July, 1990] © 1990 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 63, 2121—2123 (1990) 2121

Synthesis and Heteroannulation of 3,4-Dibenzoyl-1-phenyl-2a,5-diazabenz[*cd*]azulene

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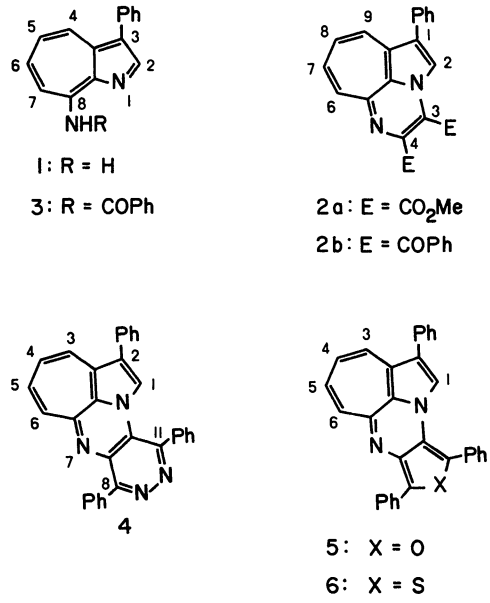
(Received February 1, 1990)

Synopsis. 3,4-Dibenzoyl-1-phenyl-2a,5-diazabenz[*cd*]azulene (**2b**) was synthesized by cycloaddition of 8-amino-3-phenyl-1-azaazulene with dibenzoylacetylene. Heteroannulation to **2b** has been achieved by reactions with hydrazine and phosphorus pentasulfide.

Cycloadditions of heterocycles with dibenzoylacetylene (DBA) and successive heteroannulations are efficient methods to obtain fused heterocycles,[1—4] especially thiophene-fused heterocycles, which are difficult to obtain by other methods. Although some cycloadditions of 2-substituted 1-azaazulenes with reactive acetylenes to give fused heterocycles are known,[5—7] cycloaddition of 8-substituted 1-azaazulene is not yet known. Therefore, it is expected that cycloaddition and successive annulation of 8-substituted 1-azaazulenes afford a novel aromatic system. Here we describe the cycloadditions of 8-amino-3-phenyl-1-azaazulene[8] with reactive acetylenes giving 2a,5-diazabenz[*cd*]azulene derivatives,[9,10] and successive heteroannulations leading to novel heterocycles fused with pyridazine, furan, and thiophene.

Reaction of 8-amino-3-phenyl-1-azaazulene (**1**) with dimethyl acetylenedicarboxylate (DMAD) in refluxing benzene for 2 h gave a complex mixture. From the mixture, dimethyl 1-phenyl-2a,5-diazabenz[*cd*]azulene-3,4-dicarboxylate[10] (**2a**) was isolated in a 10% yield by column chromatography on silica gel.



1: R = H

3: R = COPh

2a: E = CO_2Me

2b: E = COPh

4

5: X = O

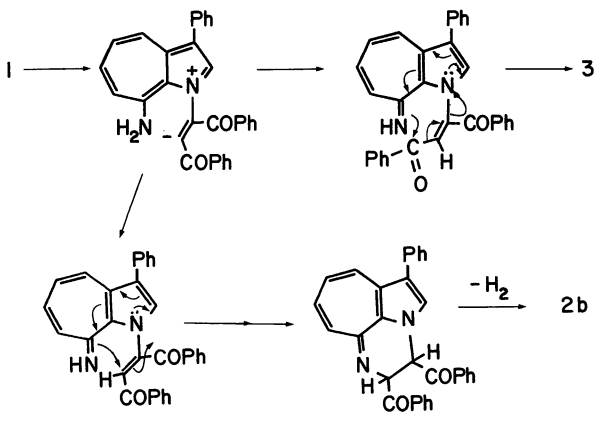
6: X = S

Fig. 1.

Similar treatment of **1** with DBA gave 8-benzoylamino-3-phenyl-1-azaazulene (**3**) and 3,4-dibenzoyl-1-phenyl-2a,5-diazabenz[*cd*]azulene (**2b**) in 21% and 30% yields, respectively. These structures were assigned on the basis of spectroscopic data as well as elemental analyses. Compound **3** was identical with the compound obtained by the reaction of **1** with benzoic anhydride. A possible mechanism for the formation of **3** is shown in Scheme 1.

