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A New Synthesis of Allyl Sulfoxides via Nucleophilic Addition of Sulfinyl Carbanions to Group 6 Fischer Carbene Complexes

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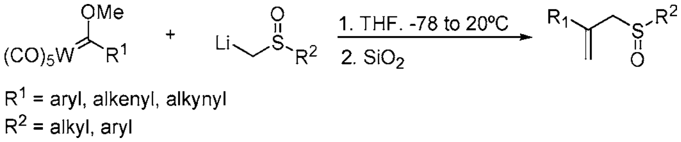
ABSTRACT



A novel synthesis of allyl sulfoxides has been developed. Primary α-lithiosulfinyl carbanions react with group 6 Fischer carbene complexes to give allyl sulfoxides as products. The Fischer carbene complex experiments involve a 1,2-addition of two molecules of sulfinyl carbanion to give an intermediate that, after a *β*-elimination, furnishes the mentioned product.

Allyl sulfoxides are versatile and valuable building blocks in organic synthesis,[1] as proved by their use in the preparation of various functionalized compounds[2] and natural products.[3] Hence, efficient and convenient methods for their preparation are still in demand and are a challenging goal. A careful literature survey reveals that the main approach to allylic sulfoxides is the oxidation of allylic sulfides with electrophilic oxidants. However, such methodology can have serious drawbacks such as a lack of chemoselectivity.[4]

On the other hand, Group 6 carbene complexes have been shown to be very efficient and versatile starting materials for carrying out a wide variety of organic transformations.[5] In particular, the addition of carbon nucleophiles such as organolithium compounds, enolates, and enamines to these complexes provides a great array of organic compounds, mainly carbo- and heterocyclic structures.[6]

These processes have been widely studied and have shown to be strongly dependent on the nature of the nucleophile, temperature, or workup conditions. However, the addition of carbanions stabilized by a sulfur atom has been scarcely investigated.[7]

In this context, we now wish to communicate a new synthesis of allyl sulfoxides via the nucleophilic addition of

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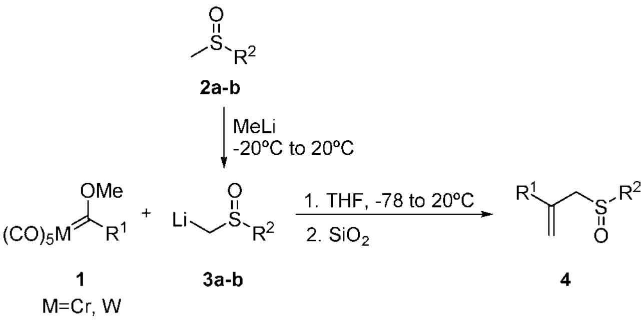
sulfinyl carbanions[8] to group 6 (M = Cr or W) electrophilic carbene complexes.

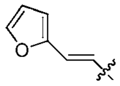
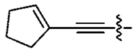
Initially, we investigated the reaction of α-unsubstituted lithiosulfinyl carbanions with Fischer carbene complexes. When the lithium sulfinyl carbanions **3** (prepared by treatment of sulfoxides **2** with methyllithium at −20 °C) were added to a solution of the Fischer carbene complexes **1** in THF at −78 °C, the allyl sulfoxides **4** were obtained after hydrolysis with silica gel and conventional workup (Scheme 1).

Scheme 1. Allyl Sulfoxides **4** from Carbene Complexes **1** and Primary α-Lithiosulfinyl Carbanions **3a**,**b**



As indicated by the examples in Table 1, the reaction takes place both with chromium and tungsten complexes. However, the allyl sulfoxides are generally obtained in better yield when tungsten complexes are used as acceptors (see **1a** vs **1c** and **1b** vs **1g**). On the other hand, attempts to accomplish the reaction of alkyl carbene complex **1i** (M = W, R^1 = Me) with sulfinyl carbanions **3** were unsuccessful, and the starting carbene was recovered after hydrolysis and workup, probably due to a competitive abstraction of the α-proton of the carbene complex by the sulfinyl carbanion.

