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A FACILE SYNTHESIS OF TRIMETHYLSILYL THIOETHERS

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SUMMARY

Imidazole catalyzes the reaction of thiols with hexamethyldisilazane. This procedure affords a convenient method for the synthesis of trimethylsilyl thioethers. Some aspects of the mechanism of this reaction are discussed.

INTRODUCTION

Several methods have been reported[1] for preparing trimethylsilyl thioethers [(organothio)trimethylsilanes]. Hexamethyldisilazane, $(Me_3Si)_2NH$, has been reported to trimethylsilylate the thiol group of 2-propenethiol (in the presence of trimethylchlorosilane)[2], L-cysteine hydrochloride[3], and arenethiols[1f]. However, alkanethiols such as 1-butanethiol do not react readily with hexamethyldisilazane[4]. Therefore, a method for catalyzing the reaction between hexamethyldisilazane and alkanethiols was sought.

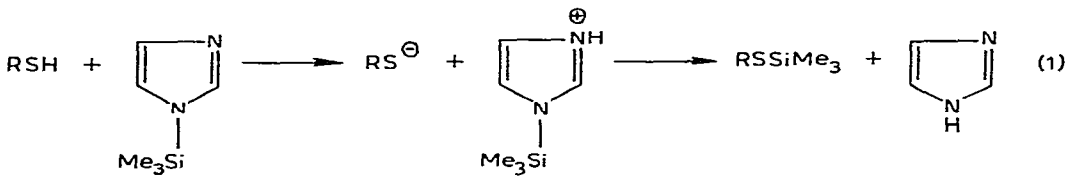
Louis and Urry[5] recently reported the preparation of hexamethyldisilthiane, $(Me_3Si)_2S$, by the reaction of hydrogen sulfide with 1-(trimethylsilyl)imidazole. Since both S–H bonds in hydrogen sulfide undergo trimethylsilylation with 1-(trimethylsilyl)imidazole, the S–H bond of thiols could reasonably be expected to undergo trimethylsilylation as well with this reagent. Furthermore, imidazole reacts readily with hexamethyldisilazane to yield 1-(trimethylsilyl)imidazole[6]. Thus, imidazole could reasonably be expected to catalyze the trimethylsilylation of thiols by hexamethyldisilazane via the intermediacy of 1-(trimethylsilyl)imidazole.

RESULTS AND DISCUSSION

Reaction of 1-decanethiol with 1-(trimethylsilyl)imidazole, at room temperature, gives $CH_3(CH_2)_9SSiMe_3$ and imidazole in 69 and 89% yield, respectively. Diphenylmethanethiol and 1-(trimethylsilyl)imidazole, at room temperature, afford Ph_2-$CHSSiMe_3$ and imidazole in 87 and 86 % yield, respectively. Treatment of 2-methyl-2-presentative primary and secondary, but not tertiary alkanethiols react with 1-(tri-$SSiMe_3$ in good yield. Analysis of the NMR spectrum of the reaction mixture suggests that only a low yield (ca. 15%) of $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$ is formed. Thus representative primary and secondary, but not tertiary alkanethiols react with 1-(trimethylsilyl)imidazole to give the corresponding trimethylsilyl thioether in prepara-

tively useful yields. Not only 1-(trimethylsilyl)imidazole but 1-(trimethylsilyl)-benzimidazole as well can effect silylation of thiols. For example, reaction of 1-decanethiol with 1-(trimethylsilyl)benzimidazole gave $CH_3(CH_2)_9SSiMe_3$ and benzimidazole in 56 and 92% yield, respectively.

A detailed investigation of the mechanism of the reaction of 1-(trimethylsilyl)-imidazole with thiols was not made. Nevertheless, some observations have been made which bear on this mechanism. The rate of reaction of benzenethiol with 1-(trimethylsilyl)imidazole is greater than that of 1-decanethiol with this reagent. Benzenethiol was shown to be a stronger acid than 1-decanethiol by the method of Salinger and West[7]. These workers demonstrated that the acidity of thiols correlates with the magnitude of the shift of the S–H stretching frequency between the free and hydrogen bonded thiol. This shift in the IR observed for benzenethiol using *N,N*-dimethylformamide as the base was 47 cm^{-1}*. The corresponding shift found for 1-decanethiol was 24 cm^{-1}. The IR method of Abel *et al.*[8] was used to demonstrate that hexamethyldisilazane is a weaker base than 1-(trimethylsilyl)imidazole. The shift in the C–D stretching frequency, in the infrared, of deuterochloroform in the presence of hexamethyldisilazane was 16 cm^{-1}**. This shift in the presence of 1-(trimethylsilyl)imidazole was 34 cm^{-1}. Thus the rate of silylation of thiols depends on the acidity of the thiol and the basicity of the silylating agent. This argues for proton transfer from the thiol to 1-(trimethylsilyl)imidazole occurring prior to or during the rate determining step. A simple mechanism incorporating this requirement is shown in eqn. (1).

