



Synthesis of 1,5-naphthylethynyl nanostructure networks with extended π -conjugation. Effective heterocoupling catalyzed by palladium under a compatible CO₂ atmosphere

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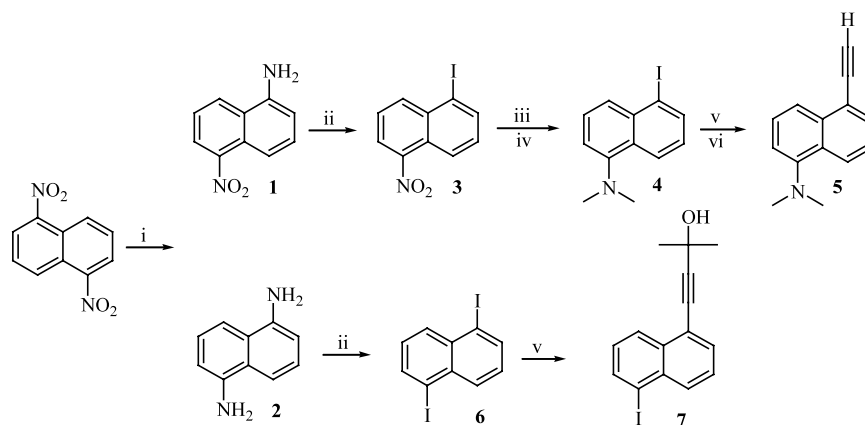
Abstract—The synthesis of a new extended π -conjugated 5-*N,N*-dimethylaminonaphthyl family was undertaken by palladium-catalyzed cross-coupling reaction between a protected 5-iodonaphthylethynyl and 1-ethynyl-5-(*N,N*-dimethylamino)naphthalene. Under an argon atmosphere, only the homocoupling product 1,4-(*N,N*-dimethylamino)naphthyl-1,3-butadiyne was isolated, in excellent yield. However, under a compatible and pure carbon dioxide atmosphere, the cross-coupling product was obtained in excellent yield. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

The synthesis and characterization of nanometer-sized conjugated molecules of precise length and constitution are of great interest, due to their inherent synthetic flexibility which permits the design of molecular architectures with important properties.^{1,2} Molecules showing extended π -conjugation in general exhibit high thermal stability and can present electroconductive, magnetic and optical properties.³

The synthesis of conjugated arylalkynes was achieved by the palladium-catalyzed heterocoupling of terminal alkynes with haloarenes.⁴ However, heterocoupling competes with the Eglinton–Glaser homocoupling reaction, reducing more or less the yield of the heterocoupling product.⁵

We report the heterocoupling reaction in high yields under a compatible and pure carbon dioxide atmosphere, avoiding the undesired homocoupling, which is the sole product under an argon atmosphere.



Scheme 1. Reagents and conditions: (i) Na₂S, NH₄OH; 80°C; (ii) NaNO₂, H₂SO₄; KI; (iii) SnCl₂·2H₂O, ethyl acetate, reflux; (iv) HCO₂H (37%), acetonitrile, NaBH₃CN, glacial acetic acid, rt; (v) 2-methyl-3-butyn-2-ol, Cl₂Pd(PPh₃)₂, Cu₂I₂, Et₂NH, rt; (vi) NaOH (powder), toluene, reflux.

Keywords: cross-coupling reaction; palladium catalyst; carbonic anhydride atmosphere; 1,5-naphthalenes; naphthylethynyl nanostructures.

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2. Discussion

The synthesis of 1,5-naphthalene conjugated nanostructures has been undertaken from ethynynaphthalene units. 5-(*N,N*-dimethylamino)naphthylethyne (**5**) was prepared by a multistep process from 5-(*N,N*-dimethylamino)-iodonaphthalene (**4**). Compound **4** was prepared by selective reduction of 1,5-dinitronaphthalene with sodium sulfide in a concentrated aqueous ammonia solution, giving 5-nitronaphthalen-1-amine (**1**) (54%) as the main product and 1,5-diaminonaphthalene (**2**) (34%).⁶ The nitro group in compound (**1**) was reduced with stannous chloride in ethyl acetate in excellent yield (93%);⁷ it was treated with sodium cyanoborohydride and formic acid (37%) in acetonitrile to give **4** in practically quantitative yield.⁸

