

Preliminary Communication

Silylcarbonylation of 1,5-dienes accompanied by acyl radical cyclization

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Abstract

2-(Silylmethyl)cyclopentanones are prepared from 1,5-dienes, carbon monoxide, and tris(trimethylsilyl)silane (TTMSS) under AIBN initiated free radical reaction conditions. © 1997 Elsevier Science S.A.

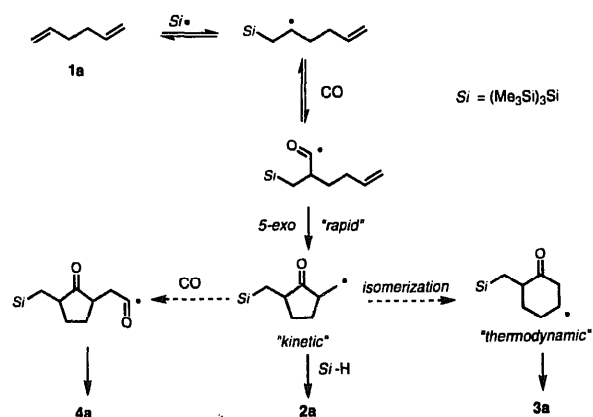
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The area of transition metal catalyzed carbonylations has recently evolved to include the silylcarbonylation of organic molecules, such as alkynes, aldehydes, etc. with hydrosilanes and CO [1–7]. Particularly impressive are recent examples which illustrate the effectiveness of the strategy for the synthesis of cyclic carbonyl compounds such as silyl-attached bicyclo[3.3.0]octenones starting from 1,6-diynes [8,9]. We were interested in determining whether this new field of silylcarbonylation chemistry could be expanded to include free radical mediated processes. In this communication, we report the first example of silylcarbonylation of 1,5-dienes which leads to 2-(silylmethyl)cyclopentanones by a 5-exo mode of acyl radical cyclization.

We envisioned that the use of TTMSS (tris(trimethylsilyl)silane) [10–12] as a hydrosilane would be most successful for silylcarbonylations under free radical reaction conditions (Scheme 1). The addition of a silyl radical to the terminus of a 1,5-diene would produce a β -silylalkyl radical which would then add to CO to give an acyl radical. Both of the steps are reversible. However, cyclization of the resulting acyl radical is expected to be rapid enough to lead to a 3-oxocyclopentylmethyl radical [13–15]. Subsequent hydrogen abstraction from TTMSS produces the desired silylcyclopentanone and regenerates the silicon radical. Preliminary experiments showed that the related stannylcarbonylation of 1,5-hexadiene was unsuccessful

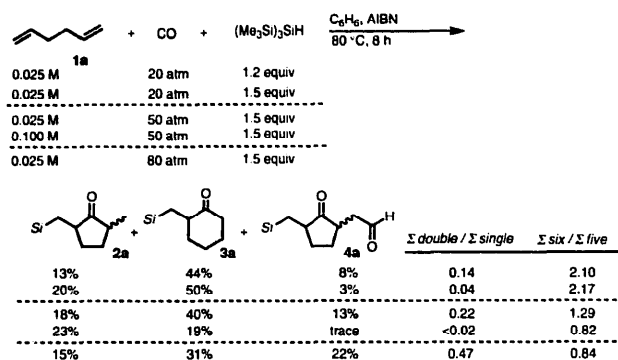
presumably owing an unfavorable equilibrium for the addition of a tin radical to an unactivated alkene such as **1a** [16,17]. However, it was our belief that tris(trimethylsilyl)silane (TTMSS) would resolve this problem, since the β -silylalkyl radical [18] would be much more stable towards the regeneration of starting material with loss of silyl radical than the related β -stannylalkyl radical.

When the reaction of 1,5-hexadiene (**1a**) with TTMSS was carried out under CO pressure of 20 atm ([diene] = 0.025 M, TTMSS (1.5 eq.), AIBN (0.3 eq.), 80°C, 8 h), it was found that the reaction gave a mixture of three types of carbonylated products, 2-(silylmethyl)cyclopentanone **2a** (20%), 2-(silylmethyl)cyclohexanone **3a** (50%), and **4a** (3%) which had incorporated two molecules of CO (Scheme 2). Uncarbonylated products



Scheme 1. The basic concept: silylcarbonylation of 1,5-hexadiene.

