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REDUCTION OF THIOPHENES IN THE PRESENCE OF SULFURIC ACID AND ZINC

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Alkyl-substituted thiophenes are hydrogenated by the Zn–H_2SO_4 system to the corresponding 2,5-dihydrothiophenes and thiophanes. In the case of 2-formyl- and 2-acetylthiophene it was established that in substituted thiophenes simultaneous reduction of the substituent to an alkyl group occurs in addition to hydrogenation of the aromatic ring. The optimum conditions for hydrogenation were selected experimentally.

Keywords: sulfuric acid, thiophene, zinc, alkyl group, chromatography, hydrogenation, reduction**.**

The hydrogenation of thiophenes with retention of the cyclic skeleton is not an easy task. One of the most widely used methods is catalytic hydrogenation of thiophenes with molecular hydrogen. The reaction begins at a temperature above 200°C and pressure of 0.5 MPa. In addition to the desired products the reaction products contain significant amounts of hydrogen sulfide and hydrocarbons. The yields of thiophene and hydrogenolysis products increase with increase in the contact time [1-4]. The sulfides of Pd, W, and Mo are the most effective in activity and selectivity in the hydrogenation of thiophenes. Reaction at 250-300°C and 0.1 MPa in the presence of nickel-containing zeolites leads to high yields of thiophanes, but the activity of the catalyst decreases significantly after use for 30 min to 1 h [5]. In the case of noncatalytic methods of hydrogenation such as the Birch method and its modifications low yields of a mixture of the dihydrothiophenes and pentenethiols are obtained [6-8]. Ionic hydrogenation with the $HSiEt_3$–CF_3COOH system, based on protonation of the substrate in an acidic medium followed by transfer of a hydride ion from the triethylsilane, gives high yields of thiophane under mild conditions [9, 10]. However, the application of this method is restricted by the high cost and the poor availability of the reagents. Replacement of the $HSiEt_3$ by Zn leads to a change of the reaction products; instead of tetrahydrothiophenes the products are 2,5-dihydrothiophenes, which are well known as biologically active substances whose synthesis involves a number of difficulties [11, 12]. Under the conditions of the proton–electron reduction of thiophenes by the Zn–CF_3COOH system the mechanism of hydrogenation is regarded as the successive transfer of one proton from the acid and two electrons from the metal [10]. The trifluoroacetic acid is simultaneously a proton donor and a good solvent. From the practical standpoint, however, it is important to seek new hydrogenation systems using more readily available acids and concentrated sulfuric acid in particular.

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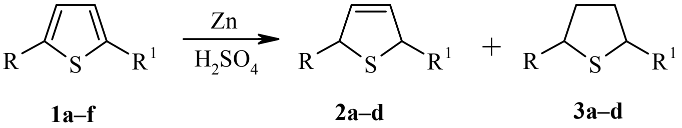
The hydrogenation of alkyl-substituted thiophenes **1a-f** by the Zn–H_2SO_4 system leads to the formation of 2,5-dihydrothiophenes **2a-d** and thiophanes **3a-d** with a significant preference for the former. The best results were obtained with part delivery of the Zn dust to a vigorously stirred mixture of the substrate and H_2SO_4 in CH_2Cl_2. This is evidently due to deactivation of the zinc surface in the concentrated acid.



1–3 a–c R = H, **a** R^1= Et, **b** R^1 = Me, **c** R^1 = Pr, **d** R = R^1 = Me;
1e,f R = H, **e** R^1 = CHO, **f** R^1 = COMe

The hydrogenation of 2-ethylthiophene **1a** hardly occurs at all in 60% H_2SO_4. By raising the acidity to 89% it was possible to increase the yield of 2-ethyl-2,5-dihydrothiophene (**2a**) to 70%. Further increase in the concentration of the acid to 90% reduced the yield of compound **2a** to 38% and increased the yield of 2-ethylthiophane (**3a**) to 20% (Table 1). Under the conditions of ionic hydrogenation the reaction requires the formation of a sufficient quantity of carbocations in the reaction medium, and this is obviously not possible at low concentrations of H_2SO_4 [8]. The protonation of the substrate becomes stronger as the concentration of the acid is increased, and the yield of the hydrogenation products is then increased. With high concentrations of sulfuric acid (>94%), however, there is a sharp reduction in the yield of the hydrogenated products, which is evidently due to acceleration of the side processes.

