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Tribute

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Professor Saverio Florio

A Tribute

This special issue of Arkivoc (Archive for Organic Chemistry) is dedicated to Professor Saverio Florio, S.; to acknowledge his contribution to synthetic organic chemistry

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Prof. Saverio Florio, S.; was born at Toritto (a small city in the Province of Bari, Italy) in 1940. He received his Italian "Laurea" degree in Chemistry from the University of Bari in 1967 (supervisor Prof. Paolo Edgardo Todesco). Following his graduate school, Florio, S.; was appointed as an Assistant Professor to the Faculty of Pharmacy at the University of Bari in 1973. From 1978 to 1979 he was Research Fellow at the University College of North Wales-Bangor (UK) in collaboration with Prof. Charles J. Stirling on a joint project with ICI (Organic Division) of Manchester on the synthesis of new organic dyes. Promoted to Associate Professor in 1982 at the University of Bari he went on to full Professor of Chemistry in 1986 as at the chair of Organic Chemistry of the Faculty of Sciences of the University of Lecce. In 1990 he returned to the University of Bari as the chair of Organic Chemistry of the Faculty of Pharmacy.

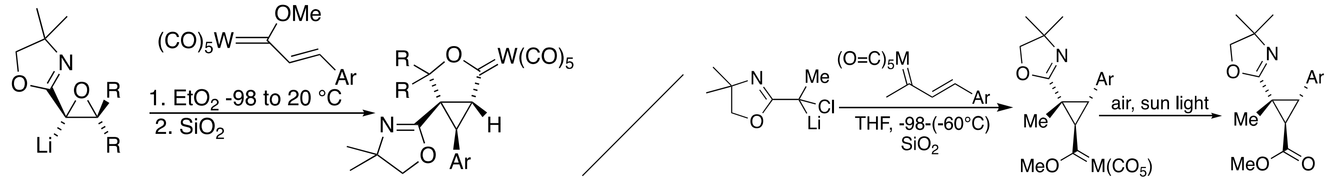
Prof. Florio, S.; has held numerous responsibilities at the University of Bari during his career: chair of the Department of Pharmacy (1994-1997), Director of the CINMPIS CONSORTIUM (a group of 15 Italian Universities) for Innovative Synthetic Methodologies and Processes; member of the scientific committee of Ischia Advanced School (IASOC); Vice-President, President and Past-President of the Division of Organic Chemistry of the Italian Chemical Society (1993-2004) and Vice-President of the Italian Chemical Society (2008-2010), member of the academic Senate of the University of Bari (2008-2010), member of the scientific committee of Doctorates for Chemical Sciences and Chemical and Enzymatic Synthesis of the University of Bari. Prof. Florio, S.; led numerous Italian ministerial research projects (PRIN, FIRB and MIUR from 1997 to 2010) on the stereoselection in organic synthesis. He led MIUR Project PON01_00862 focused on the synthesis of new drugs for rare diseases. He is founding partner of the academic spin-off Synchimia (University of Bari) based on development of synthesis of optically active molecules of pharmaceutical interest, new materials and nanomaterials for photonics and electronics.

As an invited speaker Prof. Florio, S.; attended several international advanced schools meetings on Organic chemistry: "Seminars in Organic Synthesis" (Gargnano, Italy, 1984, 1992, 2001); "Asymmetric Synthesis: Advanced Methodologies and Recent Achievements" (Urbino Italy, 2002); VII Laboratory of Synthetic Methodologies in Pharmaceutical Chemistry (Siena, Italy, 2008); Ischia Advanced School of Organic Synthesis (IASOC, at Ischia, Italy, 2006); New Horizon in Organic Synthesis at the University of Milano (1999); Task Group Chair of the IUPAC Strategic Planning Project for a new Network for organic and heterocyclic chemistry among Countries of the Mediterranean Sea Area including Europe, North Africa and West Asia (2011-2022), Member of the European Academy of Sciences and Arts (Salzburg 2012).

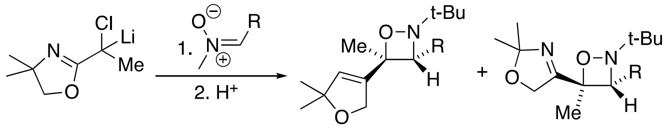
Prof. Florio is a member of the Italian Chemical Society, the Royal Society of Chemistry, the American Chemical Society, the International Society of Heterocyclic Chemistry, Honorary Member of Israel Chemical Society, member of the Board of Consulting Editors of Tetrahedron and Tetrahedron Lett., as well as a member of the Arkivoc Editorial Board of Referees.

