APPLICATION OF ORGANOLITHIUM COMPOUNDS OF BENZOTHIAZOLE AND PYRIDINE IN THE SYNTHESIS OF 4-HETERYLPYRYLIUM SALTS

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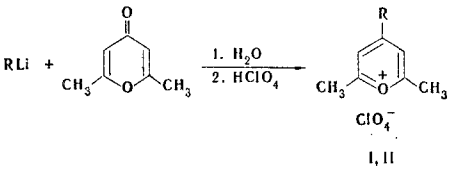
UDC 547.812.5'822'789.6.07:542.957

Little study has been devoted to methods for the preparation of pyrylium salts with heterocyclic substituents in the 4 position. The synthesis of pyrylium salts with heterocyclic substituents in the 4 position (N-substituted indole, indazole, and pyrrole) by cyclization of heterocyclic 1,5-diketones [1] or by means of direct pyrylation of heterocyclic compounds [2] has been reported. Pyrylium salts containing benzothiazole or pyridine substituents were previously unknown. In order to obtain the indicated compounds, we developed a new method for the synthesis of 4-heterylpyrylium salts from organolithium derivatives of benzothiazole and pyridine and 2,6-dimethyl-γ-pyrone. Treatment of the intermediately formed pyranols with perchloric acid gives 2,6-dimethyl-4-(2-benzothiazolyl)- and 2,6-dimethyl-4-(2-pyridyl)pyrylium perchlorates (I, II).



I, II

I R = 2-benzothiazolyl II R = 2-pyridyl

The results of elementary analysis and the IR spectra confirm the composition and structure of I and II.

EXPERIMENTAL

2,6-Dimethyl-4-(2-benzothiazolyl)pyrylium Perchlorate (I). A 2.9-g (0.02 mole) sample of benzothiazole was metallated with butyllithium, obtained from 0.3 g (0.04 g-atom) of lithium and 3.84 g (0.028 mole) of butyl bromide, in 30 ml of absolute ether at −75° in the course of 10-15 min. The resulting 2-lithiobenzothiazole was then allowed to react with 2.05 g (0.016 mole) of 2,6-dimethyl-γ-pyrone. The reaction was carried out at −75° for 1.5 h, after which the temperature was gradually raised to room temperature. At the end of the reaction, 10 ml of water and 20 ml of 28% perchloric acid were added to the mixture. The precipitated I was removed by filtration, washed with a small amount of alcohol and ether, and air-dried to give 3 g (55%) of yellow crystals with mp 215-216° (dec.). Found,%: C 48.8; H 3.8; Cl 10.4; S 9.9. $C_{14}H_{12}ClO_5NS$. Calculated,%: C 49.2; H 3.5; Cl 10.4; S 9.4.

2,6-Dimethyl-4-(2-pyridyl)pyrylium Perchlorate (II). This compound was similarly obtained in 27% yield and had mp 180-182° (dec.). Found,%: C 50.6; H 4.0; Cl 12.6. $C_{12}H_{12}ClO_5N$. Calculated,%: C 50.5; H 4.2; Cl 12.6.

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