The products were identified on the basis of GLC-MS data. Fractional distillation of the products from the hydrogenation of compound **1a** led to a mixture giving two GLC-MS peaks: *m*/*z* 114 and *m*/*z* 116. In all probability the first peak corresponds to 2-ethyl-2,5-dihydrothiophene (**2a**) (M = 114) and the second to 2-ethylthiophane (**3a**) (M = 116). In the Raman scattering spectrum of the isolated product corresponding to the first peak there is a strong absorption band in the region of 1638 cm^{-1}, which coincides with the absorption band of the C=C bond in 2-ethyl-2,5-dihydrothiophene [13].

The degree of conversion of the initial thiophene can also be affected by change in the solubility of the H_2SO_4 in CH_2Cl_2 in relation to the concentration and acidity of the reaction medium if the reaction takes place in the organic phase.

With increase in the amount of 89% H_2SO_4 in the reaction medium from 10 to 30 mol/mol, the yield of the thiophene **2a** is increased to 70% (Fig. 1). In the range from 40 to 60 mol/mol there is a decrease in the yield of this product and a small increase in the yield of the thiophane **3a**, due probably to partial hydrogenation of the thiophene **2a** to the thiophane **3a** in the high-acidity medium.

TABLE 1. The Hydrogenation of 2-Ethylthiophene **1a** by the Zn–H_2SO_4 System* at Various Concentrations of H_2SO_4

Concentration of H_2SO_4, %	Time, h	Yield, %		Concentration of H_2SO_4, %	Time, h	Yield, %	
		2a	**3a**			**2a**	**3a**
60	10	0	0	91	5	52	14
70	10	39	0	92	5	38	20
86	10	57	2	94	5	15	11
89	5	70	5	96	5	13	8
90	5	68	7	100	5	5	4

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* **1a**–H_2SO_4–Zn ratio (mol): 1:30:110; 20°C.

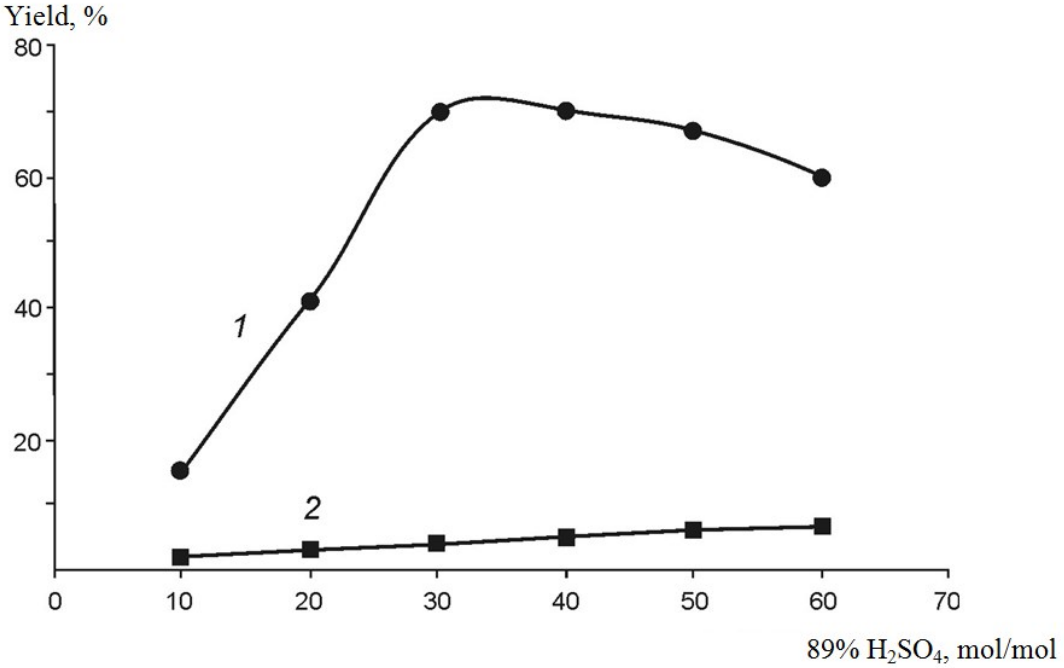

Fig. 1. The dependence of the yield of the products from hydrogenation of 2-ethylthiophene **1a** on the amount of 89% H_2SO_4. Zn–**1a** ratio, 110:1, T 20°C, 5 h. *1* – thiophene **2a**. *2* – thiophane **3a**.

