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INFLUENCE OF ADDED SALTS AND ACIDS ON THE IONIC HYDROGENATION OF THIOPHENES

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The ionic hydrogenation of thiophenes with triethylsilane (TES) and trifluoroacetic acid (TFA) forms tetrahydrothiophenes [1]; the hydrogenation of thiophenes is much slower than that of olefins [2]. Tsyryapkin has shown that the rate of hydrogenation of olefins increases with the acidity of the medium [3]. This suggests that the rate of hydrogenation of thiophenes will also depend on the acidity of the medium. However, the use of TES as hydride donor limits the possible increase in the acidity, since strong acids react with TES.

With the intention of optimizing the conditions for ionic hydrogenation of thiophenes we have made a comparative study of the dynamics of the formation of 2-ethyltetrahydrothiophene (I) in the hydrogenation of 2-ethylthiophene (II) with TES at 20°C with various quantitles of TFA (Fig. 1) and have shown that use of a large excess of TFA markedly accelerates the reaction. Thus with a 30-fold excess the yield of (I) reaches 89% less than 25 min after the start of the reaction. The yield stops increasing after the disappearance of (II) from the solution and depends on the quantity of acid. With a (II):TES:TFA ratio of 1:3:10 the maximum yield of (I) is 71% after 24 h; it does not increase further.

To reduce the quantity of TFA we used a (II):TES:TFA ratio of 1:3:10 with various quantities of p-toluenesulfonic acid (TSA) for ionic hydrogenation. This is a much stronger acid than TFA and consequently small quantities can raise the acidity to the necessary level. The use of 10% TSA solution in TFA gives an 80% yield of (I) after 0.5 h (Fig. 2). Further increase in the TSA concentration does not accelerate the reaction or increase the yield, probably because of decomposition of the silane.

We might suppose that the rate of ionic hydrogenation would be affected by addition of neutral salts, such at LiClO4 [4-6]. We found that the reaction is much faster and the yield of (I) is greater in 0.95% LiClO4 solution in TFA than in pure TFA. The effect of adding the salt to the reaction mixture containing 10 moles of TFA per mole of substrate resembles the effect given by use of a 20-fold excess of TFA or 10% TSA solution in TFA. The reaction rate increases with the LiClO4 concentration, though the concentration of the salt cannot be greatly increased because of its low solubility. Use of 1% and 2% suspensions does not give this effect. The slight differences between the curves for the suspensions and the 0.95% solution are within experimental error (Fig. 3). Addition of LiClO4 also accelerates the hydrogenation of δ -(2-thienyl)valeric acid (III) (Fig. 4) and of methyl 2-thienyl ketone (IV).

The work of Winstein et al. [6] suggests that ionic hydrogenation would be accelerated by addition of lithium tosylate, which has the same high solubility. The reaction is indeed accelerated by addition of lithium tosylate, but not even 3% of the salt would dissolve in

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Fig. 1. Yield of 2-ethyltetrahydrothiophene (I) from the ionic hydrogenation of 2-ethylthiophene (II) with TES and TFA at 20°C. Molar ratio (II):TES:TFA: 1) 1:3:5; 2) 1:3:10; 3) 1:3:15; 4) 1:3:20; 5) 1:3:30.

Fig. 2. Influence of added TSA on the ionic hydrogenation of 2-ethylthiophene (II) at 20°C with a molar ratio (II):TES:TFA = 1:3:10. Content of TSA in TFA, %: 1) 0; 2) 1; 3) 3; 4) 10.



Fig. 3. Ionic hydrogenation of 2-ethylthiophene (II) with TES and TFA at 20° C in the presence of added salt with a molar ratio (II):TES:TFA = 1:3:10. Content of LiOTs in TFA, %: 1) 0; 2) 1; 3) 2; 4) 3. Content of LiClO₄, %: 5) 0.95; 6) 1.

Fig. 4. Reduced intensity of the thiophene ring protons in percent of the original (C/Co, %) in the ionic hydrogenation of δ -(2-thienyl)valeric acid (III) at 34°C with a molar ratio (III):TES:TFA = 1:3:5; 1) in the absence of LiClO₄; 2) in saturated LiClO₄ solution in TFA.

