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LETTERS TO THE EDITOR

Synthesis of Ethyl (4*E*)-Tridec-4-ene-6-ynoate

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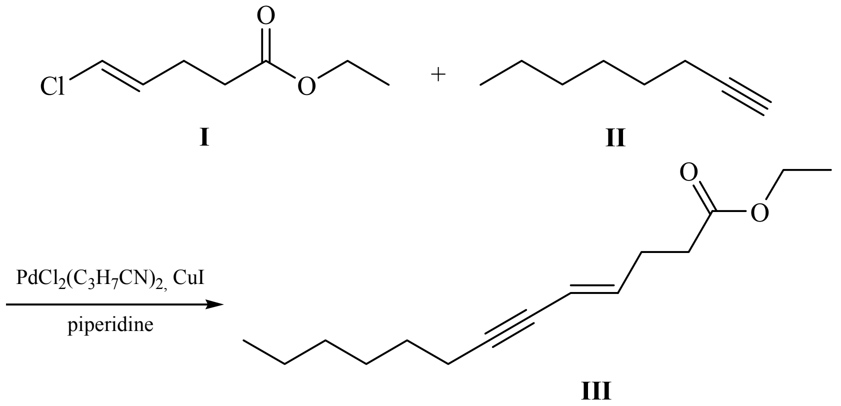
Various cross-coupling reactions based on vinyl halides, which proceed with the retention of the double bond configuration (Negishi, Sonogashira, Suzuki, Stille, Heck reactions), are widely used to create the carbon-carbon bonds in the synthesis of the practically useful unsaturated compounds [1–5]. Previously, we have synthesized the stereochemically pure chlorovinyl-derived malonic esters, which are of great interest for the synthesis of valuable intermediates used to obtain the biologically active substances. So, in order to obtain ethyl (4*E*)-tridec-4-ene-6-ynoate **III**, which is a precursor of some low-molecular bioregulators including insect pheromones with the structure of conjugated diene and enyne acids, alcohols and acetates [6, 7], we performed the reaction of (*E*)-1,3-dichloropropene with malonic ester under the phase transfer catalysis followed by the Krapcho decarboxylation [8] to produce the stereochemically pure ethyl (4*E*)-5-chloropent-4-enoate [9].

In this work we investigated the possibility of the Pd/Cu-catalyzed coupling of ethyl (4*E*)-5-chloropent-4-enoate **I** with oct-1-yne **II** (the Sonogashira reaction).



I **II** **III**

The reaction of ethyl (4*E*)-5-chloropent-4-enoate-**I** and oct-1-yne **II** proceeds in the presence of a weakly ligated complex $PdCl_2(C_3H_7CN)_2$ and CuI in piperidine under argon at room temperature to give ethyl (4*E*)-tridec-4-ene-6-ynoate **III** in a high yield (88%).

Stereochemical identity and configuration of the double bond of the compounds obtained was confirmed by GLC analysis and ^1H and ^{13}C NMR spectroscopy data. The value of coupling constants of the vinyl hydrogen atoms is 15.9 Hz indicating the *trans*-configuration of the double bond.

Ethyl (4*E*)-5-chloropent-4-enoate (I). To a solution of 10.08 g (0.0429 mol) of diethyl [(2*E*)-3-chloropropyl-2-en-1-yl]propanedioate [9] and 1.54 g (0.0858 mol) of H_2O in 16 ml of DMSO was added 3.64 g (0.0858 mol) of LiCl. The reaction mixture was stirred at reflux for 18 h, and then poured into 30 ml of water and 30 ml of hexane. The organic layer was separated, and the aqueous layer was extracted with hexane (2×30 ml). The combined organic solutions were washed with water, dried with Na_2SO_4 and concentrated. The residue was distilled in a vacuum [bp 61–63°C (10 mm Hg)]. Yield 4.54 g (65%), oily substance. IR spectrum, ν, cm^{-1}: 2982, 2932, 1732, 1634, 1445, 1373, 1350, 1300, 1240, 1192, 1161, 1096, 1036, 935, 856. ^1H NMR spectrum, δ, ppm: 1.26 t (3H, CH_3, *J* 7 Hz), 2.34–2.44 m (4H, C^2H_2, C^3H_2), 4.11 q (2H, CH_2O, *J* 7.1 Hz), 5.86–5.95 m (1H, C^4H), 6.03 d (1H, C^5H, J_{trans} 13.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.04 (CH_3), 26.07 (C^3), 33.34 (C^2), 60.39 (CH_2O), 118.30 (C^5), 131.67 (C^4), 172.27 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 127(86), 117(27), 99(100), 91 (24), 89(40), 88(31), 75(27), 53(46), 43(15).

