114. L. V. Sokolyanskaya, A. N. Volkov, and B. A. Trofimov, Zh. Org. Khim., 12, 905 (1976).
115. A. N. Volkov, L. V. Sokolyanskaya, and B. A. Trofimov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1430 (1976).
116. S. I. Miller and R. Tanaka, in: Selective Organic Transformations, Vol. 1, (B. S. Thjargarjan, ed.), Wiley Interscience, New York (1970), p. 143.
117. E. N. Nelin, A. K. Sheinkman, A. I. Mikhaleva, and B. A. Trofimov, Khim. Geterotsikl. Soedin., No. 2, 167 (1978).
118. B. A. Trofimov, M. V. Sigalov, V. M. Bzhezovskii, G. A. Kalabin, A. I. Mikhaleva, and A. N. Vasil'ev, Khim. Getorotsikl. Soedin., No. 3, 350 (1978).
119. B. A. Trofimov, M. V. Sigalov, V. M. Bzhezovskii, G. A. Kalabin, S. E. Korostova, A. I. Mikhaleva, and L. N. Balabanova, Khim. Geterotsikl. Soedin., No. 6, 768 (1978).

ELECTRONIC ABSORPTION SPECTRA AND ACIDITIES OF HETEROAROMATIC THIOLS

A. V. Anisimov, V. S. Babaitsev,
and E. A. Viktorova

UDC 547.728.1'733.735:543.422.6

The electronic absorption spectra of a number of substituted and unsubstituted thiophene-, benzothiophene-, and benzofuranthiols were studied, and their ionization constants were determined by establishment of the dependence of the optical densities of aqueous alcohol solutions of them on the pH.

A number of papers [1-3] have been devoted to the study of the acidities of phenols, thiophenols, and quinolinethiols by titrimetric and spectrophotometric methods and the effect of structural factors on the acidities. However, systematic studies of a similar sort for heteroaromatic thiols that contain furan and thiophene structural fragments are not available in the literature.

In the present research we obtained the pK_a values of a number of substituted and unsubstituted thiophene-, benzothiophene-, and benzofuranthiols by determination of the dependence of the optical densities of aqueous alcohol solutions of the thiols on the pH. A preliminary analysis of the UV spectra of heteroaromatic thiols showed that these compounds exist exclusively in the thiol form (the UV spectra of thiols I-XI do not contain the absorption band of a C=S group at 490-510 nm) (Table 1). The introduction of electron-donor substituents in the thiol molecules generally gives rise to a bathochromic shift in the electronic absorption spectra (218 → 232 nm for VII and VIII, and 218 → 233 nm for VII and IX). Replacement of a hydrogen atom in the thiophene ring by an electron-acceptor chlorine atom leads to a hypsochromic shift of the maximum of the absorption band of the mercapto group (219 → 206 nm for I and VI). Greater changes in the electronic absorption spectra occur when electron-donor substituents are introduced in the benzothiophene molecule than in the case of benzofuran (VII, VIII, and IX; X and XI); this is associated with the lower degree of aromatic character of the latter.

A comparison of the pK_a values of benzofuran-2-thiols and the corresponding benzothiophene-2-thiols shows that replacement of the sulfur atom in the heteroring by the more electronegative oxygen atom gives rise to weakening of the S—H bond and, as a consequence, an increase in the acidity of the corresponding thiol (Table 1). A similar effect is observed when the hydrogen atom in the 5 position of thiophene-2-thiol (I) is replaced by a chlorine atom (VI); in this case the acidity of the thiol increases by almost an order of magnitude. A similar effect of electron-acceptor substituents on the pK_a values was noted for substituted thiophenols [2] and phenols [1]. The introduction of electron-donor substituents in thiol molecules promotes strengthening of the S—H bond, and the acidity of the thiol decreases in this case (III, IV, V, VIII, IX, and XI). Annellation of the thiophene ring with a benzene

---

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1313-1314, October, 1980. Original article submitted April 21, 1980.

0009-3122/80/1610-0991$07.50

TABLE 1. pK_a Values at 20°C and Wavelengths and Extinctions (liters·mole^{-1}/cm^{-1}) at the Maxima in the Absorption Spectra of Heteroaromatic Thiols

Compound		λ, nm	pK_a	λ (ε)
I	Thiophene-2-thiol	290	6,76±0,05*	219 (3310), 255 (7500), 295 (5160), 305 (4200), 317 (3590)
II	Thiophene-3-thiol	280	6,80±0,05*	218 (5220), 256 (11600), 296 (6000), 305 (5450), 317 (5780)
III	3-Allylthiophene-2-thiol	290	6,92±0,05*	
IV	2-Allylthiophene-3-thiol	280	6,88±0,07*	
V	5-tert-Butyl-3-allylthiophene-2-thiol	290	7,04±0,05*	
VI	5-Chlorothiophene-2-thiol	310	5,73±0,05	206 (4090), 258 (6380), 310 (4740)
VII	Benzothiophene-2-thiol	268	6,70±0,05	213 (12800), 218 (12500), 268 (8850), 298 (7850), 318 (4300), 290 (9450)
VIII	3-Methylbenzothiophene-2-thiol	308	6,85±0,05	213 (12900), 232 (16950), 252 (8760), 277 (5890), 297 (5460), 308 (3300)
IX	3-Allylbenzothiophene-2-thiol	253	6,90±0,05	212 (11000), 233 (14300), 253 (6800), 268 (6170), 281 (6330), 300 (4550), 309 (3240), 338 (1300)
X	Benzofuran-2-thiol	248	6,60±0,05	214 (7050), 248 (4240), 258 (2600), 285 (2460), 305 (2200), 325 (1800)
XI	3-Allylbenzofuran-2-thiol	248	6,75±0,05	213 (6990), 237 (2470), 248 (2820), 255 (2120), 285 (2400), 305 (1830), 320 (1440)

*The pK_a values were determined in [4] by a similar method.

ring and a change in the position of the mercapto group in the thiophene ring do not have a substantial effect on the pK_a value.

