calcium carbonate, and was dried by passing through NaOH pellets and condensed at Dry Ice temperature. Carbon monoxide was obtained from a commercial cyclinder.

General Procedure of Carbonylation.—Silver salt, amine, and solvent, if used, were placed in a 50-ml stainless steel tube under nitrogen, into which carbon monoxide gas was compressed at room temperature. The tube was closed and heated. After reaction, carbon monoxide was released, and the organic layer was separated from the precipitated silver metal by centrifugation. The silver metal was washed several times with ether. The organic layer, combined with the ether washings, was concentrated and analyzed by glpc (9-ft column of Silicon DC 200 on Celite 545). Urea and oxamide were identified by comparison of ir spectra and glpc retention times with those of authentic samples. The authentic samples of oxamides were prepared from oxalyl chloride and amine. The authentic symmetrical ureas were obtained by the reaction of phosgene and amine. The authentic unsymmetrical ureas were synthesized from carbamoyl chloride and amine.

Stoichiometry of the Carbonylation Reaction. Determination of Silver Metal Deposited and Acetic Acid Liberated.—After reaction, the precipitated silver metal was separated by centrifugation and washed several times with the amine used in the reaction. Then silver metal was oxidized to silver nitrate by concentrated nitric acid and titrated with ammonium thiocyanate using ferric ammonium sulfate as an indicator. The acetic acid liberated in the reaction was determined by glpc analysis of the separated organic layer combined with the amine washings (9-ft column of PEG 20M on Celite 545).

Registry No.—CO, 630-08-0; AgOAc, 563-63-3; $AgNO_3$, 7761-88-8.

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endo-7-Aminomethylbicyclo[3.3.1]nonan-3-ones from Rearrangement of 1-N-Substituted *N*-Haloadamantanamines by Aluminum Chloride[1]

STANLEY J. PADEGIMAS[2] AND PETER KOVACIC*

Department of Chemistry, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

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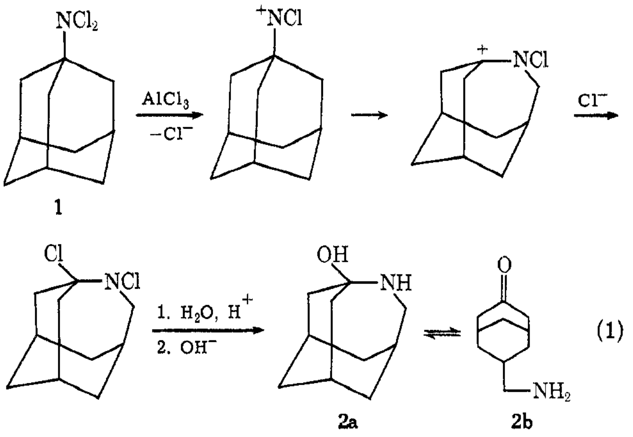
Treatment of *N*-chloro-*N*-ethyl-1-adamantanamine (**3**) with aluminum chloride afforded rearranged product which was isolated as *endo*-*N*-ethyl-7-aminomethylbicyclo[3.3.1]nonan-3-one (**4**) after acid hydrolysis. The configurational and conformational aspects of the isomeric alcohols obtained by hydride reduction are treated. The response of 3-methoxy-4-azahomoadamantanes to hydrolysis and hydride reduction was investigated. Rearrangement of *N*-chloro- and *N*,*N*-dibromo-1-adamantanamines yielded *endo*-7-aminomethylbicyclo[3.3.1]-nonan-3-one (**2**). Evidence is presented concerning the nature of the carbinolamine–amino ketone equilibrium for **2** and **4**.

Several rearrangements of *N*-haloamines have been characterized.[3] Most noted is the Hofmann–Löffler cyclization *via* an amminium radical.[4] α-Amino ketones are generated by the action of base on *N*,*N*-dichloro-*sec*-alkylamines, presumably by a pathway analogous to the Neber rearrangement.[5] Nitrenium ions have been proposed as intermediates in the Stieglitz rearrangement of *N*-halo- and *N*,*N*-dihalotritylamines.[6]

