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HYDROXY GROUP-ASSISTED ISOMERIZATION AND ALKYLATION OF ALLYLSILANES IN BASIC MEDIA. α-(1-TRIMETHYLSILYLALLYL) KETONE AS AN α-ALKENYL KETONE EQUIVALENT.

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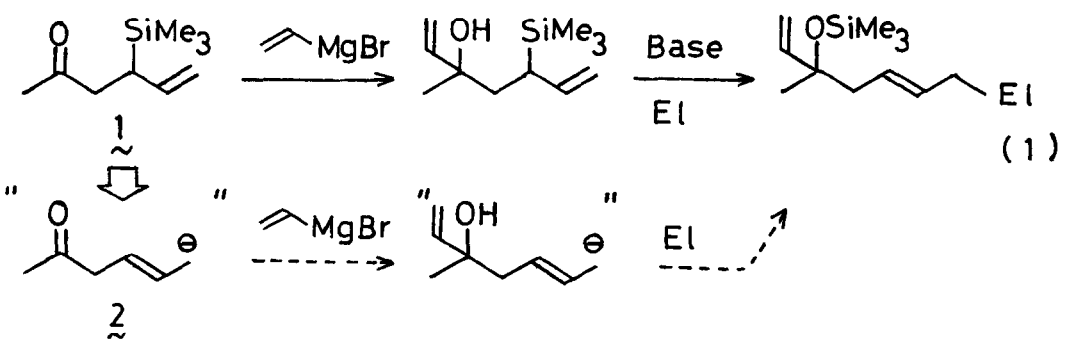
Summary: Regioselective protonation and alkylation of a certain hydroxyallylsilane have been effected in basic media. An application of these reactions to a facile preparation of 3-hydroxy-1,5-hexadiene systems has also been achieved.

In recent years, allylsilanes have found widespread use in organic synthesis.[1] Their allyl moieties are regioselectively transferred to electrophiles under the influence of Lewis acid.[1] Allylsilanes undergo addition to carbonyl group also in the presence of a fluoride under almost neutral conditions.[2] We wish to describe here another methodology for regioselective introduction of electrophiles to allylsilanes in basic media.

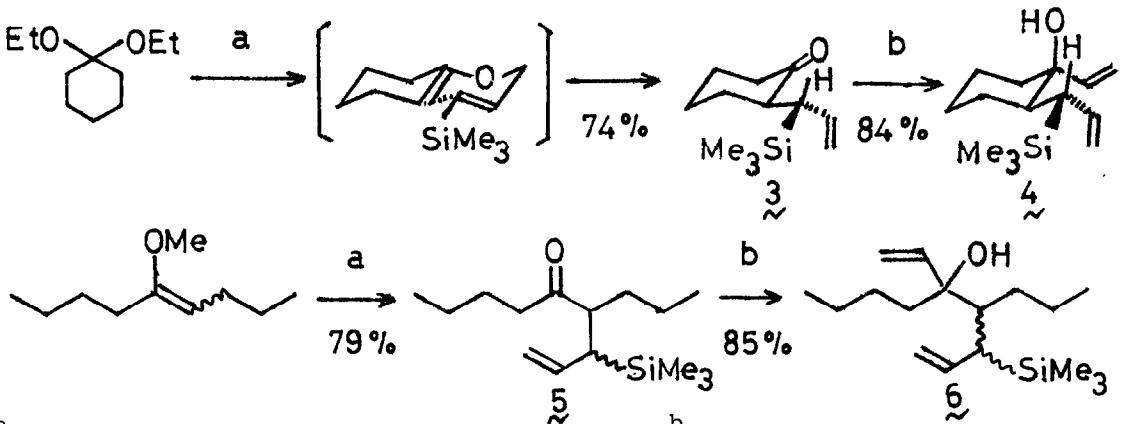
We have found that an allylsilane having a hydroxy group at a suitable position, e.g. 4 or 6, undergoes protonation or alkylation via the alkoxide accompanied by selective migration of both the double bond and the silyl group.[3] This reaction provides a convenient method for preparation of a 3-hydroxy-1,5-hexadiene system, a precursor for the oxy-Cope reaction, as illustrated in eq 1. As a result, α-(1-trimethylsilylallyl) ketone 1 can be regarded as a synthetic equivalent of an α-alkenyl ketone 2



The starting materials were readily prepared according to Scheme 1.[4,5] The ketone 3 was obtained essentially as one diastereomer,[6] and its stereochemistry could be assigned on the basis of the transition state depicted. By treating 3 with a slightly excess amount of vinylmagnesium bromide, the alcohol

4 was prepared together with a small amount of recovered 3 (3:4 = 15:85). Subsequent addition of another equivalent of the Grignard reagent to the crude mixture gave, after chromatography, the 95%[6] isomerically pure 4[7], whose structure was deduced on the basis of the well-precedented behavior of 2-substituted cyclohexanone to nucleophiles.[8,9,10] Similarly addition of vinylmagnesium bromide to 5 (a 1:2 mixture of diastereomers) gave 6.

