

tion (3) and thereby more hydrazine is produced. This chain reaction can explain the reason why the formation of hydrazine was increased rapidly in basic solutions.

In conclusion, the photochemical formation of hydrazine was observed only in basic solution (at pH higher than 8). It implies that hydrazine is formed from neutral ammonia molecule rather than ammonium ion. The formation of hydrazine rapidly increases in basic solution because the fraction of absorption by  $\text{OH}^-_{\text{aq}}$  increases and the OH radicals and  $e^-_{\text{aq}}$  are produced much more. The produced solvated electron,  $e^-_{\text{aq}}$  combines with each other to form hydroxide ion. As a result, OH radical is produced again and it contributes also to the formation of hydrazine. Besides, the formation of hydrazine increases as the initial concentration of ammonia is increased.

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## Substituent Effect for Epoxide Opening of Halo-Tricyclic Models Related to Dynemicin A

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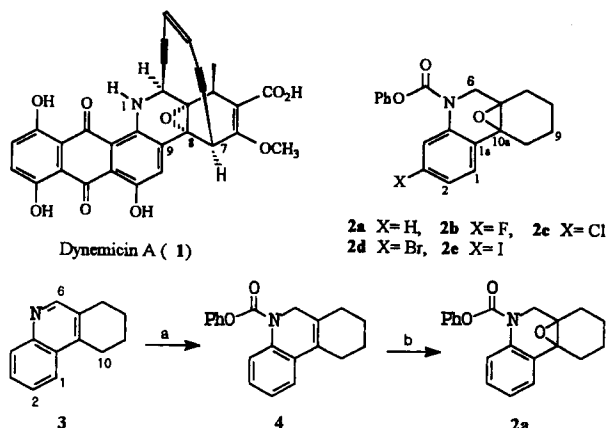
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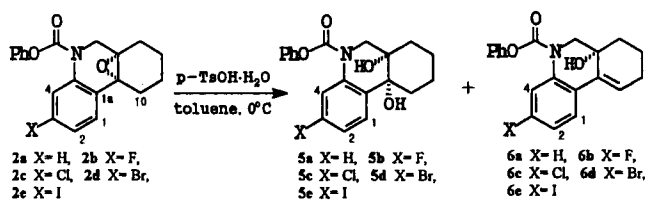
A new type of antibiotic, dynemicin A (**1**) is characterized as a unique molecular structure and interesting biological profile.<sup>1</sup> Its potent antibiotic and antitumor activities have been attributed to ability to generate, upon *in vivo* activation benzenoid diradicals that damage DNA.<sup>2</sup> It has been known that activation of **1** resulting in cycloaromatization of enediyne moiety is triggered by epoxide opening induced by development of electron density at C9.<sup>3</sup> Accordingly, the epoxide opening should be considered as a critical step for activation of dynemicin A and its biological activity. In the previous study, it was observed that methyl group at para position to the epoxide could exert as an ac-

tivating substituent in acid-catalyzed epoxide opening of dynemicin A model.<sup>4</sup> On the other hand, halides with inductive effect will serve as deactivating substituents in the epoxide opening. This study notes the electronic sensitivity of halides toward acid-induced epoxide opening for dynemicin A mimic model compounds (**2a-2e**).

Compound **2a** was easily synthesized as follows (Scheme 1). Reduction of C6 by tributyltin hydride ( $\text{Bu}_3\text{SnH}$ ) and N5 protection with phenyl chloroformate ( $\text{ClCO}_2\text{C}_6\text{H}_5$ ) transformed 7,8,9,10-tetrahydrophenanthridine (**3**) to compound **4**.<sup>5</sup> Continuously, treatment of **4** with *m*CPBA yielded the epoxide **2a**. The halide substituted compounds **2b-2e**



**Scheme 1.** Reagents and conditions: (a) 0.9 equiv of  $\text{Bu}_3\text{SnH}$  and then, 0.9 equiv of  $\text{ClCO}_2\text{C}_6\text{H}_5$ ,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ , 1 h; (b) 1.2 equiv of *m*CPBA, sat.  $\text{NaHCO}_3/\text{CH}_2\text{Cl}_2$  (1:1),  $0^\circ\text{C}$ , 1 h, 77% (two steps from 3).



**Scheme 2.**

were also readily prepared from 3-halo-7,8,9,10-tetrahydrophenanthridines,<sup>6</sup> respectively by the same synthetic method.

