the concentrations c_1 and c_2 (of I and II, respectively) from A, the absorbance at the subscripted wavelength. The total concentration of the imine isomers calculated from the original sample weight was 7.67×10^{-5} M and the concentration calculated from uv absorbance after reaction was 7.45×10^{-5} M. Analysis of synthetic samples known to contain 25.0, 50.0, and 75.0% of I gave 25.3, 49.9, and 75.3% respectively. These values were not significantly altered by putting the synthetic mixtures through the work-up procedure.

Racemization Runs. In a typical racemization run, I (1.503 g, 5.94 mmol) was introduced into a tube with 49.4 ml of 0.457 N potassium *tert*-butoxide in *tert*-butyl alcohol. The tube was sealed and placed in a constant-temperature bath for 1230 min at 100°. The tube was cooled and opened and two 0.20-ml aliquots worked up as described above for uv analysis, showing 18.1 and 18.0% isomerization. The remainder of the reaction mixture was poured immediately into a mixture of 75 ml of pentane and 125 ml of water. After washing the pentane layer 3-4 times with water, it was dried and the pentane evaporated. The resultant imine mixture was treated with 20 ml of 20% aqueous sulfuric acid solution and refluxed for 1 hr to hydrolyze the imines. The mixture was cooled and continuously extracted with ether for 24 hr. The acidic layer was made basic with *ca.* 2 g of solid sodium hydroxide and the mixture of amines extracted with ether for 24 hr. The ether solution was dried, the ether was evaporated and the amines were separated by preparative glc on a 15 ft × $^3/_8$ in. column packed with 17% SE-30 on 45-60 mesh Chromosorb W at 195°. Care was taken to keep the amine samples in a carbon dioxide free atmosphere during collection. Samples were dissolved in cyclohexane which had been stored over potassium hydroxide for polarimetric analysis. Rotations determined on amines obtained by hydrolysis of the starting materials are listed in Table X.

Table X. Rotations at 25° of Optically Active Amines from the Hydrolysis of Chiral Imines I and II

Substrate	Amine	Concn,[a] mg/ml	Specific rotation, deg
(*S*)-I-H	(−)-α-Phenylethyl[b]	45.3	−40.0
		40.4	−41.6
		Neat	−40.5
(*S*)-II-H	(−)-α-(4-Methoxyphenyl)ethyl[c]	100.0	−36.2
(*R*)-II-H	(+)-α-(4-Methoxyphenyl)ethyl[c]	121.0	+38.1
		75.0	+38.1

[a] Solution of the amine in cyclohexane. [b] Lit.[17] $\alpha^{22}\text{D}$ −38.3° (neat, 1 dm). [c] Predicted maximum specific rotation, $[\alpha]^{25}\text{D}$ +36.0° based on nmr data on partially resolved material in chiral solvent: W. H. Pirkle, T. G. Burlingame, and S. D. Beare, *Tetrahedron Lett.*, **56**, 5849 (1968).

Amination of Toluene, Adamantane, and *tert*-Butyl Chloride with Monochloramine–Aluminum Chloride[1]

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Abstract: The reaction of monochloramine with toluene in the presence of aluminum chloride at −35° yielded 13-15% of *m*-toluidine, whereas trichloramine gave 39-43% yields. In order to rationalize the meta substitution, a mechanistic scheme entailing addition–elimination is proposed. Amination of adamantane with monochloramine under Friedel–Crafts conditions gave 1-aminoadamantane in 40% yield. An analogous reaction with trichloramine–aluminum chloride provided 1-aminoadamantane in 85% yield with no detectable 2-aminoadamantane. The reaction pathway presumably involves formation of the 1-adamantyl cation followed by attack by the nitrogen-containing nucleophile. Reaction of *tert*-butyl chloride, monochloramine, and aluminum chloride yielded *tert*-butylamine (7-20%). Similarly, trichloramine generated *tert*-butylamine in 50-56% yield and 2,2-dimethylaziridine in 7-12% yield. Mechanistically, the *tert*-butyl cation is thought to participate as an intermediate. Possible reasons are discussed for the lower yields in all cases with monochloramine, as compared to trichloramine.

This report is an outgrowth of our interest in the chemistry of *N*-haloamines, as well as our involvement with environmental chemistry.[3] Prior work[4] from this laboratory involved investigations of the trichloramine–aluminum chloride combination for amination of various organic substrates, *e.g.*, arenes, alkanes, and alkyl halides. The aromatic study included mono-[5,6] and *m*-dialkylbenzenes,[7] halobenzenes,[8] and biphenyl.[9] A striking feature was the essentially exclusive meta orientation observed in all cases. There was an accumulation of evidence[4–10] which pointed to an addition–elimination pathway. This comprised the first example of involvement of this type of mechanism to a fairly appreciable extent (yields as high as 36%) with simple benzenoid compounds. It is well known[11] that with uncomplicated benzene derivatives, the straightforward substitution route pertains almost exclusively for the classical methods.

