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Silylcarbobicyclization of 1,6-Diynes: A Novel Catalytic Route to Bicyclo[3.3.0]octenones

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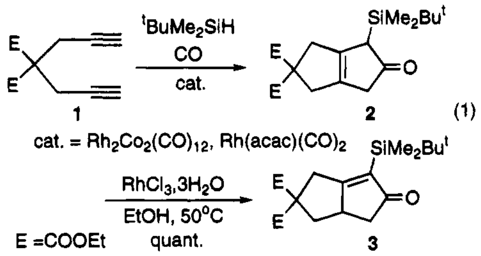
Summary: The reactions of 1,6-alkadiynes with *tert*-butyldimethylsilane under carbon monoxide pressure catalyzed by Rh(acac)(CO)$_2$, $Rh_2Co_2(CO)_{12}$, or Rh(C≡NBu^t)$_4$-Cc(CO)$_4$ give the corresponding bicyclo[3.3.0]octenones in good to excellent yields via novel silylcarbobicyclization process.

Carbocyclizations of alkenes and alkynes are extremely important reactions for the syntheses of a variety of carbocyclic and heterocyclic compounds of medicinal interest. For example, Pauson−Khand reaction[1] of alkynes with alkenes or enynes promoted by a stoichiometric amount of $Co_2(CO)_8$ has been extensively studied[2−6] and applied to the syntheses of many biologically active compounds.[7,8] In the course of our study on silylformylation of alkynes[9] and silylcarbocyclizations (SiCaC) of alkenynes, diynes, and alkynals,[10] we looked at the reactions of hydrosilanes with diynes catalyzed by Rh and Rh−Co complexes in the presence of carbon monoxide to discover a novel silylcarbobicyclization process, which is different from the previously reported SiCaC reactions,[10] giving the corresponding bicyclo[3.3.0]octenones.[11] We would like to describe here a novel silylcarbobicyclization (type 3−SiCaC) reaction of 1,6-alkadiynes and related reactions.[12]

The reaction of diethyl dipropargylmalonate (**1**, 2.00 mmol) with HSiMe$_2$Bu^t (4.00 mmol) in toluene (10.0 mL) at 50 °C and 15 atm of CO catalyzed by $Rh_2Co_2(CO)_{12}$[13] or Rh(acac)(CO)$_2$ (1.0 mol %) for 12 h gave cleanly 2-silylbicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**2**) in >90% isolated yield (98% GC yield) (eq 1). To the best of our knowledge, this is the first *truly catalytic* carbobicyclization of diynes incorporating carbon monoxide. Compound **2** thus formed is readily isomerized to 2-silylbicyclo[3.3.0]oct-1-en-3-one (**3**) in quantitative yield by adding a catalytic amound of $RhCl_3{\cdot}H_2O$ in ethanol to the reaction mixture and stirring at 50 °C for 24 h.



The efficacy of differenct catalysts was examined under the standard conditions described above except for using 50 atm of carbon monoxide. Results are as follows (isolated yields): $Rh_2Co_2(CO)_{12}$ (93%), Rh(acac)(CO)$_2$ (93%), Rh(CN-Bu^t)$_4$Co(CO)$_4$[14] (82%), [Rh(CO)$_2$Cl]$_2$ (54%). It is found that RhCl(PPh$_3$)$_3$, $Rh_2(OAc)_2$, $Ru_3(CO)_{12}$,[15] and $PdCl_2(PPh_3)_2$ are inactive for this type 3−SiCaC reaction.

Bicyclo[3.3.0]octenones, which are very useful intermediates for a variety of biologically active cyclopentanoids, can be obtained through $Co_2(CO)_8$-promoted Pauson−Khand reaction[3,5,7,8] and via zirconocene[16] or titanocene-mediated carbobicyclization−carbonylation of enynes.[17] However, these processes are basically stoichiometric, and only very recently was a catalytic version of the Pauson−Khand reaction developed.[18] The first catalytic titanocene-promoted carbobicyclization−carbonylation of enynes was recently reported,[19] but isocyanides were needed as a carbonyl synthon (hydrolysis is required to obtain ketone functionality). Nickel(0)-promoted stoichiometric carbobicyclization−carbonylation also requires isocyanides as a carbonyl synthon.[20] An efficient Pd-

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[1] Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855−5860.

[2] Schore, N. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; 1991; Vol. 5, pp 1037−1064.

[3] Krafft, M. E.; Romero, R. H.; Scott, I. L. *J. Org. Chem.* **1992**, *57*, 5277−5278.

[4] Krafft, M.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199−7207.

[5] Hoye, T. R.; Suriano, J. A. *J. Org. Chem.* **1993**, *58*, 1659−1660.

[6] Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289−5292.

[7] Schore, N. In *Organic Reactions*; Beak, P., Ed.; Wiley: New York, 1991; pp 1−90.

[8] Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, *41*, 5861−5869.

