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Preliminary communication

New cascade silylcarbocyclization (SiCaC) of enediynes [1]

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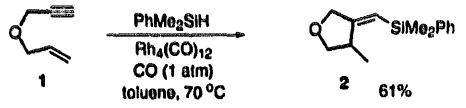
Abstract

The $Rh(acac)(CO)_2$-catalyzed cascade silylcarbocyclizations (SiCaC) of (6*E*)- and (6*Z*)-dodec-6-ene-1,11-diynes stereospecifically give (*R**,*R**)- and (*S**,*R**)-bis(*exo*-methylenecyclopentyl) respectively in good isolated yields.

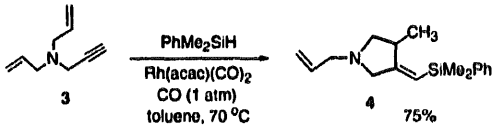
Keywords: Silicon; Silylcarbocyclization; Endiynes; Bis(*exo*-methylenecyclopentyl); Rhodium; Catalysis

1. Introduction

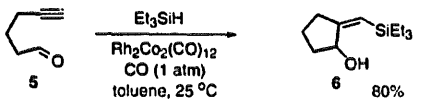
Carbocyclizations of alkenes and alkynes are extremely important reactions for the syntheses of a variety of carbocyclic and heterocyclic compounds (see, for example, Ref. [1]). In the course of our investigations into the silylformylation of alkynes catalyzed by Rh and Rh-Co complexes [2–6] (and for contributions from other laboratories, see Ref. [7]), several novel silylcarbocyclization (SiCaC) reactions have been discovered [8–10]. For example, the SiCaC-type I reaction gives a five-membered ring compound bearing an *exo*-silylmethylene moiety from a 1,6-enyne [8] or an alk-5-yn-1-al [9] (Eqs. (1)–(3)).



1 2 61% (1)

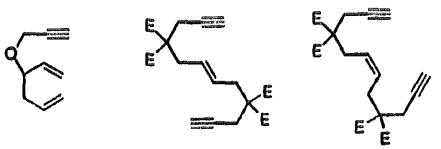


3 4 75% (2)



5 6 80% (3)

In these SiCaC-type I reactions, the β-silylvinyl-[Rh] intermediate generated by the insertion of the acetylene moiety into Si–[Rh](H) species is trapped by the olefin or aldehyde moiety to form the alkyl–[Rh](H) or alkoxy–[Rh](H) species [8,9]. We assumed that if additional alkene or alkyne moieties were placed at appropriate positions to trap the alkyl–[Rh](H) intermediate after the first silylcarbocyclization, polycyclic frameworks could be synthesized from relatively simple starting materials through cascade carbocyclizations. In this communication we describe our preliminary results on the extended SiCaC-type I reaction of dienyne **7** and enediynes **8** and **9**.



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[1] Dedicated to Professor Robert J.P. Corriu for his leadership and his outstanding contribution to the advancement of organosilicon chemistry.

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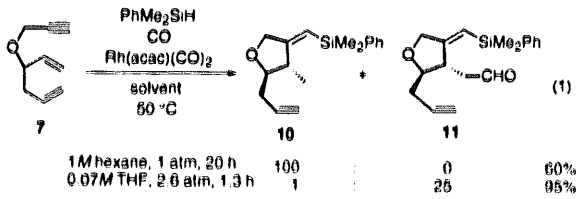
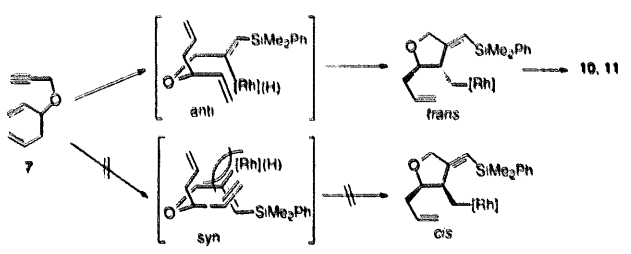
2. Experimental and discussion

