Amination of Adamantanes and Their Precursors with Trichloramine–Aluminum Chloride[1]

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Abstract: The reaction of trichloramine and aluminum chloride with adamantane and alkyladamantanes gave excellent yields of the corresponding bridgehead amines. Various tricyclic alkanes upon treatment with trichloramine under Friedel–Crafts conditions underwent rearrangement and amination in one step to the corresponding aminoadamantanes. This represents the first case in which rearrangement of an adamantane precursor is accompanied by the introduction of a functional group. Synthetically, the trichloramine amination route provides a simple, one-step method of obtaining aminoadamantanes in high yields. The postulated mechanism involves hydride abstraction by positive chlorine from the adamantane nucleus. Subsequent attack by a nitrogen-containing nucleophile affords the N,N-dichloro derivative which has been isolated. Acid hydrolysis effects conversion to the amine.

This laboratory has reported the direct amination of aromatic compounds with N-halamines under Friedel–Crafts conditions leading to basic products of unusual orientation. Thus, when monoalkylbenzenes were allowed to react with trichloramine and aluminum chloride, the corresponding *m*-alkylanilines were formed.[4–7] The proposed addition–elimination mechanism, σ substitution, accounts for the selective *meta* orientation. Similar results were obtained with dialkylbenzenes,[8] biphenyl,[9] and naphthalene[9] as substrates.

When *p*-cymene was aminated with trichloramine and aluminum chloride, the presence of 8-amino-*p*-cymene[10] in the product stimulated investigation of other aryldialkylmethines in relation to side-chain attack. The efforts were rewarding since various *para*-substituted alkylbenzenes which possess a tertiary hydrogen afforded the corresponding *t*-carbinamines.[11–13] Further studies showed that alkanes reacted in an analogous fashion, *e.g.*, 1-methylcyclohexane yielded 1-amino-1-methylcyclohexane in good yield.[14]

The object of the present work was to investigate amination in the adamantane series in relation to the synthetic and mechanistic aspects. Since 1-aminoadamantane possesses antiviral properties,[15] additional impetus was provided to this work. Furthermore, we were interested in subjecting adamantane precursors to trichloramine under Friedel–Crafts conditions, inasmuch as these hydrocarbons would be susceptible to rearrangement[16,17] in the presence of the strong Lewis acid catalyst.

Results

Tables I and II summarize the results from amination of adamantanes and adamantane precursors with trichloramine and aluminum halides. In most cases, additives were introduced into the reaction mixtures containing the precursors in order to facilitate rearrangement to adamantanes.

Adamantane and Trimethylenenorbornane. Adamantane was selected as the substrate for ascertaining optimum reaction conditions and for a more detailed scrutiny of the mechanistic features.

Addition of a solution of trichloramine (0.1 mol) in methylene chloride to a slurry of aluminum chloride (0.2 mol) and adamantane (0.11 mol) at 10–15°, followed by hydrolysis with hydrochloric acid, gave 1-aminoadamantane (98% yield based on trichloramine). Essentially the same results were obtained with a 1:1 molar ratio of trichloramine to adamantane. When an equimolar ratio of the three reactants was used, a decrease in yield to 70% resulted. In prior work with methylcyclohexane, an even more drastic decrease in the amount of amine product was noted under similar conditions.[14] With carbon tetrachloride as solvent under the standard procedure, the reaction was sluggish and the yield of pure amine dropped to about 53% (*vs.* 95%).

Omission of the hydrolysis step permitted isolation of 1-N,N-dichloroaminoadamantane which was identified by comparison with authentic material prepared from 1-aminoadamantane and calcium hypochlorite. 1-N-Chloroaminoadamantane was synthesized and characterized in connection with studies on the N,N-dichloro counterpart. N,N-Dichloro-*t*-butylamine was

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Table I. Amination of Adamantanes

Adamantane reactant	Principal Basic Product[a] 1-Aminoadamantane derivative	Yield,[b] % based on NCl_3	Yield,[b] % based on Alkane	Acetyl deriv, mp, °C—Found	Acetyl deriv, mp, °C—Lit.
Parent	Parent	95	87	149	149[c]
1-Methyl	3-Methyl	93	85	106.5–107.5	108–109[d]
1,3-Dimethyl	3,5-Dimethyl	73	67	110–111	110–111[e]
1,3,5-Trimethyl	3,5,7-Trimethyl	90	82	192.5–193	194–196[f]
1,3,5,7-Tetramethyl		24[g]	22		

