PREPARATION OF PHENANTHRO[9,10-b]THIOPHENE AND PROPERTIES OF ITS DERIVATIVES

T. N. Sidorenko, G. A. Terent'eva,
and V. S. Aksenov

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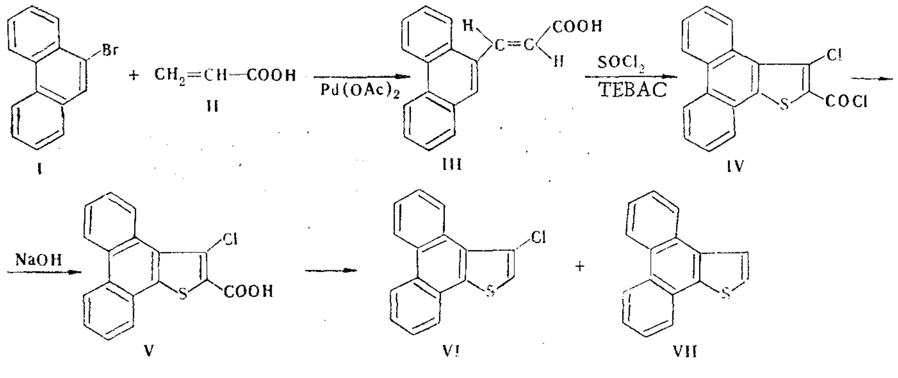
The oxidation of β-(9-phenanthryl)acrylic acid, which was obtained by arylation of acrylic acid with 9-bromophenanthrene, with thionyl chloride in the presence of triethylbenzylammonium chloride leads to the formation of 3-chloro-2-chlorocarbonylphenanthro[9,10-b]thiophene, which, after saponification to give the acid, undergoes simultaneous dehalogenation and decarboxylation under the influence of pyridine with added copper.

As reported in [1], the combination of arylation of acrylic acid with aromatic iodo derivatives with subsequent oxidation of the resulting β-substituted acrylic acids with thionyl chloride in the presence of triethylbenzylammonium chloride (TEBAC) opens up extensive possibilities for the synthesis of arenothiophene derivatives. Extending the limits of applicability of the proposed method for the synthesis of polycondensed arenothiophenes is of undoubted interest, since there is presently no universal method for the preparation of thiophene structures with more than three condensed rings in common [2]. The available methods [3, 4] involve the use of starting reagents that are difficult to obtain.

The goal of the present research was to develop a method for the synthesis of the phenanthro[9,10-b]thiophene system on the basis of accessible starting substances via the scheme that we proposed for the preparation of naphtho[b]thiophenes [1].

The use of the indicated scheme for the synthesis of polycondensed structures revealed a number of peculiarities. Thus the lability of the halogen atom increases as the number of condensed rings is increased, and not only iodo derivatives but also bromo derivatives are capable of arylation. trans-β-(9-Phenanthryl)acrylic acid (III) was obtained in high yield in the arylation of acrylic acid (II) with 9-bromophenanthrene (I). The IR spectrum of acid III contains the following absorption bands: 950 (trans-arylethylene C–H), 1680 (C=O), and 1620 cm^{-1} (C=C, Ar). The bands at 860 and 740 cm^{-1} confirm 1,2,3,4,5 substitution and 1,2 disubstitution of the benzene ring, respectively.



The oxidation of acid III with thionyl chloride was carried out in the presence of equimolar amounts of TEBAC. Ring closure in the oxidation was directed to the 10 position of the phenanthrene ring, as evidenced by disappearance of the band of deformation vibrations of a pentasubstituted benzene ring at 860-900 cm^{-1} in the IR spectrum of 3-chloro-2-chlorocarbonylphenanthro[9,10-b]thiophene (IV). The intense band at 1740 cm^{-1} in the spectrum of IV, which is characteristic for C=O stretching vibrations in acid chlorides, is shifted to the lower-frequency region (1675 cm^{-1}) in the formation of 3-chloro-2-carboxyphenanthro [9,10-b]thio-

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Institute of Petroleum Chemistry, Siberian Branch, Academy of Sciences of the USSR, Tomsk 634055. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 197-199, February, 1983. Original article submitted May 19, 1982.

