Activation and Control of the Reaction of Dioxastannolane with Carbon Disulfide and Phenyl Isothiocyanate by the Addition of Bases

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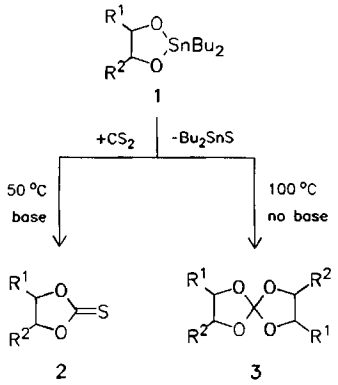
1,3-Dioxa-2-stannolanes **1** are readlily activated by Lewis bases such as Bu_3P and Et_3N to give cycloadducts on reaction with carbon disulfide or phenyl isothiocyanate under mild conditions. In particular, bases play a characteristic role in the reaction with carbon disulfide to produce 1,3-dioxolane-2-thiones **2** in good yields, while spiro compounds **3** (1:2 adducts) are predominantly obtained in the absence of bases.

The tight aggregation of 1,3-dioxa-2-stannolanes **1** is well-known even in solution[1] and perhaps responsible for the low reactivity of the Sn–O bonds. For example, electrophiles like non-activated halides, water, or carbon dioxide hardly react with these stannolanes whilst tin alkoxides like $Bu_2Sn(OCH_3)_2$ readily react with these electrophiles[2]. We have already studied the activation of tin–hetero atom bonds by complexation, where the change of the structure around the tin atom would be caused by a coordination of Lewis bases to allow a facile reaction with electrophiles[3]. This result indicates that the addition of Lewis bases weakens the aggregation, thus increasing the reactivity of dioxastannolanes. In this paper we report, on the basis of this result, on the effective additions of carbon disulfide[4] and phenyl isothiocyanate[5] to dioxastannolanes **1** in the presence of appropriate Lewis bases.

Scheme 1



	R^1	R^2	
a	H	Me	
b	H	Et	
c	H	*t* Bu	
d	H	Ph	
e	H	CH_2OMe	
f	Me	Me	*(cis)*
g	Me	Me	*(trans)*
h	$[CH_2]_4$		*(cis)*
i	$[CH_2]_4$		*(trans)*

Sakai and co-workers already reported on the addition of CS_2 to **1** affording exclusively 1:2 spiro-adducts **3** in the absence of additives[4a]. The stereochemistry of the process was not investigated. As shown in Scheme 1, the formation of **3** required heating at 100°C for 10 h, and good yields were obtained irrespective of the substituents of **1**. In particular, it should be noted that the addition of **1f** and **1g** to CS_2 proceeded stereospecifically, but that only a small difference in yield between *cis*- **1f** and the *trans* isomer **1g** was observed (69 and 75%, respectively). In contrast, in the presence of bases 1:1 adducts, 1,3-dioxolane-2-thiones **2**, were obtained, and no formation of **3** was detected in all runs (Table 1). In addition, the reaction was strikingly facilitated to proceed even at 50°C. Table 1 demonstrates the following features: The additon proceeds stereospecifically, and the reaction rates are markedly affected by the substituents of **1**. The *cis* isomer **1f** reacts considerably faster than the *trans* isomer **1g**. The stannolane **1e** bearing a CH_2OMe substituent is converted into **2e** in only 25% yield in

Table 1. Reaction of dioxastannolanes with carbon disulfide in the presence of a Lewis base[a] and without a Lewis base[b]

Entry	**1**	Base	Time [h]	Yield (%) of **2**		Yield (%) of **3**
				(cis)	*(trans)*	
1	**a**	Bu_3P	7	71		–
2	**b**	Bu_3P	20	56		60
3	**c**	Bu_3P	5	91		62
4	**d**	Bu_3P	20	56		65
5	**e**	Bu_3P	20	25		70
6	**f**	Bu_3P	5	46		75
7	**g**	Bu_3P	30	53		69
8	**f** + **g**	Bu_3P	5	70	80	–
9	**f** + **g**	–	20	trace	trace	–
10	**f** + **y**	Et_3N	10	84	93	–
11	**f** + **y**	HMPA	40	66	100	–
12	**h** + **i**	Bu_3P	7	77	trace	–

[a] Stannolane/CS_2/base (3.0:30:3.0 mmol), $ClCH_2CH_2Cl$ (20 ml), 50°C. – [b] Stannolane/CS_2 (3.0:30 mmol), $ClCH_2CH_2Cl$ (20 ml), 100°C/pressure.

