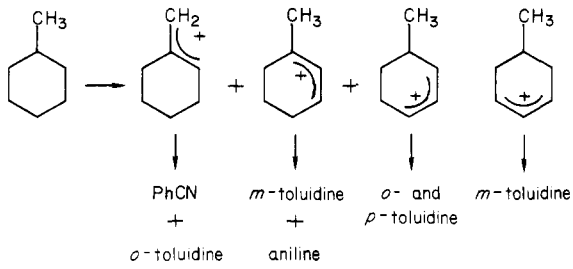
least one ammonia attack occurs at the oxidation level of an allylic carbenium ion, as the toluidine isomer distribution is that expected from attack at the most accessible position of the most stable isomer of these ions.



Experimental Section

Cyclohexane or methylcyclohexane and sulfur were loaded into a 10-cm^3 shaker tube and cooled to −78 °C. After evacuation, ammonia was distilled into the tube, and the sealed tube was heated and shaken for the desired time behind a barricade. The tube was cooled to −78 °C, and any noncondensable gases such as nitrogen or hydrogen from ammonia decomposition were vented. Solid ammonium polysulfide can plug the reactor vent opening so to ensure safe discharge of the reaction product, a hole must be made in the solid to allow the warming gases to escape. The tube was inverted over a receiver and allowed to warm to room temperature. The solid ammonium polysulfides present sublimed and decomposed, liberating H_2S and ammonia. The liquid which remained was analyzed for high-boiling amines by gas chromatography, using an SE-30 column. Products were isolated by distillation and characterized by standard methods in large-scale runs.

Registry No. *o*-Phenylenediamine, 95-54-5; cyclohexane, 110-82-7; sulfur, 10544-50-0; ammonia, 7664-41-7.

A Facile Biomimetic Method for Oxidative Deamination of Primary Amines to Aldehydes via Transposition of an Imine Functionality

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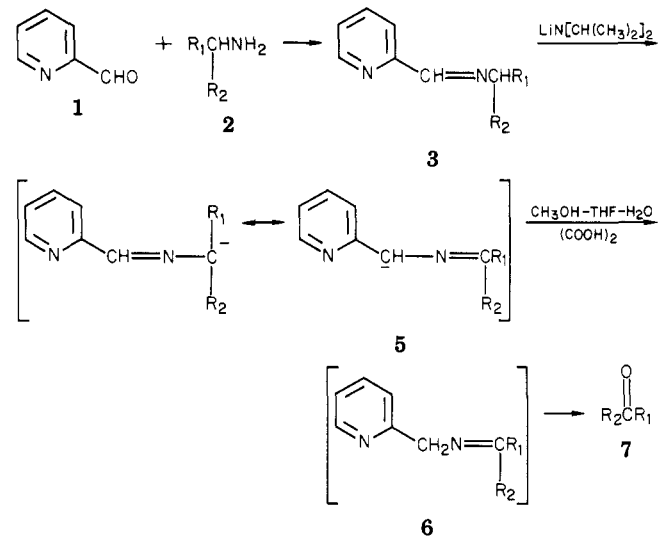
Considerable attention has been given by various research groups to developing methods for the oxidation of primary amines possessing the general structure **2** to the corresponding carbonyl compounds (**7**).[1] Prior to 1978 the synthetic methodology[2] available for effecting this transformation afforded good yields of ketones from primary amines containing secondary alkyl groups (i.e., **2**, R_1, R_2 = alkyl or aryl); however, similar attempts to prepare aldehydes from primary amines containing *primary alkyl* groups (i.e., **2**, R_1 or R_2 = H) generally gave poor yields (less than 40%). Although several methods[2,3] are available for conversion of substituted benzylamines to the corresponding aromatic aldehydes, they are less satisfactory for the preparation of aliphatic aldehydes. Recently a solution to this latter problem has been reported.[4] The new methodology effects the oxidation of primary alkyl amines to aldehydes by use of the heterocyclic reagent 5-bromo-3-(methylthio)-1,4-diphenyl-1,2,4-triazolium bromide, followed by oxidation of the corresponding derivatives with diethyl azodicarboxylate and subsequent acid-catalyzed hydrolysis.

Scheme I



1 2 3 5 6 7

a, $R_1 = CH_3(CH_2)_9$, R_2 = H; b, $R_1 = C_6H_5$, R_2 = H; c, R_1, $R_2 = -(CH_2)_7-$; d, $R_1 = C_6H_5$, $R_2 = CH_3$

In view of the fact that the known synthetic methodology for conversion of primary amines to aldehydes seems unnecessarily lengthy and often requires expensive reagents, we set out to develop a more convenient method that would closely mimic the biosynthetic equivalent of this process. It is known that enzyme-catalyzed oxidative deamination of α-amino acids to afford the corresponding α-keto acids involves reaction with pyridoxal phosphate to form a Schiff-base intermediate[5] and subsequent transposition of the carbon–nitrogen double bond. Our strategy therefore envisioned conversion of the primary amine substrate to a suitable imine derivative which could be isomerized via prototropic rearrangement. Subsequent hydrolysis would then effect the desired oxidative transformation.

