PREPARATION OF PHENYLTHIOPHANES BY IONIC HYDROGENATION METHOD

Z. N. Parnes, G. I. Bolestova,
S. P. Dolgova, V. É. Udre,
M. G. Voronkov, and D. N. Kursanov

UDC 542.941-128:547.73

Previously it was shown that alkylthiophanes are obtained by the ionic hydrogenation [1] of the corresponding thiophenes using triethylsilane and trifluoroacetic acid [2]. In the present paper this method was extended to the hydrogenation of the phenyl-substituted thiophenes. It proved that 3-phenylthiophene (I) enters into the ionic hydrogenation reaction and gives 3-phenylthiophane (II) in 80% yield when the reaction is run at 50° for 15 h.

(I) (II)

It should be mentioned that 3-methylthiophene under analogous conditions is hydrogenated very slowly, and after heating for 80 h the yield of 3-methylthiophane does not exceed 60%.

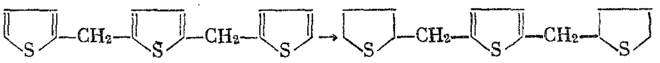
The behavior of the diphenylthiophenes under the conditions of the ionic hydrogenation reaction depends on the position of the phenyl substituents in the ring. Thus, 3,4-diphenylthiophene (III) when heated with Et_3SiH and CF_3COOH at 50° for 50 h gives 3,4-diphenylthiophane (IV) in 75% yield. The hydrogenation of 2,3-diphenylthiophene (V) and 2,4-diphenylthiophene (VI) proceeds in a similar manner; as a result the corresponding 2,3-(VII) and 2,4-(VIII) diphenylthiophanes are obtained in high yields (Table 1).

2,5-Diphenylthiophene (IX) does not enter into the ionic hydrogenation reaction even with a large excess of the hydrogenating agents and prolonged heating at 80°. 2,3,5-Triphenylthiophene (X) and 2,3,4,5-tetraphenylthiophene (XI) are also not reduced. It is probable that this is associated with the steric hindrance that arises in the protonation of the α,α'-substituted thiophene ring. This assumption is supported by the data that we obtained for the hydrogenation of 2,5-di(2-thenyl)thiophene (XII). Only the outer thiophene rings are reduced here to give compound (XIII). The middle ring remains untouched even with a 25-fold excess of acid and heating for 80 h.

TABLE 1

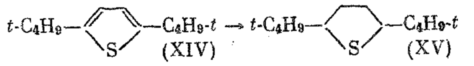
Starting thiophene	Mp, °C	Obtained compound	Mp, °C	Yield, %
(I)	92	(XVI)	182—183	80
(III)	113	(IV)	82—83	75
(V)	85	(VII)	48—49	75
(VI)	121	(VIII)	73—74	75
(IX)	152	(IX)	152—153 *	—
(X)	137	(X)	138—139 *	—
(XI)	186	(XI)	186—187 *	—

*The mixed melting point with the starting compound was not depressed.



(XII) (XIII)

Although 2,5-di-tert-butylthiophene (XIV) reacts with Et_3SiH and CF_3COOH, still the reaction is very slow and only a total of 15% of product (XV) is formed in 100 h.



(XIV) (XV)

At the same time, 2,5-dimethylthiophene is hydrogenated easily to give 2,5-dimethylthiophane in high yield [1]. It is obvious that the insertion of such bulky substituents as phenyl or tert-butyl

---

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1834-1836, August, 1974. Original article submitted December 20, 1973.

TABLE 2. Elemental Analysis Data for Obtained Compounds

Compound	Found, %			Empirical formula	Calculated, %		
	C	H	S		C	H	S
(VII)*	79,92	6,46	13,32	$C_{16}H_{16}S$	79,95	6,70	13,35
(IV)*	80,23	6,71	13,20				
(XVI)	16,77	1,75 Hg 56,93	4,58	$C_{10}H_{12}S \cdot 2HgCl_2$	16,96	1,69 Hg 56,73	4,52
(XIII)*	58,97	7,16	32,83	$C_{14}H_{20}S_3$	59,10	7,09	33,80

*New compound.

in the α,α'-positions of the thiophene ring prevents the ionic hydrogenation of these compounds.

EXPERIMENTAL METHOD

The reaction mixtures were analyzed by GLC. The chromatography conditions were: a) Chrom-2 instrument, flame-ionization detector, nitrogen as the carrier gas, and a 1.5 m × 4 mm copper column packed with 12% Fluorosilicone deposited on Celite 545 (column 1); b) LCM-8M instrument, equipped with a katharometer as the detector, and a 1 m × 4 mm steel column packed with 3% poly(ethylene glycol) 20M deposited on Celite 545 (column 2); c) Chrom-3 instrument, equipped with a katharometer as the detector, and a 2.5 m × 4 mm steel column packed with 15% poly(ethylene glycol adipate) deposited on Resorb BLK (column 3).

