NMR Shift Reagents

General Applications

Aldrich offers a variety of reagents for simplifying the interpretation of complex NMR spectra. The paramagnetic lanthanide β-diketonates (**1-4**),[1] for example, have been widely used for the determination of molecular configuration, conformation, and stereochemistry *in solution;* analysis of organometallic compounds and polymers; estimation of coupling constants; study of isotope effects and kinetics; and determination of functional group basicity.[1]

The optically active shift reagents (**3-5**) are extremely useful for the NMR assay of enantiomeric composition. A major advantage of using the NMR technique over polarimetric methods is that small quantities of optically active impurities do not interfere in the former assay. Also, there is no need to reference an external standard of enantiomeric purity using the NMR method. In addition to the chiral lanthanide reagents[2] listed at right are the two *enantioselective solvating agents* **5a** and **5b**. These chiral alcohols have been used for the determination of optical purity — and, in certain cases, the *absolute configuration* — of a wide range of organic molecules.[3]

Choosing a Shift Reagent

Selecting the most effective lanthanide shift reagent for a particular problem often requires trial and error, although some guidelines can be followed.[1] For example, the **Eu** and **Yb** complexes usually induce *downfield* proton NMR shifts, whereas those of **Pr** and **Dy** induce *upfield* shifts. The **Yb** and **Dy** shift reagents have been recommended for use in ^{13}C, ^{14}N, and ^{19}F NMR experiments.

The **fod**[4] reagents (**2**) are generally more soluble in nonpolar NMR solvents and induce greater shifts than their **thd** (**1**)[5] counterparts (however, sometimes a choice must be made between the extent of shifting and the signal broadening that usually accompanies it). There is evidence that the **fod** complexes are more stable to carboxylic acids and phenols than the corresponding **thd** chelates.

Although the more-acidic **fod** reagents are valuable for studying compounds having weakly nucleophilic functional groups, the **thd** derivatives bind more *selectively* and may be more useful for substrates having several different functional groups. The *combination* of reagents **Ag(fod) (2d)** and **Yb(fod)$_3$ (2c)** was recently found to be effective for shifting resonances of such weakly nucleophilic compounds as aromatics, olefins, phosphines, and halogenated compounds.[6]

Aldrich has a shift reagent for all your NMR needs!

References:

1) For reviews on the uses and properties of the lanthanide NMR shift reagents, see: Campbell, J.R. *Aldrichimica Acta* **1971**, *4*, 55. Campbell, J. *ibid.* **1972**, *5*, 29. von Ammon, R.; Fischer, R.D. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 675. Peterson, M.R., Jr.; Wahl, G.H., Jr. *J. Chem. Ed.* **1972**, *49*, 790. Sanders, J.K.M.; Williams, D.H. *Nature* **1972**, *240*, 385. Cockerill, A.F.; Davies, G.L.O.; Harden, R.C.; Rackham, D.M. *Chem. Rev.* **1973**, *73*, 553. Mayo, B.C. *Chem. Soc. Rev.* **1973**, *2*, 49. "Nuclear Magnetic Resonance Shift Reagents"; Sievers, R.E., Ed.; Academic Press, Inc.: New York, 1973. Kime, K.A.; Sievers, R.E. *Aldrichimica Acta* **1977**, *10*, 54.
2) Whitesides, G.M.; Lewis, D.W. *J. Am. Chem. Soc.* **1970**, *92*, 6979.
3) See, for example, Pirkle, W.H.; Rinaldi, P.L. *J. Org. Chem.* **1978**, *43*, 4475, and reference 1 cited therein.
4) Rondeau, R.E.; Sievers, R.E. *J. Am. Chem. Soc.* **1971**, *93*, 1522.
5) Sanders, J.K.M.; Williams, D.H. *Chem. Commun.* **1970**, 422.
6) Wenzel, T.J.; Bettes, T.C.; Sadlowski, J.E.; Sievers, R.E. *J. Am. Chem. Soc.* **1980**, *102*, 5903. Wenzel, T.J.; Sievers, R.E. *Anal. Chem.* **1981**, *53*, 393. Wenzel, T.J.; Sievers, R.E. *J. Am. Chem. Soc.*, in press.

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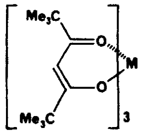


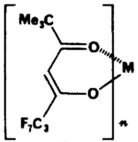
1

1a, M=Eu:
Resolve-Al™, 99+%, GOLD LABEL [Eu(thd)$_3$, tris-(2,2,6,6-tetramethyl-3,5-heptanedionato)europium] **15,697-3 1g $11.90; 5g $54.00**

1b, M=Dy:
Resolve-Al Dy™, 99+%, GOLD LABEL [Dy(thd)$_3$, tris(2,2,6,6-tetramethyl-3,5-heptanedionato)-dysprosium] **16,273-6 1g $16.40**

1c, M=Pr:
Resolve-Al Pr™, 99+%, GOLD LABEL [Pr(thd)$_3$, tris(2,2,6,6-tetramethyl-3,5-heptanedionato)praseodymium] **16,088-1 1g $11.90**

1d, M=Yb:
Resolve-Al Yb™, 99+%, GOLD LABEL [Yb(thd)$_3$, tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ytterbium] **16,275-2 1g $14.30**



