Pergamon

Tetrahedron Letters 40 (1999) 2429–2430

TETRAHEDRON
LETTERS

New Route to the Synthesis of the Indolo[7,6-g]indole ("Bis(Pyrrolo)naphthalene") system Starting from 1,5-Dihydroxynaphthalene

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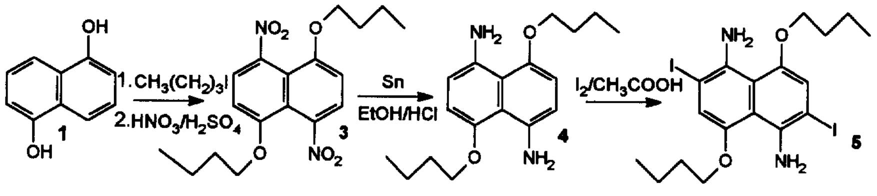
Received 1 December 1998; revised 6 January 1999; accepted 11 January 1999

Abstract. A short and convenient route for the synthesis of indolo[7,6-g]indole derivatives starting from dihydroxynaphthalene is described. 1,5-Dihydroxynaphthalene (1) after alkylation, nitration and reduction gave 4,8-diamino-1,5-dibutoxynaphthalene (4). After reaction with iodine, 4,8-diamino-1,5-disubstituted naphthalene gave the corresponding 3,7-diodonaphthalene (5) in nearly quantitative yields. Palladium-catalyzed reaction of this diiodonaphthalene derivative with (trimethylsilyl)acetylene (TMSA), followed by efficient CuI-mediated cyclization with simultaneous elimination of the TMS substituent, allowed an efficient preparation of 5,10-dibutoxyindolo[7,6-g]indole (8).

In recent years, polypyrrole and its derivatives have been widely investigated because of their easy electrosynthesis, good stability and excellent conductivity in the oxidized state.[1] We report a unique synthesis of bis(pyrrol-2-yl)arylene derivative, its electropolymerization behaviour and properties of the electroactive and electrically conducting polymer obtained.[2,3] The new synthetic route opens up a number of opportunities for the synthesis of derivatized, potentially soluble and processable, pyrrole-containing polymers.The present contribution deals with a novel approach to *bis*-pyrrolo-disubstituted naphthalene from a disubstituted naphthalene. We hoped that indolo[7,6-g]indole with the butoxy groups in positions 5 and 10 would be a good substance for polymerization.

For the synthesis of the desired 5,10-dibutoxy-indolo[7,6-g]indole **8**, we started from 1,5-dihydroxynaphthalene (**1**) which was o-alkylated by a typical procedure[4] to give 1,5-dibutoxynaphthalene (**2**). For nitration and reduction of 1,5-dibutoxynaphthalene we used the procedure described by Thomson [5] *et al.* for 1,5-dimethoxynaphthalene. Compound **2** after nitration with fuming nitric acid in acetic acid [5] gave the corresponding dinitronaphthalene **3**. Reduction of **3** with Sn metal in EtOH/ HCl [5] gave 4,8-diamino-1,5-dibutoxynaphthalene **4**. Iodination of compound **4** by I_2 in a mixture of nitric, sulfuric and acetic acids, in a procedure similar to that used for iodination of fluorene,[6] gave 4,8-diamino-1,5-dibutoxy-3,7-diiodonaphthalene in 80% yield. Iodination generally occurs at room temperature. In our case, the reaction was completed by simply mixing the diamine and the iodinating agent in an 1: 2.2 molar ratio at 40 °C.



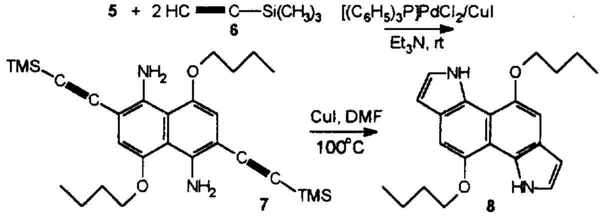
Scheme 1

4,8-Diamino-1,5-dibutoxy-3,7-diiodo-naphthalene **5** was transformed into bis-pyrrole-naphthalene **8** by the two step reaction sequence shown in Scheme 2. First, palladium-catalyzed reaction of diamine **5** with (trimethylsilyl)acetylene, using the experimental conditions previously described by Takahashi *et al.*[7] for aryl halides, provided access to the key intermediate, the dialkynylnaphthalene **7**, in good yield. Thus, reaction of diaminodiiodonaphthalene with TMSA (2.4 equiv) and catalytic amounts

0040-4039/99/$ - see front matter
PII: S0040-4039(99)00121-5

of the bis[triphenylphosphine]palladium dichloride and copper (I) iodide system (0.1 equiv) in Et_3N under N_2, from 0 °C to room temperature, furnished *bis-(*trimethylsilyldiamino)naphthalene 7 as the single reaction product.

For the cyclization reaction of compound 7 to 8 with simultaneous elimination of TMS, we used the method previously reported by Kumar *et al.*[8] for the preparation of pyridinylpyrrolo[2,3-b]pyridine from aminoethynyltrimethylsilylbipyridyl. In our case, the addition of two equivalents of CuI promoted heteroannulation of 7, providing an easy entry into "bis(pyrrolo)naphthalene" 8 [9] in excellent yield. The reaction takes place in anhydrous DMF, and the mixture was heated at 100 °C under nitrogen typically over a period of 4h.



Scheme 2

In summary, a versatile methodology for the synthesis of indolo[7,6-g]indole has been developed. The results reported herein offer a simple method of preparation of a compound belonging to class [10] of indoloindoles. The success of this method consists in the use of efficient and selective reagents in every step that, as a common feature, can be carried out without the use of protective groups. This procedure can be easily adapted for the synthesis of *bis*(pyrrolo)disubstituted naphthalenes starting from simple diamines. The overall process involving simple reaction conditions and a short number of steps with attendant good yields has provided a convenient and valuable method for the synthesis of such compounds.

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9. **5,10-Dibutoxy-indolo[7,6-g]indole ("bis(pyrrolo)naphthalene") (8).** The 4,8-diamino-1,5-dibutoxy-bis(trimethylsilylethynyl)-naphthalene 7 (1.0g, 2.0 mmol) and CuI (1.62g, 8.5 mmol) were placed under N_2 in dried flask fitted with a condenser, and DMF (10 mL) was added. The mixture was heated at 100 °C until TLC showed the dissappearance of the starting compound 7 (4h), and then the mixture was cooled to room temperature. After addition of ethyl ether (100 mL) and filtration through Celite, the combined ethereal solutions were washed with a saturated aqueous solution of NaCl (200 mL) and dried over Na_2SO_4. The solvent was evaporated and the residue was chromatographed on silica gel using hexane/ethyl acetate 5:3. Yield 83%,white solid, mp.188-190 °C; ^1H NMR (DMSO, 300 MHz) δ: 0.96 (t, J = 7.1Hz, 6H); 1.44-1.56 (m, 4H); 1.75-1.85 (m, 4H); 4.02 (t, J = 5.81Hz, 4H); 7.05 (s, 2H); 7.12 (s, 2H); 7.18 (s, br. 2H); 11.2 (s, br. 2H); ^{13}C NMR δ 13.9; 18.9; 31.4; 70.0; 97.4; 107.4; 109.2; 116.3; 122.1; 140.1; 153.9. Anal.Calcd. for $C_{22}H_{26}N_2O_2$: C, 75.39; H, 7.48; N, 7.99. Found: C, 75.0; H, 7.15; N, 7.8.
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