Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 1995, **5(3)**, 99–100

Mendeleev Communications

Interaction of Triarylpyrylium Salts with Anhydrides of Dicarboxylic Acids

Alexander I. Pyschev,* Ludmila I. Butenko and Sergei V. Verin

Institute of Physical and Organic Chemistry, Rostov State University, 344104 Rostov-on-Don, Russian Federation.
Fax: +7 8632 285667

Activation of reactivity of pyrylium salts by means of salts of carboxylic acids or tertiary amines makes possible the interaction of pyrylium salts with weak CH acids, such as anhydrides of dicarboxylic acids.

Pyrylium salts are an important synthon of various hetero and carbocycles, which they produce in reactions with the corresponding nucleophiles.[1] However, until recently the range of C-nucleophiles used for such recyclization reactions of pyrylium salts was confined to active methylene compounds, *e.g.* nitroalkanes, β-diketones, *etc*. The reactions of pyrylium salts with active methylene compounds are carried out in the presence of strong bases. At the same time, there were no synthetic methods for the interaction of pyrylium salts with such C-nucleophiles as weak CH acids (anhydrides, amides, esters, ketones). In this case strong bases are useless because they rapidly cause destruction of the pyrylium cations.

Recently, and almost at the same time in three independent laboratories,[2–4] it was found that interaction of pyrylium salts with weak CH acids may take place if the anions of strong acids usual for pyrylium salts are replaced by acylate ions. Pyrylium acylates are available by different methods, but the synthetically most convenient one is direct anion exchange *in situ* between pyrylium perchlorates and sodium or potassium acylates. The advantage of acylate ions is that on the one hand they allow pyrylium cations to exist in solution and on the another they are capable of deprotonating weak CH acids, as for example in the Perkin reaction. It is also possible that the reactivity of pyrylium acylates may be higher than that of pyrylium salts with anions of strong acids.

The reactivity of pyrylium perchlorates may be also increased on treatment with tertiary amines. It has been supposed[5] that their interaction with pyrylium cations would yield unstable and positively charged adducts, which much more readily react with nucleophiles than the tight ion pairs of pyrylium perchlorates.

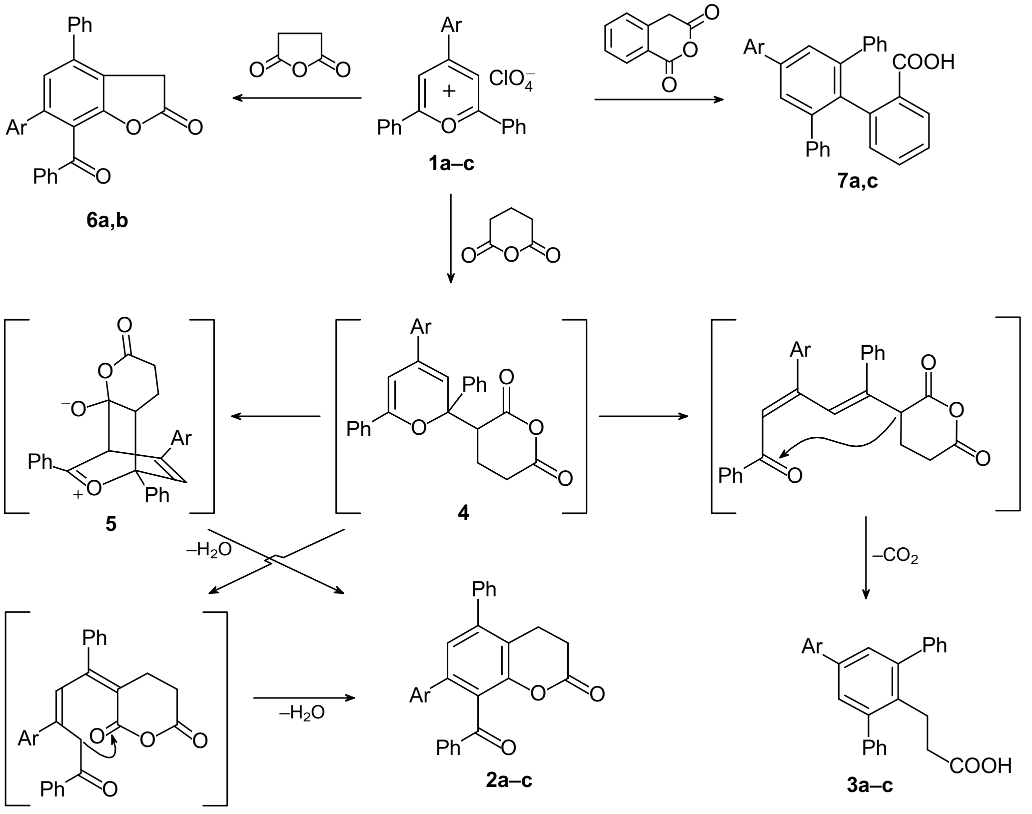
We used the methodology described here for the interactions of triarylpyrylium salts with anhydrides of dicarboxylic acids. Treatment of salts **1a–c** with glutaric anhydride both on heating to 200 °C without solvent in the presence of the disodium salt of glutaric acid and on boiling in toluene with triethylamine gave 45% of lactones **2a–c** and 40% of dihydrocinnamic acids **3a–c**. When the reaction was carried out in DMF as a solvent, the compounds **2a–c** and **3a–c** were isolated in 20% and 67% yields, respectively.

