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Silylative Cyclocarbonylation of Acetylenic Bonds Catalyzed by $Rh_4(CO)_{12}$: An Easy Access to Bicyclo[3.3.0]octenone Skeletons

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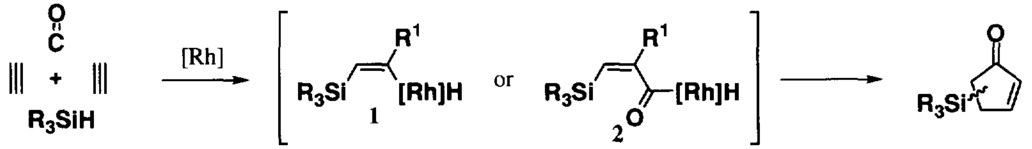
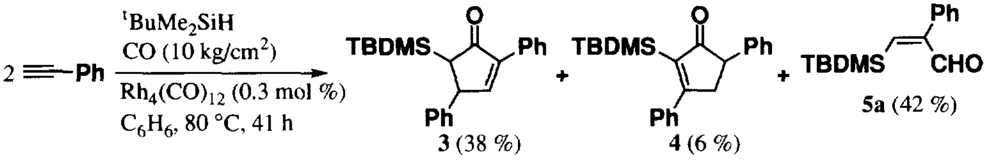
Abstract: A rhodium-catalyzed cyclopentenone annulation is found in the reaction of two moles of phenylacetylene and $^tBuMe_2SiH$ under CO pressure. This type of CO incorporation is applied to the construction of bicyclo[3.3.0]octenone frameworks from 1,6-diynes.

The simplest methodology for the construction of cyclopentenones is the transition metal-promoted coupling of three components, alkene, alkyne, and carbon monoxide, which is known as the Pauson-Khand reaction.[1] On the other hand, we reported rhodium-catalyzed "silylformylation" of acetylenic bonds[2] in which vinyl-rhodium complex **1** and alkenoyl-rhodium complex **2** are postulated as putative intermediates. If these complexes are given sufficient time to interact with further molecules of acetylenic compounds by adjusting some factors, the system for silylformylation could be diverted to a novel type cyclopentenone annulation which is conceptually drawn in Scheme 1



Scheme 1

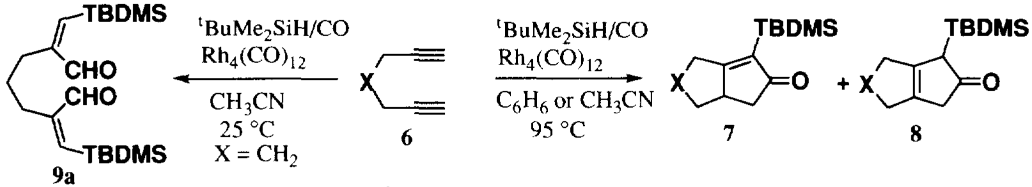
In fact, Ojima *et al.* pointed out the competitive formation of cyclopentenone derivatives in the silylformylation catalyzed by $Co_2Rh_2(CO)_{12}$.[2e] However, during scrutiny of the silylformylation catalyzed by $Rh_4(CO)_{12}$ we have become aware that a different type of coupling pattern serves to form cyclopentenones. We report here a novel type of rhodium-catalyzed cyclopentenone annulation and its extension to the intramolecular reaction which provides a catalytic route to form bicyclo[3.3.0]octenone skeletons from 1,6-diynes.



(1)

Two types of cyclopentenones **3**[4] (38 %) and **4**[4] (6 %) were isolated with the concomitant formation of **5a**[4] (42 %) and a trace amount of unidentified products in the reaction of two equivalents of phenylacetylene with (1,1-dimethylethyl)dimethylsilane (^{t}BuMe$_2$SiH) under CO pressure (10 kg/cm^2) in the presence of 0.2 mol % of Rh$_4$(CO)$_{12}$ (eq 1). However, silylformylation as a competitive path could not be suppressed to an acceptable level in an intermolecular reaction. We turned to the intramolecular version of this type cyclocarbonylation.

Thus, the reaction of 1,6-heptadiyne (**6a**, 3.58 mmol) with ^{t}BuMe$_2$SiH (3.42 mmol) catalyzed by Rh$_4$(CO)$_{12}$ (0.0091 mmol, 0.26 mol %) was carried out in C$_6$H$_6$ (10 mL) at 95 °C for 15 h under CO pressure (20 kg/cm^2). Chromatographic purification of the reaction mixture gave bicyclo[3.3.0]octenone **7a** as the predominant product (54 %) accompanied by another type of bicyclooctenone **8a** (14 %). Despite considerable reduction in the reaction time (15 h) these products were obtained in almost comparable yields (**7a**; 49 % and **8a**; 13 %). On the other hand, the presence of an excess mole of ^{t}BuMe$_2$SiH slightly improved the yield of **7a**, although stoichiometry of this reaction does not require the presence of an excess silane for the construction of **7a** and **8a**. It is notable that silylformylation products of **6a** were suppressed to an acceptable level (below 5 %) under these conditions. Overall profile of this reaction did not change under CO pressure in the range of 3 — 45 kg/cm^2, whereas the rate of this cyclocarbonylation was appreciably retarded under low CO pressure.



