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Cyclization of bis(acylsilanes) under nucleophilic activation. Competitive [1,2] carbone to oxygen and [1,4] oxygen to oxygen silyl migration

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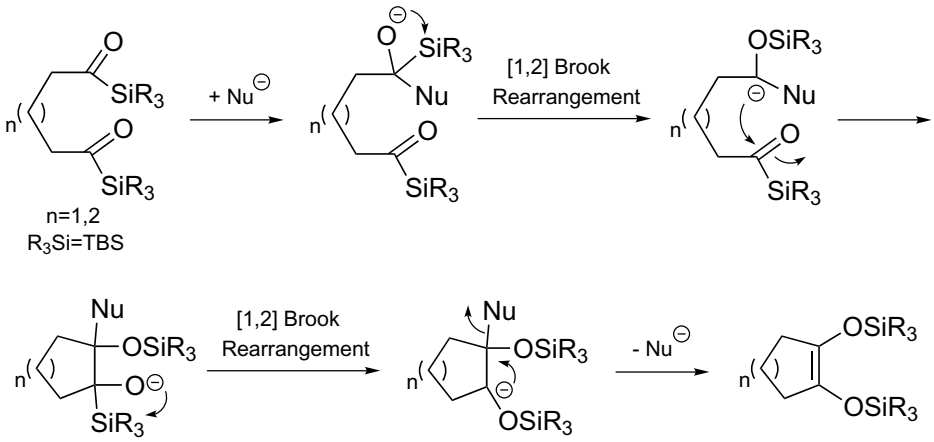
Abstract—Cyclization of 1,5- and 1,6-bis(acylsilanes) with potassium cyanide gave new silylated cycloalcanones via a multistep sequence combining nucleophilic addition, two silyl migrations and β-elimination. The nature of the products is very dependent on the competition between [1,2] carbon to oxygen and [1,4] oxygen to oxygen silyl migration.

The propensity of acylsilanes[1] to undergo a [1,2] C to O silyl migration (Brook rearrangement)[2] under nucleophilic attack is one of the more attractive properties of these compounds. The combination of such a rearrangement with subsequent steps allows various possibilities in 'tandem bond formation strategies'.[3] Of particular interest, cyclic compounds can be obtained when the subsequent steps involve a function which is present either in the incoming nucleophile or in the starting acylsilane.

Bis(acylsilanes)[4] are particular bifunctional acylsilanes the reactivity of which has been studied less. Besides cyclization not involving any Brook rearrangement, such as etherification[5] and aldolization,[4,6] some papers reported transformations where C to O silyl migration step occurred. On the one hand, macrocyclization by McMurry coupling was accompanied by products coming from some Brook rearrangement.[7] On the other hand, the Brook rearrangement is a crucial step in the conversion of bis(acylsilanes) into cyclic 2,2-difluoro-3-trialkylsilyl ketols by the reaction sequence: nucleophilic trifluoromethylation–Brook rearrangement–fluoride elimination–Mukaiyama type aldol cyclization.[8] We now present the results of an exploratory investigation of a domino rearrangement of 1,5- and 1,6-bis-(acylsilanes) induced by potassium cyanide.



Scheme 1.

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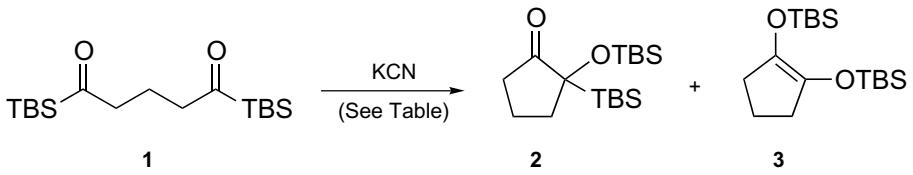


1 2 3

Scheme 2. Ref. 12

We anticipated that a reaction sequence starting with a nucleophilic attack on one acylsilane function, followed by a Brook rearrangement, should lead to an intramolecular addition which itself could induce a second Brook rearrangement (Scheme 1). If the nucleophilic reagent also has a good nucleofugal character, a β-elimination should occur to give the bis(silylated) enol ether. Cyanides are good candidates as they exhibit the dual nucleophilic+nucleofugal properties. The cyanation of simple acylsilanes by trimethylsilylcyanide yields the corresponding silylated cyanohydrine.[9] When an ammonium cyanide or potassium cyanide was used, the Brook rearrangement occurred.[10,11]

