

SYNLETT Spotlight 23

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Methoxyallene

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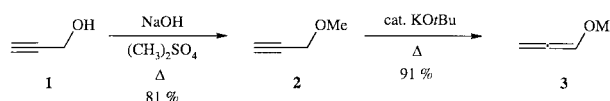
Robert Pulz studied chemistry at the Technische Universität Dresden. He is currently working on his Ph.D. thesis under the supervision of Professor H.-U. Reissig at the Freie Universität Berlin.



Introduction

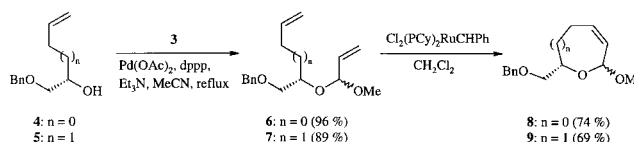
Since the first preparation of methoxyallene (**3**) by Hoff, Brandsma and Arens in 1968,¹ this compound with cumulated C=C bonds has emerged as a useful and convenient C-3 building block for many transformations in preparative organic chemistry.² This donor-substituted, electron-rich allene is easily accessible in high yield by a two step reaction from propargylic alcohol (**1**) which is methylated with dime-

thyl sulfate to give propargylic ether **2**³ followed by isomerization of **2** with potassium *tert*-butoxide.⁴ The reactivity of **3** is determined by the enol ether functionality leading to electrophilic addition to C-2 or nucleophilic attack at C-1.

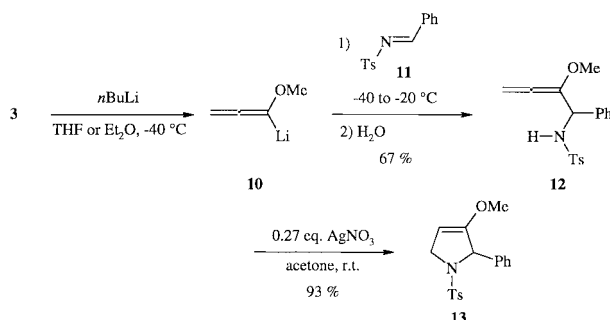


Abstracts

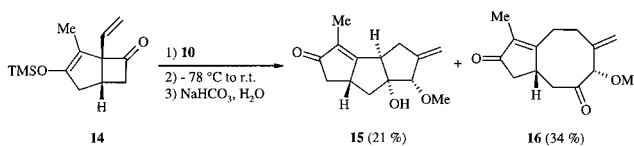
Pd(II) catalyzed reaction of methoxyallene **3** with chiral alcohols **4** and **5** led in excellent yields to acetals **6** and **7** as a 1:1 mixture of diastereomers. The dienes **6** and **7** then cyclized smoothly under standard ring-closing metathesis conditions using Grubbs' catalyst to afford dihydropyrane **8** or tetrahydrooxepin **9** in good yields.⁵



Another key feature of methoxyallene (**3**) is the smooth deprotonation at C-1 with *n*-butyllithium leading to 1-lithio-1-methoxyallene (**10**).^{4,6} After this umpolung of reactivity nucleophile **10** may be used as C-3 block for the synthesis of O-, N-, and NO-heterocycles.⁷ Thus, synthesis of 2-substituted dihydropyrroles can easily be achieved by addition of **10** to *N*-tosylimine **11** giving primary adduct **12** after hydrolysis. The cyclization of **12** was performed with catalytic amounts of AgNO₃ providing dihydropyrrole **13**.⁸



As an example for a ring expansion reaction the addition of **10** to bicycloheptenone **14** finally results in formation of polyquinane **15** in 21% and bicycloundecanone **16** in 34% yield.⁹



References and Notes

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