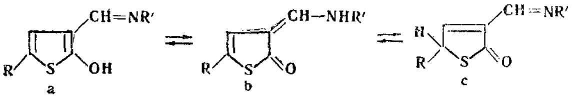
CHEMICAL BEHAVIOR OF 5-ALKOXY-2-ALKYLTHIOPHENES UNDER THE CONDITIONS OF THE VILSMEIER REACTION

Ya. L. Gol'dfarb and M. A. Kalik

UDC 547.733

Dealkylation of the methoxy group and formation of N-substituted 5-alkyl-3-aminomethylene-4-thiolen-2-ones occur during the action of substituted formamides and phosphorus oxychloride on 5-methoxy-2-alkylthiophenes on heating at 50-70 deg C. At 20 deg the major reaction products are 5-alkyl-2-methoxy-3-formylthiophenes.

In developing our studies of the synthesis of complex-forming compounds of the thiophene series, particularly mercaptothienylidenimines [1], it was of interest to obtain oxygen-containing thiophene derivatives, the structures of which can be represented as tautomeric forms Ia-c.



I

Compounds of this type are, in a certain sense, analogs of the azomethines of salicylaldehyde, but the literature data on them are extremely limited. Two Schiff bases obtained from 3-formyl-2-hydroxythiophene are only mentioned in [2], but neither elementary analytical data nor any other information confirming their nature is presented.

The first step of our projected route for the synthesis of I consisted in the action of N,N-disubstituted formamides on 5-alkoxy-2-alkylthiophenes in the presence of phosphorus oxychloride with heating. A number of 5-alkoxy-2-formylthiophenes were obtained by precisely this method [3]. One of the important advantages of this method of formylation of alkoxybenzenes, according to [4], is the absence of dealkylation of the alkoxy group during the action of the Vilsmeier complex.

The data that we obtained indicate, however, that this assertion has limited significance, at least with respect to some of the corresponding thiophene derivatives. Thus, a yellow, crystalline, nitrogen-containing substance rather than the expected 2-methoxy-5-ethyl-3-formylthiophene was isolated in yields of up to 80% by the action of N-methylformanilide (MFA) and phosphorus oxychloride on 5-methoxy-2-ethylthiophene (II)* at 50-60 deg under the conditions for formylation of alkyl thienyl sulfides and 2-alkoxythiophenes. According to the data of elementary analysis and the mass spectra, in which the presence of a molecular ion peak of M^+ 245 and a $\overset{+\cdot}{\mathrm{CH_3N}}\mathrm{C_6H_5}$ fragment with m/e 106 was established (Fig. 1), it is 5-ethyl-3-(N-methyl-N-phenylaminomethylene)-4-thiolen-2-one (VI) (see scheme). The pattern of its absorption in the UV region [λ_{max}, nm (ε): 267 (11,400), 383 (14,535)]† and in the IR region (Fig. 2) is also in agreement with structure VI.

---

* We obtained the 5-alkoxy-2-alkylthiophenes (II-IV) via the method in [5] from the corresponding iodoalkylthiophenes (Va, b).

† According to the data in [6, 7], the bands at 265 and 268 nm are characteristic for thiolactone structures.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 171-177, February, 1971. Original article submitted April 21, 1970.

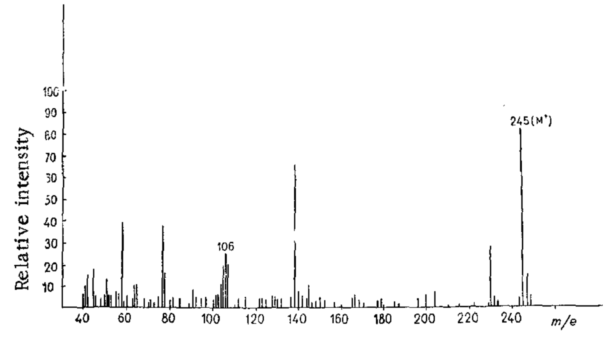


Fig. 1. Mass spectrum of 5-ethyl-3-(N-methyl-N-phenylaminomethylene-4-thiolen-2-one (VI).

