GENERATION AND REACTIONS OF 3-PHENYL-7,8-DEHYDRO-1-AZAAZULENE

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Abstract – 3-Phenyl-7,8-dehydro-1-azaazulenes were generated by the treatment of 8-bromo-3-phenyl-1-azaazulenes with potassium t-butoxide in DMSO or in THF in the presence of 16-crown-8-ether, and trapped with diphenylisobenzofuran as 3,7,12-triphenyl-1-aza-7,12-epoxynaphth[2,3-e]azulenenes. The structure of the adduct, 2-bromo-3,7,12-triphenyl-1-aza-7,12-epoxynaphth[2,3-e]azulene, was deduced by X-Ray structure analysis. Similar treatment of 8-bromo-3-phenyl-1-azaazulene with potassium t-butoxide in the presence of furan gave 3-phenyl-1-aza-7,12-epoxynaphth[2,3-e]azulene and 7-phenyl-3H-3a,3c-dihydro-1-aza-3-oxacyclopenta[3,4]cyclobuta[1,2-e]azulene as cycloadducts.

INTRODUCTION

Arynes were widely investigated from the interest of their high reactivity and synthetic utility.1–3 In spite of great interests about the non-benzenoid arynes, the studies were observed only few; some reports were about dehydrotropolone,4 dehydrotopone,5 4,5-dehydrodibenzoheteropins,6,7 5,6-dehydroazulene,8 and 5,6-dehydro-1,3-diazaazulene.9 Since we succeeded in the generation of azazaazulyne in the series of our study on the reaction of azaazulenes,10,11 we wish to present here the generation and [2 + 4]cycloadducts of 3-phenyl-7,8-dehydro-1-azaazulene and 2-bromo-3-phenyl-7,8-dehydro-1-azaazulene.

RESULTS AND DISCUSSION

A mixture of 8-bromo-3-phenyl-1-azaazulene (1a) and potassium t-butoxide in the presence of diphenylisobenzofuran (DPIBF) in DMSO was heated at 100 °C for 1.5 h. After worked up, three products, the cycloadduct (3a) (3%), 8-methylthio-3-phenyl-1-azaazulene (4a) (6%), and 3-phenyl-1-azaazulen-8(1H)-one (5a)12 (11%), were isolated from the reaction mixture (Table 1, Run 1). The
compound (3a) was analyzed as 1:1-adduct \((C_{15}H_{23}NO)\) of 3-phenyl-7,8-dehydro-1-azaazulene (2a) and DIPBF from its elemental analysis and mass spectrum. In the \(^1\)H NMR spectrum of 3a, three protons of the seven-membered ring were observed at \(\delta 7.28\) (dd, \(J 10.4, 9.2\) Hz), 7.75 (d, \(J 9.2\) Hz), and 8.47 (d, \(J 10.4\) Hz); this shows that DIPBF reacted at C-7 and C-8 of 1-azaazulene nuclei. From the result, we assigned the adduct as 3,7,12-triphenyl-1-aza-7,12-epoxynaphth[2,3-e]azulene. Thus we could show the ambiguous generation of 3-phenyl-7,8-dehydro-1-azaazulene (2a). Its spectroscopic data as well as elemental analysis assigned the compound (4a). The compound (4a) was consisted with the compound prepared by the reaction of 1a with sodium methyl sulfide, and the structure was confirmed. When the reaction was performed at rt for 2 d, the yield of 3a slightly increased (7\%) and the yield of 4a decreased (trace) (Run 2). When the base was changed, the results showed almost the same aspects (Runs 3, 4), except for lithium tetramethylpiperidine (LiTMP) (Run 5).

