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# Silicon electronic effect in the Pauson–Khand reaction of alkynylsilanes with allenes

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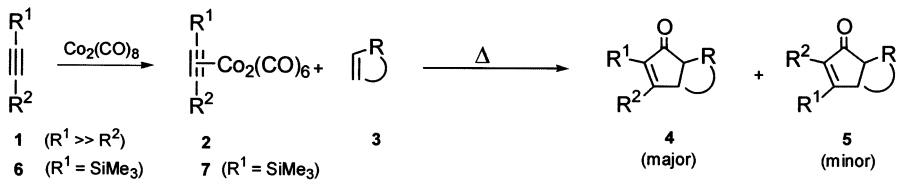
**Abstract**—The β-effect of silicon was shown to be a determining factor for the regioselectivity of the Pauson–Khand reaction of alkynylsilanes with allenes. This electronic effect accounts for the formation of 3-trimethylsilyl-4-alkylidenecyclopentenones observed from monosubstituted allenes. 

The Pauson–Khand reaction (PKR), a formal [2+2+1] cycloaddition of an alkyne, an alkene, and carbon monoxide, is a powerful methodology for the construction of cyclopentenones.[1] An attractive point of its intermolecular version is the high regioselectivity for the incorporation of the two unsaturated partners **1** and **3**, so that their more bulky substituents $R^1$ ($\gg R^2$) and R are, respectively, located in the α- and α′-positions of the keto group of the cyclopentenone **4**, which is formed as the major product (Scheme 1).[2] Particularly, a complete regioselectivity of addition to the α-silylated cyclopentenone **4** ($R^1 = SiMe_3$) was observed when silylated alkynes **6** were used.[3]

Recently, we demonstrated that allenes are suitable unsaturated compounds for the intermolecular PKR, which then allows the preparation of the rather poorly known 4-alkylidenecyclopent-2-enones **9** (Scheme 2).[4–6] In the course of our research programme on this new carbonylative acetylene/allene cocyclisation, we studied the reactivity of alkynylsilanes **6**.[7] Here we report the results of our study and particularly the different regioselectivities observed with the silylated cyclopentenones **12**–**14**.

The reaction of the trimethylsilylacetylene–dicobalt complex **7a** with 1,2-nonadiene **8a** (1.5 equiv.) in the presence of *N*-methylmorpholine oxide (NMO, 6 equiv.) was totally regioselective with respect to the alkynylsilanes **6a**, since the isomeric cyclopentenones **12a** and **13a** having this group in the α-position were the only cyclopentenones isolated (Table 1, entries 1 and 2). The ratio of these ketones was not modified by a change of solvent (conditions A or B), but yields highly increased by adding THF as a cosolvent (conditions B), as previously reported.[5]

The reactions of the alkynylsilane–dicobalt complexes **7b** and **7c** with allene **8a** were less regioselective. Indeed, we observed a large amount of the cyclopentenones **14b** and **14c** with the $SiMe_3$ group in the β-position of the keto group (entries 3 and 4). The regioselectivity with respect to the allenic hydrocarbon (ratio **12**+**14**/**13** = 95–




**Scheme 1.**

*Keywords*: Pauson–Khand reaction; allene; alkynylsilane; cobalt; electronic effect.
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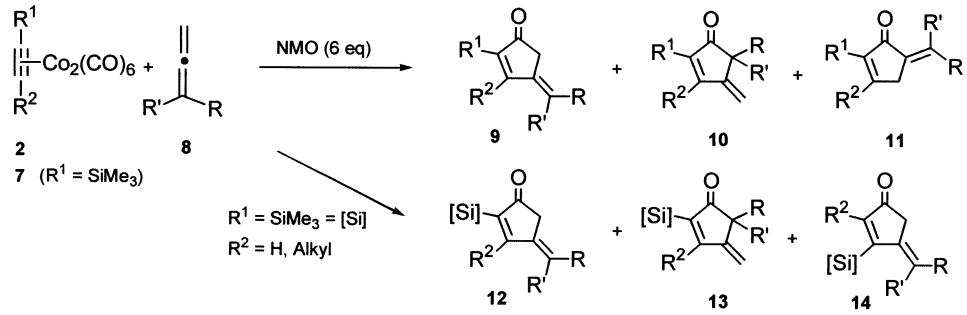
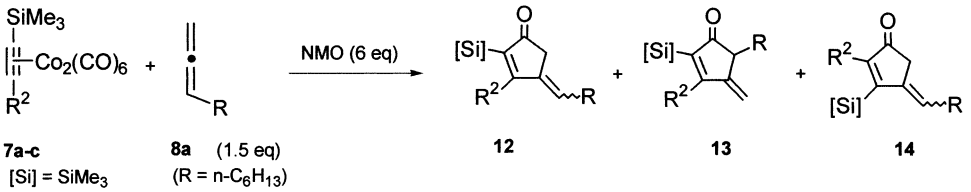