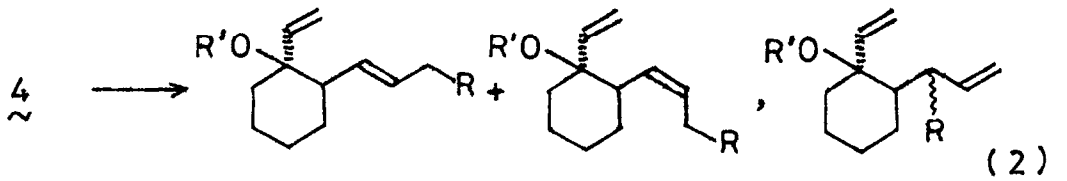
Scheme 1. Preparation of Starting Materials.



[a](E)-$Me_3SiCH{=}CHCH_2OH$, cat. TsOH, xylene, refl. [b]$CH_2{=}CHMgBr$, THF, -40 °C→r.t.

Treatment of 4 with a catalytic amount of KH (0.1 equiv) in THF led to a clean and rapid conversion to the silyl ether 7 (R = H) in 89% yield (eq 2). Comparison[6] with the authentic cis isomer[11] has determined the major product as the trans isomer.[12] The trans/cis (7a/7b) ratio estimated by GLC was 85:15. Smooth desilylation (aq. HCl-MeOH, r.t.) of 7 afforded the alcohol 8 (R = H) in 95% yield. The ^{13}C NMR analysis of the alcohol 8, isolated without attempts to separate isomers, showed that the amount of the regioisomer 8c (hence 7c) is less than 5% of the products.

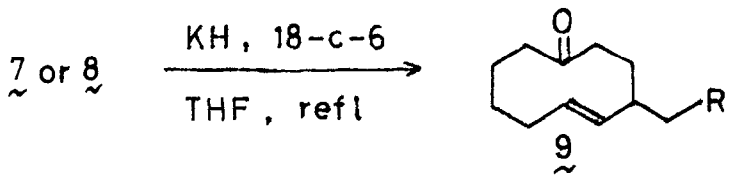
We then studied on alkylation of 4, which has turned out to provide a useful tool for homologation of the vinyl group as follows. After complete conversion of 4 to the alkoxide with BuLi (1.1 equiv, THF, -78 °C, 10 min), hexyl iodide (1.5 equiv) was added at -78 °C. On warming up to 0 °C, a slow but complete consumption of the starting material was observed. Extractive workup followed by filtration through silica gel using hexane as eluent gave the silyl ether 7 (R = C_6H_{13}), which was then desilylated (aq. HCl-MeOH, r.t., 10 min) to give the alcohols 8a and 8b (R = C_6H_{13}) in 51% and 28% yields, respectively. The analysis of the crude alcohol 8 (R = C_6H_{13}) revealed that the regioselectivity (7a+b/7c) of this alkylation was 93:7.[13] Analogous reaction of 4 with methyl iodide (2 equiv) or hexyl bromide (1.5 equiv) results in formation of 7 (R = CH_3) (91%, 7a+b/7c = 95:5, 7a/7b or vice versa = 8:2) or 8 (R = C_6H_{13}) (69% after desilylation, 8a+b/8c = 95:5, 8a/8b = 4:6).



