IONIC HYDROGENATION OF 2-(ω-DIETHYLAMINOALKYL)THIOPHENES

G. I. Bolestova, E. P. Zakharov,
S. P. Dolgova, Z. N. Parnes,
and D. N. Kursanov

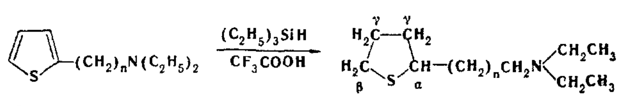
UDC 547.732:542.942.7

A method was developed for the ionic hydrogenation of 2-(ω-diethylaminoalkyl)thiophene with triethylsilane and trifluoroacetic acid; this method gives 2-(ω-diethylaminoalkyl)-thiophans, which are representatives of previously undescribed thiophan derivatives.

In [1] it was shown that α-alkylthiophenes are readily hydrogenated by the action of $(C_2H_5)_3SiH$ and CF_3COOH (ionic hydrogenation) to give the corresponding α-alkylthiophans.

In the present research this method was extended to thiophene derivatives containing an amino group in the side chain. In this case we obtained 2-(ω-diethylaminoalkyl)tetrahydrothiophenes (II), which are representatives of previously undescribed thiophan derivatives.

2-(ω-Diethylaminoalkyl)thiophenes (I), the methylene chain of which includes from two to six carbon atoms, were subjected to ionic hydrogenation:



Ia-e IIa-e

I, II a n=2; b n=3; c n=4; d n=5; e n=6

It was established that the hydrogenation of the thiophene ring depends on the number of CH_2 links of the side chain. When n ≥ 4, the thiophene ring is converted completely to a thiophan ring; when n = 3, only 50% hydrogenation occurs, whereas the reaction practically does not occur when n = 2 (Table 1).

This is probably brought about in the following way. The amino group is protonated in trifluoroacetic acid, and the positive charge arising on the nitrogen atom in the case of 2-(2-diethylaminoalkyl)thiophene

TABLE 1. Hydrogenation of 2-(ω-Diethylaminoalkyl)thiophenes at 50°C

Hydrogenation product II		Heating time, h	Yield, %	Isolated, %
compound	n			
a*	2	50	7	—
		62	7	
b*	3	50	50	—
		62	50	—
c	4	50	96	87
d	5	50	98	89
e	6	50	98	88

*The structures of IIa, b were judged from the appearance in the PMR spectrum of the reaction mixture of signals corresponding to $1H_\alpha$ (δ 3.4 ppm, multiplet) and $4H_\gamma$ (2.1, doublet of triplets, J = 6.2 Hz).

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1206-1207, September, 1975. Original article submitted October 24, 1974.

TABLE 2. 2-(ω-Diethylaminoalkyl)tetrahydrothiophenes (II)

Amine II	bp, °C (mm)	M^+	Empirical formula	Found, %				Calc., %			
				C	H	N	S	C	H	N	S
c	163—164 (11)	215	$C_{12}H_{25}NS$	67,1	11,6	6,4	14,7	66,9	11,7	6,5	14,9
d	188—190 (14)	229	$C_{13}H_{27}NS$	67,9	11,9	6,4	14,1	68,0	11,9	6,1	14,0
e	190—192 (15)	243	$C_{14}H_{29}NS$	68,7	12,0	5,8	13,2	69,1	12,0	5,8	13,2

($n=2$) completely prevents protonation of the thiophene ring. As the amino group is removed from the ring, the effect of the positive charge on the nitrogen atom decreases and when $n=4$ does not affect the hydrogenation process.

The completion of the reaction was judged from the disappearance of the signal of the protons of the thiophene ring in the PMR spectrum of the reaction mixture (δ 6.5-6.9 ppm).

In contrast to the PMR spectra of starting amines I, the PMR spectra of amines IIc-e contain $1H_\alpha$ (δ 3.4 ppm, multiplet), $4H_\gamma$ (δ 2.0 ppm, doublet of triplets, $J=6.1$ Hz), and $2H_\beta$ (δ 2.9 ppm, triplet, $J=5.4$ Hz) signals. The yields of the hydrogenated amines were determined by gas–liquid chromatography (GLC).

EXPERIMENTAL

The PMR spectra were recorded with a Perkin-Elmer R-12 spectrometer (60 MHz). Carbon tetrachloride was used as the solvent in the analysis of the individual substances, and the internal standard was tetramethylsilane. Gas–liquid chromatography was carried out with an LKhM-8MD chromatograph with a 100 by 0.3 cm steel column with 10% Versamid on silanized Celite 545 (80-100 mesh) with a catharometer detector and helium as the carrier gas (V_{He} 40 ml) at 170°.

Hydrogenation of 2-(6-Diethylaminoalkyl)thiophene.* A mixture of 11.1 g (0.46 mole) of amine, 16.8 g (0.145 mole) of $(C_2H_5)_3SiH$, and 79.2 g (0.695 mole) of trifluoroacetic acid was heated in a thermostat at 50° for 50 h, after which it was poured into 200 ml of water. The upper layer – a mixture of excess $(C_2H_5)_3SiH$ and $[(C_2H_5)_3Si]_2O$ – was separated, and the aqueous layer was extracted three times with ether. The combined organic layers were dried with potassium carbonate, the ether was removed by distillation, and the residue was vacuum distilled. A similar method was used to hydrogenate the other amines (see Table 2).

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).

---

*The method used to synthesize the aminothiophenes will be described in another paper.