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TRICHLOROSILANE-IMINE COMPLEXES. A NEW METHOD FOR THE REDUCTION OF IMINES TO AMINES

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Summary

It has been found that trichlorosilane adds regio-specifically to the carbon—nitrogen double bond of imines under mild conditions to yield hydrolytically unstable *N*-trichlorosilyl intermediates. The latter can be hydrolyzed in situ by alcoholic base to give the corresponding amines in moderate to good yields. Variously substituted aldo and keto imines, both alkyl and aryl, were tested to demonstrate the scope of the reaction. The facility of trichlorosilane addition appears to depend on the nature of the groups directly attached to the carbon—nitrogen double bond. Hydride trapping experiments suggest an intramolecular rather than intermolecular hydride transfer during the course of the reaction.

Introduction

It has been amply demonstrated in previous work [1] that trichlorosilane in combination with certain tertiary amines is capable of effecting a number of interesting and useful chemical transformations. Under the influence of tertiary amines, trichlorosilane is capable of adding the $H\cdots SiCl_3$ moieties across carbon—carbon double and triple bonds [2]. In certain systems, it can reduce carbon—halogen bonds [3] as well as form new carbon—silicon bonds [4] by an apparent nucleophilic-type displacement. Finally, the trichlorosilane/tert-amine combination has proved to be a powerful reagent for the reduction of certain aromatic aldehydes, ketones [5], aromatic acids [6,7], acid chlorides [8], anhydrides [7,10], silyl esters [9] and tertiary amides [9,10]. In many cases a benzylic silicon species is formed which can be cleaved hydrolytically, with the

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* This paper is dedicated to my friend and former mentor, Professor Henry Gilman on the occasion of his 88th birthday.

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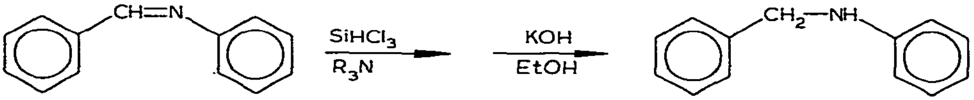
overall result being a conversion of the carbonyl group to a methyl [7].

In all of the aforementioned chemistry, it was suggested that the tert-amine functions as a base, forming a trichlorosilyl anion by removal of a proton from trichlorosilane. This trichlorosilyl anion would serve as a potent nucleophile and was postulated to explain the reaction of the trichlorosilane/tert-amine combination in a number of mechanistic schemes. It was suggested that the first step in the reductive silylation of aromatic, carbonyl-containing groups might involve an initial attack of the trichlorosilyl anion on the carbon—oxygen double bond. The subsequent mechanistic steps by which the oxygen of the carbonyl-containing group is removed have not been elucidated. In an effort to gain some insight into this mechanism, an analogous carbon—nitrogen double bond was subjected to the same reaction conditions with unexpected results.

Results and discussion

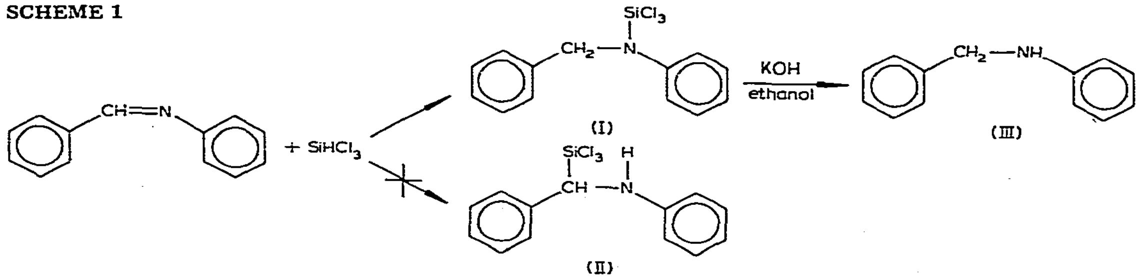
When *N*-(benzylidene)aniline was treated with the trichlorosilane/tert-amine combination under the usual reductive silylation conditions, an exothermic reaction occurred with the customary formation of a dense white precipitate. Hydrolysis of the mixture yielded no cleavage product such as toluene, but rather the amine, *N*-benzylaniline (eq. 1).



