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NITRO DERIVATIVES OF 2-(1-NAPHTHYL)THIOPHENE

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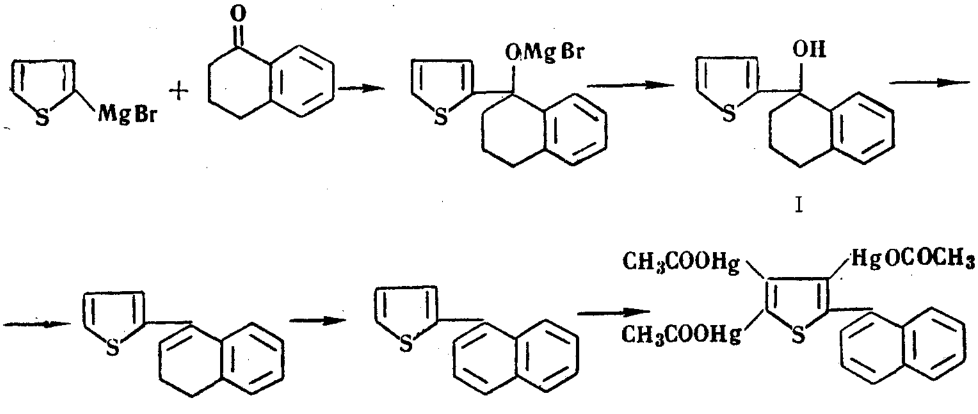
2-[1-(3, 4-Dihydronaphythyl)]thiophene, 2-(1-naphthyl)thiophene, 3, 4, 5-triacetoxymercuri-, 3, 4-diacetoxymercuri-5-nitro-, 4, 5-diacetoxymercuri-3-nitro-2-(1-naphthyl)thiophenes and 3, 3, 4-triacetoxymercuri-2[1-(4-nitronaphthyl)]thiophene are synthesized and characterized. Nitration of 2-(1-naphthyl)thiophene with copper nitrate in acetic anhydride leads to formation of two isomeric mono-nitro derivatives, 4-nitro- and 5-nitro-2-(1-naphthyl)thiophene.

Naphthylthiophenes and their derivatives are an unstudied part of thiophene chemistry, though an exception is 3-(1-naphthyl)thiophene, synthesized by heating 2-(1-naphthyl)butene-2 with sulfur at 300° [1].

2-(1-Naphthyl)thiophene, hitherto not described in the literature, was selected for study. With minor modifications a method of preparing 1-phenylnaphthalene [2] was used for synthesizing it. 2-[1-(3, 4-Dihydronaphthyl)]thiophene (II) was prepared by reacting 2-thienylmagnesium bromide with α-tetralone, followed by dehydration of the unstable intermediate alcohol I (yield 60-63%). By heating with sulfur at 240-255°, compound II is dehydrogeneated in 88-92% yield to 2-(1-naphthyl)thiophene.



I

II

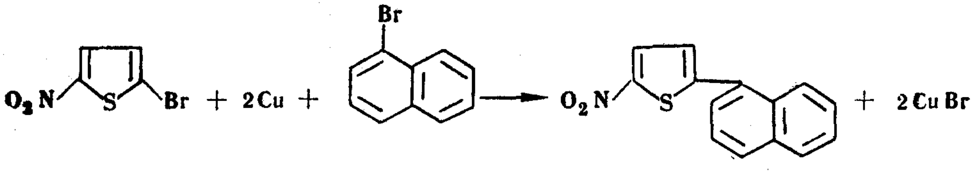
III

IV

2-(1-Naphthyl)thiophene readily undergoes mercuration to 3, 4, 5-triacetoxymercuri-2-(1-naphthyl)thiophene (IV).

Nitration of 2-(1-naphthyl)thiophene with copper nitrate in acetic anhydride [3] gave two mononitro-2-(1-naphthyl)thiophenes, one (compound A) an oil, (80-85% yield), mercurated to a diacetoxymercury derivative, and the other (compound B) forming bright yellow crystals (yield 15-20%) which did not mercurate.

