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Dimerization Reactions of 2-Methyl-4,5-diarylpyrylium Salts

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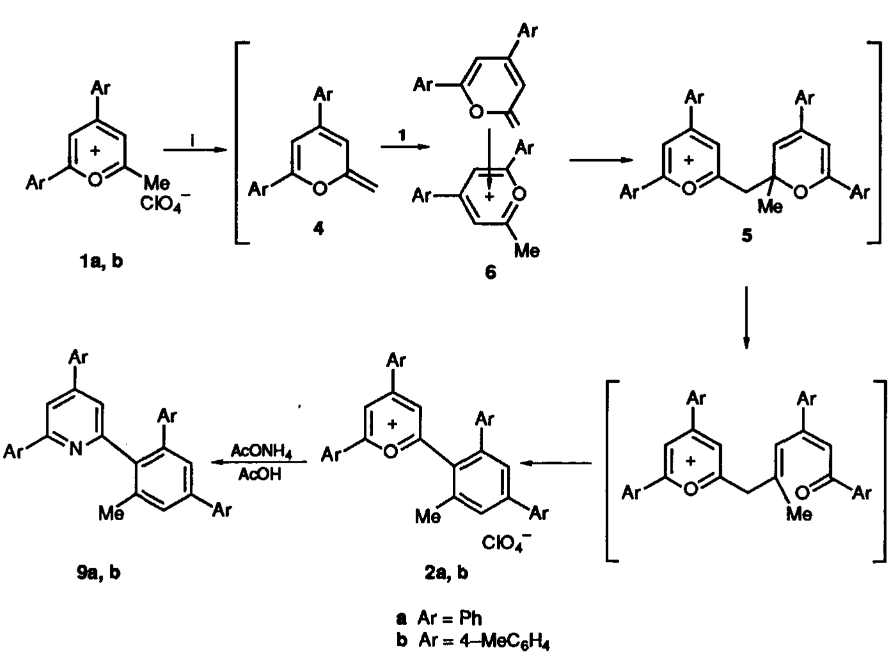
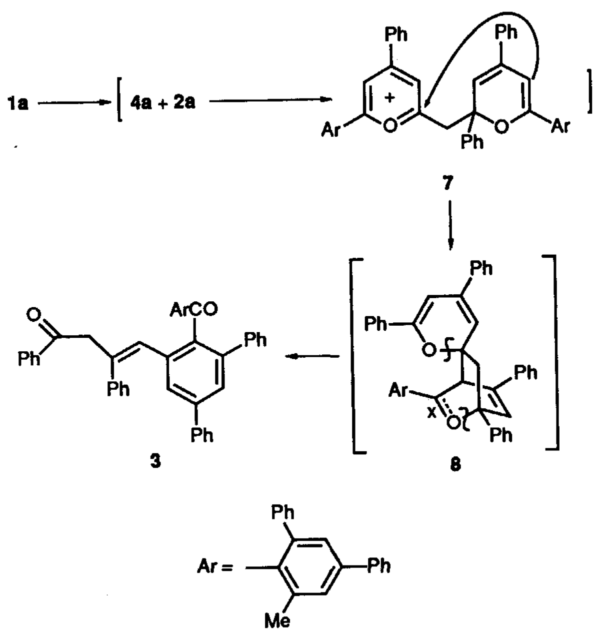
2-Methyl-4,6-diarylpyrylium salts **1a,b** rapidly undergo dimerization and trimerization reactions resulting in the formation of triarylpyrylium salts **2a,b** and dicarbonyl compounds **3**.

For several classes of heteroaromatic cation with active alkyl groups, dimerization reactions, proceeding *via* nucleo- or cyclo-addition of an anhydrobase (formed by deprotonation of one molecule) to the cation of a second molecule, have been described.[1–4] Most of the products of these transformations are capable only of retrodissociation, but in some cases their intramolecular reactions are achieved. For example, the possibilities of rare synthetic applications of 1-methylbenzo[*c*]pyrylium[5] and 6-methyloxazinium salts[6] has been recognized.

This communication describes the dimerization and trimerization reactions of 2-methyl-4,6-diarylpyrylium salts **1a,b**, ultimately yielding triaryl salts **2a,b** and dicarbonyl compounds **3**, respectively. These products form in different solvents in the presence of weak nucleophiles, *e.g.* AcONa, pyridine (Py),



Scheme 1 *Reagents*: i, $MeCO_2Na$ or other weak nucleophile (Et_3N, pyridine, Al_2O_3)



Scheme 2

Et_3N. The best yields (*ca.* 60% **2a,b**) were obtained on heating solutions of **1a,b** in AcOH with excess AcONa for 4 h under reflux. A complex mixture of non-salt products, produced on short heating (to boiling) of a solution of **1a** in Py followed by dilution with water, also gives **2a** (35%) on treatment with $HClO_4$. Yields of **3** are *ca.* ~5–15% over a wide range of conditions.

The mechanism of formation of salts **2** seems to involve attack of anhydrobase **4** to the initial cation **1** followed by further recyclization of the pyran ring of the intermediate dimer **5**.

