

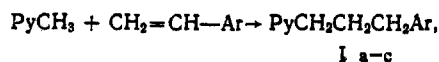
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RADICAL ADDITION OF ALKYLPIRIDINES TO STYRENE

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The reaction of alkylpyridines with styrene in the presence of metallic sodium is known [1, 2]. The phenylpropylpyridines formed are of interest as fungicides, herbicides, and surface-active agents [3]. We have proposed a method for obtaining phenylpropylpyridines by the free-radical addition of alkylpyridines to styrene. The reaction of 2-, 3-, and 4-methylpyridines with styrene have been investigated under the conditions of thermal initiation at 250-350°C for 3 h. To limit the processes of telomerization and polymerization we used a ratio of methylpyridine to styrene of 75-100:1. With the 2-, 3-, and 4-methylpyridines the process took place with the formation of the corresponding 2-, 3-, and 4-phenylpropylpyridines (Ia-c) in accordance with the equation



where Ar = C₆H₅, and Py = pyridin-2-, -3-, and -4-yl (Ia, b, and c, respectively) with yields of 31, 37, and 30% of theoretical, calculated on the styrene taken in the reaction, respectively.

In addition to the 1:1 adducts (Ia-c), the products of the oxidation and dehydrodimerization of the alkylpyridines were also detected and identified, their amount depending on the nature of the methylpyridine and the reaction conditions.

The experiments were performed in a three-liter steel autoclave under a pressure of the vapors of the reactants (20-70 atm). After the end of the reaction, the bulk of the methylpyridine was distilled off and the residue was analyzed by GLC using 4-benzylpyridine as internal standard. The individual adducts (Ia-c) were isolated with the aid of preparative GLC from the fractions obtained on vacuum distillation of the residue. Column 600 × 0.9 cm; stationary phase 20% of FFAP on Chromosorb W; column temperature 170-245°C (1°C/min), temperature of the detector 260°C and of the evaporator 250°C.

The physical constants of (Ia-c) coincided with those given in the literature [4]. The mass spectra of (Ia-c) contained peaks with m/z 197 (M⁺) 106, 105, 92, and 91. The characteristics of the PMR spectra also confirmed the structures (Ia-c) given above.

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