Treatment of **2b** with hydrazine hydrate gave the corresponding pyridazine derivative **4** in nearly quantitative yield.

Treatment of **2b** with phosphorus pentasulfide in refluxing pyridine for 30 min gave a furan derivative **5** and a thiophene derivative **6** in 68% and 26% yield, respectively. When the reaction was carried out in refluxing xylene for 4 h, compounds **5** and **6** were obtained in 63% and 32% yield, respectively. Compound **5** shows an M^+ ion at m/z 436 (rel intensity 100%) and a $PhCO^+$ ion at m/z 105 (4%). Its ^1H NMR spectrum shows four seven-membered ring protons at δ=5.93 (dd, J=11.0 and 7.9 Hz), 6.35 (dd, J=12.2 and 7.9 Hz), 6.67 (d, J=12.2 Hz), and 6.77 (d, J=11.0 Hz) together with H-1 proton and phenyl protons (16H, m) at δ=7.2—8.3. Compound **6** shows an M^+ ion at m/z 452 (rel intensity 100%), an M^{2+} ion at m/z 226 (3%), and a $PhCS^+$ ion at m/z 121 (4%). Its ^1H NMR spectrum shows a 1H singlet at δ=7.04 and four seven-memberd ring protons at δ=5.90 (dd, J=11.0 and 7.9 Hz), 6.35 (dd, J=12.2 and 7.9 Hz), 6.61 (d, J=12.2 Hz), and 6.74 (d, J=11.0 Hz) together with phenyl protons (15H, δ 7.2—8.1). In the ^{13}C NMR spectra of **5** and **6**, signals were observed at δ=115—155 and are in accord with the proposed structures. Although mechanisms for the formation of **5** and **6** are interesting, we were unable to



Scheme 1.

advance a rationale.

Compared with 1-azaazulenes,[8,11,12] higher field resonances and large divergences of coupling constants ($J_{3,4}$~$J_{4,5}$~$J_{5,6}$: Δ3.1—4.3 Hz) of the seven-membered ring protons were observed in the ^{1}H NMR spectra of **4**, **5**, and **6**, and comparable with those of **2a** and **2b**. The result exhibits appreciable bond alternation, and suggests that the heteroannulated 2a,5-diazabenz[*cd*]azulenes have the character of butadiene-bridged 3a,6-diazaindene.

Experimental

Melting points were uncorrected. ^{1}H NMR spectra (250 MHz) and ^{13}C NMR spectra (62.87 MHz) were taken on a Hitachi R-250H spectrometer using $CDCl_3$ as a solvent (TMS as an internal standard). IR spectra were recorded for Nujol mulls with a Hitachi 270-50 infrared spectrophotometer. Mass spectra were determined with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. High-resolution mass spectrum was obtained on the same instrument. Column chromatography was performed on Kieselgel 60.

Reaction of 1 with DMAD. A mixture of **1**[8] (0.881 g) and DMAD (1.71 g) in dry benzene (50 ml) was refluxed for 2 h and evaporated. The residue was chromatographed with benzene–chloroform (1 : 1) to give **2a**[10] (0.148 g, 10%).

