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REACTIONS OF 3-PHENYL-8-TRIPHENYLPHOSPHOIMINO-1-AZAAZULENE WITH ARYL ISOCYANATE, ARYL ISOTHIOCYANATE, AND CARBON DISULFIDE†

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Abstract – Reaction of 3-phenyl-8-triphenylphosphoimino-1-azaazulene (**1**) with some aryl isocyanates gave 2-arylimino-4-phenyl-2,2a-dihydro-1,2a-diazacyclopent[*cd*]azulenes (**2**) and 8-arylimino-1,8-dihydro-1-azaazulenes (**3**). Reaction of **1** with *p*-toluenesulfonyl isocyanate gave 2-imino-3-(*p*-methylphenyl)-4-phenyl-2,2a-dihydro-1,2a-diazacyclopent[*cd*]azulene as cyclization-rearrangement product. Reaction of phenyl isothiocyanate gave **2**. Tautomerization of between 8-imino-1,8-dihydro-1-azaazulenes (**3**) and 8-amino-1-azaazulenes was discussed on the basis of X-Ray structure analysis and molecular orbital calculation.

INTRODUCTION

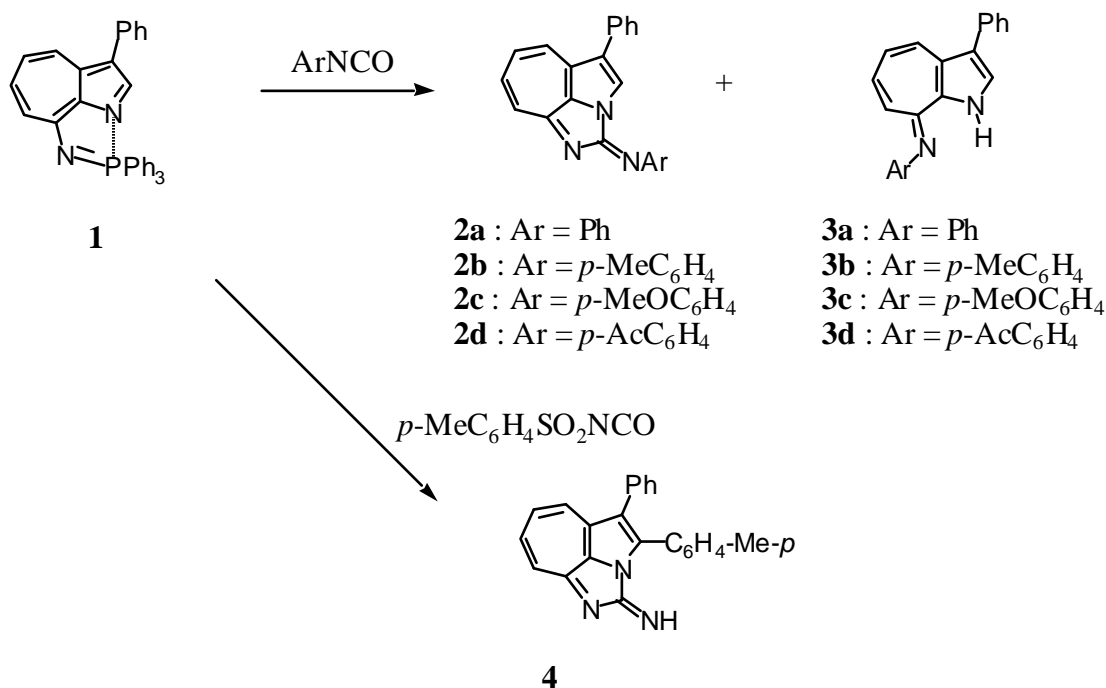
It is known that the iminophosphoranes, chemical species having the nitrogen-phosphorus double bond, reveal synthetic versatility for the construction of fused heterocycles.¹⁻⁴ Especially, the aza-Wittig reaction of aryyliminophosphoranes with heterocumulenes such as aryl isocyanates followed by electrocyclization reaction was utilized for the synthesis of a variety of useful heterocycles, such as quinolines,^{5,6} α -carbolines,^{5,6} naphthylidines,⁷ and aza analogues of ellipticines.⁸ Recently we reported the synthesis and some reactions of the 3-phenyl-8-triphenylphosphoimino-1-azaazulene (**1**), obtained from 8-amino-3-phenyl-1-azaazulene and dibromotriphenylphosphorane.^{9,10} For the extension of aza-

†Dedicated to Dr. Pierre Potier on occasion of his 70th birthday.

azulene chemistry¹¹⁻¹³ and a construction of novel fused heterocycles, we examined the reactions of **1** with aryl isocyanates, phenyl isothiocyanate, and carbon disulfide, where the aza-Wittig reaction followed by an electrocyclization would be expected.

RESULTS AND DISCUSSION

Treatment of 3-phenyl-8-triphenylphosphoimino-1-azaazulene (**1**) with phenyl isocyanate at room temperature gave 2-phenylimino-4-phenyl-2,2a-dihydro-1,2a-diazacyclo[*cd*]azulene (**2a**) as aza-Wittig reaction and a successive cyclization products in 46% yield together with recovered **1** (14%) (Entry 1). Interestingly, unexpected reaction occurred under elevated temperature. Namely, the treatment of **1** with phenyl isocyanate at 80 °C for 46 h in a sealed tube gave 8-phenylimino-1,8-dihydro-1-azaazulene (**3a**, 6%) along with **2a** (56%) and recovered **1** (10.5%) (Entry 2). Formation of **3a** would be preferred at higher temperature. Indeed **3a** was obtained in 15% yield at 125 °C and in 20.5% yield at 180 °C (Entries 3 and 4). Prolonged heating at high temperature (180 °C) led a lowering yield (Entry 5). It is known that the reaction of **1** with aryl aldehyde using zinc chloride as catalyst gave good results.¹⁰ Therefore we examined the reaction using zinc chloride, but distinct improvement was not obtained (Entries 6 and 7).



