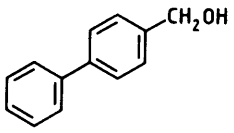
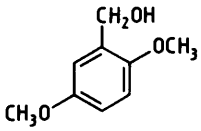
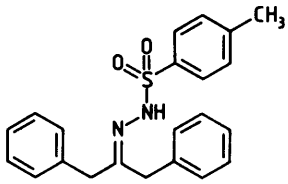
Biphenyl-4-methanol
2,5-Dimethoxybenzyl alcohol
1,3-Diphenyl-2-propanone tosylhydrazone







Indicators for Titrating Alkyllithium Solutions

The carbanion chemistry has been developing fast in recent years[1]. Alkyllithium solutions are now standard reagents in organic synthesis[2]). Many of them are commercially available at reasonable costs. As these solutions – through the action of moisture and oxygen – slowly deteriorate it is essential to determine their actual concentration prior to use. The standard method for titrating alkyllithiums according to Gilman is cumbersome because it necessitates a double titration[3]. New methods of titration with a self-indicating reagent or an indicator need but one titration. These methods are accurate and easy to carry out.

Biphenyl-4-methanol[4]

Upon addition of the alkyllithium solution to one containing a known amount of biphenyl-4-methanol the colorless alkoxide is formed primarily. After consumption of one equivalent of strong base, the titration end point is reached when the orange-red dianion begins to be formed. The end point is sharp and easily visible. The titration is run in THF.

2,5-Dimethoxybenzyl alcohol[5]

The titration gives an intensely colored red dianion as end point. The dianion becomes visible with an excess of less than 0.01 equivalent of the alkyllithium. The titration can be run in THF, ether or benzene.

1,3-Diphenyl-2-propanone tosylhydrazone[6]

The end point can be clearly observed as a change from the nearly colorless tosylhydrazone monoanion to the orange dianion. 1,3-Diphenyl-2-propanone tosylhydrazone is a non-hygroscopic crystalline solid, is conveniently weighed in for titrations and can be stored without any precautions. The titration is run in THF.

o-Phenanthroline (1,10-phenanthroline), 2,2'-Biquinoline[7]

Both are indicators and form colored complexes with alkyllithiums. Titrations are performed with sec-butanol; the color of the complex disappears after adding one equivalent of the alcohol giving a sharp end point. o-Phenanthroline forms a rust-red complex and 2,2'-biquinoline a yellow-green complex. Grignard reagents can also be titrated using this method. The authors recommend only the use of hydrocarbon solvents in the titration of alkyllithiums, whereas ethers can be used in titrating Grignard reagents as well.

References

1) J.C. Stowell, Carbanions in Organic Synthesis, Wiley, New York 1973; E. Buncel, T. Durst, Eds., Comprehensive Carbanion Chemistry, Elsevier, Amsterdam 1980; G. Wilkinson, F.G. Stone, Eds., Comprehensive Organometallic Chemistry, Pergamon Press, Oxford 1982

2) L. Fieser, M. Fieser, Reagents for Organic Synthesis, Vol. 1-11, Wiley-Interscience, New York

3) H. Gilman, F.K. Cartledge, J. Organomet. Chem. *2*, 447 (1964); T.R. Crompton, Chemical Analysis of Organometallic Compounds, Academic Press, New York 1973

4) E. Juaristi et al., J. Org. Chem. *48*, 2603 (1983)

5) M.R. Winkle et al., Chem. Commun. 87 (1980)

6) M.F. Lipton et al., J. Organomet. Chem. *186*, 155 (1980)

7) S.C. Watson, J.F. Eastham, ibid. *9*, 165 (1967)

