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A New Radical Synthesis of Allenes

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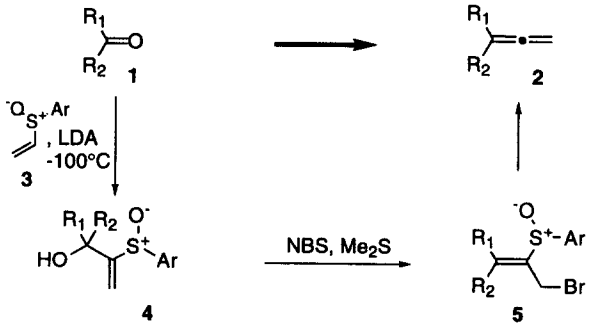
Abstract : The unprecedented radical β-elimination of vinylsulfoxides opens a new access to functionalized di- and trisubstituted allenes. The radical precursors are obtained in two steps from a carbonyl derivative and a vinylsulfoxide. The radical translocation trick can also be used to trigger the β-elimination of the sulfinyl radical. © 1999 Elsevier Science Ltd. All rights reserved.

Allenes are valuable synthetic partners in a variety of reactions including for instance oxidations, cycloadditions, metal catalyzed cycloisomerizations, formations of π-allyl complexes and electrocyclizations.[1] This explains in part the constantly observed interest in the invention of new allene syntheses. Most methods are based on the S_N2' displacement of a propargylic leaving group.[2] Other recent methods have involved the elimination of enolphosphates,[3] a tandem : Baylis-Hillman reaction of alkenylphosphonates with carbonyl compounds, followed by a Horner-Wadsworth-Emmons elimination[4], or the allenation of aldehydes with alkenyl titanocene derivatives.[5] Probably because allenes are excellent radical acceptors,[6] there has been, to the best of our knowledge, no versatile preparation of allenes relying on a radical route. Two sporadic reports mentioned that allenes can be obtained by the addition of halogens[7] or selenosulfonates[8] to cyclopropylacetylene, the reaction proceeding *via* the rearrangement of an α-cyclopropyl vinyl radical.

We report here the first radical synthesis of allenes, based on the β-elimination of a sulfinyl radical.[9,10] We used the bromides **5**, as precursors for the β-elimination (Scheme 1), which were easily obtained in two steps from a carbonyl derivative **1** and a vinylsulfoxide **3**, using Maignan's chemistry.[11] The overall process (**1**→**2**) would therefore constitute a new addition to the previously known transformations of aldehydes and ketones into allenes.[12-14]



Scheme 1

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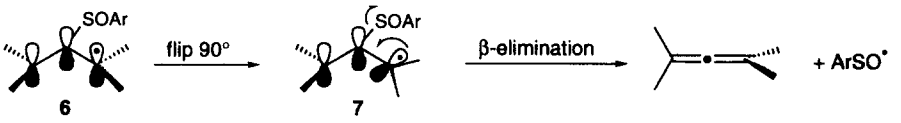
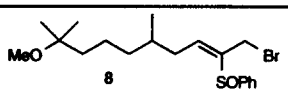
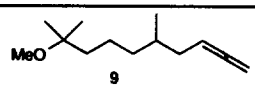
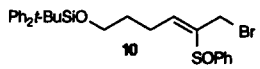
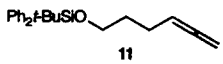
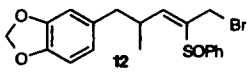
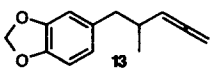
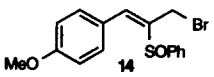
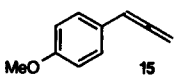
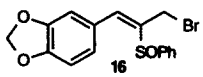
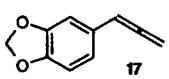
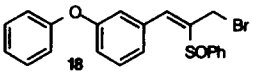
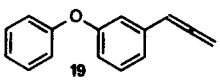
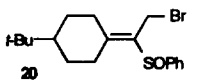
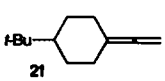
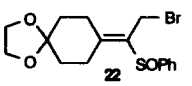
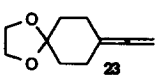
The β-elimination of sulfinyl radicals has been estimated to be a very fast process *ca.* $10^9\ s^{-1}$, in the case of an arylsulfoxide borne by a Csp3 center.[15] However, nothing is known regarding the radical β-elimination of vinylsulfoxides. We feared that the required energy barrier to break the conjugation of the allylic radical **6** would be quite high, especially since the almost reverse pathways : the seleno-[16] and iodosulfonation[17] of allenes have been described as favorable reactions (Scheme 2).



Scheme 2

Nevertheless, our initial findings showed that precursor **8** when heated, in presence of a hydrogen donor and AIBN furnished 53% of clean allene **9** (Table, entry 1). Aliphatic aldehydes (entries 1-3), aromatic aldehydes (entries 4-6) and ketones (entries 7-8) could serve satisfactorily as allene precursors. The reaction was shown to be temperature dependent since when it was performed at a lower temperature (10°C, AIBN, hν) with precursor **18**, no allene **19** was formed, yielding only the reduction product.

