Selective α-Cleavage Cycloaddition of Oxiranes with Heterocumulenes Catalyzed by Tetraphenylstibonium Iodide

Masahiro Fujiwara*, Akio Baba*, and Haruo Matsuda

Department of Applied Chemistry, Faculty of Engineering,
Osaka University, 2-1 Yamadaoka, Suita,
Osaka 565, Japan

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A catalytic amount of tetraphenylstibonium iodide (**1**) promoted unusual cycloadditions of oxiranes with isocyanates or carbodiimides, forming 3,4-disubstituted oxazolidin-2-ones **2** and oxazolidin-2-imines **4** under very mild conditions, respectively. In particular, carbodiimides gave **4** exclusively. Either oxazolidine, 3,4-disubstituted or 3,5-disubstituted ones could be obtained independently from the same reactants by the compensatable use of **1** and organotin iodide-Lewis base complexes as catalysts.

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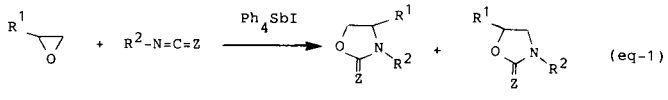
Introduction.

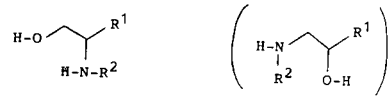
New synthetic uses of oxazolidine derivatives recently have been given attention. For example, oxazolidin-2-ones are used for the purpose of enhancing the stereoselectivity in the aldol reaction [1]. Moreover, oxazolidin-2-one rings can be regarded as "masked" β-aminoalcohols, which are found in a substantial number of bioactive compounds [2], being finally converted into corresponding β-aminoalcohols by hydrolysis [3].

A typical and useful method for preparing oxazolidines under neutral conditions is the cycloaddition of oxiranes with isocyanates or with carbodiimides [4]. Although a variety of catalysts have been developed for this reaction, higher reaction temperatures are required in most cases [5]. In addition, the cycloaddition using monosubstituted oxiranes generally gives 3,5-disubstituted oxazolidines [5a,b]. A few attempts have been made to produce 3,4-disubstituted oxazolidin-2-ones **2** in the cycloaddition of oxiranes with isocyanates [6]. For example, Herweh attempted this type of cycloaddition under refluxing DMF with lithium chloride catalyst, but the desired cycloadducts could be obtained only as minor components [6a]. Thus, the selective formation of **2** seems to be very difficult in this cycloaddition.

Recently, we found the predominant formation of **2** in the presence of catalyst **1** [7]. Herein we wish to report on the completely selective formation of 3,4-disubstituted oxazolidin-2-imines **4** in the reaction of oxiranes with carbodiimides. To our knowledge, this is the first example of the cycloaddition with heterocumulenes *via* the selective α-cleavage of oxirane rings. These cycloadducts can be readily hydrolyzed into the corresponding oxazolidin-2-ones or β-aminoalcohols bearing primary hydroxy group



1 **2** **3** **4** **5**



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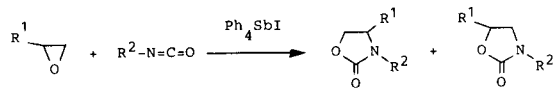
6, which were not obtained from the reaction of monosubstituted oxiranes with amines [8], or metal amides [9].

Results and Discussion.

The Cycloaddition of Oxiranes with Isocyanates.

Scheme I



1 **2a-q** **3a-q**

	R^1	R^2
a	CH_3	C_6H_5
b		*p*-ClC_6H_4
c		*p*-$CH_3C_6H_4$
d		*p*-$CH_3OC_6H_4$
e		*n*-C_4H_9
f	C_2H_5	C_6H_5
g		*p*-ClC_6H_4
h		*p*-$CH_3C_6H_4$
i		CH_2=$CHCH_2$

	R^1	R^2
j	C_2H_5	*n*-C_4H_9
k	C_6H_5	C_6H_5
l	C_6H_5	*n*-C_4H_9
m	$C_6H_5OCH_2$	C_6H_5
n	CH_3COOCH_2	
o	CH_2=$CHCH_2OCH_2$	
p	CH_2=CH	
q	2,2-$(CH_3)_2$	

As already reported briefly in our previous communication [7], **1** was an interesting catalyst which gave 3,4-disubstituted oxazolidin-2-ones **2** by unusual cleavage of monosubstituted oxiranes in the reaction with isocyanates.

