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NOVEL [σ+π] CYCLOADDITION OF SILACYCLOBUTANES WITH ACETYLENES CATALYZED BY PALLADIUM COMPLEXES[1)]

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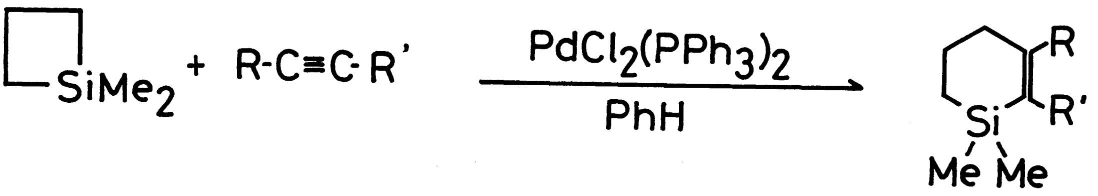
In the presence of a palladium complex, 1,1-dimethyl-1-silacyclobutane reacts smoothly with dimethyl acetylenedicarboxylate to give 1,1-dimethyl-2,3-bis(methoxycarbonyl)-1-silacyclohex-2-ene in quantitative yield. Other silacyclobutanes react similarly with various acetylenes to give silacyclohexene derivatives.

Being encouraged by the recent observations in this laboratory that the silicon-silicon bond in organodisilanes undergoes various cycloaddition reactions with acetylenes[2)] and dienes[3)] in the presence of palladium complexes, we have explored the possible cycloaddition reactions of the carbon-silicon bond with unsaturated compounds. We report here the first example of such [σ+π] cycloaddition involving the carbon-silicon bond.

1,1-Dimethyl-1-silacyclobutane (**1**) is known to undergo various insertion reactions leading to ring-expanded products with SO_2,[4)] SO_3,[4,5)] S_8,[6)] Se_8,[6)] carbenes,[7-9)] and phosphorus ylids.[10)] Recently, Cundy and Lappert[11)] have reported that the $[Fe(CO)_4]$ unit is inserted into an Si-C bond of **1** to give $(CO)_4\overline{Fe(CH_2)_3SiMe_2}$ in the reaction with nonacarbonyldiiron. Transition metal-catalyzed polymerization of **1** is also known,[12)] but there has been no report on the catalyzed cycloaddition of **1** with unsaturated compounds.

In the presence of bis(triphenylphosphine)palladium dichloride (0.04 mmol), **1** (4 mmol) reacted smoothly with dimethyl acetylenedicarboxylate (**2a**, 4 mmol) in benzene (10 ml) at reflux for 2hr to give 1,1-dimethyl-2,3-bis(methoxycarbonyl)-1-silacyclohex-2-ene (**3a**) in almost quantitative yield (over 95%).[13,14)]