[a] Molar ratio, NCl_3:$AlCl_3$:alkane = 1:2:1.1. [b] Based on purified material. [c] H. Stetter, J. Mayer, N. Schwarz, and K. Wulff, *Chem. Ber.*, **93**, 226 (1960). [d] K. Gerzon, E. V. Krumkalns, R. L. Brindle, F. J. Marshall, and M. A. Root, *J. Med. Chem.*, **6**, 760 (1963). [e] The melting point of 80–82° reported in footnote *d* is incorrect and should be 110–111° (Dr. Koert Gerzon, personal communication). [f] K. Gerzon, D. J. Tobias, Sr., R. E. Holmes, R. E. Rathbun, and R. W. Kattau, *J. Med. Chem.*, **10**, 603 (1967). [g] Crude, 6–8 components.

Table II. Amination of Precursors of Adamantanes

Precursor substrate	Method	Molar ratio,[a] NCl_3: Alkane	Rearrangement conditions, Hr	Rearrangement conditions, Temp, °C	Amination, temp, °C	Principal basic product—1-Amino-adamantane derivative	Principal basic product—Yield,[b] % based on NCl_3	Principal basic product—Yield,[b] % based on Alkane
Trimethylene-norbornane	A	1:1.5			20–27	Parent	59	40
	B	1:1.5			15–22		75	50
Tetramethylene-norbornane	B	1:1.1			10	3-Methyl	69	63
	B	1:1.1	0.5	25–30	10		85	77
Perhydroacenaphthene	B[c]	1:1.5	1.5	50–60	0–5	3,5-Dimethyl	44	29
	A[c,d]	1:1.5	24	100	0–5		73	49
Dimethyltrimethylene-norbornane	B	1:1.5			5–10	3,5-Dimethyl	53	35
	B	1:1.5			5–10		73	49
Perhydrofluorene	B	1:1.8	1.0	50–60	10–15	3,5,7-Trimethyl	28	19

[a] Molar ratio of NCl_3:AlX_3 = 1:2. [b] Pure material. [c] No methylene chloride was used with precursor during rearrangement. [d] Hydrogen chloride not added; rearrangement was carried out before addition of trichloramine.

detected in a previous amination study involving *t*-butyl chloride.[18]

Trimethylenenorbornane underwent amination during rearrangement in the presence of trichloramine, aluminum chloride, and a small amount of hydrogen chloride to give, after vigorous acid hydrolysis, a 59% yield of 1-aminoadamantane. Use of aluminum bromide and *t*-butyl bromide under the same conditions enhanced the yield to about 75%.

1-Methyladamantane and Tetramethylenenorbornane. 1-Methyladamantane, prepared by aluminum chloride catalyzed isomerization of tetramethylenenorbornane,[19] was allowed to react with trichloramine and aluminum chloride at 0–5°. Work-up gave a 93% yield of 1-amino-3-methyladamantane.

Tetramethylenenorbornane, synthesized by low pressure hydrogenation of the Diels–Alder adduct of norbornene and 1,3-butadiene,[20] aminated smoothly in the presence of trichloramine, aluminum bromide, and a small amount of *t*-butyl bromide to provide 1-amino-3-methyladamantane in 60% yield. A yield enhancement to 85% was realized when a brief rearrangement period was introduced prior to the amination.

1,3-Dimethyladamantane, Perhydroacenaphthene, and Dimethyltrimethylenenorbornane. Reaction of trichloramine and aluminum chloride with 1,3-dimethyladamantane at 0–5° gave 73% of 1-amino-3,5-dimethyladamantane. Two precursors, perhydroacenaphthene, obtained by catalytic hydrogenation of acenaphthene,[21] and dimethyltrimethylenenorbornane, from reduction of methylcyclopentadiene dimer, also served as sources of this base on exposure to the amination system. Several routes were employed. Perhydroacenaphthene, when treated directly with trichloramine, aluminum bromide, and a small amount of *t*-butyl bromide, provided a 44% yield of the amine. Allowing the hydrocarbon to undergo rearrangement by exposure to aluminum chloride at 100° for 24 hr followed immediately by the addition of trichloramine at 0–5° increased the yield to 73%.

Dimethyltrimethylenenorbornane underwent amination in one step with aluminum bromide and *t*-butyl bromide as the catalyst system, forming 1-amino-3,5-dimethyladamantane in 53–75% yields.