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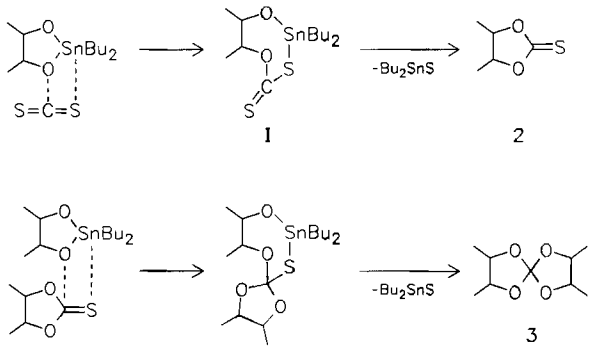
comparison with the high yield of the corresponding spiro compound **3e** obtained in the absence of Bu_3P (70%). The highest yield of *t*Bu-substituted **1c** (5h, 91%) indicates the importance of the aggregation in this process, since of monomeric dioxastannolane participated in the reaction the bulky substituent would disturb the addition of CS_2 more effectively than the other substituents. Next, in view of the large difference in reactivity between **1f** and **1g**, we attempted the selective preparation of the *cis* isomer **2f** by the reaction of CS_2 with a mixture of **1f** and **1g**, but it was unsuccessful. Surprisingly, the mixture gave higher yields of **2** compared with each individual isomer (entries 6–8). On the other hand, in the case of the 4,5-tetramethylene derivatives **1h** and **1i**, selective formation of the *cis* isomer took place. These results can also be explained by the strong aggregation between **1f** and **1g**.

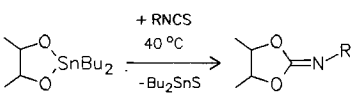
An ion pair between CS_2 and Bu_3P is known to be readily formed[6] which may react with **1**. However, because the use of HMPA and Et_3N displaying only a weak tendency to ion-pair formation also led, as shown in Table 1, to the dissociation of the aggregated stannolanes by the ion pair or bases, employment of Bu_3P would be essential for the 1:1 adduct formation. Otherwise, the 1:2 spiro adducts were exclusively produced under more severe conditions.

Scheme 2



Scheme 2 illustrates the reaction paths for the formation of **2** and **3**. 1,3-Dioxolane-2-thione **2** is formed by elimination of Bu_2SnS from the adduct **I** on account of the high affinity of tin to sulfur[4,7], and the resulting compound **2** reacts with another equiv. of **1** to give the spiro adduct **3**. When Lewis bases are added, the first step is accelerated at lower temperature so strongly that **1** is rapidly consumed without participation of the second step. Thus, a complete change of products can be achieved simply by the addition of Lewis bases.

Scheme 3



	R
4	Ph
5	Me
6	*n* Bu

Phenyl isothiocyanate was also applicable to this type of reaction[5] yielding 1,3-dioxolane-2-imines **4** as shown in Scheme 3 and Table 2. A rapid formation of **4** was effected by the addition of Et_3N, in particular the *cis* isomer **1f** was activated more strongly than the *trans* isomer **1g** (entries 1–4). In contrast to the case of CS_2, an effective kinetic resolution of *cis*- and *trans*-dioxastannolanes was successfully achieved by the reaction of PhNCS with a mixture of **1f** and **1g** (entry 5). More effective resolutions were observed under the condition of more dilute solution (entries 6, 7). This resolution led to the selective formation of **1f** from a *syn/anti* mixture of the corresponding 1,2-diols which were quantitatively transformed into the stannolanes **1**.

