THE JOURNAL OF Organic Chemistry

VOLUME 46, NUMBER 21

OCTOBER 9, 1981

Pyrolytic Eliminations from *N,N*-Dichloro Derivatives of Primary, Secondary, and Tertiary Alkyl Primary Amines[1]

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Received March 18, 1981

N,N-Dichloro derivatives of primary, secondary, and tertiary alkyl primary amines are easily converted to elimination products by neat or solution pyrolysis during GLC at 190–280 °C. Good to excellent yields result. In general, the type of product formed depends on the alkyl group: with primary alkyl, the products are alkenes and nitriles; with secondary, alkenes and chloroimines result; and with tertiary types, alkenes are formed. Mechanistic aspects are treated.

The pyrolysis of organic substrates possessing a variety of functional groups has been widely reported in the literature.[2-5] Elimination with alkene formation usually is observed, but substitution can also occur as in the case of chloroformates and related materials.[4,6b] A compilation of deamination reactions leading to olefins has been published.[6a,c] Since a quaternary nitrogen is commonly needed to effect elimination, e.g., Hofmann, primary and secondary amines must be further alkylated. There is a recent report on the stereoselective pyrolysis of *N*-alkyl-*N,N*-disulfonimides to alkenes, in three steps from the primary amine.[7]

Eliminations from haloamines to give alkenes or imines have received some attention in the recent literature. Stilbenes were produced on heating the corresponding bis(difluoroamines).[8] Pyrolysis of 1,2- and 2,2-bis(difluoroamino)propane afforded mainly propylene and fluoroimines, respectively.[9] Preparation of CF_2=NF resulted from the reaction of $ClCF_2NClF$ with mercury.[10] Decomposition of *N,N*-dichloro-*tert*-butylamine catalyzed with AgF gave isobutylene in good yield.[11] Quantitative amounts of olefins were produced by the promoted deaminations of *tert*-alkyl dichloroamines.[12] With a variety of Lewis acid halides, redox metal salts, or nucleophiles, moderate to excellent yields of alkenes were obtained from *tert*-alkyl *N,N*-dichloroamines.[13] Thermolysis of haloamines in the 1-adamantyl and neopentyl series gave substitution products rather than elimination.[14]

Table I. Neat Pyrolysis of 1-(Dichloroamino)-1-methylcyclohexane[a]

conditions	products, % yield[b]	
glass injector port[c]	80	20
metal injector port	82	21
SE-30, firebrick[d]	80	20
Carbowax, Chromosorb W[e]	78	19
stainless steel[f]	79	21
copper[g]	80	20

[a] Column temperature, 100 °C; injector temperature, 210 °C. [b] % yield, ±5%. [c] Pyrex glass insert. [d] 20% SE-30 on neutral firebrick, copper column. [e] 5% Carbowax 20M on Chromosorb W, copper column. [f] 10% SE-30 Chromosorb W, 8 ft × 1/4 in. column. [g] 15% SE-30 on Chromosorb W, 10 ft × 1/4 in. column.

The objective of our work was to determine the products from pyrolysis of *N,N*-dichloro derivatives of primary, secondary, and tertiary alkyl primary amines and to address the mechanistic features. A preliminary report has been published.[15]

