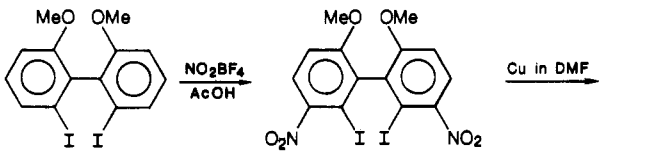
used ranged from 0.001 to 0.165. The results are summarized in Table I and the data obtained at 260 and 297 nm are plotted in Figure 1. The theoretical lines are based on an average ionic strength of 0.100. The average thermodynamic pK values (standard deviations) were pK_1 5.60 (0.09) and pK_2 8.54 (0.13).

Results and Discussion

Synthesis. We first tried to prepare 1 from the readily available 2,3-dichloroanisole. Nitration gave the desired 2,3-dichloro-4-nitroanisole in 17–25% yield, but attempted transformation of this to 4,5-dinitro-1,8-dimethoxybiphenylene (4) by reaction with activated copper bronze in refluxing dimethylformamide was unsuccessful, with the only identified product being 2-chloro-4-nitroanisole.

A second attempt started with 2,2′-diiodo-6,6′-dimethoxybiphenyl (2), already in hand as an intermediate in the synthesis of 1,8-biphenylenediol.[8,9] Nitration of 2 gave the desired 2,2′-diiodo-6,6′-dimethoxy-3,3′-dinitrobiphenyl (3) in up to 48% yield along with the 3-nitro, 5-nitro, 3,5′-dinitro, and 3,3′,5,5′-tetranitro derivatives. Reaction of 3 with copper bronze in refluxing dimethylformamide gave 79% 4. However, all the many methods used in attempting to demethylate 4 were unsuccessful. These include the use of boron tribromide, with[10] and without dimethyl sulfide, aluminum chloride, and aluminum bromide with dimethyl sulfide and/or ethanethiol,[11] trimethylsilyl iodide in acetonitrile and in dimethyl sulfoxide,[12] boiling 48% hydrobromic acid in the presence of a phase transfer catalyst,[13] pyridine with and without[14] added 4-(dimethylamino)-pyridine, and sodium thioethoxide, potassium *tert*-butoxide, and sodium iodide, all in dimethylformamide.



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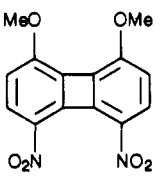

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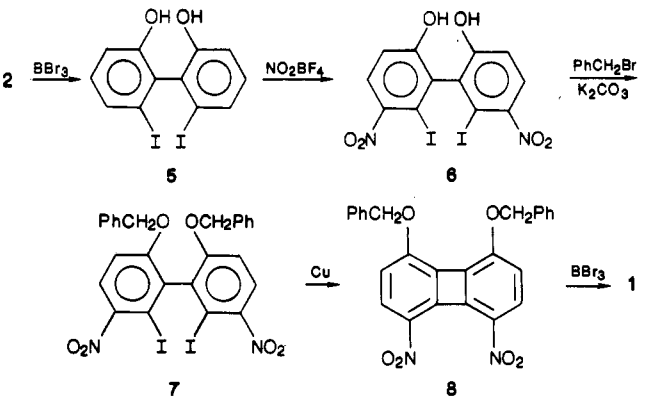
The method finally used for the synthesis of 1 started with the demethylation of 2 to 6,6′-diiodo-2,2′-biphenyldiol (5), which was then nitrated to give 25–28% 6,6′-diiodo-5,5′-dinitro-2,2′-biphenyldiol (6) and about 20% 6,6′-diiodo-3,5′-dinitro-2,2′-biphenyldiol. Benzylation of 6 using benzyl bromide and potassium carbonate[15] gave 55–60% 2,2′-bis(benzyloxy)-6,6′-diiodo-5,5′-dinitrobiphenyl (7) and an unidentified byproduct. Ring closure in 7 was achieved by use of copper bronze to give 42–45% 1,8-bis(benzyloxy)-4,5-dinitrobiphenylene (8). Debenzylation of 8 gave 1 in almost quantitative yield.