Table 2. Reaction of 4,5-dimethyldioxastannolane with RNCS[a]

Entry	R	1	Base	Time [h]	Yield (%) of 4	
					(*cis*)	(*trans*)
1	Ph	**f**	–	2.0	100	
2	Ph	**f**	Et_3N	0.5	100	
3	Ph	**g**	–	5.0	65	
4	Ph	**g**	Et_3N	5.0	82	
5	Ph	**f** + **g**	–	1.0	100	30
6[b]	Ph	**f** + **g**	–	7.0	100	5
7[b]	Ph	**f** + y	Et_3N	4.0	100	6
8	Me	**f** + **g**	–	1.0	100[c]	12[c]
9	*n*Bu	**f** + **g**	–	2.0	100[d]	10[d]

[a] Stannolane/RNCS/base (3:3:3 mmol), $ClCH_2CH_2Cl$ (20 ml), 40°C. – [b] Stannolane/RNCS/base (1:1:1 mmol), $ClCH_2CH_2Cl$ (30 ml), 40°C. – [c] Yield of **5**. – [d] Yield of **6**.

In conclusion, the addition of a Lewis base to **1** initiated a cycloaddition reaction with CS_2 and PhNCS. A change of products and a kinetic resolution of diastereomers of 4,5-disubstituted **1** were conveniently achieved.

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Experimental

General: IR: Hitachi 260-30; KRS-5 cell – ^1H, ^{13}C NMR: Hitachi R-90H. – MS: JEOL JMS-DS303. – Microanalyses: JEOL JMS-DX303 (data software processing: JMS-DA5000). – Analytical GLC: Shimadzu GC-8A using a 2 m × 3 mm glass column packed with Silicone OV-1 on Uniport HP (5%, 60–80 mesh). – Column chromatography was performed on silica gel. – Short-path distillations of products were carried out with a kugelrohr apparatus.

Materials: All Lewis bases, 1,2-dichloroethane (solvent) and carbon disulfide were purified by distillation. Isothiocyanate and diphenylthiourea were commercial products and used without further purification. Dioxastannolanes were prepared according to described methods[1,7a].

Reaction of Dioxastannolane with Carbon Disulfide in the Presence of a Lewis Base (Typical Procedure): To a solution of **1a** (921 mg, 3.0 mmol) and Bu_3P (607 mg, 3.0 mmol) in 1,2-dichloroethane (20 ml) was added CS_2 (1.8 ml, 30 mmol) under dry nitrogen, and the mixture was stirred at 50°C for 7 h. The formation and the yield (71%) of 1,3-dioxolane-2-thione **2a** were monitored by GLC. Excess CS_2 and 1,2-dichloroethane were removed in vacuo, and the resulting **2a** was isolated by column chromatography on silica gel (eluent: benzene); yield 230 mg (65%).

4-Methyl-1,3-dioxolane-2-thione (**2a**): B.p. 65°C/2 Torr[8].

4-Ethyl-1,3-dioxolane-2-thione (**2b**): B.p. 90°C/3 Torr. – IR (KRS-5): $\tilde{\nu}$ = 1180 cm^{-1} (C=S). – ^1H NMR ($CDCl_3$): δ = 1.10 (t, *J* = 8.2 Hz, 3H, CH_3), 1.71–2.00 (m, 2H, CH_2), 4.29 (t, *J* = 7.5 Hz, 1H, one of ring CH_2), 4.52–5.00 (m, 2H, CH and one of ring

CH_2). – ^{13}C NMR ($CDCl_3$): δ = 8.4 (q), 26.3 (t), 72.8 (t), 83.3 (d), 191.7 (s, C=S). – MS (70 eV): *m/z* (%) = 132 (100)[M^+].

$C_5H_8O_2S$ Calcd. 132.0245 Found 132.0242 (MS)

4-tert-Butyl-1,3-dioxolane-2-thione (**2c**): B.p. 83°C/2 Torr. – IR (KRS-5): $\tilde{\nu}$ = 1180 cm^{-1} (C=S). – ^1H NMR ($CDCl_3$): δ = 1.05 (s, 9H, CH_3), 4.52–4.70 (m, 3H, CH and CH_2). – ^{13}C NMR ($CDCl_3$): δ = 24.4 (q), 33.7 (s), 69.7 (t), 89.3 (d), 191.8 (s, C=S). – MS (70 eV): *m/z* (%) = 160 (85) [M^+], 55 (100).

