Stereospecific Cycloaddition of Heterocumulenes to Oxiranes Catalyzed by Organotin Halide Complexes

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Stereospecific cycloaddition of 2,3-disubstituted oxiranes to heterocumulenes, including carbodiimides, isocyanates and carbon dioxide, is catalytically promoted by dialkyltin diiodide-hexamethylphosphoric triamide (HMPA) system, producing various five-membered heterocycles, where the configuration of the carbons in the oxirane ring is retained. In particular, the addition of isocyanates to oxiranes gave stereospecifically two types of products, dioxolan-2-imines and oxazolidin-2-ones independently, while the rearrangement of the former to the latter product has been already proposed.

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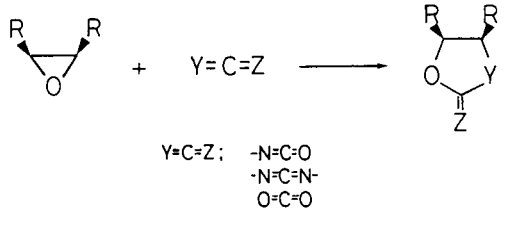
Introduction.

The cycloaddition of oxiranes to heterocumulenes is one of the significant methods for the formation of five-membered heterocycles and has the intrinsic advantage that there are no accompaning by-products. In this type of addition many types of catalysts have been investigated such as metal alkoxides, amines, ammonium halides, and metal halides [1]. However some significant drawbacks remain. Some of these are: (1) facile rearrangement of products because of the reaction conditions requiring high temperature [2]; (2) far lower reactivity of 2,3-disubstituted oxiranes in comparison with monosubstituted ones [1e]. The paucity of investigation on the stereochemistry of this type of cycloaddition is thus responsible for the difficulty of effective catalytic promotion under mild conditions. Recently, in the presence of Pd(0) catalyst, a stereo-controlled cycloaddition of isocyanates to vinylic oxiranes has attracted attention in the formation of an intermediate of a natural product [3]. Keshava reported that chrolosulphonyl isocyanate, a very active isocyanate, stereospecifically adds to oxiranes without a catalyst [4]. Thus, stereo-controlled cycloadditions might be important synthetic methods. The scope of available reagents, however, seems to be restricted. We have already reported that the catalytic activity of organotin halides was dramatically enhanced by coordination of Lewis bases such as phosphines and phosphine oxides, furnishing many five- and six-membered heterocycles from the addition of heterocumulenes to cyclic ethers [5]. This enhancement would be due to the coordination increasing the nucleophilicity of the halide.

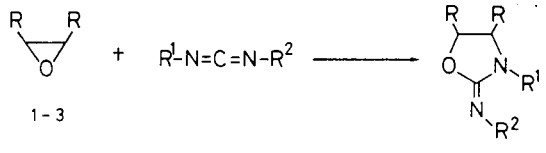
Herein we wish to adapt dialkyltin diiodide-HMPA complexes to stereospecific cycloadditions of 2,3-disubstituted oxiranes to heterocumulenes such as carbodiimides, iso-

Scheme 1



Y=C=Z; -N=C=O
-N=C=N-
O=C=O

Scheme 2



1 - 3

4 - 9

1c,1t: R=Me
2c,2t: Ph
3c: R-R=-$(CH_2)_4$-

No	R	R	R^1	R^2
4c, 4t	Me	Me	Ph	Ph
5c, 5t	Me	Me	Ph	Bu
6c, 6t	Me	Me	Bu	Bu
7c, 7t	Me	Me	c-Hex	c-Hex
8c, 8t	Ph	Ph	Ph	Ph
9c, 9t	-$(CH_2)_4$-		Ph	Ph
10c,10t	Me	Me	Ph	^{i}Pr

c:cis t:trans

Table 1

Cycloaddition of Carbodiimides to Oxiranes [a]