Scheme 2

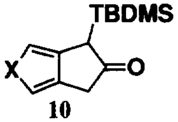
When acetonitrile was used as a solvent, the yield of **8a** decreased to a negligible level with the complementary increase of unidentified materials at 95 °C. Reaction temperature was another important factor in affecting the distribution of products. Dial **9a**[4] was isolated in 59 % yield accompanied with the concomitant formation of **7a** (20 %) in the reaction of **6a** at 25 °C (in CH$_3$CN, mole ratio of ^{t}BuMe$_2$SiH:**6a** = 2:1, 80 h).

Thus, the scope of this catalytic cyclocarbonylation was examined with various substrates and the results are summarized in Table 1. All types of 1,6-diyne listed there reacted uniformly to give cyclocarbonylation products in moderate to good yields, although product distribution depended on the substrate used. The most obvious point is that thermodynamically less stable **8b** was formed as a major product in the reaction of **6b** under similar conditions. The electronic character of the substituents on the nitrogen atom seemed to have remarkable influence on the products as observed in the reactions of **6c** and **6d**. Especially, the fact that **10d** is formed from **6d** as a major product is quite interesting in comparison with the result of N-(2-propenyl)-N,N-bis(2-propynyl)amine reported by Ojima's group.[3] A fourth bicyclic product **11e** was also isolated with the concomitant formation of **7e** and **8e** in the reaction of **6e**. The formation of **11e** suggests that an intermediate allowing the process of silatropy should be involved in the catalytic cycle. 2,8-Decadiyne (**6f**) was also carbonylated to give **8f** though the operation under relatively low pressure of CO (5 kg/cm^2) was required in order to reduce the concomitant formation of silylformylation products like **9a**.

Table 1 Silylative cyclocarbonylation of **6** catalyzed by $Rh_4(CO)_{12}$.[a]

Entry	Diyne **6**		Solvent	Products [4]			
		X		7	**8**	**10**	**11**
1	**a**	CH_2	C_6H_6	63	14	0	0
2			CH_3CN	60	0	0	0
3	**b**	$C(CO_2Me)_2$	C_6H_6	6	58	0	0
4			CH_3CN	14	70	0	0
5	**c**	N-*p*Ts	C_6H_6	51	18	5	0
6	**d**	NCH_2Ph	C_6H_6	9	0	31	0
7			CH_3CN	8	0	72	0
8	**e**	O	C_6H_6	3	0	0	6
9			CH_3CN	35	2	0	2
10	**f**	$-CH_2CH_2-$ (2,8-decadiyne)	C_6H_6	0	43	0	0

[a] Reactions were conducted in the prescribed solvent (12 mL) containing 0.5 mol % of $Rh_4(CO)_{12}$, 3 moles of **6**, and 6 mmoles of $^tBuMe_2SiH$ under CO pressure (20 kg/cm^2) for 15 h at 95 °C.



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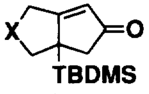

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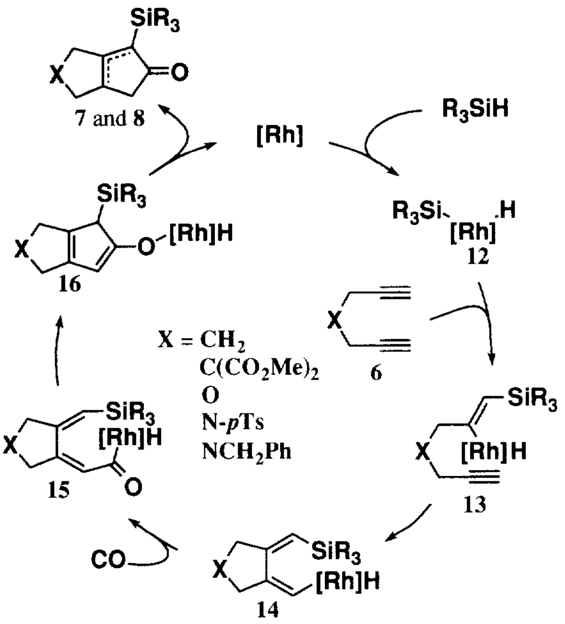
Scheme 3



