Pergamon

Tetrahedron Letters 42 (2001) 5057–5060

TETRAHEDRON LETTERS

Aluminum chloride catalyzed hydrosilylation of cyclopropanes with chlorodimethylsilane

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Received 11 May 2001; revised 28 May 2001; accepted 30 May 2001

Abstract—Aluminum chloride can be utilized as an active catalyst for the highly regioselective hydrosilylation of 1-alkyl, 1-aryl, 1,1-dialkyl, and cyclic cyclopropanes with chlorodimethylsilane in hexane at room temperature.

Hydrosilylation of alkenes and alkynes is a highly useful functional group manipulation in organic synthesis.[1] Despite the analogy between alkenes and cyclopropanes often drawn, surprisingly few studies have been made on the catalytic hydrosilylation of cyclopropanes under ring cleavage. To the best of our knowledge, only the hydrosilylation of vinylcyclopropanes and methylenecyclopropanes catalyzed by Rh(I) complexes has been studied, resulting in the addition of silanes to the cyclopropane rings to produce silylated alkenes.[2] The combination of cyclopropane rings with multiple bonds and/or other functional groups, which vinylcyclopropanes and methylenecyclopropanes include, is known to establish composite functional groups,[3] and hence, such cyclopropane rings are activated by adjacent functional substituents. In this context, we have been interested in the development of the hydrosilylation of unactivated cyclopropanes having only alkyl substituents. Here we wish to report the realization of such a reaction under the influence of $AlCl_3$ catalyst.[4]

In the reaction of 1-hexylcyclopropane (**1**)[5] with Me_2ClSiH at room temperature without solvent, ordinary hydrosilylation catalysts,[1] Speier catalyst (0.5 mol% $H_2PtCl_6{\cdot}6H_2O$) and Wilkinson complex catalyst (0.5 mol% $Rh(PPh_3)_3Cl$), respectively, indicated that the starting cyclopropane **1** was recovered quantitatively even after a prolonged reaction time (24 h). We then examined the catalytic activity of the Lewis acids $FeCl_3$, $TiCl_4$, $SnCl_4$, and $AlCl_3$ in this reaction.[6] Lewis acid catalyst (20 mol%) was added to a mixture of equimolar amounts of **1** and Me_2ClSiH without solvent and subsequent reaction at room temperature for 2 h was carried out. In the use of $TiCl_4$ and $SnCl_4$ catalysts, cyclopropane **1** was quantitatively recovered, respectively, while $FeCl_3$ catalyst provided a mixture of nonane, 1-nonene, 2-nonenes, and unidentified compounds without any hydrosilylation product formation. In marked contrast, however, $AlCl_3$ catalyst gave 1-chlorodimethylsilylnonane (**2**) (45%) and 1-dichloromethylsilylnonane (**3**) (8%) without the formation of other regioisomers after direct vacuum-distillation,[7,8] even though significant amounts of unidentified by-products remained as residue. In this $AlCl_3$-catalyzed hydrosilylation, unfortunately, switching silanes from Me_2ClSiH to other silanes, $MeCl_2SiH$, Cl_3SiH and Et_3SiH, gave unsuccessful results. The use of $MeCl_2SiH$ and Cl_3SiH resulted in high boiling by-products with complete consumption of **1** for 0.2 h, respectively. The reaction with Et_3SiH was slower (59% conversion for 2 h) and afforded complex mixtures of products. Therefore, modifications of $AlCl_3$-catalyzed hydrosilylation conditions using Me_2ClSiH were made to prevent the formation of both high boiling by-products resulting from the apparent destruction of **1** and dichloromethylsilyl compound **3**. Interestingly, in the reaction employing CH_2Cl_2 solvent (10 mL) the yield of **2** slightly increased (66%) by suppressing the formation of **3**, yet a significant proportion of high boiling by-products arose. However, the reaction in polar solvents such as diethyl ether and tetrahydrofuran resulted in total recovery of the starting cyclopropane **1**. Thus, the

Keywords: aluminum chloride; chlorodimethylsilane; cyclopropanes; hydrosilylation; ring cleavage.

