Expeditious Synthesis of Dihydrobenzo-[2,1-*b*:3,4-*b*′]-, [1,2-*b*:5,4-*b*′], and [1,2-*b*:4,5-*b*′]-dipyrroles

A. Berlin, S. Bradamante, R. Ferraccioli, G. A. Pagani, and F. Sannicolò

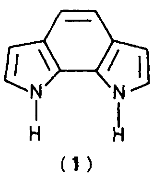
Dipartimento di Chimica Organica e Industriale dell'Università, and Centro CNR Speciali Sistemi Organici, Via C. Golgi 19, 20133 Milano, Italy

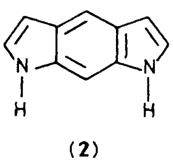
A simple, high-yield, two-step synthesis of the title compounds (**1**)—(**3**) is described, based on the catalytic reduction of the bis-enamines (**4**)—(**6**), in turn obtained by condensation of dimethylformamide diethyl acetal with the appropriate dinitro-xylene.

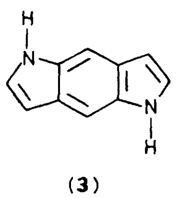
In the search for heterocyclic structures that can undergo chemical[1] or electrochemical[2] oxidative polymerization to give new electroconductive materials, we have focused our attention on compounds (**1**)—(**3**), three of the five possible isomers of benzo[*b*:*b*′]dipyrroles. The *ortho*, *meta*, and *para* relationship of the nitrogen atoms in (**1**)—(**3**) appeared to be a useful clue for correlating the structure of the monomers with the electrical properties of the oxidized polymers.

Studies on new electroconductive polymers, even at an exploratory level, require a simple synthetic route to relatively large amounts of the monomer. The known synthetic approaches to (**2**) and (**3**) are inefficient[3—5] and extremely laborious; the system (**1**) is known only as the 2,7-diethoxycarbonyl derivative.[6] We report herein a very simple two-operational-step synthesis of benzodipyrroles (**1**)—(**3**), based on an extension of the Leimgruber and Batcho synthesis.[7,8]

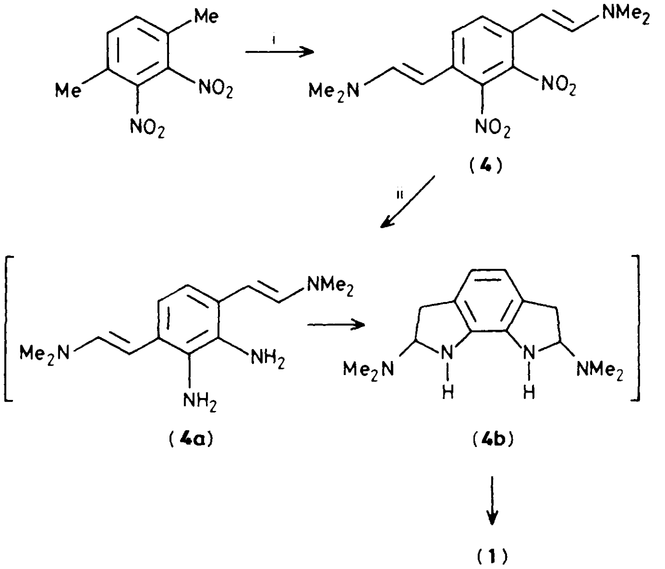
Double condensation of dimethylformamide diethyl acetal (DMFDEA) with a suitable dinitro-xylene, followed by catalytic reduction of the resulting bis-enamine, directly affords the benzodipyrroles. As a general example Scheme 1 outlines the synthesis of (**1**) and the possible intermediates.†


(**1**)


(**2**)


(**3**)

The condensation was carried out by heating a solution of the dinitro-xylene and excess of DMFDEA (4—6 mol. equiv.) in DMF under nitrogen at 90—120 °C for 5—20 h. Evaporation of the solvent left a crude product which was washed with diethyl ether to give the desired bis-enamine which was used without further purification for the next step. Thus, 2,3-dinitro-*p*-xylene[9] afforded the *trans*,*trans*-bis-enamine (**4**)‡ (75%), m.p. 237 °C (decomp.) (from $C_6H_4Me_2$); ^1H n.m.r.



