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Reactions of heteroarylhydrosilanes with dichlorocarbene under phase-transfer conditions

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Abstract

The reactions of dimethyl(2-thienyl)-, methyl[di(2-thienyl)]-, tri(2-thienyl)- and dimethyl(2-furyl)silanes (I–IV, respectively) with dichlorocarbene generated from sodium trichloroacetate under solid-liquid phase-transfer conditions afford the corresponding dichloromethylsilanes in 38–66% yield. The reactivity of the thienylsilanes decreases with the number of electron-accepting thienyl substituents at the silicon atom. Using the competition reactions, the relative rate constants for the reaction of dichlorocarbene insertion into the Si–H bond of thienyl- and furyl-silanes (I and IV) were measured. The reactivity of these silanes was found to be greater than had been expected taking as a basis the Taft σ^* constants for the substituent at the silicon atom. This is apparently due to the existence of a p_π–d_π interaction between the heterocyclic π-system and the d-orbitals of silicon.

Introduction

The reaction of hydrosilanes with dihalocarbenes (=CX_2) discovered by Seyferth and Burtlitch [1] leads to the insertion of =CX_2 into the Si–H bond. This reaction has been intensively investigated by a number of authors who have studied the Si–H bond reactivity, the reaction stereochemistry and the mechanism [2,3]. Phenyl(trihalomethyl)mercury [1,4,5] and sodium trichloroacetate [5,7] are commonly used as =CX_2 precursors, both of them leading to free singlet dihalocarbene [5]. Application of $Cl_3CCOONa$ for =CCl_2 generation in the reactions with hydrosilanes gives, as a rule, the corresponding dichloromethylsilanes in lower yields than in the case of $PhHgCX_3$ [5,6]. Nonetheless, the trichloroacetate method has certain advantages, largely due to the low cost and ease of preparation of $Cl_3CCOONa$. Moreover, the capabilities of this method have been invigorated owing to the appearance of a phase-transfer pathway of dichlorocarbene generation using solid-liquid phase-transfer catalysis (PTC) with quaternary ammonium salts [8] or crown-ethers [9,10]. By this route, starting from a number of alkyl- and arylhydrosilanes, the corresponding dichloromethylsilanes were prepared in ca. 50–70% yield [10].

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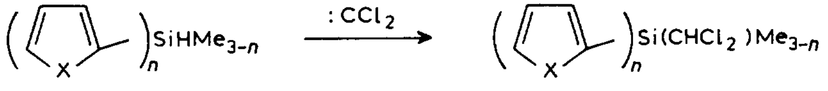
In the present work, the reactions of 2-thienyl- and 2-furyl-containing hydrosilanes with dichlorocarbene generated by thermal decomposition of sodium trichloroacetate were examined under PTC conditions. To our knowledge, such data pertaining to this type of reaction that involves heteroaryl-substituted hydrosilanes are absent in the literature.

Results and discussion

The starting (2-thienyl)hydrosilanes (I–III) were prepared by the procedures described in refs. 11–13 using the reactions of (2-thienyl)magnesium bromide with the appropriate chlorosilane in the stoichiometric ratio. Dimethyl(2-furyl)silane (IV) was synthesized by the reaction of 2-furyllithium with dimethylchlorosilane as described in ref. 14. The reactions of hydrosilanes I–IV with sodium trichloroacetate were carried out in toluene at reflux temperature. 18-Crown-6 was used as the phase-transfer catalyst. The reaction course was monitored by GLC and GLC/MS analysis.

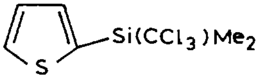
When a toluene solution of dimethyl(2-thienyl)silane (I) containing 3 mol-equiv. of $Cl_3CCOONa$ and 0.1 mol-equiv. of 18-crown-6 was heated under reflux for 3 h, the starting silane I underwent almost 100% conversion to give dimethyl(dichloromethyl)(2-thienyl)silane (V) in 66% yield (Table 1).



