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Preliminary communication

Rhodium(I) complex-catalyzed hydrosilylation of dimethyl muconates *

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Abstract

Complete regioselective 1,6-hydrosilylation of dimethyl *cis,cis*-muconate took place by using trialkylsilanes in the presence of $RhCl(PPh_3)_3$ as a catalyst. The novel, functionalized ketene silyl acetal thus obtained exhibited moderate electrophilic properties. Hydrosilylation of *trans,trans*-muconate under similar conditions gave only a 3,4-adduct, whereas that of *trans,cis*-muconate resulted in a complicated mixture of adducts but for a 1,6-adduct.

Among many transition metal complexes, chloroplatinic acid, the so-called Speier catalyst for hydrosilylation of simple alkenes, is known to be one of the most effective and even industrially important catalysts [1]. However, the mode of hydrosilylation of 1,3-dienes is markedly dependent on the Group VIII metal catalysts and on hydrosilanes employed. Thus, the addition pattern of a hydrosilane to isoprene, for example, varies from exclusively 1,4-head to form a (*Z*)-2-methyl-2-butenylsilane by using a palladium catalyst [2,3], to mainly 1,4-tail to form a prenylsilane by a rhodium catalyst [3] or even to 1,2-tail giving a 3-methyl-3-butenylsilane by a platinum one [4]. Furthermore, we have recently found that a novel addition pattern of 1,2-head gives 2-methyl-3-butenylsilane derivatives as the major product (up to 75% selectivity) in the presence of a ruthenium(II) complex as catalyst [5]. A variety of observed regioselectivities in the hydrosilylation of isoprene must stem from the different properties of each metal species characteristic of forming either a π-allyl metal intermediate or not. In addition, the nature of the silicon–metal bond, as a result of the oxidative addition of a hydrosilane to the metal catalyst, must play a crucial role. With regard to these general trends of the catalytic hydrosilylation of 1,3-dienes, we have now examined the hydrosilylation of dimethyl *cis,cis*-muconate (**1**) as an unprecedented type of a 1,3-diene substrate (certain α,β-unsaturated esters are known to undergo hydrosilylation using a rhodium catalyst to give ketene silyl acetals [6], that are very useful synthetic intermediates in organic synthesis).

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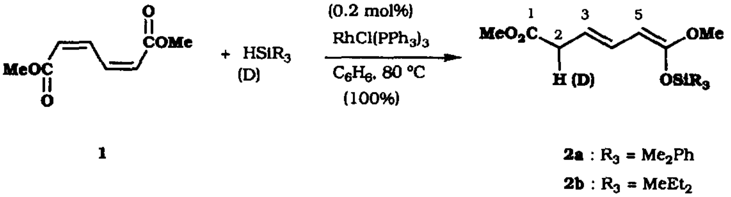
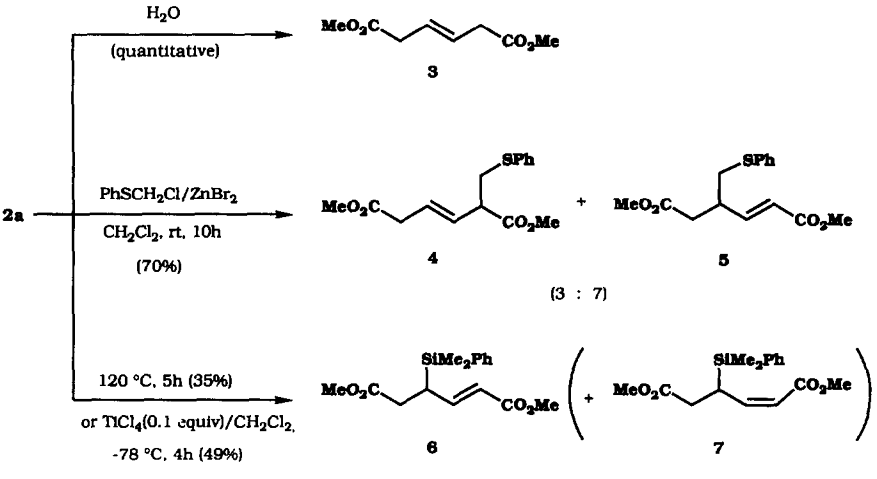
* Dedicated to Professor Akio Yamamoto on his retirement from the Tokyo Institute of Technology.

