Regioselective Cycloaddition of 1,2-Disubstituted Aziridines to Heterocumulenes Catalyzed by Organoantimony Halides

Ryoki Nomura*, Takahiro Nakano, Yoshitaka Nishio, Sachiko Ogawa, Akira Ninagawa *), and Haruo Matsuda

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-Oka, Suita, Osaka 565 (Japan)

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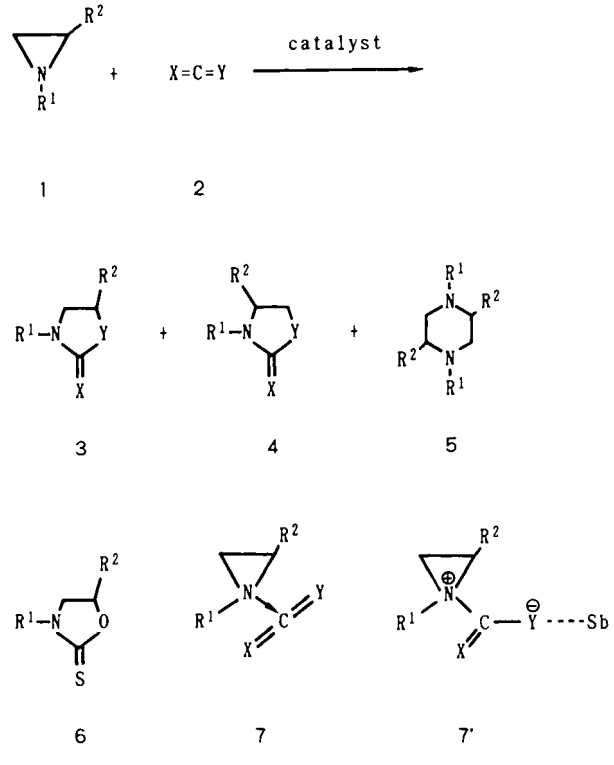
In the presence of catalytic amounts of organoantimony(V) halides such as Ph_4SbI, Ph_4SbBr, Ph_3SbBr_2, and Ph_3SbCl_2, the cycloaddition of aziridines 1a–g with heterocumulenes (phenyl isothiocyanate, carbon disulfide, and carbon dioxide) selectively gave ring-expanded cycloadducts 3a–d, f, g, and 6e by α-cleavage of the aziridine rings.

It is well known that the direction of ring opening of activated aziridines (**1**, R^1 = acyl or sulfonyl, etc.) is influenced by the nucleophiles employed and/or the reaction media. Thus, two types of products, resulting from ring cleavage across $N-CH_2$[1] and across N–CH[2], can be separately synthesized. On the other hand, reactions of the less activated aziridines (**1**, R^1 = alkyl or aryl, etc.) with nucleophiles generally gave type-**4** products by ring cleavage across $N-CH_2$, although contaminated by significant amounts of type-**3** by-products[3–7]. The direction of the latter ring cleavage dominantes when R^2 is aryl or aroyl, since these stabilize the charge generated at the ring carbon during the reaction[8]. Directional control of the ring opening of the less activated aziridines is therefore an urgent target. Thus, our recent findings that certain quinquevalent organoantimony halides promote the cycloaddition of oxiranes with heterocumulenes selectively by α-cleavage[9,10] encouraged their application to the regioselective ring opening of the aziridine systems as well.



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Cycloaddition of aziridines **1a–g** with heterocumulenes (phenyl isothiocyanate, carbon disulfide, and carbon dioxide) was carried out, catalyzed by several organoantimony halides. The organoantimony halides employed were Ph_4SbX, Ph_3SbX_2, and Me_3SbX_2, where X = Cl, Br, and I, and all nine organoantimony halides selectively gave cycloadducts (**3a–d, f, g,** and **6e**) in moderate to good yields. Since the different organoantimony catalysts were effective in all reactions, we have summarized the results of the process in Table 1, focusing on the most effective orgaoantimony halides.

