Syntheses of some N-substituted hydrazines by the anhydrous chloramine process

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Abstract. Chloramine, produced in the gas phase by the reaction of chlorine and ammonia, reacts with various primary and secondary amines in nonaqueous solvents in the presence of a fixed base to form the corresponding N-substituted hydrazines. The hydrazines synthesised include phenylhydrazine, p-tolylhydrazine, β-aminoethylhydrazine, N-aminopyrrolidine and N-aminopiperidine. Apparently, no hydrazine is formed when the reaction is carried out in the absence of fixed base. The effect of various factors, such as fixed base concentration, amine/chloramine ratio etc., on the overall yield of hydrazines has been studied. In this context, a modified chloramine gas generator giving improved yields is described. The optimum yield of chloramine is shown to be dependent upon the ratio of chlorine, ammonia and nitrogen taken, but is virtually independent of the reactor temperature.

Keywords. Synthesis; substituted hydrazines; chloramine process.

1. Introduction

Extensive use of hydrazines as storable liquid rocket fuels has led to renewal of interest in their synthesis. In most instances, the synthetic methods available are cumbersome, requiring multiple step separations from dilute aqueous solutions and, therefore, are expensive. Realising this, Jain et al (1980) recently adopted an alternate procedure wherein the synthesis of monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) (Sisler et al 1981) could be carried out in nonaqueous solvents instead, using the anhydrous chloramine process (Sisler et al 1954).

Studies leading to the synthesis of aryl and other substituted hydrazines by the chlorination process are indeed scanty. Sisler and coworkers (Sisler et al 1961; Omietanski et al 1956) reported the synthesis of phenylhydrazine and N-aminopiperidine by reacting gaseous chloramine with aniline and piperidine, respectively, taken in large excess. In contrast to these studies, ethereal solutions of chloramine have been reported (Jaffari and Nunn 1971) to react with anilines resulting in the formation of oxidation products, the azobenzenes. In view of the results of our recent studies on the synthesis of MMH and UDMH, however, it is interesting to find out if the aryl hydrazines could be synthesised in a similar way i.e. in nonaqueous solvents in the presence of a fixed base. In the present study we have examined the reactions of gaseous chloramine with anilines and some other amines of interest, the results of which are reported.

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2. Experimental

2.1 Chloramine gas generator

In Sisler's process, chloramine gas is produced by the gas phase reaction of chlorine and ammonia (Sisler et al 1954).

$$Cl_{2(g)} + 2NH_{3(g)} \rightarrow NH_2Cl_{(g)} + NH_4Cl_{(s)}.$$
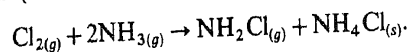
The main difficulty encountered in this production is the choking of the chlorine inlet to the chloramine generator by the ammonium chloride formed. To minimise this difficulty and to get better yields of chloramine the chloramine generator described in the literature (Sisler et al 1954) has been suitably modified. A schematic diagram of the modified generator is presented in figure 1. It consists of a vertical reactor wherein gaseous chlorine and ammonia are allowed to react. The amounts of the gases passing through the reactor were metered using previously calibrated flow meters (rotameters). The reactor is a cylindrical glass tube 40 cm long and of 5·0 cm dia, having a side tube near the bottom. This side tube (3 cm dia) contains two bulbs of dia 5 cm each which are loosely packed with glasswool to trap the ammonium chloride produced in the reaction. Both the ends of the main tube of the reactor are fitted with rubber stoppers. At the top end, the stopper is fitted with 4 glass tubes; one a 10 mm glass tube at the centre and the other three being 8 mm glass tubes symmetrically arranged around it. Ammonia is introduced through these three tubes whose ends are formed into jets
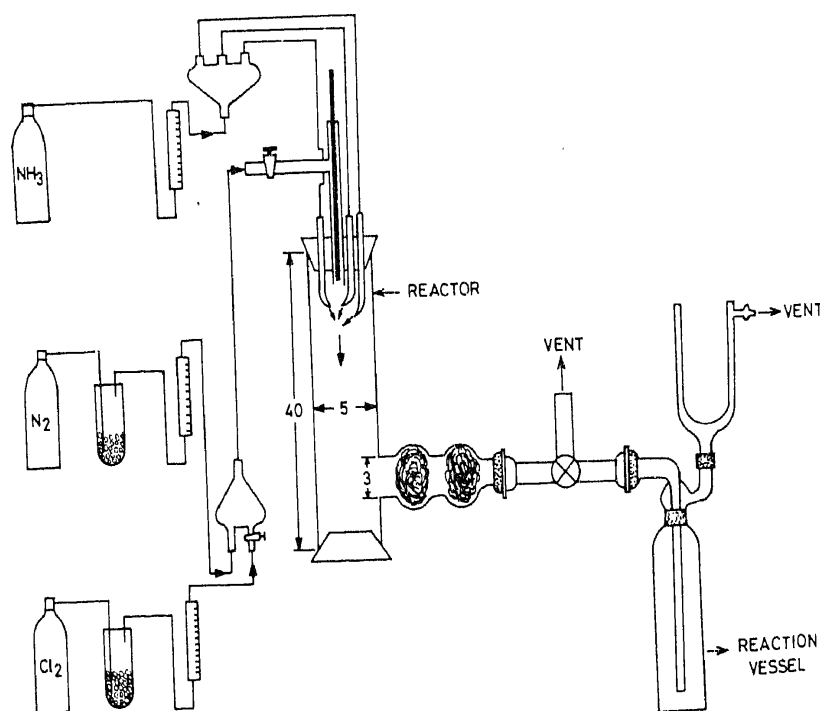

