Pergamon

Tetrahedron Letters 40 (1999) 5491–5494

TETRAHEDRON
LETTERS

Addition of lithium metal to but-1-en-3-ynes. Synthesis and epoxidation of 1,4-bis(trimethylsilyl)buta-1,2-dienes

Christiane Santelli-Rouvier,* Sophie Lefrère and Maurice Santelli *

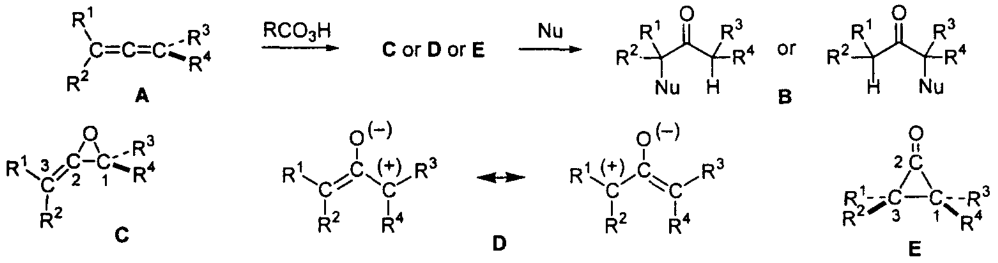
ESA au CNRS no. 6009, Faculté de St-Jérôme, 13397 Marseille Cedex 20, France

Received 24 March 1999; accepted 25 May 1999

Abstract

But-1-en-3-ynes react with lithium and chlorotrimethylsilane in THF to give 1,4-bis(trimethylsilyl)buta-2,3-dienes. Epoxidation of these allenes leads to oxyallyl species which are trapped by nucleophilic reagents to give 1,4-bis(trimethylsilyl)butan-3-ol-2-one derivatives. © 1999 Published by Elsevier Science Ltd. All rights reserved.

The epoxidation of allenes constitutes a fascinating part of their chemistry.[1] Allene monoepoxides **C** are very reactive intermediates which can be isolated in some cases,[2] or isomerized into cyclopropanones **E**.[3] More usually, the allene epoxides undergo a nucleophilic addition giving stable products **B**.[4] Interestingly, monoepoxy vinylallenes give rise to cyclopentenones[5,6] and they have been proposed as biogenetic precursors of prostanoids.[7]



In the case of the very polar oxyallyl intermediate **D**, we can hypothesize that its stability can be increased by the presence of a trimethylsilylmethyl group; a comparable stabilization effect has been observed in the silicon-directed Nazarov cyclization.[8,9] In order to evaluate this possible stabilization, we have prepared silylated allenes and studied their behavior in the presence of *m*-chloroperbenzoic acid.[10]

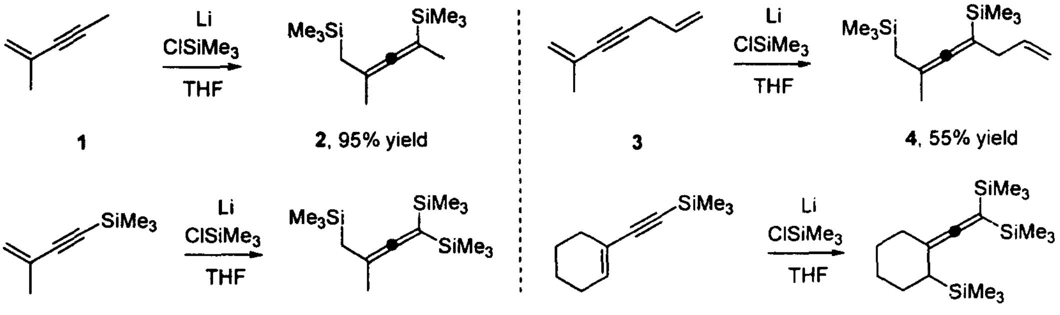
Many conjugated dienes interact with alkali metals in the presence of chlorotrimethylsilane to give a variety of 1,4-bis(trimethylsilyl)but-2-enes[11] or 1,8-bis(trimethylsilyl)octa-2,6-dienes,[12] resulting from

---

* Corresponding authors.

