washed with water and dried. Concentration of the chloroform solution followed by distillation of the residue gave 3.1 g. of X as a colorless oil; b.p. 160–170° at 0.5 mm., n_D^{25} 1.5490.

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84. Found: C, 64.55; H, 7.86.

Deoxygenation of X with phosphorus trichloride using the procedure described previously for the deoxygenation of IV gave 2-(β-ethoxyethyl)pyridine in 100% yield as a colorless oil. The infrared spectrum and refractive index of this oil were in good agreement with those of an authentic specimen.[7]

Addition of pyrrole to 2-vinylpyridine N-oxide. A mixture of 0.5 g. of sodium, 13.0 g. of pyrrole, and 5.0 g. of 2-vinyl pyridine *N*-oxide was boiled under reflux for 2 hr. It was then poured into ice water and extracted with three 75-ml. portions of ether. After the ether solution had been dried, it was concentrated and the residue distilled to give an oil (b.p. 160–180° at 0.05 mm.) which crystallized in the receiver as a hygroscopic white solid, m.p. 103–111°. There was obtained 5.6 g. (73%) of XI.

Anal. Calcd. for $C_{11}H_{12}N_2O$: C, 70.18; H, 6.43. Found: C, 70.08; H, 6.60.

Deoxygenation of XI with phosphorus trichloride was carried out as previously described for the deoxygenation of IV and gave 2[β-(*N*-pyrrolo)ethylpyridine in 52% yield as a colorless oil. The infrared spectrum and refractive index of this oil were in good agreement with those of an authentic specimen.[10]

ROCHESTER, N. Y.

(10) H. E. Reich and R. Levine, *J. Am. Chem. Soc.*, 77, 4913 (1955).

[CONTRIBUTION FROM THE ORGANIC RESEARCH DIVISION, ABBOTT LABORATORIES]

Reductions with Ruthenium. II. Its Use in the Hydrogenation of Pyridines[1]

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The preparation of a number of piperidines by catalytic hydrogenation of the corresponding pyridines with ruthenium dioxide at 90–100° and 70–100 atmospheres is reported. Its activity in the presence of various substituents is discussed.

The activity of ruthenium catalysts in the hydrogenation of phenylalkylamines[2] led us to conduct a study of it in the reduction of other nitrogen-containing compounds. This report covers the use of ruthenium dioxide in the hydrogenation of pyridine and substituted pyridines.

Low pressure reduction of the pyridine ring requires the presence of acid to prevent poisoning when platinum catalyst is used.[3] This is disadvantageous when it is necessary to isolate the corresponding piperidine base. In addition, there are reports that in some instances hydrogen uptake is slow and further addition of platinum catalyst is necessary.[4] Rhodium has been reported to be effective[5] but in some unpublished work in this laboratory it has been noted that ring reduction appears to be strongly hindered by certain substituents. Raney nickel is the catalyst most widely used for the higher pressure hydrogenation of pyridine compounds. The conditions generally described consist of reaction at 150–300 atmospheres pressure and temperatures above 150° for varying lengths of time.[6] Particularly pyridine itself required more drastic conditions than many of its derivatives.[6]

By contrast, in the presence of ruthenium dioxide pyridine is readily converted to piperidine in quantitative yield under much milder conditions. By raising the reaction temperature to 200° as little as 0.1% of this catalyst is sufficient to carry the reduction to completion in little more than one hour.

The use of alcohols as solvents is often precluded in Raney nickel reductions because of the possibility of *N*-alkylation resulting from the rather rigorous reaction conditions.[7] The hydrogenation of 2,3-dimethylpyridine in ethanol yielding 1-ethyl-2,3-dimethylpiperidine under such conditions is a striking example. The advantage of the use of alcohols is shown in the reduction of 2-β-hydroxyethylpyridine to the corresponding piperidine (XII). In methanol the reaction time was cut from three to four hours without solvent to a matter of a few minutes in its presence. Moreover, in this instance, as well as in other hydrogenations where an alcohol was used, there was no evidence of *N*-alkylation.

