ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 7, pp. 1313–1314. © Pleiades Publishing, Ltd., 2012.
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LETTERS TO THE EDITOR

Pd-Catalyzed Coupling of Vinyl Iodides with Alkynes in Water

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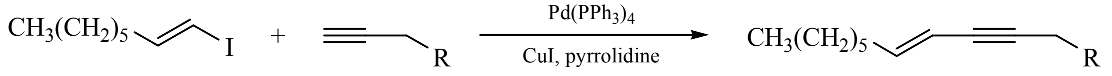
Received February 9, 2012

DOI: 10.1134/S1070363212070249

The Pd-catalyzed coupling of aryl and vinyl halides with terminal alkynes (Sonogashira coupling) is an effective method to create a carbon-carbon bond. It is widely used in the synthesis of acetylenes, natural compounds, carbo- and heterocycles [1–3]. In recent years, intensive studies were carried out to optimize the reaction with aryl halides in aqueous media [4–7]. The using of water as a solvent due to its high polarity and ability to form hydrogen bonds causes the stabilization of ionic intermediates in the catalytic cycle of the Sonogashira coupling. In addition, the replacement of the flammable, often toxic, expensive and environmentally hazardous organic solvents with inexpensive and non-hazardous solvents is an important problem of modern chemical technology [8].

We investigated a possibility of performing the coupling reaction of vinyl iodides [9] with alkynes in aqueous medium to obtain the conjugated enyne compounds, which are widely used in organic synthesis of pharmaceuticals, insect pheromones, and other biologically active substances [10–18].

It was established, that the reaction of (1*E*)-1-iodooct-1-ene **I** with 1-octyne **II** or propargyl alcohol **III** in the presence of Pd(PPh_3)$_4$, CuI, and a base in water results in the corresponding (7*E*)-hexadec-7-ene-9-yne **IV** and (4*E*)-undec-2-yne-4-ene-1-ol **V** in a high yield. The reaction proceeds stereoselectively with the full retention of spatial configuration at the double bond, as evidenced by GLC and the spin–spin coupling constants (15.7–15.8 Hz) of the reaction products **IV** and **V**, which are typical for the *trans*-configuration of the double bond.



I **II, III** **IV, V**

R = C_5H_{11} (**II, IV**), OH (**III, V**).

The structure and stereochemical purity of the synthesized compounds were confirmed by the IR, ^{1}H and ^{13}C NMR spectroscopy and chromatomass spectrometry. The IR spectra were recorded on an IRPrestige-21 Shimadzu FTIR-spectrometer (from thin layer). The ^{1}H and ^{13}C NMR spectra were registered on a Bruker AM-300 spectrometer operating at 300 and 75.47 MHz, respectively in $CDCl_3$ relative to internal TMS. The chromatographic and mass spectral analyzes were performed on a GCMSQP2010S Shimadzu spectrometer (EI, 70 eV, the range of detected masses was 33–500 Da). A capillary column HP-1MS (30 m×0.25 mm×0.25 mm) was used, the evaporator temperature 280°C, the the ionization chamber temperature 200°C. The analysis was carried out in the temperature programming mode from 50 to 280°C at the heating rate of 10 deg min^{-1}, carrier gas helium (1.1 ml min^{-1}).

(1*E*)-1-Iodooct-1-ene (I) was obtained by a modified procedure [19]. To a solution of 1.10 g (0.01 mol) of 1-octyne in 10 ml of anhydrous hexane was added 15 ml of 1 M. solution of diisobutylaluminum hydride in hexane. The obtained mixture was stirred for 6 h at 55°C in an argon atmosphere. Then the reaction mixture was cooled to –50°C, and a solution of 2.79 g (0.011 mol) of iodine in 15 ml of anhydrous THF was added over 30 min. The reaction mixture was heated to room temperature for 1 h and stirred at this temperature for another 12 h. Then to the reaction mixture 25 ml of 10% solution of sulfuric acid was added under cooling with ice. The organic layer was separated; the aqueous layer was extracted with hexane (3×15 ml). The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4, and concentrated. The product was isolated by the column chromatography. Yield 2.7 g (87%). IR spectrum, ν, cm^{-1}: 2955, 2926, 2855, 1605, 1456, 1215, 1055, 1171, 943. ^1H NMR spectrum, d_H, ppm: 0.88 t (3H, CH_3, J 7 Hz), 1.21–1.45 m (8H, $4CH_2$), 2.04 q (2H, C_3H_2, J 7 Hz), 5.97 d (1H, C^1H, J_{trans} 14.3 Hz), 6.51 d.t (1H, C^2H, J_{trans} 14.3, J 7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.02 (C^8), 22.50 (C^7), 28.26 (C^4), 28.52 (C^5), 31.52 (C^6), 36.01 (C^3), 74.24 (C^1), 146.72 (C^2). Mass spectrum, m/z (I_{rel}, %): 238 (24) $[M]^+$, 167 (11), 154 (15), 69 (100), 56 (16), 55 (53), 43 (51), 42 (10), 41 (51).

