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# THE REACTION OF TRICHLOROSILANE WITH ENAMINES

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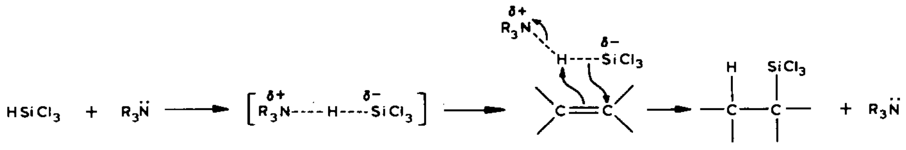
## Summary

A previously unknown reaction of trichlorosilane with enamines has been discovered and a preliminary study done on the possible mechanism. The products of the reaction are a regiospecific trichlorosilyl adduct resulting from addition of the trichlorosilane to the enamine unsaturation and the amine corresponding to simple reduction of the double bond. The addition of the trichlorosilane requires no catalyst and the relative percentages of the products varies in a generally inverse fashion depending on the exact structure of the enamine. Evidence is given to support the assigned structure of the trichlorosilyl species and mechanisms are hypothesized to explain the formation of both products from a common intermediate. Steric rather than electronic factors are suggested as responsible for the observed balance between them.

## Introduction

In a previous paper it was revealed that trichlorosilane ($HSiCl_3$) would add as hydrogen and a trichlorosilyl group across the carbon–nitrogen double bond of imines in an uncatalyzed, regiospecific manner [1]. Among the related reactions enumerated in this paper were similar additions of trichlorosilane to carbon–carbon double and triple bonds under the influence of tertiary amine and phosphine catalysts as reported by Pike [2]. These reactions were shown to take place only in solvents of sufficient polarity such as $CH_3CN$ at temperatures on the order of 125°C for several hours in sealed vessels. The mechanism proposed for such additions is summarized in eq. 1 and is a typical example of the early thinking concerning the possible influence of basic catalysts such a tertiary amines on trichlorosilane.



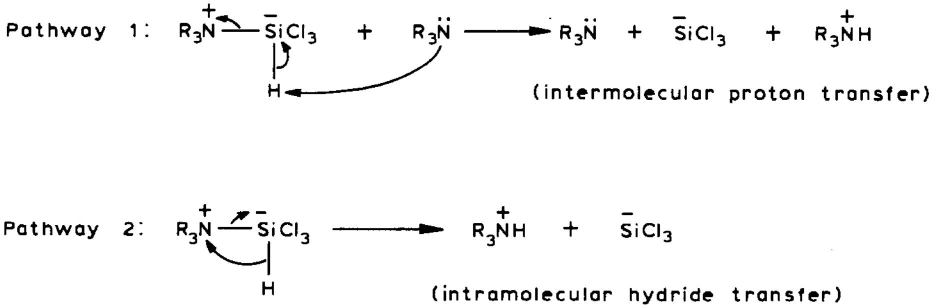
(1)

0022-328X/86/$03.50

Later work in other laboratories with NMR data [3] and kinetics studies [4] indicated the possible formation of an actual trichlorosilyl anion by the action of tertiary amines on trichlorosilane. Rather than a simple acid–base reaction, a mechanism for the transformation was proposed based on the known propensity of tetracoordinate silicon to form five or six-coordinate complexes with suitable ligands such as amine nitrogens [5–7]. This is summarized in eq. 2:

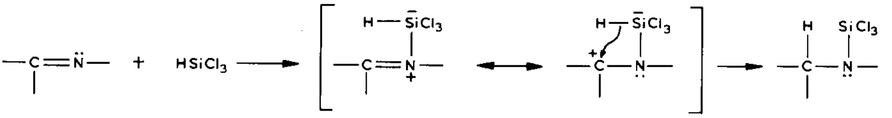
$$HSiCl_3 + R_3\ddot{N} \rightleftarrows \left[R_3\overset{+}{N}\text{-}\overset{-}{Si}HCl_3\right] \rightleftarrows R_3\overset{+}{N}H + \overset{-}{Si}Cl_3 \qquad (2)$$

Exactly how the intermediate complex may be transformed to the final ions is questionable, but two possible pathways may be suggested in Scheme 1.



