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NITROGEN DERIVATIVES OF 2-(1-NAPHTHYL) THIOPHENE. II.*

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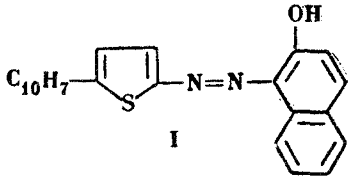
5-Amino-2-(1-naphthyl) thiophene and 4-amino-2-(1-naphthyl) thiophene are synthesized in the form of their complex salts with stannic chloride. It is shown that the stannic chloride complexes with amino derivatives of 2-(1-naphthyl) thiophene diazotize, and can be used as azo components.

It has previously been stated by the present authors that nitration of 2-(1-naphthyl) thiophene gives 5-nitro-2-(1-naphthyl)-thiophene and 4-nitro-2-(1-naphthyl) thiophene [1]. Reduction of these nitro compounds by stannous chloride in the presence of dry hydrogen chloride [2] gives 5-amino-2-(1-naphthyl) thiophene and 4-amino-2-(1-naphthyl) thiophene, isolated as double salts with stannic chloride in yields, respectively, of 57.7% and 54%.

According to information in the literature [3], amines of the thiophene series in the form of their complexes with stannic chloride can be diazotized, and give azo dyes. The present amine complexes behave in the same way. The diazo compounds from 5-amino-2-(1-naphthyl) thiophene and 4-amino-2-(1-naphthyl) thiophene readily undergo azo coupling with aromatic amines and naphthols. The dyes I-III were synthesized in that way. Amino derivatives of 2-(1-naphthyl) thiophene can be used as azo components, as was shown for preparation of the dye IV from the complex salt of 5-amino-2-(1-naphthyl) thiophene and diazotized β-naphthylamine. The dyes synthesized dye wool and silk well, cotton fabric poorly.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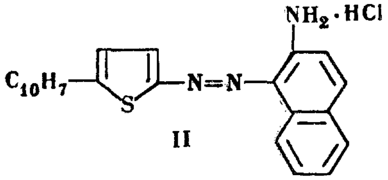
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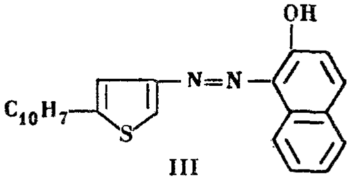
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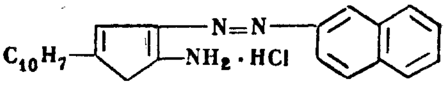
IV

Acetic anhydride acetylation [4] of the complex salt of 5-amino-2-(1-naphthyl) thiophene gives a 60-70% yield of 5-acetamino-2-(1-naphthyl) thiophene.

Experimental

Reduction of 4-nitro-2-(1-naphthyl) thiophene. 0.8 g (3.1 mmole) nitro compound was dissolved, with heating, in 12 ml dry benzene. The solution was filtered into a flask fitted with an inlet tube for HCl, 5 g (22.2 mmole) $SnCl_2 \cdot 2H_2O$ added, followed by 8 ml methanol, after which a stream of dry HCl was passed in, with cooling (ice and water) and agitation, for 2-2.5 hr. At the end of that period separation of pale cream-colored crystals of double tin salt of the amine ceased. The crystals were filtered off, washed with ether, and dried in a desiccator over potash (yield 0.71 g). The hydrochloric acid filtrate was left for 5-6 days over potash in a desiccator, and the yellowish-brown oil obtained was treated with 50-60 ml ether, by which means up to 0.25 g more salt was isolated. The salt was soluble in alcohol, acetone, somewhat less soluble in water, insoluble in ether and benzene, mp 240-242° (decomp).

When filter paper moistened with an alcohol solution of the salt was sprayed with an alcohol solution of p-dimethylaminobenzaldehyde, a red color was obtained. Found: S 5.70; Sn 21.49% (Kocheshkov method). Calculated for $C_{14}H_{11}NS \cdot H_2SnCl_6$: S 5.74; Sn 21.25%.

Reduction of 5-nitro-2 (1-naphthyl) thiophene. This was run similarly to the reduction of 4-nitro-2 (1-naphthyl) thiophene. 0.8 g (3.1 mmole) nitro compound in 5 ml benzene and 5 g (22.2 mmole) $SnCl_2 \cdot 2H_2O$ in 7 ml methanol were used for the reaction. The yield of salt was up to 1 g. It was soluble in alcohol, acetone, less soluble in water, and

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* For Part I see [1].

insoluble in ether and benzene, mp 208-211° (decomp). Filter paper moistened with an alcohol solution of the salt and sprayed with an alcohol solution of p-dimethylaminobenzaldehyde gave an orange color. Found: S 5.65; Sn 21.34%. Calculated for $C_{14}H_{11}NS \cdot H_2SnCl_6$: S 5.74; Sn 21.25%.

