49EME SEMAINE D'ÉTUDES DE CHIMIE ORGANIQUE

Les Balcons du Lac – Annecy

May 20 – 26, 2012

seco 49
Semaine d'Etudes de Chimie Organique

We gratefully acknowledge generous financial support from the following companies or organisations:

Welcome to SECO 49,

One important specific aim of the SECO 49 is to help prepare PhD students and colleagues to subsequently present their work and results at international conferences.

Therefore, and to help them overcome their shyness and inhibitions, The SECO 49 will be held in English, in the presence of renowned (but accessible) speakers, and along a schedule similar to those of actual standard meetings.

An effort is being made to preserve the friendly and convivial atmosphere that characterises the SECO and to favour contacts and exchanges.

The senoir participants are expected, not only to be exemplar speakers, but also benevolent teachers in the art of presenting scientific results in English, captivating the audience, conveying messages, inviting and answering questions, opening stimulating dialogues, esthablishing contacts, and possibly initiating future collaborations.

Such exchanges will be facilitated by the limited number of participants, all accommadated in a same small (yet not too monastic) « Village Vacances » hostel, having meals together and enjoying social get-togethers.

Thanks in advance to all participants for their contribution to making the SECO 49 a useful, fruitful, friendly and memorable one.

The Organisation Commitee.

Organisation Commitee

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Ecole européene de chimie, polymères et matériaux (ECPM)
Laboratoire de stéréochimie
25, rue Becquerel
F-67087 Strasbourg

Vice-President
Florence Giormal - florence.giormal@gmail.com
Ecole européene de chimie, polymères et matériaux (ECPM)
Laboratoire de stéréochimie
25, rue Becquerel
F-67087 Strasbourg

Treasurer
Simon Janody - simon.janody@icsn.cnrs-gif.fr
Institut de Chimie des Substances Naturelles
UPR 2301
Bât. 27, Avenue de la terrasse
91198 Gif-sur-Yvette

Vice-Treasurer
Nicolas Gigant - nicolas.gigant@univ-orleans.fr
Institut de Chimie Organique et Analytique (ICOA)
Université d'Orléans
Rue de Chartres
45067 Orléans cedex 2

Secretary
Charlotte Sevrain - charlotte.sevrain@univ-brest.fr
Chimie et Electrochimie Moléculaire et Chimie Analytique (CEMCA)
Equipe Phosphore et Vectorisation
Université de Bretagne Occidentale
6, avenue Victor le Gorgeu
29238 Brest cedex 3

Julie Masaad - julie.massaad@gmail.com
Intéractions Moléculaires et Réactivité Chimique et Photochimique (IMRCP)
Université Paul Sabatier
118, route de Narbonne
31062 Toulouse cedex 9

Stéphanie Courtiol Legourd - stephanie.courtiol-legourd@u-psud.fr
Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO)
Université Paris-Sud, Bât 420
91405 Orsay Cedex

	Monday 20th	Tuesday 21th	Wenesday 22th	Thursday 23th	Friday 24th
8h45	Opening	Kamal Sbargoud *ILV, Versailles*	Anirban Pradhan *CRPP, Bordeau*		
9h00	Camille Decroocq *ECPM, Strasbourg*	David Sigwalt *ECPM-CAMB, Strasbourg*	Ahmad El Hellani *LCM-ICMMO, Orsay*	Naoko Kotera *CEA-IBiTec-S, Gif-sur-Yvette*	Amandine Altmayer-Henzien *ICMMO, Orsay*
9h15	Amandine Noël *ICSN, Gif-sur-Yvette*	Faisal Nawaz *STéRéO, Marseille*	Oleksandr Koniev *Faculté de pharmacie, Illkirch*	Vincent Medran Navarrete *CEA-IB^{2}M, Gif-sur-Yvette*	Bixue Xu *IPCM-UPMC, Paris*
9h30	Mélanie Charpenay *LIT, Illkirch*	Mathias King *Faculté de pharmacie, Illkirch*	Thomas Bura *LCOSA-ECPM, Strasbourg*	Florian Medina *UCCS-ENSCL, Lille*	Rémy Hemelaere *ICMV, Rennes*
9h45	Alaric Desmarchelier *ILV, Versailles*	Nicolas Kern *LASYRO, Strasbourg*	Farah Ibrahim *ICMMO-PRASE, Orsay-Beyrouth*	Jérome Michaux *SERCO, Grenoble*	Coralie De Schutter *ENSICAEN, Caen*
10h00	Guillaume Compain *IC2MP, Poitiers*	Wilfried Raimondi *iSm2, Marseille*	Jing Yang *ICMMO-LCM, Orsay*	Thomas Priem *IRCOF, Rouen*	Benoît Riflade *UPMC, Paris*
10h15	Sophie Borghese *LASYRO, Strasbourg*	Xiang Hong *LCM-ICMMO, Orsay*	Denis Frath *LCOSA, Strasbourg*	Gilles Caillot *LCC-UPS, Toulouse*	Huanhuan Qu *IPCM, Paris*
10h30	**Morning Break**	**Morning Break**	**Morning Break**	**Morning Break**	**Morning Break**
11h00	Nicolas Cheval *LASYRO, Strasbourg*	Parantap Sarkar *CRPP, Bordeau*	Paco Raya *LASYRO, Strasbourg*		Aymeric Lepronier *ISM2, Marseille*
11h15	**Pr Jérome Lacour** ***Université de Genève***	**Dr Stellios Arseniyadis** ***ESPCI, Paris***	**Dr Alain de Mesmaeker** ***Syngeta***	**Dr David Bernier** ***Bayer***	**Pr David Virieux** ***ENSC Montpellier***
12h15	Lunch	Lunch	Lunch	Lunch	Lunch
14h00	Steven Giboulot *IPCM-UPMC, Paris*	Carolin Heescher *JGU, Germany*	**Cultural and Sport Activities**	Dénia Mellal *UPMC, Paris*	Benoît Bolte *DCSO, Palaiseau*
14h15	Christophe Aube *CEISAM, Nantes*	Ludovic Raffier *ICBMS, Lyon*		Jérémy Dardenne *ICSN, Gif-sur-Yvette*	Zein el abidine Chamas *SRSMC, Nancy*
14h30	Mathieu Cyklinsky *UPMC, Paris*	Cathleen Pierre *ICBMS, Lyon*		Hugo Lenormand *IPCM, Paris*	Esma Maougal *CEISAM, Nantes*
14h45	Sandra Rihn *LCOSA, Strasbourg*	Claudine Schlemmer *JGU, Germany*		Dan-Andrei Catana *SPCMIB, Toulouse*	Bénédicte Pesset *IREBS, Illkirch*
15h00	Wenjun Liu *LCBM, Strasbourg*	Alexander Stoye *JGU, Germany*		Charlélie Bensoussan *ESPCI, Paris*	Sonia Montel *AM2N, Montpellier*
15h15	Frédéric Macé *SERCO, Grenoble*	**Afternoon Break**		Min Huang *ICSN, Gif-sur-Yvette*	Bernard Pagoaga *ICMR, Reims*
15h30	**Afternoon Break**	**Dr Philippe Dauban** ***ICNS, Gif-sur-Yvette***		**Afternoon Break**	**Afternoon Break**
16h00	Emilien Demory *DCM-ICMG, Grenoble*			Audrey Giros *ICMMO, Orsay*	Sameh Aoun *CEISAM, Nantes*
16h15	**Dr Sandrine Chodorowski-Kimmès** ***L'Oréal***	**Dr Frédérick Calo** ***Basf***		**Dr Emmanuel Magnier** ***Université de Versailles***	**Dr Christophe Coudret** ***IMRCP, Toulouse***
17h15	End of the day	17h30 End of the day		End of the day	End of the day