Many kinds of oxiranes and isocyanates were adaptable to this unusual cycloaddition as shown in Table 1. In particular, it is noteworthy that even phenoxymethyloxirane (entry 13), acetoxymethyloxirane (entry 14), allyloxymethyloxirane (entry 15) gave **2** exclusively in dibromomethane at 80°-90°, since these oxiranes were hardly expected to be cleaved at α-site because of their electrowithdrawing substituents. Moreover, in the reactions of acetoxymethyloxirane and allyoxymethyloxirane bearing

Table 1

The Cycloaddition of Oxiranes with Isocyanates [a]

Entry	R^1	R^2	Solvent	Yield (%) [g]	ratio **2** : **3**
1 [b]	CH_3	C_6H_5	CH_2Cl_2	100	80 : 20
2 [b]		p-ClC_6H_4		89	65 : 35
3 [b]		p-$CH_3C_6H_4$		95	78 : 22
4 [b]		$pCH_3OC_6H_4$		72	88 : 12
5 [b]		n-C_4H_9		100 [h]	81 : 19 [j]
6	C_2H_5	C_6H_5		100	100 : 0
7		p-ClC_6H_4		89	100 : 0
8		p-$CH_3C_6H_4$		100	100 : 0
9 [c]		$CH_2CH=CH_2$	CH_2Br_2	81	100 : 0
10		n-C_4H_9	PhH	100	93 : 7
11	C_6H_5	C_6H_5		86	99 : 1
12		n-C_4H_9		69	92 : 8
13 [d]	$C_6H_5OCH_2$	C_6H_5	CH_2Br_2	100	91 : 9
14 [c]	CH_3COOCH_2			53	100 : 0
15 [c]	$CH_2=CHCH_2OCH_2$		PhH	70	81 : 19
16 [e]	$CH_2=CH$		CH_2Cl_2	75	96 : 4 [k]
17 [f]	2,2-$(CH_3)_2$		PhH	0 [i]	-

[a] Oxirane/isocyanate/**1** = 30/10/1 mmole, 45°, 1 hour, solvent 5 ml. Isocyanate was added dropwise for 1 hour. [b] 40°. [c] 80°. [d] 90°. [e] 2.5 hours. [f] 60°, 1 hour. [g] Determined by glc. [h] Isolated yield. [i] Isocyanate trimer was yielded quantitatively. [j] Determined by ^{13}C nmr. [k] Determined by ^1H nmr.

Table 2

Cycloaddition of Oxiranes with Carbodiimides [a]

Entry	R^1	R^2	R^3	Catalyst	Time (hours)	Yield [b] (%)	ratio **4** : **5**
1 [c]	CH_3	C_6H_5	C_6H_5	Ph_4SbI	15	97	100 : 0
2 [c]	C_6H_5				24	64	100 : 0
3 [c]	CH_3OCH_2				38	86	100 : 0
4 [c]	$CH_2=CH$				29	62	100 : 0
5 [c]	CH_3	C_6H_5	n-C_4H_9		50	73	100 : 0
6 [c]	CH_3OCH_2				42	80	100 : 0
7 [c,d]	CH_3	n-C_4H_9	n-C_4H_9		240	34	100 : 0
8 [c,e]	CH_3OCH_2				128	49	100 : 0
9	CH_3	C_6H_5	C_6H_5	Bu_2SnI_2-Ph_3P	1	89	0 : 100
10	C_6H_5			Bu_3SnI-Ph_3PO	3	62	75 : 25
11	CH_3OCH_2			Bu_2SnI_2-Ph_3P	1	100	0 : 100
12	$CH_2=CH$			Bu_3SnI-Ph_3PO	2	48	0 : 100
13	CH_3	C_6H_5	n-C_4H_9	Bu_2SnI_2-Ph_3P	1	87	0 : 100
14	CH_3OCH_2				2	74	0 : 100
15	CH_3	n-C_4H_9	n-C_4H_9		2	85	0 : 100
16	CH_3OCH_2				2	95	0 : 100

[a] Oxirane/carbodiimide/catalyst = 50/10/1 mmole, 40°. [b] Based on carbodiimides. Determined by glc. [c] Solvent, PhH 5 ml. [d] 48°, carried out in a glass autoclave (5 KG nitrogen). [e] 80°.

reactive functional groups, cycloadducts **2n** and **2o** were obtained in good yields. These results indicated that this tetraphenylstibonium iodide-catalyzed reaction had high chemoselectivity for oxirane rings.

The addition rate of isocyanates was significant for the formation of **2**. As mentioned in a previous report [7], when an isocyanate was added in one portion, the yield of **2** was drastically decreased, and the corresponding isocyanate trimer was produced. Further, the product in the reaction of 2,2-dimethyloxirane with phenyl isocyanate was only triphenyl isocyanurate (entry 17).

This novel cycloaddition of oxiranes with isocyanates has the high synthetic values, but has some limitations such as the by-production of **3** and the indispensability of dropwise addition of isocyanates. In particular, all the

