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AMINATION OF *EXO*-2-CHLORONORBORNANE AND NORBORNANE WITH TRICHLORAMINE-ALUMINUM CHLORIDE[1]

P. KOVACIC,[2] M. K. LOWERY,[3,4] and P. D. ROSKOS

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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Abstract Treatment of *exo*-2-chloronorbornane with trichloramine-aluminum chloride resulted in ring expansion with incorporation of nitrogen. The major product of the rearrangement, after reduction, was 2-azabicyclo[3.2.1]octane, accompanied by small amounts of the 3-isomer and *exo*-2-aminonorbornane. Amination of norbornane yielded either the *exo*-pri-amine or the aza material as the principal basic product depending upon reaction conditions. The mechanistic and synthetic features are discussed, and comparisons with related reactions are made.

OUR previous work[5] on amination of alkyl halides with trichloramine-aluminum chloride was concentrated on the simple primary, secondary, and tertiary types. Reaction of t-butyl chloride produced t-butylamine in high yield, accompanied by a minor component, 2,2-dimethylaziridine. A mechanistic scheme for the principal pathway was proposed entailing ionization of the halide, with subsequent interaction of the carbonium ion with a nitrogenous nucleophile. Isolation of N,N-dichloro-t-butylamine intimated that the nucleophile was dichloramide ion, while detection of chlorinated derivatives of isobutane suggested the involvement of $Cl^{\delta+}$. Further delving into this system showed that secondary halides gave secondary amines and N-alkylaziridines, in addition to primary amines. The occurrence of rearrangement with isobutyl chloride apparently generated t-butyl and sec-butyl cations which, in turn, combined with the nucleophile.

exo-2-Chloronorbornane was chosen for investigation because of the interesting rearrangements which frequently occur in the bicyclic series. This report describes the mechanistic and synthetic consequences resulting from exposure of this halide to trichloramine-aluminum chloride. In addition, amination of norbornane was studied.

RESULTS AND DISCUSSION

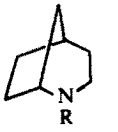
exo-2-*Chloronorbornane*

The bicyclic chloride, *exo*-2-chloronorbornane, was allowed to react with trichloramine-aluminum chloride in a molar ratio of 1/1/2. Addition of t-butyl chloride was employed to remove positive chlorine from the end product in the reaction mixture. Subsequent hydrogenation of the basic, unsaturated material yielded the indicated mixture (45% over-all yield): 2-azabicyclo [3.2.1] octane (88%), 3-azabicyclo (3.2.1] octane (6%), and *exo*-2-aminonorbornane (6%).

Identification of the aza compounds proved not to be straightforward since previous literature reports were not in agreement with our data in some instances. Furthermore, the two unsaturated products, 2- and 3-azabicyclo[3.2.1]oct-2-ene, appear to have

the same retention time on several different gas chromatographic columns. The 3-azabicyclo-[3.2.1]oct-2-ene is known, whereas the 2-isomer is not reported. Only upon hydrogenation were the two resultant aza products shown to be present by analysis, both of which are disclosed in the prior literature. Table 1 presents some physical properties of the 2- and 3-azabicyclo[3.2.1]octanes and their derivatives.

TABLE 1. CHARACTERIZATION OF 2- AND 3-AZABICYCLO[3.2.1]OCTANES

Amine		b.p., °C		m.p., °C		Picrate m.p.[a] °C		Hydrochloride m.p.[a] °C	
		Obsd.	Lit.[b]	Obsd.	Lit.[b]	Obsd.	Lit.[b]	Obsd.	Lit.[b]
	H	—	—	137[c]	134–137[d, e]	210–211[c]	209–210[f]	265	260[g, h]
	CH_3	—	—	—	—	234[c]	220	—	—
	H	160–165[i]	155	—[j]	—	209[c]	210	270[c]	134[k, l]
	CH_3	160–161[i]	150	—	—	273[c]	267	—	—