Monday Morning

DECROOCQ Camille

The multivalent effect in glycosidase inhibition: design and synthesis of cyclodextrin- and C_{60}- based iminosugar click clusters

NOEL Amandine

Comparison of the reactivity of β-thiolactones and β-lactones

CHARPENAY Mélanie

New synthetic strategies around palladium catalysis: a one-pot access to [4.6.4.6]fenestradienes and cyclooctatrienes

DESMARCHELIER Alaric

Enantioselective organocascade synthesis of 3-pyrrolines bearing a quaternary stereocenter

COMPAIN Guillaume

Stereo- and Regio-selective synthesis of *α*-fluoroenamides in superacid: new rigid urea biososters

BORGHESE Sophie

Silver(I)-USY zeolite as green catalyst for the preparation of ketals and spiroketals from alkynols and alkynediols

CHEVAL Nicolas

Synthetic tools for Organic Electronic applications:
Oligo- and poly-arylenes ethynylenes

Pr. LACOUR Jérome

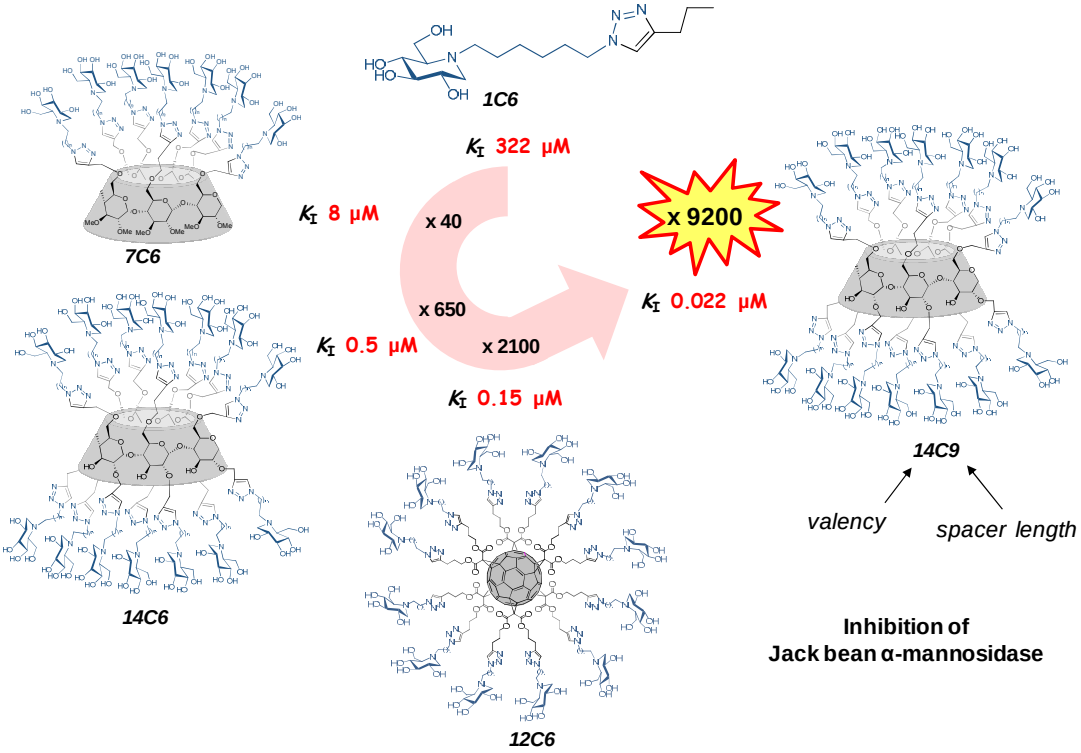
Investigations in selective synthesis & catalysis

THE MULTIVALENT EFFECT IN GLYCOSIDASE INHIBITION: DESIGN AND SYNTHESIS OF CYCLODEXTRIN- AND C_{60}- BASED IMINOSUGAR CLICK CLUSTERS‡

C. Decroocq, D. Rodríguez-Lucena, V. Russo and P. Compain*

Laboratoire de Synthèse Organique et Molécules Bioactives, UMR 7509, UdS, CNRS, ECPM, 25 rue Becquerel, 67087 Strasbourg; Emails: philippe.compain@unistra.fr, camille.decroocq@etu.unistra.fr

In the past decade, spectacular results have been obtained with multivalent ligands in the field of carbohydrate-lectin interactions.[1] In contrast, only few studies have been directed towards glycosidase inhibition with multivalent glycomymetics.[1,2] New multivalent analogs of 1-deoxynojirimicin, a famous glycosidase inhibitor,[3] have been synthesized by means of copper catalysed azide-alkyne cycloaddition (CuAAC). The different products with different cores (cyclodectrin, fullerene), different valency and



different spacer length have been evaluated toward a panel of glycosidases.

We present here the first examples of strong multivalent effects on glycosidase inhibition with binding enhancement up to four orders of magnitude over the corresponding monovalent ligand.[4,5,6]

References:

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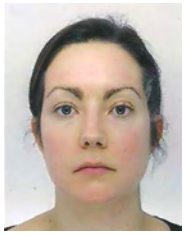
‡This work was made in collaboration with the teams of Dr. J.-F. Nierengarten, (laboratoire de Chimie des Matériaux Moléculaires, Strasbourg) and of Pr. Ortiz Mellet, (Universidad de Sevilla, Sevilla).



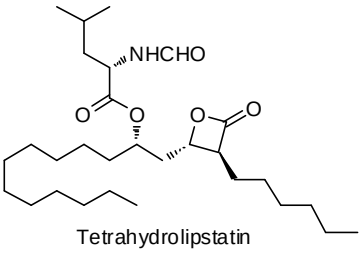
COMPARISON OF THE REACTIVITY OF B-THIOLACTONES AND B-LACTONES.

Amandine NOEL,[a] Bernard DELPECH,[a] David CRICH.[a,b]

[a]*Centre de Recherche de Gif, Institut de Chimie des Substances Naturelles, CNRS, 1 Avenue de la Terrasse, 91190 Gif-sur-Yvette, France,*

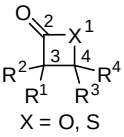
[b]*Department of Chemistry, Wayne State University, Detroit, MI 48202, USA.*

Over the years, much attention has been focused on β-lactone (2-oxetanone) chemistry because this moiety is present in many biologically active natural products. For example, tetrahydrolipstatin (Orlistat), an inhibitor of pancreatic and gastric lipases, is a current treatment for obesity.[1] In our laboratory, we are interested in the chemistry of the β-thiolactones (2-thietanones) as surrogates for the β-lactones and β-lactams in bioorganic and medicinal chemistry,[2,3] and as precursors[4] to substituted monothioacids for use in coupling reactions.[5]



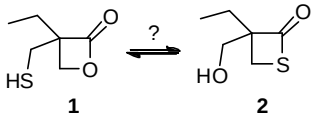
Tetrahydrolipstatin

The carbonyl bond is longer in the β-lactone (1.197 Å) than in the β-thiolactone (1.187 Å). The opposite is observed for the C2-X bond (X = O: 1.371 Å, X = S: 1.792 Å). In a β-thiolactone, the C2-X-C4 angle is about 77° instead of 90° for a β-lactone.[6] The latter is planar species both in crystal and in the gas phase,[7] whereas the former is puckered, reflecting the longer C-S bonds and reduced resonance delocalization of the sulfur lone pairs in the carbonyl system.[3] Because of these different physical properties, we decided to study the relative stabilities and reactivities of simple β-thiolactones and β-lactones toward nucleophilic ring-opening reactions.