14444	**Biphenyl-4-methanol purum** >98%(HPLC); M.P. 100-101° $C_{13}H_{12}O$ M_r 194.24 [3597-91-9]		5 g 25 g	sFr. 16.– sFr. 67.–
35020	**2,2'-Biquinoline puriss.** >99%(NT); M.P. 192-195°; Ash <0.05% $C_{18}H_{12}N_2$ M_r 256.31 [119-91-5]		1 g 5 g	sFr. 18.– sFr. 75.–
38697	**2,5-Dimethoxybenzyl alcohol puriss.** >99%(GC); B.P.$_{0.2}$99-101°; d_4^{20} 1.168; n_D^{20} 1.548 $(CH_3O)_2C_6H_3CH_2OH$ $C_9H_{12}O_3$ M_r 168.19 [33524-31-1]	1 lt ≈ 1.17 kg	10 ml 50 ml	sFr. 32.– sFr. 135.–
43190	**1,3-Diphenyl-2-propanone tosylhydrazone puriss.** >99%(HPLC); M.P. 186-187° $CH_3C_6H_4SO_2NHN{:}C(CH_2C_6H_5)_2$ $C_{22}H_{22}N_2O_2S$ M_r 378.46 [19816-88-7]		5 g 25 g	sFr. 21.– sFr. 90.–
77500	**o-Phenanthroline puriss.** >99%(NT); M.P. 94-98° $C_{12}H_8N_2.H_2O$ M_r 198.23 [66-71-7]		5 g 25 g 100 g	sFr. 15.– sFr. 55.– sFr. 175.–

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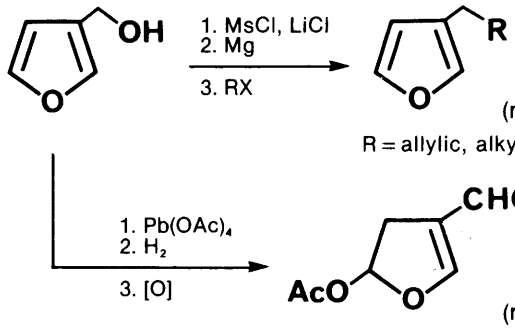
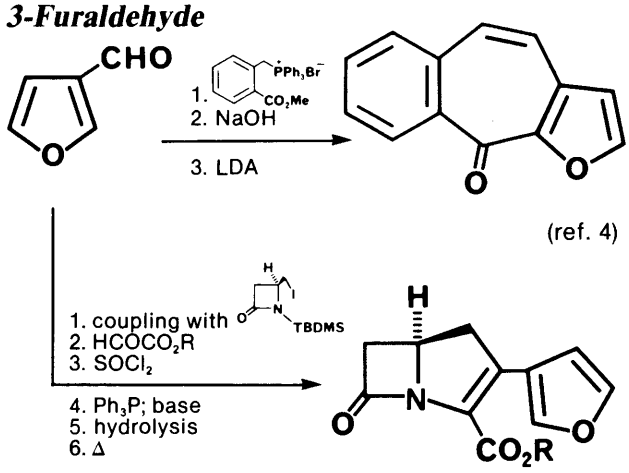
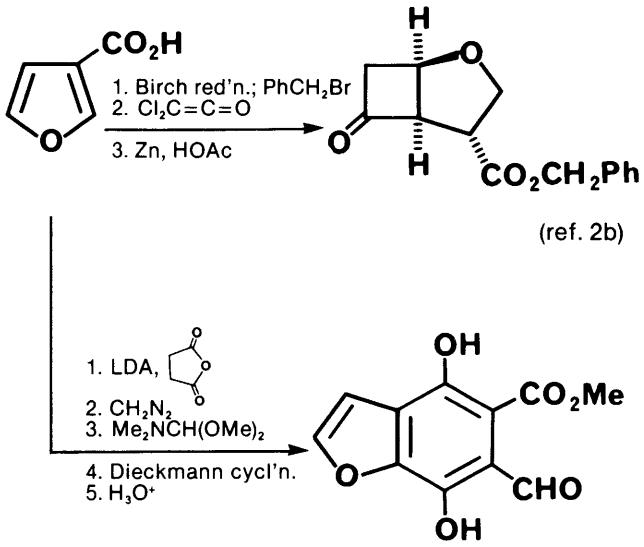


3-Furaldehyde



3-Furoic acid



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References:

1) Tanis, S.P. *Tetrahedron Lett.* **1982**, *23*, 3115 and references cited therein.
2) (a) Cama, L.D. *et al. Tetrahedron* **1983**, *39*, 2531. (b) Lowe, G.; Swain, S. *Chem. Commun.* **1983**, 1279.
3) Ojika, M. *et al. ibid.* **1982**, 628.
4) Hallberg, A.; Pedaja, P. *Tetrahedron* **1983**, *39*, 819.
5) Gammill, R.B.; Hyde, B.R. *J. Org. Chem.* **1983**, *48*, 3863.

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