We first tried a possible trapping of the alkyl–[Rh](H) intermediate by an olefin moiety using **7**. The reaction of **7** (0.20 mmol) with $PhMe_2SiH$ (0.20 mmol) in the presence of $Rh(acac)(CO)_2$ (0.002 mmol, 1 mol%) at 50 °C and ambient pressure of carbon monoxide to give a mixture of SiCaC product **10** and CO–SiCaC product **11** (Eq. (1)) (see Section 2.1.) Namely, the attempted reaction did not yield the expected bicyclic product through cascade carbocyclization. The solvent and the concentration of the reactants, as well as carbon monoxide pressure, exerted a remarkable influence on the product selectivity. Thus, when the reaction was run in hexane at 1 M concentration of **7** under 2.6 atm of carbon monoxide, **10** was formed in 60% yield and no formation of **11** was observed by GC analysis, while in the reaction of **7** in THF at 0.07 M concentration under ambient pressure of carbon monoxide for 20 h, **11** was obtained as the predominant product (**10**/**11** = 1/25) in 95% yield. The stereochemistry of **10** and **11** were unambiguously determined to be trans, based on the negligible H_2-H_3 coupling, i.e. the dihedral angle of H_2-C_2-C_3-H_3 is ca. 86°.

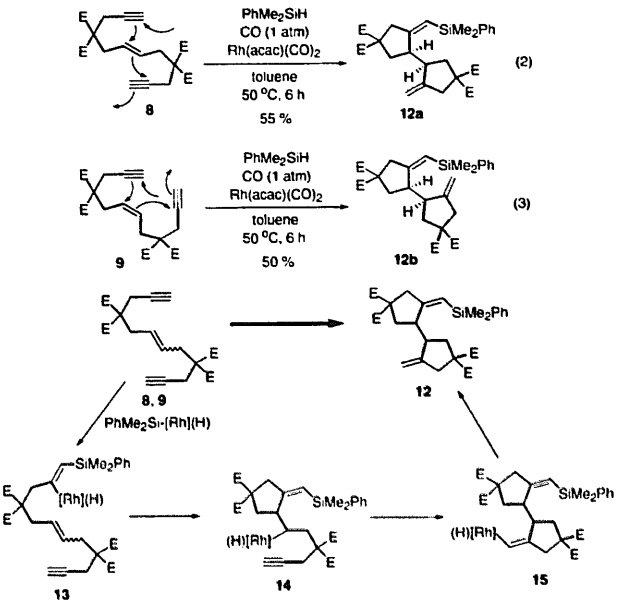


As Scheme 1 shows, in order for the second cyclization to occur the allyl and the alkyl–[Rh](H) moieties should be on the same side of the tetrahydrofuran ring. However, it appears that the syn orientation of the vinyl and the allyl moieties in the transition state is unfavorable, and thus the reaction proceeds exclusively through the transition state in which the vinyl and the allyl moieties are anti.

Since the attempted trapping of the alkyl–[Rh](H) species with an olefin moiety after the SiCaC process



Scheme 1.

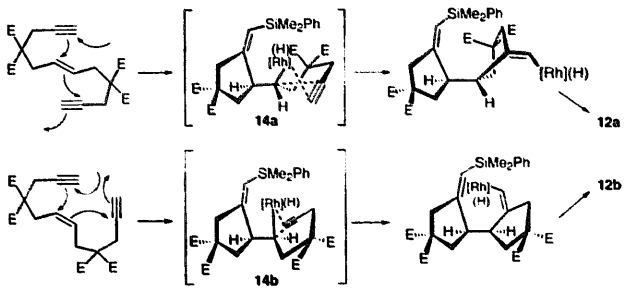


Scheme 2.

did not succeed, we examined a possible trapping with an acetylenic moiety using linear alkenediynes **8** and **9**. For these substrates, the reactions proceeded as designed to give the corresponding cascade cyclization products. The reaction of (6*E*)-dodec-6-ene-1,11-diyne (**8**) (0.2 mmol) with $PhMe_2SiH$ (0.2 mol) was carried out in the presence of $Rh(acac)(CO)_2$ (0.002 mmol, 1.0 mol%) in toluene at 50 °C and ambient pressure of carbon monoxide for 6 h to give (*R**,*R**)-bis(*exo*-methylenecyclopentyl) **12a** in 55% yield (Eq. (2)) (see Section 2.1.) In the same manner, the reaction of **9** gave (*S**,*R**)-bis(*exo*-methylenecyclopentyl) **12b** in 50% yield (Eq. (3)) (see Section 2.1.) Thus, these cascade SiCaC reactions proceeded stereospecifically. The most likely mechanism for the formation of **12** is illustrated in Scheme 2.