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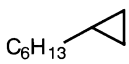
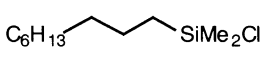
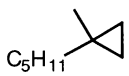
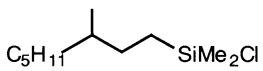
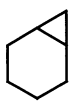
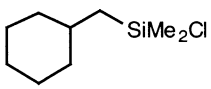
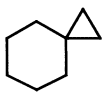
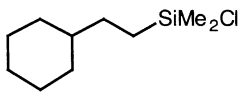
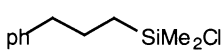
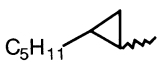
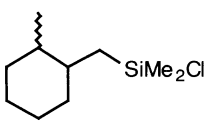
0040-4039/01/$ - see front matter
PII: S0040-4039(01)00925-X

use of hexane solvent in this hydrosilylation process is essential for achieving high product selectivity and chemical yield, affording only the regioselective hydrosilylation product **2** in 92% yield as depicted in Table 1 (entry 1). 1-Methyl-1-pentylcyclopropane (**4**), bicyclo[4.1.0]heptane (**6**), spiro[2.5]octane (**8**), in addition to 1-phenylcyclopropane (**10**) were also regioselectively hydrosilylated in this process,[5] being converted to the almost pure chlorodimethylsilyl compounds, **5**, **7**, **9**, and **11**, in good to high yields (entries 2–5).[8] These products involved silicon addition to the least-substituted cyclopropane ring carbon and hydrogen to the most substituted, respectively.

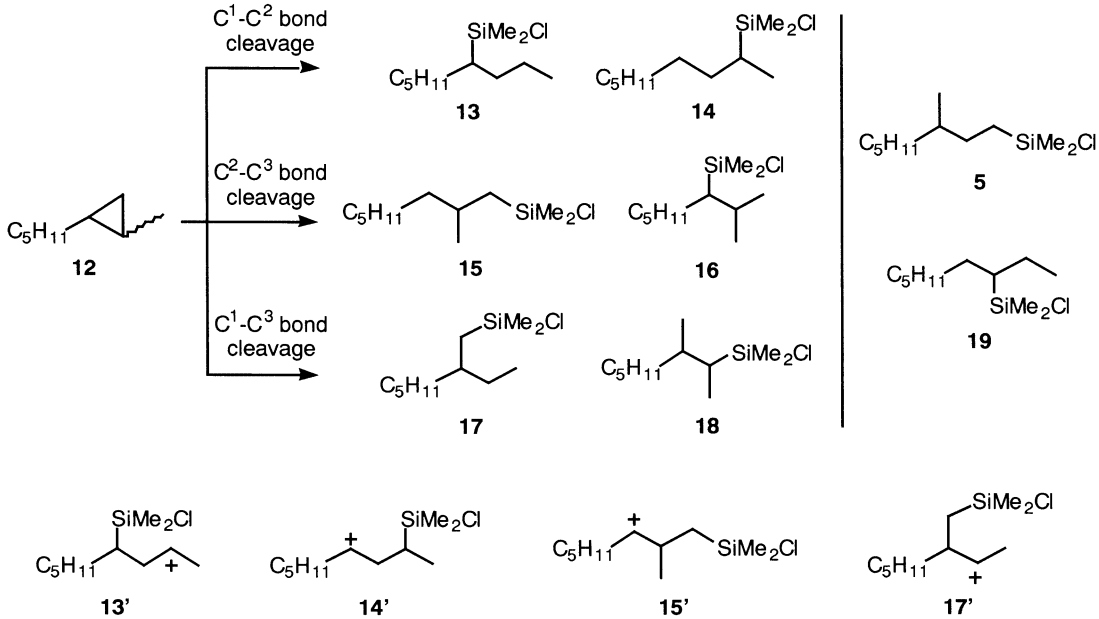
On the basis of the regiochemistry of the products and the mechanism proposed for both the reaction of cyclopropanes with electrophiles[6] and the $AlCl_3$-catalyzed hydrosilylation of alkenes with Me_2ClSiH,[7c,d] we interpreted that the reaction proceeds through the electrophilic ring opening of the cyclopropane with a catalytic chlorodimethylsilyl complex, $ClMe_2Si^+HAlCl_3^-$,[7d] formed by the reaction of $AlCl_3$ with Me_2ClSiH to give a more stable, γ-silylated secondary or tertiary carbocation intermediate. Similarly, the formation of dichloromethylsilyl products such as **3** in the reaction without solvent can be ascribed to the addition of a dichloromethylsilyl complex, $Cl_2MeSi^+HMeAlCl_2^-$, generated by the redistribution of the chlorodimethylsilyl complex.