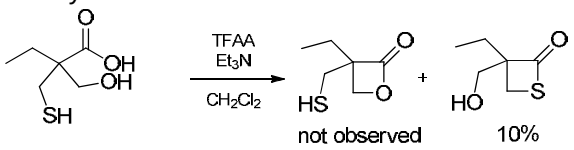


X = O, S

In order to compare their relative stability, we synthesized compounds **1** and **2** and we treated them in acidic and basic conditions. As we mainly obtained polymerization products, we studied kinetic competition for the formation of **1** and **2** via cyclodehydratation.



1 **2**



not observed 10%

We next turned our attention to the regioselectivity and relative rates for the opening of β-lactones and β-thiolactones by simple nucleophiles, isobutylamine and butanethiol, and we established kinetic profiles by LCMS. This study revealed the best reactivity of β-thiolactone toward nucleophiles and consequently, β-thiolactones might be expected to be better inhibitors of cysteine protease enzymes than the corresponding β-lactones.

References

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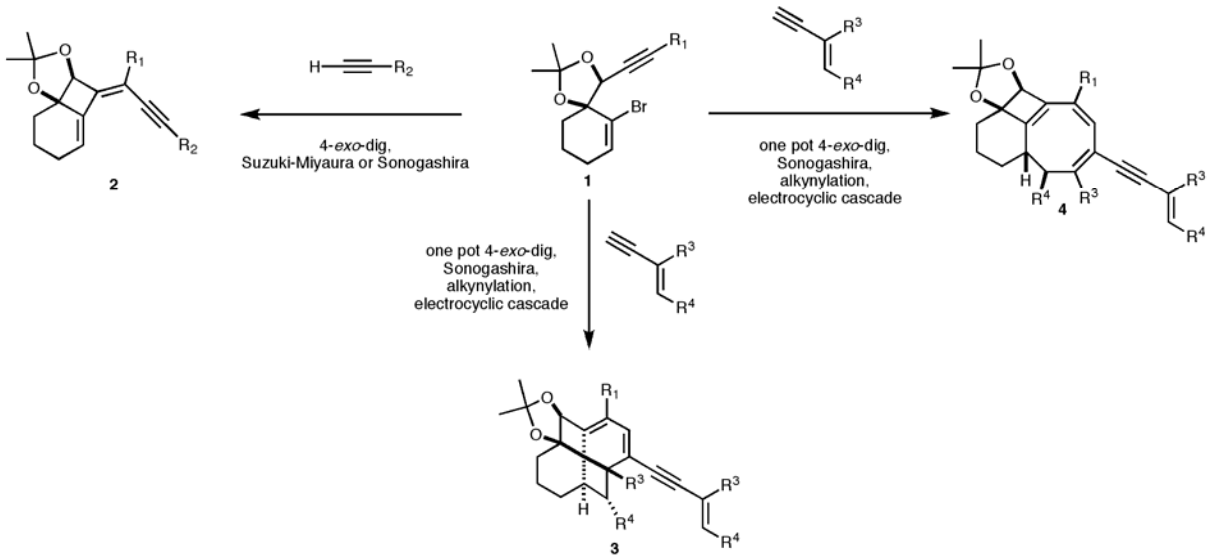
NEW SYNTHETIC STRATEGIES AROUND PALLADIUM CATALYSIS: A ONE-POT ACCESS TO [4.6.4.6]FENESTRADIENES AND CYCLOOCTATRIENES

Mélanie Charpenay, Aicha Boudhar, Acetou Siby, Gaëlle Blond, Jean Suffert

Laboratoire d'Innovation Thérapeutique (UMR 7200)
équipe de synthèse de biomolécules, Faculté de Pharmacie, UMR UDS/CNRS 7200
74 route du Rhin, 67401 Illkirch

The preparation of complex molecules starting from simple compounds in a minimum number of steps is a challenging goal in organic synthesis. Herein we describe new accesses to dienynes and trienynes **2** from **1** using new cascades reactions: 4-*exo*-dig cyclocarbopalladation followed by a Suzuki-Miyaura or Sonogashira cross-coupling.

By the same approach, fenestradienes **3** and cyclooctatrienes **4** are obtained in one step starting from the same compound **1**. The key step of this method is based on a cascade reaction through a 4-*exo*-dig cyclocarbopalladation of the protected propargylic diols **1**, a Sonogashira type coupling, a regioselective alkynylation of a disubstituted triple bond followed by a 8π and a 6π electrocyclizations. The optimized conditions, the observed results and the mechanism will be discussed in further details.



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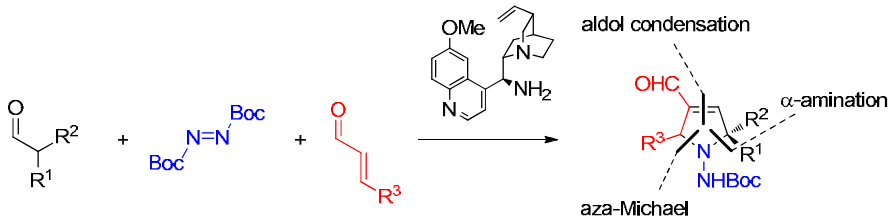
ENANTIOSELECTIVE ORGANOCASCADE SYHNTHESIS OF 3-PYRROLINES BEARING A QUATERNARY STEREOCENTER

Alaric Desmarchelier, Vincent Coeffard, Xavier Moreau, Christine Greck

Institut Lavoisier de Versailles, Université de Versailles-Saint-Quentin-en-Yvelines
45, avenue des Etats-Unis, 78035 Versailles Cedex, France

Organocatalytic processes have had increasing popularity in recent years to access highly functionalized chiral moieties from simple, achiral material. Among the available activation methods, aminocatalysis, which enables the use of either nucleophilic reagents through iminuim activation, or electrophilic ones *via* enamine processes, was the pioneer of cascade reactions in this field.[1]



As part of our ongoing research on stereoselective C-C and C-N bond formation with chiral amine catalysts,[2] we embarked on the investigation of a cascade procedure whereby we could access chiral N-heterocycles from simple aldehydes and azodicarboxylates. This resulted in a sequential cascade pathway that involves both enamine and iminium activation steps, leading to highly functionalized 3-pyrroline precursors.

