Reactions of 2-Amino-, 2-Alkylamino-, and 2-Piperidino-1-aza-azulenes with Aryl and Chlorosulfonyl Isocyanates

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Reaction of 2-amino-1-azaazulene with phenyl isocyanate gave 3-phenyl-2*H*-3,4-dihydro-1,3,4a-triazabenz[5,4-*a*]azulene-2,4-dione. Reactions of 2-alkylamino-1-azaazulenes with aryl isocyanates gave 2-(*N*-ethyl-*N*'-arylureido)-1-azaazulenes initially, which rearranged to *N*-aryl-2-alkylamino-1-azaazulene-3-carboxamides and successive reaction with another molar amount of aryl isocyanate furnished uracil-fuzed 1-azaazulenes. Reaction of 2-piperidino-1-azaazulene with aryl isocyanate gave *N*-aryl-2-piperidino-1-aza-azulene-3-carboxamide. Reaction of 2-(substituted amino)-1-azaazulenes with chlorosulfonyl isocyanate gave 3-cyano- and 3-chloro-2-(substituted amino)-1-azaazulenes.

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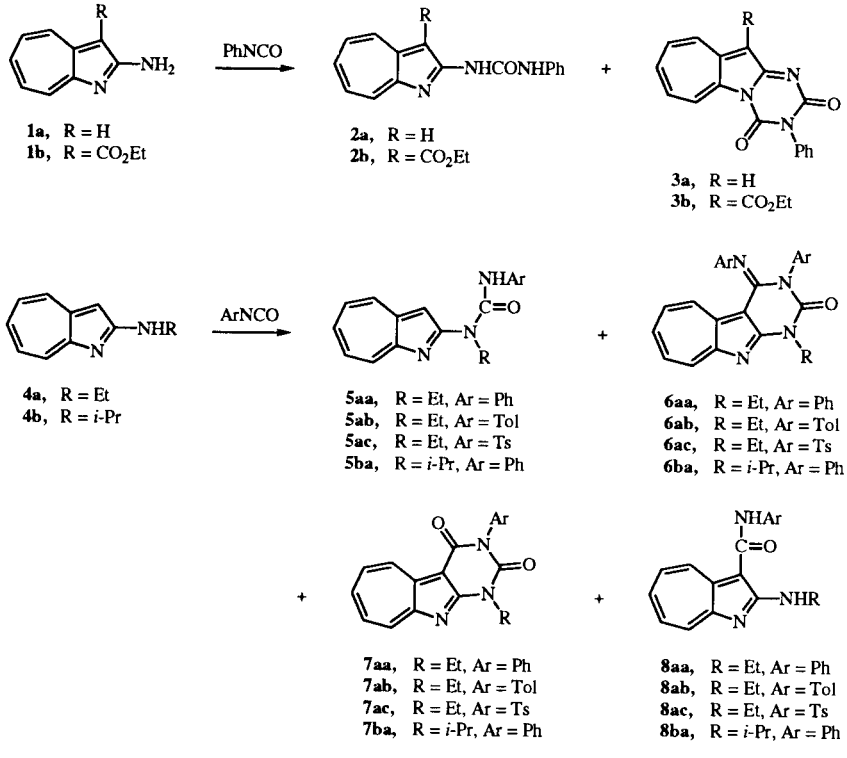
Cycloaddition reactions of azaazulenes have received attention [1-12]; we have reported various features of the reactions of 1-azaazulenes with dimethyl acetylenedicarboxylate [1,5-9] and diphenylcyclopropenone [10-12]. In the reactions, it is found that 2-amino-1-azaazulenes behaved like an amidine and/or an aminoenamine and also exist in a tautomeric form, 2-imino-1,2-dihydro-1-azaazulene, and formed a variety of cycloadducts [7,12]. The reactivities of 1-azaazulenes were discussed in terms of MO theory [13]. It is well known that isocyanates behave as 1,3-dipolar reagents and/or a dipolarolophile to give a large variety of heterocyclic compounds [14,15]. It is expected that reactions of 2-amino-1-azaazulenes with isocyanates may enable us to extend azaazulene chemistry and give novel fused heterocycles, if isocyanates behave as 1,3-dipolar reagents leading to cycloadducts. Therefore, we studied the reactions of 2-amino-, 2-alkylamino-, and 2-dialkylamino-1-azazulenes with aryl iso-

Chart 1



cyanates, and obtained novel cycloadducts. In the reactions of 2-alkylamino-1-azaazulenes with aryl isocyanates, it is found that the formation of cycloadducts proceeded *via* an aza-Fries type rearrangement. Furthermore, we studied the reactions of 2-alkylamino-, and 2-dialkylamino-1-azaazulenes with chlorosulfonyl isocyanate, and obtained interesting results, in which cyanation and chlorination occurred at C-3 of the 1-azaazulenes. In these reactions, Michael-type addition was found as the initial reaction on 2-amino-1-azaazulenes and the isocyanates did not behave as 1,3-dipolar reagents in the reaction as we expected, nevertheless, publication of the reaction of 2-amino-1-azaazulenes with isocyanates seems worthwhile.

The reactions of 2-amino-1-azaazulenes (**1a,1b**), 2-alkylamino-1-azaazulenes **4a-4c**, and 2-piperidino-1-azaazulene (**9**) with aryl isocyanates were performed under refluxing in xylene and acetonitrile with or without presence of zinc(II) dichloride. The reaction mixture then was separated by silica gel chromatography. The reaction conditions and the results are listed in Table 1.

Reaction of 2-amino-1-azaazulene (**1a**) with phenyl isocyanate gave 3-phenyl-2*H*-3,4-dihydro-1,3,4a-triazabenz-[5,4-*a*]azulene-2,4-dione (**3a**) along with 2-(*N'*-phenylureido)-1-azaazulene (**2a**). The reaction proceeded in good yield, when performed in the presence of zinc chloride for 1 hour (Run 2). Prolonged heating did not give improved results (Run 3). The reaction of ethyl 2-amino-1-azaazulene-3-carboxylate with phenyl isocyanate gave ureido derivative **2b** as major product, and cyclization product **3b** was obtained in poor yield (Run 4, 5). Treatment of **2b** with phenyl isocyanate did not give a cycloadduct. Lowering the electron density of N-1 with an ester group as an electron-withdrawing group would reduce the reactivity on N-1 with isocyanates. Therefore, it was thought that the reaction would be initiated by the Michael attack of phenyl isocyanate on N-1 of **1**, and successive addition