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phene (V). Splitting out of CO_2 and detachment of halogen occur in the decarboxylation of acid V in refluxing quinoline in the presence of copper; however, the predominant process is desulfuration of the thiophene ring. Unidentified hydrocarbons and sulfur and very small amounts of 3-chlorophenanthro[9,10-b]thiophene (VI) and phenanthro[9,10-b]thiophene (VII) were detected in the reaction products. The dehalogenation of chloride VI or acid VI with 57% hydroidic acid in the presence of red phosphorus was unsuccessful, since even more intensive desulfuration of the thiophene ring than in the experiments with quinoline occurs in both cases. A search for milder decarboxylating and dehalogenating agents gave better results when pyridine with added copper powder was used, in which case the dechlorination and decarboxylation of acid V proceed simultaneously, and virtually no cleavage of the thiophene ring occurs. According to the results of gas–liquid chromatography (GLC), the products of the reaction of acid V with pyridine contain up to 2% hydrocarbons, 7% chloride VI, and 91% of desired product VII.

Thus the method for the preparation of arenothiophenes based on the successive arylation of acrylic acids and oxidation of the resulting β-substituted acrylic acids with thionyl chloride in the presence of TEBAC can be used for the synthesis of polycondensed thiophene structures.

A study of the properties of the phenanthro[9,10-b]thiophene derivatives showed that the lability of the structure increases markedly as the number of condensed homoaromatic rings is increased, and the compounds lose not only functional groups but also the sulfur atom of the thiophene ring.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. Analysis of the reaction mixtures by GLC was carried out with an LKhM-8MD chromatograph with a thermal-conductivity detector; the carrier gas was helium, and the column (2 m × 3 mm) was packed with 5% SE-30 on Chromaton N-AW as the stationary phase.

trans-β-(9-Phenanthryl)acrylic Acid (III). A mixture of 38.6 g (0.15 mole) of 9-bromophenanthrene, 12.4 g (0.173 mole) of acrylic acid, 43 g (0.3 mole) of tributylamine, 0.336 g (0.0015 mole) of palladium acetate, and 0.786 g (0.003 mole) of triphenylphosphine was heated with stirring at 140°C for 7 h, after which it was filtered, the filtrate was treated with 20% sodium hydroxide solution, and the alkaline mixture was refluxed for 2 h. It was then extracted with ether, and the alkaline solution was acidified with dilute hydrochloric acid. Acid III was removed by filtration, washed with water, dried, and recrystallized from benzene to give 34 g (88%) of a product with mp 202-203°C. IR spectrum: 1680, 1620, 950, 860, and 740 cm^{-1}. Found: C 82.0; H 5.2%. $C_{17}H_{12}O_2$. Calculated: C 82.3; H 4.8%.

3-Chloro-2-chlorocarbonylphenanthro[9,10-b]thiophene (IV). One third of a 48-g (0.4 mole) sample of thionyl chloride was added to a mixture of 12.4 g (0.05 mole) of acid III and 11.8 g (0.05 mole) of TEBAC heated to 140°C, after which the remaining thionyl chloride was added dropwise, and stirring at 140°C was continued for 2 h. The excess thionyl chloride was removed by distillation in vacuo (with a water aspirator), and the product was extracted with boiling benzene. The benzene extract was washed with water and dried over $MgSO_4$, and acid chloride IV was precipitated with hexane and purified by repeated reprecipitation to give 11 g (66%) of a product with mp 174-175°C. IR spectrum: 1740 (C=O), 1150, and 745 cm^{-1}. Found: C 61.5; H 2.3; Cl 21.4; S 9.5%. $C_{17}H_8Cl_2OS$. Calculated: C 61.6; H 2.4; Cl 21.5; S 9.7%.

3-Chloro-2-carboxyphenanthro[9,10-b]thiophene (V). A mixture of 8.3 g (0.025 mole) of acid chloride IV, 100 ml of ethanol, and 50 ml of 30% aqueous sodium hydroxide solution was refluxed for 5 h, after which the precipitate was treated with dilute hydrochloric acid, and acid V was removed by filtration, washed with water, and dried to give 7.7 g (98%) of a product with mp 260-263°C. IR spectrum: 1675 (C=O) and 740 cm^{-1}.