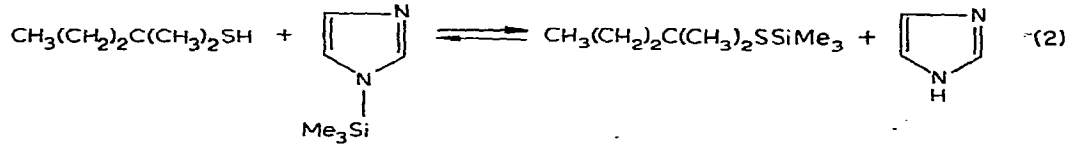


Once the ability of 1-(trimethylsilyl)imidazole to silylate alkanethiols was established the use of imidazole as a catalyst in the reaction of thiols with hexamethyldisilazane was investigated. Small amounts of imidazole markedly catalyze the reaction of primary, secondary, and tertiary alkanethiols with hexamethyldisilazane. Even the reaction of benzenethiol with hexamethyldisilazane is accelerated by the addition of small amounts of imidazole. These reactions are summarized in Table 1. In each case the IR, NMR, and mass spectra, and elemental microanalysis of the isolated trimethylsilyl thioethers supported the assigned structure.

As can be seen from Table 1 the yield of $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$ far exceeds the yield obtained by treating 2-methyl-2-pentanethiol with 1-(trimethylsilyl)-imidazole. This result at first glance would appear to preclude the intermediacy of 1-(trimethylsilyl)imidazole in the reaction of this thiol with hexamethyldisilazane and imidazole. However, there is an alternative explanation. The reaction of 2-methyl-2-pentanethiol with 1-(trimethylsilyl)imidazole to produce $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$ and imidazole is an equilibrium reaction, as shown in eqn. (2), in which the equilibrium

* This value agrees well with that determined in Ref. 7 (48 ± 4 cm^{-1})

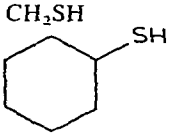
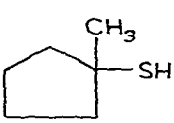
** This value does not agree with the shift reported in Ref. 8a (30 cm^{-1}) but is in agreement with that reported in Ref. 9 (15 cm^{-1}).



constant is considerably less than 1. This is substantiated by the fact that treatment of $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$ with imidazole gives a mixture very similar to the one obtained by treating $CH_3(CH_2)_2C(CH_3)_2SH$ with 1-(trimethylsilyl)imidazole. In the presence of hexamethyldisilazane, imidazole forms 1-(trimethylsilyl)imidazole and ammonia. Since the ammonia escapes from the reaction mixture as a gas, hexamethyldisilazane efficiently removes the imidazole formed as a result of the equilibrium shown in eqn. (2). This enables more $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$ to be formed and ultimately results in the formation of useful amounts of this trimethylsilyl thioether.

TABLE 1

REACTION OF THIOLS WITH HEXAMETHYLDISILAZANE IN THE PRESENCE OF IMIDAZOLE

Thiol	*Reaction time (h)*	*Yield of $RSSiMe_3$ (%)*	*B.p. (°C/mmHg)*
$CH_3(CH_2)_9SH$	3	89	78–82/0.05
CH_2SH CH_2SH	3	51[a]	145–150/40
	18	61	112–118/35
$(C_6H_5)_2CHSH$	3	93	109–112/0.02
C_6H_5SH	3	93	72–74/3[b]
$CH_3CH_2C(CH_3)_2SH$	72	50	124–132/135
	72	64	150–155/135
$CH_3(CH_2)_2C(CH_3)_2SH$	72	57	97–99/30

[a] The product isolated was $Me_3SiSCH_2CH_2SSiMe_3$ (twice the usual amount of hexamethyldisilazane was used in this case). [b] B.p. recorded in the literature for $PhSSiMe_3$: 40°/0.3 mmHg, Ref. 15; 72°/8 mmHg, Ref. 16; 71°/3 mmHg, Ref. 1g, p. 180.

