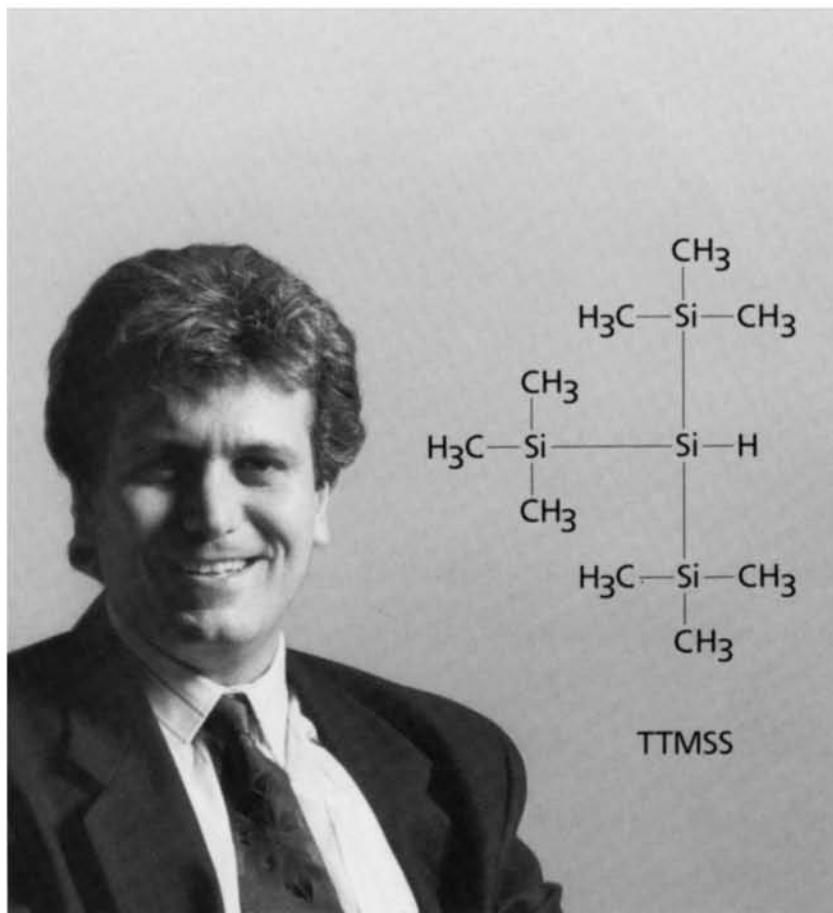


# Reagent of the Year 1990

93411 Tris(trimethylsilyl)silane, TTMSS, purum >97% (GC), package sizes 1 ml, 5 ml.



## The Prize Winner 1990

### Chrysostomos Chatgililoglu

Chrysostomos Chatgililoglu, born 1952 in Nikea (Greece), studied at the University of Bologna (Italy). As a postdoctoral fellow he joined the University of York (1977–79). From 1979 till 1982 he worked with K.U. Ingold at the National Research Council of Canada. Since 1983 he has been affiliated with the Consiglio Nazionale delle Ricerche, Ozzano Emilia (Bologna).

## The Reagent

Tris(trimethylsilyl)silane functions as a free radical reducing agent for a variety of organic substrates, i.e., halides [1,2], ketones [3,4], selenides [5], xanthates [5], isocyanides [5]. It rivals tributyltin hydride in efficiency and is superior from the ecological and practical point of view. This reagent can also be used as a mediator for the formation of carbon-carbon bonds via radicals giving less unwanted reaction products [6,7]. Its use, in catalytic amounts, with sodium borohydride as the consumable reagent, allows the efficient reduction of organic halides via radicals [6,8].

- [1] C. Chatgililoglu, D. Griller and M. Lesage, *J. Org. Chem.* **53**, 364 (1988).  
 [2] C. Chatgililoglu, D. Griller and M. Lesage, *J. Org. Chem.* **54**, 2492 (1989).