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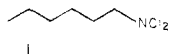
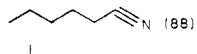
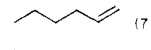
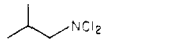
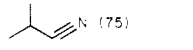
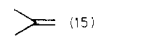
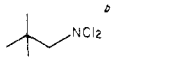
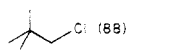
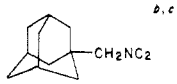
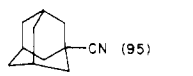
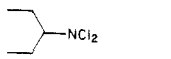
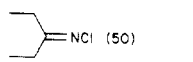
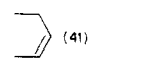
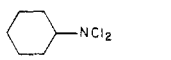
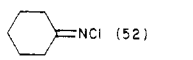
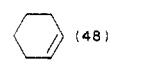
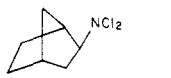
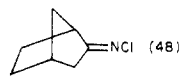
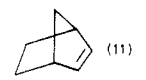
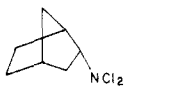
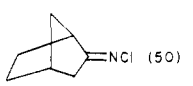
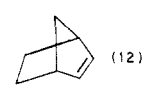
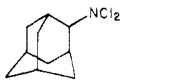
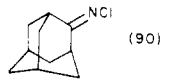
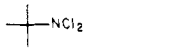
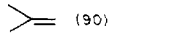
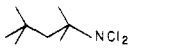
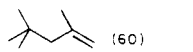
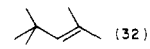
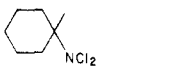
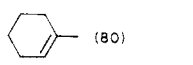
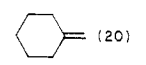
Table II. Pyrolytic Eliminations from *N,N*-Dichloroalkylamines [a]

substrate	products (% yield)		
	 (88)	 (7)	
	 (75)	 (15)	
 [b]	 (88)		
 [b,c]	 (95)		
$C_6H_5CH_2NCl_2$	C_6H_5CN (70)	$C_6H_5CH_2Cl$ (10)	
	 (50)	 (41)	
	 (52)	 (48)	
	 (48)	 (11)	
	 (50)	 (12)	
	 (90)		
	 (90)		
	 (60)	 (32)	
	 (80)	 (20)	

[a] Neat, injector temperature 190–280 °C. [b] Reference 14. [c] Solution in CH_2Cl_2 (12% w/w).

Results and Discussion

Initial work dealt with conditions for maximum yields of elimination products. The results from variation of injector port composition, column packing, and support as well as type of metal tubing are shown in Table I. The data indicate that pyrolysis is probably occurring mainly in the injector port of the GC, since changing all these parameters had no significant effect on the composition or yield of products. Also, the nature of the surface to which the substrate is exposed does not play a crucial role. Similar conclusions were deduced from pyrolytic studies of (haloamino)adamantanes.[14]

The results from neat pyrolysis of dichloroamines at 190–280 °C during GLC are shown in Table II. In general, the type of product formed depends on the identity of the R group: alkenes and nitriles from primary, alkenes and chloroimines from secondary, and alkenes from tertiary types, in good to excellent yields. Neat pyrolysis was done with liquid types. Dilute solutions, usually ~12% w/w, were used for concentration studies.

For primary alkyl dichloroamines (**1**), a number of reaction pathways may pertain, each involving the loss of small molecules. The net loss during thermolysis would be HCl (eq 1), $HNCl_2$ (eq 2), or NCl (eq 3).

$$\underset{\mathbf{1}}{R_2CHCH_2NCl_2} \xrightarrow{-HCl} R_2CHCH{=}NCl \xrightarrow{-HCl} R_2CHCN \quad (1)$$

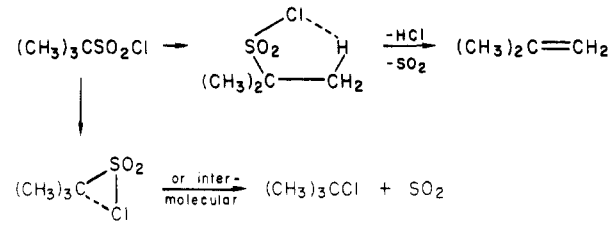
$$\mathbf{1} \xrightarrow{-HNCl_2} R_2C{=}CH_2 \quad (2)$$

$$\mathbf{1} \xrightarrow{-NCl} R_2CHCH_2Cl \quad (3)$$

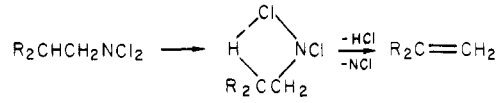
Scheme I

$$HNCl_2 \longrightarrow HCl + NCl$$
$$NCl \longrightarrow {}^1/_2N_2 + {}^1/_2Cl_2$$

