The introduction of the Boc group is accomplished with *S-tert*-butyloxycarbonyl-4,6-dimethyl-2-mercaptopyrimidine.[3] Isolation and purification of the desired *N-tert*-butyloxycarbonyl-1,6-diaminohexane as the hydrochloride is readily accomplished in approximately 60% yield. *N-tert*-Butyloxycarbonyl-1,6-diaminohexane is then reacted with the appropriate acid chloride, i.e., acryloyl and 2-methylacryloyl chloride, in the presence of tertiary base to yield *N-tert*-butyloxycarbonyl-*N'*-acrylyl-1,6-diaminohexane or *N-tert*-butyloxycarbonyl-*N'*-(2-methylacrylyl)-1,6-diaminohexane in excellent yield. Finally, the Boc group is removed with 3 M HCl in ethyl acetate to give in nearly quantitative yield the hydrochloride salts of monoacrylated 1,6-diaminohexanes.

Experimental Section

All melting points were determined in open capillary tubes and are reported uncorrected. Thin-layer chromatography was performed on precoated plates of silica gel G-60 F-254 (E. Merck). Compounds were applied in loads of up to 100 μg, and chromatograms were developed for 10–15 cm in the following solvent systems: A, $CHCl_3$–CH_3OH–CH_3CO_2H (9:1:1, v/v/v); B, butanone–CH_3CO_2H–H_2O (15:1:1); C, $CHCl_3$–CH_3OH (9:1); D, acetone–CH_3CO_2H–H_2O (9:1:1). Visualization was performed by UV, Cd/ninhydrin spray,[4] followed by treatment with Cl_2 gas and starch/NaI spray. Products gave single spots under these conditions.

***N-tert*-Butyloxycarbonyl-1,6-diaminohexane·HCl (1).** 1,6-Diaminohexane (23.2 g, 0.2 mol) was dissolved in dioxane (90 mL). To the stirred solution *S-tert*-butyloxycarbonyl-4,6-dimethyl-2-mercaptopyrimidine[3] (24.6 g, 0.1 mol) in dioxane (100 mL) was added slowly over a period of 3 h, and the reaction was allowed to proceed overnight. The precipitate (4,6-dimethyl-2-mercaptopyrimidine) was removed by filtration, and the filtrate was evaporated to 100 mL. The subsequent addition of water (150 mL) precipitated bis(*N,N'-tert*-butyloxycarbonyl)-1,6-diaminohexane (5.95 g, 0.02 mol) which was then removed by filtration. The dioxane was removed from the filtrate under reduced pressure and, following the addition of ~40 g of NaCl, the aqueous solution was extracted with EtOAc (50 mL, four times). The organic phase was pooled and evaporated under reduced pressure. The resulting oil was dissolved in water (100 mL) and acidified with 1 M HCl (70 mL) to a pH of 3. The aqueous phase was washed with EtOAc until the solution was colorless at which time the aqueous solution was saturated with NaCl. *N-tert*-Butyloxycarbonyl-1,6-diaminohexane·HCl crystallized and was isolated by filtration (18.3 g). The product was dissolved in C_2H_5OH (150 mL), decolorized with Norit, and filtered. The ethanol solution was evaporated to ~75 mL and added to 400 mL of acetone. The material, which crystallized shortly thereafter, was then filtered and dried: yield 14.6 g (58%); mp 162.5–163 °C; TLC R_f(A) 0.22, R_f(B) 0.20. Anal. Calcd for $C_{11}H_{25}N_2O_2Cl\cdot\frac{1}{4}H_2O$ (257.3): C, 51.4; H, 10.0; N, 10.9. Found: C, 51.5; H, 10.1; N, 10.5.