Entry	Oxirane	R^1-NCN-R^2 (R^1	R^2)	Time (hours)	Product	yield (%) [b]
1	**1c**	Ph	Ph	0.6	**4c**	100
2	**1t**	Ph	Ph	7	**4t**	88
3	**1c**	Ph	Bu	0.5	**5c**	99
4	**1t**	Ph	Bu	4	**5t**	76
5 [c]	**1t**	Ph	Bu	32	**5t**	91
6	**1c**	Bu	Bu	2	**6c**	94
7	**1t**	Bu	Bu	9.5	**6t**	84
8 [d]	**1c**	c-Hex	c-Hex	3	**7c**	82
9 [d]	**1t**	c-Hex	c-Hex	16	**7t**	85
10	**1c**	c-Hex	c-Hex	20	**7c**	98
11	**2c**	Ph	Ph	0.8	**8c**	77
12	**2t**	Ph	Ph	7	**8t**	56
13	**3c**	Ph	Ph	5	**9c**	100
14 [c]	**1c + 1t** (50/50)	Ph	^{i}Pr	2	**10c**	95 [e]

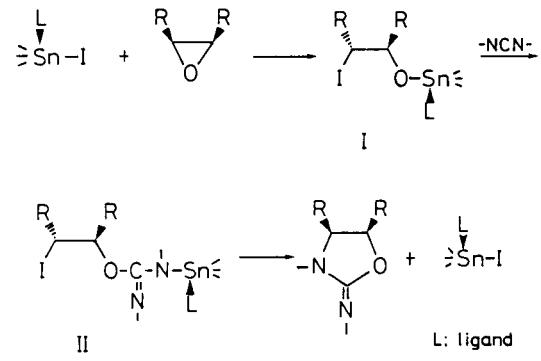
[a] Oxirane/NCN/dimethyltin diiodide/HMPA = 6/5/0.5/0.5 mmole, 40°, benzene 3 ml. [b] Glc yields. [c] Dibutyltin diiodide-tributylphosphine was used instead of dimethyltin diiodide -HMPA at 50°. [d] In an ampule, 80°. [e] A little amount (<2% yield) of **10t** was detected.

cyanates and carbon dioxide, where the configuration of oxirane carbons is retained as exemplified for the addition of *cis*-oxiranes in Scheme 1. This stereospecific transformation appears to be achieved by a route that features a double inversion of configuration.

Reaction of Carbodiimides and Oxiranes.

Table 1 exhibits typical examples of stereospecific cycloaddition of oxiranes to carbodiimides in the presence of dialkyltin diiodide complexes. At 40° heating either *cis*- or *trans*-oxiranes with carbodimides provided the corresponding oxazolidin-2-imines in high to quantitative yields without any detectable isomers. For example *cis*-2,3-dimethyloxirane (**1c**) led to *cis*-4,5-dimethyloxazolidin-2-imine **4c** quantitatively, where neither the *trans* isomer nor diazoidin-2-one, reported readily to be produced by the rearrangement of **4**, was not a contaminant at all. The choice of catalyst was very significant, and the dimethyltin diiodide-HMPA system was the most active catalyst investigated, while the use of dibutyltin diiodide-tributylphosphine required far longer reaction time (entry 5). Contrarily, in the case of monosubtituted oxiranes even trialkyltin iodides were active enough to give cycloadducts under mild conditions [5c]. Even the additions of low reactive substrates such as, for example, dialkylcarbodiimides and *trans*-2,3-diphenyloxirane (entries 6, 7, 10, 12) were easily promoted by this active catalyst. In the reaction using phenylalkylcarbodiimides, the C=N bond attached to the phenyl group was selectively incorporated in the oxazolidine ring (entries 3-5 and 14). Of interest is the large difference in reactivity between *cis*- and *trans*-oxiranes (for example, entries 1 and 2). Particularly, by the use of the dibutyltin diiodide-tributylphosphine system, the selective consumption of *cis*-oxirane **1c** was demonstrated in the reaction of phenylisopropylcarbodiimide and the mixture of *cis*- and *trans*-oxirane. Thus, all of the *cis*-oxirane was consumed leaving little of the *trans* isomer for transformation (entry 14).

Scheme 3



This stereospecific transformation is rationalized by a route that features a double inversion of configuration as illustrated in Scheme 3. In the first step, the nucleophilic attack of the iodide to a carbon of the oxirane ring causes the first inversion of configuration of the carbon atom, where the coordination of the oxirane oxygen toward the tin atom would assist this attack. A similar facile cleavage of the oxirane ring was reported to take place by trimethyltin halides [6]. Then a carbodiimide inserts into the Sn-O bond of the resulting tin alkoxide **I** to lead the adduct **II**. In the last step, the second inversion at the terminal car-