Acidity Constants. The para nitro substituent plus the other nitro substituent, also separated by four carbons from the acidic hydroxy group, decrease the pK_1 value of 1 by 2.41 units relative to that of the unnitrated compound.[9] This is less than the 2.83 unit increase in acidity produced by one para nitro group in phenol or the 3.61 unit increase produced in α-naphthol.[16,17] This greatly reduced electron withdrawing power of the nitro substituent in the biphenylene ring could be blamed on the reluctance of the four-membered ring to contain two (antiaromatic) double bonds, which is reflected in the marked tendency of the bond lengths to alternate in the "benzene" rings of biphenylene derivatives, with longer bonds falling in the four-membered rings.[18,19] This should decrease the contribution of a quinoid structure to the resonance hybrid structure of the monoanion of 1. Since the diquinoid structure for the dianion of 1 would contain a cyclobutadiene ring, pK_2 should be affected even more than pK_1. In fact, however, the difference between pK_1 and pK_2 (2.94) for 1 is essentially the same as for the unnitrated compound (2.99).[9] The most plausible explanation for the facts is steric inhibition of resonance. The two nitro groups would crowd each other excessively if they were both coplanar with the biphenylene ring. In fact, in the double hydrogen bonded adduct of 1 with 2,6-dimethyl-γ-pyrone the nitro groups are at dihedral angles of 20° and 43°.[20]



5 6 7 8

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Basicity of, S_N2 Reactivity of, and Basic Catalysis by 1-Azabicyclo[2.2.1]heptane[1]

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Relatively unhindered tertiary amines have been found to be particularly rapid reactants in a number of reactions. In the dedeuteriation of isobutyraldehyde-2-*d*, for example, a Brønsted plot showed that the best basic catalysts, for their basicity, are trimethylamine and 1,4-diazabicyclo-[2.2.2]octane,[2] which are several times as reactive as me-

(1) This research was supported in part by donors of the Petroleum Research Fund, administered by the American Chemical Society. Abstracted largely from the Ph.D. Dissertation of Y.-J. Chen, The Ohio State University, 1986.
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thylamine,[3] dimethylamine,[4] *N*-methyldiethylamine,[2] or triethylamine,[2] for their basicities. The S_N2 reactivity of quinuclidine toward methyl, ethyl, and isopropyl iodides is considerably greater than that of triethylamine.[5] The ratio of the reactivity of quinuclidine to that of triethylamine increases in the order Me < Et < *i*-Pr. This is good evidence for a steric contribution to the relative reactivities. The reactivities of 2,6-dimethylpyridine and 2,4,6-trimethylpyridine are smaller by about 10-fold than expected from the Brønsted plot for catalysis of the iodination of acetone by pyridine derivatives lacking 2-substituents.[6] The reactivities of these same two hindered pyridine derivatives in the dedeuteriation of isobutyraldehyde-2-*d* are smaller by about 150-fold than would be expected from the analogous Brønsted plot.[2] This shows that dedeuteriation of isobutyraldehyde-2-*d* is slowed more by steric hindrance than is the dedeuteriation of acetone-d_6. Since 1-azabicycloheptane must have the methylene groups attached to nitrogen pulled back from the unshared electron pair relative to the situation in quinuclidine, it must be a less hindered tertiary amine. Therefore we expected it to be more reactive in S_N2 reactions and in catalyzing dedeuteriations than a quinuclidine derivative of the same basicity.

