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Synthesis and Characterization of 3,6-*Bis*ethynyl-9*H*-fluoren-9-one Derivatives with Sonogashira Coupling

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Several 3,6-*bis*ethynyl-9*H*-fluoren-9-one derivatives were synthesized by palladium-catalyzed coupling of terminal alkynes with arylhalides (Sonogashira coupling).

Key Words: 3,6-*Bis*ethynyl-9*H*-fluoren-9-one, $PdCl_2(PPh_3)_2$, Sonogashira coupling.

INTRODUCTION

Sonogashira *et al.*[1] reported the coupling of terminal alkynes with aryl or alkenyl halides. Sonogashira coupling is carried out in the presence of catalytic amount of a palladium(II) complex as well as copper(I) iodide in an amine as solvent. This coupling is one of the most straight forward methods for the preparation of arylalkynes and conjugated enynes.

Cassar, Dieck and Heck[2,3] had communicated the similar couplings under different conditions, using only palladium catalyst. Such *sp* to sp^2 coupling of copper(I) aryl acetylenes with iodoarenes[4] or iodoalkenes[5] has been reported for the synthesis of acetylenes but its scope mean while limited by the violent reaction conditions and by the difficulties in preparations of cuprous acetylides. Herein, the synthesis of 4 new symmetrically *bis*ethynyl fluorenone derivatives which are key compounds for quinodimethane derivatives are reported. Quinodimethane derivatives assemble itself to a spherical acyclic tetramer in high yield. This spontaneous self-assembly process is driven by the four weak Csp^3-Csp^3 bonds between the fluorene units that are formed during the tetramerization[6,7].

EXPERIMENTAL

Melting points are taken on a buchi SMP-20 apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Bruker AM-400 MHz in $CDCl_3$ using TMS as an internal standard. Elemental analysis were carried out on Carlo-Erba-Analyzer model 1104. FT-IR spectra were recorded on a bruker IFS-25 spectrophotometer. The palladium (II) chloride *bis*(triphenylphosphane) was prepared according to the method of King and Negishi[8]. Trimethylsilyl acetylene was prepared according to the Overman *et al.* method[9]. All other chemicals were of reagent grade and were used without further purification.

3,6-*Bis*[(tri-methyl silyl)ethynyl]-9*H*-fluoren-9-one (4): A mixture of trimethylsilylacetylene (11.6 mL, 0.08 mmol), 3,6-dibromofluorenone (11.26 g, 0.03 mmol), $PdCl_2(PPh_3)_2$ (133 mg, 0.19 mmol), CuI (133 mg, 0.7 mmol), DMF (33 mL) and Et_3N (46 mL) were added to a 250 mL flask and was refluxed under an atmosphere of argon for 12 h. The reaction mixture was treated with water (300 mL) and extracted five times with Et_2O. Organic phase was washed three times with HCl (10 %), twice with saturated $NaHCO_3$ solution and finally with water. The organic layer was separated and dried with Na_2SO_4. The solvent was removed and residue was submitted to column chromatography using (SiO_2, CH_2Cl_2: pentane 3:1) as solvent. The solvent was evaporated and residue was crystallized with ethanol (200 mL), to give the desired compounds as yellow precipitate (yield 10.19 g, 83 %), m.p. 143 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 (2H, d, H-C (4), H-C (5), J = 1.0 Hz), 7.52 (2H, d, H-C (1), H-C (8), J = 7.5 Hz), 7.32 (2H, dd, H-C (2), H-C (7), J = 7.5 Hz, J = 1.0 Hz), 0.20 (18H, s, $6CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 191.77 (C=O), 143.64 (Ar-C), 124.78 (Ar-C), 123.89 (Ar-C), 104.31 (C≡C-$SiMe_3$), 98.75 (C≡C-$SiMe_3$), 1.00 (Me). FT-IR (KBr, ν_{max}, cm^{-1}) 2158m (C≡C), 1709s (C=O), 1615s, 1601, 1294m, 1250s, 1211m, 1187m, 1106m, 1088m, 929m, 845s, 787s, 760s, 712m, 700m, 668m, 644m. Anal. calcd. (%) for $C_{23}H_{24}OSi_2$: C, 74.14; H, 6. 49. Found: C, 74.00; H, 6.35.

