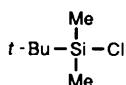




# Silicon Reagents: helpful hindrance

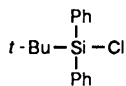
Aldrich offers a wide variety of organosilicon reagents for your synthetic needs. Sterically hindered silylating agents containing either a tert-butyl or hexyl substituent on the silicon atom are extremely useful for the protection of hydroxyl groups. Below are examples of these important reagents. For larger quantities, please call our Bulk Sales Department at 800-255-3756. Send for a free computer printout of all the organosilicon reagents available from Aldrich.



Very useful reagents for the protection of alcohols.<sup>1-3</sup>

(1) Corey, E.J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190. (2) Greene, T.W. *Protective Groups in Organic Synthesis*; Wiley-Interscience: New York, 1981 (Aldrich Catalog No. Z10,823-5). (3) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

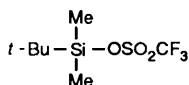
**19,050-0** *tert*-Butyldimethylsilyl chloride, 97%  
5g \$13.75; 25g \$43.45  
100g \$119.50



Selectively silylates primary alcohols.

Hanessian, S.; Lavallee, P. *Can. J. Chem.* **1975**, *63*, 2975.

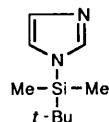
**19,553-7** *tert*-Butylchlorodiphenylsilane, 98%  
10g \$19.90; 50g \$68.25



Reagent for the protection of tertiary and unreactive secondary alcohols<sup>1</sup> and for the synthesis of silyl enol ethers from sterically hindered ketones in high yields.<sup>2</sup>

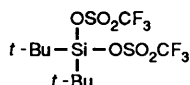
(1) Corey, E.J. *et al. Tetrahedron Lett.* **1981**, *22*, 3455.  
(2) Mander, L.N.; Sethi, S.P. *ibid.* **1984**, *25*, 5953.

**22,614-9** *tert*-Butyldimethylsilyl trifluoromethanesulfonate, 98%  
5g \$27.35



Highly reactive silylating agent.

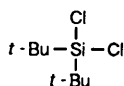
**25,023-6** 1-(*tert*-Butyldimethylsilyl)-imidazole, 97%  
250mg \$8.75  
1g \$25.85



Highly efficient reagent for the protection of a variety of 1,2-, 1,3- and 1,4-diols under mild conditions.

Corey, E.J.; Hopkins, P.B. *Tetrahedron Lett.* **1982**, *23*, 4871.

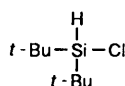
**26,202-1** Di-*tert*-butylsilyl bis(trifluoromethanesulfonate), 97%  
5g \$21.05  
25g \$68.15



Serves to protect 1,2- and 1,3- diols.

Trost, B.M.; Caldwell, C.G. *Tetrahedron Lett.* **1981**, *22*, 4999.

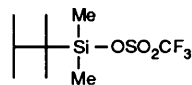
**28,766-0** Di-*tert*-butyldichlorosilane, 98%  
5g \$32.75; 25g \$125.10



For the preparation of di-*tert*-butylalkylsilanes *via* reaction with organolithium reagents.

Doyle, M.P.; West, C.T. *J. Am. Chem. Soc.* **1975**, *97*, 3777.

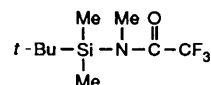
**29,693-7** Di-*tert*-butylchlorosilane, 98%  
10g \$18.65; 25g \$30.75



Valuable reagent for the protection of tertiary alcohols.

Wetter, H.; Oertle, K. *Tetrahedron Lett.* **1985**, *26*, 5515.

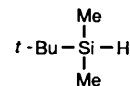
**30,332-1** Dimethylhexylsilyl trifluoromethanesulfonate, 97%  
5g \$20.00  
25g \$60.00



Excellent silylating agent which is relatively insensitive to moisture.

Mawhinney, T.; Madison, M.A. *J. Org. Chem.* **1982**, *47*, 3336.

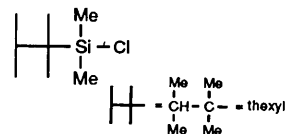
**24,205-5** *N*-(*tert*-Butyldimethylsilyl)-*N*-methyltrifluoroacetamide, 98%  
1g \$13.30; 5g \$45.45



Widely used for the preparation of *tert*-butyldimethylsilyl perchlorate, a highly reactive silylating reagent.

Barton, T.J.; Tully, C.R. *J. Org. Chem.* **1978**, *43*, 3649.

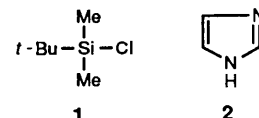
**29,476-4** *tert*-Butyldimethylsilane  
5g \$21.75; 25g \$70.95



Useful reagent for the protection of primary, secondary and phenolic hydroxy groups.

Wetter, H.; Oertle, K. *Tetrahedron Lett.* **1985**, *26*, 5515.

**30,244-9** Dimethylhexylsilyl chloride, 97%  
25g \$14.25; 100g \$38.00



The convenient DMF solution of *tert*-butyldimethylsilyl chloride, **1** (0.5M) and imidazole, **2** (1.0M) is a useful reagent for the protection of hydroxyl groups.