On the basis of analogy with the biosynthetic process, 2-pyridinecarboxaldehyde (**1**)[6] seemed to be an attractive reagent to test our proposed methodology. By use of *n*-undecylamine (**2a**) as a representative aliphatic primary amine, its imine derivative (**3a**) with the latter aldehyde (**1**) was readily prepared. Subsequent conversion in essentially quantitative yield to the corresponding anion (**4a** ↔ **5a**) was accomplished in the presence of excess lithium diisopropylamide (LDA) in tetrahydrofuran at −70 °C. It was anticipated that kinetic protonation of the resulting anion might effect the desired prototropic rearrangement (i.e., conversion of **3a** to **6a**). Indeed, as expected, subsequent acidification of the reaction mixture and simultaneous hydrolysis using oxalic acid dihydrate in aqueous methanol afforded undecanal (**7a**) in 94% yield (Scheme I).

(1) For a survey of some of these methods, see: Harrison, I. T.; Harrison, S. (Vol. 1 and 2); Hegedus, L. S.; Wade, L., Jr. (Vol. 3) "Compendium of Organic Synthetic Methods"; Wiley: New York, 1971, 1974, 1977; Vol. I, pp 150–152, 404–406; Vol. 2, pp 60, 161–162; Vol. 3, pp 264–265. For a review, see: Baumgarten, R. J. *J. Chem. Educ.* **1966**, *43*, 398.

(2) For specific examples, see: Corey, E. J.; Achiwa, K. *J. Am. Chem. Soc.* **1969**, *91*, 1429; Calo, V.; Todesco, P. E. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1652.

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(5) Stryer, L. "Biochemistry"; W. H. Freeman and Co.: San Francisco, 1975; pp 432–435.

(6) Available from Aldrich Chemical Co., Inc., Milwaukee, WI.

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Table I. Isomerization-Hydrolysis[a] of Imines 3a-d

starting amine[b]	carbonyl product[c]	distilled yield[d] (%) of 7a-d
n-undecylamine	undecanal (7a)[e]	94
benzylamine	benzaldehyde (7b)	81
cyclooctylamine	cyclooctanone (7c)	28
dl-α-methylbenzylamine (2d)	acetophenone (7d)[f]	58

[a] All reactions were run by using the general procedure listed in the Experimental Section. [b] Available from Aldrich Chemical Co., Milwaukee, WI. [c] The IR and NMR spectral properties of each product were identical with those exhibited by the authentic compounds sold by Aldrich Chemical Co. [d] Based on starting imine (3a-d). [e] VPC analysis (6 ft × 1/8 in. SE-30 column, 173 °C, flow rate 15 mL/min, retention time 8.3 min) indicated the product [bp 64-82 °C (bath temperature, 0.15 mm)] to be >99% pure. [f] VPC analysis (6 ft × 1/8 in. 2.5% Carbowax 20M column, 138 °C, flow rate 15 mL/min, retention time 8.2 min) indicated the product to be >98% pure.

As the results in Table I indicate, this process is equally successful for converting benzylic amines to the corresponding aromatic aldehydes. Less satisfactory were the yields of ketones obtained from primary amines containing *secondary* alkyl groups (Table I, entries 3 and 4). These results may be a reflection of the diminished kinetic acidity of the corresponding Schiff base (i.e., **3c** vs. **3a**; **3d** vs. **3b**), resulting in a smaller extent of anion formation[7] (**4c** and **4d** vs. **4a** and **4b**, respectively).

In view of the overall facility with which this process can be effected, it offers a convenient method for the preparation of aldehydes from an appropriate primary amine. Furthermore it complements earlier synthetic methodology by which ketones (but not aldehydes) could be obtained from primary amine precursors.

Experimental Section

General Procedures. Reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran was purified prior to use by distillation from lithium aluminum hydride. Products were recovered from the ether extracts after the organic layer was dried over anhydrous magnesium sulfate and the solvent was removed by using a rotary evaporator under reduced pressure. Evaporative distillation refers to bulb-to-bulb (Kugelrohr) short-path distillation. The NMR spectra were recorded with a Varian EM-360 spectrometer, and infrared spectra were obtained by using a Beckman Acculab 1 spectrophotometer. Vapor-phase chromatography (VPC) was performed on a Hewlett-Packard 5750 chromatograph. The microanalysis was performed by Micro-Tech Laboratories, Skokie, IL.