3,6-*Bis*[(*tert*-butyl)ethynyl]-9*H*-flouren-9-one (5): A mixture of *tert*-butyl acetylene (9.8 mL, 0.08 mmol), 3,6-dibromofluorenone (11.26 g, 0.03 mmol) $PdCl_2(PPh_3)_2$ (133 mg, 0.19 mmol), CuI (133 mg, 0.7 mmol), DMF (33 mL) and Et_3N (46 mL) were added to a 250 mL flask and was refluxed under an atmosphere of argon for 12 h. The reaction mixture was treated with water (300 mL) and extracted five times with Et_2O. Organic phase was washed three times with HCl (10 %), twice with saturated $NaHCO_3$ solution and finally with water. The resulting product was dried with Na_2SO_4, filtered and rotary evaporated. The residue was submitted to column chromatography (SiO_2, CH_2Cl_2: pentane 3:1). Solvent was evaporated and residue was crystallized with ethanol (200 mL), yield 10 g (85 %), yellow precipitate, m.p. 183 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.56 (2H, d, H-C (1), H-C (8), J = 7.5 Hz), 7.52 (2H, s, broad, H-C (5)), 7.31 (2H, dd, H-C (2), H-C (7), J =7.5 Hz, J = 1.0 Hz), 1.34 (18H, s, $6CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.01 (C=O), 143.60 (Ar-C), 132.31 (Ar-C), 130.54 (Ar-C), 123.96 (Ar-C), 123.38 (Ar-C), 102.59 (C≡C), 79.05 (C≡C), 30.83 (CH_3), 28.12 (C-*tert*). FT-IR (KBr, ν_{max}, cm^{-1}): 3055w (Ar-CH), 2970s, 2865s (CH_3), 2217w (C≡C), 1718s (C=O), 1610s, 1573s, 1475, 1432w, 1282s, 1106s, 909s, 878s, 856s, 782s, 669s. Anal. calcd. (%) for $C_{25}H_{24}O$: C, 88.19; H, 7.10. Found: C, 88.05; H, 7.00.

3,6-*Bis* ethynyl-9*H*-fluoren-9-one (6): 3,6-*Bis*[(tri-methylsilyl)ethynyl]-9*H*-flouren-9-one (**4**) (1.86 mg, 5 mmol) was solved in THF (50 mL), then K_2CO_3 (1.5 g, 11 mmol) in methanol (20 mL) was added to THF solution and stirred for 0.5 h in room temperature, a yellow suspension was formed. The yellow suspension was

treated with water (200 mL) and filtered without suction. The residue was washed twice with water (100 mL) and finally washed with acetone. The solid was dried in room temperature, yellow precipitate yield (0.86 g, 90 %), m.p. > 360 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.64 (2H, d, H-C (1), H-C (8), *J* = 7.8 Hz), 7.63 (2H, broad, s, H-C (4), H-C (5)), 7.46 (2H, dd, H-C (2), H-C (7), *J* = 1.2 Hz, *J* = 7.8 Hz), 3.30 (2H, s, H-C≡C). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 191.25 (C=O), 143.37 (Ar-C), 133.37 (Ar-C), 133.26 (Ar-C), 128.42 (Ar-C), 124.76 (Ar-C), 124.21 (Ar-C), 84.60 (2HC≡C), 83.00 (2HC≡C). FT-IR (KBr, ν_{max}, cm^{-1}): 3269s, 1714 (C=O), 1601s, 907s, 855s, 784s, 635s. Anal. calcd. (%) for $C_{17}H_8O$: C, 89.46; H, 3. 53. Found: C, 89.69; H, 3.33.

3,6-*Bis* (4-nitro-phenylethynyl)-9*H*-fluoren-9-one (7a): A mixture of 3,6-diethynyl-9*H*-fluoren-9-one (**6**) (1.35 g, 6 mmol), *p*-iodonitrobenzene (26.15 g, 11 mmol), $PdCl_2(PPh_3)_2$ (100 mg, 0.14 mmol), CuI (100 mg, 0.52 mmol) and Et_3N (300 mL) in dry DMF (1000 mL) was refluxed under argon gas for 3 h at 110 ºC. Then DMF and Et_3N were removed by evaporation under reduced pressure. The residue was soxhleted with THF. Then THF was evaporated and residue was crystallized in toluene to give the desired compounds as orange colour precipitate (yield 2.51 g, 90 %), m.p. 303 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.27 (4H, d, *J* = 8.9 Hz), 7.75 (2H, broad, s, H-C (4), H-C (5)), 7.73 (2H, d, H-C (7), H-C (8), *J* = 7.6 Hz), 7.72 (4H, d, ArH, *J* = 8.9 Hz), 7.55 (2H, dd, H-C (2), H-C (2), H-C (7), *J* = 1.2 Hz, *J* = 7.6 Hz). FT-IR (KBr, ν_{max}, cm^{-1}): 3110-3000 (Ar-CH), 2208w (C≡C), 1710s (C=O), 1623s (Ar-C=C), 1596s (Ar-C=C), 1516s, 1402m, 1340s, 1292s, 1190m, 1105s, 920s, 855s, 831m, 783m, 749s, 686m, 669m. Anal. calcd. (%) for $C_{29}H_{14}N_2O_5$: C, 74.04; H, 3.00; N, 5.95. Found: C, 73.96; H, 2.55; N, 5.81.

