NITRATION OF 2-(2-QUINOLYL)THIOPHENE AND 5-(2-QUINOLYL)-2,2'-DITHIOPHENE

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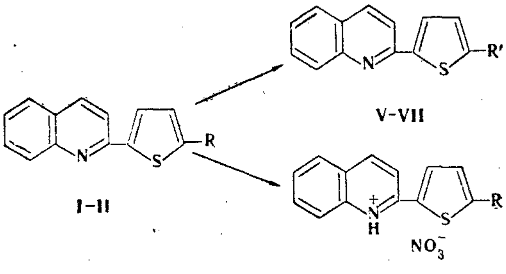
2-(2-Quinolyl)thiophene is nitrated in the 5 position, while its 2-thiophenyl analog is nitrated in the 3' and 5' positions simultaneously.

The previously described [1] method of nitration of 5-[4-carboxy(carbalkoxy)-2-quinolyl]-2,2'-dithiophenes with copper nitrate in acetic anhydride proved to be too mild for I and II, inasmuch as the absence of electron-acceptor substituents in the 4 position of the quinoline ring increases the nucleophilicity of nitrogen, and the quinolinium salts (III-IV) that we also isolated in the nitration of 2-phenylquinoline [2] are formed under the nitration conditions:



I-II

V-VII

III-IV

I, III R=H; II, IV R= 2-thienylV R'=NO_2; VI R'= 5-nitro-2-thienylVII R'=3-nitro-2-thienyl

These same salts are formed when I and II are treated with nitric acid.

We were able to thoroughly nitrate 2-(2-quinolyl)thiophene (I) with a mixture of nitric and sulfuric acids in the cold to mononitro compound V, which was synthesized alternatively by decarboxylation of 5-nitro-2-(4-carboxy-2-quinolyl)thiophene [3].

The effect of the electron-acceptor quinolinium cation in II is weakened by the introduction of a second thiophene ring, and a mixture of mononitro compounds consisting of products of substitution in the 5' (VI) and 3' (VII) positions was isolated along with IV when it was nitrated with a 1.5-fold excess of $Cu(NO_3)_2 \cdot 3H_2O$ in acetic anhydride.

The structures of VI and VII were proved by their identification with the products of decarboxylation of the previously described 5'-nitro- and 3'-nitro-5-(4-carboxy-2-quinolyl)-2,2'-dithiophenes.

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EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were measured with an IKS-22 spectrometer by V. I. Pavskii. The purity of the products and their individuality were confirmed by the results of thin-layer chromatography (TLC) on Silufol UV-254.

2-(2-Quinolyl)thiophene (I). A 4-g (15.7 mmole) sample of 4-carboxy-2-quinolylthiophene was dissolved in 4 ml of quinoline, 0.4 g of copper powder was added, and the mixture was heated at 190° for 2 h. The resulting precipitate was removed by filtration and washed with 2 ml of quinoline. The filtrate was steam distilled, and the residue was dissolved in alcohol—acetone. The solution was refluxed with activated charcoal, after which it was evaporated to give 1.95 g (59%) of I with mp 132-133° (from alcohol) [mp 132-133° (from ligroin) [4]].

5-(2-Quinolyl)-2,2'-dithiophene (II). This compound was prepared by the method used to obtain I. The yield of II, with mp 142-143° (from alcohol) [mp 142-143° (from ether) [5]], was 2.3 g (66%).

Nitration of I and II with Copper Nitrate Salts in Acetic Anhydride. A) A filtered solution obtained from 0.33 g (1.3 mmole) of $Cu(NO_3)_2 \cdot 3H_2O$ and 10 ml of acetic anhydride was added with stirring at 20° to 0.254 g (1.2 mmole) of I in 25 ml of acetic anhydride, after which the mixture was held at room temperature for 2 h. The resulting precipitate was removed by filtration to give 0.09 g (27%) of III with mp 134-135°. Found: C 56.6; H 3.5; N 10.1%. $C_{13}H_{10}N_2O_3S$. Calculated: C 56.9; H 3.7; N 10.2%. IR spectrum, cm^{-1}: 1389 (NO_3^-), 1650 (NH^+). Neutralization of the filtrate yielded 0.18 g of unchanged I.

