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Reaction of 1,4-bis(trimethylsilyl)-2-butene with aromatic aldehydes catalyzed by $TiCl_4$: an approach to (1-vinylallyl)benzene type derivatives

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Dedicated to Professor Jean-François Normant on the occasion of his 70th birthday

Abstract—1,4-bis(Trimethylsilyl)-2-butene **1** can react with alkyl and aromatic aldehydes in the presence of titanium tetrachloride to give α-(trimethylsilyl)methyl homoallylic alcohols and (1-vinylallyl)benzene type compounds in poor to good yield according to the related position of each substituents present on the aromatic ring. In the last case, the reaction involves a SE_2' type electrophilic substitution of 1,4-bis(trimethylsilyl)-2-butene by aromatic aldehydes activated by $TiCl_4$, followed by a 1,2-migration of a vinyl group.

During these last few decades, organosilicon chemistry remained omnipresent in organic synthesis.[1] Many areas have witnessed a growth in the preparation of new silicon-containing compounds and their successful use in modern synthetic transformations. Indeed, they usually served as key intermediates in the elaboration of complex molecules.[2] Among them, allylsilanes have attracted considerable attention as versatile reagents for carbon–carbon bond formation.[3] In 1955, Calas first showed that protolysis of allylsilanes by acetic acid occurred with an allylic shift.[4] Twenty years later, Sakurai and Hosomi explored the condensation of allyltrimethylsilane with aldehydes in the presence of Lewis acid, to generate the corresponding homoallylic alcohols.[5] The reaction involves a SE_2' mechanism where the regioselective attack of the activated aldehyde at the carbon–carbon double bond resulted in the intermediate formation of a carbenium ion type **A** (Scheme 2), which is stabilized by the carbon–silicon bond in β-position through hyperconjugation.[3,6] Soon after, Calas and Dunoguès confirmed the previous results and also showed that 1,4-bis(trimethylsilyl)-2-butene **1**[7] could react with propanal and $AlCl_3$ to furnish the α-(trimethylsilyl)methyl homoallylic alcohol in 40% yield.[8]

Recently, we performed the same experiment on pivaldehyde in dichloromethane at −78 °C using $TiCl_4$ as Lewis acid. Compound **2** was liberated in high yield (94%), whereas condensation with benzaldehyde resulted in the formation of another compound identified as (1-vinylallyl)benzene **3** (75%) (Scheme 1).[9–11]

A plausible mechanism for this reaction is depicted in Scheme 2 and suggests that the formation of (1-vinylallyl)-benzene **3** first comes from a SE_2' type electrophilic substitution of 1,4-bis(trimethylsilyl)-2-butene **1** by benzaldehyde activated by titanium tetrachloride. The alkoxy titanium formed evolves into an ion pair including a benzylic carbenium ion **B** which undergoes a 1,2-vinyl shift and generates the rearranged carbenium ion **C** stabilized by the neighboring carbon–silicon bond. β-Elimination of the second trimethylsilyl group liberates the dienic adduct **3**. Formation of the rearranged product is highly dependent upon the relative stability of both carbocation intermediates **B** and **C**. For success, the transient β-silylated carbocation **C** has to be more stable than its benzyl counterpart **B**. Indeed, ab initio computational studies at the B3LYP/6-311 G(d,p) level show an energy difference between both carbenium ion

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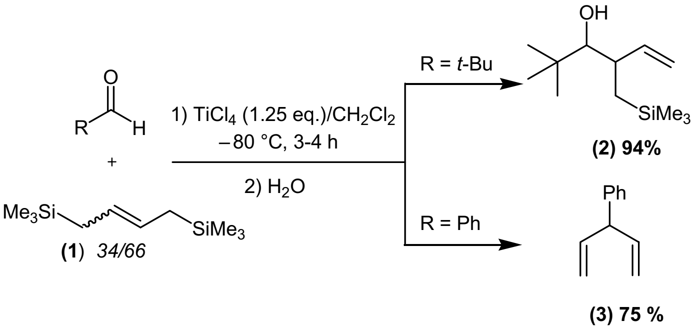
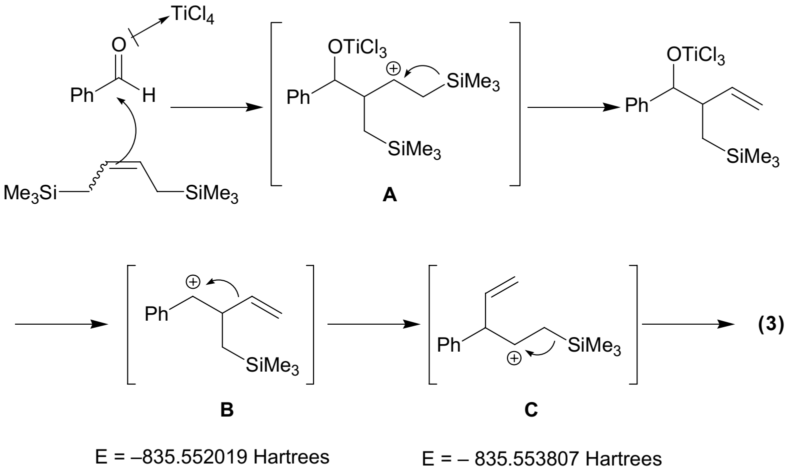


