, $VO(acac)_2$ with *tert*-butyl hydroperoxide[17] and methyltrioxorhenium with ureum hydrogen peroxide[18] as the oxidant have been reported.

However, most of these methods suffer from various drawbacks including tedious work-up, use of expensive reagents or high energy cost, non-scaleability, formation of salt waste or difficult catalyst recyclability. For example, although the NBS and peroxyacid mediated reactions appear to offer simple procedures, it was found that these methods are unreliable and unsuitable for all but very small-scale work.[19] On the other hand, the

bromomethoxylation procedure is highly sensitive to temperature and produces stoichiometric amounts of NaBr. In contrast to the above-mentioned methods, using TS-1 as a heterogeneous catalyst and aqueous H_2O_2 as an inexpensive oxygen source, small-sized furfuryl alcohols are readily converted into 6-hydroxy-2*H*-pyran-3(6*H*)-ones with high yield and high oxidant efficiency. Moreover, the use of other Ti-substituted molecular sieves possessing larger pores such as zeolite Ti-Beta or mesoporous Ti-MCM-41 may allow the oxidation of more bulky furfuryl alcohols.[20]

Conclusion

TS-1 catalyzed oxidation of furans and furfuryl alcohols with H_2O_2 occurs *via* epoxidation of one of the furan double bonds. The initially formed epoxide is unstable and immediately rearranges to unsaturated 1,4-dicarbonyl compounds. Furan and 2-methylfuran are converted to *cis*-2-butene-1,4-dial and *cis*-4-oxo-2-pentenal, respectively. These products undergo further transformations such as isomerisation, hydration and condensation. In contrast, 2,5-dimethylfuran yields an isolable mixture of *cis*- and *trans*-3-hexen-2,5-diones. Furfuryl alcohols undergo a similar oxidation-rearrangement sequence and produce stable 6-hydroxy-2*H*-pyran-3(6*H*)-ones which originate from intramolecular cyclization of enedione alcohol intermediates.

Experimental Section

General

All materials were obtained from commercially available sources and were used without further purification. 5-Methylfurfuryl alcohol was prepared by reduction of 5-methylfurfural with $NaBH_4$ in methanol.[13a] For GC analysis, a Hewlett Packard 5890 gas chromatograph equipped with a 0.32 mm i.d. by 30 m WCOT fused silica column coated with a Chrompack CP-Sil 5 CB stationary phase (1.0 μm d_f) was used. The instrument was equipped with a flame ionisation detector (FID) and coupled to a HP 3396 integrator. Products were identified by comparison of their GC retention times with authentic samples prepared by *m*-CPBA oxidation.[11,15] Additionally, GC-MS and NMR were used to confirm the identity of the products. A Fisons GC 8000 Series gas chromatograph equipped with a 0.32 mm i.d. by 60 m WCOT fused silica column coated with a Varian CP-Sil 5 CB Low bleed/MS stationary phase (0.25 μm d_f) was coupled to a Fisons MD 800 mass spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz and 75 MHz, respectively. Reactions for product identification by NMR were run in CD_3CN as the solvent.

Preparation of TS-1

TS-1 (Si:Ti ratio = 35:1) was prepared according to a literature procedure with a molar chemical composition of 1.0 SiO_2:0.028 TiO_2:0.33 TPAOH:35 H_2O.[3] Chemicals used for the synthesis were tetraethyl orthosilicate (Acros, 98%), tetrabutyl orthotitanate (Merck, 98%), and tetrapropylammonium hydroxide (TPAOH, Alfa Aesar, 40 wt %). Crystallization of the gel was conducted in stainless-steel autoclaves at 175 °C for three days. The resulting material was washed, dried and finally calcined at 550 °C for 10 h. The powder XRD patterns (Siemens D5000 matic diffractometer) of the calcined TS-1 samples matched those of published MFI data.[3]

General Procedure for the Oxidation of Furfuryl Alcohol

A 20-mL flask was charged with acetonitrile (10 mL), furfuryl alcohol (10 mmol), TS-1 (0.1 g), and H_2O_2 (35 wt %, 12.5 mmol). The mixture was stirred at 20 °C and the reaction was followed by GC analysis of the crude reaction mixture.

Spectral Data of Products Obtained by TS-1/H_2O_2 Oxidation of Furan Compounds

Oxidation of furan: *cis*-2-butene-1,4-dial: ^{1}H NMR (300 MHz, CD_3CN): δ = 10.45 (dd, $J_{1,2}$ = 4.4 Hz, $J_{1,3}$ = 2.5 Hz, 2H, CHO), 6.66 (dd, $J_{2,1}$ = 4.4 Hz, $J_{2,4}$ = 2.5 Hz, 2H, CH=CH); MS (EI): *m/z* = 84 (M^+), 56, 55, 29. ***trans*-2-butene-1,4-dial:** ^{1}H NMR (300 MHz, CD_3CN): δ 9 = 0.86 (dd, $J_{1,2}$ = 4.4 Hz, $J_{1,3}$ = 2.9 Hz, 2H, CHO), 6.89 (dd, $J_{2,1}$ = 4.4 Hz, $J_{2,4}$ = 2.9 Hz, 2H, CH=CH); MS (EI): *m/z* = 84 (M^+), 56, 55, 29.

