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Contributions to the chemistry of silicon—sulphur compounds

LVI *. The imidazole catalyzed alcoholysis of the isosteric isobutyl(isopropoxy)silanethiols i-Bu$_n$(i-PrO)$_{3-n}$SiSH ($n = 0$–3)

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Abstract

The kinetics of the imidazole-catalyzed alcoholysis of the isosteric silanethiols i-Bu$_n$(i-PrO)$_{3-n}$SiSH (I) with $n = 0$–3 in benzene and acetonitrile have been investigated. The alcoholysis of Si–S bond in I is generally first order with respect to both the silanethiol and the catalyst. At low alcohol concentrations the order with respect to alcohol tends to be zero. A mechanism involving an attack of a nucleophilic catalyst on silicon in I in the rate-determining step is proposed. In MeCN solution the reactivities of silanethiols decrease in the sequence i-Bu(i-PrO)$_2$SiSH > i-Bu$_2$(i-PrO)SiSH > (i-PrO)$_3$SiSH > i-Bu$_3$SiSH. The anomeric effect seems to determine the conformations and the reactivities of these silanethiols.

Introduction

There have been few kinetic studies of reactions of silicon-sulphur compounds. Base catalysis was found to be effective in the cleavage of the Si–S bond in arylthiosilanes [2,3]. The protolytic cleavage of the Si–S bond in trialkoxysilanethiols was shown to be accelerated by electronegative substituents on silicon [4] and to be susceptible to nucleophilic catalysis [5,6]; strong nucleophilic catalysts, such as imidazole, *N*-methylimidazole and 4-dimethylaminopyridine, proved to be especially efficient [7], but the mechanism of the catalysis was not elucidated. Nucleophilic activation in solvolytic cleavage of the Si–Cl bond is generally accepted [8,9] and it was found than in the presence of HMPTA the alcoholysis of chlorosilanes proceeds with retention of configuration, and the

* For part LV see ref. 1.

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kinetics are very similar to those observed for nucleophilic-assisted racemisation of chlorosilanes. A mechanism involving a nucleophilic attack of alcohol on a pentacoordinated silicon has been proposed [9,10]. On the other hand, some extensive studies indicate that ionic species with four coordinated silicon are active intermediates [8,11–15]. Some *N*-trimethylsilylarylium salts have been isolated and shown to be efficient silylating agents [16] and crystal structures of salts this type have been determined [17,18]. *N*-Silyl compounds of imidazole and its derivatives have been shown to undergo fast intermolecular exchange of silyl groups [19–21] these compounds are very susceptible to nucleophilic substitution, and they may be responsible as intermediates for the catalytic activity of imidazole and its ring-substituted derivatives.

This paper is concerned with a kinetic study of the catalyzed alcoholysis of the isosteric silanethiols i-Bu_n(i-PrO)$_{3-n}$SiSH with $n = 0$–3, which were undertaken in order to gain further insight into the nature of the catalytic activity of imidazole and its derivatives, and to provide information about the influence of electronegative alkoxy groups (assumed to have steric effects to the alkyl groups) on the reactivity of the Si–S bond.

Results

The reactions of isosteric silanethiols i-Bu_n(i-PrO)$_{3-n}$SiSH ($n = 0$–3) with the alcohols ROH (R = Me, Et, i-Pr) in the presence of the catalyst proceed smoothly at room temperature according to equation 1 *.

$$\text{i-Bu}_n\text{(i-PrO)}_{3-n}\text{SiSH} + \text{ROH} \xrightarrow{\text{cat}} \text{i-Bu}_n\text{(i-PrO)}_{3-n}\text{SiOR} + \text{H}_2\text{S} \qquad (1)$$

The relationships between ln k_c and ln c_{ROH}, where k_c is the catalytic constant and c_{ROH} is the concentration of the alcohol are shown for (i-PrO)$_3$SiSH (I) in Fig. 1, for i-Bu(i-PrO)$_2$SiSH (II) in Fig. 2, for i-Bu$_2$(i-PrO)SiSH (III) in Fig. 3, and for i-Bu$_3$SiSH (IV) in Fig. 4. Because the reactions of these compounds with alcohol in the absence of catalyst are slow compared to those catalyzed by nucleophiles, the spontaneous alcoholysis was neglected.