Single substituents on the pyridine ring, particularly nonbasic ones, seem to have little effect on the rate of hydrogenation. In the preparation of 2,4,6-trimethylpiperidine (XV), however, steric effects no doubt inhibited ring reduction. The use of alcohol as solvent produced only a moderate increase in the speed of hydrogen uptake.

(1) Presented at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961.

(2) M. Freifelder and G. R. Stone, *J. Am. Chem. Soc.*, 80, 5270 (1958).

(3) T. S. Hamilton and R. Adams, *J. Am. Chem. Soc.*, 50, 2260 (1928).

(4) J. Overhof and J. P. Wibaut, *Rev. trav. chim.*, 50, 957 (1931), and J. Finkelstein and R. C. Elderfield, *J. Org. Chem.*, 4, 365 (1939).

(5) G. Gilman and G. Cohn, *Advances in Catalysis*, Academic Press, Inc., New York, 1957, Vol. 9, p. 707–715.

(6) H. Adkins, L. F. Kuick, M. Farlow, and B. Wojcik, *J. Am. Chem. Soc.*, 56, 2425 (1934).

(7) J. I. Jones, *J. Chem. Soc.*, 1932 (1950), points out that even some *N*-alkylation occurs when Raney nickel, that has been stored over alcohol, is used.

The hydrogenation of the isomeric carboxypyridines is of interest. Extensive decarboxylation occurred during the conversion of nicotinic acid to nipecotic acid, yet it was not observed in the reduction of the other isomers. It was prevented by carrying out the reduction in water in the presence of an equivalent of sodium bicarbonate. That only the acid is affected is shown by the high yields obtained during conversion of the methyl and ethyl esters, and the amide and diethylamide of nicotinic acid to the corresponding piperidines, VI, IX, X, and XI.

The catalytic activity of ruthenium dioxide seems to extend beyond its ability to reduce the pyridine ring. Its tendency to cause debenzylation is noted in the hydrogenation of 4-(β-benzylaminoethyl)-pyridine. In addition to the main fraction, 4-β-aminoethylpiperidine was obtained in 11.5% yield. The main portion was proved to be 4-(β-cyclohexylmethylaminoethyl)piperidine (XIX) instead of the desired 4-(β-benzylaminoethyl)piperidine. The insufficient selectivity between reduction of pyridine ring and benzene ring noted here was further borne out by the hydrogenation of 2- and 4-benzylpyridine. While there is little doubt that the pyridine ring reduces first, vapor phase chromatography and infrared examination of the products of reduction point to the tendency toward formation of 2- and 4-cyclohexylmethylpiperidine (XIII and XIV), respectively.

The reduction of pyridines with basic side chains gave the first indication that ruthenium catalysts might be subject to the same poisoning by nitrogen containing compounds as described by Maxted[8] and others.[3,6] The retardation of hydrogen uptake is pronounced only when the amino group in the side chain is primary. This was somewhat surprising since in our original work with ruthenium[2] neither the structurally related phenylalkyl primary amines nor the resulting cyclohexyl derivatives seemed to have an adverse effect on the catalyst. In this study, as can be seen from the table, the short reaction time required to convert most of the pyridines to the corresponding piperidines is evidence that these bases also do not affect ruthenium catalysts. The slower uptake of hydrogen observed in the preparation of XVI, XVII, and XVIII is no doubt due to the combined effects of the primary amino group and the piperidine nitrogen.

The effect of a secondary or tertiary nitrogen in the side chain on the rate of hydrogenation with ruthenium is not too well defined. The differences in reduction time in the preparation of XIX, XX, and XXI may be due to the quality of the starting pyridines.

(8) E. B. Maxted and A. G. Walker, *J. Chem. Soc.*, 1093 (1948); E. B. Maxted and M. S. Biggs, *J. Chem. Soc.*, 3844 (1957).

