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REACTIONS OF 3-PHENYL-8-TRIPHENYLPHOSPHOIMINO-1-AZA-AZULENE 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 aryliminophosphoranes 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-

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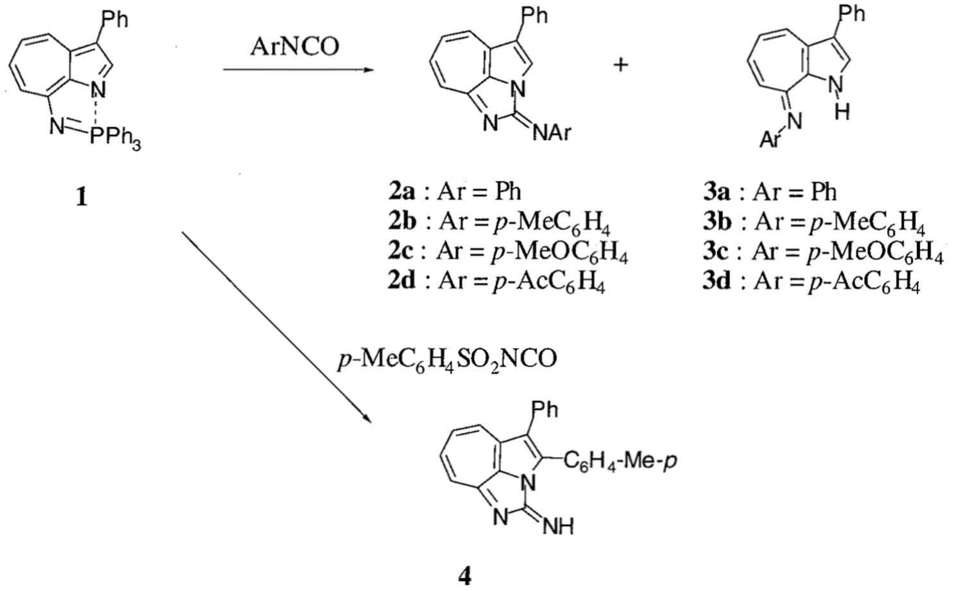
† Dedicated to Dr. Pierre Potier on occasion of his 70th birthday.

azulene chemistry[11-13] and a construction of novel fused heterocycles, we examined the reactions of **1** with aryl isocyanates, phenyl isothiacyanate, 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-diazacyclopent[*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 ℃ 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 ℃ and in 20.5% yield at 180 ℃ (Entries 3 and 4). Prolonged heating at high temperature (180 ℃) 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 these reaction, the carbodiimide derivatives considered as intermediates were not isolated.

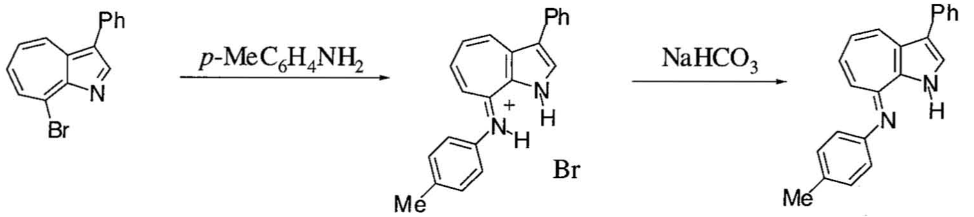
When *p*-toluenesulfonyl isocyanate was reacted with **1**, the result showed a different feature and **4** was obtained in 97% yield (Entry 13), where a cyclization attended upon an elimination of sulfur dioxide and a rearrangement of *p*-methylphenyl group.

Reaction of **1** with phenyl isothiocyanate gave **2a** in good yield and **3a** did not yield (Entry 14).

Table 1. Reactions of **1** with aryl isocyanates and phenyl isothiocyanate.

