from a mixture of alcohol and ether). The absorption bands at 3400, 3490, and 450-600 cm^{-1} in the IR spectrum of IVC are associated with the presence of water of hydration.

1-Arylthioniacycloalkane Iodides (ID-IVD, Table 3). A hot solution of 1.7 g (0.01 mole) of potassium iodide in a mixture of 10 ml of alcohol and 1 ml of water was added to a hot solution of 0.01 mole of the corresponding perchlorate (IA-IVA) in a mixture of 3 ml of alcohol and 2 ml of water, and the mixture was refluxed for 1 min. After a few hours, the precipitated $KClO_4$ was separated and washed with water and alcohol. The wash liquid was combined with the filtrate, and the mixture was evaporated. The residue was recrystallized from alcohol (ID, IID), water (IIID), or acetone—alcohol—ether (IVD). The IR spectrum of hydrated IIID contains absorption bands at 3420, 3500, and 440-490 cm^{-1}.

1-(p-Methoxyphenyl)-1-thioniacycloalkane Picrates (IIIE and IVE, Table 3). Alcohol solutions of equivalent amounts of the corresponding perchlorates (IIIA and IVA) and picric acid were mixed with heating, and the precipitated picrates (IIIE and IVE) were separated and crystallized from alcohol.

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ACYLATION OF BENZOTHIOPHENE IN THE PRESENCE OF SMALL AMOUNTS OF FERRIC CHLORIDE

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The corresponding ketones were obtained by reaction of acetyl, benzoyl, and 4-methyl- and 4-methoxybenzoyl chlorides with benzothiophene in the presence of $1 \cdot 10^{-3}$-$1 \cdot 10^{-4}$ mole of ferric chloride. It was found by gas—liquid chromatography that ∿1:4 mixtures of 2- and 3-acylbenzothiophenes are formed in all cases.

Little study has been devoted to the synthesis of ketones of the thiophene series by acylation of benzothiophene, although sulfur-containing heterocyclic carbonyl compounds are potential physiologically active substances. The acetylation [1-3] and benzoylation [3-4] of benzothiophene in the presence of various catalysts have been described. The o-methylbenzoylation [5] and p-methoxybenzoylation [6] of benzothiophene in the presence of equimolar amounts of aluminum chloride and stannic chloride are also known. It is apparent from the results of these studies that 3-acylbenzothiophenes are formed exclusively in the acylation of benzothiophene. The 2 isomer was isolated along with the 3-acyl product only in [3].

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We have studied the acylation of benzothiophene with acetyl, benzoyl, and 4-methyl- and 4-methoxybenzoyl chlorides in the presence of $1 \cdot 10^{-3}$-$1 \cdot 10^{-4}$ mole of ferric chloride. The acylation of heterocyclic compounds in the presence of small amounts of catalysts has a number of advantages as compared with the well-known Friedel—Crafts method [7]. By refluxing an equimolar mixture of the acid chloride, benzothiophene, and $1 \cdot 10^{-3}$-$1 \cdot 10^{-4}$ mole of ferric chloride for 2 h we obtained the corresponding ketones of the benzothiophene series. It was found that the products are obtained in good yields (72-75%) in the benzoylation and 4-methyl- and 4-methoxybenzoylation of benzothiophene. We obtained ∿30% of the ketone in the acetylation of benzothiophene with acetyl chloride; the use of acetic anhydride in place of acetyl chloride makes it possible to markedly increase the yield of the ketone fraction. The composition of the products of acylation of benzothiophene was studied by gas—liquid chromatography (GLC). It was found that all of the reactions involving acylation of benzothiophene proceed with the formation of 2- and 3-substituted ketones. 3-Acylbenzothiophenes are formed as the chief products in all cases; the amounts of 2-acylbenzothiophenes do not exceed 20-25%. According to the data in [8], the relative rate of substitution of the hydrogen atoms in the 3 and 2 positions in the acetylation of benzothiophene is ∿6:1, as compared with ∿2:1 in the case of benzoylation. Under our conditions the 3- and 2-acylbenzothiophenes are formed in a ratio of 4:1. Consequently, the isomer distribution depends on the electrophilicity of the acylating agent and the reaction conditions. We were able to separate the mixture of isomers of some of the acylbenzothiophenes into the individual components by fractional crystallization. We isolated and identified 3- and 2-benzoylbenzothiophenes and 3- and 2-acetylbenzothiophenes. Gas—liquid chromatography of the ketone fractions obtained in the p-methyl- and p-methoxybenzoylation of benzothiophene gives two peaks, but we were unable to isolate the pure 2-acylbenzothiophene from the fractions. The structures of the 3- and 2-acetylbenzothiophenes were proved by their oxidation to the corresponding benzothiophene-3- and benzothiophene-2-carboxylic acids.

The proposed synthesis of ketones of the benzothiophene series in the presence of small amounts of ferric chloride is not inferior to the previously described methods with respect to the yields of products and can be used as a preparative method.

EXPERIMENTAL

Gas—liquid chromatography was carried out with a Tsvet-1-64 chromatograph with a thermal conductivity detector and a 2-m-long steel column with an inner diameter of 4 mm filled with 10% Apiezon L on Celite; the carrier gas was hydrogen, the flow rate was 30 ml/min, and the temperature was 265°C. The peaks were assigned by the addition of standards. The 3-acetylbenzothiophene content was ∿80%, and up to 20% of the 2 isomer was present.