These results clearly indicate that cyclopentenone frameworks are formed uniformly in accordance with the common coupling manner regardless of whether the cyclocarbonylations are intermolecular or intramolecular. The structures of **3** and **4** suggest that intermediate **1** should interacts with the second molecule of alkyne prior to the insertion of CO into the Rh — C bond of **1**. From the same viewpoint, we can propose a plausible rationale for the intramolecular cyclocarbonylation of **6** as shown in Scheme 3. Vinyl rhodium complex **13** is formed by the insertion of **6** into the Rh — Si bond of **12** and it readily leads to **14** through consecutive carbocyclization.[5] Doubly cyclized **16** is derived from **15** which is formed by the insertion of CO into the Rh — C bond of **14**. Complex **16** could lead to **7** or **11** as a result of a process of either prototropy or silatropy just before reductive elimination. On the other hand, **8** is derived from **16** through reductive elimination.

Although Pauson-Khand type cyclocarbonylation[1e–1l] and early transition-metal mediated protocols[6] are well-known as the accessible route to **7** and congeners from 1,6-enynes, catalytic incorporation of CO is attained in very few examples.[1l, 7] Therefore, our new catalytic approach for silylative cyclocarbonylation of **6** provides an expeditious route to construct bicyclo[3.3.0]octenone or bicyclo[4.3.0]nonenone frameworks from acyclic starting materials. Especially it should be noted that cyclic compounds **8b** and **10d** are readily obtained as a major product by this one-pot operation though the control factor for selective formation is not revealed at present. It is quite interesting that switching the catalyst from Rh to Ru changes the product to catechol derivatives in the identical reaction system containing 1,6-diynes, ^{t}BuMe$_2$SiH, and CO.[8]

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4. These compounds were fully characterized from the IR, ^{1}H, and ^{13}C NMR spectra and showed satisfied combustion analyses except **8a**. Data of **3** and **7a** are described as typical examples; **3**: pale yellow viscous oil, bp 190 °C/0.3 Torr; IR (CCl_4) 1693 (C=O), 1600 (C=C), 1253 (Si-C) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 0.13 (s, 3H, $SiCH_3$), 0.15 (s, 3H, $SiCH_3$), 0.94 (s, 9H, *ter*Bu), 2.57 (d, J = 1.1 Hz, 1H, 5-CH), 4.14 (dd, J = 3.2 and 1.1 Hz, 1H, 4-CH), 7.17 – 7.42 (m, 8H, Ph), 7.64 (d, J = 3.2 Hz, 1H, 3-CH), 7.73 – 7.76 (m, 2H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) –6.81 ($SiCH_3$), –6.75 ($SiCH_3$), 17.86 (quart. C in *ter*Bu), 26.87 (CH_3 in *ter*Bu), 47.96 (4-C), 50.83 (5-C), 127.20 (Ph), 127.46 (Ph, includes *o* and *m*), 128.55 (Ph),128.78 (Ph), 129.10 (Ph), 131.74 (Ph ipso), 142.04 (Ph ipso or 2-C), 142.85 (2-C or Ph ipso), 158.53 (3-C), 208.84 (1-C). **7a**: colorless oil, bp 100 °C/0.4 Torr; IR (CCl_4) 1697 (C=O), 1602 (C=C), and 1248 (Si–C) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 0.18 (s, 3H, $SiCH_3$), 0.20 (s, 3H, $SiCH_3$), 0.86 (s, 9H, *ter*Bu), 1.09 (dddd, J = 12.2, 12.2, 12.2, and 7.8 Hz, 1H, 6-CH), 1.90 – 2.01 (m, 1H, 7-CH), 2.04 (dd., J = 17.3 and 4.2 Hz, 1H, 4-CH), 2.03 – 2.09 (m, 1H, 7-H), 2.16 (ddd, J = 12.2, 6.6, and 6.6 Hz, 1H, 6-CH), 2.52 – 2.59 (m, 1H, 8-CH), 2.58 (dd J = 17.3 and 6.6 Hz, 1H, 4-CH), 2.65 (ddd, J = 19.0, 10.5, and 2.7 Hz, 1H, 8-CH), 2.82 (b. sextet, J = 6.3 Hz, 1H, 5-H); ^{13}C NMR (50 MHz, $CDCl_3$) –5.78 ($SiCH_3$), –5.60 ($SiCH_3$), 17.48 (quart. C in *ter*Bu), 25.50 (7-C), 26.49 (CH_3 in *ter*Bu), 27.92 (8-C), 31.00 (6-C), 43.23 (4-C), 48.47 (5-C), 133.54 (2-C), 200.93 (1-C), 215.09 (3-C).
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