Table 1. Cycloaddition of aziridines with heterocumulenes in the presence of catalysts

	R^1	R^2	X	Y	Catalyst	T/°C	t/h	Products (%)
a	Ph	H	PhN	S	Ph_4SbBr	80	2	**3a** (67)
	Ph	H	PhN	S	Bu_3SnI	80	2	**3a** (57), **5a** (23)
b	Ph	Me	PhN	S	Ph_3SbBr_2	100	20	**3b** (50)
c	Ph	Et	PhN	S	Ph_3SbCl_2	100	20	**3c** (76)
	Ph	Et	PhN	S	Bu_3SnI	100	20	**5c** (56), **3c** (13)
	Ph	Et	PhN	S	Bu_4NBr	100	20	**3c** (23), **4c** (21)
d	nBu	Et	PhN	S	none	100	1	**4d** (81), **3d** (10)
	nBu	Et	PhN	S	Ph_4SbI	100	1	**3d** (74)
e	Ph	Et	S	S	Ph_4SbI	180	20	**6e** (60)
f	Ph	Me	O	O	Ph_4SbBr	60	24	**3f** (73)
	Ph	Me	O	O	Bu_3SnI	60	24	**5b** (88)
	Ph	Me	O	O	Bu_4NBr	60	24	**3f** (50), **4f** (47)
g	Ph	Et	O	O	Ph_4SbBr	60	24	**3g** (81)
	Ph	Et	O	O	Bu_4NBr	60	24	**3g** (44), **4g** (40)

Reactions without catalyst, or catalyzed by organotin halides or ammonium halides, were also carried out, but they gave distinctly different results from those catalyzed by organoantimony halides (Table 1). The uncatalyzed cycloaddition gave both type-**3** and type-**4** cycloadducts in poor yields (trace to 40%), with one exception. Thus, it may be stated that the organoantimony catalysts accelerate the cycloaddition, leading to high regioselectivity.

Organotin halides such as Bu_3SnI which is known as an alternative catalyst for the regioselective cycloaddition of oxiranes[12], show a strong tendency to dimerize aziridines to piperazines. This presumably results from their higher Lewis acidity than organoantimony halides[9a]. Ammonium salts, which are also known as classical ring opening catalysts for aziridines[13], displayed only limited regioselectivity.

As reported earlier[9b,10b], the ring opening of oxiranes is considered to be formally initiated by an insertion of both substrates

*) Present address: Department of Industrial Arts, Takaoka National College, Takaoka, Toyama 933 (Japan).

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into Sb–X bonds. Such a concerted insertion path may also operate during the cycloaddition of aziridines catalyzed by organoantimony compounds as judged on the basis of the ^{13}C- and ^{14}N-NMR investigations summarized in Table 2.

Table 2. ^{13}C- and ^{14}N-chemical shift changes in the reaction media

Specimen	$\delta(^{13}C)$[a]		$\delta(^{14}N)$[b,c]	
	$N-CH_2$	NCS	$N-CH_2$	NCS
$PhN(CH_2)_2$	27.2	–	25	–
PhNCS	–	135.7	–	122
$PhN(CH_2)_2$ + PhNCS	27.3 (+0.1)	131.1 (−4.6)	nd	100 (−22)
$PhN(CH_2)_2$ + PhNCS + Bu_3SnI	27.9 (+0.7)	131.3 (−4.4)	nd	151 (+29)
$PhN(CH_2)_2$ + Ph_4SbBr	27.2 (0)	–	nd	–
$PhN(CH_2)_2$ + Bu_3SnI	28.5 (+1.3)	–	nd	–

[a] Values of $\Delta(\delta^{13}C)$ are in parentheses, where $\Delta(\delta^{13}C)$ means [($\delta^{13}C$ in the mixture) − ($\delta^{13}C$ in $Ph(CH_2)_2$ or PhNCS)]. – [b] Values of $\Delta(\delta^{14}N)$ are in parentheses, where $\Delta(\delta^{14}N)$ means [($\Delta\delta^{14}N$ in the mixture) − ($\delta^{14}N$ in PhNCS)]. – [c] nd denotes not detected.

First of all, it is noteworthy that both $\delta N^{13}CS$ and $\delta^{14}NCS$ appeared at higher fields for the mixture of 1-phenylaziridine and phenyl isothiocyanate than for the individual materials. Such observations indicate a significant electron donation from aziridine to isothiocyanate, presumably resulting from the formation of **7** in situ[15]. In contrast, $\delta^{14}NCS$ is shifted to lower fields when the organometallic catalyst was added to the mixture, suggesting strong interaction between **7** and the organometallic catalyst. Based on these spectral changes, we could assume that the cycloaddition was initiated by an insertion of **7** into the metal–halogen bonds. Thus, an increasing electron donation from aziridine in **7** was promoted by coordination to the organoantimony catalyst as shown in **7'**, and the aziridine ring was cleaved in a borderline S_N2 manner predominantly at he N–CH bond[9].

