REACTION OF MALEIMIDES WITH NEW SILYLOXYDIENES, 2-AMINO-4-(TRIMETHYLSILYLOXY)-1,3-PENTADIENES

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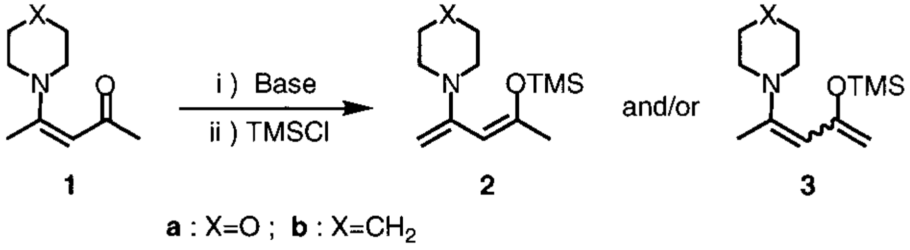
Abstract - New siloxydienes, 2-amino-4-(trimethylsilyloxy)-1,3-pentadienes which were easily obtained *via* enolization of enaminones derived from 2,4-pentane-dione, and immediate silylation, reacted with maleimides to furnish reduced benzo-[*c*]pyrrole-1,3-diones as major products, derived from initial [4 + 2] cycloadducts.

Since the pioneering studies of Danishefsky and his group,[1] a number of siloxydienes have been prepared and widely applied in synthesis of carbocyclic and heterocyclic compounds. In sharp contrast with versatilely utilized siloxydienes with an electron-donating oxygen-[1,2] or sulfur-substituent[2h,i,3] in the 1,3-pattern, however, dienes bearing siloxy and amino groups in the same pattern are not used so much in organic synthesis: To date there have been only limited studies concerning siloxydienes bearing an amino group.[4,5] Here we wish to report the preparation of new amino-substituted siloxydienes and their reaction with maleimides.

Several attempts were made to prepare enol silyl ethers from enaminones (**1**) derived from 2,4-pentanedione. Enolization with LDA in THF at -78 °C followed by quenching with chlorotrimethylsilane (TMSCl) furnished an inseparable mixture of the corresponding 2-amino-4-(trimethylsiloxy)- (**2**) and 4-amino-2-(trimethylsiloxy)-1,3-pentadiene (**3**) in quantitative yield (**2a**/**3a**=6/5; **2b**/**3b**=2/3).[6] However, it



Scheme 1

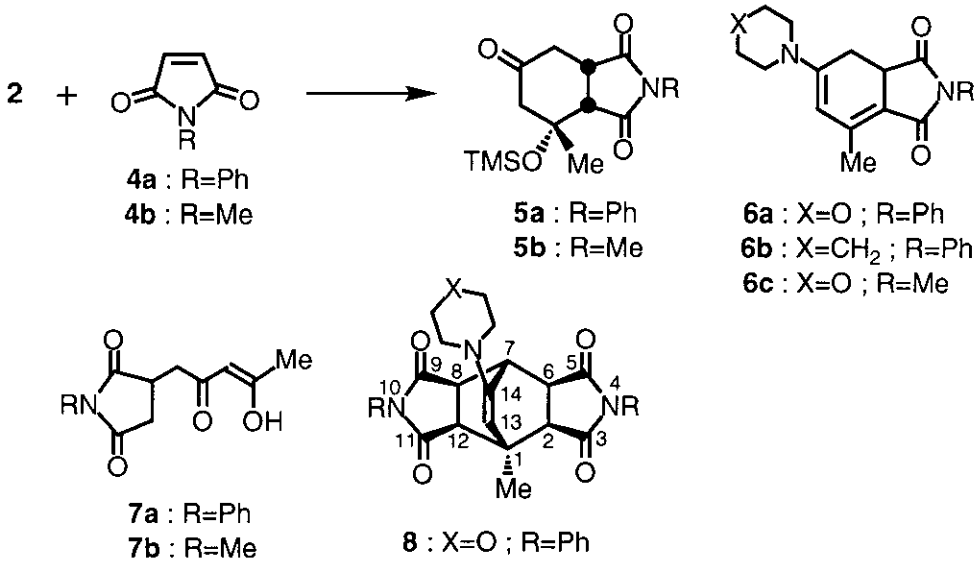
Dedicated to the memory of Professor Koji Nakanishi.

has been found that enolization with BuLi at 0 °C in THF followed by quenching with chlorotrimethylsilane (TMSCl) furnished **2** quntitatively (Scheme 1).[7] The stereochemistry of **2** was assigned to be *Z* by NOE experiment.

