[4 + 1] Cycloadditions of the Rhodium Di(methoxycarbonyl) Carbenoid to 2-Siloxy-1,3-dienes

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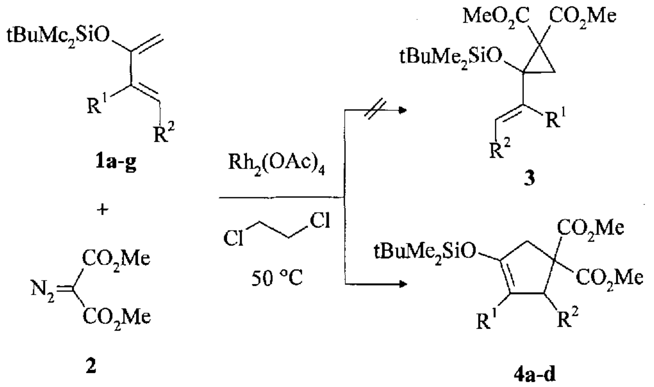
The rhodium(II) acetate catalyzed reaction of dimethyl diazomalonate with 2-siloxy-1,3-dienes **1a–1d** and **1h** furnished cyclopentene derivatives **4a–4d** and **4h** in moderate yields. The mechanism of this unusual [4+1] cycloaddition is discussed.

For our ongoing studies of intramolecular Diels-Alder reactions[1,2] we required 2-siloxycyclopropanedicarboxylates of type **3** which incorporate a masked enone moiety. The metal-catalyzed cyclopropanation of 2-siloxy-1,3-dienes with dimethyl diazomalonate (**2**) was considered as the most suitable route to these target compounds[3]. However, in this paper we report that this reaction directly leads to the five-membered ring isomers of **3**, the cyclopentene derivatives **4**.

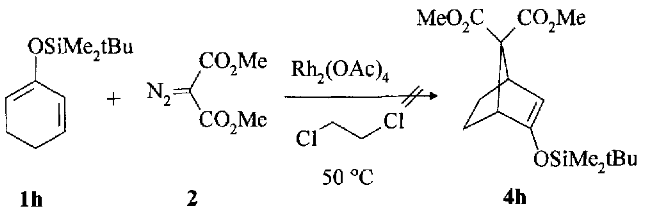


	R^1	R^2	Yield
a	H	Me	35%
b	-CH_2-$(CH_2)_2$-CH_2-		35%
c	H	Ph	43%
d	H	OMe	31%[a]
e	H	H	-
f	Me	H	-
g	H	CO_2Me	-

[a] Reaction at room temperature.

When a slight excess of dimethyl diazomalonate (**2**) was slowly added to a solution of 2-*tert*-butyldimethylsiloxy-(*E*)-1,3-pentadiene (**1a**) and $Rh_2(OAc)_4$ in 1,2-dichloroethane via a syringe pump at 50 °C, crude cyclopentene derivative **4a** was isolated after usual workup. There was no indication that vinylcyclopropane derivative **3a** had been formed as this should show significantly different NMR data. After kugelrohr distillation analytically pure **4a** was obtained in 35% yield. We tried to increase this rather moderate yield by employing rhodium(II) trifluoroacetate[4] as catalyst in *n*-hexane as solvent, the use of which was expected to furnish a more electron-deficient and hopefully more reactive rhodium carbenoid from **2**. However, the yield of **4a** dropped to 16%. With $Cu(acac)_2$ or $Cu(OTf)_2$ as catalysts for this reaction we obtained no definitive products.

The standard conditions with $Rh_2(OAc)_4$ as catalyst were therefore applied to 2-siloxy-1,3-dienes **1b**, **1c**, and **1d** with similar success furnishing siloxycyclopentene derivatives **4b**, **4c**, and **4d** in 31–43% yield. Surprisingly, the reaction of the electronically rather related 1,3-dienes **1e** and **1f** with **2** did not provide the expected products. Only intractable complex mixtures were isolated. The reaction with methoxycarbonyl-substituted diene **1g** also failed to afford **4g**. Here the crude product may have contained traces of the vinylcyclopropane derivative **3g**. However, we were not able to isolate or purify this minor component in the mixture. Finally, we also attempted to synthesize norbornene derivative **4h** by starting with 2-siloxycyclohexa-1,3-diene (**1h**). Again, only a complex product mixture was obtained.



