

Photo-Oxidation of 2-(2-Furyl)-1,3-Dicarbonyl Compounds

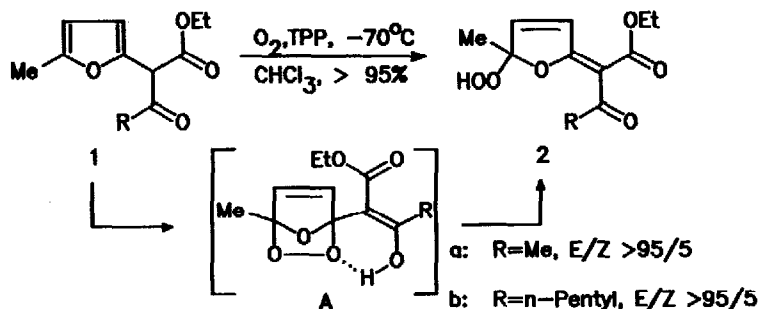
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Abstract: A very efficient photo-sensitized oxidation of 2-(2-furyl)-1,3-dicarbonyl compounds **1** afford directly hydroperoxides **2** in stereoselective way. Compounds **2**, easily isolated, can be conveniently employed in a selective epoxidation of trisubstituted allylic alcohols by a Sharpless-type procedure.

Photo-oxidation of furan derivatives has been widely investigated in these last years: in particular furan endoperoxides, deriving from a 4 + 2 cycloaddition, proved to be usually the primary products of photo-oxidation with $^1\text{O}_2$ and their following decomposition, strongly depending upon both the substituents and the solvents, involved a diversity of mechanistic pathways.^{1,2}

Investigations on the reactivity of 2-(2-furyl)-1,3-dicarbonyl compounds³ have pointed out an unusual photochemical behaviour of furan derivatives **1**. In fact, photo-oxidation of **1**, performed with a 300 W street lamp in CHCl_3 solution at -70°C in the presence of tetraphenylporphine (TPP) as sensitizer, lead directly to hydroperoxides **2**.



The careful removal of the solvent under a reduced pressure at room temperature allowed the isolation of **2**, contaminated with negligible amounts of TPP, in almost quantitative yields. The conversion **1** \longrightarrow **2** showed to proceed with high stereoselectivity affording stereoisomers E as far predominant products. Stereochemical assignment was achieved by nuclear Overhauser enhancement experiment on compound **2a**: in fact saturation of proton in 4-position of the furan nucleus resulted in a strong enhancement (7%) of the signal relative to methylene protons of $-\text{OCH}_2\text{CH}_3$ group.

The formation of hydroperoxides **2** with high degree of stereoselectivity could be explained through a mechanistic pathway involving endoperoxides **A** as usual primary products of photo-addition, and their following conversion to the final products through a retro-Michael addition, catalyzed intramolecularly by the enolic $-\text{OH}$.

It has to be noted that the formation of hydroperoxides usually required photo-oxidation of furan derivatives in alcoholic solutions or addition of alcohols to endoperoxides.⁴

Compounds **2** proved to be of synthetic value since they have been conveniently employed, in substitution of *t*-butyl hydroperoxide, in a modified Sharpless procedure for the selective epoxidation of trisubstituted allylic alcohols.

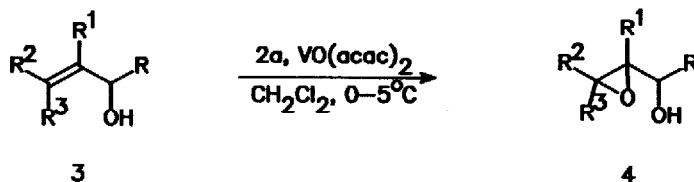


Table: Selective Vanadium-Catalyzed Epoxidation of Trisubstituted Allylic Alcohols.^a

Entry	R	R ¹	R ²	R ³	Yield (%) ^{b,c}
a	H	H	(CH ₂) ₂ CH=C(CH ₃) ₂	Me	50
b	Me	H	Me	Me	47 (19/81)
c	<i>n</i> -Bu	H	Me	Me	80 (6/94)
d	<i>n</i> -Bu	Me	Me	H	72 (82/18)
e	<i>n</i> -Bu	Me	Et	H	64 (88/12)
f	H	H	<i>n</i> -Pr	H	12

- a) All the reactions have been performed in anhydrous CH₂Cl₂ solution at 0-5 °C with 1.3% catalyst and 1.2 equivalent of hydroperoxide **2a** and were carried out to >80% completion with the exception of entry f.
- b) All the yields refer to isolated, chromatographically pure compounds whose structures have been confirmed by ¹H-NMR data (200 and 300 MHz) or by comparison with authentic samples.
- c) Values in parentheses refer to erythro/threo diastereoisomeric ratios, determined by ¹H-NMR analysis (entries b and c) or by the relative amounts of isolated isomers (entries d and e).

In fact, compounds **3**, submitted to the treatment with **2a**, chosen as representative hydroperoxide, in the presence of vanadyl acetylacetonate, VO(acac)₂, in CH₂Cl₂ solution at 0-5 °C, were converted into the corresponding epoxyalcohols **4** in satisfactory yields and with high regio- (entry a) and diastereoselectivity (entries b-e). On the contrary, the above procedure proved to be almost completely unsuccessful in the case of disubstituted allylic alcohols (entry f): the resulting selectivity was found to depend both on the very low reactivity of disubstituted allylic alcohols under the usual experimental conditions and the occurrence of a competitive process of extensive decomposition of hydroperoxide **2a**, induced by the transition metal catalyst.

General procedure: a solution of **1** (1.2 mmol) in CHCl₃ (60 ml) was submitted to photo-oxidation with a 300W street lamp at -70 °C in the presence of TPP (2.8 × 10⁻² mmol) for 2 h under a low stream of O₂. The reaction was monitored by TLC. Then the solvent was evaporated under a reduced pressure (20 mmHg) at 20 °C to afford E-2 in >95% yield (on the ground of ¹H-NMR data). The following epoxidation was performed according to the procedure reported by Sharpless.⁵

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