Imidazole can conceivably catalyze the reaction of thiols with hexamethyldisilazane even without the formation of 1-(trimethylsilyl)imidazole. Thus imidazole can function as an acidic catalyst, a basic catalyst, or both (simultaneously or sequentially). However, the fact that, in aqueous solutions at least, thiols are stronger acids than imidazole* suggests that imidazole does not function solely as an acidic

* The pK_a^0 of imidazole in water is 14.52 according to Ref. 10. The K_a of 1-butanethiol in water is reported to be 1.65×10^{-11} in Ref. 11.

catalyst. Furthermore, the reaction of 1-decanethiol and hexamethyldisilazane proceeds faster in the presence of imidazole than in the presence of other acids such as pyrrole, indole* , ammonium chloride, acetic acid, or trimethylchlorosilane. The observation that 1-decanethiol reacts faster in the presence of imidazole than in the presence of other bases such as 1-methylimidazole** , pyridine, 2,6-di-tert-butylpyridine, triethylamine, and 1,5-diazabicyclo[5.4.0]undec-5-ene demonstrates that imidazole does not act only as a basic catalyst. Imidazole could function as both an acid and a base without the formation of 1-(trimethylsilyl)imidazole. However, not only is imidazole known to form 1-(trimethylsilyl)imidazole under the conditions of the reaction but on heating 1-decanethiol, hexamethyldisilazane, and imidazole a singlet rapidly appears in the NMR spectrum of the mixture which corresponds in chemical shift to the resonance of the protons of the Me_3Si group in 1-(trimethylsilyl)imidazole. Compounds other than imidazole which could conceivably function as both acidic and basic catalysts were studied. Benzimidazole, 2-hydroxypyridine, glycine, and L-phenylalanine could act as both acid and base. Furthermore, all of these compounds could catalyze the silylation via the intermediacy of trimethylsilyl derivatives. All of these compounds undergo silylation[6,14] with hexamethyldisilazane and 1-(trimethylsilyl)benzimidazole has been shown to silylate 1-decanethiol. Amino acids are especially interesting as catalysts because hexamethyldisilazane is reported[3] to silylate the thiol group in L-cysteine hydrochloride. This result suggests that amino acids (or ammonium chloride) can assist the silylation of thiols. Reaction of 1-decanethiol with hexamethyldisilazane is faster in the presence of imidazole than in the presence of any of these other four compounds.

EXPERIMENTAL

Elemental microanalyses were performed by analysts at the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Infrared spectra were measured using a Perkin–Elmer Model 137 IR Spectrophotometer except where noted otherwise. Proton NMR spectra were measured at 60 MHz using a Varian Model T-60 NMR Spectrometer on neat samples containing tetramethylsilane as an internal standard. Mass spectra were determined employing a Hitachi–Perkin–Elmer Model RMU-6E Double Focusing Mass Spectrometer. Melting points are corrected and were determined in capillary tubes using a Thomas–Hoover m.p. apparatus. All reactions were carried out under anhydrous conditions.

Reaction of thiols with hexamethyldisilazane in the presence of imidazole

A sample of thiol (12 mmol), hexamethyldisilazane (3.64 g, 22.6 mmol), and recrystallized imidazole (30 mg, 0.45 mmol) were stirred and heated at reflux for the time indicated in Table 1. The excess hexamethyldisilazane was removed by distillation at atmospheric pressure and the resulting liquid was fractionally distilled under vacuum. The IR spectrum for each of the products listed in Table 1 was consistent

* Neither pyrrole (see Ref. 12) nor indole alone reacts with hexamethyldisilazane to produce the corresponding 1-trimethylsilyl derivative.

