

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

Noritaka Abe,* Masao Yoshitsugu, Hiroyuki Fujii, and Akikazu Kakehi †

Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi 753-8512, Japan

† Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato Nagano 380-8553, Japan

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*]azulenes. 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-3*H*-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 dehydrotropone,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 azaazulyne 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.

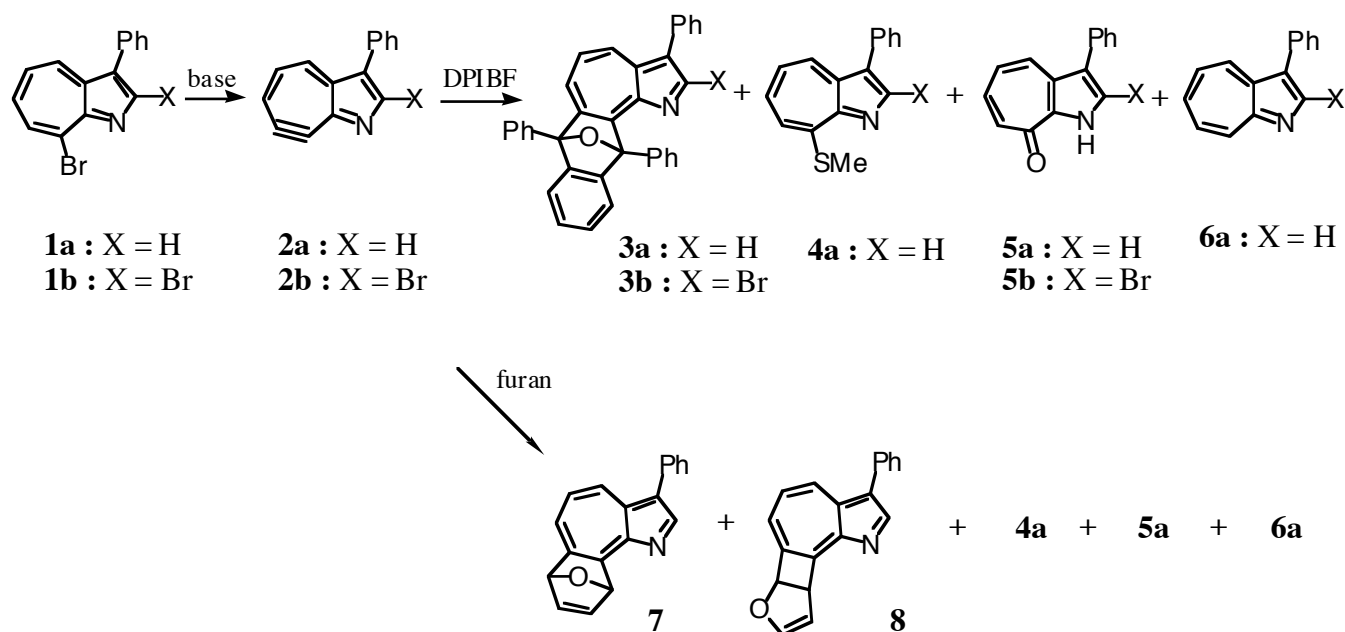
RESULTS AND DISCUSSION

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(1*H*)-one (**5a**)¹² (11%), were isolated from the reaction mixture (Table 1, Run 1). The

compound (**3a**) was analyzed as 1 : 1-adduct (C₃₅H₂₃NO) of 3-phenyl-7,8-dehydro-1-azaazulene (**2a**) and DPIBF from its elemental analysis and mass spectrum. In the ¹H NMR spectrum of **3a**, three protons of the seven-membered ring were observed at δ 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 DPIBF 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 DPIBF 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}