Evidence for the existence of a discrete electron-deficient nitrogen of this type was obtained[6] through studies of *N*-chloroalkylamine rearrangements in the presence of silver salts. Gassman's group,[6] as well as other investigators,[7] found that alkyl migration to nitrogen occurred with a strained ring system whose carbon analog is known to undergo carbonium ion rearrangement quite readily. Similar transformations of primary *N*-haloamines in the presence of aluminum chloride were observed when nitrogen was adjacent to a bicyclic[8] or tricyclic[9] ring system. For example, *N*,*N*-dichloro-1-adamantanamine (**1**) was converted to 7-aminomethylbicyclo[3.3.1]nonan-3-one (**2b**) by rearrangement followed by hydrolysis.[9] The postulated mechanism is depicted in eq 1. An analogous rearrangement was recently reported for *N*-acetyl-*N*-chloro-1-adamantanamine.[10]



The objective of the present work was to determine the effect of variation in the substitutent on rearrangement of 1-N-substituted *N*-haloadamantanamines. The chemical behavior of various compounds obtained in this study was examined. In addition, carbinolamine–ketoamine equilibria and stereochemical aspects were investigated.

Results and Discussion

Most of our attention was devoted to the rearrangement of *N*-chloro-*N*-ethyl-1-adamantanamine (**3**). Synthesis of **3** was accomplished by hydride reduction of

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[1] Paper V, "Adamantanes and Related Compounds;" for the preceding publication in the series see ref 9; presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

[2] Postdoctoral, 1970–1971.

[3] P. Kovacic, M. K. Lowery, and K. W. Field, *Chem. Rev.*, **70**, 639 (1970).

[4] M. E. Wolff, *ibid.*, **63**, 55 (1963).

[5] H. E. Baumgarten and F. A. Bower, *J. Amer. Chem. Soc.*, **76**, 4561 (1954).

[6] P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

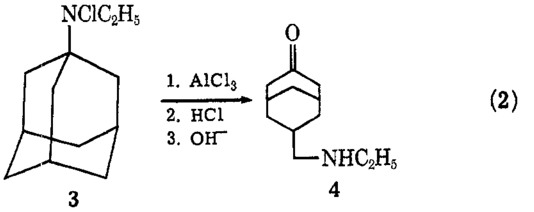
[7] H. H. Wasserman, H. W. Adickes, and O. E. de Ochoa, *J. Amer. Chem. Soc.*, **93**, 5586 (1971).

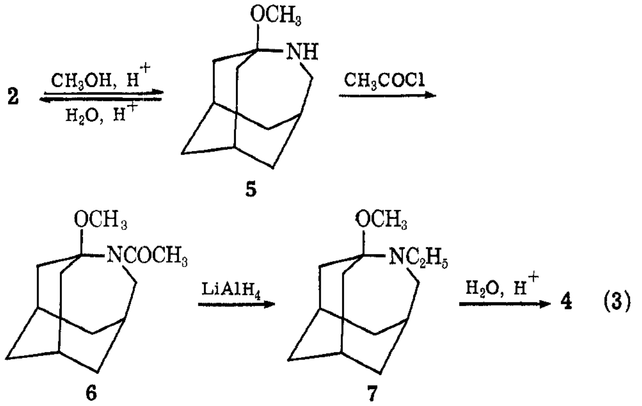
[8] P. Kovacic, M. K. Lowery, and P. D. Roskos, *Tetrahedron*, **26**, 529 (1970).

[9] P. Kovacic, J.-H. Liu, P. D. Roskos, and E. M. Levi, *Chem. Commun.*, 1034 (1970); *J. Amer. Chem. Soc.*, **93**, 5801 (1971).

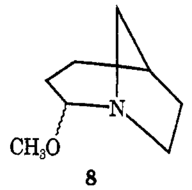
[10] T. Sasaki, S. Eguchi, T. Kiriyama, and H. Suzuki, *Syn. Commun.*, **1**, 267 (1971).

N-acetyl-1-adamantanamine followed by chlorination with calcium hypochlorite. Since the reduction process generated a minor amount of 1-adamantanamine, through a side reaction characteristic of hindered amides,[11] there was slight contamination (<5%) of **3** by **1**. When **3** was exposed to conditions similar to those used with **1**, *endo*-*N*-ethyl-7-aminomethylbicyclo[3.3.1]nonan-3-one (**4**) was isolated as the major product (65% yield), eq 2. The *N*-ethylamino ketone **4** is apparently formed in a manner analogous to the conversion of **1** to **2**. The remainder of **3** was mostly accounted for by isolation of *N*-ethyl-1-adamantanamine which could possibly arise either from acid hydrolysis of unchanged **3** or from an intermediate nitrenium ion. Gassman has demonstrated[6] that electron-deficient singlet nitrogen is able to convert to the triplet state, which can abstract hydrogen as a competing process. Structure **4**, assigned by analogy to **2**, was supported by spectral data and elemental analysis. The ir spectrum clearly showed the presence of a keto group and a secondary amine. The amine functionality was also evident from the nmr spectrum in that one proton exchanged with D_2O; the triplet of the *N*-ethyl group was distinct. In addition, confirmation was obtained by independent synthesis, eq 3. The conversion of **2** to 3-methoxy-4-azahomoadamantane (**5**) has been reported,[9] as well as the hydrolytic reverse. Acylation of **5** yielded acetamide **6**, which was then reduced with LiAlH$_4$ to the tertiary amine **7**. On acid hydrolysis, **7** readily underwent ring cleavage to afford **4**. In addition to acceptable elemental analyses, the intermediates displayed ir and nmr spectra in accord with the assigned structures.





