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CATALYTIC REDUCTION OF 2-THIOPHENALDEHYDE AND 2-ACETOTHIENONE

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A catalyst, rhenium heptasulfide, has been found for reducing 2-thiophenaldehyde and 2-acetylthiophene to the corresponding alkylthiophenes. The reduction conditions found were: temperature 170°–190° C, hydrogen pressure 130 atm, time 3-6 hr. Reduction of 2-thiophenaldehyde in methanol in the presence of rhenium heptasulfide gives 2-methoxythiphene, while corresponding hydrogenation of 2-acetylthiophene in ammonia plus dioxane gives 2-(α-aminoethyl) thiophene.

A number of papers [1-3] describe the reduction of thiophene derivatives in the presence of metal sulfides. In particular, hydrogenation of acylthiophenes over cobalt polysulfide [1] gave a mixture of alkylthiophenes and alkylthiophanes. Reduction with hydrogen-carbon monoxide (1:2) over cobalt carbonate or octacarbonyl gave thiophane from thiophene, 2-methylthiophane from 2-methylthiophene, and 2-ethylthiophane from 2-ethylthiophene. When rhenium heptasulfide catalyst [3] was used, thiophene gave about a 70% yield of thiophane. Thiophene derivatives suffered mainly hydrogenolysis over cobalt and molybdenum polysulfides.

The above was the only information which could be gotten from the literature regarding the possible reduction of the carbonyl group without hydrogenation of the thiophene ring. In this connection it should be mentioned that we previously were able to find conditions and a catalyst for selective hydrogenation of thiophene azomethines, to the corresponding secondary amines [4].

The present paper describes results of experiments on reduction of thiophene derivatives containing the carbonyl group. The results set out in the table show that using rhenium or palladium sulfide at 170°–190° C, hydrogen pressure 130 atm, and reaction time 3-6 hr, and dioxane containing acetic acid as the solvent, the C=O group in thiophen-2-aldehyde and 2-acetothienone is selectively reduced, without the thiophene ring being affected. Using this method it was possible to prepare 2-methyl- and 2-ethylthiophene.

Reduction of thiophene-2-aldehyde over Re_2S_7 in methanol gives, along with 2-methylthiophene, 2-methoxymethylthiophene, while the reduction of 2-acetothienone in ammonia gives, in addition to ethylthiophene, 2-(1-aminoethyl) thiophene. If this latter reduction is run at 210° C, 2-3% ethyltetrahydrothiophene can be detected; it is a product of reduction of the thiophene ring. Raising the temperature to 270° increases the yield of ethyltetrahydrothiophene to about 44%.

Experimental

Starting materials. Thiophen-2-aldehyde [5] had bp 90°–93° C (21 mm), n_D^{20} 1.5916 [the literature [6] gives 72.5° (7 mm), n_D^{20} 1.5920]. 2-Acetothienone [7] had bp 77°–79° (6 mm), n_D^{20} 1.5667 [the literature [7] gives 77°–78° (4 mm), n_D^{20} 1.5666]. 2-Acetothienone oxime had mp 110° [8].

Catalysts. Rhenium heptasulfide was prepared in the way which we previously described [4], by passing H_2S into a solution of rhenic acid. Palladium sulfide was prepared in quantitative yield by passing H_2S into a solution of $PdCl_2$ in dilute HCl.

Hydrogenation. The starting material (0.075-0.1 mole) dissolved in 40 ml solvent (0.45 mole), and catalyst (0.00034-0.00084 mole Re_2S_7 or 0.0014-0.0058 mole PdS) were put in the autoclave, the necessary hydrogen pressure applied, and the autoclave heated to the desired temperature. After 3-6 hr, the catalyst was filtered off, and the reaction product isolated from the filtrate. The experimental results are given in the table. Some specimens of the end products were analyzed by GLC (column 2.2 m long, i.d., 5 mm, carrier-gas helium, feed rate 200 ml/min at 140° C, packing diatomaceous tile, impregnated with 10% Tween 90.)