Chart 2

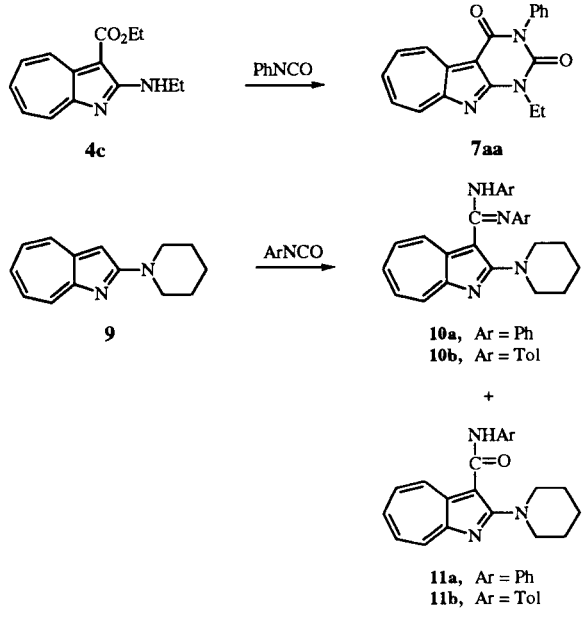
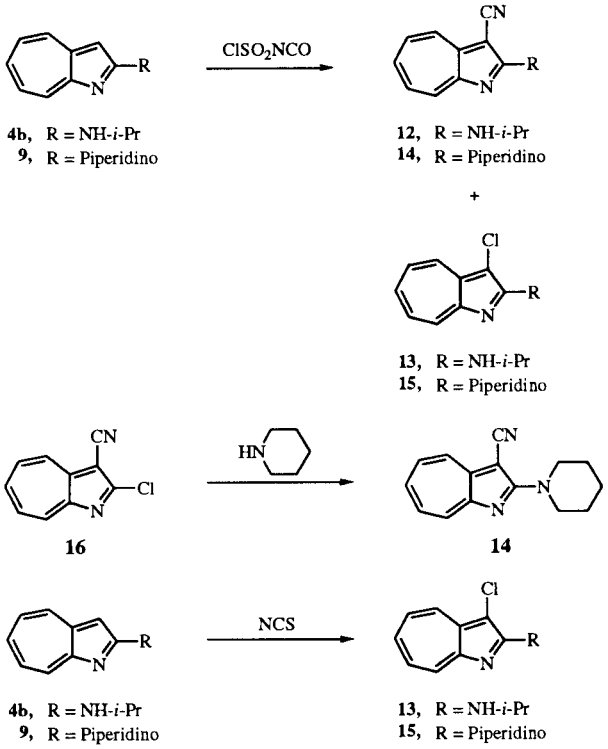


Chart 3



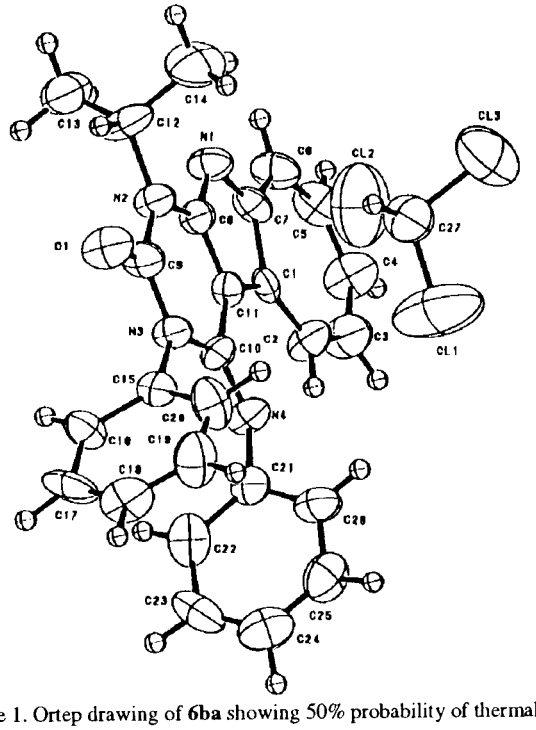
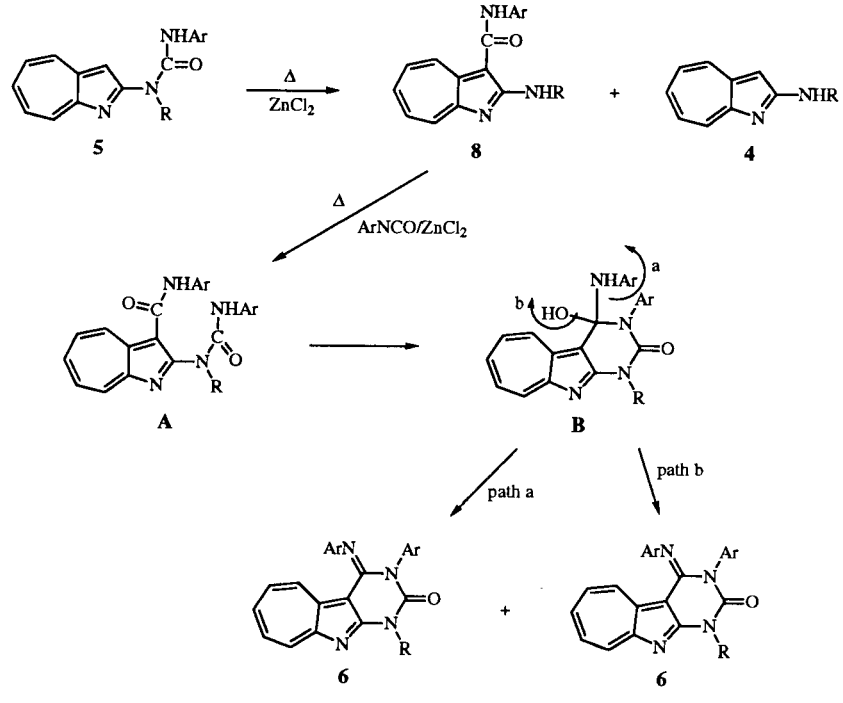
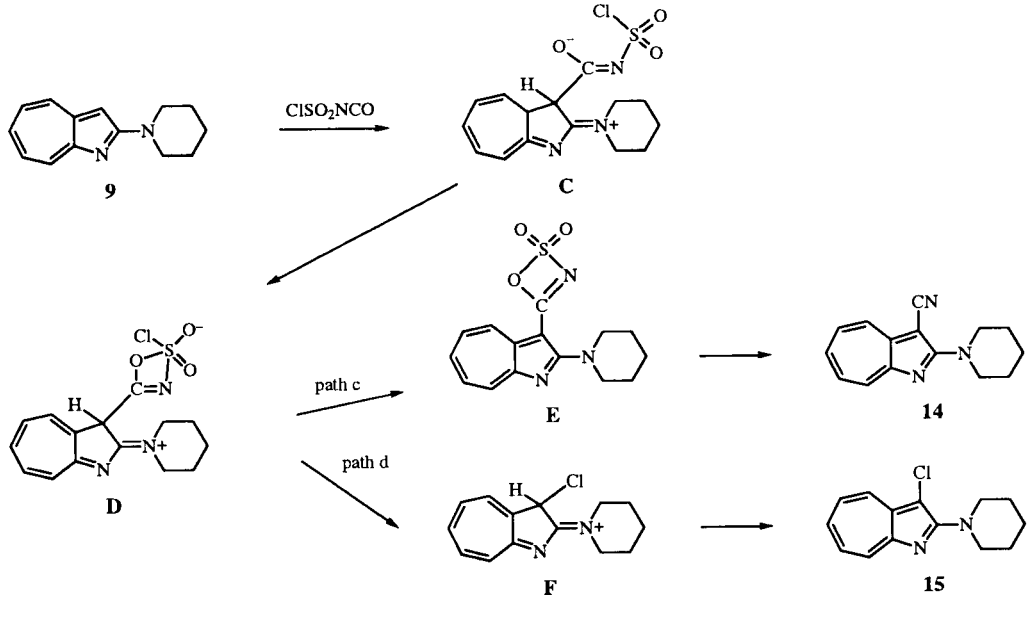


Figure 1. Ortep drawing of **6ba** showing 50% probability of thermal ellipsoids.