Coupling of (1*E*)-1-iodooct-1-ene with alkynes in water. To a suspension of 0.119 g (0.5 mmol) of (1*E*)-1-iodooct-1-ene, 3.8 mg (0.02 mmol) of CuI, 11.6 mg (0.01 mmol) of $Pd(PPh_3)_4$, and 0.43 g of pyrrolidine in 0.7 ml of water was added 0.54 mmol of alkyne. The reaction mixture was stirred at room temperature in anargon atmosphere for 2 h. Then hexane (3 ml) and saturated NH_4Cl solution (3 ml) were added. The organic layer was separated; the water layer was extracted with hexane (3×5 ml). The combined organic layers were successively washed with 0.2 M. HCl solution (3 ml), $NaHCO_3$ (5 ml), and water (5 ml), dried over Na_2SO_4, and concentrated. The reaction product was purified by the column chromatography.

(7*E*)-Hexadec-7-ene-9-yne (IV). Yield 0.101 g (92%). IR spectrum, ν, cm^{-1}: 3019, 2955, 2926, 2857, 2216, 1732, 1674, 1458, 1377, 1327, 1304, 953, 723. ^1H NMR spectrum, d_H, ppm: 0.89 m (6H, $2CH_3$, J 6.9 Hz), 1.21–1.56 m (16H, $8CH_2$), 2.07 q (2H, C_6H_2, J 6.9 Hz), 2.27 t. d (2H, $C_{11}H_2$, J 6.9, 1.9 Hz), 5.44 d.t (1H, C_8H, J_{trans} 15.8, 1.9 Hz), 6.04 d. t (1H, C_7H, J_{trans} 15.8, 6.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.01 (C^1, C^{16}), 19.35 (C^{11}), 22.53 (CH_2), 22.57 (CH_2), 28.60 (CH_2) 28.78 (CH_2), 28.83 (2 CH_2), 31.37 (CH_2), 31.67 (CH_2) 32.93 (C^6), 79.19 (C^9), 88.63 (C^{10}), 109.85 (C^8), 143.24 (C^7). Mass spectrum, m/z (I_{rel}, %): 220 (17) $[M]^+$, 135 (24), 121 (31), 109 (22), 107 (57), 95 (44), 94 (27), 93 (86), 91 (43), 81 (52), 80 (40), 79 (100), 78 (19), 77 (38), 69 (22), 67 (78), 65 (18), 55 (36), 43 (36), 41 (43).

(4*E*)-Undec-4-ene-2-yne-1-ol (V). Yield 0.074 g (89%). IR spectrum, ν, cm^{-1}: 3323 br.s (OH), 2955, 2926, 2855, 2211, 1456, 1163, 1018, 955. ^1H NMR spectrum, δ_H, ppm: 0.88 t (3H, CH_3, J 7 Hz), 1.22–1.41 m (8H, $4CH_2$), 2.03 br. s (1H, OH), 2.10 q (2H, C^6H_2, J 7.1 Hz), 4.36 d (2H, C^1H_2, J 1.6 Hz), 5.48 d. t (1H, C^4H, J_{trans} 15.7, 1.6 Hz), 6.16 d. t (1H, C^5H, J_{trans} 15.7, 7.1 Hz). ^{13}C NMR spectrum, d_C, ppm: 13.98 (C^{11}), 22.51 (C^{10}), 28.56 (CH_2), 28.69 (CH_2), 31.57 (C^9), 32.99 (C^6), 51.46 (C^1), 84.50 (C^3), 85.63 (C^2), 108.77 (C^4), 145.69 (C^5). Mass spectrum, m/z (I_{rel}, %): 166 (26) $[M]^+$, 109 (28), 105 (27), 95 (51), 93 (35), 91 (53), 81 (100), 79 (73), 78 (34), 77 (33), 67 (64), 66 (29), 65 (37), 55 (63), 54 (31), 53 (30), 43 (74), 41 (98).

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