Finally, heterocoupling reaction between **4** and 2-methyl-3-butyn-2-ol, catalyzed by palladium, yields quantitatively 4-[(5-*N,N*-dimethylamino)-1-naphthyl]-2-methylbut-3-yn-2-ol (**7**), which will be used in the heterocoupling reaction with the acetylene **5** (Scheme 1).⁹

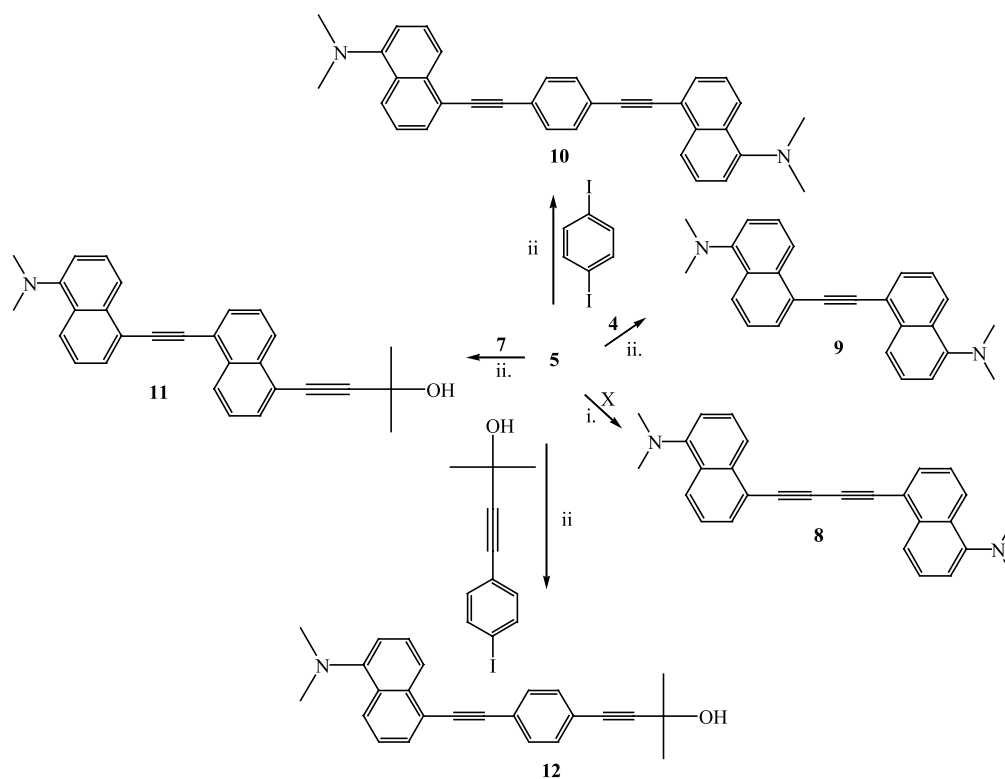
The heterocoupling between **5** and iodoaryl derivatives serves to prepare nanostructures with an electron-releasing *N,N*-dimethylamino group at the end of the conjugated system.¹⁰ However, this heterocoupling reaction, catalyzed by the $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2/\text{Cu}_2\text{I}_2$ system, in diethylamine (or triethylamine or pyridine), under an argon atmosphere at room temperature, always gives

1,4-di[5-(*N,N*-dimethylamino)naphthyl]-1,3-butadiyne (**8**), mp 176–178°C, in practically quantitative yield (Scheme 2).

The oxidative homocoupling of acetylene **5** is an Eglinton–Glaser reaction catalyzed by cuprous iodide in diethylamine, with the residual oxygen present in the argon atmosphere, presumably catalyzed by the palladium. The oxidative dimerization is a secondary reaction always present through the Sonogashira catalyst system.⁵

To avoid the residual oxygen necessary for the oxidative dimerization, we prepared a high-density carbon dioxide inert atmosphere, compatible with the catalyst system.