The double salt of 5-amino-2-(1-naphthyl) thiophene hydrochloride is converted into the neutral salt, by extraction with ether in a Soxhlet apparatus (8-10 hr). Found: S 8.04; Sn 15.24%. Calculated for $C_{28}H_{22}N_2S_2 \cdot H_2SnCl_6$: S 8.18; Sn 15.14%.

Diazotization of the tin salt of 5-amino-2-(2-naphthyl) thiophene hydrochloride. 0.4 g (0.7 mmole) double tin salt of the amine hydrochloride was dissolved with heating in 10 ml methanol, the solution cooled, and 0.35 ml hydrochloric acid (d 1.19) added. A solution of 0.1 g (1.4 mmole) $NaNO_2$ in a mixture of 0.5 ml water and 1.5 ml methanol, was added at 10-12°, with stirring. The diazo solution was kept at 10-12° for 10-15 min, filtered, and then used for azo coupling.

Preparation of azo dyes from 5-amino-2-(1-naphthyl) thiophene. a) A diazo solution prepared from 0.4 g (0.7 mmole) amine salt was gradually added with stirring and cooling (10-12°) to a solution of 0.1 g (0.7 mmole) β-naphthol and 0.32 g (8 mmole) NaOH in 1 ml water and 2.5 ml methanol. The solution turned a dark cherry red color. After 3 hr the dye was precipitated with a saturated NaCl solution. The precipitate was extracted with benzene. After distilling off the benzene 0.15 g dye I was obtained: it formed a dark-red crystalline powder. Found: S 8.23%. Calculated for $C_{24}H_{16}N_2OS$: S 8.45%.

b) A diazo solution prepared from 0.5 g (0.9 mmole) of the salt was gradually added with stirring and cooling (5-10°) to a solution of 0.14 g (1 mmole) β-naphthylamine in 7-8 ml alcohol and 0.6 ml hydrochloric acid. The solution turned brown. The dye II was precipitated with a saturated NaCl solution. Yield 0.25 g; dark brown crystalline powder. Found: S 7.54%. Calculated for $C_{24}H_{17}N_3S \cdot HCl$: S 7.71%.

c) 0.1 g (0.7 mmole) β-naphthylamine was dissolved in aqueous alcohol, and 0.2-0.4 ml hydrochloric acid added. The solution was cooled to 3-5°, and a solution of 0.03 g (0.4 mmole) $NaNO_2$ in 2 ml water added dropwise. The resultant diazo solution was filtered, and added dropwise to a cooled solution of 0.39 g (0.7 mmole) double tin salt of 5-amino-2-(1-naphthyl) thiophene hydrochloride in 4-5 ml alcohol and 0.3 ml hydrochloric acid. The whole was then diluted with water, and left for 10-12 hr, when a precipitate of dye IV came down. Yield 0.23 g, dark red crystalline powder. Found: S 7.59%. Calculated for $C_{24}H_{17}NS \cdot HCl$: S 7.71%.

Diazotization of the tin salt of 4-amino-2-(1-naphthyl) thiophene hydrochloride. This was run as above. 0.6 g (1.1 mmole), 1.4 ml 10% $NaNO_2$ solution were used, temperature 5-10°.

Preparation of azo dye from 4-amino-2-(1-naphthyl) thiophene. 0.15 g (1.05 mmole) β-naphthol in 6 ml 10% NaOH and 5 ml water were used for the azo coupling, the temperature being 5-10°. 50 ml 10% NaOH was added, and the dye precipitated by a saturated solution of NaCl. The precipitate was extracted with benzene, and the benzene distilled off, to give 0.22 g dye, forming a dark red crystalline powder. Found: S 8.30%. Calculated for $C_{24}H_{16}N_2OS$: S 8.45%.

Acetylation of the tin salt of 5-amino-2-(1-naphthyl) thiophene hydrochloride. A mixture of 0.6 ml acetic anhydride and 0.6 ml ether was dropped into a solution of 0.6 g (0.8 mmole) amine salt in 1 ml water. Then a solution of 0.8 g NaOH in 2 ml water was added, with strong cooling. The pasty mass was filtered with suction, washed with water, and dried. The resultant powder was repeatedly extracted with hot alcohol, and the combined alcoholic extracts gave crystals of a pale brown product (yield 0.3 g), mp 211-212°. Found: S 11.87%. Calculated for $C_{16}H_{13}NOS$: S 12.00%.

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