A similar cycloaddition path has been reported for the Pd-induced reaction of aziridines with isocyanide[14], by which the cycloaddition of **1** to **2** via **7'** should be rationalized.

The interaction, between organotin catalysts and 1-phenylaziridine, is stronger than the one between organoantimony halides and 1-phenylaziridine, as suggested from the difference in $\Delta(\delta N^{13}CH_2)$ resulting from the higher Lewis acidities of organotin halides than those of organoantimony halides[9]. Thus, it is concluded that organotin halides as Lewis acids activate aziridines so strongly as to dimerize them. In contrast, organoantimony halides could not activate aziridines themselves and selectively promote the cycloaddition by α-cleavage.

Experimental

^1H-, ^{13}C-, ^{14}N-NMR, and IR spectra (KRS-5 windows or KBr pellets) were recorded with a Hitachi R 90 H FT spectrometer and a Hitachi 260-30 spectrophotometer, respectively. Data acquisition conditions of ^{14}N-NMR spectra (6.50 MHz) were as following: pulse width 24 μs, pulse interval 10–30 s, number of acquisition 100 to 300, data points 4 K. Chemical shifts were measured with respect to external CH_3NO_2 and are reported on the ammonia scale [$\delta^{14}N(CH_3NO_2)$ 383]. Neat samples including equimolar mixtures were employed. – MS were obtained using a Jeol JMS-DX 303 (Faculty of Engineering, Osaka University).

Aziridines[16] and organometallic catalysts[9a,10b] employed were prepared by usual procedures.

Reactions of Aziridines with Phenyl Isothiocyanate: To a mixture of aziridine (5 mmol) and organometallic (0.5 mmol), 5 mmol of phenyl isothiocyanate (676 mg) was added dropwise, and the mixture was stirred at 80 or 100°C for the prescribed period. The mixture was then extracted with benzene and chromatographed on silica gel (Wako C-200, ∅15 × 200 mm, elution with hexane) to separate the products from the catalysts. Further **3**, **4**, and **5** was isolated by CC (size 20 × 300 mm), elution with hexane/ethyl acetate. The volumetric compositions of the eluents were as follows; 9:1 for (**3a** and **5a**), (**3b**, **4b**, and **5b**), and (**3c**, **4c**, and **5c**) and 98:2 for (**3d** and **4d**).

3-Phenyl-2-phenylimino-1,3-thiazolidine (**3a**): M. p. 135–136°C (ref.[13] 134°C).

1,4-Diphenylpiperazine (**5a**): M. p. 154°C (ref.[11] 163–164°C).

5-Methyl-3-phenyl-2-phenylimino-1,3-thiazolidine (**3b**): M. p. 98–99°C (hexane). – IR (KBr): $\tilde{\nu}$ = 1615 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 1.46 (d, *J* = 6.2 Hz, 3H, CH_3), 3.72 (d, *J* = 5.0 Hz, 2H, ring CH_2), 4.14 (sext, 1H), 6.9–7.6 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 19.9 (q), 37.3 (t, ring CH_2), 59.7 (d), 121.6 (d), 122.4 (d), 123.0 (d), 126.4 (d), 128.5 (d), 128.8 (d), 141.2 (s, *ipso*), 151.7 (s, *ipso*), 156.6 (s, C=N). – MS (70 eV): *m/z* (%) = 268 (100) [M^+].

$C_{16}H_{16}N_2S$ (268.4) Calcd. C 71.60 H 6.01 N 10.44
Found C 72.01 H 6.10 N 10.34

4-Methyl-3-phenyl-2-phenylimino-1,3-thiazolidine (**4b**): M. p. 95–96°C (hexane). – ^1H NMR ($CDCl_3$): δ = 1.29 (d, *J* = 6.2 Hz, 3H, CH_3), 2.89 and 3.39 (ddd, *J* = 10.6, 6.5 and 6.4 Hz, 2H, ring CH_2), 4.33 (sext, 1H), 6.9–7.9 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 18.9 (q), 34.1 (t), 59.5 (d), 121.8 (d), 122.4 (d), 123.0 (d), 126.3 (d), 128.5 (d), 128.8 (d), 139.8 (s, *ipso*), 151.5 (s, *ipso*), 156.6 (s, C=N). – MS (70 eV): *m/z* (%) = 268 (100) [M^+].

