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Acid-Catalyzed Oxidation Of Furan Derivatives By t-Butyl Hydroperoxide

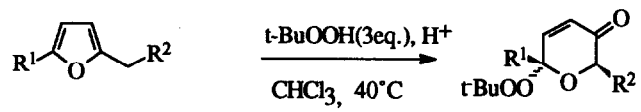
Roberto Antonioletti, Luca Arista, Francesco Bonadies, Ludovica Locati, Arrigo Scettri*

Centro CNR di Studio per la Chimica delle Sostanze Organiche Naturali, Dipartimento di Chimica, Università "La Sapienza", p.le Aldo Moro 5, 00185 Roma, Italy

Abstract: the unusual reactivity of t-butyl hydroperoxide under acid-catalysis allows the easy conversion of furan derivatives into 3(6H)-pyranones.

t-Butyl hydroperoxide (t-BuOOH) is a reagent employed in a great variety of oxidative processes, which, because of its unreactivity towards most organic compounds, usually require metal catalysis (V^{+5}, Mo^{+6}, Ti^{+4}, etc.).[1]

In the course of recent investigations devoted to the achievement of new oxidative procedures involving non-conventional catalysis[2], we have found that t-BuOOH exhibits unusual properties as mild oxidant of furan derivatives in mildly acidic medium. In fact, furans 1 submitted to treatment with an excess of t-BuOOH (3eq.) in chloroform solution at 40°C in the presence of a catalytic amount of camphorsulphonic acid (10%), are smoothly converted into 3(6H)-pyranones 2.(Table 1).



1 2

Table 1 - Oxidation of 2,5-dialkylfurans by t-BuOOH

Entry	R^1	R^2	Reac.Time	Yield[a),b)]
1	Me	n-C_4H_9	24h	50%
2	Me	n-C_7H_{15}	23h	48%
3	Me	n-C_9H_{19}	23h	71%

a) The reported yields refer to isolated, chromatographically pure compounds.

b) All the structures have been confirmed by IR and ^{1}H-NMR data. All new compounds have given satisfactory elemental analysis.

The formation of 2 takes place with high stereoselectivity, as shown by the isolation of pyranones characterized by a cis relationship of R^1 and R^2 substituents.

The mechanistic aspects of the unusual conversion 1---> 2 have not yet been investigated: however, it seemed conceivable that it could involve 2-furyl alcohols, as intermediates: as known, the typical procedure for the synthesis of 3(6H)-pyranones is based on the oxidation of compounds of type 3 with a variety of reagents such as pyridinium chlorochromate,[3] m-chloroperbenzoic acid[4] etc.

In fact, submitted to the usual treatment at room temperature, compounds 3 are changed into the expected products 2.

Scheme 1

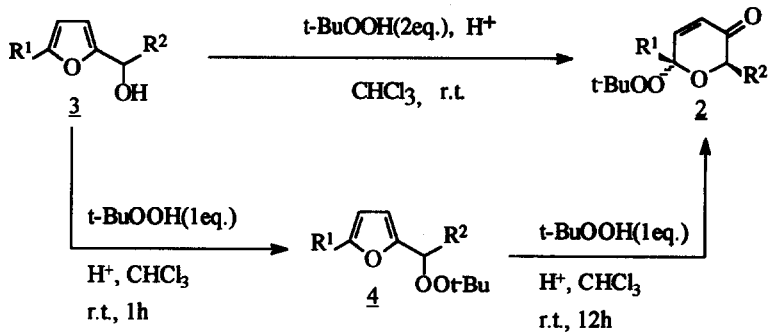


Table 2 - Oxidation of 2-furyl alcohols 3 to 3(6H)-pyranones 2 by t-BuOOH

Entry	R^1	R^2	Yield[a)b)]	
1	H	n-C_4H_9	13%	(>95/5)[c),d)]
2	Me	n-C_4H_9	67%	(85/15)[c)]
3	Me	n-C_8H_{17}	76%	(89/11)[c)]
4	Me	n-$C_{10}H_{21}$	69%	(90/10)[c)]
5	Et	n-C_4H_9	57%	(90/10)[c)]

a) The reported yields refer to isolated, chromatographically pure compounds.

b) All the structures have been confirmed by IR and ^{1}H-NMR data. All new compounds have given satisfactory elemental analysis.

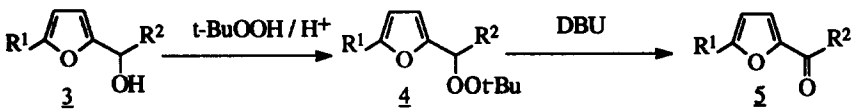
c) Values in parentheses refer to trans/cis ratio.

d) A significative process of decomposition occurs in the course of the purification by silica gel column chromatography.

It has to be noted that under suitable conditions, t-BuOOH(1eq) for 1h, the intermediate mixed peroxides 4 can be obtained with high efficency and their appreciable stability allows their easy isolation and purification by routinary procedures (Scheme 1).

The ready availability of peroxides 4 has allowed the achievement of a new methodology for the synthesis of 2-furyl ketones, not so easily accessible through the routes at present employed.[5]

In fact compound 4, submitted to treatment with a strong excess of 1,8-diazabicyclo-(5,4,0)undec-7-ene (DBU) at room temperature for 3 hrs, affords the corresponding ketone 5 with satisfactory yields (Table 3).



3 4 5

Table 3 - Conversion of 2-furyl alcohols 3 into 2-furyl ketones 5.[a)]

Entry	R^1	R^2	Yield 4 [b)]	Yield 5 [b)]
1	H	n-C_4H_9	80%	58%
2	H	n-C_8H_{17}	91%	74%
3	Me	n-C_4H_9	87%	45%
4	Me	n-C_8H_{17}	73%	59%
5	Me	n-$C_{10}H_{21}$	-[c)]	52%
6	Et	n-C_4H_9	-[c)]	61%

[a)] Compounds 4 (5 mmoles), without any previous purification, are treated with DBU (5eq.) till disappearance of starting materials. After the usual work-up crude 5 are purified by column chromatography on silica gel.

[b)] All the yields refer to isolated, chromatographically pure compounds and are calculated on starting materials 3. All the structures have been confirmed by IR and ^{1}H-NMR data and by comparison with authentic samples.

[c)] In these cases compounds 4 have been used without any previous purification.

Experimental: In a typical procedure furan derivatives 1 (or 3) (1 mmole), t-BuOOH [3 eq. (3M isoctane solution) (or 2 eq. for 3)], Camphorsulphonic acid (10% mol.) in $CHCl_3$ solution are stirred at 40°C (or at room temperature for 3). The reaction is monitored by TLC and interrupted by addition of $Na_2S_2O_3$ (0.1 M solution, 3eq. or 2 eq. for 3) . After the usual work-up, the crude products 2 are purified by column chromatography on silica gel by elution with n-hexane/diethyl ether mixtures.

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