The Invention of New Methodologies: An Opportunity for Dating Natural Products

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Abstract
This Account surveys almost two decades of methodological developments and their straightforward applications to the total synthesis of simple natural products. The main directions covered include radical chemistry and cascades, electrophilic catalysis based on coinage metals, and asymmetric synthesis based on bis(sulfoxides) auxiliaries.

1 Introduction

There are clearly two types of organic synthetic chemists who like to deal with natural products. The first group is entirely focused on a target as an alpinist chooses a mountain to climb and any pathway would work as long as the goal is reached. The second group is more opportunistic and will aim at illustrating the versatility of its newly developed methodologies through the total synthesis of a relevant natural compound. While it is not the question here to judge which approach makes more sense scientifically, since it is also highly dependent on the target and on the involved methodologies, it is rather clear that each party enriches the other. In this context, our laboratory has, over the last decade, participated in several important synthetic methodology developments and adapted them to the straightforward synthesis of natural compounds. Based on radical cascades, electrophilic catalysis with platinum and gold complexes, or Michael additions to alkylidene bis-sulfoxides, these casual encounters with natural products have been particularly stimulating. This Account surveys the different key methodologies which have been utilized over the last twenty years, and their specific applications.

2 Radical Cascades

2.1 N-Cyanamides

Based on the legacy of the Max Malacria group, a strong expertise in radical chemistry and cascades was present in our laboratory and generally involved polyunsaturated hydrocarbon substrates. In the early 2000s, the interest of the group shifted to new partners and notably heteroatomic functions to provide accesses to valuable scaffolds. N-Ynamides2 and N-cyanamides3 appeared rapidly of great appeal since they can serve as relay functions by being both a radical acceptor on a sp-hybridized carbon center and then a radical partner through a highly reactive vinyl or iminyl radical (Scheme 1). Based on this principle, using an aryl, vinyl, or alkyl radical trigger, some new types of tandem cyclizations could be worked out to deliver guanidine and quinazolinone platforms.4 In the latter case, by engaging the adequate alkyl radical precursor, which meant playing with the $R_1$ and $R_2$ substituents on substrates of type 1, the total synthesis of deoxyvasicinone, a natural alkaloid isolated from Adhatoda vasica5 with antidepressive, antibacterial, and anti-inflammatory properties,6 was achieved. Similarly, with $n = 2$ for the tether length, mackinazolinone was obtained. Mackinazolinone was isolated in 1965 in New Guinea from the leaves of Mackinlaya subulata7 and it exhibits a large spectra of pharmaceutical activities.8
The cyclization tandem begins, respectively, with a 5-exo-dig or a 6-exo-dig cyclization and, as generally observed, a stoichiometric amount of AIBN is required to ensure rearomatization after the aromatic homolytic substitution.\textsuperscript{4b,9} At the time of this study, we also synthesized the medicinally relevant \(\alpha\)-methyldeoxyvasicinone as well as the quaternary \(\alpha,\alpha\)′-dimethyl analogue.

### 2.2 Homolytic Substitution at Sulfur Atom to Give Sultines

Homolytic substitution is an intriguing radical reaction\textsuperscript{10} which has been certainly underused in the context of total synthesis. Connected to a more general interest in sulfur chemistry (see also section 4), we went one step forward within sulfur reactivity and turned our attention towards homolytic substitution at the sulfur atom to obtain cyclic sulfinites and sulfonamides.\textsuperscript{11,12} Indeed, these moieties are lactone and lactame bioisosteres\textsuperscript{13} that are found in natural products\textsuperscript{14} and have been used as imaging agents.\textsuperscript{15} Moreover, they are versatile synthetic intermediates. Our design involved substrates which would incorporate a highly reactive radical trigger and a good radical leaving group. Of particular interest was the study of the stereochemical outcome at the sulfur atom and the diastereoselectivity of the transformation. Thus, we focused on the treatment of aryl bromides 3 with tributyltin hydride in the presence of AIBN as a radical initiator. The generated

