

A NEW VARIANT OF THE SYNTHESIS OF β, γ' -BIPYRIDYL BY MEANS OF THE CHICHIBABIN REACTION

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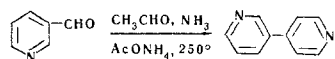
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A new method for the synthesis of β, γ' -bipyridyl by the Chichibabin reaction has been carried out.

Several methods for the preparation of β, γ' -bipyridyl are described in the literature [1-4]. In the majority of cases, it is a byproduct of the reaction. The only method developed specially for the synthesis of β, γ' -bipyridyl is the condensation of β -formylpyridine with ethyl β -aminocrotonate [4]. This synthesis has several stages and gives low yields and therefore cannot be of preparative significance.

This paper describes a synthesis of β, γ' -bipyridyl which is analogous to the preparation of polypyridyls and phenylpyridyls [5] from the corresponding aldehydes and ketones by heating them with ammonia.



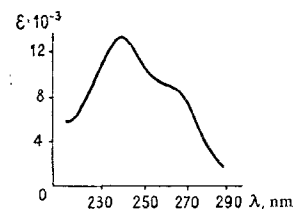
Starting materials for the synthesis are β -formylpyridine, acetaldehyde, and ammonia. The latter are used in excess taking into account the fact that they are used up in the formation of the byproducts of the reaction—collidines.

As in the case of the preparation of polypyridines, ammonium acetate was used as catalyst. The reaction was carried out at various temperatures (180-200° C, 250 and 300° C). Best results were obtained at 250° C. The yield of β, γ' -bipyridyl amounts to from 30 to 40% calculated on the initial β -formylpyridine. α, γ, α' -collidine is formed as a by-product. The UV spectrum of the β, γ' -bipyridyl was recorded; it showed the two maxima (λ_{\max} 240 and 270 nm) characteristic for β, γ' -bipyridyl.

EXPERIMENTAL

Typical experiment. A 50-ml steel autoclave was charged with a mixture of 3 g (0.028 mole) of β -formylpyridine and 13.1 g (0.298

mole) of acetaldehyde. With cooling, 9.8 ml of a 25% solution of ammonia and 23.1 g (0.300 mole) of ammonium acetate was added to

UV spectrum of β, γ' -bipyridyl.

the mixture of aldehydes. The reaction mixture was heated at 250° C for 3 hr and was then dissolved in ethanol. After the ethanol had been distilled off, the residue was treated with alkali to decompose the ammonium acetate, and the mixture was heated to drive off the ammonia liberated. The residue consisted of an oily mass the vacuum distillation of which yielded α, γ, α' -collidine with bp 66-67° C (15 mm) and β, γ' -bipyridyl with bp 144-146° C (15 mm), which gradually crystallized in the receiver. The yield of β, γ' -bipyridyl was 1.4 g (32%). Mp 61-62° C (from petroleum ether). Readily soluble in water, ethanol, and benzene, and sparingly soluble in petroleum ether. Picrate-mp 208-209° C.

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