EXPERIMENTAL[9]

The reaction conditions described for the following reduction of pyridine, except for use of solvent, are typical of those used for the preparation of the compounds listed in Table I.

Piperidine I. One mole (79.1 g.) of pyridine was hydrogenated in the presence of 1.58 g. (2% by weight of pyridine) of ruthenium dioxide[10] at 95° and 70–100 atm. pressure. Uptake of hydrogen was complete in less than 0.5 hr.

In similar reduction with 0.08 g. of catalyst at 200°, uptake of hydrogen was complete in 1.5 hr. 2-Picoline was converted to 2-pipecoline in about 20 min. under similar reaction conditions.

N-Alkylation during reduction with Raney nickel in alcohol. A solution of 107 g. (1.0 mole) of 2,3-dimethylpyridine in ethanol was hydrogenated at 150° under 200 atm. pressure in the presence of 20 g. of Raney nickel. After hydrogen uptake was complete (12–15 hr.) the mixture was cooled and filtered from the catalyst. After removal of the solvent a fraction distilling at 155–165° (750 mm.), n_D^{25} 14491 was collected. It weighed 49 g. and was shown by analysis to be 1-ethyl-2,3-dimethylpiperidine.

Anal. Calcd. for $C_9H_{19}N$: C, 76.52; H, 13.55; Found: C, 76.39; H, 13.53.

Sodium nipecotate (IV). A solution of 61.5 g. (0.5 mole) of nicotinic acid in 300 cc. of water containing 42.0 g. (0.5 mole) of sodium bicarbonate was hydrogenated in the presence of 1.22 g. of ruthenium dioxide at 95° and 100 atm. pressure. Uptake of hydrogen was complete in about 15 min. After cooling, the reaction mixture was filtered from the catalyst and evaporated to dryness. The residue was dissolved in hot absolute alcohol and filtered. Since it did not crystallize, the solution was reconcentrated and treated with acetone. After filtration and washing 65 g. of sodium nipecotate was obtained.

Anal. Calcd. for $C_6H_{11}NO_2Na$: N, 9.26. Found: N, 9.09.

Infrared examination further confirmed its structure.

Decarboxylation during reduction. A solution of 61.5 g. (0.5 mole) of nicotinic acid in 250 cc. of water was hydrogenated in the presence of 1.22 g. of ruthenium dioxide at 95° and 100 atm. pressure. In three similar experiments hydrogen uptake was never above 70%. After the reaction mixture was cooled it was filtered from the catalyst. The solution was treated with 42 g. (0.5 mole) of sodium bicarbonate and steam distilled into 0.5 mole of dilute hydrochloric acid until the distillate was no longer basic. The acidic distillate was concentrated to dryness yielding 26 g. of piperidine hydrochloride (43%).

Decarboxylation was also noted when rhodium catalyst was used at low pressure. There was, however, no evidence of it in the preparation of III or V in the presence of ruthenium.

Hydrogenation of 2- and 4-benzylpyridine. A mixture of 84.6 g. (0.5 mole) of 2-benzylpyridine and 1.7 g. of ruthenium dioxide was hydrogenated at 90–100° and 100 atm. pressure. Uptake of hydrogen was very rapid and appeared to go beyond the required uptake of 1.5 moles. Four fractions were obtained boiling at 128–130°, 130–131°, 131–132° and 132–134° at 13 mm. (for 2-benzylpiperidine 131–132°, 13 mm.).[6] The index of each fraction rose markedly. Infrared examination, analyses of the fractions, and melting points of the hydrochloride salts of each fraction indicated all were mixtures.

