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ACETYLATION OF 2-(1-NAPHTHYL)THIOPHENE

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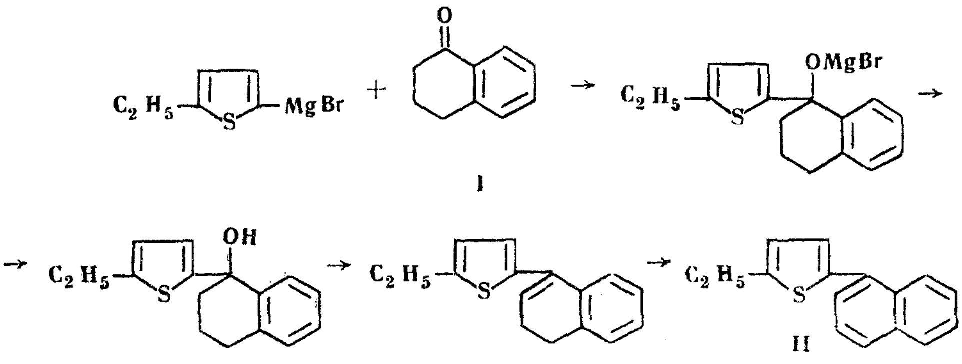
Acetylation of 2-(1-naphthyl) thiophene with acetyl chloride in the presence of $SnCl_4$, or with acetic anhydride in the presence of H_3PO_4 gives 5-aceto-2-(1-naphthyl) thiophene. 5-Ethyl-2-[1-(3, 4-dihydronaphthyl)] thiophene, 5-ethyl-2-(1-naphthyl) thiophene and 3, 4-diacetoxymercuri-5-ethyl-2-(1-naphthyl) thiophene are now synthesized and characterized.

Aceto derivatives of 2-(1-naphthyl) thiophene (I) have not been described in the literature. The present authors have now made a study of the acetylation of I: a) with acetyl chloride in the presence of $SnCl_4$ in benzene [1]; b) with acetic anhydride in the presence of catalytic quantities of 85% H_3PO_4 [2]. In both cases identical aceto derivatives of 2-(1-naphthyl) thiophene were obtained, mp 130-131° (semicarbazone mp 226-227°). Yields were 83-86% and 90-91.6% respectively.

To ascertain the structure of aceto-2-(1-naphthyl) thiophene it was submitted to Clemmensen reduction, and the reduction product, ethyl-2-(1-napthyl) thiophene, readily underwent mercuration to give a diacetoxymercuri derivative mp 217-219° (decomp).

The structure of ethyl-2-(1-naphthyl) thiophene was proved by synthesis of 5-ethyl-2-(1-naphthyl) thiophene (II) from 5-ethyl-2-thienylmagnesium bromide and α-tetralone, followed by dehydration and dehydrogenation of the reaction intermediates according to the reaction, analogous to these for synthesis [3];



II is mercurated to give 3, 4-diacetoxymercuri-5-ethyl-2-(1-naphthyl) thiophene mp 217-219° (decomp).

The identity of the two ethylnaphthylthiophenes was confirmed by the mixed melting points of the diacetoxymercuri derivatives being undepressed, so that it can be concluded that the acetylation product of I is 5-aceto-2-(1-naphthyl) thiophene (III).

Experimental

Acetylation of 2-(1-naphthyl) thiophene (I). a) 3.73 g stannic chloride was added to a cooled solution of 3 g I and 1.12 g acetyl chloride in 11 ml dry benzene. The mixture was left for 30-40 min, decomposed with ice water, and the benzene solution washed with dilute hydrochloric acid, NaOH solution, and water. The aqueous layer was extracted with benzene, the benzene extracts bulked, dried over $CaCl_2$, the benzene distilled off to give 3-3.1 g III mp 130-131° (from ethanol). Found: s 12.7%, Calculated for $C_{16}H_{12}OS$: S 12.70%. Semicarbazone mp 226-227° (from ethanol).

b) 0.15-0.20 ml 85% phosphoric acid (d 1.689) was added to a solution of 7 g I in 4.25 g acetic anhydride, heated on a water bath to 70-75°. The temperature was raised to 90°, held there for 40 min, and then heated with stirring at 100-103°. Heating was stopped 2 hr after the phosphoric acid was introduced, the mixture cooled, and 100 ml water added. The III precipitated was filtered off, washed with water, and air-dried. Yield 7.56-7.7 g, mp 130-131° (from ethanol). Found: S 12.51%. Calculated for $C_{16}H_{12}OS$: S 12.70%. Semicarbazone mp 226-227° (from ethanol).