Entry	Reagent	Conditions Catalyst	 Temp / ℃	 Time / h	Products (Yield / %)		
1	PhNCO	—	rt	24	**2a** (46)	**3a**(—)	**1**(14)
2	PhNCO	—	80	46	**2a** (56)	**3a**(6)	**1**(10.5)
3	PhNCO	—	125	200	**2a** (43)	**3a**(15)	**1**(8)
4	PhNCO	—	180	20	**2a** (57)	**3a**(20.5)	**1**(—)
5	PhNCO	—	180	120	**2a** (44)	**3a**(2)	**1**(—)
6	PhNCO	$ZnCl_2$	rt	24	**2a** (61)	**3a**(—)	**1**(33)
7	PhNCO	$ZnCl_2$	180	20	**2a** (52)	**3a**(7)	**1**(7)
8	*p*-MeC_6H_4NCO	—	125	200	**2b** (29)	**3b**(13)	**1**(14)
9	*p*-MeC_6H_4NCO	—	180	20	**2b** (60)	**3b**(11)	**1**(—)
10	*p*-$MeOC_6H_4NCO$	—	180	24	**2c** (50)	**3c**(9)	**1**(14)
11	*p*-AcC_6H_4NCO	—	180	10	**2d**(57)	**3d** (3.5)	**1**(22.5)
12	*p*-AcC_6H_4NCO	—	180	20	**2d** (93)	**3d**(5)	**1**(—)
13	*p*-TosNCO	—	150	4	**4** (97)		
14	PhNCS	—	180	20	**2a** (63)	**3a**(—)	**1**(14)

The structures of the obtained products were deduced by spectroscopic data as well as elemental analyses, and the structures of **2b** and **3b** were decided by X-Ray crystal structure analysis. Compound (**3b**) was also obtained by a substitution reaction of 8-bromo-3-phenyl-1-azaazulene (**5**) with *p*-methylaniline followed by treatment with sodium hydrogencarbonate.



5 **6** **3b**

ORTEP drawing[14] of **2b** is shown in Figure 1. Bond alternation is clearly observed in the ^{1}H NMR spectrum of **2**. The coupling constants of seven-membered ring protons existed in J = 11.3-11.9 Hz and J = 8.3-8.9 Hz in the ^{1}H 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.

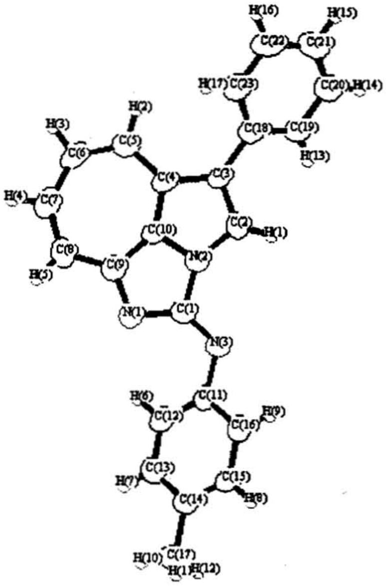
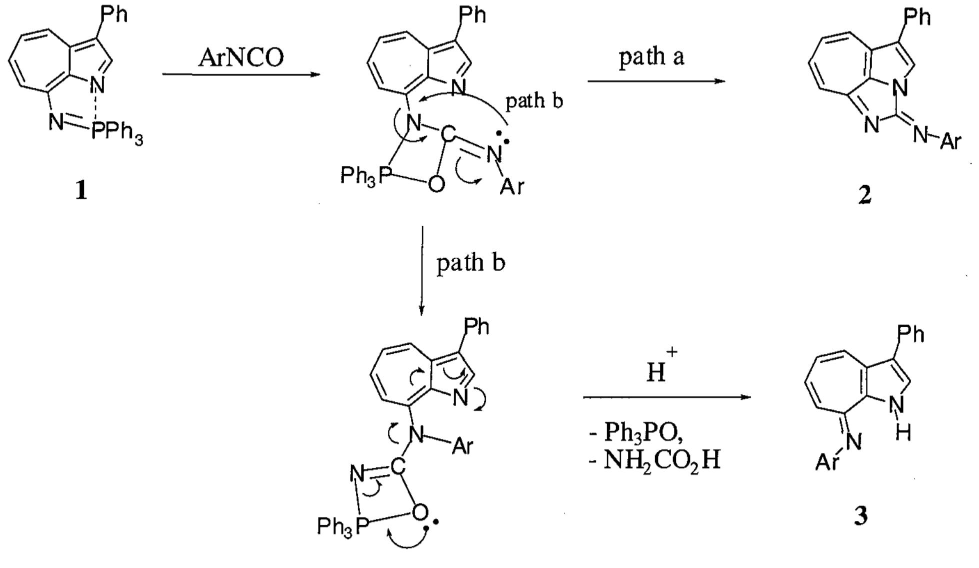
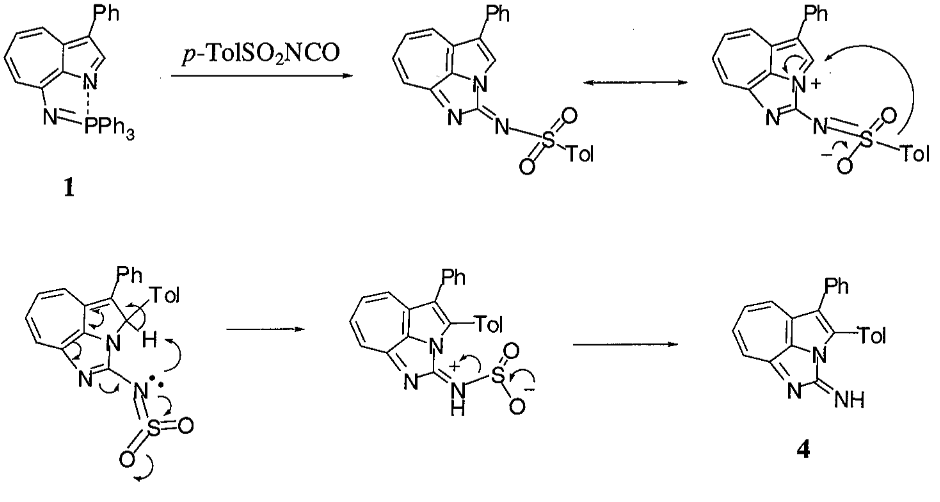