Scheme 1

In the similar manner, some aryl isocyanates reacted with **1**. Reaction of *p*-methylphenyl isocyanate and *p*-methoxyphenyl isocyanate, and *p*-acetylphenyl isocyanate gave similar results as for phenyl isocyanate (Entries 8-12). It seems that electron-withdrawing acetyl group slightly facilitated the reaction. In

ORTEP drawing¹⁴ of **2b** is shown in Figure 1. Bond alternation is clearly observed in the ¹H NMR spectrum of **2**. The coupling constants of seven-membered ring protons existed in $J = 11.3\text{--}11.9$ Hz and $J = 8.3\text{--}8.9$ Hz in the ¹H NMR spectrum of **2** and the results consisted with the observation of X-Ray structure analysis. From the results, it is considered that compound (**2**) would have inherently extended 8-azaheptafulvene character.

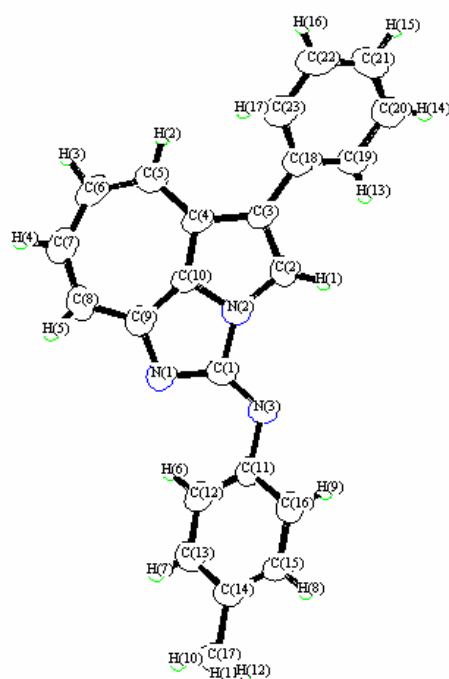
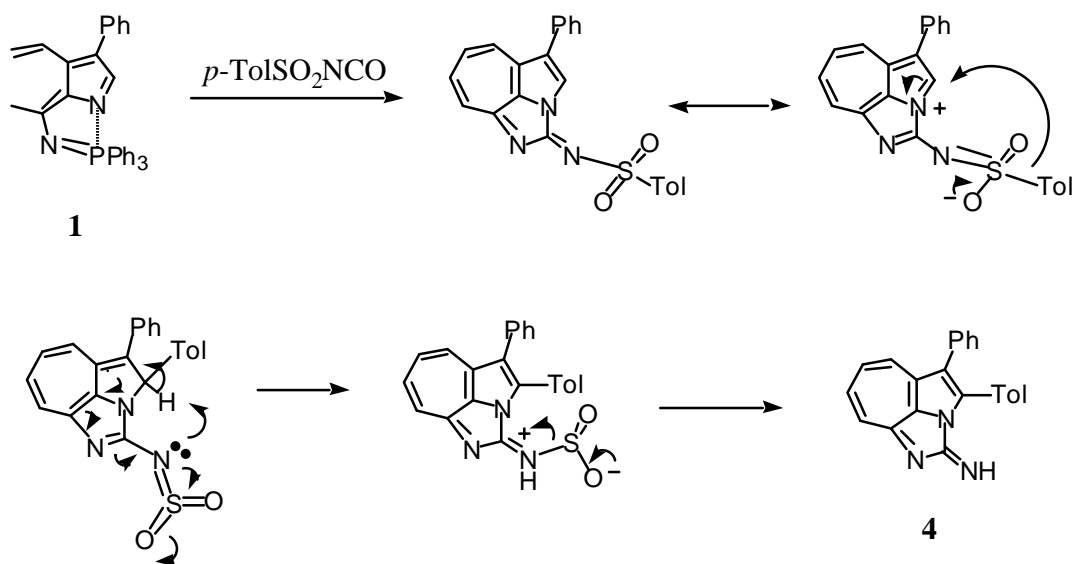
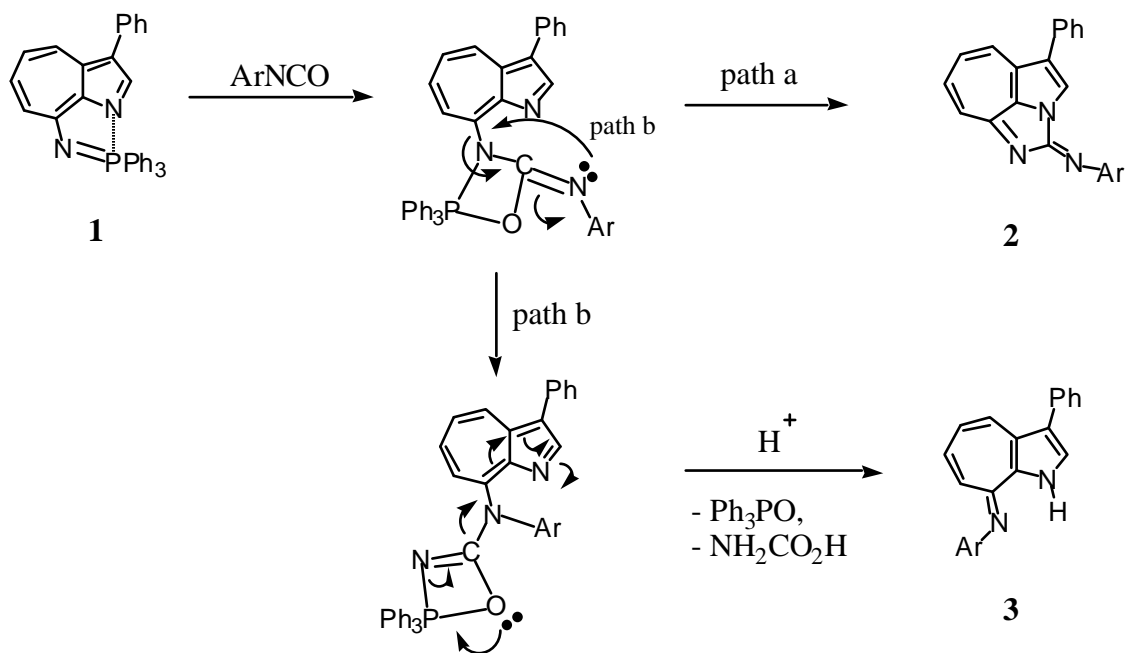