Prof. Florio's Scientific Interests

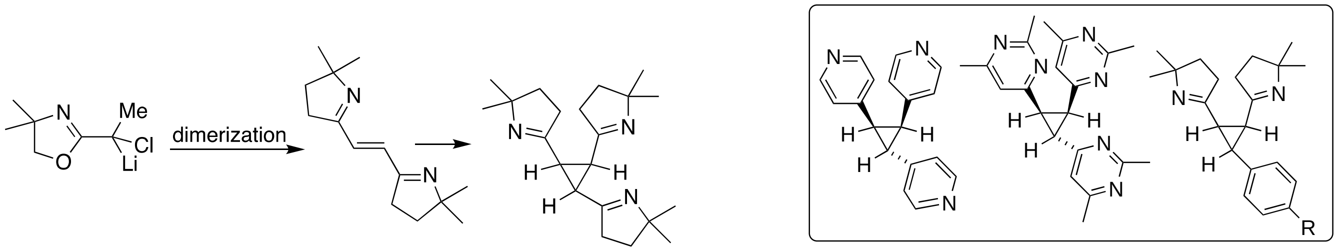
Prof. Florio's research achievements have been published in more than 200 publications on important international Journals. Research interests are mainly oriented to the design and application in stereoselective organic synthesis with polar organometallic reagents with special emphasis on organolithium and the elucidation of the structure-reactivity relationship of reactive lithiated intermediates by a combination of multinuclear magnetic resonance investigations, X-ray data and *ab initio* calculations. The latter allowed the assertion of new reaction mechanisms, alternative or in competition with the classic S_NAr mechanism with σ-anionic Meisenheimer intermediate such as "normal"-, "cine-substitution" involving "Elimination-Addition" process instead of the "Addition-Elimination" one mechanisms.[1] Back to Bari from Bangor (1979) Prof. Florio initiated an in-depth study on the reactions of heterocyclic systems with organometallic reagents. Within this research area he developed a diastereoselective synthesis of functionalized bicyclic and cyclopropylcarbene tungsten complexes from lithiated oxiranes and carbenes leading to cyclopropane-γ-lactones. Substituted cyclopropanes could also be prepared from lithiated chloroalkyloxazolines and carbene complexes.[2]



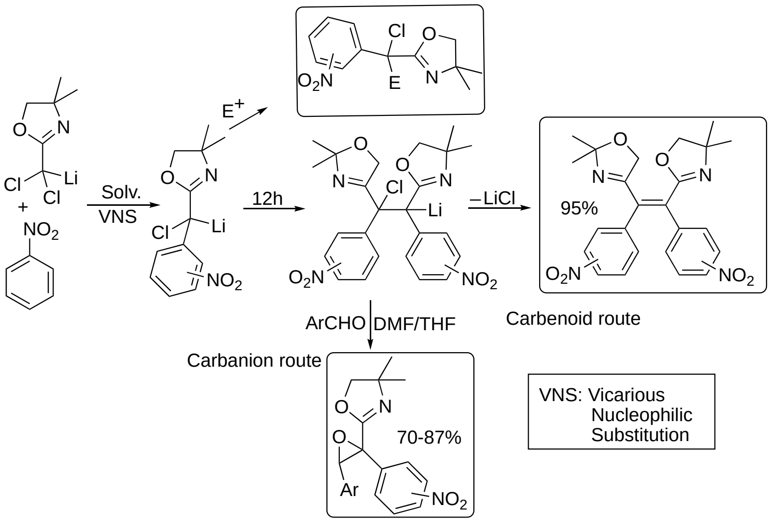
Trapping with nitrones gave benzothiazolyl epoxides.[3] The first stereoselective synthesis of oxazolinyl-(1-2)-oxazetidines was developed by the reaction of lithiated chloroethyl-2-oxazolines with nitrones.[4]



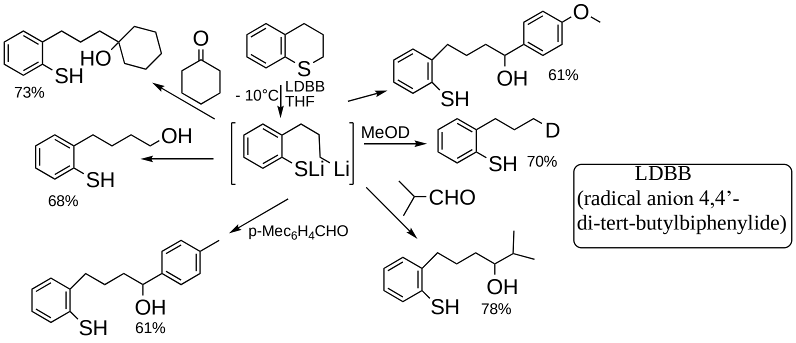
Lithiated chloromethyloxazoline has a carbenoidic property so that it tends to undergo an eliminative dimerization affording the dioxazolinyl ethene and the tri-oxazolinylcyclopropane.[5]



