Thermolysis of *N*,*N*-Dihalo Derivatives of Bridgehead and Neopentylamines to the Corresponding Halides

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N,*N*-Dihalo derivatives of (1-adamantyl)- and neopentylamine are converted to the corresponding alkyl halides in excellent yields (88–94%) during GLC at 155–330 °C. Decomposition apparently occurs by an S_Ni mechanism or by intramolecular homolytic cleavage. Intermolecular radical and free-ion reactions are eliminated from consideration because of the absence of radical-derived or rearranged products. Steric factors are deemed important in the neopentyl case since pyrolysis of *N*,*N*-dihalo[(1-adamantyl)methyl]amine gave the corresponding carbonitrile in excellent yield (90–97%). 1-(Haloamino)adamantanes gave fair amounts of 1-haloadamantanes (30–38%). 1-(Acetylamino)- and 1-(ethylchloroamino)adamantane yielded 1-chloroadamantane (10–17%), the major products being the acetamide (60%) and the ethylamine (56%), respectively. 1-(Dihaloamino)adamantanes were converted to 1-haloadamantanes by neat (64–70%) or solution (30–41%) pyrolysis.

There is an appreciable volume of research dealing with thermolytic processes. Many of these pyrolyses are first-order, gas-phase reactions.[1–3] Wertz and Allinger[4] have recently suggested heterogeneous surface catalysis with first-order kinetics as an alternate mechanism to account for certain observations. Only a few of these unimolecular processes are of the S_Ni type. Examples, carried out in the gas phase or in solution, include the decomposition of chloroformates,[1,5] chlorosulfites,[5] or sulfonyl chlorides[1,6] (eq 1). Prior investigations of *N*,*N*-

$$\mathrm{RYCl} \xrightarrow{\Delta} \mathrm{RCl} + \mathrm{Y} \qquad (1)$$
$$\mathrm{Y} = \mathrm{OC{=}O},\ \mathrm{OS{=}O},\ \mathrm{SO_2}$$

dichloroamines ($RNCl_2$) under pyrolytic conditions revealed various reaction pathways: alkene, chloroimine, or nitrile formation[7] from simple alkyl types and azo products from perfluoroalkyl[8] or aryl[9] groups. The Stieglitz rearrangement entails the thermal conversion of *N*,*N*-dichlorotritylamine to benzophenone anil.[10]

This report deals with a novel pyrolytic reaction of *N*,*N*-dihalo derivatives of bridgehead and neopentyl amines involving transformation to the corresponding halides. Mechanistic aspects are treated.

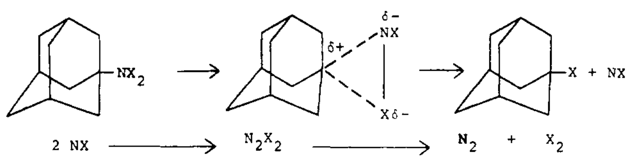
Results and Discussion

Table I. Products from Pyrolysis of *N*-Halo Compounds[a]

substrate	product (yield, %)
1-$AdNCl_2$[b] (2)	1-AdCl (3, 90), 1,3-dichloroadamantane (1, 10)
1-$AdNBr_2$[c] (4)	1-AdBr (94)
1-AdNHCl[b]	1-AdCl (38), 1-$AdNH_2$ (52)
1-AdNHBr[b]	1-AdBr (30), 1-$AdNH_2$
1-$AdNClCOCH_3$[b]	1-AdCl (17), 1-$AdNHCOCH_3$ (60)
1-AdNClEt[b]	1-AdCl (10), 1-AdNHEt (56), 1-$AdNH_2$ (10)
$(CH_3)_3CCH_2NCl_2$[d] (5)	$(CH_3)_3CCH_2Cl$ (88)
1-$AdCH_2NCl_2$[b]	1-AdCN (97)
1-$AdCH_2NBr_2$[b]	1-AdCN (95)
1-(dichloroamino)norbornane[e]	

[a] Injector temperature 250–260 °C, 15–30% SE-30 on Chromosorb W; basic products analyzed on 15% UCON on Chromosorb W (5% NaOH); Ad = adamantyl. [b] 12–14% w/w in CH_2Cl_2. [c] 12% w/w in acetone. [d] Injected neat, injector temperature 250 °C, 20% SE-30 on firebrick. [e] Neat or dilute (24% w/w in CH_2Cl_2); injection resulted in violent decomposition at 200, 230, and 250 °C with either a metal or seasoned glass injector.

Scheme I



A summary of the results from the pyrolysis of *N*-halo and *N*,*N*-dihalo bridgehead and neopentylamines in 12–14% w/w solutions is shown in Table I. The bridgehead dihaloamines are converted to 1-haloadamantanes in high yield, accompanied by a minor amount of 1,3-dichloroadamantane (1) in the chloro case. Increasing the temperature of the injector port for 1-(dichloroamino)adamantane (2) resulted in maximum amounts of 1-chloroadamantane (3) in the 200–275 °C range. Pyrolysis of more concentrated solutions of 2 and 1-(dibromoamino)adamantane (4) generated smaller amounts of the corresponding 1-haloadamantanes. Variation of the injector port composition from metal to Pyrex glass did not significantly affect the yields from 2 or 4. The yields of 1-adamantyl halides from the corresponding monohaloamines were considerably lower (30–38%), with the parent amine, 1-aminoadamantane, being the predominant product (46–56%). Pyrolysis of the *N*-chloro-*N*-acetyl and *N*-chloro-*N*-ethyl derivatives of 1-aminoadamantane gave low yields of 1-chloroadamantane (3; 10–17%). The major products were the corresponding acetyl- and ethylamines. Unexpectedly, *N*,*N*-dichloroneopentylamine (5) gave neopentyl chloride in 88% yield. In contrast, *N*,*N*-dihalo[(1-adamantyl)methyl]amine gave the related carbo-

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(1) Maccoll, A. In "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York, 1964; pp 203–240.

