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A Novel Dimerization Reaction of 1-Methyl-2-benzopyrylium Salts

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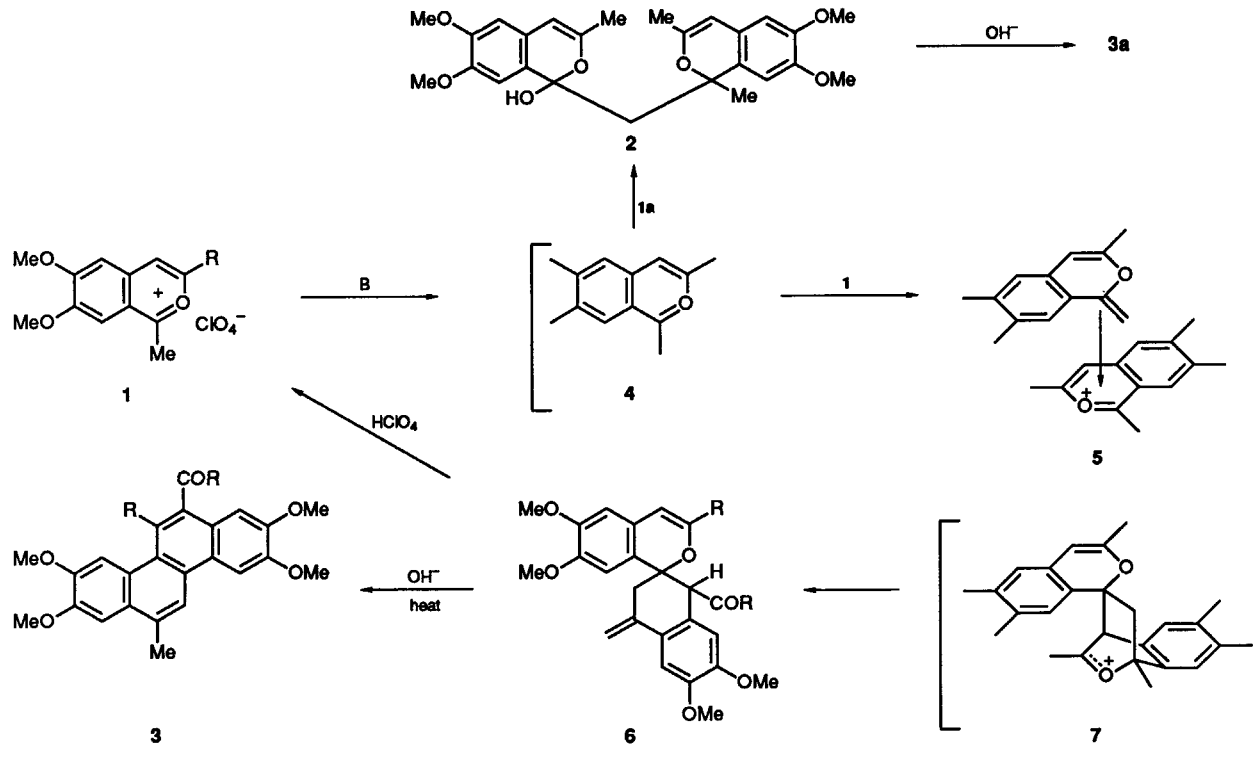
Treatment of 1-methyl-2-benzopyrylium salts **1** with weak bases gives the anhydro bases **4**, which rapidly react with the original cations as dienophile and diene respectively to form the spiro dimers **6**.

The unique ability of 2-benzopyrylium salts to undergo dimerization reactions was discovered recently in our laboratory. Beside the fundamental interest these transformations provide an original approach to the synthesis of polycondensed aromatic hydrocarbons, such as chrysene,[1,2] benz[*a*]anthracene[3] and naphthalene[4] derivatives, which result from intramolecular conversions of dimers of 2-benzopyrylium salts. Dimers of 1*H*-2-benzopyrylium salts also appeared to be intermediates in the initial cation disproportionation reaction,[5] which in this way differ from other analogous transformations.[6]



a: R = Me
b: R = Ph
c: R = 3,4-$(MeO)_2C_6H_3$

Scheme 1 B = DMF or other weak base (Et_3N, pyridine, $MeCO_2Na$ or $MeCO_2K$)

The mode of dimerization depends mainly on the presence of a substituent at the 1-position of the 2-benzopyrylium ring. Salts without a methyl group here form so-called 4-1′-dimers,[3–5] whereas the 1,3-dimethyl derivative **1a** in H_2O–AcONa was transformed into the α-1′-dimer **2**[2] which was similar to those obtained from other heteroaromatic salts with active alkyl substituents.[7,8] The dimer **2** was easily converted to the chrysene **3a**,[2] whereas the latter and its derivatives were directly obtained from the corresponding salts in a wide range of conditions.[1] This result prompted us to investigate the possibility of other more common types of dimerisation reaction of 1-methyl-2-benzopyrylium salts.