$C_7H_{12}O_2S$ Calcd. 160.0558 Found 160.0554 (MS)

4-Phenyl-1,3-dioxolane-2-thione (**2d**): B.p. 92°C/0.1 Torr. – IR (KRS-5): $\tilde{\nu}$ = 1180 cm^{-1} (C=S). – ^1H NMR ($CDCl_3$): δ = 4.54 (t, *J* = 8.5 Hz, 1H, one of CH_2), 4.97 (t, *J* = 8.5 Hz, 1H, one of CH_2), 5.87 (t, *J* = 8.5 Hz, 1H, CH). – ^{13}C NMR ($CDCl_3$): δ = 74.7 (t), 82.9 (d), 126.0 (d), 128.9 (d) 129.7 (d), 134.3 (s), 191.2 (s, C=S). – MS (70 eV): *m/z* (%) = 180 (92) [M^+], 135 (100), 91 (100).

$C_9H_8O_2S$ Calcd. 180.0245 Found 180.0236 (MS)

4-Methoxymethyl-1,3-dioxolane-2-thione (**2e**): B.p. 85°C/2 Torr. – IR (KRS-5): $\tilde{\nu}$ = 1180 cm^{-1} (C=S). – ^1H NMR ($CDCl_3$): δ = 3.47 (s, 3H, CH_3), 3.68 (dd, *J* = 2.3 and 6.3 Hz, 2H, CH_2), 4.65 (dd, *J* = 2.5 and 7.0 Hz, 2H, ring CH_2), 4.97–5.13 (m, 1H, CH). – ^{13}C NMR ($CDCl_3$): δ = 59.5 (q), 70.3 (t), 70.6 (t), 80.2 (d), 191.6 (s, C=S). – MS (70 eV): *m/z* (%) = 148 (100) [M^+].

$C_5H_8O_3S$ Calcd. 148.0194 Found 148.0198 (MS)

cis-4,5-Dimethyl-1,3-dioxolane-2-thione (**2f**): B.p. 62°C/2 Torr[8,9].

trans-4,5-Dimethyl-1,3-dioxolane-2-thione (**2g**): B.p. 70°C/3 Torr[8,9].

cis-4,5-Hexahydrobenzo-1,3-dioxolane-2-thione (**2h**): B.p. 60°C/0.1 Torr[9,10].

Reaction of Dioxastannolane with Carbon Disulfide without a Base (Typical Proccdure): A solution of **1b** (963 mg, 3.0 mmol) and CS_2 (1.8 ml, 30 mmol) in 1,2-dichloroethane (20 ml) and a magnetic bar were placed in a 50-cm^3 stainless-steel autoclave. The vessel was heated with stirring at 100°C for 12 h. After cooling the formation and the yield (60%) of spiro compound **3b** were monitored by GLC. The excess CS_2 and 1,2-dichloroethane were removed in vacuo, and the obtained **3b** was isolated by column chromatography on silica gel [eluent: *n*-hexane/benzene (8:2)] and purified by vaccum distillation (110°C/2 Torr); yield 293 mg (52%).

2,7-Diethyl-1,4,6,9-tetraoxaspiro[4.4]nonane (**3b**): B.p. 110°C/2 Torr. – ^1H NMR ($CDCl_3$): δ = 1.00 (t, *J* = 7.6 Hz, 6H, CH_3), 1.54–1.90 (m, 4H, CH_2), 3.77 (dd, *J* = 4.6, 6.3 Hz, 2H, one of ring CH_2), 4.10–4.35 (m, 4H, CH and one of ring CH_2). – ^{13}C NMR ($CDCl_3$): δ = 8.6 (q), 32.5 (s), 65.3 (t), 83.7 (d), 134.5 (s). – MS (70 eV): *m/z* (%) = 188 (2) [M^+], 144 (100).