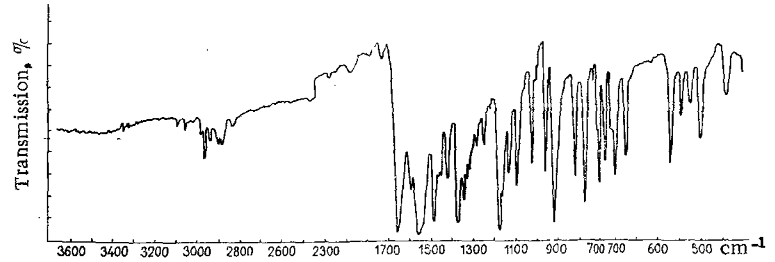
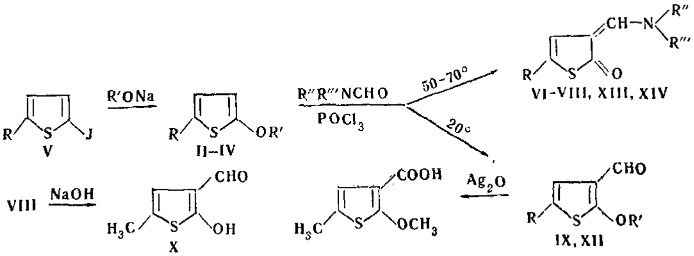


Fig. 2. IR spectrum of 5-ethyl-3-(N-methyl-N-phenylaminomethylene)-4-thiolen-2-one (VI) (KBr pellet).

The intense bands at 1560 and 1660 cm^{-1} are due to the system of conjugated multiple bonds, and the high-frequency band at 1660 cm^{-1} is due to the presence of a $-S-C=O$ fragment.

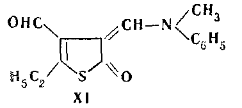
A homolog of VI, viz., VII, was obtained, like, VI, from 5-methoxy-2-methylthiophene (III), while dimethylaminomethylene derivatives VIII along with 2-methoxy-5-methyl-3-formylthiophene (IX), which was isolated as the 2,4-dinitrophenylhydrazone, were obtained in somewhat lower yields by the action of dimethylformamide (DMF) and phosphorus oxychloride.

Thus, heating N,N-disubstituted formamides, particularly MFA, with $POCl_3$ and 5-methoxy-2-alkylthiophenes results in demethylation of the methoxy group, and a substituted aminomethylene residue enters the 3-position of the thiophene ring. The splitting off of a methyl group from the methoxy group is confirmed by the fact that, as already indicated, a peak for the $CH_3\overset{+\cdot}{N}C_6H_5$ fragment is observed in the mass spectrum of VI. Finally, the formation of hydroxyaldehyde X during the alkaline hydrolysis of dimethylaminomethylene derivative VIII is extremely indicative since this pertains to the problem of the structure of VI-VIII. The process of the development of a heteroaromatic thiophene system apparently prevails here over the other possible process, viz., cleavage of a thiolactone ring.

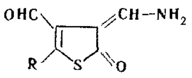


II $R=C_2H_5$, $R'=CH_3$; III $R=R'=CH_3$; IV $R=R'=C_2H_5$; VI $R=C_2H_5$, $R''=CH_3$, $R'''=C_6H_5$; VII $R=R''=CH_3$, $R'''=C_6H_5$; VIII $R=R''=R'''=CH_3$; XIII $R=C_2H_5$, $R''=H$, $R'''=C_6H_5$; XIV $R=CH_3$, $R''=H$, $R'''=C_6H_5$; IX $R=R'=CH_3$; XII $R=CH_3$, $R'=C_2H_5$

A small amount of an orange crystalline substance, for which structure XI can be proposed on the basis of elementary analysis and the NMR and IR spectra ($\nu_{C=O}$ 1720 cm^{-1}), was isolated along with VI in experiments involving the reaction of 5-methoxy-2-ethylthiophene (II) with excess MFA. A signal for an aldehyde proton at δ 9.92 ppm (relative to tetramethylsilane) appears in the NMR spectrum of XI, obtained in N-methyl-2-pyrrolidone, and the proton signal of the thiophene ring at δ 5.88 ppm, which is present in the spectrum of VI, disappears.