Dienes (**2**) belong to a class of 1-siloxydienes that have not been used so extentively in Diels-Alder reactions. It has been reported that the sole reported 3-amino-1-siloxydiene system, 3-amino-1-methoxy-1-(trimethylsiloxy)-1,3-butadiene[5] generated *in situ*, reacted with carbonyl electrophiles in the presence of $TiCl_4$ to give γ-adducts, although Diels-Alder adducts formed in the reaction with an acetylenic dienophile.

Reactions of **2a** with an equivalent of *N*-phenylmaleimide (**4a**) gave an intractable mixture owing to polymerization of **4a**. In the reaction using two equivalents of **2a** no polymerization of **4a** was observed, but instead the reaction proceeded cleanly. The reaction of **2a** or **2b** with **4a** in benzene or THF at 25 °C for 1 h furnished **5a** and **6a** or **6b** as major products, together with a small amount of **7a**, respectively.[8] Under the similar conditions **2a** reacted with *N*-methylmaleimide (**4b**) to give the corresponding products (**5b**, **6c** and **7b**). On the other hand, the reaction of **2a** with **4a** under reflux gave a new 1:2 adduct (**8**) in place of **7a**, although again **5a** and **6a** were major products. The results are summarized in Table 1.

Table 1. Reaction of Siloxydienes (**2**) with Maleimides (**4**).



4a : R=Ph
4b : R=Me

5a : R=Ph
5b : R=Me

6a : X=O ; R=Ph
6b : X=CH_2 ; R=Ph
6c : X=O ; R=Me

7a : R=Ph
7b : R=Me

8 : X=O ; R=Ph

Run	Diene	Imide	Solvent	Temp. °C	Product (Yield, %)
1	**2a**	**4a**	Benzene	25	**5a**(55), **6a**(33), **7a**(6)
2	**2a**	**4a**	Benzene	80	**5a**(40), **6a**(28), **8**(12)
3	**2a**	**4a**	THF	25	**5a**(30), **6a**(45), **7a**(13)
4	**2a**	**4a**	THF	67	**5a**(21), **6a**(48), **8**(10)
5	**2b**	**4a**	Benzene	25	**5a**(34), **6b**(52), **7a**(10)
6	**2b**	**4a**	THF	25	**5a**(42), **6b**(47), **7a**(10)
7	**2a**	**4b**	Benzene	25	**5b**(51), **6c**(26), **7b**(11)

On the basis of spectral data, major products (**5**) and (**6**) were assigned as reduced isoindolediones derived from initial [4 + 2] cycloadducts (**B**), while **7** was as that came from Michael adducts, respectively.[9] The structure of **5b** arising from hydrolysis of **B** in which has an enamine structure was unambiguously established by its X-Ray crystallographic analysis (Figure 1).[10]

Based on the stereochemistry of **5**, the initial adduct (**B**) might be attributable to *exo* cycloadduct that formed *via* an electronically favorable betaine (**A**) generated by the regioselective addition at the γ-position characteristic of 1-siloxydiene[11] rather than a concerted manner. The pathways for the formation of **6** and **8** are clearly illustrated in Scheme 2.