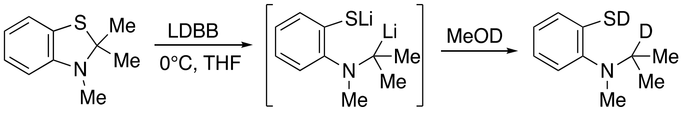
Lithiated dichloromethyloxazoline manifests its carbenoidic character leading to tetraheterosubstituted ethene, aryl-nitroaryl-oxazolinyl epoxide and simple nucleophilic substitution products.[6]



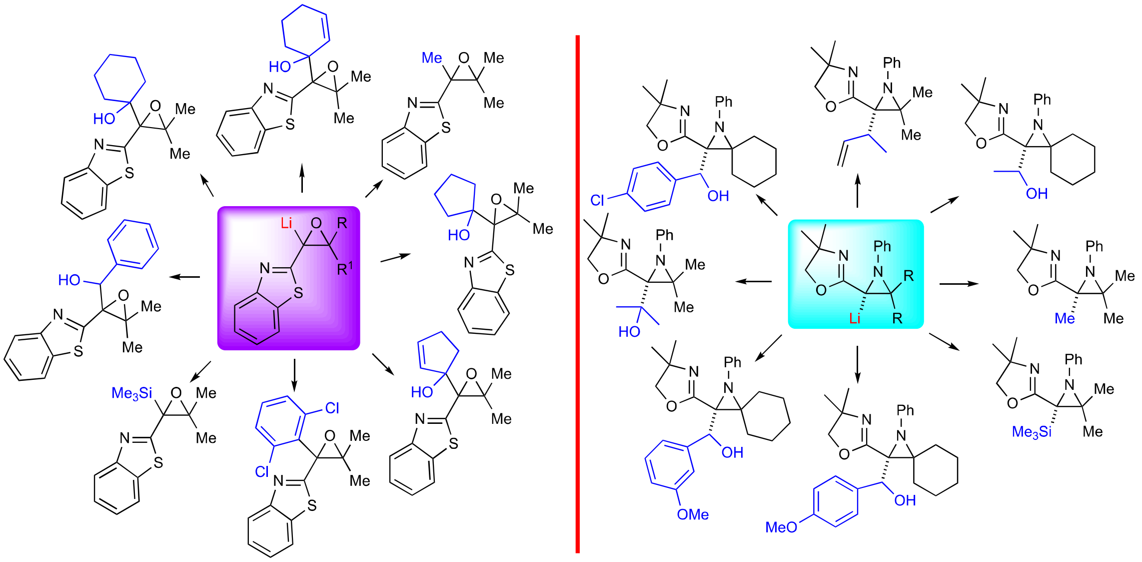
Reductive ring cleavage of thiochromane by LDBB produced a dianion which could be captured with MeOD and carbonyl compounds.[7]



α-Heterosubstituted carbanions are intermediates of great utility in organic chemistry. While stabilized α-amino carbanions are well known, unstabilized α-aminocarbanions have received little attention. Florio's group has reported on the generation and trapping of α-amino tertiary carbanions.[8]

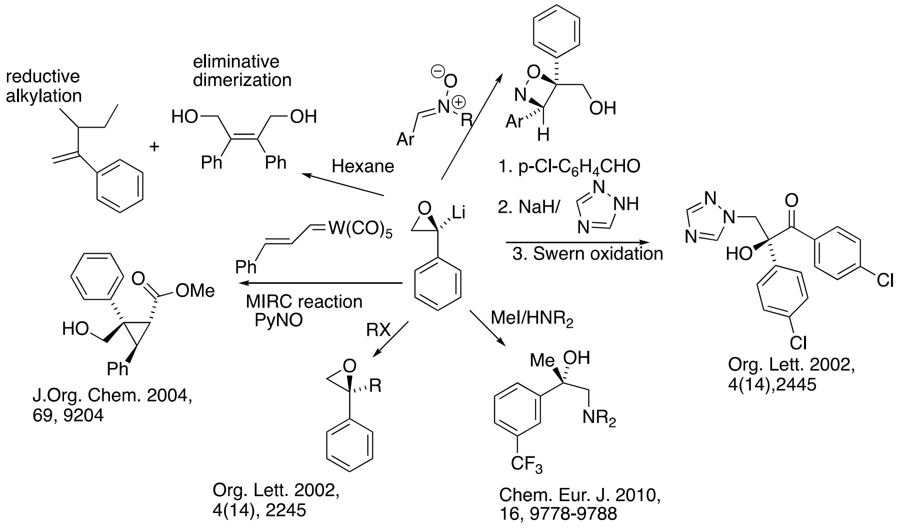


Strained small-ring heterocycles are very useful building blocks in organic synthesis. Their α-anionic forms (α to the heteroatom) proved to be even more useful. α-Lithiated oxiranes, for long time considered as fleeting intermediates in reactions of epoxides with strong bases, are nowadays useful synthons because of their chameleon-like character which gives them the ability to react either with electrophiles and with nucleophiles.[9]

