

SYNLETT
Spotlight 227Selenium Dioxide (SeO₂) – A Versatile Reagent

Compiled by Annada C. Maity



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Annada C. Maity was born in Midnapore, India in 1979 and began studying chemistry at the Vidyasagar University in 1997. He received his M.Sc. in chemistry from this university in 2002 and passed the National Eligibility Test (CSIR-UGC-NET) in 2003. He joined the research group of Prof. S. P. Goswami and is currently working towards his PhD at the Bengal Engineering and Science University. His primary research interests are focused on the vicinal polycarbonyl chemistry, pterin chemistry, total synthesis, and reaction engineering.

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Dedicated to my PhD advisor Prof. S. P. Goswami on his 55th birthday

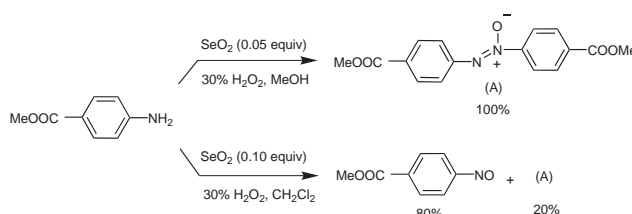
Introduction

Selenium dioxide (SeO₂) is a very useful and versatile reagent for the synthesis of various types of organic compounds. Among several oxidizing agents described for use in organic synthesis, SeO₂ has received interest as a superior oxidizing agent,¹ as dienophile agent,² oxidative bond cleaving agent,³ in the synthesis of organometallic reagents,⁴ as catalyst for synthesis of urea derivatives⁵, oxidative demethylating agent,⁶ an important agent in

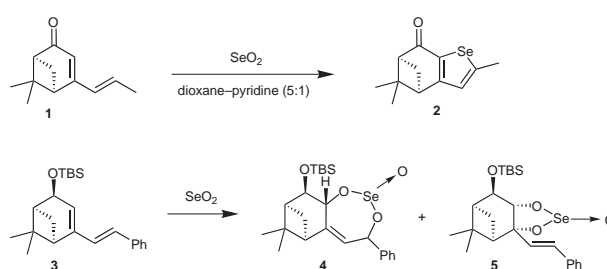
Beckman rearrangement,⁷ benzylic oxidizing agent,⁸ and as an allylic hydroxylating agent⁹ of organic molecules. Selenium dioxide is made by burning the element of Se in air. It is a white crystalline solid at room temperature with a sublimation temperature of 315 °C. The solid forms infinite polymeric chains (syndiotactic) which are not planar, but the polymeric structure breaks down in the gas phase to the monomeric covalent form, symmetrically bent like SO₂.

Abstracts

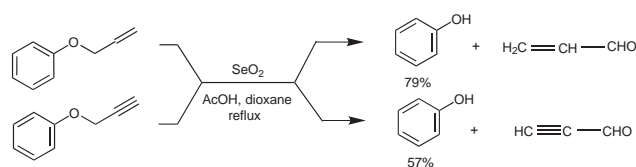
(A) *Superior Oxidizing Agent*: SeO₂ is a superior oxidizing agent for the synthesis of azobenzene and nitrosoarene from aromatic aniline using catalytic amounts of hydrogen peroxide.¹



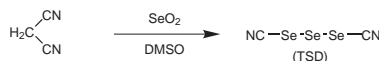
(B) *Dienophile Agent*: Selenium dioxide acts as a dienophile for the synthesis of selenophane. Selenophane **2** can easily be synthesized in high yields in a single operation from 1,3-dienes containing a carbonyl group at the C-1 position of compound **1** and selenium dioxide via a [4+2] cycloaddition, whereas an analogous diene containing a TBS-ether gives 1,4-diol cyclic selenite **4** and 1,2-diol cyclic selenite **5**.²



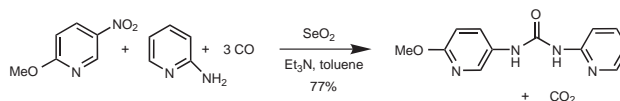
(C) *Oxidative Bond Cleaving Agent*: SeO_2 can lead to oxidative bond cleavages of allyl and propargyl ethers. Aryl allyl ether or aryl propargyl ether undergoes oxidation at the vinyl or alkynyl position to afford phenol and acrolein or propargyl aldehyde, respectively.³



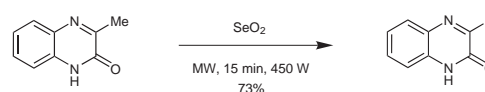
(D) *In the Synthesis of an Organometallic Reagent*: Triselenium dicyanide (TSD) is used as a selenocyanating reagent for the synthesis of aromatic and aliphatic metallo-organic selenocyanates. Triselenium dicyanide is formed by the reaction of malononitrile and selenium dioxide in dimethylsulfoxide.⁴



(E) *Catalyst*: Selenium dioxide is a good catalyst and exhibits remarkable chemoselectivity for the formation of new unsymmetric *N,N'*-dipyridyl urea derivatives by reductive carbonylation of substituted nitropyridine using carbon monoxide and amino pyridine derivatives as co-reagents.⁵



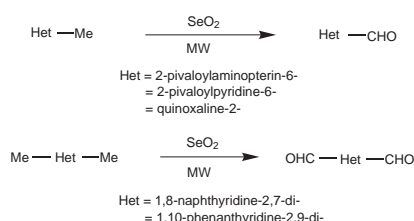
(F) *Oxidative Demethylating Agent*: Goswami and Maity have shown that SeO_2 acts not only as oxidizing agent but also as demethylating agent leading to the formation of 2(1*H*)-quinoxalinone from 3-methyl-2(1*H*)-quinoxalinone in good yield under microwave irradiation.⁶



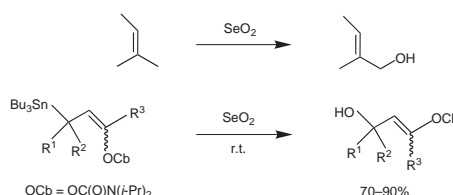
(G) *In a Beckman Rearrangement*: SeO_2 is a versatile reagent for the conversion of aldoximes into nitriles in high yield with both aliphatic and aromatic aldoximes. While the reaction proceeds with aliphatic aldoximes at room temperature in three hours, the reaction with aromatic aldoximes is achieved in boiling chloroform.⁷



(H) *Benzylic Oxidizing Agent*: Goswami and Adak⁸ have shown that SeO_2 can act as benzylic oxidizing agent for the synthesis of 2-pivaloylamino-6-formyl pterin, a new functionalized pyridine aldehyde (2-pivaloylamino-pyridine-6-carboxaldehyde) and a series of other important heterocyclic mono- and di-aldehydes (60–90%) under microwave irradiation.



(I) *Allylic Hydroxylating Agent*: Treatment of alkenes with selenium dioxide introduces a hydroxyl group in allylic position.^{9a} SeO_2 oxidation of (*Z*)-3-tributylstannyl-1-alkenyl carbamates leads to easy formation of the corresponding 3-hydroxy-1-alkenyl carbamates in high yield.^{9b}



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