NEW APPROACHES TO SYNTHESIS OF 4H-CHROMENES

Vitaly A. Osyanin, Dmitry V. Osipov, Anton V. Lukashenko, Yury N. Klimochkin

Samara State Technical University, 443100 Samara, Russia

The synthesis of benzoannelated 4H-pyrans and polyfunctional compounds of the phenol series based on the cascade transformations of o-quinone methides (o-QMs) has recently attracted considerable interest. Retrosynthetic analysis of 4H-chromenes shows that they can be obtained by addition of alkynes to o-QMs:

However, in practice, *o*-QMs, being electron-deficient heterodienes, react only with electron-enriched dienophiles, usually olefins, and do not react with alkynes even under pressure and in the presence of Lewis acids. The report will consider two approaches to solve this problem.

The first approach is based on the formal [4+1]-cycloaddition of acyl carbenes to *o*-QMs with the formation of 2-acyl-2,3-dihydrobenzofurans, followed by their reductive rearrangement into 4*H*-chromenes. Pyridinium ylides can act as synthetic equivalents of acyl carbenes. The second approach is based on the Diels-Alder reaction between *o*-QMs and highly polarized (push-pull) olefins, followed by the elimination of one of the substituents.

In addition, the report will consider ways of modifying the resulting annelated 4*H*-pyrans in order to produce various flavonoids, as well as compounds of the phenol series as a result of recyclization under the action of mono- and binucleophiles.

$$\begin{array}{c} R \\ O \\ Nu_1 \\ Nu_2 \\ \end{array}$$