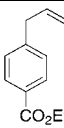
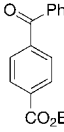
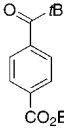
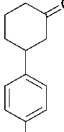
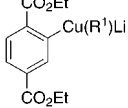
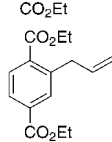
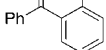
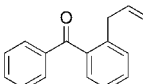
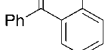
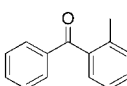
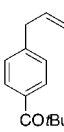
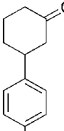
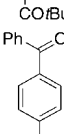
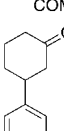
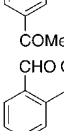
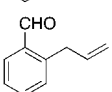
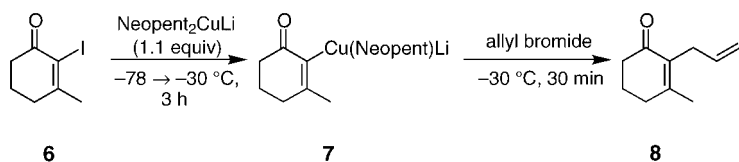


Table 1. Reaction of functionalized lithium cuprates **4** with electrophiles to give **5**.

Entry	Cuprate 4 ^[a]		Electrophile	Product 5	Yield [%] ^[b]
1	Cu(R¹)Li 	4a	allyl bromide	 5a	95 90 ^[c]
2	Cu(R¹)Li 	4a	PhCOCl	 5b	87 95 ^[c]
3	Cu(R¹)Li 	4a	<i>t</i> BuCOCl	 5c	83
4	Cu(R¹)Li 	4a	cyclohexenone	 5d	70
5	 Cu(R¹)Li	4b	allyl bromide	 5e	76
6	 Cu(R¹)Li	4c	allyl bromide	 5f	80
7	 Cu(R¹)Li	4c	MeI	 5g	80
8	Cu(R¹)Li 	4d	allyl bromide	 5h	93
9	Cu(R¹)Li 	4d	cyclohexenone	 5i	60
10	Cu(R²)Li 	4e	PhCOCl	 5j	77 ^[c]
11	Cu(R²)Li 	4e	cyclohexenone	 5k	68 ^[c]
12	 Cu(R¹)Li	4f	CH ₃ COCl	 5l	70
13	 Cu(R¹)Li	4f	allyl bromide	 5m	80

[a] R¹ = neopentyl; R² = neophyl. [b] Yields of isolated analytically pure products. [c] Yields obtained by performing the I/Cu exchange with **2**.



Scheme 2. Iodine-copper exchange with 2-iodo-3-methyl-2-cyclohexenone.

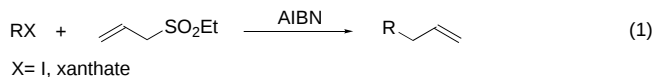
- [1] A. Boudier, L. O. Bromm, M. Lotz, P. Knochel, *Angew. Chem.* **2000**, *112*, 4584; *Angew. Chem. Int. Ed.* **2000**, *39*, 4414.
- [2] A. E. Jensen, W. Dohle, I. Sapountzis, D. M. Lindsay, V. A. Vu, P. Knochel, *Synthesis* **2002**, *4*, 565.
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- [5] Commercial neopentyl iodide was treated with *t*BuLi (2 equiv, Et₂O, -78 °C → RT, 1 h) to give neopentyllithium, which upon reaction with CuCN (0.5 equiv, 0 °C, 10 min) furnished the cuprate **1**. PhMe₂CCH₂Cl (neophyl chloride) was converted into neophyllithium by reaction with lithium metal in dry hexane (heated overnight at reflux). The mixture was then transferred through a cannula into a 50-mL Schlenk tube, and the hexane was removed under vacuum. Dry diethyl ether was added and the mixture was centrifuged (2000 rpm, 30 min). Before use, the clear solution of neophyllithium thus obtained was titrated with menthol and *o*-phenantroline as indicator. Treatment with CuCN (0.5 equiv, room temperature, 10 min) gave the corresponding copper reagent **2**.
- [6] Previously, we have shown that the neopentyl group does not readily participate in the formation of new C–C bonds: P. Jones, K. C. Reddy, P. Knochel, *Tetrahedron* **1998**, *54*, 1471; see also: S. H. Bertz, M. Eriksson, G. Miao, J. P. Snyder, *J. Am. Chem. Soc.* **1996**, *118*, 10906.
- [7] For the preparation of functionalized organocuprates by the direct insertion of activated copper, see: a) G. W. Ebert, R. D. Rieke, *J. Org. Chem.* **1984**, *49*, 5281; b) R. D. Rieke, R. H. Wehmeyer, T. C. Wu, G. W. Ebert, *Tetrahedron* **1989**, *45*, 443; c) G. W. Ebert, J. W. Cheasty, S. S. Tehrani, E. Aouad, *Organometallics* **1992**, *11*, 1560; d) G. W. Ebert, D. R. Pfennig, S. D. Suchan, T. A. Donovan, *Tetrahedron Lett.* **1993**, *34*, 2279.
- [8] a) B. H. Lipshutz, S. Sengupta, *Org. React.* **1992**, *41*, 135; b) R. J. K. Taylor, *Organocopper Reagents*, Oxford University Press, Oxford, **1994**; c) N. Krause, *Modern Organocopper Chemistry*, Wiley-VCH, Weinheim, **2002**.
- [9] For a chemoselective halogen-lithium exchange, see: Y. Kondo, M. Asai, T. Uchiyama, T. Sakamoto, *Org. Lett.* **2001**, *3*, 13.

