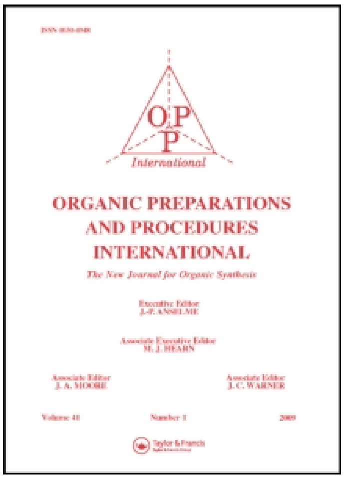

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BENZO[1,2-b:4,5-b']DITHIOPHENE

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OPPI BRIEFS

(by J. A. Moore, Associate Editor and J.-P. Anselme, Editor)

BENZO[1,2-b:4,5-b']DITHIOPHENE

Submitted by N. Aggarwal and D. W. H. MacDowell*
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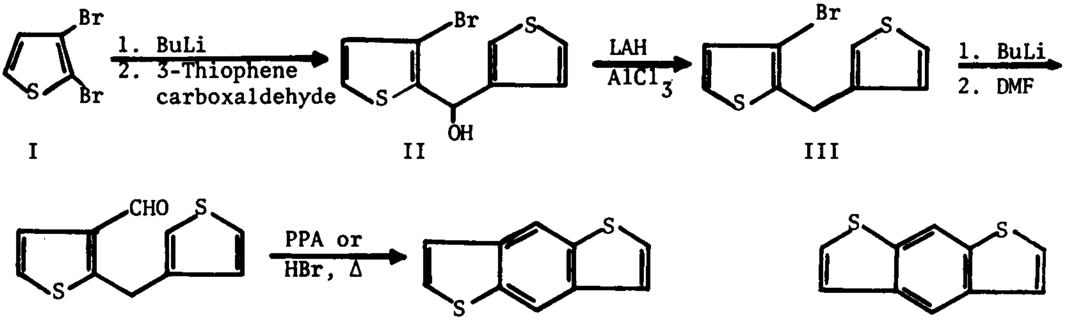
Although benzo[1,2-b:5,4-b']dithiophene(VI) is a well known compound,[1-3] the reported synthesis[4] of benzo[1,2-b:4,5-b']dithiophene(V) is fairly involved.[4] The sequence above essentially based on that of Wynberg etal.,[2] provides an efficient synthesis of V in 39% overall yield starting from I.



I II III

IV V VI

EXPERIMENTAL

2,3'-Dithienylmethane-3-carboxaldehyde(IV).- To a stirred solution of n-butyllithium (85 ml, 1.10 M, 0.085 mole) at -70° under nitrogen was added a solution of 3-bromo-2,3'-dithienylmethane[5](III), (18.7 g, 0.072 mole) in ether (75 ml). The mixture was stirred at -70° for 30 min. and dimethylformamide (6.79 g, 0.093 mole) in ether (75 ml) was slowly added at this temperature. The temperature of the reaction was allowed to rise to room temperature and the reaction mixture was kept overnight. Decomposition of the mixture with ice and 6N hydrochloric acid, followed by extraction with ether ($MgSO_4$) gave a brown oil which upon distillation gave the aldehyde IV as a colorless liquid, 11.8 g (79%), bp, 90-110°/0.02 mm.

IR (neat): 1680 cm^{-1}. Nmr ($CDCl_3$): δ10.1 (s, 1H, CHO), δ7.5-6.9 (m, 5H, thiophene), δ4.5 (s, 2H, CH_2).

Anal. Calcd. for $C_{10}H_8OS$: C, 57.66; H, 3.87; S, 30.79.

Found: C, 57.87; H, 3.92; S, 30.61.

Benzo[1,2-b:4,5-b']dithiophene(V). Method A.- A stirred mixture of IV (2.0 g) in 48% HBr solution was heated at 120° for 30 min. After cooling, it was poured on ice and extracted with ether. The brown solid obtained (1.69 g) from evaporation of the solvent was sublimed to give V as a white solid 1.56 g (80%) mp. 197-199°. Recrystallization from ethyl acetate followed by sublimation gave an analytical sample, mp. 197-199°, lit.[4] mp. 198°.

UV (λ_{max}, log ε) 95% C_2H_5OH: 247(4.62), 254(4.69), 290(3.95), 300(3.88). 320(3.83), 334(3.99). Nmr (acetone-d_6): δ8.55 (s, 2H, benzenoid), δ7.86 (d, 2H, J = 5.5 Hz, thiophene C_3), δ7.47 (d, 2H, J = 5.5 Hz, thiophene C_2).

Anal. Calcd. for $C_{10}H_6S_2$: C, 63.12; H, 3.18; S, 33.70.

Found: C, 63.47; H, 3.05; S, 33.80.

Picrate, red needles from ethanol, mp. 159-160°, lit.,[4] mp. 159°.

Method B.- A mixture of polyphosphoric acid (50 g) and the aldehyde (1.0 g), was heated on a steam bath for 30 min. and poured into ice and water. After ether extraction, the brown solid, obtained crystallized from ethyl acetate to afford benzo[1,2-b:3,5-b']dithiophene, mp. 197°, 0.90 g (96%) with properties identical with those of the sample prepared under method A above.

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SYNTHESIS OF THE ETHYLNITRONE OF ACETALDEHYDE

Submitted (1/24/79)

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A useful synthesis of acetaldehyde ethylnitrone (N-ethylidenethylamine N-oxide), the first known primary N-alkylnitrone of a simple aliphatic aldehyde, was needed for identification purposes and further testing. This compound is an intermediate in the oxidation of N,N-diethylhydroxylamine (I),[1] which has been proposed as an atmospheric additive to inhibit photochemical smog formation.[2] Efforts to synthesize II by the condensation of acetaldehyde with N-ethylhydroxylamine or by the N-ethylation of acetaldoxime failed completely. Bubbling O_2 through I afforded a solution contaminated by ca. 2% of material with promising spectral properties, but whose separation without decomposition proved impossible. The nitrone (II) was ultimately prepared in essentially quantitative yield by the oxidation of DEHA with silver oxide:[3]