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Reductive Self Coupling of 4-Oxo-4*H*-1-benzopyran-3-carboxaldehyde

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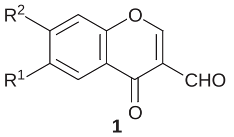
The title aldehyde **1** gives the bischromones **2**, **3** and disalicyloylbenzene **5** with sodium naphthalenide; a mixture of **3** and chromanone **22** with zinc in methanol; **3**, carbinol **6** and diol **8** with zinc in acetic acid; and acetates **7** and **9** with Zn–Ac_2O–AcONa.

Although 4-oxo-4*H*-1-benzopyran-3-carboxaldehyde (trivial name: 3-formylchromone, **1**) has been extensively studied in the last three decades,[1] its reductions by electron transfer reagents have received little attention. Reaction of (*E*)-cinnamaldehyde with SmI_2 or YbI_2 causes polymerisation.[6] So it was of interest to study how the aldehyde **1** containing a chromone moiety as well as an α,β-unsaturated aldehyde functionality would behave towards sodium naphthalenide or zinc. The aldehyde **1** on treatment with sodium naphthalenide in dry tetrahydrofuran (THF) at 10–20 °C under a nitrogen atmosphere gives a mixture of dichromonylcarbinol **2**, dichromonylmethane **3** and 1,4-disalicyloylbenzene **5**. The rationalisation of the reaction is shown in Schemes 1 and 2.



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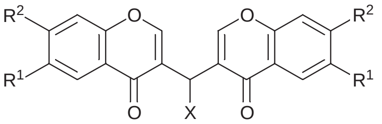
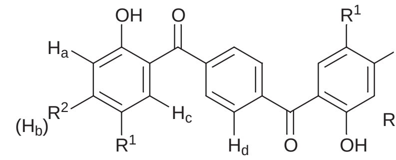


2 X = OH
3 X = H
4 X = OAc



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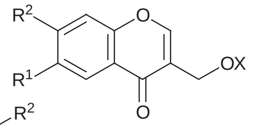
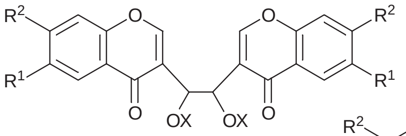
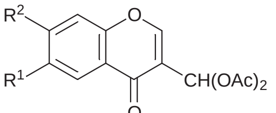


6 X = H
7 X = Ac



8 X = H
9 X = Ac



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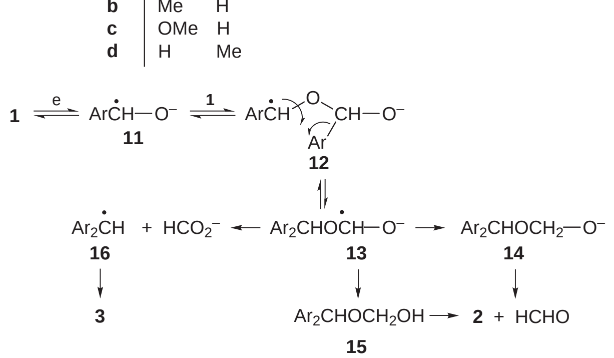
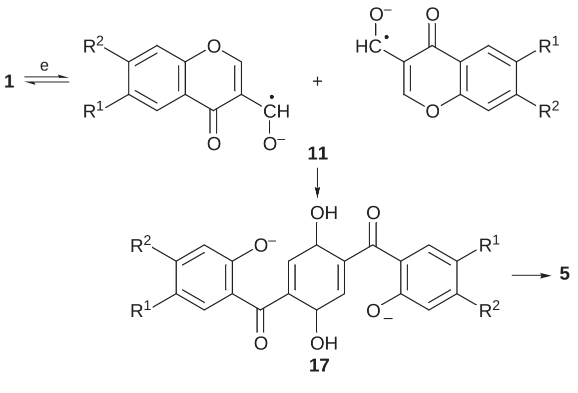
1–22	R^1	R^2
a	H	H
b	Me	H
c	OMe	H
d	H	Me

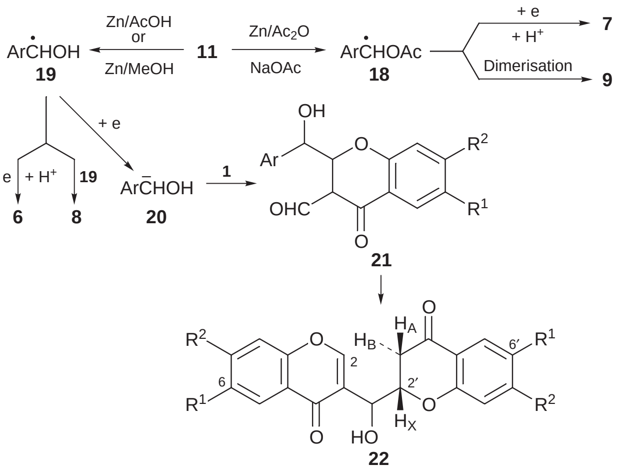


Scheme 1



Scheme 2

The title aldehyde **1** survives boiling under reflux with zinc in dry benzene or toluene even for 10 h. Addition of methanol to this mixture and boiling under reflux for a further 4 h, however, shows the formation of **2**, assumed to arise by reductive protonation of **13** and subsequent base-catalysed fragmentation of the resultant hemiacetal **15** (Scheme 1). Surprisingly, the aldehyde **1** on heating under reflux in methanol containing zinc gives a mixture of **3** and **22**. Formation of **22** is shown in Scheme 3.



Scheme 3

This envisaged reaction pathway entails the formation of the alcohol **6**[13] and the pinacol **8**. These two products are indeed obtained on treatment of aldehyde **1** with zinc and acetic acid. The acetates **7**[13] and **9** corresponding to the alcohols **6** and **8** are obtained through the radical inter-

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mediate **18** by warming the aldehyde **1** with zinc–sodium acetate–acetic anhydride. These latter two products are sometimes accompanied by the diacetate **10** which arises by the reaction of sodium acetate with aldehyde **1**.[14]

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Techniques used: ^1H and ^{13}C NMR, mass spectrometry, IR, chromatography, elemental analysis.

References: 17

Schemes: 3

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References cited in this synopsis

1 Reviews: G. P. Ellis, *Heterocyclic Compounds*, ed. A. Weissberger, Interscience, New York, 1977, vol. 35, p. 921; C. K. Ghosh, *J. Heterocycl. Chem.,* 1983, **20**, 1437; G. Sabitha, *Aldrichim. Acta,* 1996, **29**, 15.

6 P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.,* 1980, **102**, 2693.

13 S. Klutchko, M. P. Cohen, Jr. J. Shavel and M. V. Strandtmann, *J. Heterocycl. Chem.,* 1974, **11**, 183.

14 C. Pene and M. Hubert-Habart, *J. Heterocycl. Chem.,* 1980, **17**, 329.