**Scheme 1** Radical cascades leading to vasicinones

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**Biographical Sketches**

**Marion Barbazanges** was born in Annecy, France in 1981. From 2001 to 2005, she studied at the École Supérieure de Physiques et de Chimie Industrielle de la ville de Paris (ESPCI Paris). In 2005, she received the MSc in Chemical Science and Engineering of ESPCI, as well as the MSc in Organic and Bioorganic Chemistry of the Université Pierre et Marie Curie (Paris, France). She joined Prof. Cossy’s lab for her Master degree and her PhD, where she worked on enamides’ sigmatropic rearrangement as well as total synthesis of amphidinolide J. After a postdoctoral stay in Prof. A.G.M. Barrett’s group in Imperial College, London (2009), she joined Dr. C. Aubert and Prof. L. Fensterbank’s lab as a postdoctoral fellow (2010) then as an assistant lecturer (since 2011), working on organometallic chemistry and chirality.

**Louis Fensterbank** was born in Poitiers in 1967 and raised in Tours. He graduated from Ecole Supérieure de Chimie Industrielle de Lyon (ESCL) in 1990 and obtained his PhD on silicon-tethered reactions in 1993 at SUNY Stony Brook under the supervision of Scott Sieburth. After a temporary lecturer position at UPMC in 1994, he was appointed in 1995 Chargé de Recherche CNRS in Max Malacria’s team. In 2004, he obtained a professorship position at UPMC and, in 2008, he was nominated junior member at the Institut Universitaire de France. His research interests concern the discovery of new molecular transformations relying on radical or organometallic processes and their applications to the synthesis of substrates with relevant properties (e.g., natural products, probes, ligands). He serves in the editorial board of Organic Chemistry Frontiers. Recently, he received the Prix de la Division de Chimie Organique of the French Chemical Society (2016) and the Silver Medal from CNRS (2017) and was elected Fellow of the Royal Society of Chemistry (2016).
aryl radical adds to the sulfinate moiety to yield the desired sultines 4 by ejection of the stable tertiary tert-butyl radical (Scheme 2, Eq. 2). By cyclizing enantioenriched sultinamides and sultines such as (R)-3a, we showed that these transformations occurred with total inversion of configuration at sulfur (sultine (S)-4e).

This is in agreement with an intramolecular homolytic substitution mechanism which proceeds through a transition state in which the attacking and leaving radicals adopt a near collinear arrangement as suggested by DFT calculations from the Schiesser group.16 Cyclization of a secondary aryl radical adds to the sulfinate moiety to yield the desired sultine (Scheme 2, Eq. 3). This methodology provided access to natural product sultine 5a that can be found in extracts of passion fruit (2:1 diastereomeric ratio (99%, Scheme 2, Eq. 4)).

3 Electrophilic Catalysis Based on Platinum(II) and Gold(I) Complexes

Another domain of predilection of our laboratory has concerned organometallic catalysis based on the engagement of unsaturated substrates (enynes, diynes, allenynes). The logical move in the 2000s was to experiment the emerging use of electrophilic metals such as platinum(II)17 and gold(I)18 complexes in order to generate molecular complexity.19 Thus, in 2002, in collaboration with the Marco-Contelles group, we evidenced a fascinating effect of an oxygenated group at the propargylic position in the PtCl2-catalyzed cycloisomerization of diyne precursors.20 In typical conditions (5 mol% PtCl2 in toluene at 80 °C), methoxyether 7 led to the highly congested tetracyclic derivative 8 as a single diastereomer, which displays two fused cyclopropane moieties. Formally, product 8 originates from the transformation of the central alkyne moiety into a biscarbene entity, a reactivity previously reported by Chatani and Murai,21 and that was supported by calculations.17c,22 In contrast, ester precursor 9 provided the very major product 10 featuring a 1,2-acetate migration concomitant with the formation of a cyclopropane (Scheme 3). This ability of a propargyl acetate to migrate in the presence of electrophilic metals was reminiscent of the transformation of 1-ethyl-2-propenyl acetates into 2-cyclopentenones in the presence of palladium(II), also referred now as the Ohloff–Rautenstrauch rearrangement.23 It has also proved to provide a very solid route to click a propargyl acetate with an alkene to form a cyclopropyl group adjacent to an ester moiety whether inter- or intramolecular.
ly. In terms of mechanism, initial formation of an electrophilic alkyne–PtCl₂ coordination complex of type A triggers a nucleophilic attack of the richest partner: an alkene, to give platinacyclopropyl carbene B; or an O-acyl group, to generate intermediates C and D through migration of the ester. Importantly, in the case of ester substrates, chirality transfer from the propargylic position has been observed, suggesting a rather concerted cycloisomerization mechanism.