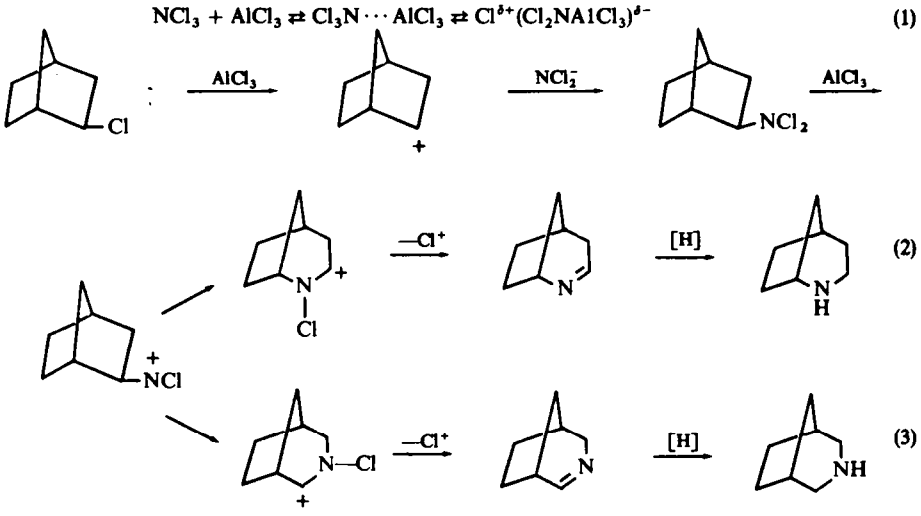
[a] Decomposed. [b] R. Griot, *Helv. Chim. Acta* **42**, 67 (1959). [c] Satisfactory data were obtained from analyses for C, H, and N. [d] M.p. 141–141·5°, C. L. Arcus, R. E. Marks, and R. Vetterlein, *Chem. Ind.*, 1193 (1960). [e] M.p. 133°, W. Klavehn, German Patent 1,030,348 (1958); *Chem. Abstr.* **54**, 14274 (1960). [f] M.p. 211–212°, see footnote *d*. [g] M.p. >300°, R. C. Elderfield and E. T. Losin, *J. Org. Chem.* **26**, 1703 (1961). [h] M.p. 273°, see footnote *e*. [i] Contains 6% of the 3-isomer. [j] Highly hygroscopic, m.p. approximately 78°. [k] Such a low melting point for this derivative appears unlikely. [l] M.p. 220–224° (crude material), see footnote *g*.

Mass spectra were obtained at low voltage on the 2- and 3-azabicyclo[3.2.1]-octanes. The 3-aza compound showed a parent peak at 111 amu and two fragment peaks at 82 and 44 amu. The 2-aza isomer also possessed a parent peak at 111 amu, but only one fragment peak at 82 amu. Since the bridgehead positions are most susceptible to cleavage, with the 3-aza compound fragmentation can occur between C_4–C_5 and C_1–C_2 or between C_1–C_7 and C_5–C_6, which accounts for the observed peaks. In the 2-aza case, the presence of a nitrogen atom adjacent to the bridgehead carbon apparently leads to bond breaking between C_1–C_7 and C_5-C_6 only, thus accounting for the single peak from fragmentation.

In relation to the synthesis of authentic materials, treatment of norbornene, 2-norborneol, or 2-bromonorbornane with hydrazoic acid in the presence of a Lewis acid catalyst is said to give 3-azabicyclo[3.2.1]oct-2-ene.[6, 7] This compound, which reportedly is susceptible to trimerization, is conveniently identified by reduction to 3-azabicyclo[3.2.1]octane. Repeating this work, we found that the saturated product was comprised of two components, 3-azabicyclo[3.2.1]octane (81%) and 2-azabicyclo-[3.2.1]octane (19%). Elderfield and Losin[8] found that the Beckmann rearrangement of norcamphor oxime led to a product presumed to be 2-azabicyclo[3.2.1]octane-3-one. In our hands, lithium aluminum hydride reduction of the crude lactam gave the composition, 3-azabicyclo[3.2.1]octane (20%) and 2-azabicyclo[3.2.1]octane (80%).