EXPERIMENTAL

The electronic absorption spectra of the individual thiols dissolved in 96% ethanol were recorded with a Specord UV-Vis spectrophotometer in quartz cuvettes (l = 0.497 cm). The UV spectra of aqueous alcohol solutions of the thiols with definite pH values were recorded with a Hitachi-124 double-beam recording spectrophotometer in quartz cuvettes (l = 1 cm). A pH-340 potentiometer with a measurement error of ±0.05 pH units was used to measure the pH values of the solutions.

Thiols I, II, VI, VII, VIII, and X were obtained by a general method by the action of sulfur on ether solutions of lithium-substituted thiophenes, benzothiophenes, and benzofurans; the thiols were extracted from the reaction mixtures with a 10% aqueous solution of potassium hydroxide and were isolated by acidification. Thiols III-V, IX, and XI were obtained by thio-Claisen rearrangement of the corresponding allyl hetaryl sulfides [4].

Determination of the Acidities of the Thiols. A 0.5-ml sample of a solution of the investigated thiol in 96% ethanol was placed in a 25-ml volumetric flask, 9.5 ml of ethanol and 5 ml of an aqueous solution (2.5 moles/liter) of potassium chloride to maintain the solution at a constant ionic strength (μ = 0.54) were added, and a definite solution pH was established by bringing the solution up to the mark by the addition of an ammonia–acetate buffer prepared by mixing appropriate amounts of a 0.1 mole/liter solution of ammonia and a 0.1 mole/liter solution of acetic acid. The pH of the solution [$C_{thiol} = (1.24-2.94) \cdot 10^{-4}$ mole/liter] and the optical density (A) at wavelength λ (nm) corresponding to the maximum change in A were measured. The pK_a value was determined by a graphical method using the dependence of the pH on A [5].

LITERATURE CITED

1. F. G. Bordwell and D. G. Copper, J. Am. Chem. Soc., 74, 1058 (1952).
2. F. G. Bordwell and H. M. Andersen, J. Am. Chem. Soc., 75, 6019 (1953).
3. Yu. A. Bankovskii, A. P. Sturis, and A. F. Ievin'sh, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 6, 672 (1967).

4. A. V. Anisimov, V. F. Ionova, and E. A. Viktorova, Khim. Geterotsikl. Soedin., No. 2, 186 (1978).
5. V. M. Peshkova, and M. I. Gromova, Methods of Absorption Spectroscopy in Analytical Chemistry [in Russian], Vyssh. Shk., Moscow (1978), p. 93.

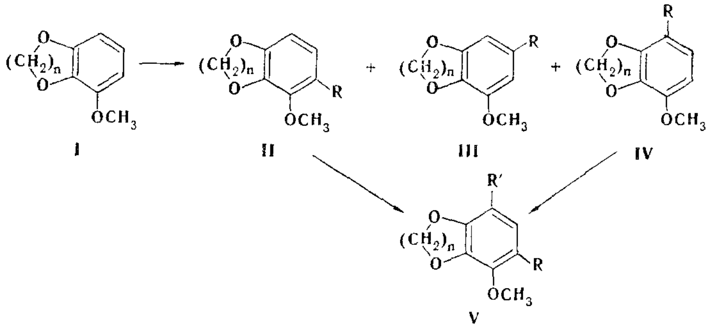
HALOGENATION AND NITRATION OF o-METHOXYBENZODIOXAHETEROCYCLES

V. K. Daukshas, É. B. Udrenaite,
V. L. Gineitite, A. Yu. Rukshenas,
G. G. Komovnikova, and A. V. Barauskaite

UDC 547.729'841'89:542.944.1'958.1

The composition of the products of electrophilic chlorination, bromination, iodination, and nitration of 4-methoxybenzo-1,3-dioxol, 5-methoxybenzo-1,4-dioxane, and 6-methoxybenzo-1,5-dioxepan were established. The reasons for the pathways via which the substitution reactions proceeds are discussed.

Halo and nitro derivatives of 5-methoxybenzo-1,4-dioxane (I, n = 2) are used in the synthesis of physiologically active substances [1]. In a continuation of our search for methods for the preparation of new compounds of this type [2, 3] we studied the compositions of the products of halogenation and nitration of I (n = 1-3).



The ratios of products II-IV are presented in Table 1. The structures of II and IV are confirmed by the presence of two doublets of aromatic protons (J = 8-10 Hz) in the PMR spectra. In the case of III ($R = NO_2$) J = 2-3 Hz. The signals of the methoxy groups of isomers II are shifted to strong field as compared with those of isomers IV (Table 2). The structure of dihalo derivatives V (n = 1, R = R' = Cl, Br, I) proves their formation from the corre-

TABLE 1. Ratios of the Products of Substitution Reactions of I

n	R	II	III	IV
1	Cl	1	0	0
	Br [3]	1,9	0	1
	I	1,3	0	1
	NO_2 [3]	0	1	0
2	Cl	4	0	1
	Br [2]	1	0	5
	I	0	0	1
	NO_2 [2]	1	8	2,7
3	Cl	1	0	1
	Br, I	0	0	1
	NO_2	0	1	0

V. Kapsukas Vilnius State University, Vilnius 232734. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1315-1319, October, 1980. Original article submitted October 17, 1979; revision submitted February 11, 1980.

0009-3122/80/1610-0993$07.50