Experimental Section

1-Azabicyclo[2.2.1]heptane was prepared as described by Clemo and Prelog.[7] The hydrochloride melted with decomposition at 296–297 °C (lit.[7] mp 306 °C, subl); ^{1}H NMR (500 MHz, D_2O) δ 1.74–1.76 (m, 2 H, endo-$H_{3,5}$), 2.06–2.09 (m, 2 H, exo-$H_{3,5}$), 2.99 (br s, 1 H, H_4), 3.14–3.15 (m, 2 H, $H_{7,7}$), 3.22–3.25 (m, 2 H, endo-$H_{2,6}$), 3.36–3.42 (m, 2 H, exo-$H_{2,6}$). Two-dimensional NMR measurements showed that $H_{7,7}$ couple with endo-$H_{3,5}$ and endo-$H_{2,6}$ but not with exo-$H_{3,5}$ and $H_{2,6}$ and that H_4 couples with $H_{7,7}$ and exo-$H_{3,5}$ but not with endo-$H_{3,5}$ or any $H_{2,6}$. The free amine was liberated from the hydrochloride with alkali and distilled over sodium: bp 129.5–130 °C (lit.[7] bp 130 °C); more than 99% pure by VPC on a 6-ft 10% OV-101 column at 230 °C.

Determination of thermodynamic pK_a values for the conjugate acids of our amine catalysts was carried out by measuring the pH of three buffer solutions used in kinetic runs. The Davies equation[8] was used to calculate activity coefficients. Values of 10.53, 10.90, and 9.48 were obtained for azabicycloheptane, quinuclidine, and 3-quinuclidinol at 35 °C. The only previous value we have found for azabicycloheptane is 10.71 at 25 °C.[9] The method of Perrin[10] for allowing for temperature effects transforms this value at 25 °C to a value of 10.38 at 35 °C. On the other hand, assumption that $\Delta C_p°$ and $\Delta S°$ are the same as for quinuclidine[11] leads to a value of 10.48 at 35 °C. Of a number of values for quinuclidine,[11-17] the most reliable seem to be those of Lobo and co-workers,[11] who made measurements over the temperature range 5–45 °C. From their summarizing equation, a value of 10.88 may be calculated in good agreement with our value. Values of pK_a for protonated 3-quinuclidinol include a thermodynamic value of 9.54 at 25 °C[18] and values at ionic strength 0.5 or 1.0 and 25 °C or 30 °C ranging from 10.02 to 10.13.[19-24] In this case Perrin's method transforms the thermodynamic value to 9.25 and the assumption that $\Delta C_p°$ and $\Delta S°$ are the same as for quinuclidine transforms it to 9.35 at 35 °C.

Table I. Rate Constants for 1-Azabicyclo[2.2.1]heptane and Quinuclidines[a]

		10^4k			
amine	pK_a[b]	C_3D_6O[c]	Me_2CD-CHO[d]	MeOTs[e]	EtOTs[f]
quinuclidine	10.90	390 (10)	370 (10)	240 (10)	27 (1)
1-azabicycloheptane	10.53	55 (1)	83 (1)	46 (1)	6.9 (0.2)
3-quinuclidinol	9.48	87 (1)		173 (4)	24 (1)
1,4-diazabicyclooctane	8.47[g,h]	22[g,h]	32[h,i]		
3-quinuclidinone	6.93[j]	3.1 (0.1)	4.3[j]	41 (1)	4.7 (0.1)

[a] The values in parentheses are estimated standard deviations. [b] Of the protonated amine in water at 35 °C. [c] For dedeuteriation of acetone-d_6 in water at 35 °C. [d] For dedeuteriation of isobutyraldehyde-2-*d* in water at 35 °C. [e] For reaction with methyl *p*-toluenesulfonate in benzyl alcohol at 30 °C. [f] For reaction with ethyl *p*-toluenesulfonate in benzyl alcohol at 49.5 °C. [g] Reference 25. [h] Per amino group. [i] Reference 2. [j] Reference 27.