PII: S0040-4039(99)01056-4

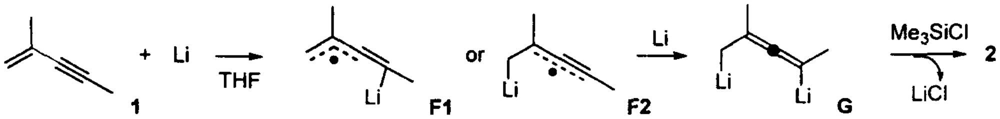
a 1,4-addition of silyl groups. Similarly, we thought that treatment of but-3-en-1-ynes should yield 1,4-bis(trimethylsilyl)buta-2,3-dienes or 1,8-bis(trimethylsilyl)octa-1,2,6,7-tetraenes.[13] We observe that butenynes **1** and **3** give rise to 1,4-bis(trimethylsilyl)buta-2,3-diene derivatives. Interestingly, the butenynylsilanes **5** and **7** afford trisilylated allenic derivatives **6** and **8**, respectively.[14] These compounds are obtained in moderate to excellent yields and, in contrast to the reaction involving buta-1,3-dienes, no products resulting from a reductive dimerization of the radical anion were obtained. To the best of our knowledge, the reduction of but-3-en-1-ynes is the only practical method for the preparation of 1,4-bis(trimethylsilyl)buta-1,2-dienes.



1 **2**, 95% yield **3** **4**, 55% yield

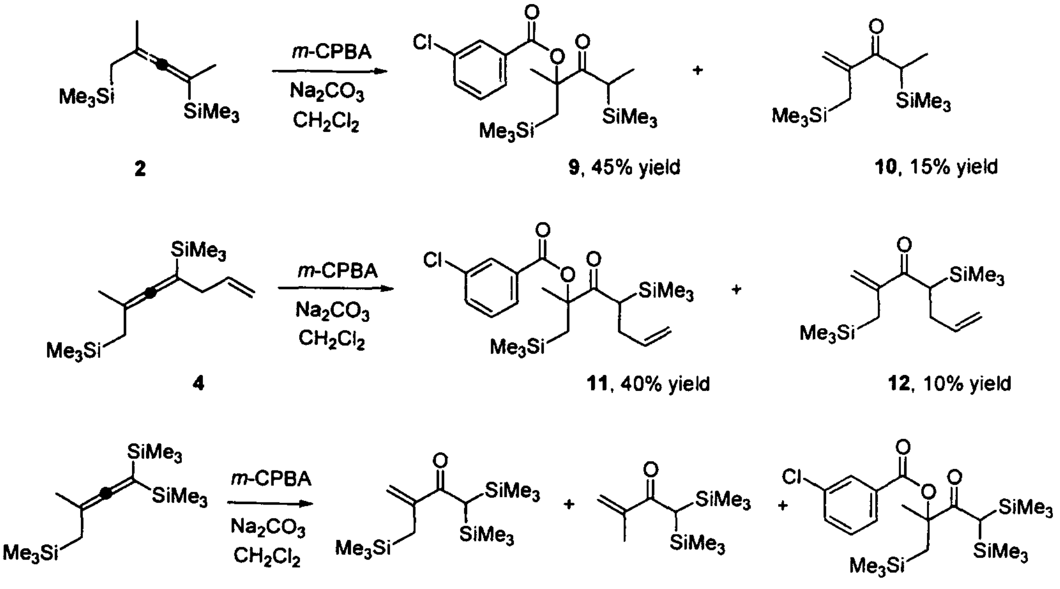
5 **6**, 68% yield **7** **8**, 80% yield

We assume that the reduction of the enyne **1** by lithium involves the trapping of the short-lived radical anion **F1** or **F2** by chlorotrimethylsilane or more probably **F1** or **F2** undergoes a second addition of an electron to give 1,4-dilithiobuta-1,2-diene derivative **G**. Derivatization with trimethylsilyl chloride (hard electrophile, 'fat proton') should occur without isomerization.[15]



1 **F1** **F2** **G**

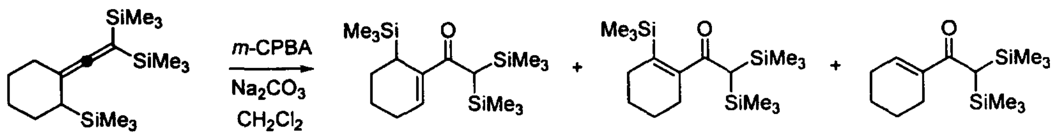
Next, the epoxidation of silylated allenes **2**, **4**, **6** and **8**, using *m*-chloroperbenzoic acid in CH_2Cl_2 in the presence of Na_2CO_3, affords silylated α,β-enones and silylated α-hydroxyketone derivatives.[16]