SCHEME 1

To explain adequately the ease of reaction and observed regiospecificity of the trichlorosilane addition to imines a mechanism was proposed (shown in eq. 3) which employed the basic concepts of eq. 2 and Scheme 1, pathway 2.



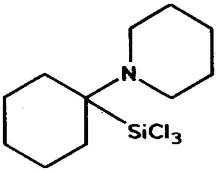
(3)

Examination of the mechanism in eq. 2 suggested the possibility that a similar intramolecular hydride transfer might be accomplished over a greater distance, although with potentially differing products. For this reason it was decided that a representative enamine would be treated with trichlorosilane to determine if any reaction would take place without the addition of external tertiary amine.

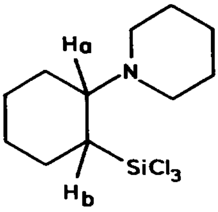
## Results and Discussion

Unlike simple olefins, when a solution of *N*-(1-cyclohexenyl)piperidine in acetonitrile was treated with $HSiCl_3$ at room temperature a strong exotherm was evident with a concurrent darkening of the resulting solution. Extraction of an aliquot after 10 min and analysis by NMR showed very little of the $HSiCl_3$ proton signal or the vinyl proton signal from the enamine. After heating to reflux for 2.5 h no further change could be seen in the NMR and the major product was isolated by direct vacuum distillation. This material proved to be a high boiling liquid (b.p. 118–119°C/0.5 torr) which crystallized on storage at −15°C to a yellow-orange solid (m.p. 36–38°C). Elemental analysis yielded a composition consistent with a

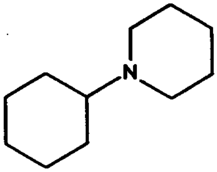
1 : 1 adduct of enamine and trichlorosilane. The lack of any vinyl proton signals in the NMR or downfield signals which might be expected from $H_A$ or $H_B$ of II lead to the assignment of I as the structure of the product.



(I)

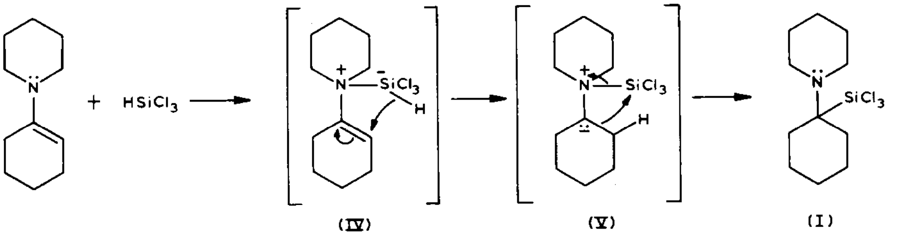


(II)



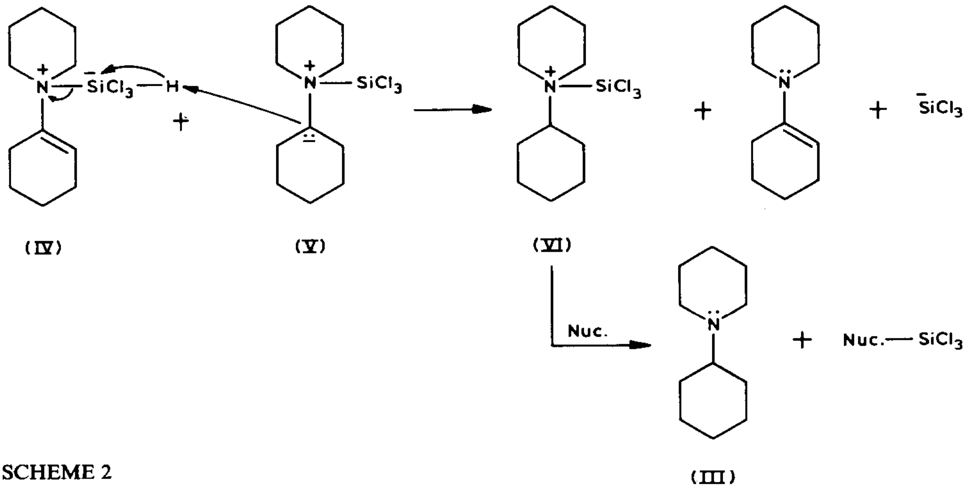
(III)

