

Direct Deoxygenation of Aryl Ketones Using Gallium(III) Chloride and Chlorodimethylsilane

Jaewoo Choi and Yonghan Kang*

Department of Chemistry and Applied Chemistry, Hanyang University, Ansan, Kyunggi-do 426-791, Korea

*E-mail: yhm kang@hanyang.ac.kr

Received October 25, 2004

Key Words : Direct deoxygenation, Gallium(III) chloride, Chlorodimethylsilane

Generally, reduction of the carbonyl group of aldehyde and ketone to the corresponding methylene derivative can be carried out by chemical methods such as Clemmensen reduction,¹ Wolff-Kishner reduction,² LiAlH₄-AlCl₃,³ NaBH₄-CF₃CO₂H,⁴ Et₃SiH-BF₃ or CF₃CO₂H,⁵⁻⁷ HI-Phosphorus^{8,9} or by catalytic hydrogenation.¹⁰ However, because of their harsh conditions or requirement of using stoichiometric or excess amount of Lewis acid, many of these methods are restricted from the use for compounds containing other functional groups. Recently, the combination of a catalytic amount of InCl₃ and 2 equivalent of Me₂SiClH is reported to be quite effective for deoxygenation of aryl ketones to the corresponding hydrocarbons under mild conditions.¹¹ The combination of hydride donor and Lewis acid was reported as useful synthetic method for the reductive Friedel-Craft alkylation of aromatic compounds with various ketones *via* carbocation intermediate.¹² Direct deoxygenation of ketones was carried out by the reaction of carbocation intermediate with hydride.

Elements which belong to the same group in the Periodic table revealed the same chemical reactivity. We paid attention to the reactivity of gallium which belongs to the same group as boron, aluminum, and indium. However, there had been only few examples of synthetic reaction using gallium compounds.^{13,14} In this paper, we report on the gallium(III) chloride-mediated direct deoxygenation of aryl ketones with chlorodimethylsilane as a hydride donor.

The analogous reductions of aryl ketones to the corresponding methylenes by using chlorodimethylsilane with gallium(III) chloride as Lewis acid instead of indium(III) chloride were investigated.

General procedure is as the following. Gallium(III) chloride was dissolved in CH₂Cl₂ dried over CaCl₂ to prepare a 0.1 M solution. Aryl ketone (2.0 mmol) in CH₂Cl₂ (1 mL) was added dropwise to a mixture of gallium(III) chloride (1 or 5 mol%) and chlorodimethylsilane (4.8 mmol) in CH₂Cl₂ (2 mL) at ambient temperature under nitrogen atmosphere. In some cases, aryl ketone was added dropwise under ice cooling (Table 1). After completion of the reaction, the reaction mixture was washed with water. The organic layer was separated and dried over MgSO₄. The filtrate was evaporated to the dryness. The yield of desired product was acquired by GC analysis [25 m OV-1701 silica capillary column, temperature programmed 50 °C (1 min hold) to 280

°C (3 min hold) at a rate of 25 °C/min, helium flow rate 30 mL/min] and the structure of isolated product was confirmed by ¹H NMR spectrum.

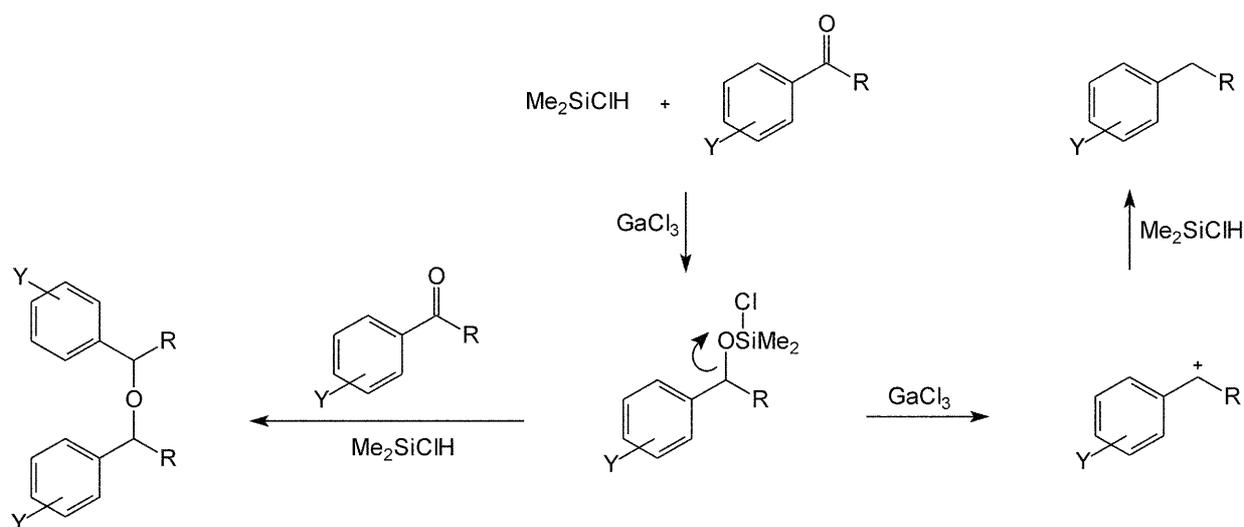
Under the above conditions, direct deoxygenation reactions of various carbonyl compounds with gallium(III) chloride and chlorodimethylsilane were carried out. The obtained results are as shown in Table 1.