Dedeuteriation of acetone-d_6 was followed by extraction of the aqueous reaction solutions with chloroform followed by mass spectral measurements, as described previously.[25] Each amine was studied in at least three different buffer solutions, in which both the buffer concentrations and the buffer ratio were changed. The observed first order rate constants for disappearance of acetone-d_6 were taken to be equal to a term proportional to the concentration of hydroxide ions (catalysis constant 0.0722 M^{-1} s^{-1} at 35 °C,[25] the temperature at which the reactions were studied) plus a term proportional to the concentration of free amine. The hydroxide term contributed less than 20% to the total reaction in any run with quinuclidine or 1-azabicycloheptane and no more than 1% to any run with either of the other two amines. The hydroxide ion concentration was calculated from the measured pH, K_w, the ionic strength, and the Davies equation for activity coefficients.[8]

The kinetics of the dedeuteriation of isobutyraldehyde-2-*d* were followed by NMR measurements on chloroform extracts of the aqueous reaction solutions as described earlier.[3] The concentrations of free amine were corrected for that which went to neutralize the 0.0030 to 0.0245 M isobutyric acid produced by oxidation of the 0.217 M deuteriated aldehyde used. The term for hydroxide ion catalysis never contributed as much as 9% to the total reaction. Treatment of the data was analogous to that described for acetone-d_6. The catalysis constants for the amines, which are listed in Table I, are capable of reproducing the first-order rate constants in the individual runs (from which they were calculated by least squares) with a standard deviation that never exceeded 3% for acetone or 4% for isobutyraldehyde.

The kinetics of the reactions of methyl and ethyl tosylates with amines were followed conductimetrically. The tosylates were vacuum distilled before use. At zero time 12 mL of thermally equilibrated tosylate solution and 12 mL of amine solution were syringed into a Jones type conductivity cell attached to an Industrial Instrument Co. RC-16 conductivity bridge. The solvent

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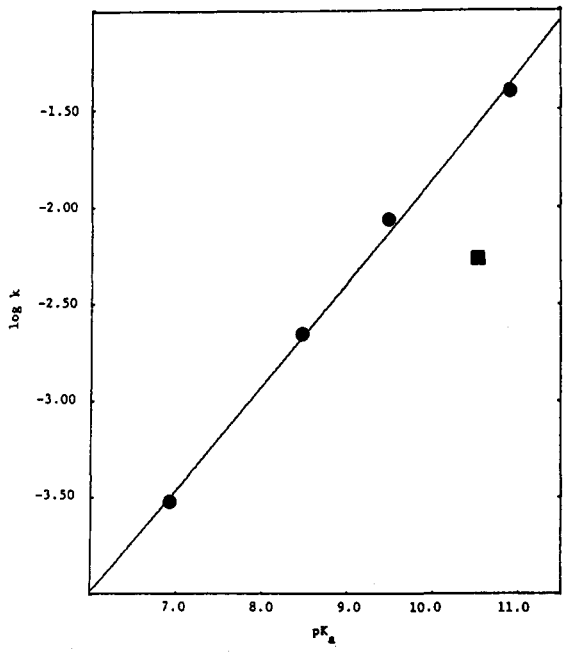

Figure 1. Plot of log k for dedeuteriation of acetone-d_6 by tertiary amines vs. pK_a for the protonated amines: (●) quinuclidines; (■) 1-azabicyclo[2.2.1]heptane.

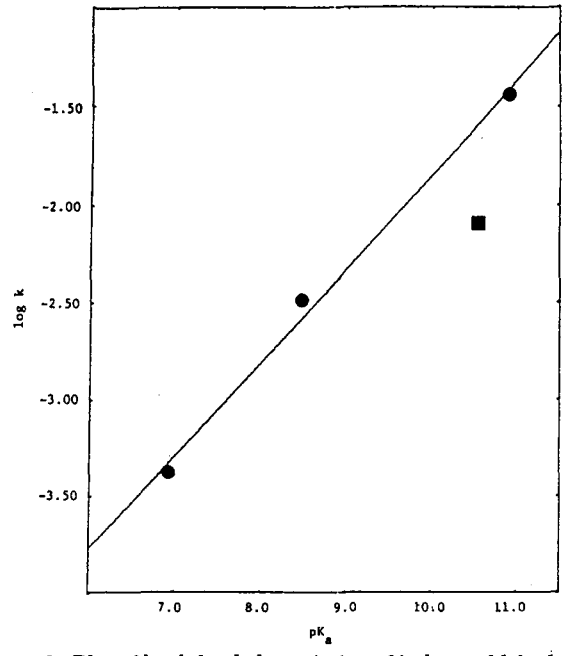

Figure 2. Plot of log k for dedeuteriation of isobutyraldehyde-2-d by tertiary amines vs. pK_a for the protonated amines: (●) quinuclidines; (■) 1-azabicyclo[2.2.1]heptane.