We exploited this transformation towards an expeditious synthesis of [3.1.0]bicyclic cyclopropylketones such as sabina ketone, from easily prepared 1,5-enyne 11. This natural product is a key precursor of monoterpenes such as sabine. A formal mechanism would involve platinacarbene of type D (Pt-D) that is trapped by the exo-methylene motif to generate the corresponding polycyclic cyclopropylvinylacetate 12 as a single diastereomer. One has to say ‘formal’ since a total chirality transfer was observed by Fürstner from the exactly the same precursor with AuCl₃(pyridine), suggesting a more concerted type of mechanisms in all these transformations. After saponification, the desired sabina ketone was isolated in 83% yield over these two steps (Scheme 4).

Moving from platinum(II) to gold(I) revealed a more efficient and general way to generate molecular complexity which has been highlighted in several total syntheses in various families of natural products. We exploited the gold-catalyzed 1,2-acyloxy transposition/trapping sequence towards neomerane sesquiterpenes skeletons. Sesquiterpenes are an important class of natural products as they are found in plants and insects, acting as semiochemicals. Two targets attracted more specifically our attention, namely neomeranol and valeneomerin B. Neomeranol 13 is a brominated sesquiterpene alcohol which was isolated from the green alga *Neomeris annulata*. Besides its attractive structure of marine-halogenated metabolite, neomeranol shows phytotoxicity to Johnson grass and toxicity to brine shrimp. More recently, mother nature offered another surprise since the related neomerane-type sesquiterpenoid valeneomerin B (14) was isolated in continental surroundings from the roots of *Valeriana officinalis var. latifolia*. For centuries, this plant has been used in Chinese medicine for the treatment of insomnia. To date, no total synthesis of these two sesquiterpenoids has been described.

We surmised that a substrate bearing a propargyl acetate function as a carbene precursor as well as a prenyl acceptor could lead to the common 5,7,3-fused ring skeleton in one step by platinum- or gold-catalyzed 1,2-aclyoxy migration/intramolecular cyclopropanation sequence. Starting from 6-methyl-5-hepten-2-one and thanks to highly diastereoselective steps, precursor 15 was efficiently obtained in seven steps. While PtCl₂ failed to give any cycloisomerization product, Echavarren’s cationic gold(I) complex [Au1] proved to be the most effective in this transformation and led to the expected tricycle 16 in 70% yield as a single diastereoisomer, probably through the vinyl gold carbene intermediate of type D (Au-D). Liberation of an enolate intermediate by MeLi followed by trapping by iodomethane or formaldehyde provided the desired skeletons. Better yields were obtained in the latter case which drove us to valeneomerin B family. After desilylation and diastereoselective reduction, triol 17 was obtained in 32% overall yield which could be acetylated to access 5-epi-valeneomerin B (Scheme 5).
While the 1,2-O-acyl migration–carbene formation proved to be a very good trigger for a series of intramolecular events, we also examined intermolecular trappings as first described by Ohe and Uemura.\textsuperscript{33} Notably, we developed a new polymerization process by polycyclopropanation\textsuperscript{34} of styryl propargyl acetates.\textsuperscript{35} In collaboration with the Ryu's and Fukuyama's group in Osaka, we also considered the possibility to incorporate CO into the Rautenstrauch rearrangement.\textsuperscript{36} While the platinum and gold carbene intermediate complexes D could not trap CO, rhodium(I) catalysis proved to be the right option. Thus, under CO atmosphere, a Rh-catalyzed O-acyl transposition can lead to a subsequent cyclocarbonylation to afford formal [4+1] or [5+1] products, depending on the alkyne substituent on precursors 18 (Scheme 6). Disubstituted alkyne (R\textsuperscript{1} ≠ H) lead to exo-Z-cyclopentenones 19 as major diastereoisomers while terminal alkyne (R\textsuperscript{1} = H) gave resorcinol derivatives 21. In the first case, 1,3-O-acyl migration, as we will also see later, leads to rhodacyclopentenes E, which insert CO to give 19. In contrast, after 1,2-O-acyl migration, intermediates of type D (Rh-D) insert CO to give ketenes 20 that undergo electrocyclization to provide valuable resorcinols 21.