With alkane substrates, replacement of hydrogen

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(1) Paper XIX. Chemistry of *N*-Haloamines. Contribution No. 81 from the Center for Great Lakes Studies, University of Wisconsin—Milwaukee.

(2) From the M. S. Thesis of J. W. S., 1972.

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(11) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, New York, N. Y., 1965, pp 4, 5.

by the amino group was effected by trichloramine in the presence of aluminum chloride. Simple cycloalkanes[12,13] were explored, as well as bicyclic,[13,14] tricyclic,[15] and benzylic[16–18] types. In some instances, rearrangement also took place. There are very few procedures reported in which direct amination of an alkane structure occurs. Our method, involving a simple technique, appears to be unique in that good to excellent yields were realized in many cases.

It was found previously that trichloramine–aluminum chloride is capable of aminating alkyl halides.[19] Products from primary, secondary, tertiary, and vicinal halides consisted of primary or secondary amines from replacement or rearrangement, in addition to aziridines. The results from *tert*-alkyl halides, *e.g.*, 90% yield of *tert*-butylamine from *tert*-butyl chloride, are especially interesting since other amination techniques often result in dehydrohalogenation.

The objective of the present work was to investigate the scope and mechanism of amination with monochloramine–aluminum chloride. Toluene, adamantane, and *tert*-butyl chloride were selected as the organic substrates. In addition, attention was given to preparative methods for the haloamine. Both gas-phase[20,21] and extraction[22–24] techniques are recorded in the existing literature.

Results and Discussion

Preparation of Monochloramine. Initially, a gas-phase procedure was explored. The reactor described in the Experimental Section was based on a design by Drago.[25] This modified form was selected since those described in the literature are generally rather complicated. An illustration of the apparatus may be found elsewhere.[2] In one experiment, the ammonia was introduced at a fast flow with chlorine entering at a rate of 1–2 bubbles/sec. The cloud of ammonium chloride was being blown in a continuous stream toward the outlet. The stream of solid particles was most easily controlled by the ammonia flow rate. The analysis for monochloramine in the trapping solvent was positive. The chlorine and ammonia were introduced at varying flow rates (all fast) in an attempt to optimize yields. It was found that the flow rates could be varied over a range as long as there was sufficient velocity to prevent suck back, and the ammonium chloride proceeded in an even stream toward the outlet. The methylene chloride solution was treated with calcium chloride in order to remove dissolved ammonia. Since the amount of monochloramine generated from one pass was small, four consecutive runs were carried out.

In other experiments, both ammonia and nitrogen were introduced at faster rates than for chlorine. It is simpler to control suck back and reaction heat with nitrogen as the diluent rather than with chlorine. After each run the reactor was cleaned of ammonium chloride. After four runs, the concentration of monochloramine was 0.1 *M* in methylene chloride.

In summary, to produce approximately 0.1 *M* monochloramine solution, fast flow rates of nitrogen and ammonia and semifast flows of chlorine are required. Reaction times are short (15–30 min) because of the buildup of ammonium chloride deposits. Earlier workers[26] report larger quantities of product during similar reaction periods, presumably due to faster gas flows or a different reactor design.

Since the gas-phase technique was relatively cumbersome and provided only small amounts of the desired material, extraction of monochloramine into an organic solvent from an aqueous phase was investigated. The monochlorination of ammonia in aqueous solution has been studied previously.[27] In our work, 3 *M* solutions of ammonia and hypochlorite were allowed to react to form a 3.5% solution of monochloramine. Free nitrogen was liberated during reaction at 0° indicating that the concentration of product is being approached which leads to rapid decomposition. Extraction with methylene chloride gave about 6 g of monochloramine. The solution must be kept cold and used promptly since the positive chlorine content decreases fairly rapidly with time because of decomposition.[20] Marckwald and Wille have discussed[22] several liquid-phase processes which lead to destruction.

