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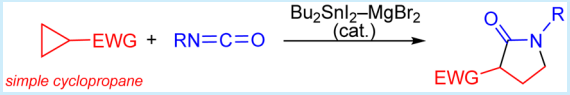
Catalytic [3 + 2] Cycloaddition through Ring Cleavage of Simple Cyclopropanes with Isocyanates

Shinji Tsunoi, Yoshiaki Maruoka, Itaru Suzuki, and Ikuya Shibata*

Research Center for Environmental Preservation, Osaka University, 2-4 Yamadaoka, Suita, Osaka 565-0871, Japan

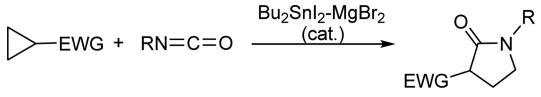
Supporting Information

ABSTRACT: The catalytic synthesis of γ-butyrolactams was established via [3 + 2]-cycloaddition of cyclopropanes with isocyanates. An organotin iodide ate complex, $MgBr^+[Bu_2SnBrI_2]^-$, was employed as an effective catalyst. Simple cyclopropanes that lack aryl or vinyl substituents were useful precursors. Even acyl cyclopropanes were applicable. The hybrid characteristics of a tin complex, acidic $MgBr^+$ with nucleophilic tin iodide, was responsible for the catalytic reaction.



[3 + 2]-Cycloadditions of cyclopropanes have proven to be a powerful strategy for the direct synthesis of five-membered carbo- and heterocycles, and such methodologies have been applied to natural product syntheses.[1] Cycloadditions are typically carried out using catalysts that include a Lewis acid or a transition metal.[2−9] Donor−acceptor (D−A) cyclopropanes with aryl or vinyl substituents have been used as the active precursors in most cases. We established a [3 + 2] cycloaddition using either epoxides or 2-methyleneaziridines with isocyanates and tin iodide catalysts.[10,11] In the case of 2-methyleneaziridines,[10c] the combination of Bu_2SnI_2 with LiI showed high catalytic activity in which an ate type of tin complex such as $Li^+[SnBu_2I_3]^-$ worked as an active catalytic species. Simple cyclopropanes seem to lack utility, but in the present study we developed a tin-catalyzed cycloaddition with isocyanates to form γ-butyrolactams (Scheme 1).[12] γ-

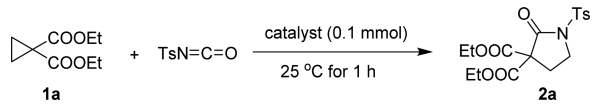
Scheme 1. Cycloadditions of Simple Cyclopropanes with Isocyanates



Butyrolactams could serve as useful building blocks toward natural products and pharmaceutically relevant heterocycles.[13] Hence, the catalytic preparation of γ-butyrolactams from simple cyclopropanes is a desirable result, particularly when using transition-metal-free catalysts.

Initially, we performed the cycloaddition of cyclopropane 1,1-carboxylate ester **1a** with tosyl isocyanate (Table 1). Without a catalyst, no reaction proceeded at 25 °C for 1 h (entry 1). Using 0.1 equiv of Bu_2SnI_2 as a catalyst afforded no reaction (entry 2). Catalytic system Bu_2SnI_2−LiI was effective for the reaction of 2-methyleneaziridines,[10c] but it was not active in cases where starting cyclopropane **1a** and tosyl isocyanate were recovered quantitatively. However, using $MgBr_2$ and MgI_2 as a catalyst gave γ-butyrolactam **2a** in 64% and 60% yield, respectively (entries 3 and 4). Furthermore, in a system that combined Bu_2SnI_2 with $MgBr_2$, product **2a** was

Table 1. Cycloaddition of Cyclopropane 1a with TsN=C=O[a]



entry	catalyst	solvent	yield of **2a**/%
1	none	dichloroethane	0
2	Bu_2SnI_2	dichloroethane	0
3	$MgBr_2$	dichloroethane	64
4	MgI_2	dichloroethane	60
5	Bu_2SnI_2-$MgBr_2$	dichloroethane	>99
6	Bu_2SnI_2-$MgBr_2$	CH_2Cl_2	>99
7	Bu_2SnI_2-$MgBr_2$	THF	60

[a] **1a**, 1 mmol; TsN=C=O, 1 mmol; Bu_2SnI_2, 0.1 mmol; $MgBr_2$, 0.1 mmol; solvent, 1 mL.

obtained in a quantitative yield (entry 5). Dichloromethane and dichloroethane were superior to THF as solvents (entries 5−7).