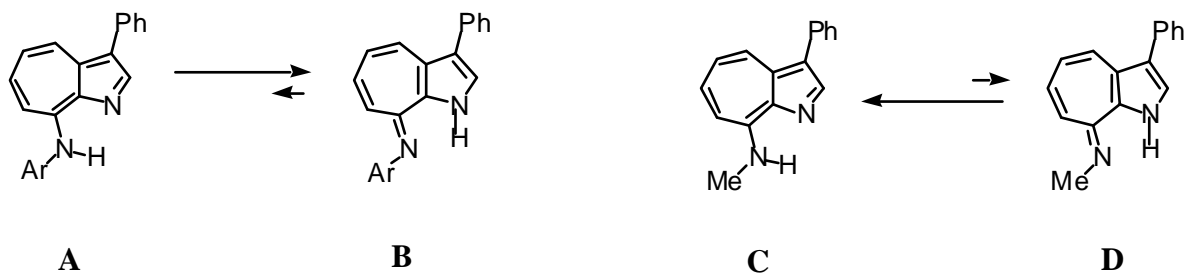
Figure 1. ORTEP drawing of **2b** with thermal ellipsoids (50% probability).

Selective bond lengths (Å): N(1)—C(1) 1.397(7), C(1)—N(2) 1.443(7), N(2)—C(2) 1.387(7), C(2)—C(3) 1.377(8), C(3)—C(4) 1.454(8), C(4)—C(5) 1.415(8), C(5)—C(6) 1.372(9), C(6)—C(7) 1.420(9), C(7)—C(8) 1.372(9), C(8)—C(9) 1.409(8), C(9)—C(10) 1.418(8), C(9)—N(11) 1.337(7), C(1)—N(3) 1.289(7).

For elucidation of reaction mechanism, some reactions were performed. Heating of **2a** in xylene at 180 °C for 60 h in a sealed tube gave only **2a** and **3a** was not obtained. When **2a** was treated with *p*-methylphenyl isocyanate in xylene at 180 °C for 20 h in a sealed tube, **2a** was recovered and a crossing reaction product was not obtained. These results suggested that **3** would be produced from **1** and aryl

isocyanate and did not formed *via* **2**. Plausible mechanism for the formation of **2** and **3** is shown in Scheme 2. Aza-Wittig reaction of the phosphoimine moiety with aryl isocyanate and a successive cyclization would produce **2** (path a). Rearrangement of the intermediate as shown by curved arrow (path b) and successive elimination of triphenylphosphine oxide and cyanide moiety furnishes **3**. The cyanide moiety would be hydrolyzed to triphenylphosphine oxide and carbamic acid. The mechanism for the formation of **4** is shown in Scheme 3. It is considered that the reaction of *p*-toluenesulfonyl isocyanate with **1** also gave 2-arylimino-4-phenyl-2,2a-dihydro-1,2a-diazacyclo[*cd*]azulene derivative, but successive rearrangement followed by elimination of SO₂ to give **4**.





It is considered that 8-hydroxy-, 8-amino-, and related derivatives of 1-azaazulene have two tautomeric forms. Previously, it is said that ketonic (or imino) form is preferred than enolic (or amino) form.¹⁵ Recently, we reported that 8-methylamino-3-phenyl-1-azaazulene exists in the form **C** by X-Ray structure analysis.¹⁶

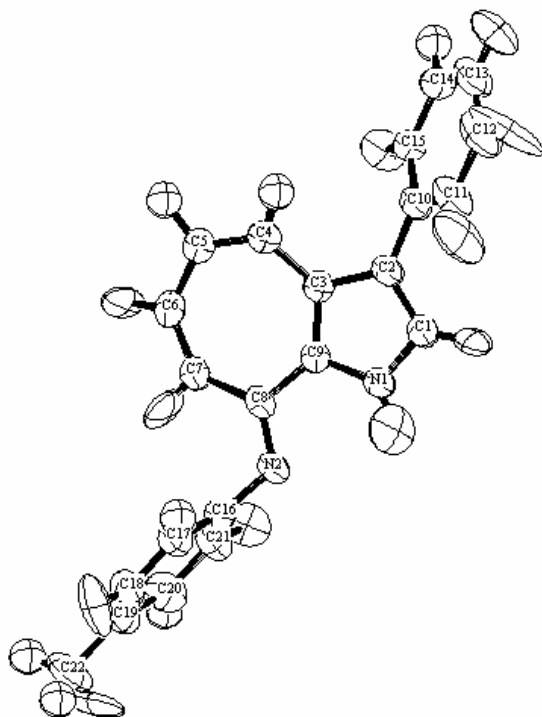


Figure 2. ORTEP drawing of **3b** with thermal ellipsoids (50% probability).