In the reaction of unsymmetrical 1,2-disubstituted cyclopropane, 1-methyl-2-pentylcyclopropane (**12**),[5] hydrosilylated regioisomers, **13**–**15** and **17**, will probably be obtained, because these regioisomers can be attributed to the reaction proceeding via the corresponding γ-silyl secondary carbocation intermediate, respectively (Scheme 1). The formation of regioisomers, **16** and **18**, might have to proceed through primary carbocation intermediates. The reaction of **12** actually afforded a mixture of the expected regioisomers, **13**–**15** and **17**, though a small amount of other regioisomers, **5** and **19**, were also formed (entry 6).[9] The regioisomer **15**

Table 1. Aluminum chloride catalyzed hydrosilylation of cyclopropanes with Me_2ClSiH[a]

entry	cyclopropane	product	% yield[b]
1	 **1**	 **2**	92 (45[c])
2	 **4**	 **5**	94 (93)
3	 **6**	 **7**	79[d] (48[e])
4	 **8**	 **9**	95 (69[d])
5	 **10**	 **11**	65[f] (54[d, g])
6[h]	 **12**	**13 + 14 + 15 + 17 + 5 + 19**	3 : 15 : 42 : 7 : 6 : 8[i, j] (3 : 10 : 36 : 5 : 9 : 5)
7	 **20**	 **21**	90 (82[d])[k]

[a] Unless otherwise noted, the reaction was carried out in hexane (10 mL) using 20 mol% $AlCl_3$ and 100 mol% Me_2ClSiH at room temperature for 2 h. [b] Isolated yield by distillation in vacuo. Values in parentheses are yields of the reaction without any solvents. [c] 8% dichloromethylsilyl product **3** was also formed. [d] 1% dichloromethylsilyl product was also formed. [e] 3% (dichloromethylsilylmethyl)cyclohexane was also obtained. [f] Use of 1 mL hexane solvent. [g] For 0.5 h. [h] (*E*)/(*Z*) = 8 : 2 for the starting cyclopropane **12**. [i] Determined by GLC analysis and NMR spectroscopy. [j] For 6 h. [k] Isomeric ratios of the products are 35 : 65 in hexane solvent, 43 : 57 without solvent, respectively.



Scheme 1.

was a major product in this reaction. Therefore, we have performed semiempirical calculations[10] in order to estimate the stability difference among secondary carbocation compounds, **13′**–**15′** and **17′**, as model compounds corresponding to the proposed γ-silyl carbocation intermediates, by comparing the heat of formation (ΔH_f). The parameters for the semiempirical calculations and the stability order of the secondary carbocation compounds estimated from the calculated ΔH_f values (298 K) are as follows: **15′**>**13′**>**14′**≅**17′** (AM1); **13′**≅**14′**≅**15′**>**17′** (PM3). The calculation results (AM1) agreed well with the experimental results, demonstrating that the most stable carbocation compound is **15′**.