Although the scope of the reaction seems to be rather limited and the yields are so far at best moderate (though not optimized), two aspects of this formal [4 + 1] cycloaddition are remarkable. First, this method allows a direct and relatively simple entry to functionalized cyclopentene derivatives[5]. Bicyclic compounds such as **4b** may be of particular importance. Second, the infrequency of [4 + 1] cycloadditions with carbene/carbenoid participation[6]

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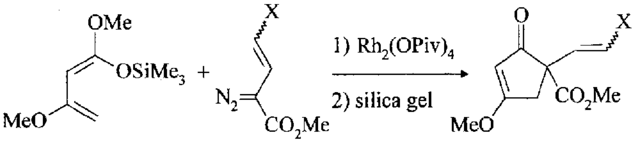
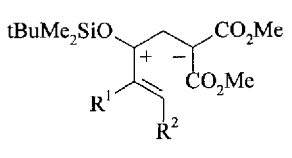
raises the question about the reaction mechanism. To the best of our knowledge only two related examples have recently been described in the literature[7]. The reaction of diene **5** with diazo compounds of type **6** furnishes cyclopentenones **7** after treatment with silica gel or acid.



5 **6** (X = OMe, SPh) **7**

The formation of cyclopentene derivatives **4** (and of **7**) can proceed via the expected vinylcyclopropanes. The formally forbidden 1,3-sigmatropic rearrangement may involve 1,3-zwitterions[8] such as **8**, which are reasonably stabilized, and it may be catalyzed by the rhodium complex present[9]. However, this mechanistic pathway does not explain why no definite compounds could be isolated in the case of the dienes **1e**, **1f**, and **1h**. The reactions of all these dienes with methyl diazoacetate gave well defined cyclopropane derivatives[10].



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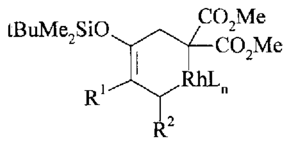

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Hence, a mechanistic alternative has to be considered. The dienes may react in a Diels-Alder-type reaction with the rhodium carbenoid to give (either in a concerted or stepwise manner) a rhodacyclohexene intermediate **9** which undergoes reductive elimination and provides the cyclopentene derivatives[11]. The [4 + 2] step fails with **1e**–**1g** because these dienes are not sufficiently electron-rich, and it does not occur with **1h** since the primary adduct would be rather strained. These mechanistic speculations certainly require further experimental support. However, they may serve as working hypothesis for future efforts in this area.

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Experimental

All reactions were performed under an argon atmosphere in a flame-dried reaction flask, and the components were added via a syringe. All solvents were dried by standard methods. – Chromatography: silica gel 60 (0.063–0.200 mm, E. Merck) and neutral alumina (6% H_2O, activity III, Macherey-Nagel). – A Büchi kugelrohr apparatus was used for distillation of small amounts of substances. – ^1H (^{13}C)-NMR spectra: Bruker AC 200, 200 (50.3) MHz, internal standards chloroform (δ = 7.26 and 77.0) or tetramethylsilane (δ = 0.00). – IR spectra: Nicolet 205.

Starting materials: **1a**[12], **1b**[13], **1c**[14], **1d**[15], **2**[16]. $Rh_2(OAc)_4$ was purchased from Aldrich. 1,2-Dichloroethane was distilled from CaH_2.

General Procedure for Reactions of 2-Siloxy-1,3-dienes **1** *with Dimethyl Diazomalonate* (**2**): $Rh_2(OAc)_4$ (5 mol-%) was dissolved under dry argon in 2 ml of dry 1,2-dichloroethane and 1 equivalent of diene **1**. At 50°C a solution of 1.5–2.0 equivalents of **2** (in 2 ml of 1,2-dichloroethane) was added via a syringe pump within 10 h. The mixture was stirred for further 12 h at room temp., then the solvent was evaporated in vacuo, the residue was dissolved in pentane and the solution filtered through a short pad of alumina (neutral, activity III). The filtrate was concentrated and the crude product was further purified by kugelrohr distillation or chromatography.