Table 3

Analytical and Spectroscopic Data of **2** and **3**

	bp (torr) °C	IR (cm^{-1}) ν C=O [a]	Molecular Formula	Analysis % Calcd./Found C	H	N
2a	(mp 51)	1740	$C_{10}H_{11}NO_2$	67.78	6.26	7.90
				68.03	6.12	8.15
2b	(mp 78)	1740	$C_{10}H_{10}ClNO_2$	56.75	4.76	6.62
				56.64	4.61	6.76
2c	(mp 109)	1750	$C_{11}H_{13}NO_2$	69.09	6.85	7.32
				68.95	6.88	7.31
2d	150 (0.1)	1740	$C_{11}H_{13}NO_3$	63.76	6.32	6.76
				63.48	6.40	6.81
2e	103 (2.0)	1750	$C_8H_{15}NO_2$	61.12	9.62	8.91
				60.82	9.65	8.98 [g]
2f	120 (0.1)	1750	$C_{11}H_{13}NO_2$	69.09	6.85	7.33
				69.19	6.95	7.41
2g	145 (0.1)	1750	$C_{11}H_{12}ClNO_2$	58.54	5.36	6.21
				58.42	5.38	6.27
2h	130 (0.1)	1750	$C_{12}H_{15}NO_2$	70.22	7.37	6.82
				69.96	7.43	6.99
2i	115 (2.0)	1740	$C_8H_{13}NO_2$	61.91	8.44	9.03
				61.68	8.50	9.11
2j	107 (2.0)	1760	$C_9H_{17}NO_2$	63.13	10.01	8.18
				62.87	10.11	8.27
2k	(mp 79)	1750	$C_{15}H_{13}NO_2$		[d]	
2l	129 (0.1)	1750	$C_{13}H_{17}NO_2$	71.21	7.82	6.39
				71.22	7.93	6.45
2m	(mp 120)	1740	$C_{16}H_{15}NO_3$	71.36	5.61	5.20
				71.15	5.54	5.13
2n	170 (0.1) [b]	1750 [c]	$C_{12}H_{13}NO_4$		---	
2o	137 (0.1) [b]	1750	$C_{13}H_{15}NO_3$	66.94	6.48	6.00
				66.67	6.50	6.11
2p	116 (0.1)	1750	$C_{11}H_{11}NO_2$		[e]	
3a	(mp 81)	1740	$C_{10}H_{11}NO_2$		[d]	
3b	(mp 94)	1740	$C_{10}H_{10}ClNO_2$	56.75	4.76	6.62
				56.81	4.75	6.65
3c	(mp 66)	1740	$C_{11}H_{13}NO_2$		[d]	
3d	(mp 88)	1740	$C_{11}H_{13}NO_3$	63.76	6.32	6.76
				63.79	6.32	6.77
3e	94 (3.0)	1740	$C_8H_{15}NO_2$		---	
3j	145 (2.0)	1760	$C_9H_{17}NO_2$	63.13	10.01	8.18
				62.78	10.13	8.17
3k	(mp 130)	1740	$C_{15}H_{13}NO_2$		[f]	
3l	143 (0.1)	1750	$C_{13}H_{17}NO_2$		---	
3m	(mp 139)	1740	$C_{16}H_{15}NO_3$		[d]	
3o	131 (0.1)	1750	$C_{13}H_{15}NO_3$		---	
3p	[h]					

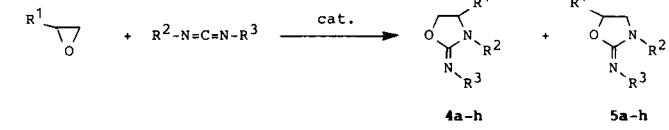
[a] Determined by using potassium bromide pellets or KRS-5 cells. [b] Using Kügel Rohr. [c] Accompanied by 1710 cm^{-1} absorption of ester carbonyl group. [d] Reference [3b]. [e] Reference [19]. [f] Reference [20]. [g] As a mixture of **2e** and **3e** (81:19). [h] Reference [21].

reactions using methyloxirane were not able to produce desired oxazolidin-2-ones **4** in perfect selectivities in spite of extensive researches (entry 1-5).

The Cycloaddition of Oxiranes with Carbodiimides.

Next, we examined the reaction of oxiranes with carbodiimides which are well known to react in a manner similar to that of isocyanates [10]. As shown in Table 2, the cyclo-

Scheme II



	R^1	R^2	R^3
a	CH_3	C_6H_5	C_6H_5
b	C_6H_5		
c	CH_3OCH_2		
d	CH_2=CH		

	R^1	R^2	R^3
e	CH_3	C_6H_5	n-C_4H_9
f	CH_3OCH_2		
g	CH_3	n-C_4H_9	n-C_4H_9
h	CH_3OCH_2		