**Scheme 2.**

**Table 1.** Cycloaddition [2+2+1] of alkynylsilane–dicobalt complexes **7a–c** with allene **8a**



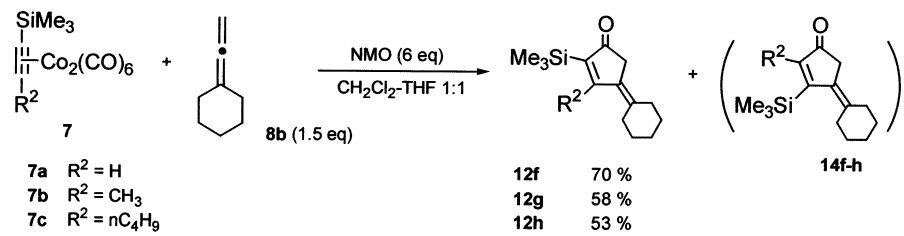

| Entry | Dicobalt complex **7a–c** | | Conditions[a] | Yield (%)[b] | **12–14a–e** Regioisomers ratio[c] | | |
|---|---|---|---|---|---|---|---|
| | | | | | **12** (*E*/*Z*)[c] | **13** | **14** (*E*/*Z*)[c] |
| 1 | **7a** | $R^2$=H | A | 31 | 94 (70/30) | 6 | – |
| 2 | | | B | 58 | 95 (75/25) | 5 | – |
| 3 | **7b** | $R^2$=Me | B | 53 | 73 (83/17) | 7 | 20 (100/0) |
| 4 | **7c** | $R^2$=*n*-Bu | B | 38 | 45 (100/0) | 10 | 45 (88/12) |
| 5 | **7d** | $R^2$=*t*-Bu | B | No reaction | | | |
| 6 | **7e** | $R^2$=$SiMe_3$ | B | 22 | 100 (82/18) | – | – |

[a] Conditions A: $CH_2Cl_2$/0–20°C (14 h). Conditions B: $CH_2Cl_2$–THF (1:1)/−78 to 20°C (4 h).
[b] Total yield of purified products **12–14** after flash-chromatography.
[c] Ratio of regioisomers **12–14** and of stereoisomers **12** and **14** (*E*/*Z*) determined by GLC analysis before purification.

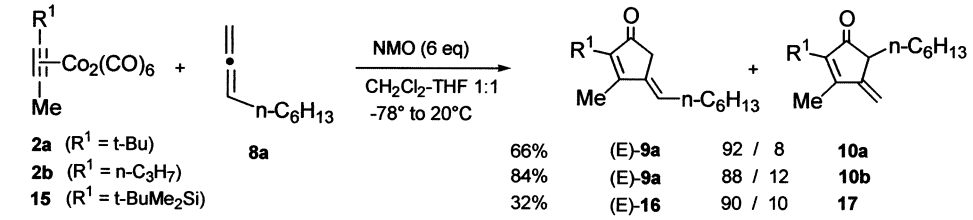
90/5–10) was consistent with the one observed for cycloadditions with unsilylated alkynes[5] (entries 1–4). No reaction was observed with trimethylsilyl-*t*-butylacetylene **6d** (entry 5), while bis(trimethylsilyl)acetylene **1f** (entry 6) gave cyclopentenone **12f**, but with a low yield (22%).