Thus, in comparison with prior techniques for the preparation of 2-azabicyclo[3.2.1]-octane, the present method appears to be the preferred one in that it provides material of reasonably good purity by a simple, two step sequence.

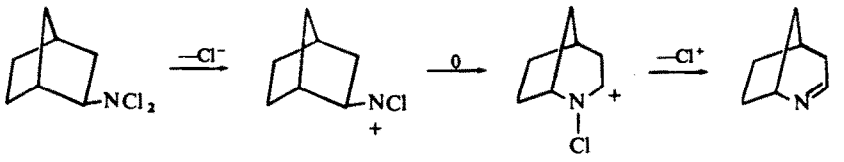
For the reaction of trichloramine-aluminum chloride with *exo*-2-chloronorbornane, the indicated mechanism is proposed for formation of the products (Eqs 1–3).



Ionization of *exo*-2-chloronorbornane gives the 2-norbornyl cation which on attack by the nucleophile, presumably dichloramide ion,[9, 10] is converted to 2-N,N-dichloroaminonorbornane. Catalytic removal of chloride ion results in an electron deficient nitrogen, permitting migration of either C_1 or C_3. Rearrangement involving positive nitrogen is facilitated by the presence of the norbornyl group, cf. acyclic systems.[5] Loss of chloronium ion produces the unsaturated species, 2- and 3-azabicyclo[3.2.1]oct-2-enes. These compounds were hydrogenated immediately to prevent polymerization. *exo*-2-Aminonorbornane apparently results from protonation and loss of chloronium ion from the corresponding N,N-dichloro compound.

Several experiments were performed in order to shed light on the stereochemical aspects of the rearrangement. *exo*-2-N,N-Dichloroaminonorbornane was subjected to the influence of aluminum chloride. After exposure of the reaction mixture to t-butyl chloride, the imino functionality was then hydrogenated. Half of the crude, basic material consisted of 2-aminonorbornane, with the remainder in the form of rearranged product: 2-azabicyclo[3.2.1]octane (90%) and 3-azabicyclo[3.2.1]octane (10%). Similarly, 2-N,N-dichloroaminonorbornane, consisting predominantly of the *endo* isomer, was induced to rearrange in this fashion. After reduction, the basic product consisted of 3-azabicyclo[3.2.1]octane (70%) and 2-azabicyclo[3.2.1]-octane (30%). These findings suggest the stereoselective schemes illustrated in eq. 4 and 5.

Related studies have been carried out in the carbonium ion series. For example, Berson and co-workers ascertained the fate of the norbornylcarbinyl cation obtained from nitrous acid deamination of *endo*- and *exo*-2-norbornylcarbinylamines in aqueous acetic acid.[11] Ring expanded alcohols resulted. The formation of 2-*exo*-*axial*-bicyclo[3.2.1]octanol and 2-*endo*-*equatorial*-bicyclo[3.2.1]octanol is a conse-



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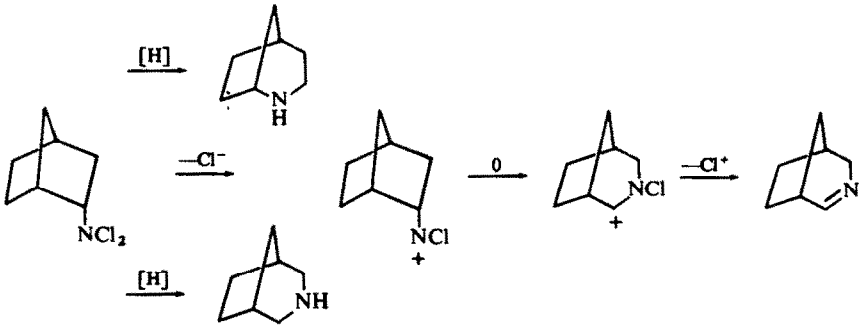

