

# Gallium Dichloride-Mediated Reductive Friedel-Crafts Reaction

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**Abstract:** In the presence of gallium dichloride, the reaction of carbonyl compounds or their dimethylacetals with aromatic compounds afforded Friedel-Crafts alkylated adducts in good yields. It was suggested that the adducts were obtained by way of a reduction of the carbonyl compounds or their dimethylacetals, followed by the Friedel-Crafts reaction in one-pot. This is the first organic synthetic method with gallium dichloride, low valent gallium.

## INTRODUCTION

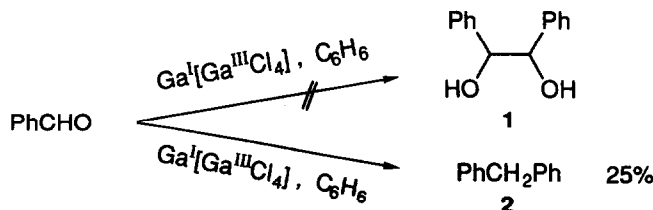
In the field of synthetic organic chemistry, boron, aluminum and thallium are very useful elements, and much attention has been focused on the development of synthetic methodologies utilizing these elements. However, there have been only a few examples of synthetic reactions using gallium which belongs to the same group.<sup>3,4)</sup> For some reasons, gallium is a scarce and expensive material, and the prominent features of gallium compounds for synthetic use have remained unknown until recently.

In a previous paper, we paid attention to the softness of gallium, compared with boron and aluminum, and reported on the gallium(III) chloride-mediated hydrolysis and allylation reaction of dithioacetals.<sup>3)</sup> During the course of our synthetic study utilizing gallium compounds, we have been interested in developing a synthetic methodology by using gallium dichloride, a low valent compound of the IIIA group.<sup>5)</sup> It is known that gallium dichloride is a double salt, comprising univalent and trivalent gallium.<sup>6)</sup> Due to its unique character, gallium dichloride would make it possible to realize a novel type of reaction, which would be difficult to proceed by activation with conventional reagents, if we can take advantage of the reducing ability of univalent gallium and the Lewis acidity of trivalent gallium.

In this paper we report on the gallium dichloride-mediated reductive Friedel-Crafts reaction of carbonyl compounds or their dimethylacetals with aromatic compounds.<sup>7)</sup>

## RESULTS AND DISCUSSION

At first, we paid attention to the reducing ability of gallium dichloride; the reductive dimerization of an



Scheme 1.

aldehyde was examined. Upon the treatment of benzaldehyde with gallium dichloride in benzene at room temperature, the system resulted in the formation of a very complex mixture; the desired diol **1** was not obtained at all. However, diphenylmethane (**2**) was formed in 25% yield (Scheme 1). This unexpected compound was considered to arise from a reductive Friedel-Crafts reaction between benzaldehyde and benzene, which was used as the solvent for a stock solution of gallium dichloride (and the reaction solvent in this case).<sup>8)</sup> We took notice of this phenomenon and thoroughly investigated the reaction using anisole and benzaldehyde as typical substances for this reductive Friedel-Crafts reaction.

When a mixture of benzaldehyde and anisole was treated with gallium dichloride in benzene at room temperature, the desired products, *p*- and *o*-benzylanisoles **3**, were obtained in 19 and 25% yields, respectively. In addition, diphenylmethane (**2**), an undesired by-product in this case, was also obtained in 30% yield (Table 1, run 1). Since the formation of diphenylmethane could be attributable to a large quantity of benzene in the reaction system, we additionally investigated this reaction in various solvents in the presence

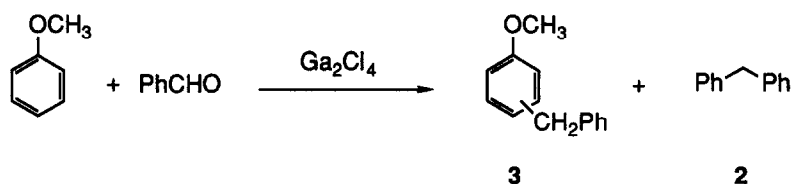


Table 1. Investigation of the Optimized Conditions: Effect of the Solvent and Temperature