(2) Smith, G. G.; Kelly, F. W. *Prog. Phys. Org. Chem.* **1971**, *8*, 75–234.

(3) DePuy, C. H.; King, R. W. *Chem. Rev.* **1960**, *60*, 431.

(4) Wertz, D. H.; Allinger, N. L. *J. Org. Chem.* **1977**, *42*, 698.

(5) March, J. "Advanced Organic Chemistry: Reactions, Mechanisms and Structure"; McGraw-Hill: New York, 1969; pp 268–269.

(6) Van Aller, R. T.; Scott, R. B., Jr.; Brockelbank, E. L. *J. Org. Chem.* **1966**, *31*, 2357.

(7) Roberts, J. T.; Kovacic, P.; Tonnis, J. A.; Scalzi, F. V. *J. Chem. Soc., Chem. Commun.* **1977**, 418.

(8) Hynes, J. B.; Austin, T. E. *Inorg. Chem.* **1966**, *5*, 488.

(9) (a) Banks, R. E.; Noakes, T. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 143. (b) Banks, R. E.; Barlow, M. G.; Noakes, T. J.; Saleh, M. M. *Ibid.* **1977**, 1746.

(10) Stieglitz, J.; Vosburgh, I. *J. Am. Chem. Soc.* **1916**, *38*, 2081.

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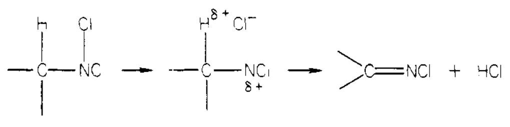
Scheme II



nitrile (>95% yield). Attempts to pyrolyze 1-(dichloroamino)norbornane resulted in violent decomposition with evolution of gas and formation of charred material. During the reaction, a large peak, presumably due to N_2, was observed which corresponded exactly in retention time to the one resulting from neat injection of air, except that the reaction peak was much larger with the various substrates.

Mechanistically, thermal decomposition of the dihaloamines may involve a dipolar pathway, entailing a three-centered transition state (Scheme I), by analogy to related systems. The net result is formation of an alkyl halide and elimination of a small neutral molecule, NX. Chloronitrene is not a well-established entity. Photolysis of NCl_3 is postulated to involve NCl.[11] Good evidence for the intermediacy of a similar compound, fluoronitrene, was provided by isolation of its dimer, difluorodiazene.[12] In our system, conversion of NCl to the thermally labile dichlorodiazene would then result in formation of N_2 and Cl_2.[13] On the basis of the similarity of rates for certain gas-phase reactions and the S_N1 or E1 counterparts in solution, it was suggested that the principles encompassing the solution reactions can be successfully applied to the gas-phase heterolytic processes.[14] From our results, radical chain pathways and reactions entailing free ions appear unlikely. A three-centered activated complex has been proposed for the vapor-phase pyrolysis of *t*-$BuSO_2Cl$.[6] Ion-pair participation was suggested for the solution thermolysis of ROSOCl in which carbon is electron deficient.[5] For ROCOCl in the gas or liquid phase, evidence pointed to a four-centered transition state of the S_Ni type in which C–O bond polarity can range from dipolar to ion pair.[2,5,15,16] Weitl and Kevill postulated a unimolecular process involving ion pairs for decomposition of 1-adamantyl chloroformate in solution.[16] If heterolysis occurs in our system, then loose ion pairs apparently do not participate since no rearrangement takes place with **5**. In contrast, pyrolysis of neopentyl chloroformate yielded neopentyl chloride and methylbutenes, consistent with a polar mechanism.[1,15] Similarly, thermolysis of neopentyl chloride at 450 °C gave methylbutenes in high yield (75%) via carbonium ion type rearrangement.[1,2]

Since prior work[7,17] with $R_{pri}NCl_2$ (R_{pri} = primary alkyl) resulted in nitrile formation predominantly, the pathway followed by **5** is surprising, namely, generation of neopentyl chloride in high yield. It is likely that a steric effect is responsible for the lack of elimination. The route involving loss of hydrogen chloride is the one normally preferred by $R_{pri}NCl_2$. If reaction proceeds as in the case of alkyl halides,[1] cis dehydrohalogenation would pertain as shown in Scheme II. It appears that the space-filling *tert*-butyl group apparently prevents the large chloride from approaching the hydrogen within bonding distance, particularly at extremely high temperatures (conformations favoring elimination would be very short-lived). Similar reasoning would apply to H abstraction by atomic chlorine. Supportive evidence is provided by thermolysis of *N*,*N*-dihalo[(1-adamantyl)methyl]amine (related to the neopentyl analogue), which possesses a quaternary *β*-carbon, but with considerably less hindrance in the region undergoing loss of HX. The quite rigid cyclohexyl rings are folded away from the aminomethyl moiety. In this case, dehydrohalogenation leading to the corresponding nitrile was essentially quantitative.