Scheme 4

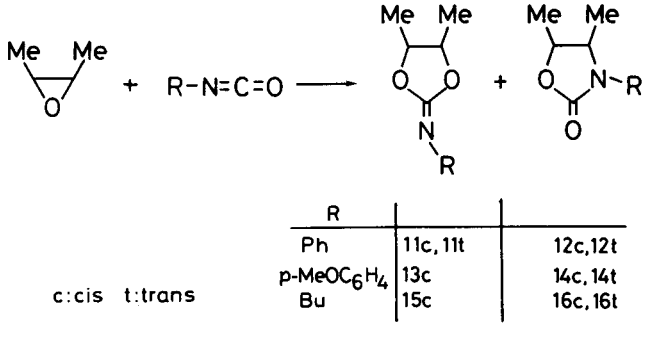


Table 2

Cycloadditon of Isocyanates to Oxiranes [a]

Entry	Oxirane	RNCO (R)	Temp (°C)	Time (hours)	Catalyst	Yield (%) [b]	Product and Ratio
1	**1t**	ph	45	6	Me_2SnI_2	73	**11t, 12t** (41/59)
2	**1c**	ph	45	3	Me_2SnI_2	68	**11c, 12c** (87/13)
3	**1c**	*p*-$MeOC_6H_4$	45	8	Me_2SnI_2	60	**13c, 14c** (79/21)
4	**1c**	Bu	40	4	Me_2SnI_2	22	**15c, 16c** (100/0)
5	**1c**	ph	85	5	Bu_2SnI_2	100	**11c, 12c, 12t** (55/20/25)
6	**1t**	ph	80	22	Me_2SnBr_2	62	**11t, 12t, 12c** (39/40/21)
7	**1c**	*p*-$MeOC_6H_4$	80	3	Me_2SnI_2	98	**13c, 14c 14t** (63/ 9/28)
8	**1c**	Bu	40	10	Me_2SnI_2	37	**15c, 16c, 16t** (89/ 0/11)

[a] Oxirane/NCO/catalyst/HMPA = 6/5/0.5/0.5 mmole, benzene 3 ml. [b] Glc yield.

bon bearing an iodo atom in **II** accomplishes the cyclization with retention of the configuration. The well-known high reactivity of carbodiimides to Sn-O bonds [7] is also responsible for this cycloaddition. As already reported [8], the coordination of HMPA to tin atom seems to increase the nucleophilicity of adjacent heteroatoms, enhancing both the cleavage of oxiranes and the last ring formation.

Table 3

Cycloaddition of Carbon Dioxide to Oxirane [a]

Entry	Oxirane	Catalyst	Temp (°C)	Time (hours)	Carbonate	Yield (%) [b]
1	**1c**	Me_2SnI_2-HMPA	45	5	**17c**	35
2	**1t**	Me_2SnI_2-HMPA	50	42	**17t**	27
3	**1c**	Me_2SnI_2-HMPA	80	5	**17c**	12
4	**1t**	Bu_3SnI-Bu_4PI	80	5	**17c, 17t**	73 (7/93) [c]
5	**3c**	Bu_3SnI-Bu_4PI	80	2	**18c**	91

[a] Oxirane/catalyst = 3/0.3 mmole, CO_2 = 50 kg/cm^2. [b] Glc yield. [c] Ratio of **17c**:**17t**.

