The Nucleophilic Displacement Reactions of 8-Chloro- and 2,8-Dichloro-3-phenyl-1-azaazulenes[1]

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The reaction of 3-phenylpyrrolo[2,3-*b*]tropone (**7**) with phosphoryl chloride gave 8-chloro-3-phenyl-1-azaazulene (**5**). When **5** and **7** were treated with *N*-chlorosuccinimide, 2,8-dichloro-3-phenyl-1-azaazulene (**6**) and 2-chloro-3-phenylpyrrolo[2,3-*b*]tropone (**8**) were obtained respectively. **6** was also obtained from **8** by treatment with phosphoryl chloride. The reactions of **5** and **6** with nucleophilic reagents gave the corresponding substituted products (**14a**—**m** and **15a**—**m**). 8-Hydrazino-3-phenyl-1-azaazulene (**14m**) and 2-chloro-8-hydrazino-3-phenyl-1-azaazulene (**10**), which had been obtained by the reaction of **5** and **6** with hydrazine hydrate, were decomposed by treatment with copper(II) sulfate in acetic acid to give 3-phenyl-1-azaazulene (**2**) and 2-chloro-3-phenyl-1-azaazulene (**11**) respectively.

1-Azaazulene (**1**),[2] a seven-membered analog of indole, and its 3-phenyl derivative (**2**),[3] were synthesized a little more than twenty years ago by one of the present authors (T. N.) and his co-workers; the molecular diagram of this interesting compound (**1**) was calculated by Kon[4] (*cf.* Fig. 1). As the reactivity of the same

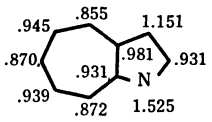
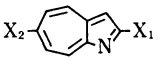


Fig. 1. Charge density of 1-azaazulene calculated by H. Kon.[4]

functional group should be different according to its position in such a nonbenzenoid nucleus, we first studied the nucleophilic substitution reaction of 2-chloro- (**3**)[2] and 2,6-dichloro-1-azaazulene (**4**).[5] Brief mention was

(**1**): R=H
(**2**): R=Ph

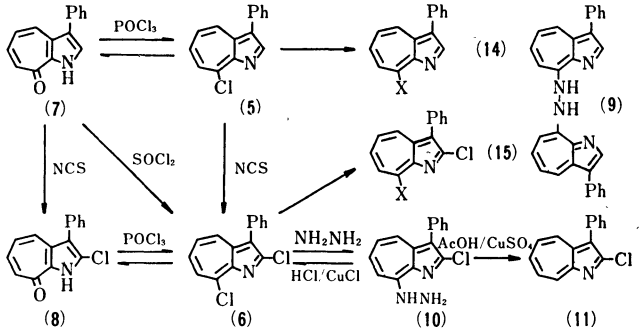


(**3**): X_1=Cl, X_2=H
(**4**): X_1=X_2=Cl

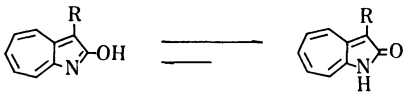
also made of the nucleophilic displacement reaction of 8-chloro-(**5**)[1,3] and 2,8-dichloro-3-phenyl-1-azaazulene (**6**),[1] the results of which have remained unpublished. We now wish to report on the nucleophilic substitution reaction of these two compounds (**5** and **6**).

Results and Discussion

The reaction of 3-phenylpyrrolo[2,3-*b*]tropone (3-phenylcyclohept[2,3-*b*]pyrrol-8-one) (**7**)[3] with phosphoryl chloride gives 8-chloro-3-phenyl-1-azaazulene (**5**) as reddish purple needles. When **5** and **7** are treated with *N*-chlorosuccinimide, dichloro- (**6**) and monochloro compound (**8**) are obtained respectively in good yields. The same compound (**6**) is also obtained by the treatment of **5** or **7** with thionyl chloride or sulfuryl chloride, but in poor yields. Compound **6** is also obtained from **8** by treatment with phosphoryl chloride. Compounds (**5** and **6**) afford **7** and **8** respectively on treatment with ethanolic alkali. Similarly, one of the two chlorine atoms in **6** is easily replaced by a hydrazino group on treatment with hydrazine hydrate to give **10**; the latter compound (**10**) reverts back to **6** upon treatment with concentrated hydrochloric acid and copper(I) chloride, while the monochloro compound (**11**) is obtained when **10** is decomposed by treatment with copper(II) sulfate in acetic acid.