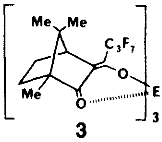
2

2a, M=Eu, *n*=3:
Resolve-Al EuFOD™, 99+%, GOLD LABEL [Eu(fod)$_3$, Sievers' Reagent, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)-europium] **16,093-8* 100mg $3.00; 1g $11.90**

2b, M=Pr, *n*=3:
Resolve-Al PrFOD™, 99+%, GOLD LABEL [Pr(fod)$_3$, Rondeau's Reagent, tris(6,6,7,7,8,-8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)praseodymium] **16,135-7* 1g $11.90**

2c, M=Yb, *n*=3:
Resolve-Al YbFOD™, 99+%, GOLD LABEL [Yb(fod)$_3$, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)ytterbium] **22,583-5* 1g $19.50; 5g $48.40**

2d, M=Ag, *n*=1:
Resolve-Al AgFOD™, 99+%, GOLD LABEL [Ag(fod), (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)silver] **22,466-9* 1g $15.00; 5g $47.50**



3

3: Tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato], europium(III) derivative, 99+%, GOLD LABEL [Eu(hfc)$_3$] **16,474-7 1g $17.50 5g $59.00**

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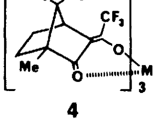
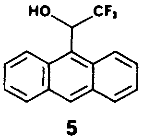


4

4a, M=Eu:
Tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato], europium(III) derivative [Eu(tfc)$_3$] **17,649-4* 100mg $4.70; 1g $19.70 5g $74.00**

4b, M=Pr:
Tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato], praseodymium(III) derivative [Pr(tfc)$_3$] **17,770-9* 1g $19.50; 5g $72.00**



5

5a, (+)-isomer:
(+)-2,2,2-Trifluoro-1-(9-anthryl)ethanol, 98+% [α-(trifluoromethyl)-9-anthracenemethanol] **21,134-6 100mg $6.25; 1g $24.70**

5b, (-)-isomer:
(-)-2,2,2-Trifluoro-1-(9-anthryl)ethanol, 98+% [α-(trifluoromethyl)-9-anthracenemethanol] **21,135-4 100mg $6.25; 1g $24.70**

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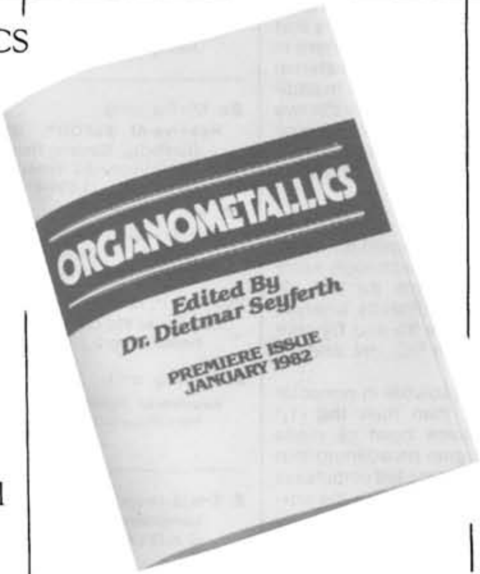

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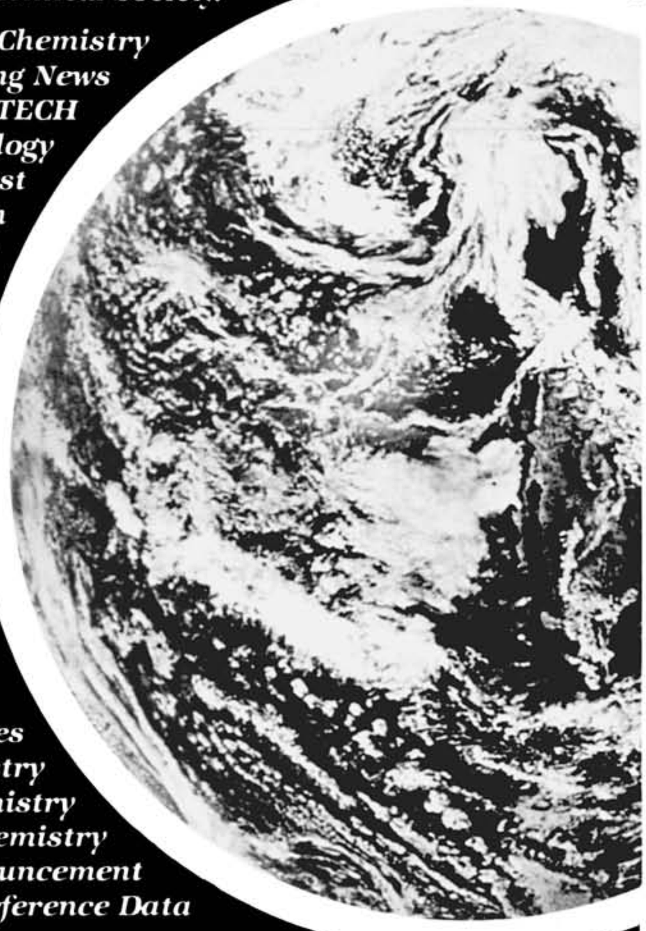

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