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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.

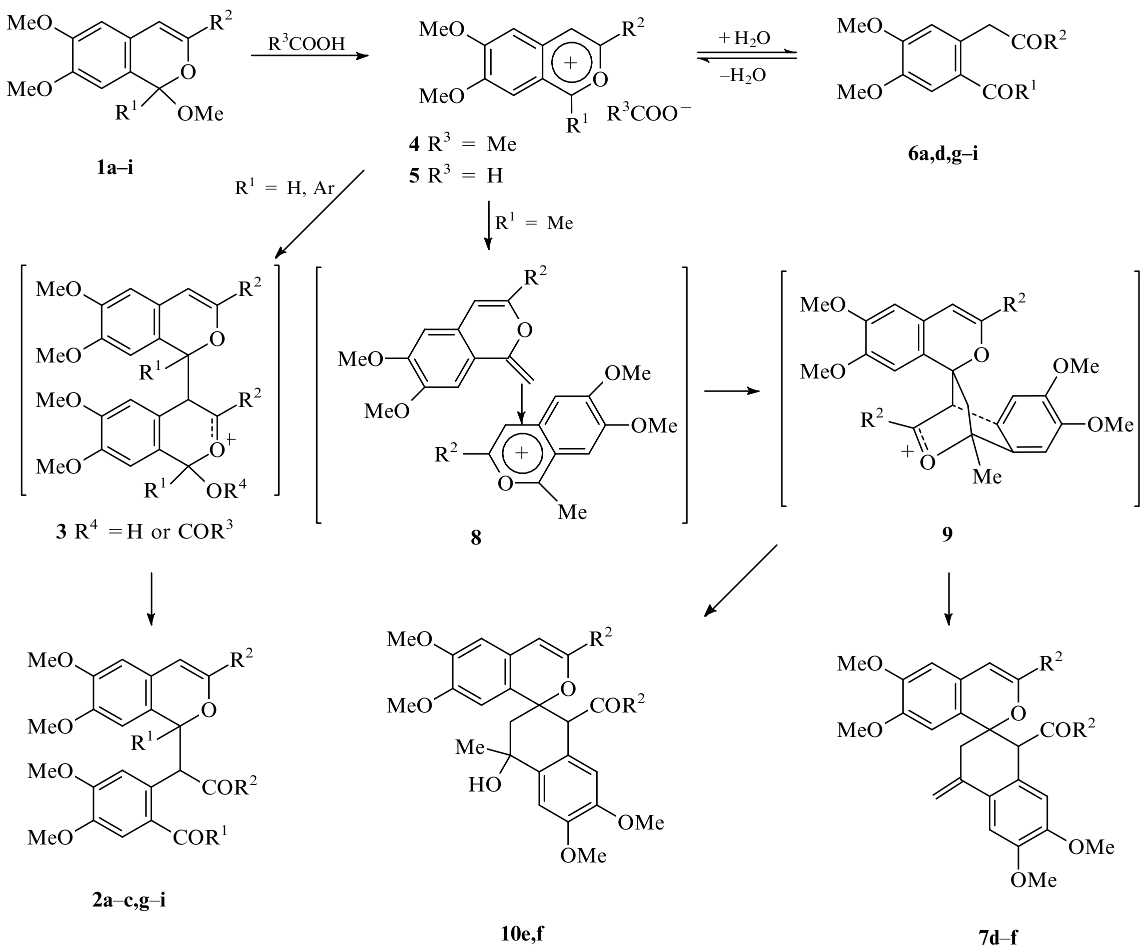
Until now, only transformations of 2-benzopyrylium salts with anions of strong acids have been investigated[1] and the behaviour of 2-benzopyrylium cations with anions of weak acids may be different. On attempting to obtain 2-benzopyrylium acetates and formates by treatment of 1-methoxy substituted isochromenes **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 correspondening 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, ^{1}H 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-



a R^1 = H, R^2 = Me
b R^1 = H, R^2 = Ph
c R^1 = H, R^2 = 3,4-$(MeO)_2C_6H_3$
d R^1 = R^2 = Me
e R^1 = Me, R^2 = Ph
f R^1 = Me, R^2 = 3,4-$(MeO)_2C_6H_3$
g R^1 = Ph, R^2 = Me
h R^1 = R^2 = Ph
i R^1 = Ph, R^2 = 3,4-$(MeO)_2C_6H_3$

Scheme 1

sponding 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 (^{1}H 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 ($Al_2O_3/CHCl_3$) 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 ^{1}H 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-benzopyrylium[6] and benzothiazolium[7] 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.

References

1 E. V. Kuznetsov, I. V. Shcherbacova and A. T. Balaban, *Adv. Heterocycl. Chem.*, 1990, **50**, 157.

2 E. V. Kuznetsov and S. V. Verin, *Khim. Geterotsikl. Soedin.*, 1993, 3 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1993, 1].

3 Yu. A. Zhdanov, S. V. Verin, I. V. Korobka and E. V. Kuznetsov, *Khim. Geterotsikl. Soedin.*, 1988, 1185 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1988, 974].

4 S. V. Verin, D. E. Tosunyan and E. V. Kuznetsov, *Khim. Geterotsikl. Soedin.*, 1991, 175 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1991, 142].

5 S. V. Verin, E. V. Kuznetsov, Yu. V. Revinskii, D. S. Yufit and Yu. T. Struchkov, *Mendeleev Commun.*, 1991, 104.

6 I. V. Shcherbakova, E. V. Kuznetsov, I. A. Yudilevich, O. E. Kompan, A. T. Balaban, A. Abolin, A. P. Polyakov and Yu. T. Struchkov, *Tetrahedron*, 1988, **44**, 6217.

7 H. Wahl and J.-J. Varsanger, *Bull. Soc. Chim. Fr.*, 1965, 3359.

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