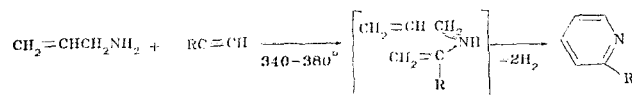


CYCLOADDITION OF ACETYLENE AND PHENYLACETYLENE TO ALLYLAMINE

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UDC 547.821.2'311'312'333.1:542.97

The addition of an acetylene fragment to unsaturated amines with subsequent cyclization has not been described in the literature. We have established a previously unknown type of addition of acetylene and phenylacetylene to allylamine at high temperature in the presence of heterogeneous catalysts that leads to the formation of pyridine or 2-phenylpyridine via the scheme



The method is of preparative value for the synthesis of alkyl- and arylpyridines with predesignated structures.

Experiments were carried out with a flow apparatus. A reactor was charged with 100 ml (pour volume) of a cadmium-fluorine-aluminum catalyst containing 80.0% $\gamma\text{-Al}_2\text{O}_3$, 15.0% CdF_2 , and 5.0% AlF_3 [the specific area measured by the BET (Brunauer-Emmett-Teller) method was 110 m^2/g], and an equimolar mixture of acetylene and allylamine was passed through the catalyst layer at 340–380°C (the best temperature was 360°C). The catalyzate was analyzed by gas-liquid chromatography (GLC) with an LKhM-8MD chromatograph with a thermal-conductivity detector; the column temperature was 120°C, the packing was Apiezon M/Celite-545, the carrier-gas (helium) flow rate was 60 ml/min, and the internal standard was toluene. The catalyzate was also subjected to rectification. A pyridine fraction, with bp 112–116°C, n_D^{20} 1.5105, d_4^{20} 0.982, and picrate mp 166°C, was isolated in 22% yield. The unchanged allylamine was recycled. A mixture of 28.5 g (0.5 mole) of allylamine and 51 g (0.5 mole) of phenylacetylene was passed through the catalyst under similar conditions. Fractional distillation of the catalyzate gave 14 g (18%) of a 2-phenylpyridine fraction with bp 265–278°C, which was analyzed by GLC. PMR spectrum (CCl_4 , tetramethylsilane as the internal standard): 7.0–7.4 (5H, m, aromatic protons), 7.73–7.83 (1H, t), and 7.84–8.24 ppm (1H, d). The picrate had mp 176°C.

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