XI



XV-XVI

XV R = C_2H_5
XVI R = CH_3

Instances of such double formylation were observed for 1-dimethylaminobutadiene [8] and cyclopentadiene [9].

An increase in the temperature is an essential condition in the demethylation and associated formation of thiolactone structures of the VI type. In fact, if the reagents are mixed at 0-5 deg and the mixture is then held at 20 deg or below, the corresponding alkoxyaldehyde of IX, viz., XII, is obtained as the major reaction product with MFA and DMF. The structure of one of them – 2-methoxy-5-methyl-3-formylthiophene – was confirmed by its oxidation with silver oxide to the known 2-methoxy-5-methyl-3-thiophenecarboxylic acid [5]. We note here that the dealkylation of an alkoxy group under the conditions indicated above occurs to a sufficient extent only with methoxy derivatives; the yield of dealkylation product VI becomes insignificant in the case of 5-ethoxy-2-ethylthiophene (IV).

In the light of what has been set forth, it was of interest to follow the action of the Vilsmeier complex, formed with monosubstituted and unsubstituted formamide, on 5-alkoxy-2-alkylthiophenes. Experiments set up for this purpose indicate in particular that, for example, 5-methoxy-2-alkylthiophenes II and III and formanilide give ~ 40% yields of compounds which correspond in structure to 5-alkyl-3-(N-phenylaminomethylene)-4-thiolen-2-ones (XIII, XIV). This again confirms the fact of the splitting off of a methyl group from the methoxyl group.

We hope to examine the problem of tautomerism of these compounds in greater detail in one of our subsequent communications. We note, however, that forms of the Ia and Ib type seem more likely to us since in these cases there is the possibility of stabilization of the molecule due to the development of an intramolecular hydrogen bond.

The picture of the interaction of 5-alkoxy-2-alkylthiophenes with unsubstituted formamide is more complex and less definite. In this case, in experiments with II and III we were able to isolate compounds which in elementary composition correspond to completely substituted thiophenes XV and XVI, but the quantities obtained were so small that it was impossible to investigate them in sufficient detail. Included in the products of the reaction with III was 5-methyl-2-methoxy-3-formylthiophene (IX) but, as in the experiments with II, the chief mass was composed of yellow, amorphous powders which contain nitrogen and sulfur, do not have sharp melting points, and are slightly soluble in the usual organic solvents; it is possible that they are formed as a result of the polycondensation of XV and XVI.

The formation, under the conditions of the Vilsmeier reaction, of enamines, to which VI-VIII and, probably, XIV and XIII are related, is characteristic for compounds with an active methylene group – malonic [10] and cyanoacetic [11] esters, cyclopentadiene derivatives [9], and, as was recently shown, for pyrrole, 1-phenyl-3-methylpyrazolone [12], and hydroxyindole [13]. The mechanism of the process proposed in [12] can essentially be assumed for our case of the formation of 3-aminomethylene-4-thiolen-2-ones; however, the mechanism of the splitting out of the methyl group still remains hidden, and one can only state that the steric proximity of the methoxy group to the newly formed grouping in the 3-position of the thiophene ring apparently plays a substantial role here. In fact, as already mentioned, only the "normal" reaction products – the corresponding alkoxyaldehydes – were isolated [3] in experiments involving the formylation of 2-alkoxythiophenes.

EXPERIMENTAL

5-Iodo-2-ethylthiophene (Va). This compound was obtained in 75% yield according to the method in [14] from 100 g (0.89 mole) of 2-ethylthiophene, 230 g (0.90 mole) of iodine, and 163 g (0.75 mole) of red mercuric oxide and had bp 95-96 deg (9 mm), n_D^{20} 1.6083, and d_4^{20} 1.7521. Found %: C 30.3, 30.4; H 2.9, 2.9; I 53.3, 53.7; S 13.3, 13.5; MR_D 47.01. C_6H_7IS. Calc. %: C 30.3; H 3.0; I 53.3; S 13.5; MR_D 46.85.

