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Abstract

Full Text

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ISOLATION OF 4-VINYLPYRIDINE FROM MIXTURES OF PYRIDINE BASES

Vinylpyridines can serve as monomers for obtaining polymers possessing a number of valuable properties. The authors have developed a method for obtaining 4-vinylpyridine by catalytic dehydrogenation of 4-ethylpyridine, which is to be reported separately. The difficulty lay in isolating 4-vinylpyridine from the liquid catalyst. The data of a study that made it possible to overcome this difficulty are presented below. The results obtained are of independent significance for the analysis and isolation of 4-vinylpyridine.

The difficulty of isolating vinylaromatic compounds by rectification from a mixture of dehydrogenation products arises from the thermal polymerization of vinyl compounds. Another reason complicating the separation of the mixture is that the boiling points of the starting and resulting vinyl compounds are, as a rule, very close.

Fig. 1. Chromatograms of mixture I of pyridine bases and 4-vinylpyridine, isolated from it through a complex with Cu_2Cl_2:
1 —water, 2 —pyridine, 3 —γ-picoline, 4 —4-ethylpyridine, 5 —4-vinylpyridine

To avoid these difficulties, a number of other methods have been proposed for isolating vinylaromatic compounds.

Thus, for isolating chlorostyrenes (1), mixtures containing these compounds were subjected to treatment under conditions causing polymerization of the chlorostyrenes, after which the unpolymerized products were distilled off, and the polymer was again depolymerized to the monomer. The difficultly separable mixture of ethyl- and vinyltoluenes was separated by azeotropic distillation (2).

Chromatogram

Figure 2: Chromatogram

For isolating vinylpyridines from catalysts for the dehydrogenation of alkylpyridine derivatives, fractional crystallization at low temperature (3, 4), distribution of vinyl- and alkylpyridines in two layers, organic and aqueous, upon acidification of the mixture (5, 6), and also countercurrent extraction of the mixture with an acidic solution and a hydrocarbon (7) have been proposed.

For isolating 4-vinylpyridine from a mixture of pyridine bases formed in the dehydrogenation of 4-ethylpyridine, we successfully applied a method previously used for the extraction of divinyl compounds (isoprene, divinyl) (8). The method is based on the ability of vinyl compounds to form π-complexes with cuprous chloride.

Pyridine bases also form complexes with Cu_2Cl_2 through nitrogen (9), which, however, as we established, are readily destroyed by treatment with hydrochloric acid. Therefore, the 4-vinylpyridine complex was obtained in a hydrochloric acid medium.

The hydrochloride of the complex of 4-vinylpyridine with Cu_2Cl_2 is a light-green substance, stable at temperatures up to 100°, and can be stored for a long time in the open air without any changes. The free complex, which is a dark-yellow powder, possesses the same stability.

Although the composition of the complex corresponds to the formula $2C_5H_7N \cdot Cu_2Cl_2$, complete isolation of 4-vinylpyridine from a mixture of pyridine bases requires an excess of cuprous chloride, up to an equimolecular ratio. The use of a stoichiometric amount of Cu_2Cl_2 leads to a considerable decrease in the completeness of isolation of 4-vinylpyridine.

Extraction of 4-vinylpyridine was carried out from dilute 25% (I) and concentrated 70% (II) solutions of 4-vinylpyridine. In both cases, about 80% of the 4-vinylpyridine present in the mixture was isolated. However, the purity of the product obtained was different in each case.

In the case where the content of 4-vinylpyridine in the mixture is low (Fig. 1), decomposition of the complex gave 4-vinylpyridine of 88% purity. When 4-vinylpyridine was extracted from a mixture enriched in the latter, the purity of the product obtained was 98.11% (Fig. 2).

Fig. 2. Chromatograms of mixture II of pyridine bases and of 4-vinylpyridine isolated from it through the complex with Cu_2Cl_2: *1* —water, *2* —pyridine, *3* — γ-picoline, *4* —4-ethylpyridine, *5* —4-vinylpyridine.

The composition of the mixtures and the purity of the isolated 4-vinylpyridine were determined by gas-liquid chromatography on an KhL-4 chromatograph, using polyethylene glycol, mol. wt. 1500, as the stationary liquid phase, applied

to NaCl crystals (diameter 0.25-0.5) in an amount of 0.4%. Beforehand, 1% KOH was applied to the NaCl. The column length was 2 m. Separation was carried out at 90°. The carrier gas—helium—was passed through at a rate of 35 ml/min.

Thus, from mixtures of pyridine bases containing 4-vinylpyridine, the latter can be isolated through the complex with Cu_2Cl_2 in sufficiently pure form.

Experimental Part

Method for isolating 4-vinylpyridine from mixtures of pyridine bases

To 1 mole of Cu_2Cl_2, 1.8 liters of water are added, and then concentrated HCl is added to the suspension of cuprous chloride in water until the Cu_2Cl_2 is completely dissolved and a clear solution is obtained. To the resulting solution, with shaking and cooling, a mixture of pyridine bases containing 1 mole of 4-vinylpyridine is added in portions. Upon subsequent cooling, the hydrochloride of the 4-vinylpyridine complex precipitates; it is filtered off and pressed well on the filter. It is then transferred to a round-bottom flask, treated with an excess of alkali, and steam-distilled. From the resulting distillate, 4-vinylpyridine is salted out with potassium carbonate and dried over KOH. In this way, 80% of the 4-vinylpyridine present in the mixture is extracted.

After reprecipitation of the complex hydrochloride from dimethylformamide with water, a dark-yellow substance was obtained.

$C_{10}H_{14}N_2Cl_2Cl_2$.	Found, %:	C 41.37, H 3.82
	Calculated, %:	C 41.18, H 3.43

The pyridine bases remaining after extraction of 4-vinylpyridine are isolated from the filtrate by alkalizing the latter and subsequent steam distillation.

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Note: Figure translations are in progress. See original paper for figures.