Amination of Toluene. Standard conditions for the reaction of toluene with monochloramine comprised an $AlCl_3/NH_2Cl$ molar ratio of 2 in methylene chloride at $-35°$ for 1 hr. *m*-Toluidine was obtained in 13% yield (glpc) based on monochloramine. The neutral portion was made up primarily of *o*- and *p*-chlorotoluenes in yields (glpc) of 40% ortho and 27% para (ortho:para ratio of 1.5), which correlates nicely with the ortho:para ratio of 1.5 reported for halogenation of toluene with chlorine in acetic acid.[28] The combined yields of basic and neutral products account for 80% of the starting material. When the reaction was extended to 4 hr, there was no significant difference in yield of *m*-toluidine (10%). In a reaction with half

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the usual concentration of monochloramine under standard conditions, the yield of *m*-toluidine decreased to 6%. In two follow-up experiments in which the time was extended to 2 hr, the yield of *m*-toluidine rose to 13–15%. These data indicate that the reaction is relatively slow.

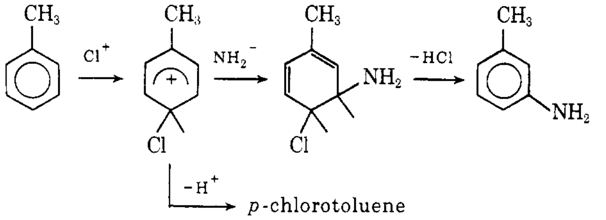
Reactions performed under the standard conditions used for monochloramine were also carried out with trichloramine. In duplicate runs, *m*-toluidine was generated in yields of 39–43%, which correspond nicely to literature data[5] obtained under somewhat different conditions. The neutral fraction contained *o*- and *p*-chlorotoluenes in yields of 34 and 24%, respectively. The ortho : para ratio of 1.4 is very close to that observed with monochloramine. For some unknown reason, the ortho : para ratio in the earlier investigation[5] with trichloramine was 2.2, which might perhaps result from the difference in reaction conditions.

A possible stoichiometric relationship for formation of the basic component is illustrated in eq 1.

$$C_6H_5CH_3 + NH_2Cl \xrightarrow{AlCl_3} m\text{-}H_2NC_6H_4CH_3 + HCl \qquad (1)$$

Based on literature analogy involving the trichloramine–aluminum chloride system,[4] it is proposed that the mechanism for amination of toluene with monochloramine entails the steps illustrated in eq 2 and 3.

$$ClH_2N + AlCl_3 \rightleftharpoons ClH_2N\cdots AlCl_3 \rightleftharpoons Cl^{\delta+}[H_2NAlCl_3]^{\delta-} \qquad (2)$$



(3)

(4)

The electronegativities of nitrogen and chlorine are reported[29] to be essentially equal. Theoretically, the aluminum chloride might coordinate with either chlorine or nitrogen, forming two complexes in equilibrium (eq 5).

$$ClH_2N\cdots AlCl_3 \rightleftharpoons NH_2Cl + AlCl_3 \rightleftharpoons NH_2Cl\cdots AlCl_3 \qquad (5)$$

Addition–elimination apparently occurs[10] when (1) the appropriate arenium ion forms, (2) nucleophilic attack of the σ complex (eq 3) competes favorably with proton elimination (eq 4), and (3) rearomatization takes place readily. Although several Lewis acids, including aluminum chloride, hydrogen chloride, and the σ complex, would be in competition for the nucleophile, apparently combination with the carbonium ion is energetically favored. Alternative mechanistic pathways appear unlikely.[5]

Amination of Adamantane. Addition of a solution of monochloramine in methylene chloride to a slurry of aluminum chloride and adamantane at 10–15°, followed by hydrolysis with concentrated hydrochloric acid at 10–15°, gave 1-aminoadamantane in 40% yield, and unchanged adamantane (69% recovery). The neutral layer contained chlorine dissolved in methylene chloride as indicated by the uv spectrum, a precipitate with silver ion, iodine formation from sodium iodide, color, and odor. The neutral layer, which was allowed to stand for 24 hr, gave 50% recovery of adamantane, 14% of 1-chloroadamantane, and 1.9% of 2-chloroadamantane (1 : 2 isomer ratio of 7.4). It appears that chlorination of adamantane was effected by contact with the chlorine. Another reaction was carried out in which the neutral layer was allowed to stand for 48 hr before work-up, resulting in 40% recovery of adamantane, 27% of 1-chloroadamantane, and 1.6% of 2-chloroadamantane (1 : 2 isomer ratio of 17).