Table 4

NMR Data of Compounds **2** and **3**

	^{1}H NMR δ (ppm) (Deuteriochloroform)	^{13}C NMR δ (ppm) (Deuteriochloroform)
2a	1.25 (d, 3H, J = 6.0 Hz), 3.90-4.17 (m, 1H), 4.35-4.70 (m, 2H), 7.08-7.55 (m, 5H)	18.30 (q), 52.30 (d), 68.60 (t), 121.90 (d), 125.10 (d), 129.10, (d), 136.50 (s), 155.70 (s)
2b	1.33 (d, 3H, J = 5.8 Hz), 3.90-4.16 (m, 1H), 4.30-4.75 (m, 2H), 6.97-7.70 (m, 4H)	18.40 (q), 52.27 (d), 68.68 (t), 122.92 (d), 129.17 (d, s, 2C), 135.24 (s), 155.36 (s)
2c	1.30 (d, 3H, J = 6.3 Hz), 2.35 (s, 3H), 3.80-4.20 (m, 1H), 4.30-4.70 (m, 2H), 6.80-7.70 (m, 4H)	18.43 (q), 20.84 (q), 52.52 (d), 68.62 (t), 122.25 (d), 129.56 (d), 133.96 (s), 135.11 (s), 155.82 (s)
2d	1.30 (d, 3H, J = 5.8 Hz), 3.82 (s, 3H), 3.85-4.15 (m, 1H) 4.25-4.75 (m, 2H), 6.80-7.45 (m, 4H)	18.58 (q), 53.19 (d), 55.50 (q), 68.77 (t), 114.50 (d), 124.75 (d), 129.32 (s), 156.21 (s), 157.52 (s)
2e	0.70-1.70 (m, 10H), 2.85-3.65 (m, 2H), 3.70-4.10 (m, 2H), 4.20-4.50 (m, 1H)	12.76 (q), 17.12 (t), 19.01 (q), 28.61 (t), 40.32 (t), 49.96 (d), 67.98 (t), 154.04 (s)
2f	0.87 (t, 3H, J = 7.0 Hz), 1.50-1.90 (m, 2H), 4.04-4.22 (m, 1H), 4.30-4.65 (m, 2H), 7.05-7.60 (m, 5H)	7.88 (q), 24.62 (t), 57.12 (d), 66.39 (t), 121.97 (d), 125.14 (d), 129.11 (d), 136.76 (s), 155.80 (s)
2g	0.90 (t, 3H, J = 7.5 Hz), 1.50-2.10 (m, 2H), 4.05-4.60 (m, 3H), 7.10-7.60 (m, 4H)	7.70 (q), 24.38 (t), 56.82 (d), 66.30 (t), 122.83 (d), 129.02 (d), 130.14 (s), 135.36 (s), 155.45 (s)
2h	0.90 (t, 3H, J = 7.0 Hz), 1.50-1.90 (m, 2H), 2.37 (s, 3H), 4.00-4.70 (m, 3H), 7.05-7.55 (m, 4H)	7.94 (q), 20.99 (q), 24.74 (t), 57.40 (d), 66.45 (t), 122.34 (d), 129.72 (d), 134.11 (s), 135.11 (s), 155.82 (s)
2i	0.93 (t, 3H, J = 7.0 Hz), 1.50-2.00 (m, 2H), 3.30-4.70 (m, 5H, 5.05-5.50 (m, 2H), 5.55-6.10 (m, 1H)	7.82 (q), 24.38 (t), 44.62 (t), 55.44 (d), 66.70 (t), 118.13 (t), 132.13 (d), 157.92 (s)
2j	0.92 (t, 6H, J = 5.8 Hz), 1.10-2.00 (m, 6H), 2.80-3.30 (m, 1H), 3.30-3.60 (m, 1H), 3.60-4.10 (m, 2H), 4.20-4.50 (m, 1H)	7.58 (q), 13.43 (q), 19.68 (t), 24.25 (t), 29.16 (t), 41.21 (t), 55.32 (d), 66.33 (t), 157.92 (s)
2k	4.15 (dd, 1H, J = 6.0 Hz and 9.0 Hz), 4.75 (t, 1H, J = 9.0 Hz), 5.40 (dd, 1H, J = 6.0 Hz and 9.0 Hz), 7.00-7.50 (m, 10H)	60.60 (d), 69.77 (t), 120.80 (d), 124.61 (d), 126.23 (d), 128.72 (d), 128.82 (d), 129.30 (d), 137.09 (s), 138.31 (s), 155.92 (s)
2l	0.75-1.10 (m, 3H), 1.10-1.60 (m, 4H), 2.55-2.90 (m, 1H), 3.30-3.65 (m, 1H), 3.90-4.20 (m, 1H), 4.40-4.90 (m, 2H), 7.15-7.60 (m, 5H)	13.60 (q), 19.81 (t), 28.95 (t), 41.79 (t), 59.73 (d), 69.80 (t), 126.98 (d), 129.25 (d, 2C), 138.07 (s), 158.33 (s)
2m	3.90-4.20 (m, 2H), 4.30-4.90 (m, 3H), 6.55-7.60 (m, 10H)	55.87 (d), 64.87 (t), 66.05 (t), 114.68 (d), 121.73 (d), 122.31 (d), 125.74 (d), 129.36 (d), 129.65 (d), 136.50 (s), 155.87 (s), 158.13 (s)