Table 4

Physical and Analytical Data of Oxazolidin-2-imines

Product No.	bp (C/mmHg)	Ir (cm^{-1}) C=N	^{1}H NMR (ppm)	^{13}C NMR (ppm)
4c	(mp 88-91)	1665	1.18 (d, 3H, J = 6.2 Hz), 1.36 (d, 3H, J = 6.2 Hz) 4.36 (quint, 1H, J = 6.25 Hz), 4.72 (quint, 1H, J = 6.25 Hz), 6.80-8.00 (m, 10H)	12.47 (q), 14.37 (q), 56.19 (d), 75.10 (d), 121.62 (d), 121.81 (d), 121.96 (d), 123.30 (d), 123.48 (d), 128.15 (d), 128.61 (d), 138.48 (s), 147.36 (s), 149.22 (s)
4t	(mp 125-127)	1670	1.31 (d, 3H, J = 6.3 Hz), 1.47(d, 3H, J = 6.3 Hz) 3.97 (quint, 1H, J = 6.1Hz), 4.28 (quint, 1H, J = 6.1 Hz), 6.85-7.80 (m, 10H)	17.13 (q), 18.72 (q), 59.49 (d), 79.00 (d), 121.62 (d), 122.54 (d), 123.18 (d), 123.85 (d), 128.00 (d), 128.42 (d), 138.15 (s), 147.30 (s), 149.64 (s)
5c	110/0.1	1695	0.80-1.70 (m, 13H), 3.30 (t, 2H, J = 6.59 Hz) 4.23 (quint, 1H, J = 6.34 Hz), 4.60 (quint, 1H, J = 6.34 Hz), 6.85-7.75 (m, 5H)	12.45 (q), 14.16 (q), 14.68 (q), 20.78 (t), 34.13 (t), 46.54 (t), 56.30 (d), 74.26 (d), 120.33 (d), 122.34 (d), 128.71 (d), 139.72 (s), 149.69 (s)
5t	113/0.1	1690	0.80-1.70 (m, 13H), 3.29 (t, 2H, J = 6.59 Hz) 3.82 (quint, 1H, J = 6.34 Hz), 4.18 (quint, 1H, J = 6.34 Hz), 6.80-7.70 (m, 5H)	14.07 (q), 17.36 (q), 19.13 (q), 20.66 (t), 33.98 (t), 46.30 (t), 59.62 (d), 78.25 (d), 121.85 (d), 123.07 (d), 128.56 (d), 139.41 (s), 150.39 (s)
6c	60/0.1	1705	0.55-1.90 (m, 20H), 2.60-3.45 (m, 4H) 3.62 (quint, 1H, J = 6.34 Hz) 4.48 (quint, 1H, J = 6.34 Hz)	11.97 (q), 14.04 (q), 14.13 (q), 14.86 (q), 20.29 (t), 20.69 (t), 29.53 (t). 34.47 (t), 42.09 (t), 46.21 (t), 54.50 (d), 74.74 (d), 153.50 (s)
6t	58/0.1	1700	0.75-1.90 (m, 20H), 2.60-3.60 (m, 5H) 3.94 (quint, 1H, J = 6.34 Hz)	13.86 (q), 13.98 (q), 16.75 (q), 18.46 (q), 20.14 (t), 20.50 (t), 28.95 (t), 34.25 (t), 42.27 (t), 45.90 (t), 58.89 (d), 78.46 (d), 153.35 (s)
7c	130/0.1	1695	1.02-2.25 (m, 26H), 3.20-3.80 (m, 3H) 4.32 (quint, 1H, J = 7.35 Hz)	14.45 (q), 15.61 (q), 25.12 (t), 25.58 (t), 25.70 (t), 25.86 (t) 29.76 (t), 31.47 (t), 34.97 (t), 35.25 (t), 52.02 (d), 53.23 (d) 54.21 (d), 74.88 (d), 151.38 (s)
7t	120/0.1	1695	0.70-190 (m, 26H), 3.05-3.75 (m, 3H) 3.96 (quint, 1H, J = 6.3 Hz)	19.27 (q), 20.98 (q), 25.31 (t), 25.79 (t), 25.98 (t), 29.09 (t), 32.01 (t), 35.12 (t), 35.31 (t), 53.48 (d), 54.39 (d), 56.28(d) 78.36 (d), 152.08 (s)
8c	mp 148-149	1660	5.48 (d, 1H, J = 8.0 Hz), 5.95 (d, 1H, J = 8.0 Hz) 6.70-7.85 (m, 20H)	66.35 (d), 81.68 (d), 120.07 (d), 122.48 (d), 122.97 (d), 123.61 (d), 126.44 (d), 127.10 (d), 127.78 (d), 128.21 (d), 128.48 (d), 134.00 (s), 135.07 (s), 139.00 (s), 147.00 (s), 149.23 (s)
8t	(mp 146)	1665	5.08 (d, 1H, J = 5.5 Hz), 5.25 (d, 1H, J = 5.5 Hz) 6.70-7.80 (m, 20H)	69.71 (d), 85.11 (d), 121.61 (d), 122.52 (d), 123.62 (d), 123.74 (d), 125.78 (d), 126.55 (d), 128.13 (d), 128.59 (d), 128.99 (d), 129.30 (d), 138.07 (s), 138.29 (s), 138.71 (s) 147.07 (s), 149.57 (s)
9c	(mp 81)	1665	1.00-2.45 (m, 8H), 4.00-4.30 (m, 1H) 4.50-4.70 (m, 1H), 6.85-7.75 (m, 10H)	19.80 (t), 20.53 (t), 26.08 (t), 26.81 (t), 56.42 (d), 74.96 (d), 121.39 (d), 121.91 (d), 123.44 (d), 128.22 (d), 128.65 (d), 138.74 (d), 147.49 (s), 149.93 (s)
10c	87/0.1	1685	1.16 (d, 9H, J = 6.3 Hz), 1.36 (d, 3H, J = 6.3 Hz) 3.70-4.05 (m, 1H), 4.10-4.45 (m, 1H) 4.45-4.81 (m, 1H), 6.95-7.84 (m, 5H)	11.97 (q), 14.22 (q), 24.31 (q), 24.44 (q), 46.66 (d), 56.21 (d), 74.59 (d), 119.96 (d), 122.22 (d), 128.44 (d), 138.77 (s), 148.90 (s)
10t	84/0.1	1680	1.12 (d, 3H, J = 6.3 Hz), 1.16 (d, 3H, J = 6.3 Hz) 1.70 (d, 3H, J = 6.3 Hz), 1.43 (d, 3H, J = 6.3 Hz) 3.68-4.00 (m, 2H), 4.05-4.32 (m, 1H) 6.90-7.63 (m, 5H)	17.33 (q), 19.13 (q), 24.53 (q), 46.66 (d), 59.56 (d), 78.40 (d), 121.33 (d), 122.86 (d), 128.44 (d), 138.96 (s), 149.32 (s)

