Rearrangement of 1-*N*,*N*-Dichloroaminoapocamphane by Aluminum Chloride[1]

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Abstract: Exposure of 1-*N*,*N*-dichloroaminoapocamphane to aluminum chloride leads to the rearrangement product, 1-chloro-3,3-dimethyl-2-azabicyclo[2.2.2]octane (10% yield), as well as materials from β fission, 4-isopropylcyclohexanone, *dl*-cryptone, and 4-isopropylphenol (40% yield total). The rearrangement is believed to entail electron-deficient nitrogen. The solvolytic behavior of the bridgehead chloride indicates enhanced reactivity in comparison with 1-bromo-3,3-dimethylbicyclo[2.2.2]octane.

Exposure of 2-*N*,*N*-dichloroaminonorbornane,[3] *N*,*N*-dichloro-1-adamantanamine,[4] *N*-chloro-*N*-ethyl-1-adamantanamine,[5] and *N*,*N*-dichlorotri-*n*-butylcarbinamine[6] to aluminum chloride has recently been shown to result in products which derive from alkyl migration to electron-deficient nitrogen. In addition, Gassman has shown that the analogous rearrangement of various *N*-chloroazabicyclic compounds, induced by silver salts, involves a nitrenium ion.[7]

The purpose of this investigation was to examine the rearrangement of a bicyclic structure containing the dichloroamino group at the bridgehead position. 1-*N*,*N*-Dichloroaminoapocamphane was selected for study.

Results and Discussion

Synthetic Aspects. 1-*N*,*N*-Dichloroaminoapocamphane (2) was obtained by chlorination of 1-aminoapocamphane (1) with *tert*-butyl hypochlorite in cyclopentane. The literature provides a five-step sequence for synthesis of the parent amine, entailing the indicated transformations; camphor → 10-camphorsulfonic acid[8] → 10-camphorsulfonyl chloride[9] → ketopinic acid[10] → 1-apocamphanecarboxylic acid[11] → 1-aminoapocamphane.[11] Compound 2 on treatment with aluminum chloride (2 mol) in methylene chloride at about −75° provided rearranged product, which was subjected to acid hydrolysis. Steam distillation separated the materials into a residual basic fraction (3 and 4) and a volatile neutral fraction (5–7) (eq 1). By controlling the severity of the hydrolytic conditions, one could obtain either or both of the basic components, 1-chloro-3,3-dimethyl-2-azabicyclo[2.2.2]octane (3) and 4-[2-amino-2-propyl]cyclohexanone (4).

α-Chloroamine 3 was identified by elemental analyses

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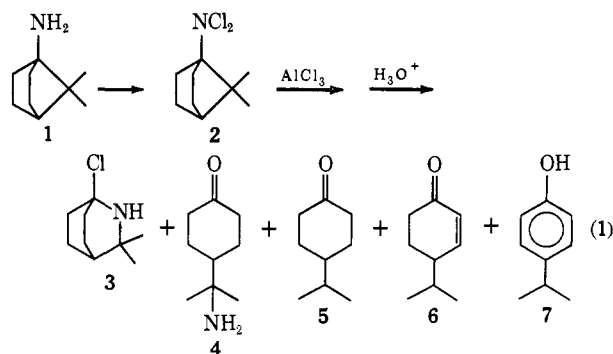
and ir and nmr spectra. In addition, chemical characterization was accomplished by hydrolysis to amino ketone (4). Subsequent Wolff–Kishner reduction provided 2-cyclohexyl-2-aminopropane (8). Authentic 8 was prepared by the sequence set forth in eq 2. Va-

$$(2)$$
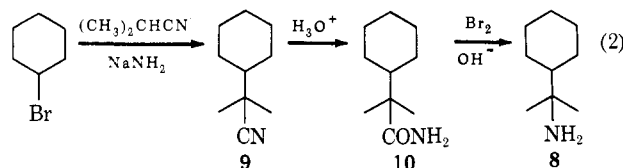
lidity of the structural assignments is supported by analogy to the corresponding adamantane system.[4] Compound 9 gave satisfactory data for the ir and nmr spectra, as well as for microanalyses. Ir and nmr spectra were used for identification of 8 and 10, together with comparison of physical properties and derivatives to those of the known materials. The identities of 5, 6, and 7 were established by means of the authentic materials. An attempt to prepare 8 *via* the Ritter reaction from the corresponding alcohol (11) led to an appreciable amount of rearranged product as shown by nmr spectral analysis. The contaminant was

11
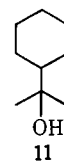
not readily separable, even by glpc. In contrast, Koch and Haaf reported[12] no difficulty in obtaining dimethylcyclohexylacetic acid from 1-isopropylcyclohexanol-1 and formic acid–sulfuric acid.

(1) Preliminary communication. XVIII. Chemistry of *N*-Haloamines: R. D. Fisher, T. D. Bogard, and P. Kovacic, *J. Amer. Chem. Soc.*, **94**, 7599 (1972).

(2) Postdoctoral Fellow, 1971–1972.

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

(4) P. Kovacic, J.-H. Liu, E. M. Levi, and P. D. Roskos, *J. Amer. Chem. Soc.*, **93**, 5801 (1971).

(5) S. J. Padegimas and P. Kovacic, *J. Org. Chem.*, **37**, 2672 (1972).