In 1922[7] Schneider *et al.* reported that treatment of **1a** with base generated a deep-red coloration. For example, **1a** shows an absorption band at 525 nm both in Py and in MeCN in the presence of Al_2O_3. The fact that regeneration of the UV spectrum of the initial cation **1a** takes place after addition of acid suggests that this coloration is caused by the formation of charge-transfer complex **6**, as in the case of benzo[*c*]pyrylium salts.[8]

The pyrylium salt **1a** trimerization process leading to **3** may be accounted for by interaction of **4** with cation **2** formed in the reaction mixture. However, further transformation of the initially-formed **7** (in contrast to **5**) appears to take place by a kind of intramolecular cycloaddition *via* the bridge intermediate **8**.[8] An increase in the yield of **3** on addition of perchlorate **2** furnishes evidence for the participation of **2a** in this reaction.

Thus, there are two different types of interaction of arylmethylenepyrans **4** with pyrylium cations. These correlate with the two main directions of pyrylium salt recyclization reactions with methylene-active compounds. The first is a 2,6-[C_5 + C]-type reaction which leads to benzene derivatives; the second, classified as a 2,5-[C_4 + C_2]-type, produces substituted benzophenones.[9]

It has also been reported[10] that addition of **4** to 2-phenylbenzo[*b*]pyrylium perchlorate results in a product which does not undergo intramolecular recyclization but which is, however, oxidized to a cyanine dye. The complete molecular structure of **3** has been determined by X-ray diffraction studies,† and a structural diagram is given in Fig. 1.

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† Crystal data for **3**: $C_{54}H_{40}O_2 \cdot 1.5C_6H_6$, $M = 838.02$, monoclinic, space group $P2_1/n$, at 20°C $a = 14.877(2)$, $b = 14.942(2)$, $c = 21.324(3)$ Å, $\beta = 90.78(1)°$, $U = 4739(2)$ Å^3, $D_{calc} = 1.174$ g cm^{-3}, $Z = 4$. Data were measured on a Siemens P3/PC diffractometer with CuKα radiation ($\lambda = 1.54178$ Å, graphite monochromator) using θ/2θ scan mode ($\theta \leq 55°$). The absorption correction [μ(CuKα) = 5.3 cm^{-1}] was performed with the XEMP programme on the basis of ψ-scan data for 12 reflections. The structure was solved by direct method and refined anisotropically by a full-matrix least-squares procedure. The atoms of the solvate benzene molecules were refined isotropically. All hydrogen atoms (except those of the benzene molecules) were located in the difference Fourier map and refined with fixed $U_{iso} = 0.05$ Å^2. One of the solvate benzene molecules is disordered over two positions with $G = 0.63$ and 0.37. Another benzene molecule seems also to be disordered but attempts to find alternative positions were unsuccessful. The final discrepancy factors are $R = 0.072$ and $R_w = 0.071$ for 4375 independently-observed reflections ($I \geq 2\sigma$). Atomic coordinates, bond lengths and angles and thermal atomic parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *Mendeleev Commun.*, 1993, issue 1.

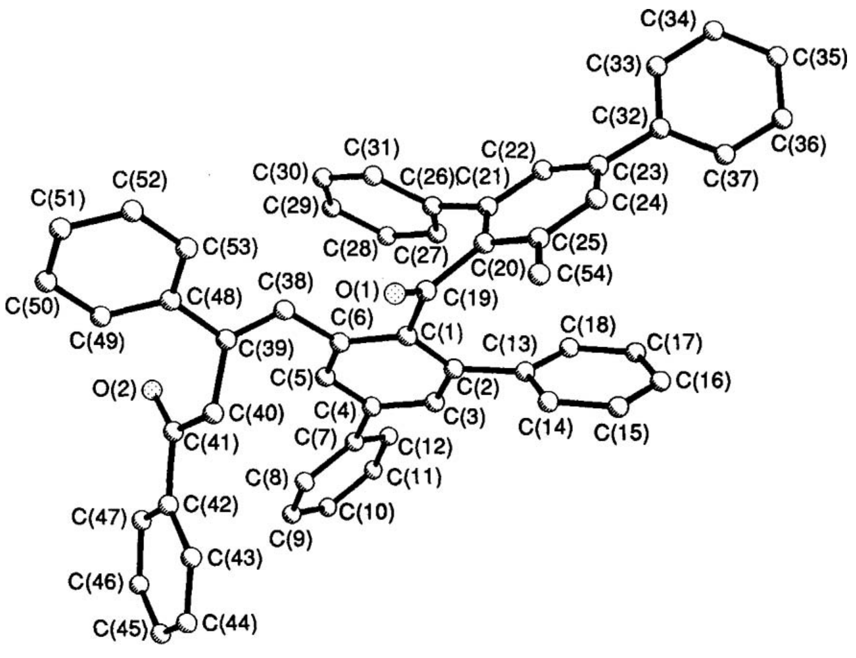

Fig. 1 Structure of compound **3**

To confirm the structure of salts **2a,b** (in addition to obtaining analytical and spectroscopic data) we carried out the conversion of those salts to the corresponding pyridines **9a,b**, on refluxing in AcOH in the presence of NH_4OAc, in almost quantitative yields. This recyclization does not, however, occur in other solvents and requires a fifteen-fold excess of NH_4OAc for **2a** and a fifty-fold excess for **2b**. The inability of 2-mesityl-4,6-diarylpyrylium salts to undergo an analogous transformation has already been reported.[11]

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