3,6-*Bis*(4-methoxy-phenylethynyl)-9*H*-fluoren-9-one (7b): A mixture of 3,6-*bis*ethynyl-9*H*-fluoren-9-one (**6**) (2.28 g, 10 mmol), 4-iodoanisole (4.68 g, 20 mmol), $PdCl_2(PPh_3)_2$ (280 mg, 0.40 mmol), CuI (150 mg, 0.79 mmol) and Et_3N (150 mL) in DMF (300 mL) was refluxed under argon gas for 3 h at 110 ºC. Then DMF and Et_3N were removed by evaporation under reduced pressure. The residue was treated with water and extracted with CH_2Cl_2 (200 mL) and organic layer was submitted to column chromatography using (SiO_2, CH_2Cl_2) as solvent. The solvent was evaporated and the residue was recrystallized in ethanol to give the desired compounds as yellow precipitate (yield 2.8 g, 64 %), m.p. 229 ºC.

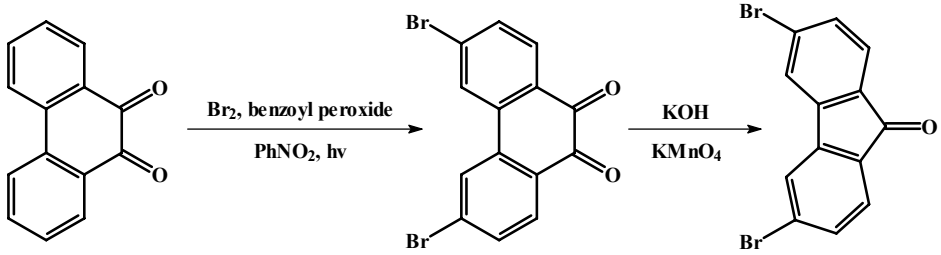
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.65 (2H, broad, s, H-C (4), H-C (5)), 7.65 (2H, d, H-C (1), H-C (8), *J* = 7.7 Hz), 7.50 (4H, dd, Ar, *J* = 6.7 Hz), 7.45 (2H, dd, H-C (2), H-C (7), *J* = 1.0 Hz, *J* = 7.7 Hz), 6.91 (4H, d, *J* = 6.7 Hz), 6.9 (4H, d, *J* = 6.7 Hz), 3.85 (6H, s, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.00 (C=O), 160.30 (Ar-C), 143.83 (Ar-C), 133.50 (Ar-C), 132.4 (Ar-C), 130.27 (Ar-C), 124.26 (Ar-C), 123.16 (Ar-C), 114.77 (Ar-C), 114.26 (Ar-C), 93.54 (C≡C), 88.02 (C≡C), 55.36 (CH_3-O). MS: 440 (100 %), 441 (34), 425 (8), 220 (17). FT-IR (KBr, ν_{max}, cm^{-1}): 2202w (C≡C), 1708s (C=O), 1597s, 1512m, 1245s, 1025w, 836w, 826m. Anal. calcd. (%) for $C_{31}H_{20}O_3$: C, 84.53; H, 4.58. Found: C, 84.30; H, 4.36.