TFA and the reaction rate in the resulting suspension is less than in 0.95% LiClO4 solution in TFA (Fig. 3).

Ionic hydrogenation of thiophene (V) under normal conditions without additives is very slow and is complicated by the formation of 2,5-dihydrothiophene (VII) together with tetra-hydrothiophene (VI) [7]. We found that LiClO4 greatly accelerates this reaction. A 79% yield of mixed (VI) and (VII) is given by 1% LiClO4 suspension in TFA [30 moles of acid per mole of (V)] after 66 min, whereas attainment of this yield requires \sim 70 h without the salt (Table 1).

EXPERIMENTAL

After 4 h reflux with H_2SO_4 (2:1 by volume), CF₃COOH (originally pure grade) had bp 71-72°C. Triethylsilane was prepared by the procedure of [8] from ethyldichlorosilane and C₂H₃•Br, bp 107-109°C. p-Toluenesulfonic acid had mp 102-104°C. Lithium tosylate was prepared

In trifluoroacetic acid				in 1% LiClO ₄ suspension in TFA			
time, min	yield, %				yield, %		
	(V)	(VI)	(VII)	time, min	(V)	(VI)	(VII)
10 36 1026 1262 3993 8460	23 22 14 8	3 10 23 23 28 30	17 42 45 48 54	11 39 66 129 232	39 15 12 8 5	20 24 30 30 31	31 41 49 52 53

TABLE 1. Ionic Hydrogenation of Thiophene (V) [(V): TES:TFA ratio = 1:3:30, 20°C]

from LiOH and p-toluenesulfonic acid and was dried at 150°C; LiClO₄ was pure grade. 2-Ethyl-thiophene was prepared by reduction of (IV) with hydrazine hydrate in KOH, bp 134-136°C; $n_D^{2^\circ}$ 1.5122. The purity of the other reagents was checked from their physical constants and by GLC.

The course of the hydrogenation of (II), (IV), and (V) was followed by GLC (Khrom-3 chromatograph, katharometer, stainless steel column, internal diameter 6 mm, 10% PEGA on Risorb BLK 0.2-0.3 mm, carrier gas helium, 100 or 110°C). Quantitative measurements were carried out with internal standards (tetrahydrothiophene and toluene). The PMR spectra were recorded with a Perkin-Elmer R-12 instrument at 34°C.

Hydrogenation of (II). To a mixture of (II) (113.1 mg), tetrahydrothiophene (42.2 mg), and TES (350.2 mg) was rapidly added TFA (1.729 g). After mixing samples were analyzed in sequence by GLC. Salts and TSA were initially dissolved or suspended in TFA. Compounds (IV) and (V) were hydrogenated in the same way.

<u>Hydrogenation of (III)</u>. To (III) (161.5 mg) was added symtetrachloroethane (101.8 mg). The PMR spectrum of the latter in TFA showed a singlet with δ 5.53 ppm relative to tetramethylsilane (external standard). To the mixture were added TES (305.4 mg) and TFA (498.3 mg). The reaction temperature was 34°C; the reaction was followed from the reduction in the intensity of the thiophene ring multiplet. The reaction was then carried out under the same conditions with the same quantities in saturated LiClO4 solution in TFA. The results are shown in Fig. 4.

The same reaction was then carried out without the standard in saturated LiClO. solution in TFA with a (III):TES:TFA ratio of 1:2.7:10. The reaction was followed from the reduction in the integrated intensity of the aromatic protons in the PMR spectrum. The first scan was made 5 min after mixing the reactants. After 19 min the intensity was reduced to a third. After 27 min a weak signal remained (on the level of noise). Thus hydrogenation was almost complete within 0.5 h.

CONCLUSIONS

1. The ionic hydrogenation of thiophenes is greatly accelerated by a large excess of trifluoroacetic acid or small quantities of p-toluenesulfonic acid or neutral salts (lithium perchlorate and lithium tosylate).

2. In the hydrogenation of 2-ethylthiophene use of excess CF₃COOH or addition of ptoluenesulfonic acid or LiClO₄ not only accelerates the reaction but also increases the yield of 2-ethyltetrahydrothiophene.

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