4f, 75458-40-1; **4g**, 75458-41-2; **4i**, 3683-70-3; **4j**, 75458-42-3; **5e**, 75458-43-4; **22**, 75458-44-5; **25**, 75458-45-6; **26e**, 75458-46-7; **26h**, 75458-47-8; **27**, 75458-48-9; **27′**, 75458-49-0; **28**, 75458-50-3; methanamine, 74-89-5; ethanamine, 75-04-7; 2-propanamine, 75-31-0; 2-methyl-2-propanamine, 75-64-9; cyclohexanamine, 108-91-8; benzenamine, 62-53-3; 4-methoxybenzenamine, 104-94-9; *d*-ephedrine, 321-98-2.

Supplementary Material Available: Table II describing the synthesis and spectrometric properties of N-substituted α,α-dichloroalkyl aryl ketimines (2 pages). Ordering information is given on any current masthead page.

Anti-Bredt Molecules. 3.[1a] 3-Oxa-1-azabicyclo[3.3.1]nonan-2-one and 6-Oxa-1-azabicyclo[3.2.1]octan-7-one, Two Atom-Bridged Bicyclic Urethanes Possessing Bridgehead Nitrogen

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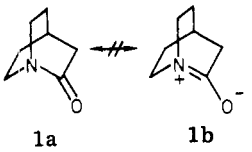
Received July 8, 1980

The first atom-bridged bicyclic urethanes possessing bridgehead nitrogen have been synthesized and their properties examined briefly. 3-Oxa-1-azabicyclo[3.3.1]nonan-2-one was synthesized from 3-(hydroxymethyl)-piperidine and phosgene by using two alternate reaction schemes. 6-Oxa-1-azabicyclo[3.2.1]octan-7-one was synthesized similarly from 3-hydroxypiperidine. Both compounds were stable, white, crystalline solids with normal infrared spectra. They were rather stable to acids and bases, but phosphoric acid initiated ring-opening polymerization demonstrated strain in the system. A novel O → N rearrangement of two aminochloroformates to hydroxy *N*-carbamoyl chlorides was demonstrated.

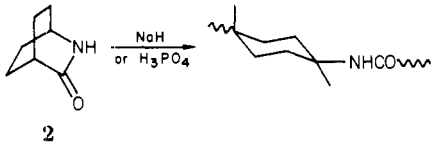
Anti-Bredt Lactams. Bicyclic lactams with a bridgehead nitrogen (1), according to Bredt's rule,[2] should be very unstable because resonance form **1b** would be prohibited.[3]



1a **1b**

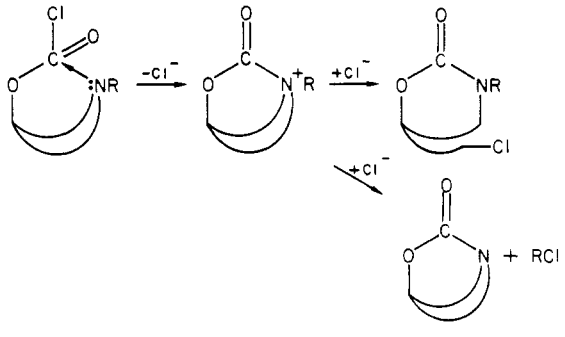
However, Yakhontov[4] and Pracejus[5–7] synthesized 1-azabicyclo[2.2.2]octan-2-one (1) itself and its 2,2-dimethyl and 2,2,6-trimethyl derivatives. These lactams showed unusual properties. Their carbonyl infrared absorptions were found at anomalously high frequencies, they hydrolyzed readily in water, and they polymerized.

However, lactam 1 and its derivatives are also destabilized by their possession of a boat six-membered ring. That this could contribute to destabilizing structure 1 was shown by Hall,[8] who showed that the analogous lactam 2-azabicyclo[2.2.2]octan-3-one (**2**) smoothly polymerized to the open-chain polyamide.