Acid-induced epoxide opening reaction of **2a-2e** was performed to see electronic effect induced by halides at C3 (Scheme 2). Each compound was treated with *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H<sub>2</sub>O) in toluene. Epoxides transformed to the *cis* diols **5a-5e** and allylic alcohol **6a-6e** as the corresponding epoxide opened products in high yields (>95%), respectively. Allylic alcohols **6a-6e** were probably generated by the dehydration induced from alcohol protonation of *trans* diols. It is thought that dehydration of *cis* diols **5a-5e** is not easy because of intramolecular hydrogen bonding between two hydroxy groups.

Table 1 shows the reaction times for the acid hydrolysis of unsubstituted and halide substituted models. Epoxide opening for the five compounds showed a significant rate difference. The order of reactivity was **2b**, **2a**, **2c**, **2d**, and **2e**. Interestingly, fluoro substituted model **2b** showed higher reactivity than unsubstituted compound **2a**. This result was contrary to our prediction that more electronegative group would less activate epoxide opening. The crucial issue for epoxide opening is the developing electron density at C1a.<sup>6</sup> Correspondingly, the experimental result shown in table 1 suggests that fluorine substitution at C3 ought to result in increasing of the electron density at C1a.

Calculation method (MOPAC-93) for the models **2a-2e** confirmed that this hypothesis is correct (Table 2). The trend of the calculated values for electron density was in exactly accord with that of experimental result. Compound **2b** with fluoro substituent gave the highest electron density, and the iodo compound **2e** represented the lowest electron density. The fact that **2b** gives higher electron density than

**Table 1.** Reactivity for acid-induced epoxide opening of halide substituted compounds

Substrate	Reaction time (min)	Products	Ratio of products
<b>2a</b>	10	<b>5a</b> , <b>6a</b>	1.1
<b>2b</b>	7	<b>5b</b> , <b>6b</b>	1.7
<b>2c</b>	25	<b>5c</b> , <b>6c</b>	1.0
<b>2d</b>	35	<b>5d</b> , <b>6d</b>	1.1
<b>2e</b>	60	<b>5e</b> , <b>6e</b>	1.2

**Table 2.** Charge and Electron Density at C1a\*

Compound	Charge	Electron Density
<b>2a</b>	-0.087927	4.0879
<b>2b</b>	-0.101224	4.1012
<b>2c</b>	-0.079445	4.0794
<b>2d</b>	-0.073606	4.0736
<b>2e</b>	-0.058781	4.0558

\*Obtained charge and electron density by MOPAC-93 calculation method.

**2a** can be explained by strong resonance effect overwhelming inductive effect of fluorine. In case of compounds **2c-2e**, the inductive effect presumably surpasses the resonance effect representing the difference of the relative contribution degree for two factors. The ratio of products in table 1 suggests that mechanism to generate the products will be different.<sup>7</sup> Fluoro compound **2b** gave much more *cis* product **5b** than **6b** derived from *trans* product.

Conclusively, fluorine substitution at C3 accumulated the electron density at C1a and accelerated the epoxide opening of dynemicin A mimic tricyclic compound **2b**. Our experimental result confirmed the hypothesis that dynemicin A activation is triggered by epoxide opening induced by development of electron density at C9. Furthermore, it is inferred that fluorine can be used as a good hydrogen isotope for new enediyne model compounds related to dynemicin A.

## Experimental Section

**General Techniques.** Melting points were recorded on a Bchi 512 capillary melting point apparatus and were not corrected. NMR spectra were recorded on a Varian Unity Plus FT-300 instrument. IR spectra were recorded on a Perkin Elmer 1430 IR spectrophotometer.

All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) under UV light.

All new compounds were identified by spectroscopic methods.

**N-[(Phenyloxy)carbonyl]-6a,10a-epoxy-5,6,6a,7,8,9,10,10a-octahydrophenanthridine (2a).** A solution of 7,8,9,10-tetrahydrophenanthridine (**3**)<sup>8</sup> (5.20 g, 28.4 mmol) in dichloromethane (60 mL) was cooled to  $0^\circ\text{C}$  and treated with tributyltin hydride (7.44 g, 25.6 mmol), and then phenyl chloroformate (4.00 g, 25.6 mmol). After 1 h, the reaction mixture was poured into saturated aqueous sodium bicarbonate (100 mL) and extracted with dichloromethane ( $2 \times 100$  mL). The combined organic layers were washed with brine (100 mL), dried ( $\text{Na}_2\text{SO}_4$ ), and eva-