2n	2.00 (s, 3H), 3.95-4.80 (m, 5H), 7.04-7.80 (m, 5H)	20.53 (q), 55.05 (d), 62.21 (t), 64.53 (t), 121.97 (d), 125.63 (d), 129.23 (d), 136.18 (s), 155.42 (s), 170.33 (s)
2o	3.64 (d, 2H, J = 3.0 Hz), 3.80-4.15 (m, 2H), 4.25-4.70 (m, 3H), 5.00-5.45 (m, 2H), 5.50-6.10 (m, 1H), 6.98-7.86 (m, 5H)	55.72 (d), 64.56 (t), 67.43 (t), 71.76 (t), 116.70 (t), 121.67 (d), 124.81 (d), 128.65 (d), 133.56 (d), 136.30 (s), 155.45 (s)
2p	3.90-4.25 (m, 1H), 4.36-5.10 (m, 2H), 5.10-5.45 (m, 2H), 5.56-6.05 (m, 1H), 6.85-7.70 (m, 5H)	59.56 (d), 67.15 (t), 120.33 (t), 121.42 (d), 124.90 (d), 128.86 (d), 134.72 (d), 137.01 (s), 155.51 (s)
3a	1.52 (d, 3H, J = 6.0 Hz), 3.60 (t, 1H, J = 7.5 Hz), 4.10 (t, 1H, J = 8.0 Hz), 4.62-4.92 (m, 1H), 7.00-7.60 (m, 5H)	20.55 (q), 51.76 (t), 67.47 (d), 118.11 (d), 123.78 (d), 128.91 (d), 138.41 (s), 154.80 (s)
3b	1.55 (d, 3H, J = 7.3 Hz), 3.60 (t, 1H, J = 7.3 Hz), 4.09 (t, 1H, J = 8.3 Hz), 4.55-4.95 (m, 1H), 7.20-7.60 (m, 4H)	20.72 (q), 51.85 (t), 69.65 (d), 119.32 (d), 128.93 (d), 128.97 (s), 137.04 (s), 154.60 (s)
3c	1.52 (d, 3H, J = 6.8 Hz), 2.33 (s, 3H), 3.58 (dd, 1H, J = 8.3 and 9.5 Hz), 4.10 (t, 1H, J = 8.3 Hz), 4.60-4.95 (m, 1H), 7.03-7.55 (m, 4H)	20.65 (q, 2C), 52.01 (t), 69.47 (d), 118.30 (d), 129.50 (d), 135.53 (s), 135.91 (s), 155.00 (s)
3d	1.50 (d, 3H, J = 6.8 Hz), 3.56 (dd, 1H, J = 8.8 and 6.8 Hz), 3.80 (s, 3H), 4.06 (t, 1H, J = 8.3 Hz), 4.53-4.90 (m, 1H) 6.70-7.50 (m, 4H)	20.84 (q), 52.55 (t), 55.63 (q), 69.56 (d), 114.35 (d), 120.27 (d), 131.90 (s), 149.18 (s), 156.28 (s)
3e	0.80-1.70 (m, 10H), 3.00-3.40 (m, 3H), 3.65 (t, 1H, J = 8.0 Hz), 4.45-4.80 (m, 1H)	13.40 (q), 19.50 (q), 20.40 (t), 29.10 (t), 43.40 (t), 51.00 (t), 69.70 (t), 157.90 (s)
3j	1.00 (t, 6H, J = 5.8 Hz), 1.20-1.90 (m, 6H), 3.00-3.40 (m, 3H), 3.60 (t, 1H, J = 7.0 Hz), 4.20-4.60 (m, 1H)	8.80 (q), 13.77 (q), 19.92 (t), 28.13 (t), 29.47 (t), 43.86 (t), 49.50 (t), 74.50 (d), 158.04 (s)
3k	3.90 (dd, 1H, J = 7.0 and 8.0 Hz), 4.30 (t, 1H, J = 9.0 Hz), 5.60 (dd, 1H, J = 8.0 and 9.0 Hz), 7.10-7.60 (m, 10H)	52.64 (t), 74.02 (d), 118.30 (d), 124.17 (d), 125.69 (d), 129.11 (d, 3C), 138.17 (s, 2C), 154.70 (s)
3l	0.80-1.05 (m, 3H), 1.10-1.70 (m, 4H), 3.20-3.50 (m, 3H), 3.90 (t, 1H, J = 7.0 Hz), 5.46 (t, 1H, J = 7.0 Hz), 7.20-7.50 (m, 5H)	13.65 (q), 19.81 (t), 29.40 (t), 43.93 (t), 52.15 (d), 74.32 (d), 125.49 (d), 128.91 (d, 2C), 139.00 (s), 157.93 (s)
3m	3.95-4.30 (m, 4H), 4.90-5.10 (m, 1H), 6.80-7.65 (m, 10H)	47.56 (t), 68.25 (t), 70.50 (d), 114.88 (d), 118.50 (d), 121.92 (d), 124.32 (d), 129.21 (d), 129.75 (d), 138.36 (s), 154.50 (s), 158.27 (s)
3o	3.70 (d, 2H, J = 4.5 Hz), 3.85-4.20 (m, 4H), 4.50-4.90 (m, 1H), 5.05-5.42 (m, 2H), 5.60-5.90 (m, 1H), 6.90-7.76 (m, 5H)	47.36 (t), 70.17 (t), 71.36 (d), 72.70 (t), 117.70 (t), 118.25 (d), 123.99 (d), 129.02 (d), 133.99 (d), 154.57 (s)
3p	[a]	

