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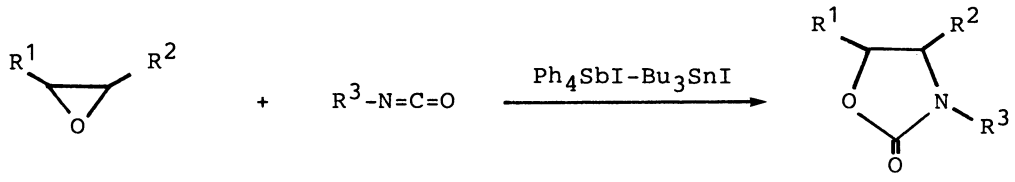
Cycloaddition Reaction of 2,3-Disubstituted Oxiranes with Isocyanates by Highly Activated Catalyst; Ph_4SbI-Bu_3SnI

Masahiro FUJIWARA, Akio BABA,* Yuri TOMOHISA, and Haruo MATSUDA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, 2-1 Yamadaoka, Suita, Osaka 565

The combination of Ph_4SbI and Bu_3SnI proved to be a new excellent catalyst for effecting cycloaddition reaction of inactive 2,3-disubstituted oxiranes with isocyanates under neutral conditions, yielding oxazolidinones in high yields, while either of both metal iodides had no activity individually.

The cycloaddition of oxiranes toward isocyanates has been ardently studied for a convenient preparation of oxazolidinones, and a variety of catalysts have been reported.[1] Quite recently we also reported that organotin halide-base complexes and organostibonium halides are very effective catalysts for this reaction.[2] These compounds show high and unique catalytic activity in the reaction of monosubstituted oxiranes under mild conditions. Unfortunately, even these active catalysts have lower effect for the cycloaddition using 2,3-disubstituted oxiranes. The development of a versatile catalyst for reactions of these inactive oxiranes is a significant problem, and if realized, a wide range of oxazolidinones could be readily obtained from the direct cycloaddition with isocyanates.



1 **2** **3**

Although showing not high activity toward this type of reaction, Ph_4SbI, as

Table 1. Reaction of 2,3-Disubstituted Oxiranes with Isocyanates[a)]

Entry	Oxirane **1** R^1 R^2	Isocyanate **2** R^3	Solvent	Cat. system	Yield of **3** / %
1	$-(CH_2)_4-$	Ph	PhH	Ph_4SbI - Bu_3SnI	99
2	"	"	"	Ph_4SbI	15
3	"	"	"	Bu_3SnI	0
4	"	"	"	Bu_4NI	0[b)]
5	"	"	"	Ph_4SbI - Bu_2SnI_2	87
6	"	"	"	Ph_4SbI - SnI_2	48
7	"	"	"	Ph_4SbI - ZnI_2	35
8	"	"	"	Ph_4SbI - AlI_3	13
9	"	"	"	Ph_4SbI - CuI	0
10	"	"	CH_3CN	Ph_4SbI - Bu_3SnI	48
11	"	"	HMPA	Ph_4SbI - Bu_3SnI	47
12	"	"	HMPA	Ph_4SbI - ZnI_2	23 + 31[c)]
13	"	p-ClC_6H_4	PhH	Ph_4SbI - Bu_3SnI	100
14	"	p-MeC_6H_4	"	Ph_4SbI - Bu_3SnI	90
15[d)]	"	iso-C_3H_7	"	Ph_4SbI - Bu_3SnI	78
16[e)]	$-(CH_2)_3-$	Ph	"	Ph_4SbI - Bu_3SnI	94
17[f)]	Ph Ph (trans)	"	"	Ph_4SbI - Bu_3SnI	65 (trans)

a) Oxirane 10 mmol, R-NCO 10 mmol, catalyst 1 mmol, solvent 5 ml, 80 °C, 2 h, isocyanate was added slowly over 60 min. b) All phenyl isocyanate turned into the trimer within 10 h. c) Iminodioxolane derivative(see reference 6), determined by GC. d) 70 °C, 1 h. e) 60 °C, 1 h. f) 80 °C, 28 h.

previously reported, can cleave monosubstituted oxiranes at their hindered site to produce 3,4-disubstituted oxazolidinones predominantly.[2a)] This result suggests that Ph_4SbI may possess an inherent catalytic ability toward the reaction with 2,3-disubstituted oxiranes. We wish to describe herein that the reaction of inactive oxiranes such as cyclohexene oxide and cyclopentene oxide with isocyanates can be promoted by a catalyst, Ph_4SbI activated by Bu_3SnI. Several oxazolidinones were obtained in high yields as shown in Table 1.