Figure 1. Flow sheet of set up for production of chloramine.

pointing towards the centre. The mixture, chlorine plus nitrogen, is introduced through the central tube. A glass rod inserted in this tube helps in periodically removing the choking, if any.

To generate chloramine in solution, about 500 ml ether is taken in the reaction vessel connected to the chloramine generator through a three-way stopcock as shown in figure 1. The outlet of this vessel is attached to a vent through a cold finger. The reactor is set to the required temperature by means of a heating tape. The system is first flushed by passing nitrogen and then specified amounts of ammonia and chlorine are introduced into the system. The production of ammonium chloride becomes immediately evident as it fogs the generator. The effluents of the chloramine generator are bubbled through a known volume of ether for a specified time, wherein the chloramine formed is dissolved in it. After completing the run, the ether solution is kept open to the atmosphere for 2 hrs for the volatile gases to escape. Chloramine present in ether solvent is then estimated by the iodometric method and the % yield calculated by the method given by Sisler *et al* (1954).

A series of experiments were conducted to explore the effect of various factors on the yield of chloramine. These include (i) the temperature of the reactor wall (ii) the introduction of excess ammonia over the stoichiometric equivalent of chlorine, (iii) the introduction of excess nitrogen as carrier gas and (iv) the time of the experimental run. Some of the typical results of this study are given in table 1.

2.2 Materials and analysis

All of the solvents and amines were of reagent grade. The liquid amines were freshly distilled before use.

The hydrazine content of the reaction mixture was estimated by the iodate method. The applicability of this method to aromatic hydrazines was ascertained by actually estimating the hydrazine content in a known amount of freshly distilled phenyl-

Table 1. Chloramine yield data.

Flow rate ratio (mmol hr^{-1}) $Cl_2:N_2:NH_3$	Mole ratio $Cl_2:N_2:NH_3$	Time (min)	Temperature (°C)	Rate of chloramine formation (mmol hr^{-1})
164:1590:1680	1:9·7:10·2	17	25	69·2
164:1600:1680	1:9·8:10·2	17	95	71·1
164:1600:1650	1:9·8:10·1	60	58	54·1
164:1590:640	1:9·7:3·9	15	26	36·2
164:1600:1130	1:9·8:6·9	15	27	53·3
164:1590:2050	1:9·7:12·5	15	26	54·2
124:820:1270	1:6·6:10·2	15	26	19·0
124:1280:1270	1:10·3:10·2	15	27	38·9
124:1680:1270	1:13·5:10·2	15	27	46·1
134:870:1020	1:6·5:7·6	60	58	41·3
134:1300:1560	1:9·7:11·6	60	58	59·4
134:1340:1340	1:10:10	60	58	63·0

hydrazine. The elemental analysis (C & H) of the hydrazine derivatives prepared, was carried out using a Heraeus combustion unit.