[a] Reference [21].

addition *via* selective α-cleavage of monosubstituted oxiranes, even in the case of methyloxirane (entry 1,5,7), was achieved by **1** to produce 3,4-disubstituted oxazolidin-2-imines **4** (entry 1-8). In contrast to the reaction with isocyanates, the choice of solvent was not a factor in the reaction; moreover, a slow dropwise addition of carbodiimides was not necessary because of their poor trimerization properties. Although the reactivity of carbodiimides was con-

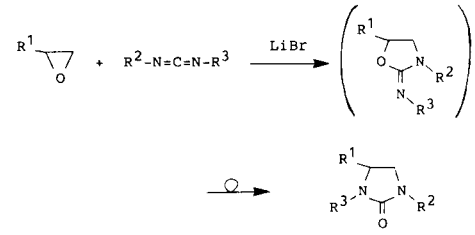
siderably lower than that of isocyanates, cycloadducts **4** could be obtained in moderate to excellent yields in prolonged reaction times.

The catalytic activity toward the unusual cycloaddition may be inherent in **1**, since even analogous antimony halides such as triphenylantimony diiodide (in the case of reaction of ethyloxirane with phenyl isocyanate, yield 39%, ratio of **2f:3f** = 2:98) and tetraphenylstibonium bromide (in the above mentioned case, yield 20%, ratio of **2f:3f** = 60:40, in the case of methyloxirane with diphenylcarbodiimide, yield 84%, ratio of **4a:5a** = 41:59 [13]) were not effective at all. Of course, conventional catalysts such as tetra-*n*-butylammonium iodide, tetraphenylphosphonium iodide and lithium bromide had no catalytic activity for this type of cycloaddition, as already reported [7].

As reported partly in our other papers [11], organotin iodide-Lewis base complexes promoted a selective β-cleavage cycloaddition of oxiranes with carbodiimides to produce 3,5-disubstituted oxazolidin-2-imines **5** in all cases except phenyloxirane (entry 10). This Sn-base complex system had higher catalytic activity than **1**, allowed us to achieve the high yield cycloaddition within a 1-3 hour period.

Consequently, it is interesting that **1** and Sn complexes compensate each other to produce 3,4-disubstituted oxazolidines **2,4** and 3,5-disubstituted ones **3,5**, respectively, from the same substrates under similar mild conditions.

Conventional catalysts such as lithium halides reported for this cycloaddition have produced cyclic ureas, where oxazolidin-2-imines were assumed to be preliminary



(eq-2)

adducts, rearranged to ureas under severe conditions [12]. Both Sb and Sn catalysts, however, could act under very mild conditions to yield the preliminary adducts **4** and **5** in good yields without rearrangement, respectively. The cycloaddition using an unsymmetrical carbodiimide, phenyl-*n*-butylcarbodiimide, took place selectively across the PhN=C group to yield *N*-butyl-3-phenyloxazolidin-2-imine in both catalytic systems.

Oxazolidin-2-imines were readily hydrolyzed under acidic conditions, to afford the corresponding oxazolidin-2-ones [11b]. On the other hand, it is well known that

Table 5

Analytical and Spectroscopic Data of **4** and **5**

	bp (torr) °C	IR (cm^{-1}) ν C=N [a]	Molecular Formula	Analysis % Calcd./Found C	H	N
4a	(mp 89)	1680	$C_{16}H_{16}N_2O$	76.17	6.39	11.10
				76.28	6.37	11.13
4b	(mp 122)	1680	$C_{21}H_{18}N_2O$	80.23	5.77	8.91
				80.44	5.71	8.81
4c	163 (0.1)	1680	$C_{17}H_{18}N_2O_2$	72.34	6.43	9.93
				72.15	6.39	9.98
4d	148 (0.1)	1690	$C_{17}H_{16}N_2O$		[c]	
4e	88 (0.1)	1690	$C_{14}H_{20}N_2O$	72.38	8.68	12.06
				72.14	8.76	11.81
4f	130 (0.1)	1690	$C_{15}H_{22}N_2O_2$	68.67	8.45	10.68
				68.39	8.54	10.63
4g	100 (2.0) [b]	1690	$C_{12}H_{24}N_2O$		---	
4h	108 (2.0)	1690	$C_{13}H_{26}N_2O_2$		---	
5a	(mp 73)	1670	$C_{16}H_{16}N_2O$		[d]	
5b	(mp 112)	1680	$C_{21}H_{18}N_2O$	80.25	5.77	8.92
				80.09	5.66	8.87
5c	200 (0.1)	1670	$C_{17}H_{18}N_2O_2$	72.34	6.43	9.93
				72.37	6.45	9.87
5d	155 (0.1) [b]	1690	$C_{17}H_{16}N_2O$	77.25	6.10	10.60
				77.16	6.10	10.70
5e	90 (2.0)	1700	$C_{14}H_{20}N_2O$		---	
5f	118 (0.1)	1690	$C_{15}H_{22}N_2O_2$	68.67	8.45	10.68
				68.45	8.47	10.60
5g	68 (2.0)	1700	$C_{12}H_{24}N_2O$		---	
5h	130 (2.0) [b]	1690	$C_{13}H_{26}N_2O_2$		---	

[a] Determined by using potassium bromide pellets or KRS-5 cells. [b] Using Kügel Rohr. [c] Reference [19]. [d] Reference [12].