***N*-Undecyl-2-picolinimine (3a).** A solution of 0.50 mL (5.25 mmol) of 2-pyridinecarboxaldehyde (1)[6] and 897 mg (5.24 mmol) of *n*-undecylamine (2a)[6] in 2.0 mL of anhydrous ether was stirred at room temperature for 40 min. The product was isolated by drying the mixture over anhydrous magnesium sulfate and removal of the ether in the usual manner. Subsequent evaporative distillation afforded 1.34 g (98%) of imine **3a**:[8] bp 125-150 °C (bath temperature, 0.20 mm); IR ν_{max} (film) 1640 (C=N), 1580, 1562, 1455, 1430, 1365, 1328, 1037, 985, 965, 765, 735 cm^{-1}; NMR (CCl_4, Me_4Si) δ 8.59 (m, $J_{5,6}$ = 5, $J_{3,6}$ = 1 Hz, aromatic H-6), 8.32 (br s, CH=NCH_2), 8.05 (m, $J_{3,4}$ = 7.5, $J_{3,6}$ = 1 Hz, aromatic H-3), 7.68 (td, $J_{4,6}$ = 1.7, $J_{3,4}$ = $J_{4,5}$ = 7.5 Hz, aromatic H-4), 7.23 (m, aromatic H-5), 3.63 (t, J = 6 Hz, NCH_2), 0.88 (br t, J = 5 Hz, CH_3). Anal. Calcd for $C_{17}H_{28}N_2$: C, 78.41; H, 10.84; N, 10.76. Found: C, 78.40; H, 11.03; N, 10.64.

Isomerization-Hydrolysis of Imines 3a-d. A solution of 1.5 mmol of imine (**3a-d**) in 3.0 mL of anhydrous tetrahydrofuran (THF) was added dropwise to a solution of 4.8 mmol of lithium diisopropylamide[9] in 5.0 mL of THF and 3.0 mL of hexane. After this mixture was stirred at -70 °C for 1 h,[7] the reaction was quenched by quickly pouring the solution into a well-stirred mixture of 1.9 g of oxalic acid dihydrate and 3.0 mL of water in 12 mL of methyl alcohol and 12 mL of THF. The mixture was stirred at room temperature for 2 h, and the product was subsequently isolated by dilution of this mixture with 125 mL of 4:1 (v/v) 2 M aqueous hydrochloric acid-saturated brine and extraction with ether. The organic layer was washed with 3:1 (v/v) 2 M aqueous hydrochloric acid-saturated brine, 1:1 (v/v) 1 M aqueous sodium hydroxide-saturated brine, and saturated brine in successive order. The product was isolated from the organic extract in the usual manner and purified by evaporative distillation.

Registry No. 1, 1121-60-4; **2a**, 7307-55-3; **2b**, 100-46-9; **2c**, 5452-37-9; **2d**, 618-36-0; **3a**, 76684-24-7; **3b**, 19198-87-9; **3c**, 57707-72-9; **3d**, 76739-45-2; **7a**, 112-44-7; **7b**, 100-52-7; **7c**, 502-49-8; **7d**, 98-86-2.

(7) Increasing the reaction time to 4 h for imine 3c failed to alter significantly the yield of cyclooctanone isolated after the standard hydrolysis procedure.

(8) Imines **3b-d** were prepared in a similar manner from benzylamine, cyclooctylamine, and *dl*-α-methylbenzylamine, respectively. For a previous synthesis of these imines (**3b-d**) using 2-pyridinecarboxaldehyde and the appropriate amine, see: Dinizo, S. E.; Watt, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 6900.

(9) This base was prepared by the addition of a 1.6 M solution of *n*-butyllithium in hexane (3.0 mL) to a solution of diisopropylamine (0.75 mL, 5.35 mmol) in 5.0 mL of anhydrous tetrahydrofuran at -10 °C. For more details, see: Cregge, R. J.; Herrmann, J. L.; Lee, C. S.; Richman, J. E.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 2425, 2429.

Reaction of Perfluoroalkyl Carbanions with Thiocyanates. Synthesis of Fluorinated Sulfides and Sulfenyl Chlorides

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Nucleophilic attack on thiocyanates can occur either on the sulfur atom or on the cyanide group.[1] An old report shows that the condensation of an arylmagnesium halide with an alkyl thiocyanate yields chiefly a nitrile or a ketone.[2] The behavior of perfluoroalkylmagnesium bromides is not always similar to that of usual Grignard reagents.[3] Our initial goal was to examine the reaction of alkyl or aryl thiocyanates with the Grignard reagent $CF_3(CF_2)_3MgBr$ (**1**). We extended this study to the more stable perfluorobutylcopper[4] (C_4F_9Cu, **2**) and to the perfluoroalkyl carbanion **3** formed by addition of potassium fluoride to perfluoroalkenes CF_2=CFX (X = Cl, CF_3).[5] These condensations could lead to the formation of sulfides **5** or nitriles **6**.

The results obtained are summarized in Table I. With the perfluoro Grignard reagent we obtained a sulfide. The only side product was a 1*H*-perfluoroalkane which arose from hydrogen abstraction. The copper derivative, easier to handle than the Grignard reagent, behaved similarly.

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(5) Young, J. A. *Fluorine Chem. Rev.* **1967**, *1*, 1967.

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