

Organic Selenium and Tellurium Compounds in Organic Synthesis Symposium

ICOS-STS-1

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Applications of Tellurium Reagents in Organic Synthesis

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Chiral Organoselenium Reagents in Enantioselective Synthesis

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Synthesis of Chiral Organic Selenium and Tellurium Compounds. The Role of Biocatalysis

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Recent Advances in Radical Reactions of Organotellurium Compounds

Applications of Tellurium Reagents in Organic Synthesis

ICOS-STS-1

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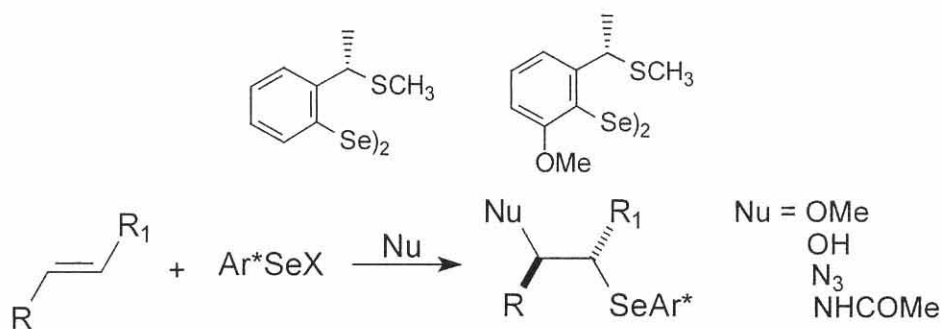
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Several synthetic methods using tellurium reagents were developed. The tellurium / metal exchange reaction and the coupling reactions of tellurides with alkynes and with organometallic species mediated by Pd and Ni are among the most studied. In this lecture, these reactions will be reviewed and recent advances in the field achieved in our group will be presented. The application of the above mentioned reactions in the synthesis of some natural products will be discussed.

Chiral Organoselenium Reagents in Enantioselective Synthesis**ICOS-STS-2****M. Tiecco**

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Starting from the recently described sulphur containing diselenides indicated in the Scheme, several asymmetric addition reactions can be effected. The products of alkoxy-, hydroxy-, azido- and amido-selenenylation of alkenes can all be obtained with high diastereoselectivity.¹⁻³ These products can be converted into other enantiomerically enriched derivatives by deselenenylation. The methoxy substituted diselenide can also be employed in catalytic amounts to promote one pot selenenylation-deselenenylation processes from which selenium free products are obtained with moderate to good enantiomeric excesses.



Asymmetric cyclofunctionalization of alkenes have been also carried out and afforded enantiomerically enriched heterocyclic compounds. The syntheses of oxazolines, thiazolines, pyrrolidines, isoxazolidines, 1,2-oxazines, cyclic nitrones and other heterocyclic compounds will be presented and discussed.

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Synthesis of chiral organic selenium and tellurium compounds. The role of Biocatalysis

ICOS-STS-3

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In recent years chiral organoselenium compounds have been prepared and some of them were applied in asymmetric synthesis. This subject constitutes a new trend in this field of organoelemental chemistry. In this way, the search for efficient methods to prepare organoselenium and tellurium compounds with high enantiomeric purities is an important goal in this area of chemistry. In the search for practical ways to generate selenium containing molecules bearing a stereogenic center, we turned our attention to environmentally friendly biocatalytic methods. The biocatalytic transformations can be performed by many classes of enzymes which are present in bacteria, fungi, yeasts and plants. In this talk, it will be presented some results obtained in our laboratory using biocatalysis in the synthesis of several chiral selenium and tellurium compounds.¹

¹ (a) Andrade, L. H.; Comasseto, J. V.; Rodrigues, D. F.; Pellizari, V. H.; Porto, A. L. M. *J. Mol. Catal B: Enzymatic* **2005**, *33*, 73. (b) Andrade, L. H.; Omori, A. T.; Porto, A. L. M. Comasseto, J. V. *J. Mol. Catal B: Enzymatic* **2004**, *29*, 47. (c) Comasseto, J. V.; Omori, A. T.; Porto, A. L. M.; Andrade, L. H. *Tetrahedron Lett.* **2004**, *45*, 473.