The reactions of dicobalt complexes **7a–c** with vinylidenecyclohexane **8b** gave cyclopentenones **12f–h** as sole products (Scheme 3). In each case cyclopentenones **14f–h** with the $SiMe_3$ group in β-position could not be isolated, which demonstrates that geminal substituents on the allenic hydrocarbon inhibit the formation of these last isomeric ketones **14**.

The PKR is described as being very sensitive to steric effects, including in the case of allenic compounds.[5] However, when electronic effects from substituents on either the acetylenic[8] or olefinic[9,10] component are involved, its regioselectivity has been rationalized as the result of a combination of both steric and electronic factors. Particularly, the effect of an electron withdrawing group in the alkyne moiety has recently been clearly explained.[11] However, to the best of our knowledge, the effect of silicon as a substituent has not been encountered and the unexpected large amount of the β-trimethylsilylcyclopentenones **14b** and **14c** obtained from alkynylsilane–dicobalt complexes **7b**,**c** (Table 1, entries 3 and 4) required more explanations. The com-




**Scheme 3.**




**Scheme 4.**

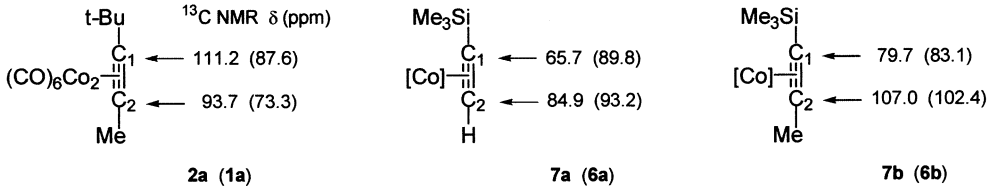



**Figure 1.** Comparison of the chemical shifts of acetylenic carbons $C_1$ and $C_2$ of free (in parentheses) and coordinated alkyne **1a** (this work) and alkynylsilanes **6a**,**b** (Ref. 13).

parison of these last cycloadditions with the reactions of disubstituted unsilylated alkyne–dicobalt complexes **2a**,**b** (Scheme 4) seemed relevant to the effect of the silicon atom. Thus, complexes **2a** and **2b** gave only the cyclopentenones **9** and **10** with the larger alkyl groups $R^1 = t$-Butyl or Pr in the α-position of the keto group.

This comparison emphasizes the prominent role of the silicon atom in the PKR of alkynylsilanes with allenes. Its hyperconjugative effect (β-effect), which is known to stabilize positive charges in the β-position,[12] may account for the observed regioselectivities. Indeed, this β-effect is responsible for the reversed polarization (compared to the unsilylated alkynes **1**) of the acetylenic bond of alkynylsilanes **6** in the free state and even more when coordinated to the $Co_2(CO)_6$ core.[13] Thus, the electronic densities on the acetylenic carbons $C_1$ (shielded) within complexes **7a**–**c** are much larger than those on $C_2$ (unshielded), as evaluated by their respective chemical shifts in $^{13}C$ NMR (Fig. 1).

The high electron density on the silicon-substituted $C_1$ carbon of complexes **7a**–**c**, together with the low one of the central carbon of the allenic hydrocarbons, explains the large amount of β-trimethylsilylcyclopentenones **14b**,**c** formed. This resulted in a favoured binding of these two carbons during the insertion of the allenic component into the C–Co bond of the alkyne–Co complex **7**. However, large steric interactions superceded this silicon electronic effect, as shown by the reaction of *t*-butyldimethylsilylpropyne–dicobalt complex **15** with allene **8a**, which gave only the α-trialkylsilylcyclopentenones **16** and **17** (Scheme 4). Steric interactions were also leading factors when trimethylsilylacetylene **2a** or *gem*-disubstituted allenes such as **8b** were used.

In summary, we have demonstrated the importance of the electronic effect of silicon in the PKR of alkynylsilanes with allenes. This allows a satisfactory rationalization of the observed regioselectivities.

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