$C_{16}H_{16}N_2S$ (268.4) Calcd. C 71.60 H 6.01 N 10.44
Found C 71.38 H 6.12 N 10.41

5-Ethyl-3-phenyl-2-phenylimino-1,3-thiazolidine (**3c**): M. p. 87 to 88°C (hexane). – IR (KBr): $\tilde{\nu}$ = 1615 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 1.00 (t, *J* = 7.2 Hz, 3H, CH_3), 1.79 (quint, 2H, CH_2), 3.51 and 4.17 (ddd, *J* = 9.3, 6.5 and 6.3 Hz, 2H, CH_2), 3.79 (m_c, 1H, CH), 6.9–7.6 (m, 10H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 12.1 (q), 27.8 (t), 44.5 (t, ring CH_2), 57.9 (d), 121.3 (d), 122.4 (d), 123.0 (d), 128.6 (d), 141.3 (s, *ipso*), 151.8 (s, *ipso*), 156.2 (s, C=N). – MS (70 eV): *m/z* (%) = 282 (100).

$C_{17}H_{18}N_2S$ (282.4) Calcd. C 72.30 H 6.42 N 9.92
Found C 72.28 H 6.43 N 9.89

4-Ethyl-3-phenyl-2-phenylimino-1,3-thiazolidine (**4c**): B. p. 120°C/0.2 Torr. – IR (KRS-5): $\tilde{\nu}$ = 1620 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 3H, CH_3), 1.49 (dq, *J* = 7.5 Hz, 2H, CH_2), 2.96 and 3.34 (ddd, *J* = 10.8, 6.4 and 5.1 Hz, 2H, CH_2), 4.17 (dq, 1H), 6.8–7.4 (m, 10H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 9.8 (q), 25.2 (t), 31.3 (t, ring C), 65.1 (d), 121.8 (d), 122.9 (d), 125.8 (d), 126.4 (d), 128.5 (d), 128.9 (d), 130.3 (s, *ipso*), 140.5 (s, *ipso*), 156.2 (s, C=N). – MS (70 eV): *m/z* (%) = 282 (100) [M^+].

$C_{17}H_{18}N_2S$ (282.4) Calcd. C 72.30 H 6.42 N 9.92
Found C 72.45 H 6.83 N 9.80

2,5-Diethyl-1,4-diphenylpiperazine (**5c**): B. p. 110°C/10^{-2} Torr. – ^1H NMR ($CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 6H, CH_3), 1.58 (quint, 4H, CH_2), 3.10 and 3.43 (ddd, *J* = 13.0, 7.9 and 3.8 Hz, 4H, ring CH_2), 3.3–3.7 (m, 2H, CH), 6.9–7.3 (m, 10H, aromatic H). – ^{13}C

NMR ($CDCl_3$): δ = 10.6 (q), 22.4 (t), 50.2 (t), 58.2 (d), 118.0 (d), 119.9 (d), 129.0 (d), 150.5 (s, *ipso*). – MS: *m/z* (%) = 294 (43) [M^+], 148 (100) [$M^+ - C_{10}H_{12}N$].

$C_{20}H_{26}N_2$ (288.4) Calcd. C 81.58 H 8.90 N 9.51
Found C 81.57 H 8.88 N 9.49

3-Butyl-5-ethyl-2-phenylimino-1,3-thiazolidine (**3d**): Colorless oil; b. p. 105°C/0.2 Torr. – IR (KRS-5): $\tilde{\nu}$ = 1625 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 1.02 (t, 6H, CH_3), 1.1–1.8 (m, 6H, CH_2), 3.3–3.7 (m, 1H, CH), 3.34 and 3.63 (ddd, *J* = 10.1, 5.9 and 5.3 Hz, 2H, ring CH_2), 6.9–7.3 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 12.2 (q), 13.9 (q), 20.2 (t), 28.1 (q), 29.3 (t), 45.1 (d, CH), 46.0 (t, NCH_2), 56.0 (t, ring CH_2), 122.0 (d), 122.5 (d), 128.6 (d), 152.4 (s, *ipso*), 158.1 (s, C=N). – MS (70 eV): *m/z* (%) = 262 (92) [M^+], 205 (100) [$M^+ - Bu$].

