REACTION OF 2-ETHOXYCARBONYL-1-CYANO-1,2-DIHYDRO-ISOQUINOLINE AND 1-METHOXYCARBONYL-2-CYANO-1,2-DIHYDROQUINOLINE WITH CARBOXYLIC ACIDS

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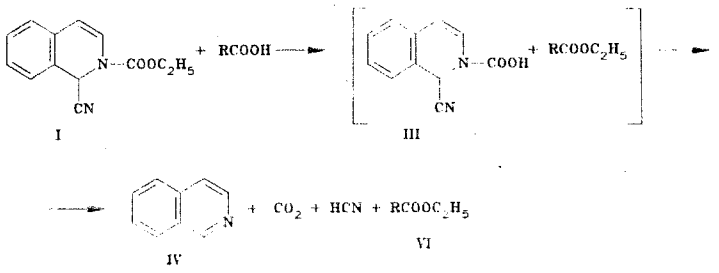
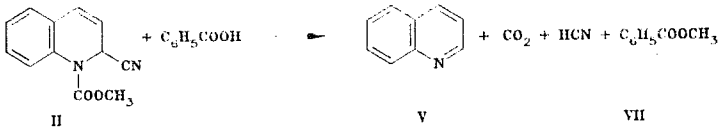
Heating Reissert compounds with inorganic acids is a well known method for preparing aldehydes; simultaneously by hydrolysis of the cyano group, quinoline (isoquinoline)carboxylic acids form [1]. We have established that the reaction of Reissert compounds that are derivatives of isoquinoline (I) or quinoline (II) with carboxylic acids proceeds in an unusual way. Heating equimolar amounts of I with a carboxylic acid (cyclohexanecarboxylic, benzoic) is accompanied by evolution of carbon dioxide and hydrogen cyanide, and a mixture of isoquinoline and the ester of the organic acid forms in high yield:



I III IV VI

$R = C_5H_{11}$, *cyclo*-C_6H_{11}, C_6H_5

The quinoline derivative II reacts similarly with benzoic acid:



II V VII

Thus, under these conditions there is tranesterification, followed by decarboxylation of the carbamic acid derivative (e.g., III) and aromatization of 1-cyano-1,2-dihydroisoquinoline (or 2-cyano-1,2-dihydroquinoline) by splitting out of hydrogen cyanide. Consequently the observed conversion proceeds like a retro-Reissert reaction.

The reaction was carried out by heating a mixture of the reagents for 4 h at 130-140°; the reaction mixture was cooled and dissolved in chloroform, and IV or V (75-80%) and VI or VII (75-85% were determined by GLC. For GLC we used a LKhM-8A instrument, with katharometer detector, column 3 m × 4 mm packed with 12% NPGS + 2% H_3PO_4 on 100/120 mesh Chromosorb W-HP, and nitrogen carrier gas. The reaction products were identified by comparison with authentic samples. Quantitative determinations were made by the procedure of [2], with naphthalene as internal standard. To trap the evolved hydrogen cyanide the reaction was carried out in a current of nitrogen that was passed through a 0.5% solution of NaOH. Titrimetric determination of cyanide ion by the method of [3] showed that the yield of hydrocyanic acid was 78-84%.

LITERATURE CITED

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