HYDROGENATION OF SUBSTITUTED THIOPHENES BY THE $Zn-H_2SO_4$ SYSTEM

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The hydrogenation of thiophenes to dihydrothiophenes poses a difficult problem. The Birch procedure is most commonly used for this purpose. Various modifications of this procedure are effective only for thiophenes with strong electron-withdrawing substituents [1] and give unsatisfactory results in the case of alkylthiophenes. For example, the reduction of 2-methylthiophene (I) gives 7.5% of a mixture of 2-methyldihydrothiophenes and 38% unsaturated thiols [2]. We have previously reported that the hydrogenation of thiophenes by the $Zn-CF_3CO_2H$ system leads to 2,5-dihydrothiophenes [3]. It is now clear that CF_3CO_2H may be replaced by H_2SO_4. In order to obtain the greatest yield, the reactions are carried out by the gradual addition of 89% H_2SO_4 (30-60 moles per mole substrate) to a vigorously stirred solution of the substrate in CH_2Cl_2 at 0°C followed by the addition of zinc powder (total amount 110-221 moles Zn per mole substrate) with subsequent stirring at 20°C for 5-7 h. This method was used to hydrogenate (I) and 2-ethylthiophene (II) to the corresponding 2,5-dihydrothiophenes in 65-70% yield. Tetrahydrothiophenes (5-7%) are formed as side-products. The reduction of 2-acetylthiophene by this system, as in the case of CF_3CO_2H, leads to 2-ethyl-2,5-dihydrothiophene (III) in 60% yield, and 6% 2-ethyltetrahydrothiophene (IV).

We should note that (II) does not form (III) and (IV) upon treatment with Zn–conc. HCl at 20°C in benzene or $Zn-CH_3CO_2H$ at 20°C. This failure is likely related to the insufficient concentration of thiophenium ions in these media [3].

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