** The pK_a for the conjugate acid of imidazole is 6.95 and that for the conjugate acid of 1-methylimidazole is 7.25. See Ref. 13.

with the assigned structure. The mass spectrum for each product listed in Table 1 showed a parent peak at the calculated *m/e* value. The proton NMR spectrum and elemental microanalysis for each trimethylsilyl thioether follows:

$CH_3(CH_2)_9SSiMe_3$ proton NMR spectrum. δ 0.25 s (Me_3Si); 0.73–1.67 m [$CH_3(CH_2)_8$]; 2.4 ppm d [CH_2S, J(H–H) 6 Hz]. (Found: C, 63.6; H, 12.4; S, 12.9. $C_{13}H_{30}SSi$ calcd.: C, 63.3; H, 12.3; S, 13.0%.)

$Me_3SiSCH_2CH_2SSiMe_3$ proton NMR spectrum: δ 0.28 s (Me_3Si); 2.6 ppm s (CH_2). (Found: C, 40.0; H, 9.1; S, 27.0. $C_8H_{22}S_2Si_2$ calcd.: C, 40.3; H, 9.3; S, 26.9%.)

$Ph_2CHSSiMe_3$ proton NMR spectrum. δ 0.09 s (Me_3Si); 5.2 s (CH); 6.9–7.6 ppm m (C_6H_5). (Found: C, 71.0; H, 7.3; S, 11.6. $C_{16}H_{20}SSi$ calcd.: C, 70.5; H, 7.4; S, 11.8%.)

$PhSSiMe_3$ proton NMR spectrum. δ 0.20 s (Me_3Si); 7.0–7.5 ppm m (C_6H_5). (Found: C, 59.1; H, 7.8; S, 16.9. $C_9H_{14}SSi$ calcd.: C, 59.3; H, 7.7; S, 17.6%.)

$(CH_2)_5CHSSiMe_3$ proton NMR spectrum. δ 0.25 s (Me_3Si); 1.1–2.1 m [$(CH_2)_5$]; 2.7 ppm br (CH). (Found: C, 57.3; H, 10.6; S, 16.4. $C_9H_{20}SSi$ calcd.: C, 57.4; H, 10.7; S, 17.0%.)

$CH_3CH_2C(CH_3)_2SSiMe_3$ proton NMR spectrum. δ 0.28 s (Me_3Si); 0.97 t [CH_3CH_2, J(H–H) 7 Hz]; 1.35 s [$(CH_3)_2C$]; 1.47 ppm q [CH_2, J(H–H) 7 Hz]. (Found: C, 54.4; H, 11.2; S, 17.6. $C_8H_{20}SSi$ calcd.: C, 54.5; H, 11.4; S, 18.2%.)

$(CH_2)_4C(CH_3)SSiMe_3$ proton NMR spectrum. δ 0.30 s (Me_3Si); 1.47 s (CH_3); 1.4–2.1 ppm m [$(CH_2)_4$]. (Found: C, 57.1; H, 10.5; S, 16.7. $C_9H_{20}SSi$ calcd.: C, 57.4; H, 10.7; S, 17.0%.)

$CH_3(CH_2)_2C(CH_3)_2SSiMe_3$ proton NMR spectrum. δ 0.30 s (Me_3Si); 0.92 m (CH_3CH_2); 1.37 s [$(CH_3)_2C$]; 1.3–1.9 ppm m [$(CH_2)_2$]. (Found: C, 56.4; H, 11.5; S, 16.2. $C_9H_{22}SSi$ calcd.: C, 56.8; H, 11.6; S, 16.8%.)

Catalysis of the reaction of benzenethiol with hexamethyldisilazane by imidazole

A solution of distilled benzenethiol (55 mg, 0.50 mmol) and hexamethyldisilazane (182 mg, 1.04 mmol) was placed in an NMR tube. In another NMR tube was placed distilled benzenethiol (56 mg, 0.51 mmol), hexamethyldisilazane (187 mg, 1.07 mmol) and purified imidazole (5.0 mg, 0.074 mmol). Both NMR sample tubes were placed in a bath maintained at 85° and shaken. At regular intervals both samples were removed from the bath and their NMR spectra measured. The NMR spectra demonstrated that the rate of silylation of benzenethiol is faster in the presence of imidazole.