(1)

Further work established that this reaction could be duplicated without the addition of any tertiary amine. Treatment of *N*-(benzylidene)aniline in acetonitrile with trichlorosilane alone resulted in an exothermic reaction without precipitate formation. Refluxing the latter solution for 4 h, followed by treatment with KOH in aqueous ethanol, resulted in a good yield of the amine (III) (Scheme 1). Significantly, no exothermic reaction occurs upon simply mixing acetonitrile with trichlorosilane.

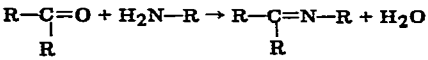
SCHEME 1



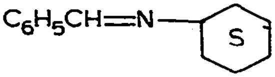
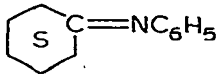
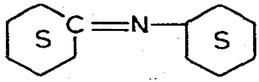
In an effort to decipher what was transpiring, the reaction was repeated but without basic hydrolysis. After the heat of reaction had subsided following the addition of the trichlorosilane, an aliquot of the reaction mixture was withdrawn and analyzed by NMR. The spectrum showed the virtual disappearance of the signal at δ 8.25 ppm, which corresponded to the single proton on the carbon doubly bonded to the nitrogen in the starting imine. The signal pattern of the aromatic protons underwent a change and also a new singlet appeared at δ 4.55 ppm.

The mixture was heated to reflux (approximately 45°C) and further aliquots removed at intervals to monitor the course of the reaction. The aromatic proton pattern continued to change and the δ 4.55 ppm signal increased. After four hours, no further change was observed. Distillation of the mixture at this point afforded, after solvent removal, 12.1 g of a pale green-yellow liquid, b.p. 124—126°C/0.5 mmHg, along with a considerable amount of tarry residue. The distillate evolved HCl vigorously when in contact with atmospheric moisture and an accurate elemental analysis could not be obtained. However, its NMR spectrum clearly showed two broad, overlapping singlets at δ 7.05 and 7.15 ppm with a total of ten protons. The only other signal was a distinct, two proton singlet at δ 4.55 ppm. A structure consistent with these data would be the product resulting from the addition of the trichlorosilane such that the $-SiCl_3$ group is bonded to the imine nitrogen (I in Scheme 1). Since it is well-known that the silicon—nitrogen bond is easily cleaved by a number of reagents [11], it is not difficult to visualize how the trichlorosilyl adduct could be hydrolyzed to the amine. Although the product of the opposite mode of addition (a benzylic silane, II in Scheme 1) might also be expected to cleave to the amine, its NMR spectrum would be expected to show two different, one-proton signals due to the lone protons on the carbon and the nitrogen. Attempts to isolate the addition product as the fully alkylated species by treatment with methylmagnesium iodide resulted only in the formation of an intractable tarry material, reflecting again

TABLE 1

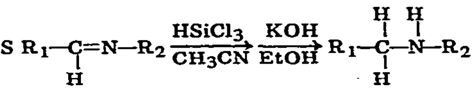
IMINE FORMATION 

$$R\underset{\displaystyle R}{-C}=O + H_2N-R \rightarrow R\underset{\displaystyle R}{-C}=N-R + H_2O$$

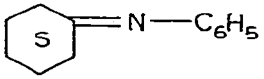
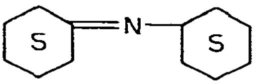
Imine	Yield (%)	B.p. (°C) (mmHg)	Ref.
$C_6H_5CHNC_6H_5$	75	[m.p. 50—52°] [a]	22
p-$ClC_6H_4CHNC_6H_5$	68	[m.p. 63—65°] [a]	23
o-$ClC_6H_4CHNC_6H_5$	82	150—155° (0.25)	24
p-$CH_3OC_6H_4CHNC_6H_5$	68	[m.p. 58—60°] [a]	25
o-$CH_3OC_6H_4CHNC_6H_5$	95	165—178° (0.25) [b]	26
m-$CH_3OC_6H_4CHNC_6H_5$	87	160—164° (1.0)	27
p-i-$C_3H_7C_6H_4CHNC_6H_5$	80	150—160° (0.25) [b]	28
	60	106—108° (0.75)	29
	71	95—100° (0.25)	30
	79	96—98° (0.75)	29
C_6H_5CHN-n-C_4H_9	72	108—110° (10.0)	31
n-C_3H_7CHN-n-C_4H_9	30	64—66° (40.0)	32

[a] Solids recrystallized from 95% ethanol for purification. [b] VPC analysis indicates 95+% purity; used without further purification. [c] Same procedure was employed as described in Ref. 32.