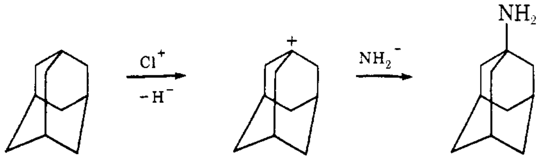
In order to determine at what stage chlorine was being formed, a sample of solvent was removed after the reaction was complete, but before acid hydrolysis. A second sample was taken after hydrolysis. Uv spectra indicated the absence of chlorine in the prehydrolysis sample (a trace of trichloramine was noted), but showed large amounts of chlorine after hydrolysis. After 24 hr the uv spectra were essentially unchanged. Chlorine formation most likely occurs as set forth in eq 6 and 7. The Cl^+ presumably does not exist as the free ion at any stage.[30]

$$NH_2Cl \xrightarrow{H^+} NH_3 + Cl^+ \qquad (6)$$

$$Cl^+ + Cl^- \longrightarrow Cl_2 \qquad (7)$$

An analogous reaction with trichloramine–aluminum chloride and adamantane under standard conditions gave 85% of 1-aminoadamantane and 14% recovery of adamantane with no detectable 2-aminoadamantane. This compares favorably with a literature yield obtained under slightly different conditions.[15]

As noted earlier in the case of trichloramine,[5] various lines of evidence support an ionic pathway, *e.g.*, the orientation (essentially all 1-substitution) and the necessity of a strong Friedel–Crafts catalyst. These transformations appear to be mechanistically analogous[31a] to bromination[31b] of adamantane, which is reported to follow a polar route. In line with the prior mechanistic treatment,[5] the illustrated sequence appears reasonable for monochloramine, entailing hydride abstraction by positive halogen,[31,32] eq 2 and 8.



(8)

Other routes to the cation can be visualized.

Several experiments were performed with the aim of obtaining information concerning the nature of the nucleophiles in the two cases, and the form of the product before hydrolysis. One investigation entailed exposure of monochloramine to aluminum chloride in methylene chloride. Only minor quantities of trichloramine were generated indicating that disproportionation is not facile under these conditions. In addition, the reaction mixtures from aminations with H_2NCl and NCl_3 were extracted rapidly with cold aqueous acid. In the case of monochloramine, the acid extract contained 1-aminoadamantane in 37–

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38% yield which is precisely the amount isolated from the standard procedure after hydrolysis. The organic layer yielded a negligible quantity of basic material after prolonged exposure to acid. In a control experiment, it was shown that *N,N*-dichloro-1-adamantanamine undergoes hydrolysis to a very minor extent (~1%) on rapid extraction with cold acid. On the basis of our working hypothesis and these findings, NH_2^-, rather than NCl_2^- (from NCl_3 through disproportionation of NH_2Cl), appears to be involved as the nucleophile (in complexed form) in the monochloramine reaction. A similar investigation was carried out with the trichloramine reaction mixture. The acid extract contained 1-aminoadamantane in 32% yield, whereas the organic layer afforded the base in 48–56% yield after hydrolysis. The combined total is in agreement with the yield obtained from the standard procedure. It was shown that, after acid extraction, the amine was in the form of the dichloro derivative in methylene chloride in accord with the prior report.[15] Perhaps, the material which is extracted by acid arises in the illustrated manner (eq 9)

$$RNCl_2 \xrightarrow[-Cl^+]{H^+} RNHCl \xrightarrow[-Cl^+]{H^+} RNH_2 \qquad (9)$$

$$R = \text{1-adamantyl}$$

during the amination reaction. In a number of earlier aminations of hydrocarbons by trichloramine, the N-chlorinated form of the amine was found to be present at the end of reaction. Specific examples include cyclohexane,[13] adamantane,[15] and *p*-cymene.[16]

Amination of *tert*-Butyl Chloride. The general procedure involved addition of *tert*-butyl chloride to a slurry of monochloramine–aluminum chloride at −5 to −10°. The resulting mixture was then stirred for 1 hr and worked up by hydrolysis with hydrochloric acid. Duplicate runs with *tert*-butyl chloride, monochloramine, and aluminum chloride revealed the presence of 9–11 basic products with the first peak comprising 75–95% of the total. The major component was identified as *tert*-butylamine (7–20% yield). Glpc of the neutral layer revealed 20–30 peaks.

Similar reactions with trichloramine–aluminum chloride and *tert*-butyl chloride gave 50–56% yields of *tert*-butylamine, plus 7–12% of 2,2-dimethylaziridine. The neutral fraction contained 11–18 compounds. It should be noted that the yield was 90% in the prior work[19] with trichloramine, which was carried out under somewhat different conditions. Apparently, increased dilution in the present case is responsible for the lowered yield, which would make for less likelihood of interaction of the intermediate *tert*-butyl cation with the nucleophile and hence an enhanced chance for participation in side reactions, such as proton loss.