Scheme 1



Scheme 2



followed by cyclization would furnish **3**. Formation of the fused [1,3,5]triazine-2,4-dione system by the reaction of isocyanate was reported on the reaction of 2-aminopyrrole with isocyanate, which gave a [1,2-*a*][1,3,5]triazine-5,7-dione derivative [16].

The structures of **2** and **3** were determined by spectroscopic data as well as elemental analyses. For example, the ir spectrum of **3a** shows two carbonyl signals at 1728 and 1688 cm^{-1}, and no NH signal is observed. In its ^1H nmr spectrum, the 1H singlet, assigned as H-10, is seen at δ 6.57, and seven-membered ring protons are seen at δ 7.40-7.60 (m, H-6, 7, and 8), 7.75 (d, J = 10.7 Hz, H-9), and 9.04 (d, J = 9.2 Hz, H-5) together with phenyl protons at δ 7.20-7.38. The observation of the low field resonating H-5 proton, owing to carbonyl at C-4, is consistent with the structure.

Reactions of 2-(substituted amino)-1-azaazulenes **4** with aryl isocyanate were different than those as for **1** (Runs 6 - 15). Thus treatment of 2-alkylamino-1-azaazulenes **4** with an aryl isocyanate in the presence of zinc

Table 1

Reactions of 2-Amino-1-azaazulenes with Aryl Isocyanates

Run	Compound	Conditions		Products (%)				
1	**1a**	PhNCO xylene reflux	2 d	**2a** (3.3)	**3a** (30)			
2	**1a**	PhNCO xylene reflux $ZnCl_2$	1 h	**2a** (8.8)	**3a** (57)			
3	**1a**	PhNCO xylene reflux $ZnCl_2$	15 h	**2a** (4.0)	**3a** (11)			
4	**1b**	PhNCO xylene reflux	2 d	**2b** (68)	**3b** (3.0)			
5	**1b**	PhNCO xylene reflux	1 h	**2b** (85)	**3b** (7.9)			
6	**4a**	PhNCO MeCN reflux	0.5 h	**5aa** (99)	**6aa** (-)	**7aa** (-)	**8aa** (-)	**4a** (-)
7	**4a**	PhNCO xylene reflux	1 h	**5aa** (96)	**6aa** (-)	**7aa** (-)	**8aa** (-)	**4a** (3)
8	**4a**	PhNCO xylene reflux $ZnCl_2$	10 d	**5aa** (-)	**6aa** (5.3)	**7aa** (48)	**8aa** (7.4)	**4a** (24)
9	**4a**	TolNCO xylene reflux $ZnCl_2$	2 d	**5ab** (23)	**6ab** (-)	**7ab** (9.9)	**8ab** (11)	**4a** (37)
10	**4a**	TolNCO xylene reflux ZnCl2	10 d	**5ab** (-)	**6ab** (-)	**7ab** (41)	**8ab** (11)	**4a** (14)
11	**4a**	TsNCO MeCN rt	18 h	**5ac** (22)	**6ac** (-)	**7ac** (9.1)	**8ac** (-)	**4a** (60)
12	**4a**	TsNCO xylene reflux	4 h	**5ac** (-)	**6ac** (-)	**7ac** (49)	**8ac** (30)	**4a** (-)
13	**4b**	PhNCO xylene reflux	1 h	**5ba** (66)	**6ba** (-)	**7ba** (-)	**8ba** (34)	**4b** (-)
14	**4b**	PhNCO xylene reflux $ZnCl_2$	10 d	**5ba** (-)	**6ba** (9.6)	**7ba** (-)	**8aa** (3.5)	**4b** (72)
15	**4c**	PhNCO xylene reflux	6 d			**7aa** (-)		**4c** (99)
16	**4c**	PhNCO xylene reflux $ZnCl_2$	3 d			**7aa** (4.5)		**4c** (76)
17	**9**	PhNCO xylene reflux $ZnCl_2$	8 d	**10a** (16)			**11a** (74)	**9** (6.8)
18	**9**	TolNCO xylene reflux $ZnCl_2$	5 d	**10b** (11)			**11b** (62)	**9** (23)

Table 2

Crystal Data and Structure Refinement for 1-Isopropyl-3-phenyl-4-phenylimino-1,2,3,4-tetrahydro-1,3,10-triazabenzazulen-2-one

Empirical Formula	$C_{26}H_{22}N_4O{\cdot}CHCl_3$
Formula Weight	525.86
Temperature	293(2)K
Wavelength	0.71069Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 11.584(4) Å
	b = 18.88(1) Å
	c = 12.406(6) Å
	β = 108.67(3)°
Volume	2571(2) $Å^3$
Z	4
Density	Calculated: 1.359 Mg/m^3
Absorption coefficient	0.383 mm^{-1}
F(000)	1088
Crystal size	0.88 x 0.82 x 1.00 mm
Scan type	ω-2θ
$2\theta_{max}$	55.0°
Scan width	(1.52 + 0.30 tanθ)
No. of reflections measured	Total: 5355
	Unique: 5066 (R_{int} = 0.080)
Refinement method	Full-matrix least-squares
Function minimized	$\Sigma\ \omega\ (|Fo| - |Fc|)^2$
Least-squares weights	$4Fo^2/\sigma^2(Fo^2)$
p-factor	0.03
No. of observations (I > 3.00σ(I))	1453
No. of variables	316
Residuals	R = 0.072, Rw = 0.080
Goodness of fit indicator	2.40
Max shift/error in final cycle	0.06
Max. peak in final diff. map	0.46 e^- $Å^{-3}$
Min. peak in final diff. map	-0.50 e^- $Å^{-3}$

chloride with refluxing xylene gave two cycloadducts **6** and **7**, together with *N*-aryl-2-alkylamino-1-azaazulene-3-carboxamides **8** and 2-alkylamino-1-azaazulenes **4** were recovered (Runs 8, 9, 10, 14). When the reaction was per-

Table 3

Atomic Coordinates and Equivalent Isotropic Thermal parameters (B_{eq}/Å) for 1-Isopropyl-3-phenyl-4-phenylimino-1,2,3,4-tetrahydro-1,3,10-triazabenzazulen-2-one