The most significant observation were as follows:

1. The pseudo - first order rate constants were found to increase linearly with the concentration of the catalyst (within the experimental error), showing that the reaction is of first order in respect to the catalyst. E.g. for (i-PrO)$_3$SiSH 0.026 *M* and EtOH 1.16 *M* in benzene solution and imidazole (im) as catalyst the k values changed as follows: $k = 59 \times 10^{-6}$ (im 0.005 *M*), $k = 129 \times 10^{-6}$ (im 0.010 *M*), $k = 210 \times 10^{-6}$ (im 0.015 *M*), $k = 260 \times 10^{-6}$ (im 0.020 *M*). For (i-PrO)$_3$SiSH 0.026 *M* and EtOH 3.43 *M* in benzene solution and *N*-methylimidazole as catalyst the k values changed as follows: $k = 55 \times 10^{-6}$ (N-meim 0.005 *M*), $k = 128 \times 10^{-6}$ (N-meim 0.013 *M*), $k = 250 \times 10^{-6}$ (N-meim 0.025 *M*), $k = 520 \times 10^{-6}$ (N-meim 0.050 *M*).

2. In the reactions of EtOH and i-PrOH, with imidazole as a catalyst, for (i-PrO)$_3$SiSH and for i-Bu$_3$SiSH, the k_c values for small concentrations of alcohol

* Tables of pseudo - first order rate constants for disappearance of the thiols are available as supplementary materials from authors.

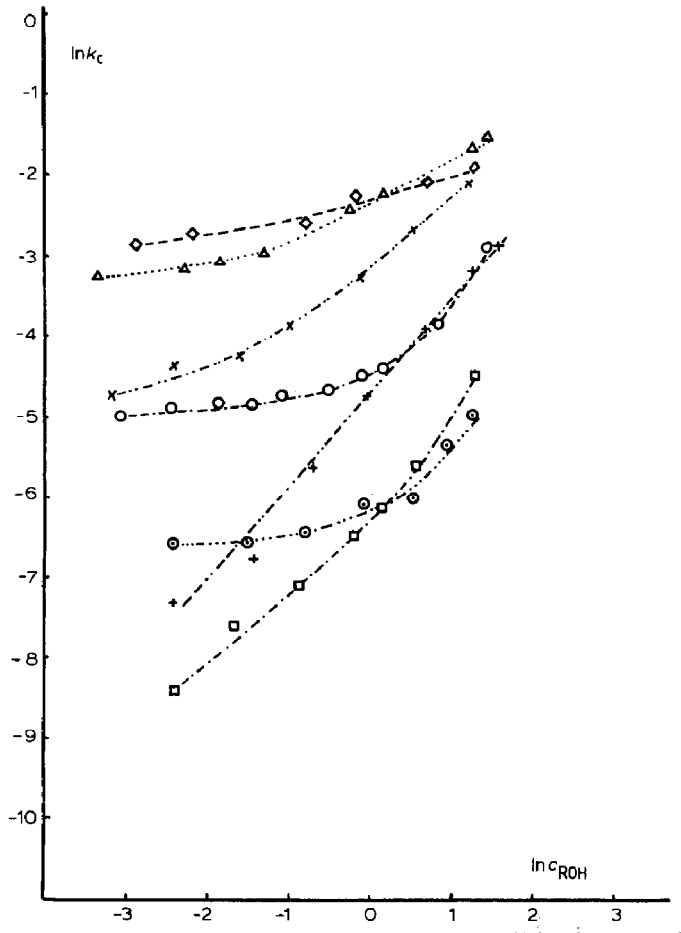

Fig. 1. Plot of ln k_c against ln c_{ROH} for Ia, ○ EtOH(im, benzene); Ib, □ EtOH(N-meim, benzene); Ic, △ EtOH(im, acetonitrile); Id, ◇ EtOH(N-meim, acetonitrile); Ie, × MeOH(im, benzene); If, + MeOH(N-meim, benzene); and Ig, ⊙ i-PrOH(im, benzene).

are almost independent of the alcohol concentration (Fig. Ia, Ig, IVa, IVg). A similar tendency is also apparent to some extent for i-Bu(i-PrO)$_2$SiSH and for i-Bu$_2$(i-PrO)SiSH (Fig. IIa, IIIa). At higher concentrations of EtOH the k_c values depend on those concentrations. For MeOH the k_c values depend on the alcohol concentration except for the cases shown by curve Ie and IVe.