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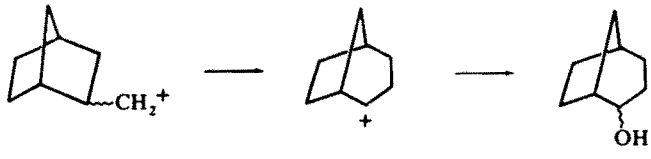


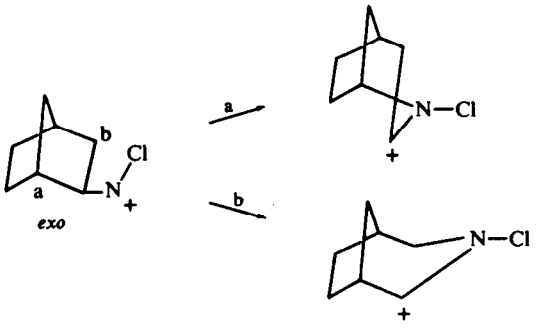
(6)

quence of C_3 migration with subsequent reaction with solvent (Eq. 6). Two rearrangements are necessary to obtain 2-bicyclo[2.2.2]octanol, the first being a C_3 shift. The generation of 3-bicyclo[3.2.1]octanol apparently entails migration of C_1 followed by attack of water.

Kraus and Schmutte reinvestigated the nitrous acid deamination of the epimeric 2-norbornylcarbinylamines.[12] For the most part their results were quite similar to the findings from Berson's laboratory. In addition, the German investigators reported the presence of isomeric 3-bicyclo[3.2.1]octanols in the *endo* reaction, and ascertained the geometry of this same product in the *exo* case. In summary, the migration ratios of C_1 to C_3 for the *endo* and *exo* isomers are 0–6:100–94 and 18:82, respectively. Hence, in all cases migration of C_3 is the preferred route by a wide margin. Similar ratios were observed from studies with 2-methyl-2-norbornylcarbinylamines.[12]

Similarities and differences are apparent in a comparison of the carbonium ion category with the present work. In both areas, C_3 involvement predominates with the *endo* form. However, whereas in our investigations the mode of reaction was shifted almost entirely to C_1 migration for the *exo* isomer, the alteration in this direction was only minor for the carbon system. On the premise that nitrogen closely resembles carbon, the theoretical considerations[11] put forth by Berson and Willner serve nicely to rationalize our findings. For *exo*-2-N,N-dichloroaminonorbornane, the shift of C_1 should be preferred on purely electronic grounds. Furthermore, in relation to con-

formational effects, C_1 migration leads to a chair form (Eq. 7), in contrast with C_3 involvement which results in a boat structure (Eq. 8). In the *endo* case the conformational effects are reversed (Eq. 9 and 10).



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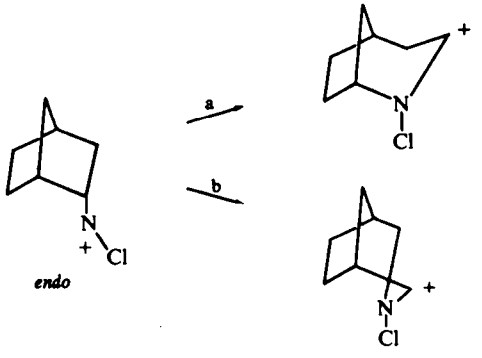

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(10)