Reaction of 1 with DBA. A mixture of **1** (0.973 g) and DBA (2.07 g) in dry benzene (60 ml) was refluxed for 70 h and evaporated. The residue was chromatographed. Elution with benzene gave **3** (0.307 g, 21%), which was recrystallized from cyclohexane to give red needles, mp 147—149 °C, ^{1}H NMR δ=7.35—7.70 (9H, m, H-5 and phenyl), 8.00 (1H, dd, J=11.0 and 9.8 Hz, H-6), 8.17 (2H, dd, J=7.9 and 1.8 Hz, H-*o*-phenyl), 8.51 (1H, s, H-2), 8.66 (1H, d, J=9.8 Hz, H-4), and 9.50 (1H, d, J=11.0 Hz, H-7);[13] ^{13}C NMR δ=120.02 (d), 125.94 (d), 126.84 (d), 127.57 (d×2), 128.81 (d×2), 128.86 (d×2), 128.93 (s), 129.25 (d×2), 132.49 (d), 134.40 (s×2), 135.55 (d), 139.02 (d), 139.12 (s), 144.39 (s), 146.71 (s), 148.78 (d), and 166.15 (s); IR 3296 (NH), 1684 (C=O), and 694 cm^{-1} (phenyl). Found: C, 81.29; H, 5.10; N, 8.63. Calcd for $C_{22}H_{16}N_2O$: C, 81.26; H, 4.97; N, 8.63%. Further elution gave **2b** (0.607 g, 30%), which was recrystallized from hexane–dichloromethane to give violet needles, mp 247—248 °C, ^{1}H NMR δ=5.53 (1H, ddd, J=11.6, 6.1 and 3.1 Hz, H-7), 5.95—6.10 (2H, m, H-8 and 9), 6.55 (1H, d, J=11.6 Hz, H-6), 7.28 (1H, s, H-2), 7.30—7.45 (9H, m, H-*m*,*p*-phenyl×3), 7.45—7.55 (2H, m, H-*o*-phenyl), 7.83 (2H, d, J=7.3 Hz, H-*o*-phenyl), and 7.89 (2H, d, J=7.3 Hz, H-*o*-phenyl); ^{13}C NMR δ=116.27 (d), 120.04 (s), 124.08 (d), 126.83 (s), 127.62 (s), 127.73 (d), 127.94 (d×2), 128.66 (d×2), 128.74 (d×2), 128.83 (d×2), 128.96 (d×2), 130.32 (d×2), 132.49 (s), 132.56 (d), 133.01 (d), 133.75 (d), 134.96 (d), 136.10 (s), 136.42 (s), 136.94 (d), 138.36 (s), 142.71 (s), 158.38 (s), 189.36 (s), and 191.28 (s); IR 1664 and 1644 cm^{-1} (C=O). Found: C, 82.44; H, 4.45; N, 6.14; M$^+$, 452. Calcd for $C_{31}H_{20}N_2O_2$: C, 82.28; H, 4.46; N, 6.19%; M, 452.

Benzoylation of 1. A mixture of **1** (0.200 g) and benzoic anhydride (0.800 g) in dry benzene (50 ml) was refluxed for 3 h and evaporated. The residue was chromatographed with benzene to give **3** (0.273 g, 93%).

Reaction of 2b with Hydrazine Hydrate. A solution of **2b** (0.130 g) and 80% hydrazine hydrate (1.0 ml) in ethanol (20 ml) was refluxed for 1 h and evaporated. To the residue water was added, and the mixture was extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated. Chromatography of the residue with chloroform gave **4** (0.128 g, 99%), which was recrystallized from hexane–dichloromethane to give red needles, mp 283—285 °C, ^{1}H NMR δ=5.86 (1H, ddd, J=11.0, 7.3, and 1.8 Hz, H-5), 6.34 (1H, dd, J=12.2 and 7.3 Hz, H-4), 6.40 (1H, dd, J=12.2 and 1.8 Hz, H-3), 6.63 (1H, s, H-1), 6.74 (1H, d, J=11.0 Hz, H-6), 7.08 (2H, dd, J=7.3 and 1.8 Hz, H-*o*-phenyl), 7.30—7.40 (3H, m, H-*m*,*p*-phenyl), 7.45—7.55 (3H, m, H-*m*,*p*-phenyl), 7.55—7.65 (5H, m, phenyl), and 8.13 (2H, dd, J=7.3 and 1.8 Hz, H-*o*-phenyl); IR 760 and 702 cm^{-1} (phenyl). Found: C, 83.25; H, 4.35; N, 12.51; M$^+$, 448. Calcd for $C_{31}H_{20}N_4$: C, 83.01; H, 4.49; N, 12.49%; M, 448.