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\text{Scheme 6 Carbonylative Rautenstrauch rearrangement via Rh catalysis}
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For instance, enyne 22 gave 23 in 37\% yield (along with noncarbonylated cyclopentenone), which is an ester derivative of the natural product olivetol. Olivetol\textsuperscript{37} is an extract of lichen and a precursor of tetrahydrocannabinol (THC). It is secreted by some insects, either as a pheromone, a repellent, or an antiseptic.

Allenes were obvious substrates to submit to electrophilic catalysis and we focused on vinyl allene substrates of type 24 flanked with a pendant alkene group.\textsuperscript{38} We demonstrated that the central allene moiety can be activated by gold, leading to allylic cation or ben allene intermediate 25,\textsuperscript{39} as modeled by V. Gadon, that triggers a Nazarov-type cyclization. The generated gold cyclopentenyldiene intermediate 26 is then trapped by the second olefin present, leading to cyclopropane containing tricyclic derivatives of type 27 (Scheme 7).\textsuperscript{40}

4 From Alkylidene Bis(sulfoxides) to Chiral Carboxylic Acids

In a context of total synthesis, methodology towards obtaining enantiopure products is of utmost importance. Diastereoselective synthesis is one of the major techniques within asymmetric catalysis and racemate separation to access optically active compounds. In this context, we...
studied the synthesis\textsuperscript{43} and the reactivity of chiral alkylidene bis(sulfoxides) 32\textsuperscript{44} as chiral Michael acceptors in radical\textsuperscript{45} and ionic processes.\textsuperscript{46,47}

For examples, various neutral or anionic nucleophiles can be stereoselectively introduced by conjugate addition. Indeed, after optimization of the reaction conditions, we showed that amines, alcoholates and dimethylmalonate lead to the (S)-adducts of type 33 in excellent diastereomeric ratios. Cyclopropane formation ((S)-34) is also possible by using sodium bromomalonate as nucleophile: concomitant nucleophilic substitution occurs to afford the corresponding pentasubstituted cyclopropane. By using diethylzinc, a small erosion of the selectivity was observed, probably due to involvement of competitive chelate, and (S)-33d was obtained in 88:12 diastereoisomeric ratio (84%). Finally, the use of cuprate reagents\textsuperscript{45b} allowed to selectively obtain the opposite (R)-adduct (R)-33e (Scheme 9).\textsuperscript{46}

The diastereoselectivity outcome of the addition process was rationalized based on the examination of the X-ray structure of alkylidene bis(sulfoxides) and notably 32a (R = Ph). The latter discloses a tolyl-tolyl π-stacking interaction (3.53 Å between centroids). It also shows that the lone pair of one of the sulfonyl group quasi-eclipses the alkene substituent R. Moreover, one can notice a hydrogen bonding between the oxygen of the other sulfonyl group and the vinyl hydrogen atom in β-position (d = 2.28 Å) which results in minimization of allylic strain. Assuming a similar preferred conformation of type F in solution, which is also consistent with conformational calculations of vinyl sulfoxides,\textsuperscript{48} the p-tolyl substituents would hinder the alkene Re face and thus direct the nucleophilic attack on the Si face to give the corresponding (S)-adduct. In the presence of cuprate reagents like methyl cuprate, chelates of high complexity, as suggested by calculations,\textsuperscript{45b} are probably involved to give rise to the (R)-adduct (Scheme 10).