***N-tert*-Butyloxycarbonyl-*N'*-(2-methylacrylyl)-1,6-diaminohexane (2).** Compound 1 (7.58 g, 29.5 mmol) was suspended in $CHCl_3$ (200 mL) and cooled in an ice bath and triethylamine (8.74 mL, 63 mmol) was added. To the stirring suspension, 2-methylacryloyl chloride (3.0 mL, 30 mmol) dissolved in $CHCl_3$ (50 mL) was added dropwise. Following the addition, the solution was washed with water (100 mL, thrice), dried with Na_2SO_4, and evaporated in vacuo. The product crystallized upon the addition of hexane: yield 7.37 g (86%); mp 59–60 °C. A sample was recrystallized from benzene–hexane (1:10): mp 61–62 °C; TLC R_f(C) 0.58. Anal. Calcd for $C_{15}H_{28}N_2O_3$ (284.4): C, 63.4; H, 9.92; N, 9.85. Found: C, 63.4; H, 9.82; N, 9.69.

***N-tert*-Butyloxycarbonyl-*N'*-acrylyl-1,6-diaminohexane (3).** A sample of compound 1 (17.8 g, 70.4 mmol) was dissolved in CH_3OH and converted to the free base by elution through a Rexyn 201 (OH^-) column (2 × 50 cm, previously washed with CH_3OH). The CH_3OH was removed in vacuo and the resulting oil, after dissolution in $CHCl_3$ (250 mL) and addition of triethylamine (9.82 mL, 70.4 mmol), was added dropwise to a solution of acryloyl chloride (7.0 mL, 80 mmol) in $CHCl_3$ (250 mL) that was being stirred and kept at −5 to −10 °C. When the reaction solution reached room temperature, it was washed with water (250 mL, four times) and evaporated under reduced pressure and the material was crystallized from benzene: yield 15.9 g (83%), mp 107–109 °C. A sample was recrystallized from benzene: mp 108.5–109.5 °C; TLC R_f(C) 0.51. Anal. Calcd for $C_{14}H_{26}N_2O_3$ (270.4): C, 62.2; H, 9.69; N, 10.4. Found: C, 62.5; H, 9.63; N, 10.3.

***N*-(2-Methylacrylyl)-1,6-diaminohexane·HCl (4).** Compound 2 (2.56 g, 9.0 mmol) was dissolved in 3 M HCl–EtOAc (5 mL). After 30 min the solution was removed in vacuo and the oil was triturated with ether, filtered, and dried: yield 1.92 g (96%); mp 110–112 °C. Since the material was hygroscopic, a sample was converted to the free base by passage through a Rexyn 201 (OH^-) column and crystallized as the tosylate from C_2H_5OH–ether: mp 132–132.5 °C; TLC R_f(D) 0.28. Anal. Calcd for $C_{17}H_{28}N_2O_4S$ (356.5): C, 57.3; H, 7.92; N, 7.86. Found: C, 57.2; H, 7.76; N, 7.65.

***N*-Acrylyl-1,6-diaminohexane·HCl (5).** Compound 3 (2.38 g, 7.54 mmol) was treated with 3 M HCl–EtOAc as described above and the product was isolated in a 98% yield. The material polymerized on heating and melted at ~160 °C. For the purpose of analysis, the tosylate was prepared and crystallized as described for 4: mp 145 °C (sharp); TLC R_f(D) 0.24. Anal. Calcd for $C_{16}H_{26}N_2O_4S$ (342.5): C, 56.1; H, 7.65; N, 8.18. Found: C, 56.1; H, 7.46; N, 7.96.

Note Added in Proof: The overall yield of *N-tert*-butyloxycarbonyl-1,6-diaminohexane·HCl (1) can be further increased by storing the by-product, bis(*N,N'-tert*-butyloxycarbonyl)-1,6-diaminohexane, in anhydrous Et_2O saturated with HCl gas at 25 °C. During the next 12 h, *N-tert*-butyloxycarbonyl-1,6-diaminohexane·HCl crystallizes free of 1,6-diaminohexane·2HCl.

