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New methodology for the conversion of pyrylium salts into pyridinium derivatives

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Treatment of triphenylpyrylium perchlorate 1 with α-methylheterocycles yields fused pyridinium derivatives which include C_3-fragments from the starting pyrylium ring.

It is well known that pyrylium salts can be readily used as the synthon of a C_5-fragment in the formation of various carbo and heterocycles. Thus, the treatment of pyrylium salts with primary amines is an important synthetic method for the preparation of pyridinium derivatives.[1]

We now report that pyrylium salts may be also considered as a C_3-synthon for the contraction of pyridinium derivatives. We have found that the reaction of triphenylpyrylium perchlorate **1** with an excess of α-methylheterocycles affords fused pyridinium derivatives **2**, **4, 6**.

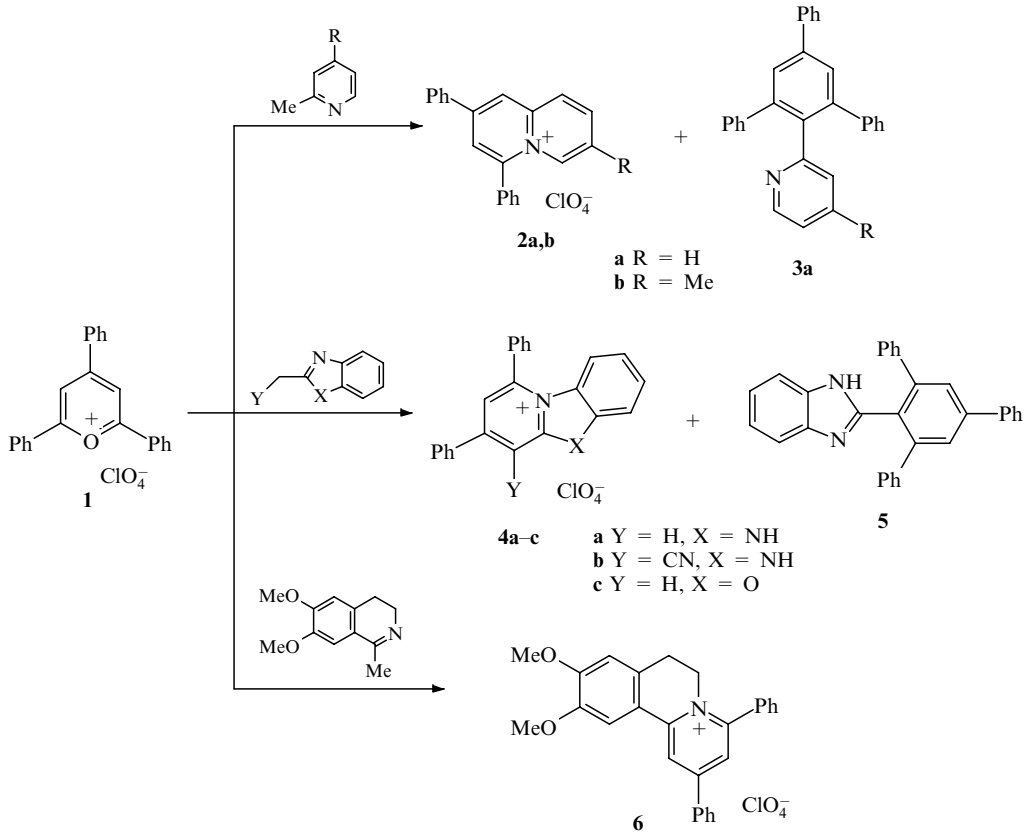
The heating of **1** with a twofold excess of α-picoline at 150–180 °C without solvent for 20 min gives the quinolizinium derivative **2a** in 75% yield and the benzene derivative **3a** in *ca.* 10% yield. The product **2a** was purified by washing of the reaction mixture with warm benzene, while compound **3a** was separated from benzene solution by means of column chromatography on alumina. The analogous reaction of **1** with 2-methylbenzimidazole produces the pyridobenzimidazole derivative **4a** and the benzene derivative **5** in 55% and 30% yield respectively. The fused pyridinium derivatives **2b**, **4b**,**c** and **6** were also obtained from triphenylpyrylium perchlorate **1** and 2,4-dimethylpyridine, 2-cyanomethylbenzimidazole, 2-methylbenzoxazole and 3,4-dihydro-6,7-dimethoxy-1-methylisoquinoline, respectively, in 50-65% yields.

There are four possible mechanisms for the formation of fused pyridinium derivatives in the reaction of pyrylium salts with α-methylheterocycles. The first involves attack at the 2-position of pyrylium ring by the nitrogen atom of pyridine (Path A), while the second starts with the attack by the methylene group of the pyridine tautomer on the pyrylium ring (Path B). Both mechanistic proposals are shown in Scheme 2. Two less-probable reaction pathways involve attack at the position-4 of the pyrylium ring with the nitrogen atom or methylene group of pyridine. A detailed discussion of the mechanism, as well as of the structure of fused pyridinium derivatives obtained from unsymmetrically substituted pyrylium salts, will be the subject of a future publication.

