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Indium-Mediated Michael Addition of Allyl Bromide to 1,1-Dicyano-2-arylethenes in Aqueous Media

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INDIUM-MEDIATED MICHAEL ADDITION OF ALLYL BROMIDE TO 1,1-DICYANO-2-ARYLETHENES IN AQUEOUS MEDIA

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Abstract: Indium-mediated addition of allyl bromide to 1,1-dicyano-2-arylethenes gives Michael addition products in aqueous media with good yields. The reaction need neither any activation nor in inert atmosphere.

Metal-mediated reactions in aqueous media have recently attracted considerable interest in organic synthesis, because such reactions in aqueous media offer a number of advantages over conventional organometallic reactions in organic solvents[1]. As for the metal used, in addition to zinc and tin, indium has been found by Chan to be the metal of choice[2]. Indium is considered to be more effective than zinc and tin since the reaction requires no activation, and produce only few side products. It has been reported that the coupling of allyl halides with carbonyl compounds and the reductive coupling of aldimines could be mediated by indium in

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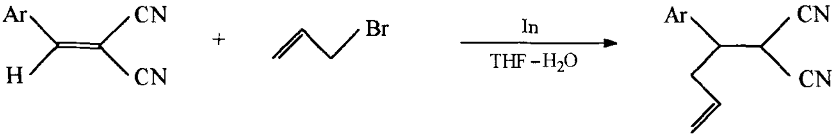
aqueous media[3]. However, the type of reactions possible have been somewhat limited and it would seem reasonable to extend the application of indium in organic synthesis. Herein we would like to report a Michael addition of allyl bromide to 1,1-dicyano-2-arylethenes mediated by indium in aqueous media.



1 **2** **3**

a: Ar = C_6H_5 **b**: Ar = p-ClC_6H_4
c: Ar = p-BrC_6H_4 **d**: Ar = p-FC_6H_4
e: Ar = p-$CH_3C_6H_4$ **f**: Ar = m-BrC_6H_4
g: Ar = m-ClC_6H_4 **h**: Ar = o-BrC_6H_4

When α,β-unsaturated carbonyl compounds react with Grignard reagents or Reformatsky reagents under anhydrous reaction conditions, generally 1,2-addition products dominate 1,4-addition products[4]. However, in α,β-unsaturated dinitriles the carbon-nitrogen triple bonds are not reactive as carbonyl group toward nucleophilic attack, so that only Michael addition products were formed. Our experimental results indicated that cyano groups in the substrates **1** remain unchanged, although the cyano group has been proven to be a good acceptor[5].

The results suggest that allyl bromide can react smoothly with 1,1-dicyano-2-arylethenes in moderate to good yields. Unfortunately, other electron-deficient alkene, such as 1-cyano-1-ethoxycarbonylstyrene, 1,1-diethoxycarbonylstyrene, diethylmaloate, and cinnamyl cyanide fail to react under the same reaction condition.

In conclusion, this work has widened the application of indium in aqueous media and more significantly, Michael addition products were given in the reaction.

Experimental

^1H NMR spectra were recorded on a JEOL PMX 60 SI instrument. All NMR samples were measured in $CDCl_3$ using TMS as internal standard. IR spectra were obtained on a Perkin -Elmer 683 infrared spectrophotometer. Mass spectra were determined on a Finnigan MAT GC-MS spectrometer. Elemental analyses were carried out on a Carlo-Erba 1106 instrument.

General procedure for the reaction:

Metallic indium powder(1.2 mmol), 1,1-dicyano-2-arylethene(1.0 mmol), allyl bromide(2 mmol), THF(4 ml) and H_2O(1 ml) were placed in a reaction flask. The mixture was stirred at room temperature for 4 h until the indium powder was almost consumed and the solution became turbid. Then 2ml of dilute hydrochloric acid(0.5 mol/L) was added to quench the reaction and the mixture was extracted with ether twice(20 ml × 2). The extracts were washed with brine, dried over anhydrous Na_2SO_4 and the solvents was removed under reduced pressure. The residue was then purified by preparative TLC on silica gel with cyclohexane/ethyl acetate as the eluent to give the pure product.

