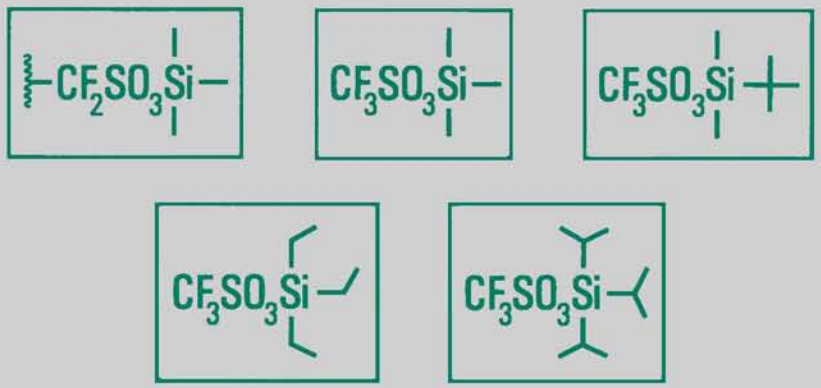
TRIALKYLSILYL TRIFLATES



Versatile Reagents and Catalysts

Since the first use of **trimethylsilyl trifluoromethanesulfonate** (TMS-triflate)[1)2)] as catalyst in nucleoside synthesis[3)] and highly reactive silylating agent for carbonyl compounds[4)] the literature on the applications of TMS- and other trialkylsilyl triflates increased rapidly (for two recent reviews see [5)] and [6)]). TMS-triflate has been used for the silylation of different substrates (e.g. aldehydes, ketones, diketones, nitriles, esters, imines, lactones), for the cleavage of tert-butyl esters, oxiranes[7)] and cyclopropanes[8)] and as catalyst for different reactions (e.g. synthesis of nucleosides and glycosides[9)], preparation of acetals and orthoesters[10)], reaction of acetals with silyl enol ethers[11)], alkylations with silyl ethers[12)13)])[5)6)].

tert-Butyldimethylsilyl triflate, introduced by W. Graf[7)] for the electrophilic opening of oxiranes, was used by L.L. Miller[14)15)] for the silylation of hydroquinones and by E.J. Corey[16)] for the silylation of hindered alcohols.

Triethylsilyl triflate, proposed by FLUKA AG[17)] as substitute for the dangerous triethylsilyl perchlorate (in the silylation of hindered alcohols), was used by G. Simchen[18)] for the silylation of nitroalkanes and by C.H. Heathcock[19)] for the silylation of hindered alcohols.

Nafion® -TMS (Nafion, a perfluorinated resin sulfonic acid, is a registered trade mark of Du Pont Co.) may be considered as a polymer supported TMS-triflate. It was developed by R. Noyori[20)] as efficient silylating agent. M. Demuth and K. Schaffner[8)] showed its use as reagent for the electrophilic opening of cyclopropanes.

Triisopropylsilyl triflate (TIPS-triflate) was recently shown by E.J. Corey[16)] to be an efficient reagent for the transformation of primary and secondary alcohols as well as aldehydes and ketones into their triisopropylsilyl derivatives.

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91742	**tert-Butyldimethylsilyl trifluoromethanesulfonate purum**	1 lt ≈ 1.15 kg	5 ml sFr. 34.–	US$ 22.70
			25 ml sFr. 145.–	US$ 96.70
70161	**Nafion® -TMS** in preparation			
91743	**Triethylsilyl trifluoromethanesulfonate purum**	1 lt ≈ 1.17 kg	10 ml sFr. 35.–	US$ 23.40
			50 ml sFr. 145.–	US$ 96.70
91746	**Triisopropylsilyl trifluoromethanesulfonate purum**	1 lt ≈ 1.17 kg	5 ml sFr. 75.–	US$ 50.00
			25 ml sFr. 320.–	US$ 213.40
91741	**Trimethylsilyl trifluoromethanesulfonate purum**	1 lt ≈ 1.22 kg	10 ml sFr. 16.–	US$ 10.70
			50 ml sFr. 60.–	US$ 40.00

