Russian Chemical Bulletin, International Edition, Vol. 53, No. 8, pp. 1749—1754, August, 2004

Selective cross-coupling of 1-ethynyl-4-iodobenzenes with activated arylacetylenes

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Conditions were found for selective cross-coupling of 1-ethynyl-2,5-dihexyl-4-iodobenzene with arylethynyl-activated arylacetylenes. The reaction is not accompanied by homocondensation of 1-ethynyl-2,5-dihexyl-4-iodobenzene.

Key words: cross-coupling, 1-ethynyl-2,5-dihexyl-4-iodobenzene, 1-ethynyl-2,5-dihexyl-4-phenylethynylbenzene, chemoselectivity, tolans.

Earlier, it has been demonstrated[1,2] that the replacement of the Cl and Br atoms in 1-ethynyl-4-halobenzenes with the ethynyl or phenylethynyl groups leads to an increase in the acidity of the ethynyl group and, as a consequence, to an increase in its reactivity in cross-coupling with aryl halides. It was also noted[2] that the lower the reaction temperature, the larger the difference in the activating effect exerted by the phenylethynyl group and the halogen atom on the ethynyl group. This opens up possibilities for the synthesis of unsymmetrical 4,4´-dialkynyl-substituted tolans based on selective cross-coupling of 1-ethynyl-4-halobenzenes with 1-alkynyl-4-ethynylbenzenes as well as for the preparation of poly(*p*-phenyleneethynylenes) with a given molecular weight and a narrow molecular-weight distribution starting from 1-ethynyl-4-halobenzenes. However, low solubilities of the reactants prevent the reactions at low temperatures. One way of solving this problem is to introduce bulky long-chain alkyl groups into the molecules under study. In the present study, we examined the possibility of preparing the above-mentioned tolans by selective cross-coupling. Compounds modified with two hexyl groups were used as the reagents. The corresponding iodine derivatives were used as haloarenes because these compounds are most efficient in cross-coupling reactions.

Results and Discussion

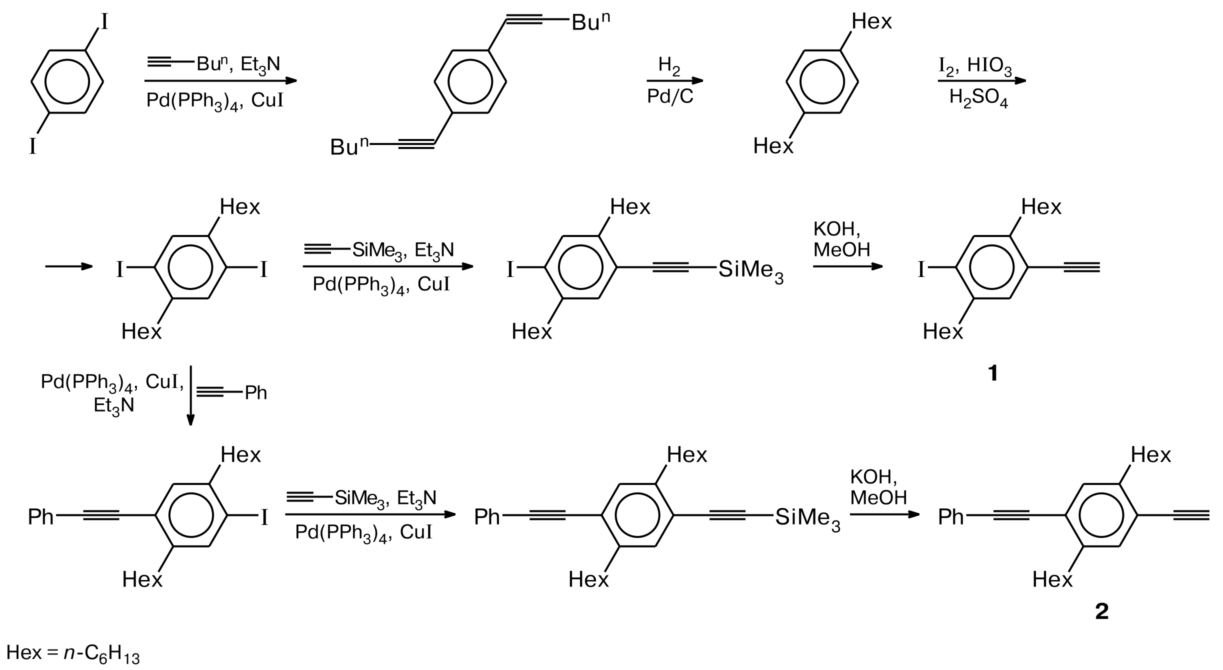
Although data on the quantitative effect of the I atom as a substituent in ethynyliodobenzenes on the reactivity of the ethynyl group are lacking in the literature, it is reasonable to expect that iodine is comparable to other halogens, *i.e.*, Cl and Br, in this characteristic. Consequently, the selectivity of aryl halide with respect to the terminal ethynyl groups of dialkynylarenes in cross-coupling reactions should be substantially higher than that with respect to 1-ethynyl-4-iodobenzene. Hence, we examined 1-ethynyl-2,5-dihexyl-4-iodobenzene (**1**) and 1-ethynyl-2,5-dihexyl-4-phenylethynylbenzene (**2**) as compounds characterized by low and high reactivity of the ethynyl group, respectively. Compound **1** was used in cross-coupling also as aryl halide.

