The First Efficient Catalyzed Acylation of Allylsilanes[1]

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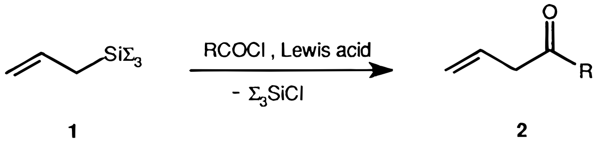
Summary: In the presence of catalytic amounts (5 mol %) of $BiCl_3$*−3 NaI or* $BiCl_3$*−1.5* ZnI_2 *acylation of allyltrimethylsilane by a variety of acyl chlorides (RCOCl with R = Me, Et, i-Pr, t-Bu, Ph, 1-adamantyl) proceeded rapidly at room temperature without decarbonylation of the acyl chloride. Allyl ketones were usually obtained in high yield with little or no isomerization to 1-propenyl ketones. Using (3-methylbut-2-enyl)trimethylsilane and* $Me_2C{=}CHCOCl$*, Artemisia ketone was synthesized in nearly quantitative yield after complete allylic transposition.*

Introduction

Among electrophilic substitutions of allylsilanes,[2] the acylation reaction (eq 1) usually occurs with Lewis acid activation of the acyl chloride and with allylic transposition. To our knowledge, aluminum trichloride,[3] titanium tetrachloride,[4] zinc chloride,[5] and tin tetrachloride[6] are the most common promoters, although acetic anhydride activated by a stoichiometric amount of BF_3 has been reported.[3b] The acylation of allylsilanes has also been examined by Calas et al.[3a] using catalytic amounts of gallium or indium trichloride, the weaker—i.e. heavier—Lewis acid being the most effective. However, the authors noted that their procedure was quite critical because (a) the isomerization of allyl ketones to 1-propenyl ketones could not be avoided and (b) the method was restricted to certain acyl chlorides. The acylation of allylstannanes catalyzed by catalytic amounts (2 mol % based on allylstannane) of chlorotris(triphenylphosphine)rhodium(I) has been reported[7] to give high yields of the corresponding allyl ketones. In spite of the toxicity of tin compounds, the method offers the advantage that various acyl chlorides can be used. A survey of the literature reveals that, to date, no efficient, nontoxic, and inexpensive procedure is available for the catalytic acylation of allylsilanes.



(1)

Recently, we reported the catalytic activity of bismuth(III) chloride−metallic iodide heterogeneous systems in the acylation of enoxysilanes by acyl chlorides.[8] In search of new applications of these heavy-metal catalysts, we decided to attempt the acylation of allylsilanes.

Results and Discussion

Our previous studies of the acylation of enoxysilanes showed that bismuth(III) chloride or bismuth(III) chloride−metallic iodides are efficient catalysts in the preparation of 1,3-diketones.[8] Since it is well-known that allylsilanes are among the most reactive organosilanes toward acylation, the catalytic activity of these bismuth systems has been tested first on the acetylation of allylsilanes bearing various substituents on the silicon atom. The results of these experiments, summarized in Table 1, allows us to note the following. (a) Of all the allylsilanes tested, allyltrimethylsilane (**1a**) appears to be the most reactive substrate (entry 1). (b) As for the acylation of enoxysilanes, the bismuth(III) chloride−metallic iodide combinations emerge as the most efficient compared to bismuth(III) chloride alone (entry 2); thus, the addition of metallic iodides seems to play an important role in the observed catalysis and will be discussed later. (c) Substitution of methyl by phenyl groups (entry 3) strongly slows down the reaction (only 10% of 4-penten-2-one (**2a**) was produced after 15 min); allyl ketones **2** have also been reported to self-isomerize slowly[3a] or to isomerize rapidly under acidic conditions[7] to the conjugated ketone **3**. Thus, after 3 h the yields of

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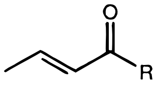
Table 1. Reactions of Various Allylsilanes ($CH_2{=}CHCH_2Si\Sigma_3$) with Acetyl Chloride (Eq 1)[a]

			product yield[b] (%)	
entry no.	Σ	catalyst	**2a**	**3a**
1	Me	A	90	5
2	Me	B	64	0
3	Ph	A	10	0
4	Cl	A	0	0

[a] Conditions and abbreviations: solvent CH_2Cl_2; room temperature; catalyst A, $BiCl_3$−3 NaI (5 mol %); catalyst B, $BiCl_3$ (5 mol %). [b] Yields determined after 15 min by ^1H NMR analysis.