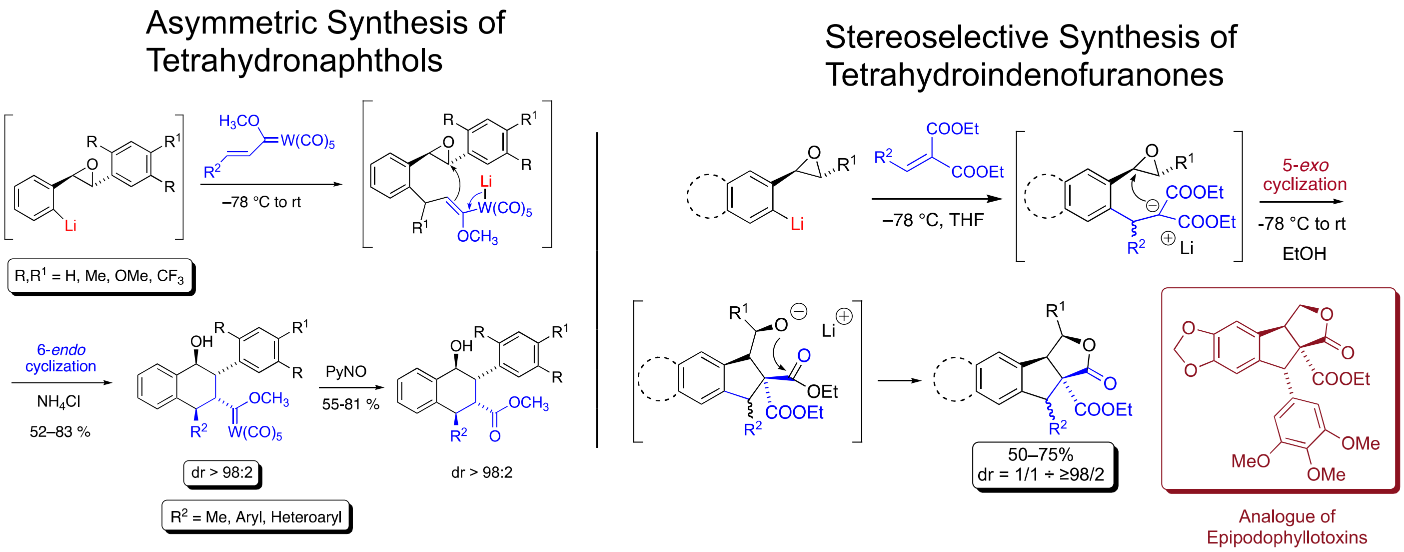


Florio, Ingrosso, Troisi and Lucchini,' Tetrahedron Lett. **1993**, 34, 1363-1366; Florio, Troisi, Tet. Lett. **1992**, 33, 7953-7956; Florio,Troisi,Capriati, Ingrosso, *Tet. Lett.* **1999**, *40*, 6101

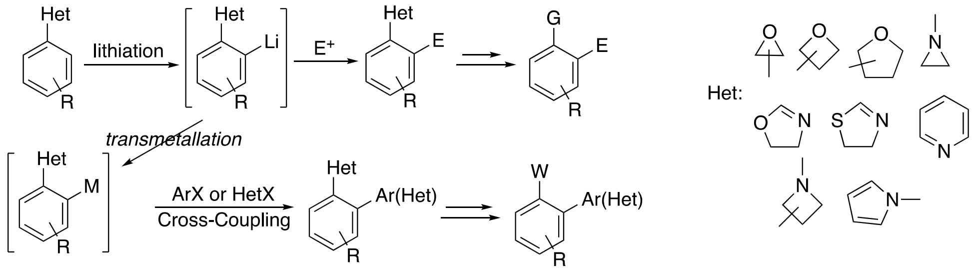
α-Lithiated oxiranes can be kept at low temperature for long time. A multinuclear magnetic resonance, supported by density functional theory calculations, has been synergically used to investigate the configurational stability, reactivity and aggregation states of α-lithiated styreneoxides concluding that in THF at 173 K they are mainly present as a THF-solvated monomeric species in equilibrium with dimers.[10] It was also proven that the configurational stability of α-lithiated styreneoxides depends on the aryl-substituents (EWG or EDG).[11] The fascinating carbenoid character of the epoxide anion is manifested in a number of reactions.[12]



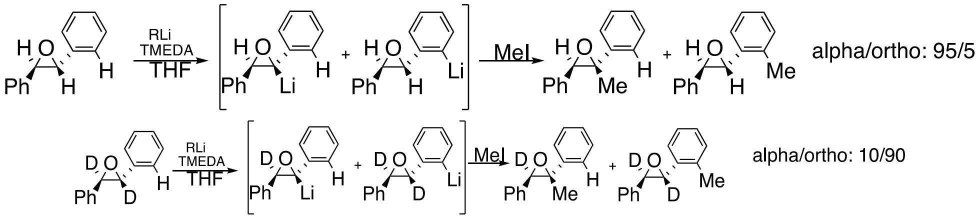
Ortho-lithiated aryloxiranes, whose generation competes with that of the α-counterparts, are useful building blocks for more complex heterocycles.[13]