run	solvent	method <sup>a</sup>	temp.	time (h)	<b>3</b>		<b>2</b>
					yield (%) <sup>b</sup>	<i>para</i> : <i>ortho</i>	
1	C <sub>6</sub> H <sub>6</sub>	A	r.t.	24	44	43 : 57	30
2	CH <sub>3</sub> CN	A	r.t.	24	0	—	0
3	Et <sub>2</sub> O	A	r.t.	91	22	73 : 27	trace
4	CH <sub>3</sub> NO <sub>2</sub>	B	r.t.	24	0	—	0
5	CS <sub>2</sub>	A	r.t.	45	59	51 : 49	7
6		B	reflux	12	69	36 : 64	0
7		B	r.t.	24	73	42 : 58	0
8		B	0 °C	72	77	44 : 56	0
9		B	-40 to -23 °C	62	28	32 : 68	0
10	CH <sub>2</sub> Cl <sub>2</sub>	A	r.t.	24	44	39 : 61	12
11		B	0 °C	24	53	30 : 70	0
12	CHCl <sub>3</sub>	B	0 °C	48	46	39 : 61	0
13	CICH <sub>2</sub> CH <sub>2</sub> Cl	B	0 °C	48	70	33 : 67	0
14	Cl <sub>2</sub> CHCHCl <sub>2</sub>	B	0 °C	48	75	27 : 73	0

<sup>a</sup> Method A: A mixture of five equimolar amounts of anisole and an equimolar amount of benzaldehyde in a solvent was treated with two equimolar amounts of gallium dichloride in benzene. Method B: After benzene was removed from a benzene solution of two equimolar amounts of gallium dichloride, solutions of five equimolar amounts of anisole and an equimolar amount of benzaldehyde were successively added. <sup>b</sup> Isolated yield.

of a minimum quantity of benzene, which arose from the solvent for a stock solution of gallium dichloride (Table 1, Method A). Except for acetonitrile (Table 1, run 2), which is reactive toward gallium dichloride and, accordingly, no Friedel-Crafts reaction occurred in this solvent, diphenylmethane (2) was also formed more or less (Table 1, runs 3, 5 and 10). In order to suppress the formation of this by-product, a strict removal of benzene would be desirable.

According to this consideration, after removing benzene thoroughly from a benzene solution of two equimolar amounts of gallium dichloride by heating at 80 °C under reduced pressure, the reaction was carried out in various solvents other than benzene upon adding, successively, solutions of five equimolar amounts of anisole and an equimolar amount of benzaldehyde. The reaction was then quenched with 2 mol dm<sup>-3</sup> aqueous sodium hydroxide (Table 1, Method B). By this method, diphenylmethane became undetectable in all of the runs. Among the solvents examined, the highest yield was achieved in carbon disulfide at 0 °C (Table 1, run 8). The reactions in dichloromethane, 1,2-dichloroethane, and 1,1,2,2-tetrachloroethane resulted in a relatively high ratio of the *ortho*-substituted product, although the yield was slightly depressed (Table 1, runs 11, 13 and 14).<sup>9</sup> The temperature effect was also examined by using carbon disulfide as a solvent (Table 1, runs 6–9). Below 0 °C, the reaction was much slower; accordingly, in this case a reaction performed at 0 °C gave the best result. However, the appropriate reaction temperature varied with the combination of reactants (*vide infra*).

Under the above optimized conditions, a reductive Friedel-Crafts reaction of various carbonyl compounds with anisole was carried out. The results are given in Tables 2 and 3.

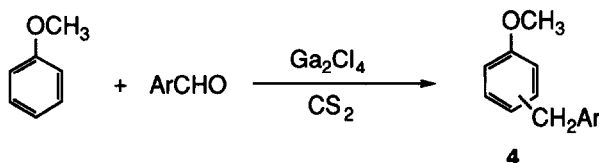


Table 2. Reductive Friedel-Crafts Reaction of Aromatic Aldehydes with Anisole<sup>a</sup>

run	ArCHO	temp.	time (h)	yield (%) <sup>b</sup>	<i>para</i> : <i>ortho</i>
1	<chem>c1ccccc1C=O</chem>	0 °C	72	77	44 : 56
2	<chem>Cc1ccc(C=O)cc1</chem>	0 °C	120	67	82 : 18
3	<chem>COc1ccc(C=O)cc1</chem>	r.t.	48	47	89 : 11
4	<chem>Clc1ccc(C=O)cc1</chem>	0 °C	96	72	50 : 50
5	<chem>O=C1C=CC2=CC=CC=C12</chem>	reflux	27	73	84 : 16

<sup>a</sup> Molar ratio; anisole : aromatic aldehyde : gallium dichloride = 5 : 1 : 2. <sup>b</sup> Isolated yield.