As the $AlCl_3$-catalyzed hydrosilylation of alkenes[7d,f] and alkynes[7e] has been reported to proceed stereoselectively in a *trans*-addition manner, the stereochemical aspect of this process was also examined with 1-methylbicyclo-[4.1.0]heptane (**20**).[5] Although the reaction of **20** was quite regioselective, unfortunately, it was nonstereoselective, yielding a mixture of stereoisomers of **21**[8] in a ratio of 35:65 in hexane and 43:57 without solvent (entry 7).

The experimental procedure is illustrated here for the synthesis of **2**. To a solution of **1** (379 mg, 3.0 mmol) and Me_2ClSiH (333 μL, 3.0 mmol) in hexane (10 mL) was added a powder anhydrous $AlCl_3$ (80 mg, 0.6 mmol) at 0°C under argon atmosphere. The resulting suspension was allowed to warm to room temperature where it was stirred for 2 h. After evaporation of hexane solvent, the residue was directly vacuum-distilled by Kugelrohr apparatus to afford **2** (610 mg, 92% yield) as a colorless oil.

Acknowledgements

This work was supported by the OKASAN-KATO Foundation.

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–0.37 (1H, m), 0.5–0.75 (3H, m), 0.87 (3H, t, $J=6.8$ Hz), 0.99 (3H, d, $J=6.1$ Hz), 1.1–1.4 (8H, m). ^{13}C NMR: δ 9.27, 11.92, 13.18, 14.06, 15.66, 22.69, 28.39, 29.81, 31.85. (*Z*)-**12**: ^{1}H NMR: δ 0.1 (1H, m), 0.35 (1H, m), 0.5–0.75 (2H, m), 0.87 (3H, t, $J=6.6$ Hz), 0.98 (3H, d, $J=5.9$ Hz), 1.1–1.4 (8H, m). ^{13}C NMR: δ 12.61, 12.84, 14.06, 19.02, 19.89, 22.69, 29.30, 31.70, 34.20.

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8. All terminal silyl products were identified by comparison of the spectral properties (NMR, GC/MS) and GLC retention times with those of authentic samples prepared by the hydrosilylation of the corresponding 1-alkenes with Me_2ClSiH or $MeCl_2SiH$ in the presence of 0.5 mol% $H_2PtCl_6{\cdot}6H_2O$ at room temperature without solvent.
9. Authentic samples of the products, **13**, **14**, and **19**, were prepared by the hydrosilylation of 2-nonene and 3-nonene with Me_2ClSiH in the presence of 20 mol% $AlCl_3$ at room temperature without solvent. For example, the hydrosilylation of 2-nonene resulted in a mixture of **14** and **19** (70:30), and the reaction of 3-nonene gave a mixture of **13** and **19** (53:47). **13**: ^{1}H NMR: δ 0.37 (6H, s), 0.7–0.9 (1H, m), 0.87 (3H, t, $J=6.7$ Hz), 0.88 (3H, t, $J=7.4$ Hz), 1.2–1.6 (12H, m). ^{13}C NMR: δ 1.15, 14.09, 14.38, 22.00, 22.56, 27.73, 28.55, 28.81, 31.19, 32.19. **14**: ^{1}H NMR: δ 0.35 (6H, s), 0.7–0.9 (1H, m), 0.87 (3H, t, $J=6.7$ Hz), 0.99 (3H, d, $J=7.3$ Hz), 1.1–1.6 (12H, m). ^{13}C NMR: δ –0.05, 0.00, 13.15, 14.10, 21.86, 22.67, 28.28, 29.26, 29.59, 30.65, 31.91. **19**: ^{1}H NMR: δ 0.38 (6H, s), 0.7–0.9 (1H, m), 0.87 (3H, t, $J=6.7$ Hz), 0.93 (3H, t, $J=7.4$ Hz), 1.1–1.6 (12H, m). ^{13}C NMR: δ 1.25, 1.29, 13.33, 14.10, 21.52, 22.67, 28.17, 28.73, 29.62, 29.65, 31.77.
10. The semiempirical calculations were performed using CAChe MOPAC ver. 94.10 on Macintosh G3. For the parameters of the calculations, see: Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 209.