Compounds **1** and **2** were synthesized according to Scheme 1.

It is known[3] that the cross-coupling reaction of ethynylaromatic compounds with aryl halides is very sensitive to atmospheric oxygen. The presence of even small amounts of the latter leads to oxidative dimerization of ethynyl compounds, which is accompanied by the formation of conjugated diyne systems. With the aim of choosing the conditions of cross-coupling, we studied the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1682—1687, August, 2004.

Scheme 1

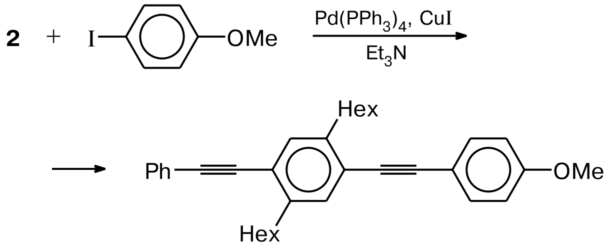


1

2

model reaction of ethynylbenzene **2** with 4-iodoanisole (Scheme 2) giving rise to product **3**.

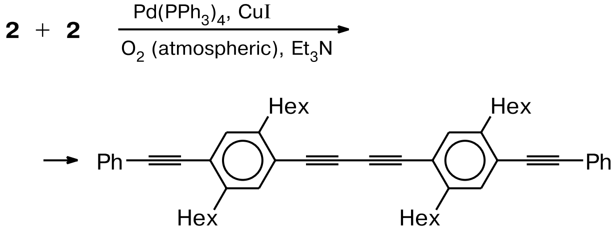
Scheme 2



3

To facilitate the identification of the reaction products, we synthesized conjugated diyne compound **4** by dimerization of arylacetylene **2** (Scheme 3).

Scheme 3



4

When choosing the conditions of the model reaction, we found (data from gel permeation chromatography (GPC)) that compound **3** can be prepared in quantitative yield by carefully removing oxygen traces from the reaction mixture (the freeze—pump—thaw method (four cycles) before and after the addition of the catalysts). When this procedure was used only prior to the addition of the catalysts, the model reaction afforded compounds **3** and **4** in an approximately equimolar ratio. In this connection, all cross-coupling reactions, including multistep reactions, were carried out under conditions precluding exposure to atmospheric oxygen.

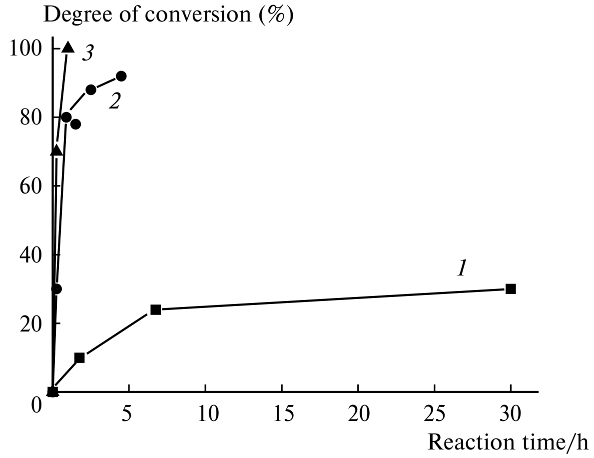
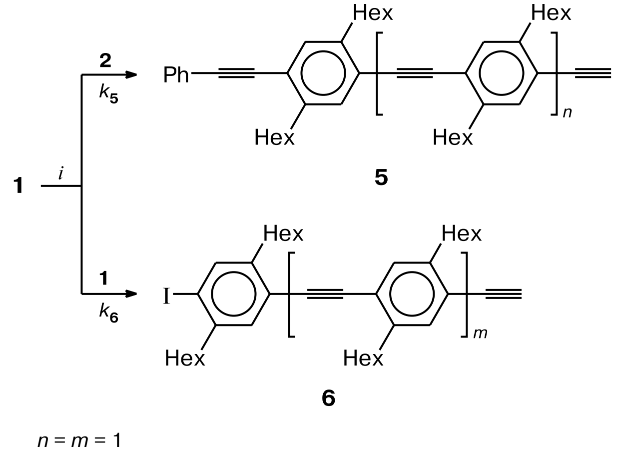