A benzene (2 mL) solution of **1** (0.34 g, 2.0 mmol), $HSiMe_2Ph$ (0.30 g, 2.2 mmol) and $RhCl(PPh_3)_3$ (3.7 mg, 0.2 mol%) was heated under argon for 10 h. The resulting clear solution was evacuated to remove the solvent and excess hydrosilane to give a yellow oil (0.61 g), which could hardly be characterized on TLC presumably owing to a highly hydrolyzable product. Although a trace of catalyst contaminated the product, the latter could be characterized uniquely by ^{1}H and ^{13}C NMR spectroscopy as methyl 6-methoxy-6-(dimethylphenylsiloxy)-(3*E*, 5*Z*)-hexadienoate (**2a**) [7*], a novel 1,6-hydrosilylation adduct consisting mainly of a single component (100% yield). The deuterium atom was incorporated in **2a**-d_1 [7*] only at C-2 position, confirmed by using $DSiMe_2Ph$ and indicated in eq. 1. Geometrical assignment of **2a** for 3*E* was made on the basis of $J(H^3\text{-}H^4)$ (15.5 Hz) and for 5*Z* based on the facile thermal rearrangement of the silyl group, as described below. Also in essentially the same manner as above, the Rh^I-catalyzed hydrosilylation of **1** with $HSiMeEt_2$ gave the 1,6-adduct **2b** [7*] in good yield.



(1)

The new, functionalized ketene silyl acetal **2a**, being an α,γ-dienolate synthon, exhibited moderate electrophilic properties which are summarized in eq. 2. Firstly, **2a** was readily hydrolyzed and protonation took place exclusively at the α(C-5) position to form dimethyl (3*E*)-hexenedioate (**3**), which reinforced the (3*E*)-geometry in **2a**. Secondly, in the presence of a mild Lewis acid ($ZnBr_2$), **2a** reacted with



(2)

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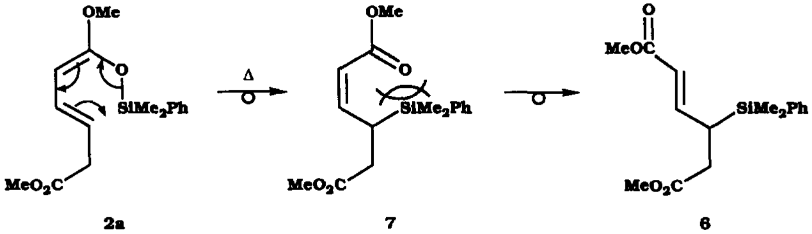
* Reference number with asterisk indicates a note in the list of references.

$PhSCH_2Cl$ to give dimethyl 5-(phenylthiomethyl)-(3*E*)-hexenedioate (**4**) [8*] (α attack) and dimethyl 4-(phenylthiomethyl)-(2*E*)-hexenedioate (**5**) [8*] (γ attack), respectively, the regioselectivity (**4** vs. **5**) being in a 3 : 7 ratio [9]. Thirdly, thermal rearrangement of **2a** (120 ° C) took place to give rise almost exclusively to dimethyl 4-(dimethylphenylsilyl)-(2*E*)-hexenedioate (**6**) [10*] in 35% yield. The result indicates that a facile 1,5 (O → C) silyl group migration [11], most probably owing to the (5*Z*)-geometry of **2a**, afforded dimethyl 4-(dimethylphenylsilyl)-(2*Z*)-hexenedioate (**7**) [10*] as the primary product that isomerized rapidly to give **6** under the sterical conditions as depicted in Scheme 1. Interestingly, a catalytic amount of $TiCl_4$ also caused silyl group migration of **2a** at −78 ° C to give a mixture of **6** and **7**. Compound **7** was obtained as a very minor component, isolated by column chromatography.