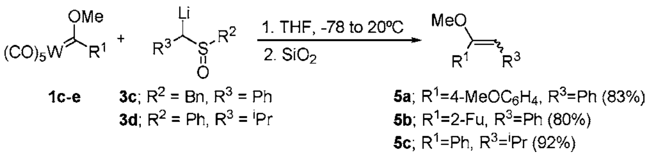
Table 1. Preparation of Allyl Sulfoxides **4** from Carbene Complexes **1** and α-Sulfinyl Carbanions **3**

Carbene Complex	M	R^1	Sulfynil Anion	R^2	Prod.	Yield (%)^a
1a	Cr	Ph	**3a**	Me	**4a**	21
1c	W	Ph	**3a**	Me	**4a**	60
1d	W	4-MeOC$_6$H$_4$	**3a**	Me	**4b**	63
1e	W	2-furyl	**3a**	Me	**4c**	60
1b	Cr	PhC≡C	**3a**	Me	**4d**	25
1g	W	PhC≡C	**3a**	Me	**4d**	62
1f	W		**3a**	Me	**4e**	45
1h	W		**3a**	Me	**4f**	58
1d	W	4-MeOC$_6$H$_4$	**3b**	*p*-Tol	**4g**	61
1e	W	2-furyl	**3b**	*p*-Tol	**4h**	55
1g	W	PhC≡C	**3b**	*p*-Tol	**4i**	58
1i	W	Me	**3a**	Me	^{b}	

^{a} Isolated yield based on carbene complex **1**. ^{b} Carbene complex **1i** was recovered.

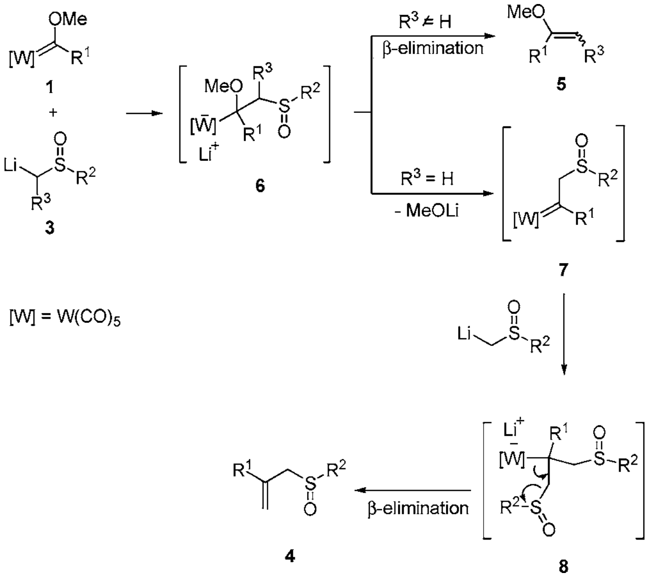
A totally different reaction pathway was observed when α-substituted lithiosulfinyl carbanions were used. Thus, treatment of carbene complexes **1c**−**e** with α-lithiosulfinyl carbanions **3c**,**d** at −78 °C led to the enol ethers **5** in high yield after warming to room temperature but as a 2:1 *Z*/*E* mixture (Scheme 2).[9]

Scheme 2. Enol Ethers **5** from Carbene Complexes **1c**−**e** and α-Substituted Lithiosulfinyl Carbanion **3c**,**d**



The formation of compounds **4** or **5** can be explained by the mechanism presented in Scheme 3. 1,2-Addition of one molecule of the sulfinyl carbanion **3** to the Fischer carbene complex **1** would give the intermediate **6**. Depending on the substitution pattern in the sulfinyl derivative, the subsequent

Scheme 3. Proposal for the Formation of Allyl Sulfoxides **4** and Enol Ethers **5** from Carbene Complexes **1** and Sulfinyl Carbanions **3**



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(9) This olefination reaction is achieved only with aryl or heteroaryl carbene complexes. When alkenyl and alkynyl carbene complexes are used, a complex mixture of products coming from 1,2- and 1,4-addition is obtained.

evolution of this intermediate can take two different courses. When $R^3 = H$, loss of the methoxy group in **6** leads to the nonstabilized carbene **7**. A second addition of the sulfinyl carbanion **3** to the highly reactive complex **7** gives rise to the new intermediate **8**, which then undergoes β-elimination to the allyl sulfoxide **4**. When $R^3 \neq H$, however, a direct β-elimination takes place with **6** to afford the enol ether **5**.

In conclusion, we have described a new pathway to allyl sulfoxides using sulfinyl carbanions and Fischer carbene complexes.

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Supporting Information Available: Experimental procedures with a description of ^1H and ^{13}C NMR data and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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