Borylations with Novel Borylstannanes via Radical Mechanism

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Organoboron compounds represent valuable synthetic intermediates in organic synthesis. Recently, radical approach for preparing organoboron compounds has been merging because of the functional group tolerance.¹ Diborons are mainly used for radical acceptors forming the borylated products. However, applicable substrates are limited because of the inefficiency of radical chain reactions by boryl radical. Therefore, the development of new efficient borylation reagents is necessary. Herein, novel type of borylstannanes were newly invented and applied to radical borylations.

In the reaction of borylstannane 1 with 1-chloro-2-phenylethane 2 in the presence of V-40 as a radical initiator, borylstannane 1a was found to be a significantly effective reagent, which afforded the borylated compound 3^2 . The known borylstannane $1b^3$ did not work for the acceptor of the alkyl radical intermediate. DFT calculation disclosed that the phenylenediamino structure plays a crucial role in accepting the radical because benzo-fusion lowers its LUMO level including the vacant *p*-orbital on the boron atom to enhance the ability to accept alkyl radicals.



Moreover, borylstannane 1a was employed for borylstannation of alkynes under radical mechanism. The reaction of borylstannane 1a with phenylacetylene 4 in the presence of AIBN gave the addition product 5 exclusively. While the conventional method using a palladium catalyst gave the product 6^3 , our radical system showed the different regioselectivity and stereoselectivity.



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