
Conversion of 1-methoxy substituted isochromenes into dimers of 2-benzopyrylium salts

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Treatment of isochromenes **1** with AcOH or HCOOH followed by addition of water as well as heating of **1** produced dimers **2**, **7** and **10**.

Until now, only transformations of 2-benzopyrylium salts with anions of strong acids have been investigated¹ and the behaviour of 2-benzopyrylium cations with anions of weak acids may be different. On attempting to obtain 2-benzopyrylium acetates and formates by treatment of 1-methoxy substituted isochromenes **1** with acetic or formic acids we unexpectedly found that these salts undergo a dimerization reaction either spontaneously or during attempted isolation from solution. This transformation is characteristic of 2-benzopyrylium perchlorates in the presence of weak bases.²

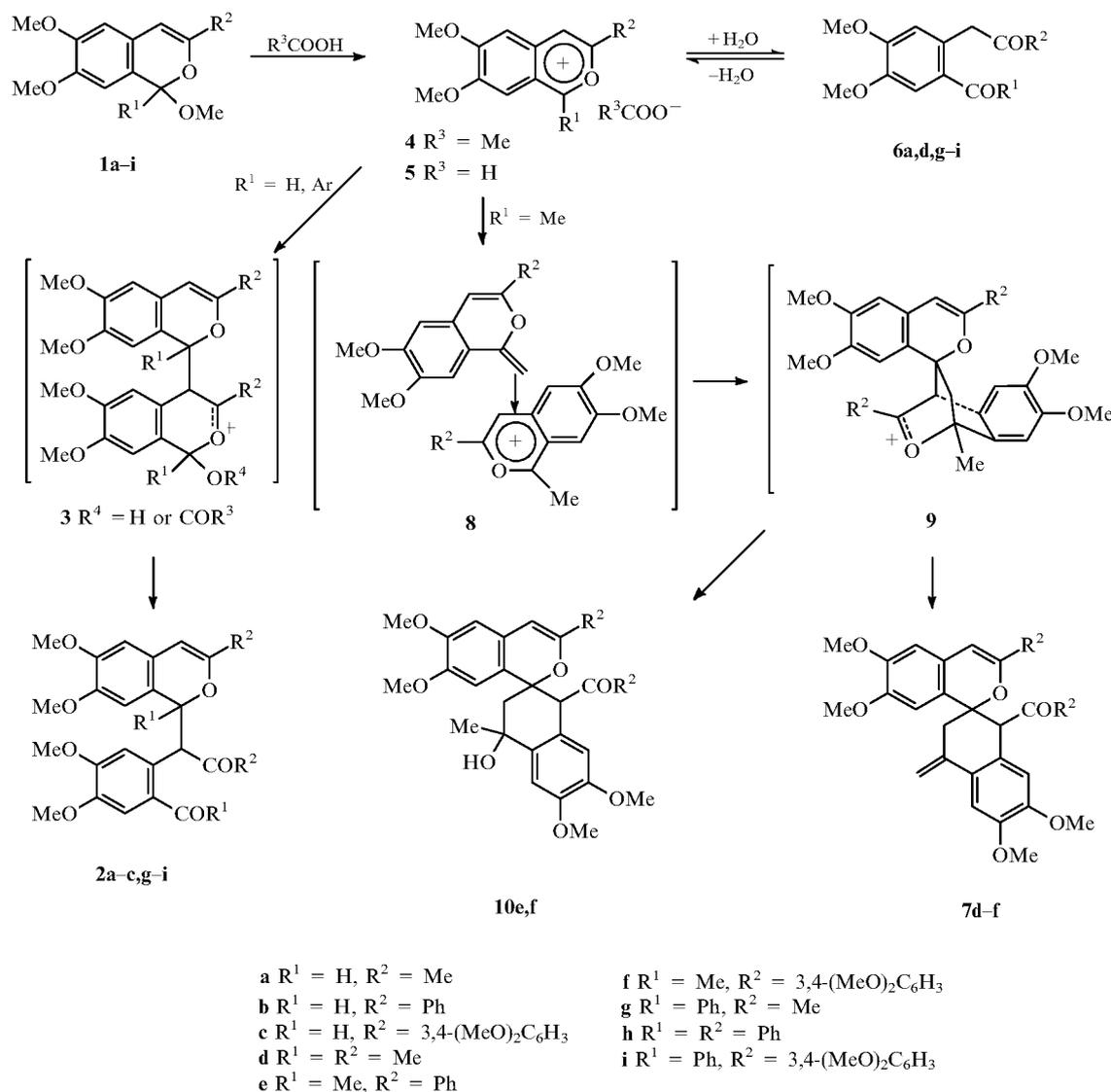
Dissolution of **1a–c** ($R = H$) in AcOH in concentration *ca.* 10^{-1} mol dm⁻³ gives the so-called 4-1'-dimers **2a–c** (UV control) on aqueous work-up in 90–95% yields as 1:1 mixtures of two diastereomers. Obviously intermediates **3** are precursors of the dimers **2**. However, at concentrations 10^{-4} mol dm⁻³ 2-benzopyrylium acetates **4**, which have identical UV absorption with the corresponding perchlorates, were obtained from isochromenes **1**. Treatment of **1a–c** with HCOOH produces solutions of pyrylium formates **5**, which are stable in formic acid medium irrespective of the

