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Direct Free-Radical Substitutions on Allyl and Vinyl Halides Using Alkyl Halides/Hexabutylditin

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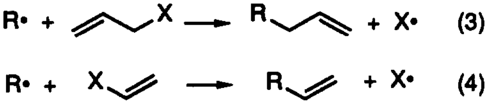
Abstract: Allyl and vinyl halides are excellent acceptors for tin-mediated substitutions by alkyl radicals generated from alkyl halides.

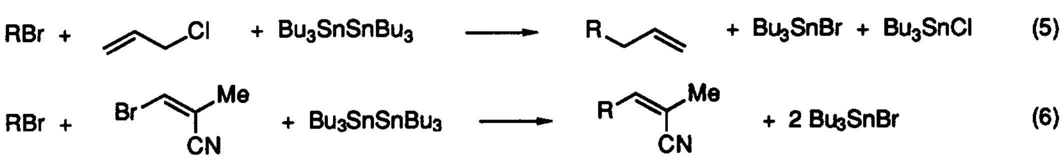
Free-radical mediated allylations and vinylations are powerful tools for the selective introduction of carbon-carbon bonds under mild conditions.[1] These reactions have been accomplished by reacting alkyl halides with allyl and vinyl tin derivatives,[2] allylsilanes,[3] or allyl sulfides/hexabutylditin[4]; thiohydroxamic esters with allyl tin and chalcogen derivatives;[5] and alkylmercurials with a variety of allyl and vinyl derivatives,[6] including allylic and vinylic halides. Because allyl and vinyl tins, silanes, and sulfides are usually generated from allyl and vinyl halides, direct substitutions on allyl and vinyl *halides* using alkyl *halides* as the radical source would provide the simplest possible methodology for synthetic chemists. We report here that such reactions are readily achieved.

Based on Keck's success with allyl phenyl sulfides and the assumption that halide atoms would react rapidly with hexabutylditin (eq 1), we envisioned chain reactions consisting of eqs 1, 2, and 3 or 1, 2, and 4. Both chains depend on the tributylstannyl radical selectively reacting with the alkyl halide (eq 2) rather than the allyl or vinyl halide. With the known atom abstracting selectivities of stannyl radicals in mind,[7] we chose to study the substitutions of alkyl bromides with allyl chlorides (eq 5) or activated vinylic bromides (eq 6).

$$X\bullet + Bu_3SnSnBu_3 \longrightarrow Bu_3SnX + Bu_3Sn\bullet \quad (1)$$

$$Bu_3Sn\bullet + RX' \longrightarrow Bu_3SnX' + R\bullet \quad (2)$$

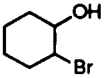
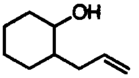
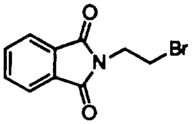
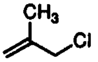
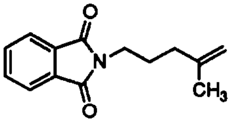
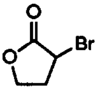
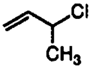
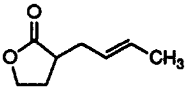
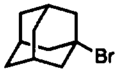
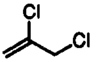
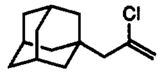
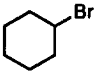
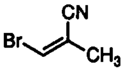
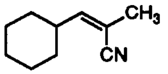
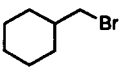
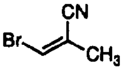
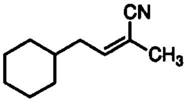
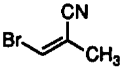
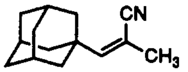




As shown in Table 1, the reaction of various alkyl bromides with allyl chlorides or 3-bromo-2-methylacrylonitrile in the presence of bistributyltin proceeded cleanly to yield the corresponding allylated and vinylated products in good to excellent yields.[8] The reactions are effective for nucleophilic, electrophilic, and 1°, 2°, and 3° radicals. The successful reaction with 3-chloro-1-butene indicates that isomerization of the allyl chloride is slower than the desired addition and that the reaction is not proceeding via an intermediate allyl stannane. Such efficient crotyl-group transfers were previously only possible with allyl sulfides. The highly efficient reactions with 3-bromo-2-methylacrylonitrile are particularly pleasing, since our experience is that both the synthesis and radical reactions of activated vinyltin derivatives can be tricky. It is notable that all the reagents employed are commercially available materials.

In summary, we have introduced a convenient alternative for free-radical allylations and vinylations for which many diverse applications should be possible.[9]

Table 1. Representative Free-Radical Mediated Substitutions.[a]

substrate	reagent	product	yield[b] (isomer ratio)
			57 % (80 : 20 trans : cis)
			49 %
			70 % (69 : 31 E : Z)
			56 %
			94 % (77 : 23 Z : E)
			78 % (78 : 22 Z : E)
			94 % (92 : 8 Z : E)

[a] In a typical procedure, 179.5 mg (0.71 mmol) of N-(2-bromoethyl)phthalimide, 167.7 mg (1.9 mmol) of methallylchloride, 455 μL (0.9 mmol) of bistributyltin, and 1 mL of C_6D_6 were placed in a standard NMR tube and sealed with a septum. After bubbling N_2 through the solution for 20 min, the mixture was irradiated for 2 d in a Rayonet reactor (9-300nm lamps). The crude mixture was treated with I_2/DBU to remove tin byproducts,[8] filtered through a plug of silica gel, and concentrated. Purification by flash chromatography (0 % then 10 % EtOAc in 30 - 60 °C petroleum ether) afforded 79.1 mg (49 %) of the methallylation product. [b] Yields refer to isolated materials.

REFERENCES AND NOTES

1. For a recent leading reference, see: Curran, D. P.; Yoo, B. *Tetrahedron Lett.* **1992,** *46,* 6931-6934.
2. Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985,** *41,* 4079-4094. (b) Baldwin, J. E.; Kelly, D. R. *J. Chem. Soc., Chem. Commun.* **1985,** 682-684.
3. Kosugi, M.; Kurata, H.; Kawata, K.; Migita, T. *Chemistry Lett.* **1991,** 1327-1328.
4. Keck, G. E.; Byers, J. H. *J. Org. Chem.* **1985,** *50,* 5442-5444.
5. Barton, D. H. R.; Crich, D. *J. Chem. Soc. Perkin Trans. 1* **1986,** 1613-1619.
6. Russell, G. A. *Acc. Chem. Res.* **1989,** *22,* 1-8. Russell, G. A.; Ngoviwatchai, P.; Wu, Y. W. *J. Am. Chem. Soc.* **1989,** *111,* 4921-4927.
7. Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984,** *106,* 343-348.
8. The removal of tin byproducts was significantly simplified by employing the I_2 / DBU workup procedure of Curran and Chang: Curran, D. P.; Chang, C. T. *J. Org. Chem.* **1989,** *54,* 3140-3157.
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