Rearrangements involving N-chloramines are described in the prior literature. The most pertinent previous work is that of Gassman and co-workers who delineated the rearrangement pathways of N-chlorazabicyclic compounds exposed to silver salt.[13] Electron deficient nitrogen apparently plays a crucial role in the transformations. Stieglitz and Vosburgh[14] found that treatment of N-bromotritylamine with base gave benzophenone anil, the same compound as produced in the thermal decomposition of N,N-dichlorotritylamine. A univalent nitrogen species was proposed as an intermediate. In a related, more recent investigation,[15] interaction of N-chloro-1-methylcyclopentylamine with ethyllithium gave the cyclimine, 2,3,4,5-tetrahydro-6-methylpyridine. Formation of a nitrene by *alpha* elimination and a concerted mechanism were considered as possible rationalizations of the observed result. Pinck and Hilbert[16] showed that 9-substituted 9-fluorenylchloramines are converted by base to phenanthridine derivatives. Regardless of whether the substituent was phenyl, α-naphthyl, or methyl, the phenanthridine product was formed with no evidence for substituent migration to give an imide structure. Although it had been suggested that the most electronegative group would migrate, relief of strain and enhanced resonance stabilization are apparently more important. The mechanism of amination of *exo*-2-chloronorbornane also incorporates a steric factor since ring expansion relieves the strain of one of the five-membered rings. Stevens[17] reported an

intramolecular migration in the N-fluoramine series, in which nitrogen seemingly displays positive character.

It is illuminating to compare, from product and mechanistic standpoints, various routes for the preparation of 2- and 3-azabicyclo[3.2.1]octanes from norbornane derivatives *via* reduction of the intermediate unsaturated product (Table 2).

TABLE 2. COMPARISON OF VARIOUS ROUTES FOR PREPARATION OF 2- AND 3-AZABICYCLO-[3.2.1]OCTANES FROM NORBORNANE DERIVATIVES

	Reaction system	Azabicyclo[3.2.1]octane,[a]	
		3-	2-
(A)	*exo*-2-Chloronorbornane + NCl_3-$AlCl_3$[b]	6	88
(B)	Norcamphor oxime (Beckmann rearrangement)	20	80
(C)	Norbornene + HN_3	81	19
(D)	Norcamphor + HN_3	100[c]	

[a] Product after reduction. [b] 2-Aminonorbornane (6%) was also formed. [c] Ref. 8.

Reduction involving systems (A) and (C) was carried out both with hydrogen and Raney nickel catalyst[6] and the Bouveault–Blanc method,[7] with no change in the relative composition of the final mixture.

According to the generally accepted mechanism[18] for the Beckmann rearrangement the substituent *trans* to the leaving group on nitrogen is involved preferentially. Reactions (A) and (B) are closely related in that the more highly substituted carbon becomes affixed to nitrogen. A rationalization of the norbornene-hydrazoic acid reaction was advanced by Arcus and Coombs[19] based on their studies on conversion of fluoren-9-ols to phenanthridines. The Schmidt rearrangement on norcamphor is reported to give one product, 3-azabicyclo[3.2.1]-octan-2-one.[8] The two suggestions[8, 20, 21] for the mechanism differ in the step involving formation of lactam from the azide. The one route[21] is analogous to the Beckmann rearrangement because of the possibility of *syn-anti* configurations. Although the Schmidt and Beckmann reactions with open chain ketones show distinct similarities, the same situation does not pertain to the cyclic and bicyclic categories. Knunyants and Fabrichnyi,[22] who investigated β-tetralone in these systems, found that the two types followed different pathways for the most part. A cautious approach to correlative interpretation of the various results is appropriate in line with the suggestion of Elderfield and Losin,[8] since direct comparisons are probably meaningful only when reaction conditions are comparable and when the actual intermediates undergoing rearrangement possess similar stereochemistry.

