

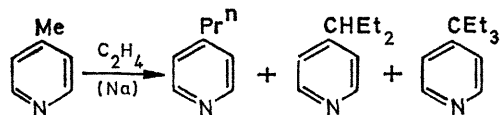
## Novel Cyclisation Reaction of 3-Ethylpyridine with Ethylene<sup>1</sup>

By HERMAN PINES\* and S. V. KANNAN

(The Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201)

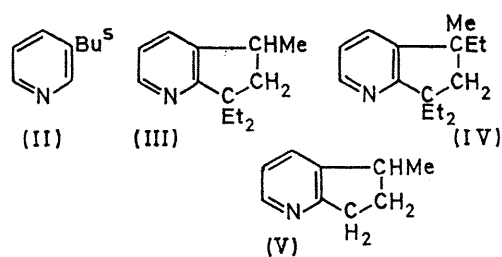
**Summary** The sodium-catalysed reaction of 3-ethylpyridine with ethylene formed 3-s-butylpyridine (II) and cyclic compound (III) as the primary products; (II) and (III) undergo further ethylation to form cyclic compound (IV).

THE sodium- and potassium-catalysed side-chain alkylation,<sup>2</sup> alkenylation,<sup>1,3</sup> and aralkylation<sup>4</sup> of 2- and 4-alkylpyridines have been extensively investigated in our laboratory. Mono-, di-, and tri-addition products are formed in these reactions; *e.g.*



The study has now been extended by us to the reactions of 3-alkylpyridines. We found that these behave differently

to give rise to pyridine derivatives under the same reaction conditions.



Ethylene was introduced into an autoclave containing a dispersion of a catalytic quantity of sodium in 3-ethylpyridine (I) at a pressure of 40 atm. The reaction started at a temp. of *ca.* 145°. The products were worked-up and analysed by g.l.c. Structural assignments were based on microanalysis, and i.r. and n.m.r. spectra.

The primary products of the reaction between 3-ethylpyridine and ethylene were 3-s-butylpyridine (II) and 7,7-diethyl-6,7-dihydro-5-methyl-5H-1-pyridine (III). When the reaction time was prolonged, another product,

5,7,7-triethyl-6,7-dihydro-5-methyl-5H-1-pyridine (IV) was also formed. The results are summarized in the Table.

*Composition of products of the reaction of ethylene with 3-ethylpyridine*

Reaction time (hr.)	Percentage conversion of (I) <sup>a</sup>	Weight percentage of the products <sup>b</sup>		
		(II)	(III)	(IV)
2.5	17	42	58	0
7.0	41	42	47	11
15.0	64	34	49	18
26.0	82	25	33	35

<sup>a</sup> Isopropylcyclohexane was used as an internal standard to calculate percentage conversion.

<sup>b</sup> Calculated from g.l.c. peak areas, uncorrected for thermal conductivity factors, by triangulation method for 100% reaction of 3-ethylpyridine.

A carbanion mechanism, suggested for the reactions of 2- and 4-alkylpyridines<sup>2</sup> and for the cycloethylation of alkylbenzenes,<sup>5</sup> will explain the observed reaction course. The cyclisation exclusively happening at position 2 is in accordance with the high reactivity of that position for nucleophilic substitutions. The absence of (V) in the products and the presence of its dialkyl derivative (III) shows that it is very reactive under the reaction conditions. It is diethylated at position 7 in preference to ethylation at position 5 because of the greater acidity of the proton in position 7.

The cyclic product (III) can undergo further ethylation at position 5 to give rise to (IV). Ethylation of pure 3-s-butylpyridine with ethylene under the same conditions gave only one product *viz.* (IV).

(Received, September 22nd, 1969; Com. 1426.)

<sup>1</sup> Previous paper: W. M. Stalick and H. Pines, *J. Org. Chem.*, submitted for publication.

<sup>2</sup> (a) H. Pines and D. Wunderlich, *J. Amer. Chem. Soc.*, 1959, **81**, 2568; (b) H. Pines and B. Notari, *ibid.*, 1960, **82**, 2209.

<sup>3</sup> (a) H. Pines and J. Oszczapowicz, *J. Org. Chem.*, 1967, **32**, 3183; (b) W. M. Stalick and H. Pines, *ibid.*, in the press.

<sup>4</sup> (a) H. Pines and N. E. Sartoris, *J. Org. Chem.*, **34**, 2113; (b) N. E. Sartoris and H. Pines, *ibid.*, 1969, **34**, 2119.

<sup>5</sup> L. A. Schaap and H. Pines, *J. Amer. Chem. Soc.*, 1957, **79**, 4967.