This paper describes the novel dimerization of perchlorates **1a–c**, leading to the spirocyclic dimers **6a–c** in excellent **6a** 83, **6b** 92 and **6c** 95% yields (Scheme 1). It proceeds in *N*,*N*′-dimethylformamide (DMF) or in the presence of some other weak bases. The structural determination of **6a–c** was carried out on the basis of analytical and spectroscopic data (IR, MS and ^{1}H NMR spectra and the complete molecular structure of 1′-acetyl-3′,4′-dihydro-3-methyl-4′-methylene-6,7,6′,7′-tetramethoxyspiro[1*H*-2-benzopyran-1,2′(1′*H*)-naphthalene] **6a** was determined by X-ray crystallography (Fig. 1).†

Treatment of **6a–c** with perchloric acid regenerated the original salts **1a–c**, while heating with alkali yields the known chrysenes **3a–c**.

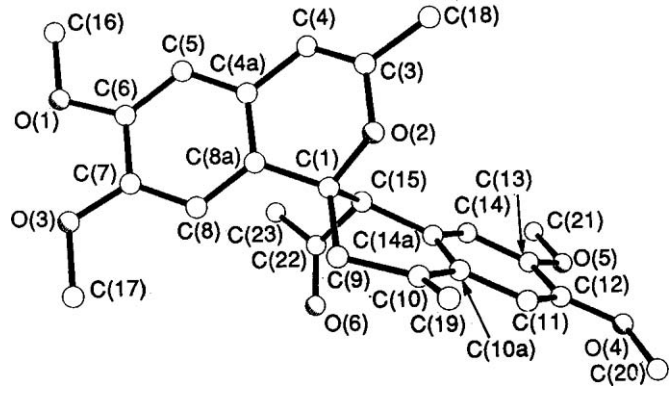


Fig. 1 Molecular structure of **6a**

The conversion of **1** into **6** can be rationalized in terms of an initial cycloaddition of the anhydro base **4** to **1**, followed by cation ring cleavage in **7**. We have already reported the analogous cycloaddition reaction of vinylethyl ether to 2-benzopyrylium salts.[9]

Only one example of the formation of the related spirocyclic dimers has previously been described.[10,11] They were obtained from 2-alkyl-4*H*-1,3-thiazin-4-one derivatives in acid media, where the original anhydro base combines with the cation generated in the reaction.

The formation of dimers **6a–c** is preceded by the appearance of a deep coloration between red and yellow, which quickly disappears. This shows a broad absorption band at 570 nm for **6c**, suggesting that the previous interaction between **1** and **4** gave the charge-transfer complex **5**. Interestingly, the pathway of cycloaddition reactions to isoquinolinium salts also involves such intermediates.[12]

The fact that the transformation of salts **1a–c** yields only one

† *Crystal data* for **6a**: $C_{26}H_{28}O_6$, M_r = 436.5, rhombic crystals from ethanol, space group $Pca2_1$, a = 16.727(5), b = 7.090(2), c = 37.403(12) Å, Z = 8, V = 4436 Å^3, D_c = 1.307 g cm^{-1}. Data were measured on an automated four-circle SYNTEX $P2_1$ diffractometer at −120 °C (λ Mo–Kα, graphite monochromator, θ/2θ − scans, θ < 30°). The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic temperature factors for all non-H atoms. All hydrogen atoms were found on a difference map, considered with B_{iso} = 4 Å^2, but not refined. Final R = 0.055, R_w = 0.052 for 2785 independent observed reflections with $I > 2\sigma(I)$. All calculations were performed on an ECLIPSE S/200 computer using the INEXTL program.[15] Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, *J. Chem. Soc., Chem. Commun.*

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diastereoisomer of the dimers **6a–c** may be accounted for both by the concerted nature of the reaction and by the ordered mutual orientation of the original molecules. In accordance with the configuration of dimer **6a**, the corresponding anhydro base and cation are aligned relative to one another before interaction as shown in structure **5**. This differs from that of the cations in the crystal of salt **1a**[13] by only a 115° rotation in the plane of the rings.

Additional evidence on the substantial role of the mutual orientation of the 2-benzopyrylium cations and their consequent association were provided by our unsuccessful attempts to achieve a 'cross-dimerization' between the salt **1c** and its 1-unsubstituted analogue. However, only a mixture of the spiro dimer **6c** and 4-1′-dimer[5] was isolated. We also failed to obtain the adduct instead of dimer **6c** on treatment of the salt **1c** with DMF in the presence of 3,6-diphenyl-1,2,4,5-tetrazine, which has recently been acclaimed[14] as the best substrate for interaction with anhydro bases of different heteroaromatic cations.

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