was redistilled benzyl alcohol. The reactions of methyl tosylate were studied at 30 °C and those of ethyl tosylate at 49.5 °C. The resistance of the benzyl alcohol was too large to measure; resistance measurements were taken until they became constant. After this time the relationship between the conductivity and the concentration of quaternary ammonium salt was determined as follows. The reaction solution, which contained a concentration of salt equal to that of the tosylate used, was successively diluted quantitatively with solvent until the conductivity became quite small. Then empirical eq 1, in which A, B, C, D, and E are

$$\text{concn} = AL + B(L)^{1/2} + C + D/(E + L) \qquad (1)$$

disposable parameters and L is the conductivity, was fitted to the plot of concentration vs. conductivity. Experiments on the rates of solvolysis of the tosylates showed that there would be no significant competition from this process. The amine was always present in at least 20% excess over the tosylate. The rate constants obtained are listed in Table I.

Results

The catalysis constants for dedeuteriation of acetone-d_6 are plotted logarithmically against the pK_a values of the protonated forms of the amines in Figure 1. The points for the four quinuclidine derivatives are seen to describe a good straight line of slope 0.53. This is similar to the slope (0.60) obtained previously for amines of the type RCH_2NMe_2.[26] However, 1-azabicycloheptane reacts too slowly, by about threefold, to fall on this line. For isobutyraldehyde-2-d there are data on only three quinuclidine derivatives and the slope of the best straight line is 0.48. The best lines through the points for unhindered pyridines and for phenoxide ions have slopes of 0.49 and 0.53, respectively.[2] Again, as shown in Figure 2, the reactivity of 1-azabicycloheptane is smaller, this time by about fivefold, than would be expected from the Brønsted equation.

The data for S_N2 reactions of methyl tosylate and ethyl tosylate are plotted in Figure 3. In each case the points for quinuclidine derivatives describe a reasonably straight line and in each case the slope is 0.20. The reactivity of 1-azabicycloheptane is too low, by about fivefold in the case of methyl tosylate and about fourfold in the case of ethyl tosylate, for its points to fall on these lines. It is interesting that, in spite of the differing steric requirements of the four reactions and their differing sensitivities to the basicities of the quinuclidines, the deviations of 1-azabicycloheptane from the Brønsted equation are all about the same. The observation that the less hindered 1-azabicycloheptane is more reactive toward the more hindered[5,28-30] ethyl tosy-

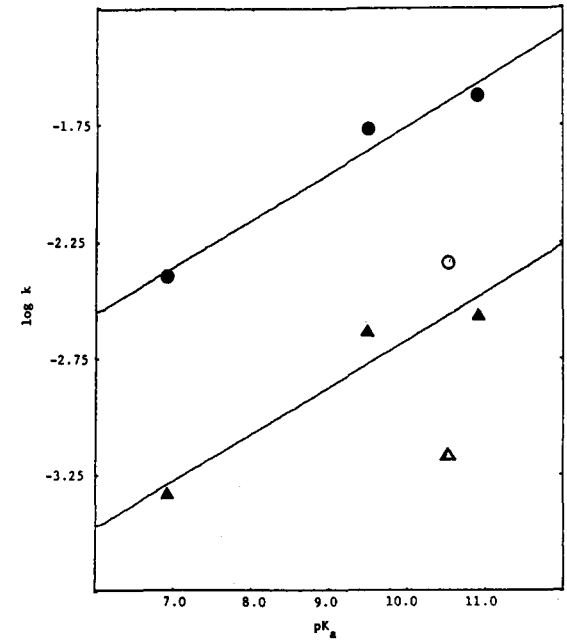

Figure 3. Plot of log k for S_N2 reactions between tertiary amines and alkyl tosylates in benzyl alcohol: (●) MeOTs plus quinuclidines at 30 °C; (○) MeOTs plus 1-azabicyclo[2.2.1]heptane at 30 °C; (▲) EtOTs plus quinuclidines at 49.5 °C; (△) EtOTs plus 1-azabicyclo[2.2.1]heptane at 49.5 °C.