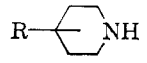
In another experiment half the amount of catalyst was used in an effort to control the hydrogenation. The reaction was stopped at uptake of 1.5 moles of hydrogen. Twelve fraction cuts, each less than 0.5° apart, were taken. The

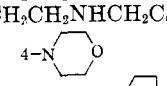
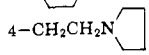
(9) Most of the starting substituted pyridines are commercially available or may be prepared by known literature methods.

(10) Available from Baker & Co., Division of Engelhard Industries, 113 Astor St., Newark, N. J.

TABLE I

PIPERIDINES



	R	Solvent[a]	Time, Hr.	Yield, %	B.P.	Pressure, Mm.	n_D^{25}	Formula
I	H	A	<0.5	100[f]				$C_5H_{11}N$
II	2-CH_3	A	[b]	91	115–117[h]	Atm.	1.4455	$C_6H_{13}N$
III	2-COOH	B	[b]	85	[i]			$C_6H_{11}NO_2$
IV	3-COONa	B	0.25	86				$C_6H_{10}NO_2Na$
V	4-COOH	B	0.5	91	[j]			$C_6H_{11}NO_2$
VI	3-$COOCH_3$	C	[b]	89	82–84[k]	6		$C_7H_{13}NO_2$
VII	4-$COOCH_3$	C	0.5	86	91–93[l]	10	1.4632	$C_7H_{13}NO_2$
VIII	2-$COOC_2H_5$	D	[b]	92	103–104[m]	20	1.4548	$C_8H_{15}NO_2$
IX	3-$COOC_2H_5$	D		90[g]	97–99.5	17	1.4482	$C_9H_{17}NO_2$[g]
X	3-$CONH_2$	B	0.8	85	[n]			$C_6H_{12}N_2O$
XI	3-$CON(C_2H_5)_2$	C	1	89	127–128[o]	3	1.4877	$C_{10}H_{20}N_2O$
XII	2-CH_2CH_2OH	C	[b,c]	94	114–115[p]	10	1.4887	$C_7H_{15}NO$
XIII	2-$CH_2C_6H_{11}$	A	0.5	88	127–128	13	1.4850	$C_{12}H_{23}N$
XIV	4-$CH_2C_6H_{11}$	A	2	83	139–140[q]	17	1.4864	$C_{12}H_{23}N$
XV	2,4,6-CH_3	A	12[d]	88	82–85[r]	100		$C_8H_{17}N$
XVI	3-CH_2NH_2	C	11	78	114–118	50	1.4905	$C_6H_{14}N_2$
XVII	2-$CH_2CH_2NH_2$	C	[e]	78.6	87–91[s]	10	1.4840	$C_7H_{16}N_2$
XVIII	4-$CH_2CH_2NH_2$	C	6	80	93–96	8.5	1.4920	$C_7H_{16}N_2$[t]
XIX	4-$CH_2CH_2NHCH_2C_6H_{11}$	C	1	56	186–187	10	1.4926	$C_{14}H_{28}N_2$
XX		B	0.3	55	80–87[l]	0.3		$C_9H_{18}N_2O$
XXI		A	1.5–2.0	85	120[u]	4	1.4950	$C_{11}H_{22}N_2$