[9] (a) Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38−41. (b) Ojima, I.; Donovan, R. J.; Eguchi, M.; Shay, W. R.; Ingallina, P.; Korda, A.; Zeng, Q. *Tetrahedron* **1993**, *49*, 5431−5444. (c) Ojima, I.; Donovan, R. J.; Ingalina, P.; Clos, N.; Shay, W. R.; Eguchi, M.; Zeng, Q.; Korda, A. *J. Cluster Sci.* **1992**, *3*, 423−438. (d) Ojima, I.; Zhang, Z.; Korda, A.; Ingallina, P.; Clos, N. In *New Science in Homogeneous Transition Metal Catayzed Reactions*; Moser, W. R., Ed.; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1992; Chapter 19, pp 277−296. See also contributions from Matsuda et al., Doyle et al., and Wright et al. (e) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332−2333. (f) Matsuda, I.; Ogiso, A.; Sato, S. *J. Am. Chem. Soc.* **1990**, *112*, 6120−6121. (g) Matsuda, I.; Sakakibara, J.; Nagashima, H.; *Tetrahedron Lett.* **1991**, *32*, 7431−7434. (h) Matsuda, I.; Sakakibara, J.; Inoue, H.; Nagashima, H. *Tetrahedron Lett.* **1992**, *33*, 5799−5802. (i) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1993**, *12*, 11−12. (j) Doyle, M. P.; Shanklin, M. S. *Organometallics*, **1994**, *13*, 1081−1088. (k) Wright, M. E.; Cochran, B. B. *J. Am. Chem. Soc.* **1993**, *115*, 2059−2060.

[10] (a) Ojima, I.; Donovan, R. J.; Shay, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 6580−6582. (b) Ojima, I.; Tzamarioudaki, M.; Tsai, C.-Y. *J. Am. Chem. Soc.* **1994**, *116*, 3643−3644.

[11] A preliminary results were presented at the 207th ACS National Meeing, San Diego, March 12−16, 1994; Abstract ORGN 0198.

[12] The discovery of the Type 3−SiCAC reaction was presented: Donovan, R. J.; Fracchiolla, F. A.; Ojima, I. 207th American Chemical Society National Meeting, San Diego, March 13−17, 1994; Abstract ORGN 198. Also Ojima, I. 27th Organosilicon Symposium, Troy, March 18−19, 1994; Abstract B-9.

[13] (a) Martinengo, S.; Chini, P.; Albano, V. G.; Cariati, F. *J. Organomet. Chem.* **1973**, *59*, 379−394. (b) Horvath, I. T.; Bor, G.; Garland, M.; Pino, P. *Organometallics* **1986**, *5*, 1441−1445.

[14] Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1991**, *10*, 3211−3219.

[15] It is worth mentioning that no (silyloxy)benzene formation, which was recently reported by Murai's laboratory using $Ru_3(CO)_{12}$−PCy$_3$, was observed under our reaction conditions. Chatani, N.; Fukumoto, Y.; Ida, T.; Murai, S. *J. Am. Chem. Soc.* **1993**, *115*, 11614−11615.

[16] (a) Negishi, E. *Pure Appl. Chem.* **1993**, *64*, 323−334 and references cited therein. (b) Rousset, C. J.; Swanson, D. R.; Lamaty, F.; Negishi, E. *Tetrahedron Lett.* **1989**, *30*, 5105−5108. (c) Agnel, G.; Owczarczyk, Z.; Negishi, E. *Tetrahedron Lett.* **1992**, *33*, 1543−1546.

[17] Grossman, R. B.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 5803−5805.

[18] Jeong, N.; Hwang, S. H.; Lee, Y.; Chung, Y. K. *J. Am. Chem. Soc.* **1994**, *116*, 3159−3160.

[19] Berk, S. C.; Grossman, R. B.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 4912−4913.

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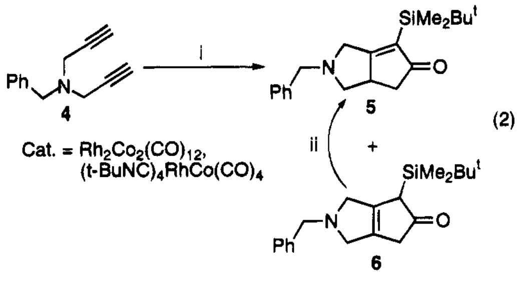
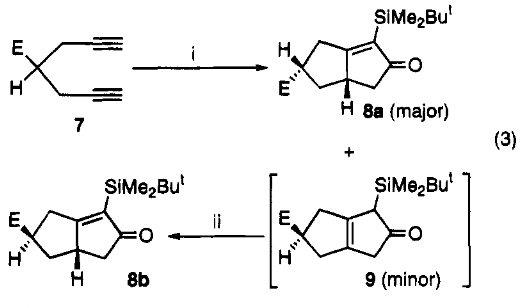
catalyzed carbonylative bicyclization of enynes bearing allylic acetate moieties has also been reported.[21] Type 3−SiCAC provides bicyclo[3.3.0]octenones from diynes (not enynes) in a truly catalytic manner. In this respect, type 3−SiCAC is a very unique carbonylative bicyclization process having a high potential as useful synthetic method, which may well complement other existing methods.