Selective bond lengths (Å): N(1)—C(1) 1.369(5), C(1)—C(2) 1.358(5), C(2)—C(3) 1.431(4), C(3)—C(4) 1.428(5), C(4)—C(5) 1.356(5), C(5)—C(6) 1.435(5), C(6)—C(7) 1.345(5), C(7)—C(8) 1.448(5), C(8)—C(9) 1.451(4), C(8)—N(2) 1.307(4), N(1)—H(1) 0.94(4), N(2)—H(1) 2.31(4).

To clarify this tautomerization, we investigated the X-Ray structure analysis and molecular orbital calculation of **3**. The X-Ray structure analysis of **3b** showed that this compound exists in the form **B** (Figure 2). The results showed that 8-arylamino-1-azaazulene favored in imino form. Molecular orbital calculation by Gaussian 98 using RHF/6-31G* is in accordance with the result, where the amino form **A** (Ar = *p*-MeC₆H₄) is unstable than the imino form **B** (Ar = *p*-MeC₆H₄) ($\Delta E(\text{A} - \text{B}) = 0.78$ kcal/mol), whereas the amino form **C** is stable than the imino form **D** ($\Delta E(\text{C} - \text{D}) = - 2.49$ kcal/mol). The results would be explained as follows: aryl group causes stabilization of azaheptafulvene moiety by the conjugation, whereas electron-donating methyl group brings down the instability to the azaheptafulvene moiety.

For the comparison, X-Ray structure of the salt (**6**) is shown in Figure 3. Two NH hydrogens were existed at two ring nitrogens (N-1 and N-2) and the structure takes pyrrolotroponeimine form. Bond-alternation is clearly seen.

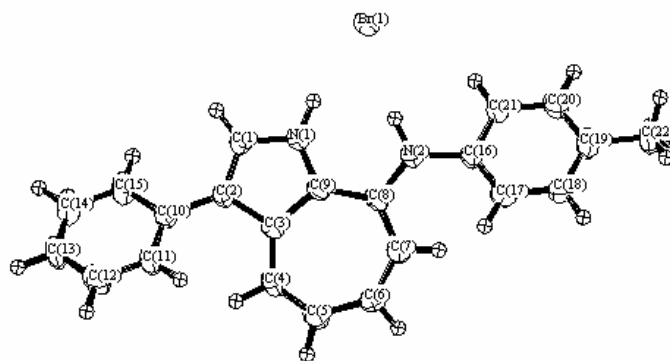
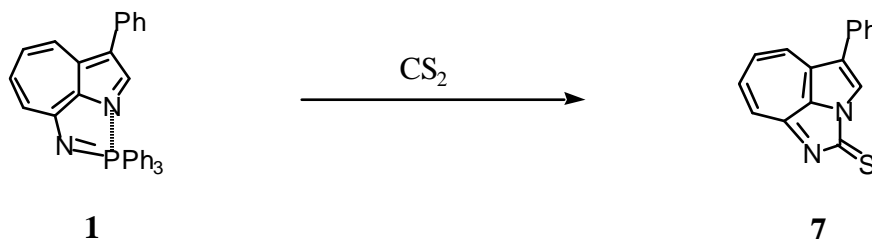


Figure 3. ORTEP drawing of **6** with thermal ellipsoids (50% probability).

Selective bond lengths (Å): N(1)—C(1) 1.363(6), C(1)—C(2) 1.361(7), C(2)—C(3) 1.436(7), C(3)—C(4) 1.407(8), C(4)—C(5) 1.351(8), C(5)—C(6) 1.427(8), C(6)—C(7) 1.356(8), C(7)—C(8) 1.404(8), C(8)—C(9) 1.426(7), C(8)—N(2) 1.360(7), N(1)—H(1) 0.97, N(2)—H(12) 0.98.

Reaction of **1** with carbon disulfide for 200 h at 90 °C in a sealed tube gave 4-phenyl-2,2a-dihydro-1,2a-diazacyclopent[*cd*]azulene-2-thione (**7**) as aza-Wittig reaction-cyclization product in 37% yield.



CONCLUSION

Reactions of 8-phosphorimidino-1-azaazulene derivative (**1**) with heterocumulenes were performed. 2-Arylimino-2,2a-dihydro-1,2a-diazacyclopent[*cd*]azulenes (**2**) were yielded on the reaction of **1** with aryl isocyanates in moderate to good yields as cycloadducts together with 8-arylimino-1,8-dihydro-1-azaazulenes (**3**) as rearrangement products. Reaction of **1** with *p*-toluenesulfonyl isocyanate gave 2-imino-3-methylphenyl-4-phenyl-2,2a-dihydro-1,2a-diazacyclopent[*cd*]azulene in excellent yield *via* cyclization-rearrangement-elimination process. The tautomerisation between imino form (**A**, **C**) and amino form (**B**, **D**) was clarified by the by X-Ray structure analysis and molecular orbital calculation..

EXPERIMENTAL

Mps are measured using a Yanagimoto micro-melting apparatus and uncorrected. ¹H NMR spectra (including HMBC and HMQC NMR) 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 on a Nicolet FT-IR Impact 410 unless otherwise stated. MS spectra were taken with on an LC-MS Waters Integrity System. Elemental analyses were taken with a Perkin Elmer 2400II. Kieselgel 60 was used for column chromatography and Kieselgel 60G was used for thin-layer chromatography.