(I–IV) (V–VIII)

(I, V: X = S, $n = 1$; II, VI: X = S, $n = 2$; III, VII: X = S, $n = 3$;
IV, VIII: X = O, $n = 1$)

GLC/MS analysis of the reaction mixture revealed the presence of small amounts (ca. 3%) of another product, namely dimethyl(trichloromethyl)(2-thienyl)silane (IX). Isotopic peaks of molecular ions at m/z 258, 260, 262 and 264 were observed in the mass spectrum of IX, the ratio of the relative intensities corresponding to the presence of three chlorine atoms in the molecule. The general route of molecular ion fragmentation under electron impact is the loss of $\cdot CCl_3$ radical with the formation of the ion radical $[(2\text{-thienyl})SiMe_2]^{+\cdot}$ (m/z 141). Under similar PTC conditions, the formation of products of type IX has not been observed in the reactions of alkyl- and arylhydrosilanes with sodium trichloroacetate [10]. Dichloromethylsilane V was isolated from the reaction mixture in 52% yield by vacuum distillation.



(IX)

Di(2-thienyl)- and tri(2-thienyl) silanes (II and III) react with dichlorocarbene similarly to silane I to afford the corresponding dichloromethyl derivatives (VI and VII, see Table 1). However, the reactivity of the thienylsilanes decreases with the

Table 1

Reactions of heteroarylhydrosilanes with dichlorocarbene under PTC conditions

Hydrosilane	Amount of $Cl_3CCOONa$ (mol-equiv.)	Reaction time (h)	Dichloromethylsilane	Yield (%) (GLC data)
I	3	3	V	66 (52) [a]
II	9	18	VI	43 (54) [b]
III	12	24	VII	54 (61) [b]
IV	3	3	VIII	42

[a] Isolated yield. [b] Isolated yield using $PhHgCCl_3$ as the dichlorocarbene precursor.

number of electron-accepting thienyl substituents at the silicon atoms. To achieve 100% conversion of II and III, a greater excess of sodium trichloroacetate is required, the duration of the reaction increasing considerably. The yields of silanes VI and VII were determined chromatographically using authentic samples of VI and VII prepared by the reactions of II and III with phenyl(trichloromethyl)mercury (benzene, 80 ° C) as standards.

Dimethyl(2-furyl)silane (IV) reacts with dichlorocarbene essentially as thienylsilane I; however, the yield of dimethyl(dichloromethyl)(2-furyl)silane (VIII) is appreciably lower (42%); several unidentified components are also present in the reaction mixture. The individual silane VIII was isolated from the mixture by preparative GLC.

Characteristic singlets of $CHCl_2$ group protons and multiplets of the ring protons (ABX system) typical of 2-silyl substituted thiophenes and furans [15] are observed in the ^1H NMR spectra of (dichloromethyl)heteroarylsilanes (Table 2). The mass spectra of V–VIII (Table 2) contain a set of isotopic molecular ion peaks, the ratio of the intensities indicating the presence of two chlorine atoms. The fragmentation pattern of the molecular ions in all cases is identical. The general fragmentation route is the loss of the $CHCl_2$ radical and the formation of the cation radical $[(\text{heteroaryl})_nSiMe_{3-n}]^{+\cdot}$ with 100% relative abundance.

Benzene and chloroform were also tested as solvents for the reaction of heteroarylsilanes with $Cl_3CCOONa$ under PTC conditions. In both solvents the reaction proceeds more slowly than in toluene; moreover, chloroform must be purified from ethanol before use. When ethanol was present, for example in the case of furylhydrosilane IV, both dichloromethylsilane VIII and silane X were found by chromatography mass spectrometry in the reaction mixture. The amount of X was

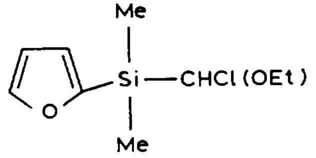
Table 2

^1H NMR and mass spectral data for $R_nSiMe_{3-n}CHCl_2$

R	n	Chemical shift, δ (ppm)					m/z (rel. abundance, %) [a]
		Me	CH	H(3)	H(4)	H(5)	
2-Thienyl	1	0.53	5.28	7.33	7.13	7.58	244 (M^+, 3), 141 ($M^+ - CHCl_2$, 100)
2-Thienyl	2	0.86	5.51	7.49	7.20	7.67	292 (M^+, 1), 209 ($M^+ - CHCl_2$, 100)
2-Thienyl	3	–	5.75	7.57	7.24	7.73	360 (M^+, 0.3), 277 ($M^+ - CHCl_2$, 100)
2-Furyl	1	0.51	5.37	6.84	6.44	7.69	208 (M^+, 4), 125 ($M^+ - CHCl_2$, 100)