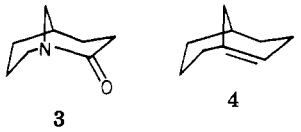


2

Scheme I



In an attempt to separate the effect of NCO resonance inhibition from conformational strains, Hall, Shaw, and Deutschmann[1a] synthesized 1-azabicyclo[3.3.1]nonan-2-one (**3**). Although **3** could adopt a two-chair form, the NMR



3 **4**

spectrum showed that a chair–boat form was preferred, in keeping with Wiseman's rule.[9–12] Lactam **3** was not very reactive, but it polymerized to the corresponding polyamide under the influence of phosphoric acid. This degree of stability for **3** corresponds well to that of the homomorphic olefin **4**, which is isolable yet reactive.[9–12]

Anti-Bredt Urea. Hall and Johnson[13] synthesized the urea 3-isopropyl-1,3-diazabicyclo[3.3.1]nonan-2-one (**5**).

(1) (a) Paper 2: Hall, H. K., Jr.; Shaw, R. G., Jr.; Deutschmann, A. *J. Org. Chem.* **1980**, *45*, 3722. (b) On leave from the University of Sanaa, Yemen.
(2) Bredt, J.; Thouet, H.; Schmitz, J. *Justus Liebigs Ann. Chem.* **1924**, *437*, 1.
(3) Lukes, R. *Collect Czech. Chem. Commun.* **1939**, *10*, 148.
(4) Yakhontov, L. N. *Usp. Khim.* **1969**, *38*(6), 1038.
(5) Pracejus, H. *Chem. Ber.* **1959**, *92*, 988.
(6) Pracejus, H. *Chem. Ber.* **1965**, *98*, 2897.
(7) Pracejus, H.; Kehlen, M.; Matschiner, M. *Tetrahedron* **1965**, *21*, 2257.
(8) Hall, H. K., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 6412.
(9) Wiseman, J. R.; Pletcher, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 956.
(10) Marshall, J. A.; Faubl, H. *J. Am. Chem. Soc.* **1970**, *92*, 948.
(11) Becker, K. B. *Helv. Chim. Acta* **1977**, *60*(1), 81.
(12) Greenberg, A.; Liebman, J. F. *Chem. Rev.* **1976**, *76*(3), 311.
(13) Hall, Jr., H.K.; Johnson, R. C. *J. Org. Chem.* **1972**, *37*, 697.

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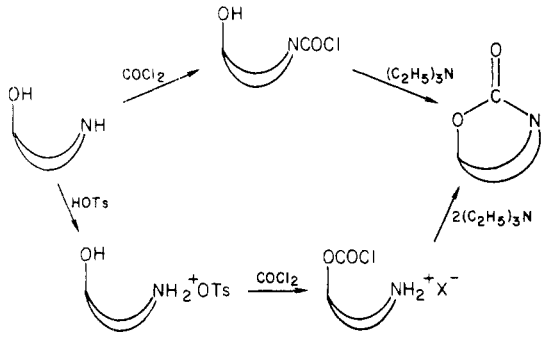
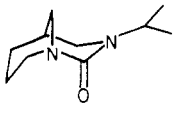
Scheme II

Route I



Route II

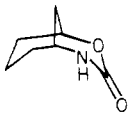
This bicyclic urea was stable and showed no signs of polymerization despite the presence of a boat form. The *N*-isopropyl group may be responsible through the "*gem*-dimethyl effect".



5

Anti-Bredt Urethanes. No N-bridgehead bicyclic urethanes were found in the literature. However, interesting reports by Fielden, Welstead, and Lunsford[14] and by Li and Biel[15] are relevant. These investigators showed that the chloroformates derived from cyclic tertiary amino alcohols isomerized to chloroalkyl monocyclic urethanes by way of the quaternary ammonium ions of N-bridgehead bicyclic urethanes (Scheme I). In no case did chloride ion dealkylate the positive nitrogen atom with formation of RCl and the N-bicyclic urethane.

That the anti-Bredt feature is responsible for these results is attested by the ready formation of bicyclic urethanes such as 2-oxa-4-azabicyclo[3.3.1]nonan-3-one[8] (**6**) where this feature is absent.



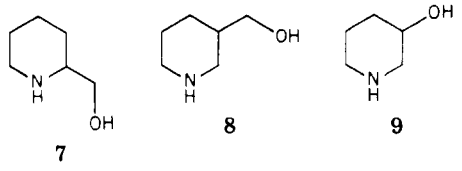
6

Our objective was the synthesis and characterization of the N-bicyclic urethanes formed from the same ring systems as those used previously[14,15] but starting from the corresponding cyclic secondary amino alcohols.