5-Iodo-2-methylthiophene (Vb). This compound was obtained in the same way as Va in 78% yield from 87 g (0.88 mole) of 2-methylthiophene, 226 g (0.89 mole) of iodine, and 144 g (0.67 mole) of red mercuric oxide and had bp 95-96 deg (16 mm) and n_D^{20} 1.6258 (bp 94 deg (16 mm), n_D^{20} 1.6230 [15]).

5-Methoxy-2-ethylthiophene (II). 5-Iodo-2-ethylthiophene [149.5 g (0.63 mole)] and 28 g of powdered cupric oxide were added to a solution of sodium methoxide obtained from 43.4 g (1.88 g-atom) of sodium and 450 ml of absolute methanol. The mixture was refluxed for 36 h and filtered. The filtrate was diluted with an equal volume of cold water, extracted with ether, and the extract was dried with $MgSO_4$ and distilled to give 68.2 g (74%) of II with bp 112 deg (65 mm), 80 deg (14 mm), n_D^{20} 1.5127, and d_4^{20} 1.0560. Found %: C 59.1, 59.4; H 7.0, 6.9; S 22.7, 22.4; MR_D 40.47. $C_7H_{10}OS$. Calc. %: C 59.1; H 7.1; S 22.5; MR_D 40.30.

5-Methoxy-2-methylthiophene (III). This was obtained in 67% yield by the method described for the preparation of II and had bp 73-75 deg (20 mm) and n_D^{18} 1.5220 (bp 51-52 deg (10 mm), n_D^{18} 1.5126 [5]).

5-Ethoxy-2-ethylthiophene (IV). This was obtained in 39% yield in the same way as II. After refluxing for 36 h, the reaction product contained a halothiophene impurity and was treated with magnesium in absolute ether according to the method in [3] to give a product with bp 110 deg (40 mm), n_D^{20} 1.5070, and d_4^{20} 1.0288. Found %: C 61.2, 61.4; H 7.7, 7.7; S 20.8, 20.7; MR_D 44.78. $C_8H_{12}OS$. Calc. %: C 61.5; H 7.7; S 20.5; MR_D 44.91.

2-Methoxy-5-ethyl-3-formylthiophene (XII). A) 5-Methoxy-2-ethylthiophene (II) [3.6 g (0.025 mole)] was added gradually with stirring to 3.4 g (0.025 mole) of N-methylformanilide and 3.9 g (0.026 mole) of $POCl_3$ at 0-5 deg in 40 min. The mixture was maintained at 20 deg for 2 h, allowed to stand overnight, and hydrolyzed with water while cooling. The liberated oil was extracted with ether, and the extract was washed with dilute hydrochloric acid (1:10) and water and dried with $MgSO_4$. The ether was removed by distillation to give 3.0 g (70%) of a red oil, from which 2.1 g (47%) of 2-methoxy-5-ethyl-3-formylthiophene with bp 110-115 deg (3 mm) and n_D^{20} 1.5620 was isolated by distillation (with decomposition). The semicarbazone had mp 198-200 deg (dec., from alcohol). Found %: C 47.5, 47.9; H 5.8, 5.9; S 14.2, 14.0. $C_9H_{13}N_3O_2S$. Calc. %: C 47.6; H 5.8; S 14.1.

B) Phosphorus oxychloride [4.3 g (0.028 mole)] was added gradually to 3.6 g (0.025 mole) of 5-methoxy-2-ethylthiophene (II) in 3 ml of dimethylformamide at 0-5 deg. The mixture was allowed to stand at 20 deg for 2 days and was cooled and treated with saturated sodium acetate solution* and extracted with ether. The extract was washed with water and dried with $MgSO_4$. The ether was removed by distillation to give 3.8 g of a red oil, from which 2.7 g (63%) of aldehyde XII with bp 120-130 deg (5 mm) and n_D^{20} 1.5610 was isolated by distillation. The 2,4-dinitrophenylhydrazone had mp 213.5-214.5 deg (from ethyl acetate). Found %: C 47.7, 47.8; H 4.0, 3.9; S 8.9, 9.1. $C_{14}H_{14}N_4O_5S$. Calc. %: C 48.1; H 4.0; S 9.1.

