Journal of Organometallic Chemistry, 320 (1987) 163–170
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REDUCTIVE CLEAVAGE OF AN $SiCl_3$ GROUP BY AMINE HYDROCHLORIDES AND BASE

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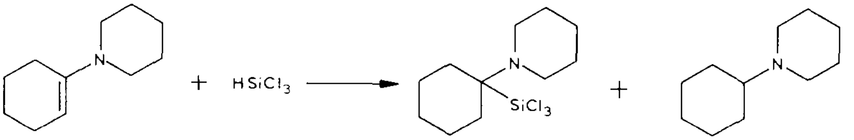
(Received June 10th, 1986)

Summary

A new procedure has been developed for removing the $SiCl_3$ group from α-trichlorosilyl-substituted amines. In this procedure the trichlorosilyl substrate is treated first with amine hydrochloride in CH_3CN, followed by hydrolysis with aqueous hydroxide. Using this sequence, amines corresponding to replacement of the trichlorosilyl group with hydrogen can be conveniently isolated in good yields for all tested cases. Evidence suggests the intermediacy of an unstable chlorosilane species formed by probable nucleophilic attack of chloride. In conjunction with the addition reaction of $HSiCl_3$ to enamines to form the α-trichlorosilyl amines, the cleavage completes a new method for the transformation of enamines to amines which could be a useful alternative to either catalytic hydrogenation or metal hydride reduction.

Introduction

In a number of reactions involving the combination of $HSiCl_3$ with tertiary amines, species containing $SiCl_3$ groups on a benzylic carbon can be isolated from aryl ketones and aldehydes [1], benzylic halides [2], aromatic acids [3], the *N,N*-dialkyl amides of aromatic acids [4], and aromatic acid chlorides [1]. In all of these reactions it was found that the trichlorosilyl group could be removed and replaced with hydrogen by the action of concentrated KOH in ethanol(aq). In a previous paper [5] it was shown that trichlorosilane will add regiospecifically across the olefinic portion of enamines to yield α-trichlorosilyl-substituted amines, as well as quantities of the amines themselves (see eq. 1). The ratio between the two products

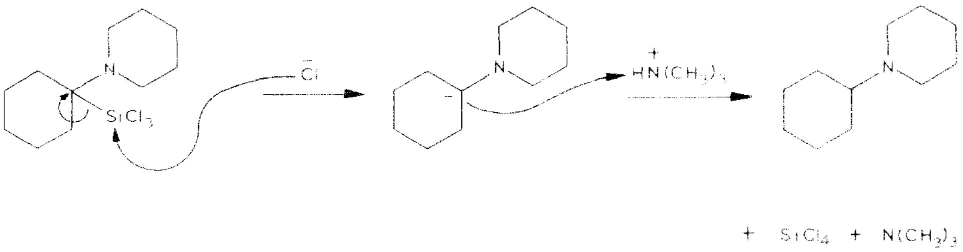


(1)

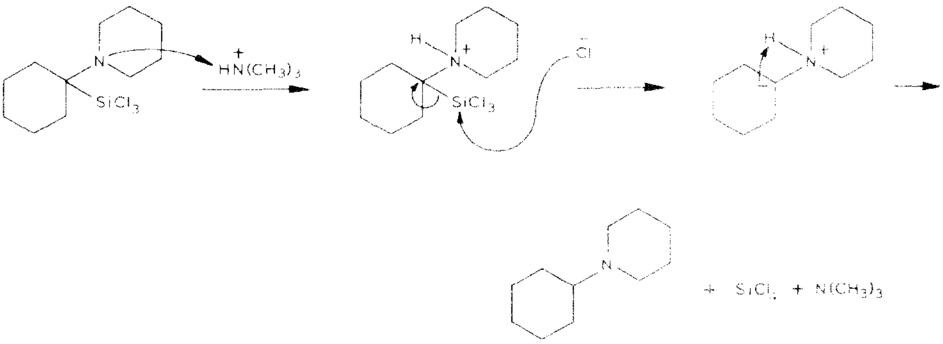
is dependent on the exact structure of the enamine. In the case of the illustrated *N*-(1-cyclohexenyl)piperidine, the trichlorosilyl adduct is the predominant product with only a few percent of the amine isolated.

One of the initial objectives of the reaction in eq. 1 had been the hope of reducing the enamine completely to the amine by treatment of the major trichlorosilyl product with the customary KOH/ethanol(aq) cleavage mixture. However, it was found that the trichlorosilyl adduct would not cleave as desired. On treatment with KOH in ethanol, or NaOH in H_2O (in varying concentrations), the trichlorosilyl adduct reacted to yield a tar-like substance which appeared to be some form of polymeric siloxy material. Continued treatment of this material with strong base produced no further reaction, forcing a search for an alternate method of cleavage.

