Tetrahedron Letters, Vol.22, No.21, pp 2021 - 2022, 1981
Printed in Great Britain

0040-4039/81/212021-02$02.00/0

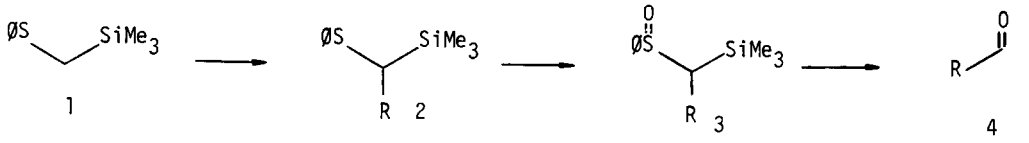
A NEW SYNTHESIS OF UNSATURATED ALDEHYDES

Ian Cutting and Philip J. Parsons*

Chemistry Department, University of Southampton, Southampton, SO9 5NH

Summary: Treatment of 3-trimethylsilylallylic alcohols with phenylsulphenyl chloride gives unstable allylic sulphoxides which rearrange and are then hydrolysed to unsaturated aldehydes.

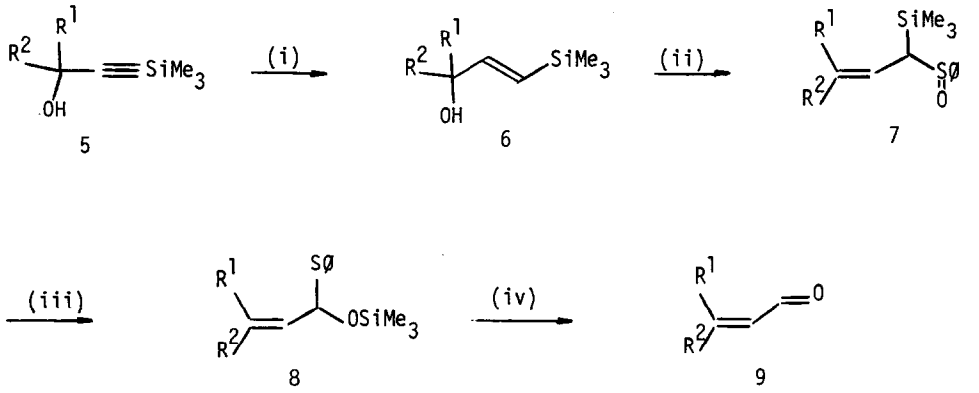
α,β-Unsaturated aldehydes are very important intermediates in organic synthesis,[1] and several new methods for their preparation have recently been reported. Each of these methods involves either metallation[2] oxidation, or other multistage elaboration to the final product.[3] In work recently described on formyl anion equivalents,[4] oxidation of the silyl sulphide (2) is required before hydrolysis to the carbonyl compounds can be achieved. (Scheme I).



Scheme I

We find that 3-trimethylsilylallylic alcohols (6) are converted into α,β-unsaturated aldehydes (9) (Scheme II) under the following mild conditions. When phenylsulphenyl chloride (1.2 eq.) was added dropwise to a stirred solution of 1-[2-trimethylsilylethyen-1-yl]-1-hydroxycyclohexane (6c) (1 eq.) and triethylamine (1.5 eq.) in dry ether at -25°C a white precipitate of triethylamine hydrochloride was immediately formed. The product was poured into water and extracted with ether yielding an oil, which on treatment with silver nitrate in aqueous acetonitrile gave (9c) isolated in 68% yield by chromatography on silica. NMR (neat and TMS) δ 1.35 (m, 6H), 1.98 (m, 2H), 2.40 (m, 2H), 5.5 (d, J = 8Hz, 1H), 9.75 (d, J = 8Hz); ν_{max} 1660 cm^{-1}. Similar results were obtained when n-butyllithium (1 eq.) was added to the allylic alcohols (6) before reaction with phenylsulphenyl chloride.

The very unstable diastereomeric sulphoxides (7) were isolated by low temperature workup (-30°C) followed by rapid flash chromatography on silica. Compound 7c is representative of these data and gave a strong sulphoxide band at 1040 cm^{-1} in the infrared. This band disappeared when the sample was gently heated. Tlc analysis and nmr confirmed the intermediacy of sulphoxides (7). Further applications of this interesting transformation are in progress and will be published later.



5 6 7 8 9

Scheme II

Reagents: i) $LiAlH_4/THF/\Delta$ ii) $ØSCl/Et_3N/Et_2O$ iii) RT iv) $AgNO_3/H_2O/MeCN$

	R'	R_2	Isolated Yield (9)%	E : Z
a	H	C_5H_{11}	72	99 1
b	CH_3	CH_3	55	- -
c	- $(CH_2)_5$	-	68	- -
d	Me	$(CH_3)_2C=CH(CH_2)_2$	50	64 36

REFERENCES

1. E. J. Corey, D. Enders and M. G. Bock, Tetrahedron Lett., 1976, 7.
2. T. Nakai, H. Shiono and M. O. Kawara, Tetrahedron Lett., 1974, 3625.
3. K. Kondo and D. Tunemoto, Tetrahedron Lett., 1975, 1007;
   F. D. King and D.R.M. Walton, J.Chem.Soc. Chem.Comm., 1974, 256.
4. P. J. Kocienski, Tetrahedron Lett., 1980, 1559;
   D. J. Ager and R. C. Cookson, Tetrahedron Lett., 1980, 1677;
   P. J. Kocienski, J.Chem.Soc. Chem.Comm., 1980, 1096;
   D. J. Ager, Tetrahedron Lett., 1980, 4759.

(Received in UK 16 March 1981)