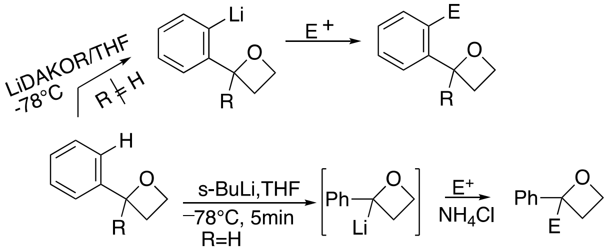
Organic synthesis relies on the transformation of functional groups (oxygen-, sulfur-, nitrogen-, halogen-containing groups) exhibiting high chemical reactivity. The direct cleavage of a strong unreactive C-H bond, followed by the formation of a new C-C or C-X bond at a specific site within a molecule, constitutes an ideal synthetic operation. The capacity to activate a specific C-H bond and transform it into a more versatile functional group represents an important and long-standing goal in chemistry. These transformations are efficiently addressed by using substrates with a suitable directing group (DG) whose role is to activate a specific C-H bond taking advantage of its electronic and coordinating properties, thus resulting in high levels of regioselectivity and increased reactivity. Electrophilic aromatic substitution (EAS) is a traditional method of synthesis of functionalized aromatic compounds but aromatic conditions are typically harsh and regioselectivity is generally poor. Moreover, hydrogen nucleophilic aromatic substitution (S_NArH) suffers, like the EAS method, from poor regioselectivity. Compared to EAS and S_NArH methods, directed *ortho*-metalation (DoM) guarantees very high regioselectivity in the *ortho* functionalization of arenes. The utility of the synthetic elaboration of the heterocyclic moiety is also important for synthesis. It is possible to access interesting molecules by combining DoM methodology with Negishi or Suzuki–Miyaura cross-coupling protocols. Among the DMG groups the heterocyclic groups play an important role in the ortho-metallation process. In this field Prof. Florio's research group privileged the use of small-ring heterocycles as DoM, as in the following scheme.



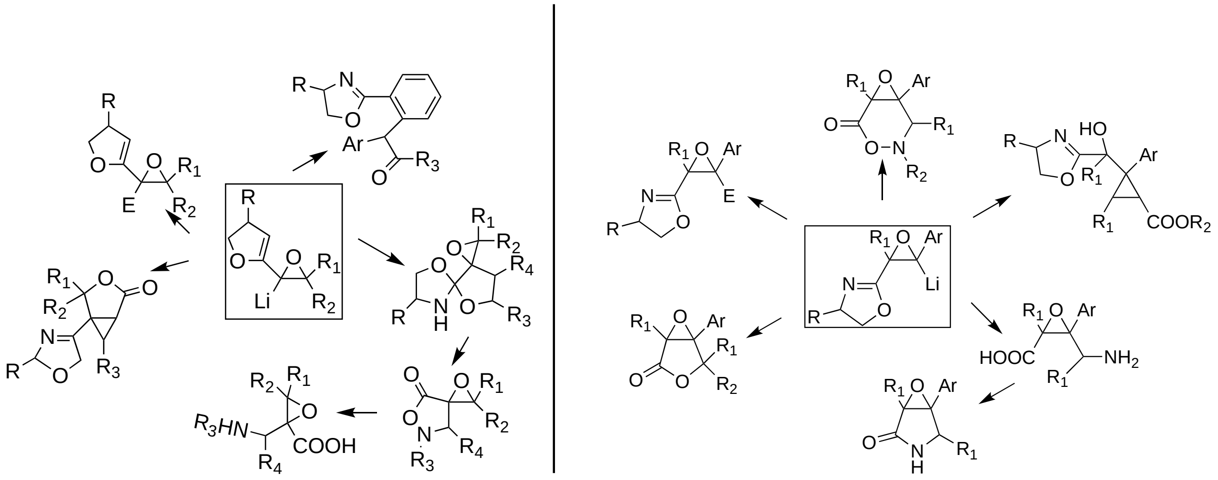
α-Lithiation trapping sequence of trans-stilbene oxide with MeI affords a mixture of *alpha* and *ortho* methylated stilbene oxides. The ortho methylated stilbene oxide can be prevalently obtained starting from the dideuterostilbene oxide likely for a strong isotopic effect.[14]