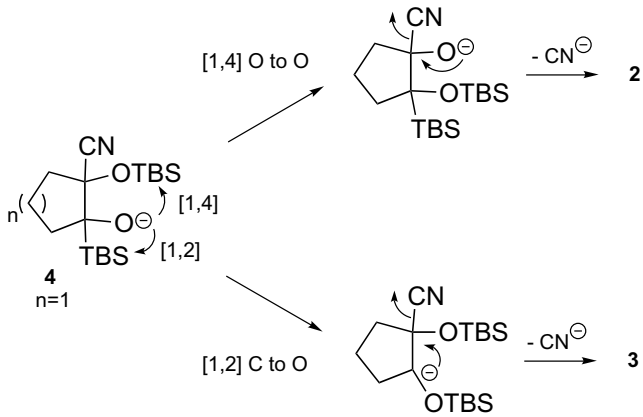
The results of the reaction of the 1,5-bis(acylsilane) **1** with potassium cyanide in various conditions are summarized in Scheme 2 and in Table 1.[12] Generally, a mixture of two cyclized products **2**[13] and **3**[14] was obtained. The expected compound **3** is indeed formed, but as the minor component of the mixture.

An examination of Table 1 (entries 1–4) shows that, even if the reaction pathway is catalytic in cyanide ion (Scheme 1), a stoichiometric amount of potassium cyanide is needed in order to obtain compounds **2** and **3** in moderate to good yields. The reaction is fast, since a 90% conversion was achieved after 5 min (entry 1). Too long a reaction time gave lower yields of both products (entries 1, 3). Other polar aprotic solvents as DMF, CH_3CN or sulfolane gave very poor yields of products **2**, **3**, even for total conversion of **1**. THF or CH_2Cl_2 allowed a similar reaction if potassium cyanide is activated with a crown ether (entries 5, 6). When the reaction was performed under high dilution conditions (entry 7), compound **2** was isolated in 49% yield.

As far as we know, this is the first domino reaction involving two Brook rearrangements. The carbonylated compound **2** has lost one C–Si bond to the benefit of one O–Si bond. It seems reasonable to consider a [1,4] oxygen to oxygen silyl migration to explain the formation of **2** (Scheme 3). Hence, compounds **2** and **3** result from a competition between a [1,4] O to O and a [1,2] C to O silyl migration, after the C–C bond forming step leading to the intermediate **4** (Scheme 3).

The extension of the procedure to the 1,6-bis(acylsilane) **5** gave a mixture of three products including the homologous carbonylated compound **6**,[15] the cyclohexadiene compound **7**,[16] and an unexpected cyclopentenic derivative **8**[17] (Scheme 4).

Compound **6** is the result of a pathway similar to the one described in Scheme 3, involving a [1,4] O to O silyl

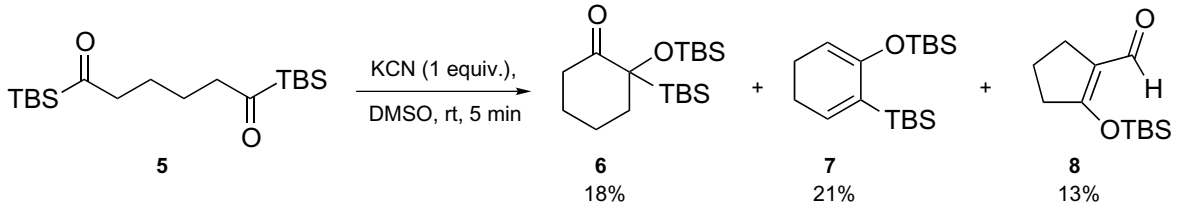


Scheme 3.

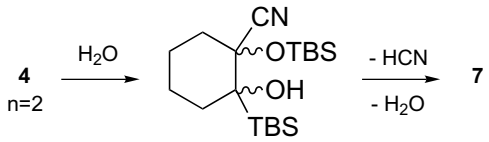
Table 1. Reaction of bis(acylsilane) **1** with KCN

Entry	KCN (equiv.)[a]	Solvent	Time (min)	Conv. (%)	Yield **2** (%)[b]	Yield **3** (%)[b]
1	1.0	DMSO	5	90	40	20
2	1.0	DMSO	15	100	46	13
3	1.0	DMSO	30	100	25	5
4	0.5	DMSO	15	89	34	12
5	1.0	THF[c]	180	100	27	10
6	1.0	CH_2Cl_2[c]	180	100	48[d]	48[d]
7	1.0	DMSO[e]	5	100	49	–

[a] Room temperature. Substrate concentration: 0.3 M.
[b] The products **2** and **3** were purified by column chromatography on silica gel (petroleum ether/AcOEt 97/3).
[c] 18-Crown-6 (0.3 equiv.).
[d] Mixture of compounds **2** and **3**.
[e] Substrate concentration: 0.075 M.