Reaction of Isocyanates and Oxiranes.

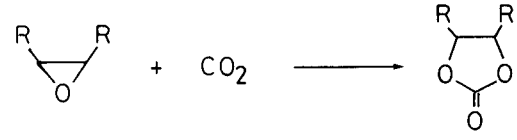
The cycloaddition reaction of isocyanates with oxiranes has been extensively studied in comparison with one of the other heterocumulenes, because various substrates are easily available and the resulting oxazolidin-2-ones are often used as biological reagents and as precursors of aminoalcohols [9].

As shown in Table 2, organotin iodide catalysts readily effected the addition of isocyanates to 2,3-disubstituted oxiranes under mild conditions, producing two types of adducts, dioxolan-2-imines, **11**, **13** and **15** and oxazolidin-2-ones **12**, **14** and **16**. The configuration was retained in both types of products also in the case of carbodiimides. In the cycloaddition of oxiranes with isocyanates, it has been generally believed that iminodioxolanes are preliminary adducts and are rearranged to oxazolidin-2-ones [2a and 3a]. However, neither *cis*-**11c** nor *trans*-4,5-dimethyldioxolan-2-imine **11t** was transformed by heating at 80° for 20 hours in the presence of dimethyltin diiodide-HMPA.

In the next stage, when cycloadditions were carried out under more vigorous conditions the stereospecificity was apparently lost as exemplified in Table 2 (entries 5-8). However, of interest is that no dioxolan-2-imine having an opposite configuration to the oxiranes used was detected in all runs.

The above result could be rationalized by the idea that both types of products were stereospecifically produced in the direct reaction of isocyanates and oxiranes at first, and

