Phosphonation of Arenes with Dialkyl Phosphites Catalyzed by Mn(II)/Co(II)/O₂ Redox Couple

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Experimental Section

All starting materials were commercially available and used without any purification. GLC analysis was performed with a flame ionization detector using a 0.2 mm x 25 m capillary column (OV-1). ^1H - and ^{13}C -NMR were measured at 270 or 400 MHz and 67.5 MHz, respectively, in CDCl_3 with Me_4Si as the internal standard.

General procedure for reaction of 1a with 2a: To a solution of **1a** (2 mmol), $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.1 mmol) and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.02 mmol) in a two-necked flask equipped with a balloon filled with an appropriate concentration of O_2 was added **2a** (6 mmol); the mixture was stirred at 45 °C for 5 h. The product was isolated by column chromatography (230-400 mesh silica gel, hexane : ethyl acetate = 1:1). The conversions and yields of products were estimated from the peak areas based on the internal standard technique using GLC.

Procedure for reaction of 1 with 2 in the presence of AcOK (e.g. run 6 in Table 2): To a solution of **1g** (2 mmol), AcOK (1 mmol), $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.1 mmol) and $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.02 mmol) in a two-necked flask equipped with a balloon filled with an appropriate concentration of O_2 was added **2a** (6 mmol); the mixture was stirred at 45 °C for 15 h. The work-up procedure was the same as described above.

All of the products were known compounds and have been reported previously.¹

(1) Kottman, H.; Skarzewski, J.; Effenberger, F. *Synthesis*, **1987**, 797.

3aa

4aa

DFILEC\WINDOWS\COMND\diethyl phenyl
DATE: Fri Jun 28 14:14
OBNUGH
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SLVNACETN
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12

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FREQU 18515.0 Hz
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PD 1.211 sec
PWI 4.3 us
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CTEMP 49.6 o
SLVNACETN
EXREF 29.80 ppm
BF 1.20 Hz
RGAIN 25

3ab

3ba

3ca

3da

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FREQU 18315.0 Hz
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EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25

3ea

3fa

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 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 11

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 PW1 4.3 us
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 CTEMP 24.0 o
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 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 26

CCOP(=O)(OCC)c1ccc2ccccc2c1