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RESEARCHES IN THE THIOPHENE SERIES

VIII. Gas-Liquid Chromatography of Isomeric Thienothiophenes*

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Chromatographic behaviors of seven alkyl-substituted thienothiophenes and two acetylmercaptothiophenes are investigated. They are separated on a stationary phase of polyethyleneglycoladipate supported on diatomaceous brick or lining tile. A mixture of 3-methyl-5-ethylthieno [2,3-b] thiophene and 3-methyl-5-ethylthieno [3, 2-b]-thiophene is analyzed quantitatively. The gas-liquid chromatographic method developed is used to elucidate the peculiarities of cyclization of acetonylmercaptothiophenes and isomeric thienothiophenes.

Previously one of the present authors in conjunction with Ya. L. Gol'dfarb worked out methods of preparing isomeric thienothiophenes, viz. cyclization of substituted thienylmercaptoacetic acids by sodium ethoxide, and of acetonylmercaptothiophenes with aluminum chloride [1-6]. To identify the isomeric thienothiophenes, we considered various chemical methods, preparation of acetyl [1, 2] and organomercury derivatives [2, 6], oxidation [6], reductive desulfurization [6], as well as certain physical methods, measurement of dipole moments [6], IR and UV spectroscopy [5]. However, there are real drawbacks with most methods of identifying isomeric thienothiophenes; they take a lot of time, and frequently they do not give quantitative analyses of mixtures of isomeric thienothiophenes.

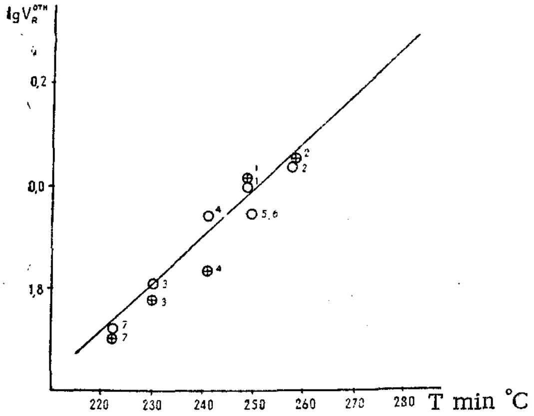

Fig. 1. Relationship between relative retention volumes and boiling points. Key to points: 1) 3-Methyl-5-ethylthieno [3, 2-b] thiophene; 2) 3-methyl-5-ethylthieno-[2, 3-b] thiophene; 3) methylthieno [3, 2-b] thiophene; 4) 3-methylthieno-[2, 3-b] thiophene; 5) 2-ethylthieno [3, 2-b] thiophene; 6) 2-ethylthieno [2, 3-b] thiophene; 7) thieno [3, 2-b] thiophene. Keys to columns: ○ - PEGA/DK + alkali, 170°; ⊕ - PEGA on lining tile, 174°.

Further, the ever increasing use of petroleum of high sulfur content makes it necessary to study and identify organic sulfur compounds which are components of petroleum, and in particular cyclic compounds. Of recent years much research has been done to determine the nature of the sulfur-containing compounds in petroleum, particularly in distillates [7-9]. The presence of condensed heterocyclic compounds of the thionaphthene, dibenzothiophene, naphthothiophenes, benzonaphthothiophenes, etc. type in sulfur-containing petroleums and coals, makes it conceivable that they contained isomeric thienothiophenes, too [10, 11]. Earlier attempts to detect these compounds in coals and lignites were unsuccessful. Evidently this was because existing information about the nature of thienothiophenes and means of identifying them were patently inadequate.

Gas liquid chromatography of heterocyclic sulfur compounds has largely been restricted to thiophene and its homologs [7, 12-17]. The present paper gives results of a chromatographic study of isomeric thienothiophenes.

Experimental

A LKhM-5 chromatograph was used for the investigations. It was built by the Special Construction Division, Institute of Organic Chemistry, AS USSR, and had an air thermostat, self-feeding potentiometer with a 2 mv scale, and thermal conductivity detector. Solid carriers used were diatomaceous brick (DK) washed free from traces of iron, the same but in addition treated with a 5% alcoholic solution of sodium hydroxide, and lining tile. The fraction used was 0.25-0.5 mm. The stationary phase was polyethyleneglycoladipate (PEGA) [18], characterized by thermal stability and selectivity. The stationary phase amounted to 15-20 wt. %. In every case spiral copper columns 6 mm i. d. were used. Part of the work was carried out with a Willy Giede GCHF-18 instrument fitted with a thermal conductivity detector, two integral stainless steel columns packed with solid carrier, sodium chloride (1 m – with a fraction 0.1-0.15 mm, and 1 m – with one 0.09-0.1 mm) to which silicone rubber SKTV (1 wt. %) had been applied.

The separation index was the Θ criterion [19], equal to 0 at no separation, and equal to 1 at complete separation.

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* For Part VII see [21].

