Samarium Di-iodide: A Useful Electron Donor in Organic Synthesis

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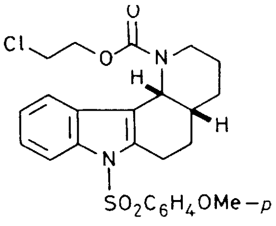
Samarium di-iodide selectively cleaves the 2-chloroethyl carbamate (**1**), and fragments the 11α-steroidal xanthate (**3**), where other reducing reagents fail.

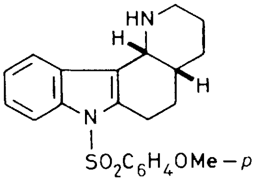
As a result of synthetic problems that required an extremely powerful reducing agent, we were attracted to the pioneering work of Kagan[1] on divalent lanthanoids in synthesis. In particular samarium di-iodide appeared to offer unique potential since it is a potent reducing agent (Sm^{2+}/Sm^{3+} = −1.55 V in H_2O) and can be readily made in anhydrous tetrahydrofuran (THF) solutions.†

We describe here the use of samarium di-iodide to solve two problems that occurred in the course of separate investigations and that could not be adequately solved by other methods.

The 2-chloroethyl carbamate (**1**)[2] required selective removal of the 2-chloroethyl protecting group to give the amine (**2**).



(**1**)



(**2**)

Exposure of (**1**) to Zn–AcOH or $CrCl_2$–HCl gave no reaction. Tri-n-butyltin hydride in xylene, initiated by azobisisobutyronitrile (AIBN) did not convert (**1**) into (**2**). Treatment of (**1**) with Zn–H_2O–THF–aquo-vitamin B_{12}[3] at 70 °C gave a small amount of (**2**) (*ca.* 10%) after several days; the major product was the 2-hydroxyethyl carbamate.

Exposure of (**1**) to samarium di-iodide (Sm–ICH_2CH_2I–

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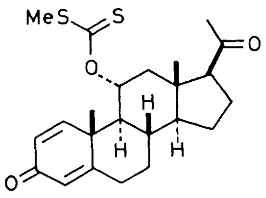
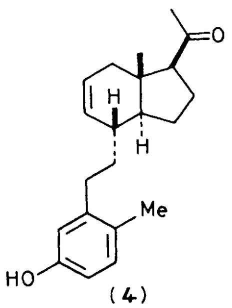
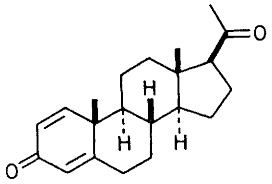
† To a suspension of samarium metal (0.452 g) in THF (10 ml; degassed), was added ICH_2CH_2I (0.404 g) in THF (15 ml). This mixture was stirred under argon until an intense blue green homogeneous solution was obtained (*ca.* 0.5 h). The substrate was added directly to the above solution.



(3)



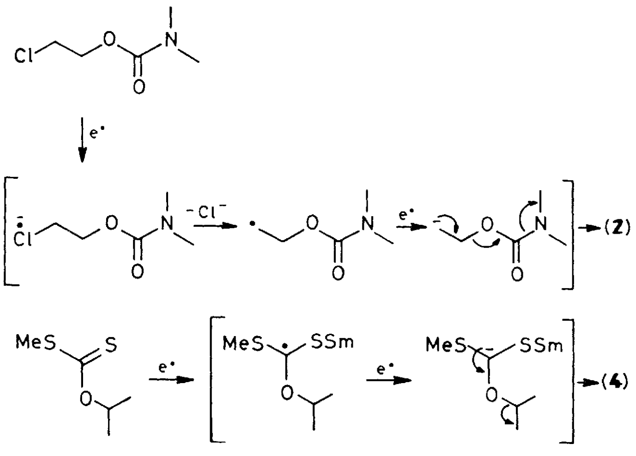
(4)



(5)

THF) at 70 °C for 7 h cleanly converted (**1**) into (**2**) in 70% yield.‡

A problem in the use of radical chemistry in synthesis is the generation of radicals for fragmentation or cyclization reactions, without competitive reduction before the desired reaction has taken place. Treatment of the steroidal 11α-xanthate (**3**)[4] with tri-n-butyltin hydride in toluene (40 h at reflux), initiated by AIBN, gave the desired 9,10-seco-steroid (**4**) and the reduction product (**5**) (1 : 1; *ca.* 50% yield). However, when (**3**) was treated with samarium di-iodide in THF at 20 °C for 5 min the 9,10-seco-steroid (**4**) was the sole product (88%). § None of the reduced material (**5**) could be detected. Treatment of (**3**) with Li–NH_3 gave a complex mixture containing neither (**4**) nor (**5**).



Scheme 1

A plausible explanation for the success of these fragmentations using samarium di-iodide in place of tri-n-butyltin hydride appears to involve the ability of the Sm^{II} to reduce rapidly a radical to an anion.[1,4] This reduction is shown in Scheme 1.

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References

1 P. Girard, J. L. Namy, and H. B. Kagan, *J. Am. Chem. Soc.*, 1980, **102**, 2693; H. B. Kagan, J. L. Namy, and P. Girard, *Tetrahedron*, 1981, **37**, Suppl. No. 9, 175.

2 For the general method of synthesizing this type of compound see: T. Gallagher and P. Magnus, *Tetrahedron*, 1981, **37**, 3889.

3 R. Scheffold and E. Amble, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 629.

4 Prepared by the procedure described by D. H. R. Barton, W. B. Motherwell, and A. Stange, *Synthesis*, 1981, 743. See also D. H. R. Barton and W. B. Motherwell, *Pure Appl. Chem.*, 1981, **53**, 15, and A. G. M. Barrett, P. A. Prokopion and D. H. R. Barton, *J. Chem. Soc., Perkin Trans.* 1, 1981, 1510 for deoxygenations of esters in general.

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‡ ^1H N.m.r. data for compound (**2**): ($CDCl_3$) δ 8.15 (1H,m), 7.72 (2H,d,*J* 8 Hz), 7.55 (1H,m), 7.22 (2H,m), 6.80 (2H,d,*J* 8 Hz), 3.96 (1H,d,*J* 3.5 Hz), 3.72 (3H,s), 3.22—2.56 (4H,m), and 1.95—1.30 (8H,m).

§ Spectral data for compound (**4**): I.r. ν($CHCl_3$) 3620, 1700, 1620, and 1600 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 7.00 (1H,d,*J* 8 Hz), 6.6 (1H,d, *J* 8 Hz), 6.65 (1H,s), 5.7 (2H,br.s), 2.17 (3H,s), 2.23 (3H,s), 0.65 (3H,s), and the methylene envelope.