[a] A, no solvent; B, water; C, methanol; D, ethanol. [b] Uptake of hydrogen was complete by the time the temperature reached 90–100°. [c] When no solvent was used, complete hydrogen uptake required 3–4 hr. reaction time. [d] Uptake of hydrogen was very slow. It was necessary to raise the temperature to 150° and increase the pressure to 170 atm. Hydrogen uptake was somewhat improved when methanol was used. [e] It was necessary to rehydrogenate with a second portion of catalyst. [f] The product filtered from the catalyst was not distilled. Infrared examination indicated complete conversion to piperidine. [g] The product was not distilled but was reductively methylated with formaldehyde in the presence of 5% palladium on carbon. Ethyl *N*-methylnipecotate was obtained in a 90% over-all yield based on ethyl nicotinate. The constants are in agreement with those of R. F. Feldkamp, J. A. Faust, and A. J. Cushman, *J. Am. Chem. Soc.*, **74**, 3831 (1952). [h] See ref. 6. [i] M.p. 279–280. Described, 264°. R. Willstatter, *Ber.*, **29**, 389 (1896). [j] M.p. 326–330. K. Freudenberg, *Ber.*, **51**, 1668 (1918) gives m.p. as above 320°. [k] Hydrochloride salt melts at 133–135°. Lit. 131–133°, see ref. j. [l] M.p. of hydrochloride salt, 167°. Lit. 169°. V. Hanowsek and V. Prelog, *Coll. Czech. Chem. Com.*, **4**, 259 (1932). [m] Lit. 107° (20 mm.). See ref. 6. [n] M.p. 110–111° as described by H. H. Fox, *J. Org. Chem.*, **17**, 543 (1952). [o] British Pat. **316,195** (1930), gives 154–156°, (14 mm.). [p] C. W. Tullock and S. M. McElvain, *J. Am. Chem. Soc.*, **61**, 962 (1939), gives 105–108° (7 mm.). [q] M.p. of hydrochloride salt, 301–302°. Lit. 296°, see ref. 12. [r] W. Koenigs, *Ber.*, **40**, 3199 (1907) gives 165–166° at atmospheric pressure. [s] Lit. b.p. 106–107° (10 mm.), K. Loffler and M. Kirschner, *Ber.*, **38**, 3336 (1905). It was further characterized as a dihydrochloride salt, m.p. 201–203°. *Anal.* Calcd. for $C_7H_{16}N_2 \cdot 2HCl$: C, 41.79; H, 9.01; N, 13.93. Found: C, 41.91; H, 9.25; N, 13.93. [t] Solidified and melted at 50–55°. It absorbed carbon dioxide too rapidly to give satisfactory carbon and hydrogen values. Calcd. for $C_9H_{18}N_2O$: N, 16.46. Found: N, 16.26. [u] A. P. Phillips, *J. Am. Chem. Soc.*, **79**, 2836 (1957) characterized the product as the dihydrochloride salt, m.p. 266–267° after reduction of the corresponding pyridine dihydrochloride with Adams catalyst. In this Laboratory it was characterized as base. *Anal.* Calcd. for $C_{11}H_{22}N_2$: C, 72.47; H, 12.16; N, 15.37. Found: C, 72.35; H, 12.08; N, 15.36. [v] *Anal.* Calcd. for $C_7H_{16}N_2$: C, 65.57; H, 12.58. Found: C, 65.48; H, 11.84. It was further characterized by conversion to a dihydrochloride salt which melted sharply at 245°.

index of refraction of each rose progressively from 1.5084 to 1.5240 at 25°. Vapor phase chromatography indicated only two components. The lower boiling product was 2-cyclohexylmethylpiperidine (XIII) and the higher one 2-benzylpiperidine. The residue was mostly starting material. The percentage of 2-benzylpiperidine increased with each fraction as its index rose. From these results it appears there is a tendency for reduction to proceed to XIII rather than to stop at 2-benzylpiperidine. The ease with which XIII is formed is shown in the following experiment.

2-Cyclohexylmethylpiperidine (XIII). Sixty-five grams of the mixture of bases obtained in the previous hydrogenations was further reduced with ruthenium dioxide at 100° and 100 atm. pressure. Hydrogen uptake was complete in less than 0.5 hr. On opening the cooled reaction vessel a solid mass was obtained. It was warmed, filtered from the catalyst, and distilled. An 88% yield of 2-cyclohexylmethylpiperidine was obtained, b.p. 127–128°, 13 mm., n_D^{25} 1.4850. It solidified and melted at 33–35°.[11]

Anal. Calcd. for $C_{12}H_{23}N$: C, 79.49; H, 12.78; N, 7.73. Found: C, 79.89; H, 12.50; N, 7.73.