Atom	x	y	z	B_{eq}
Cl(1)	0.5805(4)	0.3847(3)	0.5468(3)	12.9(3)
Cl(2)	0.5693(4)	0.3047(2)	0.7320(4)	11.7(3)
Cl(3)	0.6006(4)	0.4511(2)	0.7553(4)	12.2(3)
O(1)	0.8171(5)	0.1283(4)	0.7441(5)	4.6(4)
N(1)	0.4672(7)	0.1156(5)	0.8530(6)	3.9(4)
N(2)	0.6533(6)	0.1217(5)	0.8069(6)	3.4(4)
N(3)	0.6326(6)	0.1260(5)	0.6079(6)	3.2(4)
N(4)	0.4313(6)	0.1302(5)	0.4686(7)	3.5(4)
C(1)	0.3330(8)	0.1204(5)	0.6643(7)	2.7(4)
C(2)	0.2271(8)	0.1254(6)	0.5732(8)	4.3(5)
C(3)	0.1084(8)	0.1233(7)	0.5736(8)	5.5(6)
C(4)	0.0649(8)	0.1151(6)	0.665(1)	4.9(6)
C(5)	0.130(1)	0.1075(6)	0.777(1)	4.5(6)
C(6)	0.2544(9)	0.1084(6)	0.8340(8)	4.4(6)
C(7)	0.3484(8)	0.1154(6)	0.7858(8)	3.3(5)
C(8)	0.5276(8)	0.1205(6)	0.7762(7)	3.1(4)
C(9)	0.7074(9)	0.1259(6)	0.7210(8)	3.6(5)
C(10)	0.5033(8)	0.1268(6)	0.5693(7)	2.9(4)
C(11)	0.4546(7)	0.1230(5)	0.6643(7)	2.6(4)
C(12)	0.7338(8)	0.1249(8)	0.9275(8)	4.7(5)
C(13)	0.723(1)	0.0597(7)	0.992(1)	6.0(7)
C(14)	0.719(1)	0.1925(7)	0.986(1)	6.6(7)
C(15)	0.6968(7)	0.1293(7)	0.5247(7)	3.1(5)
C(16)	0.733(1)	0.0662(6)	0.487(1)	3.9(6)
C(17)	0.788(1)	0.0675(7)	0.404(1)	5.3(7)
C(18)	0.809(1)	0.1324(8)	0.362(1)	4.9(6)
C(19)	0.775(1)	0.1932(7)	0.400(1)	5.7(7)
C(20)	0.718(1)	0.1926(6)	0.482(1)	4.8(6)
C(21)	0.4504(8)	0.1351(7)	0.3628(8)	3.5(5)
C(22)	0.468(1)	0.0755(6)	0.302(1)	5.1(7)
C(23)	0.475(1)	0.0842(8)	0.193(1)	5.3(7)
C(24)	0.464(1)	0.1486(9)	0.144(1)	5.6(7)
C(25)	0.444(1)	0.2068(7)	0.200(1)	5.2(7)
C(26)	0.438(1)	0.2002(7)	0.310(1)	4.5(6)
C(27)	0.6329(9)	0.3772(7)	0.690(1)	5.9(6)

Table 4

Selected Bond Lengths [Å] and Angles [deg] for 1-Isopropyl-3-phenyl-4-phenylimino-1,2,3,4-tetrahydro-1,3,10-triazabenzazulen-2-one

O(1)-C(9)	1.211(9)
N(1)-C(7)	1.36(1)
N(1)-C(8)	1.35(1)
N(2)-C(8)	1.38(1)
N(2)-C(9)	1.40(1)
N(2)-C(12)	1.49(1)
N(3)-C(9)	1.39(1)
N(3)-C(10)	1.42(1)
N(3)-C(15)	1.45(1)
N(4)-C(10)	1.26(1)
N(4)-C(21)	1.40(1)
C(1)-C(2)	1.38(1)
C(1)-C(7)	1.46(1)
C(1)-C(11)	1.41(1)
C(2)-C(3)	1.38(1)
C(3)-C(4)	1.39(1)
C(4)-C(5)	1.37(1)
C(5)-C(6)	1.39(1)
C(6)-C(7)	1.41(1)
C(8)-C(11)	1.38(1)
C(10)-C(11)	1.46(1)
C(7)-N(1)-C(8)	102.5(7)
C(8)-N(2)-C(9)	118.7(7)
C(8)-N(2)-C(12)	122.9(7)
C(9)-N(2)-C(12)	118.2(7)
C(9)-N(3)-C(10)	126.1(7)
C(9)-N(3)-C(15)	114.8(7)
C(10)-N(3)-C(15)	119.0(7)
C(10)-N(4)-C(21)	132.6(8)
C(2)-C(1)-C(7)	129.1(8)
C(2)-C(1)-C(11)	128.6(8)
C(7)-C(1)-C(11)	102.2(8)
C(1)-C(2)-C(3)	128.5(8)
C(2)-C(3)-C(4)	129.1(9)
C(3)-C(4)-C(5)	128.4(9)
C(4)-C(5)-C(6)	131.2(9)
C(5)-C(6)-C(7)	127.4(9)
N(1)-C(7)-C(1)	113.4(7)
N(1)-C(7)-C(6)	120.5(8)
C(1)-C(7)-C(6)	126.1(9)
N(1)-C(8)-N(2)	122.9(8)
N(1)-C(8)-C(11)	115.1(7)
N(2)-C(8)-C(11)	122.0(8)
O(1)-C(9)-N(2)	120.9(9)
O(1)-C(9)-N(2)	120.4(8)
N(2)-C(9)-N(3)	118.7(8)
N(3)-C(10)-N(4)	128.8(8)
N(3)-C(10)-C(11)	111.5(7)
N(4)-C(10)-C(11)	119.8(8)
C(1)-C(11)-C(8)	106.8(7)
C(1)-C(11)-C(10)	130.2(8)
C(8)-C(11)-C(10)	122.9(8)

formed under mild conditions, refluxing in acetonitrile for a short time in the absence of zinc chloride, 2-(*N*-ethyl-*N*'-arylureido)-1-azaazulenes **5** were obtained in good yields (Run 6, 7, 11). Reaction of tosyl isocyanate was fast, and cycloadduct **7ac** was obtained in a 49%, along with **8ac** (30%) in boiling xylene in the absence of zinc chloride (Run 12). From the results, it is considered that compounds **6**, **7**, and **8** would be secondary products. Therefore, we treated **5** at elevated temperature. Thus, treatment of **5aa** in refluxing xylene for 2 days gave 1,3-diphenylurea (1%), **8aa** (39%), and **4a** (7%), together with **5aa** (54%). When the reaction was performed in the presence of zinc chloride for 20 hours, 1,3-diphenylurea (40%), **8aa** (8%), and **4a** (72%) were obtained. The presence of **4a** suggested that an aza-Fries type rearrangement occurred in the reaction. To confirm this, **5aa** was treated with phenyl isocyanate in refluxing xylene for 9 days, and yielded **8aa** (55%) in good yield together with **4a** (4%) and **5aa** (39%). Cycloadducts **6** and **7** would be produced by the reaction of **8** and with another mole of isocyanate in the presence of zinc chloride. Indeed, treatment of **8aa** with phenyl isocyanate in refluxing xylene for 2 days in the presence of zinc chloride gave **6aa** (2.3%) and **7aa** (66%). Treatment of **7aa** with phenyl isocyanate did not give **6aa**, therefore, it is proposed that **6aa** was produced from **8aa**.

The structures of compounds **5-8** obtained were determined by spectral as well as elemental analyses detailed in the experimental. The structure of **6ba** was established by X-ray analysis. The crystal data and data structure refinements for **6ba** are listed in Table 2, and the atomic coordinates and equivalent isotropic thermal parameters in Table 3. An ORTEP drawing of **6ba** is shown in Figure 1, and selected bond lengths and angles are listed in Table 4. For instance, the ir spectra of **5aa** shows no NH signal, whereas that of **8aa** shows NH signals at 3388 and 3300 cm^{-1}. In the ^1H nmr spectrum, the NH proton of **5aa** is observed at δ 13.55. Seven membered protons of **8aa** resonate at higher field than those of **5aa**. This would be attributed to the difference of the effects of the amino group which strongly donates electrons whereas the ureido group does not. Empirical formula ($C_{25}H_{20}N_4O$ for **6aa**, $C_{19}H_{15}N_3O_2$ for **7aa**) from their elemental analyses and mass spectra suggest that these compounds would be cyclized structures. In the ^1H nmr spectra of **6aa** and **7aa**, no singlet assigned to the H-3 proton of 1-azaazulene ring is observed. One low-field proton resonating at δ 9.30-9.40, assigned to the H-5, owing to a deshielding effect of C-4 carbonyl. On the other hand, the H-5 proton of **6aa** is found at δ 8.56, and this suggests that an imino group, not a carbonyl group, is present at C-4. No NH is observed in their ^1H nmr and ir spectra. From these facts, we assigned the structures. Formation of **7aa** by the reaction of **4c** with phenyl isocyanate also supported the assignment of the structure. Structures of other compounds were assigned from a comparison of their spectral data.