Norbornane

A study of norbornane amination with trichloramine-aluminum chloride was also carried out. In contrast to *exo*-2-chloronorbornane, reaction was effected by addition of trichloramine to a mixture of norbornane and aluminum chloride in methylene chloride at 0°. The amine product, obtained in 39% yield, was *exo*-2-aminonorbornane. Characterization was accomplished by comparison with authentic material (amide

derivative) prepared by application of the Ritter reaction to norbornene.[23] The amine has also been synthesized by hydroboration of norbornene and subsequent interaction with hydroxylamine-O-sulfonic acid.[24]

The mechanism[25] of alkane amination presumably consists of initial hydride abstraction, perhaps by $Cl^{\delta+}$, followed by combination with the nitrogenous nucleophile. Analogy for the stereochemical aspect may be found in the prior literature. For example, solvolysis of *endo*- or *exo*-norbornyl *p*-bromobenzenesulfonate in acetic acid afforded *exo*-norbornyl acetate *via* a carbonium ion intermediate.[26]

Information obtained from an investigation of reaction variables proved to be useful both theoretically and synthetically. Optimum yields were realized when a relatively small excess of alkane was used. In a solvent study best results were obtained with methylene chloride. In the case of carbon tetrachloride or *o*-dichlorobenzene, the yield of amine decreased to 5–10%. A similar solvent effect was observed in previous studies.[25, 27] We found that treatment of the mixture with trichloramine-aluminum chloride at the end of the normal reaction period resulted in the formation of appreciable quantities of azabicyclo[3.2.1]oct-2-enes, along with the expected product. The exact proportion of the 2- and 3-aza isomers was not determined. A reasonable interpretation is that these conditions favor conversion of the amine to the N,N-dichloro form and subsequent rearrangement (cf. Eq. 2). Furthermore, addition of norbornane to the other components, similar to the *exo*-2-chloronorbornane procedure, gave mainly the aza product, accompanied by 2-aminonorbornane. A general discussion of the similarities and differences between the alkane and alkyl halide systems, and accompanying rationalizations, can be found elsewhere.[5]

EXPERIMENTAL

M.ps and b.p.s are uncorrected.

Materials. The alkyl halides, which were subjected to gas chromatographic examination, were greater than 98% pure. *exo*-2-Chloronorbornane and norbornane were obtained from Aldrich Chemical Co.

Analytical procedures. The preceding publication[5] in the series should be consulted. In addition to the GLPC columns described,[5] one with Carbowax 6000 (15%) on Chromosorb W (40–60 mesh), 10% NaOH, was employed. Mass spectral data was obtained with a Varian M-66 unit.

Trichloramine solution. A published procedure[28] (method B) was used with methylene chloride as solvent. *Caution*: exercise the necessary precautions when working with N-halamines.[29]

Amination of exo-2-chloronorbornane. A modification of the general procedure[5] for alkyl halides was used with 13 g (0·1 mole) of *exo*-2-chloronorbornane. After addition (no solid was in evidence), 27·75 g (0·3 mole) of t-butyl chloride was introduced. The reaction mixture was then allowed to stir for 1 hr as the temp was taken to 15°. The amination products required a special work-up procedure because of the unsaturation present. After steam distillation of the crude basic substances, the procedure for Bouveault-Blanc reduction was followed (*vide infra*, authentic materials section). Following removal of ether by rotary evaporation, the basic material was distilled in a "Minilab" apparatus, b.p. 160–165°, 45% yield.

Authentic materials

1. *3-Azabicyclo[3.2.1]oct-2-ene.*[6] In a 250 ml, 3-necked flask equipped with stirrer, thermometer, dropping funnel and condenser were placed 10 g (0·15 mole) sodium azide and 15 ml $CHCl_3$. The mixture was cooled to 0° and kept at this temp while 40 ml conc H_2SO_4 was added. The cooling bath was then replaced with a hot water bath and the temp of the mixture was allowed to warm to 30°. A soln of 9·4 g (0·1 mole) norbornene in 10 ml $CHCl_3$ was added over a period of 1 hr between 30–32°. After being stirred for 1 hr after addition, the reaction mixture was then quenched with ice water. The organic layer was separated and the aqueous layer was made basic with 50% NaOH aq. The basic aqueous layer was extracted with ether, the

extract was dried over Na_2SO_4, and the ether removed by rotary evaporation. A solid remained which was recrystallized from abs EtOH, m.p. 103°, lit.[7] m.p. 105°.