A mechanism analogous to eq. 3 can be readily visualized to explain the ease of the addition and its regiospecificity. Based on the same nitrogen-silicon complexation and intramolecular hydride transfer, the mechanism is shown in eq. 4.



(4)

While a synchronous, five-centered transition state by-passing V might be formally envisioned, models suggest that the conformation necessary for this may be very difficult to achieve. A more reasonable view is likely a single step formation of V, which can be recognized as a nitrogen ylid, followed by a Steven's rearrangement to transfer the trichlorosilyl group. Clearly the formation of the ylid stabilized

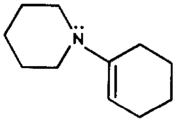
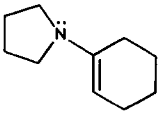
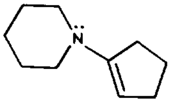
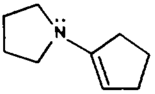
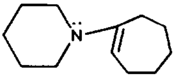
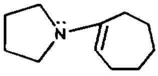
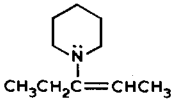
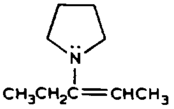


SCHEME 2

system would be preferred over the simple secondary carbanion which would result from hydride transfer to the alternate carbon. At the same time the susceptibility of silicon to attack by nucleophiles makes it reasonable that the trichlorosilyl group is transferred in preference to one of the ring carbons. The ease of the reaction relative to the conditions reported by Pike for the addition to simple olefins strongly suggests a completely intramolecular reaction where there would be a significantly smaller loss of entropy.

TABLE 1

REACTION OF ENAMINES WITH TRICHLOROSILANE (% yields of products)

| Enamine | Conditions | % Trichlorosilyl adduct | %Amine | % recovery of enamine |
|---|---|---|---|---|
|  (1) | [a] | 77.0 | (<1) | (2–3) |
|  | [b] | 57.2 | 6.6 | 9.1 |
|  (2) | [a] | 58.0 | (<1) | (2–3) |
|  (3) | [a] | 59.8 | 7.2 | 14.3 |
|  (4) | [a] | 28.0 | (<1) | (2–3) |
|  (5) | [a] | 12.7 | 21.8 | 27.9 |
|  (6) | [a] | 9.0 | 49.0 | (2–3) |
|  $CH_3CH_2C{=}CHCH_3$ (7) | [a] | 61.5 | 5.8 | 15.4 |
|  $CH_3CH_2C{=}CHCH_3$ (8) | [a] | 8.2 | 54.0 | (2–3) |

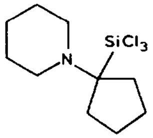
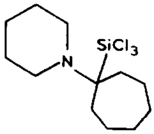
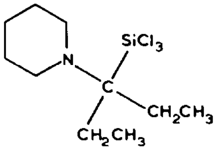
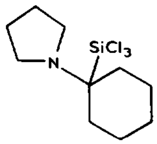
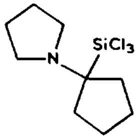
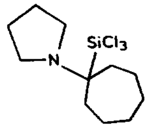
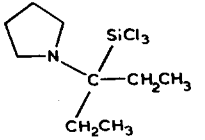
[a] Standard conditions, see Experimental. [b] Without solvent.

In addition to I a small quantity of *N*-cyclohexylpiperidine (III) could be isolated from the reaction mixture. A mechanistic pathway leading to the formation of this reduced species is less evident than eq. 4, but one can be hypothesized on the basis of a competition between intramolecular hydride transfer and intermolecular proton transfer (Scheme 1, pathway 1) between IV and V. This is summarized in Scheme 2.