When **11** is treated with ethanolic alkali, 1,2-dihydro-3-phenyl-1-azaazulen-2-one (**12**) is formed as a saponification product. The structure of **12** was confirmed by a direct comparison with the sample obtained by the reaction of aminotropone with methyl phenylacetate.



(**12**) : R=Ph
(**13**) : R=H

From the above-mentioned experimental evidence and the results of elemental analyses, **6** is identified as 2,8-dichloro-3-phenyl-1-azaazulene. The UV and NMR spectra of **5** and **6** also support the structure described above (Tables 4 and 5).

8-Hydroxy, 8-amino, and related derivatives of 1-azaazulene have two tautomeric forms, such as A and B. It seems that those substances exist mainly in their

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Table 1. Nucleophilic substitution reaction products (**14**) from 8-chloro-3-phenyl-1-azaazulene (**5**)

Compound	X	Reagent/Solvent	React Temp	React Time	Yield (%)	Mp °C Appearance (Color, crystal form)	Formula	Found (Calcd) % C	H	N	S
14a	OCH_3 (Picrate)	$CH_3ONa/MeOH$	boiling	0.5 h	(97)	190—191 yellow micro needles[a]	$C_{22}H_{16}O_8N_4$	56.59 (56.90)	3.43 3.47	12.16 12.07)	
14b	OCH_2CH_3 (Picrate)	C_2H_5ONa/C_2H_5OH	boiling	0.5 h	(98)	177—178 yellow micro needles[a]	$C_{23}H_{18}O_8N_4$	57.56 (57.74	3.48 3.70	11.44 11.71)	
14c	NH_2	$NH_3/MeOH$	room temp	3 days	65	200—201 yellow micro needles[b]	$C_{15}H_{12}N_2$	81.65 (81.79	5.24 5.49	12.63 12.72)	
14d	$NHCOCH_3$	$(CH_3CO)_2O$/—	100 °C	5 min	71	160—161 red needles[c]	$C_{17}H_{14}ON_2$	77.74 (77.84	5.69 5.38	11.10 10.68)	
14e	SH	a : $NaSH/C_2H_5OH$ b : NaSH/DMSO	boiling room temp	0.5 h 15 min	a : 17 b : 70	161—162 orange yellow prisms[c]	$C_{15}H_{11}NS$	76.04 (75.93	4.75 4.67	5.68 5.90)	
14f	$SC_6H_4CH_3$-*p*	*p*-$CH_3C_6H_4SH$/DMSO	room temp	10 min	70	177 (decomp) red plates[c]	$C_{22}H_{17}NS$	81.28 (80.71	5.20 5.24	4.25 4.28	10.17 9.78)
14g	NHC_6H_5	$C_6H_5NH_2/C_2H_5OH$	boiling	5 min	76	153—154 orange yellow prisms[c]	$C_{21}H_{16}N_2$	85.15 (85.11	5.32 5.44	9.33 9.45)	
14h	$NHCH(CH_3)_2$ (Picrate)	$(CH_3)_2CHNH_2/C_2H_5OH$	boiling	30 min	(93)	237—239 yellow needles[a]	$C_{24}H_{21}O_7N_5$	58.73 (58.65	4.32 4.31	14.32 14.25)	
14i	$NHC_6H_4CH_3$-*p*	*p*-$CH_3C_6H_4NH_2$/DMSO	room temp	10 min	93	145—146 yellow needles[d]	$C_{22}H_{18}N_2$	85.05 (85.13	5.83 5.85	8.94 9.03)	
14j	$NHC_6H_4N(CH_3)_2$	$(CH_3)_2C_6H_4NH_2$/DMSO	room temp	15 min	64	165—167 orange prisms[c]	$C_{23}H_{21}N_3$	81.11 (81.38	6.22 6.24	12.46 12.38)	
14k	$N(CH_3)_2$	a : $(CH_3)_2NH/C_2H_5OH$ b : $(CH_3)_2NH$/DMSO	boiling room temp	15 min 15 min	a : 42 b : 81	125—127 orang yellow prisms[c]	$C_{17}H_{16}N_2$	82.29 (82.22	6.49 6.50	11.29 11.28)	
14l	 (Picrate)	 /DMSO	room temp	15 min	(88)	200—202 yellow micro needles[a]	$C_{25}H_{21}O_8N_5$	57.92 (57.80	4.18 4.08	13.24 13.48)	
14m	$NHNH_2$	$NH_2NH_2 \cdot H_2O$/MeOH	room temp	2 h	40	139—140 orange needles[c]	$C_{15}H_{13}N_3$	76.67 (76.57	5.00 5.57	17.86 17.86)	
2	H (Picrate)	$CuSO_4/AcOH$-H_2O	100 °C	5 min	(60)	236 (decomp) orange needles[a]	$C_{21}H_{14}O_7N_4$	57.92 (58.07	3.44 3.25	12.52 12.90)	
	(Styphnate)					230 (decomp) red needles[a]	$C_{21}H_{14}O_8N_4$	56.48 (56.00	3.04 3.13	12.44 12.44)	

