the general polyphosphoric acid cyclization directions.[9] Procedure described in Experimental was typical and appeared to be general for this type of cyclization.

In view of elimination of the two extra steps of tosylation and detosylation and the simplicity of the experimental procedure, this new method offers clear advantages over those previously reported and provides a convenient synthetic route for the preparation of quinoline derivatives.

This study is currently being extended to isoquinolones, oxindoles and 5-ketotetrahydrobenzazepines. Additional findings will be reported later.

Experimental

4-Keto-6-chloro-1,2,3,4-tetrahydroquinoline (I).—A mixture of 6 g. of 2-(*p*-chloroanilino)propionic acid[10] and 100 g. of polyphosphoric acid in a 150-ml. beaker was heated on a hot plate with hand stirring until the temperature reached 120° (around 20 min.,) and was then kept between 120–125° for 20 min. After cooling to 80° the cherry-red reaction mixture was poured into 300 ml. of ice–water with stirring. After a few hours, the yellow precipitate was filtered and washed with water to provide 2.1 g. of pure chloroquinolone (I), m.p. 124–126°. The filtrate was saturated with sodium chloride and extracted with ether, from which another 1.5 g. of material was isolated, m.p. 116–120°. The combined yield of nearly pure product was 3.6 g. (66%). Recrystallization from benzene–petroleum ether gave canary yellow crystals, m.p. 124–126° (reported m.p. 112°[5] and 125–126°[11]).

Similarly, after 10 min. at 130°, II was obtained in 60% yield without the necessity of extraction of the aqueous solution. It seems of interest to point out that I and II did not form phosphoric acid salts. However, compound III was sufficiently basic to necessitate neutralization in order to isolate the yellow product in 55% yield. I, II, and III all gave positive dinitrophenylhydrazine tests and exhibited a strong carbonyl absorption band in the infrared spectrum at 1650 cm.$^{-1}$.

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A Simple Preparation of Nipecotic Acid

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A straightforward catalytic reduction of nicotinic acid uncomplicated by decarboxylation has never been reported. While successful hydrogenation of the isomeric 2- and 4-acids in neutral solution has been carried out with ruthenium dioxide,[1] with 5% rhodium on carbon,[2] and more recently with platinum oxide,[3] the same conditions cannot be applied to the 3-acid. Extensive decarboxylation occurred in each attempt. Some success was achieved with rhodium on carbon[2] but extensive decarboxylation did occur. A 44% yield of nipecotic acid was obtained but the result was not reproducible.

Decarboxylation can be prevented by hydrogenation of the hydrochloride salt according to the general method of Hamilton and Adams[4] for the reduction of pyridines, or by conversion in the form of the sodium salt.[5] However, isolation of the free acid in each instance leaves much to be desired. Decarboxylation has been observed by Sorm[6] even under acidic conditions. He reported that when nicotinic acid was hydrogenated in acetic acid solution, 50% of piperidine was obtained while reduction in dilute hydrochloric acid gave about 10% of piperidine as a result of decarboxylation.

It occurred to us that the resultant piperidine nitrogen should be basic enough to displace ammonia if a solution of ammonium nicotinate would be hydrogenated and that free nipecotic acid should be obtained. We were led to anticipate success by some work, still incomplete, on the reduction of some pyridylalkanoic acids.

Actual work-up, after hydrogenation, proved to be very simple. It was only necessary to concentrate the solution, after removal of catalyst, to obtain nipecotic acid in very good yield.

Experimental

Nipecotic Acid.—A suspension of 6.15 g. (0.05 mole) of nicotinic acid in 50 cc. of water was treated with 5–6 cc. of concentrated aqueous ammonia and hydrogenated in the presence of 2.4 g. of 5% rhodium on alumina at room temperature and 2 atm. Uptake of hydrogen was complete in 4 hr. or less. The solution was filtered and concentrated to dryness under reduced pressure. To ensure complete removal of water the residue was treated with pure anhydrous benzol and reconcentrated. The yield of product melting at 260–261° was 5.7 g. (88.5%). Infrared examination[7] shows that it is identical to a known standard. A mixed melting point with an authentic sample showed no depression. For further proof, the product was submitted for analysis.

Anal. Calcd. for $C_6H_{11}NO_2$: C, 55.79; H, 8.58; N, 10.84; O, 24.77. Found: C, 55.64; H, 8.54; N, 10.91; O, 24.88.[8]

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Quinoxaline Studies. XI. Unequivocal Syntheses of *cis*- and *trans-dl*-Decahydroquinoxalines. Resolution of *trans-dl*-Decahydroquinoxalines[1–3]

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In 1952, Beck, Hamlin, and Weston[4] reported the preparation of *trans*-decahydroquinoxaline (m.p. 150–151°) by the cyclization of 2-(β-aminoethylamino)-cyclohexanol. Four years later Christie, Rohde, and Schultz[5] reported that the reduction of an ethanolic

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