2. 3-*Azabicyclo*[3.2.1]octane. Two methods for the reduction of 3-azabicyclo[3.2.1]oct-2-ene were tried. A. *High pressure hydrogenation.*[6] In a steel bomb equipped for high press hydrogenation were placed 8 g (0·073 mole) crude 3-azabicyclo[3.2.1]-oct-2-ene in 20 ml EtOH. After approximately 6 g Raney Ni catalyst (prepared by the method of Vogel[30]) in EtOH was added, the temp was raised to 150° at 100 atm press with agitation. At the end of 2 hr, the catalyst was removed by filtration and washed with EtOH. Following removal of EtOH on the rotary evaporator with a hot water bath, GLPC analysis showed two peaks in the ratio 4/1. The major product was collected and found to be 3-azabicyclo[3.2.1]octane. The minor product was identified as 2-azabicyclo[3.2.1]octane. Table 1 lists physical constants for these products. B. *Bouveault-Blanc reduction.*[7] A soln of 10·9 g (0·1 mole) crude 3-azabicyclo[3.2.1]oct-2-ene in 250 ml MeOH was placed in a 500 ml, 3-necked flask equipped with condenser, thermometer, and stopper. During the course of 1 hr, 24 g (1 mole) Na was added in small pieces at reflux. After the Na had dissolved, the MeOH and basic products were steam distilled until the distillate was no longer basic. The distillate was then made acidic with HCl and the soln concentrated by rotary evaporation with a hot water bath. Treatment of the amine hydrochloride soln with 50% NaOH aq gave basic products which were extracted with ether and dried over $NaSO_4$. Removal of the ether by rotary evaporation provided a residue which, according to GLPC analysis, possessed the same composition as the product from high pressure hydrogenation.

3. 2-*Azabicyclo*[3.2.1]*octane.* The method of Elderfield and Losin[8] was followed. A. *Norcamphor oxime.* The procedure of Alder and Stein[31] gave the desired compound in 84% yield, b.p. 115–120° (12 mm); lit.[31] b.p. 114–116° (12 mm). B. *Beckmann rearrangement.* In a 250 ml Erlenmeyer flask, a soln of 5·5 g (0·044 mole) norcamphor oxime in 80 ml dry pyridine was cooled to 0°, and then 9·46 g (0·045 mole) *p*-toluenesulfonyl chloride was added. The mixture was kept at 0° for 4 hr, with subsequent storage overnight at room temp. After addition to ice and water, the mixture was concentrated by means of a rotary evaporator. The residue was dissolved in abs EtOH (150 ml), dried over Na_2SO_4, and refluxed for 2·5 hr. The EtOH was removed by rotary evaporation leaving 5 g material which was not purified. C. *Lithium aluminum hydride reduction.* The crude mixture containing 2-azabicyclo[3.2.1]oct-3-one from the Beckmann rearrangement was reduced with LAH. In a 500 ml, 3-necked flask equipped with stirrer, condenser, and dropping funnel were placed 2 g (0·02 mole) LAH in 200 ml abs ether. The crude lactam, 5 g, in 100 ml abs ether was added dropwise during 1 hr. The reaction mixture was refluxed for 6 hr, allowed to stand at room temp for 12 hr, and then diluted with water until a clear organic phase was formed. The ether layer was separated and concentrated by rotary evaporation. GLPC analysis showed the presence of two products in a 4/1 ratio. The major and minor products were identified as 2-azabicyclo-[3.2.1]octane and 3-azabicyclo[3.2.1]octane, respectively.

Preparation of 2-N,N-*dichloroaminonorbornane.* This preparation was the same as that described for N,N-dichloro-t-butylamine.[5] Both commercial 2-aminonorbornane hydrochloride (Aldrich), which is predominantly the *endo* isomer, and *exo*-2-aminonorbornane, synthesized from norbornane-aluminum chloride-trichloramine, were used as reactants.