A plausible mechanism[19] for formation of *tert*-butylamine from monochloramine is presented in eq 2 and 10. In the prior work with trichloramine,

$$(CH_3)_3CCl \xrightarrow[-Cl^-]{AlCl_3} (CH_3)_3C^+ \xrightarrow{NH_2^-} (CH_3)_3CNH_2 \qquad (10)$$

N,N-dichloro-*tert*-butylamine was isolated at the end of reaction.[19]

The composition of the neutral product was not determined in this investigation. In the previous work with trichloramine, di-, tri-, and tetrachloroalkanes were found to be present.[19]

Monochloramine *vs.* Trichloramine. What is a possible rationalization for the lower yields with monochloramine as compared to trichloramine in amination of the three organic substrates? Since monochloramine is more basic than the trichloro counterpart, one would expect aluminum chloride to coordinate more readily with the former (eq 2). Hence, the difficulty does not appear to be associated with complex formation involving the haloamine and aluminum chloride.

The answer might be found in the difference in nucleophilic properties of the two species, dichloramide ion and amide ion (in complexed form). In fact, it is conceivable on theoretical grounds that Cl_2N^- may be a supernucleophile. Supernucleophilicity (α effect)[33] is observed with entities possessing an atom, *e.g.*, oxygen, halogen, or nitrogen, with unshared electrons adjacent to the reactive site. It appears that a number of factors account for the enhanced reactivity. One possible rationalization of the α effect is based on orbital splitting which raises the energy of the highest filled orbital of the nucleophile.[33] Another interpretation involves conformational factors that influence the magnitude of electron pair–pair repulsion.[34] The α effect in nucleophilic aromatic substitution is usually more pronounced in catalyzed than in uncatalyzed processes.[35] In addition, monochloramine and trichloramine themselves might be functioning as nucleophiles.

Alternatively, the yield data may be a reflection of other phenomena, *e.g.*, the difference in solubility between the complexes, $ClH_2N{-}AlCl_3$ and $Cl_3N{-}AlCl_3$, or the difference in ease of destruction[19] of monochloramine and trichloramine by hydrogen chloride generated in the reaction mixtures.

Experimental Section

Materials. Toluene (Mallinckrodt) was distilled, treated with anhydrous calcium chloride, and stored over sodium. Methylene chloride (Aldrich Chemical Co.) was distilled from calcium hydride. Calcium hypochlorite was in the form of "HTH" (Monsanto Chemical Co., 70% purity). Nitrogen (Linde H. P. Dry) was passed through sulfuric acid. Other materials were high purity commercial grades which were used as obtained.

Analytical Procedures. Infrared spectra were obtained on a Beckman IR-8, Perkin-Elmer 337, or Perkin-Elmer 137 spectrophotometer with neat samples, dilute solutions in carbon tetrachloride, or with potassium bromide pellets. Nmr spectra were obtained on a Varian T-60 or HA-100 instrument, and ultraviolet and visible spectra with a Perkin-Elmer or Beckman spectrometer. Gas chromatography was carried out with Varian Aerograph instruments (A-90-P, Hi-Fi 1700 or 1800). Authentic materials were used in quantitative glpc analysis. The indicated columns were used (Table I).

Positive chlorine in monochloramine and trichloramine was determined by iodometric titration.[36]

Preparation of Monochloramine Solution. Gas-Phase Reaction. The reaction chamber consisted of a 1-l. Pyrex erlenmeyer flask with an outlet Pyrex tube in the center of the bottom. The stopper contained five 8-mm tubes with one in the center and the other four symmetrically distributed around it. The center one is flared and the outer tubes end in jets bent perpendicularly toward the outlet of the center tube. The outer tubes delivered the ammonia, whereas the center one contained chlorine and nitrogen, or chlorine alone.

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(33) G. Klopman, K. Tsuda, J. B. Louis, and R. E. Davis, *Tetrahedron*, **26**, 4549 (1970).