Pyrolysis of *N*-halo bridgehead amines gave lower yields of halohydrocarbon (30–38%), accompanied by 1-aminoadamantane (46–56%) in the monochloro case. The bromoamine also gave 1-aminoadamantane, but the yield was not determined. A possible rationalization is based on initial disproportionation (eq 2). Lower yields of adamantyl halides from pyrolysis of dilute solutions are observed, since disproportionation is less likely before other reactions occur. Support is provided by the conversion of mono- to dihaloamines during column chromatography. Attempts to purify 1-(bromoamino)adamantane in CH_2Cl_2 on neutral alumina or silica resulted in the formation of **4** in 92% and 86% yields, respectively. The monochloroamine was converted to **2** (98%) on silica. Gottardi[18] reported the thermal disproportionation of bromoamines to an equilibrium mixture of amine and the *N*,*N*-dibromo derivative.

$$2AdNXH \rightarrow AdNX_2 + AdNH_2 \qquad (2)$$

The possibility of radical processes should also be considered.[19] Evidence does not permit us to rule out a homolytic intramolecular reaction. This approach is analogous to the concerted mechanism which has been discarded for chlorosulfite decomposition[5] and hence, by analogy, should perhaps be given less weight in our case. An indication that an intermolecular radical mechanism is not being followed in the pyrolysis of dilute solutions of dihaloamines is provided by the absence of products expected from such a pathway, e.g., adamantane and 1,1,2,2-tetrachloroethane. Homolysis of the C–N bond in **2** would yield carbon- and nitrogen-centered radicals. According to this approach, hydrogen atom abstraction from CH_2Cl_2 by the adamantyl radical could generate adamantane in a radical chain mechanism. Dimerization of $Cl_2CH\cdot$ to tetrachloroethane is known to occur during pyrolysis of *N*-halo compounds in the presence of methylene chloride.[20] Apparently **1** might arise via either a radical or a polar pathway.[21] Furthermore, no 1-bromoadamantane or CCl_4 was obtained from the breakdown of **2** in $CBrCl_3$[22] (12% w/w) via interaction of 1-Ad· with $CBrCl_3$ or of $Cl_3C\cdot$ with a chlorine donor, respectively. A slightly different course of reaction for the pyrolysis of **4** was followed. In acetone, **4** yielded 1-bromoadamantane and no adamantane. In this case, no **3** can form, since Me_2CO can only supply hydrogens. However, in CH_2Cl_2,

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[11] Briggs, A. G.; Norrish, R. G. W. *Proc. R. Soc. London, Ser. A* **1964**, *278*, 27.

[12] (a) Klopotek, D. L. Ph.D. Thesis, Utah State University, 1967. (b) Klopotek, D. L.; Hobrock, B. G. *Inorg. Chem.* **1967**, *6*, 1750.

[13] White, R. E.; Kovacic, P. *J. Am. Chem. Soc.* **1974**, *96*, 7284.

[14] Maccoll, A.; Thomas, P. J. *Prog. React. Kinet.* **1967**, *4*, 119.

[15] Lewis, E. S.; Herndon, W. C. *J. Am. Chem. Soc.* **1961**, *83*, 1955.

[16] Kevill, D. N.; Weitl, F. L. *J. Am. Chem. Soc.* **1968**, *90*, 6416.

[17] Kovacic, P.; Lowery, M. K.; Field, K. W. *Chem. Rev.* **1970**, *70*, 639.

[18] Gottardi, W. *Monatsh. Chem.* **1973**, *104*, 1681.

[19] A reviewer suggested the following: 1-AdNCl → 1-AdN(Cl)N(Cl)Ad-1 (**6**) → 1-AdCl + N_2. It is likely that **6** would instead form 1,1′-azoadamantane which behaves differently than **2** on thermolysis (see Discussion). Analogously, hydrazines yield azo compounds on treatment with positive halogen,[32] presumably via an intermediate of type **6**. Also, no products such as 1-$AdNH_2$ and $Cl_2CHCHCl_2$ were obtained, which would be expected from hydrogen abstraction from solvent by 1-AdNCl.

[20] Roberts, J. T. Ph.D. Dissertation, University of Wisconsin—Milwaukee, 1978. Part 28 of Chemistry of *N*-Halo Compounds. Presented in part at the 174th National Meeting of the American Chemical Society, Chicago, Il, Aug 1977, Abstract ORGN -93, and at the Northeast Regional Meeting of the American Chemical Society, Clarkson College, July 1980.

[21] Kovacic, P.; Chang, J.-H. C. *J. Org. Chem.* **1971**, *36*, 3138.

[22] Kharasch, M. S.; Friedlander, H. N. *J. Org. Chem.* **1949**, *14*, 239.

a small amount (~1–2%) of **3** was detected, in addition to the major product, 1-bromoadamantane (>90%). These results are interesting since this appears to be an instance of chlorine, rather than hydrogen, abstraction from CH_2Cl_2; no di- or trichloroethane was observed. For the dibromo case, a small amount of intermolecular reaction may pertain.