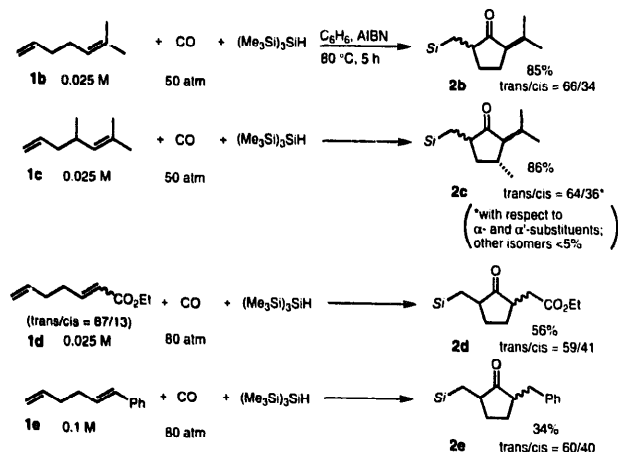
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Scheme 2. Silylcarbonylation of 1,5-hexadiene.

derived from simple hydrosilylation of 1,5-diene constituted the main byproducts of this reaction. The reaction pathways that led to these three carbonylated products are shown in Scheme 1. The six-membered ring product **3a**, which may result from isomerization of the initially formed five-membered ring radical, was the major product except when the reaction was conducted at high concentration. Such enhancement of isomerization process is commonly observed when a slow radical mediator is employed [19]. As expected, reaction under higher CO pressure (80 atm) gave more 4-oxo aldehyde **4a** (22%) [20,21]. Although we were pleased that the envisaged silylcarbonylation had occurred, the difficulty in controlling the product selectivity in the 1,5-hexadiene system led us to consider substituted 1,5-hexadienes.

Thus, in order to obtain 2-(silylmethyl)cyclopentanones as the sole silylcarbonylation product, the introduction of appropriate substituents at one diene terminus appeared essential. In this way, the kinetically favored cyclized radical would also be a thermodynamically favored radical. Remarkably, the introduction of two methyl substituents led to the exclusive formation of cyclopentanones in high yields (Scheme 3). Dienes substituted with an ethoxycarbonyl or a phenyl group at



Scheme 3. Synthesis of cyclopentanones by silylcarbonylation of 1,5-dienes.

the terminus also gave the desired cyclopentanones **2d** and **2e** as the only cyclic ketones without the formation of the six-membered ring isomer or the double carbonylation product. The modest yields observed for these two cases are due mainly to competitive hydrosilylation reaction at the carbonyl group and styryl C=C bond, respectively. It should be also noted that in the case of **1e** chain propagation was not smooth at a substrate concentration of 0.025 M and therefore we used 0.1 M for this case. The formation of two isomeric aldehydes (8%) whose structure has yet to be determined were byproducts of this reaction.

A typical procedure for the synthesis of **2b** is as follows. 6-Methyl-1,5-heptadiene (**1b**, 105 mg, 0.95 mmol), TTMSS (385 mg, 1.55 mmol), AIBN (51 mg, 0.31 mmol), and benzene (50 ml) were placed in a 100 ml stainless steel autoclave lined with a glass liner. The mixture was stirred under carbon monoxide pressure (50 atm) at 80°C for 5 h. After the residual CO was vented, the mixture was evaporated. The resultant residue was chromatographed on silica gel (C₆H₁₄/Et₂O = 10/1 as an eluent) to afford **2b** (329 mg, 85% yield) as a 34:66 mixture of *cis* and *trans* isomers.

In summary, we have demonstrated that silylcarbonylation of 1,5-dienes leading to α-(silylmethyl) substituted cyclopentanones can be achieved by using TTMSS mediated free radical carbonylation conditions. We are currently examining the scope and limitation as well as synthetic utility of the product silyl cyclopentanones.

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