Reaction of 2b with Phosphorus Pentasulfide. a) A mixture of **2b** (0.300 g) and phosphorus pentasulfide (0.442 g) in dry pyridine (20 ml) was refluxed for 30 min, then poured into dil NaOH soln (100 ml) to give red precipitates. They were collected by filtration and chromatographed. Elution with benzene gave **5** (0.198 g, 68%), which was recrystallized from cyclohexane–dichloromethane to give red needles, mp 205—206 °C, ^{1}H NMR δ=5.93 (1H, dd, J=11.0 and 7.9 Hz, H-5), 6.35 (1H, dd, J=12.2 and 7.9 Hz, H-4), 6.67 (1H, d, J=12.2 Hz, H-3), 6.77 (1H, d, J=11.0 Hz, H-6), 7.24 (1H, td, J=7.3 and 1.2 Hz, H-*p*-phenyl), 7.29—7.46 (10H, m, H-1 and phenyl), 7.48 (1H, td, J=7.3 and 1.2 Hz, H-*p*-phenyl), 7.66 (2H, dd, J=7.3 and 1.2 Hz, H-*o*-phenyl), and 8.20 (2H, dd, J=7.3 and 1.2 Hz, H-*o*-phenyl); ^{13}C NMR δ=115.80 (s), 117.02 (d), 122.08 (s), 123.94 (d), 124.66 (d×2), 126.54 (s), 127.03 (d), 127.25 (d), 127.88 (d×2), 128.26 (s), 128.35 (d×2), 128.40 (d), 128.58 (d×2), 128.76 (d×2), 129.24 (d), 129.38 (d×2), 130.06 (s), 130.41 (s), 131.05 (s), 132.81 (d), 133.24 (s), 135.17 (s), 136.27 (d), 143.47 (s), and 154.66 (s); IR 756, 702, and 684 cm^{-1} (phenyl); MS *m/z* (rel intensity) 436 (100, M$^+$), 435 (4), 407 (21), 331 (32, M$^+$-PhCO), 204 (6), 203 (12), 176 (8), 105 (4, PhCO$^+$). Found: C, 85.59; H, 4.87; N, 6.26. Calcd for $C_{31}H_{20}N_2O$: C, 85.30; H, 4.62; N, 6.42%. Further elution gave **6** (0.077 g, 26%), which was recrystallized from cyclohexane–dichloromethane to give red needles, mp 214—216 °C, ^{1}H NMR δ=5.90 (1H, dd, J=11.0 and 7.9 Hz, H-5), 6.35 (1H, dd, J=12.2 and 7.9 Hz, H-4), 6.61 (1H, d, J=12.2 Hz, H-3), 6.74 (1H, d, J=11.0 Hz, H-6), 7.04 (1H, s, H-1), 7.20-7.56 (13H, m, H-phenyl), and 8.06 (2H, dd, J=7.3 and 1.2 Hz, H-*o*-phenyl); ^{13}C NMR δ=117.38 (d), 119.53 (s), 120.85 (s), 122.94 (s), 123.97 (d), 126.20 (s), 127.15 (d), 127.30 (d), 128.03 (d×2), 128.47 (d×2), 128.54 (d×2), 128.66 (d×2), 128.83 (d), 129.22 (d×2), 129.66 (d), 130.40 (d×2), 131.16 (s), 131.21 (s), 132.44 (s), 133.22 (s), 133.45 (s), 133.56 (d), 136.01 (d), 138.04 (s), and 154.23 (s); IR 761, 747, 700, and 690 cm^{-1} (phenyl); MS *m/z* (rel intensity) 452 (100, M$^+$), 451 (14), 331 (3, M$^+$-PhCS), 226 (3, M^{2+}), 121 (5, PhCS$^+$). Found: C, 82.49; H, 4.66; N, 6.10; M$^+$, *m/z* 452.1371. Calcd for $C_{31}H_{20}N_2O$: C, 82.27; H, 4.45; N, 6.19%; M, 452.1346;

b) A mixture of **2b** (0.155 g) and phosphorus pentasulfide (0.225 g) in dry xylene (20 ml) was refluxed for 4 h and evaporated. To the residue water was added, and the mixture was extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated. The residue was chromatographed with benzene to give **5** (0.095 g, 63%) and **6** (0.050 g, 32%), successively.

We thank Dr. Masafumi Yasunami (Tohoku University) and Dr. Akira Mori (Kyushu University) for the measurement of mass spectra and elemental analyses.

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