Acid hydrolysis of α-amino ethers is reported[12] to proceed through formation of an iminium ion, $R_2N{=}CH_2{}^+$. However, for **5** and **7** delocalization in this manner would introduce double-bond character at the bridgehead position. Indeed, the resistance of 2-methoxy-1-azabicyclo [3.2.1]octane (**8**) to acid hydrolysis was rationalized[13] on this basis. In contrast, Reed and Lwowski[14] were able to effect hydrolysis of 1-methoxy-2-azabicyclo[3.2.1]octane (**9**) and 1-methoxy-2-azabicyclo[2.2.2]octane (**10**) by prolonged heating with acid. Although **9** could conceivably accommodate a strained double bond at the bridgehead,[14] as is also the case perhaps with **5** and **7**, compounds **8** and **10** are much less prone to do so because little, if any, overlap would occur between the π orbitals of C and N.[14]



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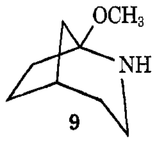
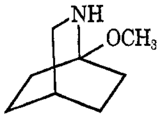


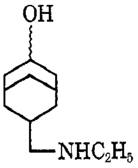
9



10

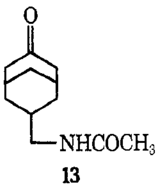
As previously discussed,[14] an alternate path appears to be available for hydrolysis of **9** and **10**, and possibly for **5** and **7**. Initial protonation on nitrogen and subsequent ring cleavage would give a resonance-stabilized, carbonium–oxonium ion which could serve as precursor of the amino ketone.

Various aspects of the chemical behavior of **4** were examined. LiAlH$_4$ reduction provided the isomeric *N*-ethylamino alcohols **11** and **12**.



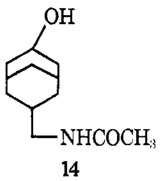
11 (endo)
12 (exo)

As predicted on the basis of steric factors, glpc analysis showed that the endo isomer predominated by a ratio of 4:1. Each of the isomeric alcohols gave satisfactory spectral and elemental analyses. In addition, similar reducing conditions applied to amide **13**[15] yielded the same isomeric amino alcohols (**11** and **12**) with an endo: exo ratio of 3:2.



13

A high degree of stereoselectivity was obtained[15] when **13** was reduced with the less reactive sodium borohydride. The resulting amide alcohol **14** was



14

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[11] P. A. S. Smith. "Open-Chain Nitrogen Compounds," Vol. I, W. A. Benjamin, New York, N. Y., 1965, pp 150–151.

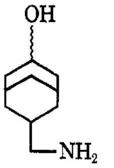
[12] T. D. Steward and W. E. Bradley, *J. Amer. Chem. Soc.*, **54**, 4172 (1932); H. Meerwein in "Methoden der Organischen Chemie," Vol. VI, Part 3, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1965, p 195.

[13] P. G. Gassman and B. L. Fox, *J. Amer. Chem. Soc.*, **89**, 338 (1967).

[14] J. O. Reed and W. Lwowski, *J. Org. Chem.*, **36**, 2864 (1971).

