Category

Key words

nitriles

lithium

Metal-Mediated Synthesis

Grignard reagents

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Transnitrilation from Dimethylmalononitrile to Aryl Grignard and Lithium Reagents: A Practical Method for Aryl Nitrile Synthesis

J. Am. Chem. Soc. 2015, 137, 9481-9488.

Transnitrilation of Grignard Reagents and Aryllithiums

Met = MgX, Li
$$S2-96\%$$
 yield

R = Alk, OMe, OBn, Ph, F, Cl, Br, NMe₂, SMe, CF₃, CO₂H, C(O)Ni-Pr₂, pyrazolyl

Via

Met N

NC CN

R CN

F2-96% yield

R = Alk, OMe, OBn, Ph, F, Cl, Br, NMe₂, SMe, CF₃, CO₂H, C(O)Ni-Pr₂, pyrazolyl

Via

Net N

Net

Significance: The authors report an electrophilic cyanation of various arylmagnesium and -lithium reagents by using dimethylmalononitrile as a reagent. The transition-metal-free method proceeds under mild reaction conditions and affords the desired nitriles in high yields.

Comment: The Grignard reagents were either obtained from commercial sources or prepared in situ from the corresponding aryl iodides or bromides. Aryllithium reagents were prepared either by bromine–lithium exchange or by directed *ortho* lithiation.

SYNFACTS Contributors: Paul Knochel, Diana Haas Synfacts 2015, 11(10), 1081 Published online: 18.09.2015 **DOI:** 10.1055/s-0035-1560243; **Reg-No.:** P11315SF