Scheme 4. Ref. 12



Scheme 5.

migration. Product **7** could come from the trapping of the intermediate **4** ($n=2$) by some water in the reaction medium (Scheme 5). The cyclopentenic derivative **8** probably comes from further transformations of the compound resulting from an intramolecular aldol condensation of **5**.[4]

In summary, these results show that a simple activation of 1,5- and 1,6-bis(acylsilanes) with cyanide ions is able to induce a multistep transformation combining two silyl migrations with nucleophilic additions (inter- then intramolecular) and β-elimination (Scheme 1). Unfortunately, it seems difficult to obtain a high selectivity between the two competitive [1,2] C to O and [1,4] O to O silyl migrations. Nethertheless, these reactions allowed new silylated cyclic compounds to be prepared.

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12. *Typical procedure for the reaction of bis(acylsilane) with KCN* (Table 1: entry 1): To a solution of bis(acylsilane) **1** (329 mg, 1.0 mmol) in dry DMSO (3.5 mL), under an argon atmosphere, was added dry potassium cyanide (65 mg, 1.0 mmol). After stirring at room temperature for 5 min, the crude mixture was purified by column chromatography on silica gel (petroleum ether/AcOEt (97/3)) to give compound **2** (131 mg, 40 %) and compound **3** (66 mg, 20 %).
13. *Spectral data for compound* **2**. Oil. ^{1}H NMR ($CDCl_3$) δ (ppm): −0.04 (s, 3H), 0.06 (s, 3H), 0.07 (s, 3H), 0.16 (s, 3H), 0.88 (s, 9H), 0.99 (s, 9H), 1.6–2.1 (m, 3H), 2.1–2.3 (m, 2H), 2.70 (m, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): −7.0 (CH_3), −6.1 (CH_3), −2.71 (CH_3), −2.69 (CH_3), 16.5 (CH_2), 18.4 (C_4), 18.8 (C_4), 25.8 (CH_3), 27.5 (CH_3), 34.7 (CH_2), 35.3 (CH_2), 83.5 (C_4), 218.5 (CO). IR (film, cm^{-1}): 1727. GC–MS *(m/e)*: 328 (M^+), 155, 147, 73.
14. *Spectral data for compound* **3**. Oil. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.13 (s, 12H), 0.94 (s, 18H), 1.75 (quint, 2H, $J=6.9$ Hz), 2.24 (t, 4H, $J=6.9$ Hz). ^{13}C NMR ($CDCl_3$) δ (ppm): −3.9 (CH_3), 17.0 (CH_2), 18.1 (C_4), 25.7 (CH_3), 30.3 (CH_2), 130.9 (C_4). IR (film, cm^{-1}): 1703. GC–MS (*m/e*): 328 (M^+), 197, 155, 147.
15. *Spectral data for compound* **6**. Oil. ^{1}H NMR ($CDCl_3$) δ (ppm): −0.03 (s, 3H), 0.15 (s, 3H), 0.18 (s, 3H), 0.29 (s, 3H), 0.87 (s, 9H), 0.90 (s, 9H), 1.5–1.9 (m, 4H), 2.0–2.1 (m, 1H), 2.3–2.6 (m, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): −5.6 (CH_3), −3.9 (CH_3), −2.4 (CH_3), −2.1 (CH_3), 18.8 ($2\times C_4$), 23.9 (CH_2), 26.2 (CH_3), 26.6 (CH_2), 27.3 (CH_3), 40.4 (CH_2), 41.7 (CH_2), 83.8 (C_4), 211.0 (CO). IR (film, cm^{-1}): 1697. GC–MS (*m/e*): 342 (M^+), 285, 189, 147.
16. *Spectral data for compound* **7**. Oil. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.13 (s, 6H), 0.14 (s, 6H), 0.90 (s, 9H), 0.94 (s, 9H), 2.4–2.5 (m, 2H), 2.5–2.6 (m, 2H), 6.1 (m, 1H), 6.5 (m, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): −5.4 (CH_3), −5.0 (CH_3), 16.9 (C_4), 18.2 (C_4), 25.6 (CH_3), 26.1 (CH_2), 26.9 (CH_3), 33.0 (CH_2), 133.2 (CH), 135.3 (C_4), 139.6 (C_4), 146.0 (CH). GC–MS (*m/e*): 324 (M^+), 267, 147, 133.
17. *Spectral data for compound* ***8***. Oil. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.24 (s, 6H), 0.92 (s, 9H), 1.85 (quint, 2H, $J=7.6$ Hz), 2.63 (tm, 2H, $J=7.6$ Hz), 2.70 (tm, 2H, $J=7.6$ Hz), 9.95 (s, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): −3.8 (CH_3), 17.2 (C_4), 23.1 (CH_2), 26.5 (CH_3), 31.9 (CH_2), 42.2 (CH_2), 155.6 (C_4), 167.1 (C_4), 191.0 (CO). IR (film, cm^{-1}): 1672. GC–MS (*m/e*, CI): 229 (M+1), 228 (M^+), 211, 132.