Such cyclic compounds are important cores of several biologically active molecules,[3] and numerous diastereoselective syntheses exist.[4] Nevertheless, to the best of our knowledge, enantioselective pathways leading to quaternary 3-pyrrolines are to this day unreported. We present here a straightforward one-pot method to obtain such compounds with good yields and high enantiomeric excess.[5]

References

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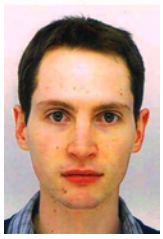


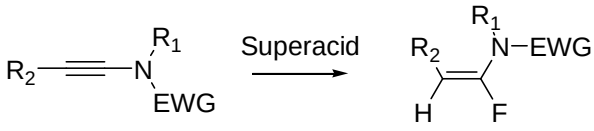
STEREO- AND REGIO-SELECTIVE SYNTHESIS OF *α*-FLUOROENAMIDES IN SUPERACID: NEW RIGID UREA BIOISOSTERS

Guillaume Compain,[a] Kévin Jouvin,[b] Agnès Martin-Mingot,[a] Gwilherm Evano,[b] Jérome Marrot [b] and Sébastien Thibaudeau [a]

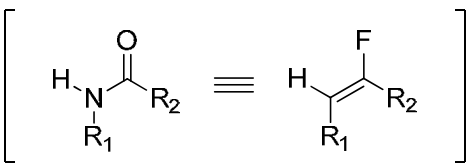
[a] Institut de Chimie des Milieux et des Matériaux de Poitiers (IC2MP) - UMR CNRS 7285
Université de Poitiers - 4, avenue Michel Brunet, F-86022 Poitiers Cedex, France
Equipe « Glycochimie, Superacide et Chimie des systèmes »
[b] Institut Lavoisier de Versailles, UMR CNRS 8180, Université de Versailles
Saint-Quentin en Yvelines, 45, avenue des Etats-Unis, 78035 Versailles Cedex, France

guillaume.compain@univ-poitiers.fr

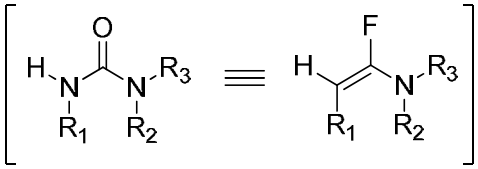
The use of nitrogen containing fluorinated compounds has increased in medicinal chemistry thanks to the unique properties of fluorine atom. However, the development of new synthetic methodologies to access these products remains a challenge. Based on the original behaviour of unsaturated substrates in superacid,[1] new methods for the preparation of fluorinated amines have been discovered.[2] These previous studies led us to develop recently a highly stereoselective and regioselective hydrofluorination of ynamides in superacid.



This methodology allows the selective synthesis of (*E*)-*α*-fluoroenamides.[3] In analogy with fluoroolefins which are known to be non-hydrolysable mimics of amides,[4] these new fluoroenamides might be considered as rigid bioisosters of ureas with further potent applications in medicinal chemistry.



Fluoroolefin: bioisoster of amides



Fluoroenamine: bioisoster of ureas

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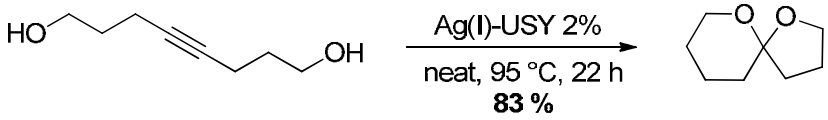
SILVER(I)-USY ZEOLITE AS GREEN CATALYST FOR THE PREPARATION OF KETALS AND SPIROKETALS FROM ALKYNOLS AND ALKYNEDIOLS

Sophie BORGHESE, Valérie BENETEAU, and Patrick PALE.

Laboratoire de Synthèse et Réactivité Organiques,
Institut de Chimie, Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg

The presence of oxacycles like oxolanes, oxanes and spiroketals in a wide variety of natural products[1] has attracted the attention of synthetic chemists in the last decades. In this context, a number of approaches to these compounds have been developed, but these often rely on multiple reaction steps and hence are not optimally efficient[2]. The transition-metal-catalyzed addition of hydroxyl groups to alkynes represents one of the most efficient methods for the synthesis of bis-oxygenated compounds like ketals, cyclic ketals and spiroketals. Homogeneous conditions employing palladium[3], gold[4], and more recently rhodium and iridium[5] complexes have already been reported for this reaction, leading efficiently to cyclic ketals and spiroketals.
Due to our interest in silver organic chemistry[6], and especially silver-catalyzed cyclizations[7], we decided to develop a greener procedure using silver(I)-doped zeolites as heterogeneous catalysts.



The recyclability of this class of solids leads to an environmental friendly alternative for the dihydroalkoxylation of alkynediols. The preparation of the catalyst, as well as the conditions screening and the scope of the reaction will be presented.

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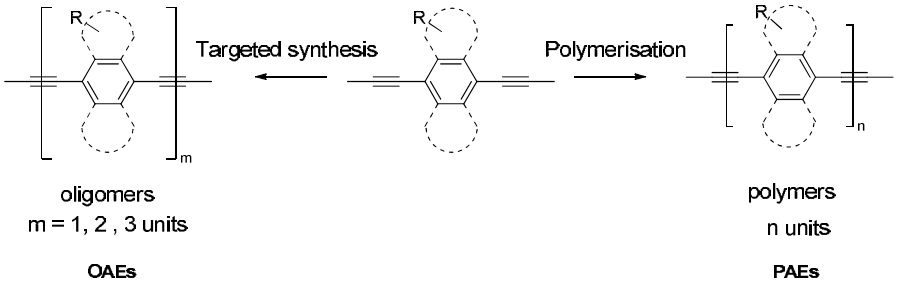
SYNTHETIC TOOLS FOR ORGANIC ELECTRONIC APPLICATIONS: OLIGO- AND POLY-ARYLENES ETHYNYLENES

Nicolas Cheval,* Jean-Marc Weibel, Patrick Pale

Laboratoire de Synthèse et Réactivité Organiques,
Institut de Chimie, Université de Strasbourg
4 rue Blaise Pascal, 67000 Strasbourg
e-mail: ncheval@unistra.fr

Electronic components are taking an omnipresent place in high-technology: Transistors, LEDs, switches.... Most of them are based on silicon, a semiconductor. However, further miniaturization and new applications require new technologies. Organic electronic, along with photovoltaic and optoelectronic, relies on the use of organic molecules as semiconductor.[1]

Poly-Arylene-Ethynylenes (PAEs), and related heterocycles are promising targets, as the π-conjugated moieties should allow to decrease the HOMO-LUMO gap facilitating electron transfer.[2] In a previous study, it has been showed that conductivity was significantly improved considering Organic Thin-Film transistors (OTFTs) made from monomers, oligomers or polymers.[3]



Various monomers and oligomers are thus being synthetized & studied as OTFTs, as well as their polymers[4].

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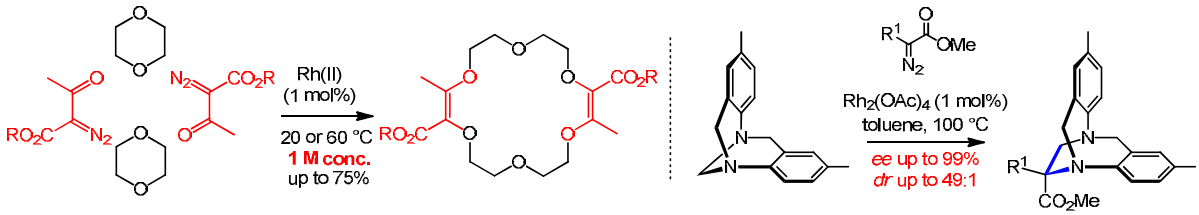
INVESTIGATIONS IN SELECTIVE SYNTHESIS & CATALYSIS

Jérôme Lacour

Université de Genève, Département de Chimie Organique

The main research interest of the group is stereoselective chemistry in a wide sense. Current research programs cover a variety of topics within the areas of enantioselective catalysis, stereoselective synthesis, asymmetric recognition, NMR enantiodifferentiation, and these encompass the use of a large range of original ionic compounds and metal complexes. In the context of SECO49, recent studies on metal-catalyzed reactions and processes will be presented – and those involving Rh(II)- and Ru(II)-catalyzed decompositions of α-diazo-β-ketoesters in particular.

