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IONIC HYDROGENATION OF THIOPHENES BY $HSiEt_3$–$HCl/AlCl_3$

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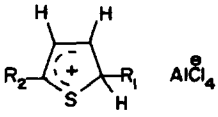
Abstract—It has been found that 2,5-dimethylthiophenium and 2,3,5-trimethylthiophenium tetrachloroaluminates react with triethylsilane and diphenylsilane in the presence of HCl to form the corresponding thiophanes. This fact in the light of the ionic hydrogenation mechanism has led to the proposal of a new hydrogenating system: $HSiEt_3$–$HCl/AlCl_3$. This system has been successfully used for hydrogenating thiophenes such as 2,5-dimethyl-, 2-ethyl- and 2,5-diphenylthiophene to the respective thiophanes. It has been also extended to branched olefines, 1-methylcyclohexene being hydrogenated in high yield to methylcyclohexane.

The hydrogenation of thiophenes with a $HSiEt_3$–CF_3COOH mixture is a promising novel method for preparing substituted thiophanes. A mechanism of the reaction has been proposed involving protonation of the thiophene molecule to the corresponding carbenium ion (σ-complexing by the proton) followed by hydride transfer from silane to the carbenium ion to yield the respective dihydrothiophene. Hydrogenation of the second double bond is considered to proceed in a similar fashion. The mechanism is in accord with the observed acceleration of the reaction by increase in acidity of the medium, by catalysts such as salts or boron trifluoride etherate and also by electron donating substituents in the α-position of the thiophene ring.[2,3] The plausibility of the first proposed stage-protonation of the thiophene ring with formation of a carbenium ion is supported by the fact that such ions have been shown to exist in highly acid media.[4] Recently 2,5-dimethylthiophene (1) was found capable of conversion to the respective cation by the system $HCl/AlCl_3$ in dichloroethane or methylene chloride. Thiophene and 2-methylthiophene also afforded analogous salts (2).[5]

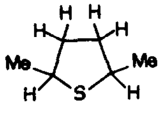


a: $R_1, R_2 = CH_3$
b: $R_1, R_2 = H$
c: $R_1 = H$; $R_2 = CH_3$

2a – c

The existence of stable salts of type **2** under mild conditions provided the means for modeling the second and subsequent stages in the above mentioned mechanism by reacting the salts with the silanes in the presence of acid. For this reason we undertook the study of the reaction between the stable, 2,5-dimethylthiophenium and 2,3,5-trimethylthiophenium cation and silanes in the presence of HCl, the results of which are reported in the present paper.

Salt **2a** reacted with silanes to give 2,5-dimethylthiophane (3). The yields depending on the silane composition and ratio of the reagents are listed in Table 1. It can be seen from the table that in all cases the reactions were practically complete in an hour. The most active donor appeared to be triethylsilane.



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Ethyldichlorosilane was completely inactive under the applied conditions. Similarly 2,3,5-trimethylthiophenium tetrachloroaluminate (**2d**) reacted with triethylsilane and diphenylsilane in the presence of HCl to yield 2,3,5-trimethylthiophane. The results are listed in Table 2.

Thus alkylthiophenium ions are capable of extracting hydride ion from silanes affording in the presence of the acid the respective thiophanes (Scheme 1).

According to Scheme 1 aluminium chloride is regenerated in the course of the reaction so that it could be expected to proceed in the presence of catalytic amounts of $AlCl_3$. In fact 2,5-dimethylthiophene(**1**) was hydrogenated to 2,5-dimethylthiophane(**3**) in high yield when reacted with triethylsilane in CH_2Cl_2- solution through which a continuous flow of gaseous HCl was maintained and only a small amount of $AlCl_3$ had been added. However, at an initial substrate concentration of 0.37M and substrate: $AlCl_3$ ratio of 1:0.2 a substantial amount of **1** remained in the reaction mixture after 10 min. The reaction rate increased when the ratio was 1:0.3 (see Table 3) but when 1:0.5 ratio was used intense decomposition of triethylsilane occured and a large excess of silane was required for the reaction to be carried out.†

