2- AND 4-ETHYNYLQUINOLINES

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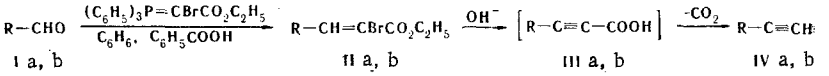
2- and 4-Ethynylquinolines are of interest as starting compounds for the synthesis of polymers with semiconductor properties [1]. However, up until now no preparative method for the synthesis of these compounds has been known [2, 3].

We synthesized 2- and 4-ethynylquinolines by means of the Wittig reaction via the following scheme:



I—IV a R = 2-quinolyl; b R = 4-quinolyl

β-(2- or 4-Quinolyl)-α-bromoacrylic acid esters were obtained by refluxing aldehydes Ia, b with carbethoxybromomethylenetriphenylphosphorane in benzene for 6 h in the presence of a catalytic amount of benzoic acid. Esters IIa, b, with mp 58-59° (IIa) and 48° (IIb, from hexane), were obtained in 95-96% yield. Treatment of esters IIa, b with a solution of potassium hydroxide in alcohol at room temperature leads to unstable quinolylpropiolic acids IIIa, b. 2-Quinolylpropiolic acid is readily decarboxylated when it is heated in alcohol to give a solid black polymer and a small amount of a light-yellow oil, the IR spectrum of which contains absorption bands of 2-ethynylquinoline ($CHCl_3$, cm^{-1}): 2124 (C ≡ C) and 3300 (≡ C − H). We were unable to isolate pure IVa. 4-Ethynylquinoline was obtained in high yield (75%) by decarboxylation of the potassium salt of acid IIIb by steam distillation and had mp 95° (from hexane). IR spectrum ($CHCl_3$, cm^{-1}): 2118 (C ≡ C) and 3303 (≡ CH). Only a polymer is formed from acid IIIa under similar conditions. Decarboxylation of the hydrochloride of acid IIIa by heating in alcohol in the presence of a catalytic amount of copper sulfate leads to β-chlorovinylquinoline (V), with mp 57-58° (from petroleum ether), in 32% yield. The purity of the compounds was monitored by thin-layer chromatography. The results of elementary analysis were in agreement with the calculated values.

LITERATURE CITED

1. Ya. M. Paushkin, T. P. Vishnyakova, A. F. Lunin, and S. A. Nizova, Organic Polymeric Semiconductors [in Russian], Khimiya, Moscow (1971), p. 113.
2. U. Haug and H. Furst, Chem. Ber., 93, 593 (1960).
3. U. Fritzsche, Tetrahedron Lett., No. 47, 4831 (1972).

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