This atmosphere was prepared as follows: a dispersion of the components in dry triethylamine was placed in a Schlenk tube (**5**, 70 mg, 0.36 mmol; **4**, 107 mg, 0.36 mmol; triethylamine, 30 mL; $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$, 25 mg, 0.036 mmol; and Cu_2I_2 , 0.7 mg, 0.0036 mmol, 1% molar). Then, carbonic dry-ice rods were added and maintained in slow sublimation until a white dense cloud was formed. The carbon dioxide atmosphere was slowly displaced with an external stream of carbon dioxide, bubbled through the diethylamine solution. Next, the $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2/\text{Cu}_2\text{I}_2$ catalyst system dispersed in dry diethylamine, under a CO_2 atmosphere, was added and the mixture stirred at room temperature,



Scheme 2. Reagents and conditions: (i) X = **4**, or **7**, or 1,4-diodobenzene; argon atm. $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2/\text{Cu}_2\text{I}_2$, Et_2NH (or Et_3N or Py); (ii) $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2/\text{Cu}_2\text{I}_2$, Et_3N , CO_2 atm. at rt.

monitoring by TLC. 1,2-Di[5-(*N,N*-dimethylamino)-naphthylethyne (**9**) mp 99–101°C, was isolated in practically quantitative yield (95%), while the 1,3-diyne **8** was only detected at a low level (3%).

In the same way, the heterocoupling between **5** and:
(i) *p*-diiodobenzene gives **10** in good yield (90%) mp 173–175°C and **8** in low yield (5%);
(ii) **7** gives **11** (87%), mp 120–121°C and **8** in low yield (5%);
(iii) 2-methyl-4-(*p*-iodophenyl)-butyn-2-ol gives **12** (96%), mp 100–102°C and **8** in low yield (2%).

In all the cases, the same reaction under an argon atmosphere, yields **8** as the unique homocoupling product in practically quantitative yield.¹¹

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References

1. Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.
2. (a) Shenlin Huang, S.; Tour, J. M. *Polym. Prepr.* **1998**, *39*, 525–526; (b) Grosshenny, V.; Romero, F. M.; Ziessel, R. *J. Org. Chem.* **1997**, *62*, 1491; (c) Brad Wan, W.; Brand, S. C.; Park, J. J.; Haley, M. M. *Chem. Eur. J.* **2000**, *6*, 2044.
3. (a) *Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*; Salaneck, W. R.; Lundström, I.; Ranby, B., Eds.; Oxford University Press: Oxford, 1993; (b) *Photonic and Optoelectronic Polymers*; Jenekhe, S. A.; Wynne, K. J., Eds.; American Chemical Society: Washington DC, 1995; (c) *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S.; Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997; (d) *Electronic Materials: The Oligomer Approach*; Müllen, K.; Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998.
4. Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467.
5. (a) Bharathi, P.; Patel, U.; Kawaguchi, T.; Pesak, D. J.; Moore, J. S. *Macromolecules* **1995**, *28*, 5955; (b) Böhm, V. P. W.; Herrmann, W. A. *Eur. J. Org. Chem.* **2000**, *65*, 3679.
6. Harthan, W. W.; Silloway, H. L. *Organic Syntheses*; Wiley: New York, 1967; Collect. Vol. III, p. 82.
7. Bellamy, F. D.; Ou, K. *Tetrahedron Lett.* **1984**, *25*, 839.
8. Borch, R. F.; Hassid, A. I. *J. Org. Chem.* **1972**, *37*, 1673.
9. (a) Ames, D. E.; Bull, D.; Takundwa, C. *Synthesis* **1981**, 384; (b) Rodríguez, J. G.; Martín-Villamil, R.; Cano, F. H.; Fonseca, I. *J. Chem. Soc., Perkin Trans. 1* **1997**, 709–714.
10. Rodríguez, J. G.; Tejedor, J. L. *J. Org. Chem.* **2002**, *67*, 7631.
11. All the new compounds give satisfactory spectral and elemental analysis.