Chiral Selenium and Tellurium Compounds as Ligands in Enantioselective Catalytic Transformations

ICOS-STS-4

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Selenium-based synthetic methods have developed rapidly over the past decades and chiral organoselenium chemistry has become a very useful tool in the hands of organic chemists. In this context, chiral selenium-containing compounds have evolved as an interesting and promising class of ligands for asymmetric catalysis for several reasons. They are readily accessible, have a modular nature, form strong bonds with soft metals, and can be used as catalyst or ligands in metal-catalyzed transformations. The large majority of these ligands are derived from readily available chiral amino alcohols in a few high-yielding synthetic steps. As a consequence, the enantiocontrolling stereocenter resides on the atom neighboring the coordinating nitrogen from the amino alcohol pattern and, therefore, in close proximity to the metal active site, thus having a direct influence on the stereochemical outcome of the reaction.

Since the first report by Uemura *et al.* in 1994 on the use of chiral selenium-based ligands in asymmetric catalysis, a diverse variety of ligands which contain a selenium atom incorporating various heteroatoms have been used with great success in a wide range of enantioselective reactions. In our presentation we will give an overview about the use of such compounds as catalysts or ligands in the control of the enantioselectivity. At the same time, we will show our contribution to this area.

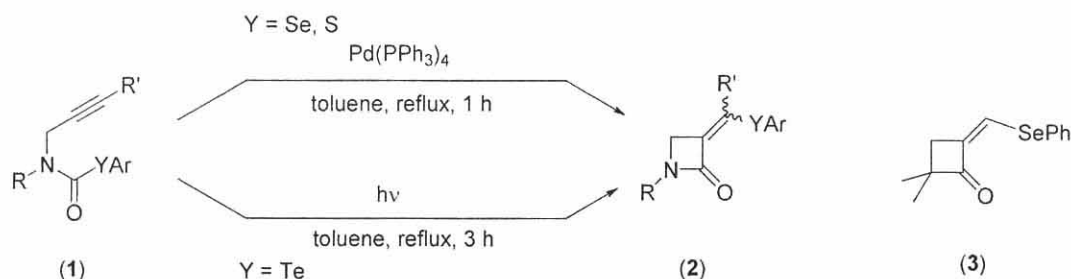
Construction of β -Lactam Frameworks by Cyclization of Organoselenium and -tellurium Compounds

ICOS-ST5-5

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Two new synthetic methods for the construction of α -alkylidene- β -lactam frameworks from carbamoselenoates and -telluroates having a propargylic group on the nitrogen atom were achieved by employing a transition metal catalyst and by photo irradiation, respectively. The first approach is based on palladium-catalyzed intramolecular selenocarbamylation of alkynes. Treatment of carbamoselenoates (1, Y = Se) with a catalytic amount of Pd(PPh₃)₄ resulted in the high-yield formation of desired lactams (2) with high regio- and stereoselectivities. The present method can be applied to construction of larger ring lactams. When a carbamothioate and a selenoester were used the expected product 2 (Y = S) and a cyclobutanone 3 were obtained. The second approach was carried out by irradiating visible light to carbamotelluates (1, Y = Te) and the corresponding β -lactams (2) were obtained via 4-*exo-dig* cyclization of carbamoyl radicals as a key step.



Recent Advances in Radical Reactions of Organotellurium Compounds

ICOS-STS-6

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Radical-mediated carbon–carbon bond formations have become extremely useful in modern synthetic applications. Radicals are neutral, “soft” and highly reactive species, and thus the radical-mediated reaction enjoys the full advantage of these characteristics over ionic reactions. Organoiodine compounds have been most widely used as radical precursors. While organotellurium compounds have been sometime used as radical precursors, their synthetic advantage has not been well understood. In this lecture, I will present highly controlled radical reaction using organotellurium compounds. Our results clearly demonstrate wider synthetic utilities of organotellurium compounds than organoiodine compounds in selective radical reactions.

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