Scheme II



Scheme III



In a consideration of the reaction pathway for 1,2-elimination leading to nitrile, a comparison can be made with the pyrolysis of *gem*-dichlorides to yield vinyl chlorides or acetylenes via HCl elimination.[3b,4b,16,17] These pyrolyses are accomplished at much higher temperatures (350–450 °C), proceeded at a fairly slow rate, and resulted in considerably lower yields of the desired compounds. From the primary amine derivatives, elimination of 1 mol of HCl would yield chloroimine (eq 1); release of the second HCl produces the observed nitrile. Chloroimino compounds were not detected during pyrolysis of materials which could lose another mole of HCl. Hence, it is evident that *N*-chloroimines undergo dehydrohalogenation with much greater facility than vinyl chlorides.

For dichloroamines, the low bond energy[18] of N–Cl (47.7 kcal/mol) compared with C–Cl (78.5 kcal/mol) is probably important in leading to ready reaction under mild conditions. Apparently, nitrile formation is more energetically favored than alkene generation. When nitrile and olefin pathways compete, the nitrile product predominates.

A closer comparison with alkyl halides can be made by viewing the NCl_2 moiety as a pseudohalogen. For RX, an ion-pair intermediate has been postulated. For example, pyrolsis of neopentyl chloride methylbutenes via rearrangement of and elimination from a carbocation.[19,20] Net loss of $HNCl_2$ would result from pyrolysis of the dichloroamine via a tight ion pair. Free ions are probably not involved since no rearranged product (2-hexene) was observed from the *n*-hexyl derivative. No radical-derived products such as hexyl chloride, *n*-hexane, or dimer, were detected. Elimination of $^-NCl_2$ or protonated dichloroamide ion, $HNCl_2$, is postulated for displacements from dichloroamides.[21] A possible decomposition pathway for $HNCl_2$ is shown in Scheme I. Chloronitrene is not a well-established entity. Photolysis of NCl_3 is postulated to involve NCl.[22] Good evidence for formation of fluoronitrene was provided by isolation of its dimer, difluorodiazene.[23] Conversion of NCl to the thermally labile

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dichlorodiazene (not necessarily by dimerization) would then result in subsequent formation of N_2 (an observed product) and Cl_2.[21]

There is a resemblance in some respects between our work and the breakdown of chloroformates, chlorosulfites, and sulfonyl chlorides, which apparently proceed in a concerted mode. For example, *tert*-butanesulfonyl chloride decomposes to isobutylene; *tert*-butyl chloride is also formed (Scheme II).[24] A similar, cyclic five-membered transition state can be written for $RNCl_2$ (Scheme III), a principal difference being that, in most cases, no alkyl halide is formed. This hypothesis is also consistent with the lack of radical-derived products.

Thermolyses of primary amines with differing numbers of R groups at the β position were studied. Pyrolysis of (dichloramino)isobutane gave nitrile (mainly) and alkene, but no isobutyl chloride. Previous work with the neopentyl analogue showed that neopentyl chloride was the main product with no rearranged olefin or nitrile present. Apparently, the relatively large *tert*-butyl group prevents nitrile formation via elimination of HCl. In contrast, the related *N,N*-dichloro[(1-adamantyl)methyl]amine produced the corresponding nitrile.[14] With the less bulky isopropyl moiety at the β carbon, a favorable conformation can be adopted which allows for HCl loss (nitrile formation) or net elimination of $HNCl_2$ (olefin formation).

Pyrolysis of the benzyl derivative gave benzonitrile (70%) and benzyl chloride (10%). Chloride formation can be rationalized on the basis of an electron-deficient benzyl carbon stabilized by the aromatic ring.

In the pyrolysis of *sec*-alkyl dichloroamines, attention was focused on the direction of elimination (alkene or chloroimine formation) and the possibility of rearrangement. Two conformationally nonrigid molecules were examined. 3-(Dichloroamino)pentane gave 2-pentene (34–47%) and the chloroimine (43–56%). Since there is only one β hydrogen, no more than 1 mol of HCl can be eliminated. The stereochemistry of 2-pentene (cis or trans) could not be determined since both olefins had identical retention times and mass spectra under the analytical conditions. Although, statistically, the likelihood of alkene formation was doubled (vs. the straight chain compound), the major product was the imine. Results are similar for the cyclic secondary amine, 1-(dichloroamino)cyclohexane: cyclohexene (48%) and (chloroimino)cyclohexane (52%).