Adamantyl radicals are generated during the pyrolysis of 1,1′-azoadamantane at higher temperatures (350–400 °C) in CH_2Cl_2 as indicated by the radical-derived products. At 400 °C, product yields were as follows: adamantane, 8%, and tetrachloroethane, 9%. Adamantyl radical abstracts hydrogen from the solvent, followed by solvent-radical dimerization. In contrast, pyrolysis of a solution of **2** in CH_2Cl_2 at 400 °C gave **3** (38%) as the only observed product; products (adamantane and tetrachloroethane) expected from radical processes were not detected.

Other evidence also militates against a radical chain mechanism for **2** and **4**. The thermolysis appears to be unaffected by scavengers (Br_2 and toluene) of carbon radicals[23] such as 1-Ad·. Addition of bromine (1% by weight) did not alter the yields from pyrolysis of **4**. Thermolysis of **2** with added bromine did not significantly change the results.

Thermolysis of a dilute solution of **2** in toluene (6% w/w) gave products **3** and **1** in a 10:1 ratio, consistent with the results obtained from the reaction in CH_2Cl_2. Also no chlorotoluene or *sym*-diphenylethane was observed.[24]

Pyrolysis of *N*-substituted (chloroamino)adamantanes gave a number of products as shown in Table I. For the *N*-acetyl compound, various plausible degradation routes should be considered to account for the products. We favor the homolytic nonchain process shown in Scheme III. The

Scheme III

$$\mathrm{AdNClCOCH_3} \rightarrow \mathrm{Ad\dot{N}COCH_3} + \mathrm{Cl}\cdot \qquad \text{(a)}$$

$$\mathrm{Ad\dot{N}COCH_3} + \mathrm{CH_2Cl_2} \rightarrow \mathrm{AdNHCOCH_3} + \mathrm{Cl_2CH}\cdot \qquad \text{(b)}$$

$$2\mathrm{Cl_2CH}\cdot \rightarrow \mathrm{CHCl_2CHCl_2} \qquad \text{(c)}$$

$$\mathrm{AdNClCOCH_3} \rightarrow \mathbf{3} + \mathrm{CH_3CON} \qquad \text{(d)}$$

$$2\mathrm{CH_3CON} \rightarrow \mathrm{CH_3CON{=}NCOCH_3} \qquad \text{(e)}$$

$$\mathrm{AdNClCOCH_3} + \mathrm{Cl_2CH}\cdot \rightarrow \mathrm{Ad\dot{N}COCH_3} + \mathrm{HCCl_3} \qquad \text{(f)}$$

products, **3**, tetrachloroethane, and the acetamide, were identified; no adamantane or $CHCl_3$ was observed. Since ionization of the NCl bond to give Cl^- and AdN^+COCH_3 is energetically unfavorable because of the electron-withdrawing properties of the acetyl group, further consideration is not given to this pathway.

For the *N*-ethyl compound, pathways analogous to those for **2** or **4** may apply. In addition, since structures possessing the functionality HCNCl are known to undergo thermal dehydrohalogenation to imines, this type of route may also pertain. On the basis of amount of product **3** formed and the loss of about 30% of the starting material, it appears that a favorable route of decomposition may be HCl loss to form the thermally labile imine. The formation of 1-aminoadamantane might be rationalized by hydrolysis of the imine by adventitious moisture.

Solution and neat pyrolyses of **2** and **4** were also examined (Table II). The neat system provided the bridgehead halides in yields of 64–70%, accompanied by 19% of **1** in the chloro case and a trace (<2%) of 1,3-dibromoadamantane with the bromo analogue. At reflux in decalin or dichlorobenzene for 1 h, only 30–40% yields of **3** were realized from **2** due to the presence of a large proportion of starting material. Small amounts of **1** were also formed.

Table II. Neat or Solution Pyrolysis of 1-AdNX$_2$

1-AdNX$_2$		yield, %		
X	wt, g	1-AdX	1,3-dihaloadamantane	1-AdNX$_2$ recovd
Br[a]	1.25	65	<2	0
Cl[b]	1.25	64	19	0
Cl[c]	1.30	30	0	59[d]
Cl[e]	1.10	41	<4	50
Cl[f]	1.00	30	<5	62

[a] Heated from 95 to 250 °C during 1 h at 6 torr. [b] For 6 min, 215 °C. [c] Heated from 95 to 240 °C during 1 h at 7 torr. [d] Distilled during heating. [e] Reflux, 1 h, *o*-$C_6H_4Cl_2$. [f] Reflux, 1 h, decalin.

Larger scale pyrolyses, neat and solution, were investigated in order to provide a synthetically useful procedure and to identify the volatile gas and minor side products. Neat **4** was pyrolyzed at 95–200 °C under vacuum to yield 1-bromoadamantane (65%) and 1,3-dibromoadamantane (2%). The dry ice trap contained bromine (56%) as an orange-red solid which liquefied at room temperature. The presence of bromine and absence of adamantane indicate that **4** is probably decomposing as shown in Scheme I. During GLC analysis of **4**, N_2 has been identified.