2-Methoxy-5-ethyl-3-formylthiophene Diethylacetal. A mixture of 5 g (0.03 mole) of aldehyde XII, 5 ml of orthoformic ester, 15 ml of absolute alcohol, and one drop of concentrated hydrochloric acid was refluxed for 6 h. The dark solution was neutralized with 10% methanolic KOH, the solvent was removed by distillation, and the residue was diluted with an equal volume of water. The mixture was thoroughly extracted with ether, and the ether extract was washed with water and dried with $MgSO_4$. The ether was removed by distillation to give 5 g of a red oil (which vacuum-distilled with decomposition) from which 3.4 g (47%) of 2-methoxy-5-ethyl-3-formylthiophene diethylacetal with bp 126-127 deg (6 mm) and n_D^{20} 1.4950 was isolated. Found %: C 59.8; H 8.3; S 13.13. $C_{12}H_{20}O_3S$. Calc. %: C 59.0; H 8.2; S 13.7. The insufficiently satisfactory analytical data can apparently be explained by decomposition of the acetal during distillation.

2-Methoxy-5-methyl-3-formylthiophene (IX). This was obtained in 50% yield, as described above, from 3 g of III, 2 ml of DMF, and 2 ml of $POCl_3$ and had bp 98-100 deg [3 mm (dec.)] and n_D^{20} 1.5693. The 2,4-dinitrophenylhydrazone had mp 201-202 deg (from ethyl acetate and from $CHCl_3$). Found %: C 46.7, 46.6; H 3.9, 3.7; S 9.4, 9.5. $C_{13}H_{12}N_4O_5S$. Calc. %: C 46.4; H 3.6; S 9.5.

2-Methoxy-5-methyl-3-thiophenecarboxylic Acid. Aldehyde IX [1 g (0.006 mole)] was added to a suspension of freshly precipitated Ag_2O [from 2.2 g (0.013 mole) of $AgNO_3$ and 0.6 g (0.015 mole) of NaOH] in the minimum amount of water, and the mass was stirred for 3 h and allowed to stand overnight. The precipitate was removed by filtration and washed with 10% NaOH and water. The filtrate was extracted with ether, acidified with HCl (1:1), and the acid was extracted with ether. The ether extract was washed with water and dried with $MgSO_4$. Removal of the ether by distillation gave 0.3 g of 2-methoxy-5-methyl-3-thiophenecarboxylic acid with mp 147-148.8. deg (from water and from ethylacetate–heptane) (mp 147-149 deg [5]). Found %: C 48.6, 48.9; H 4.7, 4.7. $C_7H_8O_3S_2$. Calc. %: C 48.8; H 4.7.

---

* If the mixture is allowed to stand for a long time (overnight) after hydrolysis, the aldehyde can be isolated in higher yields. (The oil separates better.)

5-Ethyl-3-(N-methyl-N-phenylaminomethylene)-4-thiolen-2-one (VI). 5-Methoxy-2-ethylthiophene (II) [5 g (0.035 mole)] was added dropwise in 40 min to 4.75 g (0.035 mole) of MFA and 5.4 g (0.036 mole) of $POCl_3$ at such a rate that the temperature did not exceed 50-60 deg (water cooling). The reaction mass was stirred at 50-60 deg for 2 h. The thickened mixture was allowed to stand overnight, dissolved with heating (~ 40 deg) in benzene; and the solution was stirred for 30-40 min with 10-15 ml of water. The organic layer was separated, the aqueous layer was extracted with benzene; and the extract and organic layer were combined, washed with water, and dried with $MgSO_4$. Removal of the benzene by distillation yielded 7 g (81%) of a solid,[*] yellow substance with mp 70 deg which melted at 77-78 deg after two recrystallizations from heptane (the yield of pure VI was 53%). Found %: C 68.2, 68.2; H 6.0, 6.2; N 5.7, 5.7; S 12.5, 12.5; mol. wt. 245.[†] $C_{14}H_{15}NOS$. Calc. %: C 68.5; H 6.2; N 5.7; S 13.1; mol. wt. 245. Compound VI was soluble in benzene, alcohol, ethyl acetate, $CHCl_3$, and CCl_4 and less soluble in ether and heptane. The perchlorate was obtained by the addition of 70% $HClO_4$ to a solution of VI in acetic acid and had mp 164-165 deg (from acetic acid–ether). Found %: C 49.0, 49.0; H 4.7, 4.8; Cl 10.3, 10.6; N 4.2, 4.2; S 9.3, 9.5. $C_{14}H_{15}NOS \cdot HClO_4$. Calc. %: C 48.6; H 4.7; Cl 10.3; N 4.0; S 9.3.

