Tetrahedron Letters No. 46, pp 4005 - 4008, 1974. Pergamon Press. Printed in Great Britain.

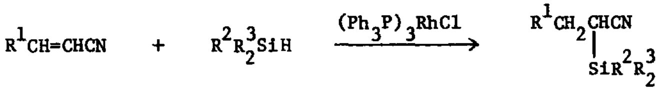
α-SILYLPROPIONITRILES: A NEW REAGENT FOR THE SYNTHESIS OF α,β-UNSATURATED NITRILES

Iwao Ojima* and Miyoko Kumagai
Sagami Chemical Research Center
Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, JAPAN
and Yoichiro Nagai
Department of Chemistry, Gunma University, Kiryu, Gunma 376, JAPAN

(Received in Japan 26 August 1974; received in UK for publication 8 October 1974)

It has been shown that over-all conversions of carbonyl compounds to olefins, similar to the well known "Wittig" reaction, could be effected using silicon-substituted carbanions[1]. Recently, an alkyl lithiomethylacetate was reported to be an excellent reagent for the synthesis of α,β-unsaturated carboxylic esters[2], which was generated by the action of lithium dialkylamide on alkyl trimethylsilylacetate. However, none has been known about the reactivity of the silicon-substituted carbanions having nitrile functionalities, as far as we concerned. Herein we wish to describe a novel synthesis of α,β-unsaturated nitriles using α-silylpropionitriles.

We found that α-silylpropionitriles are easily prepared by the rhodium(I) complex catalyzed hydrosilylation of α,β-unsaturated nitriles such as acrylonitrile, crotononitrile and cinnamonitrile in high yields[3].



$$R^1CH{=}CHCN \quad + \quad R^2R^3_2SiH \xrightarrow{(Ph_3P)_3RhCl} R^1CH_2\underset{SiR^2R^3_2}{\underset{|}{CHCN}}$$

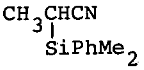
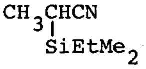
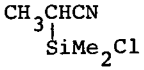
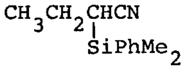
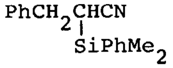
$R^1 = H, CH_3, Ph$

a) $R^2 = Cl$, $R^3 = CH_3$
b) $R^2 = Et$, $R^3 = CH_3$
c) $R^2 = Ph$, $R^3 = CH_3$

(eq. 1)

The hydrosilylation of α,β-unsaturated nitriles was performed in a sealed tube using dimethylphenylsilane, dimethylethylsilane and chlorodimethylsilane in the presence of 0.05-0.1 mol% $(Ph_3P)_3RhCl$. The reaction proceeded in a manner of 1,2-addition and afforded only an α-adduct. In the case of chlorodimethylsilane, the reaction proceeded under much milder conditions, and the resulting α-adduct was ethylated with ethylmagnesium bromide to give the corresponding α-ethyldimethylsilylpropionitrile. Results are listed in Table 1.

Table 1. Hydrosilylation of Acrylonitrile, Crotononitrile and Cinnamonitrile Catalyzed by $(Ph_3P)_3RhCl$

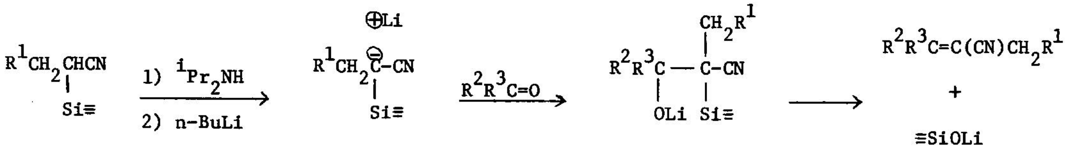
Nitrile	Hydrosilane	Conditions	Product	b.p. °C/mmHg	Yield(%)[a]
$CH_2{=}CHCN$	$PhMe_2SiH$	100°, 3 h	 $CH_3\underset{SiPhMe_2}{CH}CN$	91/0.5	87 (72)
	$EtMe_2SiH$	100°, 24 h	 $CH_3\underset{SiEtMe_2}{CH}CN$	84-85/20	72 (55)
	Me_2ClSiH	50°, 2 h	 $CH_3\underset{SiMe_2Cl}{CH}CN$	58/5	93 (70)
$CH_3CH{=}CHCN$	$PhMe_2SiH$	60°, 4 h	 $CH_3CH_2\underset{SiPhMe_2}{CH}CN$	113/2.5	82 (65)
$PhCH{=}CHCN$	$PhMe_2SiH$	100°, 12 h	 $PhCH_2\underset{SiPhMe_2}{CH}CN$	145/0.5	72 (65)

[a] Glpc yield. Isolated yield in parentheses.