For instance, 15-, 16- and 18-membered polyether macrocycles are prepared in a single step from condensation reactions with cyclic ethers. Against conventional wisdom, these macrocyclizations of four separate components occur under non-templated conditions and are more efficient as the concentration is increased.[1] Also, new configurationally-stable ethano-Tröger bases can be prepared in a single step using novel carbenoid chemistry. The process is general, enantiospecific (*ee* up to 99%), diastereoselective (with a new quaternary carbon center introduction, *dr* up to 49:1) and regioselective.[2]



$[CpRu(CH_3CN)_3][PF_6]$ [3,4] and diimine ligands catalyze also the decomposition of α-diazoacetoacetates leading to O-H insertion and condensation reactions. In comparison with Rh(II) and Cu(I) complexes, the CpRu catalysts produce rapid and often more selective reactions.[5] Other reactions and processes will be presented.

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Monday Afternoon

GIBOULOT Steven

Palladium Catalyzed Domino Reactions

AUBE Christophe

Synthesis of poly-azaheteroaromatic ligands as foldamers central linkers for an application in supramolecular chemistry

CYKLINSKY Mathieu

Rearrangement of acetylenic epoxides and aziridines communication

RIHN Sandra

Synthesis of Fluorescent Dyes Exhibiting Large Stokes Shifts

LIU Wenjun

Synthesis of deuterium labelled adenosylhopane: a probe of hopanoid side chain biosynthesis

MACE Frédéric

Towards the total synthesis of thapsigargins

DEMORY Emilien

Direct C-H arylation of cyclic nitrones

Dr. CHODOROWSKI-KIMMES Sandrine

Supramolecular polymers in cosmetic: an example of techno-push

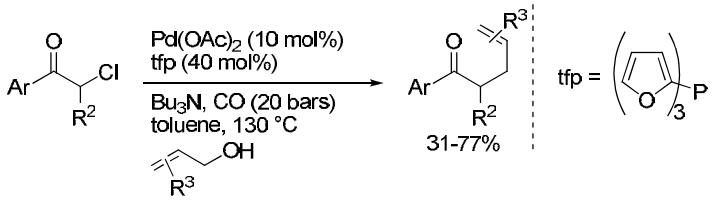
PALLADIUM CATALYZED DOMINO REACTIONS

Steven Giboulot, **Frederic Liron, Guillaume Prestat, Giovanni Poli**

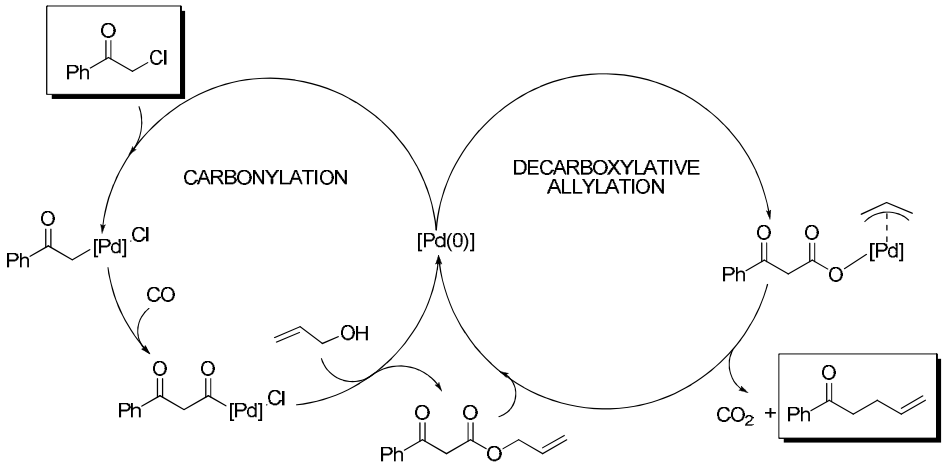
IPCM, UPMC, UMR CNRS 7201, 4 Place Jusieu, case 183, 75252 Paris Cedex 05

The selective monoallylation of ketones was realized via a *type I* pseudo-domino[1] sequence entailing a carbonylation[2] step followed by a decarboxylative allylation[3], both palladium-catalyzed. This was achieved by treatment of an α-chloroketone with catalytic amounts of a palladium complex under CO pressure and in the presence of allyl alcohol (Scheme 1).

We will present our optimization study, as well as the results of the scope and limitations of this process.



Scheme 1



Scheme 2

Acknowledgments/Financial assistance: ANR

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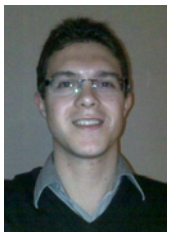

SYNTHESIS OF POLY-AZAHETEROAROMATIC LIGANDS AS FOLDAMERS CENTRAL LINKERS FOR AN APPLICATION IN SUPRAMOLECULAR CHEMISTRY

Christophe Aubé,[a] Virginie Blot,[a] Christine Thobie,[a] Sylvie Condon,[b] Eric Léonel,[b] Yann Ferrand,[c] Ivan Huc,[c] Jacques Lebreton,[a] Muriel Pipelier[a] and Didier Dubreuil[a]

[a] *CEISAM, UMR 6230 – 2 rue de la Houssinière – 44322 NANTES*
[b] *ESO - ICMPE, UMR 7182 – 2 rue Henri Dunant – 94320 THIAIS*
[c] IECB, UMR 5248 – 2 rue Robert Escarpit – 33607 PESSAC

Polydentate nitrogen ligands represent attractive targets in chemistry/ biology/physicochemistry. For many years, Profs. D. Dubreuil and E. Léonel's groups were interested in pyridazinic and pyrrolic compounds particularly for their synthetic methodology and their various applications.[1] Indeed, molecules featuring these heterocycles are present in therapeutic chemistry as anticancer agents (Prodigiosine or metallic complex of cisplatine)[2] and also in supramolecular chemistry as central linkers for the synthesis of foldamers as biological receptor mimics.[3] Our collaborative works with Dr. I. Huc in the field of synthesis and characterization of supramolecular structures led us to elaborate oligoamidic-type foldamers including an azaheteroaromatic ligand as central linker. We have demonstrated their ability to encapsulate diastereoselectively small molecules such as tartaric acid in the case of ligand **1** (Figure 1).[4]

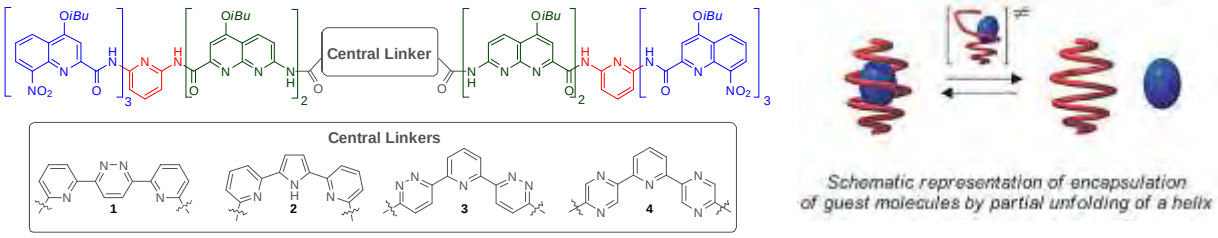

Figure 1: *Representation of the oligoamidic foldamer with different central linkers (left), encapsulation mechanism of substrates (right).*

Focusing the elaboration of the central linkers, we turned our attention to (poly)-pyridazinic and (poly)-pyrrolic structures. Their preparations are based on various methodologies of C-C bond formation, including electrochemical and chemical cross-coupling processes.