Table

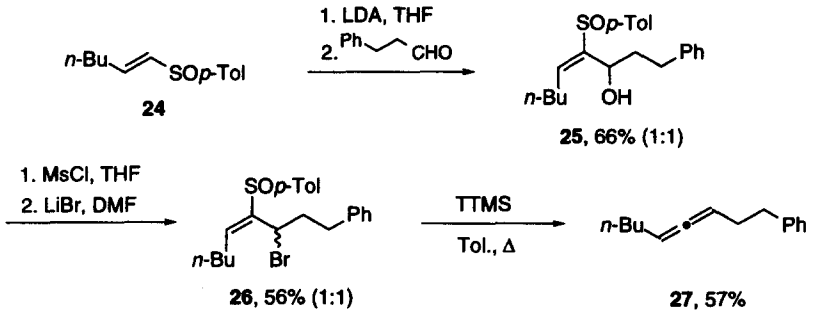
Entry	Bromide	Allene[a]	Yield, %
1			53
2			55
3			80[b]
4			56[d]
5			57
6			70
7			30[c,d]
8			40[d]

[a] See general procedure in the references section.[18] [b] Reaction was run in benzene. [c] Bu_3SnH was used. [d] Volatile material.

The same failure was met with precursor **20** at rt with triethylborane as the radical initiator, giving 76% of reduction product. This clearly confirmed the importance of providing some energy to the reacting system to trigger the β-elimination reaction.

The sulfinyl radical which is generated during the course of the reaction presumably dimerizes, and then a disproportionation occurs and furnishes ArS· and $ArSO_2$· radicals.[19] This was evidenced by isolating the $ArSSi(SiMe)_3$ or $ArSSnBu_3$ adduct in several of our reactions, suggesting that the radical chain is not properly maintained. Thus, an excess of AIBN and hydrogen donor has to be used to guarantee a complete conversion. In most cases, we also found the tris(trimethylsilyl)silane (TTMS) to be a superior reagent for this reaction, as it minimizes the formation of the reduction products.

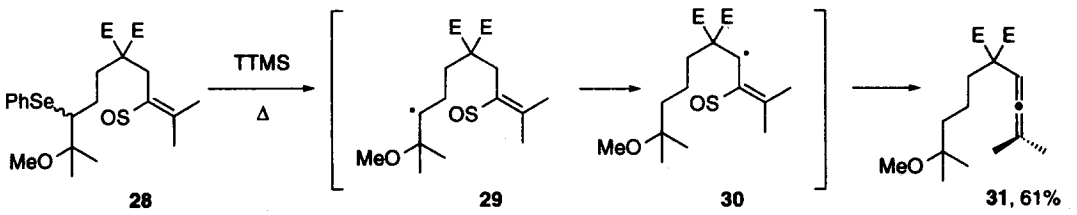
As this method appears suitable for the preparation of terminally unsubstituted allenes, we could extend it to di- and trisubstituted internal products. The following synthetic sequences were devised. Hexenylsulfoxide **24** was metallated with LDA and the resulting anion was quenched with hydrocinnamaldehyde to provide the sulfinyl alcohol **25** in 66% yield (scheme 3). The allyl bromide **26** was obtained through mesylation[20] and mesylate-bromide exchange. Exposure to TTMS in refluxing toluene and in presence of AIBN yielded the aliphatic allene **27** in 57% yield.



Scheme 3

We then sought to contract the number of steps for the synthesis of the precursors and notably to avoid the introduction of an allyl bromide functionality. The radical translocation trick, through a 1,5-H transfer, proved to be the method of choice. Thus, when precursor **28**, readily obtained by the coupling of a selenomalonate and the corresponding allylbromide, was treated with TTMS, allene **31** was obtained in 61% yield, accompanied by 18% of reduced product. The alkyl radical **29** undergoes a 1,5-H transfer to generate the more stabilized allyl radical **30**,[21] which can engage in a β-elimination of the sulfinyl radical (Scheme 4). Labelling experiments with Bu_3SnD have been carried out. No deuterium was incorporated at the allylic position of the reduction product, suggesting an efficient β-elimination after the radical translocation.

In conclusion, the previously unknown radical β-elimination of vinylsulfoxides has revealed as a new versatile entry for the preparation of di- and trisubstituted allenes. We are now exploring the asymmetric synthesis of allenes using enantiopure sulfoxides.



E = CO_2Me ; SO = *p*-TolSO

Scheme 4

Acknowledgement :

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(18) General Procedure : To a 0.02 M benzene solution of bromide **12** (204 mg, 0.5 mmol) were added AIBN (62 mg, 0.38 mmol, 0.75 equiv.) and TTMS (230µL, 0.75 mmol, 1.5 equiv.). The mixture was refluxed under nitrogen for 2 h, and the same quantity of AIBN, and TTMS (80mL, 0.25 mmol, 0.5 equiv.) were added. After 2 additional hours, the solvent was evaporated. The crude product was purified by flash chromatography (PE:EtOAc 100 : 0 to 90 : 10) to give 81 mg (80% yield) of pure allene **13**. ^1H NMR (200 MHz, $CDCl_3$) δ 1.00 (d, *J* = 6.5 Hz, 3H); 2.22-2.67 (m, 3H), 4.67 (dd, *J* = 12.6, 2.8 Hz, 2H), 5.11 (dd, *J* = 12.6, 6.6 Hz, 1H), 5.91 (s, 2H), 6.57-6.74 (m, 3H). IR 2950, 1950, 1480, 1240 cm^{-1}.
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