TABLE 2

REDUCTION OF IMINES TO AMINES 

$R_1-\underset{H}{C}=N-R_2 \xrightarrow[CH_3CN]{HSiCl_3} \xrightarrow[EtOH]{KOH} R_1-\underset{H}{\overset{H}{C}}-\overset{H}{N}-R_2$

R_1	R_2	Yield (%)	B.p. (°C) (mmHg)
1 C_6H_5	C_6H_5	79	122—125° (0.5) [a]
2 p-ClC_6H_4	C_6H_5	69	145—148° (0.25)
3 o-ClC_6H_4	C_6H_5	62	135—140° (0.25) [c]
4 p-$CH_3OC_6H_4$	C_6H_5	78	[m.p. 44—45°] [b, c]
5 o-$CH_3OC_6H_4$	C_6H_5	88	[m.p. 91—93°] [c]
6 m-$CH_3OC_6H_4$	C_6H_5	76	148—151° (0.25) [c]
7 p-i-$C_3H_7C_6H_4$	C_6H_5	73	150—155° (0.25) [c]
8 C_6H_5	n-C_4H_9	53	120—127° (16.0) [a]
9. C_6H_5		46	95—105° (0.3)
10 n-C_3H_7	n-C_4H_9	47	110—120° (50.0) [a]
11. 		48	96—99° (0.25) [a]
12. 		48	74—75° (0.25) [a]

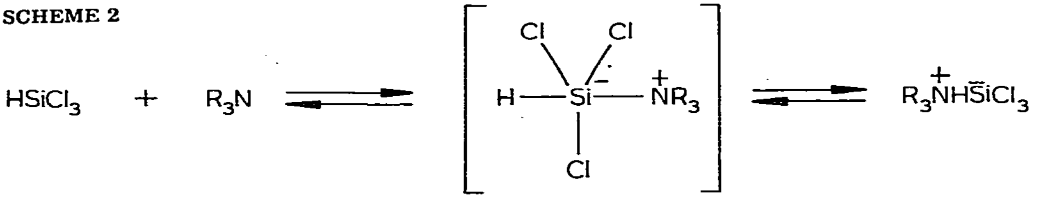
[a] Sadtler spectra available. [b] Lit. [21] m.p. 65°C. [c] Gave correct elemental analyses.

the sensitivity of the silicon—nitrogen bond. On the basis of some of these results, it seems reasonable that the initial addition proceeds as depicted above in Scheme 1.

The two step sequence of addition and hydrolysis was found to be applicable to a wide variety of imines. Both aldo and keto imines, either alkyl or aryl substituted, undergo the reaction, giving the corresponding amines in yields that are moderate to very good. The results of the reduction of a series of imines are summarized in Table 2. Most of the imines were obtained by the direct reactions of the corresponding amine and carbonyl precursors with the removal of water under a variety of reaction conditions (Table 1).

An attractive (but unproved) mechanism for the uncatalyzed addition of trichlorosilane to imines is based on the well-known ability of silicon to form pentacoordinate and hexacoordinate complexes with species containing lone pair donor atoms [12]. Such adducts have been studied and characterized [13,14,15]. This type of coordinate-covalent chemistry can be invoked to explain how a relatively weak base like a tertiary amine can "appear" to abstract a proton from trichlorosilane. In the early investigations of the trichlorosilane/ tertiary amine combination, it was found [16] that when a tertiary amine was added to an acetonitrile solution of trichlorosilane, the NMR signal of the silyl hydrogen disappeared, and a signal similar to the nitrogen-bonded hydrogen of a typical ammonium salt appeared. This evidence was used to support the idea that the trichlorosilyl anion was being formed by this interaction. However, it was not claimed that the amine was necessarily abstracting the proton directly in a simple acid-base reaction. What seemed more plausible was a two-step reaction in which the nitrogen first formed a complex by bonding to the silicon. This complex could then react further to give the postulated $\overline{\mathrm{Si}}\mathrm{Cl}_3$ group and the protonated amine as shown in Scheme 2.