Study of the effect of the amount of zinc on the hydrogenation processes at the optimum ratios of compound **1a** and H_2SO_4 shows that the highest yield of dihydrothiophene **2a** is obtained with a zinc to substrate ratio of 110:1 (Table 2). The decrease of the yield of dihydrothiophene **2a** to 36% with increase of the zinc ratio to 220:1 is evidently due to the decrease in the acidity of the reaction medium with the excess of solvent added for better mixing.

Dichloromethane, used in the reaction as solvent, promotes the production of high yields, but it mixes poorly with sulfuric acid. Realization of the reaction in other solvents (diethyl ether, $MeOC_{12}H_{25}$, or ethyl alcohol) that are readily mixable with sulfuric acid showed that the reaction takes place in ethyl alcohol but gives the desired product in small yield, while in ethers the reaction hardly occurs at all. The high basicity of the ether evidently leads to a decrease in the acidity of the reaction mixture and a decrease in the concentration of carbocations. The reaction in sulfuric acid without the solvent is obviously accompanied by secondary processes such as polymerization, polycondensation, and desulfurization, as a result of which the yield of the desired products is greatly reduced.

Study of the activity of various samples of zinc dust for the case of 2-propylthiophene (**1c)** showed that the yields of compound **2c** with the use of Ts-1 and Ts-2 differ little, but in the later case some increase in the yield of compound **3c** is observed. In the employed samples the content of metallic Zn, determined by iodometric titration, is 92 and 93% respectively, while the data from X-ray fluorescence spectrometry show insignificant differences between Ts-1 and Ts-2 with respect to Cd (2×10^{-1} and 5×10^{-3}%) and Cu (5×10^{-3} and 3×10^{-1}%) contents. The values for the remaining components (Fe, Ca, Pb, etc.) are almost identical [10]. Previous activation of the zinc surface with a 10% solution of HCl has practically no effect on the results of the reaction. This makes it possible to assume that the increase in the yield of the desired product apparently depends on the surface area of the zinc dust. The use of coarser zinc filings (1-2 mm) showed that hydrogenation hardly occurred at all, and only 13% of the starting thiophene **1a** remained in the reaction mass. In the strongly acid medium the metallic surface apparently soon loses activity on account of the formation of a salt film, and the thiophene in the strongly acid medium undergoes desulfurization, as indicated by the

TABLE 2. Hydrogenation of 2-Ethylthiophene **1a** by the Zn–H_2SO_4 System in CH_2Cl_2 with Various Zinc Dust–Substrate Ratios*

Molar ratio Zn–**1a**	Time, h	Yield, %	
		2a	**3a**
28:1	8	15	—
60:1	8	21	—
90:1	8	42	—
110:1	5	70	5
130:1	5	64	6
220:1	5	36	2
110:1*[2]	5	70	4

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* **1a**–H_2SO_4 (89%) ratio (mol), 1:30; 20°C

*[2] The acid was added at 0°C.

appearance of the smell of H_2S. This hypothesis is supported by the increased degree of hydrogenation when the zinc dust is added to the reaction mixture in portions, by its large consumption rate, and by the ineffectiveness of the use of Zn–Hg and Zn–Cu couples in the reaction.

Various alkylthiophenes were subjected to hydrogenation under the optimum conditions obtained for the thiophene **1a** (**1a**:H_2SO_4:Zn = 1:30:110). However, the reaction conditions that made it possible to hydrogenate compound **1a** with a high yield of the product **2a** were not effective for the other substituted thiophenes. For each alkylthiophene therefore it was necessary to chose conditions that lead to high yields of the desired products (Table 3).

Hydrogenation of the thiophene **1b** with the Zn–H_2SO_4 system under the conditions obtained for the thiophene **1a** led to the formation of 2-methyl-2,5-dihydrothiophene (**2b**) and a small amount of the 2-methylthiophane (**3b**), i.e., the degree of conversion of compound **1b** was significantly reduced. Increase of the molar ratio of the reagents in relation to the substrate also did not lead to success. An increased yield of the reaction product **2b** is achieved if the H_2SO_4 is added gradually in portions at reduced temperature (0°C).