Corey, E.J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

**21,476-0** BDCS Silylation Reagent  
5ml \$8.95; 100ml \$21.85; 800ml \$97.15



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# MMPP: a replacement for MCPBA

The commercial 80-85% grade of 3-chloroperoxybenzoic acid (MCPBA), an "old friend" to many synthetic chemists, will soon be unavailable due primarily to hazards associated with its manufacture. As old friends pass on, new ones are quickly made. Please consider **monoperoxyphthalic acid, magnesium salt** (magnesium monoperoxyphthalate, **MMPP, 1**), a recently developed organic peracid, which promises to be a useful replacement for MCPBA.<sup>1</sup>

**MMPP** is a fine, white crystalline solid that is non-shock-sensitive and nondeflagrating, containing about 80% of the pure oxidant as its hexahydrate. Its stability in the solid state compares favorably with that of MCPBA.<sup>2</sup> **MMPP** is a weak acid, and therefore useful for the oxidation of acid-sensitive substrates without recourse to buffer systems. Since it is very soluble in water and low-molecular-weight alcohols, it is suitable for oxidations which frequently employ homogeneous systems such as alcohol or aqueous alcohol. Oxidations can also be done in two-phase

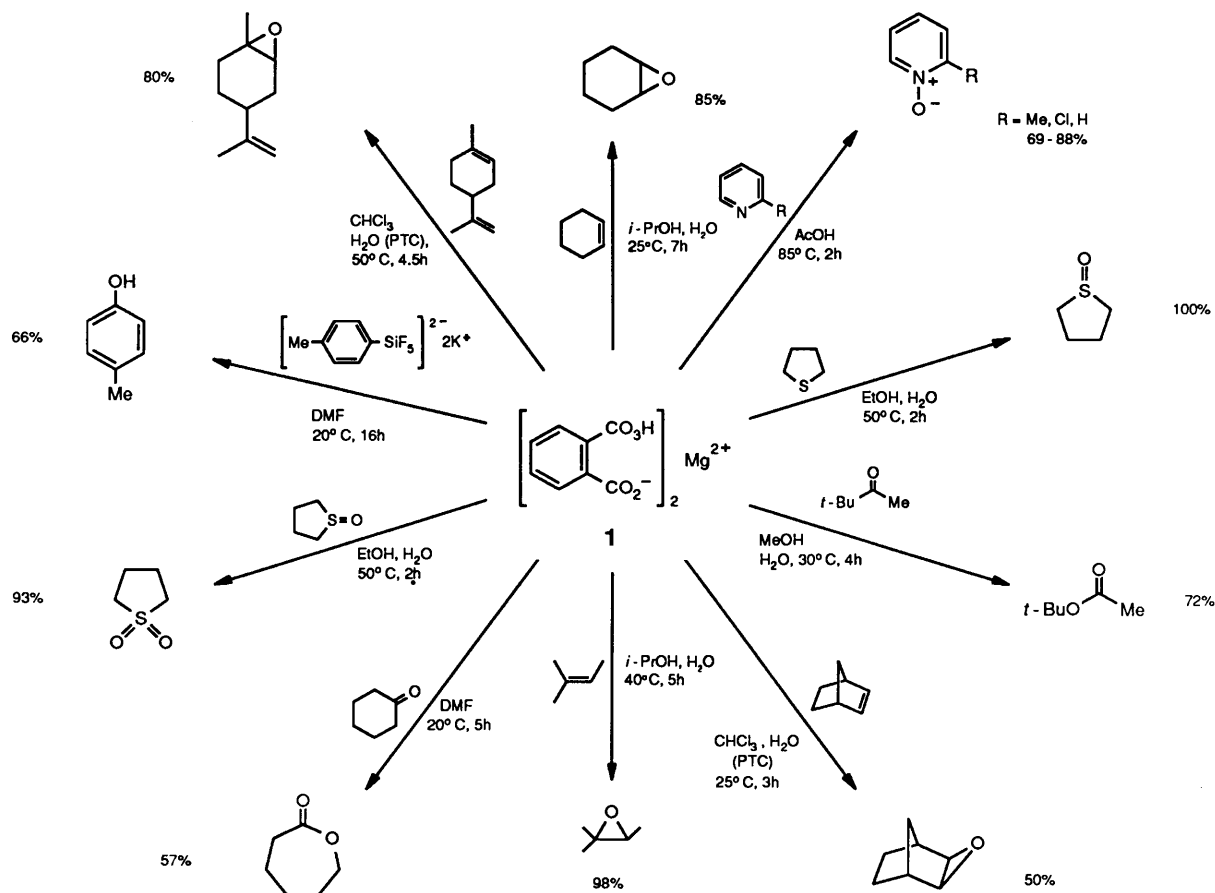
water/chlorinated-hydrocarbon systems employing phase-transfer catalysis (PTC). More importantly, the oxidation byproduct, magnesium phthalate, is water-soluble and thus easily removed. As indicated in the scheme below, **MMPP** has proven to be a suitable replacement for MCPBA in several classic oxidations.<sup>1</sup> For details, send for Technical Information Bulletin No. AL-171.

**MMPP** is significantly less expensive than MCPBA, and is also available in bulk quantities. Please call our Bulk Sales Department at 800-255-3756 for quotations.

#### References and Notes:

- 1) Brougham, P.; Cooper, M.S.; Cummerson, D.A.; Heaney, H.; Thompson, N. *Synthesis* **1987**, 1015, and references cited within.
- 2) Loss of only 2.7% available oxygen after 16 weeks at 28°C (ref. 1).

**28,320-7 Monoperoxyphthalic acid, magnesium salt hexahydrate, tech., 80% (MMPP) 100g \$10.80; 500g \$34.60**



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