# STUDY OF SOME NITROGEN COMPOUNDS OF 2,2'-DITHIENYL

## III.* NITRATION OF 5-FORMYL-2,2'-DITHIENYL

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UDC 547.734:542.958.1

5-Formyl-5'-nitro-2,2'-dithienyl and 5-formyl-3'-nitro-2,2'-dithienyl were obtained by nitration of 5-formyl-2,2'-dithienyl with copper nitrate in acetic anhydride. The structures of the nitroaldehydes were established by their oxidation to the corresponding nitro acids of the 2,2'-dithienyl series, the decarboxylation of which yielded 5-nitro- and 3-nitro-2,2'-dithienyls.

In [1,2] one of us described the synthesis and structures of a number of nitrogenous derivatives of 2,2'-dithienyl. In order to obtain new nitrogenous derivatives of 2,2'-dithienyl, it seemed of interest to nitrate 5-formyl-2,2'-dithienyl (I) [3] with copper nitrate in acetic anhydride by the method in [4]. As a result, we obtained two nitro compounds, one with mp 150-152°C (IIa), and the other with mp 124-126° (IIb). Compound IIa proved to be 5-formyl-5'-nitro-2,2'-dithienyl diacetate, from which 5-formyl-5'-nitro-2,2'-dithienyl (IIIa) was obtained. To prove its structure, aldehyde IIIa was subjected to mild oxidation with potassium permanganate in aqueous pyridine [5]. This gave 5-carboxy-5'-nitro-2,2'-dithienyl (IVa). The known 5-nitro-2,2'-dithienyl (Va) [6,7] was obtained after decarboxylation of the nitro acid by heating in quinoline in the presence of copper powder.

Compound IIb proved to be 5-formyl-3'-nitro-2,2'-dithienyl diacetate, the structure of which was similarly proved.

## EXPERIMENTAL

Nitration of 5-Formyl-2,2'-dithienyl. A solution of 20 g (0.1 mole) of 5-formyl-2,2'-dithienyl [3] in 40 ml of acetic anhydride was cooled to 5°, and a solution of diacetylorthonitric acid [8-11] (filtered off from copper salts), obtained from 24.5 g (0.09 mole) of $Cu(NO_3)_2 \cdot 3H_2O$ and 40 ml of acetic anhydride, was added with stirring. The nitration was carried out at 8-10°. After introduction of all of the nitrating mixture, the mixture was held at 8° for 1 h and then at room temperature for 2 h. The resulting crystalline precipitate was filtered, washed with acetic anhydride and water, and air dried to give 17.85 g of diacetate IIa with mp 150-152° (from alcohol). IR spectrum: 1766 $cm^{-1}$ (carbonyl group), 1502, and 1338 $cm^{-1}$ (nitro group). Found %: S 19.5. $C_{13}H_{11}NO_6S_2$. Calculated %: S 19.3. The filtrate was poured into ice water to precipitate an oil that began to crystallize after about 12 h. The yield of diacetate IIb with mp 124-126° (from alcohol) was 11.3 g. IR spectrum: 1763 $cm^{-1}$ (carbonyl group); 1510, 1337 $cm^{-1}$ (nitro group). Found %: S 19.0. $C_{13}H_{11}NO_6S_2$. Calculated %: S 19.3.

5-Formyl-5'-nitro- and 5-Formyl-3'-nitro-2,2'-dithienyl (IIIa and IIIb). Diacetate IIa or IIb (2 g) was dissolved in 10 ml of alcohol, 2 ml of concentrated $H_2SO_4$ was added, and the mixture was heated for 1 h on a steam bath. It was then cooled, and the resulting crystals were filtered to give 1.47 g of aldehyde IIIa with mp 193° (from alcohol). IR spectrum: 1645 (C=O); 1504, 1337 $cm^{-1}$ ($NO_2$). Found %: S 26.3. $C_9H_5NO_3S_2$. Calculated %: S 26.8. The semicarbazone had mp 318-320° (from alcohol–acetone). Found %: S 21.5. $C_{10}H_8N_4O_3S_2$. Calculated %: S 22.0.

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*See [1] for communication II.

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The yield of aldehyde IIIb with mp 152-154° (from alcohol) was 1.2 g. IR spectrum: 1657 (C=O); 1495 and 1332 cm$^{-1}$ ($NO_2$). Found %: S 26.4. $C_9H_5NO_3S_2$. Calculated %: S 26.8. The semicarbazone had mp 235-236° (from alcohol–acetone). Found %: S 21.7. $C_{10}H_8N_4O_3S_2$. Calculated %: S 22.0.