The ^{1}H NMR spectra were recorded on a Varian T-60 spectrometer using DMSO-d_6 as solvent and TMS as internal standard. The NH proton signals were confirmed by D_2O exchange spectra. The IR spectra were recorded with a Perkin-Elmer-781 spectrophotometer as nujol mulls.

2.3 Reaction of the chloramine-ammonia mixture with aniline

In a typical reaction, a cylindrical reaction vessel of 650 ml capacity was charged with a 350 ml methanol solution containing 252 mmol of KOH and 378 mmol of freshly distilled aniline. The inlet of this vessel was attached to the chloramine generator, and the outlet to a vent via a cold finger. Approximately 63 mmol of chloramine was bubbled through the methanol solution over a period of one hr. A white solid material precipitated and the solution turned brown. The solution was kept undisturbed for 2 hrs to allow the volatile gases to escape. The solid material was then filtered off and found to be potassium chloride by the flame test and chloride analysis. The filtrate was estimated for its hydrazine (total N–N bonded material) content by the iodate method. It was found to contain 44 mmol, or 70% yield of phenylhydrazine based on chloramine.

The presence of phenylhydrazine in the reaction mixture was confirmed by preparing its benzaldehyde derivative. For this, a known volume of the chloraminated solution was carefully neutralized by concentrated hydrochloric acid till it became slightly acidic. To this solution, an equivalent amount of benzaldehyde dissolved in minimum amount of methanol, was added. A yellow precipitate was formed immediately, which was filtered, recrystallised from dilute ethanol and dried under vacuum. The derivative was characterized by its melting point, elemental analysis, IR and NMR spectra (table 2). The spectral features were identical to those obtained using an authenticated sample of benzaldehydephenylhydrazone. The yield data of phenylhydrazine obtained using different mole ratios of chloramine:amine:KOH are given in table 3.
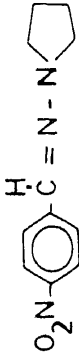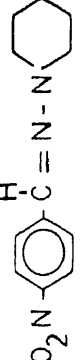
The chloramination procedure used for other amines was the same as that used in the case of aniline. The salient features of each reaction are described below. The analytical data of the derivatives are given in table 2.

When a mixture of 13·5 g (126 mmol) of p-toluidine, 7·1 g (127 mmol) of KOH in 350 ml methanol was chloraminated for 45 min (47 mmol of chloramine), the amount of the N–N bonded product formed was found to be 20·3 mmol corresponding to a yield of 43% p-tolylhydrazine, based on chloramine. The benzaldehyde derivative was prepared by refluxing the neutralized reaction mixture (using HCl) and benzaldehyde for 2½ hrs, and subsequently cooling it in ice and salt mixture.

When a methanolic solution (300 ml) containing 10·5 ml (126 mmol) of pyrrolidine and 7·0 g (125 mmol) of KOH was chloraminated for one hour (63 mmol, chloramine), 53 mmol of N–N bonded material was obtained corresponding to a yield of 85% N-aminopyrrolidine. The formation of N-aminopyrrolidine was confirmed by preparing and characterizing its p-nitrobenzaldehyde derivative; by neutralizing the chloraminated mixture by glacial acetic acid and reacting it with p-nitrobenzaldehyde.

The chloramination of piperidine was carried out using various ratios of amine:KOH:chloramine. The yield data are given in table 4. The formation of N-aminopiperidine was confirmed by its p-nitrobenzaldehyde derivative, which was

Table 2. Characterization of hydrazine derivatives[a].

Compound	m.p. °C	Found %		Calculated %		¹H NMR chemical shifts (δ)	IR absorptions (cm^{-1})	
		C	H	C	H		νN-N	νC=N
N-(4-nitrophenylmethylene)-1-pyrrolidinamine	102	60·27	6·28	60·26	5·98	7·5, 8·1 (4H, Ar); 7·03 (H, CH); 2 (4H, CH₂); 3·43 (4H, NCH₂)	1100	1590
N-(4-nitrophenylmethylene)-1-piperidinamine	65	62·04	6·59	61·79	6·48	7·7, 8·1 (4H, Ar); 7·5 (H, CH); 1·66 (6H, CH₂); 3·27 (4H, NCH₂)	1100	1600

[a] The observed and reported (in parentheses) melting points of the benzaldehyde derivatives of phenylhydrazine and p-tolylhydrazine respectively, are 154 (158–160) and 115 (114)°C (Reutt and Pavlewski 1903). The elemental analysis, IR and ¹H NMR data of these compounds are in agreement with the assigned structures. The m.p. of the dioxalate derivative of β-aminoethylhydrazine is 204 (206)°C (Gever and Hayes 1949). It was characterized by its elemental analysis and IR spectrum.