In accordance with the proposal by Akio Baba and his co-workers,¹² a plausible mechanism is shown in Scheme 1, which has three steps; hydrosilylation of carbonyl group, generation of the carbocation by desiloxylation, and reaction of carbocation with hydride derived from excess chlorodi-

Table 1. Direct deoxygenation of various aryl ketones using the combination of chlorodimethylsilane and gallium(III) chloride

Run	R	Y	Reaction Temp	Time/min	Yield/%
1	1a CH ₃	H	0 °C	10	2a 99
2	1b CH ₂ CH ₃	H	0 °C	10	2b 94
3	1c CH ₂ CH ₂ CH ₃	H	0 °C	10	2c 79
4	1d CH(CH ₃) ₂	H	rt	10	2d 75
5 ^a	1e Ph	H	rt	30	2e 64
6	1f CH ₃	<i>o</i> -Ph	0 °C	10	2f 72
7	1g CH ₃	<i>m</i> -OCH ₃	rt	5	2h ^{-b}
8	1h CH ₃	<i>p</i> -OCH ₃	rt	60	2g 95
9	1i CH ₃	<i>m</i> -NO ₂	0 °C	10	2j 37 ^c
10 ^a	1j CH ₃	<i>p</i> -NO ₂	0 °C	10	2i 37 ^d
11	1k CH ₃	<i>m</i> -NH ₂	rt	–	No reaction
12	1m CH ₃	<i>p</i> -NH ₂	rt	–	No reaction
13	1n CH ₃	<i>p</i> -CH ₃	rt	10	2n 62
14	1o CH ₃	<i>p</i> -Br	0 °C	10	2o 82
15 ^a	1p 3,4-Dihydro-1(2 <i>H</i>)-naphthalenone		rt	60	2p 78
16	1q Methyl 1-naphthyl ketone		0 °C	10	2q 90
17	1r 2-Methoxy-2-phenylacetophenone		rt	10	2r 88

^a5 mol% of GaCl₃ was used. ^bInseparable many products were obtained. ^c28% of (1-Methyl)-*m*-nitrobenzyl ether was obtained. ^d9% of (1-Methyl)-*p*-nitrobenzyl ether was obtained.



Scheme 1

methylsilane.

In this study, we found that the combination of gallium(III) chloride and chlorodimethylsilane is more effective for the deoxygenation of aryl ketones to the corresponding methylene compounds than the combination of indium(III) chloride and chlorodimethylsilane. In most cases, the reaction was over within 10 min and the direct deoxygenation by using gallium(III) chloride proceeded faster than using indium(III) chloride. Direct deoxygenation using indium(III) chloride for the aryl ketones took at least 1 hour for the completion of the reaction.¹¹ Furthermore, aryl ketones were deoxygenated to the corresponding hydrocarbons by using lower concentrations of gallium(III) chloride (1-5 mol%) than those of indium(III) chloride (5-10 mol%). Thus, we assumed that gallium(III) chloride was more effective and powerful in producing a carbocation intermediate from an alcohol than indium(III) chloride.

The reduction of acetophenone (**1a**), propiophenone (**1b**), butyrophenone (**1c**), and isobutyrophenone (**1d**) provided the corresponding methylenes (**2a-d**) in good yields (run 1-4). However, the yields of isolated methylene compounds were inversely proportional to the length of the acyl side chain of aryl ketones.

The relatively slow reaction rates for benzophenone (**1e**, run 5) and *p*-methoxy-acetophenone (**1h**, run 8) were observed. It was considered that the resonance effects with two phenyl groups of **1e** and the presence of *para*-substituted electron-donating group of **1h** appeared to hinder the reduction by increasing the electron density of carbonyl group. On the other hand, *m*- or *p*-nitroacetophenone (**1i** and **1j**, run 9 and 10) was reduced to the corresponding hydrocarbon with poor yields and inseparable by-products due to the decomposition of unstable intermediate. Furthermore, from the reduction of **1i** and **1j**, the corresponding dimerized ethers, (1-methyl)-*m*-nitrobenzyl ether and (1-methyl)-*p*-nitrobenzyl ether were isolated in 28% and 9%

yield, respectively. It was assumed that the formation of carbocation was difficult by electron-withdrawing character of the nitro group.

m- or *p*-Aminoacetophenone (**1k** and **1m**, run 11 and 12) provided no reaction under the conditions mentioned above because of the formation of the complex between gallium(III) chloride and amino group.

In conclusion, we have found that the direct deoxygenation of aryl ketone using GaCl₃ as a Lewis acid and chlorodimethylsilane as a hydride donor proceeded effectively under mild conditions.

Acknowledgements. This work was supported by the research fund of Hanyang University (HY-2002-I).

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