α-Silylpropionitrile thus obtained were converted to lithio-α-silylpropionitriles by the action of lithium diisopropylamide. The lithio-α-silylpropionitrile was allowed to react with a variety of aldehydes and ketones to give excellent yields of the corresponding α,β-unsaturated nitriles as shown in Table 2. Conjugated carbonyl compounds react with the lithio-α-silylpropionitrile in a manner of 1,2-addition without any side reactions, and thus provide a synthesis of nitriles with extended conjugation, as shown by the entries for crotonaldehyde and β-ionone. All α,β-unsaturated nitriles obtained by this method were found to be a mixture of E and Z isomer (ca. 1:1).

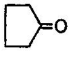
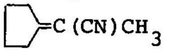
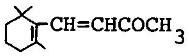
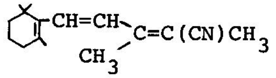
When n-butyl lithium was used as a base, the yield of the α,β-unsaturated nitriles decreased markedly. Thus, lithium diisopropylamide seems to be a suitable base for the reaction.

In a typical procedure, n-hexane solution of n-butyl lithium was added to a THF solution of diisopropylamine at -78° with stirring under nitrogen. To this solution, α-silylpropionitrile was added dropwise over 5 min. After additional 10 min. a carbonyl compound was injected into the solution and stirred



(eq. 2)

Table 2. Reaction of α-Silylpropionitriles with Carbonyl Compounds

α-Silylnitrile	Carbonyl Compound	Product	b.p. °C/mmHg	Yield (%)[a]
$CH_3\underset{SiPhMe_2}{CHCN}$	PhCHO	$\genfrac{}{}{0pt}{}{Ph}{H}\!>C{=}C(CN)CH_3$	111/4.5	98
	CH_3COCH_3	$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>C{=}C(CN)CH_3$	49/20	92
	$CH_3CH_2COCH_3$	$\genfrac{}{}{0pt}{}{CH_3CH_2}{CH_3}\!>C{=}C(CN)CH_3$	69/20	95
			107/20	96
	$PhCOCH_3$	$\genfrac{}{}{0pt}{}{CH_3}{Ph}\!>C{=}C(CN)CH_3$	75-80/0.4	98
	$CH_3CH{=}CHCHO$	$\genfrac{}{}{0pt}{}{CH_3CH{=}CH}{H}\!>C{=}C(CN)CH_3$	45-50/1.0	91
			150/0.3	93
$CH_3CH_2\underset{SiPhMe_2}{CHCN}$	PhCHO	$\genfrac{}{}{0pt}{}{Ph}{H}\!>C{=}C(CN)CH_2CH_3$	90/0.5	97
$PhCH_2\underset{SiPhMe_2}{CHCN}$	PhCHO	$\genfrac{}{}{0pt}{}{Ph}{H}\!>C{=}C(CN)CH_2Ph$	132/0.5	92
$CH_3\underset{SiEtMe_2}{CHCN}$	PhCHO	$\genfrac{}{}{0pt}{}{Ph}{H}\!>C{=}C(CN)CH_3$	111/4.5	98

[a] GLPC yields.

for one hour. The reaction mixture was then gradually warmed to room temperature and stirred for additional two hours. The reaction mixture was hydrolyzed by the action of aqueous ammonium chloride solution, and extracted with dichloromethane. After the solvent was evaporated , the residue was distilled under reduced pressure or chromatographed on silica gel, and the resulting α,β-unsaturated nitrile was obtained in high yield.

REFERENCES

1. D. J. Peterson, J. Org. Chem., 33, 780 (1968); T. H. Chan, E. Chang and E. Vinokur, Tetrahedron Lett., 1137 (1970); F. A. Carey and A. S. Court, J. Org. Chem., 37, 939, 1926 (1972); F. A. Carey and O. Hernandez, J. Org. Chem., 38, 2670 (1973); D. Seebach, B. -Th. Gröbel, A. K. Beck, M. Braun and K.-H. Geiss, Angew. Chem. Internat. Edit., 11, 443 (1972); D. Seeback, M. Kolb and B. -Th. Gröbel, Chem. Ber., 106, 2277 (1973); H. Sakurai, K. Nishiwaki and M. Kira, Tetrahedron Lett., 4193 (1973).
2. S. L. Hartzell, D. F. Sullivan and M. W. Rathke, Tetrahedron Lett., 1403 (1974); K. Shimoji, H. Taguchi, K. Oshima, H. Yamamoto and H. Nozaki, J. Amer. Chem. Soc., 96, 1620 (1974).
3. As for the hydrosilylation of acrylonitrile using $HRh(CO)(PPh_3)_3$, see A. J. Chalk, J. Organometal. Chem., 21, 207 (1970). A detailed description of the selective hydrosilylation of α,β-unsaturated nitriles will be presented separately.