C. R. Chimie xxx (2018) 1–12

Contents lists available at ScienceDirect

Comptes Rendus Chimie

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Recent trends in perfluorinated sulfoximines

Développements récents de la chimie des sulfoximines perfluorées

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ARTICLE INFO

Article history:
Received 29 November 2017
Accepted 11 January 2018
Available online xxxx

Keywords:
Fluorine
Synthetic methods
Sulfur
Sulfoximines

ABSTRACT

The search for original perfluorinated moieties is a very modern and attractive challenge. Among the emergent groups, the *S*-perfluoroalkylated sulfoximines are very peculiar because of their structural diversity and promising properties. A literature survey shows that interest in these molecules is strongly increasing. This short review summarizes the recent works devoted to this topic.

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Mots clés:
Fluor
Méthodes de synthèse
Soufre
Sulfoximines

RÉSUMÉ

La recherche de groupes fluorés originaux est un défi moderne de la chimie organique. Parmi ces entités fluorées, les sulfoximines *S*-perfluoroalkylées représentent une classe particulière de composés, en raison de leur structure, mais aussi de leurs propriétés intéressantes. L'intérêt pour ces molécules est en forte augmentation dans la littérature. Le but de cette mini-revue est de résumer les travaux récents dédiés à cette thématique.

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1. Introduction

Sulfoximines are very intriguing sulfur(VI) compounds and can be considered as monoaza analogues of sulfones [1a] (Fig. 1).

They nevertheless display much more diversity in terms of structure and reactivity than sulfones because of the multiple potential variations offered by the replacement of an oxygen by a nitrogen (Fig. 1). Two major differences may be highlighted. In the case of two different groups R_1 and R_2, this replacement brings the chirality to the sulfur center and also allows the introduction of a mostly unlimited number of substituents attached to the nitrogen. The variety of possible skeletons has then allowed the fine modulation of the electronic and configuration properties of these original structures, accounting for their use in various applications [1]. Numerous reactions using the chiral pool of the sulfoximines have been described in the field of asymmetric synthesis [2] and ligands for catalysis [3]. To a lesser extent, they also exhibit interesting properties for life science purposes [4] or as building blocks for the preparation of pseudopeptides [5]. Interestingly, a recent article

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https://doi.org/10.1016/j.crci.2018.01.004
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Please cite this article in press as: A.-L. Barthelemy, E. Magnier, Recent trends in perfluorinated sulfoximines, Comptes Rendus Chimie (2018), https://doi.org/10.1016/j.crci.2018.01.004

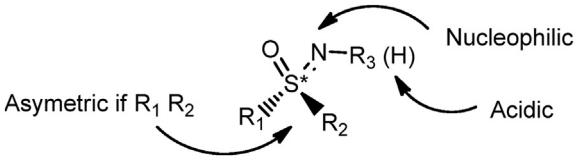


Fig. 1. General structure of sulfoximines.

has highlighted this particular heteroatomic group as a "neglected opportunity in life science" [6].

When one of the two groups (R_1 or R_2) bonded to the sulfur atom is a perfluoroalkyl chain, huge differences immediately appear whether it be for the synthesis or concerning the applications. Most of the synthetic routes reported for the preparation of nonfluorinated sulfoximines start from the corresponding thioethers or sulfoxides [7] and are not effective for the fluorinated series because of the tamed reactivity of the sulfur atom. Therefore, the synthesis of such compounds is a challenge for chemists. In 2009, a three-step methodology for the preparation of *N*H *S*-perfluoroalkylated sulfoximines was reported by our group paving the way for an extension of the structural diversity of these sulfur(VI) derivatives [8]. In the last decade, perfluoroalkylated sulfoximines were intensively studied because of their promising properties. They were described as highly electron-withdrawing substituents [9] or as building blocks for liquid crystals [10]. However, the most widespread applications involved their use as reagents for the transfer of the perfluoroalkyl group by electrophilic [11], nucleophilic [12], and very recently radical pathways [13]. In 2014, two reviews, independently written by Bolm et al. [14] and Shen and Hu et al. [15] have made a state in terms of syntheses, properties, and applications of fluorinated sulfoximines. This review will consequently focus on an overview of the new trends in this research area, since 2014. Accordingly, we will discuss the structural diversification of the skeleton of sulfoximines via N-functionalization or *ortho*-lithiation, their applications in catalytic and organocatalytic systems, their use as perfluoroalkylating reagents, and their potential as biologically active molecules.