Oxidation of 2-methylfuran: *cis*-4-oxo-2-pentenal: ^{1}H NMR (300 MHz, CD_3CN): δ = 10.03 (d, $J_{1,2}$ = 6.9 Hz, 1H, CHO), 7.10 (d, $J_{3,2}$ = 11.7 Hz, 1H, H3), 6.15 (dd, $J_{2,3}$ = 11.7 Hz, $J_{2,1}$ = 6.9 Hz, 1H, H2), 2.33 (s, 3H, H5); MS (EI): *m/z* = 98 (M^+), 83, 70, 69, 55, 43, 29.

Oxidation of furfuryl alcohol: 6-hydroxy-2*H*-pyran-3(6*H*)-one: ^{1}H NMR (300 MHz, CD_3CN): δ = 6.98 (dd, $J_{5,4}$ = 10.3 Hz, $J_{5,6}$ = 2.9 Hz, 1H, H5), 6.17 (d, $J_{4,5}$ = 10.3 Hz, 1H, H4), 5.64 (s, 1H, H6), 4.57 (d, $J_{2a,2e}$ = 16.8 Hz, 1H, H2), 4.14 (d, $J_{2a,2e}$ = 16.8 Hz, 1H, H2), 4.06 (br s, 1H, OH); MS (EI): *m/z* = 114 (M^+), 97, 84, 69, 56, 55, 42, 39, 29.

Oxidation of 1-(2-furyl)ethanol: 6-hydroxy-2-methyl-2*H*-pyran-3(6*H*)-one: ^{1}H NMR (300 MHz, CD_3CN): *cis* isomer: δ = 6.97 (d, $J_{5,4}$ = 10.3 Hz, 1H, H5), 6.00 (d, $J_{4,5}$ = 10.3 Hz, 1H, H4), 5.50 (s, 1H, H6), 4.64 (q, $J_{2,7}$ = 6.6 Hz, 1H, H2), 2.8 (br, OH), 1.28 (d, $J_{7,2}$ = 6.6 Hz, 3H, H7), *trans* isomer: δ = 6.96 (d, $J_{5,4}$ = 10.3 Hz, 1H, H5), 6.06 (dd, $J_{4,5}$ = 10.3 Hz, $J_{4,2}$ = 1.5 Hz, 1H, H4), 5.59 (s, 1H, H6), 4.22 (qd, $J_{2,7}$ = 6.6 Hz, $J_{2,4}$ = 1.5 Hz, 1H, H2), 2.8 (br, OH), 1.32 (d, $J_{7,2}$ = 6.6 Hz, 3H, H7); MS (EI): *m/z* = 128 (M^+), 111, 99, 84, 56, 55, 43, 29.

Preparation of Reference Compounds

Oxidation of furan compounds with *m*-CPBA[11,15]: Furan and its derivatives (1 mmol) were added to a solution of *m*-CPBA (0.5 or 1 mmol) in CH_2Cl_2 (1 mL) at 0 °C. After reaction, precipitated *m*-chlorobenzoic acid was removed and the sample was subjected to GC and GC-MS analysis.

Photooxygenation of furfural[21]: Practical-grade furfural (10 mmol) and a few milligrams of methylene blue as sensitiser were dissolved in methanol (5 mL). The reaction vessel was cooled to 0 °C with a cryostatic bath and was externally irradiated with two 150 W lamps while a gentle stream of oxygen was passed through the reaction mixture. The reaction was followed by GC until complete consumption of furfural. After evaporation of the solvent under reduced pressure at 30 °C, 5-hydroxy-2(5*H*)-furanone was obtained. ^{1}H NMR (300 MHz, CD_3CN): $\delta = 7.33$ (dd, $J_{4,3} = 5.9$ Hz, $J_{4,5} = 1.1$ Hz, 1H, H4), 6.19 (d, $J_{3,4} = 5.9$ Hz, 1H, H3), 6.15 (s, 1H, H_5), 5.50 (br s, 1H, OH); ^{13}C NMR (75 MHz, CD_3CN): $\delta = 171.8$, 153.6, 124.4, 99.3; MS (EI): $m/z = 100$, 99, 83, 82, 72, 71, 55, 54, 45, 44, 37, 29.

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