To date, transition metal or Lewis acid catalyzed cycloaddition with heterocumulenes has been applied only to donor−acceptor (D−A) cyclopropanes.[12] In a reaction with isocyanates, Tsuji et al. reported a cycloaddition of vinyl cyclopropane that was catalyzed via a Pd complex.[12a] In that Pd-catalyzed reaction, the formation of π-allyl palladium species was a key step. Stoltz et al. have reported a Lewis acid catalyzed cycloaddition,[12c] where the reaction passed a 1,3-dipole, which included a stable allylic or benzylic cation. In these methods, using donor−acceptor cyclopropanes was essential for an effective ring cleavage. Among our results, it was noteworthy that cyclopropane **1a** bears only acceptor substituents. Thus, simple cyclopropanes that lack aryl or vinyl substituents proved to be useful precursors.

With respect to our catalytic system, Bu_2SnI_2−$MgBr_2$,[14] we have already achieved the formation of an ate complex, $MgBr^+[Bu_2SnBrI_2]^-$, which works as an active catalyst in the

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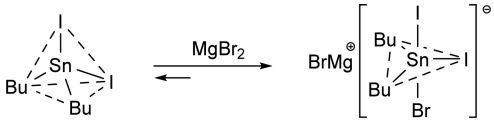
reactions (Scheme 2). When a tin complex, $MgBr^+[Bu_2SnBrI_2]^-$, was reacted with an equimolar amount

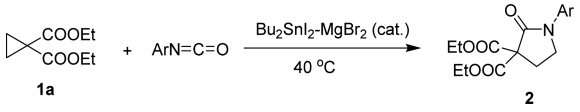
Scheme 2. Ate Tin Iodide Complex



of **1a** at rt for 24 h, a ring-opened adduct, iodoethyl malonate, was formed in a 45% yield, whereas, using only Bu_2SnI_2 or $MgBr_2$ afforded lower yields (<10%) for the ring-opened adduct under the same conditions. The characteristic feature of the tin ate complex is its hybrid makeup, in which both an acidic magnesium cation and a nucleophilic Sn−I bond are included in the same molecule.[14a] Thus, $MgBr^+$ acted as a Lewis acid to activate the dicarboxylate moiety and accelerate the ring opening. Simultaneously, a prolonged Sn−I bond that occupied the axial position in the TBP tin structure[15] attacked the cyclopropane ring in an effective manner. Although a similar catalytic principle of MgI_2 has been reported,[2g,7b−d,8a] the hybrid characteristic of the tin catalyst is one of the reasons for the higher activity than MgI_2 and the accessibility of simple cyclopropanes that lack aryl or vinyl substituents.

Table 2 shows the results of the reaction of cyclopropane **1a** with various isocyanates catalyzed by Bu_2SnI_2−$MgBr_2$ under

Table 2. Cycloaddition of Cyclopropane 1a with ArN═C═O[a]



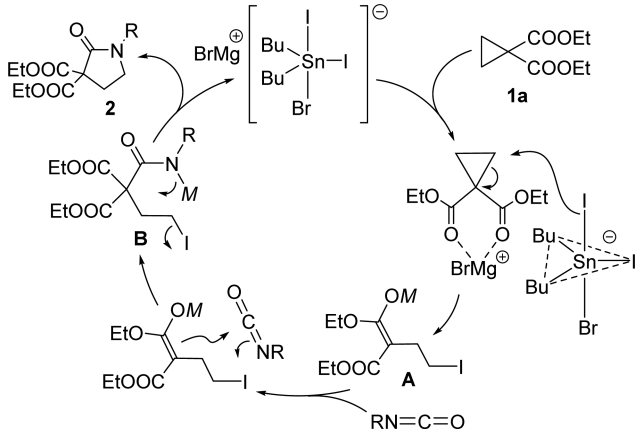
entry	Ar	time/h	product	yield of 2/%
1	C_6H_5	24	**2b**	35[b]
2	*p*-$MeOC_6H_4$	24	**2c**	trace
3	*p*-BrC_6H_4	48	**2d**	53
4	*p*-ClC_6H_4	48	**2e**	78
5	*p*-FC_6H_4	48	**2f**	52
6	*p*-$CF_3C_6H_4$	72	**2g**	66
7	*p*-NCC_6H_4	48	**2h**	76
8	*p*-$NO_2C_6H_4$	24	**2i**	82