Scheme 1

In an attempted hydrosilylation of **1**, neither chloroplatinic acid nor $Pd(PPh_3)_4$ was effective and intractable adducts were obtained. Furthermore, $Ru(OAc)_2(PPh_3)_2$ was found to catalyze a slow isomerization of **1** into dimethyl *trans,trans*-muconate (**8**) (20%) in the presence of $HSiMe_2Cl$ at room temperature for 20 h. Finally, **8** was found to undergo hydrosilylation sluggishly under exactly the same conditions as depicted in eq. 1 to give **6** in 50% yield along with recovered **8**. Dimethyl *trans,cis*-muconate (**9**) was also subjected to the Rh^I-catalyzed hydrosilylation with $HSiMe_2Ph$, giving rise to a complicated mixture of adducts in terms of ^1H NMR analysis of the reaction mixture. The apparent TLC analysis, however, exhibited none of **3** which must result from the ketene silyl acetal **2a**. We therefore conclude that a novel Rh^I-catalyzed 1,6-hydrosilylation of muconates takes place only for *cis,cis*-muconate (**1**), and neither for *trans,trans*- (**8**) nor *trans,cis*-muconate (**9**). Relevance of these findings in terms of mechanistic implications will be the subject of further investigation.

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References and notes

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7 Data on **2a**: ^{1}H NMR (90 MHz, $CDCl_3$, TMS): δ 0.33 (s, 6H), 3.07 (dd, $J = 7.5$, 1.3 Hz, 2H), 3.66 and 3.68 (s, 3H×2), 4.44 (d, $J = 10.3$ Hz, 1H), 5.36 (dt, $J = 15.5$, 7.5 Hz, 1H), 6.35 (ddt, $J = 15.5$, 10.3, 1.3 Hz, 1H), and 7.3–7.6 ppm (m, 5H). ^{13}C{^{1}H} NMR (22.5 MHz): −0.8, 38.5, 51.7, 55.0 79.5, 114.8, 127.9, 129.0, 129.9, 133.3, 134.0, 158.1 and 170.7 ppm.

2a-d_1: ^{1}H NMR: 0.48 (s, 6H), 3.04 (d, $J = 7.1$ Hz, 1H), 3.50 and 3.66 (s, 3H×2), 4.45 (d, $J = 10.3$ Hz, 1H), 5.36 (dd, $J = 15.2$, 7.1 Hz, 1H), 6.28 (ddd, $J = 15.2$, 10.3, 1.3 Hz, 1H) and 7.3–7.6 (m, 5H).

2b: ^{1}H NMR 0.16 (s, 3H), 0.69 (q, $J = 7.3$ Hz, 4H), 0.96 (t, $J = 7.3$ Hz, 6H), 3.08 (d, $J = 6.8$ Hz, 2H), 3.56 and 3.67 (s, 3H×2), 4.42 (d, $J = 10.1$ Hz, 1H), 5.36 (dt, $J = 15.4$, 7.5 Hz, 1H) and 6.28 (dd, $J = 15.4$, 10.1 Hz, 1H).

8 Data on **4**: ^{1}H NMR: δ 2.85–3.40 (m, 5H), 3.67 and 3.68 (s, 3H×2), 5.65 (m, 2H), 7.2–7.4 ppm (m, 5H). IR ($CHCl_3$): 1730, 1585 cm^{-1}.

5: ^{1}H NMR: 2.57 (br, 2H), 2.8–3.1 (m, 3H), 3.65 and 3.72 (s, 3H×2), 5.87 (d, $J = 15.8$ Hz, 1H), 6.85 (dd, $J = 15.8$, 7.8 Hz, 1H) and 7.2–7.5 (m, 5H). IR ($CHCl_3$): 1725, 1660 cm^{-1}.

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10 Data on **6**: ^{1}H NMR: δ 0.33 and 0.35 (s, 3H×2), 2.3–2.6 (m, 3H), 3.57 and 3.70 (s, 3H×2), 5.62 (d, $J = 16.0$ Hz, 1H), 7.04 (dd, $J = 16.0$, 7.8 Hz, 1H) and 7.3–7.5 ppm (m, 5H). ^{13}C{^{1}H} NMR: 2.3, 39.3, 52.5, 55.8, 80.3, 115.6, 128.7, 130.0, 133.1, 134.8, 158.9, 170.6 and 171.5 ppm. IR ($CHCl_3$): 1715, 1635 cm^{-1}.

7: ^{1}H NMR: 0.32 and 0.33 (s, 3H×2), 0.85 (m, 1H), 2.36 (br, 2H), 3.56 and 3.67 (s, 3H×2), 5.73 (d, $J = 11.2$ Hz, 1H), 6.07 (dd, $J = 11.2$, 7.6 Hz, 1H) and 7.3–7.6 (m, 5H). IR ($CHCl_3$): 1730, 1585 cm^{-1}.

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