Ethyl (4*E*)-tridec-4-ene-6-ynoate (III). To a suspension of 0.200 g (1.23 mmol) of ethyl (4*E*)-5-chloropent-4-enoate **I**, 23 mg (0.12 mmol) of CuI, and 19 mg (0.06 mmol) of $PdCl_2(C_3H_7CN)_2$ in 1 ml of piperidine was added 0.149 g (1.35 mmol) of oct-1-yne **II**. The reaction mixture was stirred at room temperature under argon for 3 h, and then poured into diethyl ether (3 ml) and a saturated NaCl solution (3 ml). The organic layer was separated, and the aqueous layer was extracted with ether (3×5 ml). The combined organic solutions were washed with a saturated NH_4Cl solution (5 ml) and water (5 ml), dried with Na_2SO_4, and concentrated. The crude product was purified by the column chromatography (SiO_2, hexane–diethyl ether, 9:1). Yield 0.254 g (88%), oily substance. IR spectrum, ν, cm^{-1}: 2932, 2820, 1738, 1468, 1445, 1371, 1250, 1159, 1038, 955. ^1H NMR spectrum, δ, ppm: 0.89 t (3H, $C^{13}H_3$, *J* 7 Hz), 1.24–1.41 m (9H, $C\underline{H}_3CH_2O$, $3CH_2$), 1.48–1.53 m (2H, C^9H_2), 2.27 t (2H, C^2H_2, *J* 7 Hz), 2.37–2.43 m (4H, C^3H_2, C^8H_2), 4.13 q (2H, $CH_3C\underline{H}_2O$, *J* 7 Hz), 5.51 d (1H, C^5H=, J_{trans} 15.9 Hz), 5.99–6.05 m (1H, C^4H). ^{13}C NMR spectrum, δ_C, ppm: 13.97 (C^{13}), 14.12 ($\underline{C}H_3CH_2O$), 19.24 (C^8), 22.46 (C^{12}), 28.06 (CH_2), 28.50 (CH_2), 28.64 (CH_2), 31.12 (C^{11}), 33.39 (C^2), 60.36 ($CH_3\underline{C}H_2O$), 78.61 (C^6), 89.55 (C^7), 111.18 (C^5), 140.36 (C^4), 172.58 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 119(35), 107(18), 105(45), 95(21), 93(68), 92(58), 91 (100), 88(49), 81(26), 79(76), 78(37), 77(42), 70(29), 67(44), 65(22), 61(17), 60(16), 55(31), 43(33), 41(47).

The IR spectra were recorded on an IRPrestige-21 Shimadzu FTIR spectrophotometer from a thin film. The ^1H and ^{13}C NMR spectra were registered in $CDCl_3$ on a Bruker AM-300 instrument operating at 300 and 75.47 MHz, respectively, internal reference TMS.

The chromatographic and mass spectrometric analysis was carried out on a GCMS-QP2010S Shimadzu spectrometer (EI, 70 eV) with the detected masses range of 33–500 Da using a HP-1MS capillary column (30 m×0.25 mm×0.25 μm), the evaporator temperature 280°C and the ionization chamber temperature 200°C. The analysis was carried out in the temperature programming mode from 50 to 280°C with the heating rate of 10°C min^{-1}, the carrier gas helium (1.1 ml min^{-1}).

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