Scheme 5



c: cis
t: trans

17c, 17t: R = Me
18c: R-R = -(CH2)4-

Table 5

Physical and Spectral Data of Products

Product No.	bp (C/mmHg)	Ir (cm^{-1})	^{1}H NMR (ppm)	^{13}C NMR (ppm)
11c	(mp 41-42)	1710 (C=N)	1.35 (br, 6H) [a], 4.38-4.93 (m, 2H) 6.80-7.45 (m, 5H)	14.04 (q), 75.41 (d), 77.49 (d), 123.00 (d), 128.34 (d), 145.38 (s), 152.49 (s)
11t	(mp 62-63)	1689 (C=N)	1.45 (br, 6H) [b], 4.02-4.47 (m, 2H) 6.80-7.50 (m, 5H)	17.55 (q), 79.38 (d), 81.45 (d), 122.98 (d), 128.35 (d), 145.30 (s), 152.68 (s)
12c	(mp 36-39)	1740 (C=O)	1.24 (d, 3H, J = 7.2 Hz), 1.46 (d, 3H, J = 6.8 Hz), 4.28-4.65 (m, 1H) 4.65-5.02 (m, 1H), 7.06-7.85 (m, 5H)	12.92 (q), 14.84 (q), 55.85 (d), 73.32 (d), 121.65 (d), 124.88 (d), 129.12 (d), 137.07 (s), 155.18 (s)
12t	(mp 53-55)	1730 (C=O)	1.32 (d, 3H, J = 6.3 Hz), 1.52 (d, 3H, J = 6.3 Hz), 3.90-4.16 (m, 1H) 4.16-4.45 (m, 1H), 7.10-7.60 (m, 5H)	12.82 (q), 14.77 (q), 55.75 (d), 73.25 (d) 121.55 (d), 124.78 (d), 129.0 (d), 137.0 (s) 155.10 (s)
13c	145/0.1	1708 (C=N)	1.36 (d, 6H, J = 4.7 Hz), 3.73 (s, 3H) 4.58-4.99 (m, 2H), 6.68-7.27 (m, 4H)	14.22 (q), 55.38 (q), 75.26 (d), 77.52 (d), 113.80 (d), 124.05 (d), 138.41 (s), 152.21 (s) 155.54 (s)
14c	175/0.1	1738 (C=O)	1.14 (d, 3H, J =6.8 Hz), 1.40 (d, 3H, J = 6.8 Hz). 3.81 (s, 3H), 4.32 (quint, 1H, J = 7.5 Hz), 4.81 (quint, 1H, J = 7.5 Hz) 6.78-7.06 (m, 2H), 7.15-7.60 (m, 2H)	13.03 (q), 14.86 (q), 55.47 (q), 56.45 (d), 73.28 (d), 114.44 (d), 124.56 (d), 138.86 (s) 155.61 (s), 157.16 (s)
14t	172/0.1	1740 (C=O)	1.25 (d, 3H, J = 6.6 Hz), 1.50 (d, 3H, J = 6.6 Hz), 3.80 (s, 3H), 3.90 (quint, 1H, J = 6.3 Hz), 4.28 (quint, 1H, J = 6.3 Hz) 6.70-7.02 (m, 2H), 7.10-7.40 (m, 2H)	17.85 (q), 19.40 (q), 55.41 (q), 59.99 (d), 77.27 (d), 114.35 (d), 124.78 (d), 138.17 (s), 155.81 (s), 157.40 (s)
15c	69/0.1	1720 (C=N)	0.90 (t, 3H, J = 6.3 Hz), 1.05-1.70 (m, 10H) 3.15 (t, 2H, J = 8.9 Hz), 4.25-4.97 (m, 2H)	13.78 (q), 14.02 (q), 14.18 (q), 20.31 (t), 33.39 (t), 46.04 (t), 74.79 (d), 76.26 (d), 152.02 (s)
16c	120/3	1745 (C=O)	0.75-1.55 (m, 13H), 3.41 (t, 2H, J = 6.8 Hz) 3.70-3.98 (m, 1H), 4.51-4.81 (m, 1H)	11.31 (q), 12.47 (q), 16.28 (q), 18.72 (t), 28.51 (t), 39.97 (t), 52.35 (d), 72.11 (d), 156.17 (s)
16t	40/0.1	1745 (C=O)	0.75-1.55 (m, 13H), 3.06 (t, 2H, J = 6.3 Hz) 3.24-3.54 (m, 1H), 3.97-4.22 (m, 1H)	12.47 (q), 13.57 (q), 18.02 (q), 18.72 (t), 28.26 (t), 39.97 (t), 56.62 (d), 75.98 (d), 156.08 (s)
17c	129-132/20	1800 (C=O)	1.35 (d, 6H, J = 6.34 Hz), 4.68-5.01 (m, 2H)	16.57 (q), 78.28 (d), 152.89 (s),
17t	129-132/20	1800 (C=O)	1.44 (d, 6H, J = 5.58 Hz), 4.18-4.52 (m, 2H)	12.61 (q), 74.44 (d), 152.80 (s)
18c	(mp 51)	1800 (C=O)	1.20-2.21 (m, 8H), 4.52-5.03 (m, 2H)	18.83 (t), 26.39 (t), 75.45 (d), 154.90 (s)

[a] 400 MHz mnr: 1.32 (d, 3H, J = 6.35 Hz), 1.36 (d, 3H, J = 6.35 Hz). [b] 400 MHz mnr: 1.42 (d, 3H, J = 5.86 Hz), 1.46 (d, 3H, J = 5.86 Hz),

that then the oxazolidinone of the opposite configuration was obtained *via* rearrangement of the resulting dioxolan-2-imine under vigorous conditions. This rearrangement appears to be assisted by other factors than heating and a catalyst. We are investigating the precise mechanism of this rearrangement, and it will be reported in the near future.