3. In benzene solution the k_c values are higher for imidazole as than for *N*-methylimidazole. The k_c values for N-methylimidazole depend strongly on the alcohol concentration (exception Fig. IVb). The k_c values are much higher in MeCN. Both for imidazole and N-methylimidazole the rates of ethanolysis show little dependence on the concentration of ethanol. The two bases show similar catalytic effects (Fig. Ic, Id, IIc, IId, IIIc, IIId, IVc, IVd).

4. MeCN itself has no catalytic effect, since it has no significant influence on the rate of un-catalyzed alcoholysis.

5. Et$_3$N has an inhibiting effect on the catalyzed alcoholysis of silanethiols, although it acts as weak catalyst itself. The degree of inhibition depends strongly on the acidity of silanethiols, and is larger for (i-PrO)$_3$SiSH than for i-Bu$_3$SiSH (in benzene). THF shows a weak inhibiting effect.

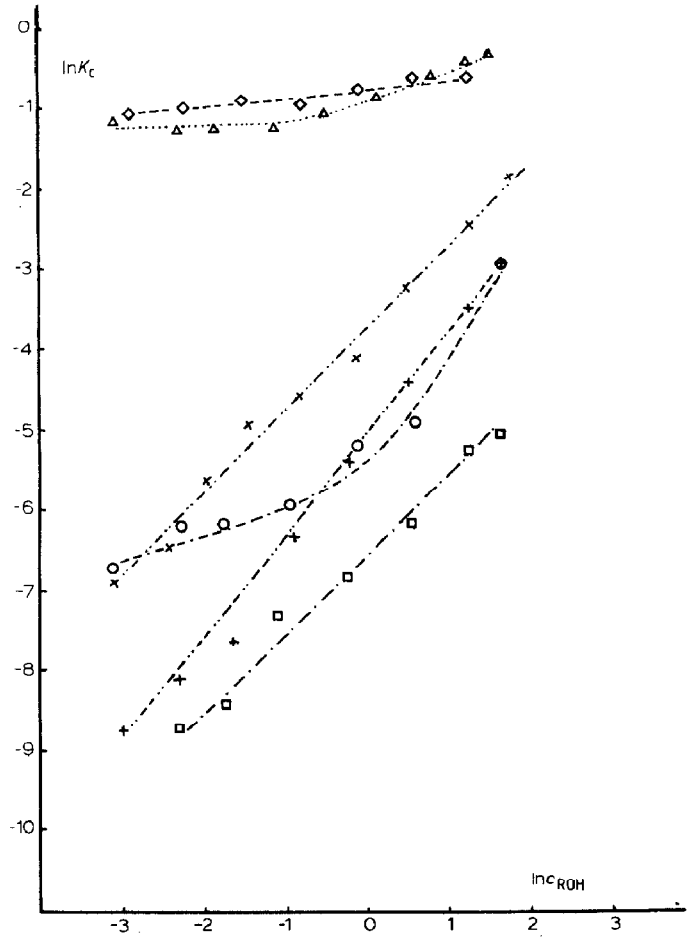

Fig. 2. Plot of ln k_c against ln c_{ROH} for IIa, ○ EtOH(im, benzene); IIb, □ EtOH(N-meim, benzene); IIc, △ EtOH(im, acetonitrile); IId, ◇ EtOH(N-meim, acetonitrile); IIe, × MeOH(im, benzene); and IIf + MeOH(N-meim, benzene).

6. The effects of the catalysts (in benzene solution) generally decreases in the sequence 4-meim > im > 2,4-me_2im > 2-meim > *N*-meim.

7. The reactivities of the silanethiols towards EtOH in C_6H_6 decreases in the sequence (i-PrO)$_3$SiSH > i-Bu(i-PrO)$_2$SiSH > i-Bu$_2$(i-PrO)SiSH ≫ i-Bu$_3$SiSH. For EtOH and imidazole the relative reactivities are 17 : 13 : 10 : 1 (EtOH 3.43M). In the case of MeOH the reactivity sequence depends to some extent on the methanol concentration. For 3.43 *M* MeOH the reactivity falls in the sequence (i-PrO)$_3$SiSH, i-Bu(i-PrO)$_2$SiSH, i-Bu$_2$(i-PrO)SiSH and i-Bu$_3$SiS, with the relative reactivities are 51/38/24/5 (with imidazole as catalyst).