The phosgene route, involving "high-energy" acyl chloride intermediates, appeared to be the method of choice. Two sequences were possible as shown in Scheme II. In route I, reaction of phosgene with the amino alcohol should lead to the hydroxy *N*-carbamoyl chloride because of the much greater nucleophilic reactivity of amines than of alcohols. Alternatively (route II), the nitrogen may be protected by protonation, and then phosgene will react with the alcohol group.[16] Treatment with base should then liberate the amine–chloroformate whose cyclization should be very rapid. Both routes were tried successfully in this work.

Results and Discussion

Our studies were carried out with secondary amino alcohols **7a–9a** which were obtained commercially and purified by distillation.



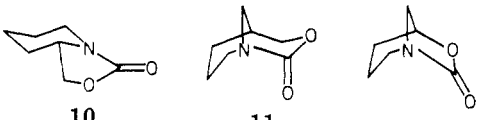
7 8 9

a, free amino alcohol; b, *p*-toluenesulfonate salt; c, chloroformate *p*-toluenesulfonate; d, hydroxy *N*-carbamoyl chloride

Route I. Reaction of phosgene with the free amino alcohols in dichloromethane at −30 °C or lower in presence of 1 equiv of triethylamine gave the hydroxy *N*-carbamoyl chlorides **7d–9d**. These could not be crystallized or distilled without polymerization or decomposition but were characterized by their IR and NMR spectra.

To bring about cyclization, the hydroxy *N*-carbamoyl chlorides were first treated with 1 equiv of triethylamine in inert solvents at low temperature for 1–2 days. If these conditions did not cause cyclization, the conditions were made increasingly drastic (higher concentrations and increased reaction temperatures and times) until cyclization, polycondensation, or decomposition occurred.

The easiest bicyclic urethane to synthesize was the reference compound 8-oxa-1-azabicyclo[4.3.0]nonan-9-one (**10**), in which N–CO overlap is not inhibited. Next came



10 11 12

3-oxa-1-azabicyclo[3.3.1]nonan-2-one (**11**), but we obtained only a 15% yield. More vigorous conditions were required to form 6-oxa-1-azabicyclo[3.2.1]octan-7-one (**12**), but then a 61% yield was achieved.

Route II. The amino alcohols were converted to crystalline hydrotosylates **7b–9b**. Phosgenations of the salts were carried out by using 1.0–1.5 equiv of phosgene in dichloromethane or chloroform at 0 °C for 1.0–1.5 h. The chloroformate salts, isolated by rotary evaporation, could not be recrystallized without decomposition but were characterized by strong C=O absorptions at 1770–1780 cm^{-1} and by the absence of OH group absorptions.

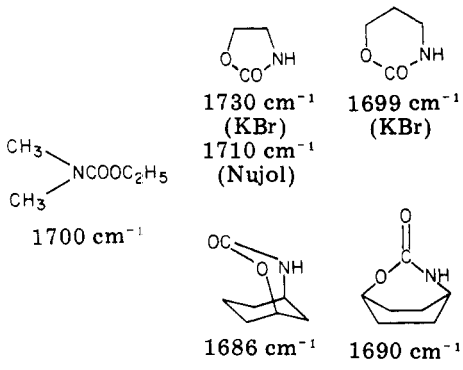
Treatment of the chloroformate salts with triethylamine in dichloromethane solution gave the following results. 2-[[(Chloroformyl)oxy]methyl]piperidinium *p*-toluenesulfonate gave a 75% yield of **10**, and 3-[[(chloroformyl)oxy]methyl]piperidinium *p*-toluenesulfonate gave a 74% yield of **11**. Surprisingly, the chloroformate *p*-toluenesulfonates **8c** and **9c**, treated at −60 °C with triethylamine in dichloromethane, underwent O → N isomerization to the hydroxy *N*-carbamoyl chlorides, identical with those synthesized above.

Physical Properties of Bicyclic Urethanes. The [4.3.0] urethane is a liquid at room temperature (mp 11–13 °C), whereas the other bicyclic urethanes are crystalline solids.