Larger scale pyrolysis of **2** was also completed. Heating **2** in a sublimation vessel at 215 °C for 6 min gave large volumes of a nonacidic (to litmus) gas, presumably N_2, **3** (64%), and **1** (19%).

Under the conditions employed for the pyrolysis of **4**, **2** gave a lower yield of monohalo product, with no dihalo product. Interestingly enough, as the temperature of the system under vacuum increased, **2** distilled from the reaction mixture (59% recovery based on titration for positive chlorine). The formation of only **3** is not surprising. As the chlorinating agent is generated, it is apparently evacuated from the reaction mixture, thus preventing further conversion to **1**.

Solution pyrolysis of **2** in high-boiling inert solvents was attempted for comparison with results from the GLC conditions. Dilute solutions (~3% w/w) in *o*-dichlorobenzene and decalin were used to minimize intermolecular interactions. In both cases, heating at reflux for 1 h produced moderate yields of **3** (41% and 30%, respectively) with small amounts of **1** (4% and 5%). Surprisingly, not all of **2** decomposed under these conditions, as demonstrated by titration for positive chlorine (50% and 62%, respectively).

Experimental Section

Melting points (uncorrected) were obtained with a Thomas-Hoover capillary apparatus or a Fisher-Johns hot-stage apparatus. Perkin-Elmer infrared spectrophotometers, Models 137B and 700, with sodium chloride optics, were used (calibrated with the 1601-cm^{-1} band of polystyrene). NMR spectra were recorded in parts per million at 60 MHz on a Varian Associates T-60 and at 20 MHz with a CFT-20, with internal Me_4Si. GLC was carried out with a Varian Associates 1720 instrument with a thermal conductivity detector and 8 ft × 0.25 in. copper columns: (1) 15% SE-30 on Chromosorb W, (2) 30% SE-30 on Chromosorb W, (3) 15% Ucon on Chromosorb W (5% NaOH), (4) 20% SE-30 on firebrick; injector temperature 200–400 °C with Pyrex glass inserts; helium carrier gas. GLC peak areas were determined with a Sargent Recorder (Model SR-6) with a Disc integrator. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E at 10, 20, and 70 eV with a direct probe for sample introduction. Positive halogen in the haloamines was determined by standard titration methods.[25] Authentic materials were obtained from Aldrich

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[23] Rembaum, A.; Szwarc, M. *J. Am. Chem. Soc.* **1954**, *76*, 5975.

[24] Maccoll, A. *Chem. Rev.* **1969**, *69*, 33.

Chemical Co., unless otherwise noted.

(A) Preparation of Dichloroamines. General Procedure.[25] A suspension of [(1-adamantyl)methyl]amine (2.5 g, 15.1 mmol) and calcium hypochlorite (70% HTH, 4.8 g, 23.5 mmol) in CH_2Cl_2 (50 mL) was magnetically stirred and cooled in an ice bath to 0 °C as 3 N HCl (50 mL) was added dropwise during 1 h to dissolve the solids. Both liquid phases became bright yellow after being stirred, and cooling (0 °C) was continued for 2 h. The layers were separated. The organic phase was washed with H_2O (2 × 15 mL), dried (Na_2SO_4), filtered, and concentrated on the flash evaporator to yield a yellow odorous liquid: 2.88 g (12.3 mmol, 81%, $\{Cl^+\}$ = 94%); ^{13}C NMR ($CDCl_3$) δ 82.76 (t, C-1′), 40.52 (t, C-2, C-8, C-9), 36.90 (t, C-4, C-6, C-10), 36.56 (s, C-1), 28.36 (d, C-3, C-5, C-7); ^1H NMR ($CDCl_3$) δ 3.45 (s, 2 H), 2.1–1.4 (m, 15 H).

***N,N*-Dichloroneopentylamine (5).** This material was prepared in 50% yield: $\{Cl^+\}$ = 100%; ^{13}C NMR ($CDCl_3$) δ 88.60 (t, C-1), 34.24 (s, C-2), 27.95 (q, C-3); ^1H NMR ($CDCl_3$) δ 3.85 (s, 2 H), 1.05 (s, 9 H).

1-(Chloroamino)adamantane. This compound was prepared according to a literature procedure:[26] mp 133–134 °C (lit.[25] mp 133.5–135 °C); $\{Cl^+\}$ = 93–94%; ^{13}C NMR ($CDCl_3$) δ 56.95 (s, C-1), 41.20 (t, C-2, C-9, C-10), 36.27 (t, C-4, C-6, C-8), 29.68 (d, C-3, C-5, C-7); mass spectrum, *m/e* (relative intensity) 187 (2), 185 (5), 151 (100), 149 (25), 150 (30), 136 (10), 135 (85), 94 (36).

1-(Dichloroamino)adamantane (2). A 75% yield of product was obtained: mp 39–40 °C (lit.[25] mp 40–41 °C); ^{13}C NMR ($CDCl_3$) δ 72.07 (s, C-1), 38.68 (t, C-2, C-8, C-9), 36.05 (t, C-4, C-6, C-10), 30.27 (d, C-3, C-5, C-7).