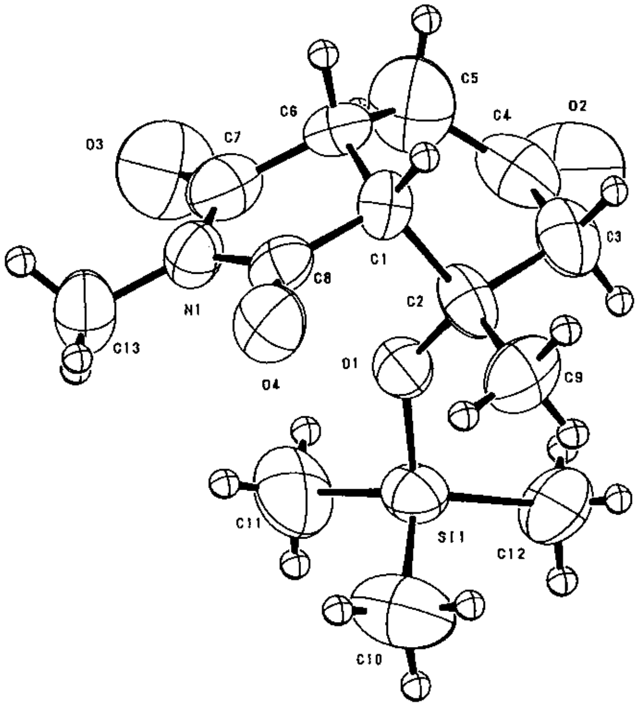
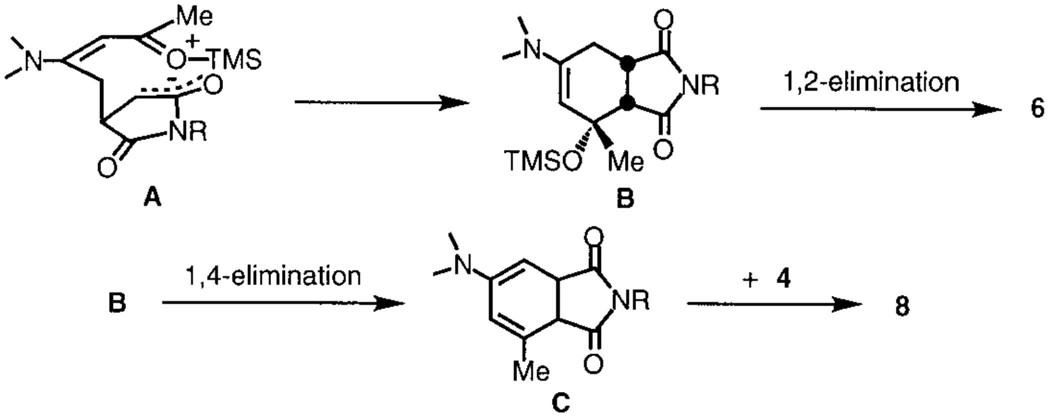


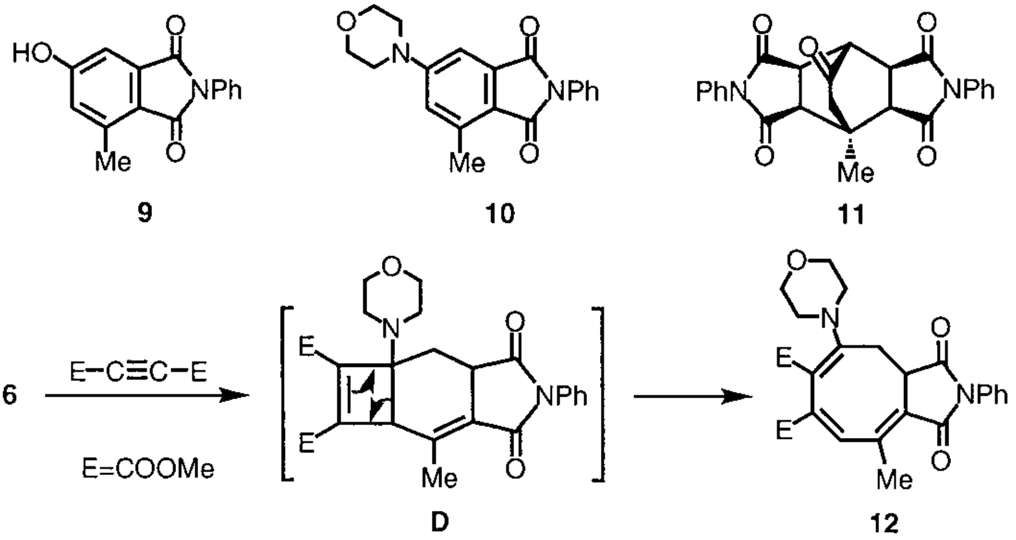
Figure 1. An ORTEP drawing of **5b**.