[a] **1a**, 1 mmol; ArN═C═O, 1 mmol; Bu_2SnI_2, 0.1 mmol; $MgBr_2$, 0.1 mmol; dichloroethane, 1 mL; 40 °C. [b] 60 °C.

the optimized conditions. The reactivity was dependent upon the substituents of isocyanates. The reaction with PhN═C═O proceeded at 60 °C for 24 h to give product **2b** in a 35% yield (entry 1). When *p*-methoxyphenyl isocyanate (PMPN═C═O) was reacted, the desired product **2c** could not be obtained, and both substrates were recovered quantitatively (entry 2). Other alkyl-substituted isocyanates were unreactive. However, isocyanates with electron-withdrawing substituents were reactive. *p*-Bromophenyl, *p*-chlorophenyl, and *p*-fluorophenyl isocyanates gave the corresponding γ-butyrolactams **2d**−**2f** (entries 3−5). Besides halogen substituents on the aromatic rings, CF_3−, CN groups were also allowed and gave **2g** and **2h** (entries 6 and 7). In particular, the reaction with *p*-nitrophenyl isocyanate gave the desired product **2i** in an 82% yield (entry 8).

A plausible catalytic cycle is shown in Scheme 3. Initially, the tin catalyst attacked **1a** at the C-2 carbon to give a metal ketene

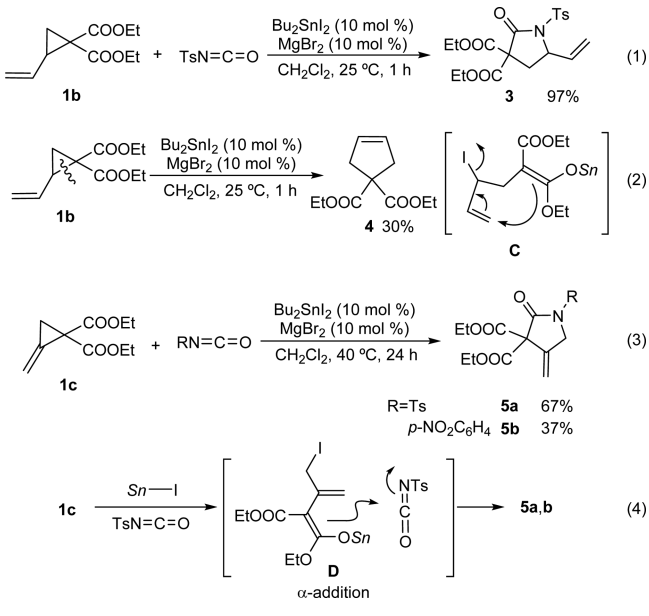
Scheme 3. A Plausible Catalytic Cycle



acetal **A**. The hybrid characteristics of the tin catalyst worked well in the ring opening of cyclopropane. The preference for dichloroethane over THF as a solvent can be explained by the difference in their coordinating ability. A coordinating solvent such as THF would prevent the $MgBr^+$ activation toward **1a**. Dichloroethane did not affect the $MgBr^+$ moiety; hence, the effective activation of the 1,1-carboxylate esters of **1a** is possible. In a subsequent step, metal ketene acetal **A** was added to an isocyanate, giving a tin amide **B**. To make this step effective, the use of highly electrophilic isocyanates was necessary. In the last stage, the intramolecular alkylation of metal amide **B** afforded γ-butyrolactam **2**, regenerating the tin catalyst.

Conventionally useful donor−acceptor cyclopropanes were also applicable in our catalytic system (Scheme 4). In the case of vinylcyclopropane **1b**, the corresponding γ-butyrolactam **3** was obtained when tosyl isocyanate was reacted (eq 1). However, in the reaction with other aromatic isocyanates, no

Scheme 4. Cycloaddition of Active Cyclopropanes with RN═C═O



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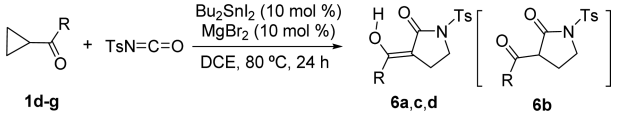
desired products could be isolated. Under the same conditions, without isocyanates, cyclopentene derivative **4** was obtained as a rearrangement product from **1b** through an intramolecular reaction of stannyl ketene acetal **C** to allylic iodide (eq 2).[16] Thus, stannyl ketene acetal **C** reacted with only highly electrophilic tosyl isocyanate prior to the intramolecular reaction. As another activated cyclopropane, methylenecyclopropane **1c** also reacted well to give 4-methylene-γ-butyrolactam **5a** (eq 3). Besides tosyl isocyanate, *p*-nitrophenyl isocyanate was reactive to give **5b**. The ring opening of methylenecyclopropane **1c** afforded tin dienolate **D**. Thus, it is clear that the products, **5a** and **5b**, were derived from the α-addition of the tin dienolate **D**.