In this communication, the synthetic approach of central linkers (**1** to **4**) will be presented following organometallic chemistry for cross-coupling reactions. Results obtained in supramolecular chemistry will also be discussed.

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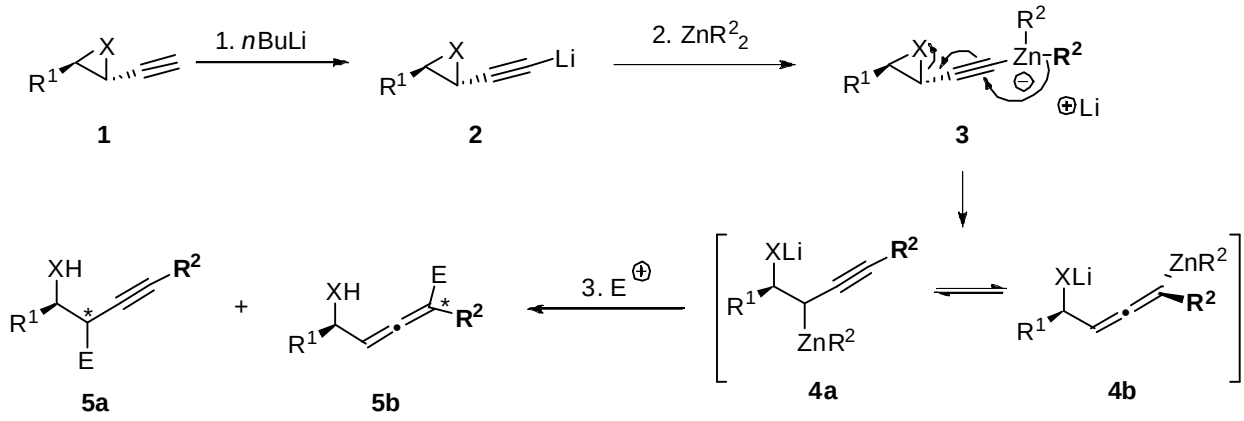
REARRANGEMENT OF ACETYLENIC EPOXIDES AND AZIRIDINES COMMUNICATION

Mathieu CYKLINSKY

Fabrice CHEMLA, Franck FERREIRA, Alejandro PEREZ-LUNA

UPMC-Univ Paris 06, Institut Parisien de Chimie Moléculaire (UMR CNRS 7201)
Equipe Synthèses Sélectives et Organométalliques, Bâtiment F, 2ème étage C.183,
4 place Jussieu, 75252 Paris cedex 5
email : mathieu.cyklinsky@upmc.fr

Due to their high electrophilicity, epoxides and aziridines could undergo regio- and stereoselective ring opening with a wide variety of nucleophiles.[1] Our group is more particularly interested in the acetylenic epoxides and aziridines[2] ring opening through a 1,2-metalate rearrangement as follows :



1 **2** **3** **4a** **4b** **5a** **5b**

This rearrangement takes place on zincates **3** generated by deprotonation in the acetylenic position of the corresponding epoxide (X = O) or aziridine (X = NR^3) **1** followed by transmetallation of lithium intermediate **2** with dialkylzinc species. In this rearrangement, the migration of a R^2 group occurs through a S_N2' mechanism and leads to propargylzinc **4a** which is in metallotropic equilibrium with allenylzinc **4b**. The trapping of the mixture of **4a** and **4b** by various electrophiles (H_2O, aldehydes, ketones...) could lead to a wide variety of propargylic and/or allenic compounds **5a** and/or **5b** by controlling the stereoselectivity.

Our preliminary recent results with R^2 = $SiMe_2Ph$ will be presented and discussed.

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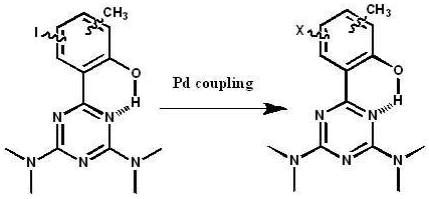
SYNTHESIS OF FLUORESCENT DYES EXHIBITING LARGE STOKES SHIFTS

Rihn Sandra

Laboratoire de Chimie Moléculaire et Spectroscopies Avancées (LCOSA),
Ecole Européenne de Chimie, Polymères et Matériaux,
CNRS, (UMR 7515) 25 rue Becquerel, 67087 Strasbourg Cedex 02, France
http://www-lmspc.u-strasbg.fr/LCOSA/

Fluorescent dyes displaying high photostability and emission wavelength tunability have received many renewed interest in recent years[1,2]. To find applications in chemistry and biology, a fluorescent probe should respect some basics rules. In fact efficient fluorescent probes should process a large absorption cross-section and high fluorescent quantum yields, tunable spectroscopic properties, radiative deactivation pathways should be privileged and finally they should have large Stokes' shifts to achieve high resolutions and low limits of detection. We decide to focus on this last point and to engineer molecules where intramolecular proton transfer is promoted in the excited state (ESIPT process). Such dyes are well-known since the discovery of methylsalicylate and relative derivatives[3,4] but less interest was giving to 6-(2-hydroxy-5-methylphenyl)-s-triazines.

The phenyl residue on this molecule can easily be functionalized using palladium cross-coupling (ie Sonogashira, Suzuki, Stille) to modify the optical properties. In particular, we graft different aromatics compounds such as thiophene, bis-thiophene, EDOT, pyrene, perylene, styrene and standard Bodipy's[5].



X = thiophene, bis-thiophene, EDOT, vinyl, alkyne

We also investigated the construction of caged 6-(2-hydroxy-5-methylphenyl)-s-triazines dyes by substitution on the hydroxyle group with a carbonate linkage which leads to a loss of fluorescence. By using specific lipase, this linkage can be removed very efficiently and the fluorescence restored. To the best of our knowledge, there have been no reports of the synthesis of such OFF-ON system based on 6-(2-hydroxy-5-methylphenyl)-s-triazines.