Dimethyl 4-(tert-Butyldimethylsiloxy)-2-methyl-3-cyclopentene-1,1-dicarboxylate (**4a**): According to the general procedure the reaction of 0.500 g (2.52 mmol) of **1a** with 0.597 g (3.78 mmol) of **2** in the presence of 0.055 g (0.125 mmol) of $Rh_2(OAc)_4$ as the catalyst provided after kugelrohr distillation (60–90°C/0.07 Torr) 0.286 g (35%) of **4a** as a colourless oil. – ^1H NMR ($CDCl_3$): δ = 4.49 (dd, *J* = 2, 3.5 Hz, 1 H, 3-H), 3.71, 3.70 (2 s, 3 H each, 2 CO_2Me), 3.50 (m_c, 1 H, 2-H), 3.23 (td, *J* = 2, 17 Hz, 1 H, 5-H), 2.57 (broad d, *J* = 17 Hz, 1 H, 5-H), 0.92 (d, *J* = 7 Hz, 3 H, 2-Me), 0.89 (s, 9 H, *tert*-Bu), 0.13, 0.12 (2 s, 3 H each $OSiMe_2$). – ^{13}C NMR ($CDCl_3$): δ = 172.4, 170.6, 52.6, 52.1 (2 s, 2 q, 2 CO_2Me), 150.7 (s, C-4), 106.5 (d, C-3), 61.3 (s, C-1), 41.3 (d, C-2), 40.1 (t, C-5), 25.6, 18.0 (q, s, *tert*-Bu), 16.9 (q, 2-Me), –4.7, –4.8 (2 q, $OSiMe_2$). – IR (film): ṽ = 3050 cm^{-1} (=C–H), 2960–2860 (C–H), 1740 (CO_2Me), 1655 (C=C), 1260 (Si–C). – $C_{16}H_{28}O_5Si$ (328.5): calcd. C 58.50, H 8.59; found C 58.76, H 8.78.

Dimethyl 3-(tert-Butyldimethylsiloxy)-2,4,5,6,7,7a-hexahydro-1H-indene-1,1-dicarboxylate (**4b**): According to the general procedure 0.500 g (2.10 mmol) of **1b**, 0.664 g (4.20 mmol) of **2** and 0.046 g (0.104 mmol) of $Rh_2(OAc)_4$ were allowed to react to provide a crude product which was purified by chromatography (silica gel, hexane/ethyl acetate, 10:1) affording 0.268 g (35%) of **4b** as a colourless oil. – ^1H NMR ($CDCl_3$): δ = 3.73, 3.70 (2 s, 3 H each, 2 CO_2Me), 3.32–3.12 (m, 2 H, 7a-H, 2-H), 2.56 (m_c, 2 H, 2-H, 4-H), 1.88–1.57, 1.30–1.18 (2 m, 5 H, 2 H, 4-H, 5-H, 6-H, 7-H), 0.93 (s, 9 H, *tert*-Bu), 0.14, 0.09 (2 s, 3 H each, $OSiMe_2$). – ^{13}C NMR ($CDCl_3$): δ = 172.7, 170.9, 52.6, 52.0 (2 s, 2 q, 2 CO_2Me), 139.7 (s, C-3), 116.4 (s, C-3a), 59.3 (s, C-1), 47.5 (d, C-7a), 41.0 (t, C-2), 30.0, 25.9, 25.63, 24.1 (4 t, C-4, C-5, C-6, C-7), 25.62, 18.0 (q, s, *tert*-Bu), –4.1, –4.4 (2 q, $OSiMe_2$). – IR (film): ṽ = 2950–2850 cm^{-1} (C–H), 1735 (CO_2Me), 1650 (C=C), 1260 (Si–C). – $C_{19}H_{32}O_5Si$ (368.5): calcd. C 61.92, H 8.75; found C 62.03, H 8.90.