Recognizing the usefulness of the nucleophilic fluoride cleavage of O–Si bonds in trialkyl siloxanes [6], the strategy initially considered was to attempt a similar reaction in an aprotic, nonoxygen solvent where there would be no danger of reaction of the solvent with the hydrolytically unstable Si–Cl bonds of the trichlorosilyl amine. Due to the somewhat greater ease of handling (and ready availability), it was decided to attempt using chloride as the cleaving nucleophile. It was assumed that the chloride would not be as effective as fluoride, but it was felt that the three electron-withdrawing chlorine substituents might increase the susceptibility of the silicon to nucleophilic attack sufficiently to allow the cleavage to take place. An alkyl ammonium counterion was chosen to allow solubilizing of the chloride in



SCHEME 1



SCHEME 2

acetonitrile, as well as to serve as a proton source for the carbanionic group to be displaced from the silicon. Two possible mechanisms through which it was thought the proposed cleavage might take place are shown in Schemes 1 and 2.

Results and discussion

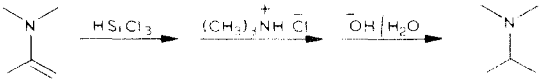
After formation of the trichlorosilyl product by the reaction of *N*-(1-cyclohexenyl)piperidine with $HSiCl_3$, an equivalent of trimethylamine hydrochloride in acetonitrile was added to the reaction flask. There was almost immediate, visible sign of reaction with the appearance of dense white vapor and formation of solids, both in the reaction flask and the attached condenser. After 12 h of reflux the reaction mixture was filtered and analyzed. The filtrate showed little organic product, so major emphasis was placed on the solid which had been collected. It appeared to be somewhat hydrolytically unstable, generating HCl in contact with atmospheric moisture, but it proved soluble (exothermically) in 10% NaOH (aq) to form a liquid–liquid two-phase system. Isolation of the organics by separation, extraction and distillation gave the expected *N*-cyclohexylpiperidine in a 62% overall yield from the starting enamine. A number of related enamines were then reacted following the same procedure, all proving to give the corresponding reduced amines in varying yields (see Table 1).

While the successful isolation of the amines was gratifying, the initial formation of a solid upon treatment with the trialkylamine hydrochloride was difficult to reconcile with the mechanisms of either Scheme 1 or Scheme 2. Further experiments revealed a number of interesting facts relating to this. Variations in the alkyl groups of the cleaving amine hydrochloride showed a modest change in the yield of product, but this could be counteracted by extending the reaction time (see Table 2). In addition, the reaction did not appear to be catalytic in the cleaving agent, less than a full equivalent giving a significantly lower yield under standard reaction conditions (see Table 2).

Of the two mechanisms already proposed, it was felt that Scheme 2 seemed the more probable, since initial protonation would allow displacement of a more stable nitrogen-ylid rather than a simple carbanion. This, however, would make the exchangable proton of the trialkylamine hydrochloride of critical importance to the reaction. An attempt was made to test this hypothesis by substituting tetramethylammonium chloride for trimethylamine hydrochloride as the cleaving agent. This was not entirely feasible due to the low solubility of the tetramethylammonium chloride in acetonitrile, but stirring a suspension of the salt with the trichlorosilyl adduct gave a somewhat suspiciously high yield of reduced amine; more than could be expected from the initial reaction of the enamine with the $HSiCl_3$ (see Table 3). Tetraethylammonium chloride was far more soluble in acetonitrile than the tetramethyl salt, so it was then substituted for the trimethylamine hydrochloride as the cleaving agent. This reaction (see Table 3) surprisingly gave the customary yield of reduced amine, clearly indicating that neither Scheme 1 nor Scheme 2 is an adequate representation of the true mechanism.

Since it was clear that the cleavage reaction is a more complex process than first thought, the solid which could initially be isolated before treatment with base was reinvestigated in more detail. The hydrolytic instability strongly suggested the presence of more Si–Cl bonds than could be accounted for by contamination by