Reaction of 1-decanethiol with 1-(trimethylsilyl)imidazole

To a sample of distilled 1-(trimethylsilyl)imidazole (1.61 g, 11.5 mmol) prepared according to the method of Birkofer *et al.*[6] and cooled in an ice/water bath was added distilled 1-decanethiol (1.75 g, 10.1 mmol). The solution was stirred and allowed to warm to room temperature over 24 h. At the end of this time dried pentane was added to the mixture. The solution was decanted from the solid. The colorless solid was washed with additional pentane to give 608 mg (89% yield) of imidazole: m.p. 90–91°. The decanted solution and the pentane washings were combined and the solvent removed by distillation at atmospheric pressure. The resulting oil was fractionally distilled under vacuum to give 1.59 g (69% yield) of $CH_3(CH_2)_9SSiMe_3$: b.p. 79–80°.

Reaction of diphenylmethanethiol with 1-(trimethylsilyl)imidazole

A sample of distilled diphenylmethanethiol (1.365 g, 6.83 mmol) was added to a sample of distilled 1-(trimethylsilyl)imidazole (1.027 g, 7.34 mmol) cooled in an ice/water bath. The mixture was stirred and allowed to warm to room temperature over 16 h during which time a precipitate formed. At the end of this time dried n-hexane was added and the mixture separated by decantation. The solid was washed with n-hexane and then recrystallized from benzene to give 401 mg (86% yield) of imidazole: m.p. 89–91°. The solution and the n-hexane washings were fractionally distilled to afford 1.612 g (87% yield) of $Ph_2CHSSiMe_3$: b.p. 115–118°.

Reaction of 1-decanethiol with 1-(trimethylsilyl)benzimidazole

A sample of distilled 1-(trimethylsilyl)benzimidazole (1.073 g, 5.65 mmol) prepared according to the method of Birkofer *et al.*[6] was dissolved in dried, distilled carbon tetrachloride (1.5 ml). To this stirred solution was added distilled 1-decanethiol (871 mg, 5.00 mmol). A small portion (0.5 ml) of carbon tetrachloride was used to wash the thiol into the reaction flask. The solution was stirred at room temperature for 24 h during which time a precipitate formed. Dried pentane was then added to the mixture and the solution decanted. The solid was washed with pentane and gave 547 mg (92% yield) of benzimidazole: m.p. 172–173°. The decanted solution and the pentane washings were combined and fractionally distilled first at atmospheric then reduced pressure to give 688 mg (56% yield) of $CH_3(CH_2)_9SSiMe_3$: b.p. 89–95°.

Reaction of 2-methyl-2-pentanethiol with 1-(trimethylsilyl)imidazole

A sample of distilled 2-methyl-2-pentanethiol (1.192 g, 10.1 mmol) prepared according to the method of Moore and Saville[17] and a sample of distilled 1-(trimethylsilyl)imidazole (1.552 g, 11.1 mmol) were stirred at room temperature for 49 h. No precipitate formed. The NMR spectrum of the solution revealed absorptions due to starting materials as well as a small amount of $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$. The ratio of 1-(trimethylsilyl)imidazole to $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$ could not be accurately determined because of overlapping of peaks in the NMR spectrum. However, this ratio was approximately 4/1. Heating the solution under reflex for 69 h caused the solution to turn orange but no precipitate formed. The solution was allowed to cool to room temperature (no precipitate formed) and NMR spectrum measured. The ratio of 1-(trimethylsilyl)imidazole to $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$ could not be accurately ascertained but appeared to be about 6/1.

Comparison of the reaction rate of 1-decanethiol with hexamethyldisilazane in the presence of imidazole and in the presence of other potential catalysts

A solution of distilled 1-decanethiol (0.5 mmol) and hexamethyldisilazane (1.1 mmol) was placed in an NMR tube containing the potential catalyst (0.03–0.09 mmol). A mixture consisting of 1-decanethiol (0.5 mmol), hexamethyldisilazane (1.1 mmol) and purified imidazole (an amount equimolar to the other potential catalyst to which imidazole is being compared) was placed in another NMR tube. The NMR tubes were placed in a bath maintained at 90–105° and the tubes were removed at appropriate time intervals and the NMR spectrum recorded.