concentration. However, dilution of these solutions with water or ether yields either dimers **2b,c** as a 1:3 mixture of two diastereomers when $R^2 = Ar$ or the 4,5-dicarbonyl compound **6a** when R^2 is methyl (Scheme 1).

Isochromenes **1g–i** ($R^1 = Ph$) generate cations **4** or **5** at high concentrations (10^{-1} mol dm⁻³) both in AcOH and HCOOH media. Addition of water to these solutions results in the slow precipitation of mixtures containing the 4-1'-dimers **2g–i** and dicarbonyl compounds **6g–i**, the ratio of which depend on the exact conditions.

The structural assignments of the 4-1'-dimers **2a–c,g–i** were made on the basis of analytical, IR, ¹H NMR spectroscopy and by comparison with samples previously obtained from 2-benzopyrylium perchlorates.^{3,4}

Isochromenes **1d–f** (with $R^1 = Me$) give rise to another type of dimer. On their dissolution in AcOH a deep coloration appears caused by a broad absorption band centred at 570 nm for **1f** ($c = 10^{-1}$ mol dm⁻³). This band disappears on dilution with AcOH until the concentration becomes 10^{-4} mol dm⁻³, when the UV spectrum coincides with that of the corre-



Scheme 1

spending 2-benzopyrylium perchlorate. The coloration also fades spontaneously over a period of 20–30 min, after which UV spectroscopy indicated the formation of spirodimers **7d–f**, which were isolated as a 1 : 1 mixture of two diastereomers by pouring of the solutions into water. Recently, we reported the formation of compounds **7d–f**,⁵ which was also preceded by the same coloration, from 2-benzopyrylium perchlorates. It was suggested that this dimerization proceeds *via* generation of the charge-transfer complex **8** between cation and anhydrobase, which is responsible for the absorption band at 570 nm. The formation of **8** is supposedly followed by a cycloaddition reaction leading to **9**, whereupon ring-opening and deprotonation afford **7**.

The structure of spirodimers **7d–f** was proved by spectroscopic (¹H NMR) comparison with the samples obtained from 1-methyl-2-benzopyrylium perchlorates whose structure has been determined previously by spectroscopic and X-ray analysis.⁵

1-Methyl-2-benzopyrylium formates **5d–f**, obtained from **1d–f** by dissolution in HCOOH, also either quantitatively undergo dimerization, when $R^1 = Ar$, or yield **6d** from **5d** on addition of water. However, dimerization in this case gives a mixture of **7e,f** and **10e,f**, in which the former are the main

products. Dimer formation may be rationalized by the addition of water to **9**. The separation of these mixtures by column chromatography (Al₂O₃/CHCl₃) gives one of the diastereomers of **7e,f** and two diastereomers of **10e,f** in the ratio 1:1. The structure of each of the diastereomers of **10e,f** was proved by means of elemental analysis, IR and ¹H NMR spectroscopy.

The stereoselectivity of the dimerization reaction of 2-benzopyrylium formates **5b,c,e,f**, contrasts with dimer formation by treatment of isochromenes **1a–f** with acetic acid which produces equal amounts of the diastereomers of the dimers **2a–c** and **7d–f**. The dimerization reaction of 2-benzopyrylium perchlorates is also stereoselective, supposedly because of the ordered mutual orientation of the original cations.⁵ The stereoselectivity of the dimerization reaction of 2-benzopyrylium formates can be rationalized by the existence of these salts in solution as associates with ordered mutual orientation of the cations. This is impossible for 2-benzopyrylium acetates, because of their instability at high concentrations. Nevertheless the fact that dimers **10e,f** were obtained as an equal mixture of two diastereomers does not contradict the stereoselectivity of dimerization taking into account that molecules of **10e,f** contain three chiral centres and the

formation of two diastereomers occurs on water addition to **9**.

Isochromenes **1a-i** on heating up to 200 °C also yield dimers contaminated by the products of their further transformations. This dimerization occurs by a different mechanism to that in acidic media but resembles the dimer preparations from the adducts of 2-benzopyrylium⁶ and benzothiazolium⁷ salts with cyanide anion.

Thus the dimerization reaction is a characteristic transformation for 2-benzopyrylium salts regardless of the type of anion. This work describes the first transformation which occurs when 2-benzopyrylium salts become thermodynamically unstable.

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