2 **9**, 45% yield **10**, 15% yield

4 **11**, 40% yield **12**, 10% yield

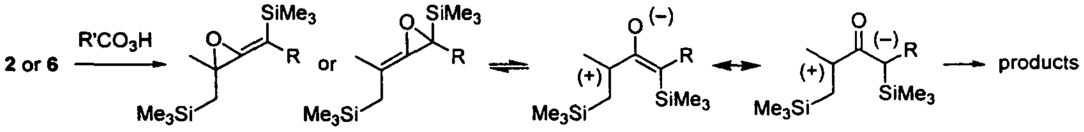
6 **13**, 54% yield **14**, 10% yield **15**, 23% yield



8 **16**, 25% yield **17**, 10% yield **18**, 10% yield

The 1,4-bis(trimethylsilyl)buta-2,3-dienes bear both bis-allylsilane and vinylsilane moieties. The semiempirical PM3 calculations on **2** indicated a strong interaction of the central π-bond with the σ-(Si–C) bonds. This orbital interaction caused a destabilization of the HOMO level (−8.41 eV) and a slight stabilization of the LUMO (0.55 eV) (for 2-methyl-2,3-pentadiene, −9.51 eV and 1.07 eV, respectively). The high energy level of the HOMO should increase the rate of the epoxidation. Consequently, for an electrophilic addition, the most reactive double bond was that of the bis-allylsilane moiety and the formation of the epoxide **H** should be favored.

The products from the epoxidation of silylated allenes could result from an elimination process or a nucleophilic attack on the oxyallyl **J**. In this intermediate, one of the trimethylsilyl groups stabilizes the positive charge while the other stabilizes the enolate moiety.[17] The most surprising feature is the weak process of loss of the silyl group in the presence of some nucleophilic species.[18]



H **I** **J1** **J2**

In conclusion, the addition of lithium metal to but-1-en-3-ynes affords a simple and efficient route to the preparation of 1,4-bis(trimethylsilyl)buta-1,2-dienes which lead, in the presence of *m*-chloroperbenzoic acid, to the corresponding α-hydroxyketones without loss of the trimethylsilyl groups. Thus, the but-1-en-3-yne moiety can be functionalized, in two simple steps.

Acknowledgements

We thank Dr. R. Faure for his assistance in NMR measurements.

References

1. For reviews of allene oxide chemistry, see: (a) Stang, P. J. *The Chemistry of Functional Groups, Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Analogs*; Patai, S., Ed.; Wiley: New York, 1983; pp. 859–879. (b) L'Abbé, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 276–289. (c) Jacobs, T. L. In *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: London, 1982; Vol. 2, pp. 483–491. (d) Smadja, W. *Chem. Rev.* **1983**, *83*, 263–320.
2. (a) Camp, R. L.; Greene, F. D. *J. Am. Chem. Soc.* **1968**, *90*, 7349. (b) Crandall, J. K.; Conover, W. W.; Komin, J. B.; Machleder, W. H. *J. Org. Chem.* **1974**, *39*, 1723–1729. (c) Marshall, J. A.; Tang, Y. *J. Org. Chem.* **1994**, *59*, 1457–1464. (d) Behr, H.; Bolte, O.; Draeger, G.; Ries, M.; Schaumann, E. *Liebigs Ann. Org. Bioorg. Chem.* **1996**, 1295–1300.
3. Crandall, J. K.; Machleder, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 7347–7349.
4. (a) Crandall, J. K.; Machleder, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 7292–7296. (c) Crandall, J. K.; Machleder, W. H.; Sojka, S. A. *J. Org. Chem.* **1973**, *38*, 1149–1154.
5. Grimaldi, J.; Bertrand, M. *Tetrahedron Lett.* **1969**, 3269–3272. (b) Grimaldi, J.; Bertrand, M. *Bull. Soc. Chim. Fr.* **1971**, 957–962.