Fig. 1. Plot of the degree of conversion of compound **1** *vs.* the reaction time at –20 (*1*), 0 (*2*), and 10 °C (*3*).

To find the optimum conditions of the reaction, cross-coupling of components **1** and **2** was carried out at different temperatures. As can be seen from Fig. 1, the reaction at 10 °C proceeds rather rapidly and the quantitative conversion of compound **1** is achieved in 1 h. At higher temperatures, selectivity of the reaction decreases.

In the general form, cross-coupling of the **1** + **2** system can follow two pathways (Scheme 4).

Scheme 4



Reagents and conditions: *i*. $Pd(PPh_3)_4$, CuI, Et_3N.

Evidently, due to similarity of the nearby substituents in the phenyl ring adjacent to the ethynyl group in compounds **2**, **5** and **6**, these groups have similar reactivities. Consequently, if $k_5 \gg k_6$, selective cross-coupling should afford compound **5** ($n = 1$) as well as a series of structurally similar compounds bearing a larger number of the phenyleneethynylene fragments (with a higher degree of polymerization). In this reaction, compound **2** remains partially unconsumed. If $k_5 \ll k_6$, selective cross-coupling should produce exclusively the dimer of compound **1** (**6**; $m = 1$). If $k_5 \approx k_6$, the reaction should give (particularly, at low conversions of compound **1**) compounds **5** ($n = 1$) and **6** ($m = 1$) as well as structurally similar compounds with a higher degree of polymerization.

At high degrees of conversion of ethynyliodobenzene **1** in cross-coupling with **2**, it is difficult to unambiguously determine whether the reaction proceeds by the mechanism of selective cross-coupling ($k_5 \gg k_6$) or compound **2** serves only as a versatile blocking agent ($k_5 \approx k_6$). To elucidate this question, we studied the products of the reaction of equimolar amounts of **1** and **2** in early stages of the conversion of compound **1**. For comparison, we also investigated oligomeric products of homocondensation of compound **1** of general formula **6** ($m \geq 1$) performed in the absence of compound **2**.

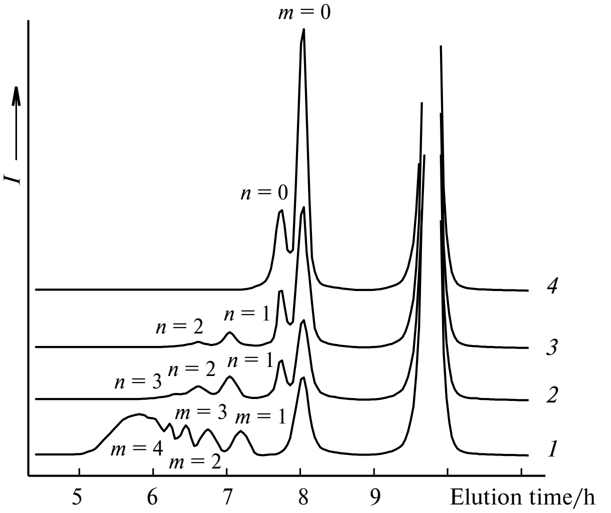


Fig. 2. GPC data for oligomers **6** (*1*) and the products of the competitive reaction (*2—4*; see Scheme 4) at different degrees of conversion of compound **1**: 50 (*2*), 10 (*3*), and 0% (*4*); *n* and *m* are the degrees of polymerization of products **5** and **6**, respectively; the starting reagent molar ratio **1** : **2** = 1 : 1.