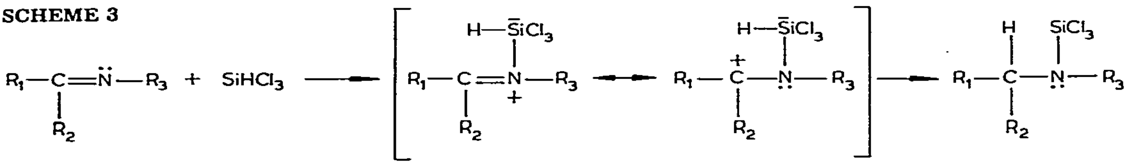
SCHEME 2



From kinetic studies of trichlorosilane vs. deuterotrichlorosilane, it was concluded [17] that formation of the complex was the rate determining step, followed by a subsequent fast decomposition to the final product. The last step would involve a direct intramolecular hydride transfer from silicon to nitrogen. The complexed silicon would have a negative charge, which would induce considerable hydride-like character to the silicon—hydrogen bond. An essentially nucleophilic attack by this hydride on the nitrogen would displace the $\overline{\mathrm{Si}}\mathrm{Cl}_3$ group to yield the protonated amine, thus mimicking a direct proton abstraction by the amine.

In accord with the aforementioned facts, a rational mechanism for the addition of trichlorosilane to imines can be proposed as shown in Scheme 3. The

SCHEME 3



(III)

lone pair of electrons of the imine nitrogen would react with the silicon of the trichlorosilane in a manner similar to the normal tertiary amine, forming a similar complex. Koacher and coworkers have isolated such complexes [18] from the reaction of dimethyldichlorosilane and Schiff base imines. However, the trichlorosilane complex would still possess a hydride-like hydrogen. It would not require a nucleophilic displacement on the tetracoordinated nitrogen (see Scheme 2) to form any final product. Instead, the carbon—nitrogen double bond of the imine, which would be highly polarized in the complex, would be available to accept the hydride from the carbon atom directly via a four-centered transition state without any external catalyst (Scheme 3).

Although the above intramolecular hydride transfer appears reasonable, there also exists the possibility of an intermolecular route. In an attempt to test this possibility, benzophenone, which undergoes reductive silylation readily with the usual trichlorosilane/tertiary amine combination, was added to one of the imine/trichlorosilane reaction mixtures. An intermolecular hydride transfer mechanism might be expected to give some of the benzophenone reductive silylation product and a lowered yield of the imine reduction product. Neither effect was observed. The yield of the nitrogen-silylated product was unchanged, and the benzophenone was recovered quantitatively. Addition of a hydride trapping agent like triphenylmethyl tetrafluoroborate to the reaction mixture did not affect the yield, and no triphenylmethane could be found. This was in contrast to the addition of triphenylmethyl tetrafluoroborate to the normal reductive silylation combination of trichlorosilane and a tertiary amine where a moderate yield of triphenylmethane could be isolated. The latter proved to be an ambiguous result, however, since triphenylmethane could also be isolated from the reaction between trichlorosilane and triphenylmethyl tetrafluoroborate even in the absence of an amine. While results of the hydride trapping experiments are not conclusive, they do suggest the lack of any free hydride, and lend some support to the concept of an intramolecular hydride transfer.

The electronic effects of the substituent groups and their relationship to the proposed mechanism are not particularly clear. The *ortho* and *para* chloro groups on the benzylidene portion of *N*-(benzylidene)aniline appear to lower the overall yield of amine (compare examples 2 and 3 to 1 in Table 2). However, there is little effect by alkyl or methoxy groups. The most noticeable effect is the significant reduction in yields in those imines substituted on the carbon—nitrogen bond with alkyl groups. Only one alkyl group is required to lower the yield, regardless of whether it is located on the carbon or the nitrogen. At the same time, alkyl substitution on both atoms causes no further reduction in overall yield. The *N*-alkylimines might be expected to be somewhat more reactive than the *N*-arylimines, since the lone pair of electrons on the N atom in the former case should be more available for complexing with the Si atom of the trichlorosilane. Experimentally, reaction of trichlorosilane with the *N*-alkylimines does appear to be more exothermic than in the case of the *N*-arylimines. Until a more in-depth study of the mechanism of this reaction is made, the differences noted between the alkyl and aryl systems must remain unanswered.