A plausible reaction mechanism for the formation of **6** and **7** is shown in Scheme 1. Reaction of **8** with isocyante would give dipolar intermediate **A**, and successive cyclization of **A** affords **B**. Dehydration of **B** gives **6** (path

b), whereas deamination of **B** yields **7** (path a).

The reaction of 2-piperidino-1-azaazulene (**9**) with aryl isocyanates was slightly different, and gave amidine derivatives **10a,b** and amide derivative **11a,b** (Runs 17, 18). In the azulene system, only a Michael type reaction such as the reaction of 4,6,8-trimethylazulene with tosyl isocyanate occurred to give N-tosyl-4,6,8-trimethylazulene-1-carboxamide [17]; this resembles the formation of **11**. It is also known that aryl isocyanates react with an amide to give amidines [18,19]. Therefore, it is proposed that **10** was formed from the reaction of 11 with aryl isocyanate. Indeed, treatment of **11a** with phenyl isocyanate in refluxing xylene gave **10a** in a 40% yield. This result also supports the structure of **10a**.

The reactions of **4b** and **9** with chlorosulfonyl isocyanate were distinct results. Thus, treatment of **4a** with chlorosulfonyl isocyanate in refluxing xylene gave 2-isopropylamino-1-azaazulene-3-carbonitrile (**12**) (68%) and 3-chloro-2-isopropylamino-1-azaazulene (**13**) (4%). Similarly, **9** with chorosulfonyl isocyanate gave **14** (61%) and **15** (8%). The structure of **14** was confirmed by the observation that the reaction 2-chloro-1-azaazulene-3-carbonitrile (**16**) with piperidine gave **14**. Structures of **13** and **15** were confirmed from the fact that treatment of **4b** and **9** with *N*-chlorosuccinimide (NCS) gave **13** and **15**, respectively.

One reasonable mechanism is shown in Scheme 2. Reaction of the **9** with chorosulfonyl isocyanate would produce intermediate **C**, from which dehydrochlorination followed by aromatization gives **D**, and successive elimination of sulfur trioxide on **E** furnishes **14** (path c). Nucleophilic substitution of chloride anion on C-3 of **D** gives **F**, and successive aromatization furnishes **15** (path d).

EXPERIMENTAL

Melting points are uncorrected. The ^{1}H nmr spectra (250 MHz) were recorded on a Hitachi R-250H spectrometer using deuteriochloroform as a solvent with tetramethylsilane as an internal standard. The ir spectra were recorded on a Hitachi 270-50 infrared spectrophotometer for Nujol mulls. Mass spectra were taken with a JEOL JMS-01SG-2 spectrometer. Kieselgel 60 was used for column chromatography and Kieselgel 60G for preparative thin-layer chromatography. The reaction procedure of 2-amino-1-azaazulenes **1**, 2-alkylamino-1-azaazulenes **4**, and 2-piperidino-1-azaazulene **9** with aryl isocyanates (Table 1) were described in detail for the particular type as examples; the other compounds are in Table 1 giving only analytical and physical data.

Reaction of 2-Amino-1-azaazulene (**1a**) with Phenyl Isocyanate.

A mixture of **1a** (0.576 g, 4.00 mmoles), phenyl isocyanate (1.43 g, 12.00 mmoles) and zinc chloride (0.545 g, 4.00 mmoles) in dry xylene (50 ml) was refluxed for 1 hour, then the solvent was evaporated. To the residue, chloroform (30 ml) was added and the colorless precipitate (0.450 g), assigned as 1,3-diphenylurea, was filtered off. The filtrate was evaporated and the residue was chromatographed with chloroform to give 2-(*N'*-phenylurido)-1-azaazulene (**2a**) (0.080 g, 8.8%), 1,3-diphenylurea (0.313 g), and 3-phenyl-2*H*-3,4-dihydro-1,3,4a-triazabenz[5,4-*a*]azulene-2,4-dione (**3a**) (0.540 g, 57%), successively.

Compound **2a** had mp 197-200° (orange prisms from hexane-dichloromethane); ^{1}H nmr: δ 6.85 (1H, s), 7.12 (1H, t, J = 7.9 Hz), 7.37 (1H, dd, J = 10.4 and 9.8 Hz), 7.39 (2H, t, J = 7.9 Hz), 7.57 (1H, dd, J = 10.4 and 9.8 Hz), 7.61 (1H, dd, J = 10.4 and 9.8 Hz), 7.70 (2H, d, J = 7.9 Hz), 8.22 (1H, d, J = 10.4 Hz), 8.29 (1H, d, J = 9.8 Hz), 8.6-9.2 (1H, br), and 11.9-12.3 (1H, br); ir: cm^{-1} 3392, 3255 (NH), and 1706 (C=O).

Anal. Calcd. for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96. Found: C, 72.95; H, 5.16; N, 15.62.

Compound **3a** had mp 255° dec (orange needles from ethyl acetate); ^{1}H nmr: δ 6.57 (1H, s), 7.20-7.38 (5H, m), 7.40-7.60 (3H, m), 7.75 (1H, d, J = 10.7 Hz), and 9.04 (1H, d, J = 9.2 Hz); ir: cm^{-1} 1728 and 1668 (C=O).

Anal. Calcd. for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.80; N, 14.40. Found: C, 70.56; H, 3.99; N, 14.52.

Ethyl 2-(*N'*-Phenylurido)-1-azaazulene-3-carboxylate (**2b**).

This compound had mp 174-175° (yellow needles from hexane-dichloromethane); ^{1}H nmr: δ 1.50 (3H, t, J = 7.0 Hz), 4.50 (2H, q, J = 7.0 Hz), 7.11 (1H, t, J = 7.3 Hz), 7.37 (2H, dd, J = 7.9 and 7.3 Hz), 7.67 (2H, t, J = 7.9 Hz), 7.70-7.95 (3H, m), 8.40 (1H, d, J = 10.4 Hz), 9.19 (1H, d, J = 10.4 Hz), 9.47 (1H, s), and 12.07 (1H, s); ir: cm^{-1} 3492, 3308 (NH), 1706 and 1654 (C=O).

Anal. Calcd. for $C_{19}H_{17}N_3O_3 \cdot H_2O$: C, 64.58; H, 5.42; N, 11.89. Found: C, 64.71; H, 5.00; N, 11.89.

Ethyl 3-Phenyl-2*H*-3,4-dihydro-2,4-dioxo-1,3,4a-triazabenz-[5,4-*a*]azulene-10-carboxylate (**3b**).

This compound had mp 170-171° (orange needles from hexane-dichloromethane); ^{1}H nmr: δ 1.48 (3H, t, J = 7.0 Hz), 4.52 (2H, q, J = 7.0 Hz), 7.33 (2H, d, J = 7.6 Hz), 7.40-7.80 (6H, m), 9.29 (1H, d, J = 11.0 Hz), and 9.53 (1H, d, J = 10.4 Hz); ir: cm^{-1} 1672 and 1634 (C=O).

Anal. Calcd. for $C_{20}H_{15}N_3O_4$: C, 66.48; H, 4.18; N, 11.63. Found: C, 66.24; H, 4.25; N, 11.52.

2-(*N*-Ethyl-*N'*-phenylureido)-1-azaazulene (**5aa**).