When 8-bromo-3-phenyl-1-azaazulene (1a) was treated with potassium \(t\)-butoxide in the presence of 18-crown-6-ether (CE) and excess DIPBF in dry THF under refluxed for 30 h, the formation of 3a was improved (Runs 7, 8): the compounds (3a) (15\%) and (5a) (20\%) were obtained along with small amount of 3-phenyl-1-azaazulene (6a).\(^{11,12}\)

\[
\begin{align*}
1a : X = H & & 2a : X = H \\
1b : X = Br & & 2b : X = Br \\
3a : X = H & & 4a : X = H \\
3b : X = Br & & 5a : X = H \\
5b : X = Br & & 6a : X = H \\
\end{align*}
\]

Scheme 1

Similarly, the reaction of 2,8-dibromo-3-phenyl-1-azaazulene (1b) with potassium \(t\)-butoxide in the presence of CE and DIPBF in dry THF gave 3b (4\%), 5b (13\%), and recovered 1b (43\%) (Run 9). When the reaction was performed under elevated temperature and using excess amounts of DIPBF, the yield of 3b was improved (Runs 10, 11).

Spectroscopic data of 3b were resembled to those of 3a, and this supported the structure. The structure of the adduct (3b) was finally deduced by X-Ray structure analysis (Figure 1). In the seven-membered ring,
the bond alternation was clearly observed [C(3)-C(4) 1.42(2), C(4)-C(5) 1.37(2), C(5)-C(6) 1.40(2), C(6)-
C(7) 1.36(1), C(7)-C(16) 1.42(1), C(16)-C(17) 1.39(1)]. The results agree with the $^1$H NMR
spectroscopic results.

Formation of 4a, 5a, and 5b was considered as follows (Scheme 2). Two possible formation mechanisms
for 4a could be considered. When the generated dehydro-1-azaazulene (2a) reacts with DMSO,
intermediate (A) would be produced. Rearrangement of A affords B, and the successive elimination of
formaldehyde furnishes 4a (path a). Another path is the substitution mechanism (path b). Although
DMAD was purified, methyl sulfide could be produced by decomposition, and reaction of methyl sulfide with
1a gave 4a. Reaction of 1a and 1b with alkoxide gives C. Compound (C) could be easily hydrolyzed to
give 5a and 5b.

\[
\text{Ph} \\
\text{Br} \\
\begin{array}{c}
\text{X} = \text{H} \\
\text{path a}
\end{array}
\]
\[
\begin{array}{c}
\text{X} = \text{H} \\
- \text{SMe} \\
\text{path b}
\end{array}
\]
\[
\begin{array}{c}
- \text{OR} \\
\text{path c}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{OR} \\
\begin{array}{c}
\text{X}
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\text{DMSO} \\
\text{hydrolysis}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{SMe}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{Me}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{H}
\end{array}
\]

Scheme 2

The intermediate (2a) could be also trapped by furan. Thus we treated 1a with potassium t-butoxide in the
presence of furan in DMSO and obtained 7 (1%) and 8 (1%) together with 4a and 5a (Run 12). The
products (7 and 8) were 1:1-adducts of 2a and furan on the basis of mass spectra (M+, m/z 271). In the
$^1$H NMR spectrum of 7, three protons of the seven-membered ring appear at $\delta$ 7.93 (dd, J 11.1 and 9.8, H-5),
8.53 (d, J 11.1, H-4), 8.65 (d, J 9.8, H-6), two methine protons at $\delta$ 6.72-6.77 (1H, m) and 7.72-7.74
(1H, m), and two olefinic protons at $\delta$ 7.51 (1H, dm, J 3.5) and 8.42 (1H, dm, J 3.5), along with phenyl
protons and H-2 proton at $\delta$ 8.78 (1H, s). The divergence of the coupling shows the existence of bond
alternation of seven-membered ring of 7. From the results, the compound (7) was assigned as 3-phenyl-1-aza-7,10-epoxybenz[e]azulene. In the ¹H NMR spectrum of 8, three protons of the seven-membered ring were seen at δ 7.29 (1H, dd, J 10.7 and 8.8), 7.70 (1H, d, J 8.8), and 8.45 (1H, d, J 10.7), two methine protons were seen at δ 5.89 (1H, br s), 6.64 (1H, br s), and two olefinic protons were seen at δ 7.17 (1H, d, J 5.5 and 1.7) and 7.20 (1H, dd, J 5.5 and 1.8). In the ¹³C NMR spectrum of 8, two methine carbon signals were seen at δ 83.38 and 84.95. Bond alternation of seven-membered ring of 8 was also seen. From the results, we assigned the structure as 7-phenyl-3H-3a,9c-dihydro-9a-aza-3-oxa-cyclopenta[3,4]cyclobuta[1,2-e]azulene.