During the hydrogenation of 2-propylthiophene **1c,** a mixture of 2-propyl-2,5-dihydrothiophene (**2c**) and 2-propylthiophane (**3c)** is formed. The mass spectrum of the distillation fraction revealed ions that correspond to 2-propyl-2,5-dihydrothiophene (**2c**) and 2-propylthiophane (**3c**). As in the case of 2-ethyl-2,5-dihydro-thiophene **2a**, the Raman spectrum of the distilled fraction revealed an absorption band in the region of 1638 cm^{-1} coinciding with the absorption band of the isolated C=C bond in 2,5-dihydrothiophene [13]. The 2,5-dimethyl-thiophene (**1d**) is hydrogenated by this system with the formation of 2,5-dimethyl-2,5-dihydrothiophene (**2d**) with a small amount of 2,5-dimethylthiophane (**3d**) as impurity. During the hydrogenation of 2,5-dimethyl-thiophene (**1d**) in order to obtain better results, it was necessary to double the amount of sulfuric acid and the reaction time, and this was obviously due to the presence of the two alkyl groups (Table 3).

The hydrogenation of 2-formylthiophene (**1e**) and 2-acetylthiophene (**1f**) by the Zn–H_2SO_4 system leads to the formation of compounds **2b** and **2a** respectively, i.e., both the carbonyl group and the thiophene ring are reduced (Table 4). The hydrogenation of thiophene **1e** gives lower yields compared with the compound **1f** under identical conditions. It was possible to increase the yield of the product **2b** by reducing the reaction temperature to 0°C.

The GLC analysis of the reaction mixture at certain time intervals showed that hydrogenation of the substituted thiophenes **1e** and **1f** leads to the formation of the intermediate alkylthiophenes **1b** and **1a** respectively. During reduction of the thiophene **1e** the amount of methylthiophene increases at the beginning of the reaction but then decreases in the course of time.

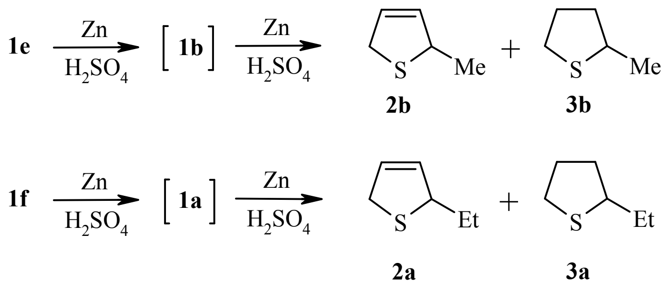

TABLE 3. Hydrogenation of Alkylthiophenes by the Zn–H_2SO_4 (89%) System in CH_2Cl_2, 20°C

Substrate	**1**–H_2SO_4-Zn molar ratios	Time, h	Alkyldihydro-thiophene	Yield, %	Alkylthiophane	Yield, %
1b	1:30:110	5	**2b**	28	**3b**	2
	1:60:230	5		40		4
	1:100:230	5		37		4
	1:30:110*	5		65		7
1c	1:30:110	4	**2c**	63	**3c**	4
	1:30:110*[2]	4		63		12
1d	1:30:110	8	**2d**	52	**3d**	6
	1:60:110	8		74		6
	1:30:220	8		58		4
	1:60:220	8		53		6

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*The acid was added at 0°C.

*[2]Zinc – Ts-2.

Thus, it was shown that the hydrogenation of 2-alkyl- and 2-carbonyl-substituted thiophenes by the Zn–H_2SO_4 system in CH_2Cl_2 results in the formation of the corresponding 2,5-dihydrothiophenes.

TABLE 4. Hydrogenation of Carbonyl-Substituted Thiophenes by the Zn–H_2SO_4 System

Substrate	**1**–H_2SO_4–molar ratios	Time, h	T, °C	Alkyl dihydro-thiophene	Yield, %	Alkyl thiophane	Yield, %
1e	1:60:220	6	20	**2b**	7	**3b**	2
	1:60:220	6	0		35		5
	1:30:220	6	0		33		4
	1:30:110	6	0		32		7
	1:60:110	6	0		41		7
1f	1:30:110	8	20	**2a**	10	**3a**	1
	1:30:220	8	20		50		6
	1:60:220	8	20		58		6