At room temperature 1,2-elimination of silanol from **B** exclusively occurs to give **6**. On the other hand, at elevated temperature an alternate elimination of silanol *via* 1,4-fashion takes place concomitantly to form **C**, which undergoes Diels-Alder reaction with **4** to furnish **8**.



Scheme 2

Desilylation of **5a** with CsF in DME (reflux, 5 h) gave a 46% yield of phenol derivative (**9**) (mp > 300 °C) with concomitant dehydrogenation. Dehydrogenation of **6a** with 5% Pd-C in benzene (reflux, 10 h) furnished isoindoledione (**10**) (mp 231-231.5 °C) quantitatively. The 1:2 adduct (**8**) was readily



Scheme 3

hydrolyzed to the ketone derivative (**11**) (mp > 300 °C) when treated in refluxing 10% ethanolic hydrochloric acid. The stereochemistry of **8** was assumed on the basis of NMR spectral data[12] and inspection of molecular modeles. It was also found that **6a** reacted with dimethyl acetylenedicarboxylate in benzene (reflux, 45 h) to give a 21% yield of cyclooctatriene (**12**) (mp 183-184 °C) *via* an electrocyclic reaction of [2 + 2] cycloadduct **D** (Scheme 3). The structure of **12** was unambiguously established by its X-Ray crystallographic analysis (Figure 2).[13]

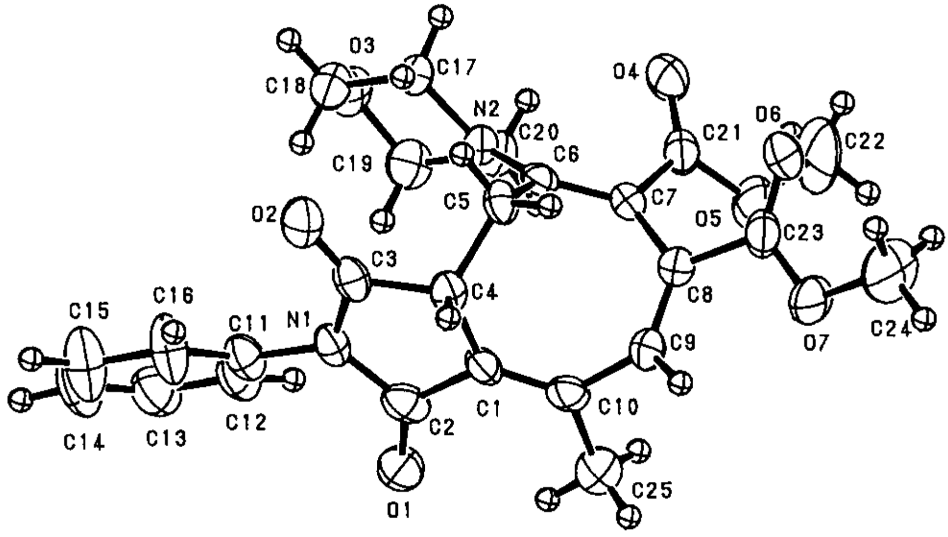


Figure 2. An ORTEP drawing of **12**.

Thus the reaction of **2** with **4** whose major reaction path is [4 + 2] cycloaddition presents a striking contrast to the reaction of 3-amino-1-methoxy-1-silyloxybutadiene.[5]