3a: Oil[6]. Yield 72%. IR(neat) υ/cm^{-1} 2230, 1650, 690. ^1H NMR δ 2.27-2.90(m, 3H, -CH- and -CH_2-), 4.36(d, 1H, -CH$(CN)_2$), 4.86-5.90(m, 3H, -CH=CH_2), 7.05-7.80(m, 5H, Ph). MS m/z 196(M^+).

3b: Oil[6]. Yield 82%. IR(neat) υ/cm^{-1} 2219, 1645, 836. ^1H NMR δ 2.25-2.85(m, 3H, -CH- and -CH_2-), 4.30(d, 1H, -CH$(CN)_2$), 4.90-6.02(m, 3H, -CH=CH_2), 6.85-7.80(m, 4H, Ar). MS m/z 230(M^+), 232(M^++2).

3c: Oil. Yield 80%. IR(neat) υ/cm^{-1} 2225, 1650, 840. ^1H NMR δ 2.30-2.95(m, 3H, -CH- and -CH_2-), 4.42(d, 1H, -CH$(CN)_2$), 4.81-5.97(m, 3H, -CH=CH_2), 6.98-7.88(m, 4H, Ar). Anal. for $C_{13}H_{11}N_2Br$: Calc.(found) C 56.75(56.98), H 4.03(4.25), N 10.18(9.94)%.

3d: Oil. Yield 78%. IR(neat) υ/cm^{-1} 2215, 1655, 830. ^{1}H NMR δ 2.32-2.86(m, 3H, -CH- and -CH_2-), 4.38(d, 1H, -$CH(CN)_2$), 4.95-6.05(m, 3H, -$CH=CH_2$), 7.05-7.97(m, 4H, Ar). Anal. for $C_{13}H_{11}N_2F$: Calc.(found) C 72.88(72.64), H 5.17(5.25), N 13.07(12.85)%.

3e: Oil[6]. Yield 65%. IR(neat) υ/cm^{-1} 2227, 1650, 1385, 833. ^{1}H NMR δ 2.20-2.95(m, 6H, -CH-, -CH_2- and -CH_3), 4.29(d, 1H, -$CH(CN)_2$), 4.83-5.97(m, 3H, $CH=CH_2$), 6.89-7.84(m, 4H, Ar). MS m/z 210(M^+).

3f: Oil. Yield 72%. IR(neat) υ/cm^{-1} 2230, 1655, 790, 705. ^{1}H NMR δ 2.34-2.78(m, 3H, -CH- and -CH_2-), 4.41(d, 1H, -$CH(CN)_2$), 4.95-6.04(m, 3H, $CH=CH_2$), 6.89-7.85(m, 4H, Ar). Anal. for $C_{13}H_{11}N_2Br$: Calc.(found) C 56.75(56.58), H 4.03(3.95), N 10.18(10.30)%.

3g: Oil. Yield 74%. IR(neat) υ/cm^{-1} 2234, 1650, 795,698. ^{1}H NMR δ 2.37-2.94(m, 3H, -CH- and -CH_2-), 4.38(d, 1H, -$CH(CN)_2$), 4.86-5.98(m, 3H, $CH=CH_2$), 7.01-7.80(m, 4H, Ar). Anal. for $C_{13}H_{11}N_2Cl$ Calc.(found) C 67.68(67.82), H 4.80(4.63), N 12.14(12.03)%.

3h: Oil. Yield 70%. IR(neat) υ/cm^{-1} 2225, 1650, 750. ^{1}H NMR δ 2.29-2.84(m, 3H, -CH- and -CH_2-), 4.32(d, 1H, -$CH(CN)_2$), 4.95-5.99(m, 3H, -$CH=CH_2$), 6.94-7.86(m, 4H, Ar). Anal. for $C_{13}H_{11}N_2Br$: Calc.(found) C 56.75(56.88), H 4.03(4.29), N 10.18(10.29)%.

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