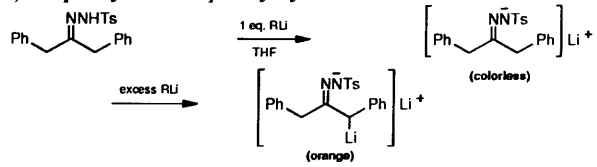
Indicators for Organolithium Assay

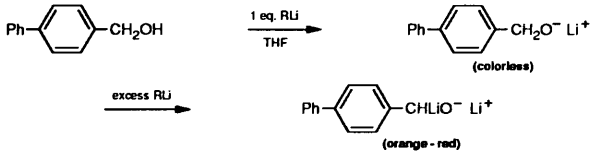
The wide use of organolithium reagents in organic synthesis has prompted the development of several analytical methods for the determination of organolithium solution concentrations.[1-5] Since they react readily with moisture and oxygen, organolithium reagents are often analyzed just prior to use. Titration is a convenient and accurate method; Aldrich offers several indicators as well as the organolithium solutions.

1,3-Diphenylacetone p-tosylhydrazone[6]

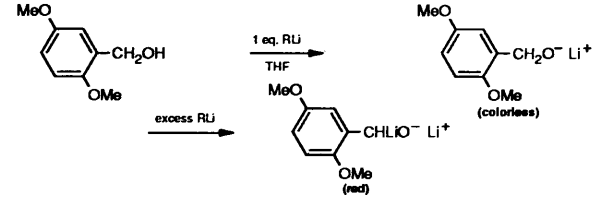


The end point, the formation of the orange dianion, is sharp and easily observed. Titers obtained with this reagent are in good agreement with those found by established procedures. In addition, this tosylhydrazone is convenient to store and handle and is not hygroscopic.

4-Biphenylmethanol[7]

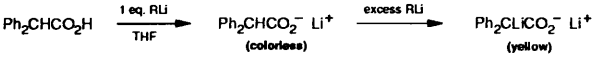


2,5-Dimethoxybenzyl alcohol[8]



In THF, ether or benzene the end point is very sharp, requiring less than 0.01mmol excess of the organolithium to be visible. Even samples containing suspended particulates or which are highly colored give easily visible and reproducible end points.

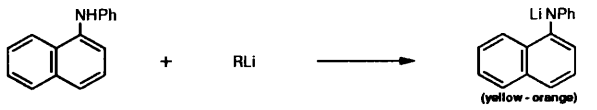
Diphenylacetic acid[9]



1,10-Phenanthroline and 2,2′-Biquinoline[10]

These indicators form colored (rust-red and yellow-green, respectively) complexes with butyllithiums. The color disappears sharply upon the addition of one equivalent of *sec*-BuOH. The problem of turbidity in hydrocarbon solvents is avoided since *sec*-BuOLi is soluble; ethers interfere in the reaction. This method is especially useful for the frequent, routine analyses of alkyllithium solutions; it is used by Aldrich analytical chemists.

N-Phenyl-1-naphthylamine[11]



Titration of the yellow-orange diarylamide with a xylene solution of *sec*-BuOH to a cloudy-white or colorless end point gives good results. It can be used in ether or hydrocarbon solvents.

References:

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6) Lipton, M.F.; Sorensen, C.M.; Sadler, A.C.; Shapiro, R.H. *J. Organometal. Chem.* **1980,** *186,* 155.
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8) Winkle, M.R.; Lansinger, J.M.; Ronald R.C. *Chem. Commun.* **1980,** 87.
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10) Watson, S.C.; Eastham, J.F. *J. Organometal. Chem.* **1967,** *9,* 165.
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Indicators

23,030-8 **1,3-Diphenylacetone *p*-tosylhydrazone,** 98%
10g $18.20; 50g $64.20

12,383-8 **4-Biphenylmethanol** **10g $18.10**

18,787-9 **2,5-Dimethoxybenzyl alcohol,** 99%
10g $18.10; 50g $58.10

D20,430-7 **Diphenylacetic acid,** 99% **100g $14.55**
500g $52.15

13,137-7 **1,10-Phenanthroline,** 99+% **5g $13.05**
25g $43.60; 100g $118.50

B3,540-7 **2,2′-Biquinoline,** 98% **1g $13.35; 5g $57.10**

10,404-3 ***N*-Phenyl-1-naphthylamine,** 98% **100g $5.90**
500g $12.75; 2kg $37.40

Organolithium Reagents

23,071-5 **BuLi,** 10.0*M* in hexanes **100ml $21.70**
800ml $129.20; 8l $647.00; 18l $1,247.00

23,070-7 **BuLi,** 2.5*M* in hexanes **100ml $12.25**
800ml $31.40; 8l $190.10; 18l $343.00

30,212-0 **BuLi,** 2.0*M* in cyclohexane **100ml $9.50**
800ml $46.00

30,210-4 **BuLi,** 2.0*M* in pentane **100ml $9.50**
800ml $46.00

18,617-1 **BuLi,** 1.6*M* in hexanes **100ml $9.80**
800ml $22.35; 8l $136.75; 18l $269.00

19,559-6 ***sec*-BuLi,** 1.3*M* in cyclohexane **100ml $11.65**
800ml $28.40; 8l $177.75; 18l $333.00

18,619-8 ***tert*-BuLi,** 1.7*M* in pentane **100ml $13.10**
800ml $41.40; 8l $328.00; 18l $645.00

19,734-3 **MeLi,** 1.4*M* in diethyl ether **100ml $10.00**
800ml $43.40; 8l $337.00; 18l $631.00

18,620-1 **MeLi,** LiBr complex, 1.5*M* in diethyl ether
100ml $9.80; 800ml $34.40
8l $319.00; 18l $615.00

31,676-8 **MeLi,** LiI complex, 1.0*M* in diethyl ether
100ml $9.50; 800ml $38.00

22,102-3 **PhLi,** 2.0*M* in cyclohexane-ether (70:30)
100ml $18.35; 800ml $120.75
8l $973.00; 18l $1,823.00

28,769-5 **PhLi-LiBr** complex, 1.0*M* in diethyl ether
100ml $10.00; 800ml $33.50