Reaction of **1** with aryl isocyanate

Typical procedure A -Under argon atmosphere, a mixture of **1** (0.120 g, 0.25 mmol) and phenyl isocyanate (0.058 mL, 0.50 mmol) in dry xylene (3.0 mL) was heated at 80 °C for 46 h in a sealed tube. Then the mixture was evaporated. Chromatography of the residue gave **2a** (0.0456 g, 56%), **3a** (0.0043 g, 6%) and recovered **1** (0.0126 g, 10.5%).

Typical procedure B -Under argon atmosphere, a mixture of **1** (0.240 g, 0.50 mmol), benzaldehyde (0.052 mL, 0.50 mmol), zinc(II) chloride (0.0056 g, 0.025 mmol), and dry xylene (5.0 mL) in a sealed tube was heated at 125 °C for 200 h. The mixture was evaporated and chromatographed to give **2a** (0.094 g,

61%).

2a: Red needles (from acetonitrile-hexane), mp 177.5-178.5 °C; δ_{H} 7.02 (1H, dt, J 10.7 and 9.6), 7.14 (1H, tdd, J 7.3 1.3, and 1.1), 7.37 (1H, br t, J 7.3), 7.44 (1H, td, J 6.9, 1.3), 7.46 (2H, br t, J 7.3), 7.47 (2H, dd, J 7.2, 1.1), 7.50 (2H, br t, J 7.3), 7.54 (2H, dd, J 6.9 and 1.3), 7.56 (1H, dd, J 11.6 and 9.6), 7.83 (1H, d, J 10.7), and 7.94 (1H, s); δ_{C} 121.83, 122.02, 123.74, 124.54, 126.42, 127.19, 127.91, 128.35, 128.85, 129.19, 130.79, 132.70, 134.42, 141.85, 143.31, 146.98, 154.08, and 165.28; ν_{max} / cm^{-1} 1625, 1605, and 1578 (C=N and C=C); m/z (rel intensity) 321 (M^+ , 35), 320 (32), 244 (21), 194 (36), 119 (20), 93 (100), and 77 (53). *Anal.* Calcd for $\text{C}_{22}\text{H}_{15}\text{N}_3$: C, 82.22; H, 4.70; N, 13.08. Found: C, 82.43; H, 4.62; N, 13.00.

3a: Yellow prisms (from cyclohexane), mp 153.5-154.5 °C (lit.,¹⁵ mp 153-154 °C); δ_{H} 5.6-6.7 (1H, br), 6.98 (1H, ddd, J 10.3, 8.8, and 2.0), 7.27 (1H, tm, J 7.3), 7.32 (2H, d, J 7.8), 7.35 (1H, d, J 11.3), 7.38 (1H, dd, J 11.3 and 8.8), 7.40 (2H, br t, J 7.6), 7.45 (1H, t, J 7.8), 7.47 (2H, t, J 7.8), 7.56 (2H, dd, J 7.3, 1.0), 8.05 (1H, s), and 8.20 (1H, d, J 10.3); δ_{C} 117.03, 119.86, 120.73, 122.07, 124.06, 125.66, 126.28, 128.54, 129.45, 129.72, 130.23, 133.44, 135.16, 137.17, 140.91, and 151.26; ν_{max} / cm^{-1} 3281(NH), 1624 and 1589 (C=N and C=C); m/z (rel intensity) 297 ($\text{M}^+ + 1$, 10), 296 (M^+ , 47), 295 (100), 165 (14), 147 (12), and 77 (11). *Anal.* Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.03; H, 5.38; N, 9.64.

In a similar manner, the reactions of **1** with some aryl isocyanates were performed. The results were listed in Table 1.

2b: Red needles (from acetonitrile-hexane), mp 155-156 °C; δ_{H} 2.35 (3H, s), 6.97 (1H, dd, J 10.7 and 9.6), 7.18 (2H, d, J 8.3), 7.38 (1H, d, J 11.3), 7.40 (2H, d, J 8.3), 7.41 (1H, tm, J 7.3), 7.49 (2H, br t, J 7.8), 7.52 (2H, dd, J 7.1 and 1.0), 7.53 (1H, dd, J 11.3 and 9.6), 7.78 (1H, d, J 10.7), and 7.91 (1H, s); δ_{C} 21.01, 121.48, 121.79, 123.75, 126.25, 127.07, 127.79, 128.25, 129.12, 130.55, 131.02, 132.71, 134.18, 134.25, 141.5, 143.19, 145.75, 153.83, and 165.00; ν_{max} / cm^{-1} 1630, 1605, and 1581 (C=N and C=C); m/z (rel intensity) 336 ($\text{M}^+ + 1$, 100), 335 (M^+ , 64), 320 (31), 258 (25), 168 (34), 107 (35), 91, (24), and 77 (26). *Anal.* Calcd for $\text{C}_{23}\text{H}_{17}\text{N}_3 \cdot 1/4\text{H}_2\text{O}$: C, 81.27; H, 5.18; N, 12.36. Found: C, 81.35; H, 4.84; N, 12.16.

