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Reaction of acylsilanes with potassium cyanide: Brook rearrangement under phase-transfer catalytic conditions

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Abstract

The reactions of acylsilanes with KCN under liquid–liquid phase-transfer catalytic conditions proceeded smoothly via the Brook rearrangement to produce *O*-silylated cyanohydrin derivatives in excellent yields. We also found that α-cyano carbanions generated by the Brook rearrangement in the reaction of (β-(trimethylsilyl)acryloyl)silane **7** can undergo alkylation at the γ-position and that in the reaction of β-bromoacylsilane **14** intramolecular alkylation occurs to afford cyclopropanone cyanohydrin derivative **16**. © 2000 Elsevier Science Ltd. All rights reserved.

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Reactions of acylsilanes with nucleophiles have attracted considerable attention because of the unique transformation, including the Brook rearrangement, which allows the carbonyl group to serve as a 1,1-dipole.[1,2] We became interested in the reaction of acylsilanes with a cyanide ion in connection with our ongoing investigation directed to the development of Brook rearrangement-mediated reactions.[3] Since the Brook rearrangement is facilitated by carbanion-stabilizing groups,[2] we reasoned that the reaction of acylsilanes with a cyanide ion would be more synthetically useful if the ion could be nucleophilic enough to generate an appropriate concentration of a carbanion for the Brook rearrangement in the reaction with acylsilanes. To the best of our knowledge, there has been only one report, that by Reich, on the reaction of acylsilanes with a cyanide ion.[4] We decided to try the reaction of acylsilanes with KCN in a liquid–liquid two-phase system under phase-transfer conditions. One of our interests was also to see whether the Brook rearrangement can occur in the presence of water or whether it is intercepted by water to give an α-silylcarbinol, because it is known that acylsilanes are cleaved by dilute alkaline solutions to give aldehydes via the attack of a hydroxide ion at the carbonyl carbon[5] and, to our knowledge, there has been no report on the occurrence of the Brook rearrangement in α-hydroxysilanes under aqueous conditions.

When β-alkyl substituted acryloylsilanes **1**[6] were treated with KCN in the presence of n-Bu$_4$NBr in CH_2Cl_2–H_2O, *O*-silylated cyanohydrin derivatives **4** were obtained (Table 1).[7,8] The use of n-Bu$_4$PBr

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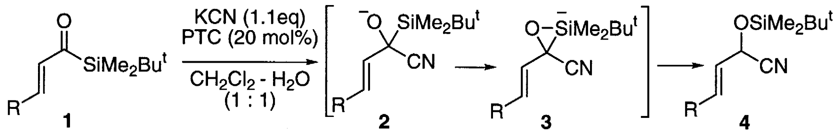
as a PTC gave a better result. In both cases, no α-silylcarbinol arising from protonation of **2** before the Brook rearrangement was detected.

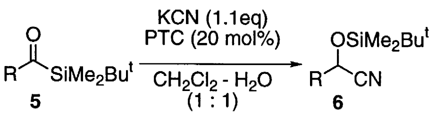
Table 1



1	R	yield (%)	
		n-Bu_4NBr	*n*-Bu_4PBr
a	Me	75	82
b	*i*-Pr	56	93
c	*c*-C_3H_5	85	95
d	*c*-C_6H_{11}	64	96
e	*t*-Bu	85	95

The almost same result was obtained when the reaction was performed with benzoylsilane **5a** and acylsilanes **5b**,**c**[9] (Table 2).