It might be reasonably assumed that the longer the lifetime of IV before trichlorosilyl transfer, the more competitive Scheme 2 could become. While it is difficult to estimate what the p$K_a$ of the silyl proton in the complex IV might be, the possibility it would be low enough for removal by a carbanionic species is not unacceptable. In a similar sense the indicated displacement of a tertiary amine leaving group from VI to yield the final product would seem equally probable. The

TABLE 2

PHYSICAL CONSTANTS OF TRICHLOROSILYL ADDUCTS

| Adduct | b.p. (°C/torr) | NMR ($\delta$ (ppm), rel. $CHCl_3$) |
|---|---|---|
|  | 111/2.0 | 1.40–1.65 (br s, 4H),<br>1.65–2.45 (br m, 10H),<br>2.55–3.20 (br s, 4H) |
|  | 133/4.0 | 1.15–1.95 (br m, 14H),<br>1.95–2.80 (complex m, 8H) |
|  | 177/2.0 | 0.45–2.10 (complex m, 16H),<br>2.30–2.85 (br s, 4H) |
|  | 112/1.5 | 0.15–1.65 (br m, 14H),<br>1.65–2.25 (complex m, 4H) |
|  | 139/2.5 | 0.65–1.75 (br m, 12H),<br>1.75–2.40 (br m, 4H) |
|  | 100/2.0 (with decomposition) | 0.80–1.60 (br s, 16H),<br>1.65–2.40 (complex m. 4H) |
|  | 108/2.0 | 0.40–1.45 (complex m, 4H),<br>1.50–2.10 (complex m, 10H),<br>2.15–3.40 (br m, 4H) |

identity of the nucleophile is unspecified since there would be several possible in the reaction solution. However the quantity of tarry residue which always remains after reaction contains discernable silicon–chloride bonds. In come cases small quantities of a species tentatively identified as hexachlorodisilane have also been isolated.

The reaction has proven general for a series of structurally related enamines with an interesting relationship between the yields of the two products similar to I and III. The results of these experiments are shown in Table 1.

In all cases the resulting trichlorosilyl products were similar in their NMR spectra to that resulting from the *N*-(1-cyclohexenyl)piperidine, indicating single isomers of the specified regiochemistry (see Table 2, Experimental section). The total yields of products varied, indicating both differing reactivities and some possible differences in stabilities of the trichlorosilyl products. Specifically trials **4** and **6** gave much larger quantities of tarry residue and their trichlorosilyl products appeared much more prone to decomposition, particularly on heating. However an interesting trend can be seen in the fact that structural changes which lead to lower yields of trichlorosilyl product generally increase the yields of the corresponding amines. This trend is most strikingly demonstrated in the comparision of **7** and **8**. Since electronic factors would not appear to play any role in the change in product distribution, a steric effect of some kind seems the more likely determinant. Preliminary studies with models show indications of potential steric crowding of the hydrogen on the carbons flanking the nitrogen and those on the carbons directly opposite on the double bond fragment. The cases with the most significant crowding are generally those with low yields of trichlorosilyl product such as **7**. Those with less crowding, such as **8**, have higher yields of their trichlorosilyl products. This effect could be explained as the result of the crowding causing a hindrance to the rotation around the central nitrogen–carbanion bond, preventing achievement of the conformation necessary for the Steven's rearrangement. A slowing of the rate of the rearrangement could allow a greater competition from the intermolecular proton transfer as shown in Scheme 2 to increase the yields of the amines at the expense of the trichlorosilyl product.

## Conclusions

The study which has been made demonstrates that trichlorosilane will add to enamines in a regiospecific manner without catalysis under relatively mild conditions. Overall yields are highest when acetonitrile is used as a solvent, but reaction without solvent is possible. Amines are possible products and may predominate depending on the exact structure of the enamine. The results indicate sufficient versatility to justify further research into possible applications as a synthetic route to compounds functionalized at a single carbon center with both nitrogen and silicon.

