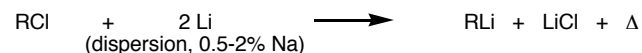


General References:

Organometallics in Organic Synthesis, Schlosser, M., Ed.; Wiley: New York, 1994.

Organolithium Methods, Wakefield, B. J.; Academic Press: London, 1988.

The Chemistry of Organolithium Compounds, Wakefield, B. J.; Pergamon, New York, 1974.

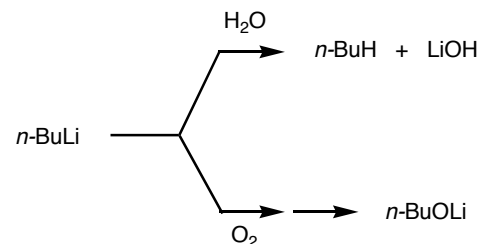
Industrial Production of Organolithium Reagents:

- Organolithium formation is carried out in hydrocarbon solvents. Afterwards, lithium chloride is removed and the solution is concentrated to as much as 90% w/w.
- Metalation occurs through a radical pathway. Sodium initiates and accelerates this highly exothermic reaction.

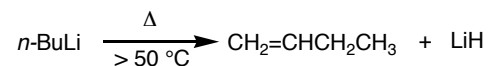
Availability (conc. in w/w):

<i>n</i> -butyllithium	15%, 23%, 50%, and 90% in hexane 20% in cyclohexane 20% in toluene
<i>sec</i> -butyllithium	10% in isopentane 12% in cyclohexane
<i>tert</i> -butyllithium	15% in pentane 15% in hexane
methylithium	5% in ethyl ether 6.4% in ethyl ether containing <i>ca</i> 10% LiBr 2.6% in cumene-THF containing 0.5% methylmagnesium
ethylithium	2% in hexane
phenyllithium	20% in cyclohexane-ethyl ether
lithium acetylide	solid complex with ethylenediamine

Organometallics in Organic Synthesis, Schlosser, M., Ed., p. 170, Wiley: New York, 1994.

Handling of Organolithium Reagents:

- Contact with oxygen or water leads to stoichiometric loss of alkyllithium titre.



Ziegler, K.; Gellert, H. G. *Liebigs Ann. Chem.* **1950**, 567, 179.

- Thermal decomposition of *n*-butyllithium produces butene and lithium hydride.

Decomposition Rates (% material lost per day)

Storage Temperature (°C)	<i>n</i> -BuLi 15-20% in hexane	<i>n</i> -BuLi 90% in hexane	<i>sec</i> -BuLi 10-12% in isopentane
0	0.00001	0.0005	0.003
5	0.0002	0.0011	0.006
10	0.0004	0.0025	0.012
20	0.0018	0.013	0.047
35	0.017	0.11	0.32

Organometallics in Organic Synthesis, Schlosser, M., Ed., p. 171, Wiley: New York, 1994.

- These factors, along with solvent evaporation, can cause concentrations of alkyllithium reagents to fluctuate over time. For careful experimental work it is important to titrate alkyllithium reagents regularly.

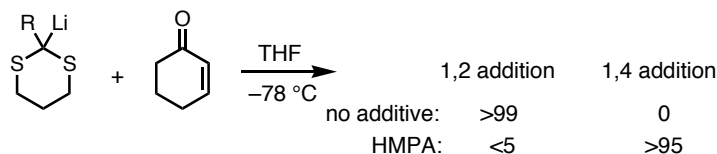
Additives:

- Additives are often used to enhance the reactivity of alkyllithium reagents. Common additives are tetramethylethylenediamine (TMEDA), hexamethylphosphoramide (HMPA), and potassium *tert*-butoxide.

