dimethylaminobenzaldehyde or 3,4-dimethoxybenzaldehyde upon heating in a mixture of glacial acetic acid and acetic anhydride (3:1) for 1 h [4] (see Table 1).

2-Phenyl-8-dimethylaminomethine-5,6,7,8-tetrahydrothiachromylium Perchlorate (XII). A mixture of 0.005 mole of perchlorate (III), 0.01 mole of dimethylformamide, and 16 ml of acetic anhydride was boiled for 10 min, then cooled to room temperature and left for 48 h. Compound (XII) crystallized upon cooling. Yield was 1.6 g (84%), mp 197-198°.

Thiapyrylocyanin (XVI) was obtained analogously (see Table 1).

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SYNTHESIS OF NITROGEN DERIVATIVES OF 2,3'-DITHIENYL

E. A. Popolitova and A. E. Lipkin

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We have synthesized 2,3'-dithienyl, which has previously been detected as a byproduct in the preparation of 2,2'-dithienyl [1, 2], from ketotetrahydrothiophene and 2-thienylmagnesium bromide with subsequent dehydration and dehydrogenation of the tertiary alcohol formed from them [3, 4] (yield, 45-55%).

There is some information in the literature on electrophilic substitution reactions in the 2,3'-dithienyl series; 5-acetyl-2,3'-dithienyl has been synthesized by acetylation of 2,3'-dithienyl. The 5-carboxy-, 2'-carboxy-, and 5'-carboxy-2,3'-dithienyls have been described [3, 4], as well as bromination, deuteration, and metallation (with lithium) reactions of 2,3'-dithienyl [5].

With the objective of further study of electrophilic substitution reactions in the 2,3'-dithienyl series, we have prepared 5-formyl-2,3'-dithienyl (I) by formylation of 2,3'-dithienyl via the Vilsmeier reaction; the structure of (I) was established by oxidizing it to the acid [6], which proved to be identical with 5-carboxy-2,3'-dithienyl (II) prepared by oxidation of 5-acetyl-2,3'-dithienyl.

Thin-layer chromatography on aluminum oxide in the system chloroform–benzene–hexane (30:60:1) showed the presence of a spot of (I) (in UV light) having R_f = 0.61.

It is known that some Schiff bases have physiological activity [7-10]. We have prepared some azomethine bases of the 2,3'-dithienyl series which have not been described in the literature (III)-(IX); see Table 1), which were tested for antimicrobial activity.

Microbiological tests were conducted with respect to Gram-positive (*Staphylocci, Bacillus mesentericus,* anthracoid) and Gram-negative forms of bacteria (intestinal bacilli, *Salmonella typhus*, Flexner and Sonne *Shigella, Bacillus pyocyaneus*). The antimicrobial prop-

V. V. Kuibyshev Polytechnic Institute, Kuibyshev.

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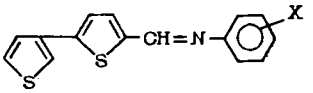
TABLE 1. Azomethine Bases



Compound	X	Yield (%)	mp (deg)	S found (%)	Empirical formula	S calc. (%)
III	H	91	132—3	23,65	$C_{15}H_{11}NS_2$	23,80
IV	2-CH_3	80	103—4	22,50	$C_{16}H_{13}NS_2$	22,61
V	3-CH_3	98	120—1	22,65	$C_{16}H_{13}NS_2$	22,61
VI	4-CH_3	78	150—1	22,71	$C_{16}H_{13}NS_2$	22,61
VII	2-COOH	86	208—10	20,30	$C_{16}H_{11}NO_2S_2$	20,46
VIII	3-COOH	94	213—4	20,25	$C_{16}H_{11}NO_2S_2$	20,46
IX	4-COOH	99	245—6	20,34	$C_{16}H_{11}NO_2S_2$	20,46
X	4-NO_2	83	138—40	20,34	$C_{15}H_{10}N_2O_2S_2$	20,39
XI	3-NO_2	82	116—8	20,25	$C_{15}H_{10}N_2O_2S_2$	20,39

Note. Compounds (III), (IV), (V), (VI), (X), and (XI) were recrystallized from ethyl alcohol; (VII), (VIII), and (IX), from isopropyl alcohol.

erties were studied on simple nutrient agar at a standard preparation concentration of 400 μg/ml. Compounds (III)-(XI) did not display antimicrobial action. The microbiological tests of preparations were performed by T. B. Ryskina.

EXPERIMENTAL METHOD

2,3'-Dithienyl. This compound was prepared by the procedure of [4]. The yield was 7 g (58%), mp 67-68°. Found, %: S 38.40. $C_8H_6S_2$. Calculated, %: S 38.56.

5-Formyl-2,3'-dithienyl (I). To a mixture of 1 g of 2,3'-dithienyl, 0.71 ml of freshly distilled dimethylformamide, and 4.6 ml of dry toluene, with stirring, was added 0.81 of phosphorus oxychloride; the mixture was heated on a water bath for 5 h, and after addition of 9.2 ml of a hot saturated sodium acetate solution the aldehyde was distilled with steam. The yield was 0.84 g (52%), mp 91° (from ethyl alcohol). IR spectrum: 1642 cm^{-1} (C=C). Found, %: S 32.67. $C_9H_6OS_2$. Calculated, %: S 33.

