Benzopyrans. Part 38.[1] Reactions of 4-Oxo-4*H*-1-benzopyran-3-carbaldehyde, -3-carbonitrile and -3-carboxylate with Chloroacetone and a Note on the Stereochemistry of Benzo[*b*]cyclopropa[*e*]pyrans

J. Chem. Research (S), 1998, 178–179
J. Chem. Research (M), 1998, 0859–0869

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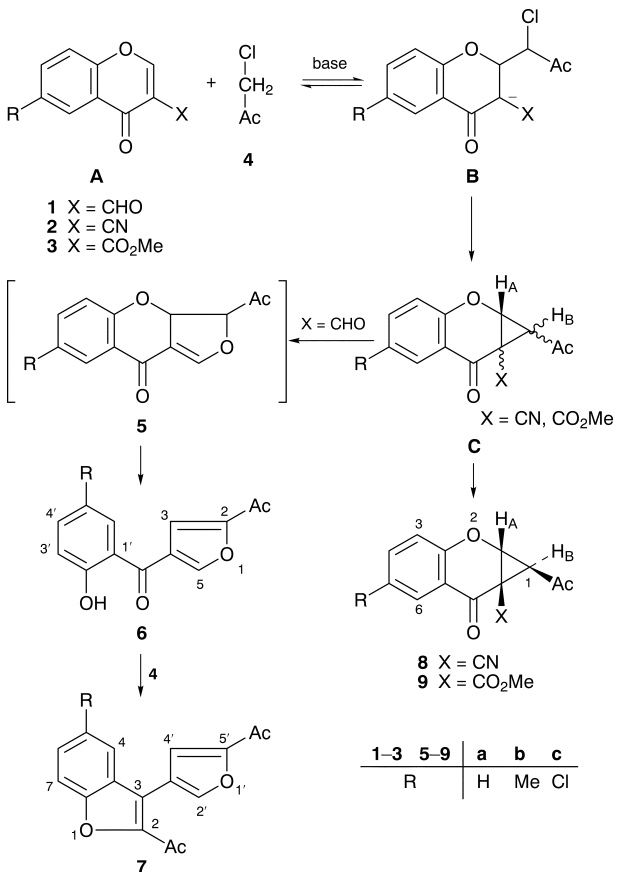
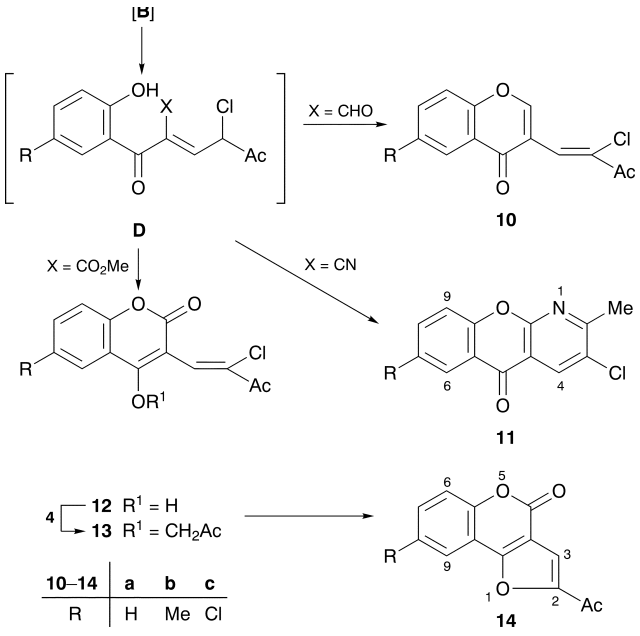
The title benzopyranones **1**–**3** give the benzo[*b*]furan **7** and the benzo[*b*]cyclopropa[*e*]pyrans **8** and **9** with chloroacetone in acetone containing anhydrous potassium carbonate and a catalytic amount of potassium iodide but give the 1-benzopyranones **10**, **11** and **14** in dichloromethane in the presence of Brockman neutral alumina, respectively.

