Letters to the Editor

Dehydrochlorination of chloroform by *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine

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N,*N*-Bis(silatranylmethyl)methylamine **1** reacts with chloroform resulting in amine hydrochloride **2** and dichlorocarbene. The formation of the latter was proved by a cyclopropanation reaction and insertion into the Si—H bond. In the presence of cyclohexene, compound **2** and 7,7-dichlorobicyclo[4.1.0]heptane are the major reaction products. Compound **2** and 1-dichloromethylsilatrane were isolated upon the reaction of amine **1** with chloroform and 1-hydrosilantrane.

Key words: *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine, chloroform, dichlorocarbene, dehydrochlorination.

Over decades, polychloromethanes CH_nCl_{4-n} ($n = 0$—2) are used in organic chemistry as inert solvents,[1] in particular, in studies of properties of amines.[2] The introduction of an organosilicon substituent in the α-position to the nitrogen atom in amines results in dramatic changes in the reactivity of the amino group in comparison with purely organic amines.[3—7] Recently, we have shown that α-silylamines $RR'NCH_2SiX_3$ (R, R′ = Alk, CH_2SiX_3; SiX_3 = $= SiMe_n(OAlk)_{3-n}$, $Si(OCH_2CH_2)_3N$) react readily with di- and tetrachloromethanes.[5—7] The nature of these reactions and the structures of products are determined by the structure of polychloromethane. For example, the reaction of *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine with CCl_4 is radical and initiated by daylight.[5,6] The final reaction product is hydrochloride of the initial amine. The reaction of this amine with dichloromethane is a typical quaternization reaction resulting in *N*-methyl-*N*,*N*-bis(silatranylmethyl)-*N*-chloromethylammonium chloride and bis[*N*,*N*′-dimethyl-*N*,*N*,*N*′*N*′-tetra(silantranylmethyl)ammonio]methane dichloride.[7]

In the present work, the results of studies of the reaction of chloroform with *N*-methyl-*N*,*N*-bis(silatranylmethyl)amine **1** are described.

Mere dissolution of compound **1** in chloroform, as in the case of dichloromethane, brings about modest warming and light yellowing of the solution. Monitoring of this process by ^1H NMR in CD_3CN shows the gradual weakening of the signal for chloroform and the change in the pattern of the spectrum, which is evidence of the reaction of compound **1** with chloroform. The reaction is completed in 24 h. According to the data from ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, compound **1** reacts with chloro-

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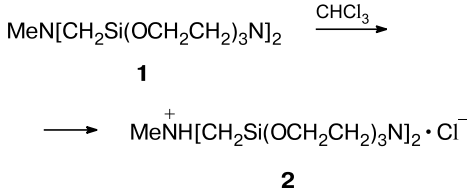
form to give ammonium salt **2** in a virtually quantitative yield (Scheme 1).

Scheme 1

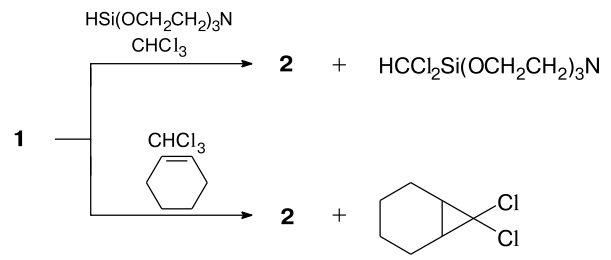


What is the fate of chlorofom in this reaction? The analysis of the reaction mixture by ^{13}C NMR spectroscopy showed that, in addition to signals for compound **2**, a low-intensity signal with δ 120.67 belonging to tetrachloroethylene, that is the dichlorocarbene dimerization product, is observed. Furthermore, the small amount of unidentified resin-like colored products remained after recrystallization of compound **2**.

The elimination reaction of a hydrogen halide from trihalomethanes in the presence of strong bases are well known.[8] Usually, NaOH, KOH, Bu^tOK, or RLi are used as such bases. Information about generation of carbenes using amines as bases is extremely scarce. In the reaction of piperidine with chloroform, piperidine hydrochloride is obtained in 1% yield after 24 h.[9] It is suggested[9] that this reaction affords dichlorocarbene. The formation of 2,2,3,3-tetramethylcyclopropane-1,1-dicarbonitrile in the reaction of bromomalononitrile $(CN)_2CHBr$ with tetramethylethylene in the presence of Et_3N is evidence of the involvement of carbene $:C(CN)_2$ in this process.[10]

The cyclopropanation of olefins is the most typical reaction of dihalocarbenes.[8] If amine **1** induces dehydrochlorination of chloroform giving dichlorocarbene, it was to be expected that this reaction carried out in the presence of cyclohexene would result in its cyclopropanation product. In fact, in the reaction of compound **1** with $CHCl_3$ in the presence of cyclohexene, 7,7-dichlorobicyclo[4.1.0]heptane (Scheme 2) was obtained in 46% yield. Its ^1H and ^{13}C NMR spectra are in accord with the literature data.[11]

Scheme 2



The carbenes react with silanes to form insertion products into the Si—H bond.[12–14] The reaction of amine **1** with chloroform in the presence of 1-hydrosilatrane (molar ratio amine : 1-hydrosilatrane is 2 : 1) affords compound **2** and 1-dichloromethylsilatrane in 52% yield; spectral characteristics of the latter agree with those described in the literature.[15] However, in the reaction of chloroform with an equimolar mixture of amine **1** and 1-hydrosilatrane, the latter reacts partly and remains in the reaction mixture.

