Pergamon

Tetrahedron Letters 43 (2002) 2043–2046

TETRAHEDRON
LETTERS

A novel synthesis of allenes by alkenylation of magnesium alkylidene carbenoids with lithium α-sulfonyl carbanions

Tsuyoshi Satoh,* Tatsuya Sakamoto and Masanori Watanabe

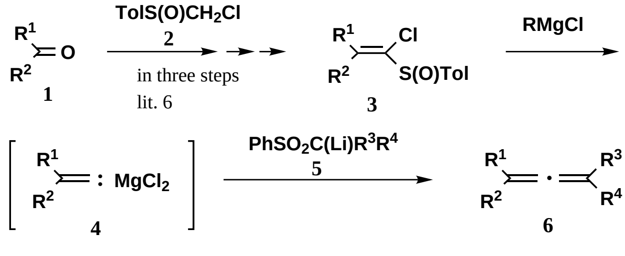
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Received 10 December 2001; accepted 11 January 2002

Abstract—Treatment of magnesium alkylidene carbenoids, which were generated from 1-chlorovinyl *p*-tolyl sulfoxides with a Grignard reagent by sulfoxide–magnesium exchange, with lithium α-sulfonyl carbanions gave allenes in moderate to good yields. This procedure offers a novel synthetic method for allenes with three-component coupling in relatively short steps. © 2002 Elsevier Science Ltd. All rights reserved.

Allenes are quite important and interesting compounds in organic and synthetic organic chemistry, and a large number of studies have been reported on their chemistry and synthesis.[1] The general methods for the synthesis of allenes are, for example, isomerization of acetylenes,[2] ring-opening of cyclopropylidenes,[3] the reaction of propargylic derivatives with organocopper reagents,[4] and β-elimination of olefins.[5]

We previously reported the generation of magnesium alkylidene carbenoids **4**[6] from 1-chlorovinyl sulfoxides **3** by a sulfoxide–magnesium exchange reaction and an application of the methodology to a new synthesis of tetra-substituted alkenes.[6] In continuation of our study on the use of the magnesium alkylidene carbenoids[7] generated by the sulfoxide–metal exchange reaction[8] in organic synthesis, we investigated the reaction of carbenoids **4** with some carbanions and found that lithium α-sulfonyl carbanions **5** gave allenes **6** in moderate to good yields (Scheme 1). This procedure offers a novel method for the synthesis of allenes **6** from three components, ketones **1**, chloromethyl *p*-tolyl sulfoxide **2**, and sulfones **5**, in relatively short steps.



Scheme 1.

In a previous paper, we reported the generation of magnesium alkylidene carbenoids **4** from 1-chlorovinyl *p*-tolyl sulfoxides **3** and their properties.[6] In order to use the carbenoids **4** in a new synthetic method, we reinvestigated an improved method for the generation of the magnesium alkylidene carbenoids **4** from **3** as follows (Scheme 2).

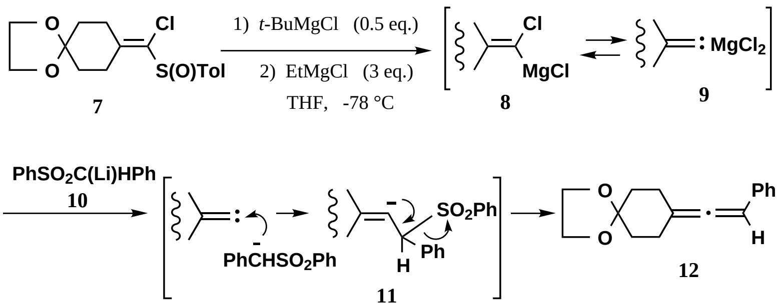
In a flame-dried flask, 0.5 equivalent of *t*-BuMgCl was added to a solution of **7** (1 equivalent) in dry THF with stirring at −78°C. Using this treatment no reaction of **7** with *t*-BuMgCl took place, but a trace of moisture in the solution was removed. After 10 min, 3 equivalents of EtMgCl or *i*-PrMgCl (both Grignard reagents work equally well) were added to the reaction mixture. A quite rapid reaction took place to give the magnesium alkylidene carbenoid **8** in over 92% chemical yield, and the protonation was suppressed to less than 10% (the protonation product of this reaction is the desulfinylated chloroalkene).

To this carbenoid a solution of the lithium α-sulfonyl carbanion **10** (3 equivalents) derived from benzyl phenyl sulfone was added, and the temperature of the reaction mixture was gradually allowed to warm to room temperature. We obtained a crystalline compound which showed sharp absorption at 1954 cm^{-1} in IR spectrum. Other spectral data showed that the product was the allene **12**. We propose a plausible mechanism of this reaction, as shown in Scheme 2.