The structure of the nitro compound giving the diacetoxymercury derivative was proved by synthesizing 5-nitro-2-(1-naphthyl)thiophene (V) from 5-nitrothiophene [4] and 1-bromonaphthalene by heating them together in the presence of copper powder at 220-225°.



V

Because of the low yield of V, it was isolated as 3, 4-diacetoxymercuri-5-nitro-2-(1-naphthyl)thiophene.

The identity of V with liquid mononitro-2-(1-naphthyl)thiophene was proved by the diacetoxymercury derivatives giving an undepressed mixed melting point.

Hypotheses that the nitro group in crystalline compound B is at position 3 in the thiophene ring, or in the naphthalene ring, are untenable, since 3-nitro-2-(1-naphthyl)thiophene and 2-[1-(4-nitronaphthyl)]thiophene when synthesized proved not to be identical with it; they both mercurate readily. Hence in compound B the nitro group is at position 4 in the thiophene ring. Its failure to mercurate is probably due to possible steric hindrance.

Experimental

2-[1-(3, 4-Dihydronaphthyl)]thiophene (II). A solution of 6.86 g (0.047 mole) α-tetralone in 7 ml ether was added to 2-thienylmagnesium bromide, prepared from 8.8 g (0.054 mole) 2-bromothiophene and 1.25 g (0.054 g atom) magnesium in 20 ml ether, vigorous refluxing being maintained (30 min). After refluxing for 30 min, the reaction mixture was allowed to stand for 1 hr, the magnesium complex decomposed with ice, and the ether layer separated off. The remaining magnesium salt was decomposed with glacial acetic acid, and the aqueous layer extracted with ether. The total ether extracts were dried over sodium sulfate, the ether distilled off, and the oil remaining heated with 2.4 ml acetic anhydride on a steam bath for 20-25 min, after which the reaction products were transferred to a beaker. After 5-6 hr the crystals formed were filtered off, washed with acetic anhydride, and dried in air, yield 5.5-5.8 g, mp 81-82° (after steam distillation). Soluble in ether, benzene, and alcohol, somewhat less soluble in acetic anhydride. A further 0.5 g reaction product could be isolated from the acetic acid filtrate. Found: C 79.45; H 5.91; S 14.93%. Calculated for $C_{14}H_{12}S$: C 79.19; H 5.70; S 15.09%.

2-(1-Naphthyl)thiophene (III). 1.28 g powdered sulfur and 8 g (0.038 mole) II were heated together for 30 min in a Claisen flask immersed in a Woods metal bath at 240-255°. At the end of that period hydrogen sulfide evolution had ceased; the dense oil formed was distilled, and a cut bp 168-170° (4 mm), forming a pale yellow oil, collected, yield 7-7.3 g. Found: C 80.24; H 5.16; S 15.11%. Calculated for $C_{14}H_{10}S$: C 79.95; H 4.80; S 15.26%.

3, 4, 5-Triacetoxymercuri-2-(1-naphthyl)thiophene (IV). 0.2 g (0.9 mmole) 2-(1-naphthyl)thiophene was added to a solution of 0.7 g (3.2 mmole) mercuric oxide in 2 ml glacial acetic acid, the whole heated on a steam bath for 2 hr, then 4-5 ml water added. The white crystalline powder formed was filtered off, washed with water, then with benzene, and dried at 120°, yield quantitative, mp 246-248° (decomp). Found: Hg 61.29; S 3.09%. Calculated for $C_{20}H_{10}Hg_3O_6$: Hg 61.02; S 3.24%.

Nitration of 2-(1-naphthyl)thiophene. A 2-necked rb flask was fitted with a thermometer passing to the bottom, and a dropping funnel, and in it was placed 1.8 g (7.5 mmole) powdered copper nitrate (trihydrate) in 7 ml acetic anhydride. The contents were cooled to 8-10° by placing the flask in ice, and a solution of 5.6 g (25 mmole) III and 30 ml acetic anhydride added with stirring, the nitration being carried out at 10-12°. After half the solution had been added, the flask was cooled to 5°, a further 1.8 g (7.5 mmole) copper nitrate added, and the rest of the solution added dropwise to the mixture maintained at 10-12°. After 2 hr the copper salts were filtered off, washed with acetic anhydride, and the filtrate treated with ice, precipitating an oil which partly crystallized after 12 hr.