EXPERIMENTAL

The ^1H NMR spectra were obtained in carbon tetrachloride on a Bruker WR-200 SY instrument (200 MHz), and the chemical shifts are presented in parts per million with reference to TMS. The mass spectra were recorded on an AEI MS 1073 chromato-mass spectrometer with an ionization energy of 28.5 eV (I) and on an MX-1320 mass spectrometer with a heated direct injection system at 70 eV (II). The Raman spectra were obtained on a Ramanor HG.2S instrument with an argon laser source (514.5 nm). The refractive index was measured on an IRF-22 refractometer. The GLC analysis was conducted on a Chrom 5 instrument with a flame-ionization detector. Carrier gas – nitrogen. Columns: 2.7 mm × 3.7 m with 10% PEGA on Risorb BLK 0.2-0.315 mm (version 1); 3 mm × 2.5 m with 20% SKTFT-50-X on Chromaton N-AW 0.16-0.20 mm (version 2); 3 mm × 2.5 m 5% DS 200 on Chromaton N-Super 0.125-0.160 mm (version 3); 3 mm × 1.7 m 15% pentaerythritol benzoate on Chromaton NAW 0.20-0.25 mm (version 4). Stainless steel columns. The X-ray fluorescence spectra were obtained on a VRA-2 instrument.

Hydrogenation of 2-Ethylthiophene (1a) at Various Sulfuric Acid Concentrations. To a solution of compound **1a** (0.075 g, 0.68 mmol) in CH_2Cl_2 (6 ml), zinc dust (2.45 g, 34.47 mmol) was added. Over 10-15 min with constant stirring H_2SO_4 of the corresponding concentration (2.01 g, 20.52 mmol) was added. The remaining zinc dust (2.45 g, 37.47 mmol) was added gradually over 30 min. The reaction mixture was stirred at 20°C for 3 h, decomposed with water, and neutralized with a solution of KOH. The GLC analysis (version 1, 132°C) showed that the starting compound had reacted completely. The yields of the products were determined with an internal standard (dodecane). The retention times of compounds **2a** and **3a** agree with published data [10]. The results of the analyses are presented in Table 1.

Preparative Hydrogenation of 2-Ethylthiophene (1a). Half the calculated amount of Zn dust (195.8 g, 2.996 mmol) was added to a mixture of 2-ethylthiophene **1a** (6.1 g, 54.46 mmol) in CH_2Cl_2 (300 ml). With constant stirring 89% H_2SO_4 (160.1 g, 1.634 mmol) was added dropwise and the remaining Zn dust (195.8 g, 2.996 mmol) was added over 1 h. The reaction mixture was stirred for 8 h until the peak of the starting compound on the chromatogram had disappeared. The Zn was then filtered off and washed several times with CH_2Cl_2, water, and KOH solution. The organic layer was decomposed with water and KOH solution and extracted with CH_2Cl_2. The combined organic layer was dried with $MgSO_4$. The residue after removal of the CH_2Cl_2 was distilled. Two fractions were collected: at 140-150°C, n^{20}_D = 1.4950 (3.72 g, yield 60%) and 150-152°C, n^{20}_D = 1.4962 (0.17 g, yield 4%). The first fraction contained compound **2a**. Mass spectrum (II), *m*/*z* (I_{rel}, %): 114 $[M]^+$ (15), 99 $[M-CH_3]^+$ (22), 85 $[M-C_2H_5]^+$ (100), 59 $[SC_2H_3]^+$ (10), 45 $[CH{=}S]^+$ (13). The second fraction contained compound **3a**. Mass spectrum, *m*/*z* (I_{rel}, %): 116 $[M]^+$ (25), 101 $[M-CH_3]^+$ (12), 87 $[M-C_2H_5]^+$ (100), 59 $[SC_2H_3]^+$ (10), 45 $[SCH]^+$ (26).

Hydrogenation of 2-Methylthiophene (1b). To a solution of compound **1b** (0.078 g, 0.8 mmol) in CH_2Cl_2 (5 ml), Zn dust (2.86 g, 44.0 mmol) was added. The mixture was cooled to 0°C, and 89% H_2SO_4 (1.57 g, 24.0 mmol) was added with constant stirring. The remaining Zn dust (2.86 g, 44.0 mmol) was then added in portions over 30 min. The reaction mixture was stirred for 3 h and decomposed by the method described above. The yields of the products **2b** and **3b** were determined with the method of an internal standard (dodecane) (GLC, version 1, 119°C).