Isomeric 2-(dichloroamino)[2.2.1]bicycloheptanes were pyrolyzed to give products (alkenes and chloroimines) similar to those from the other secondary cases (Table II). Thermal decomposition of *exo*- or *endo*-2-(dichloroamino)norbornane gave 2-norbornene (10–13%) and 2-(chloroimino)norbornane (43–56%). The isomeric nature (syn–anti) of the chloroimino product was not ascertained. Minor amounts of uncharacterized byproducts were also detected. Wagner–Meerwein rearrangements may be occurring, as in similar cases,[25] but cannot be detected. Since the product data for the two norboryl isomers correspond quite closely, there may well be a common reaction pathway involving the same intermediate. Olefin formation could result from highly polarized bonds or ion pairs in the precursor **2**. For characterization of the (chloroimino)norbornanes, authentic materials were synthesized by the method of Knowles and Alt;[26] treatment of either isomeric dichloroamine precursor with KOAc in EtOH effected dehydrohalogenation. Pyrolysis of related bicyclic compounds, namely bornyl and isobornyl acetates, in the gas phase to give alkenes and rearranged products was reported by Emovon;[25] the recent "surface-catalyzed" mechanism[27] for this type of reaction has been challenged by Taylor.[28]

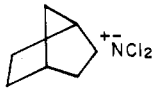

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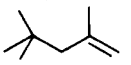
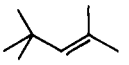
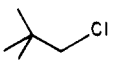
Table III. Pyrolysis of *N,N*-Dichloro-*tert*-octylamine: Variation in Injector Temperature[a]

temp, °C	products, % yield		
			
190	60	32	0
270	9	4	22
315[b]	0	0	40

[a] Neat injection, metal injector, 15% SE-30 on Chromosorb W, yield variation ±5%. [b] Plus <5% of isobutylene.

Material balance was not achieved with our norbornyl substrate during pyrolysis. Herndon and Manion studied the retro-Diels–Alder reaction of bornylene and proposed that dimerization or polymerization might occur yielding products not amenable to GLC analysis.[29] Under the conditions employed in our study, apparently such problems are not encountered since the amounts of norbornene do not appreciably vary in the temperature range of 190–315 °C. Pyrolysis of dicyclopentadiene under the conditions of the reaction did not yield materials with retention times corresponding to those of any products from (dichloroamino)norbornane.

A *sec*-alkyl, tricyclic dichloroamine was also pyrolyzed. Neat thermolysis of 2-(dichloroamino)adamantane gave only the 2-chloroimine. Net elimination of $HNCl_2$ to form bridgehead unsaturation would be energetically unfavorable. Adamantene, recently trapped in modest yield,[30] was not observed. Previous work with 1-(dichloroamino)-adamantane revealed the major product to be 1-chloroadamantane.[14] This type of pathway, generation of 2-chloroadamantane, is not followed by the 2-isomer.

In the *tert*-alkyl series, pyrolysis of 1-methyl-1-(dichloroamino)cyclohexane gave methylenecyclohexane (20%) and 1-methylcyclohexene (80%). The more stable isomer is formed in larger yield, suggesting that the transition state has appreciable carbonium ion character. Since these results are very similar to those obtained by DePuy and co-workers[31] (methylenecyclohexane, 24%; methylcyclohexene, 76%) from pyrolysis of the corresponding acetate, similar mechanistic pathways may pertain. *N,N*-Dichloro-*tert*-butylamine gave only isobutylene (80–100%), with no *tert*-butyl chloride. The neat reaction of the *tert*-octyl derivative afforded excellent yields of diisobutylenes in approximately 65:35 ratio for 2,4,4-trimethyl-1-pentene/2,4,4-trimethyl-2-pentene. More of the less substituted, thermodynamically more stable isomer was formed. The *tert*-octyl substrate gave different results as the temperature (Table III) or concentration (Table IV)

