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PYRIDINIUM CHLOROCHROMATE IN THE ORGANIC SYNTHESIS: A CONVENIENT OXIDATION OF 5-BROMO-2-FURAN-DERIVATIVES TO γ-HYDROXY BUTENOLIDES^

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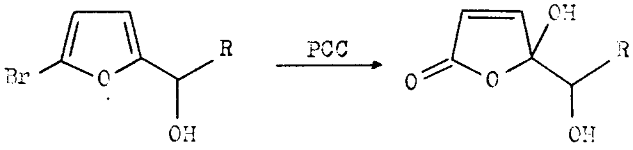
Abstract: γ-hydroxy butenolides 2 are directly obtained by oxidation of 5-bromo-2-furan-derivatives under mild and simple conditions.

Pyridinium chlorochromate (PCC), a stable reagent originally introduced for the oxidation of alcoholic functions, is now widespreadly used in organic synthesis[1]: in particular, we have pointed out the reactivity of PCC, as weakly electrophilic species, towards activated olefins, and some original applications for enol-ethers and 2-furylcarbinols have been reported[2].

We wish now to describe a novel synthetic use of PCC, that, behaving as dienophile and oxidant, is able to convert 5-bromo-2-furan-derivatives 1 into γ-hydroxy butenolides 2 with high yields. Compounds of type 2 are useful intermediates in synthesis[3] and, furthermore, many natural substances presenting the butenolide system as major structural feature[4] show varied physiological properties[5].



1 2

a: R = n-pentyl
b: R = cyclohexyl
c: R = n-decyl

In a typical experiment, the furan derivative[6] 1 (2 mmol in 5 ml of CH$_2$Cl$_2$) was rapidly added at room temperature to a suspension of PCC (4 mmol) in CH$_2$Cl$_2$ (5 ml). After 90 minutes the reaction, which was followed by tlc,

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^ Dedicated to Professor Luigi Panizzi on the occasion of his 70th birthday.

was complete and the isolated crude product was purified by column chromatography on SiO_2[2]. Elution with benzene-diethyl ether afforded the pure butenolides in excellent yields (60-75%). The spectroscopic data (I.R., ^{1}H-N.M.R., and M.S.) were completely in agreement with the proposed structures 2. For ex., 2a, I.R. (film, ν_{max} cm^{-1}): 3430, 3100, 1805, 1775[7], 1600; ^{1}H-N.M.R. (CCl_4, δ): 7.42 (d, 1 H, J = 6 Hz), 6.13 (d, 1 H, J = 6 Hz), 3.90 (t, 1 H, CH-OH), 2.20 (m, secondary -OH), and 1.58 (m, tertiary -OH). M.S. (m/e): M^+ = 200.

This conversion points out an unusual regiospecific reactivity of PCC, since only the oxidation of the furan ring occurs in spite of the presence of a secondary alcoholic function.

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References and remarks

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