Acetylation of Benzothiophene. A mixture of 6.7 g (0.05 mole) of benzothiophene, 5.1 g (0.05 mole) of acetic anhydride, and 0.02 g of ferric chloride was heated at 140-150°C for 2 h, after which the unchanged benzothiophene and acetic anhydride were removed by distillation, and the residue was vacuum distilled to give 6.2 g (70%) of an acetylbenzothiophene fraction with bp 125-129°C (2 mm). Fractional recrystallization from alcohol gave 2-acetylbenzothiophene, with mp 88°C, and 3-acetylbenzothiophene with mp 65°C (mp 88 and 65°C, respectively [3]). Oxidation of 2-acetylbenzothiophene with sodium hypobromite gave benzothiophene-2-carboxylic acid with mp 240°C, and similar treatment of 3-acetylbenzothiophene gave benzothiophene-3-carboxylic acid with mp 171°C (mp 241 and 172°C, respectively [3]).

Benzoylation of Benzothiophene. The reaction of 6.7 g (0.05 mole) of benzothiophene, 7 g (0.05 mole) of benzoyl chloride, and 0.02 g of ferric chloride by the above method gave 8.4 g (70%) of a benzoylbenzothiophene fraction with bp 235-241°C (15 mm). Gas—liquid chromatography was carried out under the above-indicated conditions at 280°C. The percentage of the principal product — 3-benzoylbenzothiophene — was ∿81%. Fractional recrystallization from alcohol gave 3-benzoylbenzothiophene, with mp 53°C, and 2-benzoylbenzothiophene with mp 48°C (mp 53 and 48°C, respectively [3]).

p-Methylbenzoylation of Benzothiophene. The reaction of 6.7 g (0.05 mole) of benzothiophene, 7.7 g (0.05 mole) of p-methylbenzoyl chloride, and 0.02 g of ferric chloride gave 9.2 g (72%) of a fraction with bp 238-243°C (15 mm) containing, according to GLC, 79% 3-(p-methylbenzoyl)benzothiophene. A second peak evidantly was related to the 2 isomer, which we were unable to isolate in pure form. Crystallization from alcohol gave 3-(p-methylbenzoyl)-benzothiophene with mp 102-104°C. Found: C 75.9; H 4.6%. $C_{16}H_{12}OS$. Calculated: C 76.2; H 4.8%.

p-Methoxybenzoylation of Benzothiophene. The reaction of 6.7 g (0.05 mole) of benzothiophene, 8.5 g (0.05 mole) of p-methoxybenzoyl chloride, and 0.02 g of ferric chloride gave 8.7 g (65%) of a fraction with bp 275-285°C (13 mm), which, according to GLC, contained up to 80% 3-(p-methoxybenzoyl)benzothiophene. Crystallization from alcohol gave 3-(p-methoxybenzoyl)benzothiophene with mp 112°C (mp 112°C [6]). A second isomer was not isolated.

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SYNTHESIS AND SOME TRANSFORMATIONS OF 2-ACYLMETHYL-1,3-OXATHIOLANES

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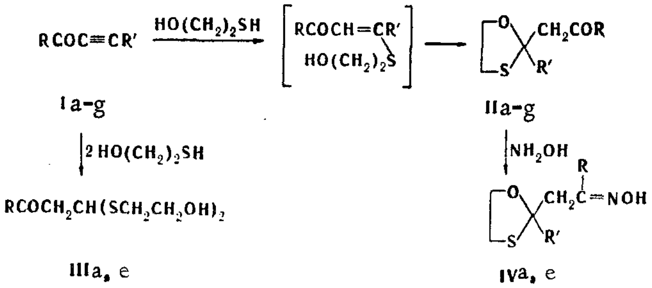
2-Acylmethyl-1,3-oxathiolanes, which form oximes with hydroxylamine and perchlorates with perchloric acid, were synthesized by reaction of α-alkynyl ketones with β-mercaptoethanol.

It is known [1-4] that one or two molecules of alcohol or phenol can be added to α-alkynyl ketones. One mole of thiol is added in the reaction of β-alkyl-α-ethynyl ketones with thiols [5-7]. The formation of cyclic products — the corresponding 2-substituted 1,3-dioxolanes [4] and 1,3-dithiolanes [8] — as a result of "double addition" to the acetylenic bond is possible with some 1,2-dinucleophilic reagents (ethylene glycol and ethanedithiol).

We have studied the reaction of α-alkynyl ketones Ia-g with β-mercaptoethanol; this reaction proceeds readily in the presence of basic catalysts — potassium carbonate or triethylamine — to give 2-acylmethyl-1,3-oxathiolanes (IIa-g, Table 1). The reaction probably proceeds through the intermediate formation of ketovinyl sulfides and cyclization of the latter.



I—IV a $R=C_6H_5$, $R'=H$; I, II b $R=C_6H_5$, $R'=C_4H_9$; c $R=R'=C_6H_5$; d $R=m\text{-}C_6H_4\text{—}NO_2$, $R'=C_6H_5$; e $R=C_4H_3S$, $R'=H$; f $R=C_4H_3S$, $R'=C_4H_9$; g $R=C_4H_3S$, $R'=C_6H_5$

The absorption band of the C=O bond lies at 1650-1685 cm^{-1} in the IR spectra of IIa-g. The absorption at 1070-1120 cm^{-1} corresponds to the stretching vibrations of the C=O bond,

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