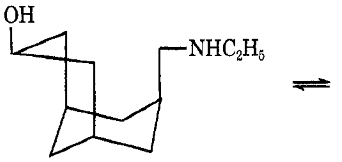
[15] J. A. Tonnis and T. A. Wnuk, unpublished work.

essentially the endo isomer, since subsequent conversion of the amide functionality with $LiAlH_4$ yielded N-ethylamino alcohol which was greater than 98% endo. Confirmation of the stereospecificity of the $NaBH_4$ reduction was provided by hydrolysis[15] of **14** to the endo amino alcohol **15**. None of the exo isomer **16** could be detected by glpc analysis. The $NaBH_4$ reduction of 2 in ethanol has been found[15] to afford **15** and **16** with an endo:exo ratio of 3:1. Analogous stereospecificity pertains in the hydride reduction of camphor.[16a]

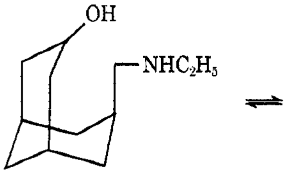


15 (endo)
16 (exo)

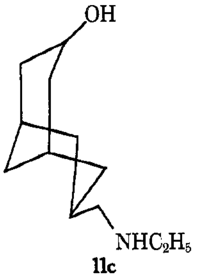
Endo and exo assignment of isomers was based on spectral and chemical evidence. The parent hydrocarbon, bicyclo[3.3.1]nonane, is known to exist in the chair–chair conformation.[17] However, when an endo substituent is introduced at either C_3 or C_7, the substituted ring prefers the boat form.[17,18] An exo substituent maintains the chair–chair relationship. With the N-ethylamino alcohols, the aminomethyl group must be in the endo position. For both isomers, the most stable conformation will result when the aminomethyl-substituted ring is in the boat conformation, *e.g.*, **11c**. Distinction between isomeric alcohols can then be obtained from the vicinal splitting of the carbinyl proton in the nmr.[18b]. As expected, the minor isomer **12** showed a larger vicinal coupling constant than did the endo. Similar observations[15] were obtained for **15** and **16**. Amino alcohols **15** and **11** must have the same configurations since both are produced from **14**. In other studies mass spectral analysis has been used[19] to distinguish between the 3-*endo*- and 3-*exo*-bicyclo[3.3.1]nonanols, and oxidation is also reported[16b] as a means of differentiating between endo and exo isomers. In contrast to the $LiAlH_4$ reduction of the N-ethyl derivative **4**, parent **2** is known[9] to yield azahomoadamantane (**17**).



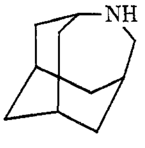
11a



11b



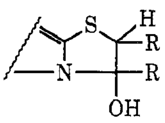
11c



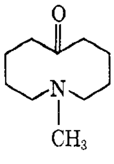
17

Attention was also devoted to the carbinolamine–ketoamine equilibrium situation for **2** and **4**. The ir spectrum of **2** in solution ($CHCl_3$) shows a carbonyl band of medium intensity at 1700 cm^{-1}, which is comparatively weak for this functional group. In the solid state (Nujol or KBr), the spectrum displays very weak absorption at 1650 cm^{-1}, indicating that the compound has little carbonyl characteristics in this physical form; the spectrum also shows strong absorption bands at 3300 and 3480 cm^{-1} which can be assigned either to NH_2 of **2b** or to the OH and NH of **2a**. However, from the weak carbonyl absorption observed, it is apparent that there is significant interaction between the carbonyl and amine functionalities, which can be described as an equilibrium between amino ketone **2b** and carbinolamine **2a** or as intimate complexing (hydrogen bonding or nucleophilic–electrophilic attraction) of the two groups. In any case, the interaction is carried to its full extent when **2** is converted to its hydrochloride salt. The ir spectrum of this derivative in the solid state is completely devoid of any carbonyl absorption.

Intramolecular interaction between amine and carbonyl groups has been noted by a number of prior investigators. In relation to the carbinolamine–amino ketone isomers, it is claimed[20] that when the ring is larger than five members the open-chain form is favored in certain heterocyclic series. Evidence indicates[21] that for compounds of type **18** some members assume this form both in the solid state and in solution, whereas others exist as the cyclic structure in the solid phase and as a tautomeric mixture in solution. Leonard and coworkers have studied[22] compounds such as **19** in which transannular interaction occurs between nitrogen and carbonyl carbon. Indeed, for the salt form a transannular covalent bond is apparently established.



R = H, alkyl
18



19

In contrast, N-ethylamino ketone **4** shows strong carbonyl absorption in the ir for both the free amine and its hydrochloride salt, indicating little, if any, binding between amino and carbonyl. This situation can be ascribed to steric interference resulting from the ethyl group. Hence, the keto of **4** behaves typically in the $LiAlH_4$ reduction.

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(16) (a) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 31; (b) p 83.

(17) G. L. Buchanan in "Topics in Carbocyclic Chemistry," Vol. 1, D. Lloyd, Ed., Plenum Press, New York, N. Y., 1969, p 199.