Reduction of aceto-2-(1-naphthyl) thiophene. 5 g powdered aceto-2-(1-naphthyl) thiophene was added to 10 g amalgamated zinc in a flask fitted with a reflux condenser, followed by a mixture of 7 ml concentrated hydrochloric acid and 14 ml water.

The mixture was refluxed vigorously for 4 hr with occasional shaking, and 4-5 ml concentrated hydrochloric acid added hourly. The flask was cooled, and the organic layer extracted with ether and dried over $CaCl_2$. The ether was distilled off, and the residual oil fractionally distilled under vacuum, a cut bp 205-207° (12 mm) being taken: it formed a yellowish oil. Yield of ethyl-2-(1-naphthyl) thiophene was 0.5 g. Found: C 80.46; H 5.67%. Calculated for $C_{16}H_{14}S$: C 80.62; H 5.92%.

Diacetoxymercuri derivative of ethyl-2-(1-naphthyl) thiophene. 0.1 g ethyl-2-(1-naphthyl) thiophene was added to a solution of 0.25 g mercuric oxide in 2 ml glacial acetic acid. The mixture was heated on a steam bath for 1.5 hr and 5-6 ml water added. The white crystalline powder obtained was filtered off, washed with water, then with benzene, and dried at 100-105°. Quantitative yield mp 217-219° (decomp). Found: Hg 53.19%. Calculated for $C_{20}H_{18}O_4SHg_2$: Hg 53.09%.

5-Ethyl-2-[1-(3, 4-dihydronaphthyl)] thiophene. The Grignard reagent was prepared from 10.9 g 5 ethyl-2-bromothiophene in 12 ml ether and 1.4 g magnesium in 14 ml ether, 6.9 g α-tetralone in 7 ml ether was added to the resultant solution of 5-ethyl-2-thienylmagnesium bromide at such a rate as to maintain refluxing. The mixture was heated for half an hour on a water bath, and then left for an hour at room temperature. The magnesium complex was decomposed with ice, and the ether layer decanted. The basic magnesium salt was decomposed with glacial acetic acid, and the aqueous layer extracted with ether. The ether extract was dried over sodium sulfate, the ether distilled off, and the residual oil steam distilled (1-1.5 *l* distillate). The undistilled oil was removed, dried, and heated for .5 hr with 3-3.5 ml acetic anhydride on a steam bath. The acetic anhydride was distilled off, and a cut bp 207-210° (12 mm) taken. Redistillation gave 4.45 g pale yellow oil bp 207-209° (12 mm). Found: C 79.78; H 6.80; S 13.21%. Calculated for $C_{16}H_{16}S$: C 79.95; H 6.70; S 13.34%.

5-Ethyl-2-(1-naphthyl) thiophene (II). A mixture of 0.55 g powdered sulfur and 3.5 g 5-ethyl-2-[1-(3, 4-dihydronaphthyl)] thiophene was heated in a Claisen flask in a Wood's metal bath at 240-255° for half an hour. After that time hydrogen sulfide evolution ceased: the heavy oil was distilled off from the same flask, and a cut bp 205-207° (12 mm) taken. It was a yellowish oil. Yield 2.6 g. Found: C 80.39; H 6.12; S 13.27%. Calculated for $C_{16}H_{14}S$: C 80.62; H 5.92; S 13.45%.

3, 4-Diacetoxymercuri-5-ethyl-2-(1-naphthyl) thiophene. Prepared in the way described above, using 0.5 g mercuric oxide, 3.5 ml glacial acetic acid and 0.2 g 5-ethyl-2-(1-naphthyl) thiophene. Yield quantitative, mp 217-219° (decomp). Found: S 4.08; Hg 53.10%. Calculated for $C_{20}H_{18}O_4SHg_2$: S 4.24; Hg 53.09%.

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