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Registry No.—1 HCl, 65915-94-8; **2**, 65915-95-9; **3**, 65915-96-0; **4**, 65915-97-1; **4** HCl, 65915-98-2; **4** tosylate, 65915-99-3; **5**, 7530-30-5; **5** tosylate, 65916-00-9; **5** HCl, 65916-01-0; 1,6-diaminohexane, 124-09-4; *S*-Boc-4,6-dimethyl-2-mercaptopyrimidine, 41840-28-2; 2-methylacryloyl chloride, 920-46-7; acryloyl chloride, 814-68-6.

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A New Synthesis of α-(2-Pyridyl) Ketones by Acylation of 2-Picolyllithium and 2,6-Lutidyllithium with *N,N*-Dimethylcarboxamides

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In connection with a study[2] of the synthesis and characterization of nickel(II), copper(II), and cobalt(II) complexes of various α-(2-hetaryl) ketones we required a series of α-(2-pyridyl) ketones of type **4**. The most widely used method for the synthesis of such compounds involves reaction of 2-lithiomethylpyridines (**1**) with an appropriate ester.[3–5] The mechanism of this process, as proposed by Levine and Raynolds,[5] involves initial reaction of **1** with the acylating ester to form **2**, which then reacts with more **1** either by proton abstraction to form the enolate of the desired ketone or by

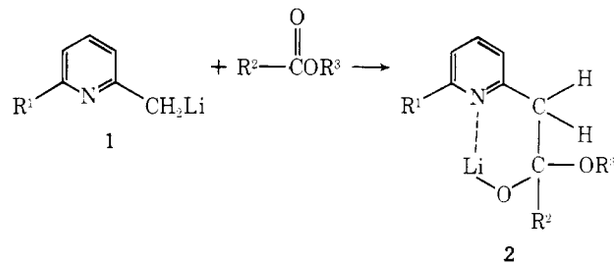

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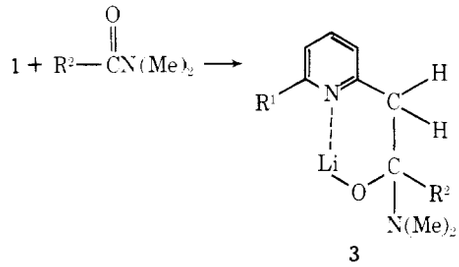
Table I
Acylation of 2-Picolylithium and 2,6-Lutidyllithium with *N,N*-Dimethylcarboxamides

Amide R^2	Registry no.	Ketone product R^1	R^2	No.	Registry no.	Yield, % S.A.[a]	I.A.[b]	Lit. yield, %	Bp, °C (Torr)	Lit. bp, °C (Torr)
CH_3	127-19-5	H	CH_3	**4a**	6302-02-9	79	69	18[c]	60–65 (0.4)	74–75 (1.5)[c]
$(CH_3)_2CH$	21678-37-5	H	$(CH_3)_2CH$	**4b**	10330-59-3	85	67	30[c]	80 (2)	79–85 (2)[c,d]
$(CH_3)_3C$	24331-71-3	H	$(CH_3)_3C$	**4c**	34552-04-0		57		78–83 (0.3)	51–53 (0.15)[d,e]
$C_6H_5CH_2$	18925-69-4	H	$C_6H_5CH_2$	**4d**	50550-53-3		69		133–138 (0.3)	*f*
C_6H_5	611-74-5	H	C_6H_5	**4e**	1620-53-7	51	41	40[c]	100–120 (1)	145–153 (3–4)[c]
CH_3		CH_3	CH_3	**4f**	65702-08-1	69		21[g]	67–72 (0.7)	105–106 (9.9)[g]
$(CH_3)_2CH$		CH_3	$(CH_3)_2CH$	**4g**	65702-09-2	66		31[g]	78–84 (0.7)	119–120.5 (9.5)[g]
$(CH_3)_3C$		CH_3	$(CH_3)_3C$	**4h**	65702-10-5	75			85 (0.7)	*h*