TABLE 1



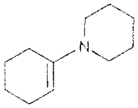
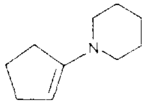
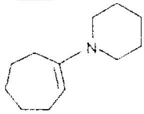
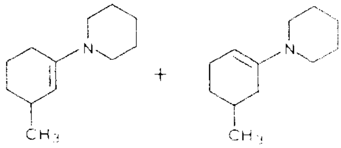
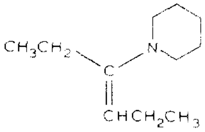
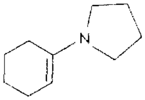
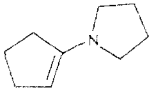
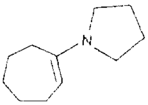
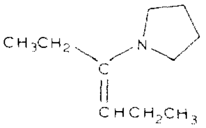
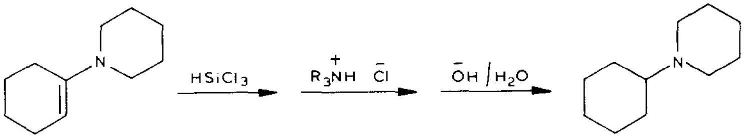
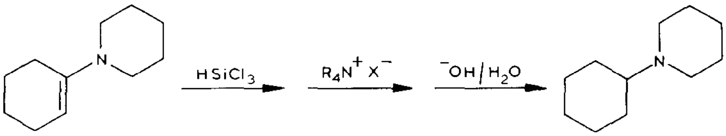
Enamine	Yield of amine (%)
	69
	66
	74
	62
	59
	72
	58
	69
	52

TABLE 2



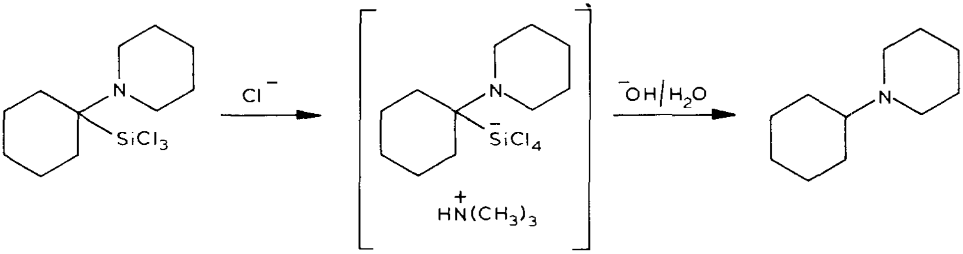
R	eq. of $R_3NH^+Cl^-$	Reaction time (h)	Yield of amine (%)
CH_3	1.0	12	69
CH_3	0.1	14	13
CH_3CH_2	1.0	13	41
CH_3CH_2	1.0	26	59

TABLE 3



R	X	eq. of $R_4N^+X^-$	Reaction time (h)	Yield of amine (%)
CH_3	Cl	1.0	15	17
CH_3CH_2	Cl	1.0	24	52
$CH_3CH_2CH_2CH_2$	Br	1.0	24	8

traces of unreacted $HSiCl_3$. The decomposition prevented purification, but pyrolysis of samples demonstrated the presence of 2–3% Si in the solid; good evidence that the $SiCl_3$ groups had not yet been removed. One theory which could potentially account for the formation of the solid and its composition can be found in the known ability of silicon to form 5- or 6-coordinate complexes from tetravalent silanes and suitable lone pair donor ligands [7–9]. While the complexes which have been studied involved nitrogen or oxygen ligands, it may not be unreasonable to suggest such complex formation by nucleophilic attack of chloride to generate the type of hypervalent anion shown in Scheme 3. (While the anion shown should



SCHEME 3

contain ca. 6% Si, based on the proposed structure, the lower 2–3% Si found may reflect either the presence of impurities in the total samples or the possible loss of Si in decomposition prior to analysis.)

If it is the intermediate species shown in Scheme 3 which is ultimately cleaved by the action of the base, it is evident why there would be no need for an exchangeable proton on the ammonium counterion. The proposed mechanism would also suggest a possible dependence of the reaction on the identity of the attacking nucleophile. This can be seen in Table 3, where the use of a bromide rather than a chloride gives very little amine product. The possibility that the cleavage (or possible complex formation) could be due to any small equilibrium concentration of free R_3N can be discounted by the fact that there is no reaction when a full equivalent of triethylamine is used in place of any ammonium chloride.

What is most unclear is why the postulated hypervalent salt should be susceptible to cleavage by hydroxide while the trichlorosilyl adduct gives only polymerization. In the case of the adduct, the poor leaving group ability of the carbon structure would tend to guarantee replacement of the chloride first by nucleophilic attack of OH^-. This would yield silanols which could then react with other $SiCl_3$ groups to give the undesired polymeric structure, which would still be unreactive due to the continued poor leaving group ability of the carbon. Although the carbon leaving group would still be the same in the proposed hypervalent anion, the silicon itself would be in a very different state. As an anionic complex it might be expected to be less stable and possibly more prone to unknown reactions with strong base that would ultimately allow the reductive cleavage. While it is not clear what the mechanism of such a reaction might be, the cleavage of carbon–silicon bonds in complex silicon anions is not unknown. A number of organofluorosilicates have been studied and shown to be susceptible to Si–C bond cleavage by a variety of reagents [10–12]. Such behavior, by analogy, could be viewed as further evidence in support of the transformation proposed in Scheme 3.

