Tetrahedron Letters, Vol.22, No.29, pp 2827 - 2828, 1981
Printed in Great Britain

0040-4039/81/292827-02$02.00/0

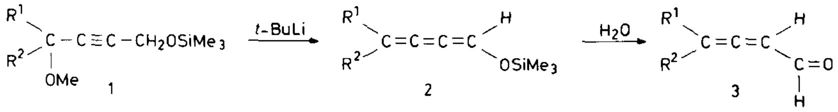
SYNTHESIS OF α-ALLENIC ALDEHYDES AND ALLENYL TRIMETHYLSILYL KETONES VIA (TRIMETHYLSILYLOXY)BUTATRIENES

R.G. Visser, L. Brandsma and H.J.T. Bos

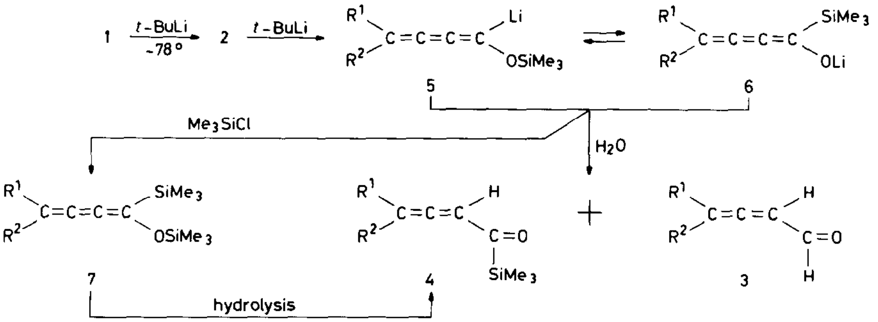
Laboratory for Organic Chemistry, University of Utrecht
Croesestraat 79, 3522 AD UTRECHT, The Netherlands

Abstract: α-Lithiated (trimethylsilyloxy)butatrienes, generated by 1,4-elimination of methanol from 1-trimethylsilyloxy-4-methoxy-2-alkynes with *tert*-butyllithium, give mixtures of α-allenic aldehydes and allenyl trimethylsilyl ketones which can be separated by distillation. The ratio aldehyde/ketone is solvent dependent.

Previous work from our laboratory[1,2] has resulted in practical syntheses of cumulenic ethers $R^1R^2C=C=C=CH-O-alkyl$. As only a few[3-5] synthesis of α-allenic aldehydes have been reported, we wondered whether acid hydrolysis could provide an alternative preparative method for these aldehydes. Preliminary experiments, however, showed that only 1,4-addition of water took place with formation of acetylenic aldehydes $R^1R^2CH-C\equiv C-CH=O$. We anticipated that hydrolysis of (trimethylsilyloxy)butatrienes $R^1R^2C=C=C=CH-OSiMe_3$ 2 should proceed via Si-O splitting. Therefore we turned our attention to these butatrienes 2. Compounds 2 were further required for studying photochemical cycloaddition reactions[6].
The (trimethylsilyloxy)butatrienes 2 were prepared *in situ* by 1,4-elimination of methanol from 1-trimethylsilyloxy-4-methoxy-2-alkynes 1 with *tert*-butyllithium (*cf*. ref 2).



Compounds 2 could not be isolated thus far. Due to the acidity of the $=CH-OSiMe_3$ proton in 2 with respect to the $-CH_2-OSiMe_3$ protons in 1, two mole equivalents of base were used for a complete conversion of 1 with formation of the lithiobutatrienes 5.
The O-trimethylsilyl compound 5 however appeared to be in equilibrium with the C-trimethylsilyl compound 6 (Brook rearrangement)[7], as hydrolysis afforded a mixture of the desired allenic aldehyde 3 together with the allenic trimethylsilyl ketone 4. The formation of 3 is in accordance with the observations of Kuwajima[8] who postulated a silyloxybutatriene as the unstable intermediate in the formation of an allenic ketone.
The ratio 5/6 depends on the nature of the solvent. In Et_2O/pentane the Brook equilibrium is towards 5, whereas in THF/pentane it is towards 6.



a) R^1,R^2=Me,Me. b) R^1,R^2=Me,Et. c) R^1,R^2=Me,*t*-Bu. d) R^1,R^2= $-(CH_2)_5-$

For R^1=Me and R^2=Et the ratios 5/6 are 15/85 and 85/15 respectively. The ratio 5/6 also slightly depends on the nature of R^1 and R^2 (*cf.* ref 9). By using the proper solvent system, either 3 or 4 was obtained in a reasonable yield. When performing the reaction in Et_2O/pentane, the silyl ketones 4 could be isolated by distillation in yields of 40-60%, while in THF/pentane the aldehydes 3 were isolated in yields of 25-70%.

Silylation of the equilibrium mixture of 5 and 6 gave in yields of 50-75% the pure butatrienes 7, which survived aqueous work-up. Dilute acetic acid or $[Et_4N]F.2H_2O$ in THF, however, caused a smooth cleavage of the Si-O bond, resulting in the allenic ketones 4, (*cf.* ref 10).

$Me_2C=C=CH-CO-SiMe_3$ 4*a*: yield 50%; IR(neat) 1945 and 1600 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.10($SiMe_3$), 1.82(d,J=3.0Hz,2xMe), 5.60(septet,=CH); ^{13}C NMR($CDCl_3$) δ-2.7($SiMe_3$) 19.4(2xMe), 99.3 (C^4), 100.2(C^2), 213.2(C^3), 234.6(C=O)

$Me_2C=C=C=C(SiMe_3)-OSiMe_3$ 7*a*: yield 50%; IR(neat) 2037 and 1614 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.11 and 0.20(2x$SiMe_3$), 1.87(br,2xMe); ^{13}C NMR($CDCl_3$) δ-2.6 and + 0.3(2x$SiMe_3$), 22.6 and 22.8 (2xMe), 103.1 (C^4), 136.2(C^1), 147.6(C^2) and 157.7(C^3).

Starting compounds 1 were prepared from $LiC\equiv C-CH_2-OCH(OEt)CH_3$ and R^1CO-R^2, followed by methylation (*cf.* ref 11), deprotection and trimethylsilylation. Overall yields based upon $HC\equiv CCH_2OH$ were 60-70%.

References

1. R. Mantione, A. Alves, P.P. Montijn, H.J.T. Bos and L. Brandsma, Tetrahedron Lett., *1969*, 2483
2. R.G. Visser, H.J.T. Bos and L. Brandsma, Recl. Trav. Chim., 100, 34 (1981).
3. H. Schelhorn, H. Frischleder and S. Hauptmann, Tetrahedron Lett., *1970*, 4315.
4. P.D. Landor, S.R. Landor and S. Mukasa, J. Chem. Soc., Chem. Comm., *1971*, 1638.
5. J.-C. Clinet and G. L'Instrumelle, Nouv. J. Chim., 1, 373 (1977).
6. R.G. Visser and H.J.T. Bos, Tetrahedron Lett., *1979*, 4857.
7. A.G. Brook, Acc. Chem. Res., 7, 77 (1974)
8. I. Kuwajima and M. Kato, Tetrahedron Lett., *1980*, 623.
9. H.J. Reich, R.E. Olson and M.C. Clark, J. Am. Chem. Soc., 102, 1423 (1980).
10. J.-C. Clinet and G. L'Instrumelle, Tetrahedron Lett., *1980*, 3987.
11. P.E. van Rijn, S. Mommers, R.G. Visser, H.D. Verkruijsse and L. Brandsma, to be published in Synthesis, *1981*.

(Received in UK 6 May 1981)