Reaction of 2-N,N-*dichloroaminonorbornane with aluminum chloride and t-butyl chloride.* The two epimers, *endo*- and *exo*-2-N,N-dichloroaminonorbornane were treated in the same manner. In a 250 ml, 3-necked flask equipped with thermometer, stirrer, condenser, and dropping funnel, a mixture of 13·3 g (0·1 mole) $AlCl_3$ and 50 ml CH_2Cl_2 was cooled to −10°. A soln of 2-N,N-dichloroaminonorbornane (0·05 mole) in CH_2Cl_2 (100 ml) was added. While the temp was maintained between −5 to −10°, 13·8 g (0·15 mole) t-butyl chloride was introduced. The reaction mixture was then allowed to stir for 1 hr as the temp was taken to 15°. Work-up followed the geeral procedure described for *exo*-2-chloronorbornane.

Amination of norbornane. A modification of a published procedure[25] was followed. A molar ratio of 1:2:1·5 (0·133:0·266:0·20 mole) for NCl_3:$AlCl_3$:norbornane was used with the norbornane dissolved in about 150 ml CH_2Cl_2. The reaction was carried out in a 500-ml flask with a constant flow of N_2. The product was distilled through a Minilab column, b.p. 50–55° (4–7 mm), lit.[32] 77° (50 mm), to give *exo*-2-aminonorbornane in 39% yield (based on trichloramine). Characterization was effected with the acetyl derivative, m.p. 140°, lit.[33] m.p. 139°. IR and NMR spectra also were in agreement.

Several reaction variables were investigated.

1. *Amount of norbornane.* With NCl_3:$AlCl_3$ constant at 1:2 molar ratio, norbornane variation gave the indicated yields, 5:3:1·5 = 35:36:39%.

2. *Solvent study.* CH_2Cl_2, CCl_4 and *o*-dichlorobenzene were tested as solvents.

3. *Mode of addition.* A. *Norbornane and trichloramine to aluminum chloride.* The general procedure for norbornane was used except that a soln of norbornane and NCl_3 in CH_2Cl_2 was added during 1·5 hr at

0–10° to a mixture of $AlCl_3$ and CH_2Cl_2. After another hr at 0–10°, work-up gave crude amine in 66% yield, *exo*-2-aminonorbornane (67%) and rearranged azabicyclo-[3.2.1]oct-2-enes (33%). Identification was made by comparison with authentic materials. B. *Norbornane to trichloramine and aluminum chloride.* The general procedure for *exo*-2-chloronorbornane was used (NCl_3:$AlCl_3$: C_7H_{12} = 1:2:1·5 molar ratio). The crude base (47% yield) consisted of *exo*-2-aminonorbornane (33%) and azabicyclo[3.2.1]oct-2-enes (66%).

4. *Post-treatment.* After the standard amination for norbornane was carried out, $AlCl_3$ (0·133 mole) and NCl_3 (0·036 mole) were added and the mixture was stirred at 0° for 12 hr. A 35% yield was obtained of crude amine product, *exo*-2-aminonorbornane (66%) and azabicyclo[3.2.1]oct-2-enes (34%). In a control experiment involving no excess materials, after 12 hr only the *exo* amine was detected.

Authentic acetyl derivative of exo-2-*aminonorbornane.* MeCN (4·5 g, 0·11 mole) was added to a soln of conc HSO_4 acid (5·5 ml, 0·1 mole) in 4 ml glacial AcOH at 20°. After norbornene (9·4 g, 0·10 mole) in 6 ml glacial AcOH was added slowly at 50°, the reaction mixture was heated at 80° for 3 hr. Dilution with 200 ml cold water, followed by storage at 0°, yielded crystals which melted at 139–140°, lit. m.p.[33] 139°, m.p.[26] 140–141°, after purification.

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