The C=O stretch absorption in the IR region showed an approximate measure of the hybridization of the bicyclic urethanes. Thus, the [4.3.0] urethane absorbed at 1750 cm^{-1} while the more strained [3.2.1] urethane ab-

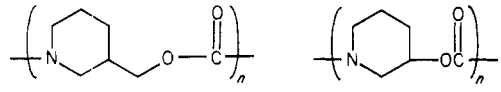
(14) Fielden, M. L.; Welstead, W. J.; Lunsford, C. D. "Abstracts of Papers", 152nd National Meeting of the American Chemical Society, New York, NY, Sept 1966; American Chemical Society: Washington, DC; 1966; p 15.
(15) Li, J. P.; Biel, J. H. *J. Org. Chem.* **1970**, *35*, 4100.
(16) Schaefgen, J. R.; Koontz, F. H.; Tietz, R. F. *J. Polym. Sci.* **1959**, *40*, 377.

sorbed at 1770 cm^{-1}. These are five-membered-ring urethanes. The six-membered-ring [3.3.1] urethane absorbed at 1710 cm^{-1}. For comparison, the following values are available.[17]



Chemical Properties of Bicyclic Urethanes. All the bicyclic urethanes synthesized were soluble and stable in water except the [3.2.1] urethane. Reactivities toward various potential polymerization initiators were studied by using **10** neat or the other urethanes in solution.

The three bicyclic urethanes were completely stable to potassium *tert*-butoxide and to *p*-toluenesulfonic acid monohydrate from 28 to 105 °C. Phosphoric acid polymerized **12** to poly(3,*N*-piperidyloxycarbonamide) **14** after



13 **14**

20 h at 105 °C in Me_2SO and **11** to poly(3,*N*-piperidylmethyleneoxycarbonamide) **13** after 27 h at 105 °C in Me_2SO. As expected, **10** was completely stable under all conditions tried. More complete polymerization studies will be reported elsewhere.[18]

Conclusions. The first two atom-bridged bicyclic urethanes, **11** and **12**, have been synthesized. They are stable, isolable molecules with normal infrared spectra. They are rather stable to acids and bases, but their phosphoric acid initiated polymerizations prove the existence of strain in both systems.

Experimental Section

Instrumentation. All melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were determined on Varian Model T-60 spectrometer at 60 MHz. Infrared (IR) spectra were obtained with a Perkin-Elmer 337 grating infrared spectrophotometer. Mass spectra were determined on a Hewlett-Packard 5930A quadrupole mass spectrometer. Gas chromatograms were obtained on a Varian Aerograph 1700 using a 5 ft × $^1/_4$ in. column packed with 3% SE-30 on 80–100-mesh Chromosorb W AW/DMCS HP.

Elemental analyses were performed by Chemalytics, Inc., or the University Analytical Center, Department of Chemistry, University of Arizona, Tucson.

Chemicals. All the chemicals are from Aldrich Chemical Co., Inc., unless otherwise mentioned. Solvents are distilled from CaH_2 or kept over 4A molecular sieves.

Phosgenations of Chloroformate Salts. 2-(Hydroxymethyl)piperidinium *p*-toluenesulfonate (8.83 g, 29 mmol) was dissolved in 600-mL of dry dichloromethane in a 1-L, three-necked Morton flask fitted with a thermometer and a condenser. Through the third neck were fitted two tubes, one for nitrogen and the other for phosgene, extending nearly to the bottom of the flask. The exit from the condenser was protected with a U-tube mineral oil trap. The apparatus was dried with a Bunsen flame and cooled under a stream of nitrogen. Phosgene (5.72 g, 57.8 mmol, 4.11 mL) was condensed in a small graduated finger by using a dry ice–isopropyl alcohol bath. Phosgene was swept into the reaction vessel, which was kept at 0 °C by using a dry ice–isopropyl alcohol bath, by a stream of dry nitrogen (NaOH). After 90 min of magnetic stirring, all the phosgene had been added, and the reaction vessel was left to warm to room temperature with magnetic stirring for 30 min to expel any excess phosgene. The chloroformate salt, **7c**, absorbed in the IR in the C=O stretching region at 1775 cm^{-1}.

Similar phosgenation of 3-(hydroxymethyl)piperidinium *p*-toluenesulfonate (**8b**) in methylene chloride and 3-hydroxypiperidinium *p*-toluenesulfonate (**9b**) in chloroform gave the corresponding chloroformate salts with IR absorptions at 1780 and 1775 cm^{-1}, respectively. No OH absorption was visible. The salts could not be recrystallized without decomposition. In all cases in which excess phosgene was used, *p*-toluenesulfonyl chloride formed.