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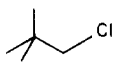
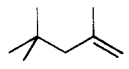
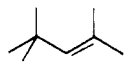
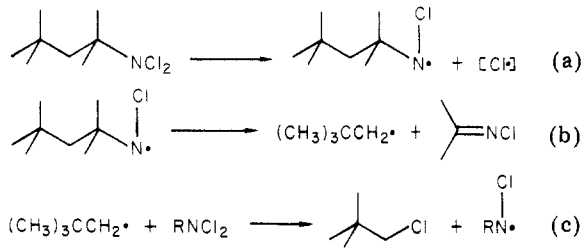
Table IV. Pyrolysis of *N,N*-Dichloro-*tert*-octylamine: Variation in Concentration

substrate, concn, w/w %[a]	products			
				
Metal Injector Port				
12	8-14	28-40	13-18	
47	21-23	18-19	11-16	3
neat	34	1	0.1	
Seasoned Glass				
12	14-17	39-40[b]		
47	25-37	24-28	6-11	5
neat	31	9	4	

[a] In CH_2Cl_2; injector temperature, 270 °C. [b] Total amount of alkenes; yield variation, ±5%.

Scheme IV



changed. With increasing temperature the yields of alkenes decreased. At much higher temperatures (315 °C) the major observed organic product was neopentyl chloride (40%), with a small amount of isobutylene (<5%), but no diisobutylenes. At intermediate temperatures, both types of products resulted. The width of half maximum height in GLC for the product peaks detected at either temperature extreme was larger when compared to the width of the peaks from authentic materials at the same temperature. Hence, it appears that reaction is occurring on the column to some extent. The alkenes did not undergo significant decomposition when solutions were injected at the higher temperatures. At lower temperatures reaction was relatively clean, but at 315 °C there was an appreciable gap in the material balance.

In order to minimize side reactions, pyrolysis was carried out on more dilute solutions at a lower temperature (270 °C) (Table IV). The results indicate that as the solution increased in concentration, the yield of neopentyl chloride was enhanced, whereas the yield of alkenes decreased. The concentration effects suggest that two competing pathways pertain. Alkene production may occur as already discussed. The rise in the amount of neopentyl chloride with increasing concentration indicates that a bimolecular process may be involved (Scheme IV). Homolysis of the N–Cl bond generates a nitrogen-centered radical (step a) as in the Hofmann–Loeffler–Freitag reaction. In step b neopentyl radical is formed via β scission. Reaction with a chlorine donor, e.g., starting material, gives rise to neopentyl chloride. Characterization of the major peaks from the reaction did not reveal the presence of the chloroimine of acetone. The chloroimine might not be detected under our conditions, it may undergo further reaction, or it may not be formed, and hence, in the last case, the postulated pathway would not pertain. Adam and Schreiber[32] reported analogous β cleavage via Cl· loss from a chloroamine under photolytic conditions in the presence of acid. The steroidal substrate was deaminated with net formation of an alkyl chloride.

Results from thermal decomposition of $C_6H_5C(CH_3)_2N$-Cl_2 and $C_6H_5CH_2C(CH_3)_2NCl_2$ are reported elsewhere.[15]

The major elimination pathways for the primary, secondary, the tertiary alkyl categories have solution counterparts.[12,33]

Experimental Section

Melting points (uncorrected) were obtained with a Hoover-Thomas 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 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 CFT-20, with internal Me_4Si. GLC was carried out with a Varian Associates 1720 instrument, thermal conductivity detector, injector temperature 200–400 °C with pyrex glass inserts; helium carrier gas; (A) 8–15 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, and (5) 5% Carbowax 20 on Chromosorb W; (B) 8 ft × 0.25 in. stainless steel columns: (1) 5% Carbowax 20M on neutral Chromosorb W, (2) 20% SE-30 on firebrick, (3) 10% SE-30 on Chromosorb W. GLC peak areas were determined with a Sargent Recorder (Model SR-6) having 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 haloamines was determined by standard titration methods.[34] Authentic materials were obtained from Aldrich Chemical Co., unless otherwise noted. Products were generally characterized by IR, NMR, and mass spectrometry, in addition to GLC (peak enhancement or retention time).

