

2,5-Dichloro-3-picoline (II). A stirred solution of 5-amino-2-chloro-3-picoline (I) (3.0 g, 0.021 mol) (7) in concentrated hydrochloric acid (153 ml) was diazotized at 0–5 ° by the slow, dropwise addition of a solution of sodium nitrite (8.3 g) in water (23 ml). Copper powder (16.6 g) was cautiously added to the freshly diazotized solution, and the mixture was allowed to reach room temperature where stirring was continued for 2½ h. The solution was again cooled to ice bath temperature and slowly neutralized with chilled 30% sodium hydroxide. Indirect steam distillation of the neutralized solution afforded the dihalopicoline II as a white solid. Further purification was achieved by recrystallization (Table I).

2-Chloro-5-iodo-3-picoline (III). A stirred solution of I (2.0 g, 0.014 mol) in concentrated hydrochloric acid (7 ml) was diazotized at 0 ° by the slow, dropwise addition of sodium nitrite (1.7 g) in water (4 ml). The freshly diazotized solution was poured into a solution of potassium iodide (8.0 g) in water (6 ml). The resulting mixture was warmed on a steam cone for 5 min, cooled to room temperature, and made basic with 25% sodium hydroxide. Sodium bisulfite was added to the dark suspension which was then stirred overnight. The dihalopicoline III was isolated by indirect steam distillation and purified as described in Table I.

5,6-Dichloro-3-picoline (VII) and 5-iodo-6-chloro-3-picoline (VIII). These compounds were prepared by diazotization of 5-amino-6-chloro-3-picoline (VI) (9) by procedures identical to those employed in the preparation of II and III from I.

2,5-Dichloronicotinic acid (IV), 2-chloro-5-iodonicotinic acid (V), 5,6-dichloronicotinic acid (IX), and 6-chloro-5-

iodonicotinic acid (X). These dihaloacids were prepared by oxidation of the appropriate dihalopicoline (II, III, VII, and VIII, respectively) using potassium permanganate. The general procedure employed has been previously described (6–8).

5-Chloro-6-iodonicotinic acid (XI). A mixture of IX (0.82 g, 0.004 mol), sodium iodide (2.0 g), and methyl ethyl ketone (25 ml) was heated under reflux for 5 days. The precipitated sodium chloride was removed by filtration, and the filtrate was evaporated to dryness. The residual dark solid was leached with 10% sodium bisulfite solution (20 ml) and then recrystallized (Table I) to give pure XI.

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Physical Properties of Some Tertiary Amides

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Thirteen tertiary amides were prepared, and their densities and refractive indices determined. From the measured refractive indices, molar refractivities were calculated and compared with molar refractivities calculated from tables utilizing additive values.

During the course of an investigation of the reduction of some tertiary amides, it was necessary to prepare the amides to be studied. Since the compounds were made from the interaction of amines and acids or acid derivatives, the standard procedure of identifying an amide by hydrolyzing it to an acid and an amine was felt to be inadequate; accordingly, the densities, refractive indices, and molar refractivities of the amides were determined.

The methods used to prepare these amides are described elsewhere (7). (Supplemental information on the preparation of compounds and methods of determining data has been filed with the ACS Microfilm Depository Service.) Table I lists the observed values of the amides, as well as a tabulation of values calculated from the observed values or, in the case of

calculated molar refractivity, values obtained from the Lorenz-Lorentz equation using standard tables and methods (2, 4, 6).

Experimental

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Boiling points were determined during distillation and are reported both corrected and uncorrected. Determination of density was performed using a pycnometer which held 2.0086 g of water at 4.0 °C (6), and refractive indices were measured with a Bausch and Lomb Abbe-3L refractometer connected to a Lauda-thermostated bath utilizing a dry ice heat exchanger charged with ice-water instead of dry ice-isopropanol and connected as illustrated on page 23 of Lauda Bulletin BR 215-B. The prism temperature was maintained at 20.0 °C. M_{rD} (%) was calculated from the equation:

$$\left| \frac{M_{rD}(\text{found}) - M_{rD}(\text{calculated})}{M_{rD}(\text{calculated})} \right| \times 100$$

Table I. Values of Amides

Amide	Bp ^a					Mr _D		
	Obs, °C	Corr, °C	Press, torr	n _D ²⁰	d ⁴	Found	Calcd	% Diff
CH ₃ (CH ₂) ₃ CON(C ₆ H ₄) ₂	118	120	0.01	1.4918 ²⁴	0.9667 ²⁴	79.64	80.13	0.6
CH ₃ (CH ₂) ₄ CON(CH ₃) ₂	58-60	58-60	0.02	1.4434 ²⁶	0.8902 ²⁶	42.69 42.62	43.41	1.7
CH ₃ (CH ₂) ₆ CON(CH ₃) ₂	87	88	0.6	1.4478 ²⁶	0.8815 ²⁶	51.61 51.87	52.55	1.8
CH ₃ (CH ₂) ₈ CON(CH ₃) ₂	108-9	110-2	0.6	1.4485 ²⁶	0.8757 ²⁶	61.00	61.79	1.3
CH ₃ (CH ₂) ₈ CON(CH ₂ CH ₃) ₂	120	133	0.6	1.4505 ²⁶	0.8654 ²⁶	70.67	70.67	0
CH ₃ (CH ₂) ₆ CONφ(CH ₃)	141	144	2.25	1.5032 ²⁵	0.9593 ²⁵	71.93	72.23	0.4
CH ₃ (CH ₂) ₆ CONφ(CH ₂ CH ₃)	124	126	0.6	1.4991 ²⁴	0.9483 ²⁴	76.61	76.67	0.1
CH ₃ (CH ₂) ₆ CONφ((CH ₂) ₃ CH ₃)	118-20	120-22	0.2	1.4947 ²⁷	0.9367 ²⁷	85.70	85.47	0.3
CH ₃ (CH ₂) ₈ CONφ(CH ₃)	135	138	0.05	1.5006 ²⁴	0.9467 ²⁴	81.29	81.47	0.2
CH ₃ (CH ₂) ₂ CON(C ₆ H ₁₁)	87	88	1.0	1.4730 ²⁴	0.9542 ²⁴	49.76	50.00	0.5
CH ₃ (CH ₂) ₆ CON(C ₆ H ₁₁)	114	116	0.6	1.4727 ²⁴	0.9300 ²⁴	63.72	63.86	0.2
CH ₃ (CH ₂) ₆ CON(C ₆ H ₁₀)	140	143	0.8	1.4724 ²⁵	0.9807 ²⁵	60.95	60.88	0.1
CH ₃ (CH ₂) ₆ CON(C ₆ H ₉)	90	91	0.95	1.4743 ²⁴	1.0676 ²⁴	40.88	40.78	0.2

^a Values given are those observed (obs) at the pressure (press) of distillation as well as that temperature corrected (corr) by use of standard stem correction (6). ^b Ref. 3. ^c Ref. 5.

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Supplementary material available: Preparation of compounds and methods of determining data (12 pages). Ordering information is given on any current masthead page.