8. The reactivities of the silanethiols in MeCN decrease in the sequence: i-Bu(i-PrO)$_2$SiSH > i-Bu$_2$(i-PrO)SiSH > (i-PrO)$_3$SiSH > i-Bu$_3$SiSH; e.g. for 3.43 *M* EtOH and 5×10^{-3} *M* imidazole the relative reactivities are 10.0/6.1/3.1/1.3 and for 3.43 *M* EtOH and 5×10^{-3} *M* *N*-methylimidazole they are 8.7/5.1/2.5/1.

9. The rate of reaction is not very sensitive to steric hindrance in the alcohol. For the base-catalyzed alcoholysis of R_3SiCl the reactivities fall markedly in the series: MeOH > EtOH > i-PrOH, the relative reactivities being $10^4/10^3/1$ [22].

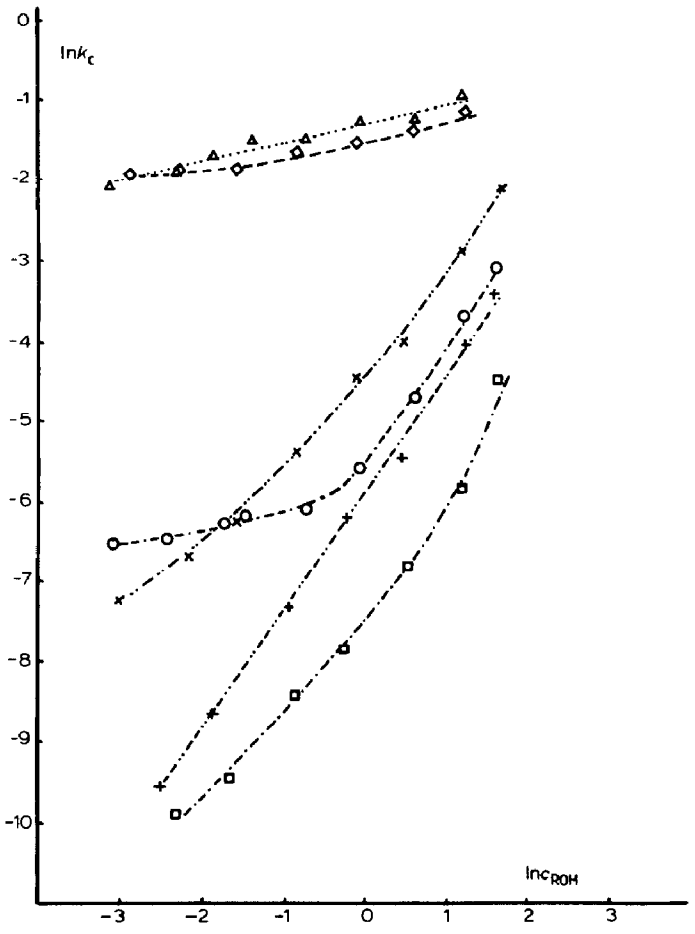

Fig. 3. Plot of ln k_c against ln c_{ROH} for IIIa, ○ EtOH(im, benzene); IIIb, □ EtOH(N-meim, benzene); IIIc, △ EtOH(im, acetonitrile); IIId, ◇ EtOH(N-meim, acetonitrile); IIIe, × MeOH(im, benzene) and IIIf, + MeOH(N-meim, benzene).

Discussion

In the light of the above observations we suggest the following mechanism for imidazole-catalyzed alcoholysis involving a steady state system of consecutive reactions with the first and second step reversible (Nu = imidazole or its derivatives)

$$R_3SiSH + Nu \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R_3Si(Nu)SH \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} [R_3SiNu]^+ SH^- \xrightarrow{k_3[EtOH]} R_3SiOEt + H_2S + Nu \tag{2}$$

This mechanism leads to eq. 3 for the overall reaction rate

$$\frac{d[R_3SiOEt]}{dt} = \frac{k_1k_2k_3[R_3SiSH][EtOH][Nu]}{k_{-2}k_{-1} + (k_2 + k_1)k_3[EtOH]} \tag{3}$$