Table 3. Reaction between chloramine[a] and aniline in methanol in the presence of KOH.

Mole ratio CA:amine:base (mmol)	Ratio CA:amine:base	Amount of phenylhydrazine formed (mmol)	Yield based on CA (%)
63:63:0	1:1:0	0	0
63:63:63	1:1:1	0	0
63:63:252	1:1:4	13·6	22
63:126:252	1:2:4	28·5	45
63:252:252	1:4:4	38·6	61
63:378:252	1:6:4	44·3	70
63:378:126	1:6:2	38·2	61

[a] Chloramine = CA.

Table 4. Reaction between chloramine[a] and piperidine in methanol in the presence of KOH.

Mole ratio CA:amine:base (mmol)	Ratio CA:amine:base	Amount of N-aminopiperidine formed (mmol)	Yield based on CA (%)
63:63:0	1:1:0	0	0
63:63:63	1:1:1	0	0
63:63:126	1:1:2	25·4	40
63:126:127	1:2:2	31·4	50
63:189:126	1:3:2	27·3	43
63:63:189	1:1:3	30·4	50

[a] Chloramine = CA.

obtained by refluxing the neutralized mixture and p-nitrobenzaldehyde for $2\frac{1}{2}$ hrs.

When a mixture of ethylenediamine (250 m mol) and KOH (250 m mol) in 300 ml methanol was chloraminated for one hour (63 m mol chloramine), the conversion to β-aminoethylhydrazine was found to be 51 %. The formation of β-aminoethylhydrazine was confirmed by preparing its dioxalate derivative, by the method reported by Gever and Hayes (1949).

In all of the above cases, when the chloramination was carried out in the absence of KOH, there was no evidence of the presence of any N–N bonded compound in the reaction products.

3. Results and discussion

It is obvious that chloramine gas could be generated in fair yields using the modified generator. In order to optimise the chloramine yield, a series of experiments were carried out, the results of which are summarized in table 1. It is observed that the introduction of excess ammonia over the stoichiometric equivalent of chlorine favours the formation of chloramine. The increase in the yield appears to be in direct

proportion with the excess of ammonia up to a certain ammonia to chlorine mole ratio. Further, it is interesting to note that a significant increase in the yield is also observed with the introduction of excess nitrogen which is known to act only as a carrier gas. Since, the introduction of excess ammonia or nitrogen improves the rate of total gas flow away from the primary reaction zone, these results suggest that the increased flow rates prevent or suppress the decomposition of chloramine by the reaction (Sisler *et al* 1954):

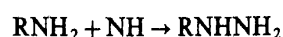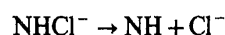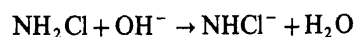$$6NH_{3(g)} + 2Cl_{2(g)} + NH_2Cl_{(g)} \rightarrow N_{2(g)} + 5NH_4Cl_{(g)}.$$
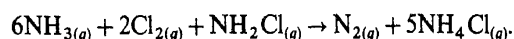
The above reaction could occur at the lower flow rates by bringing the chloramine gas formed back into the primary reaction zone and thereby getting it oxidized to nitrogen. It may also be noticed that this oxidation causes a sharp decrease in the total gas volume, which again will result in the reduction of the total gas flow, and this in turn further enhances the decomposition of chloramine.

The temperature of the reactor wall does not seem to have any effect on the chloramine yield in the range 25 to 95°C, although Sisler *et al* (1954), observed considerable decomposition of chloramine when the reactor walls are kept below the ambient temperature i.e. in the range 10 to −30°C.

