HYDROGENATION OF ALKYLTHIOPHENES BY THE Zn–TsOH·H_2O/$AlHal_3$ SYSTEM

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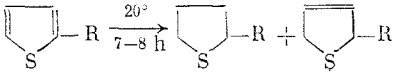
In our previous work [1, 2], we reported systems for the proton–electron (P2eP) hydrogenation, Zn–CF_3CO_2H and Zn–H_2SO_4 (CH_2Cl_2), which are capable of hydrogenating thiophenes to 2,5-dihydrothiophenes under mild conditions. The search for other similar systems led us to the Zn–TsOH·H_2O/$AlHal_3$ system (Hal = Cl and Br). In contrast to the previous systems, this system hydrogenates thiophenes to tetrahydrothiophenes (with a trace of 2,5-dihydrothiophenes)



(Ia–c) (IIa–c) 60–73% (IIIa–c) 3–9%

R = Me (a); Et (b); Pr(c).

The greatest yields of tetrahydrothiophenes are achieved for (I):Zn:TsOH·H_2O:$AlCl_3$ (or $AlBr_3$) mole ratio = 1:110:27:4 (or 2) if half the calculated amount of zinc powder is added to a solution of (I) in CH_2Cl_2, followed by TsOH·H_2O and $AlHal_3$ with rapid stirring and, over 15-20 min, the remaining portion of zinc powder.

The reaction mechanism is apparently analogous to that presented in our previous work [1, 3]. The reaction does not proceed in the absence of aluminum trihalide. Dihydrothiophene (IIIb) is not hydrogenated by this new system, indicating that, as in the case of CF_3·CO_2H or H_2SO_4, (III) is not an intermediate in the formation of (II) and, thus, the reaction proceeds with the intermediate formation of 2-alkyl-4,5-dihydrothiophene.

Therefore, by changing the acid, we may hydrogenate thiophenes either to 2,5-dihydrothiophenes or to tetrahydrothiophenes.

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