D. A. Oparin, T. G. Melent'eva, and L. A. Pavlova

It is shown that the reaction of 1,3,3-triphenylthiophthalylium perchlorate with aniline and o- and p-toluidines proceeds with retention of the thiophthalane ring to give, depending on the reaction conditions, N- or C-substituted derivatives of amines.

It is known that salts of cyclic heterocarbonium ions react readily with primary aromatic amines; the direction of the reaction depends both on the structures of the starting compounds and on the conditions under which the synthesis is carried out. Thus the reaction of pyrylium and 2-benzopyrylium salts with aromatic amines leads to pyridinium [1, 2] and isoquinolinium salts [3], while the reaction of 1,2- and 1,3-dithiolium salts lead to substituted arylamines [4, 5]. Phthalylium salts react with arylamines at room temperature in the presence of pyridine to give N-substituted derivatives of amines, viz., 1-arylaminophthalanes, whereas when the components are heated, the final products are the isomeric (with respect to arylaminophthalanes) C-substituted derivatives of amines, viz., 1-(p-aminoaryl)phthalanes [6].

In order to study the effect of the nature of the heteroatom on the direction of the reaction we investigated the reaction of thiophthalylium salts with aniline and o- and p-toluidines in the case of 1,3,3-triphenylthiophthalium perchlorate (I). The reaction conditions were similar to those described for the oxygen analog [6].

As in the case of phthalylium salts, the reaction proceeds with retention of the heteroring. The reaction of perchlorate I with equimolar amounts of aniline and o- and p-toluidines in the presence of pyridine at room temperature gives 1-arylamino-1,3,3-triphenylthiophthalanes (II-IV) - products of nucleophilic addition of the amines to the conjugated carboniumthionium ion. In acidic media the resulting C-N bond is readily hydrolyzed. Starting perchlorate I was isolated when II-IV were treated with a mixture of acetic and perchloric acids.



II $R^1 = R^2 = H$; III $R^1 = CH_3$, $R^2 = H$; IV $R^1 = H$, $R^2 = CH_3$; V $R^1 = H$; VI $R^1 = CH_3$

Heating perchlorate I with excess aniline and o-toluidine leads to isomeric (with respect to II and III) C-substituted derivatives of amines, viz., l-(p-aminoaryl)-1,3,3-triphenylthiophthalanes (V, VI). Let us note that the yields of V and VI depend on the heating time. Thus a mixture of isomers II and V was obtained when perchlorate I was heated with aniline for 1 h, which makes it possible to **regard** the N-substituted derivatives as inter-

Division for the Regulation of Metabolism, Academy of Sciences of the Belorussian SSR, Grodno 230009. Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 917-919, July, 1983. Original article submitted December 27, 1982.

TABLE 1. IR and PMR Spectra of II-VI

Compound	IR spec	ctrum, cm ⁻¹	PMR spectrum, δ, ppm					
	NH	NH ₂	R ¹ (R ²)	NH	$\rm NH_2$	Harom		
II III IV V VI	3402 3411 3398 	 1618, 3396, 3482 1620, 3397, 3483	1,57 (2,18) 1,96	4,12 - 3,89 4,03 —	 3,33 3,48	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$		

TABLE 2. Characteristics of II-VI

Com- pound	mp,* deg C	Found, %		Empirical formula	Calculated, %			Yield,	
		с	н	s		с	н	s	'%
II III IV V VI	$\begin{array}{r} 147 - 149 \\ 193 - 194 \\ 178 - 179 \\ 149 - 152 \\ 143 - 145 \end{array}$	84,6 84,2 84,1 84,5 84,2	5,6 5,9 6,0 5,7 6,1	6,7 6,5 6,6 6,7 6,6	C ₃₂ H ₂₅ NS C ₃₃ H ₂₇ NS C ₃₃ H ₂₇ NS C ₃₂ H ₂₅ NS C ₃₃ H ₂₇ NS	84,3 84,4 84,4 84,3 84,4	5,5 5,8 5,8 5,5 5,8	7,0 6,8 6,8 7,0 6,8	98 96 93 76 55

*The compounds were recrystallized from hexane-ether (II, V, and VI) and hexane-CC14 (III and IV).

mediates in the formation of compounds of the V and VI type. In the case of p-toluidine IV was obtained under these conditions. In contrast to the N-substituted derivatives (arylamino-thiophthalanes), the C-substituted derivatives (p-aminoarylthiophthalanes) are resistant to acidic hydrolysis.

The structures of II-VI were confirmed by the IR and PMR spectroscopic data (Table 1).

Bands of stretching vibrations of the NH group that are characteristic for secondary aromatic amines are present in the IR spectra of N-substituted derivatives II-IV at 3390- 3420 cm^{-1} . The IR spectra of C-substituted derivatives V and VI contain intense bands (~1620 cm⁻¹) that correspond to the deformation vibrations of the NH₂ group, as well as a doublet at 3390-3490 cm⁻¹ due to the symmetrical and asymmetrical stretching vibrations in primary amines. The mutual orientation of these bands is satisfactorily described by the Bellamy-Williams equation [7]:

$v_s(NH_2) = 0.876v_{as}(NH_2) + 345.5$ (cm⁻¹).

The data from the PMR **spectra** do not contradict the conclusions regarding the structures of II-VI drawn on the basis of an analysis of their IR spectra. The signals of the protons **of the NH**₂ group (V and VI) are found at stronger field as compared with the corresponding signals of the NH group (II-IV).