One of the advantages of the presented tin-catalyzed reaction is that simple cyclopropanes that lack an aryl or vinyl substituent could be applicable as useful precursors. Hence, we next tried to use other simple cyclopropanes besides **1a**. Fortunately, we found that benzoyl cyclopropane **1d** was useful for the cycloaddition (Table 3). The desired product **6a** was

Table 3. Cycloaddition of Cyclopropanes 1d−g with TsN═C═O[a]



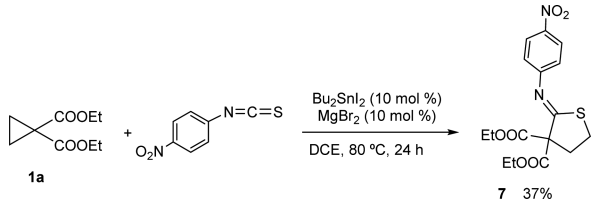
entry	R	conditions	product	yield of **6**/%
1	C_6H_5 (**1d**)	40 °C, 24 h	**6a**	25[b]
2	**1d**	40 °C, 24 h	**6a**	77 (15[c])
3	**1d**	80 °C, 24 h	**6a**	86
4	*p*-$MeOC_6H_4$ (**1e**)	80 °C, 24 h	**6b**	69
5	*p*-ClC_6H_4 (**1f**)	80 °C, 24 h	**6c**	64
6	Me (**1g**)	60 °C, 48 h	**6d**	70

[a]**1a**, 1 mmol; TsN═C═O, 2 mmol; Bu_2SnI_2, 0.1 mmol; $MgBr_2$, 0.1 mmol; dichloroethane, 1 mL. [b]TsN═C═O, 1 equiv. [c]Only $MgBr_2$ cat.

obtained in a 25% yield at 40 °C after 24 h (entry 1). Catalytic cycloaddition using simple acyl cyclopropanes is rare. Reactions with enones[3e] or alkynes[4c] have been reported using a Ni catalyst system. The cycloaddition with imines was reported via stoichiometric MgI_2.[7d] Hence, the presented tin-catalyzed reaction with isocyanates is noteworthy in terms of application to simple acyl cyclopropanes. To increase the yield of desired product **6a**, we found that using 2 equiv of isocyanate gave a 77% yield (entry 2). Furthermore, the reaction at 80 °C attained an 86% yield (entry 3). The reaction with PhN═C═O resulted in a lower yield (20%) because of low electrophilicity of PhN═C═O. Besides benzoyl cyclopropane, *p*-methoxyphenylcarbonyl- and *p*-chlorophenylcarbonyl cyclopropanes **1e** and **1f** were reactive to give the corresponding α-acyl-γ-butyrolactams **6b** and **6c** in 69% and 64% yields, respectively (entries 4 and 5). A similar product, **6d**, was obtained using acetyl cyclopropane **1g** (entry 6). Products **6a**, **6c**, and **6d** were isolated as enol compounds, and **6b** was a keto-type compound, all of which were detected by ^1H NMR.

In addition to isocyanates, we next tried to use an isothiocyanate (Scheme 5). In the reaction of **1a** with PhN═C═S, although the yield of the desired 1:1 adduct was unsatisfactory, using more electrophilic *p*-nitrophenyl isothiocyanate afforded a moderate yield of the desired adduct **7**.

Scheme 5. Cycloaddition of Cyclopropane 1a with Isothiocyanate



Product **7** was derived from the addition of isothiocyanates across the C═S bond.[17]

In conclusion, we demonstrated the catalytic synthesis of γ-butyrolactams via a [3 + 2]-cycloaddition with isocyanates. The organotin iodide complex $MgBr^+[Bu_2SnBrI_2]^-$ was generated from Bu_2SnI_2 and $MgBr_2$ and was employed as an effective catalyst. The hybrid character of a tin ate complex, acidic $MgBr^+$ and nucleophilic tin iodide, was responsible for the catalytic reaction. Simple cyclopropanes that lack aryl or vinyl substituents were useful precursors. Even acyl cyclopropanes were useful. We are now planning tin-catalyzed cycloadditions with other electrophiles.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01905.

Experimental procedures and spectral data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*shibata@epc.osaka-u.ac.jp

Notes

The authors declare no competing financial interest.

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