LETTERS TO THE EDITOR

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:

$$\begin{array}{c} \textbf{R}-CHO & \frac{(C_6H_5)_3P=CBrCO_2C_2H_5}{C_6H_6, C_6H_5COOH} \quad \textbf{R}-CH=CBrCO_2C_2H_5 \quad \frac{OH^-}{C_6H_6, C_6H_5COOH} \quad \frac{-CO_2}{R-C=CH} \\ \textbf{i.a., b} & \textbf{ii.a., b} & \textbf{iii.a., b} & \textbf{iii.a., b} \\ I-IV \ \textbf{a} \ \textbf{R}=2-\textbf{quinolyl}; \ \textbf{b} \ \textbf{R}=4-\textbf{quinolyl} \end{array}$$

 β -(2- or 4-Quinoly1)- 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 (CHCl₃, 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 (CHCl₃, 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.

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