The obtained results open the way to development of a novel procedure for the synthesis of dihalomethylsilanes and -silatranes and may be useful in synthetic chemistry of silicon compounds. It should also be noted that all the polychloromethanes of the CH_nCl_{4-n} (n = 0—2) series react with α-silylamines. That is why, in studies of properties of amines (especially highly basic) in these solvents, account must be taken of possibility of reaction of the amine with polychloromethane.

Experimental

NMR spectra of 20% solutions of compounds in CD_3CN and $CDCl_3$ were recorded on a Bruker DPX-400 spectrometer (400 MHz) with Me_4Si as the internal standard. *N*-Methyl-*N*,*N*-bis(silatranylmethyl)amine **1** was synthesized as described previously,[16] $CHCl_3$ was dried according to the known procedure.[17] All the reactions were carried out in an atmosphere of dry argon.

The reaction of amine 1 with chloroform. Amine **1** (0.81 g, 2 mmol) was dissolved in chloroform (30 mL). After 24 h, the excess of chloroform was removed, the residue was recrystallized from chloroform-hexane (1 : 1) mixture. *N*-Methyl-*N*,*N*-bis(silatranylmethyl)amine **2** (0.83 g, 94%) was obtained, m.p. > 165 °C (decomp.), spectral characteristics are identical to those described previously.[4,6]

The reaction of amine 1 with chloroform in the presence of cyclohexene. A tube with amine **1** (1.62 g, 4 mmol) was placed in liquid nitrogen, a solution of cyclohexene (0.49 g, 6 mmol) in chloroform (75 mL) was added, the mixture was degassed and sealed up *in vacuo*. The tube was kept for 24 h at ~20 °C, then volatile compounds (chloroform and cyclohexene) were removed, the residue was extracted with boiling pentane (35 mL). The solid residue was filtered off and dried, hydrochloride **2** (1.75 g, 98%) was obtained. The filtrate was concentrated, the residue was distilled *in vacuo*. 7,7-Dichlorobicyclo[4.1.0]heptane (0.31 g, 46%) was isolated by distillation, b.p. 74—76 °C (12 Torr), n^{20}_D 1.5029. ^1H NMR spectrum ($CDCl_3$), δ: 1.10—1.37 (m, 4 H, $CH_2—C\underline{H}_2—C\underline{H}_2—CH_2$); 1.60—1.73 (m, 4 H, $C\underline{H}_2—CH_2—CH_2—C\underline{H}_2$); 1.86—2.01 (m, 2 H, $C\underline{H}—C\underline{H}$). ^{13}C NMR spectrum ($CDCl_3$), δ: 18.97 ($CH_2—\underline{C}H_2—\underline{C}H_2—CH_2$); 19.94 ($\underline{C}H_2—CH_2—CH_2—\underline{C}H_2$); 25.75 ($\underline{C}H—\underline{C}H$); 67.32 ($CCl_2$).

The reaction of amine 1 with chloroform in the presence of 1-hydrosilatrane. Amine **1** (1.62 g, 4 mmol) was placed into a tube, previously blown with dry argon. The tube was cooled in liquid nitrogen, a mixture of chloroform (30 mL) and 1-hydrosilatrane (0.35 g, 2 mmol) was added, the resulting mixture was degassed and the tube was sealed *in vacuo*. After 48 h at ~20 °C, the excess of chloroform was removed *in vacuo* using a water-jet

pump. Toluene was added to the residue, the resulting mixture was heated to boiling and filtered. 1-Dichloromethylsilatrane (0.27 g, 52%) was isolated from the filtrate, m.p. 265—267 °C. ^{1}H NMR spectrum ($CDCl_3$), δ: 2.96 (t, 6 H, NCH_2); 3.93 (t, 6 H, OCH_2); 5.12 (s, 1 H, CH). ^{13}C NMR spectrum ($CDCl_3$), δ: 31.36 (CH); 51.15 (NCH_2); 57.33 (OCH_2). ^{29}Si NMR spectrum ($CDCl_3$), δ: –83.2. Compound **2** (1.59 g, 88%) was isolated by recrystallization of the solid residue from chloroform—hexane (1 : 1) mixture.

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