Table 6

NMR Data of Compounds **4** and **5**

	^{1}H NMR δ (ppm) (Deuteriochloroform)	^{13}C NMR δ (ppm) (Deuteriochloroform)
4a	1.25 (d, 3H, J = 6.3 Hz), 3.80-4.10 (m, 1H), 4.30-4.60 (m, 2H), 6.80-7.90 (m, 10H)	17.76 (q), 53.28 (d), 70.84 (t), 122.22 (d), 122.51 (d), 123.39 (d), 124.22 (d), 128.43 (d), 128.91 (d), 138.26 (s), 147.61 (s), 150.15 (s)
4b	4.15 (dd, 1H, J = 8.1 and 4.8 Hz), 4.68 (t, 1H, J = 8.0 Hz), 5.30 (dd, 1H, J = 4.8 and 7.8 Hz), 6.84-7.70 (m, 15H)	61.86 (d), 72.10 (t), 121.22 (d), 122.56 (d), 123.41 (d), 123.60 (d), 126.28 (d), 128.57 (d, 2C), 128.63 (d), 129.24 (d), 138.72 (s), 139.02 (s), 149.97 (s), 161.40 (s)
4c	3.36 (s, 3H), 3.40-3.70 (m, 2H), 4.20-4.60 (m, 3H), 6.70-7.90 (m, 10H)	56.89 (d), 59.20 (q), 67.34 (t), 70.67 (t), 121.95 (d), 122.07 (d), 123.23 (d), 124.05 (d), 128.26 (d), 128.78 (d), 138.23 (s), 147.32 (s), 149.88 (s)
4d	3.95-4.23 (m, 1H), 4.30-4.95 (m, 2H), 5.14-5.53 (m, 2H), 5.55-6.10 (m, 1H), 6.70-7.85 (m, 10H)	60.05 (d), 69.07 (t), 119.11 (t) 121.73 (d), 122.00 (d), 123.25 (d), 123.53 (d), 128.25 (d, 2C), 134.84 (d), 138.59 (s), 147.25 (s), 149.41 (s)
4e	0.70-1.90 (m, 10H), 3.30 (t, 2H, J = 7.0 Hz), 3.80-4.15 (m, 1H), 4.20-4.70 (m, 2H), 6.90-8.00 (m, 5H)	14.07 (q), 17.76 (q), 20.69 (t), 33.89 (t), 46.27 (t), 53.28 (d), 70.35 (t), 121.52 (d), 123.16 (d), 128.68 (d), 138.93 (s), 150.63 (s)
4f	0.70-1.90 (m, 7H), 2.90-3.80 (m, 5H), 3.30 (s, 3H), 4.20-4.50 (m, 2H), 6.85-7.80 (m, 5H)	14.10 (q), 20.75 (t), 33.98 (t), 46.54 (t), 56.76 (q), 59.29 (d), 66.85 (t), 71.01 (t), 120.42 (d), 122.86 (d), 128.77 (d), 139.44 (s), 149.96 (s)
4g	0.75-1.80 (m, 17H), 2.80-3.90 (m, 5H), 4.10-4.40 (m, 2H)	13.58 (q, 2C), 13.95 (q), 17.21 (t), 20.26 (t), 29.59 (t), 34.38 (t), 42.49 (t), 46.05 (t), 52.24 (d), 70.66 (t), 153.65 (s)
4h	0.60-1.80 (m, 14H), 2.70-4.40 (m, 9H), 3.35 (s, 3H)	13.98 (q, 2C), 20.14 (t), 20.66 (t), 29.44 (t), 34.32 (t), 43.31 (t), 46.21 (t), 55.78 (d), 59.32 (q), 67.21 (t), 72.73 (t), 153.71 (s)
5a	1.45 (d, 3H, J = 6.0 Hz), 3.55 (dd, 1H, J = 7.0 and 8.0 Hz), 4.05 (t, 1H, J = 8.0 Hz), 4.50-4.90 (m, 1H), 6.90-7.80 (m, 10H)	20.25 (q), 52.99 (t), 71.87 (d), 118.84 (d), 122.36 (d), 122.90 (d), 123.44 (d), 128.58 (d), 128.87 (d), 139.97 (s), 147.50 (s), 149.02 (s)
5b	3.90 (t, 1H, J = 8.3 Hz), 4.30 (t, 1H, J = 8.3 Hz), 5.50 (t, 1H, J = 8.3 Hz), 6.80-7.80 (m, 15H)	55.44 (t), 77.12 (d), 119.53 (d), 123.10 (d), 123.68 (d), 124.11 (d), 126.49 (d), 129.17 (d), 129.47 (d), 129.60 (d, 2C), 139.05 (s), 140.33 (s), 147.77 (s), 149.17 (s)
5c	3.40 (s, 3H), 3.55 (d, 2H, J = 5.8 Hz), 3.75-4.05 (m, 2H), 4.50-4.80 (m, 1H), 6.80-7.90 (m, 10H)	48.23 (t), 59.60 (q), 72.53 (t), 73.53 (d), 118.63 (d), 122.26 (d), 122.74 (d), 123.35 (d), 128.44 (d), 128.69 (d), 139.70 (s), 147.26 (s), 148.45 (s)
5d	3.45-3.85 (m, 1H), 4.10 (t, 1H, J = 8.8 Hz), 4.47-4.95 (m, 1H), 5.10-5.60 (m, 2H), 5.60-6.13 (m, 1H), 6.70-7.90 (m, 10H)	48.58 (t), 55.84 (d), 117.92 (d), 119.05 (t), 121.27 (d), 122.80 (d), 123.74 (d), 128.59 (d, 2C), 136.00 (d), 138.47 (s), 139.81 (s), 154.87 (s)

Table 6 (continued)