1-(Bromoamino)adamantane. Bromine (1.43 g, 8.8 mmol) was added to a cooled, stirred solution of KOH (0.39 g, 7.0 mmol) in H_2O (35 mL). The resulting yellow solution was added dropwise during 15 min to a stirred solution of 1-aminoadamantane (1.0 g, 6.6 mmol) in CH_2Cl_2 (50 mL) cooled in an ice bath. The two layers were stirred well for 1.5 h at 0–3 °C and then separated. The yellow organic phase was washed with H_2O (2 × 20 mL), dried (Na_2SO_4), filtered, and concentrated on a flash evaporator to yield a pale yellow solid in 41% yield: $\{Br^+\}$ = 99%; mp 115–118 °C (sinters), 129 °C (chars) (lit.[27] mp 122 °C dec); ^{13}C NMR ($CDCl_3$) δ 46.17 (s, C-1), 42.16 (t, C-2, C-8, C-9), 36.31 (t, C-4, C-6, C-10), 29.95 (d, C-3, C-5, C-7).

1-(Dibromoamino)adamantane (4). Use of a prior procedure[26] gave the product in 68% yield: $\{Br^+\}$ = 96%; mp 64–66 °C (lit.[26] mp 67–67.5 °C); ^{13}C NMR ($CDCl_3$) δ 71.88 (s, C-1), 39.77 (t, C-2, C-8, C-9), 36.04 (t, C-4, C-6, C-10), 30.66 (d, C-3, C-5, C-7).

***N,N*-Dibromo[(1-adamantyl)methyl]amine.** This compound was formed[28] as a red oil: 24% yield; $\{Br^+\}$ = 100%. The material decomposed on standing at room temperature for 2 h: mass spectrum, *m/e* (relative intensity) 323 (10), 161 (30), 135 (100).

1-(*N*-Chloroacetylamino)adamantane. This compound[29,30] was prepared in 92% yield: $\{Cl^+\}$ = 63%; ^{13}C NMR ($CDCl_3$) δ 65.75 (s, C-1), 40.80 (t, C-2, C-8, C-9), 36.26 (t, C-4, C-6, C-10), 30.54 (d, C-2, C-5, C-7), 26.15 (q, C-2′).

1-(*N*-Chloroethylamino)adamantane. A 69% yield was obtained:[26] mp 38–40 °C (lit.[26] mp 45–51 °C); $\{Cl^+\}$ = 100%; ^{13}C NMR ($CDCl_3$) δ 62.04 (s, C-1), 48.35 (t, C-1′), 39.30 (t, C-2, C-8, C-9), 36.64 (t, C-4, C-6, C-10), 29.92 (d, C-3, C-5, C-7), 14.67 (q, C-2′).

1,1′-Azoadamantane. A literature procedure[27] provided a yield of 68%; mp 276–283 °C (lit. mp 271–272 °C,[27] 286–294 °C[31]).

(B) Pyrolysis. General Procedure. Injection of 5.0 μL of a 12% w/w solution of 1-(dichloroamino)adamantane (2) in CH_2Cl_2 into the GLC apparatus (column 2; injector temperature 250 °C; column temperature 155 °C; detector temperature 250 °C; He flow rate 150 mL/min) gave two peaks in addition to a N_2 peak, (t_r 3.33 min), and 1,3-dichloroadamantane (t_r 6.67 min). The peak for N_2 was identified by comparison with the t_r for a neat injection of air with a variety of temperatures and columns. A Beilstein flame test on each of the collected materials indicated the presence of halogen. Compound identification was established by comparison of retention times, mass spectra, peak enhancement (GLC), mixture melting points, and proton magnetic resonance spectra. Yields were determined by comparison of the integrated area for the various pyrolysis products vs. the integrated area of known concentrations of the authentic materials. Basic products were analyzed on column 3.

Data for **2** at various temperatures (injector temperature, % **3**, % **1**): 160, 79, 9; 200, 92, 8; 250, 92, 8; 270, 92, 8; 300, 84, 11; 330, 80.

Data for **2** at various concentrations at 250 °C (w/w % in CH_2Cl_2, % **3**, % **1**): 12, 93, 9; 26, 57, 15; 48, 36, 15.

Data for various concentrations at 250 °C (w/w % in acetone, % 1-bromoadamantane): 15, 94; 26, 81.

Data for the variation in injector port composition for **2** at 250 °C are as follows (w/w % in CH_2Cl_2, % **3**, % **1**). For Pyrex glass: 12, 91, 11; 26, 55, 12; 48, 37, 13. For metal: 12, 91, 12; 26, 60, 18; 48, 38, 21.

Disproportionation of 1-(Chloroamino)adamantane. Crude 1-AdNHCl [0.5 g, 2.70 mmol; mp 130–135 °C (lit.[26] mp 133–133.5 °C); $\{Cl^+\}$ = 94–96%] was eluted from 20 g of silica (60–80 mesh) with CH_2Cl_2 (180 mL) followed by CH_3OH (150 mL). Concentration of each fraction yielded 0.29 g [1.32 mmol; mp 32–35 °C (lit.[26] mp 40–41 °C); $\{Cl^+\}$ = 99%] of **2** (98% conversion) and 0.04 g (0.21 mmol) of 1-$AdNH_2$·HCl (mp >250 °C, halogen present).

