Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. 200460246

Nickel-Catalyzed Cross-coupling Reaction of Alkyl Halides with Organozinc and Grignard Reagents Using 1,3,8,10-Tetraenes as Additives

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Typical Experimental Procedures and Analytical Data of Products.

Tridecanenitrile

To a THF solution (4.5 mL) of 5-bromo-pentanenitrile (166 mg, 1.03 mmol), $MgBr_2$ (552 mg, 3.0 mmol), $NiCl_2$ (4 mg, 0.03 mmol), 2,2-bis-(penta)-2,4-dienyl-malonic acid dimethyl ester **2a** (24 mg, 0.09 mmol), and NMP (4.2 mL) was added $n\text{Oct}_2\text{Zn}$ (0.33 M in THF, 3.9 mL, 1.3 mmol) at 25 ^{o}C under nitrogen. After stirring for 1 h, ca. 2 mL of 1 N HCl was added to the solution at 0 ^{o}C and the mixture was warmed to 25 ^{o}C. Then a saturated aqueous $NaHCO_3$ solution (20 mL) was added and the product was extracted with ether (20 mL), dried over $MgSO_4$, and evaporated to give a crude product.

Purification by silica gel column chromatography with hexane/ether (5:1) as an eluent afforded 193 mg, (96%) of tridecanenitrile.

7-Phenyl-heptanoic acid diethylamide

To a THF solution (3.9 mL) of 5-bromo-pentanoic acid diethylamide (236 mg, 1.0 mmol), $MgBr_2$ (552 mg, 3.0 mmol), $NiCl_2$ (4 mg, 0.03 mmol), **2a** (24 mg, 0.09 mmol), and NMP (4.2 mL) was added $(PhCH_2CH_2)_2Zn$ (0.29 M in THF, 4.5 mL, 1.3 mmol) at 25 ^oC under nitrogen. Similar workup as mentioned above afforded an orange crude product. Purification by silica gel column chromatography with hexane/ether (3:1) as eluent afforded 238 mg, (91%) of 7-phenyl-heptanoic acid diethylamide. ^1H NMR (400 MHz, $CDCl_3$): δ= 7.15-7.29 (m, 5H), 3.37 (q, *J* = 7.2 Hz, 2H), 3.29 (q, *J* = 7.2 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.27 (t, *J* = 7.6 Hz, 2H), 1.70-1.57 (m, 4H), 1.39-1.33 (m, 4H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=171.9, 142.6, 128.4, 128.0, 125.4, 42.0, 40.1, 36.0, 33.2, 31.5, 29.5, 29.3, 25.5, 14.6, 13.3; HR-MS: calcd for $C_{17}H_{27}NO$: 261.2092, found 261.2089; elemental analysis: calcd for $C_{17}H_{27}NO$: C, 78.11, H, 10.41, N, 5.36 found: C, 77.96; H, 10.19, N, 5.19.

Nonanoic acid ethyl ester.

To a THF solution (4.3 mL) of 5-bromo-pentanenitrile (221 mg, 1.0 mmol), $MgBr_2$ (552 mg, 3.0 mmol), $NiCl_2$ (4 mg, 0.03 mmol), **2a** (24 mg, 0.09 mmol), and NMP (4.2 mL) was added nPr_2Zn (0.32 M in THF, 4.1 mL, 1.3 mmol) at 25 ^oC under nitrogen. Similar workup as mentioned above afforded an orange crude product. Purification by silica gel column chromatography with hexane/ether (24:1) as eluent afforded 161 mg, (87%) of nonanoic acid ethyl ester. ^1H NMR (400 MHz, $CDCl_3$): δ= 4.165 (q, *J* =

7.2 Hz, 2H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.72-1.60 (m, 2H), 1.45-1.24 (m, 13H), 0.92 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=173.6, 60.2, 34.5, 31.9, 29.4, 29.28, 29.25, 25.1, 22.8, 14.4, 14.3; HR-MS: calcd for $C_{11}H_{22}O_2$: 186.1620, found 186.1619; elemental analysis: calcd for $C_{11}H_{22}O_2$: C, 70.92, H, 11.90 found: C, 70.71; H, 11.72.

***N,N*-Bis(penta-2,4-dienyl)-benzylamine** (**2b**).

To a suspension of NaH (60% dispersion in mineral oil, 848 mg, 21 mmol) in DMF (12 mL) was added a solution of benzylamine (967 mg, 9 mmol) in DMF (12 mL). The mixture was stirred at 0 ^{o}C for 30 min, after which solution of bromopenta-2,4-diene[1] (2940 mg) in DMF (6 mL) was added. After stirring for 1.5 h at 25 ^{o}C, 30 mL of saturated aqueous of NH_4Cl was added to the solution at 0 ^{o}C. The product was extracted with ether, dried over $MgSO_4$, and evaporated to give an orange crude product. Purification by silica gel column chromatography with hexane/EtOAc (10:1) as eluent afforded 1802 mg, (84%) of **2b** as a pale yellow oil. IR (neat): 3006, 2794, 1602, 1359, 1119, 1003, 901, 737, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.32-7.215 (m, 5H), 6.39-6.21 (m, 2H), 6.21-6.15 (m, 2H), 5.79-5.72 (m, 2H), 5.17-5.02 (m, 4H), 3.57 (s, 2H), 3.10 (d, *J*=6.8 Hz, 4H), ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.5, 133.3, 131.6, 128.7, 128.0, 126.7, 116.1, 57.9, 55.4, MS (EI) *m/z* (relative intensity, %) 239 (M^+, 58), 172 (24), 148 (44), 91 (100), 67 (56); HR-MS: calcd for $C_{17}H_{21}N$ 239.1674, found 239.1667; elemental analysis: calcd for $C_{17}H_{21}N$: C, 85.30; H, 8.84, N, 5.85. found: C, 85.02, H, 8.74, N, 5.92.

(1) K. Mori, *Tetrahedron* **1974**, *30*, 3807-3810.

Dodecane from *n*-nonyl fluoride

To a mixture of *n*-nonyl fluoride (292 mg, 2.0 mmol), [$Ni(acac)_2$] (3 mg, 0.012 mmol), *N,N*-bis(penta-2,4-dienyl)-benzylamine **2b** (72 mg, 0.3 mmol) was added *n*PrMgCl (2 M in THF, 1.5 mL, 3.0 mmol) at 25 ^{o}C under nitrogen. After stirring for 6 h, a saturated aqueous NH_4Cl solution (10 mL) was added, and the product was extracted with ether (10 mL), dried over $MgSO_4$, and evaporated to give 94% GC yield of dodecane.

Registry No of other products and their references

The following compounds are known and their spectral data (^{1}H NMR, ^{13}C NMR, and Mass spectra) were consistent with those previously reported.

2,2-Bis-(penta)-2,4-dienyl-malonic acid dimethyl ester (**2a**). [Reg. No. 149167-31-7]

J. M. Takacs, E. C. Lawson, *Organometallics* **1994**, *13*, 4787-4793.

Tridecanenitrile. [Reg. No. 629-63-0]

E. D. Soli, A. S. Manoso, M. C. Patterson, P. DeShong, D. A. Favor, R. Hirschmann, A. B. Smith, *J. Org. Chem.* **1999**, *64*, 3171-3177.