A small amount of orange crystals of 5-ethyl-4-formyl-3-(N-methyl-N-phenylaminomethylene)-4-thiolen-2-one (XI) with mp 175-176 deg (from ethyl acetate and from CCl_4) was isolated (in experiments with a twofold excess of MFA) from the solution obtained during the washing of VI. Found %: C 66.2, 66.4; H 5.6, 5.7; S 11.9, 11.9. $C_{15}H_{15}NO_2S$. Calc. %: C 65.9; H 5.4; S 11.7.

5-Methyl-3-(N-methyl-N-phenylaminomethylene)-4-thiolen-2-one (VII). This was obtained in the same way as VI from 3 g (0.023 mole) of III, 3.28 g (0.024 mole) of MFA, and 3.6 g (0.024 mole) of $POCl_3$. Workup and removal of the solvent by distillation yielded 4.13 g of a solid, yellow residue from which 2 g (37%) of pure VII with mp 105-106 deg was isolated by recrystallization from heptane. Found %: C 67.7, 67.8; H 5.6, 5.7; S 13.5, 13.8. $C_{13}H_{13}NOS$. Calc. %: C 67.5; H 5.7; S 13.9. The heptane-insoluble, dark, amorphous powder did not have a sharp melting point and is apparently a polycondensation product.

Action (with heating) of DMF and $POCl_3$ on 5-Methoxy-2-methyl-thiophene (III). Phosphorus oxychloride [3.6 g (0.024 mole)] was added gradually to a solution of 3 g (0.023 mole) of III in 2 ml of DMF, and the mixture was heated at 60-70 deg for 2 h and allowed to stand overnight. The next day the viscous, red oil was stirred with a solution of 4 g of sodium acetate in 10 ml of water until complete decomposition of the complex, and the mixture was extracted with benzene. The extract was washed with water and dried with $MgSO_4$, and the benzene was removed by distillation to give 1.6 g of a yellow, crystalline substance mixed with an oil. The crystals were washed with ether and recrystallized from heptane to give 0.54 g (16%) of 5-methyl-(N,N-dimethylaminomethylene)-4-thiolen-2-one (VIII) with mp 131-132 deg. Found %: C 56.5, 56.7; H 6.5, 6.4; S 18.8, 18.6; $C_8H_{11}NOS$. Calc. %: C 56.7; H 6.5; S 18.9. The filtrate from washing VIII was evaporated, an alcohol solution of 2,4-dinitrophenylhydrazine sulfate was added to the residue, and the resulting red precipitate was filtered to give 0.45 g of the 2,4-dinitrophenylhydrazone of aldehyde IX with mp 199-200 deg (from ethyl acetate). A sample of this product did not depress the melting point of a sample of the hydrazone previously obtained (see above).