## Experimental section

*General.* All NMR spectra were recorded on a Varian EM-300X 30 MHz NMR spectrometer with $CHCl_3$ 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 trichlorosilane, which was redistilled at normal pressure from quinoline. Elemental analysis was performed by Galbraith Laboratories.

*Enamines.* All enamines derived from cyclic ketones were synthesized by reaction of the ketone with a 10% excess of the appropriate amine in a 5–6 *M* benzene solution. A trace of conc. $H_2SO_4$ was added and the solution refluxed until the theoretical maximum of $H_2O$ was collected as the benzene azeotrope in a Dean–Stark trap [8]. The products were then collected by distillation at reduced pressure. Yields varied from 65–95%. The enamines of acyclic ketones were formed by allowing similar mixtures of ketone, amine, benzene and $H_2SO_4$ to sit over a large quantity of 4Å molecular sieve for four to six weeks at ambient temperature [8]. Yields varied from 16–42%.

### *Reaction of trichlorosilane with N-(1-cyclohexenyl)piperidine*

A single neck 100 ml flask with an addition funnel was charged with a suspension of *N*-(1-cyclohexenyl)piperidine (16.53 g, 0.10 mol) in 10 ml of dry $CH_3CN$. The addition funnel was charged with trichlorosilane (13.45 g, 0.10 mol) and the trichlorosilane added dropwise to the rapidly-stirred flask over a period of 10–15 min to prevent the reaction exotherm from refluxing the resulting solution. After completion of the addition the addition funnel was replaced with a condenser and drying tube and the reaction solution heated to reflux for 2.5 h. After cooling to room temperature the condenser was replaced with a short-path microhead and the solution distilled at ambient pressure to remove the $CH_3CN$ with traces of unreacted trichlorosilane and any other volatiles. The pressure was then reduced and the distillation continued. A small (3.7 g) forerun was collected, followed by the isolation of 23.2 g (77%) of *N*-(1-trichlorosilylcyclohexyl)piperidine as a heavy yellow moisture sensitive oil. NMR ($CCl_4/CHCl_3$) 1.35–2.54 (complex m, 16H), 2.55–3.35 (complex m, 4H). Anal. Found: C, 43.99; H, 6.75; Cl, 35.10; N, 4.58; Si, 9.47. $C_{11}H_{20}Cl_3NSi$ calcd.: C, 43.94; H, 6.71; Cl, 35.36; N, 4.64; Si, 9.34%.

### *Isolation of amines from reaction mixtures (general procedure)*

In all cases the similarities in boiling points of the enamine and the corresponding amines made separation impossible by distillation. The foreruns before the distillation of the trichlorosilyl products were analyzed by stirring in excess 10% HCl (aq.) to hydrolyze the enamine, followed by treatment with 10% NaOH to pH 9. The resulting insoluble organic layer was separated, the aqueous phase extracted with $Et_2O$ and the combined extracts dried over $MgSO_4$ and distilled to isolate the high boiling amines. The isolated amines were identified by comparison to literature IR and NMR spectra.

## Acknowledgment

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## References

1 R.A. Benkeser, and D.C. Snyder, J. Organomet. Chem., 225 (1982) 107.

2 R.A. Pike, J. Org. Chem., 27 (1962) 2186.

3 R.A. Benkeser, K.M. Foley, J.B. Grutzner and W.E. Smith, J. Amer. Chem. Soc., 92 (1970) 697.

4 S.C. Bernstein, J. Amer. Chem. Soc. 92 (1970) 699.
5 H.J. Campbell-Ferguson and E.A.V. Ebsworth, J. Chem. Soc. A, (1966) 1508.
6 H.J. Campbell-Ferguson and E.A.V. Ebsworth, J. Chem. Soc. A, (1967) 705.
7 B.J. Aylett, J. Inorg. Nucl. Chem., 15 (1960) 87.
8 W.D. Gurowitz and M.A. Joseph, J. Org. Chem., 32 (1967) 3289.