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, 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- or sulfur-substituent 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. 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-pentanediene. Enolization with LDA in THF at -78 °C followed by quenching with chlorotrimethylsilane (TMSCI) furnished an inseparable mixture of the corresponding 2-amino-4-(trimethylsilyloxy)- (2) and 4-amino-2-(trimethylsilyloxy)-1,3-pentadiene (3) in quantitative yield (2a/3a=6/5; 2b/3b=2/3). However, it

\[
\begin{align*}
\text{1} & \xrightarrow{\text{i) Base}} \xrightarrow{\text{ii) TMSCI}} \text{2} \\
X = & \text{O} ; & X = & \text{CH}_2 \\
\text{a} & \quad \text{and/or} \quad \text{b}
\end{align*}
\]

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 (TMSCI) furnished 2 quantitatively (Scheme 1). 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 extensively 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 generated in situ, reacted with carbonyl electrophiles in the presence of TiCl₄ 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. 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.

![Diagram showing the reaction of siloxydienes (2) with maleimides (4).]

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

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

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 rather than a concerted manner. The pathways for the formation of 6 and 8 are clearly illustrated in Scheme 2.

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.

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
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\textsuperscript{12} and inspection of molecular models. 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) \textit{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).\textsuperscript{13}

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.\textsuperscript{5}
REFERENCES AND NOTES


6. The ratios were calculated by integral values of methyl proton in $^1$H NMR spectra at $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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 $\delta$ 0.11 (9H, s), 1.69(3H, s), 2.24-3.43 (6H, m), 7.21-7.55 (5H, m); $^{13}$C NMR $\delta$ 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 $\delta$ 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: C₁₃H₂₁NO₄Si, F.W.=283.40, tetragonal, space group P₄₂₁c (114), a=18.899 (4) Å, c=8.87 (13) Å, V=3168 (4) Å³, Z=8, Dcal=1.188 g/cm³, μ(MoKα)=1.51 cm⁻¹, R=0.057, Rw=0.064.


12. 8: Pale yellow needles, mp 233-234 °C; IR (KBr) 1717 cm⁻¹; ¹H 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); ¹³C 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 (M⁰).

13. Crystal data for 12: C₂₅H₂₆N₂O₇, F.W.=466.49, monoclinic, space group P2₁/n, a=10.777 (8) Å, b=13.504 (3) Å, c=16.148 (2) Å, β=95.28 (3)°, V=2340 (2) Å³, Z=4, Dcal=1.324 g/cm³, μ(MoKα)=0.91 cm⁻¹, Rigaku AFC5S diffractometer, 1642 reflections (I>3.00σ (I)), R=0.058, Rw=0.065.

Received, 30th June, 1997