Preparation of Dichloroamines. General Procedure.[34] A suspension of *tert*-octylamine (5.0 g, 38 mmol) and calcium hypochlorite (70% HTH, 16 g, 78.4 mmol) in CH_2Cl_2 (100 mL) was magnetically stirred and cooled in an ice bath at 0 °C as 3 N HCl (100 mL) was added dropwise during 1 h to dissolve the solids. Both liquid phases became bright yellow while stirring and cooling were continued for 2 h. The layers were separated, and the organic phase was washed with H_2O, dried (Na_2SO_4), filtered, and concentrated on the flash evaporator to yield a yellow odorous liquid (7.0 g, 35.4 mmol, 91%, $[Cl^+]$ = 99%): ^1H NMR ($CDCl_3$) δ 2.5 (s, 2 H), 1.9 (s, 6 H), 1.2 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 76.02 (s, C-2), 50.23 (t, C-3), 31.54 (q, C-1,2′), 25.78 (q, C-5).

2-(Dichloroamino)-2-methylpropane. The general procedure gave a 64% yield: $[Cl^+]$ = 96%, yellow oil (solid at −20 °C); ^1H NMR ($CDCl_3$) δ 2.5 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 72.56 (s, C-1), 25.88 (q, C-2); mass spectrum, *m/e* (relative intensity) 146 (3), 144 (6), 142 (5), 71 (31), 57 (100).

1-(Dichloroamino)-1-methylcyclohexane. This material was prepared in 66% yield: $[Cl^+]$ = 99%; ^1H NMR ($CDCl_3$) δ 2.3–1.6 (br m, 13 H).

3-(Dichloroamino)pentane. A 70% yield of the desired compound was obtained: $[Cl^+]$ = 97%; ^1H NMR ($CDCl_3$) δ 3.6 (t, 1 H), 25 (dq, 4 H), and 1.9 (t, 6 H).

3-(Chloroimino)pentane. The procedure of Alt and Knowles[26] was used to obtain a yellow oil, $[Cl^+]$ = 94%, which readily decomposed: IR (neat) 1640 cm^{-1} (C=N).

(Dichloroamino)cyclohexane. The yellow oil was produced in 88% yield: $[Cl^+]$ = 93%; ^1H NMR ($CDCl_3$) δ 3.2 (br m, 1 H) and 2.20–0.95 (br m, 10 H); mass spectrum, *m/e* (relative intensity) 172 (2), 170 (5), 168 (5), 133 (32), 131 (100), 82 (85), 81 (60).

(Chloroimino)cyclohexane. A 52% yield of a pale yellow oil was obtained:[26] $[Cl^+]$ = 100%; ^1H NMR (CCl_4) δ 2.5–1.0 (br m, 10 H); ^{13}C NMR ($CDCl_3$) δ 182.65 (s, C-1), 37.03 (d, C-6), 32.81, 27.06, 26.01, 25.22 (d, C-2, 3, 4, 5); mass spectrum, *m/e* (relative intensity) 133 (34), 131 (100), 83 (46), 82 (51), 81 (30).

2-*exo*-(Dichloroamino)norbornane. This compound was prepared in 49% yield: $[Cl^+]$ = 100%; bp 30–37 °C (7 torr); ^1H NMR ($CDCl_3$) δ 3.55 (br t, 1 H, ($CHNCl_2$) 2.67 (br s, 1 H), 2.33

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(br s, 1 H), 1.83–0.96 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 86.82 (d, C-2), 42.50 (d, C-1), 40.24 (t, C-3), 39.72 (d, C-4), 36.81 (t, C-7), 27.74 (t, C-6), and 26.86 (t, C-5); mass spectrum, *m/e* (relative intensity) 179 (11), 177 (22), 152 (12), 150 (21), 145 (34), 143 (98), 117 (8), 115 (24), 110 (17), 109 (48), 108 (100), 94 (23) 93 (31), 92 (24), 91 (70), 78 (34), 68 (39), 67 (67), 66 (96).