[a] Standard addition. [b] Inverse addition. [c] See ref 3. [d] See ref 8. [e] Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.15; H, 8.69; N, 7.86. [f] Calcd for $C_{14}H_{13}NO$: C, 79.59, H, 6.20; N, 6.63. Found: C, 79.32; H, 6.27; N, 6.64. [g] See ref 4. [h] Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.57; H, 9.11; N, 7.23.

displacement of alkoxide to form the lithium salt of a tertiary alcohol. Since the ionization and displacement reactions usually proceed at rates greater than the rate of formation of **2**, a molecular equivalent of **1** is consumed in a nonproductive fashion with respect to ketone formation. Therefore, a 2:1 molar ratio of 1:acylating ester is routinely employed in these reactions.[3-5] Recently,[6] it has been found that efficient acylations of methylated heteroaromatics with nonenolizable esters can be accomplished with a 1:1 molar ratio of heterocyclic substrate:ester employing excess sodium hydride as the condensing agent. However, when the sodium hydride procedure was attempted with 2-picoline or quinaldine using ethyl acetate as the acylating agent, the rate of ester self-condensation to form ethyl acetoacetate was much more rapid than lateral acylation.[7] Photostimulated $S_{RN}1$ reactions of 2-halopyridines with ketone enolates provide a facile new route to certain ketones of type **4**, but such reactions afford mixtures of products with ketones capable of forming isomeric enolates, and certain enolates, such as those derived from alkyl aryl ketones, fail to react.[8]

Earlier reports[9,10] that *N,N*-dimethylcarboxamides react with organolithium reagents to form ketones prompted us to investigate the possibility of using these compounds for the acylation of lithio salts **1**. It seemed possible that addition of 1 to the amide carbonyl would produce intermediates such as **3**,[5,10] in which the dimethylamino function would serve to



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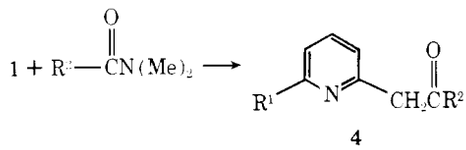
suppress proton abstraction as well as nucleophilic displacement, thereby leading mainly to ketonic products without requiring an extra equivalent of **1**.

Reaction of 2-picolyllithium (**1**, R^1 = H) with a representative series of *N,N*-dimethylcarboxamides afforded ketones **4a–e** in yields of 41 to 85%. Similar acylations of 2,6-lutidyllithium (**1**, R^1 = CH_3) afforded the corresponding α-(6-methyl-2-pyridyl) ketones **4f–h** in yields of 66 to 75%. Results of these experiments are summarized in Table I. In all cases the molar ratio of lithium reagent:acylating amide was 1:1, and



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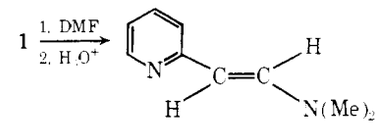
yields are based on the heterocycle. Addition of the metalated methylheteroaromatics to the acylating amide (inverse addition)[12] did not increase the yields over those obtained when the amide was added to the organometallic reagent (normal addition). For comparison purposes, yields of ketones **4a, 4b,** and **4e–g** obtained previously by acylation of **1** (R^1 = H and R^1 = CH_3) with appropriate esters are included in Table I. These yields were recalculated on the basis of 1 as the limiting reagent in order to compare them with the present results. In four of five cases where comparisons can be made, the amide acylation procedure affords yields at least double those involving esters. In addition, no carbinol by-products were detected, whereas acylations of 1 (R^1 = H and R^1 = CH_3) with methyl acetate produce the corresponding tertiary alcohols in yields of 28 and 35%, respectively.[3-5] The steric requirements of the acylating amide exert only minor effects on these reactions as evidenced by the fact that the yields obtained with 1 (R^1 = CH_3) remain essentially constant as the amide R^2 residue is changed from methyl, to isopropyl, to *tert*-butyl. Successful acylation of 1 (R^1 = H) with *N,N*-dimethylphenylacetamide implies that amides containing relatively acidic α protons can be employed without difficulty.