(18) (a) J. A. Peters, J. D. Remijnse, A. van der Wiele, and H. van Bekkum, *Tetrahedron Lett.*, 3065 (1971); (b) W. D. K. Macrosson, J. Martin, and W. Parker, *ibid.*, 2589 (1965).

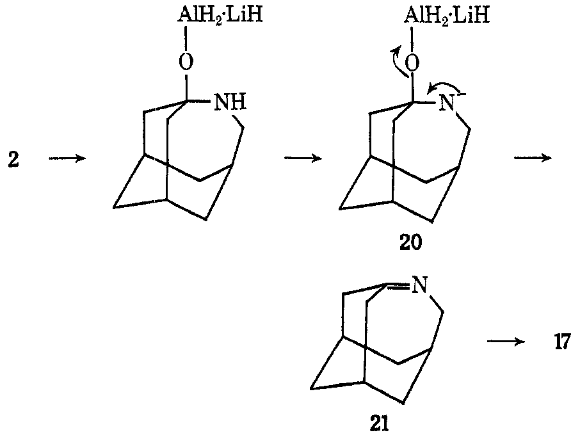
(19) J. K. MacLeod, M. Vegar, and R. J. Wells, *Recent Develop. Mass Spectrosc., Proc. Int. Conf. Mass Spectrosc.*, 1197 (1969); *Chem. Abstr.*, **75**, 97901 (1971).

(20) H. Singh and A. Singh, *Tetrahedron Lett.*, 585 (1970).

(21) A. E. Alper and A. Taurins, *Can. J. Chem.*, **45**, 2903 (1967).

(22) N. J. Leonard, *Rec. Chem. Progr.*, **17**, 243 (1956).

In the reaction[9] of **2** with $LiAlH_4$, the reducing agent may shift the equilibrium in favor of the carbinolamine structure by Lewis acid coordination[14] with carbonyl oxygen or by conversion of the primary amine to the more nucleophilic amide anion form.[9] Subsequent generation of anion **20** could result in displacement[9] of oxygen to form azahomoadamantene (**21**) which would be converted with ease to **17**, eq 4.



(4)

A related pathway has been postulated[14] in the $LiAlH_4$ reduction of **9**. The inertness[13,14] of **8** and **10** is presumably due to the reluctance of the bridgehead to assume double bond character. Reed and Lwowski suggested[14] that either the lone pair on nitrogen or the anion form could expel the adjacent oxygen. We believe, however, that involvement of the anion is necessary for formation of a bridgehead double bond. Although **2** and **5** were readily converted to **17**, the *tert*-amino ether **7** resisted reduction. Indeed, **7** was prepared in high yield by treating **6** with a large excess of $LiAlH_4$.

Since electron-deficient nitrogen appears to be involved in the rearrangement of **3** to **4**, we explored the behavior of **3** on exposure to silver salts according to the procedure of Gassman.[6] However, only a 5% yield of **4** was obtained with silver perchlorate. On prolonged heating with silver nitrate, the yield of **4** was increased to 22%. In both cases the majority of **3** was isolated as *N*-ethyl-1-adamantanamine. Similar reduced yields of **2** were noted when **1** was treated with silver salts. The reason for the greater effectiveness of aluminum chloride remains obscure.

N,*N*-Dibromo-1-adamantanamine (**22**) underwent facile rearrangement. With aluminum bromide catalyst, **2** was isolated in yields comparable to those obtained from **1**. *N*-Chloro-1-adamantanamine (**23**) afforded **2** in only 10% yield. The presence of an ethyl or halogen[23] substituent on the nitrenium ion would be expected to exert a favorable influence on ease of formation, and hence can rationalize the improved yields from rearrangements involving **1**, **3**, and **22**.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-8 spectrophotometer (calibrated with the 1601-cm^{-1} band of polystyrene). Varian T-60 and HA-100 instruments were used to obtain nmr data, which are reported in parts per million relative to tetramethylsilane as internal standard. Gas chromatography was carried out with a Varian Aerograph instrument (A-90-P or 1700) with a 15 ft × 0.25 in. column of 15% Carbowax 20M and 10% sodium hydroxide on Chromosorb P (30/60).

Positive halogen in *N*-haloamines was determined by standard iodometric titration methods.[8] Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill., and by Mr. A. Gasiecki.