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Table I. Glpc Columns

Column	Dimensions, ft:in.	Packing
1	10:0.25	15% Carbowax 20M Chromosorb W (45–60 mesh)
2	10:0.25	15% Ucon 50HB2000 on base-coated (5% NaOH) Chromosorb W (45–60 mesh)
3	10:0.25	10% SE-30 Chromosorb W (45–60 mesh)
4	15:0.25	15% Carbowax 20M on base-coated (10% NaOH) Chromosorb P (30–60 mesh)

A glass ramrod was used to free the nitrogen–chlorine delivery tube of ammonium chloride deposits that build up during reaction and block the opening. The reaction chamber was packed with glass wool, loosely in the fore part of the reactor and more tightly near the outlet in order to trap the ammonium chloride which is formed. During reaction, the tube became warm with estimated temperatures of 40–50°. A fast flow rate of nitrogen monitored by a sulfuric acid trap was established, followed by a fast flow of ammonia, then 2 bubbles/sec for chlorine, in that order. The stream of monochloramine, containing some ammonium chloride, was led (8-mm delivery tube) into 200 ml of methylene chloride cooled to −10°. After 15 min, the gas flow was stopped and the glass wool plug was cleaned of ammonium chloride. After the procedure was repeated three more times, the methylene chloride solution was treated three times with calcium chloride. After filtration, the solution was approximately 0.1 *M* (∼1 g) in monochloramine according to titration.

Liquid-Phase Extraction. In an 800-ml beaker cooled to 0° was placed a solution of 160 g of sodium hydroxide in 600 ml of water. Into this was bubbled chlorine until the solution no longer turned litmus blue. This yielded a 3 *M* solution of sodium hypochlorite which was filtered. In a 600-ml beaker cooled in a Dry Ice–acetone bath was placed 200 ml of 3 *M* ammonia to which 200 ml of 3 *M* sodium hypochlorite was slowly added with stirring. The solution of monochloramine was extracted with two 100-ml portions of methylene chloride. After the generation and extraction procedure was repeated twice more, the combined extract was dried over sodium sulfate and filtered, giving 550 ml (∼0.25 *M*, 6.4 g) of monochloramine solution. The solution should be kept at 0° and used immediately after preparation. The positive chlorine content was determined by titration.

Preparation of Trichloramine Solution.[36] In a 3-l., three-necked flask equipped with a mechanical stirrer, 500-ml addition funnel, and thermometer were placed 450 ml of water, 675 of methylene chloride, and 202.5 g of commercial "HTH" (70% calcium hypochlorite). The slurry was cooled to 0° and a solution of 49.5 g of ammonium chloride in 112.5 ml of concentrated hydrochloric acid and 330 ml of water was added over 30 min at 0°. After the mixture was stirred for an additional 30 min, the layers were separated, and the organic phase was washed twice with cold water, dried over anhydrous sodium sulfate, and filtered. Titration of the trichloramine solution gave a molarity between 0.6 and 0.7. The product is stable at −20° for up to 3 weeks.

Amination of Toluene with Monochloramine. In a 1-l., three-necked flask fitted with a 500-ml addition funnel, mechanical stirrer, and thermometer were placed 34.1 g (0.26 mol) of aluminum chloride and 256 ml (3.2 mol) of toluene. A solution of monochloramine (0.13 mol) in 500 ml of methylene chloride was added slowly below the surface over 30 min at −35 ± 2° with stirring. After an additional hour at −35°, the reaction mixture was added to cold hydrochloric acid, the layers were separated, and the organic phase was washed twice with dilute hydrochloric acid. The combined acid solution was extracted with ether, then made strongly basic in the cold with 50% sodium hydroxide. Ether extraction, followed by removal of solvent, yielded *m*-toluidine (1.4 g according to glpc analysis), 13% yield based on monochloramine. Identification was accomplished by comparison of nmr and ir spectra and glpc retention time with those of authentic material. Distillation yielded 0.7 g (7%) of *m*-toluidine, bp 56° (0.41 mm), $n^{20}\mathrm{D}$ 1.5701 [lit.[5] bp 69–73° (5 mm), $n^{20}\mathrm{D}$ 1.5686]. Two unknown peaks were observed during glpc, each representing less than 1% of total product. The basic fraction also contained black tar.

After the neutral layer was dried and freed of solvent, distillation yielded 9.8 g of material boiling at 38–40° (7.2 mm) which contained two components of similar retention time, in addition to toluene. The products were shown to be *o*- and *p*-chlorotoluene (40 and 27% yields, respectively) based on glpc and ir spectral comparison with authentic materials.

Amination of Toluene with Trichloramine. The reactions with trichloramine were run with essentially the same concentrations and molar ratios as in the case of monochloramine.