(6) T. A. Kling, M, B. Nazareno, and P. Kovacic, *J. Amer. Chem. Soc.*, **94**, 2157 (1972); T. A. Kling, R. E. White, and P. Kovacic, *ibid.*, **94**, 7416 (1972).

(7) P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(8) P. D. Bartlett and L. H. Knox, *Org. Syn.*, **45**, 12 (1965).

(9) P. D. Bartlett and L. H. Knox, *ibid.*, **45**, 14 (1965).

(10) P. D. Bartlett and L. H. Knox, *ibid.*, **45**, 55 (1965).

(11) D. N. Kursanov and S. V. Vitt, *J. Gen. Chem. USSR*, **25**, 2401 (1955).

(12) H. Koch and W. Haaf, *Justus Liebigs Ann. Chem.*, **618**, 251 (1958).

Table I. Rearrangement of 1-N,N-Dichloroaminoapocamphane by Aluminum Chloride[a]

| Cl+ in 2, % | Temp, °C | Solvent | Products, % | | | | | | | |
			3	4	5	6	7	Total β scission	1	Tar[b]
95	−75	CH₂Cl₂	11	6	14	23	3	40	7	0.5
94	−75	CH₂Cl₂	6	10	4	16	15	35	8	0.5
93	−75	CH₂Cl₂	11		6	18	16	40	10	0.8
95	−75	CH₂Cl₂	13		5	16	15	36	9	0.6
98	−75[c]	CH₂Cl₂	10		6	26	d	32[d]	6	0.9
93	−70[e]	CH₂Cl₂		12	14	19	d	33[d]	11	0.7
94	−10 to 0	CH₂Cl₂	1		12		d	12[d]	17	1.2
99	−25	CH₂Cl₂	4		10	18	3	31	24	0.6
99	−75[f]	CH₂Cl₂	9		13	17	d	30[d]	17	0.4
91	−75[g]	CH₂Cl₂	14		5	8	12	25	9	0.7
93	−75[h]	CH₂Cl₂	6		6	15	d	21[d]	9	0.8
98	−75[h]	CH₂Cl₂	9		6	23	16	45	6	0.5
95	−75[h]	CH₂Cl₂	16		3	15	16	34	9	0.5
98	−25[h]	CH₂Cl₂	23		9	15	5	29	5	0.5
93	−30	C₂H₄Cl₂	2		12	23	d	35[d]	15	0.6
100	−60	CHCl₃			9	14	d	23[d]	12	0.6
96	−50[i]	CHCl₃			17	27	d	44[d]	2	0.7
92	−25	CCl₄	9			4	3	7	29	0.4
95	−20[i]	CCl₄	17		1	6	21	28	25	0.6

[a] See standard procedure. [b] In grams. [c] Scrupulously dry. [d] **7** was not determined. [e] 90 min reaction time. [f] 0.9 ml of water was added to the aluminum chloride. [g] 100 ml of CH₂Cl₂ was added to the aluminum chloride. [h] In the presence of oxygen. [i] 2 hr.

Analogous α-chloroamines (or derivatives thereof) have been isolated or proposed as intermediates in prior studies entailing rearrangement of N-haloamines. As examples, **12** was formed from N-chloro-N-acetyl-1-
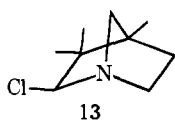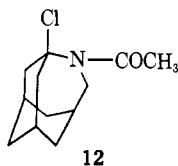

adamantanamine and aluminum chloride,[13] and **13** from 4,7,7-trimethyl-2-chloro-2-azabicyclo[2.2.1]heptane and silver salt.[7] Also, 1-chloro-2-azadamantane is reported.[13b] However, **3** appears to be unique in that the chlorine atom is at a bridgehead position of a bicyclic system. It is significant that we have found no literature examples of open-chain compounds containing the R₂CClNHR functionality.[14] As in the case of the carbonyl group and hydrogen chloride, energetics apparently favor the unsaturated form (imino moiety). The stability and covalent nature of **3** are most likely associated with the strain involved in introducing a carbon–nitrogen double bond at a bridgehead position. Reed and Lwowski found[15] that decomposition of 1-azidonorbornane led to rearrangement involving ring expansion with incorporation of nitrogen.

Table I presents the results from a study of reaction variables. Due to some variation in product yields under presumably identical conditions (runs 1–4), caution must be exercised in drawing conclusions based on small changes in yield. Addition of water resulted in an increase in the amount of recovered amine, apparently from hydrolysis of **2**. With chloroform (rela-

tively low dielectric constant) as solvent, no **3** was produced and the reaction appeared to be appreciably slower. There was little recovered **2** when the time was extended. Similarly, the yield of **3** decreased in 1,-2-dichloroethane. With carbon tetrachloride solvent, almost no **5** was formed and the amount of recovered amine increased even when the reaction time was prolonged.

