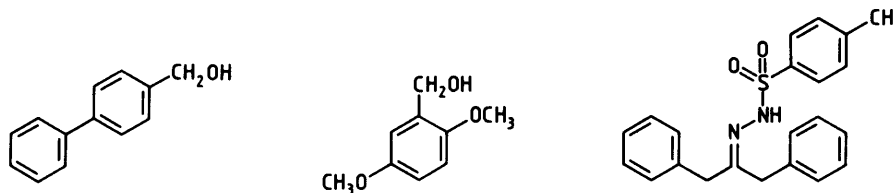




Biphenyl-4-methanol 2,5-Dimethoxybenzyl alcohol 1,3-Diphenyl-2-propanone tosylhydrazone



Indicators for Titrating Alkylolithium Solutions

The carbanion chemistry has been developing fast in recent years¹⁾. Alkylolithium solutions are now standard reagents in organic synthesis²⁾. 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 alkylolithiums according to Gilman is cumbersome because it necessitates a double titration³⁾. 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-methanol⁴⁾

Upon addition of the alkylolithium 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 alcohol⁵⁾

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 alkylolithium. The titration can be run in THF, ether or benzene.

1,3-Diphenyl-2-propanone tosylhydrazone⁶⁾

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'-Biquinoline⁷⁾

Both are indicators and form colored complexes with alkylolithiums. 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 alkylolithiums, whereas ethers can be used in titrating Grignard reagents as well.

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14444	Biphenyl-4-methanol purum >98%(HPLC); M.P. 100-101°	5 g	sFr.	16.—
	C ₁₃ H ₁₂ O M _r 194.24 [3597-91-9]	25 g	sFr.	67.—
35020	2,2'-Biquinoline puriss. >99%(NT); M.P. 192-195°; Ash <0.05%	1 g	sFr.	18.—
	C ₁₈ H ₁₂ N ₂ M _r 256.31 [119-91-5]	5 g	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	1 lt ≈ 1.17 kg	10 ml	sFr. 32.—
	(CH ₃ O) ₂ C ₆ H ₃ CH ₂ OH C ₉ H ₁₂ O ₃ M _r 168.19 [33524-31-1]	50 ml	sFr.	135.—
43190	1,3-Diphenyl-2-propanone tosylhydrazone puriss. >99%(HPLC); M.P. 186-187°	5 g	sFr.	21.—
	CH ₃ C ₆ H ₄ SO ₂ NHN:C(CH ₂ C ₆ H ₅) ₂ C ₂₂ H ₂₂ N ₂ O ₃ S M _r 378.46 [19816-88-7]	25 g	sFr.	90.—
77500	o-Phenanthroline puriss. >99%(NT); M.P. 94-98°	5 g	sFr.	15.—
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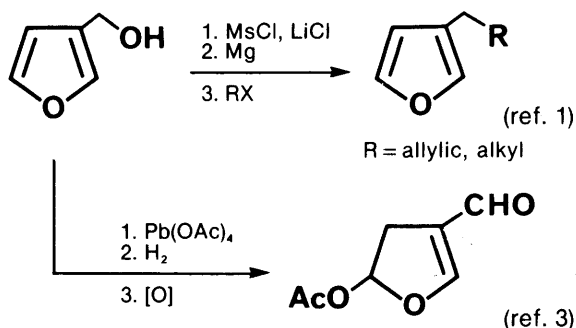


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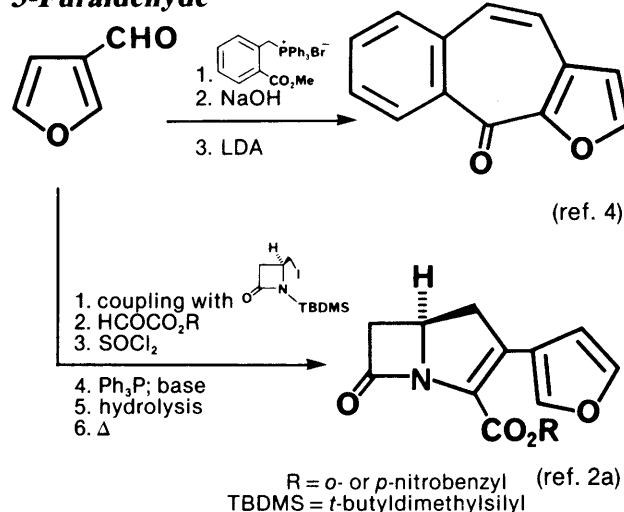
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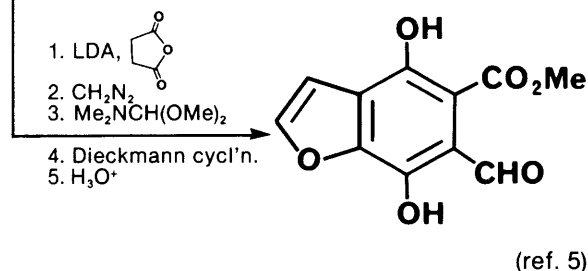
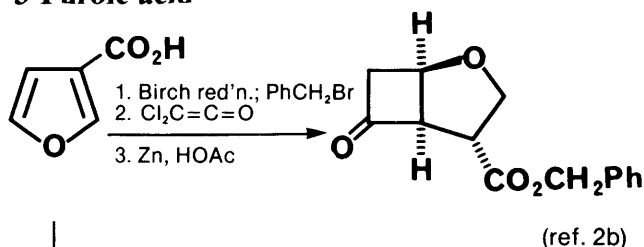
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References:

- 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.
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