3,6-*Bis*(phenylethynyl)-9*H*-fluoren-9-one (7c): A mixture of 3,6-*bis*ethynyl-9*H*-fluorene-9-one (**6**) (2.28 g, 10 mmol), bromobenzene (2.11 mL, 20 mmol), $PdCl_2(PPh_3)_2$ (280 mg, 0.40 mmol), CuI (150 mg, 0.79 mmol) and Et_3N (150 mL) in DMF (300 mL) was refluxed under argon gas for 3 h at 110 ºC. Then DMF and Et_3N were evaporated under reduced pressure. The residue was treated with water and extracted with CH_2Cl_2 (200 mL), organic layer was submitted to column chromatography using (SiO_2, CH_2Cl_2) as solvent. The solvent was evaporated the residue was recrystallized in ethanol to give the desired compounds as yellow precipitate (yield 3.27 g, 85 %), m.p. 215 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70 (2H, broad, s, H-C (4), H-C (5)), 7.67 (2H, d, H-C (1), H-C (8), *J* = 7.5 Hz), 7.65-7.57 (4H, m), 7.49 (2H, dd, H-C (2), H-C (7), *J* = 1.2 Hz, *J* = 7.5 Hz), 7.39 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 190.95 (C=O), 142.69 (Ar-C), 132.58 (Ar-C), 131.63 (Ar-C), 130.78 (Ar-C), 128.76 (Ar-C), 127.94 (Ar-C), 127.47 (Ar-C), 123.29 (Ar-C), 122.36 (Ar-C), 121.48 (Ar-C), 92.20 (C≡C), 87.95 (C≡C). FT-IR (KBr, ν_{max}, cm^{-1}): 3110-3050 (Ar-CH), 2208m (C≡C), 1710s (C=O), 1611s, 1576m, 1446m, 1410s, 1402s, 1223s, 1006s, 920s, 885s, 861s. Anal. calcd. (%) for $C_{29}H_{16}O$: C, 91.56; H, 4.24. Found: C, 91.41; H, 4.10.

RESULTS AND DISCUSSION

3,6-Dibromophenanthren-9,10-dione (**2**) was prepared from the reaction of 9,10-phenanthrenquinone (**1**), bromine and benzoyl peroxide in nitrobenzene as solvent according to the literature procedures[10,11].

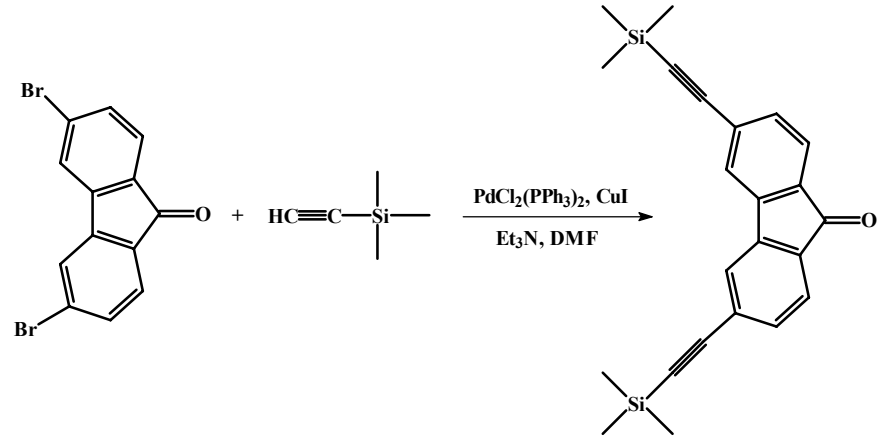


(**1**) (**2**) (**3**)

Scheme-I

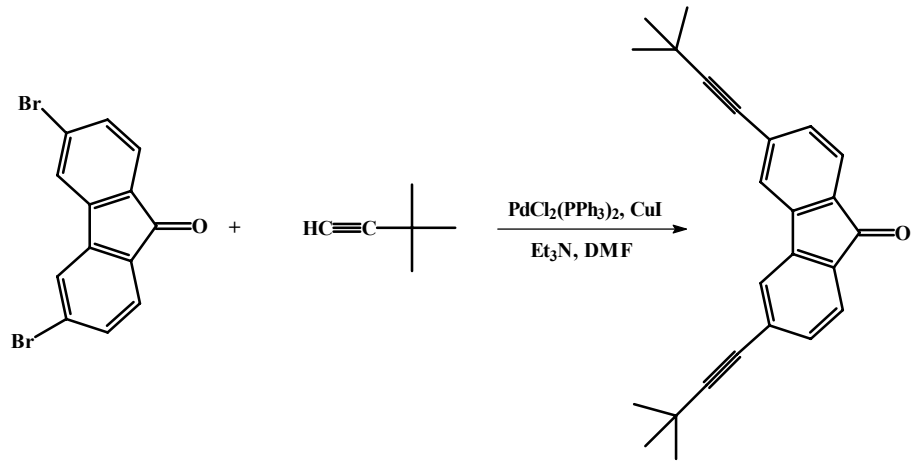
3,6-Dibromo-9*H*-fluoren-9-one (**3**) was prepared from 3,6-dibromophenanthren-9,10-dione (**2**) by literature procedure[5]. 3,6-*Bis*[(trimethylsilyl)ethynyl]-9*H*-fluoren-9-one (**4**) was synthesized from the reaction of 3,6-dibromo-9*H*-fluoren-9-one (**3**) and trimethylsilyl acetylene with improved procedure for Sonogashira Coupling[6].