Base catalysed Michael addition of chloroacetone **4** to the benzopyranone **A** (X is an electron withdrawing group) gives the carbanion **B** that leads to the cyclopropane **C** by ring closure (Scheme 1) or the diacylalkene **D** by pyran ring opening and subsequent protonation (Scheme 2). Depending on the nature of the X group, compounds **C** and **D** may undergo further transformations. **C** (X = CHO) is likely to give **7** through a sigmatropic rearrangement[10] (to **5**) followed by base-catalysed opening of the pyran ring (to **6**) and further reaction with **4**. The salicyloylalkene **D** with X = CHO, CN and CO_2Me may cyclise to **10**, **11**[5] and **12**[7], respectively.



Scheme 1

We report herein that the chromones **1**–**3** when stirred with chloroacetone **4** at ambient temperature in acetone containing anhydrous potassium carbonate and a catalytic amount of potassium iodide (Method A) followed the reaction course as depicted in Scheme 1. However, stirring in dichloromethane in the presence of Brockman neutral alumina of activity grade I (Method B) gave the products according to the reaction sequence in Scheme 2. Thus in Method A, the aldehyde **1** gave the benzo[*b*]furan **7** (52–57%) *via* the *o*-hydroxyaromatic ketone **6**, and only one stereoisomeric form of the appropriate benzo[*b*]cyclopropa[*e*]pyran **C** (13–54%) was obtained from **2** and **3**. Molecular modelling studies of the fused cyclopropanes **C** (X = CN and CO_2Me) using Hyperchem Software indicated a *cis* geometry at the ring junction, in agreement with the sole possibility of *cis* ring fusion in the cyclopropanation of enones[9,13] and in the bicyclo[4.1.0]heptane system. Vicinal coupling constants for the cyclopropyl protons in the *cis*-fused cyclopropanes (**C**, X = CN, R = Me) and (**C**, X = CO_2Me, R = H) were calculated with the help of QCPE Software 3JHHPC; *trans* J_{AB} values were found to be 4.10 and 3.79, and *cis* J_{AB} 9.13 and 9.26 Hz, respectively. The benzocyclopropapyrans isolated after treating **2** as well as **3** with **4** show J_{AB} values of *ca.* 4.0 Hz and are hence



Scheme 2

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assigned the stereostructures **8** and **9**, respectively. Several benzo[*b*]cyclopropa[*e*]pyran derivatives reported by Dicker *et al.*[9] conform to the general trend that J_{cis} for cyclopropyl protons is higher than J_{trans} as revealed in the above modelling studies. The assignments given to *cis* and *trans* protons in an analogous compound derived from 3-nitrochromone and diazomethane,[16] therefore, need be reversed.

The reaction between the aldehyde **1** and chloroacetone **4** according to Method B afforded the chromone derivative **10** (22–32%) sometimes contaminated with small amounts (2–5%) of the alumina mediated transformation products of the former.[1] In contrast, the alumina-mediated transformation of the substrate **2** into the corresponding 2-amino-3-formylchromone (27–32%) always predominated over the formation of the pyranopyridine **11** (12–14%) from **2** and **4**. The ester **3** with excess **4** in the presence of alumina gave the furocoumarin **14** (35–54%) exclusively. Here the initially formed 4-hydroxycoumarin **12** from **2** and **4** (Scheme 2) undergoes *O*-alkylation (to **13**) by **4** followed by intramolecular Michael addition and subsequent elimination of **4** to afford **14**.

Financial support [Scheme No. 01(1362)/95 EMR-II from CSIR, New Delhi and computer facilities provided by the Centre for Knowledge Based Systems, Jadavpur University, Calcutta are duly acknowledged.

Techniques used: ^{1}H and ^{13}C NMR, molecular modelling, elemental analysis, IR, MS

References: 19

Schemes: 2

Table 1: Yields, mps and analytical data for **8** and **9**

Table 2: ^{1}H NMR spectral data for **8** and **9**

Received, 10th September 1997; Accepted, 9th December 1997
Paper E/7/06609K

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