As we reported previously,[10a] the reaction of allyldipropargylamine with Et_3SiH catalyzed by $Co_2Rh_2(CO)_{12}$ under similar conditions gave unique 2-silylazabicyclo-[3.3.1]non-1-ene-3,9-dione (type 2−SiCaC product) in a good yield. Accordingly, we revisited the type 2−SiCaC reactions of dipropargylamines. When benzyldipropargylamine (**4**) and $^tBuMe_2SiH$ were used as the substrate and the hydrosilane, respectively, we found that only type 3−SiCaC proceeds to give 7-azabicyclo[3.3.0]oct-1-ene **8** (60% isolated yield) accompanied by a small amount of its $\Delta^{1,5}$-isomer **6** which is readily isomerized *in situ* to the more stable **5** quantitatively by $RhCl_3{\cdot}3H_2O$ (*vide supra*), yielding **5** as the single product in 70% isolated yield (eq 2). It appears that *N*-substituent and the bulkiness of hydrosilane play a key role on the type 2 and type 3 product selectivity. When 4-carbethoxy-1,6-heptadiyne (**7**) was employed as the substrate, interesting stereoselective transformations were observed (eq 3). The reaction of **7** with $HSiMe_2Bu^t$ under the standard conditions gave a mixture of *exo*-bicyclo[3.3.0]oct-1-ene **8a** (48% isolated yield) as single stereoisomer and its $\Delta^{1,5}$-isomer **9** (17% isolated yield). The isomerization of **9** gave the corresponding *endo*-bicyclo[3.3.0]oct-1-ene **8b** as single stereoisomer in quantitative yield, which turned out to be the other diastereomer of **8a**. The stereochemistry of **8a** and **8b** were unambiguously determined by ^1H NMR analyses on coupling constants and molecular modeling (MACROMODEL). According to MM2 calculations, **8b** is ca. 3.3 kcal/mol more stable than **8a**, which means **8a** is the kinetic product. The *endo*-isomer **8a** remained unchanged when the crude reaction mixture of **8a** and **9** was subjected to the isomerization conditions, i.e., only **9** was converted to **8b**. These results imply that there may well be conditions which give silylbicyclo[3.3.0]octen-1-one **8a** or **8b** (via **9**) in a highly selective manner. The crucial factors for the regio- and stereoselective formation of each of these products **5**−**9** warrants further investigation.

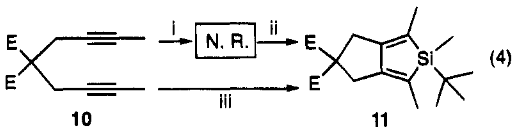


i. $^tBuMe_2SiH$, CO (50 atm), Cat., 50°C, toluene
ii. $RhCl_3.3H_2O$, 50°C, toluene-EtOH



i. $^tBuMe_2SiH$, CO (50 atm), $Rh(acac)(CO)_2$, 50°C, toluene
ii. $RhCl_3.3H_2O$, 50°C, toluene-EtOH

The reaction of diethyl bis(2-butynyl)malonate (**13**) with $^tBuMe_2SiH$ catalyzed by $Rh(acac)(CO)_2$ at 50 °C and 50 atm of carbon monoxide did not proceed at all even after 7 days. To our surprise, however, when this reaction mixture was subjected to milder conditions, i.e., at 70 °C and ambient pressure of carbon monoxide for 2 days, totally unexpected reaction took place to give 3-silabicyclo[3.3.0]octa-1,4-diene **12** in 66% isolated yield (eq 5). This novel reaction should include C−Si activation, losing a methyl substituent from $^tBuMe_2Si$ moiety. To the best of our knowledge, this type of facile C−Si activation by rhodium complexes under thermal conditions are unprecedented. This reaction proceeds at 70 °C and ambient pressure of carbon monoxide without "pretreatment" of the reaction system under 50 atm of carbon monoxide to give **11** (100% at 50% conversion).



(i) $tBuMe_2SiH$, CO (50 atm), $Rh(acac)(CO)_2$, 50°C, 7 d.
(ii) CO (1 atm), 70°C, 48 h.
(iii) $tBuMe_2SiH$, CO (1 atm), $Rh(acac)(CO)_2$, 50°C, 48h.

Further studies on the scope and limitation of the type 3−SiCaC reactions and mechanisms of these reactions as well as the novel bicyclization involving C−Si bond activation are actively underway.

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Supplementary Material Available: General experimental procedures for silylcarbobicyclizations, and the characterization data for new compounds **2**, **3**, **5**, **6**, and **9**−**11** (5 pages). This material is contained in libraries on microfiche, immediately follow this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(20) Tamao, K.; Kobayashi, K.; Ito, Y. *Syn lett* **1992**, 539−546 and references cited therein.

(21) Ihle, N. C.; Heathcock, C. H. *J. Org. Chem.* **1993**, *58*, 560−563.

(22) Matsuda, I.; Ishibashi, H.; Ii, N. *Tetrahedron Lett.*, in press.