porated in vacuo. The residue was purified by column chromatography (silica, 15% ethyl acetate in hexane) to produce 8.32 g of **4**. An aliquot of **4** (730 mg, 2.4 mmol) in dichloromethane (20 mL) and saturated aqueous sodium bicarbonate (20 mL) was treated with mCPBA (497 mg of a 55% sample, 2.88 mmol) at 0 °C, and stirred for 1 h. The solution was poured into saturated sodium bicarbonate solution (50 mL) and the organic layer was separated. The aqueous layer was extracted with further dichloromethane (2 × 50 mL), and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated *in vacuo*. The residue was purified by flash chromatography (silica, 25% ethyl acetate in hexane) to give the epoxide **2a** (613 mg, 77% from **3**) as a white solid: mp 105-107 °C; IR (KBr)  $\nu_{\max}$  3450, 3070, 2940, 1715, 1490, 1375, 1200 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ = 7.52-7.11 (m, 9H, aromatic), 4.65 (d, *J*=14.1 Hz, 1H, H6), 3.14 (br d, *J*=14.1 Hz, 1H, H6), 2.54-2.47 (m, 1H, H7), 2.25-2.14 (m, 1H, H10), 2.04-1.93 (m, 2H, H7 and H10), 1.70-1.58 (m, 3H, H8 and H9), 1.35-1.20 (m, 1H, H8 or H9); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ = 155.0, 151.9, 139.7, 130.6, 129.9, 126.7, 127.6, 126.8, 126.1, 126.0, 122.3, 68.3, 58.3, 46.9, 26.0, 25.4, 21.2, 19.8.

**N-[(Phenyloxy)carbonyl]-3-fluoro-6a,10a-epoxy-5,6,6a,7,8,9,10,10a-octahydrophenanthridine (2b).**

Prepared from 3-fluoro-7,8,9,10-tetrahydrophenanthridine in 63% yield in a similar manner as that described for **2a**. **2b**: white crystalline solid; mp 60-62 °C; IR (KBr)  $\nu_{\max}$  3080, 2940, 1730, 1590, 1500, 1380, 1200 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ = <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ = 7.48-6.88 (m, 8H, aromatic), 4.66 (d, *J*=14.1 Hz, 1H, H6), 3.15 (d, *J*=14.1 Hz, 1H, H6), 2.53-2.47 (m, 1H, H7), 2.22-2.11 (m, 1H, H10), 2.04-1.94 (m, 2H, H7 and H10), 1.71-1.57 (m, 3H, H8 and H9), 1.32-1.19 (m, 1H, H8 or H9); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =162.4, 154.1, 151.4, 139.1, 129.7, 126.7, 126.3, 126.1, 122.0, 113.8, 112.7, 67.8, 57.8, 46.6, 26.0, 25.1, 21.0, 19.6.

**N-[(Phenyloxy)carbonyl]-3-chloro-6a,10a-epoxy-5,6,6a,7,8,9,10,10a-octahydrophenanthridine (2c).**

Prepared from 3-chloro-7,8,9,10-tetrahydrophenanthridine in 79% yield in a similar manner as that described for **2a**. **2c**: white solid; mp 90-92 °C; IR (KBr)  $\nu_{\max}$  3080, 2940, 1730, 1490, 1380, 1200 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ = 7.54-7.05 (m, 8H, aromatic), 4.55 (d, *J*=13.3 Hz, 1H, H6), 3.15 (d, *J*=13.3 Hz, 1H, H6), 2.36-2.30 (m, 2H, H7 and H10), 2.00-1.65 (m, 5H, H7, H8, H9, H10), 1.51-1.35 (m, 1H, H8 or H9); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =153.3, 150.8, 138.1, 132.2, 129.4, 129.0, 128.9, 128.7, 125.7, 125.3, 121.7, 67.6, 56.9, 45.5, 24.7, 24.1, 19.9, 18.8.

**N-[(Phenyloxy)carbonyl]-3-bromo-6a,10a-epoxy-5,6,6a,7,8,9,10,10a-octahydrophenanthridine (2d).**

Prepared from 3-bromo-7,8,9,10-tetrahydrophenanthridine in 57% yield in a similar manner as that described for **2a**. **2d**: white solid; mp 63-65 °C; IR (KBr)  $\nu_{\max}$  3080, 2940, 1725, 1595, 1490, 1375, 1200 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.48-7.14 (m, 8H, aromatic), 4.55 (d, *J*=13.3 Hz, 1H, H6), 3.15 (d, *J*=13.3 Hz, 1H, H6), 2.40-2.29 (m, 2H, H7 and H10), 1.98-1.64 (m, 5H, H7, H8, H9 and H10), 1.49-1.39 (m, 1H, H8 or H9); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ = 153.3, 150.8, 138.2, 129.4, 129.3 (two peak), 129.0, 128.2, 125.7, 121.7, 120.5, 67.6, 57.0, 45.5, 24.6, 24.1, 19.9, 18.8.