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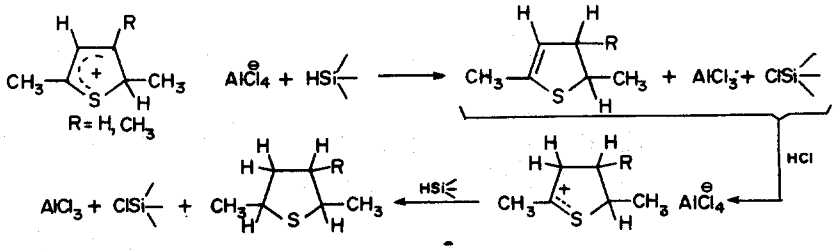
†When thiophenium ions were obtained prior to hydrogenation 1 mole of $AlCl_3$ per mole of substrate was used, yet the hydrogenation reaction proceeded without intensive decomposition of triethylsilane. Probably this was due to complexing of $AlCl_3$ by thiophene. The yield of **3**, however, turned out to be less than that in the ionic hydrogenation at a ratio of 1:0.3.



Scheme 1.

Table 1. Interaction of 2,5-dimethylthiophenium tetrachloroaluminate **2a** with silanes in the presence of HCl at room temperature

Silane	Molar ratio <u>2a</u> : silane	Yield of 2,5-dimethylthiophane, %	
		1 hr	15 hrs
Et_3SiH	1 : 2.6	63	63
Et_3SiH	1 : 5	59	66
Ph_2SiH_2	1 : 9.4	39	43
$EtSiHCl_2$	1 : 1.7	0	0

Table 2. Interaction of 2,3,5-trimethylthiophenium **2d** with silanes in the presence of HCL at room temperature

Silane	Molar ratio 2d : silane	Yield of 2,3,5-trimethylthiophane, %	
		1 hr	15 hrs
Et_3SiH	1 : 2.5	56	61
Ph_2SiH_2	1 : 2.7	18	33
Ph_2SiH_2	1 : 9.4	17	34
$EtSiHCl_2$	1 : 4.3	0	0

Table 3. Ionic hydrogenation of 2,5-dimethylthiophene **1** by means of $HSiEt_3$–$HCl/AlCl_3$ at room temperature; the initial concentration of **1**—0.37 M and ratio of **1**:$HSiEt_3$:$AlCl_3$ = 1:3,2:0.3

Reaction time, minutes	10	20	47	90	120	150
Yield of 2,5-dimethylthiophane, %	58	68	70	76	75	76

2-Ethylthiophene(**4**) underwent rapid hydrogenation to 2-ethylthiophane(**5**) in high yield. On this compound as example the optimal substrate to triethylsilane to $AlCl_3$ ratio, while keeping the other parameters (initial substrate concentration, HCl flow rate, temperature) invariable, was established, taking as a response function the yield of **5** 30 min after starting the reaction. The optimal substrate: triethylsilane: $AlCl_3$ ratio for an initial substrate concentration of 0.37M and room temperature was found to be 1:3:0.3 with either increase or decrease in the $AlCl_3$ content lowering the yield of **5**. At the optimal reagents ratio, the reaction was completed in 10 minutes. The yield of **5** was 80%.

The advantage of the $HSiEt_3$–$HCl/AlCl_3$ system is in the ability to vary the medium "acidity" by varying the amount of $AlCl_3$. As a result it has become possible in principle to hydrogenate compounds such as those which are not amenable to reduction by triethylsilane–trifluoroacetic acid. Earlier it was shown that 2,5-diphenylthiophene(**6**) did not undergo hydrogenation with $HSiEt_3$–CF_3COOH.[1] The authors attributed this to hindrance of protonation of thiophene **6**. With the system

$HSiEt_3$–$HCl/AlCl_3$ in the presence of 2 mole of $AlCl_3$ per mole of **6**, however, the latter was hydrogenated to 2,5-diphenylthiophane(**7**) with a yield of 66%.

The system $HSiEt_3$–$HCl/AlCl_3$ also turned out to be capable of hydrogenating branched olefines. Thus 1-methylcyclohexene was converted to methylcyclohexane almost quantitatively in 10 minutes when the initial concentration of olefine was 0.42 M and the ratio olefine: $HSiEt_3$: $AlCl_3$ was 1:1.4:0.2.

EXPERIMENTAL

2,5-Dimethylthiophene, 2,3,5-trimethylthiophene, 2-ethylthiophene were obtained according to [6,7]. Triethylsilane was prepared by Jenkins' method[8] from ethyldichlorosilane and EtBr. Diphenylsilane was obtained by reducing diphenyldichlorosilane with LAH. $AlCl_3$ was of anhydrous commercial grade and used without purification for ionic hydrogenation, it was sublimed *in vacuo* for the preparation of cations **2a,d**. CH_2Cl_2 was purified and dried by a standare procedure. Gaseous HCl was dried by passing it twice through conc HSO_4.