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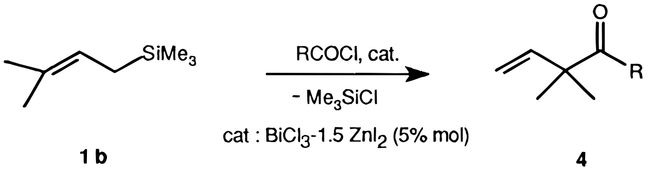
2a and **3a** obtained from allyltriphenylsilane became 40% and 10%, respectively, and the same problem happened with allyltrimethylsilane when reaction was carried out for a period longer than 15 min (after 1 h the yields of of **2a** and **3a** were respectively 48 and 50%). (d) When methyl or phenyl groups were replaced by more electron-withdrawing chlorine atoms, no reaction was observed even after 5 h (entry 4), revealing that the reactivity of the double bond toward electrophiles, i.e. the magnitude of the β-effect, is drastically diminished by the change of substituents from alkyl or aryl groups to chlorine atoms. A similar influence on allylsilanes and vinylsilanes has recently been reported.[9] (e) No reaction occurred when acetic anhydride was used instead of acetyl chloride.

In light of these results, we decided to extend this reaction to other acyl chlorides and allylsilanes. Thus, allyltrimethylsilanes (**1a**) and (3-methyl-2-butenyl)trimethylsilane (**1b**) were reacted with various acyl chlorides (Table 2, eqs 1 and 2).



(2)

An interesting point is the synthesis of allyl ketone **2d** or **2f** in yields >80% (Table 2, entries 6 and 9), while 1-adamantanecarbonyl and pivaloyl chlorides usually undergo decarbonylation during Friedel−Crafts synthesis. For example, the intermediate complex of 1-adamantanecarbonyl chloride with $AlCl_3$ has been reported to decarbonylate quantitatively,[5] leading exclusively to 1-phenyladamantane when reacted with benzene. In addition, our experiments on allylsilane **1b** showed that complete allylic transposition occurred during the reaction (entries 10 and 11) and Artemisia ketone **4b** was obtained almost quantitatively.

These observations suggest a weak interaction between $BiCl_3$ and acyl chlorides. Moreover, we found that bismuth(III) iodide was a very poor catalyst (details not shown). Thus, BiI_3 probably does not take part in the catalytic cycle and its formation is due to the spontaneous and partial reaction between $BiCl_3$ and metallic iodides.[1] Our experiments also showed that neither acyl iodide nor iodotrimethylsilane could explain the observed iodine activation, as acyl iodides and iodotrimethylsilane reacted instantaneously and quantitatively with bismuth(III) chloride, forming halogen exchange products. In summary, the active species is probably $BiCl_3$ and the iodine activation still remains to be rationalized.

We were also interested to know if the resulting conjugated ketones **3** could arise from the catalytic acylation of vinylsilanes produced by catalytic isomerization of allylsilanes (such isomerization is catalyzed by $Pd(PPh_3)_4$[10]). In addition, allylsilane **1a** has been reported to be 8 kJ mol^{-1} less stable than the corresponding *(E)*-propenyltrimethylsilane.[2a] The acetylation of 1-propenyltrimethylsilane using 5 mol % of the catalytic system $BiCl_3$−1.5 ZnI_2 was attempted, and after 6 h only 16% of 3-propen-2-one was obtained (see Experimental Section). Moreover, we demonstrated that neither $BiCl_3$ nor BiI_3 is a catalyst for the isomerization of allylsilane **1a** to propenylsilane. Thus, the conjugated ketones **3** observed resulted from the isomerization of the allyl ketones **2**.

Conclusion

Bismuth(III) chloride−metallic iodide systems are the first efficient catalysts for the acylation of allylsilanes. In almost all cases studied, reactions proceed rapidly at room temperature with complete allylic transposition. These catalysts are inexpensive and have low toxicity.[11] Taking into account that numerous allylsilanes are synthetically or commercially available,[2] we believe that these catalysts are new and very useful reagents for the synthesis of allyl ketones. Finally, a search for the composition of the acylating complex and the extension to acylation of other organosilanes are currently underway.

Experimental Section

Dichloromethane was purified using known procedures.[12] Bismuth(III) chloride, metallic iodides, allylsilanes, and acyl chlorides were purchased and used without further purification. (3-Methyl-2-butenyl)trimethylsilane (**1b**) was prepared by following the procedure of Calas et al.[3g] All transfers of bismuth(III) chloride and metallic iodides were done in a glovebag under argon. Allylsilanes and acyl chlorides were added by syringe.

^1H NMR spectra were recorded at 80 MHz. Chemical shifts are reported in parts per million on the δ scale relative to an internal TMS standard. Infrared spectra were recorded on a FT/IR spectrophotometer.