Action (with heating) of MFA and $POCl_3$ on 5-Ethyoxy-2-ethylthiophene (IV). A total of 3.7 g of a dark oil, which partially crystallized on standing in a refrigerator, was obtained from 3 g (0.019 mole) of IV, 2.6 g (0.019 mole) of MFA, and 3 g (0.02 mole) of $POCl_3$ after heating for 2 h at 60-70 deg and the usual workup. A portion of the crystals was squeezed on a porous plate to give a product with mp 76-77 deg (from heptane); this product did not depress the melting point of a sample of the thiolenone (VI) previously obtained. The oil (0.3 g) yielded 0.3 g (43%) of the 2,4-dinitrophenylhydrazone of 2-ethoxy-5-ethyl-3-formylthiophene with mp 177-178 deg (from ethyl acetate). Found %: C 49.6, 49.3; H 4.5, 4.4; S 8.9, 8.9. $C_{15}H_{16}N_4O_5S$. Calc. %: C 49.4; H 4.4; S 8.8. A small amount of 5-ethyl-4-formyl-3-(N-methyl-N-phenylaminomethylene)-4-thiolen-2-one (XI) with mp 174-176 deg (from ethyl acetate) was also isolated in experiments with a 1.5-2-fold excess of MFA. Found %: C 65.6, 65.5; H 5.7; 5.7; S 11.4, 11.3. $C_{15}H_{15}NO_2S$. Calc. %: C 65.9; H 5.4; S 11.7. A sample of this product did not depress the melting point of a sample obtained by the action of MFA and $POCl_3$ on II (see above).

5-Ethyl-3-(N-phenylaminomethylene)-4-thiolen-2-one (XIII). Phosphorus oxychloride [3.7 g (0.024 mole)] was added gradually to a suspension of 3 g (0.025 mole) of formaldehyde in 3.4 g (0.024 mole) of

---

[*] In some cases the residue was a viscous oil which crystallized on cooling or trituration with heptane.

[†] Determined by mass spectroscopy.

5-methoxy-2-ethylthiophene (the temperature rose to 90-100 deg). The thickened mixture was heated at 60-70 deg for 2 h, allowed to stand overnight, and worked up as described above for VI. Removal of the benzene by distillation yielded 3.25 g (72%) of an oily residue which crystallized on cooling. The precipitate was filtered and washed with cold alcohol–ether and dried in vacuo to give 2.4 g (43%) of XIII with mp 99-100 deg (after two recrystallizations from alcohol). Found %: C 67.5, 67.7; H 5.6, 5.6; S 13.7, 13.8. $C_{13}H_{13}NO_3S$. Calc. %: C 67.5; H 5.7; S 13.9.

5-Methyl-3-(N-phenylaminomethylene)-4-thiolen-2-one (XIV). This compound was obtained, like XIII, from 3 g (0.025 mole) of formaldehyde, 3 g (0.023 mole) of 5-methoxy-2-methylthiophene, and 3.6 g (0.024 mole) of $POCl_3$ and had mp 159-160 deg (from alcohol and from heptane) (mp 165 deg (from alcohol) [2]). According to gas-liquid and thin-layer chromatography [on Al_2O_3, hexane–ether (4:1)] it was a pure compound. Found %: C 66.6, 66.4; H 5.1, 5.1; S 14.4, 14.7. $C_{12}H_{11}NOS$. Calc. %: C 66.3; H 5.1; S 14.8.

Action of Alkali on 5-Methyl-3-(N,N-dimethylaminomethylene)-4-thiolen-2-one (VIII). Compound VIII (0.48 g) was refluxed with 5 ml of 5% NaOH until it dissolved completely and the odor of dimethylamine vanished. The dark solution was cooled and acidified with HCl (1:10); and the resulting precipitate was filtered, washed with water, and dried to give 0.32 g (80%) of 5-methyl-2-hydroxy-3-formylthiophene (X), which melted at 98-100 deg (mp 112 deg (from benzene) [2]) after reprecipitation from 10% NaOH with dilute HCl (1:1) and two recrystallizations from heptane and from benzene. Found %: C 50.4, 50.4; H 4.3, 4.1; S 22.4, 22.2. $C_6H_6O_2S_2$. Calc. %: C 50.7; H 4.2; S 22.5. Aldehyde X (0.1 g) was heated with 0.1 g of aniline in alcohol until it dissolved completely. Cooling of this solution precipitated yellow crystals of a Schiff base with mp 157-158 deg (from alcohol). A sample of this product did not depress the melting point of a sample of 5-methyl-3-(N-phenylaminomethylene)-4-thiolen-2-one (XIV) (see above).