Disproportionation of 1-(Bromoamino)adamantane. With Silica. According to the procedure with 1-AdNHCl, 1-AdNHBr (1.9 g, 8.3 mmol; $\{Br^+\}$ = 96%) was converted to **4** (1.10 g, 3.6 mmol; mp 65–66 °C; $\{Br^+\}$ = 98%) and 1-$AdNH_2$·HBr (0.25 g, 1.1 mmol; mp >250 °C; halogen present; 86% conversion).

With Alumina. As in the silica case, 1-AdNHBr was converted to **4** (0.31 g, 1.00 mmol; $\{Br^+\}$ = 94%) in 92% yield.

Neat Pyrolyses. 1-(Dibromoamino)adamantane (4). Dibromo compound **4** (1.254 g, 4.1 mmol; $\{Br^+\}$ = 86%) was placed in a 15-mL, one-necked, round-bottomed flask with a magnetic stirrer and connected by a water-cooled short-path distillation still head to a 25-mL receiving flask cooled in a dry ice bath. The system was evacuated (6 torr) and lowered into a silicon oil bath heated to 95 °C. As the solid decomposed, an orange-brown gas was evolved, and a yellow solid condensed on the walls of the short-path column. Heating was continued for 1 h as the temperature was increased to 250 °C. After the yellow and white solids in the head and receiving flask were washed down with acetone, concentration yielded 0.53 g of material which was added to CH_2Cl_2, and the mixture was filtered to remove 1-$AdNH_2$·HBr (0.02 g, mp >250 °C, white solid). GLC of the filtrate indicated the presence of 1-bromoadamantane (>95% pure, 65% yield) and a minor amount of 1,3-dibromoadamantane. The dry ice trap contained bromine (56% yield) as an orange-red solid was liquefied at room temperature. The residue was black (0.29 g). Beilstein flame tests indicated the presence of halogen in the residue and the white solid.

1-(Dichloroamino)adamantane (2). Dichloro compound **2** (1.2 g, 5.4 mmol; $\{Cl^+\}$ = 96%) in a small sublimation vessel with a water-cooled jacket was lowered into a silicon oil bath heated to 215 °C. The yellow solid quickly melted with slight bubbling. After 1 min the material decomposed violently with evolution of copious amounts of a nonacidic gas. After 6 min, the reaction mixture was cooled to room temperature, CH_2Cl_2 (50 mL) was added to the black residue and sublimed solid, and the mixture was filtered. The filtrate was extracted first with 3 N HCl (2 × 15 mL) and then with water (2 × 10 mL), dried (Na_2SO_4), and concentrated on the flash evaporator to yield a white solid (0.8 g, 83% yield). GLC analysis indicated a mixture of **3** (64% yield) and **1** (19% yield).

Solution Pyrolysis. 1-(Dichloroamino)adamantane (2). A mixture of **2** (~1 g) and decalin or *o*-dichlorobenzene (ODCB) (30 mL) was heated to reflux for 1 h with a silicon oil bath. After the mixture was cooled to room temperature, GLC analysis of

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[25] Kovacic, P.; Roskos, P. D. *J. Am. Chem. Soc.* **1969**, *91*, 6457.

[26] Padegimas, S. J.; Kovacic, P. *J. Org. Chem.* **1972**, *37*, 2672.

[27] Stetter, H.; Smulders, E. *Chem. Ber.* **1971**, *104*, 917.

[28] Zawalski, R.; Kovacic, P. *Synth. Commun.* **1978**, *8*, 549.

[29] Sasaki, T.; Eguchi, E.; Kiriyama, T.; Suzuki, H.; *Synth. Commun.* **1971**, *1*, 267.

[30] Starewicz, P. M.; Sackett, A.; Kovacic, P. *J. Org. Chem.* **1978**, *43*, 739.

[31] Prochazka, M.; Ryba, O.; Lim, D. *Collect. Czech. Chem. Commun.* **1968**, *33*, 3387.

[32] Millar, I. T.; Springall, H. D. "Sidgwick's Organic Chemistry of Nitrogen", 3rd ed.; Clarendon Press: Oxford, 1966; p 574. Timberlake, J. W.; Stowell, J. C. "The Chemistry of the Hydrazo, Azo, and Azoxy Groups"; Patai, S., Ed.; Wiley: New York, 1975; Part 1, p 86.

product showed the following yields: **3** (41%) and **1** (4%) with ODCB; **3** (30%) and **1** (5%) with decalin. A 1-mL aliquot was titrated for a 50% and 62% {Cl+}, respectively.

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Registry No. 2, 24375-05-1; **4**, 34913-44-5; **5**, 69083-99-4; 1-$AdCH_2NH_2$, 17768-41-1; 1-AdNHCl, 24375-06-2; 1-AdNHBr, 5511-20-6; 1-$AdNH_2$, 768-94-5; 1-$AdCH_2NBr_2$, 75558-64-4; 1-$AdNClCOCH_3$, 64741-22-6; 1-AdNClEt, 34913-37-6; 1,1′-azoadamantane, 21245-62-5; 1-AdCl, 935-56-8; 1,3-dichloroadamantane, 16104-50-0; 1-AdBr, 768-90-1; 1-$AdNH_2$, 768-94-5; 1-$AdNHCOCH_3$, 880-52-4; 1-AdNHEt, 3717-44-0; $(CH_3)_3CCH_2Cl$, 753-89-9; 1-AdCN, 23074-42-2.