- [3] K.J. Kulicke and B. Giese, *Synlett*, 91 (1990).  
 [4] A. Alberti and C. Chatgililoglu, *Tetrahedron*, in press.  
 [5] M. Ballestri, C. Chatgililoglu, B. Clark, D. Griller, B. Giese & B. Kopping, *J. Org. Chem.* submitted for publication  
 [6] C. Chatgililoglu, in "Free Radicals in Synthesis and Biology"; Edited by F. Minisci, Kluwer, Dordrecht: 1989, pp. 115–123.  
 [7] B. Giese, B. Kopping and C. Chatgililoglu, *Tetrahedron Lett.* **30**, 681 (1989).  
 [8] M. Lesage, C. Chatgililoglu and D. Griller, *Tetrahedron Lett.* **30**, 2733 (1989).

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## The Fluka Prize:

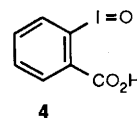
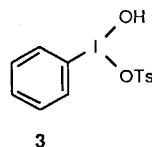
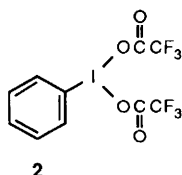
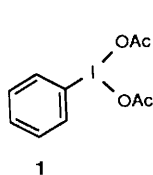
Since 1987, the Fluka Prize "Reagent of the Year" has been awarded annually to a research project, in which a new compound has been shown to be a reagent of prime importance, useful in organic chemistry, biochemistry or analytical chemistry. The winner will be awarded the sum of sFr. 10 000.–. He will be free of any obligations whatsoever.

Nominations for the Fluka Prize "Reagent of the Year" should be submitted to the Fluka Prize Committee c/o Fluka Chemie AG, CH-9470 Buchs/Switzerland no later than September 30th. Full details regarding the Fluka Prize are available upon request.

**Fluka** 

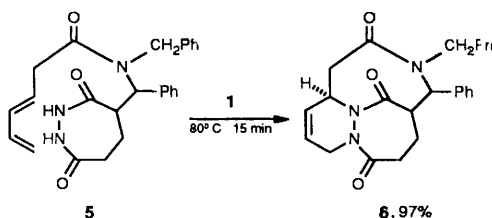
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 CH-9470 Buchs/Switzerland

# Hypervalent Iodine Reagents



Hypervalent iodine reagents (e.g., 1-4) resemble Pb(IV), Tl(III) and Hg(II) reagents in their reactions, but do not share the undesirable characteristics (i.e., high toxicity and associated waste-disposal problems) that are commonplace for the heavy metals. This fact, coupled with the versatility of these mild oxidants, has resulted in renewed interest in their synthetic utility. Hypervalent iodine reagents have been used in the oxidation of a broad range of organic functional groups, such as simple olefins, alkynes, carbonyl compounds and alcohols.<sup>1</sup> The following paragraphs highlight some recent synthetic applications of these useful reagents.

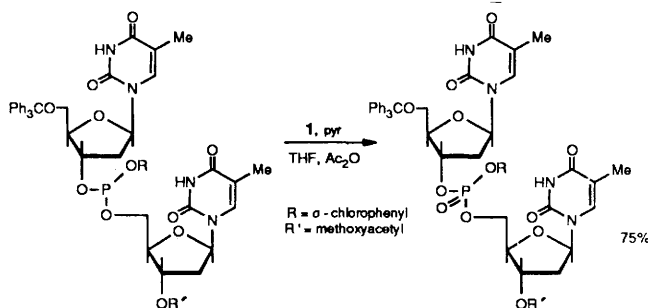
## Synthesis of a Nonpeptide Mimic



Hydrazide 5, on oxidation with 1, generates a highly reactive azodicarbonyl dienophile which undergoes a facile intramolecular (4+2) cycloaddition to afford 6.<sup>2</sup>

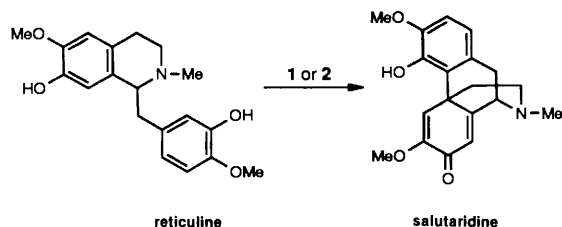
## Oligonucleotide Synthesis

One of the important steps in oligonucleotide synthesis consists of phosphite oxidation. This can be accomplished conveniently by using an iodine-based oxidant in a nonaqueous system.<sup>3</sup>