$C_9H_{16}O_4$ (188.2) Calcd. C 57.43 H 8.57
Found C 57.14 H 8.50

2,7-Di-tert-butyl-1,4,6,9-tetraoxaspiro[4.4]nonane (**3c**): B.p. 52°C/0.1 Torr. – ^1H NMR ($CDCl_3$): δ = 0.95 (s, 18H, CH_3), 3.71–4.13 (m, 6H, CH and CH_2). – ^{13}C NMR ($CDCl_3$): δ = 25.0 (q), 32.5 (s), 65.3 (t), 83.7 (d), 134.5 (s). – MS (70 eV): *m/z* (%) = 244 (1) [M^+], 200 (100).

$C_{13}H_{24}O_4$ (244.3) Calcd. C 63.91 H 9.90
Found C 63.77 H 9.86

2,7-Diphenyl-1,4,6,9-tetraoxaspiro[4.4]nonane (**3d**): B.p. 170°C/0.1 Torr. – ^1H NMR ($CDCl_3$): δ = 4.35 (t, *J* = 8.5 Hz, 2H, one of CH_2), 4.80 (t, *J* = 8.5 Hz, 2H, one of CH_2), 5.70 (t, *J* = 8.5 Hz, 2H, CH), 7.22–7.53 (m, 10H). – ^{13}C NMR ($CDCl_3$): δ = 71.4 (t), 77.9 (d), 125.7 (d), 129.1 (d), 129.6 (d), 134.7 (s), 135.7 (s). – MS (70 eV): *m/z* (%) = 284 (3) [M^+], 240 (100).

$C_{17}H_{16}O_4$ (284.3) Calcd. C 71.82 H 5.67
Found C 71.67 H 5.66

2,7-Methoxymethyl-1,4,6,9-tetraoxaspiro[4.4]nonane (**3e**): B.p. 60°C/0.1 Torr. – ^1H NMR ($CDCl_3$): δ = 3.60 (d, *J* = 7.5 Hz, 2H), 3.70 (d, *J* = 5.0 Hz, 2H), 4.00–4.62 (m, 12H). – ^{13}C NMR ($CDCl_3$): δ = 43.0 (q), 67.47 (t), 67.53 (t), 75.2 (d), 135.0 (s). – MS (70eV): *m/z* (%) = 220 (1)[M^+], 176 (100).

$C_9H_{16}O_6$ (220.2) Calcd. C 49.09 H 7.32
Found C 48.75 H 7.26

cis-2,3,7,8-Tetramethyl-1,4,6,9-tetraoxaspiro[4.4]nonane (**3f**): B.p. 45°C/3 Torr. – ^1H NMR ($CDCl_3$): δ = 1.35 (d, *J* = 7.2 Hz, 12H, CH_3), 4.31–4.59 (m, 4H, CH). – ^{13}C NMR ($CDCl_3$): δ = 14.3 (q), 14.4 (q), 70.6 (d), 74.3 (d), 75.0 (d), 132.1 (s). – MS (70 eV): *m/z* (%) = 187 (1) [M^+], 144 (100).

$C_9H_{16}O_4$ (188.2) Calcd. C 57.43 H 8.57
Found C 57.21 H 8.53

trans-2,3,7,8-Tetramethyl-1,4,6,9-tetraoxaspiro[4.4]nonane (**3g**): B.p. 50°C/2 Torr. – ^1H NMR ($CDCl_3$): δ = 1.25 (d, *J* = 7.5 Hz, 12H, CH_3), 3.75–4.10 (m, 4H, CH). – ^{13}C NMR ($CDCl_3$): δ = 16.3 (q), 17.1 (q), 78.9 (d), 132.3 (s). – MS (70 eV): *m/z* (%) = 187 (1) [M^+], 144 (100).

$C_9H_{16}O_4$ (188.2) Calcd. C 57.43 H 8.57
Found C 57.25 H 8.55

Reaction of Dioxastannolane with Isothiocyanate (Typical Procedure): To a solution of **1f** (963 mg, 3.0 mmol) and Et_3N (304 mg, 3.0 mmol) in 1,2-dichloroethane (20 ml) was added PhNCS (406 mg, 3.0 mmol) under dry nitrogen, and the mixture was stirred at 40°C for 0.5 h. The formation and the yield (100%) of dioxolan-2-imine **4f** were monitored by GLC. 1,2-Dichloroethane was removed in vacuo and the resulting **4f** isolated by column chromatography on silica gel (eluent: benzene); yield 533 mg (93%). Vacuum distillation (120°C/0.1 Torr) afforded pure **4f**.