Mechanistic Considerations. The first mechanistic question to be addressed is whether a nitrenium ion is involved as an intermediate or whether the reactions occur in a concerted fashion. In Gassman's work,[7] the chief criterion used to establish the existence of a nitrenium ion was the presence of recovered amine. Good evidence was presented to support the contention that a triplet state, formed from the singlet nitrenium ion by spin inversion, abstracts hydrogen. Equation 3 describes the changes in our case. A favor-


$$2 \xrightarrow[-Cl^-]{AlCl_3} \mathbf{14a} \longrightarrow \mathbf{14b} \xrightarrow{[2H\cdot]} \xrightarrow{-Cl^+} 1 \quad (3)$$
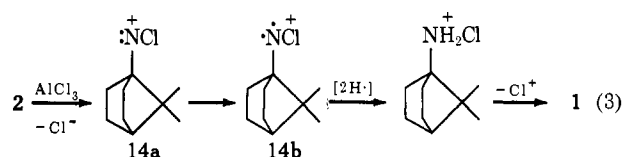
able driving force in our system is the presence of a heavy atom solvent, methylene chloride, which is known to catalyze spin inversion.[7] Under our standard conditions, the amount of recovered amine was usually small, less than 10%. This can be ascribed to unchanged **2**, hydrolysis of **2** by adventitious water during rearrangement, and the presence of 1-N-chloroaminoapocamphane as an impurity[5,6] in **2**. On the other hand, it appears that formation of **14** may be a function of temperature. At higher temperatures (0 to −10° and −25°, Table I), there was an appreciable increase in the per cent of recovered parent amine (17–24% recovery).

β Scission. On theoretical grounds and by literature analogy, it is possible to designate a number of pathways leading to β fission. The first to be considered entails a polar mechanism (eq 4). Cleavage might occur in a

(13) (a) T. Sasaki, S. Eguchi, T. Kiriyama, and H. Suzuki, *Syn. Commun.*, 1, 267 (1971); (b) H. Stetter, P. Tacke, and J. Gärtner, *Chem. Ber.*, 97, 3480 (1964).

(14) (a) S. Patai, Ed., "The Chemistry of the Carbon-Nitrogen Double Bond," Interscience, New York, N. Y., 1970; (b) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," W. A. Benjamin, New York, N. Y., 1965 (Vol. I), 1966 (Vol. II).

(15) J. O. Reed and W. Lwowski, *J. Org. Chem.*, 36, 2864 (1971).
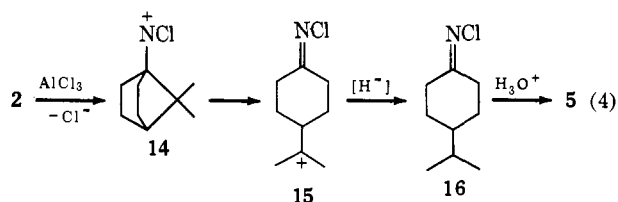
concerted manner or through **14** as a discrete intermediate. Solvent or organic substrate could serve as hydride donors. Also, **15** can function as a source of *dl*-cryptone (**6**) through proton loss, rearrangement, and hydrolysis. This approach is akin to several literature reports. Under mild conditions **17** was converted[16a] to isoquinoline, presumably by way of **18** (eq 5). The
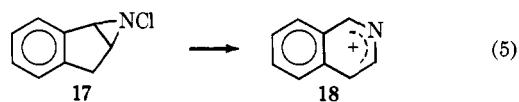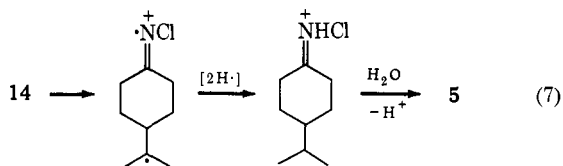

mechanistic scheme in eq 6 was proposed[16b] by Biehler
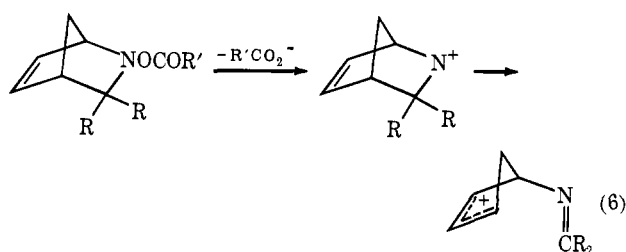
and Fleury. Both literature examples are characterized by a strain factor, as is also the case with **2**. Of course, a similar type cleavage is well established[17] in carbonium ion chemistry.

Alternatively, a radical pathway appears plausible with **14** as precursor (eq 7). Finally, a purely radical

chain reaction might set in (eq 8). The two sources of
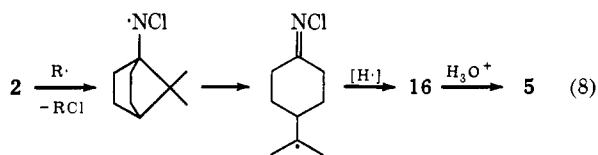
hydrogen for donation are the organic substrate (or derivative) and methylene chloride which possesses a relatively small chain transfer constant (styrene polymerization).[18a] Although relatively few in number, there are literature examples[19] of β cleavage involving nitrogen-centered radicals.

In relation to experimental evidence, as already mentioned (*vide supra*), there appears to be a direct cor-

(16) (a) D. C. Horwell and C. W. Rees, *Chem. Commun.*, 1428 (1969); (b) J. M. Biehler and J.-P. Fleury, *Tetrahedron*, **27**, 3171 (1971).
(17) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structures," McGraw-Hill, New York, N. Y., 1968, p 772.
(18) C. Walling, "Free Radicals in Solutions," Wiley, New York, N. Y., 1957, (a) p 152; (b) p 169.
(19) P. Kovacic, M. K. Lowery, and K. W. Field, *Chem. Rev.*, **70**, 639 (1970).

relation between an increase in temperature and enhanced generation of nitrenium ion (**14**). Structure **14** can conceivably undergo ring opening either by a polar (eq 4) or radical (eq 7 and 8) route. Studies with oxygen also aided in elucidation of the reaction course. In four experiments with this inhibitor, there was little or no change in yield of products from β fission. Oxygen is known to act as an effective scavenger of carbon radicals.[18b] Hence, one can conclude that a homolytic process is not involved to any appreciable extent. The low yield of **5** when carbon tetrachloride comprised the medium points to the solvent as the species responsible for hydrogen donation.