Anal. Calcd for $C_7H_{11}Cl_2N$: C, 46.68; H, 6.17; H, 7.78. Found: C, 46.19; H, 6.08; H, 8.18.

2-(Chloroimino)norbornane. By use of the method of Alt and Knowles[26] a 33% yield of chloroimine was obtained from the exo isomer: [Cl$^+$] = 100%; ^{1}H NMR ($CDCl_3$) 3.07 δ (br s, 1 H), 2.77 (br s, 1 H), 2.28 (br s, 1.5 H), 2.08–1.27 (m, 7.5 H); ^{13}C NMR ($CDCl_3$) δ 190.90 (s, C-2), 46.28 (d, C-1), 42.26 (t, C-3), 39.56 (t, C-7), 37.00 (d, C-4), 26.93 (t, C-6), 25.29 (t, C-5); mass spectrum, *m/e* (relative intensity) 146 (6), 145 (33), 144 (9), 143 (100), 110 (4), 109 (19), 108 (59), 107 (32), 91 (23), 86 (14), 84 (20), 81 (23), 69 (23), 68 (11), 67 (27), 66 (23), 65 (3), 53 (8).

2-*endo*-(Dichloroamino)norbornane. A 53% conversion from the amine was obtained: yellow oil, [Cl$^+$] = 94%; ^{1}H NMR ($CDCl_3$) δ 4.07 and 3.90 (overlapping t, 1 H), 2.6 (br s, 1 H), 2.22 (br s, 1 H), 1.91–0.96 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 84.38 (d, C-2), 42.97 (d, C-1), 39.06 (t, C-3), 38.37 (t, C-7), 37.70 (d, C-4), 29.67 (t, C-5), 20.29 (t, C-6); mass spectrum, *m/e* (relative intensity) 179 (2), 177 (5), 152 (2), 150 (4), 145 (32), 144 (10), 143 (100), 117 (5), 115 (13), 110 (18), 109 (30), 108 (54), 107 (36), 94 (5), 93 (4), 92 (6), 91 (5), 81 (9), 78 (7), 67 (30), 66 (30).

2-(Chloroimino)norbornane. Dehydrohalogenation[26] of the endo isomer gave the imine in 87% yield: [Cl$^+$] = 97%; ^{1}H NMR ($CDCl_3$) δ 3.60 and 3.07 (br s, 1 H, 1-CH), 2.67 (br s, 1 H), 2.33 (br s, 1 H), 1.85–1.2 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 186.22 (s, C-2), 47.66 (d, C-1), 41.89 (t, C-3), 39.74 (t, C-7), 35.93 (d, C-4), 27.44 (t, C-6), 26.36 (t, C-5); mass spectrum, *m/e* (relative intensity) 146 (4), 145 (33), 144 (10), 143 (100), 128 (2), 110 (16), 109 (17), 108 (55), 107 (26), 91 (42), 68 (7), 67 (21), 66 (6).

2-(Dichloroamino)adamantane. This material was formed as a yellow oil in 40% yield: [Cl$^+$] = 97–99%; on storage in a freezer, it solidified (fp ~−20–10 °C); ^{1}H NMR ($CDCl_3$) δ 3.45 (br t, 1 H), 25 (br m, 2 H, 1,3-bridgehead H), 2.2–1.0 (br m, 12 H); ^{13}C NMR ($CDCl_3$) δ 83.88 (d, C-2), 37.31 (t, C-8,9), 37.12 (t, C-6), 32.33 (d, C-1,3), 30.57 (t, C-4,10), 27.18, 26.76 (d, C-5,7).

2-(Chloroimino)adamantane. A yellow oil was isolated in 17% yield:[26] [Cl$^+$] = 97%; ^{13}C NMR δ 184.60 (s, C-2, 38.31, 37.51, 33.76, 32.66, 28.04, 25.98; mass spectrum, *m/e* (relative intensity) 185 (3), 183 (9), 148 (14), 136 (9), 135 (100), 94 (20).