The elution profiles of the products (GPC data), which were prepared under the conditions of competitive reactions (see Scheme 4) and homocondensation of **1** (oligomers of general formula **6** ($m \geq 1$)), are shown in Fig. 2. It should be noted that in the chromatograms measured at the same concentration of the compounds, the peaks of iodine-containing compounds **1** and **6** are much more abundant than the peaks of compounds **2** and **5**. In particular, the intensity of the peak of compound **1** is 6.5 times higher than that of the peak of compound **2** (see Fig. 2, curve *4*). However, even taking into account this fact, signals of homooligomers **6** ($m \geq 1$) were not found (*cf.* Fig. 2, curve *1*) in the GPC chromatograms of the products prepared according to Scheme 4 (see Fig. 2, curves *2* and *3*). These data indicate that cross-coupling occurs selectively under the conditions used.

Under the conditions of Pd—Cu catalysis, ethynylaromatic compounds are very sensitive to atmospheric oxygen. Hence, to preclude the possible partial formation of conjugated diyne structures in the course of isolation of products **5**, the terminal ethynyl groups were protected with 4-iodoanisole in the final step of the reaction (Scheme 5).

The data from MALDI—TOF mass spectrometry* of the products, which were synthesized starting from compounds **2** and **1** in molar ratios of 1 : 1 and 1 : 2, are given in Table 1. It can be seen that the reaction product consists of a number of oligomeric molecules corresponding exclusively to structure **7** and contain virtually no compo-

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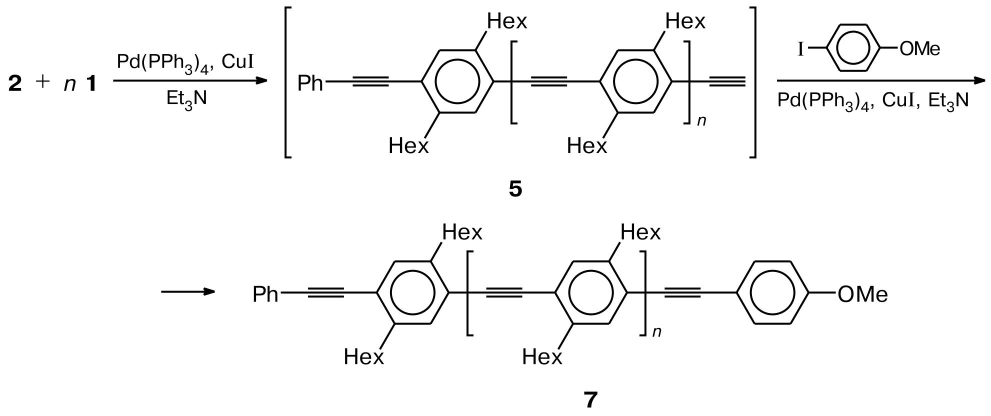
* Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry.

Scheme 5



n = 1, 2

Table 1. Compositions of oligomers **7** determined by MALDI—TOF mass spectrometry ($[M + H]^+$)

n	Starting molar ratio of reagents **1** and **2**			
	1 : 1		2 : 1	
	Observed *m/z*	Oligomer fraction (%)	Observed *m/z*	Oligomer fraction (%)
0	475.8	41.6	475.9	13.8
1	744.4	35.2	745.0	29.2
2	1012.9	15.8	1014.1	28.3
3	1281.7	6.1	1282.5	19.9
4	1550.8	1.3	1551.4	7.2
5	—	—	1820.1	1.4
6	—	—	2088.0	0.2

Note. Peaks at other mass numbers are observed in the spectrum only in trace amounts and are not belong to components of other chemotypes.

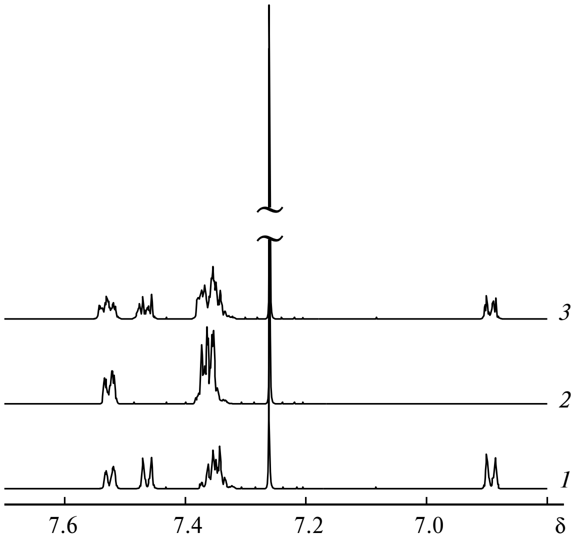


Fig. 3. ^1H NMR spectra (in $CDCl_3$) of compounds **3** (*1*), **4** (*2*), and **7**, which was synthesized using the starting molar ratio **1** : **2** = 2 : 1 (*3*).