Each carbonyl compound reacted smoothly with anisole to afford the corresponding adduct in moderate to good yields. When aromatic aldehydes were used as electrophiles (Table 2), the ratio of the *para* products tended to increase with increasing electron-donating character of the substituent at the *para* position of benzaldehyde. Similar to the result for the usual Friedel-Crafts reaction between anisole and substituted benzyl chlorides,<sup>10</sup> it is considered that anisole is more preferentially alkylated at the thermodynamically stable *para* position with a benzaldehyde derivative having an electron-donating *para*-substituent, which stabilizes the intermediate benzylic cation. The relatively slow reaction rate for *p*-anisaldehyde is also explained on the basis of the stability of the intermediate benzylic cation.

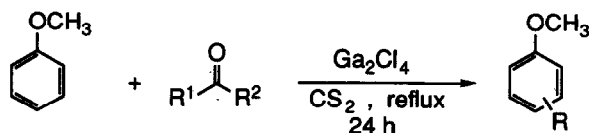


Table 3. Reductive Friedel-Crafts Reaction of Carbonyl Compounds with Anisole<sup>a</sup>

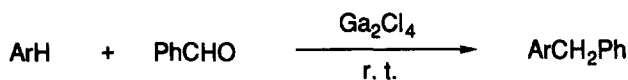
run		yield (%) <sup>b</sup>	<i>para</i> : <i>ortho</i>	main product
1		15	100 : 0	
2		72	29 : 71	
3		81	100 : 0	
4		66	100 : 0	7
5		41	39 : 61	

<sup>a</sup> Molar ratio; anisole : carbonyl compound : gallium dichloride = 5 : 1 : 2. <sup>b</sup> Isolated yield.

When acetophenone was employed as an electrophile instead of an aromatic aldehyde, the yield was poor due to the formation of complex by-products arising from its high enolizability (Table 3, run 1). In the cases of the reactions with aliphatic ketones or aldehydes, the reactions were found to proceed readily as well, though somewhat vigorous reaction conditions were required (carbon disulfide, reflux).

It should be particularly noted that unexpected adducts having a rearranged carbon framework, 7 and 8, were formed (Table 3, runs 3, 4 and 5). The formation of these products can be rationalized by a reduction-electrophilic substitution mechanism (*vide infra*).

In the next stage we carried out this reaction using various aromatic compounds other than anisole as nucleophiles for the purpose of further synthetic exploration (Table 4). The treatment of 1,3-dimethoxybenzene with benzaldehyde in carbon disulfide in the presence of gallium dichloride afforded the

Table 4. Reductive Friedel–Crafts Reaction of Benzaldehyde with Various Aromatic Compounds<sup>a</sup>

run	ArH	solvent	additive	time (h)	yield <sup>b</sup>	main product
1 <sup>c</sup>		CS <sub>2</sub>	none	86	65	 <b>9</b> + <b>10</b> <b>9 : 10 = 98 : 2<sup>d</sup></b>
2	benzene	CS <sub>2</sub>	none	48	21	<b>2</b>
3		benzene	none	24	25	<b>2</b>
4		benzene	iPr <sub>2</sub> O	52	53	<b>2</b>
5	toluene	CS <sub>2</sub>	none	42	22	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Ph <b>11</b> ( <i>para</i> : <i>ortho</i> = 73 : 27 <sup>e</sup> )
6		toluene	iPr <sub>2</sub> O	72	46	<b>11</b> ( <i>para</i> : <i>ortho</i> = 81 : 19 <sup>e</sup> )
7	mesitylene	CS <sub>2</sub>	none	69	31	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> CH <sub>2</sub> Ph <b>12</b>
8		mesitylene	iPr <sub>2</sub> O	72	50	<b>12</b>

<sup>a</sup> Molar ratio; aromatic compound : benzaldehyde : gallium dichloride = 5 : 1 : 2 (runs 1, 2, 5, and 7). Benzaldehyde : gallium dichloride = 1 : 2, benzene (nucleophile) was used as a solvent (run 3). Diisopropyl ether : benzaldehyde : gallium dichloride = 5 : 1 : 2, alkylated benzene (nucleophile) was used as a solvent (runs 4, 6, and 8). <sup>b</sup> Isolated yield. <sup>c</sup> The reaction was performed at 0 °C. <sup>d</sup> Molar ratio. <sup>e</sup> Determined by GC.