Cyclization of Chloroformate Salt 7c To Form 10. Salt **7c** slurry was transferred to a pressure-equalized dropping funnel and added dropwise to dry triethylamine (8.78 g, 86.7 mmol, 12.1 mL; distilled from CaH_2) in 600 mL of dry dichloromethane in a 2-L flask. The addition was completed in 70 min. The dichloromethane was rotoevaporated, leaving a white residue. This was dried under vacuum for 1 h. Anhydrous ether was added and the mixture stirred for 14 h and filtered. Ether was rotoevaporated under vacuum, leaving, after 30 min, 7.8 g of a yellowish liquid. The NMR showed the presence of *p*-toluenesulfonyl chloride by absorption at δ 7.5 (4 H) and a singlet at δ 2.5 (3 H), while IR showed its presence by a peak at 1600 cm^{-1}. The *p*-toluenesulfonyl chloride was separated by dissolving the urethane in water and filtering the insoluble toluenesulfonyl chloride. The water was rotoevaporated at 60 °C, and urethane **10** was purified by molecular distillation [bp 91 °C (0.03 mmHg)]: crude yield 91% (75% purified); mp 11–13 °C; n^{24}_D 1.4890; VPC on a 3% SE-30 column showed only one peak, retention time 1.5 min, at 175 °C with a flow rate of 20 mL of He/min; IR (neat) 1750 (C=O), 2950, 2860 (CH) cm^{-1}; NMR (neat) δ 4.8 (m, 1), 4.2 (m, 3), 3.25 (m, 1), 2.1 (m, 6); mass spectrum, *m/e* 141, 140 (–H), 86, 83 (M – CH_2CO_2), 69 (M – $CH_2CH_2CO_2$), 55 (M – $CH_2CH_2CH_2CO_2$).

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.57; H, 7.80; N, 9.93. Found: C, 59.30; H, 7.53; N, 9.66.

Cyclization of Chloroformate 8c at 28 °C To Form 11. 3-[[(Chloroformyl)oxy]methyl]piperidine *p*-toluenesulfonate (**8c**; 2.3 g, 6.26 mmol) was dissolved in 200 mL of dry dichloromethane and added dropwise from a press-equalized funnel to 12.52 mmol (1.75 mL) of triethylamine in 300 mL of dichloromethane. The addition was over in 1 h. The solvent was rotoevaporated to dryness. The residue was transferred to a Soxhlet thimble, extracted with ether for 48 h, filtered, and rotoevaporated, leaving 0.74 g of white crystals which melted at 144–146 °C (yield 84%, purified 74%). The urethane **11** can be distilled in a Kugelrohr apparatus and sublimed: mp 146–147 °C; IR (KBr) 1710 (C=O), 2935, 2860 (CH) cm^{-1}; NMR ($CDCl_3$) δ 4.8 to 1.2 (m); mass spectrum, *m/e* 141.

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.57; H, 7.80; N, 9.93. Found: C, 59.35; H, 7.76; N, 10.00.

O → N Rearrangement at –60 °C. When the chloroformate salt **8c** in CH_2Cl_2 was treated with 2.2 equiv of triethylamine at –60 °C for 1.2 h, the bicyclic urethane was obtained in about 10% yield, and the main product obtained, as a colorless viscous oil, was 3-(hydroxymethyl)piperidine-*N*-carbamoyl chloride (63% yield; IR C=O at 1735 cm^{-1} and OH at 3400 cm^{-1}). The [3.3.1] bicyclic urethane was separated from the carbamoyl chloride by cooling the mixture at –30 °C in ether; white crystals came out, and the solvent above them was decanted. An NMR ($CDCl_3$) and an IR spectrum were completely identical with those of an authentic sample prepared by another method.

To the chloroformate **9c** formed from 9.7 g (33 mmol) of **9b** was added 10.2 mL (73 mmol) of triethylamine at –60 °C. The solvent used in this case was purified chloroform. Chloroform was purified from ethanol by being passed through an alumina column. 3-Hydroxypiperidine-*N*-carbamoyl chloride (**9d**) was obtained: 4.02 g (96% crude yield); IR (neat) 1745 (C=O), 2850, 2920 (CH), 3400 cm^{-1} (OH).