Dimethyl 4-(tert-Butyldimethylsiloxy)-2-phenyl-3-cyclopentene-1,1-dicarboxylate (**4c**): According to the general procedure 0.500 g (1.92 mmol) of **1c**, 0.460 g (2.93 mmol) of **2** and 0.046 g (0.104 mmol) of $Rh_2(OAc)_4$ were allowed to react to provide a crude product which was purified by chromatography (silica gel, hexane/ethyl acetate, 15:1) furnishing 0.319 g (43%) of **4c** as a colourless oil. – ^1H NMR ($CDCl_3$): δ = 7.23 (m_c, 5 H, C_6H_5), 4.80, 4.64 (2 m_c, 1 H each, 2-H, 3-H), 3.76, 3.06 (2 s, 3 H each, 2 CO_2Me), 3.43 (td, *J* = 2, 17 Hz, 1 H, 5-H), 2.64 (d, *J* = 17 Hz, 1 H, 5-H), 0.95 (s, 9 H, *tert*-Bu), 0.23, 0.20 (2 s, 3 H each, $OSiMe_2$). – ^{13}C NMR ($CDCl_3$): δ = 172.3, 169.6, 53.0, 52.9, 51.6 (2 s, 2 q, 1 d, 2 CO_2Me, C-2), 152.6 (s, C-4), 140.6, 128.9, 127.8, 127.1 (s, 3 d, C_6H_5), 104.2 (d, C-3), 62.9 (s, C-1), 40.8 (t, C-5), 25.6, 18.1 (q, s, *tert*-Bu), –4.62, –4.64 (2 q, $OSiMe_2$). – IR (film): ṽ = 3100–3050 cm^{-1} (=C–H), 2955–2860 (C–H), 1740 (CO_2Me), 1660, 1500 (C=C), 1235 (Si–C). – $C_{21}H_{30}O_5Si$ (390.5): calcd. C 64.58, H 7.48; found C 63.99, H 7.60.

Dimethyl 4-(tert-Butyldimethylsiloxy)-2-methoxy-3-cyclopentene-1,1-dicarboxylate (**4d**): According to the general procedure (the reaction was performed at room temp.) 0.500 g (2.33 mmol) of **1d**, 0.550 g (3.50 mmol) of **2** and 0.051 g (0.117 mmol) of $Rh_2(OAc)_4$ were allowed to react to deliver a crude product which was purified by chromatography (silica gel, hexane/ethyl acetate, 10:1) affording 0.250 g (31%) of **4d** as a colourless oil. – ^1H NMR ($CDCl_3$): δ = 4.76 (t, *J* = 2 Hz, 1 H, 2-H), 4.57 (broad dd, *J* = 2, 3.5 Hz, 1 H, 3-H), 3.66, 3.65, 3.12 (3 s, 3 H each, 2 CO_2Me, OMe), 3.18 (td, *J* =

2, 17 Hz, 1 H, 5-H), 2.30 (dd, $J = 1$, 17 Hz, 1 H, 5-H), 0.82 (s, 9 H, *tert*-Bu), 0.12, 0.11 (2 s, 3 H each, OSiMe$_2$). – ^{13}C NMR (CDCl$_3$): $\delta = 171.4$, 168.9, 52.6, 52.3 (2 s, 2 q, 2 CO$_2$Me), 157.0 (s, C-4), 100.9 (d, C-3), 86.2 (d, C-2), 63.8 (s, C-1), 57.2 (q, OMe), 39.9 (t, C-5), 25.4, 18.0 (q, s, *tert*-Bu) −4.78, −4.83 (2 q, OSiMe$_2$). – IR (film): $\tilde{\nu} = 3050$ cm^{-1} (=C–H), 2955–2850 (C–H), 1740 (CO$_2$Me), 1650 (C=C), 1250 (Si–C). – $C_{16}H_{28}O_6Si$ (344.5): calcd. C 55.78, H 8.19; found C 55.85, H 8.16.

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