nents of other chemotypes. These conclusions follow also from the ^1H NMR spectroscopic data. In the spectrum of compound **7**, which was synthesized starting from the molar ratio **2** : **1** = 1 : 2 (Fig. 3, curve *3*), the integral intensity ratio of the signals at δ 7.52 and 7.46 (or 6.89) is 1, *i.e.*, the number of the terminal phenyl groups in product **7** is equal to the number of the phenylenemethoxy groups. The same situation is observed in the spectrum of compound **3** (see Fig. 3, curve *1*), in contrast to the spectrum of compound **4** (see Fig. 3, curve *2*), which has no signals of the phenylenemethoxy groups. Besides, the spectrum of compound **7** has no signals of the ethynyl groups of unprotected products **5** or **6** (δ 3.25—3.30) and signals of the iodophenyl groups of compounds **6** (δ 7.26—7.31 and 7.64—7.66) as well as of products of their protection with the anisolyl reagent.

To summarize, we carried out selective cross-coupling of 1-ethynyl-2,5-dihexyl-4-iodobenzene with aromatic compounds containing the arylethynyl-activated ethynyl group. The reaction is not accompanied by homocondensation of 1-ethynyl-2,5-dihexyl-4-iodobenzene. The results of our study open up possibilities for the synthesis of unsymmetrical 4,4′-diacetylenyl-substituted tolans and also give grounds to expect that the use of selective cross-coupling for the synthesis of polymers will allow one to prepare defect-free poly(*p*-phenyleneethynylenes) with a given molecular weight and a narrow molecular-weight distribution.

Experimental

Tetrakis(triphenylphosphine)palladium(0), (trimethylsilyl)acetylene, and phenylacetylene (Wako Pure or Aldrich) were used without additional purification; CuI was refluxed in toluene and stored under nitrogen after removal of the toluene. The solvents were dried over the corresponding reagents and distilled under nitrogen immediately before use. All reactions were carried out in an atmosphere of dry oxygen-free nitrogen. The reactions under the conditions of Pd—Cu catalysis were carried out in Schlenk vessels. The catalysts were added under a stream of nitrogen. Before and after the addition of the catalysts, oxygen was removed from the reaction solutions by the freeze—pump—thaw method (four cycles), unless otherwise indicated. After completion of the last cycle, the reaction solutions were kept in blackened Schlenk vessels under nitrogen at a slightly excessive pressure, unless otherwise indicated. Column chromatography was carried out with the use of silica gel (Aldrich, 70—230 mesh).

The ^{1}H NMR spectra were recorded on a JEOL LA600 spectrometer (600 MHz) in $CDCl_3$ or DMSO-d_6 with Me_4Si as the internal standard. The IR spectra were measured on a Perkin—Elmer Paragon 1000 FT-IR spectrometer. Gel permeation chromatography was performed on a Jasco Gulliver instrument equipped with a Shodex K-804L column and a UV detector (254 nm) using $CHCl_3$ as the mobile phase. The data were recorded at 35 °C at a flow rate of 1 mL min^{-1}. The molecular structures of the products were analyzed on a Shimadzu/Kratos Kompact MALDI III mass spectrometer using 2,5-dihydroxybenzoic acid and THF as the matrix and the solvent, respectively.

1,4-Di(hex-1-ynyl)benzene. Copper iodide (0.20 g, 1.06 mmol) and $Pd(PPh_3)_4$ (0.49 g, 0.43 mmol) were added to a solution of *p*-diiodobenzene (4.95 g, 15 mmol), hex-1-yne (3.12 g, 38 mmol), and Et_3N (15 mL) in toluene (22 mL). The reaction solution was stirred at 0 °C for 2 h and at 25 °C for ~16 h. Then hexane (100 mL) was added and the precipitate was separated. The mother liquor was concentrated, hexane was added to the residue, and the product was purified by column chromatography on SiO_2 (hexane, R_f 0.35). The yield was 3.32 g (93%), colorless liquid. ^{1}H NMR ($CDCl_3$), δ: 0.94 (t, 6 H, Me, J = 6.6 Hz); 1.52 (m, 8 H, $(CH_2)_2$); 2.40 (t, 4 H, CH_2, J = 6.8 Hz); 7.29 (s, 4 H, C_6H_4).