1-(Dichloroamino)-*n*-hexane. A volatile, odorous liquid was formed in 23% yield: [Cl$^+$] = 100%.

1-(Dichloroamino)-2-methylpropane. A 67% yield of the desired compound was obtained as a yellow oil: [Cl$^+$] = 92–94%; ^{1}H NMR ($CDCl_3$) δ 3.4 (d, 2 H, *J* = 7 Hz), 2.03 (br septet, 1 H, *J* = 7 Hz), 0.90 (d, 6 H, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 83.34 (t, C-1), 28.36 (d, C-2), 19.77 (q, C-3).

***N,N*-Dichlorobenzylamine.** The compound was produced in 70% yield: [Cl$^+$] = 90%; ^{1}H NMR ($CDCl_3$) δ 7.35 (s, 5 H), 4.6 (s, 2 H); mass spectrum, *m/e* (relative intensity) 178 (4), 176 (4), 143 (9), 141 (27), 106 (20), 91 (100).

***N,N*-Dichloro[(1-adamantyl)methyl]amine.** This material was prepared in 81% yield: [Cl$^+$] = 95–97%; ^{1}H NMR ($CDCl_3$) δ 3.45 (s, 2 H), 2.1–1.4 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 82.76 (t, CH_2NCl_2), 40.52 (t, C-2, 9, 10), 36.90 (t, C-4, 6, 8), 36.56 (s, C-1), 28.36 (s, C-3, 5, 7).

Pyrolysis of Chloroamines. General Procedure. Neat injection of 5–10 μL of the (dichloroamino)alkane (except as noted in Table II) into the GLC (injector port temperature, 190–280 °C; column temperature, 75–125 °C; He flow rate, 60 mL/min) gave a number of peaks, with the first being N_2. The others were identified by retention time and peak enhancement. The materials were collected and compared to authentic materials by IR, NMR, and mass spectrometry. Absolute yields were obtained by comparison of the integrated areas with those obtained from known concentrations of authentic materials.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank Dr. Piotr Starewicz for the ^{13}C NMR spectra, Mr. Paul Karges for the mass spectra, and Mr. Myron Mikaelian for assistance with the experimental work.

Registry No. 1-(*N,N*-Dichloroamino)-1-methylcyclohexane, 57337-77-6; *N,N*-dichloro-*tert*-octylamine, 69083-98-3; 2-(dichloroamino)-2-methylpropane, 2156-72-1; 3-(dichloroamino)pentane, 78685-86-6; 3-(chloroimino)pentane, 78685-87-7; (dichloroamino)-cyclohexane, 26307-01-7; (chloroiminocyclohexane, 6681-70-5; 2-*exo*-(dichloroamino)norborane, 78685-88-8; 2-(chloroimino)norborane, 78685-89-9; 2-*endo*-(dichloroamino)norborane, 78685-90-2; 2-(dichloroamino)adamantane, 25164-85-6; 2-(chloroimino)-adamantane, 75667-98-0; 1-(dichloroamino)hexane, 64851-26-9; 1-(dichloroamino)-2-methylpropane, 52548-05-7; *N,N*-dichlorobenzylamine, 6263-00-9; *N,N*-dichloro[(1-adamantyl)methyl]amine, 78685-91-3; hexanenitrile, 628-73-9; 1-hexene, 592-41-6; 2-methylpropanenitrile, 78-82-0; 1-chloro-2,2-dimethylpropane, 753-89-9; tricyclo[3.3.1.1^{3,7}]decane-1-carbonitrile, 23074-42-2; benzonitrile, 100-47-0; (chloromethyl)benzene, 100-44-7; 2-pentene, 109-68-2; cyclohexene, 110-83-8; bicyclo[2.2.1]hept-2-ene, 498-66-8; 2-methyl-1-propene, 115-11-7; 2,4,4-trimethyl-1-pentene, 107-39-1; 2,4,4-trimethyl-2-pentene, 107-40-4; 1-methylcyclohexene, 591-49-1; methylenecyclohexane, 1192-37-6.