As Scheme 2 shows, the alkyl–[Rh](H) intermediate **14** generated by the first carbocyclization is effectively trapped by the acetylene moiety to form the vinyl–[Rh](H) intermediate **15**, and the hydride shift, i.e. reductive elimination, gives **12**. Although the trapping of the vinyl–[Rh] species with the vinylsilane moiety in **15** to undergo third carbocyclization was conceptually possible, such a carbocyclization did not take place. The exclusive formation of two diastereomers can easily be rationalized by taking into account the stereospecific generation of the alkyl–[Rh](H) species, **14a** or **14b** followed by the stereospecific insertion of the acetylene moiety into the alkyl–[Rh] bond as illustrated in Scheme 3.

Further investigations on the cascade SiCaC reactions are actively underway.



Scheme 3.

2.1. Analytical results

10: ^{1}H NMR ($CDCl_3$) δ: 0.40 (d, J = 4.6 Hz, 6H), 1.01 (d, J = 7 Hz, 3H), 2.00-2. 18 (m, 1H), 2.18-2.30 (m, 1H), 2.38 (m, 1H), 3.72 (td, J = 7.0, 3.1 Hz, 1H), 4.27 (dd, J = 13.5, 1.7 Hz, 1H), 4.45 (dt, J = 13.7, 1.2 Hz, 1H), 5.01 (m, 2H), 5.52 (s, 1H), 5.70-5.80 (m, 1H), 7.36 (m, 3H), 7.53 (m, 2H); ^{13}C NMR ($CDCl_3$) δ: -1.00, 19.95, 38.95, 41.97, 72.51, 86.55, 115.88, 117.05, 127.85, 129.03, 133.78, 135.16.

11: ^{1}H NMR ($CDCl_3$) δ: 0. 40 (d, J = 4.6 Hz, 6H), 2. 08 (dd, J = 18.0, 2.0 Hz, 1H), 2. 18 (m, 2H), 2. 55 (ddd, J = 18.0, 10.8, 1.5 Hz, 1H), 2. 81 (d, J = 10.8 Hz, 1H), 3. 82 (t, J = 7 Hz, 1H), 4. 26 (dd, J = 13.8, 1.3 Hz, 1H), 4.41 (dt, J = 13.8, 1.0 Hz, 1H), 5.04 (m, 2H), 5.61 (s, 1H), 5.72 (m, 1H), 7.36 (m, 3H), 7.53 (m, 2H); ^{13}C NMR ($CDCl_3$) δ: -1.7, -1.4, 38.5, 41.5, 48.1, 71.7, 84.2, 117.4, 118.1, 128.1, 129.4, 133.9, 134.2, 138.6, 160.5, 200.1.

12a: ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 0.11 (s, 3H), 0.36 (s, 3H), 1.22 (t, 12H), 1.6-1.72 (m, 1H), 1.8-1.9 (m, 1H), 2.3-2.4 (m, 1H), 2.45-2.55 (m, 1H), 2.6-3.1 (m, 6H), 4.15 (m, 8H), 4.35 (s, 1H), 4.85 (s, 1H), 5.88 (s, 1H), 7.25-7.6 (m, 5H). ^{13}C NMR ($CDCl_3$ 62.5 MHz) δ: -1.9, -0.7, 14.0, 14.1, 34.1, 34.2, 41.1, 41.6, 46.4, 47.2, 58.5, 61.4, 61.5, 107.1, 120.2, 127.8, 128.2, 128.9, 129.6, 133.6, 133.8, 149.0, 161.1, 171.3.

12b: ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 0.32 (s, 3H), 0.39 (s, 3H), 1.23 (m, 12H), 1.5-1.6 (m, 1H), 1.8-1.9 (m, 1H), 2.1-2.2 (m, 1H), 2.4-3.1 (m, 7H), 4.15 (m, 8H), 4.92 (s, 1H), 4.97 (s, 1H), 5.61 (s, 1H), 7.25-7.6 (m, 5H). ^{13}C NMR ($CDCl_3$ 62.5 MHz) δ: -2.0, -0.5, 14.0, 29.7, 35.3, 43.7, 45.0, 47.1, 58.4, 61.4, 61.5, 108.0, 121.0, 127.7, 128.19, 133.8, 139.0, 149.0, 162.0, 172.0.

Acknowledgements

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