A Facile One-Step Conversion of Chalcones *into* 2,3-Dihydroflavonols

Shabnam Saxena, J.K. Makrandi, S.K. Grover*

Department of Chemistry, University of Delhi, Delhi-110007, India

The preparative conversion of chalcones into 2,3-dihydroflavonols (10–30% yield) has been accomplished via 2'-alkoxychalcone epoxides[1–4]. For the success of this method it is essential to protect the 2'-hydroxy group of the chalcone prior to epoxidation; otherwise alkaline hydrogen peroxide treatment results in an Algar-Flynn-Oyamada reaction yielding flavonols. Although 2,3-dihydroflavonols have been reported to be formed in poor yields during the Algar-Flynn-Oyamada reaction of 2'-hydroxychalcones in buffered medium[5] in the presence of sodium tungstate or Triton B[6], this reaction normally results in the formation of flavonols or aurones depending upon the temperature and substitution pattern of the chalcones[7,8]. The preparation of 2,3-dihydroflavonols from chalcones in 25–28% yields has been achieved by treatment of chalcone dibromides[9,11] with base.

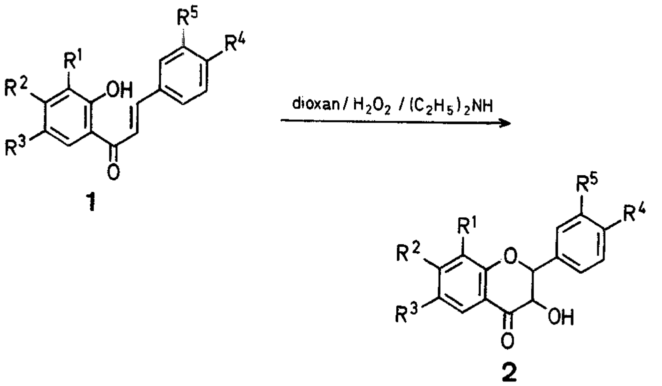
We present here a facile one-step conversion of 2'-hydroxychalcones (**1**) into 2,3-dihydroflavonols (**2**). The appropriate chalcone **1** in dioxan solution is treated with hydrogen peroxide (30%) and diethylamine and the mixture left in the refrigerator. The reaction is monitored by T.L.C. After the starting chalcone has been completely consumed (3–48 h), dilution with water gives the target compounds **2** in 38–63% yields. The ^{1}H-N.M.R. spectra of compounds **2** thus obtained were in agreement with expectation.

It is necessary to keep the reaction temperature below 5 °C in order to avoid the formation of mixtures of products which are difficult to separate. Dioxan proved to be the most suitable solvent for the conversion **1** → **2**; the use of methanol, ethanol, or acetone leads to the formation of product mixtures. Of the bases investigated, diethylamine was found to be

Table. 2,3-Dihydroflavonols (**2**) prepared

2	R^1	R^2	R^3	R^4	R^5	Reaction Time [h]	Yield [%]	m.p. [°C]	m.p. [°C] reported or Molecular Formula
a	H	H	H	H	H	40	38	178°	178–180°[1]
b	H	OCH_3	H	H	H	3	57	150°	142–144°[4]
c	H	H	H	OCH_3	H	36	47	168°	168°[10]
d	H	OCH_3	H	OCH_3	H	20	47	130–131°	130–131°[6]
e	H	H	OCH_3	OCH_3	H	46	38	160–162°	$C_{17}H_{16}O_5$ (300.3)[a]
f	OCH_3	OCH_3	H	OCH_3	H	48	57	172°	172°[11]
g	OCH_3	OCH_3	H	OCH_3	OCH_3	48	63	166°	166°[9]

[a] calc. C 68.00 H 5.39
found 68.10 5.50
^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 3.75$ (s, 6H, 2OCH_3); 4.50 (d, 1H, $J = 14$ Hz, 3-H); 4.95 (d, 1H, $J = 14$ Hz, 2-H); 6.80 (d, 2H, $J = 10$ Hz, 3'-H + 5'-H); 6.79–6.89 (m, 2H, 7-H + 8-H); 7.30 (d, 2H, $J = 10$ Hz, 2'-H + 6'-H); 7.35 ppm (s, 1H, 5-H).



the most efficient one; the use of piperidine, pyrrolidine, morpholine, or triethylamine resulted in prolonged reaction times and lower yields of products **2**.

2,3-Dihydroflavonols (2,3-Hydroxy-2-aryl-4-chromanones); General Procedure:

A 30% hydrogen peroxide solution (5 ml) is added dropwise to a stirred solution of the 2'-hydroxychalcone (**1**; 0.4 mmol) in dioxan (6 ml) containing diethylamine (147 mg, ~ 2.0 mmol) over a period of 20 min. The mixture is then left in the refrigerator until the starting chalcone has completely reacted (T.L.C.). Addition of ice-cold water (20 ml) and saturation of the resultant mixture with magnesium sulfate gives a solid which is filtered and washed with cold water (2 x 5 ml). The dried compound is crystallized from benzene/light petroleum to give the pure product **2**.

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* Address for correspondence.

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