Stereoselective Synthesis of (*E*)-2-(1-Hydroxyalkyl)alk-2-enenitriles *via* (*Z*)-1-Cyanoalk-1-enyl Anion Intermediates

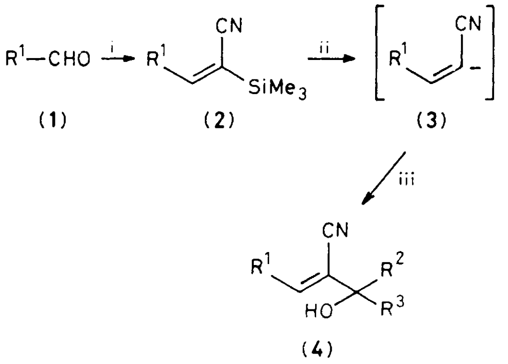
Yoshiro Sato* and Kyoko Hitomi

Faculty of Pharmaceutical Sciences, Nagoya City University, Tanabe-dori, Mizuho-ku, Nagoya 467, Japan

Fluoride ion-induced desilylation of (*E*)-2-trimethylsilylalk-2-enenitriles affords (*Z*)-1-cyanoalk-1-enyl anion intermediates, which are trapped by carbonyl compounds to give (*E*)-2-(1-hydroxyalkyl)alk-2-enenitriles with 100% retention of the configuration.

Alkenylsilanes are versatile synthetic intermediates, which react with a variety of electrophiles, undergoing desilylation with retention of stereochemistry.[1] We recently reported on the highly stereoselective synthesis of (*E*)-2-trimethylsilylalk-2-enenitriles (**2**) from aldehydes (**1**).[2] Electrophile-induced desilylation of (**2**), employing H^+ or $RCOCl/AlCl_3$ was unsuccessful, but desilylation with an appropriate nucleophile for silicon (OH^- or F^-) took place readily to give (*Z*)-alk-2-enenitriles in a moist solvent. This suggested that the desilylation of (**2**) proceeded *via* a (*Z*)-1-cyanoalk-1-enyl anion intermediate (3), and we now report the reactions of (3) with carbonyl electrophiles.

Tetra-n-butylammonium fluoride (1.1 equiv., 0.2 M THF solution, dried over molecular sieves 4A) was added dropwise to a solution of (**2**) (1 equiv.) and a carbonyl compound (1.1



Scheme 1. i, $(Me_3Si)_2C{=}C{=}N{-}SiMe_3$, $BF_3{\cdot}Et_2O$, C_6H_6; ii, $Bu^n{}_4NF$, tetrahydrofuran (THF), −15 to −20 °C; iii, R^2COR^3

Table 1. Yields of (*E*)-2-(1-hydroxyalkyl)alk-2-enenitriles (**4**)[a] from (*E*)-2-trimethylsilylalk-2-enenitriles (**2**)[b] and the carbonyl compounds R^2COR^3.

R^1	R^2	R^3	% Yield (isolated)
n-Heptyl	Me	H	70
	Ph	H	81
	Me	Me	22
	Ph	Me	33[c]
Et(Bu^n)CH	Me	H	76
	Ph	H	79
Cyclohexyl	Me	H	75
	Ph	H	74
Ph	Me	H	68
	Ph	H	72

[a] Satisfactory spectral and analytical data were obtained for all products. [b] Pure (*E*)-isomers were used. [c] G.l.c. yield.

equiv.) listed in Table 1, in THF at −15 to −20 °C. Stirring was continued at the same temperature for 0.5 h and at room temperature for 0.5 h. Normal work-up followed by distillation gave high yields (except for two ketones) of the substitution products (*E*)-2-(1-hydroxyalkyl)alk-2-enenitriles (**4**), accompanied by a small amount of desilylated products, (*Z*)-alk-2-enenitriles (*ca.* 15%). The 100% (*E*)-stereochemistry of (**4**) was confirmed by ^{13}C n.m.r. [$^3J(\mathrm{CN{-}H}^{\beta}) = 10$—15 Hz] and ^{1}H n.m.r. spectral and g.l.c. (Triton X-305) analyses.

Thus we conclude that the formation of (**4**) proceeds *via* (**3**) which retains its original configuration under the reaction conditions.

Received, 24th November 1982; Com. 1348

References

1 For reviews of electrophilic substitution of alkenylsilanes, see T. H. Chan and I. Fleming, *Synthesis*, 1979, 761; E. Colvin, 'Silicon in Organic Synthesis,' Butterworths, London, 1981.

2 Y. Sato and Y. Niinomi, *J. Chem. Soc., Chem. Commun.*, 1982, 56.