1,4-Dihexylbenzene. Oxygen was removed from a mixture of 1,4-di(hex-1-ynyl)benzene (0.95 g, 4.0 mmol), Pd/C (5%, 1.0 g), and anhydrous EtOH (140 mL). Then a stream of hydrogen was passed through this mixture at 25 °C. The completeness of hydrogenation was monitored by GLC. After completion of the reaction, $CHCl_3$ (50 mL) was added to the suspension. The precipitate was separated and washed several times with $CHCl_3$. The combined solutions were concentrated, $CHCl_3$ was added to the residue, and the product was separated from residues of the catalyst on a short column with SiO_2 (hexane, R_f 0.35). The yield was 0.895 g (91%), colorless liquid. ^{1}H NMR ($CDCl_3$), δ: 0.87 (t, 6 H, Me, J = 6.6 Hz); 1.29 (m, 12 H, $(CH_2)_3$); 1.59 (m, 4 H, CH_2); 2.56 (t, 4 H, CH_2, J = 7.8 Hz); 7.08 (s, 4 H, C_6H_4).

1,4-Dihexyl-2,5-diiodobenzene was synthesized according to a known procedure[4] and recrystallized from 95% EtOH. The yield was 55%, m.p. 51 °C. ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, 6 H, Me, J = 6.6 Hz); 1.33 (m, 12 H, $(CH_2)_3$); 1.54 (m, 4 H, CH_2); 2.59 (t, 4 H, CH_2, J = 7.8 Hz); 7.59 (s, 2 H, C_6H_2).

[2-(2,5-Dihexyl-4-iodophenyl)ethynyl](trimethyl)silane. Copper iodide (26 mg, 0.136 mmol) and $Pd(PPh_3)_4$ (63 mg, 0.055 mmol) were added to a solution of 1,4-dihexyl-2,5-diiodobenzene (3.35 g, 6.72 mmol), (trimethylsilyl)acetylene (0.48 mL, 3.4 mmol), and Et_3N (4 mL) in toluene (30 mL). The reaction solution was stirred at 0 °C for 8 h and at 25 °C for ~16 h. Then the precipitate was separated from the reaction mixture and the solution was concentrated. Hexane was added to the residue and the product was purified by column chromatography on SiO_2 (hexane, R_f 0.80). The yield was 0.875 g (55%), colorless oil. ^{1}H NMR ($CDCl_3$), δ: 0.24 (s, 9 H, $SiMe_3$); 0.89 (t, 6 H, Me, J = 6.6 Hz); 1.31 (m, 12 H, $(CH_2)_3$); 1.54 and 2.62 (both m, 4 H each, CH_2); 7.23 and 7.61 (both s, 1 H each, *o*-H arom., *m*-H arom.). IR (KBr), ν/cm^{-1}: 2928.6, 2858.5, 2154.6, 1474.7, 1376.3, 1249.6, 1141.9, 856.8, 759.8, 663.4.

1-Ethynyl-2,5-dihexyl-4-iodobenzene (1). Methanol (4 mL) and a 10% aqueous KOH solution (2 mL) were added to a solution of [2-(2,5-dihexyl-4-iodophenyl)ethynyl](trimethyl)silane (867 mg, 1.85 mmol) in THF (8 mL). The reaction mixture was stirred in a blackened flask at 25 °C for one day. Then volatile components were removed from the reaction mixture under reduced pressure. Water (20 mL) and Et_2O (20 mL) were added to the residue. The mixture was shaken and the organic layer was separated from the aqueous layer. The latter was extracted two times with Et_2O. The combined extracts were dried with $CaCl_2$. After removal of diethyl ether, hexane was added to the residue and the product was purified by column chromatography on SiO_2 (hexane, R_f 0.80). The yield was 0.623 g (85%), colorless oil. Found (%): C, 60.61; H, 7.37; I, 32.02. $C_{20}H_{29}I$. Calculated (%): C, 60.58; H, 7.51; I, 31.71. ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, 6 H, Me, J = 6.6 Hz); 1.31 (m, 12 H, $(CH_2)_3$); 1.55 and 2.64 (both m, 4 H each, CH_2); 3.25 (s, 1 H, ≡CH); 7.26 and 7.64 (both s, 1 H each, *o*-H arom., *m*-H arom.).