A reasonable route to **6** and **7** entails **5** as precursor. Since carbonyl compounds are known[20] to undergo α-chlorination by *N*-haloamines, such a process, followed by dehydrohalogenation, would lead to **6**. Continuation in a similar fashion gives rise to **7**, which has literature analogy.[21]

Basic Products. According to the mechanistic interpretation suggested for the rearrangement pathway in prior examples involving *N,N*-dihaloamines, the indicated scheme is set forth (eq 9).
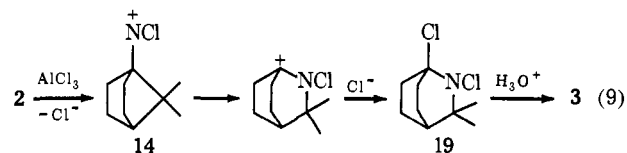
On the basis of *a priori* reasoning and the arguments presented in the preceding section, one should consider several possibilities for rearrangement of **2** to **3**, including a synchronous process and a three-step sequence involving the intermediate nitrenium ion **14**. In our recent investigations[22] with open-chain types, R_3CNCl_2, several lines of evidence, including migratory aptitudes, led us to believe that the reaction was proceeding in a concerted manner. The strain associated with the apocamphane nucleus would represent an additional factor favoring such a route in the present case. It is worthwhile mentioning Gassman's conclusions[7] dealing with the formation of **13**. Evidence was presented that the rearrangement involved either a very tight ion pair or a highly concerted transition state leading directly to C–Cl bond formation. At this stage, it is not possible to designate with certainty the detailed aspects of the reaction leading to **3**.

A similar overall transformation has been described in which a 1,2 shift occurs to electron-deficient carbon attached to the bridgehead of the norbornyl nucleus. Thus, acetolysis of bicyclo[2.2.1]heptane-1-methyl tosylate (**20**) afforded the acetate (**21**) of bicyclo[2.2.2]-octan-1-ol in 85% yield[23] (eq 10). The relative rate *vs.* acetolysis of neopentyl tosylate was 8:1.
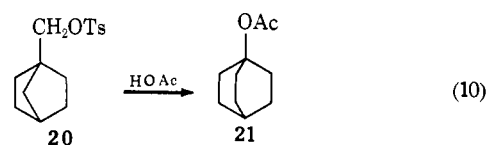

(20) H. G. O. Becker, *et al.*, *Z. Chem.*, **9**, 325 (1969).
(21) E. M. Kosower and G.-S. Wu, *J. Org. Chem.*, **28**, 633 (1963).
(22) T. A. Kling, M. B. Nazareno, R. E. White, and P. Kovacic, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, No. ORGN-63.
(23) K. B. Wiberg and B. R. Lowry, *J. Amer. Chem. Soc.*, **85**, 3188 (1963).

Solvolysis of 1-Chloro-3,3-dimethyl-2-azabicyclo-[2.2.2]octane (3). The solvolysis of **3** is of considerable interest in regard to bridgehead reactivity[24] and Bredt's rule, particularly in comparison with the related carbon analog **22**. We observed formation of an immediate

22
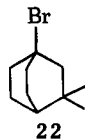
precipitate when **3** was placed in contact with aqueous silver nitrate. In contrast, 4 hr was employed[25] to effect reaction with **22** which contains a halogen atom (bromine) inherently more labile than the one (chlorine) in **3**. Additional indications of the relatively high reactivity of **3** are set forth in Table II.

Table II. Solvolysis of **3**

	Temp, °C	Time, min	End result 3, %[a]	4, %[a]
Dioxane-5% NaOH (60:40)[b]	45	15	93	7
Dioxane-5% HCl (60:40)	45	15	100	
H₂O[c]	70	15	22	78
5% NaOH[c]	70	15	53	47
3 N HCl	70	15	100	
H₂O[c]	95	30		100
5% NaOH[c]	95	30		100

[a] Per cent of the organic mixture after reaction. [b] Heterogeneous mixture. [c] **3** was added in methylene chloride which quickly vaporized. However, too little material was employed to ascertain whether the mixture was homogeneous or heterogeneous.

Due to the errors involved in these trial reactions, no rate constants have been calculated. However, in contrast to the sluggish behavior[24] of **22**, **3** appears to display increased lability in solvolysis.

It is well established that α-heteroatoms with unshared pairs of electrons can enhance solvolytic reactivity.[26] In fact, compounds of the type [RCH= NR₂]⁺X⁻ exist as open-chain immonium salts,[27] rather than in covalent form (α-chloroamine). Methyl chloromethyl ether, which solvolyzes about 10¹³ times faster than *n*-propyl chloride,[28] provides a striking example of this effect. Rate enhancement is attributed to the favorable resonance contribution by the oxonium ion structure. To invoke this type of argument in accounting for the reactivity of **3**, one must accept the immonium ion **23** as a canonical resonance

23
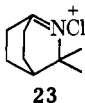
form which bestows a degree of carbon–nitrogen double bond character to the bridgehead position.