Amination of Adamantane with Monochloramine. In a 1-l., three-necked flask equipped with a mechanical stirrer, thermometer, below-surface addition funnel, and nitrogen inlet was placed 14.2 g (0.104 mol) of adamantane in 150 ml of methylene chloride. A slow flow of nitrogen was then established. After the introduction of 25.3 g (0.19 mol) of anhydrous aluminum chloride at 0°, 500 ml of monochloramine (0.095 mol) was added at 10–15° over a period of 1 hr. The mixture was allowed to stir for an additional 30 min at 10–15°. A solution of 50 ml of concentrated hydrochloric acid and 100 ml of water was added and after 30 min of agitation, the layers were separated and the organic phase was treated again with concentrated hydrochloric acid. The combined acid solution was washed with ether, made strongly basic with 50% sodium hydroxide in the cold, and extracted with methylene chloride. Drying over sodium sulfate, followed by solvent removal and sublimation, yielded 5.8 g (40% yield based on monochloramine) of 1-aminoadamantane. Identification was made by comparison of ir and nmr spectra and glpc retention time with those of authentic material.

In another run, the reaction mixture was shaken with a mixture of 200 ml of ice–water and 25 ml of hydrochloric acid, and the layers were immediately separated. The acid extract contained 1-aminoadamantane (37–38%), with essentially no aminated material remaining in the organic phase.

The neutral layer was dried and freed of solvent. Sublimation yielded 9.8 g (69%) of unchanged adamantane characterized by ir and nmr spectra and glpc retention time. When the neutral layer was allowed to stand, 1- and 2-chloroadamantane were also found to be present in yields dependent upon storage time. Identification was based on ir and nmr data.[31a] Yields were 14–27% for 1-chloroadamantane and 1.6–1.9% for 2-chloroadamantane.

Amination of Adamantane with Trichloramine. The reaction with trichloramine was essentially the same as that with monochloramine. No 2-aminoadamantane was detected by glpc, in a comparison with a mixture of the authentic 1- and 2-isomers.

In another experiment, the reaction mixture was shaken with a mixture of 200 ml of ice–water and 25 ml of hydrochloric acid, and the layers were immediately separated. Isolation from the organic phase provided 1-*N*,*N*-dichloroaminoadamantane in 48–56% yield according to iodometric titration. Identification was by ir comparison involving authentic material.[15] The acid extract contained 1-aminoadamantane in 32% yield.

Amination of *tert*-Butyl Chloride with Monochloramine. A slurry of 37.9 g (0.284 mol) of aluminum chloride and 500 ml of monochloramine (0.142 mol) was cooled to −10° in a three-necked flask fitted with a mechanical stirrer, thermometer, and addition funnel. To the mixture was added dropwise 52.6 g (0.568 mol) of *tert*-butyl chloride at −5 to −10°. The mixture was stirred for 1 hr and then poured over 200 g of ice and hydrochloric acid. The layers were separated, and the organic phase was washed twice with 200 ml of distilled water and 25 ml of hydrochloric acid. The combined aqueous portion was extracted twice with ether. The aqueous layer was cooled, made basic with 50% sodium hydroxide, and then steam distilled into hydrochloric acid solution until the distillate was no longer basic. Water was removed from the amine hydrochloride by rotary evaporation. The salt was dissolved in 25 ml of water and 25 ml of 50% sodium hydroxide with cooling. After the amine was salted out with potassium carbonate, the basic layer was separated and dried over potassium hydroxide pellets. Glpc analysis indicated 7–20% yield of *tert*-butylamine identified by ir and nmr spectra.

The neutral layer was dried, filtered, and freed of solvent. Glpc analysis revealed 20–30 peaks (two major ones).

Amination of *tert*-Butyl Chloride with Trichloramine. The procedure with trichloramine was essentially the same as that with monochloramine. *tert*-Butylamine was found in 50–56% yield and 2,2-dimethylaziridine in 8–12% yield from glpc analysis. 2,2-Dimethylaziridine was identified by comparison of the ir spectrum with that of authentic material.[19] A repeat run gave essentially the same results.

The neutral layer showed 11–18 peaks in glpc (4–5 major ones).

Monochloramine and Aluminum Chloride. In a 1-l., three-necked flask equipped with a mechanical stirrer, thermometer, addition funnel, and nitrogen inlet were placed 38.7 g (0.29 mol) of aluminum chloride and 150 ml of methylene chloride. After the gas flow was established, monochloramine was added below the surface during 1 hr at 10–15°. After an additional 30 min, a 10-ml sample was removed. Uv analysis[24] indicated no chlorine and a trace of trichloramine present. The remaining mixture was hydrolyzed with 50 ml of hydrochloric acid and 50 ml of water for 5 min at 30°. Uv analysis of a 10-ml sample showed the presence of chlorine, but no trichloramine. Uv analysis of the first sample after 24 hr showed a larger amount of trichloramine.