Scheme 1.



Scheme 2.

intermediates **B** and **C** of 1.12 kcal/mol in favor of the formation of **C**, as suggested above.

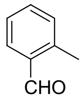
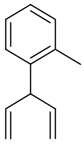
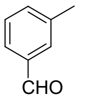
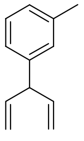
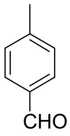
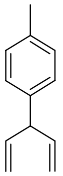
The proposed mechanism is in accordance with precedent studies reported in 1981 by Fleming and co-workers[12] showing that γ-silylated tertiary alcohols could rearrange in the presence of protic acid through a similar sequence. However, no allusion to vinyl migration or to similar experiments with γ-silylated secondary alcohols was mentioned.

In order to extend the scope of this transformation, we were interested in studying the reactivity of methyl-substituted benzaldehydes. As shown in Table 1, the outcome of the condensation of 1,4-bis(trimethylsilyl)-2-butene **1** with tolualdehydes proved to be quite dependent on the relative position of the substituents on the aromatic ring. By far, the best result was obtained with *ortho*-tolualdehyde under the previously described conditions. The *meta*-oriented substrate provides the adduct **5** in a moderate yield whereas reaction with its *para*-isomer appears to be less favored. Although **1** was completely consumed in each case, a small amount of starting aldehyde still remained present together with more or less side products. In an effort to optimize the procedure, the reaction mixture was warmed up to room temperature. Unfortunately, no significant improvement was observed.

Reasons for such a variation of reactivity between the three tolualdehydes may be explained by considering first the influence of the methyl substituent on the formation and stabilization of the intermediate **B**. Indeed, carbenium ions formed adjacent to the aromatic ring are stabilized by hyperconjugation/resonance or Baker–Nathan effect[13] and this much better with *ortho*- and *para*-substituted precursors than the corresponding *meta*-isomer. By consequence, the presence of the electrodonating methyl substituent at the *para*-position can also limit the subsequent 1,2-migration process. By opposition, the presence of the methyl substituent at the *ortho*-position results in a steric hindrance, which should partially prevent a charge stabilization favoring at the same time the formation of the β-silylated carbocation type **C**.

Encouraged by these results, we tested the condensation procedure on 2- and 4-methoxybenzaldehydes. Table 2 shows that, when the reaction is conducted at −80 °C, 2-methoxybenzaldehyde can be converted into 1-methoxy-2-(1-vinylallyl)-benzene **8** in only 21% yield together with the intermediate alcohol **9** (63%), whereas 4-methoxybenzaldehyde leads to the adduct **7** as results of two successives SE_2' reactions. This example mainly shows the effect of electrodonating substituents on the stabilization of the benzylic carbenium ions through

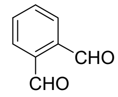
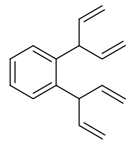
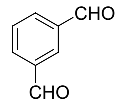
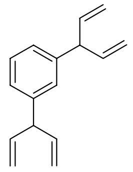
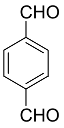
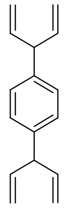
Table 1.

Entry	Aldehyde	Conditions	Product	Yield (%)
1		3.5 h, −80 °C	 **(4)**	96
2		4.5 h, −80 °C	 **(5)**	64
3		3.5 h, −80 °C −80 °C→rt, 4 h	 **(6)**	40 41

mesomeric resonance. As discussed before, an '*ortho* effect' is proposed to explain the interesting difference of reactivity with both 2- and 4-methoxybenzaldehydes.