Semicarbazone, mp 212-214° (from ethyl alcohol). Found, %: S 25.60. $C_{10}H_9N_3OS_2$. Calculated, %: S 25.51.

Thiosemicarbazone, mp 170-172° (from ethyl alcohol). Found, %: S 35.72. $C_{10}H_9N_3S_3$. Calculated, %: S 35.97.

5-Carboxy-2,3'-dithienyl (II). To 1.3 g of 5-formyl-2,3'-dithienyl in 65 ml of hot (60-70°) pyridine was added a solution of 2.58 g of potassium permanganate in 52 ml of pyridine and 130 ml of water. After all the oxidant had been added, the mixture was stirred for 30 min at 70° and then was allowed to stand for 12 h at room temperature; the precipitate of manganese dioxide which had settled was filtered off and washed with pyridine. The combined pyridine filtrate was evaporated to dryness under vacuum; the residue was dissolved in water, the solution was filtered, and it was acidified with 10% hydrochloric acid. The crystalline precipitate which separated was filtered off, washed with water, and air dried. The yield was 0.9 g (61%), mp 203-204° (from glacial acetic acid), according to [4] mp 203-205° (from benzene). IR spectrum: 1674 cm^{-1} (carboxyl group). Found, %: S 30.33. $C_9H_6O_2S_2$. Calculated, %: S 30.49.

Azomethine Bases (III)-(XI). To an alcoholic solution of 0.01 mole of 5-formyl-2,3'-dithienyl, with vigorous stirring, was added, in small portions, an alcoholic solution of the appropriate amine, and the mixture was heated on a water bath for 1 h. The precipitate which separated on cooling was filtered off and washed with alcohol; it was then recrystallized from an appropriate solvent. Absorption bands for the azomethine bond were identified in the IR spectra of compounds (III)-(XI) in the 1630-1620 cm^{-1} region.

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TUBERCULOSTATIC ACTIVITY OF PHENOXAZINONE-3, PHENOTHIAZONE-3, 5-PHENYLPHENAZINONE-3, AND SOME OF THEIR DERIVATIVES

T. K. Pashkevich, G. B. Afanas'eva,
I. Ya. Postovskii, K. I. Pashkevich,
T. S. Viktorova, and N. N. Frolova

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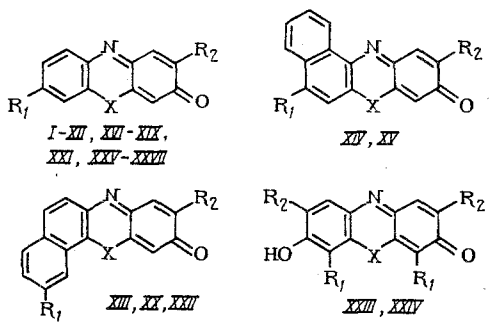
Many biologically active compounds, obtained synthetically and also isolated from bacterial cultures, are derivatives of phenoxazine, phenothiazine, and phenazine. 3-Oxo compounds of these heterocycles have been studied little to date, but nevertheless, materials having antiinflammatory effect (2-aminophenothiazone-3) and active antituberculosis preparations (2-phenyl-5-ethylphenazinone-3, 2-acetamidophenoxazinone-3) [1-3] have already been found among them.

During a comparative study of reactions of nucleophilic agents with phenoxazinone-3 (I), phenothiazone-3 (II), and 5-phenylphenazinone-3 (III), differing in the nature of the bridge heteroatom, we developed a method for the direct amination of the heterocycle [4-6], making it possible to obtain in one step with good yield amino derivatives of the indicated heterocycles. The essence of the method consists of heating the initial heterocycle with amine in alcohol, benzene, or dimethylformamide in the presence of the corresponding amine hydrochloride or catalytic amounts of concentrated hydrochloric acid with subsequent column chromatography. A multistep condensation [1, 3] was used earlier to obtain compounds of such nature.

By this reaction 24 derivatives were obtained containing the cycloalkylimine residue (morpholine, piperidine, cyclohexamethylenimine, N-methylpiperidine) and also the p-thiocresol residue in position 2 or 7 of compounds (I)-(III).



Investigations of the antituberculosis activity of initial heterocycles (I)-(III) and synthesized materials (IV)-(XXVII) were carried out *in vitro* in a Sutton synthetic medium without serum and with addition of 10% normal horse blood serum. Laboratory strains of tu-

S. M. Kirov Ural Polytechnical Institute, Sverdlovsk. Sverdlovsk Scientific-Research Institute of Tuberculosis. Translated from Khimiko-Farmatsevticheskii Zhurnal, Vol. 10, No. 1, pp. 77-80, January, 1976. Original article submitted November 26, 1974.