2-Methoxymethylthiophene. 0.089 mole thiophen-2-aldehyde in 40 ml absolute MeOH (0.0167 mole) was hydrogenated in the presence of 0.22 g Re_2S_7, for 1 hr at 150° C, and 2 hr at 170°, pressure 130 atm. The products were filtered to remove the catalyst, the solvent distilled off through a column, the residue treated with water, and extracted with ether. The extract gave 1.4 g (16% yield) bp 109°–115°, n_D^{20} 1.5182 [the literature [10] gives bp 112.5° (760 mm), n_D^{20} 1.5202], and 5.7 g (48% yield) 2-methoxymethylthiophene, bp 66.5°–67° (16 mm), n_D^{20} 1.5202 [the literature [11] gives bp 67°–68° (16 mm), n_D^{25} 1.5180. Found: C 56.26, 56.32; H 6.62, 6.29%. Calculated for C_6H_8OS: C 56.21; H 6.29%.

2-Methylthiophene. A solution of 0.089 mole thiophen-2-aldehyde plus 1 ml AcOH in 40 ml dioxane was hydrogenated using 0.8 g PdS, temperature 180 °C, pressure 130 atm, time 6 hr, 30 min. The catalyst was then filtered off, the filtrate diluted with 5 times its volume of water, extracted with ether, the extract washed with dilute NaOH solution, and finally distillation gave 8.3 g (77% yield) 2-methylthiophene, bp 108°–115°.

Reduction of Thiophen-2-aldehyde and 2-Acetothienone, H_2 Pressure 130 atm, in 40 ml Dioxane, in the Presence of 1 ml Glacial AcOH

Starting material (10 g)	Catalyst, g	Temperature, °C	Hydrogenation time, hr	End product (yield, %)[a]
Thiophen-2-aldehyde [b]	Re_2S_7 (0.22)	170	1.5	Resin formation
Thiophen-2-aldehyde [c]	Re_2S_7 (0.22)	170	3	Resin formation
Thiophen-2-aldehyde [c]	Re_2S_7 (0.5)	180	5	A(49); Resin formation
Thiophen-2-aldehyde [d]	Re_2S_7 (0.22)	170	2	2-Methoxymethylthiophene (48), A(16)
Thiophen-2-aldehyde [c]	PdS (0.22)	170	3	A(35), B(35)
Thiophen-2-aldehyde [c]	PdS (0.22)	170	4.5	A53, B(<30)
Thiophen-2-aldehyde [e]	PdS (0.22)	170	5	A(<11), B(<17) Resin formation
Thiophen-2-aldehyde	PdS (0.5)	170	5	A(<70), B(6)
Thiophen-2-aldehyde	PdS (0.5)	180	5.5	A(70), B(3)
Thiophen-2-aldehyde	PdS (0.8)	180	5.5	A(77)
2-Acetothienone	Re_2S_7 (0.3)	190	5.5	C(70)
2-Acetothienone	Re_2S_7 (0.3)	190	3	C(70)
2-Acetothienone	Re_2S_7 (0.3)	210	3	C(78), D(2)
2-Acetothienone	Re_2S_7 (0.3)	240	3	C(56), D(14)
2-Acetothienone	Re_2S_7 (0.3)	270	3	C(31), D(44)
2-Acetothienone [f]	Re_2S_7 (0.2)	160	5	C(30) 2-(α-aminoethyl) thiophene (34)
2-Acetothienone [f]	PdS (0.5)	180	3	C(~10), E(76)
2-Acetothienone [f]	PdS (0.9)	210	3	C(27), D(b), E(32)

[a] A) Methylthiophene; B) thiophenaldehyde; C) ethylthiophene; D) ethyltetrahydrothiophene; E) 2-acetothienone; [b] without solvent; [c] in dioxane without AcOH; [d] in dry MeOH; [e] no solvent, 2 ml AcOH; [f] in dioxane, with 50 ml liquid NH_3.

2-Ethylthiophene. a) A solution of 10 g 2-acetylthiophene plus 1.0 ml AcOH in 40 ml dioxane was hydrogenated over 0.3 g Re_2S_7, temperature 190°C, pressure 130 atm, time 6 hr. The catalyst was filtered off, the solvent distilled off through a column, the residue washed with 5% NaOH solution, dried over $MgSO_4$, and distilled. Yield 6.3 g (70%), 2-ethylthiophene bp 134°–135°, n_D^{20} 1.5119 [the literature gives [12] bp 133°–134.5°, n_D^{20} 1.5122]. Found: C 64.21, 64.27; H 7.41, 7.41; S 28.47, 28.32%. Calculated for C_6H_8S: C 64.23; H 7.19; S 28.58%.

b) A solution of 5 g acetothienone oxime in 40 ml dioxane was hydrogenated in the presence of 0.09 g Re_2S_7 and 0.5 g activated charcoal in an autoclave, temperature 210°, time 3 hr, pressure 130 atm. Then the catalyst was filtered off, the filtrate diluted with 80 ml water, made acid with HCl, and extracted with ether (extract A); next the aqueous layer was made alkaline, and extracted with ether (extract B). Extract A was washed with 10% NaOH solution, evaporated, and washed with water to remove dioxane. Distillation of the residue gave 1 g 2-ethylthiophene, yield 25%. No α-aminoethylthiophene was found when extract B was distilled.