3b: Yellow prisms (from acetonitrile), mp 145-146 °C (lit.,¹⁵ mp 145-146 °C); δ_{H} 2.41 (3H, s), 5.4-7.0 (1H, br), 6.99 (1H, dd, J 11.3, 8.8), 7.24 (2H, br d, J 7.8), 7.26 (2H, br t, J 7.3), 7.35 (1H, tm, J 7.3), 7.38 (1H, d, J 11.6), 7.45 (1H, dd, J 11.6 and 8.8), 7.49 (2H, t, J 7.8), 7.58 (2H, dd, J 7.8, 1.0), 8.12 (1H, s), and 8.23 (1H, d, J 10.2); δ_{C} 21.50, 116.82, 121.10, 122.26, 124.94, 126.83, 129.11, 129.30, 129.90,

130.75, 134.58, 134.95, 135.74, 136.32, 137.60, 137.89, 142.14, 143.00, and 151.85; ν_{\max} / cm^{-1} 3272 (NH), 1629, 1585, and 1545 (C=N and C=C); m/z (rel intensity) 311 ($M^+ + 1$, 59), 310 (M^+ , 100), 223 (19), 165 (14), 147 (25), 107 (14), and 91 (18). *Anal.* Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2$: C, 85.13; H, 5.85; N, 9.03. Found: C, 85.02; H, 5.64; N, 9.01.

2c: Red needles (from acetonitrile-hexane), mp 184-184.5 °C; δ_{H} 3.82 (3H, s), 6.93 (2H, d, J 8.9), 6.94 (1H, dd, J 10.6 and 9.6), 7.36 (1H, d, J 11.1), 7.40 (1H, br t, J 7.1), 7.53 (2H, br d, J 7.3), 7.48 (1H, dd, J 11.1 and 9.6), 7.49 (2H, br t, J 7.8), 7.55 (2H, d, J 8.9), 7.76 (1H, d, J 10.6), and 7.90 (1H, s); δ_{C} 55.47, 114.12, 121.35, 121.65, 125.47, 126.82, 127.79, 128.30, 129.02, 130.51, 132.83, 134.34, 140.00, 141.62, 143.22, 153.34, 156.96, and 164.93; ν_{\max} / cm^{-1} 1626 1609, and 1582 (C=N and C=C); m/z (rel intensity) 351 (M^+ , 78), 336 (100), 307 (8), 203 (14), 176 (20), and 149 (14). *Anal.* Calcd for $\text{C}_{23}\text{H}_{17}\text{N}_5\text{O}$: C, 78.61; H, 4.88; N, 11.96. Found: C, 78.33; H, 4.59; N, 11.70.

3c: Yellow prisms (from cyclohexane), mp 163-163.5 °C; δ_{H} 3.2-3.9 (1H, br), 3.87 (3H, s), 7.00 (2H, br d, J 8.4), 7.01 (1H, J 10.1 and 8.4), 7.30 (1H, d, J 11.7), 7.31 (2H, tm, J 7.8), 7.36 (1H, br t, J 7.3), 7.48 (1H, dd, J 11.7 and 8.4), 7.50 (2H, dd, J 7.8 and 7.3), 7.58 (2H, br d, J 8.4), 8.15 (1H, s), and 8.28 (1H, d, J 10.1); δ_{C} 55.90, 114.65, 115.41, 116.52, 122.12, 126.80, 127.03, 127.33, 129.10, 129.33, 129.83, 132.36, 134.86, 135.10, 135.76, 138.06, 143.51, 152.31, and 158.48; ν_{\max} / cm^{-1} 3287, 3255 (NH), 1610, and 1587 (C=N and C=C); m/z (rel intensity) 326 (M^+ , 78), 325 (100), 311 (31), 282 (17), 254 (24), 167 (25), 149 (47), 129 (18), 105 (23), 97 (17), 83 (24), and (48). *Anal.* Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}$: C, 80.96; H, 5.56; N, 8.58. Found: C, 80.96; H, 5.42; N, 8.52.

2d: Red needles (from acetonitrile-hexane), mp 141-142 °C; δ_{H} 2.60 (3H, s), 7.13 (1H, dd, J 10.6 and 9.6), 7.43 (1H, dm, J 7.0), 7.48, 7.50-7.56 (6H, m), 7.67 (1H, dd, J 11.1 and 9.6), 7.90 (1H, d, J 10.6), 7.94 (1H, s), and 7.99 (1H, dm, J 8.6); δ_{C} 26.94, 122.83 123.17, 124.12, 127.10, 128.31, 128.50, 128.77, 129.64, 129.92, 131.61, 132.80, 133.45, 135.15 142.69, 144.64, 152.41, 155.11, 165.65, and 197.80; ν_{\max} / cm^{-1} 1675 (C=O), 1653, and 1625 (C=N); m/z (rel intensity) 363 (M^+ , 100), 362 (21), 348(81), 320 (41), 286 (15), 204 (14), 176 (12), and 160 (22). *Anal.* Calcd for $\text{C}_{24}\text{H}_{17}\text{N}_5\text{O}$: C, 79.32; H, 4.72; N, 11.56. Found: C, 78.89; H, 4.80; N, 11.78.

3d: Yellow needles (from cyclohexane), mp 204-205 °C; δ_{H} 2.62 (3H, s), 5.0-6.0 (1H, br), 6.75 (1H, dd, J 10.6 and 8.4), 7.13 (2H, br d, J 7.1), 7.19 (2H, d, J 8.5), 7.38 (1H, tm, J 7.3), 7.47 (1H, d, J 11.5), 7.49 (1H, dd, J 11.5 and 8.4), 7.50 (2H, tm, J 7.5), 7.66 (1H, s), 7.82 (1H, d, J 10.6), 8.03 (2H, d, J 8.5); δ_{C} 26.45, 121.04, 121.61, 122.71, 126.92, 128.10, 128.74, 128.92, 129.49, 130.29, 130.82, 132.36, 134.66, 138.53, 140.76, 151.50, 151.81, and 196.97; ν_{\max} / cm^{-1} 3348 (NH), 1665 (C=O), 1625 and 1593 (C=N); m/z (rel intensity) 338 (M^+ , 54), 337 (100), 294 (14), 293 (13), 161 (10), 146 (16), 105 (96), 91 (9), and 77 (12). *Anal.* Calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}$: C, 81.63; H, 5.36; N, 8.28. Found: C, 81.38; H, 5.17; N, 8.33.