This compound had mp 131-132° (yellow prisms from hexane-dichloromethane); ^{1}H nmr: δ 1.40 (3H, t, J = 7.0 Hz), 4.17 (2H, q, J = 7.0 Hz), 6.88 (1H, s), 7.08 (1H, t, J = 7.3 Hz), 7.37 (2H, t, J = 7.3 Hz), 7.50-7.70 (3H, m), 7.72 (2H, t, J = 7.3 Hz), 8.25 (1H, d, J = 10.4 Hz), 8.29 (1H, d, J = 9.8 Hz), and 13.55 (1H, s); ir: cm^{-1} 1690 (C=O).

Anal. Calcd. for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.60; H, 6.05; N, 14.60.

1-Ethyl-3-phenyl-4-phenylimino-1,2,3,4-tetrahydro-1,3,10-triazabenzazulen-2-one (**6aa**).

This compound had mp 204-205° (orange needles from hexane-dichloromethane); ^{1}H nmr: δ 1.49 (3H, t, J = 7.0 Hz), 4.46 (2H, q, J = 7.0 Hz), 6.51 (2H, d, J = 7.3 Hz), 6.70 (1H, t, J = 7.3 Hz), 6.95 (2H, t, J = 7.3 Hz), 7.00-7.20 (5H, m), 7.63 (1H, dd, J = 11.0 and 9.8 Hz), 7.78 (1H, dd, J = 10.4 and 9.8 Hz), 7.82 (1H, dd, J = 10.4 and 9.8 Hz), 7.89 (1H, d, J = 9.8 Hz),

and 8.56 (1H, d, J = 11.0 Hz); ir: cm^{-1} 1684 (C=O); ms: m/z (relative intensity) 394 (M^++2, 30), 393 (M^++1, 75), 392 (M^+, 100), 391 (80).

Anal. Calcd. for $C_{25}H_{20}N_4O$: C, 76.51; H, 5.14; N, 14.28. Found: C, 76.61; H, 5.33; N, 14.15.

1-Ethyl-3-phenyl-1,2,3,4-tetrahydro-1,3,10-triazabenzazulene-2,4-dione (**7aa**).

This compound had mp 270-271° (yellow needles from hexane-dichloromethane); ^1H nmr δ 1.50 (3H, t, J = 7.0 Hz), 4.50 (2H, q, J = 7.0 Hz), 7.34 (2H, d, J = 7.9 Hz), 7.40-7.60 (3H, m), 7.90-8.10 (3H, m), 8.68 (1H, d, J = 10.4 Hz), and 9.30-9.40 (1H, m); ir: cm^{-1} 1706 and 1658 (C=O); ms: m/z (relative intensity) 317 (M^+, 92), 289 (100).

Anal. Calcd. for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.67; H, 4.92; N, 13.08.

2-Ethylamino-3-phenylcarbamoyl-1-azaazulene (**8aa**).

This compound had mp 176-177° (yellow prisms from hexane-dichloromethane); ^1H nmr: δ 1.34 (3H, t, J = 7.3 Hz), 3.74 (2H, qd, J = 7.3 and 5.5 Hz), 7.16 (1H, t, J = 7.3 Hz), 7.32 (1H, t, J = 9.8 Hz), 7.40-7.65 (7H, m), 7.70 (1H, br s), 8.02 (1H, d, J = 9.8 Hz), and 8.08 (1H, d, J = 10.4 Hz); ir: cm^{-1} 3388, 3300 (NH), and 1644 (C=O).

Anal. Calcd. for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 73.92; H, 5.98; N, 14.21.

2-[*N*-Ethyl-*N'*-(*p*-tolyl)ureido]-1-azaazulene (**5ab**).

This compound had mp 98-99° (orange prisms from hexane); ^1H nmr δ 1.40 (3H, t, J = 7.0 Hz), 2.34 (3H, s), 4.17 (2H, q, J = 7.0 Hz), 6.87 (1H, s), 7.17 (2H, t, J = 7.9 Hz), 7.50-7.75 (5H, m), 8.24 (1H, d, J = 10.4 Hz), 8.28 (1H, d, J = 9.8 Hz), and 13.43 (1H, s); ir: cm^{-1} 1682 (C=O).

Anal. Calcd. for $C_{19}H_{19}N_3O$: C, 74.73; H, 6.27; N, 13.76. Found: C, 74.39; H, 6.42; N, 13.95.

1 -Ethyl-3-*p*-tolyl-1,2,3,4-tetrahydro-1,3,10-triazabenzazulene-2,4-dione (**7ab**).

This compound had mp 263-264° (yellow needles from hexane-dichloromethane); ^1H nmr: δ 1.50 (3H, t, J = 7.0 Hz), 2.43 (3H, s), 4.49 (2H, q, J = 7.0 Hz), 7.22 (2H, d, J = 7.9 Hz), 7.34 (2H, d, J = 7.9 Hz), 7.90-8.05 (3H, m), 8.67 (1H, d, J = 10.4 Hz), and 9.30-9.40 (1H, m); ir: cm^{-1} 1710 and 1662 (C=O); ms: m/z (relative intensity) 331 (M^+, 100), 330 (32).

Anal. Calcd. for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17; N, 12.68. Found: C, 72.76; H, 5.27; N, 12.68.

2-Ethylamino-3-*p*-tolylcarbamoyl-1-azaazulene (**8ab**).

This compound had mp 191-193° (orange prisms from hexane); ^1H nmr: δ 1.34 (3H, t, J = 7.3 Hz), 2.36 (3H, s), 3.75 (2H, qd, J = 7.3 and 6.1 Hz), 7.20 (2H, d, J = 7.9 Hz), 7.33 (1H, t, J = 9.8 Hz), 7.44 (2H, d, J = 7.9 Hz), 7.40-7.75 (3H, m), 7.70 (1H, br s), 8.03 (1H, d, J = 9.8 Hz), and 8.09 (1H, d, J = 9.8 Hz); ir: cm^{-1} 3352, 3320 (NH), and 1640 (C=O).

Anal. Calcd. for $C_{19}H_{19}N_3O$: C, 74.73; H, 6.27; N, 13.76. Found: C, 74.95; H, 6.27; N, 14.21.

2-(*N*-Ethyl-*N'*-tosylureido)-1-azaazulene (**5ac**).

This compound had mp 128-129° (orange needles from ethyl acetate); ^1H nmr: δ 1.29 (3H, t, J = 7.0 Hz), 2.41 (3H, s), 4.00 (2H, q, J = 7.0 Hz), 6.81 (1H, s), 7.31 (2H, d, J = 7.9 Hz), 7.60-7.80 (3H, m), 8.05 (2H, d, J = 7.9 Hz), 8.31 (1H, d, J = 9.8 Hz), 8.35-8.45 (1H, m), and 13.40 (1H, s); ir: cm^{-1} 3124 (NH) and 1696 (C=O).

Anal. Calcd. for $C_{19}H_{19}N_3O_3S$: C, 61.77; H, 5.18; N, 11.37. Found: C, 61.59; H, 5.23; N, 10.96.

1-Ethyl-3-tosyl-1,2,3,4-tetrahydro-1,3,10-triazabenzazulene-2,4-dione (**7ac**).