corresponding adduct **9**, accompanied by a small amount of di-substituted adduct **10** (Table 4, run 1). Moreover, the reaction of benzene or alkylated benzenes gave the desired products, although the yields were somewhat low, due to the formation of complex by-products. This phenomenon was considered to be attributable to the stronger acidity of this reaction system than that of the reaction system for anisole or dimethoxybenzene, because of the lack of ether oxygen(s) as a Lewis base. On the basis this consideration, the reaction of benzene with benzaldehyde was carried out in the presence of various Lewis bases, such as ethers, sulfides and amides; as a result, the highest yield was achieved when five equimolar amounts of diisopropyl ether were added (compare runs 3 and 4 in Table 4). This result and the very sluggish reaction in diethyl ether (Table 1, run 3) suggest that the reaction is highly governed by the acidity of the reaction system.

Though it is well known that the reductive dimerization of carbonyl compounds and related reactions can be mediated by a low valent metallic compound,<sup>11)</sup> acetals, protected carbonyl compounds, are normally stable toward such a reductant.<sup>12)</sup> However, in a gallium dichloride-mediated reaction, the strong acidity of gallium dichloride is expected to enable acetals to react in the same way as carbonyl compounds. In this

context, dimethylacetals were next submitted to a reaction with anisole. As a result, various dimethylacetals were found to react smoothly with anisole to give the corresponding adducts in relatively good yields (Table 5). The structures of the adducts were the same as those obtained by a reaction with the corresponding carbonyl compounds. However, because of the Lewis basicity of the acetal oxygens, the use of three equimolar amounts of gallium dichloride was suitable for the reproducibility.

When dimethylacetals of benzaldehyde derivatives were used as electrophiles, the relationship between the *para* substituent and the *para/ortho* ratio of the product, as well as the reactivity, was similar to that of the reaction using benzaldehyde derivatives.

Though the product was obtained in moderate yield in a reaction of octanal with anisole (Table 3, run 5), no reaction proceeded with its dimethylacetal (Table 5, run 8). On the contrary, when dimethylacetals of cyclohexanone derivatives were employed, the reaction smoothly proceeded to afford cyclohexylanisole

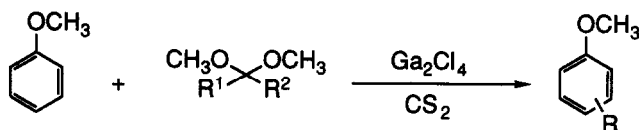


Table 5. Reductive Friedel-Crafts Reaction of Dimethylacetals with Anisole<sup>a</sup>

run	acetal	temp.	time (h)	yield <sup>b</sup> (%)	<i>para</i> : <i>ortho</i>	main product
1		r.t.	24	81	48 : 52	<b>3</b>
2		r.t.	24	83	79 : 21	
3		0 °C	48	66	89 : 11	<b>13</b> (X=OCH <sub>3</sub> )
4		r.t.	24	81	57 : 43	<b>13</b> (X=Cl)
5		r.t.	48	67	28 : 72	<b>6</b>
6		r.t.	24	84	100 : 0	<b>7</b>
7		reflux	24	58	100 : 0	<b>7</b>
8		reflux	48	0	—	

<sup>a</sup> Molar ratio; anisole : dimethylacetal : gallium dichloride = 5 : 1 : 3. <sup>b</sup> Isolated yield.

derivatives **6** and **7** under milder conditions than those for the reaction of cyclohexanone derivatives (Table 5, runs 5 and 6).

The reaction of alkylated benzenes with benzaldehyde dimethylacetal should be noted (Table 6); without any additive, the reaction proceeded smoothly to give the benzylated products in much better yields than the reaction with benzaldehyde, itself. The presence of an acetal function would result in the adequate acidity of the reaction system and would lead to smooth progress of the reaction. As a result, in cases using alkylated benzenes as nucleophiles, dimethylacetals were found to be more potent electrophiles than the corresponding carbonyl compounds.