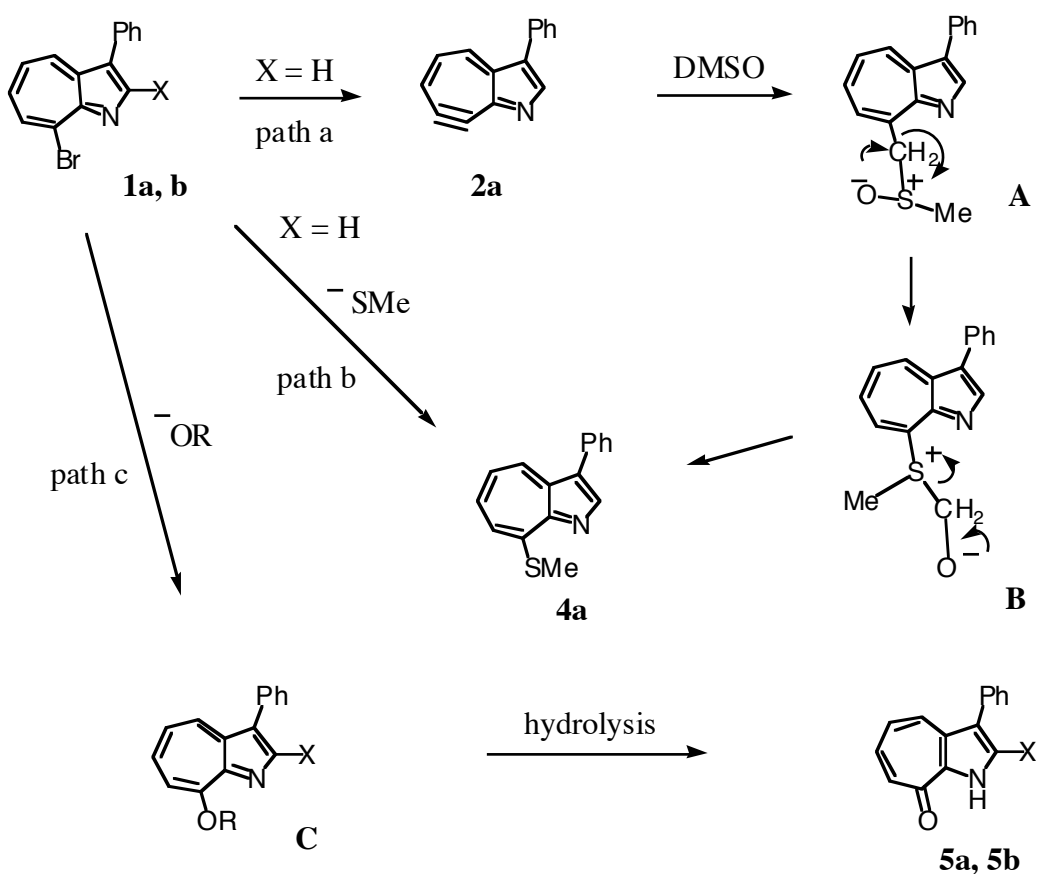
Scheme 1

Similarly, the reaction of 2,8-dibromo-3-phenyl-1-azaazulene (**1b**) with potassium *t*-butoxide in the presence of CE and DPIBF 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 DPIBF, 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 ^1H 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**.



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 ^1H NMR spectrum of **7**, three protons of the seven-membered ring appear at δ 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 δ 6.72-6.77 (1H, m) and 7.72-7.74 (1H, m), and two olefinic protons at δ 7.51 (1H, dm, J 3.5) and 8.42 (1H, dm, J 3.5), along with phenyl protons and H-2 proton at δ 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-3*H*-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 diphenylisobenzofurane (DPIBF) or furan.

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

a) 5 eq. of DPIBF was used.

