# Hydrogenation of Thiophens *via* the Consecutive Electron and Proton Transfer to Thiophenium Ions

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*Summary* Thiophen and 2-ethylthiophen are hydrogenated to the corresponding 2,5-dihydrothiophens with Zn and $CF_3CO_2H$ *via* a mechanism involving the protonation of the thiophen ring to the respective thiophenium ion, followed by the transfer of two electrons from Zn and the second proton from the acid

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THIOPHENS were shown to undergo hydrogenation with $HSiEt_3$ and $CF_3CO_2H$.[1] A mechanism was proposed involving protonation of the substrate to form the thiophenium ion, the latter abstracting a hydride ion from $HSiEt_3$ to yield the hydrogenated product.[1,2] Though the detailed mechanism of the second step of the reaction has not yet been ascertained, it is formally possible to consider the hydride transfer as a transfer of two electrons and a proton and, thus, $HSiEt_3$ as performing two donating functions, one of them being electron donating and the other proton donating. Thus, it seemed reasonable to try to develop a process in which these two donating functions would be divided between two separate donors, the first being the donor of electrons and the second supplying protons, especially as a proton donor is required for the first step of the reaction. We report here that the reaction using the pair Zn + $CF_3CO_2H$ is suitable. 2-Ethylthiophen (**1**) in $CF_3CO_2H$ solution reacts with Zn to give a mixture of 2-ethyl-2,5-dihydrothiophen (**2**) and 2-ethyltetrahydrothiophen (**3**), (**2**) being in considerable excess. Solvents such as benzene, toluene, hexane, or dichloromethane increase the yield of (**2**), while the yield of (**3**) remains unchanged or even slightly decreases (Table).

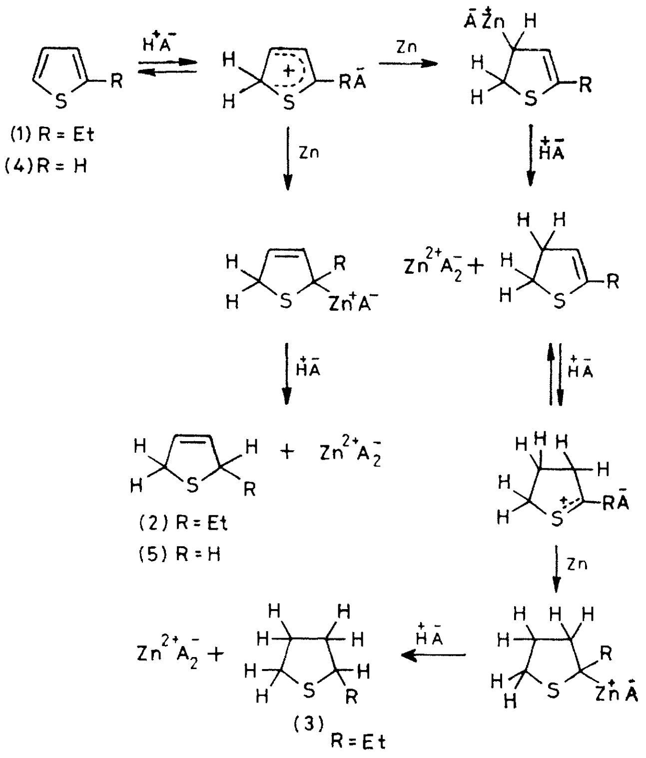
TABLE. Hydrogenation of (**1**) by Zn and $CF_3CO_2H$ at room temperature.[a]

| Molar ratio (**1**) : Zn : $CF_3CO_2H$ | Reaction time/h | Solvent | Yield/% (**2**) | (**3**) |
|---|---|---|---|---|
| 1 : 50 : 100 | 3 | — | 41 | 11 |
| 1 : 92 : 50 | 2·5 | Benzene | 58 | 8 |
| „ | 3 | Toluene | 61 | 8 |
| „ | 3 | Hexane | 55 | 10 |
| „ | 3 | Dichloromethane | 70 | 6 |
| „ | 5 | Ether | 0 | 0 |

[a] High dilution and large amounts of Zn were used in order to decrease the extent of bimolecular side reactions.

Hydrogenation of unsubstituted thiophen (**4**) results in 2,5-dihydrothiophen (**5**), but the rate of the reaction is noticeably less. When the reaction of (**4**) was carried out in benzene under the conditions analogous to those used for the hydrogenation of (**1**), 10 h of vigorous agitation resulted in a 7% yield of (**5**) and a considerable amount of (**4**) remained unchanged. Under the more drastic conditions, boiling $CF_3CO_2H$ without solvent and in the presence of $LiClO_4$, the yield of (**5**) was 42% after 4 h.

The products were identified by g.l.c.–m.s. [$M^+$: (**2**) 114 and (**3**) 116] and, after isolation by preparative g.l.c., by mass [$M^+$: (**5**) 86] and Raman spectroscopy [C=C stretching: ν (**2**) 1638 $cm^{-1}$ and (**5**) 1637 $cm^{-1}$].[3] Since the Raman spectrum did not absolutely specify the double bond position in (**2**) a chemical method was employed for additional support: (**2**) did not react with $HSiEt_3$ in $CF_3CO_2H$ solution which is characteristic of an isolated double bond.[1] The quantitative measurements were performed by g.l.c.



SCHEME. A = $CF_3COO$.

A plausible mechanism for the reaction is illustrated in the Scheme. The following experimental findings support the possibility that the process begins with protonation of the substrate. (i) The reaction does not occur when $CF_3CO_2H$ is replaced by $MeCO_2H$ or a mixture of conc. HCl and benzene. The concentration of thiophenium ions is very small in these media as shown by the lack of reaction with $HSiEt_3$. (ii) The rate of hydrogenation of (**1**) is considerably higher than that of (**4**). The introduction of the donating ethyl-radical into the thiophen ring increases the basicity of the molecule and, thus, the concentration of the thiophenium ion. (iii) No reaction was observed in ether, a solvent which is more basic than the others used and so decreases the acidity of the solution to a greater extent.

It is interesting that the hydrogenation with Zn and $CF_3CO_2H$ leads to 2,5-dihydrothiophens, whereas the hydrogenation of alkylthiophens with $HSiEt_3$ in acidic media results in tetrahydrothiophen compounds. Under conditions of the Clemmensen reduction (Zn or amalgamated Zn in aq. HCl) thiophen rings do not undergo hydrogenation.[4]

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