Keywords: allene; magnesium alkylidene carbenoid; sulfoxide; sulfoxide–magnesium exchange; sulfone.

* Corresponding author.

PII: S0040-4039(02)00103-X



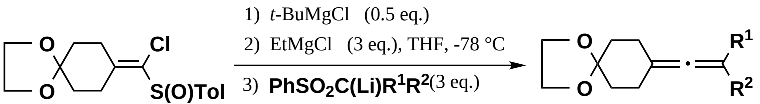
Scheme 2.

First, the lithium α-sulfonyl carbanion **10** attacks the electron-deficient carbenoid carbon of **9** to give the vinyl anion **11**. As the sulfonyl group is a good leaving group, β-elimination takes place to afford the allene **12**.

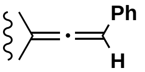
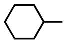
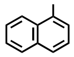
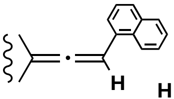
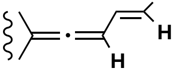
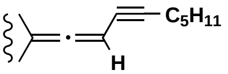
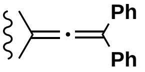
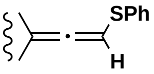
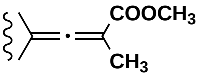
We next investigated this reaction using various kinds of sulfones, and the results are summarized in Table 1. The result in entry 1 has been described above. The results in entries 2–4 are quite interesting. In contrast to the result with benzyl phenyl sulfone (entry 1), the α-sulfonyl carbanion having a hydrogen or an alkyl group as R^1 gave no allenes but only a complex mixture.

One difference between benzyl phenyl sulfone and the sulfones in entries 2–4 is the acidity of the hydrogen on the carbon bearing the sulfonyl group. The p*K*a values of these hydrogens are estimated to be as follows:[9] $PhSO_2C\underline{H}_2Ph$ (23.4), $PhSO_2C\underline{H}_3$ (29), $PhSO_2C\underline{H}_2CH_3$ (31). These values imply that some carbanion-stabilizing group is essential for the reaction of the α-sulfonyl carbanion with the magnesium alkylidene carbenoid.

Table 1. Synthesis of allenes **13** from 1-chlorovinyl *p*-tolyl sulfoxide **7** and various lithium α-sulfonyl carbanions

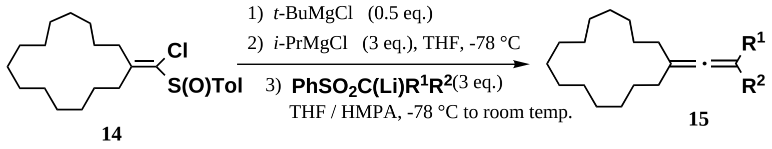


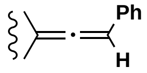
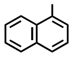
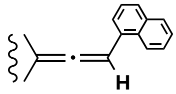
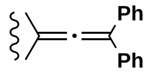
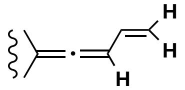
7 13

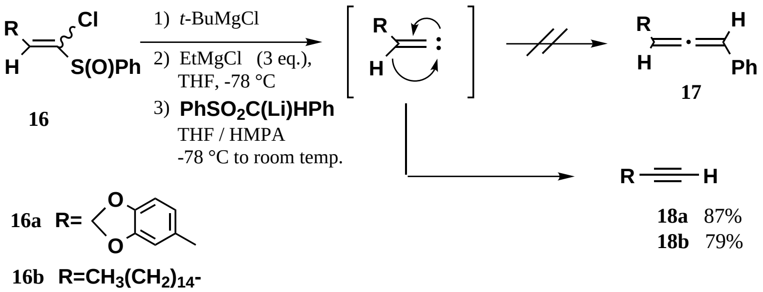
Entry	Sulfone		Allene	Yield
	R^1	R^2		%
1	Ph	H		63
2	H	H	complex mixture	—
3	$CH_3(CH_2)_8$	H	complex mixture	—
4		H	complex mixture	—
5		H		51
6	CH_2=CH	H		51
7	$C_5H_{11}-\equiv$	H		65
8	Ph	Ph		41
9	PhS	H		14[a)]
10	$COOCH_3$	CH_3		41[b)]

a) The reaction was carried out in the presence of DMPU. b) The reaction was carried out in the presence of HMPA.

Table 2. Synthesis of allenes **15** from 1-chlorovinyl *p*-tolyl sulfoxide **14** and various lithium α-sulfonyl carbanions



Entry	Sulfone		Allene	Yield
	R^1	R^2		%
1	Ph	H		54
2		H		56
3	Ph	Ph		24
4	CH_2=CH—	H		61



Scheme 3.