(24) R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, 1, 283 (1966).
(25) W. v. E. Doering, M. Levitz, A. Sayigh, M. Sprecher, and W. P. Whelan, *J. Amer. Chem. Soc.*, 75, 1008 (1953).
(26) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 102.
(27) K. Harada, p 259 in ref 14a.
(28) P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Prestt, *J. Chem. Soc.*, 3641 (1955).

A related situation was reported[29] by Grob and Sieber in which the positions of the nitrogen and electron-deficient carbon were reversed. On the basis of the observation that the 2-quinuclidinyl cation **24**

24
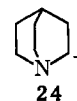
is somewhat more stable than its carbon counterpart (the bicyclo[2.2.2]-2-octyl cation), they proposed delocalization involving the bridgehead nitrogen. Similarly, evidence was recently presented[30] for stabilization of an adjacent positive charge by bridgehead nitrogen in the 1-azabicyclo[2.2.1]heptane system.

The comparative resistance of **3** to hydrolysis in acid is noteworthy. The lessened reactivity presumably results from protonation of the amino group. This provides insight into the survival of the bridgehead chloride in acid medium during the steam distillation step of the work-up procedure. It is apparent that the N–Cl bond of **19** is more susceptible to hydrolytic cleavage than is the C–Cl bond.

Experimental Section

Melting points, determined in a Thomas-Hoover capillary apparatus, are uncorrected. Glpc analyses were performed on a Model 1720-10 Varian Aerograph gas chromatograph with either a 10 ft × 0.25 in. column of 15% Carbowax 20M on 45–60 Chromosorb W (column A) or a 10 ft × 0.25 in. column of 15% UCON-50HB 2000 and 5% sodium hydroxide on 45–60 Chromosorb W (column B). All products were collected from the columns used for analyses. Nmr spectra were obtained with a Varian T-60 or HA-100 spectrometer, and ir spectra were recorded with a Perkin-Elmer 137 spectrometer. Elemental analyses were performed by Baron Consulting Co., Orange, Conn., and Micro-Tech Laboratories, Skokie, Ill. Methylene chloride and 1,2-dichloroethane were distilled from calcium hydride prior to use. Carbon tetrachloride (Fisher, spectroanalyzed) was used without further purification. Chloroform was washed in succession with equal volumes of concentrated sulfuric acid, water, 5% sodium bicarbonate, and water, then dried, and distilled prior to use. Anhydrous sodium sulfate was used as a drying agent.

1-Aminoapocamphane[11] (1). **1** was prepared from *dl*-10-camphorsulfonic acid (Aldrich) by a sequence of reactions involving 1-apocamphanecarboxylic acid,[11] ketopinic acid[10] (10–35% yields *vs.* literature yields of 38–43%), and *dl*-10-camphorsulfonyl chloride.[9] By-product aniline was removed from the crude amine by washing with water. Alternatively the amount of this by-product could be substantially reduced during reaction by decreasing the time to 15 min and allowing the temperature of the benzene solution to rise to about 80°. Ir and nmr spectra, and physical properties were as expected for the various compounds. The basic product was stored as the hydrochloride.

1-*N,N*-Dichloroaminoapocamphane (2). **2** was prepared by a modification of a published procedure.[31] A 25-ml solution of *tert*-butyl hypochlorite[32] (2.17 g, 0.02 mol) in cyclopentane was slowly added with stirring to a solution of 1-aminoapocamphane (1.39 g, 0.01 mol) in 100 ml of cyclopentane at −20°. The resultant solution was stirred for 1 hr at −20 to 0°. Ice cold water (50 ml) was added; the cyclopentane solution was separated, dried, and cautiously evaporated near room temperature. After 25 ml of dry methylene chloride was added, the solution was evaporated. The orange, oily residue was diluted to 50 ml with dry methylene chloride and used immediately in the rearrangement reaction. Yields of 93–99% of the *N,N*-dichloroamine generally were obtained, as indicated by titration for positive chlorine.[33] The ir

(29) C. A. Grob and A. Sieber, *Helv. Chim. Acta*, 50, 2531 (1967).
(30) P. G. Gassman, R. L. Cryberg, and K. Shudo, *J. Amer. Chem. Soc.*, 94, 7600 (1972).
(31) H. Zimmer and L. F. Audrieth, *ibid.*, 76, 3856 (1954).
(32) H. M. Teeter and E. W. Bell, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1967, p 125.
(33) P. Kovacic, C. T. Goralski, J. J. Hiller, Jr., J. A. Levisky, and R. M. Lange, *J. Amer. Chem. Soc.*, 87, 1262 (1965).

spectrum of **2** showed bands at 2950, 1450, 1395, 1385, 1300, 1030, 730, 690, and 670 cm⁻¹.

Reaction of 1-N,N-Dichloroaminoapocamphane (2) with Aluminum Chloride. A 50-ml solution of **2** (*ca.* 0.01 mol) in dry methylene chloride was slowly added with vigorous stirring to a slurry of anhydrous aluminum chloride (2.66 g, 0.02 mol) in 50 ml of dry methylene chloride under a constant nitrogen pressure at *ca.* —75°. After the mixture was stirred for 30 min at *ca.* —75°, 100 ml of ice cold, 18% hydrochloric acid was added. The solution was stirred and purged with nitrogen for 20 min while it warmed to room temperature. Water (50 ml) was added and the mixture was steam distilled until 200 ml of total distillate was obtained. After separation, the aqueous portion was extracted with 50 ml of methylene chloride. The combined, dried extract yielded the nonbasic product fraction on solvent removal. The steam distillation residue was cooled and extracted with methylene chloride yielding *ca.* 0.5 g of tarry residue after solvent removal from the dried solution. The aqueous layer was basified by slow addition to 100 ml of 50% sodium hydroxide solution cooled either in a Dry Ice–acetone bath (procedure A) or in a room temperature water bath (procedure B). Extraction with methylene chloride followed by drying and solvent removal yielded the basic product fraction. Amino ketone was produced by procedure B.