A valuable feature of a bis(sulfinyl) moiety is that it can be transformed into a carboxylic derivative through a Pummerer type of rearrangement.\textsuperscript{44} We applied this methodology to the total synthesis of optically enriched α-substituted carboxylic acids profens, which is most important group of nonsteroidal anti-inflammatory drugs. Although they are prescribed as a racemic mixture, there is indeed a constant interest in obtaining them in the enantioenriched form. In spite of the fact that (S)-profens are generally accepted to be the bioactive enantiomers, knowing the pharmaceutical profile of the (R) derivatives is essential.\textsuperscript{49} When styryl bis(sulfoxide) 32f was treated by methyl lithium (2 equiv) in the presence of copper iodide, the expected adduct (R)-33f was isolated quantitatively as a single diastereoisomer. Subsequent treatment with trifluoroacetic anhydride in the presence of pyridine and saponification led to enantioselectively pure (R)-fenoprofen in 40% yield (Scheme 11).\textsuperscript{46,50}
It possesses amongst others an interesting antituberculosis activity.\(^5\) It was isolated in 1999 from fermentation of broth of Sphaeropsis sp.,\(^5\) it displays an interesting antibiotic activity against Staphylococcus aureus and Bacillus subtilis, and interacts with interleukine-1 that is involved in the immune system.

However, when the corresponding Z-enolates Z-35 or Z-36 were used, even if the face selectivity of the addition onto the alkylidene was total, the undesired anti-adduct was obtained as the major diastereoisomer. This lack of diastereoselectivity can be explained by the dissociative effect of HMPA used to generate the Z-enolate: OLi becomes less sterically demanding, so the differentiation between OLi and OtBu is weaker than without HMPA. So, the slightly favored transition state F3 preventing the steric interaction between the methyl substituent and the alkylidene alkene side chain and leading to the anti-product is in competition with transition state F2 giving the desired cis isomer. By using a large excess of HMPA and higher temperature (–20 °C), both diastereoisomers were obtained in an almost 1:1 ratio, providing synthetically useful quantities of syn-33h adduct (30%). Total synthesis of (+)-sphaeric acid was successfully completed after double saponification. The first one relied on the previously described Pummerer/LiOH–H\(_2\)O\(_2\) sequence. But a TMSCI/Nal treatment was necessary to cleave the tert-butyl ester (15% overall).\(^6\) It is worthy to note that absolute configuration of (+)-sphaeric acid was established for the first time through this total synthesis (Scheme 13).

Respective synthesis of the syn diastereoisomer was also envisioned and we targeted optically enriched syn-sphaeric acid. Isolated in 1999 from fermentation of broth of Sphaeropsis sp.,\(^5\) it displays an interesting antibiotic activity against Staphylococcus aureus and Bacillus subtilis, and interacts with interleukine-1 that is involved in the immune system.

5 Conclusion and Perspectives

In conclusion, this journey has highlighted several methodologies, radical cascades, electrophilic catalysis, and bis-sulfoxide chemistry which bear as common feature the possibility to rapidly access molecular complexity from readily available precursors. This has allowed to assemble various types of natural products (acyclic, heterocyclic, and polycyclic). Our next efforts in this area consist in the development of new catalytic processes, notably photoredox or...
photosensitized cascades, as well as dual catalysis sequen-
ces. We have recently evidenced the high synthetic potential
embodied in this type of approaches.  

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