In a typical procedure, to a mixture of cyclohexene oxide (10 mmol), Ph_4SbI (1 mmol), Bu_3SnI (1 mmol) and benzene (3 ml), phenyl isocyanate (10 mmol) in benzene (2 ml) was added dropwise during a course of 60 min at 80 °C. After additional 2 h the resultant mixture was subjected to separation by column chromatography on silica gel, and 4,5-tetramethylene-3-phenyl-1,3-oxazolidin-2-one (**3a**) was eluted by $CHCl_3$ (99% yield).

As summarized in Table 1, the combination catalyst of Ph_4SbI and Bu_3SnI showed the highest activity, yielding **3a** quantitatively, while either of them exhibited little activity individually. Representative conventional catalysts, Bu_4NI or LiBr, gave only the trimer of phenyl isocyanate. It is notable that this reaction media is considered to be almost neutral because of lower acidity of the both of Ph_4SbI and Bu_3SnI.[3] This cycloaddition appeared to be highly dependent on the nature of the additives to Ph_4SbI and solvents as revealed in Table 1. The efficiency of additives decreases in the following order; $Bu_3SnI > Bu_2SnI_2 \gg SnI_2$, $ZnI_2 > AlI_3$. Aluminum triiodide[4] caused predominantly polymerization of cyclohexene oxide due to its strong acidity. In particular, it is noteworthy that the addition of CuI completely depressed the catalytic ability of Ph_4SbI, and isocyanate was recovered nearly quantitatively. Consequently, Bu_3SnI of lowest acitity was the most suitable additive. Among various solvents examined, benzene was found to be a solvent of choice, while polar solvents such as acetonitrile and hexamethylphosphoramide (HMPA) were unsatisfactory. These polar solvents have coordinate ability to organotin halides,[5] which would weaken an interaction of Ph_4SbI with Bu_3SnI, leading to a lower yield of **3a**. Of interest is the observation that 4,5-tetramethylene-2-phenylimino-1,3-dioxolane (**4**) was produced by Ph_4SbI-ZnI_2 catalyst in HMPA (entry 12).[6] To our knowledge, this is the first example of isolation of **4** in the direct reaction of phenyl isocyanate with oxiranes, although it has been assumed to be an intermediate of the formation of oxazolidinones.[7]

The reaction of trans-stilbene oxide with phenyl isocyanate gave trans-4,5-diphenyloxazolidinone[8] in 65% yield without the formation of cis isomer. Stereospecificity of this reaction promoted by this type of catalysts is now under investigation.

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6) 4,5-Tetramethylene-2-phenylimino-1,3-dioxolane; mp 84-85 °C; IR (KBr) 1700 cm^{-1} (C=O); MS (m/e) 217 (M^+); ^1H NMR ($CDCl_3$)δ = 1.1-2.2 (8H, m), 4.45-4.7 (2H, m), 6.8-7.4 (5H, m); ^{13}C NMR ($CDCl_3$)δ = 19.6 (t), 19.9 (t), 26.7 (t), 27.0 (t), 75.1 (d), 77.0 (d), 123.11 (d), 123.17 (d), 128.5 (d), 145.5 (s), 153.2 (s). Found: C, 71.78; H, 6.93; N, 6.37%. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45%.

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8) trans-4.5-Diphenyl-3-phenyloxazolin-2-one; mp 128 °C; IR (KBr) 1740 cm^{-1} (C=O); MS (m/e) 315 (M^+); ^1H NMR ($CDCl_3$)δ = 5.14 (1H, d, J = 6.3 Hz), 5.27 (1H, d, J = 6.3 Hz), 6.9-7.6 (15H, m).

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