2. Synthesis

2.1. N-Functionalization

We have previously demonstrated that the reactivity of the *S*-perfluoroalkylated sulfoximines depends on the group attached to the nitrogen atom [11f], highlighting thus the need for the development of efficient methods of N-functionalization of sulfoximines.

2.1.1. N-Functionalization of S-perfluoroalkylated sulfoximines

In 2011, our group described the copper-assisted N-arylation of perfluorinated sulfoximines [16]. However, this transformation required the reflux of toluene during several hours as reaction conditions. A slight improvement, using a microwave activation, enabled a significant reduction in the reaction time and an increase in the molecular diversity of the targeted *N*-arylated sulfoximines **2a**–**f** obtained in 81–92% yield (Scheme 1) [17].

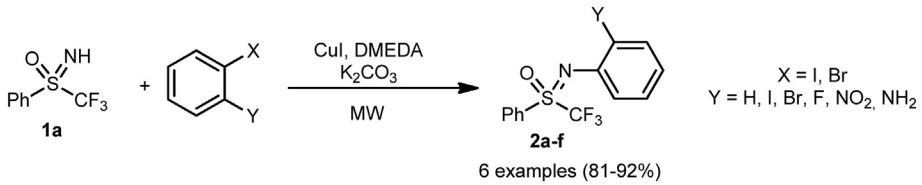
The copper-catalyzed preparation of *N*-alkenyl and *N*-alkynyl sulfoximines was consequently studied by our group [18]. A wide variety of *N*-alkenyl trifluoromethyl sulfoximines **3a**–**f** were synthesized in moderate to excellent yields (up to 94%) from the corresponding 1,2-disubstituted vinyl halides, with CuI as a catalyst, K_2CO_3 as a base, and DMEDA as a ligand (Scheme 2). This procedure was also extended to other perfluoroalkyl chains, in the presence of vinyl bromide, leading to the formation of **3g** and **3h** in moderate yield. The same reaction conditions, applied to bromophenylacetylene or 1-bromohexyne led to the formation of *N*-alkynyl sulfoximines **4a** and **4b** in 98% and 81% yield, respectively. The previous procedure did not succeed with phenylacetylene. Therefore, the reaction conditions were modified to perform the N-alkynylation of sulfoximines, using $CuCl_2$ as a catalyst, pyridine as a ligand, and Na_2CO_3 as a base, giving rise to products **5a**–**l** with good to excellent yields (55–96%).

We also demonstrated that the N-functionalization of sulfoximines could also occur via a nucleophilic pathway providing the use of smooth conditions (Scheme 3). The use of NaH and a catalytic amount of Bu_4NBr allowed the N-alkylation of the sulfoximine **1a** to give rise to compounds **6a** and **6b** with excellent yields. The nucleophilicity of the nitrogen atom of the sulfoximine was also underlined by the reaction between **1a** and phenylisocyanate to deliver sulfoximine thioureas **7a** and **7b**.

The presence of an iodine, bromine, or amino group in *ortho*-position in compounds **2** enabled a post-functionalization (Scheme 4). Bis-sulfoximines **8a** and **8b** were thereby synthesized with 76% and 81% yields, respectively, starting from dibromo- or diiodobenzene and the *N*-arylated sulfoximine **2a**. A two-step reductive amination delivered the molecule **10** in 97% yield, whereas the treatment of compound **2c** with isothiocyanate allowed the preparation of sulfoximine thioureas **9a** and **9b** in good yields.

2.1.2. N-fluoroalkylation of sulfoximines

In 2015, Bolm et al. [19] reported that nonfluorinated sulfoximines can be successfully *N*-trifluoromethylated using a silver catalysis (Scheme 5). Twenty *N*-CF_3 sulfoximines **12** were synthesized by treatment of the



Scheme 1. Copper-catalyzed N-arylation of sulfoximines.

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