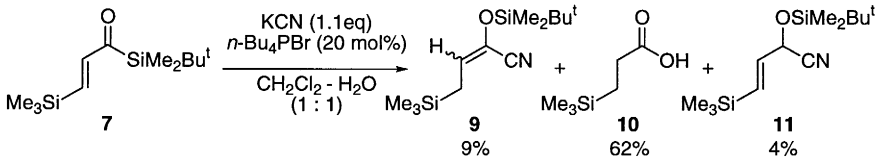
Table 2



5	R	yield (%)	
		n-Bu_4NBr	*n*-Bu_4PBr
a	Ph	68	95
b	Me	65	74
c	CH_2CH_2OMe	65	76

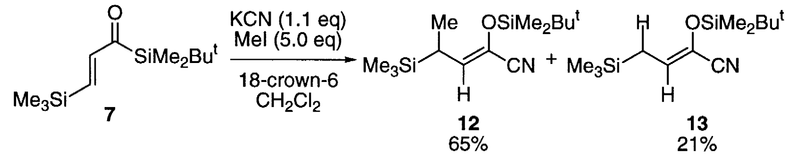
The fact that no α-silylcarbinol was detected suggests that an intramolecular nucleophilic attack of the oxyanion on silicon in adduct **2** to lead to the pentavalent silicon species **3** is faster than the protonation of the oxyanion by water or that the reaction proceeds via a concerted process involving **3**.

In the reaction of the β-alkyl-substituted acryloylsilane **1**, no allylic rearrangement to lead to the formation of enol silyl ethers was observed. We envisaged that the introduction of an anion-stabilizing group at the β-position in **1** causes the allylic rearrangement to produce a γ-anion derivative of α-siloxyacrylonitrile. To test this possibility, we examined the reaction of (β-(trimethylsilyl)acryloyl)silane **7**[10,3a] with KCN. Under the same conditions employed for **1**, we obtained α-siloxyacrylonitrile **9** (*Z*:*E*=2.4:1), a product arising from the Brook rearrangement followed by an allylic rearrangement of a generated carbanion, β-silylpropanoic acid **10**, a hydrolysis product of **9**, and **11**, the Brook rearrangement product (Scheme 1).



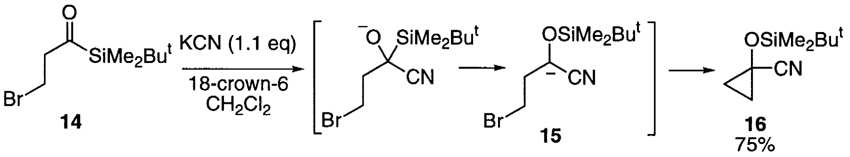
Scheme 1.

The above results led us to investigate the reaction of **7** with KCN under non-aqueous conditions in the presence of an electrophile and a PTC that would allow the introduction of substituents on the α- or γ-position of α-siloxyacrylonitriles. We examined the reactions of **1** and **7** with KCN using methyl iodide and 18-crown-6 as an electrophile and a PTC, respectively. Whereas the reaction of **1** resulted in recovery of the starting material, methylated product **12** was obtained in 65% yield together with protonated derivative **13** from the reaction of **7** (Scheme 2). The *Z* geometries of **12** and **13** were assigned on the basis of results of NOESY experiments, and the exclusive formation of the *Z* derivative was attributed to the coordination of the allylic anion to the silicon atom.



Scheme 2.

Finally, intramolecular alkylation[11] of the silyl-protected cyanohydrin carbanion **15** derived from the reaction of **14** with KCN in the presence of the crown ether in CH_2Cl_2 was examined, and the results are shown in Scheme 3. It is noteworthy that the reaction proceeds at room temperature, because the base-induced cyclization of *O*-protected β-chlorocyanohydrin is reported to require heating at 95°C.[12]



Scheme 3.

In conclusion, we have demonstrated that KCN can serve as a nucleophile in combination with PTC in the reaction with acylsilanes and thereby provide potentially synthetically useful silyl-protected cyanohydrin carbanions. Attempts to explore the scope of the reactions are underway.

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8. In contrast, reactions of **1** with KCN in organic solvents such as CH_2Cl_2, MeCN, DMF, or DMSO in the presence or absence of PTC, or with *n*-Et_4NCN in CH_2Cl_2 resulted in lower yields of **4** and/or in the recovery of starting material. This may be partly attributed to the lower stability of the generated carbanion in the solvents. Under the PTC conditions, the carbanion can be immediately protonated.
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