B) Experiment A was repeated, but the reaction mixture was held at room temperature for 2 days. The resulting precipitate was removed by filtration to give 0.09 g (27%) of III with mp 134-135°. Found: C 56.6; H 3.5; N 10.1%. $C_{13}H_{10}N_2O_3S$. Calculated: C 56.9; H 3.7; N 10.2%. IR spectrum, cm^{-1}; 1389 (NO_3^-); 1650 (NH^+). Neutralization of the filtrate yielded 0.18 g of unchanged I.

The nitration of 0.37 g (1.2 mmole) of II under the conditions of experiment A gave 0.16 g (50%) of IV with mp 113-114°. Found: C 57.5; H 3.5; S 17.9%. $C_{17}H_{12}N_2O_3S_2$. Calculated: C 57.3; H 3.4; S 17.9%. IR spectrum, cm^{-1}: 1394 (NO_3^-); 1650 (NH^+). The filtrate yielded 0.12 g (30%) of a mixture of isomeric mononitro compounds and 0.1 g of unchanged II.

Nitration of 1 g (3.4 mmole) of II under the conditions of experiment B gave 0.68 g (60%) of VI with mp 225-226° (from alcohol—acetone). Found: C 60.5; H 3.1; S 19.0%. $C_{17}H_{10}N_2O_2S_2$. Calculated: C 60.3; H 3.0; S 18.9%. IR spectrum, cm^{-1}: 1532, 1347 (NO_2). The acetic acid solution yielded 0.3 g (25%) of mononitro compound VII with mp 170-171° (from alcohol). Found: C 60.3; H 3.2; S 18.9%. $C_{17}H_{10}N_2O_2S_2$. Calculated: C 60.3; H 3.0; S 18.9%. IR spectrum, cm^{-1}: 1527, 1340 (NO_2).

Nitrates of I and II (III, IV). Equimolecular amounts of I (II) and nitric acid (sp. gr. 1.5) were mixed with cooling in dry acetone to give nitrates III (IV), the physical constants of which, the IR spectra, and the results of quantitative elementary analysis were identical to the constants of salts III (IV) obtained under the conditions of nitration of I (II) in acetic anhydride.

Nitration of 2-(2-Quinolyl)thiophene (I) with a Mixture of Nitric and Sulfuric Acids. A total of 0.54 g (38 mmole) of HNO_3 (sp. gr. 1.5) in 15 ml of H_2SO_4 (sp. gr. 1.84) was added dropwise in the course of 1 h at —3° to 1.8 g (8.5 mmole) of I dissolved in 10 ml of H_2SO_4. The mixture was held at —3° for 1.5 h, after which it was poured over ice. The precipitate was removed by filtration, washed with water, and dried to give 1.6 g (82.5%) of V with mp 202-203° (from alcohol—acetone). Found:C 60.6; H 3.1; S 12.3%. $C_{13}H_8N_2O_2S$. Calculated: 60.9; H 3.2; S 12.5%. IR spectrum, cm^{-1}: 1504, 1346 (NO_2). The filtrate was neutralized to give 0.27 g (15%) of starting I.

5-Nitro-2-(2-quinolyl)thiophene. A 2-g sample of copper powder was added to 1.5 g (5 mmole) of 5-nitro-2-(4-carboxy-2-quinolyl)thiophene in 3 ml of quinoline, and decarboxylation was carried out as in the case of I. Workup of the mixture gave 0.54 g

(42%) of 5-nitro-2-(2-quinolyl)thiophene. The melting points, results of elementary analysis, and IR spectra were identical to those obtained for V obtained by nitration of I.

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