Attempted acylation of 1 (R^1 = H) with DMF failed to afford 2-pyridylacetaldehyde. Instead, the normal hydrolytic work-up produced an unstable yellow oil with mass spectra and ^{1}H-NMR characteristics consistent with enamine structure **5**.



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Pyridyl ketones **4** exist in solutions in equilibrium with their enamine tautomers **6**.[16] Comparison of the integrated intensities of the side-chain methylene and vinyl protons in the ^{1}H-NMR spectra of $CDCl_3$ solutions of **4a–h** provided a convenient method for determination of enamine content (Table II). Comparison of the enamine concentration data indicates that as the steric requirements of R^2 are increased, the amount of enamine present in solution also increases.[17] From a consideration of inductive effects alone, the enamine concentration might be expected to decrease with increasing methyl substitution at R^2. An increase in enamine content with R^2 = phenyl (**4c**) would be anticipated, since phenyl should increase the polarity of the carbonyl group, thereby

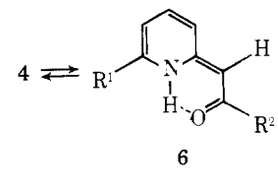

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Table II
^{1}H-NMR Data for α-(2-Pyridyl) Ketones[a]

Ketone No.	Ketone R^1	Ketone R^2	δ CH_2 keto	δ CH enamine	% enamine[b]	Registry no.
4a[a]	H	CH_3	3.88	5.28	12	65702-11-6
4b	H	$CH(CH_3)_2$	4.00	5.40	16[c]	65702-12-7
4c	H	$C(CH_3)_3$	4.10	5.50	18	65702-13-8
4d	H	$CH_2C_6H_5$	3.94	5.28	22	65702-14-9
4e	H	C_6H_5	4.50	6.03	46	65702-15-0
4f	CH_3	CH_3	3.92	5.10	16	65702-16-1
4g	CH_3	$CH(CH_3)_2$	4.01	5.41	18[c]	65702-17-2
4h	CH_3	$C(CH_3)_3$	4.40	5.50	27[c]	65702-18-3

[a] Solvent = $CDCl_3$. Concentrations of ketones were ca. 25% by volume. Chemical shifts and integrated intensities of all other peaks were consistent with the assigned structures of **4a–h.** [b] Relative error ±2% or less, except where noted. [c] Relative error ±2.5%.

leading to stronger hydrogen bonding than when R^2 = alkyl. It appears that steric factors are more important than inductive effects with aliphatic R^2 groups and that the observed increase in enamine content with bulkier R^2 groups results mainly from relief of steric repulsions between these groups and the heterocyclic moiety in the pyridyl tautomers. Similar effects have been noted with β diketones.[18] Substitution of a methyl group at the 6 position of the pyridine ring in **4f–h** causes an increase in enamine content over that observed with the corresponding unmethylated ketones **4a–c.** Since addition of a 6-methyl group should contribute little to the steric requirements of the pyridine residue, it is suggested that the methyl group increases the basicity of the ring nitrogen and that the enamine form is stabilized by stronger hydrogen bonding in the methylated ketones.

Experimental Section

Melting points were taken on a Thomas-Hoover Mel-Temp apparatus and are uncorrected; boiling points are also uncorrected. Infrared spectra were measured on films, melts, or in Nujol mulls on potassium bromide plates. Spectra were recorded on a Beckman IR-5, a Beckman 20-AX, or a Perkin-Elmer 621 spectrophotometer where band positions were calibrated using polystyrene. Proton magnetic resonance (^{1}H-NMR) spectra were recorded on a JEOL PS 100 spectrometer. Chemical shifts are reported in δ in parts per million (ppm) downfield from tetramethylsilane as in internal standard. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-7 double-focusing mass spectrometer. The analyzer tube and the ion source were maintained at a pressure less than 10^{-6} Torr. Microanalyses were carried out in this Department on a Perkin-Elmer Model 240 C, H, and N elemental analyzer.