1,3,5-Trimethyladamantane and Perhydrofluorene. Trimethyladamantane was synthesized from perhydrofluorene by a modified literature procedure.[22] Since only modest yields were obtained even under vigorous reaction conditions, this case appears to be one of the less efficient examples in the reaction category. With the standard amination procedure a 90% yield of 1-amino-3,5,7-trimethyladamantane was realized.

Perhydrofluorene, from high pressure hydrogenation of fluorene,[21] was brought into contact with aluminum bromide and *t*-butyl bromide for 1 hr at 50–60° followed by exposure to trichloramine at around 10°. The 28% over-all yield of desired amine is quite low in comparison with the result for the direct amination of trimethyladamantane.

1,3,5,7-Tetramethyladamantane. Amination of tetramethyladamantane at either 0–5° or 10–15° afforded a multicomponent mixture of basic products in low yield. Characterization was not attempted.

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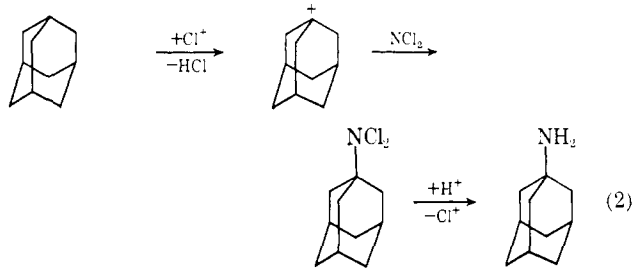
Discussion

Synthetic Aspects. The direct amination of adamantane and alkyladamantanes constitutes a convenient, efficient method for the synthesis of the corresponding bridgehead amines. A further simplification involves amination during rearrangement of adamantane precursors. This appears to be the first example involving introduction of a functional group during transformation of a precursor to the adamantane nucleus. The advantages of this novel procedure are further illustrated by comparison with prior literature routes in relation to yield and convenience. According to previous techniques,[23-29] multistep pathways are required for preparation from the parent adamantanes (yields of 60–80% based on alkane) or precursor hydrocarbons (23–75% yields).

Mechanistic Aspects. Amination of Adamantanes. The postulated mechanism for the amination of adamantanes is outlined (eq 1 and 2). Supporting evidence

$$NCl_3 + AlCl_3 \rightleftharpoons Cl_3N{-}{-}{-}AlCl_3 \rightleftharpoons Cl^{\delta+}\ [Cl_2NAlCl_3]^{\delta-} \quad (1)$$



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for the general scheme has been cited in earlier studies.[14,30-32] In addition, hydrogen chloride was evolved during the reaction. A favorable feature is undoubtedly the high preference for formation of the tertiary adamantyl cation[17] which has been detected in a strong acid system.[33]

The observations that the reaction is sluggish and the yield of amine is lower in carbon tetrachloride point to an interesting solvent effect. An ionic route would presumably be facilitated in methylene chloride as compared to carbon tetrachloride because of the difference in dielectric constants (9.08 *vs.* 2.2). Similar mechanistic interpretations of solvent influences were advanced for the ketone–phosphorus pentachloride reaction[34] and the acetyl chloride–aluminum chloride–cyclopropane system.[35]

There are two aspects of adamantane amination which were not encountered with simple alkanes.[14] First, a very high yield of amine could be obtained with a 1:1 molar ratio of trichloramine to adamantane, and second, at the end of reaction the amine was present for the most part in the form of the N,N-dichloro derivative. These findings are attributed to the inability of the adamantane structure to accommodate a double bond (Bredt's rule).[36-38] Side reactions from the simpler alkanes, leading to olefinic material, enhance the amount of by-products, such as polymers and chlorinated alkanes.[14] Prior work indicates that alkenes are involved in the conversion of $RNCl_2$ to RNH_2 in the amination of alkyl halides.[18]

The mechanism described for adamantane should apply as well to alkyladamantanes. In the case of tetramethyladamantane the low yield of multicomponent amine is attributed to the unavailability of a tertiary position. This observation lends further support to the proposed mechanistic scheme.

Amination During Rearrangement of Adamantane Precursors. Although a clear understanding is lacking of the pathway for formation of adamantanes from tricyclic alkanes on exposure to Lewis acid catalysts, several plausible routes entailing carbonium ion intermediates have been advanced.[16,21,29,39] A similar mechanism[3] is probably operative in our case.