$C_{15}H_{22}N_2S$ (262.4) Calcd. C 68.65 H 8.45 N 10.68
Found C 68.56 H 8.43 N 10.77

3-Butyl-4-ethyl-2-phenylimino-1,3-thiazolidine (**4d**): B. p. 121°C/10 Torr. – IR (KRS-5): $\tilde{\nu}$ = 1620 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 0.95 (t, 6H, CH_3), 0.95–1.8 (m, 4H, CH_2), 1.55 (dq, *J* = 7.1 and 7.3 Hz, 2H, CH_2), 2.75 and 3.13 (ddd, *J* = 13.4, 6.4 and 5.8 Hz, 2H, ring CH_2), 3.10 (t, *J* = 7.0 Hz, 2H, NCH_2), 3.71 (m_c, 1H, CH), 6.9–7.4 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 9.6 (q), 13.9 (q), 20.2 (t), 24.4 (t), 29.2 (t, ring CH_2), 31.1 (t), 44.1 (t, NCH_2), 62.1 d (CH), 122.0 (d), 122.5 (d), 128.5 (d), 152.3 (s, *ipso*), 158.2 (s, C=N). – MS (70 eV): *m/z* (%) = 262 (49) [M^+], 187 (100).

$C_{15}H_{22}N_2S$ (262.4) Calcd. C 68.65 H 8.45 N 10.67
Found C 68.66 H 8.42 N 10.56

Reactions of Aziridines with Carbon Disulfide: The reactions were carried out in a stainless steel autoclave (SUS 304, 30 ml) at 180°C. Thiazolidinethiones were the main products in the crude samples, but they disappeared after workup with silica gel and oxazolidinethiones were obtained.

5-Ethyl-3-phenyl-1,3-oxazolidine-2-thione (**6e**): B. p. 150°C/0.015 Torr. – IR (KRS-5): $\tilde{\nu}$ = 1080 cm^{-1} (C=S). – ^1H NMR ($CDCl_3$): δ = 0.91 (t, *J* = 7.4 Hz, 3H, CH_3), 1.67 (quint, 2H, CH_2), 3.19 and 3.61 (ddd, *J* = 11.1, 7.9 and 7.1 Hz, 2H, ring CH_2), 4.52 (m_c, 1H, ring CH), 7.1–7.6 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$): δ = 9.1 (q), 25.6 (t), 33.2 (t, ring CH_2), 127.6 (d), 128.2 (d), 129.3 (d), 139.4 (s, *ipso*), 197.9 (s, C=S). – MS: *m/z* (%) = 207 (100) [M^+].

$C_{11}H_{13}NOS$ (207.3) Calcd. C 63.74 H 6.32 N 6.76
Found C 63.79 H 6.50 N 6.86

Reactions of Aziridines with Carbon Dioxide: 5 mmol of aziridines, 0.5 mmol of catalyst, and 1 ml of acetonitrile were placed into an autoclave and pressurized with CO_2 (50 atm). After the reaction, unreacted CO_2 was decompressed at room temperature and the residues were similarly worked up.

5-Methyl-3-phenyl-1,3-oxazolidine-2-one (**3f**): M. p. 81°C (ether, ref.[10c] 81°C).

4-Methyl-3-phenyl-1,3-oxazolidine-2-one (**4f**): M. p. 51°C (ether, ref.[10c] 51°C).

5-Ethyl-3-phenyl-1,3-oxazolidine-2-one (**3g**): B. p. 124°C/1.5 Torr (ref.[10c] 124°C/1.5 Torr).

4-Ethyl-3-phenyl-1,3-oxazolidine-2-one (**4g**): B. p. 120°C/0.1 Torr (ref.[10c] 120°C/0.1 Torr).

CAS Registry Numbers

1a: 696-18-4 / **1b**: 102879-24-3 / **1c**: 123265-53-2 / **1d**: 123265-54-3 / **2a**: 103-72-0 / **2e**: 75-15-0 / **2f**: 124-38-9 / **3a**: 6200-49-3 / **3b**: 123265-55-4 / **3c**: 123265-56-5 / **3d**: 123265-60-1 / **3f**: 708-57-6 / **3g**: 101835-17-0 / **4b**: 123265-61-2 / **4c**: 123265-58-7 / **4d**: 123265-59-8 / **4f**: 28386-16-5 / **4g**: 105873-71-0 / **5a**: 613-39-8 / **5b**: 65018-26-0 / **5c**: 123265-57-6 / **6e**: 123288-81-3 / Ph_4SbBr: 21450-52-2 / Bu_3SnI: 7342-47-4 / Ph_3SbBr_2: 1538-59-6 / Ph_3SbCl_2: 594-31-0 / Bu_4NBr: 1643-19-2 / Ph_4SbI: 13903-91-8

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