N,N-Dimethylamides were prepared by the method of Lecomet.[19] This involved dissolving the appropriate acid chloride in ether and passing dimethylamine gas through the solution until moist litmus paper above the solution turned blue. The solution was filtered to remove the precipitated dimethylammonium chloride. The ether was removed at aspirator pressure and the final products were purified by distillation.

Tetrahydrofuran (THF) was distilled from sodium hydride and stored under argon. *n*-Butyllithium (2 M in hexane) was obtained from Alpha-Ventron. All other chemicals were reagent grade and were used without further purification.

3-Methyl-1-(2-pyridyl)-2-butanone (4b). The following procedure is intended to be used as a model for the preparation of ketones **4.**

Standard Addition. 2-Picolyllithium (**1**, R^1 = H) was prepared by the method of Smith et al.[11] This involved the placing of 2-picoline (47.2 g, 0.50 mol) in a 2-L three-necked flask containing 200 mL of THF which was purged with argon and stirred mechanically. The solution was cooled in a dry ice/2-propanol bath and 2 M *n*-butyllithium (0.50 mol in hexane) was added dropwise through a pressure-equalizing dropping funnel. The bath was removed and the temperature was allowed to rise to ambient. The cooling bath was then replaced and a solution of 58 g (0.5 mol) of *N,N*-dimethylisobutyramide in 200 mL of anhydrous ether was added dropwise to the picolyllithium. The solution was allowed to warm to ambient temperature and 200 mL of water was added cautiously followed by 31 mL of concentrated HCl. The water layer was checked to ensure basicity, after which the ethereal layer was removed. The water layer was extracted with three 100-mL portions of chloroform and the extracts were combined with the ethereal layer and dried over Na_2SO_4. The volume was reduced at aspirator pressure and 65 °C. The crude product was vacuum distilled to afford 69.4 g (85%) of **4b,** bp 80 °C (2 Torr) [lit.[3] bp 79–85 °C (2 Torr)]. The ^{1}H-NMR and IR spectra of **4b** were identical with those of an authentic sample.[8]

Inverse Addition. 2-Picolyllithium (0.25 mol) was prepared and diluted with 200 mL of anhydrous ether. The solution was added dropwise to a solution of 26.5 g (0.25 mol) of *N,N*-dimethylisobutyramide in 200 mL of anhydrous ether. The product was worked up as in the previous procedure to afford 67% of **4b.**

Enamine 5. To a solution of 109 g (1.5 mol) of DMF in 300 mL of anhydrous ether cooled in a dry ice/2-propanol bath was added 1.0 mol of 2-picolyllithium over a period of 10 h. The reaction mixture was allowed to warm to room temperature and was then poured into 200 mL of 6 N HCl. The ethereal layer was separated. The aqueous layer was made basic and extracted with three 50-mL portions of chloroform. The organic layers were combined, dried (Na_2SO_4), and concentrated at 25 °C (0.25 Torr). Vacuum distillation afforded a light yellow oil, bp 75 °C (0.4 Torr), which began to decompose rapidly even at −5 °C. A sample of this product had: ^{1}H NMR ($CDCl_3$) δ 2.84 (s, 6 H, $N(CH_3)_2$), 5.22 (d, J = 7 Hz, 1 H, vinyl H), 6.88 (m, 2 H, PyH-3,5), 7.5 (d, J = 7 Hz, 1 H, vinyl H, superimposed on the multiplet for PyH-4, 1 H), and 8.43 (m, 1 H, PyH-6); mass spectrum *m/e* 148 (M^+).

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Registry No.—1 (R′ = H), 1749-29-7; 1 (R′ = Me), 34667-18-0; **5,** 20973-84-6.

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