Hydrogenation of 3-Phenylthiophene [3]. A mixture of 1.38 g (0.0081 mole) of 3-phenylthiophene (I), 2.82 g (0.0243 mole) of Et_3SiH, 15.00 g (0.1316 mole) of CF_3COOH, and 0.83 g (0.007 mole) of $CHCl_3$ (added for homogenization) was heated under reflux at 50° for 50 h. The course of the reaction was followed by GLC (column 2, 120°, p_{He} 0.85). The $CHCl_3$ and excess CF_3COOH were distilled from the reaction mixture, while the residue was vacuum-distilled. The obtained 3-phenylthiophane (II) was purified via its complex with mercuric chloride: to a stirred refluxing solution of 5.3 g of $HgCl_2$ in 15 ml of EtOH was added 0.76 g of 3-phenylthiophane [fraction with bp 122-129° (10 mm)] in drops. The mixture was heated for 30 min, and then it was cooled to ~20°. The obtained precipitate was filtered, and recrystallized twice from EtOH. The yield of the 3-phenylthiophane complex with 2 molecules of $HgCl_2$ (XVI) was 3.54 g, mp 181-182° [4].

Hydrogenation of 3,4-Diphenylthiophene [5]. A mixture of 0.66 g (0.0028 mole) of 3,4-diphenylthiophene (III), 1.68 g (0.0145 mole) of Et_3SiH, 6.47 g (0.567 mole) of CF_3COOH, and 2.7 g (0.02 mole) of $CHCl_3$ was heated at 50° for 50 h (GLC analysis using column 1, 240°, p_{N_2} 0.85). All of the low-boiling components were distilled from the reaction mixture, and the solid residue was recrystallized from petroleum ether. The yield of the pure 3,4-diphenylthiophane (IV) was 0.47 g, mp 82-83°.

Hydrogenation of 2,3-Diphenylthiophene [5]. A mixture of 0.26 g (0.0011 mole) of 2,3-diphenylthiophene (V), 0.41 g (0.0036 mole) of Et_3SiH, 2.12 g (0.0185 mole) of CF_3COOH, and 0.36 g (0.003 mole) of $CHCl_3$ was heated at 50° for 50 h (GLC analysis using column 2, 190°, p_{He} 0.8). The yield of 2,3-diphenylthiophane (VII) was 0.19 g, mp 48°.

Hydrogenation of 2,4-Diphenylthiophene [6]. A mixture of 0.36 g (0.0015 mole) of 2,4-diphenylthiophene (VI), 1.60 g (0.014 mole) of Et_3SiH, 4.23 g (0.04 mole) of CF_3COOH, and 3.48 g (0.03 mole) of $CHCl_3$ was kept at 50° for 50 h (GLC analysis using column 2, 220°, p_{He} 0.8). The yield of 2,4-diphenylthiophane was 0.2 g, mp 73-74°.

Hydrogenation of 2,5-Di(2-thenyl)thiophene [7]. A mixture of 3.02 g (0.0109 mole) of 2,5-di(2-thenyl)-thiophene (XII), 9.55 g (0.0823 mole) of Et_3SiH, and 20.27 g (0.1778 mole) of CF_3COOH was heated at 50° for 50 h. After the usual workup we obtained 2.1 g of (XIII), bp 235-236°.

The elemental analysis data are given in Table 2.

CONCLUSIONS

1. A method was proposed for the preparation of phenyl-substituted thiophanes by the ionic hydrogenation of phenylthiophenes with triethylsilane and trifluoroacetic acid. 3-Phenylthiophane, and the 2,3-, 2,4-, and 3,4-diphenylthiophanes were obtained in high yields by this method.

2. Polyphenylthiophenes that have phenyl groups in the α,α'-positions of the thiophene ring do not enter into the ionic hydrogenation reaction.

LITERATURE CITED

1. Z. N. Parnes, G. I. Bolestova, L. I. Belen'kii, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., 1918 (1973).
2. D. N. Kursanov and Z. N. Parnes, Usp. Khim., 38, 1783 (1969).
3. M. G. Voronkov and A. N. Pereferkovich, Khim. Geterotsikl. Soed., 1133 (1967).
4. Yu. K. Yur'ev and E. M. Lukina, Zh. Obshch. Khim., 24, 1449 (1954).
5. E. N. Zvyagintseva, V. É. Udre, M. G. Voronkov, and A. I. Shatenshtein, Zh. Obshch. Khim., 41, 2289 (1971).
6. M. G. Voronkov, V. É. Udre, and É. P. Popova, Khim. Geterotsikl. Soed., 1003 (1967).
7. Ya. L. Gol'dfarb and Ya. L. Danyushevskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1361 (1956).