(17) Hall, H. K., Jr.; Zbinden, R. *J. Am. Chem. Soc.* **1958**, *80*, 6428.
(18) Hall, H. K., Jr.; El-Shekeil, A. *Polym. Bull.*, in press.

Hydroxy *N*-Carbamoyl Chloride Syntheses. 3-(Hydroxymethyl)piperidine (2.0 g, 17.3 mmol) was added to an equimolar amount of triethylamine (2.5 mL) in 140 mL of dichloromethane. The round-bottomed flask was cooled to −65 °C by using dry ice–isopropyl alcohol. An equimolar amount of phosgene (1.26 mL) was condensed in a graduated finger in a dry ice–isopropyl alcohol bath and poured into the round-bottomed flask with the aid of 20 mL of cold dichloromethane with vigorous magnetic stirring. After 15 min, the flask was left to warm to room temperature, the solvent rotoevaporated, the product extracted with ether, and the triethylamine hydrochloride filtered out. If the reaction was run at a higher temperature than −65 °C or if the stirring was not vigorous, 3-[[(chloroformyl)oxy]methyl]-piperidine-*N*-carbamoyl chloride was formed. The yield as triethylamine hydrochloride was 95%. For **8d**: IR (neat) 1735 (C=O, br), 2850, 2925 (CH), 3400 cm^{-1} (br, OH); NMR ($CDCl_3$) δ 4.3 (m, 3), 4.3 (s, 1, exch), 3.5 (d, 2), 3.0 (m, 2), 1.8 (m, 5); mass spectrum, *m/e* 177 (calcd for $C_7H_{12}NO_2Cl$ *m/e* 177).

Analogous treatment of 3-hydroxypiperidine gave **9d** in 87% yield: IR (neat) 1745 (C=O, s), 2860, 2935 (CH), 3400 cm^{-1} (OH, br); NMR ($CDCl_3$) δ 3.7 (m, 5 H), 1.8 (m, 4 H), variable (s, 1 H, exch); mass spectrum, *m/e* 163 (calcd for $C_6H_{10}NO_2Cl$ *m/e* 163).

Analogous treatment of 2-(hydroxymethyl)piperidine gave **7d** in 91% yield.

These compounds could not be crystallized or molecularly distilled without decomposition.

Cyclization of an (Unisolated) Hydroxy *N*-Carbamoyl Chloride. To 1.00 g (8.6 mmol) of 2-(hydroxymethyl)piperidine was added 1.76 g (2. 41 mL, 17.2 mmol) of triethylamine in dichloromethane in a 250-mL round-bottomed flask. This was cooled in a dry ice–isopropyl alcohol bath to −60 °C, and 0.86 g (0.62 mL, 8.6 mmol) of phosgene was condensed in a graduated finger by using a dry ice–isopropyl alcohol bath and was transferred to the reaction vessel with the aid of 20 mL of cool dichloromethane with vigorous magnetic stirring. The flask was left to warm to room temperature, the dichloromethane was rotoevaporated, and the urethane **10** was extracted with anhydrous ether; yield 1.15 g (94%). The product, characterized by IR and NMR, was identical with a sample prepared from the cyclization of the chloroformate salt.

Cyclization of the Hydroxy *N*-Carbamoyl Chloride to 3-Oxa-1-azabicyclo[3.3.1]nonan-2-one (11). 3-(Hydroxymethyl)piperidine-*N*-carbamoyl chloride (**8d**) was prepared as usual and taken into 30 mL of ethyl ether, 60 mL (10 equiv) of triethylamine was added, and the mixture was stirred magnetically at room temperature for 24 h. Triethylamine hydrochloride started precipitating out directly. The white solid was filtered, the solvents were rotoevaporated, and the oily residue was dissolved in 20 mL of 1:1 pentane/ether mixture and cooled at −50 °C. The crystals that came out were separated by decanting the liquid above them. The crystals were dissolved in ether, rejecting the insoluble residue, and the solvent was decanted and cooled. This process was repeated five times until nice white crystals were obtained which were sublimed at 25–60 °C (0.1–0.2 mmHg). The overall yield was 15% (0.12 g). In another experiment, 3-(hydroxymethyl)piperidine-*N*-carbamoyl chloride (13.4 mmol) was dissolved in 150 mL of toluene, and then 0.5 g of tetra-*n*-butylammonium iodide was added together with 15 mL of triethylamine. The mixture was refluxed at 110 °C (oil bath at 120 °C) for 3 h, cooled to room temperature, filtered, and rotoevaporated at 50 °C. Ethyl ether (50 mL) was added to the orange-brown residue. The insoluble material was rejected. When the ether solution was cooled at −60 °C, it gave 0.80 g of crude yellowish crystals, crude yield 35%. This was distilled in a Kugelrohr apparatus at 25–85 °C (0.01 mmHg), giving 0.64 g (28% yield) of product: mp 146–147 °C; IR (KBr) 1710 (C=O), 2855, 2940 (CH); NMR ($CDCl_3$) δ 4.8 (d, 1), 4.2 (d, 1), 4.1–2.7 (m, 4), 2.2 (m, 1), 1.7 (m, 4); mass spectrum, *m/e* 141, 97 (M − CO_2), 83 (M − CH_2CO_2), 69 (M − $CH_2CH_2CO_2$).