Generally, for the isomerization of precursors to adamantanes by prior techniques rather drastic conditions (temperature and/or time) were employed.[16,21,40,41] It is significant that, in some cases in our precursor experiments, as good or better yields of adamantanes in aminated form were obtained at relatively low temperatures and short reaction times. Several explanations for the difference can be offered. Trichloramine or a derived entity, *e.g.*, from reaction with the alkane, might function as an efficient isomerization catalyst. In addition, solubility of the catalyst in the amination system could well be an important beneficial factor. Finally, under our conditions harmful side reactions may be diminished.

Experimental Section

Warning. Exercise the necessary precautions in working with halamines.

Materials. Acenaphthene, adamantane, fluorene, methylcyclopentadiene dimer, norbornene, perhydrophenanthrene, trimethylenenorbornane (Aldrich Chemical Co.), and 1,3-butadiene (Union Carbide Corp.) were used without further purification. Methylene chloride (Fisher Certified) was distilled from calcium hydride to ensure dryness. We are grateful to Dr. Henry J. Peterson, Sun Oil Co., for a sample of 1,3-dimethyladamantane, and to Mr. William Richmond, an undergraduate summer research trainee, for assistance in the preparation of tetramethyladamantane.

Analytical Procedures. Infrared spectra were obtained on a Beckman IR-8 spectrophotometer with neat samples or dilute solutions in carbon tetrachloride. Varian A-60 or HA-100 instruments

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were used to obtain nmr data, and mass spectra were recorded by means of a Varian M-66 unit. Gas chromatography was carried out with Varian Aerograph instruments (A-90-P, Hy-Fi 1200 or 1700). The indicated columns were employed: 16 ft × 1/4 in., 20% Carbowax 20M and 5% NaOH on Chromosorb P (30–60 mesh); 10 ft × 1/8 in., 10% Carbowax 20M and 2.5% NaOH on Chromosorb P (60–80 mesh); 6 ft × 1/4 in., 3% SE-30 on Varaport 30 (100–120 mesh).

Positive chlorine in trichloramine and other N-halo compounds was determined by standard iodometric titration methods.[4] Melting points and boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of Trichloramine Solution. A published procedure[4] (method B) was used with the appropriate solvent. No appreciable deterioration occurred during storage for 3 weeks at −20°.

Amination of Adamantane. In a 1-l., 3-necked flask equipped with a mechanical stirrer, condenser, thermometer, addition funnel, and nitrogen inlet was placed 27.3 g (0.2 mol) of adamantane in 650 ml of methylene chloride. A slow flow of nitrogen through the flask was then established. After the introduction of 35.6 g (0.226 mol) of anhydrous aluminum chloride at 0°, trichloramine solution equivalent to 0.133 mol was added at 10–15° over a period of 1 hr. The mixture, essentially homogeneous, was allowed to stir for an additional 15–30 min at 10–15°. A mixture of 50 ml of concentrated hydrochloric acid and 20 ml of water was then added slowly to the stirred reaction mixture at 25–35°. After 30 min of agitation, the layers were separated and the organic phase was treated in a similar manner with strong hydrochloric acid until the yellow color was no longer observed. The combined acid solutions were washed with ether, made slightly basic with 50% sodium hydroxide while keeping the solution around room temperature, and then extracted with methylene chloride. Drying over sodium sulfate, followed by evaporation of solvent, yielded about 20 g (98% based on trichloramine) of 1-aminoadamantane which was identified by comparison with authentic material.

Amination of Alkyladamantanes. The same general procedure was employed except that the reaction was carried out at approximately one-third scale at 0–5°. A molar ratio of NCl_3–$AlCl_3$–alkyladamantane of 1:2:1.1 was used. The mixture became essentially homogeneous during the amination.

Purification was accomplished by low pressure sublimation, 70–110° at 0.05 mm, except in the case of 1-amino-3,5-dimethyladamantane which was distilled, 72° at 1.5 mm, through a spinning band column. Because of interaction with atmospheric components, exposure of the amines to air should be minimized.

Identification was by comparison with published data[42–44] of infrared and nmr spectra obtained from sublimed, distilled, or glpc-collected material, and by means of the acetyl derivative. 1-Amino-3,5-dimethyladamantane was synthesized according to a literature method[25,26] for use in identification of the amination product.

Amination of Precursor Hydrocarbons. Two general methods were employed. The molar ratio of reactants, reaction conditions, and yield data for the individual precursors are given in Table II. Molar quantities of reactants were NCl_3:$AlCl_3$:precursor = 0.1:0.2:0.11–0.18, with the exception of perhydrofluorene for which one-half scale runs were made.