***N*-Ethyl-1-adamantanamine.**—A sample of 19.33 g (0.1 mol) of *N*-acetyl-1-adamantanamine (Aldrich Chemical Co.) was placed in a Soxhlet apparatus and continuously extracted into a suspension of 10.32 g (0.272 mol) of lithium aluminum hydride in 800 ml of dry ether. After the extraction had continued for 72 hr, the mixture was cooled in an ice bath as 10 ml of water was slowly added, followed by 10 ml of 15% sodium hydroxide, and then by an additional 20 ml of water. The resulting mixture was filtered. The filtrate was dried over sodium sulfate and then evaporated to yield 18.2 g of the crude amine as a yellow oil. Distillation afforded 14.82 g (83%) of *N*-ethyl-1-adamantanamine, bp 57–59° (0.1 mm) [lit.[24] bp 101–102.5° (7 mm), lit.[25] mp 28°].

***N*-Chloro-*N*-ethyl-1-adamantanamine (3).**—To a mixture of 20.4 g of HTH [0.1 mol of $Ca(OCl)_2$] and 250 ml of water was added a solution of 11.01 g (0.0614 mol) of *N*-ethyl-1-adamantanamine in 100 ml of methylene chloride below 5°. After being stirred at 0–5° for 4.5 hr, the mixture was filtered and the layers were separated. The aqueous solution was extracted with four 100-ml portions of methylene chloride. The combined organic solution was dried over sodium sulfate and evaporated to yield 10.05 g (79%) of **3**, mp 45–51°, as a pale yellow solid; a sample of **3** titrated for the theoretical amount of chlorine.

Rearrangement of 3.—A solution of 35 mmol of **3** in 100 ml of methylene chloride was chilled to −30°. Aluminum chloride (11.1 g, 82 mmol) was added in one portion, and the mixture was then allowed to warm to 0°. After the mixture was stirred for 1.5 hr under a nitrogen sweep at 0°, 175 ml of concentrated hydrochloric acid was slowly added below 3°. The mixture was then stirred at room temperature for 2 hr and diluted with 200 ml of water, and the layers were separated. The methylene chloride phase was extracted with two 30-ml portions of concentrated hydrochloric acid and then with 60 ml of water. The aqueous solution was slowly added to 300 ml of 50% sodium hydroxide solution below 20°. The resulting suspension was extracted with two 200-ml portions of methylene chloride which was washed with 100 ml of water, dried over sodium sulfate, and then evaporated to yield 6.3 g of an orange oil. Glpc analysis showed that **4** was formed in 65% yield and *N*-ethyl-1-adamantanamine in 24% yield, in addition to several minor components. Distillation of the mixture afforded a pure sample of **4**, bp 83–85° (0.05 mm), which changed on standing to a white solid: mp 44–46°; ir (neat) 3320 (NH) and 1700 cm^{-1} (C=O); nmr ($CDCl_3$) δ 0.87 (s, 1, NH, exchangeable), 1.06 (t, 3, CH_2CH_3) and 2.17 (m, 17, CH, CH_2).

Anal. Calcd for $C_{12}H_{21}NO$: C, 73.80; H, 10.84; N, 7.17. Found: C, 74.06; H, 10.73; N, 7.15.

***N*-Acetyl-3-methoxy-4-azatricyclo[4.3.1.1^{3,8}]undecane (6).**—A solution of 2 ml (28 mmol) of acetyl chloride in 5 ml of benzene and 5 ml of pyridine was slowly added to a solution of 1.27 g (7 mmol) of **5**[9] in 10 ml of benzene and 10 ml of pyridine. After the mixture was stirred for 30 min at room temperature, it was poured into 100 ml of water. The benzene layer was separated and the aqueous layer was extracted with 25 ml of benzene. The combined benzene solution was washed with 25 ml of 5% sodium bicarbonate, dried (Na_2SO_4), and then evaporated to yield 1.21 g (78%) of **6**, mp 92–94°. Recrystallization from petroleum ether (bp 40–60°) gave prismatic plates: mp 97–99°; ir (CCl_4) 1620 (C=O), 1060 and 1080 cm^{-1} (COC); nmr ($CDCl_3$) δ 1.92 (m, 13, CH, CH_2), 2.28 [s, 3, (C=O)CH_3], 3.16 (s, 3, OCH_3), and 3.83 (d, 2, NCH_2).

Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 70.20; H, 9.22; N, 6.23.

***N*-Ethyl-3-methoxy-4-azatricyclo[4.3.1.1^{3,8}]undecane (7).**—A solution of 0.62 g (2.8 mmol) of **6** in 50 ml of ether was slowly added to a mixture of 0.5 g (13 mmol) of lithium aluminum hydride in 75 ml of ether so as to maintain a gentle reflux. After

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[23] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 102.