Reaction of **1** with *p*-toluenesulfonyl isocyanate

Under argon atmosphere, a mixture of **1** (0.120 g, 0.25 mmol), *p*-toluenesulfonyl isocyanate (0.0986 g, 0.50 mmol) in dry xylene (5.0 mL) was heated at 150 °C for 4 h in a sealed tube. The precipitate was collected by filtration and washed with hexane, and yielded **4** (0.0812 g, 97%).

4: Orange powders (from hexane-dichloromethane), mp 260-261 °C; δ_{H} 2.41 (3H, s), 7.30 (2H, d, *J* 8.1), 7.44-7.51 (1H, m), 7.51-7.55 (4H, m), 7.71 (1H, dd, *J* 10.3 and 10.1), 8.04 (1H, br s), 8.06 (1H, d, *J* 10.8), 8.09 (2H, d, *J* 8.1), 8.16 (1H, dd, *J* 10.8 and 10.1), and 8.31 (1H, d, *J* 10.3); δ_{C} 21.97, 121.40, 126.23, 128.20, 128.39, 128.82, 129.18, 129.45, 129.84, 130.04, 131.48, 132.30, 132.95, 136.76, 139.39, 143.28, 144.20, 158.67, 164.69; ν_{max} / cm^{-1} 3135 (NH) and 1622 (C=N); *m/z* (rel intensity) 335 (M^+ , 74), 334 (100), 320 (72), 192 (28), 165 (23), 108 (34), 91 (65), and 86 (68). *Anal.* Calcd for $\text{C}_{23}\text{H}_{17}\text{N}_5 \cdot \text{CH}_2\text{Cl}_2$: C, 68.57; H, 4.56; N, 10.00. Found: C, 68.56; H, 4.19; N, 10.30.

Reaction of **1** with phenyl isothiocyanate

Under argon atmosphere, a mixture of **1** (0.120 g, 0.25 mmol), phenyl isothiocyanate (0.060 mL, 0.50 mmol) in dry xylene (5.0 mL) was heated at 180 °C for 20 h in a sealed tube, then the mixture was evaporated. Chromatography of the residue (hexane-ethyl acetate) gave **2a** (0.0507 g, 63%) and recovered **1** (0.0164 g, 14%).

Reaction of 8-bromo-3-phenyl-1-azaazulene (**5**) with *p*-methylaniline

A mixture of 8-bromo-3-phenyl-1-azaazulene (**5**) (0.0986 g, 0.355 mmol) and *p*-methylaniline (0.0429 g, 0.40 mmol) in dry ethanol (15 mL) was heated under reflux for 5 min. The solvent was evaporated and the residue was recrystallized from acetonitrile to give **6** (0.127 g, 92%). Compound (**6**) (0.127 g, 0.325 mmol) was dissolved sodium hydrogencarbonate solution then the mixture was extracted with chloroform. The extract was dried with sodium sulfate and filtered. Evaporation of the filtrate gave **3b** (0.0866 g, 86%).

6: Orange prisms (from acetonitrile), mp 279-280 °C; δ_{H} 2.42 (3H, s), 7.29 (1H ddd, *J* 10.5, 8.4, and 1.0), 7.33 (2H, d, *J* 8.2), 7.42 (2H, d, *J* 8.2), 7.47 (2H, dm, *J* 7.9), 7.51 (1H, dd, *J* 11.7 and 1.0), 7.54 (2H, tm, *J* 7.8), 7.68 (1H, br t, *J* 7.3), 7.70 (1H, dd, *J* 11.7 and 8.4), 8.01 (1H, s), 8.26 (1H, d, *J* 10.5), 11.96 (1H, br s), and 14.58 (1H, br s); ν_{max} / cm^{-1} 3254, 3188, 3110—2700 (broad) (NH) and 1628 (C=N); *m/z* (rel intensity) 311 (9), 310 (52), 309 (100), 147 (15). *Anal.* Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_2\text{Br}$: C, 67.53; H, 4.89; N, 7.16. Found: C, 67.96; H, 4.76; N, 7.08.

Reaction of **1** with carbon disulfide

A mixture of **1** (0.120 g, 0.25 mmol) and carbon disulfide (0.15 mL, 2.50 mmol) in dry benzene (5.0 mL) was heated at 90 °C for 200 h in a sealed tube, then the mixture was concentrated. Chromatography of the residue (hexane-ethyl acetate) gave **7** (0.0243 g, 37%).

7: Red needles (from hexane), mp 107- 108°C; δ_{H} 7.45 (1H, tm, *J* 7.3), 7.53 (2H, dd, *J* 8.3 and 7.3), 7.57

(2H, dm, J 8.3), 7.60 (1H, dd, J 10.3 and 10.0), 7.89 (1H, d, J 10.6), 8.01 (1H, s), 8.07 (1H, dd, J 10.6 and 10.0), and 8.23 (1H, d, J 10.3); δ_{C} 121.11, 124.48, 128.44, 128.78, 129.04, 129.79, 131.09, 132.14, 136.63, 144.05, 147.01, 149.38, 152.38, and 201.05; ν_{max} / cm^{-1} 1615, 1575 (C=N and C=C), and 1450, 1269, and 1234 (N-C=S); m/z (rel intensity) 262 (M^+ , 100), 203 (14), 176 (8), and 149 (11). *Anal.* Calcd for $\text{C}_{16}\text{H}_{10}\text{N}_2\text{S}$; C, 73.26; H, 3.84; N, 10.68. Found: C, 73.21; H, 3.78; N, 10.58.