Experimental

There are many methods known for the synthesis of amines by the reduction of imines [19]. These include catalytic hydrogenation, reduction by metal hydrides or active metals, as well as electrochemical and photochemical procedures [20]. Each of these methods suffers from certain disadvantages. The addition-hydrolysis sequence herein described offers an alternative to the usual methods since it is highly specific for the C=N functional group and combines the advantages of inexpensive reagents and simple procedures.

Synthesis of representative imines

N-(Benzylidene)aniline. Aniline (93.13 g, 1000 mmol, J.T. Baker) was added in a single portion to benzaldehyde (106.12 g, 1000 mmol, MCB) which was stirring rapidly in a 500 ml flask. After 0.5 h, the mixture was poured into 150 ml of rapidly stirring 95% ethanol. The resulting solution was allowed to stand undisturbed until crystallization had begun, at which time it was placed in an ice bath for 0.5 h. The crude solid was collected, recrystallized from 95% ethanol, and dried in vacuo to give 136.2 g of *N*-(benzylidene)aniline (75% yield).

N-(2-Chlorobenzylidene)aniline. Aniline (46.56 g, 500 mmol, J.T. Baker) was mixed with 2-chlorobenzaldehyde (70.29 g, 500 mmol, MCB) in a 250 ml flask and stirred for 1 h. A 25 ml portion of benzene was added and the volatile materials removed from the mixture in vacuo over a hot water bath. When the solution appeared homogeneous it was distilled through a short-path microhead to give 88.5 g of *N*-(2-chlorobenzylidene)aniline as a heavy, yellow oil, collected at 150—155°C (0.25 mmHg), (82% yield). NMR spectrum (CCl_4): δ 7.10—7.45 (complex m, 9 H), 8.25 ppm (broad t, 1 H). Anal. Found: C, 72.22; H, 4.86; Cl, 16.39; N, 6.30. Calcd. for $C_{13}H_{10}ClN$: C, 72.40; H, 4.67; Cl, 16.43; N, 6.50%.

N-(n-Butylidene)-n-butylamine. n-Butyraldehyde (72.11 g, 1000 mmol, MGB) was stirred in a 500 ml flask equipped with a thermometer and an addition funnel and cooled to 20°C in a water bath. n-Butylamine (73.14 g, 1000 mmol, J.T. Baker) was added dropwise over a period of several hours at such a rate that the temperature of the reaction mixture was kept below 25°C. After the addition was completed, the solution was stirred in the cold water bath for 24 h before 10 g of KOH pellets were added. The mixture was then allowed to stand for 48 h in the cold water bath. The solution was decanted into a 500 ml flask containing 1.0 g of barium oxide and distilled through a 15 cm Vigreux column to give 37.5 g of *N*-(n-butylidene)-n-butylamine as a colorless liquid collected at 64—66°C (40 mmHg) (30% yield). NMR spectrum ($CDCl_3$): δ 0.95 (2 supermposed t's, 6 H), 1.15—1.80 (m, 6 H), 2.15—2.40 (m, 2 H), 3.25—3.45 (m, 2 H), 7.65 ppm (s, 1 H).

Reductive silylation of imines followed by hydrolysis to amines

N-Benzylaniline. *N*-(Benzylidene)aniline (18.1 g, 100 mmol) was dissolved in 20 ml of dry acetonitile in a 500 ml flask and cooled in an ice bath. Trichloroilane (13.5 g, 100 mmol) was added dropwise via an addition funnel over a ten minute period. The ice bath was removed, a condenser attached to the flask, and the solution heated to reflux for 4 h. It was then cooled in an ice bath and he addition funnel attached again. A solution of KOH (30.0 g, 540 mmol, Mallinckrodt) in 150 ml of 85% ethanol was placed in the funnel and added dropwise over a period of 2 h to the ice cold reaction mixture. (Great care must be taken with the KOH/ethanol addition. The hydrolysis reaction is extremely vigorous and exothermic, particularly in the early stages of the addition. A large mass of white solid forms which must be broken up occasionally in order to prevent a dangerous localized concentration of unreacted KOH/ethanol above he surface of the mixture which could unexpectedly come in contact with it, with violent results.)

After the addition was completed, the ice bath was removed and the mixture tirred for 12 h at room temperature. The solid was dissolved by the addition of 300 ml of water and the resulting solution extracted twice with 100 ml portions of ether. The aqueous phase was saturated with NaCl and extracted with 100 ml of ether. The organic extracts were combined and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue distilled to give 14.4 g of *N*-benzylaniline as a pale yellow liquid collected at 122—125°C (0.5 mmHg) 79% yield).

