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Regio- and Stereoselective Carbobismuthination of Alkynes

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anti-Carbobismuthination of Alkynes

 $R^1=$ Ph, 1,3-di-t-BuC₆H₃, 4-ClC₆H₄, Hex $R^2/R^3=$ H, Me, Ph electrophile = I₂, TsCl, PhSSPh, RCOCl

Selected examples:

Significance: The first carbobismuthination of alkynes has been accomplished by the reaction of an alkyne, BiBr₃, and a ketene silyl acetal to produce an alkenylbismuth compound with high stereo- and regioselectivity. The Br₂Bi group in the alkenylbismuth compounds can be substituted by I, Ts and SPh groups, and palladium-catalyzed cross-couplings with acid chlorides have been performed successfully.

Comment: The reaction of BiBr₃ with a phenylacetylene derivative and a ketene silyl acetal gives monoalkenylbismuth dibromide as a white solid. X-ray crystallographic analysis of this product reveals that the carbobismuthination takes place regio- and stereoselectively in an *anti*-addition manner.

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