Table 6

Analytical and Mass Spectral Data of Products

Product No.	Mass Spectrum m/z	Molecular Formula	Analysis (%) Calcd./(Found) C	H	N
4c	266 (M^+)	$C_{17}H_{18}N_2O$	76.66	6.81	10.52
			(76.92	6.53	10.49)
4t	266 (M^+)	$C_{17}H_{18}N_2O$	76.66	6.81	10.52
			(76.71	6.69	10.38)
5c	246 (M^+)	$C_{15}H_{22}N_2O$	73.13	9.00	11.37
			(73.52	8.99	11.27)
5t	246 (M^+)	$C_{15}H_{22}N_2O$	73.13	9.00	11.37
			(73.15	8.94	11.28)
6c	226 (M^+)	$C_{13}H_{26}N_2O$	68.98	11.58	12.38
			(68.80	11.32	12.10)
6t	226 (M^+)	$C_{13}H_{26}N_2O$	68.98	11.58	12.38
			(68.52	11.51	12.17)
7c	278 (M^+)	$C_{17}H_{30}N_2O$	73.33	10.86	10.06
			(73.31	10.84	10.13)
7t	278 (M^+)	$C_{17}H_{30}N_2O$	73.33	10.86	10.06
			(73.31	10.91	10.04)
8c	390 (M^+)	$C_{27}H_{22}N_2O$	83.05	5.68	7.17
			(82.96	5.51	7.10)
8t	390 (M^+)	$C_{27}H_{22}N_2O$	83.05	5.68	7.17
			(83.00	5.71	7.09)
9c	292 (M^+)	$C_{19}H_{20}N_2O$	78.05	6.89	9.58
			(78.19	6.94	9.56)
10c	232 (M^+)	$C_{14}H_{20}N_2O$	72.38	8.68	12.06
			(72.62	8.83	12.15)
10t	232 (M^+)	$C_{14}H_{20}N_2O$	72.38	8.68	12.06
			(72.54	8.72	12.01)
11	191 (M^+)	[a]			
11t	191 (M^+)	[a]			
12c	191 (M^+)	$C_{11}H_{13}NO_2$	69.09	6.85	7.32
			(69.00	6.79	7.30)
12t	191 (M^+)	$C_{11}H_{13}NO_2$	69.09	6.85	7.32
			(68.85	6.78	7.41)
13c	221 (M^+)	$C_{12}H_{15}NO_3$	65.14	6.83	6.33
			(64.86	6.91	6.52)
14c	221 (M^+)	$C_{12}H_{15}NO_3$	65.14	6.83	6.33
			(65.21	6.82	6.31)
14t	221 (M^+)	$C_{12}H_{15}NO_3$	65.14	6.83	6.33
			(64.98	6.60	6.14)
15c	171 (M^+)	$C_9H_{17}NO_2$	63.13	10.01	8.18
			(62.90	10.14	8.07)
16c	171 (M^+)	$C_9H_{17}NO_2$	63.13	10.01	8.18
			(63.11	10.13	8.10)
16t	171 (M^+)	$C_9H_{17}NO_2$	63.13	10.01	8.18
			(62.94	10.09	8.04)
17c	116 (M^+)	[b]			
17t	116 (M^+)	[b]			
18c	142 (M^+)	[c]			

[a] Reference [15]. [b] Reference [11]. [c] Reference [12].

Reaction of Carbon Dioxide and Oxiranes.

Backvall already reported the stereochemistry of the formation of cyclic carbonates from a cycloaddition of oxiranes to carbon dioxide in the reaction using 1,2-dideuterioethylene oxide, where the configuration of the carbonates is significantly responsible for the catalysts employed [10]. A nickel complex catalyst, for example, gives a mixture of *cis*- and *trans*-dideuteriocarbonate (1:1).