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late, relative to the quinuclidines, than it is toward methyl tosylate would be expected from the concept of steric hindrance. However, the observation that the relative reactivity of 1-azabicycloheptane toward the more hindered isobutyraldehyde-2-*d* is less than it is toward acetone-d_6 is counter to the expectations of steric hindrance. Of course, the van der Waals equation contains attractive as well as repulsive terms and suitable combination of these would seem to explain our results but in the absence of appropriate calculations we cannot claim to have explained them.

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An Efficient Regio- and Stereoselective Synthesis of (±)-Monomorine I via the Highly Regioselective α-Alkynylation of a 1-Acylpyridinium Salt

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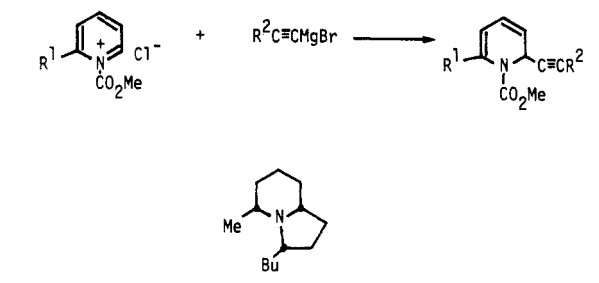
We have recently reported that nucleophilic addition of alkynyl Grignard reagents to 1-methoxycarbonylpyridinium chloride takes place at the α-position in a highly regioselective manner to give 2-substituted 1-methoxycarbonyl-1,2-dihydropyridines exclusively. This methodology is applicable to the synthesis of (±)-solenopsin A as well as indolizidine and quinolizidine.[1,2] In further extension of this α-alkynylation methodology to the synthesis of naturally occurring nitrogen heterocycles, we now describe an efficient regio- and stereoselective synthesis of (±)-monomorine I (1), a trail pheromone of the pharaoh ant,[3,4] using the above regioselective α-alkynylation of 1-acylpyridinium salt[5,6] as a key reaction (Scheme I).

Reaction of 2-methylpyridine with 3-(2-tetrahydropyranyloxy)heptynylmagnesium bromide (2) in the presence of methyl chloroformate afforded the α-alkynylated 1,2-dihydropyridine (3) exclusively in high yield. Without purification, 3 was hydrogenated over 5% Pt-C, followed by deprotection of the hydroxyl group, to give a cis-2,6-disubstituted piperidine derivative (4) in 83% isolated yield.[7] No other regioisomer could be detected by NMR or GLC analysis, clearly indicating the general and high α-regioselectivity in the reaction of alkynyl Grignard reagents with 1-acylpyridinium salts.

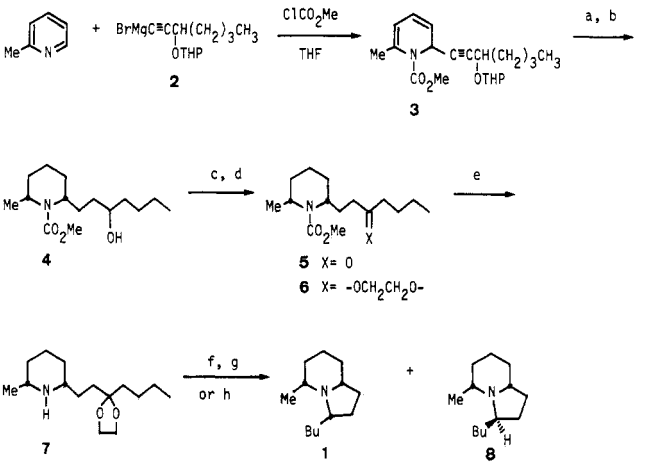
Jones oxidation of 4 followed by protection of the carbonyl group with ethylene glycol gave 6. Basic hydrolysis of 6 in the presence of hydrazine hydrate afforded a crucial intermediate, 7, in 96% yield. The last step required stereoselective reductive cyclization of 7 to monomorine I (1). At first we examined intramolecular reductive amination with $NaBH_3CN$.[8] Thus, acidic deprotection of 7,