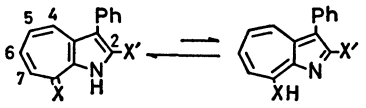
These solvents were used for the recrystallization: a) ethanol, b) benzene, c) cyclohexane, d) hexane. Compound **14d** was obtained by the acetylation of **14c**. Compound **2** was obtained from **14m**.

TABLE 2. NUCLEOPHILIC SUBSTITUTION REACTION PRODUCTS (15) FROM 2,8-DICHLORO-3-PHENYL-1-AZAAZULENE (6)

Compound	X	Reagent/Solvent	React Temp	React Time	Yield (%)	Mp °C Appearance (Color, crystal form)	Formula	Found (Calcd) % C	H	N	S
15a	OCH_3	$CH_3ONa/MeOH$	boiling	0.5 h	92	150—151 orange micro needles[e]	$C_{16}H_{12}ONCl$	71.64 (71.24	4.52 4.49	5.32 5.19)	
15b	OC_2H_5	C_2H_5ONa/C_2H_5OH	boiling	0.5 h	26	99—100 orange plates[f]	$C_{17}H_{14}ONCl$	72.07 (71.95	5.01 4.97	4.91 4.94)	
15c	NH_2	$NH_3/MeOH$	room temp	a week	67	185—186 yellow micro needles[b]	$C_{15}H_{11}N_2Cl$	70.81 (70.72	4.68 4.32	11.25 11.00)	
15d	$NHCOCH_3$	$(CH_3CO)_2O/—$	100 °C	5 min	77	171—172 orange needles[c]	$C_{17}H_{13}N_2OCl$	68.56 (68.80	4.59 4.41	9.52 9.44)	
15e	SH	a : $NaSH/C_2H_5OH$ b : NaSH/DMSO	boiling room temp	10 min 15 min	a : 53 b : 71	118 (decomp) reddish brown needles[c]	$C_{15}H_{10}NSCl$	66.46 (66.29	3.71 3.71	5.39 5.16)	
15f	$SC_6H_4CH_3$-*p*	*p*-$CH_3C_6H_4SH$/DMSO	room temp	15 min	69	216—217 orange plates[c]	$C_{22}H_{16}NSCl$	73.00 (73.01	4.50 4.46	3.90 3.87	8.90 8.86)
15g	NHC_6H_5	$C_6H_5NH_2/C_2H_5OH$	boiling	10 min	75	148—150 orange needles[g]	$C_{21}H_{15}N_2Cl$	76.11 (76.24	4.55 4.57	8.57 8.47)	
15h	$NHCH(CH_3)_2$	$(CH_3)_2CHNH_2/C_2H_5OH$	boiling	10 min	73	149—150 orange yellow needles[d]	$C_{18}H_{17}N_2Cl$	72.84 (72.76	5.77 5.77	9.44 9.52)	