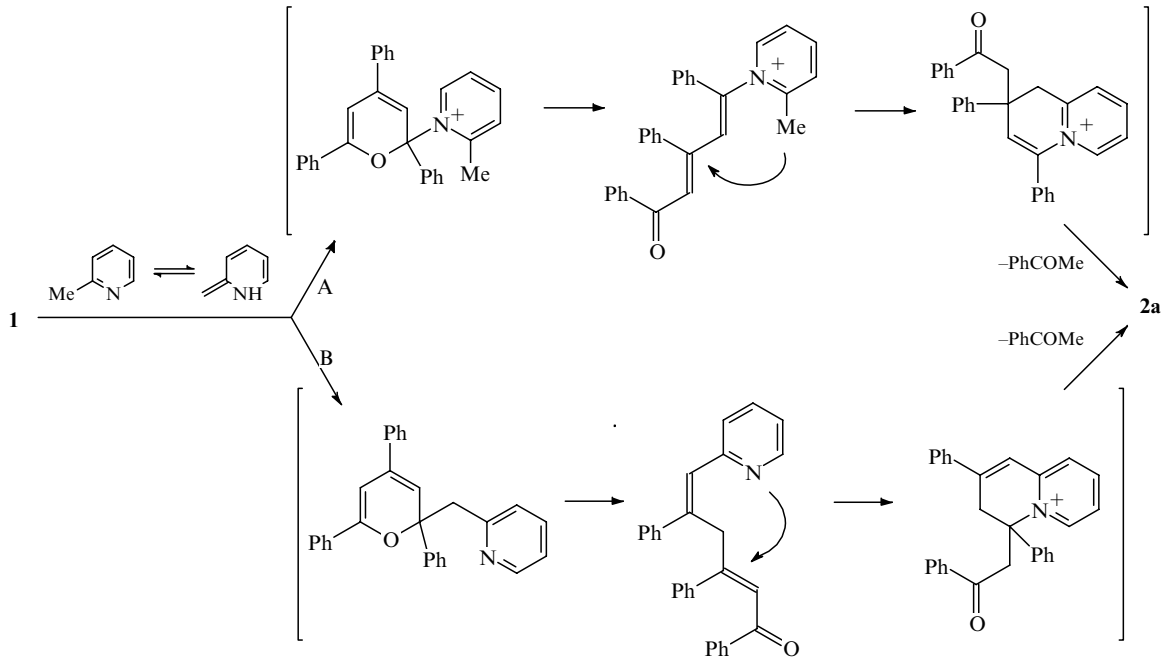
As for as the formation of aromatic derivatives **3a** and **5**, the mechanism of this reaction is obviously the same as that for the interaction of pyrylium salts with nitromethane[2] or anhydrides of carboxylic acids[3,4] and is a further example of the ability of pyrylium salts to be the synthon of a C_5-fragment for the formation of new rings.

Taking into account that 3,4-dihydro-6,7-dimethoxy-1-methylisoquinoline can be considered as the cyclic azomethine of dimethoxyacetophenone, we considered that the interaction of pyrylium salts with azomethines of acetophenones would result in the formation of monocyclic pyridinium derivatives, as in the treatment of pyrylium salts with primary amines.[1] However, if the known pathway for the conversion of pyrylium salts into pyridinium derivatives can be expressed as a [C_5 + N]-type, the path proposed here would be of a [C_3 + C_2N]-type. To check this idea we carried out the reaction of triphenylpyrylium perchlorate **1** with the azomethine of *p*-methoxyacetophenone and *p*-toluidine. The two different methyl groups of this reagent simplified the structural determination of the final products. We did in fact obtain the target product **7**, formed by a C_3-fragment of the starting pyrylium salt and the C_2N-fragment of azomethine. Unfortunately, the product **7** was accompanied by the pyridinium salt **8** in the ratio 1 : 2 with a high total yield (Scheme 3).

In conclusion, it should be noted that there are only a few known reactions in which pyrylium salts are the synthon for the C_3-fragment in the formation of new heterocyclic systems.



Scheme 1



Scheme 2

Examples are the reaction of pyrylium salts with hydroxylamine to produce substituted isooxazoles,[5] the use of hydrazine to yield pyrazoles[6] and treatment with 2-aminopyridine to give pyridopyrimidinium salts.[7] Nevertheless, the use of pyrylium salts as a synthon of a C_5-fragment in their numerous known reactions,[1] the ability of pyrylium salts to act as a C_4-synthon, as in the reactions with methylene active compounds[1,8] or Shiff bases[9] and as a C_3-synthon, as mentioned here, have all to be taken into account when considering the utility of pyrylium salts in organic synthesis.

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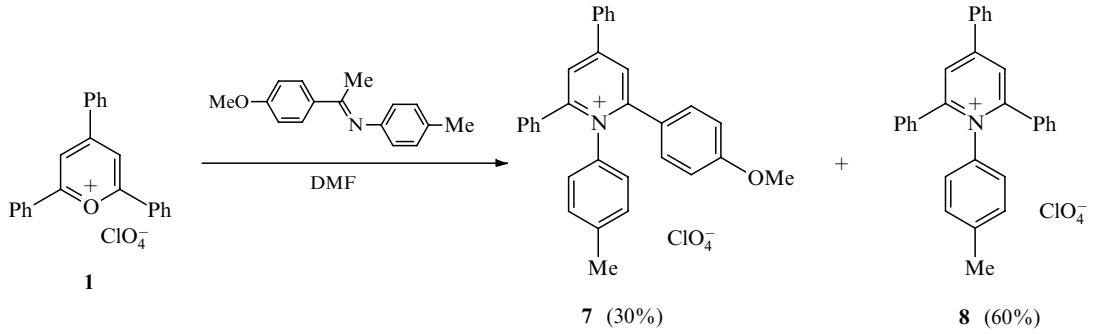

Scheme 3

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