[a] Peaks of ^{35}Cl-containing ions are given.

found to be comparable with that of VIII and evidently resulted from the nucleophilic displacement of one chlorine atom in VIII for an ethoxy group. The characteristic peaks in the mass spectrum of silane X, 220/218 (M^+), 183 ($M^+ - Cl$) and 175/173 ($M^+ - OEt$), provide evidence in favour of this structure.



(X)

We also examined the applicability of polymeric crown-ether, namely poly(dibenzo-18-crown-6) [16], insoluble in the reaction mixture, as a phase-transfer catalyst for the reaction of silane I with sodium trichloroacetate. Using triphase catalysis [17] under reflux of $Cl_3CCOONa$ and polymeric crown-ether suspension in the toluene solution of hydrosilane I, the formation of dichloromethylsilane IV failed to occur. Thus, this PTC variant is unsuitable for the given reaction. We also sought to facilitate the reaction of silane I and $Cl_3CCOONa$ with the aid of ultrasonic irradiation, which has often been applied over the last few years in organic synthesis to accelerate various heterogeneous reactions (for recent reviews see refs. 18 and 19). It was found, however, that when a mixture of I, 18-crown-6 and $Cl_3CCOONa$ was refluxed under ultrasonication (Branson® B-52 ultrasonic cleaner, 45 kHz, 250 W), no reaction enhancement could be achieved as compared with the reaction performed under the same conditions in the absence of ultrasonication.

It was concluded on the basis of stereochemical and kinetic evidence obtained for the reactions of hydrosilanes with dihalocarbene generated from phenyl(trihalomethyl)mercury that the insertion mechanism involves electrophilic attack at the Si–H bond by the carbene, resulting in the formation of a three-centre, weakly polar transition state [4,5,20]. The same mechanism was confirmed by kinetic data [7] obtained for dichlorocarbene insertion into the Si–H bond using $=CCl_2$ generated by thermal decomposition of $Cl_3CCOONa$ in dimethoxyethane after the competition reaction technique. It has been shown [7] that the relative rate constants of these reactions are correlated with the Taft σ^* constants for substituents at the silicon atom both in alkyl- and aryl-silanes. In the case of thienyl- and furyl-silanes, specific electronic effects have been discovered [15], presumably due to the interaction of the heterocyclic π-electrons with the d-orbitals of silicon. Therefore, it was of interest to assess the influence of the heterocyclic substituent at the silicon atom in the hydrosilanes on the reactivity of the Si–H bond in the dichlorocarbene insertion reaction. With recourse to the competition reaction technique, we determined the relative rate constants (k_{rel}) for the reactions of thienyl- and furylsilanes (I and IV) with dichlorocarbene using dimethylphenylsilane as a reference compound. The procedure was similar to that described in ref. [7]: a mixture of silane I (or IV), $PhSiMe_2H$, sodium trichloroacetate and 18-crown-6 in the molar ratio 5/5/1/0.1 was allowed to react, and the value of k_{rel} was determined on the basis of the concentration ratio of the two products. Taking k_{rel} for $PhSiMe_2H$ to be equal to 1, the values of k_{rel} for silanes I and IV were found to be 0.83 ± 0.04