Reaction of imidazole with $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$

A sample of distilled $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$ (276 mg, 1.45 mmol) and

purified imidazole (101 mg, 1.49 mmol) in an NMR tube were shaken in a bath maintained at 60°. The solid dissolved within 2 min. After 10 min the sample was allowed to cool to room temperature and the NMR spectrum of the solution was measured. The NMR spectrum closely resembled that obtained by the reaction of 2-methyl-2-pentanethiol with 1-(trimethylsilyl)imidazole. Thus the solution consists predominantly of 1-(trimethylsilyl)-imidazole and 2-methyl-2-pentanethiol. The ratio of 1-(trimethylsilyl)imidazole to $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$ could not be accurately determined due to overlapping peaks in the NMR spectrum but appeared to be approximately 4/1. The sample was again placed in a bath maintained at 60° for 23 h. At the end of this time the sample was allowed to cool to room temperature and then its NMR spectrum measured. The spectrum was very similar to that obtained before. Perhaps the ratio of 1-(trimethylsilyl)imidazole to $CH_3(CH_2)_2C(CH_3)_2SSiMe_3$ in the mixture was 5/1.

Relative rate of reaction of 1-*decanethiol and benzenethiol with* 1-(*trimethylsilyl*)-*imidazole*

A sample of distilled 1-(trimethylsilyl)imidazole (358 mg, 2.55 mmol) was dissolved in carbon tetrachloride distilled from phosphorus pentoxide and the solution was diluted to 10.0 ml with dry carbon tetrachloride. A carefully measured amount of this solution (1.00 ml) was added to distilled 1-decanethiol (44 mg, 0.25 mmol) and another portion (1.00 ml) of this solution was added to a separate sample of distilled benzenethiol (28 mg, 0.25 mmol). The rate of both reactions was followed by measuring the NMR spectra of the solutions at appropriate times. The rate of silylation of benzenethiol exceeded that of 1-decanethiol.

IR determination of the relative acidity of 1-*decanethiol and benzenethiol*

The carbon tetrachloride used for these experiments was distilled from phosphorus pentoxide prior to use. The *N*,*N*-dimethylformamide used in these determinations was spectrograde material distilled from calcium hydride under vacuum just prior to use. All transfers were done in a glove bag under an atmosphere of dry nitrogen.

A sample of the distilled mercaptan (2.0 mmol) was dissolved in carbon tetrachloride and diluted to 2.00 ml. This material was placed in a 1.0 mm sodium chloride cell and the S–H stretching vibration of the mercaptan in this solution measured with a Beckman Model IR-12 IR spectrophotometer. The hydrogen bonded S–H stretching frequency was measured in a solution containing the mercaptan diluted to 2.00 ml with a 2.50 *M* solution of *N*,*N*-dimethylformamide in carbon tetrachloride.

IR determination of the relative basicity of hexamethyldisilazane and 1-(*trimethylsilyl*)-*imidazole*

The carbon tetrachloride used in this experiment was distilled from phosphorus pentoxide. The hexamethyldisilazane and deuterochloroform were freshly opened purified samples obtained from Aldrich Chemical Company. All transfers were done in a glove bag under an atmosphere of dry nitrogen. The C–D stretching vibrations were determined using a Beckman Model IR-12 IR spectrophotometer on solutions in a 1.0 mm sodium chloride cell.

The solution used for determining the basicity of hexamethyldisilazane was

prepared by dissolving deuterochloroform (54 mg, 0.45 mmol) in hexamethyldisilazane (785 mg, 4.86 mmol). A similar solution containing 1-(trimethylsilyl)imidazole in place of hexamethyldisilazane did not show a free C–D stretching vibration. However, the following solution exhibited both free and hydrogen bonded C–D stretching vibrations: distilled 1-(trimethylsilyl)imidazole (11 mg, 0.080 mmol), deuterochloroform (77 mg, 0.64 mmol) and carbon tetrachloride (671 mg). Solutions of 1-(trimethylsilyl)imidazole in carbon tetrachloride did not absorb in the region characteristic of the C–D stretching vibration. A solution containing imidazole (5.7 mg, 0.084 mmol), deuterochloroform (77 mg, 0.64 mmol), and carbon tetrachloride (671 mg) could not be prepared owing to the insolubility of imidazole in this solvent system. However, the IR spectrum of a solution of deuterochloroform (77 mg, 0.64 mmol) and carbon tetrachloride (671 mg) saturated with imidazole was recorded. A doublet in the C–D stretching vibration region is not observed (there is only a shoulder on the peak due to the free C–D stretching vibration). Thus, the doublet observed in the spectrum of 1-(trimethylsilyl)imidazole and deuterochloroform is not due to imidazole.

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