REACTION OF 5-BROMO-2,3'-DIPYRIDYL WITH MAGNESIUM IN THE PRESENCE OF ETHYL BROMIDE

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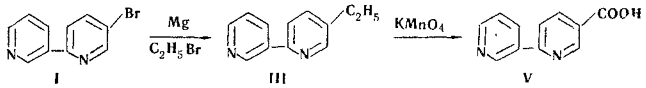
5-Ethyl-2,3'-dipyridyl was obtained by the reaction of 5-bromo-2,3'-dipyridyl with magnesium in the presence of ethyl bromide. The yield of the Grignard reagent did not exceed 20%.

In a continuation of our study of the properties of 5-bromo-2,3'-dipyridyl (I) [1,2], we made an attempt to obtain a Grignard reagent from it. It was found that I itself does not react with magnesium. We therefore used the "escort" method, which was employed in the case of halopyridines [3]. Ethyl bromide (II) was chosen as the "escorting" agent.

A series of experiments demonstrated that the major product of the reaction is 5-ethyl-2,3'-dipyridyl (III); the best yield (52%) of it is observed when the ratio of I to II is 1 : 3. The yield of the Grignard reagent, from the amount of 2,3'-dipyridyl (IV) liberated, was no higher than 20% in all cases. Oxidation of III gave the known [4] 2,3'-dipyridyl-5-carboxylic acid (V).



EXPERIMENTAL

5-Ethyl-2,3'-dipyridyl (III). A solution of 6.4 g (0.04 mole) of I and 7.3 ml (0.12 mole) of II in 30 ml of ether was added dropwise to a refluxing mixture of 3.9 g (0.1 g-atom) of magnesium powder and several drops of II in 20 ml of absolute ether. The mixture was refluxed for 1 h, and the bulk of the ether was removed by distillation. The mixture was then heated for 2 h on a water bath, 30 ml of ether was added, and the mixture was refluxed for another 2 h. The contents of the flask were cooled with ice and decomposed, and the mixture was made alkaline and steam distilled. The distillate was saturated with sodium carbonate, extracted with benzene, and distilled to give 0.65 g (20%) of IV [bp 160-164° (10 mm); picrate mp 163-165°] and 2.3 g (52%) of III [bp 158-162° (4 mm)]. Found %: N 15.3, 15.4. $C_{12}H_{12}N_2$. Calculated %: N 15.2. The picrate had mp 158-160°. Found %: N 18.0, 18.2. $C_{12}H_{12}N_2 \cdot 2C_6H_3N_3O_7$. Calculated %: N 18.1. The methiodide melted at 214-216°. Found %: N 6.1, 6.2. $C_{14}H_{18}I_2N_2$. Calculated %: N 6.2.

2,3'-Dipyridyl-5-carboxylic Acid (V). A solution of 8.9 g (0.05 mole) of $KMnO_4$ in 250 ml of water was added dropwise to 1.9 g (0.01 mole) of III in 100 ml of water, and the mixture was allowed to stand for 10 h. The excess permanganate was decomposed by the addition of methanol. The precipitate was removed by filtration, and the filtrate was washed with water. The aqueous extracts were concentrated to 10 ml and acidified to pH 2 with hydrochloric acid. The precipitated V was removed by filtration and recrystallized from water to give 1.2 g (60%) of V with mp 280-282° (mp 281-283° [4]).

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