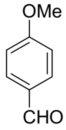
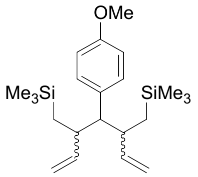
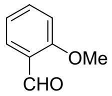
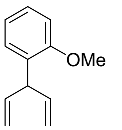
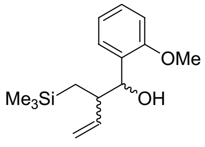
Finally, to illustrate the synthetic potential of this methodology, we undertook experiments with aromatic dialdehydes. As can be seen in Table 3, treatment of phthaldialdehyde and isophthalaldehyde with 2.2 equiv of 1,4-bis(trimethylsilyl)-2-butene and 2.5 equiv of titanium tetrachloride at −80 °C gave the desired 1,2- and 1,3-bis-(1-vinylallyl)-benzene adducts **10** and **11** in good to moderate yield, respectively. We next examined the behavior of terephthalaldehyde. After optimization, only a 24% yield of compound **12** was isolated when the reaction was carried out at room temperature. At the light of these results, we can draw a parallel between the reactivity of tolualdehydes and phthalaldehydes given that after allylation of each aldehyde function, the influence of substituent electronic effects on the 1,2-vinyl shift is almost similar.

Table 3.

Entry	Aldehyde	Conditions	Product	Yield (%)
1		3.5 h, −80 °C	 **(10)**	79
2		3.5 h, −80 °C	 **(11)**	62
3		3.5 h, −80 °C −80 °C→rt, 3 h	 **(12)**	7 24

In summary, aromatic aldehydes placed in the presence of 1,4-bis(trimethylsilyl)-2-butene and $TiCl_4$ evolve to (1-vinylallyl)benzene type compounds via a SE'_2 type electrophilic substitution/1,2-vinyl shift reaction sequence in poor to good yield, according to the substitution on the aromatic ring. Influence of the electronic nature of these substituents on the outcome of the reaction process is still under study. Then, these compounds, rarely encountered in the literature, represent interesting precursors of highly functionalized 1,3-dienic systems.

Table 2.

Entry	Aldehyde	Conditions	Product	Yield (%)
1		4 h, −80 °C	 **(7)**	35
2		3 h, −80 °C (−80 °C→rt, 4 h)	 **(8)**	21 (40)
			 **(9)**	63 1/6 dr

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9. For different transformations using 1,4-bis(trimethylsilyl)-2-butene **1** as reagent, see: (a) Calas, R.; Dunoguès, J.; Pillot, J. P.; Biran, C.; Pisciotti, F.; Arreguy, B. *J. Org. Chem.* **1975**, *40*, 149; (b) Abed, D. E.; Santelli-Rouvier, C.; Santelli, M. *Tetrahedron* **1990**, *46*, 5993; (c) Santelli, M.; Abed, D. E.; Jellal, A. *J. Org. Chem.* **1986**, *51*, 1199; (d) Roux, M.; Santelli, M.; Parrain, J.-L. *Org. Lett.* **2000**, *2*, 1701.
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11. To a stirred solution of $TiCl_4$ (3 ml, 27 mmol, 1.25 equiv) in dry CH_2Cl_2 (30 ml) was added dropwise a solution of benzaldehyde (2.0 ml, 20 mmol) in dry CH_2Cl_2 (5 ml) under argon at −60 °C. After 5 min stirring, the mixture was cooled to −90 °C and a solution of 1,4-bis(trimethylsilyl)-2-butene **1** in dry CH_2Cl_2 (5 ml) was slowly added, and the resulting solution was stirred for 3.5 h at −80 °C. The reaction was monitored by TLC analysis. The mixture was quenched with a saturated NH_4Cl solution (50 ml) and was stirred for 1 h at rt. The aqueous layer was extracted with CH_2Cl_2 (3×25 ml). The combined organic layers were washed with a saturated $NaHCO_3$ solution (75 ml), brine (50 ml), dried over $MgSO_4$, filtered and concentrated under vacuum. The residue obtained was purified by flash silica gel chromatography (P.E.) to provide **3** (2.17 g, 75%) as a colorless oil. R_F 0.76 (P.E.); δ_H (300 MHz, $CDCl_3$) 7.33–7.18 (m, 5H), 6.10–5.98 (ddd, *J* 6.8, 10.2, 17.2 Hz, 2H), 5.15 (d, *J* 10.2 Hz, 2H), 5.09 (d, *J* 17.2 Hz, 2H), 4.06 (br t, *J* 6.8 Hz, 1H). δ_C (75 MHz, $CDCl_3$) 142.4, 139.9 (2C), 128.4 (2C), 127.9 (2C), 126.4, 115.4 (2C), 53.1. CAS registry number 33558-13-3.
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