

Dimethylsulfoxide–iodine catalysed deprotection of 2'-allyloxychalcones: synthesis of flavones

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Received 2 October 2004; revised 20 November 2004; accepted 8 December 2004

Available online 22 January 2005

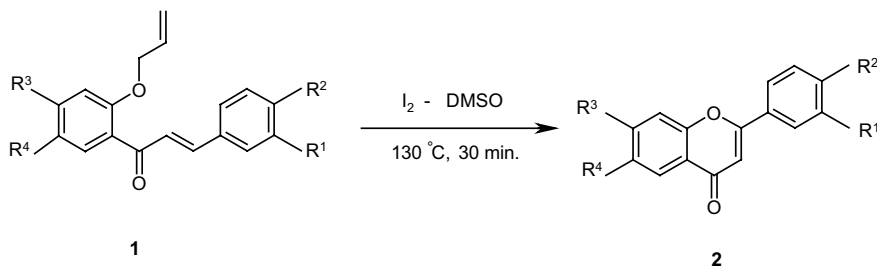
Abstract—A new one-pot method is described for the removal of *O*-allyl protecting groups under oxidative conditions at neutral pH. 2'-Allyloxychalcones undergo deprotection and subsequent oxidative cyclisation to give flavones. The general applicability of the reagent has been studied.

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The DMSO–I₂ reagent has been used in the oxidative cyclisation of 2'-hydroxychalcones to flavones¹ and the oxidation of pyrazolines to pyrazoles,² isoxazolines to isoxazoles³ and flavanones to flavones.⁴ A comparison of the reported methods showed the DMSO–I₂ reagent to be particularly useful in the synthesis of flavones from 2'-hydroxychalcones. Under these conditions the reaction temperature is fairly high and the iodine does not cause any side reactions. Naturally occurring flavonoids contain free phenolic–OH groups or methoxy groups as substituents. Therefore, the protection of phenolic groups is an important step in the synthesis of chalcones,^{5a} flavanones,^{5b} and flavones.⁶ The allyl-protecting group has been shown to be useful for the protection of phenolic functions⁷ due to its ready availability and stability under acidic and basic conditions.⁸ Several methods have been developed for the removal

of allyl groups under different conditions; these include DDQ,⁹ NaBH₄/I₂,¹⁰ NBS/hν,¹¹ (TBA)₂S₂O₈,¹² OsO₄, NMO/NaIO₄,¹³ Pd(PPh₃)₄/NaBH₄¹⁴ and Me₃SiCl/NaI.¹⁵ These systems, however, have several drawbacks such as the instability of the reagent, nasty smells, long reaction times, high cost of the reagent¹⁶ and competitive side reactions.¹⁷ The ready availability as well as the ease of handling of the DMSO–I₂ reagent provides a particular advantage of the present system.

We herein report an efficient procedure for the cleavage of 2'-allyloxychalcones containing benzyl and methoxy protection using the DMSO–I₂ reagent (**Scheme 1**). Cleavage reactions using a stoichiometric amount of I₂ gave excellent yields (85–98%) of flavones within 30 min. 2'-Hydroxychalcones were not isolated from the reaction. The results obtained are summarised in **Table 1**.



Scheme 1.

Keywords: Allylchalcones; Deprotection; Flavones.

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Table 1.

Entry	R ¹	R ²	R ³	R ⁴	Yield of 2 (%)
a	H	H	H	CH ₃	86
b	H	OCH ₃	H	CH ₃	89
c	OCH ₃	OCH ₃	H	CH ₃	92
d	H	OCH ₃	H	Cl	85
e	OCH ₃	OCH ₃	H	Cl	97
f	H	H	H	Cl	92
g	NO ₂	H	H	Cl	90
h	H	OCH ₃	OCH ₂ Ph	H	87
i	OCH ₃	OCH ₃	OCH ₂ Ph	H	93
j	H	H	OCH ₂ Ph	H	88
k	NO ₂	H	OCH ₂ Ph	H	85

The typical experimental procedure is as follows:

To a solution of compound **1a** (248 mg, 1 mmol) in DMSO (5 mL) was added I₂ (254 mg, 1 mmol) and the reaction mixture was heated in an oil bath at 130 °C for 30 min. After cooling, the reaction mixture was diluted with water and the iodine was removed by washing with a saturated solution of sodium thiosulfate. The product **2a** was then extracted with ethyl acetate and purified by column chromatography (hexane/ethyl acetate, 9:1)

The present work provides an efficient deallylation procedure, which uses a weak oxidising agent under neutral conditions. The mild conditions, compatibility with other functional groups and easy handling of the reagent constitute advantages of the present procedure. It may provide a new entry into the synthesis of naturally occurring flavonoids.

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