	^{1}H NMR δ (ppm) (Deuteriochloroform)	^{13}C NMR δ (ppm) (Deuteriochloroform)
5e	0.95-1.70 (m, 10H), 3.30 (t, 2H, J = 7.0 Hz), 3.45 (t, 1H, J = 7.0 Hz), 3.95 (t, 1H, J = 7.0 Hz), 4.50-4.80 (m, 1H), 6.80-7.80 (m, 5H)	14.00 (q), 20.10 (q), 20.60 (t), 34.00 (t), 46.50 (t), 52.90 (t), 70.90 (d), 118.00 (d), 121.80 (d), 128.60 (d), 140.70 (s), 149.50 (s)
5f	0.80-1.80 (m, 7H), 3.10-4.10 (m, 6H), 3.40 (s, 3H), 4.50-4.80 (m, 1H), 6.80-7.80 (m, 5H)	14.07 (q), 20.81 (t), 34.19 (t), 46.72 (t), 48.65 (t), 59.59 (q), 72.98 (d), 73.40 (t), 118.04 (d), 121.82 (d), 128.62 (d), 140.88 (s), 148.74 (s)
5g	0.80-1.70 (m, 17H), 2.95-3.50 (m, 5H), 3.65 (t, 1H, J = 8.0 Hz), 4.60-4.90 (m, 1H)	13.80 (q, 2C), 19.90 (q), 20.20 (d, 2C), 29.20 (t, 2C), 33.40 (t), 45.30 (t), 53.20 (t), 73.60 (d), 155.50 (s)
5h	0.70-1.90 (m, 14H), 2.90-3.90 (m, 8H), 3.44 (s, 3H), 4.30-4.70 (m, 1H)	14.07 (q), 14.19 (q), 20.23 (t), 20.72 (t), 29.62 (t), 34.41 (t), 45.23 (t), 46.39 (t), 48.46 (t), 59.62 (q), 73.37 (t), 73.77 (d), 154.84 (s)

β-aminoalcohols are obtained by alkaline hydrolysis of oxazolidin-2-one readily [3a]. Accordingly, β-aminoalcohols bearing a primary alcohol **6** were synthesized from monosubstituted oxiranes selectively by following procedures, that is, cycloaddition of oxiranes with isocyanates or carbodiimides in the presence of **1** and acidic and alkaline hydrolysis.

Conclusion.

The α-cleavage cycloaddition of oxiranes with heterocumulenes such as isocyanates and carbodiimides proceeded in high selectivities and good yields in the presence of a catalytic amount of **1**. In particular, a completely selective cycloaddition was readily effected in the reaction with carbodiimides. Moreover, it is noteworthy that a beautiful control for the direction of cycloaddition of oxiranes with isocyanates or carbodiimides has been achieved by the compensatory use of **1** and organotin iodide-Lewis base complexes as catalysts, and thus the former catalyst gave α-cleavage cycloadducts and the latter gave β-cleavage ones.

EXPERIMENTAL

General Data.

Melting points were obtained by using a Yanaco Micromelting point apparatus and are uncorrected. The ir spectra were recorded on a Hitachi 260-30 spectrometer using potassium bromide pellets or KRS-5 cells. Mass spectra were obtained on a Hitachi RUM-6 mass spectrometer operating at 70 eV. The ^{1}H nmr and ^{13}C nmr glc spectra were performed on Hitachi R-90H. Analytical glc was performed on a Shimadzu GC-8A with FID (OV-1 or FFAP). Elemental analyses were performed by the section on elemental analysis in our department.

Materials.

All oxiranes were freshly distilled from calcium hydride. Diphenylcarbodiimide [14], phenyl-*n*-butylcarbodiimide [15] and di-*n*-butylcarbo-

diimide [15] were prepared according to described methods. Isocyanates were commercial ones and used without further purification. Tetraphenylstibonium iodide (**1**), tetraphenylstibonium bromide [16] and triphenylantimony diiodide [17] were prepared according to described methods. Organotin iodides, tri-*n*-butyltin iodide, di-*n*-butyltin diiodide were produced according to described methods [18].

General Preparation.

3,4-Disubstituted Oxazolidin-2-ones **2** and 3,5-Disubstituted Oxazolidin-2-ones **3**.

To a solution of an oxirane (30 mmoles) and **1** (0.56 g, 1 mmole) in 5 ml of a solvent as shown in Table 1 was added dropwise an isocyanate (10 mmoles) for 60 minutes at the appropriate temperature. After heating, volatiles were removed under reduced pressure, then the resulting mixture was subjected to silica gel column chromatography, yielding nearly pure **2** and **3**.

3,4-Disubstituted Oxazolidin-2-imines **4**.

To a solution of an oxirane (50 mmoles) and **1** (0.56 g, 1 mmole) in 5 ml of benzene was added a carbodiimide (10 mmoles) in one portion. After heating for the time prescribed in Table 2, volatiles were removed under reduced pressure, then the resulting mixture was subjected to triethylamine-treated silica gel column chromatography, yielding nearly pure **4**.

3,5-Disubstituted Oxazolidin-2-imines **5**.

The solution of an organotin iodide and Lewis base (1 mmole) in an oxirane (50 mmoles) was stirred for 5 minutes at ambient temperature. Then a carbodiimide (10 mmoles) was added slowly, and the resulting mixture was heated at 40° for a few hours. Nearly pure product **5** was obtained in a similar manner as in the isolation of **4**.

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