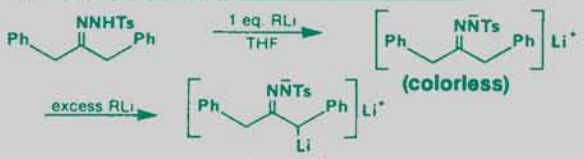
For other organosilicon compounds see FLUKA-Catalogue 13, 1982/83, or the FLUKA-Brochure "Silylating Agents"

FLUKA AG, CH-9470 BUCHS, SWITZERLAND, TELEPHONE (085) 6 02 75, TELEX 855 282

Indicators for Organolithium Assay

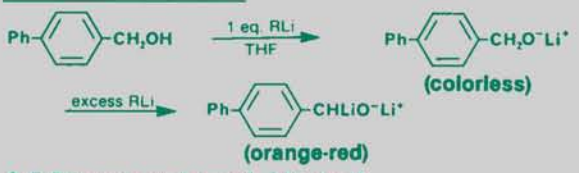
The wide use of organolithium reagents in organic synthesis has prompted the development of many analytical methods for the determination of organolithium solution concentrations.[1-5] Because they react readily with moisture and oxygen, organolithium reagents must be analyzed just prior to use. Titration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

1,3-Diphenylacetone *p*-Tosylhydrazone[6]

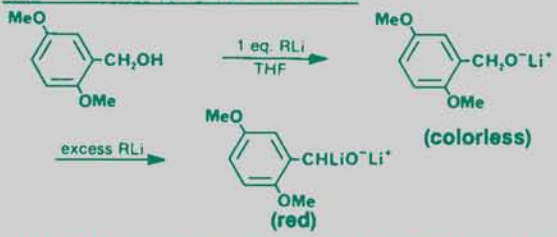


The end point, the formation of the orange dianion, is sharp and easily observed. Titers obtained with this reagent are in good agreement with those found by established procedures. In addition, this tosylhydrazone is convenient to store and handle and is not hygroscopic.

4-Biphenylmethanol[7]

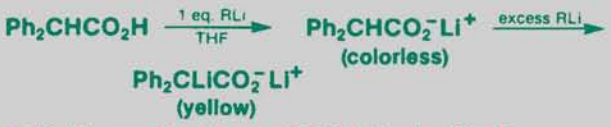


2,5-Dimethoxybenzyl Alcohol[8]



In THF, ether or benzene the end point is very sharp, requiring less than 0.01-mmol 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 QC 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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Organolithium reagents:*

19,734-3	**MeLi**, 1.4*M* in ether	22g $38.50
18,620-1	**MeLi-LiBr complex**, 2*M* in ether	22g $24.90
18,617-1	**BuLi**, 1.6*M* in hexane	10g $8.40; 90g $20.25
23,070-7	**BuLi**, 2.5*M* in hexane	15g $9.00; 130g $23.00
23,071-5	**BuLi**, 10.5*M* in hexane	70g $12.00; 500g $68.00
19,559-6	***sec*-BuLi**, 1.3*M* in cyclohexane	9g $8.80
		75g $27.25
18,619-8	***tert*-BuLi**, 1.7*M* in pentane	10g $11.25
		90g $68.75
22,102-3	**PhLi**, 2*M* in cyclohexane-ether(70:30)	15g $14.45
	*Weights shown do not include solvent.	130g $95.65

Indicators:

23,030-8	**1,3-Diphenylacetone *p*-tosylhydrazone**, 98%	10g $15.00; 50g $54.00
12,383-8	**4-Biphenylmethanol**, 97%	10g $13.95
18,787-9	**2,5-Dimethoxybenzyl alcohol**, 97%	10g $12.50
		50g $40.45
D20,430-7	**Diphenylacetic acid**, 99+%	100g $13.50
		500g $46.95
13,137-7	**1,10-Phenanthroline**, 97%	5g $10.50; 25g $33.85
B3,540-7	**2,2′-Biquinoline**, 98%	1g $11.00; 5g $48.05
10,404-3	***N*-Phenyl-1-naphthylamine**, 98%	100g $9.00
		500g $10.60; 2kg $30.80

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