Tin-Free Radical-Mediated C–C-Bond Formations with Alkyl Allyl Sulfones as Radical Precursors**

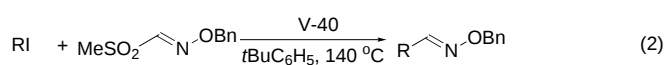
Sunggak Kim* and Chae Jo Lim

The synthetic importance of tin-free radical reactions has been well recognized in recent years.^[1] Among several

approaches, an organosulfone-mediated approach is very effective for allylation,^[2] vinylation,^[3] and azidation^[4] [Eq. (1), AIBN = 2,2'-azobisisobutyronitrile]. However, the reported methods did not work well with primary alkyl iodides and xanthates owing to inefficient iodine-atom transfer and xanthate-group transfer, respectively. Recently, we also reported a tin-free acylation approach

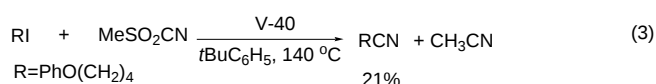


using methanesulfonyl oxime ether, in which primary alkyl iodides and xanthates caused the same problem as a result of the small energy difference between the methyl radical and the primary alkyl radical [Eq. (2), V-40 = 1,1'-azobis(cyclohexane-1-carbonitrile)].^[5]



As our extensive efforts to generate primary alkyl radicals from primary alkyl iodides and xanthates were unsuccessful, we have been interested in developing a new reliable method to generate primary alkyl radicals by using new types of radical precursors that do not require an atom- or a group-transfer step. In this regard, we have studied the possibility of using an alkyl allyl sulfone as a radical precursor. Alkyl allyl sulfones have been widely used as radical acceptors to transfer an allyl group to a radical precursor.^[6] Although alkyl allyl sulfones have been used once as the radical precursor in an allylation reaction,^[2a] primary alkyl allyl sulfones have not been examined. To the best of our knowledge, S-alkoxycarbonyl dithiocarbonates are the only generators of primary alkyl radicals from alcohols, but they cannot be applied to C–C-bond formations owing to the rapid formation of the corresponding xanthates.^[7] We have found that alkyl allyl sulfones are highly efficient and reliable radical precursors for the generation of primary alkyl radicals under tin-free conditions and can be successfully applied to various C–C-bond-formation reactions.

Initially, we focused on radical cyanation,^[8] and began our study with a primary alkyl iodide and methanesulfonyl cyanide.^[9] The reaction of 4-phenoxybutyl iodide with methanesulfonyl cyanide (2 equiv) and V-40 (0.2 equiv) in *tert*-butylbenzene at 140 °C for 5 h afforded 4-phenoxybutyl cyanide in only 21 % yield together with recovered 4-phenoxybutyl iodide (77 %). Notably, methanesulfonyl cyanide was completely consumed, with acetonitrile as the major product [Eq. (3)].^[10] However, allyl sulfone **1** was an effective



precursor for radical cyanation, and our approach is outlined in Scheme 1. We envisaged that the addition of a *p*-toluenesulfonyl radical to **1** would produce an alkyl sulfonyl radical as well as *p*-tolyl allyl sulfone **4**. Although the alkyl sulfonyl

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[**] We thank CMDS and BK21 project for financial support.

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