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Synthesis of Alkylbismuths by Regiodivergent Carbobismuthination of Simple Alkenes

Bismuth-Mediated Switchable Regioselective Carbometalation

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.

Selected examples:

- 90% yield (using BiBr₃)
- 99% yield (using BiBr₃)
- 61% yield (using BiCl₃)
- 79% yield (using BiBr₃)
- 63% yield (using BiCl₃)
- 71% yield (using BiCl₃)
- 61% yield (using BiCl₃)