Interestingly, when the reaction was performed with potassium t-butoxide in the presence of CE under reflux, 7 was obtained; whereas, when the reaction was performed with potassium t-butoxide in the presence of CE at rt, 8 was obtained (Runs 13, 14). Plausible formation mechanism of 8 is shown in Scheme 3. Hydrogen abstraction from 1a produces the anion (D). Michel addition of D with furan, and successive cyclization of E gives F. Debromination of F furnishes 8.

Although the dehydro-1-azaazulene reacts with furan at rt to give [2 + 2] and [2 + 4] cycloadducts, the dehydro-1-azaazulene with furan underwent preferentially [2 + 4] cycloaddition at elevated temperature (Runs 9, 10, 13, 14).

Table 1. Reactions of 8-bromo- and 2-8-dibromo-3-phenyl-1-azaazulenes (1a,b) with base in the presence of diphenylisobenzofuran (DPIBF) or furan.

<table>
<thead>
<tr>
<th>Run</th>
<th>Compd</th>
<th>Reagent</th>
<th>Solvent</th>
<th>Base</th>
<th>Temp.</th>
<th>Time</th>
<th>Yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>DPIBF</td>
<td>DMSO</td>
<td>t-BuOK</td>
<td>100 °C</td>
<td>1.5 h</td>
<td>3a(3) 4a(6) 5a(11)</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>DPIBF</td>
<td>DMSO</td>
<td>t-BuOK</td>
<td>rt</td>
<td>2 d</td>
<td>3a(7) 4a(trace) 5a(20)</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>DPIBF</td>
<td>DMSO</td>
<td>MeONa</td>
<td>60 °C</td>
<td>6 h</td>
<td>3a(5) 4a(3) 5a(27)</td>
</tr>
<tr>
<td>4</td>
<td>1a</td>
<td>DPIBF</td>
<td>DMSO</td>
<td>NaH</td>
<td>rt</td>
<td>2 d</td>
<td>3a(5) 4a(trace) 5a(17)</td>
</tr>
<tr>
<td>5</td>
<td>1a</td>
<td>DPIBF</td>
<td>DMSO</td>
<td>LiTMP</td>
<td>rt</td>
<td>2 d</td>
<td>complex mixture</td>
</tr>
<tr>
<td>6</td>
<td>1a</td>
<td>DPIBF</td>
<td>THF</td>
<td>t-BuOK</td>
<td>reflux</td>
<td>2 d</td>
<td>3a(1) 5a(24) 6a(5) 1a(5)</td>
</tr>
<tr>
<td>7</td>
<td>1a</td>
<td>DPIBF</td>
<td>THF</td>
<td>t-BuOK–CE</td>
<td>reflux</td>
<td>30 h</td>
<td>3a(7) 5a(21) 6a(trace) 1a(8)</td>
</tr>
<tr>
<td>8</td>
<td>1a</td>
<td>DPIBF</td>
<td>THF</td>
<td>t-BuOK–CE</td>
<td>reflux</td>
<td>30 h</td>
<td>3a(15) 5a(20) 6a(trace)</td>
</tr>
<tr>
<td>9</td>
<td>1b</td>
<td>DPIBF</td>
<td>THF</td>
<td>t-BuOK–CE</td>
<td>rt</td>
<td>10 d</td>
<td>3b(4) 5b(13) 1b(43)</td>
</tr>
<tr>
<td>10</td>
<td>1b</td>
<td>DPIBF</td>
<td>THF</td>
<td>t-BuOK–CE</td>
<td>reflux</td>
<td>1 d</td>
<td>3b(18) 5b(17) 1b(16)</td>
</tr>
<tr>
<td>11</td>
<td>1b</td>
<td>DPIBF</td>
<td>THF</td>
<td>t-BuOK–CE</td>
<td>reflux</td>
<td>1 d</td>
<td>3b(22) 5b(trace) 1b(36)</td>
</tr>
<tr>
<td>12</td>
<td>1a</td>
<td>furan</td>
<td>DMSO</td>
<td>t-BuOK</td>
<td>rt</td>
<td>2 d</td>
<td>7(1) 8(1) 4a(1) 5a(28)</td>
</tr>
<tr>
<td>13</td>
<td>1a</td>
<td>furan</td>
<td>THF</td>
<td>t-BuOK–CE</td>
<td>rt</td>
<td>6 d</td>
<td>8(1) 5a(27) 1a(4)</td>
</tr>
<tr>
<td>14</td>
<td>1a</td>
<td>furan</td>
<td>THF</td>
<td>t-BuOK–CE</td>
<td>reflux.</td>
<td>12 h</td>
<td>7(4) 5a(9) 6a(5)</td>
</tr>
<tr>
<td>15</td>
<td>1a</td>
<td>furan</td>
<td>furan</td>
<td>t-BuOK</td>
<td>rt</td>
<td>7 d</td>
<td>5a(27) 1a(50)</td>
</tr>
</tbody>
</table>