cis-4,5-Dimethyl-N-phenyl-1,3-dioxolan-2-imine (**4f**): B.p. 120°C/0.1 Torr, m.p. 41–42°C[11].

trans-4,5-Dimethyl-N-phenyl-1,3-dioxolan-2-imine (**4g**): M.p. 62 to 63°C[11].

cis-4,5-Dimethyl-N-methyl-1,3-dioxolan-2-imine (**5f**): B.p. 80°C/2 Torr. – IR (KRS-5): $\tilde{\nu}$ = 1720 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 1.43 (d, *J* = 4.1 Hz, 6H, CH_3), 2.88 (s, 3H, NCH_3), 4.56–4.79 (m, 2H, CH). – ^{13}C NMR ($CDCl_3$): δ = 14.3 (q), 33.3 (q), 75.2 (d), 76.5 (d), 153.9 (s). – MS (70 eV): *m/z* (%) = 129 (44) [M^+], 57 (100).

$C_6H_{11}O_2N$ Calcd. 129.07903 Found 129.07901 (MS)

trans-4,5-Dimethyl-N-methyl-1,3-dioxolan-2-imine (**5g**): B.p. 75°C/2 Torr. – IR (KRS-5): $\tilde{\nu}$ = 1720 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 1.30 (d, *J* = 6.5 Hz, 6H, CH_3), 2.88 (s, 3H, NCH_3), 4.08–4.28 (m, 2H, CH). – ^{13}C NMR ($CDCl_3$): δ = 17.7 (q), 33.3 (q), 79.2 (d), 80.5 (d), 154.0 (s). – MS (70 eV): *m/z* (%) = 129 (43) [M^+], 57 (100).

$C_6H_{11}O_2N$ (129.2) Calcd. C 55.80 H 8.58 N 10.84
Found C 55.59 H 8.55 N 10.90

cis-4,5-Dimethyl-N-butyl-1,3-dioxolan-2-imine (**6f**): B.p. 69°C/0.1 Torr[11].

trans-4,5-Dimethyl-N-butyl-1,3-dioxolan-2-imine (**6g**): B.p. 67°C/0.1 Torr. – IR (KRS-5): $\tilde{\nu}$ = 1720 cm^{-1} (C=N). – ^1H NMR ($CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz, 3H, CH_3 of NBu), 1.12–1.70 (m,

10H, $2CH_2$ of NBu and $2CH_3$), 3.32 (t, J = 7.4 Hz, 2H, NCH_2), 3.95–4.45 (m, 2H, 2 CH). – ^{13}C NMR ($CDCl_3$): δ = 13.9 (q), 17.6 (q), 20.4 (t), 33.5 (t), 46.1 (t), 78.9 (d), 80.4 (d). – MS (70 eV): *m/z* (%) = 171 (47) [M^+], 99 (100).

$C_9H_{17}O_2N$ (171.2) Calcd. C 63.13 H 10.00 N 8.18
Found C 62.89 H 9.98 N 8.21

CAS Registry Numbers

1a: 3590-60-1 / **1b**: 134110-54-6 / (*cis*)-**1f**: 5271-63-6 / **2a**: 13303-26-9 / **2b**: 134110-51-3 / **2c**: 134110-52-4 / **2d**: 116447-63-3 / **2e**: 134110-53-5 / (*cis*)-**2f**: 56194-03-7 / (*trans*)-**2g**: 66841-50-7 / (*cis*)-**2h**: 56155-84-1 / **3b**: 134110-55-7 / **3c**: 134110-56-8 / **3d**: 134110-57-9 / **3e**: 134110-58-0 / **3f** (isomer 1): 29882-37-9 / **3g** (isomer 2): 134175-77-2 / (*cis*)-**4f**: 132783-14-3 / (*trans*)-**4g**: 132783-13-2 / (*cis*)-**5f**: 134110-29-1 / (*trans*)-**5g**: 134110-60-4 / (*cis*)-**6f**: 132783-18-7 / (*trans*)-**6g**: 134110-61-5

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