15i	$NHC_6H_4CH_3$-*p*	*p*-$CH_3C_6H_4NH_2/C_2H_5OH$	boiling	10 min	85	143—144 orange prisms[d]	$C_{22}H_{17}N_2Cl$	77.13 (76.62	4.98 4.97	8.23 8.13)	
15j	$NHC_6H_4N(CH_3)_2$	$(CH_3)_2NC_6H_4NH_2/C_2H_5OH$	boiling	10 min	81	182—184 orange micro needles[c]	$C_{23}H_{20}N_3Cl$	74.09 (73.88	5.41 5.39	11.13 11.24)	
15k	$NH(CH_2)_3CH_3$ (Picrate)	$CH_3(CH_2)_3NH_2/C_2H_5OH$	boiling	3 h	(20)	169—170 yellow needles[a]	$C_{25}H_{22}N_5O_4Cl$	55.73 (55.61	4.11 4.11	12.55 12.97)	
15l	$N(CH_3)_2$	$(CH_3)_2NH_2/C_2H_5OH$	boiling	15 min	93	149—150 yellow plates[a]	$C_{17}H_{15}N_2Cl$	72.19 (72.20	5.28 5.35	9.89 9.91)	
15m			room temp	15 min	68	131—132 orange prisms[d]	$C_{19}H_{17}ONCl$	69.69 (70.25	5.29 5.28	8.59 8.63)	
10	$NHNH_2$	$NH_2NH_2 \cdot H_2O/MeOH$	room temp	3 h	82	175—176 orange needles[b]	$C_{15}H_{12}N_3Cl$	66.72 (66.79	4.20 4.45	15.49 15.58)	
15n	Br	$CuSO_4$-HBr	100 °C	5 min	25	154—155 red plates[c]	$C_{15}H_9NClBr$	56.42 (56.54	2.85 2.85	4.40 4.40)	
11	H	$CuSO_4/AcOH$-H_2O	100 °C	15 min	61	100 °C/1 Torr (Bp) red oil	$C_{15}H_{10}NCl$	74.84 (75.16	4.33 4.21	5.79 5.84)	
	(Picrate)					199 (decomp) orange needles[a]	$C_{21}H_{13}O_7N_4Cl$	54.06 (53.79	2.54 2.77	11.89 11.95)	

These solvents were used for the recrystallization: a) ethanol, b) benzene, c) cyclohexane, d) hexane, e) benzene-cyclohexane, f) petroleum ether, g) hexane-cyclohexane. Compound **15d** was obtained by the acetylation of **15c**. Compounds **15n** and **11** were both obtained from **10**.