The hydrochloride salt melted at 209–210°.

Anal. Calcd. for $C_{12}H_{23}N \cdot HCl$: C, 66.18; H, 11.11; N, 6.43. Found: C, 66.29; H, 10.96; N, 6.50.

4-Benzylpyridine was hydrogenated under the same conditions used for the 2-benzyl compound. The product of reduction consisted of three fractions distilling at 145–147°; 147–150°, 150–152° at 17 mm., all within the range of the

(11) V. Prelog, L. Frenkiel, and S. Szpilfogel, *Helv. Chim. Acta*, **29**, 484 (1946), give no physical data for the base, only analysis and melting point of a picrolonate.

described boiling point of 4-benzylpiperidine.[12] The index of refraction of each rose progressively. The first fraction on analysis gave a high hydrogen value suggesting a tendency toward formation of XIV. The third fraction gave a hydrochloride melting at 140–165° (m.p. for 4-benzylpiperidine hydrochloride, 169°[8]). Infrared examination of each fraction indicated all were mixtures. By allowing the reduction to proceed until 6 equivalents of hydrogen were taken up XIV was obtained in good yield.

3-Aminomethylpyridine. A solution of 52.5 g. (0.5 mole) of 3-cyanopyridine in 425 cc. of analytical grade methanol containing 51.0 g. (3.0 moles) of anhydrous ammonia was reduced in the presence of 1.0 g. of ruthenium dioxide, at 95° and 120 atm. hydrogen pressure. Uptake of hydrogen was complete in less than 4 hr. After cooling, the contents of the reactor were filtered from the catalyst, which was washed with some alcohol. The solvent was then distilled and the residue fractionated. 3-Aminomethylpyridine boiling at 108–111° (18 mm.) n_D^{25} 1.5471[13] was obtained in 68% yield.

Anal. Calcd. for $C_3H_8N_2$: C, 66.64; H 7.46. Found: C, 66.66; H, 7.83.

The described procedure for the reduction of 2-cyanopyridine using palladium on carbon catalyst in alcoholic hydrogen chloride[14] gave very poor yield with 3-cyanopyridine. Substitution of platinum oxide for palladium caused little change. Low pressure hydrogenation with rhodium in the presence of ammonia[15] also gave low yield (15%). A reduction of an alcoholic solution of 3-cyanopyridine containing acetic acid with rhodium likewise failed to give good yield. Instead, the product obtained was bis(3-pyridylmethyl)amine, b.p. 168–170° (0.3 mm.), n_D^{25} 1.5804. Lit.[13] 170–171° (2 mm.), n_D^{25} 1.5696.

Anal. Calcd. for $C_{12}H_{13}N_3$: C, 72.33; H, 6.57; N, 21.09. Found: C, 71.98; H, 6.69; N, 21.40.

3-Aminomethylpiperidine XVI was also prepared directly from 3-cyanopyridine in 68% yield by hydrogenation in the presence of 6 moles of liquid ammonia with a 5% ratio of ruthenium dioxide at 100–125° and 150 atm. pressure. It distilled at 89° at 18 mm., n_D^{25} 1.4910.

Anal. Calcd. for $C_6H_{14}N_2$: C, 63.11; H, 12.36; N, 24.53. Found: C, 63.39; H, 12.06; N, 24.70.

In the preparation of XVI from 3-aminomethylpyridine 2 equivalents of glacial acetic acid were added to the reaction mixture. The reaction time of 11 hr. noted in Table I was reduced to 2 hr. However, because of the solubility of XVI in water, after removal of the catalyst, concentration of the solution and treatment with excess alkali poor yield resulted unless continuous extraction over a long period was employed.