This compound had mp 214-216° (yellow needles from hexane-dichloromethane); ^1H nmr: δ 1.41 (3H, t, J = 7.0 Hz), 2.46 (3H, s), 4.37 (2H, q, J = 7.0 Hz), 7.40 (2H, d, J = 7.9 Hz), 7.95-8.10 (3H, m), 8.28 (2H, d, J = 7.9 Hz), 8.55-8.65 (1H, m), and 9.25-9.35 (1H, m); ir: cm^{-1} 1724 and 1696 (C=O).

Anal. Calcd. for $C_{20}H_{17}N_3O_4S$: C, 60.75; H, 4.33; N, 10.63. Found: C, 60.83; H, 4.57; N, 10.63.

2-Ethylamino-3-tosylcarbamoyl-1-azaazulene (**8ac**).

This compound had mp 237-238° (yellow needles from hexane-dichloromethane); ir: cm^{-1} 3220 (NH) and 1644 (C=O).

Anal. Calcd. for $C_{19}H_{19}N_3O_3S$: C, 61.77; H, 5.18; N, 11.37. Found: C, 61.65; H, 5.26; N, 11.52.

2-(*N*-Isopropyl-*N'*-phenylureido)-1-azaazulene (**5ba**).

This compound had mp 148-149° (orange prisms from hexane); ^1H nmr: δ 1.66 (6H, d, J = 6.7 Hz), 4.94 (1H, sep, J = 6.7 Hz), 6.99 (1H, s), 7.06 (1H, t, J = 7.3 Hz), 7.35 (2H, t, J = 7.3 Hz), 7.50-7.70 (5H, m), 7.64 (1H, d, J = 10.4 Hz), 7.67 (1H, d, J = 9.8 Hz), and 13.42 (1H, br s); ir: cm^{-1} 3108 (NH) and 1690 (C=O).

Anal. Calcd. for $C_{19}H_{19}N_3O$: C, 74.73; H, 6.27; N, 13.76. Found: C, 74.49; H, 6.39; N, 13.89.

1-Isopropyl-3-phenyl-4-phenylimino-1,2,3,4-tetrahydro-1,3,10-triazabenzazulen-2-one (**6ba**).

This compound had mp 163-164° (orange prisms from hexane-chloroform); ^1H nmr: δ 1.70 (6H, d, J = 6.7 Hz), 5.60 (1H, sep, J = 7.0 Hz), 6.50 (2H, d, J = 7.3 Hz), 6.69 (1H, t, J = 7.3 Hz), 6.93 (2H, t, J = 7.3 Hz), 7.05-7.20 (5H, m), 7.65 (1H, dd, J = 11.0 and 9.8 Hz), 7.78 (1H, dd, J = 10.4 and 9.8 Hz), 7.82 (1H, dd, J = 10.4 and 9.8 Hz), 7.88 (1H, d, J = 9.8 Hz), and 8.54 (1H, d, J = 11.0 Hz); ir: cm^{-1} 1704 (C=O) and 1640 (C=N); ms: m/z (relative intensity) 406 (M^+, 100), 405 (99).

Anal. Calcd. for $C_{26}H_{22}N_4O$: C, 76.82; H, 5.46; N, 13.78. Found: C, 76.53; H, 5.46; N, 13.48.

2-Isopropylamino-3-phenylcarbamoyl-1-azaazulene (**8ba**).

This compound had mp 170-171° (yellow prisms from hexane); ^1H nmr: δ 1.35 (6H, d, J = 6.7 Hz), 4.51 (1H, m), 7.17 (1H, t, J = 7.3 Hz), 7.25-7.65 (9H, m), 8.04 (1H, d, J = 10.4 Hz), and 8.10 (1H, d, J = 10.4 Hz); ir: cm^{-1} 3364, 3280 (NH), and 1628 (C=O)

Anal. Calcd. for $C_{19}H_{19}N_3O$: C, 74.73; H, 6.27; N, 13.76. Found: C, 74.39; H, 6.39; N, 13.72.

3-(*N,N'*-Diphenyl)amidino-2-piperidino-1-azaazulene (**10a**).

This compound had mp 233-234° (yellow prisms from hexane-dichloromethane); ^1H nmr: δ 1.50-1.70 (6H, m), 3.60-3.80 (4H, m), 6.40-7.50 (10H, m), 7.18 (1H, t, J = 9.8 Hz), 7.26 (1H, dd, J = 10.4 and 9.8 Hz), 7.38 (1H, t, J = 9.8 Hz), 7.70 (1H, d, J = 10.4 Hz), 7.78 (1H, d, J = 9.8 Hz), and 7.60-8.20 (1H, br); ir: cm^{-1} 3108 (NH) and 1630 (C=N); ms: m/z (relative intensity) 406 (M^+, 100), 316 (71).

Anal. Calcd. for $C_{27}H_{26}N_4$: C, 79.77; H, 6.45; N, 13.78.

Found: C, 79.93; H, 6.51; N, 13.55.

2-Piperidino-3-phenylcarbamoyl-1-azaazulene (**11a**).

This compound had mp 261-263° (yellow prisms from hexane-dichloromethane); ^{1}H nmr: δ 1.65-1.80 (6H, m), 3.55-3.65 (4H, m), 7.15 (1H, t, J = 7.9 Hz), 7.40 (2H, t, J = 7.9 Hz), 7.45-7.70 (3H, m), 7.77 (2H, d, J = 7.9 Hz), 8.18 (1H, d, J = 9.8 Hz), 8.89 (1H, s), and 8.91 (1H, d, J = 9.8 Hz); ir: cm^{-1} 3210, 3164, 3108 (NH), and 1668 (C=O); ms: m/z (relative intensity) 331 (M^+, 54), 240 (100).

Anal. Calcd. for $C_{21}H_{21}N_3O$: C, 76.09; H, 6.39; N, 12.68. Found: C, 75.82; H, 6.41; N, 12.54.

3-(*N,N'*-Di-*p*-tolyl)amidino-2-piperidino-1-azaazulene (**10b**).

This compound had mp 262-263° (yellow prisms from ethyl acetate); ^{1}H nmr: δ 1.50-1.70 (6H, m), 2.10-2.30 (6H, br), 3.70-3.85 (4H, m), 6.50-7.30 (8H, m), 7.17 (1H, t, J = 9.8 Hz), 7.25 (1H, t, J = 9.8 Hz), 7.39 (1H, t, J = 9.8 Hz), 7.71 (1H, d, J = 9.8 Hz), 7.78 (1H, d, J = 9.8 Hz), and 7.50-8.00 (1H, br); ir: cm^{-1} 3276 (NH) and 1634 (C=N); ms: m/z (relative intensity) 434 (M^+, 12), 328 (100).

Anal. Calcd. for $C_{29}H_{30}N_4$: C, 80.15; H, 6.96; N, 12.89. Found: C, 80.18; H, 7.07; N, 12.96.

2-Piperidino-3-*p*-tolylcarbamoyl-1-azaazulene (**11b**).

This compound had mp 222-223° (orange prisms from ethyl acetate); ^{1}H nmr: δ 1.65-1.80 (6H, m), 2.36 (3H, s), 3.55-3.65 (4H, m), 7.21 (2H, d, J = 7.9 Hz), 7.45-7.64 (3H, m), 7.65 (2H, d, J = 7.9 Hz), 8.17 (1H, d, J = 9.8 Hz), 8.79 (1H, s), and 8.88 (1H, d, J = 10.4 Hz); ir: cm^{-1} 3210, 3164, 3105 (NH), and 1668 (C=O).

Anal. Calcd. for $C_{22}H_{23}N_3O$: C, 76.49; H, 6.71; N, 12.16. Found: C, 76.10; H, 6.71; N, 11.89.

