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Tetrahedron Letters 46 (2005) 5839-5840

Tetrahedron Letters

A new approach to the synthesis of oligomers. Application to the synthesis of *p*-phenylene thioether wires

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> Received 6 May 2005; revised 22 June 2005; accepted 27 June 2005 Available online 14 July 2005

Abstract—Oligothioethers $4-RC_6H_4(SC_6H_4-4)_nX$ (n = 1-3; X = Br, I; $R = NO_2$; X = Br; R = MeO. n = 1 and 2; X = I; R = MeO. n = 4; X = Br; $R = NO_2$) have been prepared through a process involving (i) palladium-catalyzed C–S coupling between $4-RC_6H_4(SC_6H_4-4)_{n-1}I$ and $4-BrC_6H_4SH$ to give $4-RC_6H_4(SC_6H_4-4)_nBr$ and (ii) copper-catalyzed replacement of Br by I. © 2005 Elsevier Ltd. All rights reserved.

The design and tailoring of linear or branched oligomeric molecules (molecular wires or dendrimers, respectively) are receiving considerable attention because they may play an important role in different key research areas. To build such oligomers, a variety of repeating step-by-step coupling methods have been used.^{1–11} We report here a new approach to prepare thioether wires involving (i) C–S coupling between R–I and HS–R'–Br to give R–S–R'–Br and (ii) replacement of bromo by iodo to give R–S–R'–I.

The reaction of equimolecular amounts of 4-BrC₆H₄SH with KO^{*t*}Bu and 4–RC₆H₄I, catalyzed by 1% molar amounts of a mixture of Pd(dba)₂ (dba = dibenzylide-nacetone) and diphenylphosphinoferrocene (dppf) (Scheme 1), gave the corresponding thioethers 4-BrC₆H₄SC₆H₄R-4 (R = MeO (1bM, 71%), NO₂ (1bN, 75%)).^{12–14} These bromides were transformed into the iodides 4-IC₆H₄SC₆H₄R-4 (R = MeO (1iM, 75%), NO₂ (1iN, 78%))¹⁵ following a slight modification of the copper/diamine-catalyzed method of Klapars and Buchwald.¹⁶ The amounts of the palladium and copper catalysts must be increased (up to 10% and 40%, respectively) as the length of the chain grows. The oligomers **2bM** (84%), **2bN** (80%), **2iM** (77%), **2iN** (89%), **3bM** (80%), **3bN** (76%), **3iN** (71%), and **4bN** (69%), were obtained similarly (Scheme 2).



Scheme 1. Reagents and conditions: $[Pd] = 1 \mod \% (Pd(dba)_2 + dppf) + KO'Bu$, toluene, 50 °C, 3 days; $[Cu] = 8 \mod \% (CuI + 2 \operatorname{racemic} trans-N,N'-dimethyl-1,2-cyclohexanediamine) + 2 equiv NaI, dioxane, 140 °C, 48 h.$

Similar oligomers have been reported by Gingras and co-workers through a three step process: (i) *p*-bromination of a thiomethyl arene to give Br–Ar–SMe, (ii) Pdor Cu-catalyzed coupling of the bromoarenes with a thiophenol R–Ar'–SH to give R–Ar'–S–Ar–SMe and (iii) dealkylation of the SMe group to give R–Ar'–S–Ar– SH.^{17,18} With respect to our method, the reported yields are similar or lower, the reaction conditions are harsher (100–160 °C for the C–S coupling and 160–200 °C for the deprotection of thiols from the thiomethyl compounds) and the end group R is limited to H or a group with +M effect (OⁱPr) while our method is compatible with both +M (OMe) and –M groups (NO₂). We unsuccessfully attempted to apply the above-mentioned

Keywords: Oligomer; Thioether; C–S Coupling; Palladium catalyst; Molecular wires.

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^{0040-4039/\$ -} see front matter @ 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.tetlet.2005.06.143



Scheme 2. Reagents and conditions: $[Pd] = 1-10 \mod\% (Pd(dba)_2 + dppf) + KO'Bu$, toluene, 50 °C, 1–3 days; $[Cu] = 8-40 \mod\% (CuI + 2 racemic$ *trans-N,N'*-dimethyl-1,2-cyclohexanediamine) + 2 equiv NaI, dioxane, 140 °C, 48 h.

deprotection method¹⁸ to prepare Br(C₆H₄-1,4)S(C₆H₄-1,4)SH, which would allow growing the chains using less steps.¹⁹ Our method is only limited by the very low solubility of the longest chains. Thus the poor solubility of **4iN** rules out its purification and the preparation of pure **5bN**. The synthesis of a few linear or cyclic oligo(*p*-phenylene)thioethers $4-XC_6H_4(SC_6H_4-4)_nX$ (n = 2, X = H; n = 4, X = Br, I)²⁰ or $(SC_6H_4-4)_n$ (n = 4, 5 and 6^{21})²² has also been reported.

This new approach for preparing oligomers is also open to: (1) growing chains in two or more directions using S or other links, for example, by reacting $C_6H_nI_{6-n}$ with HX-R'-Br (X = C $\equiv C$, NH, O, etc.), or HX-R'-XHwith IC_6H_4 Br; (2) growing long chains by transforming $R-(X-R')_n$ -Br into $R-(X-R')_n$ -XH and then reacting it with $R - (X - R')_m - I$; (3) if R is a protecting group, to prepare chains $H-(X-R')_n$ -Br that could be used to grow longer chains in less steps; (4) preparing chains with the same or different X links ($X = C \equiv C$, NH, O, S, etc.; R or/and R' \neq aryl group); (5) building molecular wires through the catalytic Heck, Stille or Suzuki reactions. Of course, it is necessary, to find the experimental conditions allowing the coupling step to occur selectively with the carbon atom bonded to I but not to Br. In conclusion, the great flexibility of this approach opens the way to preparing wires or dendrimers fulfilling some desired properties.

Acknowledgements

We thank the financial support of Ministerio de Educación y Ciencia (MEC), Spain and FEDER (CTQ2004-05396); R.M.L.-N. thanks to MEC for a grant.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet-let.2005.06.143. Detailed descriptions of experimental procedures and ¹H and ¹³C NMR spectra of the new compounds.

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