TABLE 3. UV, IR, AND NMR SPECTRA OF SUBSTITUTION REACTION PRODUCTS

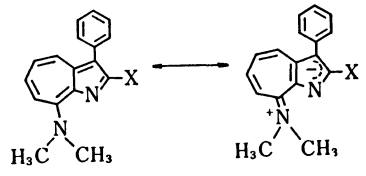


Compound	X	X′	UV λ_{max}, nm (log ε)	IR (KBr) cm^{-1}	NMR ppm in $CDCl_3$ (100 MHz)
7	O	H	228(4.51), 290(4.49) 345(3.68), 360(3.77) 380(3.78) (MeOH)	3183, 1619 1552, 1520	6.88(1H, ddd, J=10.5, 7.3, 2.0 Hz, H-5) 7.28—7.54(7H, m, H-6, 7 and phenyl) 7.59(1H, s, H-2) 7.86(1H, dm, J=10.5 Hz, H-4)
8	O	Cl	230(4.42), 287(4.38) 362(3.76), 373(3.65) (MeOH)	3080, 1621 1548, 1513	6.85(1H, ddd, J=10.5, 6.8, 2.8 Hz, H-5) 7.28—7.48(7H, m, H-6, 7 and phenyl) 7.58(1H, dm, J=10.5 Hz, H-4)
14c	NH	H	243(4.51), 316(4.52) 445(3.03) (MeOH)	3460, 3300 1610, 1595 1548	6.39(bs, NH) 6.88—7.61(8H, m, H-5, 6, 7 and phenyl) 8.19(1H, s, H-2) 8.28(1H, dm, J=10.5 Hz, H-4)
15c	NH	Cl	249(4.48), 312(4.62) 412(3.46) (MeOH)	3471, 3316 1614, 1601 1554	6.36(b, NH) 6.91—7.56(8H, m, H-5, 6, 7 and phenyl) 8.04(1H, dm, J=9.8 Hz, H-4)
14e	S	H	257(4.36), 308(4.00) 407(4.13) (cyclohexane)	3280, 1601 1496	7.06—7.52(7H, m, H-5, 6 and phenyl) 7.67(1H, d, J=2.7 Hz, H-2) 7.89(1H, dd, J=8.0, 2.4 Hz, H-7) 8.25(1H, dd, J=9.2, 2.4 Hz, H-4)
15e	S	Cl	256(4.34), 309(3.94) 413(4.13) (cyclohexane)	3248, 1602 1494	7.03—7.72(8H, m, H-5, 6, 7 and phenyl) 8.21(1H, dd, J=9.3, 2.0 Hz, H-4)
14k	$N(CH_3)_2$	H	252(4.41), 264(4.38) 329(4.56), 408(3.32) (cyclohexane)	1612, 1513	3.63(6H, s, $N(CH_3)_2$) 6.81(1H, ddd, J=10.0, 8.6, 1.0 Hz, H-5) 7.12(1H, dm, J=12.0 Hz, H-7) 7.30—7.62(7H, m, H-6 and phenyl) 8.28(1H, dm, J=10.0 Hz, H-4)
15l	$N(CH_3)_2$	Cl	253(4.38), 265(4.40) 331(4.54), 390(3.72) 412(3.70) (sh), 447 (3.52) (sh) (cyclohexane)	1613, 1518	3.60(6H, s, $N(CH_3)_2$) 6.83(1H, ddd, J=10.0, 8.4, 1.0 Hz, H-5) 7.09(1H, dm, J=11.6 Hz, H-7) 7.25—7.53 (7H, m, H-6 and phenyl) 7.94(1H, dm, J=10.0 Hz, H-4)

ketonic form (B) rather than in the enolic form (A), as in the case of 2-hydroxy derivatives of 1-azaazulene (**13**)[6] or its 3-substituted products (**12** or other compounds),[5] as is shown by their spectroscopic data, presented in Table 3.

(A) (B)

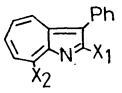
As for the 8-dimethylamino derivatives (**14k** and **15l**), the visible and PMR spectra indicate that there is a contribution of the zwitterion structure (D),[5] as will be described below. In the absorption spectra of **14k** and **15l**, the absorption maxima in the visible region were shifted to shorter wavelengths than those of **5** and **6** (Tables 3 and 4). The PMR spectra of **14k** and **15l** exhibited the signals for H-5 at *ca.* 6.8 PMR, and they were observed upfield from those of **5** and **6**, as in the case of the 8-hydroxy derivatives of 1-azaazulene (**7** and **8**) (Tables 3 and 5).



