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A One-pot Procedure to Prepare Ethynylferrocene and Iodoethynylferrocene

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Abstract: Ethynylferrocene and iodoethynylferrocene were prepared in high yield as 88-90% through a one-pot procedure. 1, 1'-diiodoferrocenylene was *in-situ* prepared from reaction of CHI_3 PPh_3, *t*-BuOK and ferrocenecarboxaldehyde, further reaction with *t*-BuOK or *n*-BuLi gave the title compounds.

Keywords: Ferrocene derivatives, Wittig-type reaction.

Introduction

Ferrocene-containing compounds have been widely used as important probes to investigate the electron transfer/transport properties of the molecular materials[1]. Recently, this technique was employed in molectronics research, where the ferrocenes were incorporated on the ends of conjugated molecular wires, and the electron transfer/transport abilities of the molecular wires were conveniently studied by electrochemical method[2]. Ethynylferrocene and iodoethynylferrocene were two important starting materials to prepare these functional molecular wires according to Pd-catalyzed Sonogashira coupling[2c] and Cadiot-Chodkiewicz coupling[3]. Therefore, preparation of Ethynylferrocene and iodoethynylferrocene in facile way with high yields is of practical importance in modern molectronics research[4]. In this communication, ethnylferrocene and iodoethynylferrocene, will be prepared in one-pot procedure with high yield employing Witting-type reaction.

Results and discussion

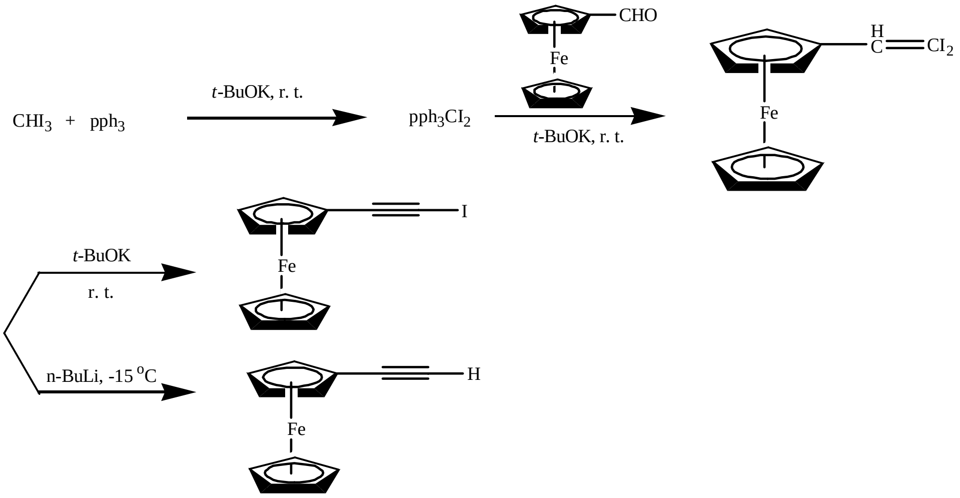
Generally, there are two main synthetic paths for preparation of ethynylferrocene:
(i) Acetylferrocene was treated with excessive phosphorous oxychloride and dimethylformamide to give the chloroaldehyde FcCCl = CHCHO, it was then heated in a

basic aqueous dioxane solution to give ethynylferrocene in 76.6% yield[5].

(ii) Acetylferrocene was reacted with Negishi's reagent in one pot to give ethynylferrocene in 94% yield[6]. However, the above procedure was performed under absolutely oxygen and water-free atmosphere due to the use of lithium diisopropylamide (LDA), moreover, an alternative changing in temperature from -78°C to room temperature was required. As to the iodoethynylferrocene, it was usually prepared by lithiation of ethynylferrocene followed by quenching with iodide at low temperature[7].

Recently, Wittig-type condensation reaction of aldehydes with diiodomethyltripheny- phosphine was used to prepare iodoalkynes[8]. We found that by changing the reaction conditions, such reaction was quite efficient to generate both iodoethynylferrocene and ethynylferrocene in a one-pot procedure (**Scheme 1** outlines the whole procedure). When PPh_3, CHI_3 and *t*-BuOK were dissolved in THF under inert atmosphere, the diiodomethyltriphenylphosphorane ylide formed immediately. When ferrocen carboxaldehyde was added, Wittig-type condensation occured to give 1,1'-diiodoferrocenylene. After excess of *t*-BuOK or *n*-BuLi was added at room temperature or -15°C, the HI elimination of the 1,1'-diiodoarylene took place, after quenching with brine, Iodoethynylferrocene or ethynylferrocene was obtained, respectively.

Scheme 1



Experimental

General procedure

THF was dried according to standard method prior to use. All other reagents were purchased from Acrôs Co. and without further purification. Analytical thin layer chromatography (TLC) was performed on precoated sheets of silica gel 60 F_{254} (Merck

Co.). Column chromatography was carried out with silica gel (200~400 mesh).

Synthesis of iodoethynylferrocene

1.734 g of iodoform (4.4 mmol), 1.145 g of triphenylphosphine (4.4 mmol) and 0.449 g of *t*-BuOK (4.0 mmol) were dissolved in 30 mL of THF under argon atmosphere. The mixture was stirred for 10 min at room temperature, and then 0.428 g of ferrocene carboxaldehyde was added. After stirring for 15 min, the mixture was added with another 1.122 g of *t*-BuOK (10.0 mmol) and stirred for 2 h at room temperature, it was then quenched by saturated brine (50 mL). The aqueous layer was extracted by ethyl ether (30 mL) for three times. The combined organic layer was washed with brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 1:1, R_f = 0.68) to give 0.605 g (90 % yield) of the title product. FT-IR (neat) cm^{-1}: 3098, 2176, 1407, 1103, 922, 822, 530, 506, 486. ^{1}H-NMR (400MHz, $CDCl_3$) δ ppm: 4.440 (t, 2H, J = 2.0Hz), 4.224 (s, 5H), 4.185 (t, 2H, J = 2.0Hz). EI-MS: 336 (M^+), 209 (M-I).

Synthesis of ethynylferrocene:

The procedure was quite the same as above. Once 1,1-diiodoferrocenylene was formed, the solution was cooled to -15°C, and then the solution of *n*-BuLi (6.252 mL, 10.0 mmol, 1.6 mol/L in hexane) was added. After addition of *n*-BuLi, the mixture was allowed to warm to room temperature and stirred for another 30 min, then saturated brine (50mL) was added. The aqueous layer was extracted by ethyl ether and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 1:1, R_f = 0.56) to give 0.370g (88% yield) of title product. FT-IR (neat) cm^{-1}: 3298, 3055, 2108, 1590, 1437, 1118, 821. ^{1}H-NMR (400MHz, $CDCl_3$) δ ppm: 4.463 (t, 2H, J = 2.0 Hz), 4.219 (s, 5H), 4.193 (t, 2H, J = 2.0 Hz), 2.719 (s, 1H). EI-MS: 210(M^+), 209 (M-H).

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