[24] E. I. du Pont de Nemours and Co., Belgian Patent 646,581 (1964); *Chem. Abstr.*, **63**, 14726 (1965).

[25] E. Gottwald and H. Machoczek, German Patent 1,294,371 (1969); *Chem. Abstr.*, **71**, 38444 (1969).

being refluxed for 40 hr, the mixture was cooled in an ice bath while 0.5 ml of water was slowly added followed by 0.5 ml of 15% sodium hydroxide, and then by an additional 1 ml of water. The mixture was filtered and the filtrate was dried (Na_2SO_4) and evaporated to yield 0.51 g (88%) of **7** as a pale yellow oil: glpc indicated a purity greater than 98%; ir (neat) 1040 and 1070 cm^{-1} (COC); nmr ($CDCl_3$) δ 1.03 (t, 3, CH_2CH_3), 1.80 (m, 13, CH, CH_2), 2.76 (m, 4, NCH_2), and 3.13 (s, 3, OCH_3).

Anal. Calcd for $C_{13}H_{23}NO$: C, 74.59; H, 11.08; N, 6.69. Found: C, 74.72; H, 10.91; N, 6.80.

***N*-Ethyl-7-aminomethylbicyclo[3.3.1]nonan-3-one (4) from 7.**—A 0.913-g (0.924 mmol) sample of **7** was dissolved in 10 ml of 18% hydrochloric acid. After standing at room temperature for 16 hr, the solution was poured into 30 ml of 15% sodium hydroxide. The resulting suspension was extracted with two 25-ml portions of ether. The combined ether extract was dried (Na_2SO_4) and then evaporated to yield 0.172 g (95%) of **4**; ir and nmr spectra were identical with those of a sample of **4** prepared from **3**.

***N*,*N*-Dibromo-1-adamantanamine (22).**—To a solution of 9.6 g (0.24 mol) of sodium hydroxide in 75 ml of water, 6.8 ml (0.12 mol) of bromine was added below 0°. A solution of 5 g (0.033 mol) of 1-adamantanamine in 75 ml of methylene chloride was introduced below 0°. After the mixture was stirred at 0–5° for 6.5 hr, the layers were separated, and the aqueous portion was extracted with two 25-ml portions of methylene chloride. The combined organic solution was dried over sodium sulfate and evaporated to yield 8.16 g (80%) of **22**, mp 63–66° dec, which titrated for 89% of the theoretical amount of bromine. Sublimation afforded an analytical sample of **22**, mp 67–67.5°, which titrated for 99.8% of the theoretical amount of bromine.

Anal. Calcd for $C_{10}H_{15}NBr_2$: C, 38.86; H, 4.89; N, 4.53. Found: C, 39.01; H, 4.87; N, 4.58.

Rearrangement of 22.—A solution of 0.0262 mol of **22** in 230 ml of methylene chloride was chilled to −30°. Aluminum bromide (16 g, 0.06 mol) was then added in one portion, and the reaction temperature was allowed to rise to 0°. The mixture was stirred under a nitrogen sweep for 1.5 hr at 0°. Hydrochloric acid (18%) (200 ml) was slowly added below 3°. After the mixture was allowed to warm to room temperature, stirring was maintained for 2 hr. The layers were separated and the methylene chloride phase was extracted with two 50-ml portions of 18% hydrochloric acid. The combined acid solution was slowly added to 200 ml of 50% sodium hydroxide below 10°. The white solid which separated was collected, washed with water, and recrystallized from 95% ethanol to yield 3.15 g (72%) of **2**, mp 165–167° (lit.[9] mp 166.5–167.5°).

***N*-Chloro-1-adamantanamine (23).**—The preparation was according to the previously reported procedure.[26] Extension of the reaction time to 1 hr afforded a 74% yield.

Treatment of *N*-Chloro-1-adamantanamine (23) with Aluminum Chloride.—A solution of 3.01 g (16.4 mmol) of **23** in 150 ml of methylene chloride was chilled to −30°. After aluminum chloride (4.6 g, 34.6 mmol) was added in one portion, the mixture was allowed to warm to 0°. The mixture was stirred at 0° under a nitrogen sweep for 1.5 hr. Concentrated hydrochloric acid (35 ml) was slowly added below 3°. After the mixture was allowed to warm to room temperature, 40 ml of water was added to dissolve the suspended solid, the mixture was then stirred for 2 hr, and then the layers were separated. The organic layer was extracted with two 25-ml portions of concentrated hydrochloric acid. The combined acidic solution was slowly added to 125 ml of 50% sodium hydroxide below 5°. The white solid which separated was collected, washed with water, and recrystallized from 95% ethanol to yield 0.41 g (15%) of **2**, mp 166–167° (lit.[9] mp 166.5–167.5°).

