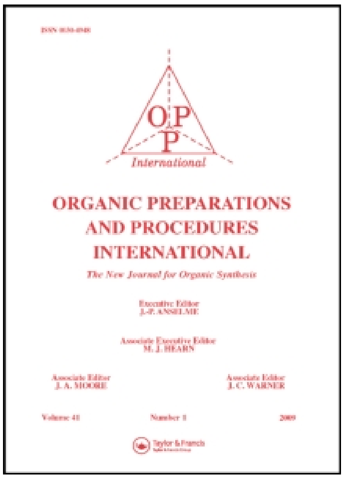

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NEW HALO ACETAMIDO AND BENZAMIDOMETHYLPYRIDINES

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NEW HALO ACETAMIDO AND BENZAMIDOMETHYLPYRIDINES

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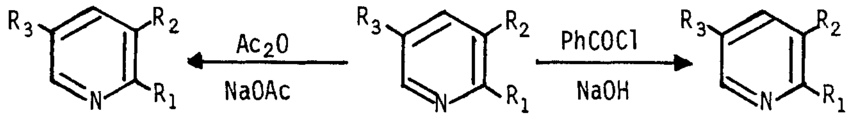
New acetyl derivatives (IIa-d) and benzoyl derivatives (IIIa-d) of several halo aminopicolines (Ia-d) have been prepared. Amine Id (3-amino-2-bromo-5-methylpyridine) yielded only the dibenzoyl derivative (IIId).



II I III

	II			I			III		
	R_1	R_2	R_3	R_1	R_2	R_3	R_1	R_2	R_3
a)	Cl	CH_3	NHAc	Cl	CH_3	NH_2	Cl	CH_3	NHCOPh
b)	Br	CH_3	NHAc	Br	CH_3	NH_2	Br	CH_3	NHCOPh
c)	Cl	NHAc	CH_3	Cl	NH_2	CH_3	Cl	NHCOPh	CH_3
d)	Br	NHAc	CH_3	Br	NH_2	CH_3	Br	$N(COPh)_2$	CH_3

EXPERIMENTAL SECTION

Typical Procedure. Acetylation.- A stirred solution of 5-amino-2-chloro-3-methylpyridine (Ia, 0.5 g, 3.35 mmol) in a mixture of conc. hydrochloric acid (1 ml) and water (10 ml) was brought to slight turbidity by the dropwise addition of 10% sodium hydroxide and the turbidity was then removed by a few drops of 5% hydrochloric acid. Acetic anhydride (15 ml) was added to the stirred solution followed immediately by the addition of a solution of sodium acetate (10.0 g) in water (10 ml). The resulting mixture was warmed to 50° for 5 min. with continued stirring, cooled to 10° (ice bath) and brought to pH 8-9 by the addition of conc. ammonium hydroxide. The resulting mixture was saturated with sodium chloride and allowed to remain in the ice bath for 20 min. The crude acetylated product was filtered, washed thoroughly with cold water, and recrystallized from water to afford 0.58 g (89%) of pure 5-acetamido-2-chloro-3-methylpyridine (IIa) as small white needles, mp. 174-175°.

Typical Procedure. Benzoylation.- A mixture of 5-amino-2-chloro-3-methylpyridine (Ia, 0.5 g, 3.5 mmol), benzoyl chloride (1 ml), and 10% sodium hydroxide (10 ml) in a 25 ml glass-stoppered flask was agitated on a mechanical shaker for 15 min. The resulting solid was filtered, washed with cold water, and recrystallized from aqueous ethanol to afford 0.71 g (83%) of 5-benzamido-2-chloro-3-methylpyridine (IIIa) as white plates, mp. 141-142°.

TABLE 1. Data on Acetyl and Benzoyl Derivatives[a]

Cpd.	mp (°C)	Yield (%)	Elemental Analyses			Found		
			C	H	N	C	H	N
IIa	174-175[b]	89	52.03	4.91	15.17	51.96	5.00	15.15
IIb	157-158[b]	69	41.92	3.95	12.22	42.02	4.00	11.99
IIc	118-119[c]	78	52.03	4.91	15.17	52.15	5.00	15.03
IId	139-140[c]	79	41.92	3.95	12.22	42.13	4.06	12.19
IIIa	141-142[d]	83	63.28	4.49	11.35	62.98	4.33	11.12
IIIb	162-163[d]	74	53.61	3.80	9.62	53.49	3.84	9.48
IIIc	100-101[d]	65	63.28	4.49	11.35	63.40	4.35	11.38
IIId	219-220[d]	33[e]	60.75	3.79	7.09	60.98	3.77	7.08

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a. Mps. and yields are those of analytical samples obtained by recrystallization; Mps. are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. The starting aines (Ia-d) were obtained as previously described [J. Chem. Eng. Data, 17, 515 (1972); Org. Prep. Proced. Int., 9, 13 (1977)]. b. Recrystallized from water. c. Recrystallized from methylcyclohexane. d. Recrystallized from aqueous ethanol. e. Dibenzoylated product.

TABLE 2. Spectral Data

Cpd.	IR (KBr)	^{1}H-NMR, 60 MHz ($CDCl_3$/TMS)
IIa	3235, 1692 cm^{-1}	δ 2.13 (s, 3 H), 2.32 (s, 3H), 7.56 (b, 1H), 7.82-8.15 (m, 2 H)
IIb	3236, 1686 cm^{-1}	δ 2.15 (s, 3 H), 2.33 (s, 3 H), 7.52-8.15 (m, 3 H)
IIc	3263, 1653 cm^{-1}	δ 2.13 (s, 3 H), 2.25 (s, 3 H), 7.57 (b, 1 H), 7.90 (b s, 1 H), 8.51 (b s, 1 H)
IId	3250, 1652 cm^{-1}	δ 2.20 (s, 3 H), 2.31 (s, 3 H), 7.50 (b, 1 H), 7.80 (b s, 1 H), 8.34 (b s, 1 H)
IIIa	3300, 1650 cm^{-1}	δ 2.30 (s, 3 H), 7.20-8.35 (m, 8 H)
IIIb	3290, 1653 cm^{-1}	δ 2.28 (s, 3 H), 7.18-8.39 (m, 8 H)
IIIc	3311, 1650 cm^{-1}	δ 2.30 (s, 3 H), 7.20-8.70 (m, 8 H)
IIId	1675, 1709 cm^{-1} (sh)	δ 2.20 (s, 3 H), 7.15-8.10 (m, 12 H)

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ACTIVATED NITRILES IN HETEROCYCLIC SYNTHESIS. NOVEL SYNTHESIS OF PYRAZOLES, PYRIDONES AND PYRROLO[2,3-b]PYRIDONES

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Functionallized nitriles are versatile reagents which are extensively utilized in heterocyclic synthesis.[1-3] Recently the cyanoacetanilide I has been utilized as starting material for the synthesis of azoles[4] and