5-Carboxy-5'-nitro-2,2'-dithienyl (IVa). A solution of 5.16 g of $KMnO_4$ in 103 ml of pyridine and 258 ml of water was added dropwise with stirring to 2.58 g (0.01 mole) of IIIa and 129 ml of hot (60-70°) pyridine. After all of the oxidant solution had been introduced, the mixture was held at 70° for 30 min and then allowed to stand at room temperature for 12 h. The resulting precipitate of $MnO_2$ was filtered and washed with pyridine. The combined filtrates were evaporated in vacuo almost to dryness. The precipitate was dissolved in water, and the solution was filtered and acidified with 10% hydrochloric acid.

The crystalline precipitate of IVa was filtered, washed with water, and air dried to give 2 g of a product with mp 286-288° (from glacial acetic acid). IR spectrum: 1649 cm$^{-1}$ (carboxyl group); 1489 and 1331 cm$^{-1}$ (nitro group). Found %: S 24.6. $C_9H_5NO_4S_2$. Calculated %: S 25.1.

5-Carboxy-3'-nitro-2,2'-dithienyl (IVb). This was obtained in a yield of 1.6 g and had mp 278-280° (from glacial acetic acid). IR spectrum: 1707 cm$^{-1}$ (carboxyl group); 1501, 1324 cm$^{-1}$ (nitro group). Found %: S 24.7. $C_9H_5NO_4S_2$. Calculated %: S 25.1.

5-Carbethoxy-5'-nitro-2,2'-dithienyl (VIa). A mixture of 1 g (0.003 mole) of IVa, 30.6 ml of ethanol, and 4 ml of concentrated $H_2SO_4$ was heated on a boiling-water bath for 5 h, filtered, and neutralized with 10% $Na_2CO_3$. The resulting crystalline precipitate of VIa was filtered, washed with water, and air dried to give 1.01 g of a product with mp 158-160° (from alcohol). IR spectrum: 1692 cm$^{-1}$ (carbonyl group); 1500, 1322 cm$^{-1}$ (nitro group). Found %: S 22.1. $C_{11}H_9NO_4S_2$. Calculated %: S 21.9.

5-Carbethoxy-3'-nitro-2,2'-dithienyl (VIb). This was similarly obtained in a yield of 1.04 g and had mp 80-82° (from alcohol). IR spectrum: 1712 cm$^{-1}$ (carbonyl group); 1502, 1327 cm$^{-1}$ (nitro group). Found %: S 21.4. $C_{11}H_9NO_4S_2$. Calculated %: S 21.9.

5-Nitro-2,2'-dithienyl (Va). Copper powder (0.05 g) was added to a mixture of 0.5 g (0.001 mole) of IVa in 7.5 ml of quinoline, and the mixture was refluxed for 10 min. The reaction mixture was cooled, acidified with respect to Congo Red with 10% hydrochloric acid, and steam distilled. The distillate was cooled, and the resulting crystals of Va were filtered, washed with water, and air dried to give 52% of a product with mp 109° [6, 7].

3-Nitro-2,2'-dithienyl (Vb). This was similarly obtained in 51% yield and had mp 39° [7].

The IR spectra of KBr pellets were recorded with an IKS-14 spectrophotometer.

## LITERATURE CITED

1. A. E. Lipkin, Zh. Obshch. Khim., 33, 2274 (1963).
2. A. E. Lipkin, Zh. Obshch. Khim., 33, 196 (1963).
3. E. Lescot, Ng. Ph. Buu-Hoi, and N. D. Xuong, J. Chem. Soc., 3234 (1959).
4. N. I. Putokhin, Sbornik Nauchn. Trudov Kuibyshevsk. Industr. Instit., 5, 271 (1955).
5. J. Volhard, Ann., 261, 380 (1891).
6. W. Steinkopf and W. Köhler, Ann., 522, 17 (1936).
7. C. Carpanelli and G. Leandri, Ann. Chem., 51, 181 (1961).
8. G. Baharach, J. Am. Chem. Soc., 44, 1522 (1922).
9. G. Baharach, Rec. Trav. Chim., 50, 732 (1931); 52, 413 (1933).
10. G. Baharach, Ber., 64, 2136 (1931).
11. J. B. Menke, Rec. Trav. Chim., 44, 141, 269 (1925).