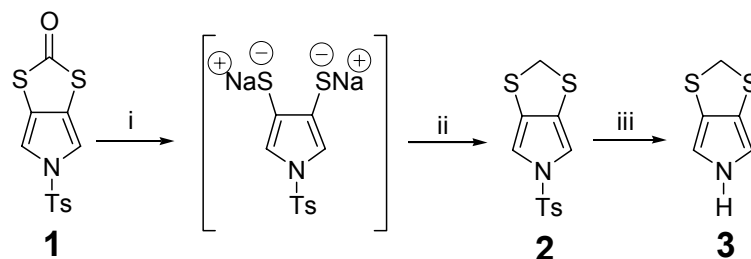


3,4-Methylenedithiopyrrole: convenient synthesis and application as a novel monomer for electroactive polymers

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Electronic Supplementary Information:



Scheme 1 (i) MeONa, MeOH-THF, reflux; (ii) CH₂Cl₂; (iii) MeONa, MeOH-THF, reflux.

N-Tosyl-(1,3)-dithiolo[4,5-*c*]pyrrole-2-thione (0.1557 g, 0.5 mmol) was dissolved in 16 mL of anhydrous THF-MeOH (1:1 v/v) and degassed (N₂, 30 min) before addition of sodium methoxide (5 M in MeOH, 10 mmol). The yellow solution was refluxed for 60 min and cooled down, 1 mL of dichloromethane was added to the resulted orange reaction mixture and the mixture was stirred at room temperature for 60 min. The reaction was stopped by addition of H₂O (100 mL) and extracted with dichloromethane. The combined organic phase was washed with H₂O and dried over anhydrous MgSO₄. After concentration in vacuum, the crude product was purified by column chromatography (silica gel, CH₂Cl₂/petrom ether 1:2) to give 0.096 g of white solid product **2** in 65% yield.

¹H NMR (CDCl₃) δ 2.35 (s, 3H, Ph-CH₃), 4.60 (s, 2H, -SCH₂S-), 6.78 (s, 2H, Py-H), 7.24 (d, 2H, aromatic H), 7.65 (d, 2H, aromatic H).
MS (EI) *m/z* 297 (M⁺, 100), 142 (M⁺-Ts, 77%).

The obtained **2** (0.32 mmol) was refluxed in MeOH-THF (10 mL, 1/1 v/v) in the presence of MeONa (6.4 mmol) for another 60 min before addition of H₂O, and the pH of the reaction mixture was adjusted to pH = 7 by addition of 4 M HCl. The mixture was extracted with CH₂Cl₂, and the combined organic phases were dried over anhydrous MgSO₄. After concentration in vacuum, the crude product was purified by column chromatography (silica gel, CH₂Cl₂/petrom ether 1:1) to give 0.039 g (yield 85 %) of 3,4-methylenedithiopyrrole as colourless crystals.

¹H NMR (acetone-*d*₆) δ 4.52 (s, 2H, -SCH₂S-), 6.38 (s, 2H, Py-H), 9.62 (b, 1H, NH).
¹³C NMR (acetone-*d*₆) δ 124.9, 113.8, 48.7.
MS (EI) *m/z* 143 (M⁺, 100).