R'=Me_3Si 7a 7b 7c

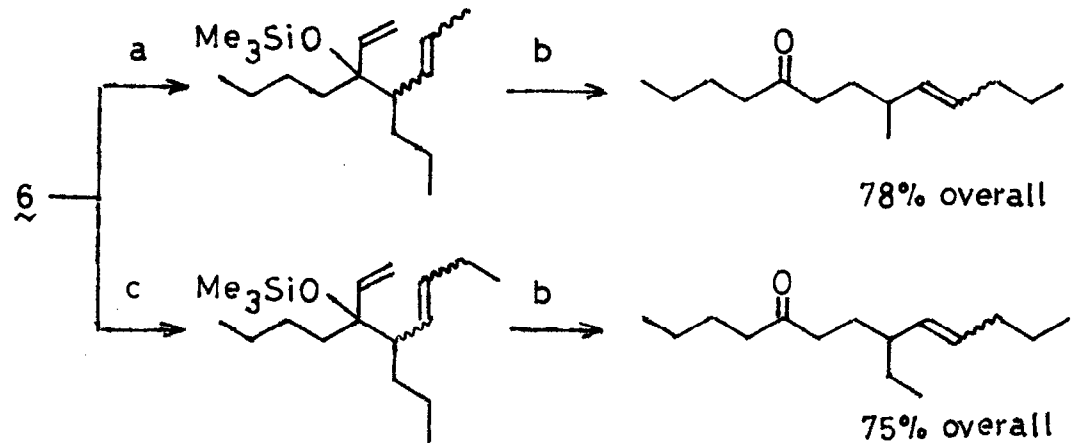
H 8a 8b 8c

The anionic oxy-Cope reaction[14] using the alcohols obtained here has been demonstrated as follows.[11] For example, the alcohol 8 (R = H or C_6H_{13}) was treated with excess KH and 1 equiv of 18-crown-6 in THF gave the ketone 9 in good yield. To our surprise, 7 (R = H) also afforded 9 (R = H) in 82% yield under the same conditions as above, showing that transmetalation from the silyl ether to the potassium alkoxide would occur in situ.



These transformations also work well for an acyclic ketone derivative (Scheme 2).

Scheme 2. Isomerization and Alkylation of 6.



[a]KH (0.1 equiv), THF, r.t., 30 min. [b]KH, 18-crown-6, THF, reflux, 1 h. [c]BuLi -78 °C, 10 min; MeI (2 equiv), -78 °C; 0 °C→r.t., overnight.

In summary, the reaction described herein has shown three characteristic features: i) oxygen-assisted remote migration of the silyl group, ii) generation of an allyl anionic species under mild conditions, and iii) high regioselectivity on the protonation and the alkylation reactions.

Synthetic application of this new concept is now studied in more details

References and Notes

1. E. W. Colvin, "Silicon in Organic Synthesis"; Butterworths: London (1981), p. 97. W. P. Weber, "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin (1983), p. 173. H. Sakurai, Pure Appl. Chem., 54, 1 (1982).
2. A. Hosomi, A. Shirahata, and H. Sakurai, Tetrahedron Lett., 3043 (1978).
3. 1,2-Migration of a silyl group from an allylic carbon to oxygen: W. C. Still and T. L. Macdonald, J. Am. Chem. Soc., 96, 5561 (1974); I. Kuwajima and M. Kato, J. Chem. Soc., Chem. Commun., 708 (1979); I. Kuwajima, M. Kato, and A. Mori, Tetrahedron Lett., 21, 2745 (1980); H. J. Reich, R. E. Olson, and M. C. Clark, J. Am. Chem. Soc., 102, 1423 (1980).
4. S. E. Denmark and T. K. Jones, J. Org. Chem. 47, 4595 (1982).
5. I. Kuwajima, T. Tanaka, and K. Atsumi, Chem. Lett., 779 (1979).
6. These were determined by GLC and ^{13}C NMR.
7. The alcohol 4 was decomposed to some extent during distillation.
8. E. C. Ashby and J. T. Laemmle, Chem. Rev., 75, 521 (1975).
9. D. A. Holt, Tetrahedron Lett., 22, 2243 (1981). T. Kato, H. Kondo, M. Nishio, M. Tanaka, G. Hata, and A. Miyake, Bull. Chem. Soc. Jpn., 53, 2958 (1980).
10. E. N. Marvell and W. Whalley, Tetrahedron Lett., 509 (1970). W. C. Still, J. Am. chem. Soc., 99, 4168 (1977). W. C. Still, Ibid., 101, 2493 (1979).
11. Authentic samples were prepared according to Ref's 9, 10, and 14.
12. This assignment is consistent since the ^{1}H NMR chemical shift of the allylic methyl protons in the major isomer appears at 1.73 ppm (δ) and the authentic cis isomer at 1.60 ppm. See: L. K. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2 nd Ed., Pergamon Press: Oxford (1969); p. 225.
13. Determined by GLC using authentic samples.
14. D. A. Evans and A. M. Golob, J. Am. Chem. Soc., 97, 4765 (1975).

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