For $(k_2 + k_1)k_3[EtOH] \gg k_{-2}k_{-1}$, this becomes:

$$\frac{d[R_3SiOEt]}{dt} = \frac{k_1k_2}{k_2 + k_1}[R_3SiSH][Nu] \tag{4}$$

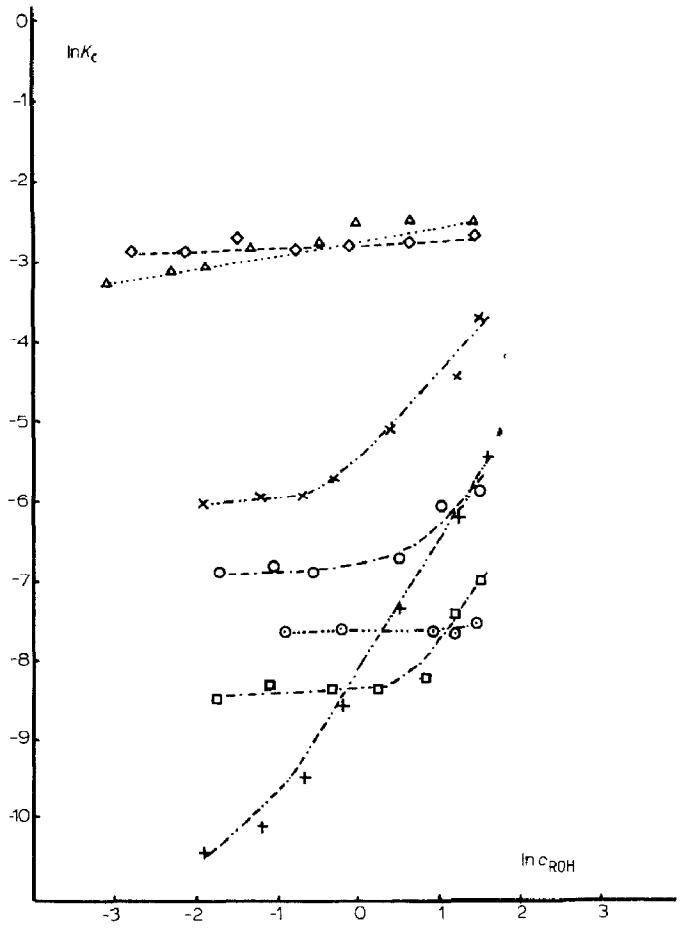

Fig. 4. Plot of ln k_c against ln c_{ROH} for IVa, ○ EtOH(im, benzene); IVb, □ EtOH(N-meim, benzene); IVc, △ EtOH(im, acetonitrile; IVd, ◇ EtOH(N-meim, acetonitrile); IVe, × MeOH(im, benzene); IVf, + MeOH(N-meim, benzene); IVg, ⊙ i-PrOH(im, benzene).

Our kinetic results are consistent with eq. 4. The order with respect to alcohol seems to be zero (see results p.2). The increase in the catalytic constant with increasing alcohol concentration in benzene is probably due to the change in the polarity of the medium and to variation of the hydrogen-bond systems; however, the influence of the alcohol concentration can be complex [23], and the solvation of the catalyst and silanethiols by the alcohol can greatly influence the reaction rates. This would lead to a different sensitivity of k_c towards the alcohol concentrations for the various silanethiols, alcohols, and catalysts. Our conclusion is supported by the fact that in MeCN solution the alcoholysis is of near zero order with respect to ethanol over the whole range of alcohol concentration for all four isosteric silanethiols. The results of IR studies [24] indicated that in binary systems the solute-nitrile interactions are generally stronger than solute-solute interactions, and therefore only solute-nitrile complex molecules are formed, and there are presumably single solute molecules bonded with single nitrile molecules. Thus MeCN probably counteracts the influence of the alcohol concentration on the various hydrogen bond equilibrias and also the influence of alcohol on the polarity of

medium. This would account for the observed near zero slope of the plot of ln k_c against ln c_{EtOH} for catalysis by imidazole and *N*-methylimidazole. The strong accelerating effect on the catalyzed reaction suggests that the reactive intermediate must have a silylimidazolium salt structure. The remarkable efficiency of imidazoles as catalysts is a consequence not only of their unhindered tertiary amine structure but also of the additional stabilization by resonance of these silylimidazolium salts.

