CARBOALKOXY-SUBSTITUTED PYRYLIUM SALTS

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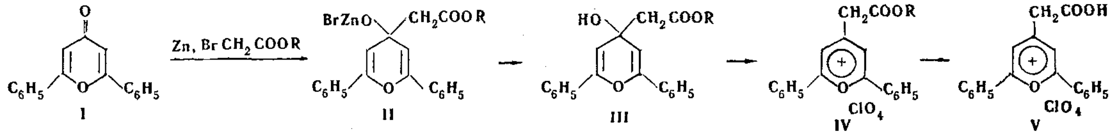
Grignard reagents are widely used for the synthesis of alkyl- and aryl-substituted pyrylium salts from pyrones [1, 2]. However, these and other known methods for the synthesis of a pyrylium ring do not make it possible to obtain pyrylium cations with functional substitutents. We have used the Reformatskii reaction [3] for the synthesis of carboalkoxy-substituted pyrylium salts from 2,6-diphenyl-4-pyrone, 2,6-diphenyl-4-thiapyrone, flavone, and xanthone. The reaction of the latter with methyl bromoacetate (or ethyl bromoacetate) in the presence of activated zinc in dry benzene gives the typical (for the Reformatskii reaction) organometallic complex (II), which is hydrolyzed to pyranol III on treatment with dilute acetic acid (the pyranol was identified by elementary analysis and IR spectrum.) Treatment of III with perchloric acid converts it to perchlorate IV:



To carry out the reaction, a mixture of the pyrone, bromoacetic acid ester, and a two- to threefold excess of zinc in dry benzene is heated until the reaction commences and for another 10-15 min to complete it (the end of the reaction is judged from the cessation of spontaneous refluxing of the reaction mixture.) The residue was decomposed with water and acetic acid, and the pyranol was extracted with ether. A 1.5-fold excess of perchloric acid was then added to the dried extract. The resulting precipitated salt was purified by recrystallization from nitromethane. The following compounds were synthesized (salt, percent yield, and melting point given): 2,6-diphenyl-4-(carbomethoxymethylene)pyrylium perchlorate, 67, 235°; 4-(carbomethoxymethylene)flavylium perchlorate, 92, 208-209°; 9-(carbomethoxymethylene)xanthylium perchlorate, 68, 220-221°. The properties of the pyrylium perchlorates are similar to those of the triarylpyrylium salts. Their structures were proved by IR spectra and hydrolysis to the corresponding carboxymethylpyrylium salts of the V type.

The character of the course of the reaction, the isolation and identification of pyranol III, and the high yields of final products are evidence for the unambiguous character of the process and confirm the proposed reaction scheme.

LITERATURE CITED

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