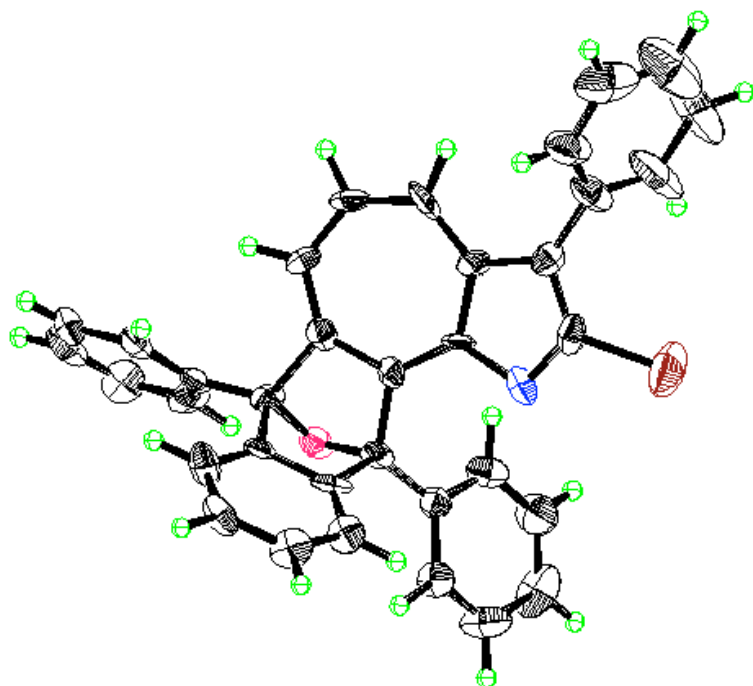
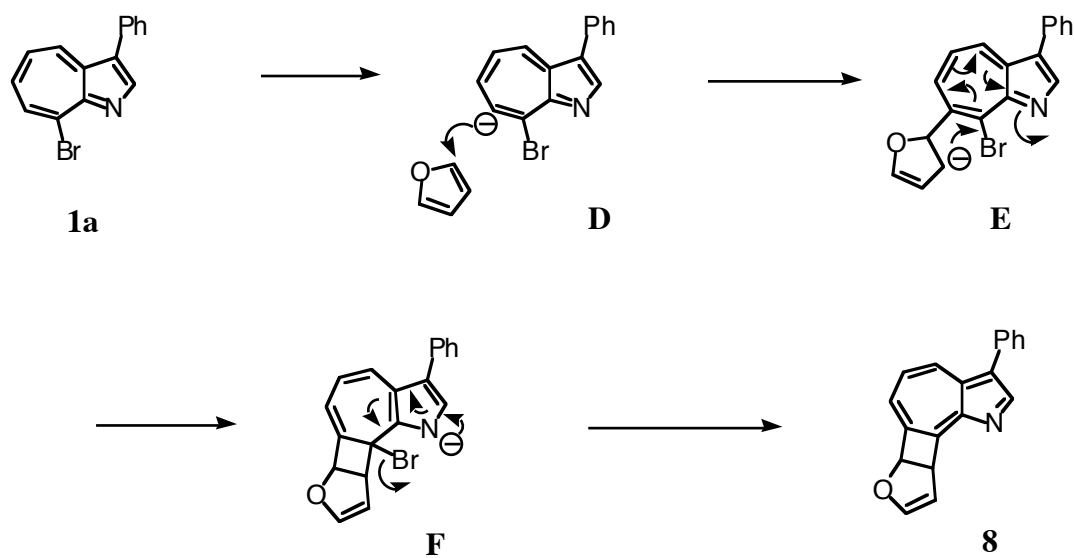


Figure 1. An ORTEP drawing of **3b** with thermal ellipsoids (50% probability).



