

Zinc-induced reduction of ethyl 2-cyano-3-(4-oxo-4H-1-benzopyran-3-yl)propanoates – a medium-dependent reaction

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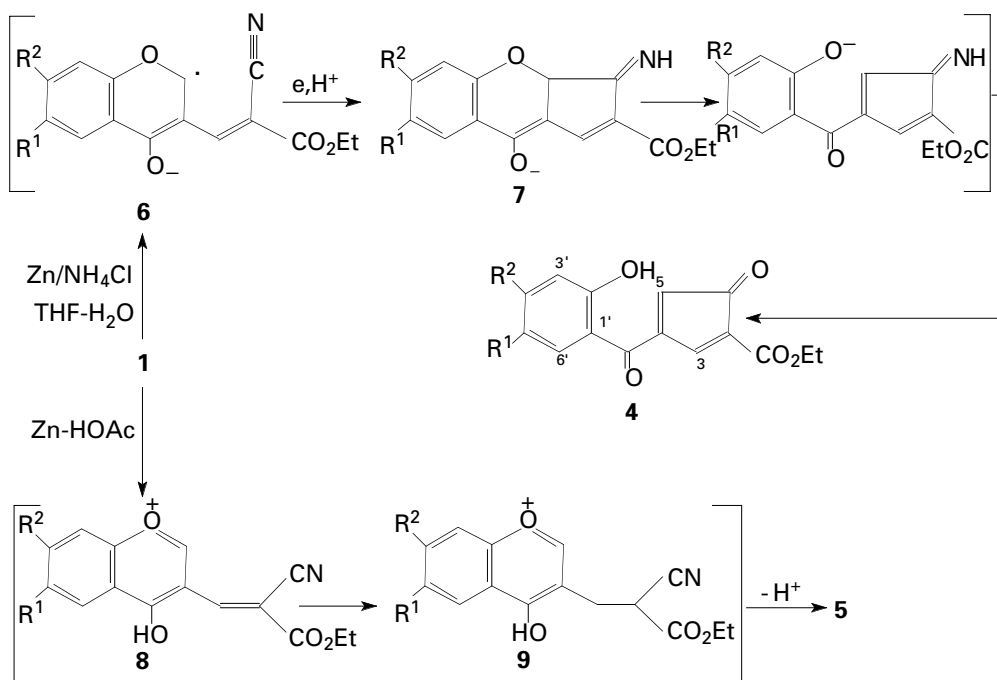
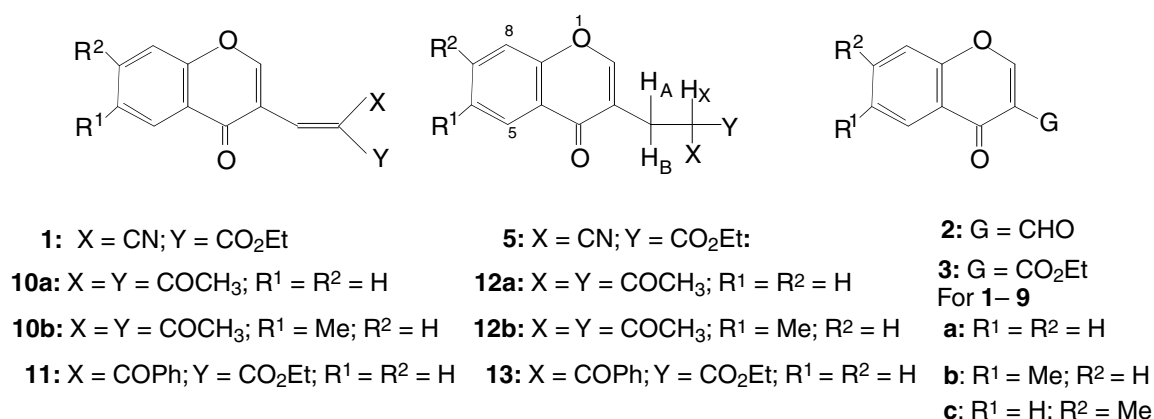
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Reduction of acrylates **1** with Zn in THF containing aqueous NH₄Cl produces the cyclopentadienones **4**, whereas with Zn in acetic acid reduction produces the cyanopropanoates **5**.