The oil (substance A) was dissolved in a small amount of ether, while the crystals (substance B) which had a low solubility in ether, were filtered off, washed with water, and dried in air. A further quantity of crystals could be obtained by dissolving the copper salts filtered off in water at 20°. Yield 0.6-0.9 g, mp 166-167° (from alcohol and benzene). The ether was distilled off, yield of oil 4.9-5.2 g bp 238-240° (7.4-8 mm).

Analysis of substance A: Found: N 5.29; S 12.45%. Calculated for $C_{14}H_9NO_2S$: N 5.49; S 12.56%.

Analysis of substance B: Found: N 5.32; S 12.62%. Calculated for $C_{14}H_9NO_2S$: N 5.49; S 12.56%.

Diacetoxymercury derivative of substance A. The method of mercuration was described above. 1.85 g (8.6 mmole) mercuric oxide, 3.7 ml acetic acid, and 0.5 g (2 mmole) substance A were taken and the yield was almost quantitative, mp 179-181° (decomp). Found: Hg 51.85; S 4.21%. Calculated for $C_{18}H_{13}Hg_2NO_6S$: Hg 51.93; S 4.14%.

5-Nitro-2-(1-naphthyl)thiophene (V). 0.82 g (4 mmole) bromonaphthalene, 0.55 g (2.6 mmole) 2-bromo-5-nitrothiophene, and 0.7 g copper powder were placed in a small flask fitted with a thermometer and reflux condenser, stirred, and heated for 1 hr at 220-225° in a Woods metal bath. After cooling the products were treated with benzene, the copper salt separated off, and treated a few times with boiling benzene. The benzene extracts were bulked, the benzene distilled off, and the oil obtained steam distilled to remove unreacted starting materials. The nonvolatile oil in the flask was transferred to a beaker and left 2-3 days, then dissolved in a small amount of ether, and the crystals, almost insoluble in ether, of a by-produce, 5, 5'-dinitro-2, 2'-dithienyl [5], filtered off. The ether was distilled off, and the oil obtained again left for a few days, after which it was treated with ether until crystals ceased to separate. The oil which remained was mercurated, to give up to 0.4 g 3, 5-diacetoxymercuri-5-nitro-2-(1-naphthyl)thiophene, forming yellow crystals mp 179-181° (decomp). Found: Hg 52.22; S 3.95%. Calculated for $C_{18}H_{13}Hg_2NO_6S$: Hg 51.93; S 4.14%. The mixed mp with the diacetoxy derivative of substance A was undepressed.

3-Nitro-2-(1-naphthyl)thiophene. 0.85 g (4.1 mmole) 1-bromonaphthalene, 0.6 g (2.9 mmole) 2-bromo-3-nitrothiophene [6], and 0.75 g copper powder were used for a synthesis which was carried out as described above. Crystals of 3, 3'-dinitro-2, 2'-dithienyl [6] were isolated as a by-product. 3-Nitro-2-(1-naphthyl)thiophene was identified as 4, 5-diacetoxymercuri-3-nitro-2-(1-naphthyl)thiophene, a crystalline yellow product, decomposing above 270°.

Found: Hg 52.3%. Calculated $C_{18}H_{13}Hg_2NO_6S$: Hg 51.93%.

2-[1-(4-Nitronaphthyl)]thiophene. 1 g (4 mmole) 1-bromo-4-nitronaphthalene, 0.6 g (3.7 mmole) 2-bromothiophene, and 0.75 g copper powder were used in a synthesis carried out as described above. The by-product 2, 2'-dithienyl [5], was steam-distilled off. 2-[1-(4-Nitronaphthyl)]thiophene was identified as 3, 4, 5-triacetoxymercuri-2-[1-(4-nitronaphthyl)]thiophene, a yellow crystalline product, decomposing above 250°. Found: Hg 58.32%. Calculated for $C_{20}H_{15}Hg_3NO_8S$: Hg 58.36%.

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