Figure 1. ORTEP drawing of **2b** with thermal ellipsoids (50% probability).
Selective bond lengths (Å): N(1)—C(1) 1.397(7), C(1)—N(2) 1.443(7), N(2)—C(2) 1.387(7), C(2)—C(3) 1.377(8), C(3)—C(4) 1.454(8), C(4)—C(5) 1.415(8), C(5)—C(6) 1.372(9), C(6)—C(7) 1.420(9), C(7)—C(8) 1.372(9), C(8)—C(9) 1.409(8), 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 ℃ 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 ℃ 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-diazacyclopent[*cd*]azulene derivative, but successive rearrangement followed by elimination of SO_2 to give **4**.



Scheme 2



Scheme 3

A **B** **C** **D**

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]

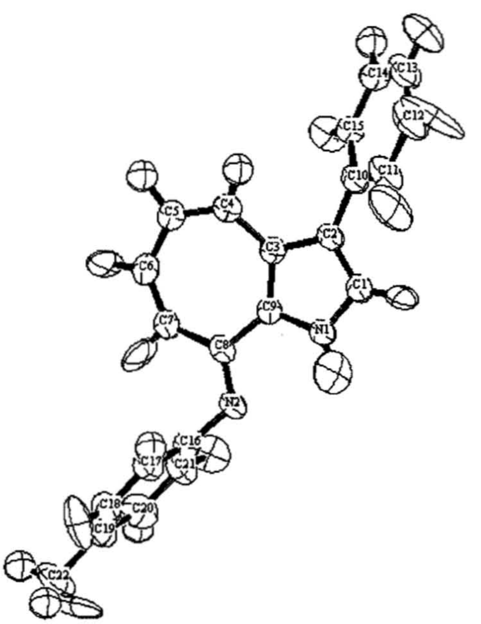


Figure 2. ORTEP drawing of **3b** with thermal ellipsoids (50% probability).

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 caluculation by Gaussian 98 using RHF/6-31G* is in accordance with the result, where the amino form A (Ar = p-MeC$_6$H$_4$) is unstable than the imino form **B** (Ar = p-MeC$_6$H$_4$) (ΔE(A – B) = 0.78 kcal/mol)), whereas the amino form **C** is stable than the imino form **D** (ΔE(C - 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.

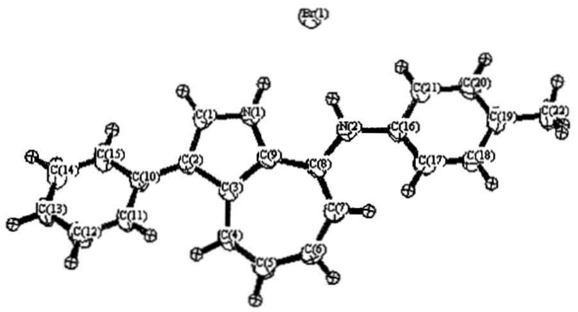
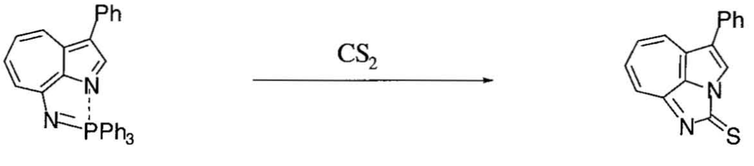


Figure 3. ORTEP drawing of **6** with thermal ellipsoids (50% probability).