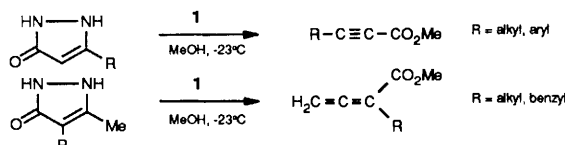
## Natural-Product Synthesis

When 1 or 2 is used for the *o/p*-phenolic oxidative cyclization of reticuline, a key alkaloid biosynthetic intermediate, salutaridine, is obtained in good yield.<sup>4</sup> The same reaction, when carried out using thallium trifluoroacetate and lead tetraacetate, affords the product in lower yield with the formation of highly toxic by-products.<sup>5</sup>



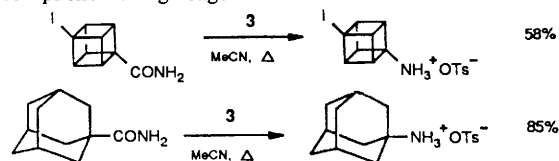
## Alkyne and Allene Formation

Methyl 2-alkynoates and methyl 2,3-alkadienoates are useful intermediates for the synthesis of a variety of complex acyclic, carbocyclic and heterocyclic molecules.<sup>6</sup> Although many methods are known for their preparation, oxidation of corresponding pyrazolones seems to be the simplest one.<sup>7</sup> This oxidation can be carried out using hypervalent iodine reagent 1.<sup>8</sup> Interestingly, the 5-substituted pyrazolones yield alkynes, whereas 5-methyl-4-substituted pyrazolones yield allenes in moderate to good yield under similar conditions.



## Bridgehead Amine Synthesis

The preparation of bridgehead primary amines from the corresponding amides (Hofmann rearrangement) can be conveniently accomplished using reagent 3.<sup>9</sup>



## References:

- (1) Merkushev, E.B. *Russ. Chem. Rev.* **1987**, *56*, 826. Ochia, M.; Nago, Y. *Yuki Gosei Kagaku Kyodaishi* **1986**, *44*, 660. Umemoto, T.; Yuki, Y. *ibid.* **1983**, *41*, 251. Moriarty, R.M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. Varvoglis, A. *Synthesis* **1984**, 709. Varvoglis, A. *Chem. Soc. Rev.* **1981**, *10*, 377. Koser, G.F., "Hypervalent Halogen Compounds"; In *The Chemistry of Functional Groups, Supplement D*; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, 1983; Chapter 18, p 721. Koser, G.F.; "Halogen Ions"; *ibid.*; Chapter 25, p 1265. (2) Kahn, M. *et al. J. Am. Chem. Soc.* **1988**, *110*, 1638. (3) Fourrey, J.L.; Varenne, J. *Tetrahedron Lett.* **1985**, *26*, 1217. (4) Szantay, C. *et al. ibid.* **1980**, *21*, 2509. (5) Schwartz, M.A.; Mami, I.S. *J. Am. Chem. Soc.* **1975**, *97*, 1239. Kametani, T. *Tetrahedron* **1969**, *25*, 3667. (6) *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: London, 1978, Parts 1 and 2; *Allenes in Organic Synthesis*; Schuster, H.F.; Coppola, G.M., Eds.; Wiley: New York, 1984. (7) Taylor, E.C. *et al. J. Org. Chem.* **1972**, *37*, 2797; Myrbo, H. *et al. Synthesis* **1982**, 1101. (8) Moriarty, R.M. *et al. Tetrahedron* **1989**, *45*, 1605. (9) Moriarty, R.M. *et al. Synth. Commun.* **1988**, *18*, 1179.

17,872-1	Iodobenzene diacetate, 98% (1)	25g \$24.30
		100g \$66.40
23,213-0	[Bis(trifluoroacetoxy)iodo]benzene, 97% (2)	10g \$19.80; 50g \$65.80
30,103-5	Hydroxy(tosyloxy)iodobenzene (3)	5g \$11.90
		25g \$38.70
22,004-3	2-Iodosobenzoic acid, 97% (4)	1g \$6.50
		5g \$21.00



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