Both directions of this reaction are in general analogous to the two main types of interaction of pyrylium salts with active methylene compounds.[1] The so-called 2,6[C_5+C] process, followed by decarboxylation, leads to exchange of the heteroatom in the pyrylium ring and formation of **3**. An alternative 2,5[C_4+C_2]-transformation, which may occur through either cleavage of the pyran ring in adduct **4**, or *via* bridge intermediate **5**, gives **2**.

In contrast, only one direction of the 2,5[C_4+C_2]-type was found for the recyclization reaction of salts **1a,b** with succinic anhydride, which produce lactones **6a,b** in different aprotic solvents in the presence of the disodium salt of succinic acid or triethylamine, but with yields less than 40%.

At the same time, interaction of salts **1a,c** with homophthalic anhydride in DMF in the presence of triethylamine gives only products of 2,6[C_5+C]-type – substituted benzoic acids **7a,c** in *ca.* 70% yields.

Thus, activation of reactivity of pyrylium salts by means of acylate ions and tertiary amines is rather promising since one may suggest that this approach would be useful for the reactions of pyrylium salts with various C-nucleophiles.



a Ar = Ph
b Ar = 4-$MeOC_6H_4$
c Ar = 4-BrC_6H_4

We are grateful to the Russian Foundation for Basic Research for financial support by grant no. 93-03-5439.

References

1 A. T. Balaban, A. Dinculescu, G. N. Dorofeenko, G. W. Fischer, A. V. Coblic, V. V. Mezheritskii and W. Schroth, *Pyrylium Salts. Synthesis, Reactions and Physical Properties* in *Adv. Heterocycl. Chem.*, Academic Press, New York, 1982, Suppl. vol. 2.
2 T. Zimmerman and G. W. Fischer, *J. Pract. Chem.*, 1987, **329**, 975.
3 V. F. Lipnitski and O. P. Shvaika, *Khim. Geterotsikl. Soedin.*, 1988, 1685 (in Russian).
4 A. I. Pyschev, E. T. Oganesyan, L. I. Butenko, N. V. Shibaeva and L. I. Pyscheva, *USSR Pat.* 1553528, 1989.
5 E. V. Kuznetsov and S. V. Verin, *Khim. Geterotsikl. Soedin.*, 1993, 3 (in Russian).

Received: Moscow, 24th January 1995
Cambridge, 13th March 1995; Com. 5/00543D