

Synthesis of 3-Picoline and 3-Ethylpyridine

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ONE of the most successful syntheses of pyridine is from tetrahydrofurfuryl alcohol and ammonia in the vapour phase over alumina-supported catalysts at 500°.^{1,2} It is shown here that it is possible to modify this reaction so that besides pyridine, either 3-picoline or 3-ethylpyridine may be produced.

The Table compares the yields of pyridines obtained using an Al₂O₃-MoO₃ catalyst containing 8.6% MoO₃ by weight, when ethylamine, ethanol, or methanol, respectively, are included in the tetrahydrofurfuryl alcohol fed to the reactor.

530° causes a decrease in conversion into pyridine (IV) and n-valeronitrile (VI) with an accompanying increase in gaseous products. At these temperatures the rate of degradation of the intermediate (III) becomes faster than the rate of cyclization.

The comparatively high yields of pyridinic products obtainable from this reaction⁵ stem from the flexibility of the saturated 5-carbon chain of the intermediate which enables cyclization to occur. This steric consideration is emphasized by the fact that reaction between furfuryl alcohol and ammonia does not give pyridine.⁶ In this case,

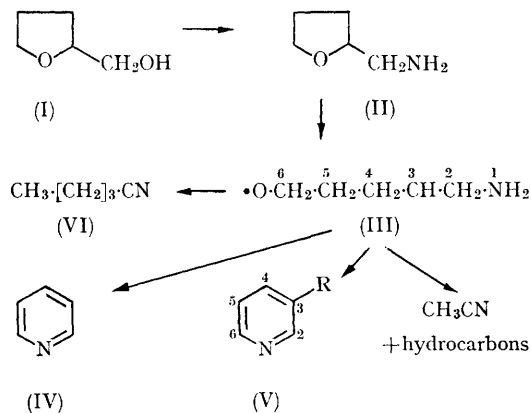
TABLE

Mole percent of pyridinic product; mole ratio THFA: NH₃ ~ 1:4; temperature 475°; catalyst volume 44 c.c., duration of run 3 hr., contact time ~ 1.3 sec.

Compound added	None	EtNH ₂	EtNH ₂	EtNH ₂	EtOH	MeOH
Mole ratio THFA : additive	1:0	1:0.4	1:0.75	1:1.5	1:1	1:1
Pyridine	20.0	7.9	7.6	8.8	7.5	13.0
3-Picoline	5.6	3.3	3.5	4.2	3.8	17.7
3-Ethylpyridine	3.5	18.9	21.5	24.1	19.8	1.8

The principal by-products of the reaction, analyzed by gas-liquid chromatography and infrared spectroscopy, were n-valeronitrile and acetonitrile. Smaller amounts of unidentified products were also present.

Available evidence³ indicates that tetrahydrofurfuryl alcohol (I) and ammonia react initially to form 2-aminomethyltetrahydrofuran (II). Rupture of the tetrahydrofuran ring at the ether linkage⁴ will give the free-radical intermediate (III) which subsequently cyclizes to pyridine. Degradation of (III) will also occur producing methyl and to a smaller extent ethyl radicals which attack the ruptured bond of the intermediate either before or during cyclization so that alkylation of the pyridine ring takes place selectively at the 3-position (V). The inclusion of methyl or ethyl compounds in the feed to the reactor merely increases the availability of methyl or ethyl radicals which can react with the intermediate postulated, so that 3-alkylpyridines result (V). It is evident, from the relative amounts of 3-picoline and 3-ethylpyridine compared with pyridine (IV) found in the products from tetrahydrofurfuryl alcohol and ammonia (Table) that the rate of cyclization at 475° is faster than the rate of degradation. Raising the temperature above



resinous products are formed because once the ether linkage of the furan ring is broken, the resulting unsaturated carbon chain is more rigid and polymerization predominates.

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