**N-[(Phenyloxy)carbonyl]-3-iodo-6a,10a-epoxy-5,6,6a,7,8,9,10,10a-octahydrophenanthridine (2e).**

Prepared from 3-iodo-7,8,9,10-tetrahydrophenanthridine in 58% yield in a similar manner as that described for **2a**. **2e**: white solid; mp 141-143 °C; IR (KBr)  $\nu_{\max}$  3070, 2940, 1725, 1590, 1485, 1375, 1200 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =7.65-7.10 (m, 8H, aromatic), 4.63 (d, *J*=14.1 Hz, 1H, H6), 3.14 (m, 1H, H6), 2.52-2.45 (m, 1H, H7), 2.19-2.08 (m, H, H10), 2.04-1.94 (m, 2H, H7 and H10), 1.72-1.56 (m, 3H, H8 and H9), 1.32-1.20 (m, 1H, H8 or H9); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =154.5, 151.7, 138.9, 135.5, 135.0, 130.5, 130.0, 129.1, 126.3, 122.3, 93.3, 68.4, 58.1, 46.8, 25.9, 25.3, 21.2, 19.7.

**Acid-Induced Epoxide Opening of Compound 5a.**

**Representative procedure.** A solution of epoxide **2a** (20 mg, 0.062 mmol) in toluene (3 mL) was treated with *p*-toluenesulfonic acid monohydrate (5.9 mg, 0.031 mmol) and stirred at 0 °C for 10 min. The solution was poured into saturated sodium bicarbonate solution (5 mL) and extracted with ethyl acetate (5 mL). The aqueous layer was extracted with further ethyl acetate (5 mL). The organic layers were combined, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated *in vacuo*. The residue was purified by flash chromatography (silica, 33% ethyl acetate in hexane) to give the diol **5a** (10.5 mg, 50%) and the allylic alcohol **6a** (9 mg, 45%). **5a**: white solid; mp 135-137 °C; IR (KBr)  $\nu_{\max}$  3450, 3070, 2940, 1715, 1490, 1375, 1200 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$ = 7.79 (d, 1H, *J*=8.1 Hz, aromatic), 7.68-7.64 (m, 1H, aromatic), 7.56-7.50 (m, 2H, aromatic), 7.38-7.20 (m, 5H, aromatic), 4.84 (s, 1H, OH), 4.79 (s, 1H, OH), 4.11 (ABq, *J*=13.3 Hz, 1H, H6), 4.01 (ABq, *J*=13.3 Hz, 1H, H6), 2.00-1.88 (m, 3H, H7 and H10), 1.79-1.64 (m, 3H, H7 or H10, H8 and H9), 1.55-1.35 (m, 2H, H8 and/or H9); <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>):  $\delta$ =153.4, 151.0, 135.9, 135.6, 129.4, 126.8, 126.5, 125.5, 124.0, 122.8, 121.9, 71.6, 69.6, 51.8, 36.9, 33.2, 22.1, 21.4. **6a**: white crystalline solid; mp 172-174 °C; IR (KBr)  $\nu_{\max}$  3500, 3105, 2990, 1740, 1510, 1400, 1220 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$ =7.82 (d, *J*=8.0 Hz, 1H, aromatic), 7.73 (d, *J*=8.2 Hz, 1H, aromatic), 7.55-7.49 (m, 2H, aromatic), 7.38-7.27 (m, 4H, aromatic), 7.23-7.17 (m, 1H, aromatic), 6.59 (br s, 1H, H10), 4.43 (d, *J*=13.0 Hz, 1H, H6), 3.23 (d, *J*=13.0 Hz, 1H, H6), 2.45-2.28 (m, 2H, H9), 2.13-2.00 (m, 1H, H7), 1.91-1.80 (m, 2H, H7 and H8), 1.56-1.47 (m, 1H, H8); <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>):  $\delta$ =153.7, 151.2, 135.8, 132.7, 129.3, 126.4, 126.0, 125.3, 124.4, 124.2, 123.6, 123.3, 121.8, 64.2, 55.0, 33.2, 25.9, 16.5.