Scheme 1. *Reagents*. i, $Me_2NCH(OEt)_2$ in Me_2NCHO; ii, H_2, 10% Pd–C in $MeCO_2Et$.

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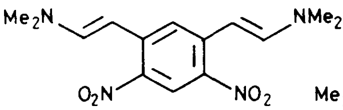
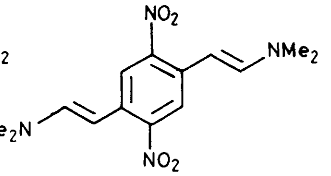
† The conversion of (**4**) into (**1**) may involve several different intermediates, the nature of which we have no evidence for: by reporting (**4a**) and (**4b**) we do no necessarily imply that the reduction of both the nitro groups precedes the cyclisation or that formation of the pyrrole rings occurs simultaneously.

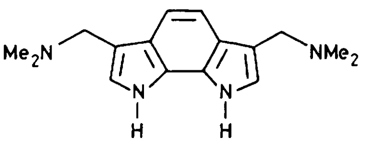
‡ Compounds (**1**)—(**6**) gave satisfactory C,H,N analyses.



(5)



(6)



(7)

δ (CD_3SOCD_3) 3.32, 4.98—7.38 (AB, *J* 13.5 Hz), and 7.63. Analogously, 4,6-dinitro-*m*-xylene[10] gave the *trans*,*trans*-bis-enamine (**5**) (93%), m.p. 216 °C (decomp.)(from $C_6H_4Me_2$); ^{1}H n.m.r. δ (CD_3SOCD_3) 3.35, 5.9—7.72 (AB, *J* 13.5 Hz), 7.68, 8.57. Finally, 2,5-dinitro-*p*-xylene[11] afforded the *trans*,-*trans*-bis-enamine (**6**) (78%), m.p. 267 °C (decomp.) (sublimed at 180 °C and 10^{-2} mmHg); ^{1}H n.m.r. δ (CD_3SOCD_3) 2.9, 5.18—7.3 (AB, *J* 13.5 Hz), 7.93.

The reductive cyclization of the bis-enamines (**4**)—(**6**) was carried out by catalytic hydrogenation (room temp., atm. pressure, AcOEt solution, 10% Pd–C, 25—50% of the weight of the bis-enamine). Column chromatography of the crude product on silica gel (CH_2Cl_2) afforded the desired compound. Thus, the bis-enamine (**4**) gave (**1**) (70%), m.p. 217 °C (decomp.) (sublimed at 180 °C and 10^{-2} mmHg); ^{1}H n.m.r. δ (CD_3SOCD_3) 6.42, 7.18, 10.5; M^+ *m/z* 156. Analogously, (**5**) afforded (**2**) (60%), m.p. 252 °C (decomp.) (sublimed at 180 °C and 10^{-2} mmHg); ^{1}H n.m.r. δ (CD_3SOCD_3) 6.35, 7.21, 7.33, 7.62, 10.57; M^+ *m/z* 156. Finally, the bis-enamine (**6**) gave (**3**) (50%), m.p. 198—203 °C (decomp.) (sublimed at 160 °C and 10^{-2} mmHg); ^{1}H n.m.r. δ (CD_3SOCD_3) 6.31, 7.21, 7.41, 10.41; M^+ *m/z* 156.

We have shown that, by analogy with (**2**)[12] and (**3**),[13] the β-positions in (**1**) are the sites where electrophilic substitutions occur. The benzodipyrrole (**1**) afforded, upon treatment with dimethylamine hydrochloride (3 equiv.) and formaldehyde (3 equiv.) in methanol, followed by addition of alkali, the Mannich bis-base (**7**), m.p. 160 °C (decomp.); ^{1}H n.m.r. δ (CD_3SOCD_3) 2.2, 3.6, 7.05, 7.24, 10.44. This result indicates that (**1**), at least under these conditions, behaves towards electrophilic reagents as a double indole rather than an α,α′-bipyrryl.

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