Rearrangement of **5aa**.

a) A solution of **5aa** (0.100 g) in dry xylene (20 ml) was refluxed for 2 days, then evaporated. Chromatography of the residue with chloroform then ethyl acetate gave **5aa** (0.054 g, 54%), 1,3-diphenylurea (0.01 g, 1%), **8aa** (0.039 g, 39%), and **4a** (0.004 g, 7%), successively.

b) A mixture of **5aa** (0.400 g) and zinc chloride (0.200 g) in dry xylene (50 ml) was refluxed for 20 hours, then the solvent was evaporated. Chromatography of the residue gave **5aa** (0.016 g, 4%), 1,3-diphenylurea (0.090 g, 40%), **8aa** (0.033 g, 8%), and **4a** (0.170 g, 72%), successively.

c) A solution of **5aa** (0.200 g) and phenyl isocyanate (30 ml) was refluxed for 9 days, then evaporated. Chromatography of the residue gave **5aa** (0.077 g, 39%), 1,3-diphenylurea (0.130 g), **8aa** (0.110 g, 55%), and **4a** (0.005 g, 4%), successively.

Reaction of **8aa** with Phenyl Isocyanate.

A mixture of **8aa** (0.100 g, 0.343 mmole), phenyl isocyanate (0.164 g, 1.38 mmoles), and zinc chloride (0.100 g, 0.73 mmole) in dry xylene (30 ml) was refluxed for 2 days, then the solvent was evaporated. Chromatography of the residue gave **6aa** (0.003 g, 2.3%), **7aa** (0.072 g, 66%), and **8aa** (0.014 g, 14%).

Reaction of **11a** with Phenyl Isocyanate.

A mixture of **11a** (0.100 g, 0.30 mmole) and phenyl isocyanate (0.260 g, 2.18 mmoles) in dry xylene (30 ml) was refluxed for 2 days, then the solvent was evaporated. Chromatography of the residue with chloroform-ethyl acetate gave **10a** (0.038 g, 40%) and **11a** (0.055 g, 55%).

Reaction of 2-isopropylamino-1-azaazulene (**4b**) with Chorosulfonyl Isocyanate.

A solution of **4b** (0.200 g, 1.07 mmoles) and chorosulfonyl isocyanate (0.456 g, 3.22 moles) in dry xylene (30 ml) was refluxed for 1 hour, then evaporated. To the residue water was added, the mixture was then neutralized with sodium hydrogencarbonate and extracted with chloroform. The extract was dried (sodium sulfate) and evaporated. Chromatography of the residue with chloroform gave 2-isopropylamino-1-azaazulene-3-carbonitrile (**12**) (0.154 g, 68%) and 3-chloro-2-isopropylamino-1-azaazulene (**13**) (0.001 g, 4.0%).

Compound **12** had mp 153-154° (yellow prisms from hexane); ^{1}H nmr: δ 1.37 (6H, d, J = 6.7 Hz), 4.53 (1H, sep, J = 6.7 Hz), 5.30-5.45 (1H, br), 7.47 (1H, t, J = 9.8 Hz), 7.60 (1H, t, J = 9.8 Hz), 7.68 (1H, t, J = 9.8 Hz), and 8.04 (2H, d, J = 9.8 Hz); ir: cm^{-1} 3308 (NH) and 2212 (CN); ms: m/z (relative intensity) 211 (M^+, 45), 169 (100).

Anal. Calcd. for $C_{13}H_{13}N_3$: C, 73.91; H, 6.20; N, 19.89. Found: C, 74.02; H, 6.30; N, 19.66.

The compound **13** had mp 90-91° (orange needles from hexane); ^{1}H nmr δ 1.38 (6H, d, J = 6.7 Hz), 4.51 (1H, sep, J = 6.7 Hz), 4.95-5.05 (1H, br), 7.23 (1H, t, J = 9.8 Hz), 7.34 (1H, t, J = 9.8 Hz), 7.41 (1H, t, J = 9.8 Hz), 7.75 (1H, d, J = 9.8 Hz), and 8.04 (1H, d, J = 9.8 Hz); ir: cm^{-1} 3224 (NH).

Anal. Calcd. for $C_{12}H_{13}N_2Cl$: C, 65.31; H, 5.94; N, 12.69. Found: C, 65.26; H, 6.10; N, 12.66.

Reaction of 2-Piperidino-1-azaazulene (**9**) with Chorosulfonyl Isocyanate.

A solution of **9** (0.500 g, 2.35 mmoles) and chorosulfonyl isocyanate (1.00 g, 7.07 mmoles) in dry xylene (30 ml) was refluxed for 2 hours, then evaporated. To the residue water was added, the mixture was then neutralized with sodium hydrogencarbonate and extracted with chloroform. The extract was dried (sodium sulfate) and evaporated. Chromatography of the residue with chloroform gave 2-piperidino-1-azaazulene-3-carbonitrile (**14**) (0.337 g, 61%) and 3-chloro-2-piperidino-1-azaazulene (**15**) (0.045 g, 8.0%).

Compound **14** had mp 89-90° (orange prisms from hexane-dichloromethane); ^{1}H nmr: δ 1.70-1.80 (6H, m), 4.00-4.10 (4H, m), 7.41 (1H, t, J = 9.8 Hz), 7.58 (1H, dd, J = 10.4 and 9.8 Hz), 7.64 (1H, t, J = 9.8 Hz), 7.94 (1H, d, J = 10.4 Hz), and 8.02 (2H, d, J = 9.8 Hz); ir: cm^{-1} 2200 (CN); ms: m/z (relative intensity) 237 (M^+, 83), 208 (100).

Anal. Calcd. for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.96; H, 6.52; N, 17.82.

Compound **15** was orange oil; ^{1}H nmr: δ 1.70-1.78 (6H, m), 4.00-4.10 (4H, m), 7.24 (1H, t, J = 9.8 Hz), 7.37 (1H, t, J = 9.8 Hz), 7.42 (1H, dd, J = 10.4 and 9.8 Hz), 7.81 (1H, d, J = 9.8 Hz), and 7.82 (1H, d, J = 10.4 Hz). Picrate of **15** had mp 190-191°.

Anal. Calcd. for $C_{20}H_{18}N_5O_7Cl$: C, 50.48; H, 3.81; N, 14.72. Found: C, 50.78; H, 4.12; N, 15.03.

Synthesis of **14**.

A solution of 2-chloro-1-azaazulene-3-carbonitrile **16** (0.150 g) and piperidine (1.0 ml) in 1-butanol (15 ml) was refluxed for 6 days, then evaporated. Chromatography of the residue with chloroform gave **14** (0.183 g, 97%).

Synthesis of **13**.

A solution of **4b** (0.400 g, 2.15 mmoles) and NCS (0.290 g, 2.17 mmoles) in chloroform (50 ml) was stirred for 1 hour at

room temperature. The precipitate was filtered off, and the filtrate was evaporated. Chromatography of the residue with chloroform gave **13** (0.310 g, 65%) and **4b** (0.127 g, 32%).

Synthesis of **15**.

A solution of **9** (0.200 g, 0.94 mmoles) and NCS (0.130 g, 0.97 mmole) in chloroform (30 ml) was stirred for 1 hour at room temperature. The precipitate was filtered off, and the filtrate was evaporated. Chromatography of the residue with chloroform gave **15** (0.204 g, 88%) and 9 (0.020 g, 10%).

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