The hydrogenation of 2-propylthiophene (1c) was conducted similarly to the hydrogenation of compound **1a**. The following were used: compound **1c** (3.4 g, 27 mmol), 89% H_2SO_4 (79.4 g, 0.810 mol), Zn dust (197.3 g, 3.016 mol), CH_2Cl_2 (350 ml). Two fractions were collected at 160-171°C (yield 2.05 g, 62%) and 171-172.5°C (yield 0.065 g, 3%). The first fraction contained compound **2c**. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.93 (3H, m, CH_3); 1.42 and 1.67 (4H, m, CH_2CH_2); 3.64 (2H, m, CH_2); 4.15 (1H, m, CH); 5.71 (2H, m, HC=CH). Mass spectrum (II), *m*/*z* (I_{rel}, %): 128 $[M]^+$ (40), 113 $[M-CH_3]^+$ (5), 99 $[M-C_2H_5]^+$ (8), 85 $[M-C_3H_7]^+$ (100). The second fraction was compound **3c**. Mass spectrum, *m*/*z* (I_{rel}, %): 130 $[M]^+$ (22), 115 $[M-CH_3]^+$ (1), 101 $[M-C_2H_5]^+$ (20), 87 $[M-C_3H_7]^+$ (100), 59 $[SC_2H_3]^+$ (10), 45 $[SCH]^+$ (22).

The hydrogenation of 2,5-dimethylthiophene (1d) was conducted by the method used for the hydrogenation of compound **1a**. We used compound **1d** (0.057 g, 0.508 mmol), 90% H_2SO_4 (2.987 g, 30.480 mmol), Zn dust (3.654 g, 55.880 mmol), and CH_2Cl_2 (5 ml). The hydrogenation products **2d** and **3d** were identified by GLC–MS (I) (GLC, version 1, 130°C). The compounds corresponding to the first peak (yield 0.034 g, 60%) and the second peak (yield 0.0013 g, 3.7%) were isolated from the benzene extract by preparative GLC. First peak – compound **2d**. ^{1}H NMR spectrum, δ: 1.34 (6H, m, CH_3); 4.27 (2H, m, CH); 5.57 (2H, m, HC=CH). Mass spectrum, *m/z* (I_{rel}, %): 114 $[M]^+$ (110), 99 $[M\text{-}CH_3]^+$ (100), 85 $[M\text{-}C_2H_5]^+$ (11), 59 $[SC_2H_3]^+$ (30), 45 $[SCH]^+$ (3). Second peak – compound **3d**. Mass spectrum, *m/z* (I_{rel}, %): 116 $[M]^+$ (40), 101 $[M\text{-}CH_3]^+$ (100), 87 $[M\text{-}C_2H_5]^+$ (1), 59 $[SC_2H_3]^+$ (10), 45 $[SCH]^+$ (20).

The hydrogenation of 2-formylthiophene (1e) was conducted by the method used for the hydrogenation of compound **1b**. We used compound **1e** (0.087 g, 0.78 mmol), 90% H_2SO_4 (4.586 g, 46.80 mmol), Zn dust (5.611 g, 85.80 mmol), and CH_2Cl_2 (5 ml). The reaction time was 6 h. The hydrogenation products **1e** were identified by GLC by the agreement of the retention times of the products and the authentic compounds on three (in the extreme case, two) columns of different polarity (versions 1, 3, and 4.)

The hydrogenation of 2-acetylthiophene (1f) was conducted by the method used for the hydrogenation of compound **1a**. We used compound **1f** (0.101 g, 0.8 mmol), 89% H_2SO_4 (4.704 g, 48.0 mmol), Zn dust (11.510 g, 176.0 mmol), and CH_2Cl_2 (5 ml). The reaction time was 6 h. The hydrogenation products from compound **1f** were identified by GLC–MS (I) and GLC (versions 1, 3, 4). First peak – compound **2a**. Mass spectrum, *m/z* (I_{rel}, %): 114 $[M]^+$ (15), 99 $[M\text{-}CH_3]^+$ (22), 85 $[M\text{-}C_2H_5]^+$ (100), 59 $[SC_2H_3]^+$ (10), 45 $[CH{=}S]^+$ (13). Second peak – compound **3a**. Mass spectrum, *m/z* (I_{rel}, %): 116 $[M]^+$ (25), 101 $[M\text{-}CH_3]^+$ (12), 87 $[M\text{-}C_2H_5]^+$ (100), 59 $[SC_2H_3]^+$ (10), 45 $[SCH]^+$ (26).

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