4-β-(N-Cyclohexylmethyl)aminoethylpiperidine (XIX). A solution of 21.23 g. (0.1 mole) of 4-(β-benzylaminoethyl)-pyridine (b.p. 135–139° (0.1 mm.), n_D^{25} 1.5705) in 50 cc. of analytical grade methanol was hydrogenated in the presence of 0.42 g. of ruthenium dioxide. Over 0.6 mole of hydrogen was taken up in less than 1 hr. After cooling, the solution was filtered from the catalyst. The solvent was distilled and the residue fractionated. A lower boiling fraction, 95–99° (10 mm.), was identified as 4-β-aminoethylpiperidine (XVIII), 11.5% yield. The main fraction was shown to be XIX by analysis and not 4-(β-benzylaminoethyl)piperidine.

Anal. Calcd. for $C_{14}H_{28}N_2$: C, 74.97; H, 12.58; N, 12.49. Found: C, 75.15; H, 12.43; N, 12.52.

4-Chloropyridine 1-oxide. To 120 cc. of acetyl chloride stirred in a round bottom flask was added, in small portions, 25 g. (0.1785 mole) of 4-nitropyridine 1-oxide. The first addition caused refluxing. When addition was complete, the mixture was refluxed for 3 hr. and then allowed to stand overnight. It was then poured into ice, made basic with sodium carbonate, and extracted with chloroform. The chloroform extract was dried over anhydrous magnesium sulfate. After filtration and distillation of solvent an 84% yield of product was obtained. It melted at 167–168° (lit. m.p. 169.5°).[16]

4-Morpholinopyridine 1-oxide.[16] The reaction conditions and work-up described by Ochiai were followed in a run with 54.0 g. (0.416 mole) of 4-chloropyridine 1-oxide and 72.4 g. (0.832 mole) of morpholine in 80 cc. of water. However, the product obtained after recrystallization from acetone melted at 91–92° (described m.p. 75–78°). It was shown by analysis to be hydrated.[17]

Anal. Calcd. for $C_9H_{12}N_2O_2 \cdot H_2O$: C, 54.60; H, 7.07; N, 14.13. Found: C, 54.48; H, 7.36; N, 14.35.

On vacuum drying at 50°, the melting point rose to 197–199°.

Anal. Calcd. for $C_9H_{12}N_2O_2$: C, 59.99; H, 6.71; N, 15.55. Found: C, 59.69; H, 6.05; N, 15.71.

4-Morpholinopyridine. Sixty cubic centimeters of phosphorus trichloride was added dropwise with stirring to a solution of 30 g. (0.167 mole) of 4-morpholinopyridine 1-oxide in 500 cc. of chloroform cooled in an ice bath. The mixture was allowed to warm to room temperature on standing overnight. It was then refluxed for 3–4 hr., cooled and poured into ice. It was treated with 40% sodium hydroxide solution and gradually made basic. When the mixture was finally strongly basic it was extracted with about 2 l. of chloroform. The extract was dried over anhydrous magnesium sulfate and filtered from the drying agent. After distillation of the solvent the crude dried solid weighed 27.0 g. (98.5% yield) and melted at 102–104°. Upon recrystallization from cyclohexane the weight was 23.3 g., m.p. 105–106°.

Anal. Calcd. for $C_9H_{12}NO$: C, 65.83; H, 7.37; N, 17.07. Found: C, 65.90; H, 7.41; N, 16.97.

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NORTH CHICAGO, ILL.

(12) W. L. C. Veer and St. Goldschmidt, *Rec. trav. chim.* **65**, 793 (1946).

(13) H. Adkins, I. A. Wolff, H. Pavlic, and E. Hutchinson, *J. Am. Chem. Soc.*, **66**, 1293 (1944), found 112–113° (18 mm.), n_D^{25} 1.5485.

(14) K. Winterfeld and G. Gierenz, *Ber.*, **92**, 240 (1959).

(15) M. Freifelder, *J. Am. Chem. Soc.*, **82**, 2386 (1960).

(16) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

(17) The monohydrate and anhydrous compound were identified and characterized by R. W. DeNet of the Organic Research Division of this laboratory.