a) 5 eq. of DPIBF was used.
Figure 1. An ORTEP drawing of 3b with thermal ellipsoids (50% probability).

\[ \text{Scheme 3} \]
CONCLUSION
7,8-Dehydro-1-azaazulenes (2a, 2b) has been generated and trapped with diphenylisobenzofuran to give the adducts (3a, 3b), and with furan to give 7 and 8. Bond alternation of the adducts were confirmed by X-Ray structure analysis and ¹H NMR spectra.

EXPERIMENTAL
Mps are measured using a Yanagimoto micro-melting apparatus and uncorrected. ¹H NMR spectra were recorded on a Bruker AVANCE 400S (400 MHz) and ¹³C NMR spectra were recorded on a Bruker AVANCE 400S (100.6 MHz) using deuteriochloroform as a solvent with tetramethylsilane as an internal standard unless otherwise stated; J values are recorded in Hz. IR spectra were recorded for KBr pellets unless otherwise stated on a Nicolet FT-IR Impact 410. Electronic spectra were recorded with Shimadzu UV-1600PC spectrophotometer. MS spectra were taken with an LC-MS Waters Integrity System. Elemental analyses were taken with a Perkin Elmer 2400II. Kieselgel 60 and Alumina Activated 300 were used for column chromatography and Kieselgel 60G was used for thin-layer chromatography.

Synthesis of 8-bromo-3-phenyl-1-azaazulene (1a)
Under argon atmosphere, a mixture of 3-phenyl-1-azaazulen-8(1H)-one¹² (0.234 g, 1.10 mmol), and phosphorus oxybromide (0.887 g, 3.09 mmol) was heated for 1 h at 110 °C. To the mixture was added water, then the solution was neutralized with sodium carbonate. The mixture was extracted with chloroform, and the solvent was dried over sodium sulfate and evaporated. The residue was chromatographed on alumina column with benzene to give 8-bromo-3-phenyl-1-azaazulene (1a) (0.226 g, 72%).

1a: Dark violet needles (from hexane-dichloromethane), mp 123-124 °C; δ₁ 7.43 (1H, d, J 7.4), 7.54 (2H, dd, J 7.6 and 7.4), 7.59 (2H, d, J 7.6), 7.64 (1H, dd, J 10.2 and 9.7), 7.71 (1H, dd, J 10.8 and 10.2), 8.29 (1H, d, J 10.8), 8.69 (1H, d, J 9.7), 8.94 (1H, s); δ₁C 127.49, 127.88, 129.04, 129.50, 131.08, 133.69, 133.76, 135.28, 136.23, 137.33, 139.95, 155.05, 157.03; ν max / cm⁻¹ 729 and 696 (phenyl); λ max(CHCl₃) / cm⁻¹ (log ε) 299 (4.49), 369 (3.55, sh) and 515 (2.80); m/z (rel intensity) 285 (M⁺, 98), 283 (M⁺, 100), 203 (28). Anal. Calcd for C₁₅H₁₀NBr: C, 63.40; H, 3.55; N, 4.93. Found: C, 63.66; H, 3.45; N, 4.67.