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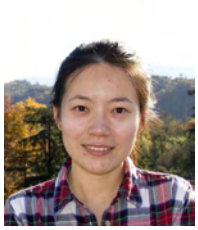


SYNTHESIS OF DEUTERIUM LABELLED ADENOSYLHOPANE: A PROBE OF HOPANOID SIDE CHAIN BIOSYNTHESIS

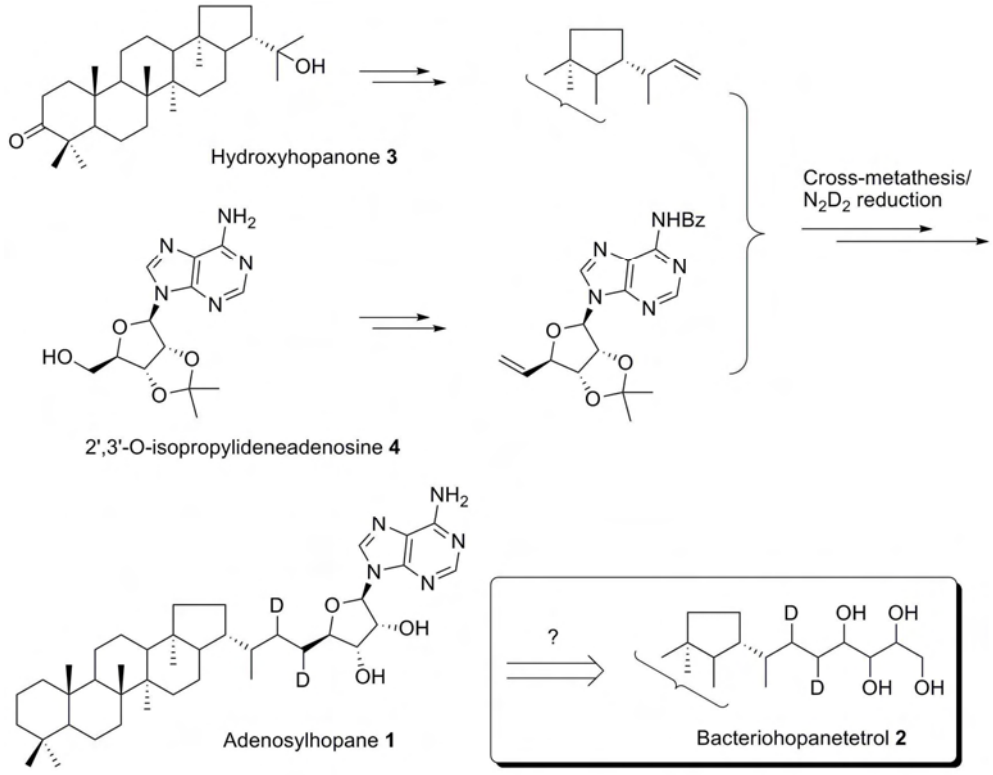
Wenjun Liu, Anne Bodlenner, Michel Rohmer

Laboratoire de chimie et biochimie des microorganismes,
Institut de Chimie, Université de Strasbourg/CNRS UMR 717,
4 rue Blaise Pascal, 67070 Strasbourg, France.

As a putative intermediate in C_{35} bacterial hopanoid biosynthesis, adenosylhopane is frequently found in bacteria.[1,2] In this work, ^{2}H-labelled adenosylhopane **1** was successfully synthesized from hydroxyhopanone for the first time via 14 steps.

The pentacyclic skeleton **3** and the adenosine derivative **4** are available as natural compound and commercial product, respectively. However, coupling of the bulky triterpene moiety with an acyclic or cyclic synthon is challenging. Cross-metathesis was chosen in the key step because of its mildness and high efficiency. Mild yield was obtained under microwave irradiation condition. The following reductive labelling of adenosyl-hopene can only be achieved via diimide reduction due to the steric hinderance. Isotopic abundance of [30, 31-$^{2}H_2$]adenosylhopane can reach 60 atom% D.

Incorporation experiments of reducing ^{2}H-labelled adenosylhopane into bacterial C_{35} bacteriohopane derivatives such as bacteriohopanetetrol **2** are currently performed.



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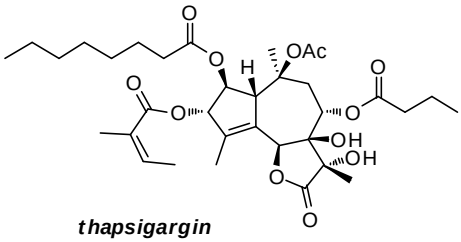
TOWARDS THE TOTAL SYNTHESIS OF THAPSIGARGINS

Frédéric Macé, Jean-Pierre Deprés

Département de Chimie Moléculaire (SERCO), UMR-5250,
Université Joseph Fourier, 301 Rue de la Chimie,
BP-53, 38041, Grenoble Cedex 9

Thapsigargin is a densely oxygenated guaianolide isolated from the roots of *Thapsia*. Among the 17 members of the thapsigargin family, it is the most effective inhibitor of endo/sarcoplasmic reticulum Ca^{2+} ATPases (SERCA) in cells, leading to apoptosis. Taking advantage of this activity, prodrugs derivatives were studied against prostate cancer, giving promising results.[1]

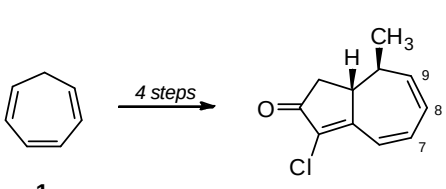


thapsigargin

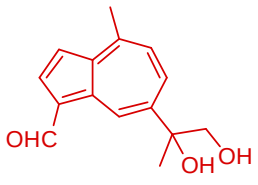
Unfortunately, the use of thapsigargin-related compounds as drug candidates is limited by low availability from natural sources. And there is only one total synthesis so far. [2] This can be explained by their complexity which make them a challenge for the chemist community.

We decided to tackle a new synthesis by taking advantage of our experience in sesquiterpene total synthesis: our versatile intermediate **2** -readily accessible from cyclohepatriene **1**- permitted the access of several natural guaianolides in the past.[3] Important transformations of **2** are a 1,6-conjugate-addition/oxidation at C_7 and an electrophilic activation at $C_{8\text{-}9}$.

This work led us to a promising path to thapsigargins, with good selectivity in stereocenters formation. We also took profit of an interesting intermediate in order to synthesize some recently discovered azulenes, such as the intense red-colored **3**. [4]



1 **2**



3

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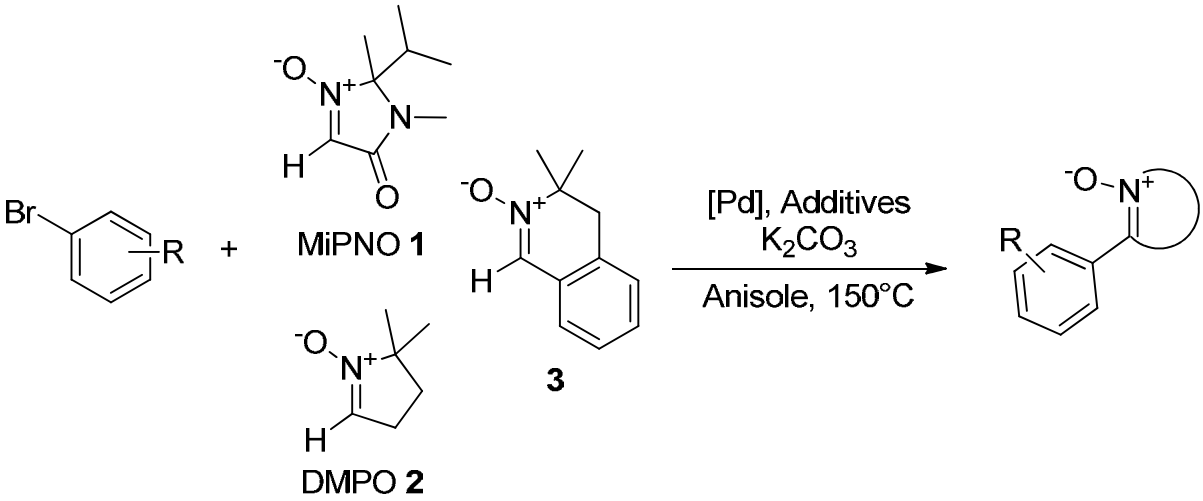
DIRECT C-H ARYLATION OF CYCLIC NITRONES

Emilien Demory

Département de Chimie Moléculaire, UMR-5250, ICMG FR-2607, CNRS,
Université Joseph Fourier, BP-53, 38041 Grenoble Cedex 9, France

In the past decade, a rapidly increasing number of methods for the transition metal-catalysed direct C-H arylation of arenes and heteroarenes have been developed.[1,2] In this regard, nitrogen-containing heteroaryl coumpounds have been the subject of extensive research, whereas scarce examples of direct C-H arylation involving non-aromatic nitrogen heterocycles are to be found.