When the reaction was run in the presence of oxygen, the gas was introduced below the surface through a fritted tube.

Nonbasic Products. The nonbasic product fraction was analyzed on column A (with a column temperature of 120° initially, followed by programming to 180° after 24 min). Cyclohexanone was used as an internal standard, with no correction for thermal conductivity differences.[34,35] The major products[36] were identified as indicated.

4-Isopropylcyclohexanone (5). **5** showed ir bands at 2850, 1704, 1381, 1368, and 940 cm⁻¹, and nmr bands at 0.95 (d, 6 H), 1.5 (m, 6 H), and 2.3 (m, 4 H) ppm; semicarbazone, mp 185–185.5° (lit.[37] mp 188–189°); 2,4-dinitrophenylhydrazone, mp 118–119° (lit.[38] mp 119–120°).

4-Isopropyl-2-cyclohexen-1-one (*dl*-Crypton) (6). **6** showed ir bands at 2900, 1680, 1466, 1388, 1368, and 835 cm⁻¹; and nmr bands at 0.98 (d, 6 H), 1.9 (m, 4 H), 2.45 (m, 4 H), 6.0 (d, 1 H), and 6.9 (d, 1 H) ppm.[39,40]

4-Isopropylphenol (7). **7** gave ir and nmr spectra identical with those of authentic material.

Basic Products. The basic product fraction was analyzed on column B (180°) with cyclohexanone as internal standard.[34]

1-Aminoapocamphane. This material was identical with the starting material (**1**).

1-Chloro-3,3-dimethyl-2-azabicyclo[2.2.2]octane (3). **3** has a glpc retention time of 8.4 min and mp 55–56°. **3** showed ir bands at 3280, 2850, 1370, 1350, 1090, 1050, and 775 cm⁻¹; and nmr bands at 1.25 (s, 6 H), 1.4 (m, 2 H), 1.7 (s, 1 H, exchangeable), *ca.* 1.7 (m, 1 H), and 2.1 (m, 6 H) ppm.

Anal. Calcd for C₉H₁₆NCl: C, 62.24; H, 9.23; N, 8.07. Found: C, 62.55; H, 9.41; N, 8.12.

On treatment with either aqueous or ethanolic silver nitrate, **3** gave an immediate precipitate. Hydrolysis with 5% sodium hydroxide for 15 min on a steam bath gave 4-[2-amino-2-propyl]-cyclohexanone (**4**).

4-[2-Amino-2-propyl]cyclohexanone (4). **4** has a glpc retention time of 17 min and mp 37–38°; it showed ir bands at 2850, 1700, 1580, 1380, 1360, and 1040 cm⁻¹; and nmr bands at 1.12 (s, 6 H), 1.25 (s, 2 H), 1.6 (m, 2 H), and 2.4 (m, 8 H) ppm.

Anal. Calcd for C₉H₁₇NO: C, 69.65; H, 11.04; N, 9.03. Found: C, 69.06; H, 11.11; N, 8.91.

2-Cyclohexyl-2-aminopropane (8) from 4. A mixture of 36 mg of **4**, 0.1 ml of hydrazine hydrate, and 0.1 g of KOH in 3 ml of triethylene glycol was refluxed for 4 hr. Water (2 ml) was added to the cooled mixture, which was then acidified with 18% hydrochloric acid and washed with ether. The aqueous layer was then basified with 50% sodium hydroxide and extracted with ether. The extracts were dried and freed of solvent. Preparative glpc on column B afforded 2-cyclohexyl-2-aminopropane (**8**) which possessed ir and nmr spectra and glpc retention time identical with those of authentic material.

α,α-Dimethyl-α-cyclohexylacetonitrile (9). **9** was prepared by a modification of a published procedure.[41] A stirred suspension of sodium amide (66 g, 1.66 mol) in 300 ml of toluene in an addition funnel was slowly added during 3 hr to a solution of isobutyronitrile (35 g, 0.5 mol) and cyclohexyl bromide (82 g, 0.5 mol) in 200 ml of toluene at 80°. After addition, the mixture was refluxed for 3 hr and then cooled to 10° prior to the dropwise addition of 500 ml of water. Separation of phases, extraction of the aqueous layer with benzene, drying of the combined organic portions, and evaporation of solvent yielded *ca.* 20 g of crude product.[42] Distillation afforded 4.8 g (6%) of **9**: bp 110–112° (5 mm); ir bands at 2860, 2790, 2200, 1450, 1385, 1365, and 900 cm⁻¹; nmr bands (HA-100) 1.2 (m, 2 H), 1.3 (s, 6 H), 1.4–1.7 (broad, ∼3 H), and 1.82 (m, 6 H) ppm.

Anal. Calcd for C₁₀H₁₇N: C, 79.46; H, 11.25; N, 9.27. Found: C, 79.22; H, 11.37; N, 9.40.