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6. The ratios were calculated by integral values of methyl proton in ^{1}H NMR spectra at δ 1.85 (**2a**), 1.84 (**2b**), 2.04 (**3a**) and 2.04 (**3b**), respectively.
7. **2a** and **2b**: Both yellow oil, and can be kept in a stoppered container for up to several days in the freezer without obvious decomposition, but are slowly hydrolyzed when exposed to air. **2a:** ^{1}H NMR ($CDCl_3$) δ 0.20 (9H, s), 1.85 (3H, d, J=0.9 Hz), 2.78-2.88, 3.68-3.77 (each 4H, m), 4.08, 4.36 (each 1H, s), 4.85 (1H, br s); ^{13}C NMR ($CDCl_3$) δ 0.86, 23.79, 49.29, 66.83, 89.56, 106.43, 150.37, 150.60. NOE enhancement (15%) was observed between 3-CH= and CH_3 in **2a**. Brassard's diene[2a] and Chan's diene[3a] whose structures are 1-siloxydienes have been reported as (Z)-stereochemistry.
8. Typical run is as follows (Run 1 in Table 1): After a solution of **2a** (1.2 g, 5 mmol) and **4** (0.43 g, 2.5 mmol) in dry benzene (30 mL) was stirred at 25 °C for 1 h, the reaction mixture was concentrated in vacuo. Flash chromatography (SiO_2) using benzene-AcOEt (1:1) and then benzene-AcOEt (1:2) gave **5** (0.47 g, 55%), **6a** (0.27 g, 33%) and then **8** (43 mg, 6%), respectively.
9. All the new compounds gave satisfactory analytical and spectral data. All the NMR spectra in this paper were measured in $CDCl_3$. Selected data: **5a**: Colorless needles, mp 140-141 °C; IR (KBr) 1715 cm^{-1}; ^{1}H NMR δ 0.11 (9H, s), 1.69(3H, s), 2.24-3.43 (6H, m), 7.21-7.55 (5H, m); ^{13}C NMR δ 1.98, 26.73, 35.80, 37.67, 50.87, 52.53, 75.74, 126.20, 128.56, 129.16, 131.96, 174.76, 177.56, 206.20. MS *m/z* 345 (M^+). **6a**: Yellow needles, mp 210.5-211.5 °C; IR (KBr) 1709 cm^{-1}; ^{1}H NMR δ 2.09-3.60 (7H, m), 2.33 (3H, d, J=1.8 Hz), 3.70-3.85 (4H, m), 5.02 (1H, q, J=1.8 Hz), 7.22-7.58 (5H, m); MS *m/z* 324 (M^+).
10. X-Ray crystallographic analysis was carried out on a Rigaku AFC5S diffractometer. The diffraction data were collected with the use of MoKα radiation and 2121 independent reflections were used for

solving the structure by the TEXSAN program (TEXSAN TEXRAY. Structure Analysis Package, Molecular Structure Corporation). Crystal data for **5b**: $C_{13}H_{21}NO_4Si$, F.W.=283.40, tetragonal, space group $P42_1c$ (#114), a=18.899 (4) Å, c=8.87 (13) Å, V=3168 (4) Å^3, Z=8, Dcal=1.188 g/cm^3, μ (MoKα)=1.51 cm^{-1}, R=0.057, Rw=0.064.

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12. **8**: Pale yellow needles, mp 233-234 °C; IR (KBr) 1717 cm^{-1}; ^{1}H NMR δ 1.88 (3H, s), 2.77 (2H, d, J=8.2 Hz, H-2, H-12), 2.78-2.88 (4H, m), 3.12 (2H, dd, J=8.2, 3.2 Hz, H-6, H-8), 3.59-3.70 (4H, m), 4.00 (1H, dd, J=2.0, 3.2 Hz, H-7), 4.52 (1H, d, J=2.0 Hz, H-13), 7.08-7.52 (10H, m); ^{13}C NMR δ 20.35, 34.42, 41.05, 44.29, 47.83, 49.27, 66.38, 99.78, 126.31, 128.83, 129.23, 131.75, 148.06, 174.96, 175.46; MS *m/z* 497 (M$^+$).
13. Crystal data for **12**: $C_{25}H_{26}N_2O_7$, F.W.=466.49, monoclinic,space group $P2_1/n$, a=10.777 (8) Å, b=13.504 (3) Å, c=16.148 (2) Å, β=95.28 (3)°, V=2340 (2) Å^3, Z=4, Dcal=1.324 g/cm^3, μ(MoKα)=0.91 cm^{-1}, Rigaku AFC5S diffractometer, 1642 reflections (I>3.00σ (I)), R=0.058, Rw=0.065.

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