Synthesis of 2,8-dibromo-3-phenyl-1-azaazulene (1b)
Under argon atmosphere, a mixture of 2-chloro-3-phenyl-1-azaazulen-8(1H)-one¹² (1.67 g, 6.52 mmol), and phosphorus oxybromide (5.71 g, 19.90 mmol) was heated for 1 h at 110 °C. To the mixture was added water, then the solution was neutralized with sodium carbonate. The mixture was extracted with chloroform, and the solvent was dried over sodium sulfate and evaporated. The residue was chromatographed on alumina column with benzene to give 2,8-dibromo-3-phenyl-1-azaazulene (1b) (1.82 g, 77%).

1b: Red scales (from hexane-dichloromethane), mp 164-166 °C; δ₁ 7.45-7.56 (5H, m), 7.64 (1H, dd, J 10.4 and 9.5), 7.69 (1H, dd, J 10.8 and 10.4), 8.27 (1H, d, J 10.8), 8.37 (1H, d, J 9.5); δ₁C 128.13, 128.70, 129.02, 129.81, 130.66, 132.26, 134.33, 135.07, 135.64, 136.10, 140.83, 148.78, 153.30; ν max / cm⁻¹ 731 and 700 (phenyl); λ max(CHCl₃) / cm⁻¹ (log ε) 254 (4.52), 306 (4.64), 377 (3.21, sh) and 498 (3.12); m/z (rel intensity) 365 (M⁺, 44), 363 (M⁺, 81), 361 (M⁺, 43), 203 (100). Anal. Calcd for C₁₅H₉NBr₂: C,
49.62; H, 2.50; N, 3.86. Found: C, 49.9; H, 2.41; N, 3.74.

**Generation and trapping of 7,8-dehydro-1-azaazulenes with diphenylisobenzofuran**

*Typical procedure A* - Under argon atmosphere, a mixture of 8-bromo-3-phenyl-1-azaazulene (1a) (0.291 g, 1.02 mmol), potassium t-butoxide (0.141 g, 1.26 mmol), and diphenylisobenzofuran (0.325 g, 1.20 mmol) in dry DMSO (35 mL) was stirred for 2 d at rt. To the mixture was added water, and the mixture was extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel column (benzene then hexane-ethyl acetate (2:1)) to give 3a (0.035 g, 7%), 4a (0.001 g, 0.4%), and 5a\textsuperscript{12} (0.045 g, 20%).

*Typical procedure B* - Under argon atmosphere, a mixture of 8-bromo-3-phenyl-1-azaazulene (1a) (0.145 g, 0.51 mmol), potassium t-butoxide (0.069 g, 0.61 mmol), diphenylisobenzofuran (0.675 g, 2.50 mmol), and 18-crown-6-ether (0.164 g, 0.62 mmol) in dry THF (30 mL) was refluxed for 30 h. To the mixture was added water, and the mixture was extracted with chloroform. The extract was dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel column (benzene then hexane-ethyl acetate (2:1)) to give 3a (0.036 g, 15%), 5a (0.023 g, 20%), and 6a (0.0004 g, 0.4%).

In a similar manner, the reactions of 1a and 1b were performed under some variety of conditions. The results were listed in Table 1.