Actually, the sulfones having a carbanion-stabilizing group on the α-carbon gave the desired allenes, as shown in entries 5–10, though the yields were variable. It is interesting to note that tetra-substituted allenes, the synthesis of which is recognized to be difficult, is also obtained by this method (entries 8 and 10).

Table 2 shows the results of the reaction of 1-chlorovinyl *p*-tolyl sulfoxide **14** derived from cyclopentadecanone[6] with some sulfones. We anticipated some problems with the Fritsch–Wiechell rearrangement[10] of the intermediate, magnesium alkylidene carbenoid; however, **14** gave allenes in a similar yields and no rearranged product, cyclohexadecyne, was observed.

Finally, we studied this reaction with the 1-chlorovinyl *p*-tolyl sulfoxides (**16a** and **16b**) derived from aldehydes (Scheme 3). The reaction was conducted in the same way as described above and we obtained completely different results. By this reaction acetylenes **18a** and **18b** were obtained in good yields and the desired allenes were not observed. These results clearly indicated to us that the Fritsch–Wiechell rearrangement of the β-hydrogen in the magnesium alkylidene carbenoid proceeds faster than the reaction with the α-sulfonyl carbanion. From these results it is emerged that we cannot synthesize allenes from aldehydes by this procedure.

We are continuing to study the scope and limitation of this procedure and improving the yields of the allenes.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research No. 11640545 from the Ministry of Education, Science, Sports, and Culture, Japan, which is gratefully acknowledged.

References

1. (a) Patai, S. *The Chemistry of Ketenes, Allenes, and Related Compounds*; John Wiley and Sons: Chichester,

Parts 1 and 2, 1980; (b) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes, and Cumulenes*; Elsevier: Amsterdam, 1981; (c) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; John Wiley and Sons: New York, 1984; (d) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805.

2. (a) Franck-Neumann, M.; Martina, D.; Neff, D. *Tetrahedron: Asymmetry* **1998**, *9*, 697; (b) Oku, M.; Arai, S.; Katayama, K.; Shioiri, T. *Synlett* **2000**, 493.
3. (a) Doering, W.; von, E.; LaFamme, P. M. *Tetrahedron* **1958**, *2*, 75; (b) Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1960**, *25*, 2073; (c) Skattebol, L. *Tetrahedron Lett.* **1961**, *2*, 167; (d) Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1962**, *27*, 4179; (e) Satoh, T.; Kurihara, T.; Fujita, K. *Tetrahedron* **2001**, *57*, 5369.
4. For example: (a) Posner, G. H. *Org. React.* **1975**, *22*, 287; (b) Marek, I.; Mangeney, P.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1986**, *27*, 5499; (c) Alexakis, A.; Marek, I.; Mangeney, P.; Normant, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 8042; (d) Gooding, O. W.; Beard, C. C.; Jackson, D. Y.; Wren, D. L.; Cooper, G. F. *J. Org. Chem.* **1991**, *56*, 1083.
5. (a) Nativi, C.; Ricci, A.; Taddei, M. *Tetrahedron Lett.* **1987**, *28*, 2751; (b) Konoike, T.; Araki, Y. *Tetrahedron Lett.* **1992**, *33*, 5093; (c) Zhao, Y.; Quayle, P.; Kuo, E. A. *Tetrahedron Lett.* **1994**, *35*, 3797; (d) Araki, Y.; Konoike, T. *J. Syn. Org. Chem. Jpn.* **2000**, *58*, 956; (e) Tius, M. A.; Pal, S. K. *Tetrahedron Lett.* **2001**, *42*, 2605.
6. Satoh, T.; Takano, K.; Ota, H.; Someya, H.; Matsuda, K.; Koyama, M. *Tetrahedron* **1998**, *54*, 5557.
7. A review for unsaturated carbenes including alkylidene carbenoids: Stang, P. J. *Chem. Rev.* **1978**, *78*, 383.
8. A review for the sulfoxide–metal exchange reaction in organic synthesis: Satoh, T. *J. Syn. Org. Chem. Jpn.* **1996**, *54*, 481.
9. Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; pp. 46–47.
10. (a) Stang, P. J.; Fox, D. P.; Collins, C. J.; Watson, C. R., Jr. *J. Org. Chem.* **1978**, *43*, 364; (b) Mundy, B. P.; Ellerd, M. G. *Name Reactions and Reagents in Organic Synthesis*; John Wiley and Sons: New York, 1988; pp. 90–91; (c) Satoh, T.; Hayashi, Y.; Yamakawa, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1866.