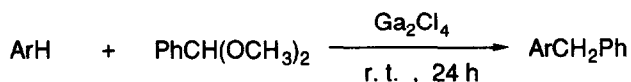
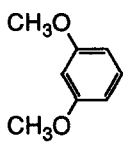


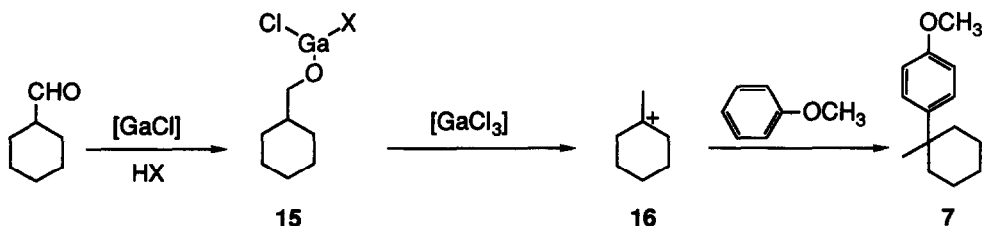
Table 6. Reductive Friedel-Crafts Reaction of Benzaldehyde Dimethylacetal with Various Aromatic Compounds<sup>a</sup>

run	ArH	solvent	yield (%) <sup>b</sup>	main product
1		CS <sub>2</sub>	74	<b>9 + 10</b> <b>9 : 10 = 84 : 16<sup>c</sup></b>
2	benzene	CS <sub>2</sub>	10	<b>2</b>
3		benzene	46	<b>2</b>
4	toluene	CS <sub>2</sub>	54	<b>11 (para : ortho = 76 : 24<sup>d</sup>)</b>
5		toluene	71	<b>11 (para : ortho = 77 : 23<sup>d</sup>)</b>
6	<i>p</i> -xylene	CS <sub>2</sub>	60	<b>2,5-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>Ph</b> <b>14</b>
7		<i>p</i> -xylene	82	<b>14</b>
8	mesitylene	CS <sub>2</sub>	58	<b>12</b>
9		mesitylene	61	<b>12</b>

<sup>a</sup> Molar ratio; aromatic compound : benzaldehyde dimethylacetal : gallium dichloride = 5 : 1 : 3, alkylated benzene (nucleophile) was used as a solvent in runs 3, 5, 7, and 9. <sup>b</sup> Isolated yield. <sup>c</sup> Molar ratio. <sup>d</sup> Determined by GC.

In summary, the present gallium dichloride-mediated reductive Friedel-Crafts reaction has the following characteristic features: 1) In the reaction of benzaldehyde derivatives, benzylated products are obtained, and the behavior resembles that of the normal Friedel-Crafts benzylation reaction.<sup>10)</sup> 2) However, in some cases, the *ortho*-substituted derivatives can be obtained in marvelous yields.<sup>13)</sup> 3) When carbonyl compounds having  $\alpha$ -proton(s) are applied to this reaction, carbon-carbon bond formation occurs at the neighboring, most-branching site to give products having a rearranged carbon framework. 4) Dimethylacetals are also applicable in this reaction.

Taking into account the above-mentioned features, the reaction mechanism is considered to be as shown in Scheme 2. The reduction of cyclohexanecarbaldehyde, for instance, occurs at first due to the actions of univalent gallium and a proton donor, which would originate from atmospheric moisture and would slightly contaminate the reaction system, to afford the corresponding gallium(III) alkoxide **15**. Then, the alkoxide is converted into tertiary carbocation **16** via a primary carbocation generated through a trivalent gallium-mediated elimination of the metaloxy group. Finally, **16** reacts with anisole to give alkylated anisole **7**. If carbonyl compounds have no proton at the carbonyl  $\alpha$  position, such as benzaldehyde and its derivatives, benzylic cations are generated without a rearrangement. The reaction using dimethylacetals as electrophiles is also considered to proceed in a similar manner as that mentioned above.



Scheme 2.

In conclusion, we achieved a reductive Friedel-Crafts alkylation using gallium dichloride, a novel Lewis acidic reducing agent. It is very interesting that Friedel-Crafts alkylated adducts are obtained in one-pot, even though electrophiles are carbonyl compounds or their dimethylacetals. This is the first organic synthetic method with low valent gallium.