Table 1

Retention Time, Relative Retention Volume, and Separation Indices for Thienothiophenes on Different Phases

Compound	Bp, °C, at 760 atm	20% PEGA/DK + alkali, 2 m						20% PEGA/DK, 2.6 m			15% PEGA/ lining tile, 3 m			1% silicone rubber SKTV/NaCl, 2 m		
		150°		170°		211°		175°			153°			200°		
		t_R, min	V_R^{Rel}	t_R, min	V_R^{Rel}	t_R, min	V_R^{Rel}	t_R, min	V_R^{Rel}	θ	t_R, min	V_R^{Rel}	θ	t_R, min	V_R^{Rel}	θ
3-Methyl-5-ethylthieno [2, 3-b] thiophene	248	23.7	1.0	12	1.0	2.5	1.0	44.5	1.0		59.4	1.0		5.1	1.0	1.00**
		(V_R = 1565 ml)		(V_R = 660 ml)		(V_R = 63 ml)		(V_R = 2900 ml)			(V_R = 3560 ml)					
3-Methyl-5-ethylthieno [3, 2-b] thiophene	258	30	1.05	13	1.08	2.5	1.0	49.5	1.11	0.36	67.2	1.13	0,36	5.55	1.09	1.0**
3-Methylthieno [3, 2-b] thiophene	230	11.1	0.47	6.3	0.647	1.75	0.697	26.5	0.60	1.0	—	—		3.0	0.59	1.0**
3-Methylthieno [2, 3-b] thiophene	245	—	—	7.05	0.88	—	—	30.2	0.68		—	—		—	—	—
3-Acetonylmercaptothiophene	257	—	—	5.4	0.556	—	—	18	0.405		—	—		—	—	—
2-Acetonylmercaptothiophene	265	—	—	18.3	1.88	—	—	—	—		—	—		—	—	—
Thieno [3, 2-b] thiophene	221—224	—	—	5.1	0.526	—	—	22.4	0.503	0.82*	—	—		—	—	—
2-Ethylthieno [3, 2-b] thiophene	250	—	—	—	—	—	—	—	—		—	—		4.05	0.79	1.0**
2-Ethylthieno [2, 3-b] thiophene	245	—	—	—	—	—	—	—	—		—	—		4.05	0.79	1.0**

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*For the pair thieno [3, 2-b] thiophene and 3-methylthieno [2, 3-b] thiophene.

**Θ is given for the following pairs: 3-methyl-5-ethylthieno [3, 2-b] thiophene and 3-methylthieno [3, 2-b] thiophene; 3-methyl-5-ethylthieno [2, 3-b] thiophene and 2-ethylthieno [2, 3-b] thiophene; 3-methylthieno [3, 2-b] thiophene and 2-ethylthieno [3, 2-b] thiophene.

The quantitative composition of a mixture was determined either from peak area, taken as the product of height and width at half height, or by multiplying height (h) by retention time (t_R).

Heats of solution were calculated from the temperature relationship for the corrected retention volumes [20].

The methods used for preparing the compounds studied were previously described [6-11, 21]. In what follows derivatives of thieno [3, 2-b] thiophene will be called the unscrewed isomer, and those of thieno [2, 3-b] thiophene the linear isomers.

Results and Discussion

Linear isomers are characterized by higher retention volumes than unscrewed ones, which falls into line with their having much higher boiling points and dipole moments [6]. Introduction of an alkyl group raises the boiling point of a substance, and correspondingly its retention volume. The linear relationship between boiling point and retention volume (Fig. 1) with selectivity coefficient 0.93×10^{-3} lg V_R^{rel}/t°C, enables the isomeric thienothiophenes to be identified.

The behavior of acetonylmercaptothiophenes differs markedly from that of thienothiophenes, the beta substituted isomer emerging sooner, and the alpha substituted one much later, than the thienothiophenes with very similar boiling points.

Treatment of solid carrier with alkali has two effects: it cuts retention time, and gives rise to big tails. The latter effect is just the opposite of what is found for the effect of alkali in chromatographing pyridine bases [18]. Naturally it considerably spoils separation of unscrewed and linear isomers, shoulders and inflexions appearing on the chromatograms instead of maxima. Still, as will be shown below, this generally does not interfere with calculation of the content of isomers in a mixture. After treating the carrier with alkali, the retention time even becomes less than that for a column with 1% silicone rubber SKTV (Table 1). No doubt but that those effects are the result of specific interaction with the alkali.

Table 2

Quantitative Analysis of a Mixture of 3-Methyl-5-ethylthieno [2, 3-b] thiophene (I) and 3-Methyl-5-ethylthieno [3, 2-b] thiophene (II)

Calibration mixture, %		Found, %			
		From peak area *		From the product $h \times t_R$ **	
I	II	I	II	I	II
50	50	49.5	50.5	49	51
40	60	43	57	44	56
30	70	30	70	—	—
Found for the cyclization product***		57.3	39		

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*On a PEGA column (lining tile).