**3a**: Red purple needles (from ethanol), mp 192-194 °C; \( \delta_t \) 7.01 (1H, dd, J 7.5 and 7.4), 7.21 (1H, dd, J 7.5 and 7.4), 7.28 (1H, dd, J 10.4 and 9.2), 7.36 (1H, dd, J 7.3 and 7.2), 7.46-7.55 (8H, m), 7.59 (2H, d, J 7.4), 7.63 (1H, d, J 7.3), 7.75 (1H, d, J 9.2), 7.92-8.00 (5H, m), 8.47 (1H, d, J 10.4, 8.73 (1H, s); \( \delta_C \) 91.46, 94.20, 121.00, 123.75, 126.32, 126.61, 126.88, 127.05, 127.67, 128.02, 128.66, 128.71, 128.85, 128.88, 129.10, 129.12, 129.92, 130.28, 132.16, 134.23, 135.17, 142.87, 146.30, 150.41, 150.48, 150.79, 155.63, 158.89; \( \nu_{\text{max}} / \text{cm}^{-1} \) 1658 (C=O), 758 and 703 (phenyl); \( \lambda_{\text{max}} / \text{CHCl}_3 / \text{cm}^{-1} / \log \varepsilon \) 303 (4.40), 374 (3.76), 519 (2.95); \( m/z \) (rel intensity) 473 (M\(^+\), 92), 368 (94), 105 (100) and 77 (60). Anal. Calcd for C\(_{35}\)H\(_{33}\)NO: C, 88.77; H, 4.90; N, 2.96. Found: C, 88.83; H, 5.01; N, 3.32.

**4a**: Orange prisms (from hexane-dichloromethane), mp 135-136 °C; \( \delta_t \) 2.73 (3H, s), 7.37 (1H, d, J 7.4), 7.41 (1H, dd, J 9.8 and 9.6), 7.50 (1H, dd, J 7.4 and 7.2), 7.57 (2H, d, J 7.2), 7.61 (1H, d, J 11.0), 7.76 (1H, dd, J 11.0 and 9.6), 8.57 (1H, d, J 9.8), 8.63 (1H, s); \( \delta_C \) 15.54, 123.72, 125.20, 126.91, 128.86, 129.31, 129.47, 134.47, 135.48, 135.88, 138.02, 151.96, 152.64, 154.77; \( \nu_{\text{max}} / \text{cm}^{-1} \) 769 and 703 (phenyl); \( \lambda_{\text{max}} / \text{CHCl}_3 / \text{cm}^{-1} / \log \varepsilon \) 273 (4.70), 339 (4.62), 495 (3.03); \( m/z \) (rel intensity) 251 (M\(^+\), 100), 204 (97), 177 (75). Anal. Calcd for C\(_{16}\)H\(_{12}\)NS: C, 76.45; H, 5.21; N, 5.57. Found: C, 76.94; H, 5.19; N, 5.69.

**6a\textsuperscript{12,13}:** Red violet oil; \( \delta_t \) 7.34 (1H, t-like, J 7.4), 7.53 (2H, t-like, J 7.7), 7.62-7.67 (3H, m), 7.76 (1H, t-like, J 9.9), 7.91 81H, t-like, J 9.9), 8.76 (2H, t-like, J 9.2), 8.91 (1H, s); \( m/z \) (rel intensity) 205 (M\(^+\), 100),
176 (30), 76 (32).

**Synthesis of 4a**

A mixture of 8-bromo-3-phenyl-1-azaazulene (1a) (0.293 g, 1.03 mmol) and sodium methyl sulfide (0.088 g, 1.25 mmol) in dry THF (20 mL) was refluxed for 2 h. To the mixture was added water, and the mixture was extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel column (benzene then hexane-ethyl acetate (3:1)) to give 4a (0.242 g, 93%).

**Generation and trapping of 7,8-dehydro-1-azaazulenes with furan**

*Typical procedure A* - Under argon atmosphere, a mixture of 8-bromo-3-phenyl-1-azaazulene (1a) (0.581 g, 2.04 mmol), potassium t-butoxide (0.367 g, 1.26 mmol), and furan (1.1 mL) in dry DMSO (15 mL) was stirred for 2 d at rt. To the mixture was added water, and the mixture was extracted with chloroform. The extract was washed with water, dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel column (benzene then hexane-ethyl acetate (2:1)) to give 7 (0.006 g, 1%), 8 (0.007 g, 1%), 4a (0.005 g, 1%), and 5a (0.163 g, 28%).