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 on 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(1*H*)-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; δ_{H} 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); δ_{C} 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; $\bar{\nu}_{\text{max}}$ / cm⁻¹ 729 and 696 (phenyl); $\bar{\nu}_{\text{max}}$ (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(1*H*)-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; δ_{H} 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); δ_{C} 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; $\bar{\nu}_{\text{max}}$ / cm⁻¹ 731 and 700 (phenyl); $\bar{\nu}_{\text{max}}$ (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**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; δ_{H} 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); δ_{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; ν_{max} / cm⁻¹ 1658 (C=O), 758 and 703 (phenyl); ν_{max} (CHCl₃) / cm⁻¹ (log ϵ) 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 C₃₅H₂₃NO: 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; δ_{H} 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); δ_{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; ν_{max} / cm⁻¹ 769 and 703 (phenyl); ν_{max} (CHCl₃) / cm⁻¹ (log ϵ) 273 (4.70), 339 (4.62), 495 (3.03); *m/z* (rel intensity) 251 (M⁺, 100), 204 (97), 177 (75). *Anal.* Calcd for C₁₆H₁₃NS: C, 76.45; H, 5.21; N, 5.57. Found: C, 76.94; H, 5.19; N, 5.69.

6a^{12,13}: Red violet oil; δ_{H} 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 (8H, 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; δ_{H} 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; δ_{H} 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); δ_{C} 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, 150.55, 155.38, 159.39; ν_{max} / cm^{-1} (CHCl_3) 1629 (C=C), 769 and 703 (phenyl); m/z (rel intensity) 271 (M^+ , 100), 243 (71), 215 (17). *Anal.* Calcd for $\text{C}_{19}\text{H}_{13}\text{NO}$: 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, $\text{C}_{35}\text{H}_{22}\text{NOBr}$, $M=552.47$, monoclinic, space group $P2_1/c$, $a=10.48(1)$,

$b=17.638(4)$, $c=14.321(4)$ Å, $V=2632(2)$ Å³, $Z=4$, $D_{\text{calcd}}=1.394$ g/cm³, crystal dimensions 0.46 x 0.38 x 0.07 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-K α radiation. Total 4852 (4581 unique) reflections were collected using ω -scan technique with in a 2θ range of 50.0°. 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 $w = 4Fo^2/\sigma^2(Fo^2)$ 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).

ACKNOWLEDGEMENTS

This work was partially supported by a Grand-in Aid for Scientific Research on Priority Areas (A) of Exploitation of Multi-Element Cyclic Molecules (Nos. 13029083 and 14044074) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES AND NOTES

1. R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,' Academic Press, New York, 1967.
2. E. K. Fields and S. Meyerson, *Adv., Phys. Org. Chem.*, 1968, **6**, 1.
3. M. O. Reinecke, *Tetrahedron*, 1982, **38**, 427.
4. T. Yamatani, M. Yasunami, and K. Takase, *Tetrahedron Lett.*, 1970, 1725.
5. T. Nakazawa and I. Murata, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 711; T. Nakazawa, N. Abe, K. Kubo, and I. Murata, *Tetrahedron Lett.*, 1979, 4995; T. Nakazawa, Y. Niimoto, and I. Murata, *Tetrahedron Lett.*, 1978, 569; T. Nakazawa, K. Kubo, and I. Murata, *Angew. Chem., Int. Ed. Engl.*, **1981**, **20**, 189.
6. W. Tochtermann, K. Oppenlander, and M. N. D. Hoang, *Ann.*, 1967, **701**, 117.
7. M. Lorch and H. Meier, *Chem. Ber.*, 1981, **114**, 2382.
8. Y. Lu, D. M. Lemal, and J. P. Jasinski, *J. Am. Chem. Soc.*, 2000, **122**, 2440.
9. M. Yasunami, Y. Sasagawa, and K. Takase, *Chem. Lett.*, 1980, 205.
10. N. Abe, *Recent Res. Devel. Org. & Bioorg. Chem.*, 2001, **4**, 17.
11. N. Abe, *Trends in Heterocycl. Chem.*, 2001, **7**, 25.
12. K. Yamane, K. Fujimori, J.-K. Sin, and T. Nozoe, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1184.
13. T. Nozoe, Y. Kitahara, and T. Arai, *Proc. Jpn. Acad.*, 1954, **30**, 478.