and 0.77 ± 0.04, respectively. Comparison of these values with known Taft $\sigma^\star$ constants for phenyl (+0.6 [21]), 2-thienyl (+1.3 [22]) and 2-furyl (+1.5 [23]) substituents has shown that there is no correlation between the Taft $\sigma^\star$ constants and k_{rel} observed for alkyl- and aryl-hydrosilanes [7] in the series of compounds I, IV and $PhSiMe_2H$. The reactivity of the Si–H bond in thienylsilane I and furylsilane IV appears to be greater than could be expected on the basis of the Taft $\sigma^\star$ constants for heterocyclic substituents. These results confirm the presence of the p_π–d_π interaction mentioned above, whose direction is opposite to that of the inductive effect of the thienyl or furyl radical. Multinuclear NMR findings indicate that the degree of interaction of the heteroaryl substituent with the silicon atom in silanes of the (heteroaryl)$_n$SiMe$_{4-n}$ type decreases in the following order: 2-furyl > 2-thienyl > phenyl [15]. This circumstance probably explains essentially the same reactivity of hydrosilanes I and IV, on the one hand, and the similar reactivities of heteroaryl- and phenyl-silanes, on the other. It should also be noted that the p_π–d_π interaction explains [2] the relatively high reactivity of hexynylhydrosilanes of the $n\text{-}C_4H_9C{\equiv}CSiMe_{3-m}H_m$ ($m = 1$–3) type as compared with that expected on the basis of the Taft $\sigma^\star$ constant for alkynyl substituent.

Experimental

^1H NMR spectra were recorded on a Bruker WH-90/DS spectrometer using $CDCl_3$ as solvent and Me_4Si as internal standard. Mass spectra were recorded on a Kratos MS-25 (70 eV) chromato-mass spectrometer. GLC analysis was performed on a Chrom-5 instrument equipped with a flame-ionization detector. A glass column (1.2 m × 3 mm) was packed with 5% OV-17/Chromosorb W-HP (80-100 mesh) (column A) or 10% SE-30 + 2.5% Reoplex-400/Chromosorb W-AW (60-80 mesh) (column B). Helium (50 cm^3/min) was used as the carrier gas. The GLC analysis temperature was varied depending on the composition of mixture to be analysed (see below).

Dimethyl(2-thienyl)silane (I) [11], methyl[di(2-thienyl)]silane (II) [12], tri(2-thienyl)silane (III) [13] and dimethyl(2-furyl)silane (IV) [14] were prepared as described. Sodium trichloroacetate was prepared by a known procedure [24] and was carefully dried in vacuo prior to use. 18-Crown-6 and phenyl(trichloromethyl)-mercury were Fluka products and were used without further purification.

Dimethyl(dichloromethyl)(2-thienyl)silane

To a solution of dimethyl(2-thienyl)silane (I, 1.42 g, 10 mmol) and 18-crown-6 (0.26 g, 1 mmol) in 20 ml of dry toluene was added finely powdered sodium trichloroacetate (5.56 g, 30 mmol). The resulting mixture was refluxed to eliminate the starting silane I from solution (2.5–3 h, GLC control: column A, 170 °C). The reaction mixture was cooled and filtered through Celite 545. Toluene was removed by distillation and the residue was fractionated in vacuo to afford 1.17 g (52%) of silane V; yellowish liquid, b.p. 130 °C/30 mmHg; found: C, 37.55, H, 4.42. $C_7H_{10}Cl_2SSi$ calcd.: C, 37.33; H, 4.44%; for ^1H NMR and mass spectral data, see Table 2.

Methyl(dichloromethyl)[di(2-thienyl)]silane (VI)

To a solution of methyl[di(2-thienyl)]silane (II) (1.1 g, 5 mmol) and 18-crown-6 (0.13 g, 0.5 mmol) in 10 ml of dry toluene was added sodium trichloroacetate (2.78

g, 15 mmol), and the reaction mixture was heated under reflux for 6 h. After filtration through Celite 545, sodium trichloroacetate (2.78 g, 15 mmol) was repeatedly added and the mixture was heated under reflux for an additional 6 h. The described procedures were repeated once again and refluxing was continued for another 6 h. The yield of silane VI was determined by GLC (column A, 180 °C/2 min, 180–250 °C/20 °C/min) using the absolute calibration technique. The sample of VI obtained by the reaction of II with $PhHgCCl_3$ (see below) was used as a standard. The yield of VI (GLC) was 43%; for ^1H NMR and mass spectral data, see Table 2.

