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Phenanthroimidazoles, IV.

Short Communication

Ewa Kesler

Division of Organic Chemistry 1, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden

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Syntheses of 1*H*-phenanthro(9,10-d)imidazoles with naphthyl and thienyl substituents at position 2 are described.

[Keywords: Cancerostatic activity; 1H-Phenanthro(9,10-d)imidazoles]

Phenanthroimidazole, IV. (Kurze Mitteilung)

Die Darstellung von drei 1*H*-Phenanthro(9,10-d)imidazolen mit Naphthyl- und Thienyl-Substituenten in 2-Stellung wird beschrieben.

Previous publications described several 1*H*-phenanthro(9,10-d)-imidazole derivatives, synthesised by the method of *Steck* and *Day* as potential cytostatic agents[1a, b, c]. Since then a number of 1*H*-phenanthro(9,10-*d*)imidazoles has been prepared by other authors[2a, b, c] and new photochemical and thermal syntheses have been developed[3a, b].

A recent publication[2a] has prompted me to report my results on the preparation of **1**, since they differ from those reported in the literature. Our substance had a higher melting point and the yield was considerably better. Some new 1*H*-phenanthro(9,10-d)imidazoles (**2**, **3**) of potential pharmacological interest have also been prepared[1,4].

The above compounds have been tested as yet only for cancerostatic activity; they showed no evident effect.

Compounds **2** and **3** exhibit intensive fluorescence.

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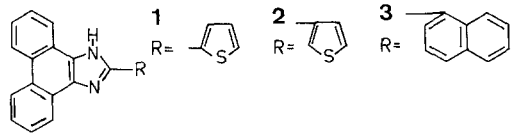
Experimental

Melting points were determined on a Reichert apparatus and are uncorrected. A Perkin-Elmer 257 spectrometer was used for IR spectra. ^{1}H-NMR spectra were recorded on a Jeol MH 100 spectrometer. Elemental analyses on



1 and **2** were carried out by the Department of Analytical Chemistry, University of Lund, Sweden, and on **3** by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, West Germany.

Phenanthroimidazoles

1. Phenanthrenoquinone (6.24 g) was dissolved under nitrogen in glacial acetic acid (80 ml) and heated with stirring on a paraffin bath at 100°. Ammonium acetate (46.5 g) and a solution of redistilled 2-thiophene aldehyde (4.71 g) in glacial acetic acid (10 ml) were added rapidly. The mixture changed on reflux from brown to yellow and deposited pale yellow crystals. The reaction mixture was refluxed at 115° with stirring under a nitrogen current for another hour and allowed to cool to room temperature. The precipitate was filtered under suction, washed with glacial acetic acid and dried at 80° to give 8.7 g (97% yield) of crude crystalline product. Recrystallisation from methanol (650 ml) gave 7.54 g (84%) of the pure substance (Ref.[2a] 33%). Two additional recrystallisations (one with active carbon) gave analytically pure compound: light-yellow needles, subliming at 294–314°, final m. p. 316–317° (Ref.[2a] m. p. 245°).

IR (KBr): 832, 839, 850, 1045, 1079, 1340, 1355, 1415, 1490, 1530, 1590, 1615 and 3035 cm^{-1}.

^{1}H-NMR (*DMSO-d_6*, δ, ppm): 13.56 (NH), 8.96–8.74 2H, 8.69–8.43 2H, 7.86–7.53 4H (CH-phenanthrene), 7.98 (C_3—H), 7.73 (C_5—H), 7.31 (C_4—H). $J_{3,4} = 3.7$ Hz, $J_{3,5} = 1.2$ Hz, $J_{4,5} = 5.0$ Hz.

$C_{19}H_{12}N_2S$. Calcd. C 75.97 H 4.03 N 9.33 S 10.60.
Found. C 75.70 H 4.17 N 9.38 S 10.80.

MS: $m/e = 300$, calcd. 300.3.

2 was prepared as described above from phenanthrenoquinone (6.24 g), ammonium acetate (46.5 g) and 3-thiophene aldehyde (4.71 g) giving after the usual workup 8.0 g (89% yield) of the crude product. A sample for analysis was recrystallised from methanol (1 g/100 ml): long, pearl-silky needles, subliming at 260–290°, final m. p. 342–344°.

IR (KBr): 751, 795, 865, 890, 1350, 1369, 1395, 1415, 1428, 1485, 1530, 1540, 1570, 1590, 1615 and 3035 cm^{-1}.

$C_{19}H_{12}N_2S$. Calcd. C 75.97 H 4.03 N 9.33 S 10.60.
Found. C 75.20 H 4.09 N 9.27 S 10.70.

MS: $m/e = 300$, calcd. 300.3.

3 was prepared as described for **1** from phenanthrenoquinone (4.16 g) in glacial acetic acid (60 ml), ammonium acetate (31 g) and a solution of α-naphthaldehyde (4.4 g) in the same solvent (20 ml). The reaction mixture changed on reflux at 110-130° from brown to straw-coloured and a white precipitate began to form. The precipitate was washed thoroughly with cold water and dried at 80° to give 4.5 g (66% yield) of the crude product. Very pure compound was obtained by recrystallising three times (once with active carbon) from glacial acetic acid (1 g/20 ml) and drying under vacuum at 100° during 14 days: white crystals, m.p. 170°, subliming as needles, final m.p. 210-215°. The compound was readily soluble in acetone, tetrahydrofuran and carbon tetrachloride.

IR (KBr): 775, 801, 1355, 1390, 1430, 1455, 1500, 1540, 1571, 1590, 1615 and 3035 cm^{-1}.

$C_{25}H_{16}N_2$. Calcd. C 87.10 H 4.68 N 8.13.
Found. C 87.25 H 4.53 N 8.14.

MS: $m/e = 344$, calcd. 344.394.

Acknowledgement

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