α,α-Dimethyl-α-cyclohexylacetamide (10). A mixture of 1.55 g (*ca.* 0.01 mol) of **9** and 25 ml of 80% sulfuric acid was heated with stirring on a steam bath for 24 hr. The mixture was poured on ice and extracted with ether. The ether layer was washed with 10% sodium carbonate and water and then dried. Removal of solvent yielded 0.56 g (33%) of crude amide, mp 152–153° (lit.[12] mp 154°).

2-Cyclohexyl-2-aminopropane (8) from 10. Bromine (0.78 g, 0.0045 mol) was added to an ice cold solution of sodium hydroxide (0.8 g, 0.018 mol) in 10 ml of water. After the bromine color disappeared, crude **10** (0.56 g, 0.0033 mol) was added and stirring was continued for 5 hr at 0–5°. The mixture was extracted with ether. The ether layer was washed with water, dried, and freed of solvent by evaporation. The crude isocyanate was added to 5 ml of 20% hydrochloric acid. After the mixture was stirred for 5 hr on a steam bath, sodium hydroxide was added, and the mixture was extracted with ether. The ether extract was washed with water, dried, and freed of solvent. Preparative glpc on column B afforded **8** (retention time 3.5 min, 180°): ir bands at 3240, 2900, 2850, 1600, 1450, 1385, 1365, 900, 840, and 810 cm⁻¹; nmr bands at 1.02 (s, 6 H), *ca.* 1.1 (m, ∼4 H), 1.37 (s, 2 H), and 1.8 (m, *ca.* 6 H) ppm.

Anal. Calcd for C₉H₁₉N: C, 76.53; H, 13.56; N, 9.91. Found: C, 76.50; H, 13.64; N, 9.78.

The hydrochloride melted at 263–264° (lit.[43] mp 252–253°).

2-Cyclohexyl-2-propanol (11). Cyclohexyl chloride (59 g, 0.5 mol) was added to magnesium (12 g, 0.5 mol) in 100 ml of ether. After the Grignard reagent was prepared, acetone (29 g, 0.5 mol) in 100 ml of ether was added slowly with stirring. After 1 hr, 200 ml of 1 N sulfuric acid was added, and the mixture was extracted with ether. The combined ether extract was dried and freed of solvent. Distillation yielded 28 g (40%) of a mixture of products (glpc, column A) which contained >85% of the desired material. Preparative glpc afforded pure **11**: n²⁰D 1.4692 (lit.[44] n²⁰D 1.4683); ir bands at 3300, 2870, 1450, 1370, 1350, 1140, 960, and 895 cm⁻¹; nmr bands at 1.15 (s, 6 H), *ca.* 1.2 (m, 4 H), 1.35 (s, 1 H), and 1.8 (m, 7 H) ppm.

Ritter Reaction of 11. A solution of concentrated sulfuric acid (25 ml) in glacial acetic acid (25 ml) was added during 3 hr at room temperature to a stirred mixture of crude **11** (14.2 g, 0.1 mol), glacial acetic acid (10 ml), and powdered sodium cyanide (7 g, 0.15 mol). After addition of 50 ml more of concentrated sulfuric acid, the temperature was raised gradually to 60° over a period of 3 hr. After 12 hr at room temperature, the mixture was combined with 200 g of ice and then refluxed for 6 hr. Sodium hydroxide

(34) Little difference in thermal conductivity between cyclohexanone and the product is expected, see ref 35.

(35) H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography," Varian Aerograph, Consolidated Printers, Berkeley, Calif., 1969, p 146.

(36) Two components with retention time of 31–33 min (broad peak) were not separated or identified. They comprised 5% of the product under the standard conditions, and less under other conditions. Other minor products were present in <1% yield.

(37) R. S. Cahn, A. R. Penfold, and J. L. Simonsen, *J. Chem. Soc.*, 1366 (1931).

(38) P. A. Berry, A. K. Macbeth, and T. B. Swanson, *ibid.*, 986 (1937).

(39) The spectra agreed well with those of authentic material, kindly furnished by Drs. H. J. Wobben, R. Ter Heide, and R. Timmer, for which we extend our thanks.

(40) Glpc analysis (column B) showed the presence of two impurities (10% each) which likely account for the discrepancy between the calculated and experimental values in the nmr integration.

(41) N. Sperber, D. Papa, and E. Schwenk, *J. Amer. Chem. Soc.*, 70, 3091 (1948).

(42) Glpc analysis showed the presence of cyclohexyl bromide (about 50%) indicating incomplete reaction.

(43) G. Drefahl, K. Ponsold, and G. Kollner, *J. Prakt. Chem.*, 23, 136 (1964).

(44) G. Chiurdoglu and S. van Walle, *Bull. Soc. Chim. Belg.*, 66, 612 (1957).

(50%, 300 ml) was added; the mixture was refluxed for an additional 6 hr and then extracted with ether. The ether layer was washed with water, dried over potassium carbonate, and freed of ether by evaporation. Preparative glpc (column B) afforded material with a retention time identical with that of the Wolff–Kishner product from 4. The product displayed an nmr band at 0.90 (d) ppm which is not present in the spectrum of pure 8. The area ratio of the band at 0.90 to the one at 1.05 was 11:20.