X-Ray structure determination

Crystal data of 2b: dark red prism, $\text{C}_{23}\text{H}_{17}\text{N}_3$, $M = 335.41$, monoclinic, space group $\text{P}2_1/a$, $a=8.687(7)\text{\AA}$, $b=19.544(9)\text{\AA}$, $c=10.538(7)\text{\AA}$, $\beta=106.94(5)^\circ$, $V=1711(2)\text{\AA}^3$, $Z=4$, $D_{\text{calc}}=1.302\text{g/cm}^3$, crystal dimension $0.06 \times 0.56 \times 1.00$ mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-K α radiation. Total 4312 reflections (4057 unique) were collected using ω - 2θ scan technique with in a 2θ range of 55.0° . The structure was solved by direct methods (SIR92),¹⁷ and refined a full-matrix least squares methods using TEXAN structure analysis software¹⁸ with 235 variables and 1293 observed reflections [$I > 2\sigma(I)$]. The final refinement converged to $R = 0.073$ and $R_w = 0.069$.

Crystal data of 3b: brown prism, $\text{C}_{22}\text{H}_{18}\text{N}_2$, $M = 310.40$, triclinic, space group $\text{P}1$, $a=10.502(7)\text{\AA}$, $b=12.644(8)\text{\AA}$, $c=6.864(8)\text{\AA}$, $\alpha=91.03(9)^\circ$, $\beta=99.81(8)^\circ$, $\gamma=107.78(6)^\circ$, $V=853(1)\text{\AA}^3$, $Z=2$, $D_{\text{calc}}=1.209\text{g/cm}^3$, crystal dimension $0.58 \times 0.64 \times 1.00$ mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-K α radiation. Total 4231 reflections (3093 unique) were collected using ω - 2θ scan technique with in a 2θ range of 55.0° . The structure was solved by direct methods (SIR92),¹⁷ and refined a full-matrix least squares methods using TEXAN structure analysis software¹⁸ with 379 variables observed 1811 reflections [$I > 2\sigma(I)$]. The final refinement converged to $R = 0.054$ and $R_w = 0.056$;

Crystal data of 6: yellow prism, $\text{C}_{22}\text{H}_{19}\text{N}_2\text{Br}$, $M = 391.31$, monoclinic, space group $\text{P}2_1/n$, $a=14.088(4)\text{\AA}$, $b=7.478(7)\text{\AA}$, $c=18.051(4)\text{\AA}$, $\beta=105.73(3)^\circ$, $V=1831(1)\text{\AA}^3$, $Z=4$, $D_{\text{calc}}=1.420\text{g/cm}^3$, crystal dimension $0.08 \times 0.62 \times 0.86$ mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-K α radiation. Total 4709 reflections (4533 unique) were collected using ω - 2θ scan technique with in a 2θ range of 55.0° . The structure was solved by direct methods (SIR92),¹⁷ and refined a full-matrix least squares methods using TEXAN structure analysis software¹⁸ with 226 variables and 2086 observed reflections [$I > 2\sigma(I)$]. The final refinement converged to $R = 0.054$ and $R_w = 0.056$.

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REFERENCES AND NOTE

1. P. Molina and M. J. Vilaplana, *Synthesis*, 1994, 1197.
2. Y. G. Gololobov and L. F. Kasukhin, *Tetrahedron*, 1992, **48**, 1353.
3. M. Nitta, *Reviews on Heteroatom Chemistry*, 1993, **9**, 87.

4. A. W. Johnson, "*Ylides and Imines of Phosphorus*", Wiley, New York, 1993.
5. P. Molina, M. Alajalin, A. Vidal, and P. Sanchez-Andrada, *J. Org. Chem.*, 1992, **57**, 929.
6. T. Saito, H. Ohmori, E. Furuno, and S. Motoki, *J. Chem. Soc., Chem. Commun.*, 1992, 22.
7. P. Molina, A. Lorenzo, and E. Aller, *Tetrahedron*, 1992, **48**, 4601.
8. Q. Zhang, C. Shi, H.-Ren Zhang, and K. K. Wang, *J. Org. Chem.*, 2000, **65**, 7977, and references cited therein.
9. N. Abe, H. Fujii, K. Tahara, and M. Shiro, *Heterocycles*, 2001, **55**, 1659.
10. N. Abe, K. Nagamatsu, K. Tahara, and H. Fujii, *Heterocycles*, 2004, **63**, 809.
11. T. Nishiwaki and N. Abe, *Heterocycles*, 1981, **15**, 547.
12. N. Abe, *Recent Res. Devel. Org. & Bioorg. Chem.*, 2001, **4**, 17.
13. N. Abe, *Trends in Heterocycl. Chem.*, 2001, **7**, 25.
14. C. K. Johnson, ORTEP **II**, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
15. K. Yamane, K. Fujimori, J.-K. Sin, and T. Nozoe, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1184.
16. Y. Sugihara, T. Murafuji, N. Abe, M. Takeda, and A. Kakehi, *New J. Chem.*, 1998, **22**, 1031.
17. A. Altomare, M. Cascarano, C. Giacovazzo, and A. Guagliardi, *J. Appl. Cryst.*, 1994, **26**, 343.
18. TEXAN for Windows version 1.06: Crystal Structure Analysis Package, Molecular Structure Corporation (1997-9).