Dichloromethyl[tri(2-thienyl]silane (VII)

Silane VII was prepared as described above for VI using 0.69 g (2.5 mmol) of tri(2-thienyl)silane (III), 0.066 g (0.25 mmol) of 18-crown-6 and 1.39 g (7.5 mmol) of $Cl_3CCOONa$ in 5 ml of dry toluene. Unlike in the synthesis of VI, fresh portions of sodium trichloroacetate were added three times at 6-h intervals. The total reaction time was 24 h; the yield of VII was 54% (GLC, Column A, 250 °C); for ^1H NMR and mass spectral data, see Table 2.

Reactions of hydrosilanes II and III with phenyl(trichloromethyl)mercury

A solution of 0.42 g (2 mmol) of silane II and 0.792 g (2 mmol) of $PhHgCCl_3$ in 2 ml of dry benzene in a 5 cm^3 Pierce reacti-vial was heated at 80 °C for 24 with magnetic stirring. Fresh portions of $PhHgCCl_3$ were added to the reaction mixture at 6-h intervals (3×2 mmol). The mixture was cooled, filtered and the benzene was removed by distillation in vacuo. The viscous residue was purified by column chromatography on silica gel, using n-hexane as eluant, to give silane VI (0.315 g, 54%) as a viscous yellowish oil. Found: C, 41.56; H, 3.36. $C_{10}H_{10}Cl_2S_2Si$ calcd.: C, 40.96; H, 3.41%. This product was used for the determination of the yield of VI (by GLC) in the reaction of II with sodium trichloroacetate.

The reaction of hydrosilane III with $PhHgCCl_3$ was carried out as described for II using 0.14 g (0.5 mmol) of III and 0.2 g (0.5 mmol) of $PhHgCCl_3$ in 1 ml of dry benzene. The duration of the reaction was 24 h, 0.5 mmol of $PhHgCCl_3$ being added to the mixture at 4-h intervals. Compound VII was isolated as a yellowish powder by column chromatography on silica gel using n-hexane as eluant. Yield: 0.11 g (61%), m.p. 77–78 °C; found: C, 43.19; H, 2.35. $C_{13}H_{10}Cl_2S_3Si$ calcd.: C, 43.21; H, 2.77%. This product was used as a standard for the determination of the yield of VII (by GLC) in the reaction of III with $Cl_3CCOONa$.

Dimethyl(dichloromethyl)(2-furyl)silane (VIII)

Compound VIII was prepared as described above for V using 0.56 g (4.5 mmol) of hydrosilane IV, 0.12 g (0.45 mmol) of 18-crown-6 and 2.45 g (13.5 mmol) of sodium trichloroacetate in 9 ml of dry toluene (heating for 3 h at reflux temperature; GLC control: column A, 120 °C). Yield of VIII: 42% (by GLC). The reaction mixture was filtered through Celite 545, and toluene was removed by vacuum distillation to afford VIII containing unidentified impurities. An analytical sample of VIII was isolated on a Pye Unicam 105 chromatograph (1 m × 7 mm column packed with 10% SE-30/Chromaton N AW-DMCS, 60-80 mesh; 150 °C) as a pale yellowish liquid gradually darkening in air. Found: C, 41.16; H, 4.83. $C_7H_{10}Cl_2OSi$ calcd.: C, 40.19; H, 4.78%; for ^1H NMR and mass spectral data, see Table 2.

Procedure for competition reactions

A mixture of two hydrosilanes (3.5 mmol of each) and 10.6 mg (0.07 mmol) of 18-crown-6 was dissolved in 2.5 ml of dry toluene. Sodium trichloroacetate (127 mg, 0.7 mmol) was added and the mixture was heated under reflux accompanied by vigorous stirring. After 1 h, the reaction was terminated, a sample was collected for GLC analysis, and the concentration ratio of the two dichloromethylsilanes was determined (a mixture of $PhSi(CHCl_2)Me_2$ with V was analysed on column B at 140 ° C, and a mixture of $PhSi(CHCl_2)Me_2$ with VIII on column A at 130 ° C). The reaction was continued for another hour and analysed once again; the product ratio remained unaltered. A mixture of the two dichloromethylsilanes of known composition was used for calibration. The procedure for the calculation of k_{rel} was similar to that described in ref. [7].

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