As allylic ketones are known to be thermally unstable, we decided not to determine the yields by gas chromatography but to follow the procedure of Kachinsky et al.[13] The yield of **2e** was determined by adding to the reaction mixture, after its complete reaction, a known amount of cyclododecane.[13] Since there is no overlap of the product ^1H NMR signals with

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Table 2. Reactions of Allylsilanes 1a,b with Various Acyl Chlorides RCOCl Catalyzed by $BiCl_3-xMI_n$ (5 mol %)[a] (Eqs 1 and 2)

entry no.	allylsilane	R	xMI_n	reacn time	product yield[b] (%)	
					2	**3**
1	**1a**	Me	3 NaI	15 min.	**2a**, 90	**3a**, 5
2	**1a**	Et	3 NaI	15 min.	**2b**, 95	**3b**, trace
3	**1a**	*i*-Pr	3 NaI	1 h	**2c**, 85	**3c**, 8
4	**1a**	*i*-Pr	1,5 ZnI_2	5 min.	**2c**, 89	**3c**, 7
5	**1a**	*t*-Bu	3 NaI	30 min.	**2d**, 95	**3d**, trace
6	**1a**	*t*-Bu	1,5 ZnI_2	15 min.	**2d**, 97	**3d**, 0
7	**1a**	Ph	3 NaI	5 h	**2e**, 65[d]	**3e**, 30[d]
8	**1a**	Ph	1,5 ZnI_2	15 min	**2e**, 67[d]	**3e**, 32[d]
9	**1a**	Ad[c]	1,5 ZnI_2	25 min.	**2f**, 80[d]	**3f**, 20[d]
10	**1b**	Me	1,5 ZnI_2	1 h	**4a**, 90[d]	
11	**1b**	$Me_2C{=}CH$	1,5 ZnI_2	1 h	**4b**, 95[d]	

[a] Conditions: solvent CH_2Cl_2; room temperature. [b] Yields determined by ^1H NMR analysis. [c] Ad = 1-adamantyl. [d] Yield of isolated product.

those of cyclododecane, the absolute yields were determined from the ratio of their respective integrations.

Typical Procedure (Table 2, Entry 6). 2,2-Dimethyl-5-hexen-3-one[3a,15] (**2d**) was prepared in the following way. A 100 mL flask with a septum inlet and a magnetic stirbar was flame-dried under vacuum and filled with argon. A 50 mL portion of dichloromethane was introduced into the flask by a syringe. Bismuth(III) chloride (790 mg, 2.5 mmol) and zinc iodide (1.195 g, 3.75 mmol) were transferred in a glovebag to the reaction flask. Then, the flask was connected to an argon line. This was followed by the addition of pivaloyl chloride (6.65 g, 55 mmol), and the suspension was stirred for 5 min at room temperature. Then, allyltrimethylsilane (5.7 g, 50 mmol) in 10 mL of the same solvent was added all at once with rapid stirring. The reaction was monitored by following the formation of chlorotrimethylsilane (^1H NMR). After 15 min at ambient temperature, the reaction mixture was quenched with 50 mL of a saturated sodium hydrogen carbonate solution. The layers were separated, and the aqueous layer was washed three times with 20 mL of dichloromethane. The organic layers were combined and dried over sodium sulfate. Then, the organic layer was concentrated under reduced pressure to give 6 g of a pale yellow oil (95% yield). The oil was analyzed by ^1H NMR and IR. Spectral analyses clearly indicated the presence of **2d** as the sole component of the crude mixture. ^1H NMR ($CDCl_3$): δ 1.11 (s, 9H, *t*-Bu), 3.23 (m, 2H, CH_2), 4.9–5.25 (m, 2H, $C{=}CH_2$), 5.7–6.2 (m, 1H, $={CH}-$). IR (neat): 1718 (C=O), 1643 cm^{-1} (C=C). After distillation, 5.2 g (83% yield) of an oil was collected and submitted for elemental analysis. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H,11.18. Found: C, 76.07; H, 11.22.

All other synthesized compounds presented characteristics identical with those previously reported: **2a**,[3a,14] **2b**,[7] **2c**,[3a] **2d**,[15] **2e**,[13] **2f**,[5] **4a**,[15a] **4b**.[3g] For compounds **2a**–**c** and **4a** a known amount of chloroform was added to the reaction mixture after the reaction was complete, and an aliquot of the resulting mixture was analyzed by ^1H NMR to determine the absolute yields of **2** and **3**.

Acetylation of 1-Propenyltrimethylsilane. Using the same experimental procedure, 2.88 g (25.16 mmol) of 1-propenyltrimethylsilane16 (Z/E = 70/30) was reacted with 1.8 g (25.16 mmol) of acetyl chloride in 20 mL of dichloromethane in the presence of 5 mol % of the system $BiCl_3-1.5\ ZnI_2$. After 6 h the suspension turned to brown and NMR analysis of an aliquot of the reaction mixture revealed that only 40% of the starting vinylsilane was reacted. Then, 3 g (25.16 mmol) of chloroform was added and the absolute yield of 3-penten-2-one formed was determined (yield 16%). This compound was accompanied by heavy unidentified products. A control experiment with a mixture of 3-penten-2-one, acetyl chloride, and (TMS)Cl (1/1/1) and 5 mol % of $BiCl_3-1.5\ ZnI_2$ in dichloromethane gave after 6 h the same complex mixture accompanied by the disparition of the starting ketone.

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