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Tetrahydrofuran Ring Opening with Acyl Chlorides or Anhydrides Catalyzed by Gallium Triiodides: A Novel and Facile Method for the Preparation of Iodo Esters

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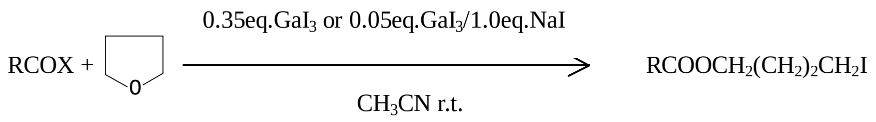
Abstract: Tetrahydrofuran ring can be opened with acyl chlorides or anhydrides catalyzed by gallium triiodides to afford iodo esters under mild conditions in good yields.

Keywords: Tetrahydrofuran ring, acyl chloride, anhydride, gallium triiodides.

Recently gallium and its compounds are gradually attracting attention as useful reagents in organic synthesis[1-7]. Gallium enolate-mediated intermolecular aldol reaction and addition reaction of α-bromoketone with imine, a straightforward and versatile preparation of propargylic alcohols from 1-alkynes and aldehydes *via* GaI_3 and amine have been documented[3]. Kobayashi reported that gallium reagents could efficiently promote the glycosidation of glycopyranosyl fluorides[4]. The reaction of alkyne with aldehyde being carried out to produce conjugated enones in the presence of GaI_3-NBu_3 in CH_2Cl_2[5]. Ga/$PbCl_2$ bimetal redox system-mediated carbon-carbon bond formation reactions between carbonyl compounds and ethyl trichloroacetate or iodoacetonitrile[6], and gallium-mediated highly regioselective reactions of trimethylsilylpropargyl bromide and trimethylsilylally bromide with carbonyl compounds[7] are known. We have also reported gallium mediated allylation and propargylation of 1-(α-aminoalkyl) benzotriazole[8]. All those reactions above indicated that the scope of utility of gallium reagents in organic chemistry would be broad.

Tetrahydrofuran ring opening with acid chlorides promoted by NaI has been reported previously necessitating long reaction time (21-46 h)[9]. Using iodine only as a catalyst, tetrahydrofuran ring opening with acid chlorides did not occur. Our previous work of tetrahydrofuran ring opening with acid chlorides catalyzed by samarium triiodides has been reported[10]. Here we wish to report that gallium triiodide, which are considered as hard Lewis acid to catalyze the tetrahydrofuran ring opening reaction with acyl chlorides or anhydrides affording the corresponding 4-iodo esters under mild conditions with good yields. (**Scheme 1**)

Scheme 1



Two methods of GaI_3 catalyzed reactions were carried out: (A) 0.35 equivalent of GaI_3 was added in the reaction. (B) 0.05 equivalent of GaI_3 and 1.0 equivalent of NaI were added in the reaction. The results were summarized in **Table 1**.

Table 1 Tetrahydrofuran ring opening with acyl chlorides or anhydrides catalyzed by gallium triiodide

Entry	Method	R	X	Product	Reaction Time (h)	Yield* (%)
1	A	CH_3	Cl	$CH_3COO(CH_2)_4I$	1	89
2	B	CH_3	Cl	$CH_3COO(CH_2)_4I$	1	78
3	B	CH_3	Cl	$CH_3COO(CH_2)_4I$	3	81
4	A	CH_3	$OCOCH_3$	$CH_3COO(CH_2)_4I$	1	85
5	A	$CH_3\ CH_2$	Cl	$CH_3CH_2COO(CH_2)_4I$	1	87
6	B	$CH_3\ CH_2$	Cl	$CH_3CH_2COO(CH_2)_4I$	1	81
7	A	Ph	Cl	$PhCOO(CH_2)_4I$	2	76
8	B	Ph	Cl	$PhCOO(CH_2)_4I$	2	70
9	A	Ph	OCOPh	$PhCOO(CH_2)_4I$	2	74
10	B	Ph	OCOPh	$PhCOO(CH_2)_4I$	2	71
11	A	$CH_3\ CH_2\ CH_2$	Cl	$CH_3CH_2CH_2COO(CH_2)_4I$	1	87
12	A	$CH_3\ CH_2\ CH_2$	$OCO(CH_2)_2CH_3$	$CH_3CH_2CH_2COO(CH_2)_4I$	1	85
13	A	$CH_3(CH_2)_{10}$	Cl	$CH_3(CH_2)_{10}COO(CH_2)_4I$	1	85
14	B	$CH_3(CH_2)_{10}$	Cl	$CH_3(CH_2)_{10}COO(CH_2)_4I$	1	81
15	A	$p\text{-}ClC_6H_4$	Cl	$p\text{-}ClC_6H_4COO(CH_2)_4I$	2	69

A. A molar ratio of 1︰0.35 substrate/GaI_3 was used.
B. A molar ratio of 1︰0.05︰1.0 substrate/GaI_3/NaI was used.
* Isolated yield.

The result of our experiment indicated that tetrahydrofuran ring could be opened with either acyl chlorides or anhydrides catalyzed by gallium triiodides. Smaller amounts of catalyst (0.05 equivalent of GaI_3) afford lower yield products even after extended reaction time (entries 2 and 3)

In conclusion, it has been found that the hard Lewis acid character of gallium triiodide could be in action in tetrahydrofuran ring opening. The present work also provides a new and facile method for the preparation of iodo esters. The notable advantages of this methodology are mild conditions, short reaction time, simple operation and good yields. It is a new application of gallium reagent in organic synthesis.

Experimental

^1H NMR spectra were recorded on a JEOL PMX 60 SI instrument in CCl_4 solution using TMS as internal standard. IR spectra were determined on a Perkin-Elmer 683 spectrometer. MS spectra were obtained on a Finnigen MAT GC-MS mass spectrometer. Metallic gallium and other chemicals were purchased from commercial sources and used without purification. CH_3CN was freshly distilled prior to use.

General Procedure of Method A——Under a nitrogen atmosphere, metallic gallium bar (0.7 mmol), iodine (1.05 mmol) and acetonitrile (10 ml) were added in a three-necked reaction flask, the mixture was stirred at room temperature until the color of iodine disappeared completely, then tetrahydrofuran (2 mmol) and acyl chloride or anhydride (2 mmol) were added. The resulting solution was stirred at room temperature for a given time (**Table 1**). A dilute solution of HCl was added into the solution and the resulting mixture was stirred for a few minutes. The mixture was extracted with ether (20 ml×2). The organic layer was washed with aqueous sodium thiosulfate and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*. The residue was then purified by preparative TLC on silica gel with cyclohexane and ethyl acetate as eluent to give pure product.

General Procedure of Method B——Under a nitrogen atmosphere, metallic gallium bar (0.1 mmol) iodine (0.15 mmol) and acetonitrile (10 ml) were added in a three-necked reaction flask, the mixture was stirred at room temperature until the color of iodine disappeared completely, then NaI (2.0 mmol), tetrahydrofuran (2 mmol) and acyl chloride or anhydride (2 mmol) were added at room temperature. Then the reaction mixture was worked-up just like that described in method A.

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