Our interest in the preparation and use of chiral cyclic nitrones led us to develop nitrone **1**, MiPNO[3-5], and we wondered whether the direct arylation of this heterocycle was possible. We hypothesized that cyclic aldonitrones should behave like pyridine *N*-oxide which are excellent substrates for palladium-catalyzed direct arylation.[6,7]



We report herein the very efficient palladium-catalyzed direct C-H arylation of cyclic nitrones **1**-**3** with various aryl halides, the study of its mechanism and the role of additives.

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SUPRAMOLECULAR POLYMERS IN COSMETIC: AN EXAMPLE OF TECHNO-PUSH

Sandrine Chodorowski-Kimmès

L'OREAL, 1 Avenue Eugène Schueller, BP 22, 93601 Aulnay Sous Bois

Polymers are well known components in cosmetic formulations. We have investigated the interest of the use of supramolecular polymers in cosmetic, and the impact in our final applications. This program is focused on two subjects: one concerning the specificity of a class of organogelators with a bis-urea skeleton and the other is based on polymers functionalized by ureidopyrimidone.

In these last years, supramolecular polymers have drawn considerable attention in the scientific world[1], especially because of their unique properties due to their dynamical and reversible properties. Compared to conventional polymers, it has been shown for example, that supramolecular polymers can combine surprising material properties with low-viscosity melts, properties which can help for their applications in industry. Some other supramolecular polymers also have remarkable characteristics, such as the ability to self-heal fractures in their structure[2]. In other hand, polymers represent a large class of raw material used in cosmetic. We use them for example in formulations for their film forming properties like in nail varnish, or in our gel and spray in styling, or also for encapsulation of active ingredients…
In this research program, we have investigated the interest of supramolecular polymers in cosmetic. In l'Oreal Research, we are concentrated on two subjects: one concerning the specificity of a class of organogelators with a bis-urea skeleton[3] and the other is based on polymers functionalised by ureidopyrimidone[4].The key point is too find what superiority those supramolecular assemblages through H-Bond interactions could bring in our different applications. This means that we need first to have a deep understanding of their behaviour in our typical cosmetic media compared to classical and already well-known polymers. We are specially focused on the analytical and the physico-chemical properties of the polymers in solution, and in the final material properties.

After a short and general introduction of the research in l'Oreal, I will present these two examples which are a good illustration of the difficulty for an industrial like l'Oreal, to find the way to a breakthrough applications, and this, despite all the scientific knowledge developed during these last years.

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Tuesday Morning

SBARGOUD Kamal

Orthogonal functionalization of polymeric nanoparticles

SIGWALT David

Gene delivery with polycationic fullerene hexakis-adducts

NAWAZ Faisal

Enantioselective annulation reaction of homoenolate catalysed by bifunctional N-heterocyclic carbenes

KING Mathias

Screening for bioorthogonal chemical ligation reactions

KERN Nicolas

Coinage metals-catalysed reactions of aryl alkynylaziridines: silver(I)-single vs gold(I)-double cyclizations

RAIMONDI Wilfried

Novel reactivity of 1,2-dicarbonyl compounds in asymmetric synthesis

HONG Xiang

Electrochemically and chemically polymerized salen cobalt complexes for the hydrolytic kinetic resolution of terminal epoxides

SARKAR Parantap

Tetraazaarenes by the ceramidonine approach

Dr. ARSENIYADIS Stellios

Exploring Chemical Reactivities to Maximize Structural Diversity: Application to Natural Product Total Synthesis

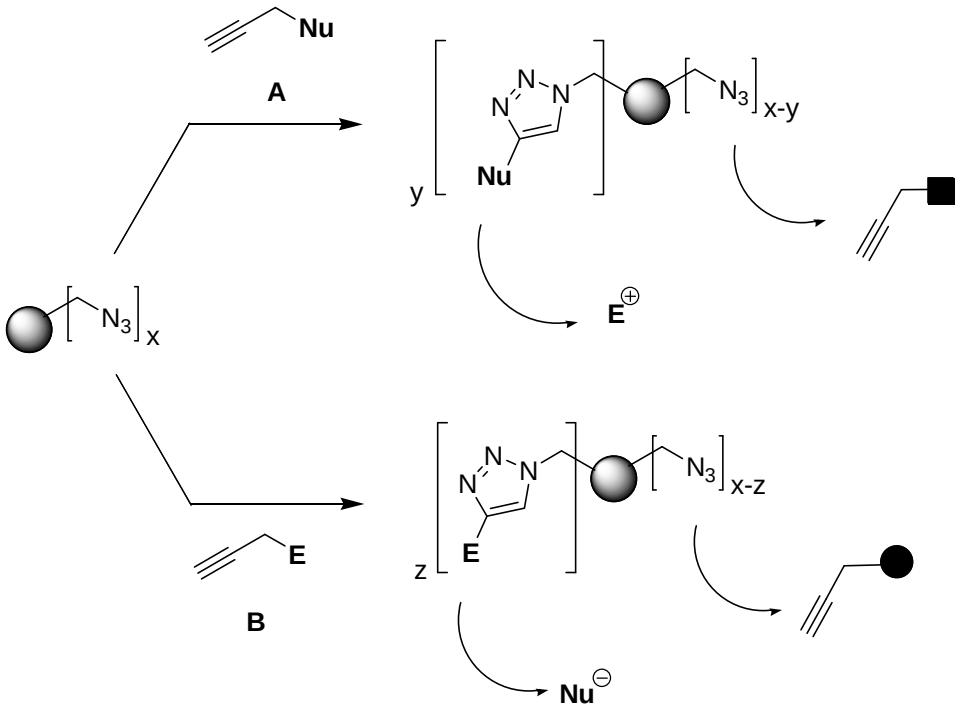
ORTHOGONAL FUNCTIONALIZATION OF POLYMERIC NANOPARTICLES

Kamal Sbargoud, Emmanuel Allard, Chantal Larpent

Institut Lavoisier, UMR CNRS 8180, Université de Versailles St Quentin en Y.
45 avenue des Etats Unis, 78035 Versailles Cedex

Polymeric nanoparticles are of great interest in several research areas because of their unique properties; especially their very high surface to volume ratio which allows one to perform surface reactions over an extended area. Recently, our group have developed an efficient method to synthesize azide functionalized nanoparticles with a very small diameter of 16 nm which can be further functionalized through CuAAc, 'Click reaction', with alkynes.[1,2]

In this presentation we show that the surface modification through click reactions allows one to synthesize multi-functionalized NPs with controllable ratio of functional groups. Our strategy uses orthogonally functionalized NPs as modular platforms (Scheme). Bifunctional NPs with N_3 and nucleophilic reactive groups or with N_3 and electrophilic reactive groups in adjustable ratio (x/y, x/z) are easily prepared by clicking variable amounts of the corresponding alkyne (A or B). These NPs are then further functionalized by grafting another alkyne through CuAAC and an electrophilic or a nucleophilic substrate.



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