Method A. In a 500-ml, 3-necked flask with standard equipment was placed the precursor alkane in 100 ml of methylene chloride and then aluminum chloride was added at 15°. A small amount of anhydrous hydrogen chloride was introduced below the surface followed by the addition of trichloramine over a period of 1.5 hr. The mixture was stirred for an additional 0.5 hr at the amination temperature. Isolation of the amine was by the previously described route for adamanatane.

Method B. The procedure outlined in method A was used for the most part. Aluminum bromide was added at 0° to the alkane dissolved in 50 ml of methylene chloride. The mixture was warmed to 10°, and 2 ml of *t*-butyl bromide was added over 5 min with autogenous heating. In some cases rearrangement was effected prior to addition of the trichloramine solution. After the 1-hr addition period, stirring for 15 min at the amination temperature, followed by the usual work-up, gave the amine product. Purification and identification of the amine products were as described in a previous section.

Rearrangement of Trimethylenenorbornane. Trimethylenenorbornane was treated with aluminum bromide and *t*-butyl bromide as described in method B (amination of precursor hydrocarbons). After the *t*-butyl bromide was added, the mixture was stirred for 1.5 hr at 20°. Upon work-up, adamantane was found to be present in about 25% yield.

Preparation of Precursors. The indicated literature procedures were used: dimethyltrimethylenenorbornane,[19] tetramethylenenorbornane,[20] perhydrofluorene,[21] and perhydroacenaphthene.[21]

Preparation of Alkyladamantanes. Published methods were followed: 1-methyl,[19] 1,3,5-trimethyl,[22] and 1,3,5,7-tetramethyl.[41]

1-N,N-Dichloroaminoadamantane from 1-Aminoadamantane. A solution of 5 g (0.033 mol) of 1-aminoadamantane dissolved in 7 ml of concentrated hydrochloric acid and 20 ml of water was added during about 5 min with stirring at 0° to 9.2 g (0.045 mol) of calcium hypochlorite in 20 ml of water and 40 ml of methylene chloride. The organic phase was immediately separated, washed twice with cold water, and dried over sodium sulfate. Removal of solvent followed by sublimation at 45° (0.05 mm) and crystallization from hexane gave yellow crystals, mp 40–41°, which titrated for 100% of the theoretical amount of active chlorine.

The product showed the following characteristics: ir (CCl_4) 685 cm^{-1} (N—Cl); nmr ($CDCl_3$) δ 2.22 (s, 3H), 1.93 (d, 6H), 1.67 ppm (d, 6H); mass spectrum (70 eV) *m/e* (rel intensity) 135 (100), 86 (42), 84 (67), 51 (36), 49 (80).

Anal. Calcd for $C_{10}H_{15}NCl_2$: C, 54.50; H, 6.82; Cl, 32.3, N, 6.38. Found: C, 54.77; H, 6.88; Cl, 31.96; N, 6.45.

Isolation of 1-N,N-Dichloroaminoadamantane from the Amination Reaction. Adamantane was aminated according to the general procedure with a 1:2:1 molar ratio of trichloramine–aluminum chloride–adamantane. After addition of the trichloramine, a portion of the reaction mixture was treated with cold water. Isolation and purification by the usual method gave a product identical in all respects with the authentic material.

1-N-Chloroaminoadamantane from 1-Aminoadamantane.[45] The procedure for the N,N-dichloro derivative was followed. Calcium hypochlorite (2.75 g, 0.013 mol) dissolved in 45 ml of water was added during about 5 min to 4.07 g (0.027 mol) of 1-aminoadamantane dissolved in 50 ml of methylene chloride at 0°. Recrystallization of the crude, semisolid product from methylene chloride gave crystals, mp 133.5–135°, that titrated for 100% of the theoretical quantity of active chlorine.

1-N-Chloroaminoadamantane showed these characteristics: ir (CCl_4) 3390, 1700, 735, and 685 cm^{-1}; nmr ($CDCl_3$) δ 4.06 (s, 1H), 2.13 (s, 3H), 1.69 ppm (m, 12H).

Anal. Calcd for $C_{10}H_{16}NCl$: C, 64.70; H, 8.63; Cl, 19.10; N, 7.55. Found: C, 64.60; H, 9.11; Cl, 19.26; N, 7.63.

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