EXPERIMENTAL

The IR spectra of 1.5% solutions of the compounds in CCl₄ (layer thickness 0.58 mm) were recorded with a Specord 75 IR spectrometer. The PMR spectra of solutions in CCl₄ were obtained with a Tesla BS-487C spectrometer (80 MHz) with tetramethylsilane as the internal standard. Starting perchlorate I was obtained by the method in [8]. The characteristics of the synthesized compounds are given in Table 2.

<u>1-Phenylamino-1,3,3-triphenylthiophthalane (II)</u>. A 1.0-g (2.2 mmole) sample of perchlorate I was added in small portions with stirring to a solution of 0.2 g (2.2 mmole) of freshly distilled aniline in 3 ml of pyridine. After 3 h, the reaction mass was poured into 25 ml of a mixture of ice and water, and the resulting precipitate was separated, washed with water, and dried. The reactions of perchlorate I with o- and p-toluidines were carried out similarly.

<u>1-(p-Aminopheny1)-1,3,3-triphenylthiophthalane (V).</u> A mixture of 1.0 g (2.2 mmole) of perchlorate I and 4 ml of aniline was heated on a boiling-water bath for 4 h, after which it was cooled, diluted with 100 ml of absolute ether, and filtered to separate the aniline perchlorate. The filtrate was evaporated, and the excess aniline was removed by steam distillation. The residue was treated with ether, and the ether solution was washed with water and dried with Na₂SO₄. Removal of the solvent gave V.

1-(4-Amino-3-methylphenyl)-1,3,3-triphenylthiophthalane (VI). This compound was obtained as in the preceding experiment, but the reaction mixture was heated for 1.5 h.

Hydrolysis of Arylaminothiophthalanes II-IV. A 0.5-ml sample of 57% HClO4 was added to a hot solution of 0.5 mmole of the corresponding arylaminothiophthalane in 5 ml of acetic acid, after which the mixture was cooled and worked up to give perchlorate I (80-90%), which was crystallized from glacial acetic acid. No melting-point depression was observed for a mixture of this perchlorate with a genuine sample.

LITERATURE CITED

- 1. A. R. Katritzky, A. Prout, R. J. Agha, and M. Alajarin-Ceron, Synthesis, No. 12, 959 (1981).
- É. A. Zvezdina, A. N. Popova, A. I. Pyshchev, and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., No. 4, 461 (1982).
- 3. G. N. Dorofeenko, E. I. Sadekova, and V. M. Goncharova, Khim. Geterotsikl. Soedin., No. 10, 1308 (1970).
- 4. U. Schmidt, A. Lüttringhaus, and F. Hübinger, Ann., 631, 138 (1960).
- 5. E. E. Campaigne, T. Bosin, and R. D. Hamilton, J. Org. Chem., 30, 1677 (1965).
- 6. S. V. Yakovlev and L. A. Pavlova, Zh. Org. Khim., 3, 852 (1967).
- 7. L. Bellamy, New Data on the IR Spectra of Complex Molecules [Russian translation], Mir, Moscow (1971), p. 121.
- 8. T. G. Melent'eva, I. P. Soloveichik, D. A. Oparin, and L. A. Pavlova, Zh. Org. Khim., <u>8</u>, 1327 (1972).

SYNTHESIS AND PROPERTIES OF 9-THIA-1,4-DIAZASPIRO[5.5]UNDECANES

R. A. Kuroyan, V. V. Sarkisyan, and S. A. Vartanyan UDC 547.818.1'861.3'866.1.07:543.422'51

4-Bromo-4-formyltetrahydrothiopyrans, which were used to develop a method for the synthesis of 8,8-dialkyl-9-thia-1,4-diazaspiro[5.5]undecanes, were synthesized from 4-formyltetrahydrothiopyrans. Alkylation of these products with ethyl bromo-acetate and ethyl acrylate gave, respectively, their di- and monosubstituted de-rivatives.

Considering the ever increasing interest in recent years in methods for the synthesis and investigation of the biological properties of spiro biheterocyclic compounds [1-4], we have developed a method for the synthesis of a new spiro biheterocyclic system in which the tetrahydrothiopyran and piperazine rings are spiro-bonded; this method also makes it possible to obtain diverse derivatives of the indicated spiro biheterocycle. The synthesis was accomplished via the scheme at the top of the following page.

Aldehydes I [5] were converted to the corresponding α -bromo aldehydes (II) by bromination by means of dioxane dibromide. It should be noted that bromination in acetic acid does not give the desired result. α -Bromo aldehydes II are relatively unstable and undergo partial resinification upon vacuum distillation. However, they can be used in the next step for the preparation of spiro imines III without additional purification. The corresponding spiro amines IV were obtained in high yields by reduction of the spiro imines III with lithium aluminum hydride. The nitrogen atom in the 4 position of spirans IV is more nucleophilic than the nitrogen atom in the 1 position. Thus a product of monoaddition to the nitrogen atom in the 4 position (Va) is obtained in the reaction of spiro amine IVa with excess ethyl acrylate;

A. L. Mndzhoyan Institute of Fine Organic Chemistry, Academy of Sciences of the Armenian SSR, Yerevan 375014. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 920-922, July, 1983. Original article submitted July 26, 1982.