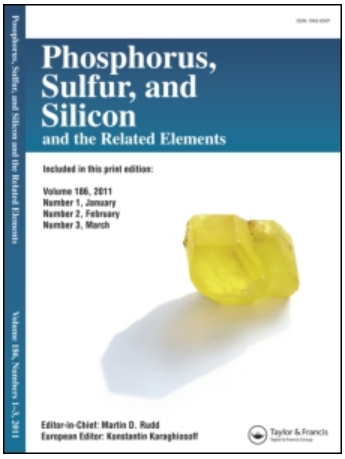

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IONIC HYDROGENATION OF THIOPHENES BY $HSIET_3$ - $HCL/ALCL_3$

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

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Earlier we have proposed and developed a novel method to hydrogenate thiophenes to thiophanes by means of hydridesilanes in trifluoroacetic acid. We have displayed the reaction to proceed smoothly, rapidly and with good yields in the presence of small additions of boron trifluoride etherate or lithium perchlorate. Similarly to ionic hydrogenation of olefines a mechanism was proposed involving an intermediate formation of thiophenium ion.

To reveal the plausibility of that mechanism, we undertook a study of the reaction between 2,5-dimethyl- and 2,3,5-trimethylthiophenium tetrachloroaluminates and hydridesilanes in the presence of HCl. Indeed, it was found that the reaction afforded 2,5-dimethyl- or 2,3,5-trimethylthiophanes conformably. According to reaction scheme $AlCl_3$ is regenerated in the course of the reaction. In the light of that we have proposed a novel hydrogenating system: $HSiEt_3$ + HCl in the presence of catalytic amounts of $AlCl_3$. In fact 2-ethylthiophene was converted to 2-ethylthiophane (80 %) in 10 minutes at room temperature when the ratio of substrate to silane to $AlCl_3$ was I:3:0.3.

The advantage of that novel hydrogenating system is in the ability to vary the medium "acidity" by varying the amount of $AlCl_3$. As a result it become possible to hydrogenate the derivatives of thiophene such that are not ammenable to reduction by $HSiEt_3$-CF_3COOH even in the presence of above mentioned additions. The example of such compound is 2,5-diphenylthiophene.

The system $HSiEt_3$-$HCl/AlCl_3$ was successfully applied to hydrogenation of thiophene, 2-ethylthiophene, 2,5-dimethylthiophene, 2,5-diphenylthiophene, methyl-(2-thienyl)ketone.