Phenanthro[9,10-b]thiophene (VII). Pyridine (100 ml) was added to a mixture of 9.3 g (0.03 mole) of acid V and 5 g of powdered copper, and the mixture was refluxed for 5 h. The copper was removed by filtration, and the filtrate was acidified with dilute hydrochloric acid and extracted with ether. The extract was washed with water and dried, and the solvent was removed by distillation to give 6.5 g of crude product. Chromatography with a column filled with silica gel (elution with hexane) gave 2.8 g (40%) of a product with mp 151-152°C (mp 151-152°C [4]). IR spectrum: 740 and 720 cm^{-1}. Found: C 81.9; H 4.2; S 13.4%. $C_{16}H_{10}S$. Calculated: C 82.0; H 4.3; S 13.7%.

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REACTION OF POLYSUBSTITUTED 4H-THIOPYRANS WITH TRIFLUOROACETIC ACID IN SALT-FORMATION AND IONIC-HYDROGENATION REACTIONS

V. G. Kharchenko and N. I. Kozhevnikova

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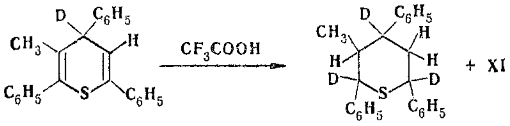
Depending on their structure, tetra- and pentasubstituted 4H-thiopyrans either undergo disproportionation or form salts with the participation of air oxygen upon reaction with trifluoroacetic acid. It is shown that these processes are competitive. The previously proposed scheme for the disproportionation of 4H-thiopyrans with protic acids was proved experimentally. The positions at which protonation of the double bonds of the heterorings occurs were established as a result of ionic hydrogenation of the 4H-thiopyrans.

The formation of thiapyrylium salts and thiacyclohexanes in a ratio of 2:1 in the reactions of di- and trisubstituted 4H-thiopyrans with protic acids made it possible to assume that disproportionation of the investigated sulfides, which includes initial protonation of the heteroring double bond and stabilization of the resulting carbonium ion due to hydride migration* from the 4H-thiopyran molecule, occurs in this case [1].

The proposed scheme has been confirmed experimentally by realization of the reaction of 4-deutero-3-methyl-2,4,6-triphenyl-4H-thiopyran (I-D) with trifluoroacetic acid. The reaction products were the corresponding trifluoroacetate XI and 2,4,6-trideutero-3-methyl-2,4,6-triphenylthiacyclohexane (VI-D).



I-D VI-D

As pointed out in [4], polysubstituted 4H-thiopyrans I-IV react with $HClO_4$ in acetic acid to give thiapyrylium salts with the participation of air oxygen via a mechanism that competes with disproportionation. At the same time, thiopyrans I, III, and IV undergo disproportionation in the usual manner upon reaction with trifluoroacetic acid, whereas thiopyran II does not undergo disproportionation even with trifluoroacetic acid. Whereas sulfide II is converted quantitatively to 3,5-dimethyl-2,4,6-triphenylthiapyrylium trifluoroacetate (XII) after 48 h upon reaction with CF_3COOH in air, virtually no reaction with trifluoroacetic acid occurs after the same period of time in a helium atmosphere. The results provide evidence that in this case, as in the reaction of thiopyrans I-IV with perchloric acid [4], air oxygen plays a substantial role in the formation of thiapyrylium salt XII. It should be noted that for the thiopyrans that undergo disproportionation with trifluoroacetic acid in air the absence of oxygen does not affect the direction of the process. Thus when this reaction is carried out in a helium atmosphere, sulfides I and V form disproportionation products (VI and XI and X and

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*Here and subsequently, the overall migration of a proton and two electrons is intended. The problem of the mechanism of hydride transfer, which has recently been the subject of active discussion [2, 3], is not discussed in the present communication.

N. G. Chernyshevskii Saratov State University, Saratov 410601. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 200-203, February, 1983. Original article submitted April 29, 1982.

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