Category

Metal-Mediated Synthesis

Key words

bismuth

alkenes

Y. NISHIMOTO, M. TAKEUCHI, M. YASUDA, A. BABA* (OSAKA UNIVERSITY, JAPAN) Synthesis of Alkylbismuths by Regiodivergent Carbobismuthination of Simple Alkenes *Chem. Eur. J.* **2013**, *19*, 14411–14415.

Bismuth-Mediated Switchable Regioselective Carbometalation

$$X = Br$$

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$$R^{1} + R^{2} + BiX_{3}$$

$$(1 \text{ equiv}) \quad (1.5 \text{ equiv}) \quad (1.5 \text{ equiv}) \quad (1.5 \text{ equiv})$$

$$R^{1} = Ph, (CH_{2})_{2}Ph, Me, Ar$$

$$R^{2} = Me, Et, Ph, H, -(CH_{2})_{5}$$

$$R^{3} = Me, Et, Ph, -(CH_{2})_{5}$$

$$R^{4} = Me, Et, Pr$$

$$Si = TBS, TMS$$

Selected examples:

Significance: Baba and co-workers report a novel carbobismuthination reaction of alkenes using bismuth trihalides and ketene silyl acetals. Furthermore, in this protocol, the first switch in regioselectivity of the carbometalation using BiCl₃ instead of BiBr₃ is reported.

Comment: The resultant alkylbismuth compounds react with a range of reagents in order to give functionalized aliphatics. Therefore, reaction with *N*-bromosuccinimide furnishes the bromide, reaction with AIBN and PhSSPh introduces a thiophenyl group, and PhI(OAc)₂ in combination with TMSOAc gives the acetate.

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