*Typical procedure B* - Under argon atmosphere, a mixture of 8-bromo-3-phenyl-1-azaazulene (1a) (0.286 g, 0.51 mmol), potassium t-butoxide (0.069 g, 0.61 mmol), furan (1.0 mL), and 18-crown-6-ether (0.164 g, 0.62 mmol) in dry THF (30 mL), was refluxed for 12 h. To the mixture was added water, and the mixture was extracted with chloroform. The extract was dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel column (benzene then hexane-ethyl acetate (2:1)) to give 7 (0.011 g, 4%), 5a (0.019 g, 9%), and 6a (0.011 g, 5%).

7: Red violet oil; δH 6.72-6.77 (1H, m), 7.40 (1H, t-like, J 7.4), 7.51 (1H, dm, J 3.5), 7.52 (2H, tm, J 7.6), 7.63 (2H, dm, J 7.8), 7.72-7.74 (1H, m), 7.93 (1H, dd, J 11.1 and 9.8), 8.42 (1H, dm, J 3.5), 8.53 (1H, d, J 11.1), 8.65 (1H, d, J 9.8), 8.78 (1H, s); m/z (rel intensity) 271 (M+, 100), 245 (25), 243 (54), 241 (39), 213 (13).

8: Orange needles (from hexane-dichloromethane), mp 133-134 °C; δH 5.89 (1H, br s), 6.64 (1H, br s), 7.17 (1H, d, J 5.5 and 1.7), 7.20 (1H, dd, J 5.5 and 1.8), 7.29 (1H, dd, J 10.7 and 8.8), 7.39 (1H, d, J 7.4), 7.51 (2H, dd, J 7.7 and 7.5), 7.59 (2H, d, J 7.7), 7.70 (1H, d, J 8.8), 8.45 (1H, d, J 10.7), 8.85 (1H, s); δC 83.38, 84.95, 126.44, 127.20, 128.54, 128.83, 128.97, 131.42, 134.03, 140.03, 141.90, 143.48, 147.40, 150.53, 155.38, 159.39; νmax / cm⁻¹ (CHCl₃) 1629 (C=C), 769 and 703 (phenyl); m/z (rel intensity) 271 (M+, 100), 243 (71), 215 (17). *Anal.* Calcd for C₁₉H₁₃NO: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.36; H, 4.42; N, 4.98.

**X-Ray structure determination**

**Crystal data of 3b:** Red prism, C₃₅H₂₂NOBr, M=552.47, monoclinic, space group P2₁/c, a=10.48(1),
\[ b = 17.638(4) \, \text{Å}, \quad c = 14.321(4) \, \text{Å}, \quad V = 2632(2) \, \text{Å}^3, \quad Z = 4, \quad D_{\text{calc}} = 1.394 \, \text{g/cm}^3, \quad \text{crystal dimensions 0.46 x 0.38 x 0.07 mm.} \] 

Data were measured on a Rigaku AFC5S radiation diffractometer with graphite-monochromated Mo-K\(\alpha\) radiation. Total 4852 (4581 unique) reflections were collected using \(\omega-2\theta\) scan technique with in a \(2\theta\) range of 50.0\(^\circ\). The structure was solved by direct methods and refined by a full-matrix least-squares method using 343 variables refined with 1357 reflections \([I > 2\sigma(I)]\). The weighting scheme \(\omega = 4F_0^2/\sigma^2(F_0^2)\) gave satisfactory agreement analyses. The final refinement converged to \(R = 0.066\) and \(R_w = 0.048\).

Selected bond lengths (azaazulene ring) of 3b (Å): N(1)-C(1) 1.34(1), C(1)-C(2) 1.41(1), C(2)-C(3) 1.38(1), C(3)-C(4) 1.42(2), C(4)-C(5) 1.37(2), C(5)-C(6) 1.40(2), C(6)-C(7) 1.36(1), C(7)-C(16) 1.42(1), C(16)-C(17) 1.39(1), C(17)-N(1) 1.39(1), C(3)-C(17) 1.45(1).

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**REFERENCES AND NOTES**