**On a PEGA/DK column treated with alkali.

***3.7% of an unidentified mixture also found.

The values of Θ show that better separation is attained on PEGA supported on brick not treated with alkali, or on lining tile. Though it is not possible to secure complete separation, this does not prevent quantitative analysis of a mixture (Table 2).

The quantitative chromatographic analysis data are in good agreement with the results of spectrophotometric analysis [5].

In addition to the quantitative analysis of a two-component mixture, a qualitative analysis of a six-component mixture was run in 50 min; the peaks in the chromatogram can be seen to be quite symmetrical (Fig. 2).

The calculated heats of solution of 3-methyl-5-ethyl [2, 3-b] thiophene and 3-methyl-5-ethylthieno [3, 2-b] thiophene in the PEGA stationary phase supported on alkali-treated brick, are approximately equal in magnitude, amounting to about 16 kcal/mole.

The method of chromatographic separation of thienothiophenes developed, enable the following questions to be settled: a) identity of the thienothiophenes prepared by different methods (cyclization and reverse synthesis); b) conversion direction when acetonylmercaptothiophene derivatives are cyclized. 3-Methyl-5-ethylthieno [3, 2-b]-thiophene obtained by cyclizing 5-ethyl-3-acetonylmercaptothiophene with aluminum chloride was identical with the 3-methyl-5-ethylthieno-[3, 2-b] thiophene prepared by reverse synthesis from methyl (5-ethyl-2-acetyl-3-thienylmercapto) acetate [21]. The thienothiophene prepared by aluminum chloride cyclization, contained an insignificant trace of what was, apparently, unreacted 5-ethyl-3-acetonylmercaptothiophene, judging by its position on the chromatogram. The isomeric thienothiophene is not formed in the reaction, i.e., in the reaction with aluminum chloride, the acetonylmercapto group does not migrate from position 3 in the thiophene ring to position 2. The same conclusion can be reached by comparing the UV spectra of the cyclization product with those of the isomeric thienothiophenols.

The 3-methylthieno [3, 2-b] thiophene, prepared by aluminum chloride cyclization of 3-acetonylmercaptothiophene, is identical with the 3-methylthieno [3, 2-b] thiophene prepared by reverse synthesis starting from methyl

(2-acetyl-3-thienylmercapto) acetate [21]. The cyclization product contained a trace of 3-acetonylmercaptothiophene. In that case too the acetonylmercapto group did not migrate. However, aluminum chloride cyclization of 5-ethyl-2-acetonylmercaptothiophene is accompanied by migration of the acetonylmercapto group to position 3, and a mixture of dialkyl substituted thienothiophenes is formed (Table 2). Action of acid compounds of the aluminum chloride type can be expected to be accompanied by migration of alkyl groups [22], but the method of gas liquid chromatographic analysis developed made it possible to show that such migration did not occur in a single case.

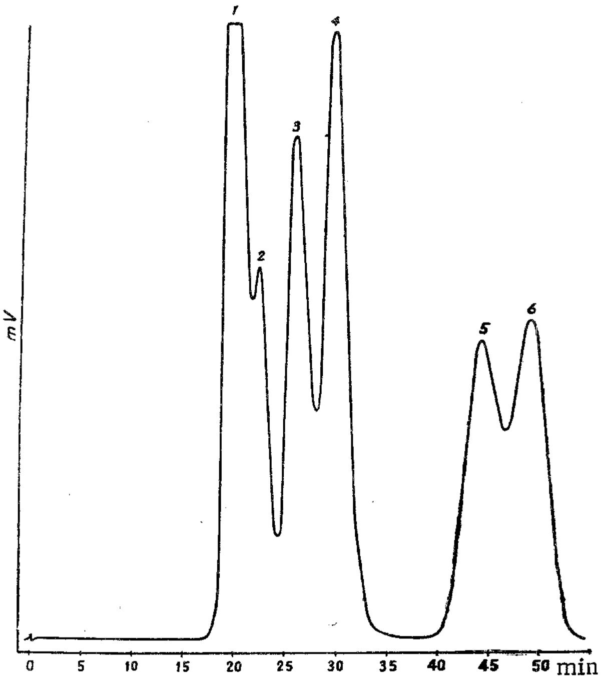

Fig. 2. Chromatogram of mixed isomeric thienothiophenols. Column: 20% PEGA/DK, 2.6 m, 6 mm i.d. Operating conditions: Temperature of column and catharometer 175°, helium flow rate 66 ml/min, pressure at inlet 0.45 kg/cm^2. Key to peaks: 1) 3-acetonylmercaptothiophene, 2) thieno [3, 2-b] thiophene, 3) 3-methylthieno-[3, 2-b] thiophene, 4) 3-methylthieno [2, 3-b] thiophene, 5) 3-methyl-5-ethylthieno [3, 2-b] thiophene, 6) 3-methyl-5-ethylthieno [2, 3-b]-thiophene.

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