Action of Formamide and $POCl_3$ on 5-Methoxy-2-ethylthiophene (II). Phosphorus oxychloride (2.3 ml) was added dropwise to 3.6 g of II and 2.2 ml (twofold excess) of freshly distilled, dry formamide (exothermic reaction), and the mass was stirred at 60 deg for 2 h and allowed to stand overnight. After the usual workup 1.7 g of an oil was isolated from the benzene extract and was converted by treatment with heptane to an amorphous powder with mp 126-145 deg (dec.) containing nitrogen and sulfur, the structure of which was not established. A total of 0.8 g of a mobile, red oil, from which 0.7 g of the 2,4-dinitrophenylhydrazone of 2-methoxy-5-ethyl-3-formylthiophene with mp 213-214 deg (from ethyl acetate) was obtained, was isolated from the aqueous layer after standing overnight. A sample of this product did not depress the melting point of a sample of the hydrazone obtained previously (see above).

A small amount of a yellow, crystalline substance with mp 119-121 deg (from ethyl acetate), which corresponds in composition to 5-ethyl-4-formyl-3-aminomethylene-4-thiolen-2-one (XV), was isolated by extraction with hot heptane when the experiments were carried out with threefold to fourfold excesses of formamide. Found %: C 52.5, 52.6; H 5.0, 5.0; N 7.8; S 17.6, 17.5. $C_8H_9NO_2S$. Calc. %: C 52.4; H 4.9; N 7.7; S 17.5.

Action of Formamide and $POCl_3$ on 5-Methoxy-2-methylthiophene (III). Workup of the reaction mixture, obtained as described above from 2 g (0.016 mole) of III, 2 ml of formamide, and 1.5 ml of $POCl_3$, yielded (from the benzene extract) 0.4 g of a yellow oil which was treated with heptane. Cooling of the heptane solution liberated an oil and a small amount of yellow crystals of 5-methyl-4-formyl-3-aminomethylene-4-thiolen-2-one (XVI) with mp 175-176 deg (from heptane). Found %: C 49.7; H 4.1; S 19.1. $C_7H_7NO_2S$. Calc. %: C 49.7; H 4.2; S 18.9. The 2,4-dinitrophenylhydrazone of 2-methoxy-5-methyl-3-formylthiophene with mp 200-201 deg (from ethyl acetate) was obtained from the oil remaining after separation of XVI and did not depress the melting point of a sample of the hydrazone previously described (see above).

LITERATURE CITED

1. Ya. L. Gol'dfarb, M. A. Kalik, and M. L. Kirmalova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 701 (1962).
2. P. Demerseman, J.-P. Lechartier, A. Cheutin, M. L. Desvoye, and R. Roger, Comptes Rend., 254, 1652 (1962).
3. E. Profft, Ann., 622, 196 (1959).
4. N. P. Buu-Hoi, N. D. Xuong, M. Sy, G. Lejeune, and N. B. Tien, Bull. Soc. Chim. France, 1594 (1955).
5. J. Sicé, J. Am. Chem. Soc., 72, 5543 (1950).
6. A. J. Kosak, R. J. F. Palchak, W. A. Steele, and C. M. Selwitz, J. Am. Chem. Soc., 76, 4450 (1954).

7. A.-B. Hörnfeldt, Ark. Kemi, 22, 211 (1964).
8. Z. Arnold, Coll. Czech. Chem. Commun., 25, 1309 (1960).
9. Z. Arnold, Coll. Czech. Chem. Commun., 25, 1313 (1960).
10. H. Bredereck and K. Bredereck, Ber., 94, 2278 (1961).
11. F. Eiden, Angew. Chem., 72, 77 (1960).
12. M. A. Kira and A. Bruckner-Wilhelms, Acta Chim. Acad. Sci. Hung., 56, 47 (1968).
13. S. Seshadri, M. S. Sardessai, and A. M. Betrabet, Indian J. Chem., 7, 662 (1969).
14. Synthesis of Organic Preparations [Russian translation], Vol. 2, Inostr. Lit., Moscow (1949), p. 287.
15. A. Vlastelitsa, Zh. Russk. Fiz.-Khim. Obshchestva, 46, 790 (1914).