Conformational Properties of *cis,cis,cis*-1,5,9-Cyclododecatriene. Dynamic Nuclear Magnetic Resonance Spectroscopy and Empirical Force Field Calculations

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Dynamic NMR effects are observed in both the ^1H and ^{13}C NMR spectra of *cis,cis,cis*-1,5,9-cyclododecatriene in the vicinity of −140 to −150 °C. Empirical force field calculations show that the NMR data can be interpreted in terms of a "helix" conformation of C_2 symmetry. This conformation pseudorotates with a calculated strain energy barrier of 6.3 kcal/mol, in agreement with an experimental free-energy barrier of 5.9 kcal/mol. The pseudorotation of the helix takes place via a pair of enantiomeric "saddle" conformations which are calculated to be 0.6 kcal/mol above the helix. Other conformations are calculated to have relatively high strain energies: crown-I (2.0 kcal/mol), crown-II (3.0 kcal/mol), and propeller (7.8 kcal/mol).

cis,cis,cis-1,5,9-Cyclododecatriene (**1**) is a compound of importance as a synthetic intermediate[1] and as a potential homoaromatic system.[2] Unlike the other three stereoisomers of 1,5,9-cyclododecatriene, the all-cis isomer has not been observed as a product of the cyclotrimerization of 1,3-butadiene on Ziegler-type catalysts.[3] However, **1** can be made by a chemical trans-to-cis inversion of the three double bonds in *trans,trans,trans*-1,5,9-cyclododecatriene.[2]

The ^1H NMR spectrum of **1** in the temperature range −115 to 150 °C has been reported to show no change beyond a loss of fine structure below −80 °C.[2] On the basis of molecular models, UV spectroscopy, and the low melting point of **1**, Untch and Martin concluded that this hydrocarbon did not adopt a crown conformation with C_{3v} symmetry.[2] They suggested that **1** was likely to have an all s-trans conformation of C_2 symmetry.

Dale has briefly discussed possible site-exchange paths in **1** in a "helix" conformation with C_2 symmetry and a "propeller" conformation with D_3 symmetry.[4] Ollis and co-workers have reported the dynamic ^1H NMR spectra of a variety of tribenzo-1,5,9-cyclododecatrienes and heterocyclic analogues.[5–7] In solution these compounds were found to exist as "helix" and/or "propeller" conformations. Since the presence of fused benzene rings and of heteroatoms can lead to substantial effects on conformational equilibria and barriers, the data of Ollis et al. cannot be easily extrapolated to the parent system. We now report an investigation of the conformational properties of *cis,cis,cis*-1,5,9-cyclododecatriene by both dynamic NMR spectroscopy and empirical force field calculations.

Experimental Section

cis,cis,cis-1,5,9-Cyclododecatriene was synthesized by the method of Untch and Martin.[2] Its ^{13}C NMR spectrum in $CDCl_3$ at room temperature exhibits chemical shifts at δ 27.9 (CH_2) and 130.7 (CH).

All low-temperature NMR spectra were measured on a superconducting solenoid spectrometer operating at 59 kG.[8] The proton noise decoupled ^{13}C NMR spectra are Fourier transforms of accumulated free-induction decays and were obtained with standard 10-mm tubes under the following conditions: 45° pulse angle, 8K data points, 11-KHz spectrum width, an exponential broadening function corresponding to a broadening of 4 Hz. For variable-temperature studies a mixture of $CHCl_2F$ and $CHClF_2$ (3:1) was used as a solvent and a ^{19}F peak of the solvent was employed for lock purposes. The ^1H NMR spectra were obtained with 5-mm tubes in a frequency-sweep mode, with the magnetic

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(1) Barkovich, A. J.; Vollhardt, K. P. *J. Am. Chem. Soc.* **1976**, *98*, 2667–2668.

(2) Untch, K. G.; Martin, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 3518–3520.

(3) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 105–115. Breil, H.; Heimbach, P.; Kröner, M.; Müller, H.; Wilke, G. *Makromol. Chem.* **1963**, *69*, 18–40.

(4) Dale, J. *Top. Stereochem.* **1976**, *9*, 199–270.

(5) Brickwood, D. J.; Ollis, W. D.; Stoddart, F. *J. Chem. Soc., Chem. Commun.* **1973**, 638–640.

(6) Ollis, W. D.; Stoddart, F.; Nógrádi, M. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 168–169.

(7) Ollis, W. D.; Price, J.; Stephanatou, J.; Stoddart, F. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 169. Downing, A. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc. B* **1970**, 24–34. Downing, A. P.; Ollis, W. D.; Sutherland, I. O.; Mason, J. *Chem. Commun.* **1968**, 329–330. Ollis, W. D.; Stephanatou, J.; Stoddart, J. F.; Ferrige, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 223–224.

(8) Anet, F. A. L.; Basus, V. J.; Bradley, C. H.; Cheng, A. K., paper presented at the 12th Experimental Nuclear Magnetic Resonance Conference, Gainesville, FL, Feb 1971. Bradley, C. H. Ph.D. Thesis, University of California, Los Angeles, CA, 1971.

0022-3263/80/1945-5243$01.00/0