Other crystallization and sublimation fractions had infrared absorption bands characteristic of cyanotriphenylmethane (2230 cm.$^{-1}$, potassium bromide disk), triphenylmethyl peroxide, and mercuric cyanide. No attempt was made to isolate all products from these fractions.

DEPARTMENT OF CHEMISTRY
NORTH TEXAS STATE COLLEGE
DENTON, TEX.

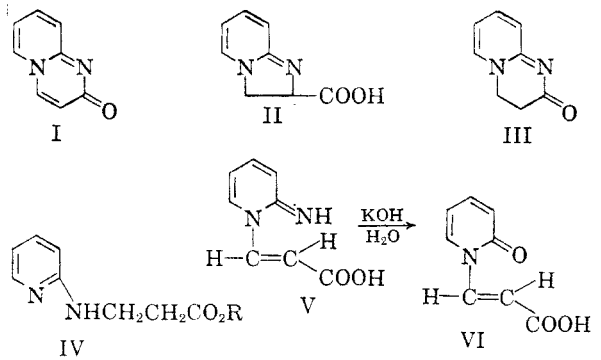
Reaction of 2-Aminopyridine with Propiolic Acid

IRWIN J. PACHTER[1]

Received March 17, 1961

In a previous paper[2] it was shown that 2-aminopyridine reacts with α-bromoacrylic acid at the ring nitrogen atom to produce 2*H*-pyrido[1,2-*a*]-pyrimidin-2-one (I). A by-product, considered to be 2,3-dihydroimidazo-[1,2-*a*]pyridine-2-carboxylic acid (II) on the basis of analogy to previous work[3] was also obtained.

Subsequently, Lappin[4] showed that 2-aminopyridine reacts with acrylic esters at both the ring and α-amino nitrogen atoms to form 3,4-dihydro-2*H*-pyrido[1,2-*a*]pyrimidin-2-one (III) and esters of *N*-(2-pyridyl)-β-alanine (IV).



In extending these studies on the addition of 2-aminopyridine to derivatives of unsaturated acids, the reaction with propiolic acid was investigated. Two colorless compounds were obtained, one of which is 2*H*-pyrido[1,2-*a*]pyrimidin-2-one (I). The second product, an amino acid, fails to cyclize when heated and must therefore be a *trans* adduct. It is the *ring* nitrogen derivative, *trans*-2-imino-1-(2*H*)-pyridineacrylic acid (V), as treatment with alkali results in evolution of ammonia and formation of *trans*-2-oxo-1(2*H*)pyridineacrylic acid (VI). No evidence for reaction of propiolic acid at the α-amino nitrogen atom was obtained.

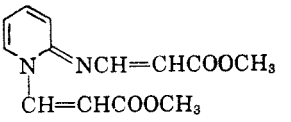
(1) Present address: Research and Development Division, Smith Kline and French Laboratories, Philadelphia 1, Pa.

(2) R. Adams and I. J. Pachter, *J. Am. Chem. Soc.*, **74**, 5491 (1952).

(3) R. Adams and I. J. Pachter, *J. Am. Chem. Soc.*, **74**, 4906 (1958).

(4) G. R. Lappin, *J. Org. Chem.*, **23**, 1358 (1958).

Lappin[5] recently reported the reaction of 2-aminopyridine with methyl propiolate. He found that the highly exothermic reaction produced I and the colored diadduct VII. Although none of the monoadduct corresponding to V was obtained in



VII

the reaction, such adducts could be obtained when certain substituted 2-aminopyridines were used.

EXPERIMENTAL

Reaction of 2-aminopyridine with propiolic acid. To 7.0 g. of propiolic acid was added 10.0 g. of 2-aminopyridine. Heat was evolved as 2-aminopyridinium propiolate formed. Upon heating to 100°, reaction occurred with evolution of gas and spontaneous temperature rise to 150°. The mixture was kept at this temperature for 5 min. and then cooled. The resulting solid was broken up and extracted three times with 25-ml. portions of hot 2-propanol. The insoluble residue was recrystallized from water to give 5.5 g. of *trans*-2-imino-1-(2*H*)-pyridineacrylic acid (V), m.p. 255° (dec.). The compound is a monohydrate.

Anal. Calcd. for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.78; H, 5.62; N, 15.19.

Evaporation of the aqueous mother liquor from the crystallization of V left a residue which largely dissolved in hot 2-propanol. The 2-propanol solution was combined with the extracts previously obtained and the total was evaporated to dryness. The residue was dissolved in methanol and the resulting solution diluted with chloroform. An additional 0.3 g. of V separated. The methanol-chloroform solution, upon concentration, gave 4.0 g. of 2*H*-pyrido[1,2-*a*]pyrimidin-2-one (I), m.p. 245°, which was identified with a previously obtained sample.

trans-2-Oxo-1(2H)-pyridineacrylic acid (VI). To 1.0 g. of *trans*-2-imino-1(2*H*)pyridineacrylic acid (V) was added 0.5 g. of potassium hydroxide and 10 ml. of water. The solution was heated under reflux for 30 min. It turned red in color and ammonia was evolved. The solution was acidified with dilute sulfuric acid and a solid separated Recrystallization from ethanol with charcoal treatment gave 0.53 g. of needles of VI which, after one further recrystallization from ethanol, melted at 220–225° dec.

Anal. Calcd. for $C_8H_7NO_3$: C, 58.18; H, 4.27; N, 8.48. Found: C, 57.70; H, 4.26; N, 8.24.

ETHYL CORP.
FERNDALE 20
DETROIT, MICH.

(5) G. R. Lappin, *Distillation Products Industries Organic Chemical Bulletin*, **33** (1), 1961, and private communication.

Direct Synthesis of *p*-Styryldiphenylphosphine

ROBERT RABINOWITZ AND RUTH MARCUS

Received March 22, 1961

A recent article[1] describes a multistep synthetic route to *p*-styryldiphenylphosphine, I. The proce-

(1) A. E. Senear, W. Valient, and J. Wirth, *J. Org. Chem.*, 25, 2001 (1960).