Alkyltin iodide catalysts promoted stereospecific formations of cyclic carbonates as shown in Table 3. This cycloaddition also proceeded with retention of configuration of the oxiranes, although the yields of carbonates were low. An attempt to effect this reaction under more vigorous conditions suffered from a transformation of 2,3-dimethyloxirane to methyl ethyl ketone due to the low reactivity of carbon dioxide (entry 3). Instead of the HMPA complex, tributyltin iodide-tetrabutylphosphonium iodide system roughly effected the stereospecific reaction, prehaps because of lower acidity of this tin iodide. However, even in this case the *cis* isomer was still detected in a 7% ratio (entry 4). Although organotin iodide complexes were preliminarily confirmed to promote this stereospecific addition, a more effective tin complex would be required to promote this cycloaddition under mild conditions.

Conclusion.

The stereospecific cycloaddition of 2,3-disubstituted oxiranes with heterocumulenes was promoted by catalytic amounts of dimethyltin diiodide-HMPA complex, furnishing the corresponding five-membered heterocycles with retention of the configuration of the oxiranes.

EXPERIMENTAL

All temperatures are uncorrected. Melting points were recorded on a Yanaco microapparatus. Short-path distillations were carried out in a Kugelrohr apparatus. Spectrometric measurements were performed with the following instruments: ir, Hitachi 260 spectrophotometer; glc, Shimadzu GC-8A with FID (OV-1 or FFAP); mass spectra, Hitachi RUM-6; ^1H nmr and ^{13}C nmr, Hitachi R-90H (in deuteriochloroform, TMS as an internal standard). Microanalytical determinations were performed by the Analysis Center of our department.

HMPA was freshly distilled from calcium hydride prior to use. Tetrabutylphosphonium iodide was used after drying under reduced pressure for 24 hours. Reagent grade isocyanates and carbon dioxide were used without further purification. Carbodiimides [13] and organotin halides [14] were prepared by methods described in the literatures.

Reactions except using carbon dioxide were conducted in flame-dried glassware under a nitrogen atmosphere.

Reaction of Carbodiimides with Oxiranes.

The following procedure, described for diphenylcarbodiimide and *cis*-2,3-dimethyloxirane (**1c**), is representative. To a solution of dimethyltin diiodide (0.5 mmole), HMPA (0.5 mmole) and **1c** (6 mmoles) in 3 ml of benzene was added diphenylcarbodiimide (5 mmoles), and the resulting mixture was heated at 40°. After completion of the reaction (monitored by ir), column chromatography (silica gel, benzene as eluant) of the mixture afforded *cis*-4,5-dimethyl-3-phenyl-oxazolidin-2-(*N*-phenyl)imine (**4c**) as a colourless oil, bp 110°/0.1 mm Hg. The yields of products were determined by glc before column chromatography.

The physical and spectral data of oxazolidin-2-imines prepared by this general method are listed in Table 4.

Reaction of Isocyanates with Oxiranes.

The addition of 2,3-dimethyloxirane (**1c**) to phenyl isocyanate is representative. To the mixture of **1c** (6 mmoles), dimethyltin diiodide (0.5 mmole), HMPA (0.5 mmole) and benzene 3 ml was dropwise added phenyl isocyanate (5 mmoles) at 45°. The period of addition over 2 hours was preferable, otherwise trimerization of isocyanate was sometimes accompanied. After completion of the reaction, the reaction mixture was chromatographed on silica gel eluting with benzene to give *cis*-4,5-dimethyl-3-phenyoxazolidin-2-one (**12c**). On the other hand the corresponding 1,3-dioxolan-2-imine **11c** could not be isolated in completely pure form, and the identification was performed by comparison of spectral data (gc-ms, ^{1}H-nmr, and glc) with ones of the authentic samples prepared in accordance with reported method [15]. All dioxolan-2-imine derivatives were identified in a similar manner. The yields of products were determined by glc before column chromatography. The physical and spectral data of oxazolidin-2-ones and dioxolan-2-imines are listed in Table 5.

Reaction of Carbon Dioxide and Oxiranes.

A mixture of an oxirane (5 mmoles), dimethyltin diiodide (0.5 mmole), HMPA (0.5 mmole) and benzene 2 ml was placed in a 30 ml stainless steel autoclave, and then carbon dioxide gas was introduced up to 50 Kg/cm^2. The vessel was heated with stirring by a magnetic stirrer. After cooling, the reaction mixture was dissolved in benzene, and the yield of carbonates was determined by glc. The physical and spectral data of carbonates **17** and **18** are listed in Table 5.

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