2-(α-Aminoethyl) thiophene. A current of dry NH_3 was passed into a solution of 10 g 2-acetylthiophene in 30 ml dioxane, cooled to −50° C. The mixture solidified, and part of the NH_3 condensed on top. A homogeneous mixture was obtained by shaking the flask, and the resultant solution was introduced into the autoclave, precooled to −40°. Hydrogenation was effected in the presence of 0.2 g Re_2S_7, temperature 160°, H_2 pressure 100 atm, time 5 hr. The catalyst was filtered off, 3/4 of the solution evaporated off through a column, the residue treated with dilute HCl, and extracted with ether (extract A). The aqueous solution was made alkaline, and the ether extraction repeated (extract B). Distillation of extract A gave 2.7 g (30% yield) 2-ethylthiophene, bp 130°–135°; while extract B similarly gave 3.4 g (34% yield) 2-(α-aminoethyl)thiophene bp 65°–69° (7 mm); n_D^{20} 1.5443 [the literature gives [13] 83°–84° (16 mm),

n_D^{20} 1.5441]. Found: C 56.75, 56.85; H 6.95, 6.97; S 25.14, 25.07%. Calculated for C_6H_9NS: C 56.65; H 7.13; S 25.20%. Also isolated was 1.6 g (19% yield) of a cut bp 113°(0.5 mm); judging by its elementary analysis, it was bis(α-thienyl-2-ethyl) amine. Found: C 61.09, 61.09; H 6.75, 6.64; S 25.29, 25.54%. Calculated for $C_{12}H_{15}NS_2$: C 60.71; H 6.37; S 26.97%.

Discussion

The present work showed that rhenium and palladium sulfides can be used as catalysts for selective reduction of carbonyl derivatives of thiophene. The yields of 2-alkyl-substituted compounds greatly depended on a number of conditions (see table).

The results set out in the table show that reduction of thiophen-2-aldehyde and 2-acetothienone to 2-alkyl-substituted thiophenes can be effected in the presence of rhenium heptasulfide, a small quantity of glacial acetic acid, at 180°–190° C and hydrogen pressure 130 atm, using dioxane as the solvent. Only resinification was observed in the absence of dioxane and acetic acid. Replacement of the rhenium heptasulfide by palladium sulfide raised the yield of 2-methylthiophene from thiophen-2-aldehyde, for example, 1.5-fold (from 49 to 70%). Using 10 g starting thiophen-2-aldehyde, increase in the quantity of palladium sulfide from 0.5 g to 0.8 g increased the yield of 2-methylthiophene to about 80%. 2-Acetothienone is harder to reduce in the presence of palladium sulfide, and the yield of 2-methylthiophene amounts to about 27%.

The results show that palladium sulfide can be used as a catalyst for selective reduction of the carbonyl group in thiophen-2-aldehyde, and rhenium heptasulfide, for that in 2-acetothienone.

Use of methanol as the solvent results in the 2-methylthiophene being accompanied by an approximately 48% yield of 2-methoxymethylthiophene.

As would be expected, hydrogenation of 2-acetothienone over rhenium heptasulfide proceeds at a higher temperature, 190°, than hydrogenation of thiophen-2-aldehyde. At 210° the products contain 2–3% of material hydrogenated in the ring, and when the temperature is raised further to 240°, the quantity rises to 14%, while at 270° the content of 2-ethyltetrahydrothiophene is about 44%.

Reduction of 2-acetothienone oxime in the presence of rhenium heptasulfide, in dioxane, temperature 210°, pressure 130 atm, gives a 25% yield of 2-ethylthiophene. In the presence of ammonia, 2-acetothienone is reduced to 2-ethylthiophene and 2-(α-aminoethyl) thiophene.

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