6. The epoxidation of allylallenes can afford bicyclo[3.1.0]hexa-2-ones; see: (a) Grimaldi, J.; Malacria, M.; Bertrand, M. *Tetrahedron Lett.* **1974**, 275–277. (b) Grimaldi, J.; Malacria, M.; Bertrand, M. *Bull. Soc. Chim. Fr.* **1975**, 1725–1730 and 1731–1739.
7. Brash, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 1891–1892.
8. (a) Lambert, J. B.; Cheluis, E. C. *J. Am. Chem. Soc.* **1990**, *112*, 8120–8126. (b) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677–2689.
9. For example, in the silicon-directed Nazarov cyclization, the formation of a silicon stabilized cyclopentenyl cation (an oxyallyl species) led to the exclusive formation of the thermodynamically less stable cyclopentenone isomer; see: (a) Denmark, S. E.; Jones, T. K. *J. Am. Chem. Soc.* **1982**, *104*, 2642–2645. (b) Denmark, S. E.; Klix, R. C. *Tetrahedron* **1988**, *44*, 4043–4060. (c) Denmark, S. E.; Habernas, K. L.; Hite, G. A. *Helv. Chim. Acta* **1988**, *71*, 168–194. (d) Miesch, M.; Miesch-Gross, L.; Franck-Neumann, M. *Tetrahedron* **1997**, *53*, 2103–2110.
10. The epoxidation of 3-methyl-1-trimethylsilylpenta-1,2,4-triene by the Payne reagent (H_2O_2, PhCN, MeOH) led to 2-methyl-5-trimethylsilylcyclopent-2-enone; see: Dulcère, J.-P.; Grimaldi, J.; Santelli, M. *Tetrahedron Lett.* **1981**, *22*, 3179–3180.
11. Weyenberg, D. R.; Toporcer, L. H.; Nelson, L. E. *J. Org. Chem.* **1968**, *33*, 1975–1982.
12. Tubul, A.; Santelli, M. *Tetrahedron* **1988**, *44*, 3975–3982.
13. Compound **6** has been obtained by the use of Me_3SiCl/Mg/HMPA on **5**, in contrast **7** led to a disilylated allenic compound; see: Dunogues, J.; Bourgeois, P.; Pillot, J.-P.; Merault, G.; Calas, R. *J. Organomet. Chem.* **1975**, *87*, 169–181. The reductive silylation of hexa-1,3,5-triene with Me_3SiCl/Mg/THF afforded 1,6-bis(trimethylsilyl)-2,4-hexadiene; see: Birkofer, L.; Bockhorst, M.; Steigel, A.; Eichstädt, D. *J. Organomet. Chem.* **1982**, *233*, 291–297.
14. General procedure for the preparation of silylated allenes: to a stirred and cooled (0°C) solution of chlorotrimethylsilane (16 g, 140 mmol) in anhydrous THF (190 mL) were added pieces (0.3 mm) of lithium (1 g, 0.14 at.g). Then a solution of enyne (72 mmol) in anhydrous THF (40 mL) was slowly added. The stirring was maintained overnight and the solution was allowed to warm to room temperature. Then pentane (or light petroleum) was added to fill in the flask, and the possibly small remaining pieces of lithium were removed with tweezers. The milked solution was poured onto crushed ice, and after stirring, the layers were separated. The organic one was washed with chilled water (6×500 mL) and then dried over anhydrous $MgSO_4$. After filtration, the solvent was removed and the allenic compound was purified.
15. (a) Maercker, A.; Wunderlich, H.; Girreser, U. *Tetrahedron* **1996**, *52*, 6149–6172. (b) Maercker, A.; Wunderlich, H.; Girreser, U. *Eur. J. Org. Chem.* **1998**, 793–798.
16. General procedure for the epoxidation of silylated allenes. To a stirred and cooled (0°C) solution of allenylsilane (10 mmol) and Na_2CO_3 (4.88 g, 46 mmol) in CH_2Cl_2 (80 mL) were added over 4 h a solution of *m*-chloroperbenzoic acid (4.32 g, 25 mmol) in CH_2Cl_2 (40 mL). The mixture was filtered and the salt was washed with ether. The organic layers were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed and the compounds were separated by chromatography on silica gel.
17. Stork, G.; Ganem, B. *J. Am. Chem. Soc.* **1973**, *95*, 6152–6153.
18. (a) Brook, M. A.; Henry, C.; Jueschke, R.; Modi, P. *Synlett* **1993**, 97–104. (b) Lambert, J. B.; Zhao, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7867–7868.