SYNTHESIS OF 3-CYANO-6-ARYL-2-PYRONES BY THE ROSENMUND—VON BRAUN REACTION

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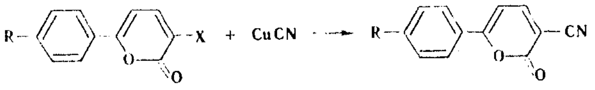
Cyano-2-pyrones are difficult-to-obtain compounds; this is explained, in particular, by the instability of 2-pyrones with respect to the action of the cyanide ion, which even in the cold readily cleaves the 1,6 bond of the pyrone ring to give muconic acid derivatives [1]. The condensation of di- and tricarbonyl compounds with cyanoacetic ester and malononitrile is applicable for the synthesis of only tetrasubstituted 2-pyrones [2]. In order to expand the number of methods for the synthesis of 3-cyano-2-pyrones we investigated the reaction of the accessible 3-halo-6-aryl-2-pyrones [3] with the slightly dissociating cuprous cyanide.



Ia-c IIa,b IIIa-c

I X=Br, II X=I; I–III a R=H; b $R=CH_3$, c $R=CH_3O$

We used the Rosenmund—von Braun reaction to synthesize several 3-cyano-6-aryl-2-pyrones (IIIa-c) by refluxing equimolar amounts (0.05 mole) of cuprous cyanide and 3-bromo-6-aryl-2-pyrones (Ia-c) or 3-iodo-6-aryl-2-pyrones (IIa,b) for 1.5-2 h in 20 ml of dimethylformamide (DMF) with subsequent treatment with a hydrochloric acid solution of ferric chloride.

After recrystallization from alcohol, the yields of pyrones III from II ranged from 53 to 60%, and the yields from I ranged from 15 to 23%. An increase in the reaction time with bromides Ia-c to 2.5-3 h did not lead to an increase in the yields. The IR spectra of pyrones IIIa-c contain absorption bands at 2200-2225 (CN) and at 1705-1730 and 1630-1650 cm^{-1} (pyrone ring). Compound IIIa had mp 184-186°C, IIIb had mp 208-210°C, and IIIc had mp 214-216°C. The results of elemental analysis were in agreement with the calculated values.

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