1,4-Dihexyl-2-iodo-5-phenylethynylbenzene. Copper iodide (20 mg, 0.104 mmol) and $Pd(PPh_3)_4$ (48 mg, 0.042 mmol) were added to a solution of 1,4-dihexyl-2,5-diiodobenzene (3.91 g, 7.85 mmol), phenylacetylene (0.29 mL, 2.6 mmol), and Et_3N (5 mL) in toluene (35 mL). The reaction mixture was stirred at 25 °C for 16 h. The precipitate that formed was filtered off and washed with hexane. The mother liquor was concentrated under reduced pressure, the residue was diluted with a threefold excess of hexane and purified on a column with SiO_2 (hexane, R_f 0.70). The yield was 0.822 g (67%), liquid. ^{1}H NMR ($CDCl_3$), δ: 0.88 (t, 6 H, Me, J = 6.6 Hz); 1.33 (m, 12 H, $(CH_2)_3$); 1.60 (m, 4 H, CH_2); 2.64 and 2.74 (both t, 2 H each, $ArC\underline{H}_2$, J = 7.8 Hz); 7.31 (s, 1 H, *o*-H arom.); 7.34 (m, 3 H, Ph); 7.50 (m, 2 H, Ph); 7.66 (s, 1 H, *m*-H arom.).

[2-(2,5-Dihexyl-4-phenylethynylphenyl)ethynyl](trimethyl)silane. Copper iodide (13 mg, 0.068 mmol) and $Pd(PPh_3)_4$ (31 mg, 0.027 mmol) were added to a solution of 1,4-dihexyl-2-iodo-5-phenylethynylbenzene (816 mg, 1.73 mmol), trimethylsilylacetylene (0.37 mL, 2.61 mmol), and Et_3N (1 mL) in toluene (8 mL). The reaction mixture was stirred at 0 °C for 9 h and then gradually heated to 25 °C. After ~16 h, the reaction solution was filtered, the precipitate was washed with hexane, and the filtrate was concentrated. Hexane (4 mL) was added to the residue and the product was purified on a column with SiO_2 (hexane, R_f 0.45). The yield was 0.724 g (94%), yellowish oil. ^{1}H NMR ($CDCl_3$), δ: 0.26 (s, 9 H, $SiMe_3$); 0.88 (t, 6 H, Me, J = 6.6 Hz); 1.33 (m, 12 H, $(CH_2)_3$); 1.60 and 2.74 (both m, 4 H each, CH_2); 7.29, 7.31 (both s, 1 H each, *o*-H arom., *m*-H arom.); 7.34 (m, 3 H, Ph); 7.51 (m, 2 H, Ph). IR (KBr), ν/cm^{-1}: 2928.9, 2858.7, 2150.8, 1497.2, 1249.9, 856.9, 843.0, 755.2, 689.4.

1-Ethynyl-2,5-dihexyl-4-phenylethynylbenzene (2) was synthesized analogously to 1-ethynyl-2,5-dihexyl-4-iodobenzene. The yield was 82%, colorless oil. Found (%): C, 90.75; H, 9.25. $C_{28}H_{34}$. Calculated (%): C, 90.62; H, 9.34. ^{1}H NMR ($CDCl_3$), δ: 0.87 (t, 6 H, Me, J = 6.6 Hz); 1.33 (m, 12 H, $(CH_2)_3$); 1.61 and 2.75 (both m, 4 H each, CH_2); 3.29 (s, 1 H, ≡CH); 7.34 (m, 5 H, Ph + H arom.); 7.51 (m, 2 H, Ph).

1,4-Dihexyl-2-(4-methoxyphenyl)ethynyl-5-phenylethynylbenzene (3). A solution of compound **2** (7.4 mg, 0.02 mmol), 4-iodoanisole (9.4 mg, 0.04 mmol), and Et_3N (0.2 mL) in toluene (1.4 mL) was degassed and then CuI (0.4 mg, 0.002 mmol) and $Pd(PPh_3)_4$ (0.8 mg, 0.0007 mmol) were added, after which the reaction solution was degassed and stirred at 25 °C for 1 day. The chromatographic test demonstrated that the product was obtained in quantitative yield. Then the reaction mixture was filtered, the precipitate was washed with a 1 : 1 hexane—benzene mixture, and the combined filtrates were concentrated. The precipitate was dissolved in a 4 : 1 hexane—benzene mixture and chromatographed on a column with SiO_2 (hexane—benzene, 4 : 1). The yield was 0.0063 g (66%), R_f 0.10 (hexane). Found (%): C, 88.19; H, 8.46. $C_{35}H_{40}O$. Calculated (%): C, 88.07; H, 8.66. ^{1}H NMR ($CDCl_3$), δ: 0.87 (t, 6 H, Me, J = 6.6 Hz); 1.32 (m, 8 H, $(CH_2)_2$); 1.40, 1.69, and 2.79 (all m, 4 H each, CH_2); 3.84 (s, 3 H, OMe); 6.89 and 7.46 (AB-q, 4 H, $C_6\underline{H_4}OMe$, J = 8.5 Hz); 7.34 (m, 5 H, Ph + H arom.); 7.52 (m, 2 H, Ph). IR (KBr), ν/cm^{-1}: 2927.3, 2857.5, 2206.7, 1607.2, 1497.8, 1465.5, 1441.8, 1377.2, 1289.4, 1249.4, 1172.0, 1033.2, 830.6, 755.2, 689.9.