$LiAlH_4$ Reduction. General Procedure.—An ethereal solution of the compound to be reduced was slowly added to a suspension of $LiAlH_4$ (x g) in ether. After the mixture had refluxed for 24 hr, it was cooled in an ice bath as x ml of water followed by x ml of 15% sodium hydroxide and an additional $2x$ ml of water were slowly added. The mixture was filtered; the filtrate was dried (Na_2SO_4) and evaporated to yield the designated products.

11 and 12 from 13.—A sample of 210 mg (1.0 mmol) of **13** was reduced with 130 mg (3.4 mmol) of $LiAlH_4$ to yield a mixture (174 mg, 88%) of **11** and **12**. Glpc analysis showed 62% of **11** and 38% of **12**.

Alcohol **11** had mp 110–111°; ir ($CHCl_3$) 3200 (NH, OH) and 1110 cm^{-1} (COH); nmr ($CDCl_3$) δ 4.09 (m, 1, $J_{AX} \cong J_{BX} = 3$ Hz, CHOH), 2.58 (m, 4, $CH_2NHCH_2CH_3$), 1.90 (m, 15, CH, CH_2, NH, OH), 1.09 (t, 3, CH_2CH_3); mass spectrum *m/e* (rel intensity) 197 (49), 79 (12), 58 (100), 30 (31).

Anal. Calcd for $C_{12}H_{23}NO$: C, 73.04; H, 11.75; N, 7.10. Found: C, 72.78; H, 11.85; N, 7.02.

12 had mp 131.5–133°; ir ($CHCl_3$) 3200 (NH, OH) and 1100 cm^{-1} (COH); nmr ($CDCl_3$) δ 3.92 (m, 1, $J_{AX} = 5$, $J_{BX} = 15$ Hz, CHOH), 2.54 (m, 4, $CH_2NHCH_2CH_3$), 1.86 (m, 11, one exchangeable proton), 1.10 (m, 7, one exchangeable proton); mass spectrum *m/e* (rel intensity) 197 (20), 95 (29), 58 (100), 46 (50), 30 (25).

Anal. Calcd for $C_{12}H_{23}NO$: C, 73.04; H, 11.75; N, 7.10. Found: C, 73.18; H, 12.04; N, 6.97.

11 and 12 from 4.—**4** (195 mg, 1.0 mmol) was reduced with 100 mg (2.6 mmol) of $LiAlH_4$ to yield a mixture (160 mg, 82%) of **11** and **12**; glpc analysis showed 82% of **11** and 18% of **12**.

11 and 12 from 14.—**14** (214 mg, 1.0 mmol) was reduced with 110 mg (2.9 mmol) of $LiAlH_4$ to yield a mixture (149 mg, 76%) of **11** and **12**; glpc analysis showed 98% of **11** and 2% of **12**.

17 from 5.—A sample of 525 mg (2.9 mmol) of **5** was reduced with 300 mg (7.9 mmol) of $LiAlH_4$ to yield 390 mg (90%) of **17**, identified by comparison to an authentic sample.[9]

2 HCl and 4 HCl.—Hydrogen chloride gas was passed through an ethereal solution of the amine until precipitation ceased; **2** HCl had mp 192–193° dec.

Anal. Calcd for $C_{10}H_{18}NOCl$: C, 58.96; H, 8.91; N, 6.88. Found: C, 58.86; H, 8.69; N, 6.87.

4 HCl had mp 221–224° dec.

Anal. Calcd for $C_{12}H_{22}NOCl$: C, 62.18; H, 9.56; N, 6.04. Found: C, 61.89; H, 9.43; N, 6.15.

Registry No.—**2a** HCl, 34934-77-5; **2b**, 34650-78-7; **3**, 34913-37-6; **4**, 34913-38-7; **4** HCl, 34913-39-8; **6**, 34913-40-1; **7**, 34913-41-2; **11**, 34913-42-3; **12**, 34913-43-4; **22**, 34913-44-5.

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(26) P. Kovacic and P. D. Roskos, *J. Amer. Chem. Soc.*, **91**, 6457 (1969).