Scheme I



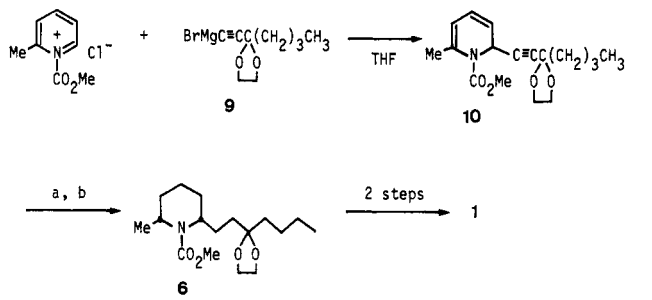
1, Monomorine I

Scheme II



Reagents: (a) H_2, Pt-C/MeOH; (b) Amberlyst H-15/MeOH; (c) CrO_3-H_3O^+/acetone; (d) $(CH_2OH)_2$, p-TsOH/PhH; (e) KOH, NH_2NH_2 H_2O/$(CH_2OH)_2$; (f) aq. HCl/THF; (g) $NaBH_3CN$/aq. HCl-MeOH; (h) H_2, Pd-C/aq. HCl-MeOH

Scheme III



Reagents: (a) H_2, Pt-C/MeOH; (b) $(CH_2OH)_2$, p-TsOH/PhH

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(2) For the related synthesis of quinolizidine system via 2-substituted 1,2-dihydropyridines, see: Comins, D. L.; Brown, J. D. *Tetrahedron Lett.* **1986**, *21*, 2219, 4549.
(3) Ritter, F. J.; Rotgans, I. E. M.; Talman, E.; Vermiel, P. E. J.; Stein, F. *Experientia* **1973**, *29*, 530.
(4) Oliver, J. E.; Sonnet, P. E.; *J. Org. Chem.* **1974**, *39*, 2662. (b) Sonnet, P. E.; Oliver, J. E. *J. Heterocycl. Chem.* **1975**, *12*, 289. (c) Sonnet, P. E.; Netzel, D. A.; Mendoza, R. Ibid. **1979**, *16*, 1041. (d) For stereoselective synthesis, see: Stevens, R. V.; Lee, A. W. M. *J. Chem. Soc., Chem. Commun.* **1982**, 102. (e) For asymmetric synthesis, see: Royer, J.; Husson, H.-P. *J. Org. Chem.* **1985**, *50*, 670.
(5) For reviews on dihydropyridine chemistry: Eisner, U.; Kuthan, J. *Chem. Rev.* **1972**, *72*, 1. (b) Stout, D. M.; Meyers, A. I. Ibid. **1982**, *82*, 223. See also ref 1c.
(6) For our recent studies on reactions of 1-acylpyridinium salts with organotin reagents, see: (a) Yamaguchi, R.; Moriyasu, M.; Yoshioka, M.; Kawanisi, M. *J. Org. Chem.* **1985**, *50*, 287. (b) Yamaguchi, R.; Moriyasu, M.; Kawanisi, M. *Tetrahedron Lett.* **1986**, *27*, 211.
(7) It should be noted that catalytic hydrogenation of 2,6-disubstituted 1,2-dihydropyridine gives cis-2,6-disubstituted piperidine exclusively. See ref 1b,c.
(8) Borch, R. F.; Bernstein, M. D.; Durst, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 2897.

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