The arguments above imply that the alcoholysis reaction probably proceeds through the rate determining formation of imidazolium salt in two reversible steps followed by a fast irreversible reaction with alcohol. Our mechanism is similar to that of the hydrolysis of acetic anhydride catalyzed by pyridine [25] and is different from the rate determining cleavage of the Si–X bond [9]. Our conclusion is supported by the fact that the reaction is not very sensitive to steric hindrance in the alcohol. The differences in the catalytic ability between imidazole and *N*-methylimidazole in benzene and the absence of such differences in MeCN probably indicate the greater sensitivity of *N*-methylimidazole than of imidazole to the polarity of medium and to the changes in the hydrogen bond equilibria.

It is not clear whether in the case of imidazole the second catalytic pathway involving *N*-silylated derivatives [19,20,21] is of importance.

The steric hindrance arising from a α-methyl substituent causes only a two-fold decrease in the catalytic ability of imidazole. In contact such α-substitution causes a large decrease in the catalytic efficiency of pyridine in the hydrolysis of acetic anhydride [25]. This difference is probably due to the greater susceptibility of silicon than of carbon towards nucleophilic substitution.

The reactivity series i-Bu(i-PrO)$_2$SiSH > i-Bu$_2$(i-PrO)SiSH > (i-PrO)$_3$SiSH > i-Bu$_3$SiSH observed can be best explained in terms of a geminal anomeric effect [26]. From our previous studies [1] it is evident, that for the compounds i-Bu$_n$(i-PrO)$_{3-n}$SiSH ($n = 0$–3 the σ^* (Si–S) orbitals (LUMO) are of comparable energies, so the differences in the HOMO–LUMO energies are not significant for kinetic effects. For i-Bu(i-PrO)$_2$SiSH the geminal anomeric effect constrains both i-Pr groups to be in the (g,g) conformation, with a marked rotation barrier about the Si–O axes. This effect lowers the overall steric hindrance in the i-Bu(i-PrO)$_2$Si system. This anomeric effect is of little significance in i-Bu$_2$(i-PrO)SiSH because the rotation barrier for geminal S–Si–O interactions is lower. The anomeric effect probably has only a small influence on the reactivity of (i-PrO)$_3$SiSH, in which the rotation around Si–O axes is relatively unhindered because (a,g) and (a,a) conformers allow interaction of the lone pairs of oxygen with σ^* (Si–O) or σ^*(Si–S) of the third SiOPr-i or SiSH moiety. In benzene solution the reactivity series is probably determined by both solvation and anomeric effects.

Kinetic studies

Solvents and alcohols used in kinetic studies were carefully purified by standard methods [28]. Solutions of the catalysts in benzene were refluxed over CaH_2 and the recovered bases then carefully sublimed or distilled under reduced pressure. Catalysts were dissolved in the appropriate alcohol to give a stock solution. The compounds i-Bu$_n$(i-PrO)$_{3-n}$SiSH were prepared as described previously [1]. i-Bu(i-PrO)$_2$SiSH must be distilled immediately before use because it condenses to a silthiane. The samples were introduced with a microliter syringe into a carefully

dried 5 ml vessel filled with argon which was sealed with a septum. The reactions were carried out at $20 \pm 1°C$.

The progress of the reaction was monitored by GC. The rate constants for the pseudo-first order reactions were calculated from the slope of the ln $h_t t_1/h_s t_s$ vs t, (isothermic conditions, h_t is the height of i-Bu$_n$(i-PrO)$_{3-n}$SiSH signal; t_t is the retention time for i-Bu$_n$(i-PrO)$_{3-n}$SiSH, h_s and t_s are the corresponding values for the standards). The reactions were carried out in most cases up to 80% conversion of the silanethiol. Rate constants were generally reproducible to about $\pm 10\%$. Small amounts of i-Bu$_n$(i-PrO)$_{3-n}$SiOH were found in some cases (10%).

GC - equipment: 1 m long column ϕ 4mm, 7% SE-30 on chromosorb W-NAW 80–100 mesh, argon 40 cm^3 min^{-1}, FID-detector. Standards used were $C_{12}H_{24}$ for (i-PrO)$_3$SiSH, $C_{14}H_{30}$ for i-Bu(i-PrO)$_2$SiSH and i-Bu$_2$(i-PrO)SiSH, and $C_{16}H_{34}$ for i-Bu$_3$SiSH.

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