## EXPERIMENTAL SECTION

**General.** The  $^1\text{H}$  NMR spectra were measured on a JEOL PMX-60SI or GX-400 instrument, using tetramethylsilane as an internal standard.  $\text{CDCl}_3$  was used as the solvent. Infrared spectra were recorded on a Jasco IR-810 spectrophotometer. GC analyses were performed with a 25-m OV-1701 fused silica capillary column. A High-resolution mass spectrum was recorded at an ionization potential of 70 eV with a JEOL JMS-AX505H instrument.

Preparative thin-layer chromatography (TLC) was performed on a silica gel (Wakogel B-5F). Benzene was dried with  $\text{CaCl}_2$ , distilled from sodium wire then from  $\text{LiAlH}_4$ , and stored over sodium. Toluene and mesitylene were dried with  $\text{CaCl}_2$ , distilled from  $\text{P}_2\text{O}_5$ , and stored over sodium. Carbon disulfide was dried with  $\text{CaCl}_2$ , distilled from  $\text{P}_2\text{O}_5$ , and stored over Molecular Sieves 4A.

All of the carbonyl compounds are commercially available. The carbonyl compounds were distilled under atmospheric or reduced pressure before use. Dimethylacetals were prepared by a procedure given in the literature with a slight modification.<sup>14)</sup>

**Preparation of Gallium Dichloride.** Gallium dichloride was prepared according to a method described in the literature<sup>15)</sup> with a slight modification. In a 30 ml, two-necked, round-bottomed flask were charged 0.96 g (14 mmol) of metallic gallium and 8.55 g (49 mmol) of gallium(III) chloride. Under an argon atmosphere, the mixture was heated at 200  $^\circ\text{C}$  for 3 days. During this operation, metallic gallium was dissolved into liquidified gallium(III) chloride. Excess gallium(III) chloride was distilled off, and the residue was dissolved in dry benzene (freshly distilled from  $\text{LiAlH}_4$ ). The concentration of the gallium dichloride solution (20 ml) was determined by iodometry (0.98 mol  $\text{dm}^{-3}$ , 93%).

**General Procedure for the Reductive Friedel-Crafts Reaction of Carbonyl Compounds with Aromatics.** Benzene was removed from a benzene solution containing gallium dichloride (1.34 mmol) upon heating at 80  $^\circ\text{C}$  for 1 h under reduced pressure. Then, a solution of anisole (3.35 mmol) in  $\text{CS}_2$  (2 ml) and a



solution of a carbonyl compound (0.67 mmol) in CS<sub>2</sub> (2 ml) were successively added under an argon atmosphere. Stirring was continued until completion of the reaction (24 – 120 h, checked by TLC) at the temperature indicated in the Tables in the text. The reaction was quenched by adding 2 mol dm<sup>-3</sup> aqueous sodium hydroxide (20 ml), and stirring was continued for 3 h at room temperature. Then, the organic layer was separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 2 ml). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvents were removed under reduced pressure. The residue was purified by preparative TLC to afford the product.

All of the products, except for 1-methoxy-2-(1-methylheptyl)benzene, are known compounds and were characterized by a comparison of their spectral data with those of authentic samples prepared or those from the literature.

**1-Methoxy-2-(1-methylheptyl)benzene.** IR (neat): 2930, 1490, 1240, 1030, 750 cm<sup>-1</sup>. <sup>1</sup>H NMR: δ 0.86 (3H, t, *J* = 6.9 Hz), 1.18 (3H, d, *J* = 6.9 Hz), 1.18-1.31 (8H, m), 1.46-1.54 (1H, m), 1.55-1.64 (1H, m), 3.17 (1H, sextet, *J* = 6.9 Hz), 3.81 (3H, s), 6.84 (1H, d, *J* = 8.2 Hz), 6.92 (1H, td, *J* = 7.5, 1.0 Hz), 7.12-7.17 (2H, m). HRMS: calcd for C<sub>15</sub>H<sub>24</sub>O 220.1827, found 220.1847.

**General Procedure for the Reductive Friedel-Crafts Reaction of Dimethylacetals with Aromatics.** The procedure was the same as that for the reaction of carbonyl compounds with aromatics, except that three equimolar amounts of gallium dichloride were employed.

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- 9) The reason is not clear at present. However, the result would be explained as follows: A benzylic cation, generated from a benzaldehyde derivative may easily approach to the *ortho* position near to the oxygen atom of anisole, where gallium dichloride would coordinate, since it is not so strongly solvated in such a halogenated hydrocarbon.

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