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 disufide for 200 h at 90 ℃ 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.



1 **7**

CONCLUSION

Reactions of 8-phosphoimino-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. ^{1}H NMR spectra (including HMBC and HMQC NMR) were recorded on a Bruker AVANCE 400S (400 MHz) and ^{13}C 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 ℃ 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 ℃ 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 ℃; 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 $C_{22}H_{15}N_3$: 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 ℃ (lit.,[15] mp 153-154 ℃); 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 (M$^+$ + 1, 10), 296 (M$^+$, 47), 295 (100), 165 (14), 147 (12), and 77 (11). *Anal.* Calcd for $C_{21}H_{16}N_2$: 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 ℃; 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 (M$^+$ + 1, 100), 335 (M$^+$, 64), 320 (31), 258 (25), 168 (34), 107 (35), 91, (24), and 77 (26). *Anal.* Calcd for $C_{23}H_{17}N_3 \cdot 1/4H_2O$: 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 ℃ (lit.,[15] mp 145-146 ℃); 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 $C_{22}H_{18}N_2$: 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 ℃; 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 $C_{23}H_{17}N_5O$; 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 ℃; 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 $C_{22}H_{18}N_2O$: 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 ℃; 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 $C_{24}H_{17}N_5O$; 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 ℃; 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 $C_{23}H_{18}N_2O$: 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 ℃ 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 ℃; 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 $C_{23}H_{17}N_5 \cdot CH_2Cl_2$: 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 isothiacyanate (0.060 mL, 0.50 mmol) in dry xylene (5.0 mL) was heated at 180 ℃ 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 ℃; 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 $C_{22}H_{19}N_2Br$: C, 67.53; H, 4.89; N, 7.16. Found: C, 67.96; H, 4.76; N, 7.08.

Reaction of 1 with carbon disufide

A mixture of **1** (0.120 g, 0.25 mmol) and carbon disufide (0.15 mL, 2.50 mmol) in dry benzene (5.0 mL) was heated at 90 ℃ 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℃; 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 $C_{16}H_{10}N_2S$; 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, $C_{23}H_{17}N_3$, *M* = 335.41, monoclinic, space group P2$_1$/a, *a*=8.687(7)Å, *b*=19.544(9)Å, *c*=10.538(7)Å, *β*=106.94(5)°, *V*=1711(2) Å^3, *Z*=4, D$_{calc}$=1.302g/cm^3, crystal dimension 0.06 x 0.56 x 1.00 mm. Data were measured on a Rigaku AFC 5S radiation diffractmeter with graphite-monochromated Mo-Kα radiation. Total 4312 reflections (4057 unique) were collected using *ω*-2*θ* scan technique with in a 2*θ* 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 software[18] with 235 variables and 1293 observed reflections [I>2σ(I)]. The final refinement converged to *R* = 0.073 and *Rw* = 0.069.

Crystal data of 3b: brown prism, $C_{22}H_{18}N_2$, *M* = 310.40, triclinic, space group P1, *a*=10.502(7)Å, *b*=12.644(8)Å, *c*=6.864(8)Å, *α*=91.03(9)°, *β*=99.81(8)°, *γ*=107.78(6)°, *V*=853(1) Å^3, *Z*=2, D$_{calc}$=1.209g/cm^3, crystal dimension 0.58 x 0.64 x 1.00 mm. Data were measured on a Rigaku AFC 5S radiation diffractmeter with graphite-monochromated Mo-Kα radiation. Total 4231 reflections (3093 unique) were collected using *ω*-2*θ* scan technique with in a 2*θ* 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 software[18] with 379 variables observed 1811 reflections [I>2σ(I)]. The final refinement converged to *R* = 0.054 and *Rw* = 0.056;

Crystal data of 6: yellow prism, $C_{22}H_{19}N_2Br$, *M* = 391.31, monoclinic, space group P2$_1$/n, *a*=14.088(4)Å, *b*=7.478(7)Å, *c*=18.051(4)Å, *β*=105.73(3)°, *V*=1831(1) Å^3, *Z*=4, D$_{calc}$=1.420g/cm^3, crystal dimension 0.08 x 0.62 x 0.86 mm. Data were measured on a Rigaku AFC 5S radiation diffractmeter with graphite-monochromated Mo-Kα radiation. Total 4709 reflections (4533 unique) were collected using *ω*-2*θ* scan technique with in a 2*θ* 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 software[18] with 226 variables and 2086 observed reflections [I>2σ(I)]. The final refinement converged to *R* = 0.054 and *Rw* = 0.056.

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