There is, however, a decrease in percentage chloramine yield with the time of the run. As the reaction proceeds, the glasswool placed in the side tube continuously traps the ammonium chloride formed in the reaction. Consequently, the retention time of chloramine near the reaction zone increases with the time. Because of this, the decomposition of chloramine by the reaction (mentioned above) occurs to some extent, resulting in the low percentage yield of chloramine.

From the results of the chloramination reactions, it is evident that chloramine reacts readily with various amines in non-aqueous solvents in the presence of a fixed base such as KOH, resulting in the formation of the corresponding hydrazines in good yields. The yield data of phenylhydrazine and N-aminopiperidine, given in tables 3 and 4, show that these could be synthesised using amine to chloramine ratios as low as 1:1 at appropriate fixed base concentrations. This is in striking contrast to the twenty to thirty-fold excess of aniline or piperidine needed to obtain the corresponding hydrazines in satisfactory yields using the earlier methods (Omietanski *et al* 1956; Sisler *et al* 1961) involving chloramination of these amines taken as neat liquids.

The present study also reveals the importance of the fixed base in the synthesis of hydrazines in nonaqueous solvents. Apparently no hydrazine is formed when the reaction is carried out in the absence of KOH. These results are parallel to those obtained recently by Jain *et al* (1980) and earlier by Audrieth and Diamond (1954b) and Wiberg and Schmidt (1951). These data provide strong support to the postulate (Audrieth *et al* 1954) that the chloramination of amines resulting in the formation of the corresponding hydrazines, proceed via the intermediate formation of the imide molecule (NH), as follows:

$$NH_2Cl + OH^- \rightarrow NHCl^- + H_2O$$
$$NHCl^- \rightarrow NH + Cl^-$$
$$RNH_2 + NH \rightarrow RNHNH_2$$
$$RR'NH + NH \rightarrow RR'NNH_2.$$

As described in an earlier work (Jain *et al* 1980) the fixed base (OH^- or OR^-) used abstracts a proton from the chloramine resulting in the formation of the imide molecule which on subsequent reaction with an amine results in the formation of the corresponding hydrazine.

The above mentioned scheme of reactions requires that the minimum concentration of the base (OH^-) should be equal to that of chloramine or amine for the formation of the corresponding hydrazine. However, the yield data (tables 3 and 4) show that there is no formation of either phenylhydrazine or N-aminopiperidine when the reactants are taken in $1:1:1$ mole ratio, although when the fixed base concentration is increased, there is ready formation of the respective hydrazines. This may be explained as follows. Although glass wool filters are used in the chloramine generator to check the flow of NH_4Cl from the generator to the reaction vessel, this does not completely prevent NH_4Cl from going to the reaction vessel. This is evident from the white deposition inside the chloramine delivery tube to the reaction vessel. This NH_4Cl then reacts with KOH to form KCl, NH_3 and H_2O. A portion of the fixed base used is thus destroyed by this process. The remaining base possibly would react with chloramine and subsequently with amine to form hydrazine. However, the hydrazine formed, in turn, will get oxidized by the excess chloramine in the absence of the fixed base. As reported earlier, chloramine reacts with the fixed base in preference to hydrazine, but once the fixed base is destroyed it reacts with hydrazine in preference to the respective amine. It, therefore, appears that whatever hydrazine is formed at chloramine:amine:base, $1:1:1$, is oxidized by the excess chloramine.

Although the feasibility of the anhydrous chloramine method to synthesis hydrazines in non-aqueous solvents was earlier established in the case of MMH (Jain *et al* 1980) and UDMH (Sisler *et al* 1981) the present study suggests that it be a general method for the synthesis of various hydrazines in anhydrous medium. The formation of water as a reaction product could also be avoided if the fixed base is properly chosen; as shown in the case of MMH (Jain *et al* 1980) synthesis where sodium methoxide was used instead. Sodium methoxide on reacting with chloramine will generate methanol instead of water. It is further conceivable that if the solvent is properly chosen, the recovery of the hydrazines formed could be achieved by a simple distillation method. In the present instance some of the hydrazines such as *p*-tolylhydrazine, β-aminoethylhydrazine and N-aminopyrrolidine, have been synthesised for the first time using the gaseous chloramination method. The synthetic methods available for these and other substituted hydrazines in the literature being highly complicated, the present method suggests an easy way out for their synthesis.

Acknowledgement

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