1. *Reaction of* **2a** *with silanes in the presence of HCl*

Twenty drops of n-decane was added to a solution of **1** in CH_2Cl_2 and the ratio of peak area of **1** and n-decane on a GLC-gram (10% of carbowaxadipate on Rysorb BLK, 110°) was determined. This was followed by producing complex **2a** according to [5]. Silane was then added and gaseous HCl was continuously bubbled through. The yield of **3** (Table 1) was calculated by means of the expression:

$$S\% = \frac{\tau_2 h_2}{\tau_0 h_0} \times \frac{1.08}{\alpha} \times \frac{M_1}{M_2} \times 100$$

where τ_2, h_2; τ_0, h_0 -retention times and peak heights of **3** and n-decane respectively. α—the ratio of peak area of **1** to that of n-decane determined before the preparation of complex **2a** as the ratio of the products of the retention times by the peak heights. 1.08—weigh sensitivity coefficient of **1** per **3**. M_1M_2—molecular weights of **1** and **3** respectively.

2. *Reaction of* **2d** *with silanes in the presence of* HCl

This reaction was performed in a similar fashion to **2a** (Table 2).

3. *Ionic hydrogenation of thiophenes.*

2,5-Dimethylthiophane(**3**). To a solution of **1** (1 mmol) and triethylsilane (3,2 mmole) in 2 ml of CH_2Cl_2 was added ten drops of n-decane and the GLC-gram recorded. Then gaseous HCl was bubbled through the soln for 10 min. No peak of **3** was observed. After addition of 0.3 mmole of $AlCl_3$ the increase in yield of the product with time was determined by GLC, gaseous HCl being bubbled through the soln during the entire length of the experiment (Table 3). The mixture was treated with water, the organic layer separated and dried over Na_2SO_4. The product was identified by GLC-MS. The following main ion peaks were observed in mass-spectrum: $m/e = 116$, $(M)^+$; 101, $(M–CH_3)^+$; 74, $(M–C_3H_6)^+$; 67, $(M–CH_3–H_2S)^+$; 59, $(M–CH_3–C_3H_6)^+$; 45; 41.

2-Ethylthiophane(**5**). The experiments on the hydrogenation of **4** were performed analogously to those of **1** apart from the preliminary passage of HCl. The amounts of triethylsilane and $AlCl_3$ were varied and n-undecane was used as internal standard. The retention times of the product in three stationary phases (10% Carbowax adipate on Rysorb BLK, 141°; 10% SKTFT-50 on Celite 545, 104°; 2.5% OV-17 on Chromosorb W AW DMCS, 130°) were the same as those of 2-ethylthiophane. The maximum yield of **5** (80%) was achieved in 10 min at the ratio of **4**:$HSiEt_3$:$AlCl_3$ of 1:3:0.3†).

2,5-Diphenylthiophane(**7**). To a soln of **6** (0.52 mmole) and triethylsilane (1.56 mmole) in 2 ml of CH_2Cl_2 was added 3 more mmole of $HSiEt_3$ and 1.04 mmole of $AlCl_3$ in small portions in the course of 4 hr while bubbling gaseous HCl through the mixture. The additions were monitored by GLC, i.e. triethylsilane was added when its peak disappeared and $AlCl_3$ was added until the peak of **6** disappeared. On its disappearance the reaction was considered to have gone to completion. The mixture was then treated with water and the organic layer subjected to GLC. The substantial increase in two not fully separated peaks with retention times less than that of **6**, which prior to the treatment with water were of minor intensity, was observed. 28.3 mg of **6** was added to the solution and the yield of the product (66%) was determined assuming the sensitivity coeff. of **6** per **7** as 1.0. The organic layer was separated, dried and evaporated *in vacuo*. The solid residue was analysed by mass-spectrum which displayed the molecular ion of **7**, the molecular ion of added compound **6** and also the fragmentary ion of **7** with $m/e = 136$, $(M–PhCHCH_2)^+$, rel. abundance = 100. The observation of two partially resolved peaks in GLC can be accounted for by assuming *cis* and *trans* isomers.

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†With the initial substrate concentration of 0.37 M. The effect of varying that parameter on the yield of **5** has not been studied.