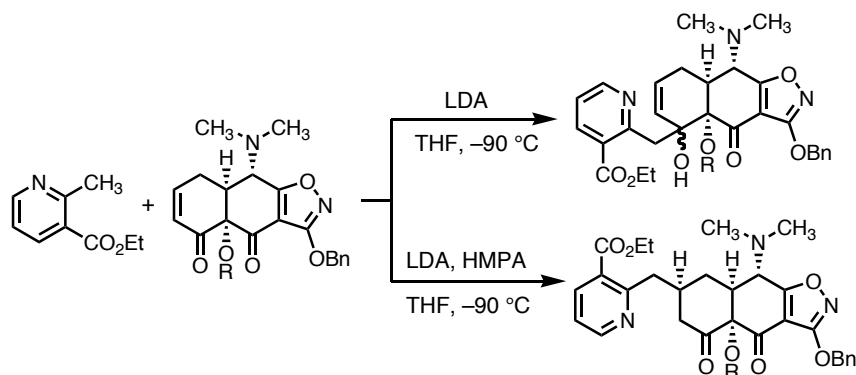


Chalk, A. J.; Hoogeboom, T. J. *J. Organomet. Chem.* **1968**, *11*, 615.

- Treatment of benzene with *n*-BuLi leads to little or no reaction, where as addition of TMEDA leads to quantitative lithiation.

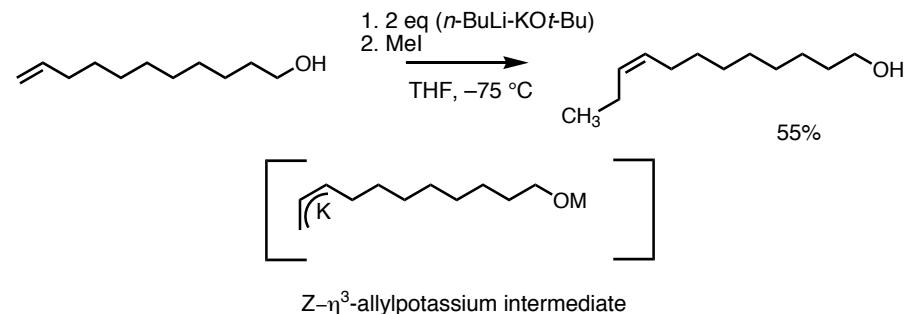


Sikorski, W. H., Reich, H. J.; *J. Am. Chem. Soc.* **2001**, *123*, 6527.



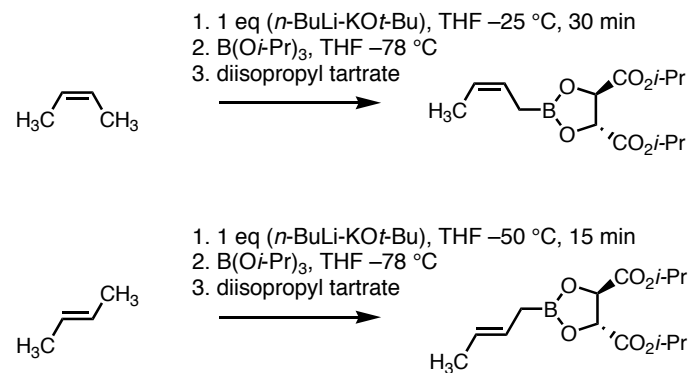
Brubaker, J. D.; Myers, A. G.; *unpublished*

- HMPA (1-2 equiv) can sometimes change the regioselectivity from 1,2- to 1,4- in the addition of stabilized organolithium reagents to α,β -unsaturated carbonyl compounds.



Schlosser, M. *Pure Appl. Chem.* **1988**, *11*, 1627.

- Alkyllithium reagents combined with potassium alcoholates ("LICKOR" reagents) provide highly activated and yet selective organometallic reagents. The reaction depicted above provides an η^3 -allylpotassium reagent. The Z isomer is favored (ratio 20:1 Z:E at -50°C). Alkylation of allylpotassium reagents usually occurs at the unsubstituted terminus.



Roush, W. R.; Ando, K.; Powers, D. B.; Halterman, R. L.; Palkowitz, A. D. *Tetrahedron Lett.* **1988**, *29*, 5579.

- The LICKOR base system allows for the stereospecific preparation of synthetically important crotylboronate reagents from butene.