Solvolysis of 3. A small amount of 3 was added to 5 ml of solvent in a small vial and placed in a water bath at the indicated temperature. After the desired reaction time (15–30 min), the contents were added to 5 ml of ether and cooled. The mixture was basified with a few drops of 50% sodium hydroxide and separated. The aqueous layer was extracted with 3 ml of ether. The combined, dried ether layer was concentrated to ca. 1 ml on a rotary evaporator. This material was then analyzed by glpc (column B). A control run with 3 showed that 70–85% of 3 and/or 4 was recovered.

Bridged Polycyclic Compounds. LXXVI. The Nature of the Norbornenyl–Nortricyclyl Cation[1]

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Abstract: *exo*-3-Deuterio-*exo*-2-norbornenyl *p*-bromobenzenesulfonate (1-OBs) acetolyzes, under a wide variety of conditions, to give, in addition to deuterionortricyclyl acetate (3-OAc), *equal* quantities of *exo*-3-deuterio-*exo*-2-norbornenyl acetate (1-OAc) and of the Wagner–Meerwein rearrangement product, *syn*-7-deuterio-*exo*-2-norbornenyl acetate (2-OAc). This finding removes the necessity for consideration of any unsymmetrical norbornenyl–nortricyclyl cation, as has been proposed earlier by others. Heating *exo*-3-deuterio-*exo*-2-norbornenyl thiocyanate (1-SCN) in sulfolane gives a mixture of *exo*-3-deuterio-*exo*-2-norbornenyl isothiocyanate (1-NCS) and *syn*-7-deuterio-*exo*-2-norbornenyl isothiocyanate (2-NCS), with the latter in slight excess, along with 2-SCN. These results are discussed briefly.

Some time ago, we reported[2] that acetolysis of *exo*-3-deuterio-*exo*-2-norbornenyl *p*-bromobenzenesulfonate (1-OBs) leads to equal quantities of 3-deuterio-(1-OAc) and 7-deuterionorbornenyl acetate (2-OAc), in addition to deuterionortricyclyl acetate (3-OAc). Furthermore, we reported that acetolysis of 1-OBs is accompanied by substantial deuterium scrambling, resulting in the formation of 2-OBs. These observations led us to conclude that ionization of the carbon–oxygen bond gives an ion pair in which the cation is best represented as 4, and that our evidence excluded the possibility[3] of a relatively stable unsymmetrical cation such as 5, which suffers capture before complete rearrangement to its enantiomer or delocalization of the 1,2 bond to produce 4.
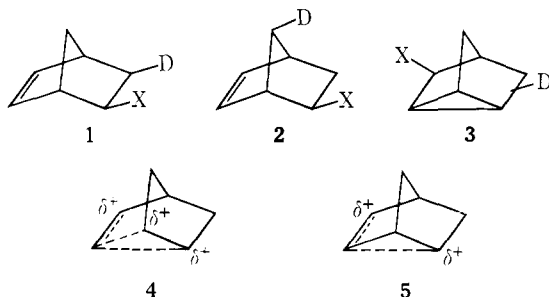
Cation 5 was proposed originally to explain certain ¹⁴C results which we therefore assumed to be incorrect. Recently Lee and Hahn[4] reported that acetolysis of 2-

endo-deuterio-2-*exo*-norbornenyl *p*-bromobenzenesulfonate (6-OBs) at 14 or 24° (the latter being the temperature at which the previous work in this laboratory was conducted) leads to complete Wagner–Meerwein scrambling of the deuterium label between C-2 and C-1 (*i.e.*, to give equimolar amounts of 6-OAc and 7-OAc), thus confirming the presence of the symmetrical cation 4 (or its equivalent) in the solvolysis. However, they also reported that at 45 and at 65°, scrambling was not complete, 6-OBs giving substantially more 6-OAc than 7-OAc, consistent with the ¹⁴C results. We have now done acetolyses of 1-OBs at temperatures from 24 to 65°, with initial concentrations of 1-OBs varying from 0.03 to 0.48 *M*, and with potassium acetate or sodium acetate as base in initial concentrations 0.30–0.52 *M*, and have failed to observe product ratios of 1-OAc to 2-OAc differing significantly from unity (see Experimental Section).[5]

Professor Lee has kindly sent us material from Dr. Hahn's thesis and we find no errors in the calculations made from their data. We are presently unable to rationalize the discrepancies between our work and theirs.

In attempting to find conditions in which capture of intermediate cations might be anticipated to occur

(1) Paper LXXV: F. R. Jensen, J. J. Miller, S. J. Cristol, and R. S. Beckley, *J. Org. Chem.*, **37**, 4341 (1972).

(2) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Amer. Chem. Soc.*, **88**, 3087 (1966).

(3) J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, **77**, 3034 (1955).

(4) C. C. Lee and B.-S. Hahn, *ibid.*, **92**, 2583 (1970).

(5) Again scrambling of 1-OBs and 2-OBs was observed, and, in addition, return was observed leading to 3-OBs, such that experiments interrupted after about 90% solvolysis resulted in the isolation of most of the bromobenzenesulfonate as 3-OBs. The composition was probably close to the equilibrium mixture of 1-OBs, 2-OBs, and 3-OBs. Earlier experiments,² in which the sulfonate was isolated after about 10% solvolysis, did not show observable isomerization to 3-OBs. Our present results thus require modification of the earlier statement² that "return from the 4-OBs ion pair (produced from 1-OBs) is too fast to allow significant migration of the *p*-bromobenzenesulfonate ion to C-5 to give 3-OBs."