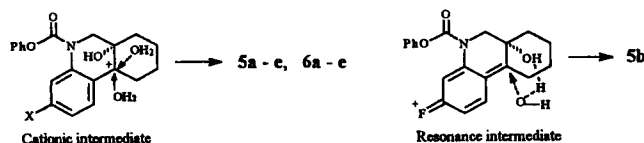
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7. A cationic intermediate is suggested to give epoxide opened products as below. Water near cation will randomly attack the positive carbon center to generate

the *cis* diols **5a-e** and allylic alcohols **6a-e** derived from *trans* diols. On the other hand, compound **2b** with fluorine at C3 can make a resonance intermediate. The hydrogen bonding between hydroxy group and water will place water at the same side with hydroxy group and predominantly induce the *cis* diol **5b**.



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## Synthesis and Properties of Novel Poly[3,4-(silylisopropyl)benzo-1-silapentene]

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### Introduction

Chlorosilane derivatives have received considerable academic and industrial attention since the direct synthesis process was developed.<sup>1-3</sup> Recently, novel chlorosilane derivatives such as 3,4-benzo-1,1-dichloro-1-silacyclopentene and allyldichlorosilane have been prepared by direct synthesis method.<sup>4,5</sup> 3,4-Benzo-1,1-dimethyl-1-silacyclopentene undergoes anionic ring opening polymerization to give a thermally stable polycarbosilane.<sup>6</sup> Friedel-Crafts reaction of aromatic compounds with allyldichlorosilane has also reported.<sup>7,8</sup> We have previously reported the regioselective Friedel-Crafts reaction of allyldichlorosilane with 3,4-benzo-1,1-dichloro-1-silacyclopentene.<sup>9</sup>

Here we wish to report the synthesis of poly[3,4-(silylisopropyl)benzo-1-silapentene] by anionic ring opening polymerization of 3,4-[(silyl)isopropyl]benzo-1-silacyclopentene, which was prepared by the regioselective Friedel-Crafts reaction of allyldichlorosilane with 3,4-benzo-1,1-dichloro-1-silacyclopentene followed by reduction with LiAlH<sub>4</sub>.

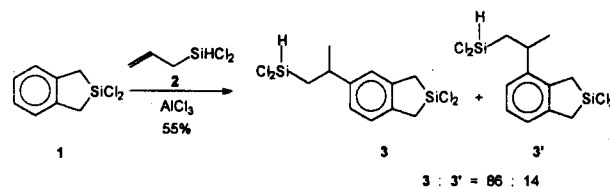
### Results and Discussion

3,4-Benzo-1,1-dichloro-1-silacyclopentene (**1**) has the two reactive functional groups: the aromatic benzene ring and the chlorine atoms bonded to silacyclopentene ring. We previously reported that the Friedel-Crafts reaction of **1** with allyldichlorosilane (**2**) in the presence of AlCl<sub>3</sub> gave an 86:14 isomeric mixture of 3,4-[3'-(dichlorosilyl)isopropyl]benzo-1,

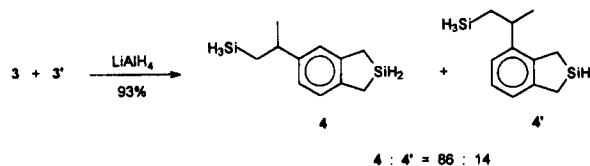
1-dichloro-1-silacyclopentene (**3**) and 3,4-[2'-(dichlorosilyl)isopropyl]benzo-1,1-dichloro-1-silacyclopentene (**3'**) in 55% yield (Scheme 1).<sup>9</sup>

The chlorine atoms bonded to silicon in the mixture of **3** and **3'** were easily converted in high yield into SiH groups by reduction with LiAlH<sub>4</sub> (Scheme 2).

The structure of the reduced product was determined by <sup>1</sup>H, <sup>13</sup>C NMR spectra, IR spectrum, and mass spectrum analysis. The IR spectrum of the product shows the characteristic strong Si-H stretching at 2150 cm<sup>-1</sup>.<sup>10</sup> The isomeric ratio of the products **3** and **3'** was again confirmed. Based on the integration of <sup>1</sup>H NMR spectrum, the distilled product of 3,4-[3'-(silyl)isopropyl]benzo-1-silacyclopentene (**4**) contains the isomer of 3,4-[2'-(silyl)isopropyl]benzo-1-sila-



Scheme 1.



Scheme 2.

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