The analogous synthesis, which was carried out without repeated degasification of the reaction solution after the addition of the catalysts, afforded two products (**3** and **4**) in a ratio of 52 : 48 (GPC data).

1-[4-(2,5-Dihexyl-4-phenylethynylphenyl)butane-1,3-diyn-1-yl]-2,5-dihexyl-4-phenylethynylbenzene (4). Copper iodide (0.4 mg, 0.002 mmol) and $Pd(PPh_3)_4$ (0.8 mg, 0.0007 mmol) were added to a solution of compound **2** (7.4 mg, 0.02 mmol) and Et_3N (0.2 mL) in toluene (1.4 mL). The reaction mixture was stirred in air at 25 °C for one day and then filtered. The filtrate was concentrated. Hexane was added to the residue and the mixture was chromatographed on a column with SiO_2 (hexane, R_f 0.30). The yield was 0.0068 g (92%), white crystals with violet fluorescence. Found (%): C, 91.00; H, 9.00. $C_{56}H_{66}$. Calculated (%): C, 90.94; H, 9.11. ^{1}H NMR ($CDCl_3$), δ: 0.88 (t, 12 H, Me, J = 6.6 Hz); 1.33 (m, 16 H, $(CH_2)_2$); 1.39, 1.67, and 2.78 (all m, 8 H each, CH_2); 7.35 (m, 10 H, Ph + H arom.); 7.52 (m, 4 H, Ph). IR (KBr), ν/cm^{-1}: 2927.3, 2857.4, 2137.6, 1600.5, 1495.8, 1459.4, 1441.9, 1377.7, 1189.0, 1069.2, 1025.3, 903.1, 757.8, 725.6, 690.9, 626.2.

Selective cross-coupling of compounds 1 and 2 (general procedure). Oligomeric mixture 5. Copper iodide (1 mg, 0.005 mmol) and $Pd(PPh_3)_4$ (2 mg, 0.0017 mmol) were added to a solution of the corresponding amount of 1-ethynyl-2,5-dihexyl-4-phenylethynylbenzene (**2**), 1-ethynyl-2,5-dihexyl-4-iodobenzene (**1**) (19.2 mg, 0.05 mmol), and Et_3N (0.5 mL) in toluene (3.5 mL). The reaction mixture was stirred at a specified temperature. The course of the reaction was monitored by GPC and MALDI—TOF mass spectrometry. Oligomers **5** were not isolated in pure form and were used *in situ* for the preparation of products **7**.

Oligomeric mixture 6. Copper iodide (0.4 mg, 0.002 mmol) and $Pd(PPh_3)_4$ (0.8 mg, 0.0007 mmol) were added to a solution of 1-ethynyl-2,5-dihexyl-4-iodobenzene (**1**) (7.9 mg, 0.02 mmol) and Et_3N (0.2 mL) in toluene (1.4 mL). The reaction mixture was stirred at 30 °C. The course of the reaction was monitored by GPC and MALDI—TOF mass spectrometry.

Synthesis of products 7 (general procedure). A solution of 4-iodoanisole (23.4 mg, 0.1 mmol) and Et_3N (0.25 mL) in toluene (1.7 mL) was added to the reaction solutions of products **5**. Then CuI (0.5 mg, 0.0025 mmol) and $Pd(PPh_3)_4$ (1 mg, 0.0009 mmol) were added. The reaction mixture was stirred at a specified temperature. The course of the reaction was monitored by GPC and MALDI—TOF mass spectrometry.

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Received September 2, 2003;
in revised form December 23, 2003