Reductive silylation of N-(benzylidene)aniline

N-(Benzylidene)aniline (18.1 g, 100 mmol) was dissolved in 20 ml of dry acetonitrile in a 250 ml flask and trichlorosilane (13.5 g, 100 mmol) added slowly over a period of 40 minutes so that the temperature remained between 30—35°C. After the addition was completed and the solution had cooled, an aliquot was removed for NMR analysis. The solution was then heated to reflux for 4 h until the NMR showed no further changes. The solution was transferred to a 100 ml flask and distilled at atmospheric pressure to remove the volatile materials. The pressure was reduced and the residue distilled to give 12.1 g of a heavy yellow-green liquid collected at 124—126°C (0.25 mmHg). The distillate fumed in contact with the atmosphere indicating the formation of HCl. Considerable tarry residue remained after distillation. Assuming the distillate to be product I (Scheme 1), the yield was 38%. NMR spectrum ($CDCl_3$): δ 4.5 (s, 2 H), 7.0—7.2 ppm (d, 10 H).

Treatment of N-(benzylidene)aniline/trichlorosilane reaction product with methylmagnesium iodide

A 100 ml flask was charged with a solution of *N*-(benzylidene)aniline (18.1 g, 100 mmol) in 20 ml of acetonitrile and cooled in ice. Trichlorosilane (13.5 g, 100 mmol) was added slowly; the resulting solution was heated to reflux for 4 h. After reflux, the acetonitrile and all other volatile materials were quickly removed by distillation at atmospheric pressure. The high-boiling, green-yellow residue was transferred to a 300 ml flask, dissolved in 50 ml of diethyl ether, and the solution cooled in ice. Via an addition funnel, 178 ml of 1.4 *M* methylmagnesium iodide (250 mmol) in diethyl ether, was added over 2 h. The resulting red-brown solution was heated to reflux for 16 h with little visible change. Several ml of saturated NH_4Cl solution was added to precipitate a quantity of yellow solid. The diethyl ether was decanted away from the solid and the ether removed in vacuo. When an effort was made to distill the residual black oil under vacuum, it hardened to a black tar.

Reductive silylation and hydrolysis of N-(cyclohexylidene)cyclohexylamine with the addition of benzophenone

Following the standard procedure, *N*-(cyclohexylidene)cyclohexylamine (17.9 g, 100 mmol) in 20 ml of acetonitrile was treated with trichlorosilane (13.5 g, 100 mmol) at 0°C. The resulting suspension of white solid was stirred for 5 minutes, followed by the addition of a solution of benzophenone (18.1 g, 100 mmol, Eastman) in 20 ml of acetonitrile over a 10 minute period, without visible effect. The mixture was heated to reflux for 4 h and then treated with KOH/ethanol solution and stirred for 16 h at room temperature. The normal work-up and removal of solvent in vacuo gave a residue which distilled into two fractions. The first fraction of 14.1 g of colorless liquid collected at 85—105°C (0.5 mmHg) was analyzed by NMR and shown to be composed of 60% dicyclohexylamine (47% yield) and 40% benzophenone. The second fraction of 12.1 g collected at 115—117°C (0.5 mmHg) was virtually all benzophenone. The amount of benzophenone recovered was 17.7 g (97%).

Reductive silylation and hydrolysis of N-(benzylidene)aniline with the addition of triphenylmethyl tetrafluoroborate

N-(Benzylidene)aniline (9.05 g, 50 mmol) was dissolved in 40 ml of acetonitrile in a 500 ml flask and cooled in an ice bath. Triphenylmethyltetrafluoroborate (8.25 g, 25 mmol, Alfa/Ventron) was added, followed by the usual addition of trichlorosilane (6.75 g, 50 mmol). The resulting dark brown solution was heated to reflux for 4 h with no visible change. It was treated with KOH/ethanol solution as previously indicated and stirred for 24 h at room temperature. The normal work-up and distillation after the removal of the solvent gave .3 g of pale yellow liquid collected at 120—140°C (0.25 mmHg). The IR spectrum of this material was identical to that of authentic *N*-benzylaniline (69% yield). There remained in the distillation flask 6.6 g of a black, tarry residue which could not be characterized.

cknowledgment

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