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.57; H, 7.80; N, 9.93. Found: C, 59.57; H, 8.32; N, 9.90.

6-Oxa-1-azabicyclo[3.2.1]octan-7-one. 3-Hydroxypiperidine-*N*-carbamoyl chloride was extracted into 180 mL of toluene. To the toluene solution was added 20 mL (4 equiv, 142.4 mmol) of triethylamine, and triethylamine hydrochloride started precipitating out immediately. The mixture was refluxed for 1 h at 90 °C (100 °C oil bath), the white triethylamine hydrochloride was filtered, the toluene was rotoevaporated at 50 °C, and the brown residue was distilled in a Kugelrohr apparatus at 98 °C (0.01 mmHg), giving 1.72 g (38%) of the [3.2.1] bicyclic urethane. The residue in the distillation flask was dissolved in dichloromethane and added dropwise to 400 mL of ethyl ether in a 400-mL beaker. Polymer precipitated out (1.40 g, 31% yield). The ether was evaporated to give an additional 1.05 g of the monomer. An analytical sample was purified by sublimation at 25° (0.01 mmHg): total overall yield of **12** 61.3%; mp 112–113 °C; IR (KBr) 1770 (C=O), 2940, 2860 (CH) cm^{-1}; NMR ($CDCl_3$) δ 4.8 (m, 1), 3.3 (m, 4), 1.95 (m, 4); mass spectrum, *m/e* 127, 83 (M − CO_2), 70 (M − $CHCO_2$), 55 (M − $CH_2CH_2CO_2$), 42 (M − $CHCH_2CH_2CO_2$).

Anal. Calcd for $C_6H_9NO_2$: C, 56.69; H, 7.09; N, 11.02. Found: C, 56.37; H, 7.20; N, 10.94.

For polymer: IR (KBr) 1700 (C=O), 2860, 2945 (CH) cm^{-1}; NMR ($CDCl_3$) δ 3.63 (1, br m), 3.4 (4, br m), 1.7 (4, br m).

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Registry No. 7a, 3433-37-2; **7b**, 75431-11-7; **7c**, 75431-13-9; **7d**, 75431-14-0; **8a**, 4606-65-9; **8b**, 75431-15-1; **8c**, 75431-17-3; **8d**, 75431-18-4; **9a**, 6859-99-0; **9b**, 75431-19-5; **9c**, 75431-17-3; **9b**, 75431-20-8; **10**, 42329-17-9; **11**, 75431-05-9; **12**, 75431-07-1; **13** polymer, 75431-06-0; **13** repeating unit, 75431-10-6; **14** polymer, 75431-08-2; **14** repeating unit, 75431-09-3; phosgene, 75-44-5.

Preparation of Fluoro Amines by the Reaction of Aziridines with Hydrogen Fluoride in Pyridine Solution[1]

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Hydrogen fluoride combines regiospecifically with aziridines (**1**) to give 2-fluoro amines (**6**) in good yields. Fluorine attack is in all cases completely directed to the most substituted ring carbon or to the benzylic carbon. The results, for benzylic aziridines, are consistent with an S_N1-type mechanism.

Interest in the synthesis of β-fluoro amines and β-fluoro-α-amino acid derivatives arises from their biological and pharmacological properties.[3] However, their direct preparation is difficult since most of the common fluori-

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