Keywords: zinc reduction, ethyl 2-cyano-3-(4-oxo-4H-1-benzopyran-3-yl)propanoate

Reductive self-coupling of alkylidene cyanoacetates with Sm² or Zn³ in the presence of aqueous NH₄Cl in THF has been reported to produce aminocyclopentenones. Alkylidene malononitrile also produces the same type of compound when reduced with Sm,² Zn/NH₄Cl⁴ or Cp₂VCl₂/Zn/TMSCl.⁵ Ketone-nitrile

reductive coupling was achieved using LVT (TiCl₄/Sm)⁶ or SmI₂.⁷ Partial reduction of an α,β : γ,δ – unsaturated amide by Zn/HOAc produces the β,γ-unsaturated amide.⁸ Chemoselective reduction of N-acyl-2,3-dihydropyridones to N-acyl-4-piperidones by Zn/HOAc has been reported



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recently.⁹ In continuation of our studies on the reductive self-coupling of 3-functionalised 4-oxo-4H-1-benzopyrans **2**¹⁰ and **3**,¹¹ we report herein two chemoselective reductions of alkylidene cyanoacetate **1** with Zn under different conditions.

Sodium naphthalenide-induced reduction of **1a-c** produces complex mixtures, from which the cyclopentadienones **4** were isolated in 5% yield. Reaction of **1a-c** with Zn in the presence of aqueous NH₄Cl in THF at room temperature produces **4a-c** as major products (21-37%) along with **5a-c** (4-10%). To the best of our knowledge, this is the first report of the formation of a cyclopentadienone derivative instead of an aminocyclopentene derivative from an alkylidene cyanoacetate. However, in the absence of aqueous NH₄Cl, **1a-c** fail to react with Zn in THF even after stirring for 10 h at room temperature. In order to consider the requirement of a protic solvent in the above reaction, an ethanolic solution of **1a** was heated under reflux for 5 h with an excess amount (4 equivalent) of Zn powder. The reaction mixture produced the aldehyde **2a** (30%) along with cyclopentadienone **4a** (10%). But a regioselective reduction of the exocyclic alkenic bond of **1a-c** was achieved with Zn in glacial acetic acid to furnish **5a-c** in moderate to good yields. However, reduction of ethyl 2-cyano-5-phenyl-2,4-pentadienoate either with Zn/HOAc, or with Zn/NH₄Cl/THF produces a complex mixture, from which no pure compound was isolated.

All these observations are rationalised as follows: in the presence of aqueous NH₄Cl initial single electron transfer takes place preferably to the most electron deficient centre C-2 of the pyrone ring in acrylate **1** to form the radical anion **6** (Scheme 1). Radical cyclisation involving the nitrile function in **6** and reduction produce **7**. In this context, the ketone-nitrile reductive coupling reaction can be envisaged where initial electron transfer takes place to the carbonyl function, then the resultant radical anion couples with the nitrile function.^{6,7} Compound **4** was obtained from **7** by pyran ring opening and subsequent hydrolysis. But in the presence of acetic acid, the pyrone ring of **1** is supposed to be stabilised by forming the pyrylium ion **8** and reduction takes place on the exocyclic activated double bond to produce **5** via **9**. It may be presumed that in the case of NH₄Cl, electron transfer initially occurs followed by protonation whereas with acetic acid transfer of electron occurs after initial protonation. For generalization, a few other condensates **10a,b** and **11** were prepared

according to the literature procedure¹² and were subjected to reduction by Zn/HOAc to produce **12a,b** and **13**, respectively in good yields.

In conclusion, $\alpha,\beta:\gamma,\delta$ -unsaturated cyanoester **1** undergoes regioselective reduction of the double bond at the α,β - position by Zn in acetic acid when the double bond at γ,δ - position is a part of the chromone moiety, but reductive cyclisation of **1** with Zn in THF containing aqueous NH₄Cl produces salicyloylcyclopentadienone **4**. Thus, two chemoselective reduction procedures of the title compound **1** are achieved.

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Techniques used : ¹H NMR, IR, chromatography, elemental analysis

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Scheme : 1

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