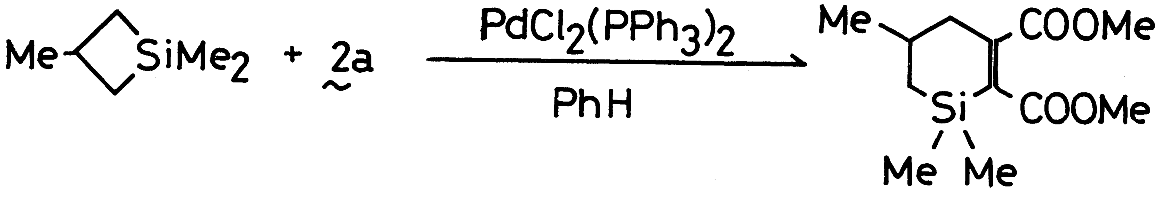
1

2a, R = R' = COOMe
b, R = COOMe; R' = H
c, R = Ph; R' = H
d, R = R' = H

3a, R = R' = COOMe
b, R = COOMe; R' = H
c, R = Ph; R' = H
d, R = R' = H

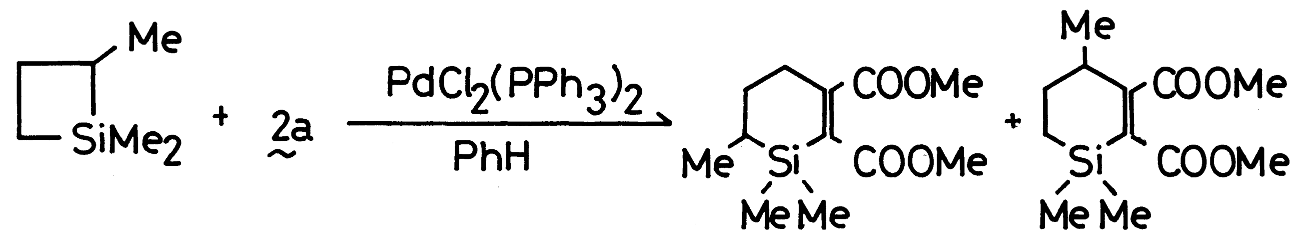
The reaction of 1 with methyl propiolate (2b) and phenylacetylene (2c) under similar conditions gave the corresponding silacyclohexenes 3b (35% yield)[15] and 3c (17% yield),[16] respectively. Regiospecificity in the reaction should be noted in these examples, since only single isomers were obtained for both acetylenes. Unsubstituted acetylene (2d) also reacted with 1, when 2d was bubbled into refluxing benzene solution of 1 in the presence of the catalyst. 1,1-Dimethyl-1-silacyclohex-2-ene (3d)[17] was obtained in 45% yield.

1,1,3-Trimethyl-1-silacyclobutane (4) reacted similarly with 2a to give 5 in 65% yield,[18] and 1,1,2-trimethyl-1-silacyclobutane (6) gave, as expected, a 7:3 mixture of 7 and 8 in 61% yield in the reaction with 2a.[19,20]



4

5



6 7 8

Palladium complexes such as $PdCl_2(PhCN)_2$, $Pd(PPh_3)_4$, $Pd(PPh_3)_2$(olefin) and Pd-charcoal are more or less effective as a catalyst in the reaction, but Co, Ni, Rh, Ir, and Pt complexes did not catalyze the reaction.

The reaction is formally a $[_\sigma 2+_\pi 2]$ reaction which is thermally "forbidden" according to the Woodward-Hoffmann classification of concerted reactions but may become "allowed" when a transition-metal catalyst is involved. However, the driving force of this reaction is apparently the ring strain of silacyclobutanes, since silacyclopentanes and other compounds with "strain-free" carbon-silicon bonds did not react with acetylenes.

Acknowledgment

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References and Notes

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13) All new compounds gave correct elemental analyses.
14) Compound **3a**: an oil n_D^{20} 1.4861; M^+ 242(2.6), m/e 199(100); ir(cm^{-1})(neat) 1722, 1443, 1239, 1149, 1120; NMR δ (CCl_4) 0.27$_5$(6H, s), 0.49(2H, m), 1.90(2H, m), 2.47(2H, t), 3.72(3H, s), 3.73$_5$(3H, s).
15) Compound **3b**: an oil n_D^{19} 1.4605; M^+ 184(1.1), m/e 143(100); ir(cm^{-1})(neat) 1733, 1433, 1220, 1169, 1021; NMR δ (CCl_4) 0.22(6H, s), 0.8-1.9(6H, m), 3.74(3H, s), 6.30(1H, s).
16) Compound **3c**: an oil n_D^{20} 1.5397; M^+ 202(13.1), m/e 161(100); ir(cm^{-1})(neat) 1627, 1492, 1248, 1152; NMR δ (CCl_4) 0.26$_5$(6H, s), 0.08-0.45(2H, m), 1.36-2.12(4H, m), 6.51(1H, s), 7.45(5H, m).
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18) Compound **5**: an oil n_D^{20} 1.4840; M^+ 256(1.8), m/e 199(100); ir(cm^{-1})(neat) 2920, 1725, 1245, 1225, 827, 795; NMR δ (CCl_4) 0.25(3H, s), 0.27(3H, s), 0.76(2H, m), 1.16(3H, d, J=6Hz), 1.96(1H, m), 2.37(2H, m), 3.71(3H, s), 3.73(3H, s).
19) Compound **7**: an oil n_D^{20} 1.4866; M^+ 256(1.6), m/e 199(100); ir(cm^{-1})(neat) 2950, 1734, 1439, 1250, 1225, 1150, 1032; NMR δ (CCl_4) 0.19(3H, s), 0.23(3H, s), 0.87 (1H, m), 1.09(3H, d, J=6.7Hz), 1.80(2H, m), 2.49(2H, m), 3.70(3H, s), 3.72(3H, s).
20) Compound **8**: an oil n_D^{20} 1.4853; M^+ 256(1.7), m/e 89(100) ir(cm^{-1})(neat)2950, 1731, 1438, 1250, 1230, 826; NMR δ (CCl_4) 0.21(3H, s), 0.31(3H, s), 0.80(2H, m), 1.15 (3H, d, J=6.7Hz), 1.86(2H, m), 2.78(1H, m), 3.70(3H, s), 3.72(3H, s).

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