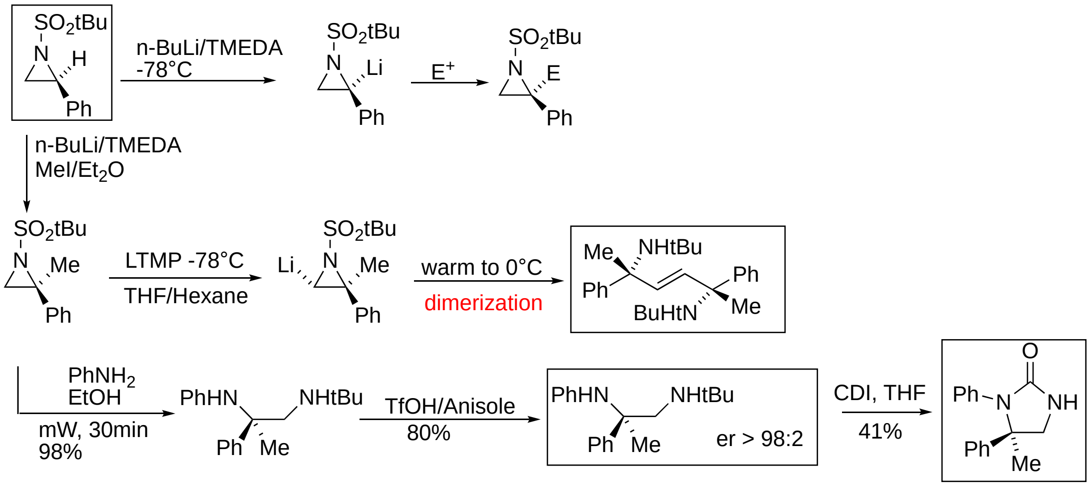
Compared to ethers and epoxides, the reactivity of oxetanes with organometallic reagents has been much less investigated. Quite recently 2-phenyloxetane has been reported to undergo clean α-(benzylic)lithiation with sec-BuLi to give, after trapping with electrophiles, various disubstituted oxetanes.[15]



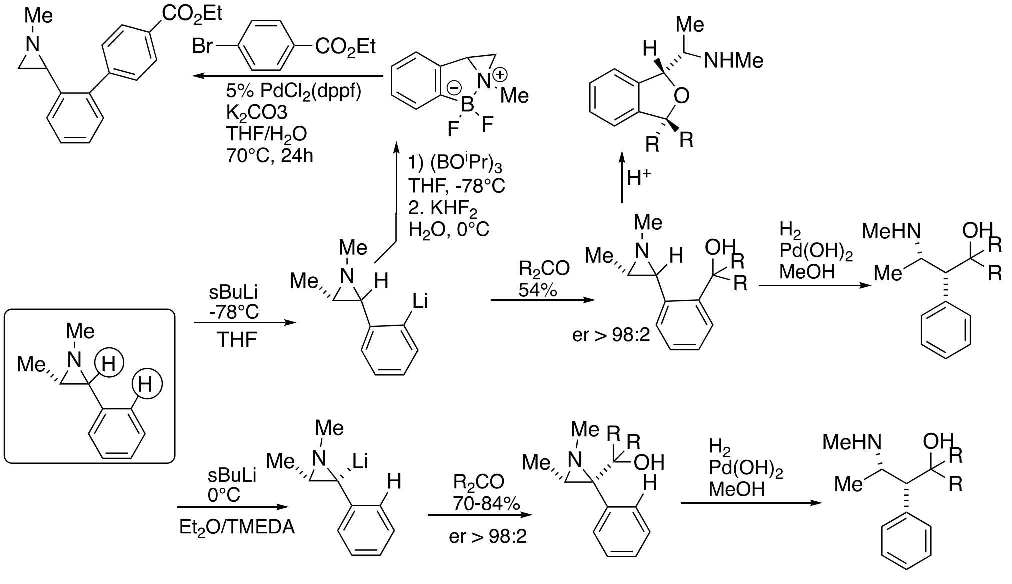
An EWG such as an oxazolinyl group, which is a well-known masked form of the carbonyl group, is an ideal stabilizing group for α-lithiated oxiranes: it is amenable to synthetic elaboration and the presence of stereocenters on the heterocyclic ring could induce asymmetry in the reactions of the related lithiated oxiranes. Lithiated 2-oxazolinyloxiranes are particularly attractive reactive intermediates in synthetic organic chemistry for being susceptible of elaboration to a variety of other substances such as more functionalized oxiranes, acyloxiranes, spirocyclic compounds, polysubstituted cyclopropanes, epoxylactones, epoxyisoxazolinones.[16]