3,6-*Bis*[(*tert*-butyl)ethynyl]-9*H*-fluoren-9-one (**5**) was synthesized from the reaction between 3,6-dibromo-9*H*-fluoren-9-one (3) and 3,3-dimethyl-1-butyne with the same procedure[6].



(**3**) (**4**)

Scheme-II

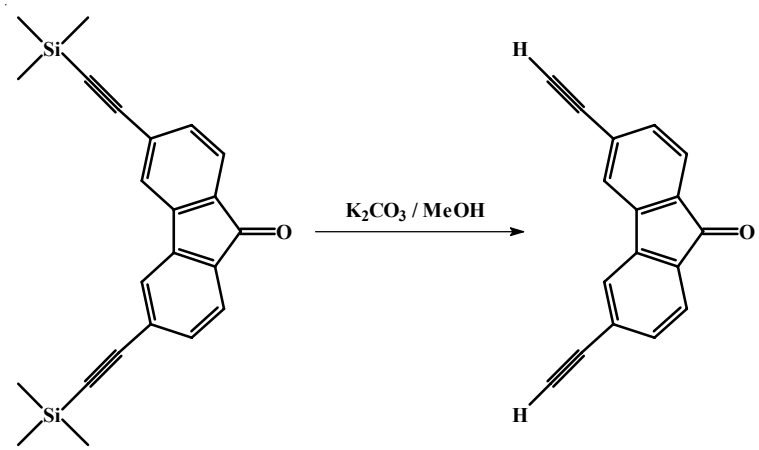


(**3**) (**5**)

Scheme-III

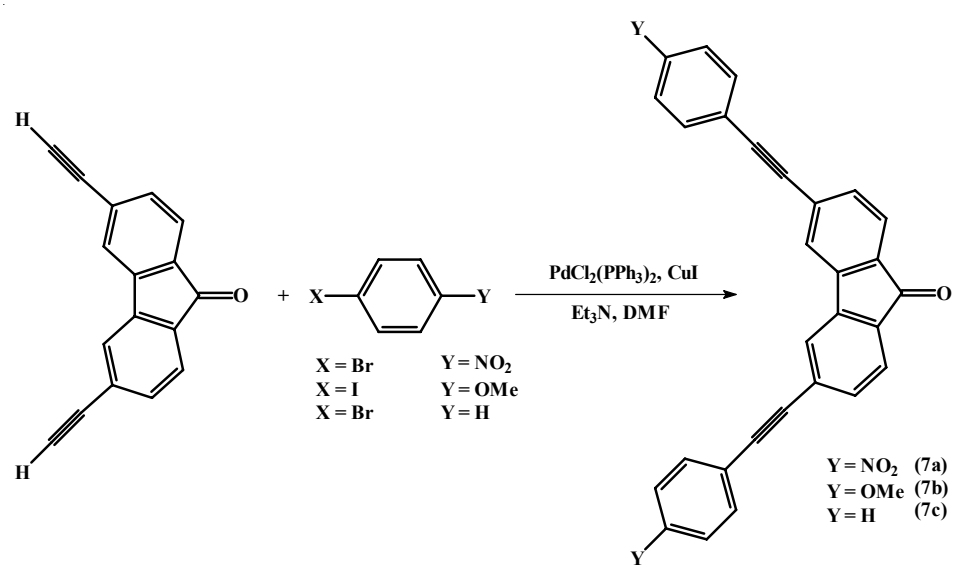
3,6-*Bis*ethynyl-9*H*-fluoren-9-one (**6**) was obtained from the reaction between 3,6-*bis*[(trimethylsilyl)ethynyl]-9*H*-fluoren-9-one (**4**) and potassium carbonate in methanol according to the literature procedure[6].

Acetylenic hydrogens in 3,6-diethynyl-9*H*-fluoren-9-one (**6**) may be easily substituted by iodo and bromo aryls in the presence of a catalytic amount of a palladium(II) complex as well as copper (I) iodide in an amine as solvent. The reactivity of the coupling of aryl bromides is often slower than the reactivity of the aryl iodides and thus we used DMF as solvent which increase the rate of the transformation according to the procedure[12].



(**4**) (**6**)

Scheme-IV



(**6**)

Scheme-V

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