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Reactions of Azirines. Carbene and Carbenoid Reactions[1]

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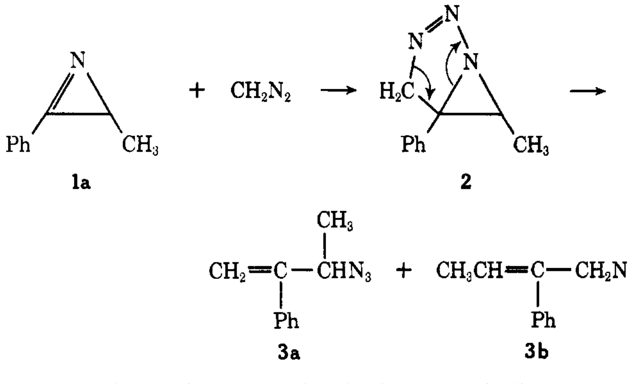
Abstract: The reaction of 1-azirines **1** with dichlorocarbene (generated from phenyl(trichloromethyl)mercury) led to formation of ring opened *N*-vinylimines **4**. Hydrolysis of **4a** produced propiophenone while treatment with azide ions gave a tetrazole. Attempts to prepare dichloroazabicyclobutanes **10**, by addition of trichloromethide ions to several azirines **1** followed by base-catalyzed ring closure of the intermediate aziridines **6**, led to azetines **9** except in the diphenyl substituted case **6c**, when **13**, a product of electrocyclic ring opening, resulted. The structure of azetines **9** was inferred from spectra including ^{13}C nmr spectra and chemical conversions. The formation of azetines **9** from **6** most likely involves an azabicyclobutane intermediate **10**. Chloroazetines **9** were further transformed to azetidinones **11** or methoxyazetine **12**.

The chemistry of azirines **1** has been of recent interest because of the high reactivity of this small ring system toward nucleophilic as well as electrophilic reagents.[2] It was also shown that this three-membered ring serves as a substrate in cycloadditions leading to pyrroles,[3] azepines,[4] pyridones,[5] and bicyclic dioxazines.[6] Experiments between azirines and carbene-like reagents have been somewhat limited. For instance, interaction of diazomethane with **1a** was shown to lead to allyl azides **3** presumably *via* cycloadduct **2**,[7] while the addition of dimethylsulfonium methylide to **1b** represents the first successful synthesis of an azabicyclobutane.[8]



1a **2**

$$CH_2{=}\underset{\displaystyle Ph}{C}{-}\overset{\displaystyle CH_3}{CH}N_3 \quad + \quad CH_3CH{=}\underset{\displaystyle Ph}{C}{-}CH_2N_3$$

3a **3b**

In connection with our continuing studies on the chemistry of azirines **1**, we would like to report on the interaction of **1** with carbenes leading to the formation of some unusual products.

Results

Generation of dichlorocarbene from phenyl(trichloromethyl)mercury[9] in refluxing benzene in the presence of 3-methyl-2-phenyl-1-azirine (**1a**) led to the open-chain product *N*-(dichlorovinylidene)-1-(1-phenylpropenyl)amine (**4a**). None of the azabicyclobutane expected from cycloaddition of $:CCl_2$ to the C=N of **1a** was detected. The structure of **4a** was apparent from its ir (C=N at 1640 cm^{-1}), nmr (methyl doublet at τ 8.24 and vinyl H at 4.8 (quartet)), and mass spectrum, as well as from its chemistry. Hydrolysis of **4a** in acid gave propiophenone and treatment with sodium azide gave the tetrazole **5**, behavior consistent with a dichloroimine structure. Altering the conditions to room temperature or 0° by generating $:CCl_2$ from phenyl(bromodichloromethyl)mercury[9] in the presence of sodium iodide still led to **4a** as the major product. Dichlorocarbene generated from potassium *tert*-butoxide and chloroform also produced **4a**. The reaction of 2,3-diethyl-1-azirine (**1d**) at room temperature gave the analogous **4d**.

Addition of trichloromethide ion to **1a** by means of trichloromethyllithium at −100° led to *cis*-3-methyl-2-phenyl-2-trichloromethylaziridine (**6a**). Further reaction with trimethyloxonium tetrafluoroborate yielded the aziridinium salt (**7**). When **6a** was allowed to stand over alumina, decomposition to dichloroacetophenone (**8**) took place. The stereochemical assign-

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(1) (a) Chemistry of Small Rings. 20. For the previous paper in the series, see ref 5. (b) For a preliminary report, see A. Hassner, J. O. Currie, Jr., A. S. Steinfeld, and R. F. Atkinson, *Angew Chem., Int. Ed. Engl.*, **9**, 731 (1970).

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