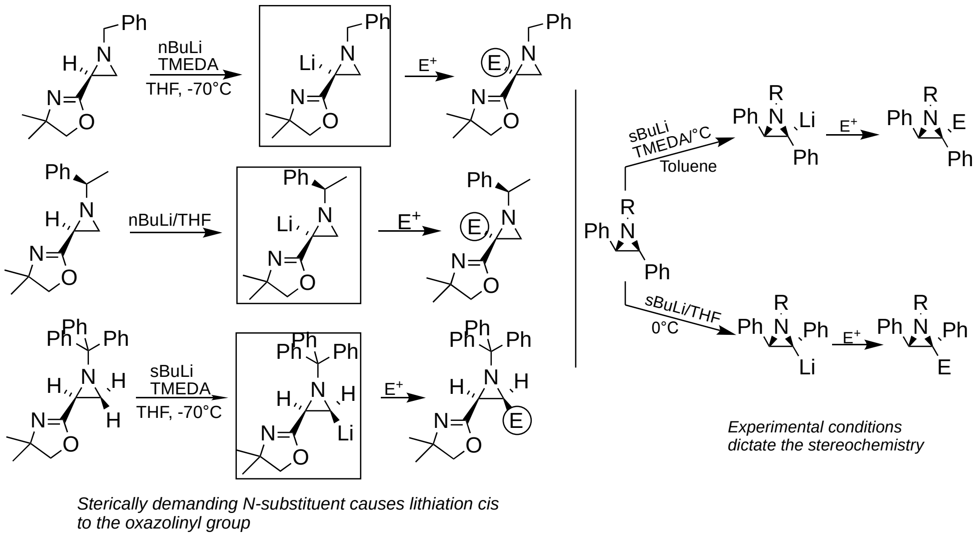
Aziridinyl anions, proposed for the first time by Turner[17] can be generated by desulfinylation, desilylation and deprotonation of aziridines; they share some aspects of reactivity with oxiranyl anions. In analogy, their carbenoidic character has been demonstrated for some aziridinyl anions bearing an (EWG) as the N-substituent as in their reductive alkylation and eliminative dimerization. Lithiated aziridines, once generated, can be captured by electrophiles, leading to more highly functionalized derivatives. Nitrogen dynamics and complexation phenomena play crucial roles in determining the regiochemistry of the lithiation process of aziridines and the stereochemistry of the reactions of the resulting lithiated species with electrophiles. The lithiation-trapping sequence of N-sulfonylaziridine is a good route to more functionalized aziridines and ene-diamines as a result of an eliminative dimerization of the lithiated starting aziridine.



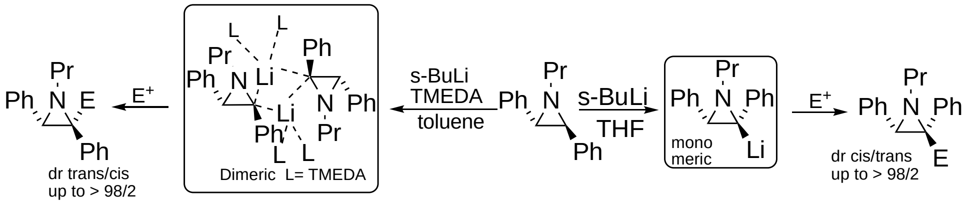
The trapping of *ortho*-lithiated aziridine with alkylborates followed by reaction with KHF_2 gives the cyclic aziridinedifluoroborate which behave as a Suzuki-Miyaura reagent in a palladium-catalyzed cross-coupling reaction. In contrast, α-lithiation of the starting aziridine followed by trapping with a ketone ends up with the formation of a 1-3-aminoalcohol.[18]



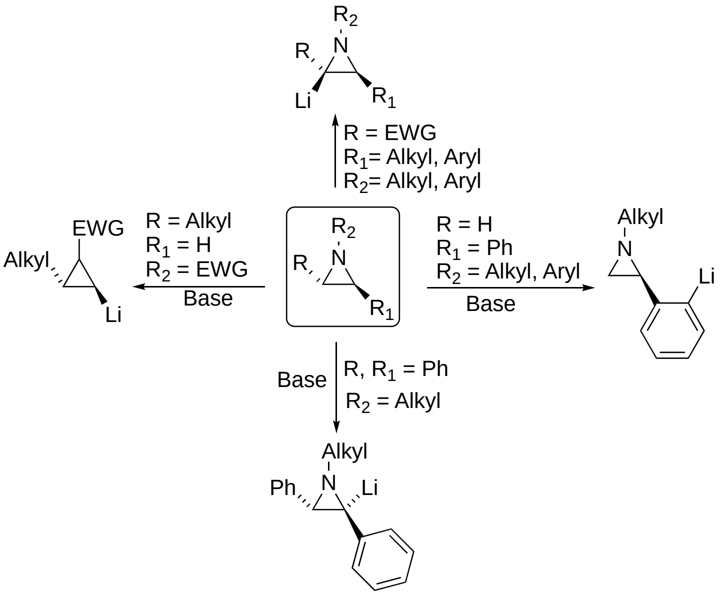
Lithiation of aziridines followed by trapping with electrophiles is an appealing methodology for making more functionalized aziridines, which are useful building blocks for stereoselective synthesis. The regioselectivity of the lithiation step substantially depends upon the nature of the aziridine ring substituents as well as on the stereochemistry at the nitrogen atom. In the ample territory of metallated aziridines the lithiated oxazolinyl aziridines play a very important role as the oxazolinyl group affects reactivity, stability and stereochemistry of the reactions with electrophiles.[19] Synthetic utility of lithiated aziridines is in the following scheme:



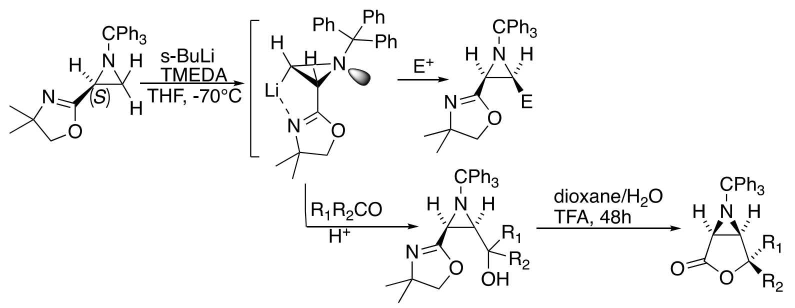
The α-lithiation-trapping sequence of substituted aziridines takes place with a stereochemistry which depends on the solvent coordinating ability (inversion of configuration in THF and retention in toluene) has been carefully investigated. Multinuclear NMR investigation at low temperature suggests that two differently configured lithiated aziridines (monomeric cis in THF and dimeric trans in toluene) are involved.[20]

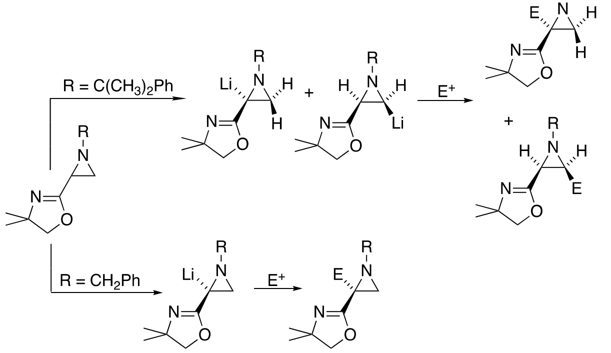


The lithiation of terminal oxazolinylaziridines can be regio- and stereoselective depending upon the aziridine N-substituent and the oxazolinyl group effect.



The oxazolinyl group has proven to be an exstraordinary good stabilizing group either for oxiranyl or aziridinyl anions. In its presence, lithiation occurs always α to it if there is an α hydrogen; it occurs β only when there is no α hydrogen. Here is reported the first example of a stereoselective lithiation taking place β to EWG aziridine ring substituent: the case of (*S*)1-trityl-2-oxazolinylaziridine. It is remarkable that lithiation occurs at the β position cis to the oxazolinyl group although in the presence of the more acidic α hydrogen. This can be explained with the strong stabilizing effect of the oxazolinyl group which chelates the (*S,S*) β-lithiated species and the presence of the sterically demanding competition between α and β lithiation (with respect to the oxazolinyl ring) occurred with the N-cumylaziridine as proved by the trapping of the lithiated intermediates.





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Selected Publications

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Prof. Florio supervised 40 doctoral students and 30 Diploma or PhD students. Through his more than 50 years at the University of Bari and Lecce, he has been a dedicated teacher of organic chemistry for chemistry students in the Laurea of Chemistry and PhD programs with a high passion. His infectious enthusiasm for science and learning has been shared with PhD students, postdoctoral research associates along with more than 100 undergraduate students. The training in critical thinking and problem solving provided by Prof. Florio, S.; has resulted in his students being prepared for success in areas far outside of the "box" of synthetic organic chemistry. Many of his students and coworkers have gone on to successful careers in academia, governmental service, industrial research, scientific and business management, medical research. He organized numerous international meetings on various aspects of organic chemistry.

Prof. Florio's scientific awards

2005: "Ziegler-Natta Lecture" from the German Chemical Society for his studies on oxiranyl and aziridinyl anions and their applications in organic synthesis.
2007: "Gold Medal-Angelo Mangini" from the Division of Organic Chemistry of the Italian Chemical Society for his studies on small ring heterocycles and his organizational scientific activity.
2010: "First Lecturer of the Slovenia-Italy Lectureship" for his high scientific reputation, creativity and for his interpersonal skills.
2014: "Silver Plate" from the Consortium CINMPIS for his commitment to the enhancement and promotion of the CINMPIS activities.
2010: Meeting on the "Chemistry of organolithiums" organized at the University of Bari on the occasion of his 70th birthday.
2011: "Honorary Membership" from the Israel Chemical Society.

Prof. Saverio Florio's hobbies and interests

In his youth Florio, S. enjoyed playing football, cycling, travelling, meeting friends, attending conferences, listening music, going to cinema. After his retirement he takes care of a country property producing almonds, olive oil, fruits. He has also started being scientifically interested in Blood Anticoagulants.