Conclusions

The experiments which have been performed clearly demonstrate that α-trichlorosilyl amines can be reductively cleaved to amines by the action of trialkylamine hydrochloride, or tetraalkyl ammonium chloride, followed by base hydrolysis. The reaction is general for the α-trichlorosilyl amines, and can conveniently be done in the same reaction flask in which they are generated, without the necessity of isolation or purification. A variety of chloride salts can be used, depending on solubility or availability, giving reasonable yields in all cases. More work must be done on the nature of the possible intermediate before base hydrolysis to fully understand its composition and potential reactions. However, at the present time, the ease of the cleavage, coupled with the simplicity of synthesis of the α-trichlorosilyl amines, recommends the entire sequence as a useful alternative to catalytic hydrogenation or metal hydride reduction as a means of synthesizing amines from enamines [13].

Experimental

General. All NMR spectra were recorded on a Varian EM-300X 30 MHz NMR spectrometer, using $CHCl_3$ as an internal standard. IR spectra were recorded on a

Beckman Acculab 4 infrared spectrophotometer. All solvents and reagents were used as commercially supplied except for the $HSiCl_3$, which was redistilled at normal pressure from quinoline. All enamines were prepared as previously described [5]. Identification of amine products was made by comparison of physical data and spectra with reported literature values.

1. Reaction of N-(1-trichlorosilylcyclohexyl)piperidine with trimethylamine hydrochloride

A 250 ml flask equipped with a pressure-equalizing addition funnel was charged with a suspension of *N*-(1-cyclohexenyl)piperidine (16.53 g, 0.10 mol) in 10 ml of dry CH_3CN and cooled in an ice bath. Trichlorosilane (13.45 g, 0.10 mol) was added dropwise through the addition funnel, to the rapidly-stirred suspension over a 10–15 min period. After addition, the funnel was replaced with a condenser, the ice bath removed, and the reaction mixture heated to reflux for 2.5 h. A solution of trimethylamine hydrochloride (9.96 g, 0.1 mol) in 125 ml of refluxing CH_3CN was then added in a single portion to the homogeneous reaction mixture. Almost immediately, dense white vapor began to issue from the open condenser and solid began to form, both in the condenser and in the reaction flask. The flask was kept at reflux for 12 h until there was no further visible sign of reaction. The reaction mixture was then cooled to 0°C and filtered to remove the orange-yellow solid. The solid was dried for 24 h under dry N_2 and weighed (16.0 g). An NMR spectrum of the material showed only a broad band of overlapping signals from δ 1.5–3.5. Pyrolysis in the open atmosphere gave a residue of SiO_2 corresponding to 2.4% by weight Si in the sample.

2. Reaction of isolated solid with aqeous base

A 500 ml Erlenmeyer flask was charged with 300 ml of 10% NaOH (aq) and stirred in an ice bath. The solid from reaction 1 was added in a single portion and proceeded to dissolve slowly with some evidence of exothermic reaction. After 30 min of stirring all solid had dissolved and a small organic phase had separated. The two-phase system was separated and the H_2O phase extracted with two 50 ml portions of diethyl ether. The organics were combined, dried over $MgSO_4$, and the solvent removed under reduced pressure. The residue was then distilled through a short-path microhead at reduced pressure to give a single fraction of clear liquid, 12.0 g, 61–62°C/1.0 Torr, without forerun and only a small quantity of pot residue. This material was identified by IR as *N*-cyclohexylpiperidine in a yield of 72% from the starting enamine.

3. General procedure for the reduction of enamines to amines via the α-trichlorosilyl amines

For all entries found in Table 1, the general procedure followed was a combination of reactions 1 and 2, without isolation of the intermediate solids (or solutions). The enamines were allowed to react with $HSiCl_3$ on a 0.1 mol scale to form the α-trichlorosilyl amines, which were then treated with the proper chloride salt in CH_3CN. After refluxing for the appropriate period of time, the reaction mixtures were then cooled and hydrolyzed in the same flask with 10% NaOH(aq). When the flask was filled, the contents were transferred to a larger Erlenmeyer and more 10% NaOH(aq) added until all solids had dissolved and the pH of the system was equal to or greater than 9 (usually a total volume of 250–300 ml of base required). The organic phase was removed and the H_2O phase extracted with diethyl ether. The organics were combined, dried over $MgSO_4$, and the solvent removed under reduced pressure. The amines were then isolated by simple distillation under reduced pressure.

Acknowledgment

Acknowledgment is made to the Penn State Faculty Scholarly Support Fund and the Scholarly Activities Committee of the Penn State/Wilkes-Barre Campus Faculty Organization for their financial support of this work. Thanks are also expressed to Miss Marjorie Zikor for her work in manuscript preparation.

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