(C) (D)

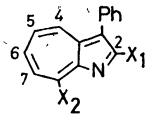
The C_8-positions of Compounds **5** and **6** are easily replaced by the treatment of various nucleophilic reagents; the results are summarized in Tables 1 and 2. Only the chlorine atom at C_8 in the dichloro compound (**6**) is displaced by the nucleophilic reagent. However, a strong nucleophile such as *p*-thiocresol afforded a disubstituted product (**16**). This is quite understandable in view of Fig. 1 and the electron-releasing effect

TABLE 4. ULTRAVIOLET AND VISIBLE ABSORPTION MAXIMA OF SUBSTITUTED 1-AZAAZULENES



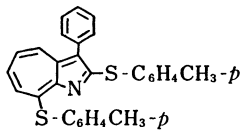
Compound	X_1	X_2	λ_{max}, nm (log ε)
2	H	H	227(4.81), 285(4.95), 358(4.14), 512(3.30) (MeOH)
5	H	Cl	237(4.59), 296(4.61), 528(2.82) (cyclohexane)
6	Cl	Cl	242(4.58), 298(4.65), 379(3.31), 500(2.89) (cyclohexane)
11	Cl	H	232(4.39), 288(4.53), 370(3.40), 500(2.87) (cyclohexane)

TABLE 5. NMR SPECTRA OF **5** AND **6**



Compound	X_1	X_2	ppm in $CDCl_3$ (100 MHz)
5	H	Cl	7.37—7.65(6H, m, H-5 and phenyl) 7.77(1H, ddd, J=10.3, 9.0, 1.0 Hz, H-6) 8.01(1H, dd, J=10.3, 2.0 Hz, H-7) 8.68(1H, dd, J=9.0, 1.5 Hz, H-4) 8.89(1H, s, H-2)
6	Cl	Cl	7.42—7.86(7H, m, H-5, 6 and phenyl) 8.02(1H, dd, J=9.9, 2.0 Hz, H-7) 8.39(1H, dd, J=9.0, 2.4 Hz, H-4)

of the reaction products (**15**).



(**16**)

The reaction of **5** with hydrazine hydrate in methanol gave **9** besides **14m**.[3]

Experimental†

All the melting points are uncorrected.

Phenylacetaldehyde Troponylhydrazone. To a solution of 2-hydrazinotropone (16.7 g) in ethanol (200 ml), phenylacetaldehyde (16.1 g) was added, and the mixture was refluxed for 30 min. After cooling, the separated precipitates were collected and recrystallized from ethanol to give yellow needles (27.5 g, 94%); mp 127—128 °C. UV: λ_{max}^{MeOH} 252 (log ε=4.32), 350 (4.24), and 410 (4.29) nm. Found: C, 75.33; H, 6.20; N, 11.70%. Calcd for $C_{15}H_{14}ON_2$: C, 75.60; H, 5.92; N, 11.76%.

3-Phenylpyrrolo[2,3-b]tropone (7). A mixture of phenylacetaldehyde troponylhydrazone (23.5 g), water (650 ml), and concd sulfuric acid (32 ml) was refluxed at 110—120 °C for 3 h. After cooling, the reaction mixture was made slightly acid with 2 M sodium hydroxide and, then extracted with chloroform. The extract was dried over anhydrous sodium sulfate, and the solvent was removed. The residue was recrystallized from benzene to give pale yellow needles (15.2 g, 70%); mp 188—189 °C. Found: C, 81.21; H, 5.09; N, 6.24%. Calcd for $C_{15}H_{11}ON$: C, 81.43; H, 5.01; N, 6.33%.

8-Chloro-3-phenyl-1-azaazulene (5). A mixture of **7** (7.0 g) and phosphoryl chloride (28.0 g) was heated at 105 °C for 1 h. After cooling, the reaction mixture was poured onto ice water and the solution was made alkaline with a sodium hydrogencarbonate solution, followed by extraction with benzene. The extract was dried, the solvent was removed, and the residue was recrystallized from cyclohexane to give reddish purple needles (6.5 g, 85%); mp 106—107 °C. Found: C, 75.57; H, 4.29; N, 6.01%. Calcd for $C_{15}H_{10}NCl$: C, 75.17; H, 4.18; N, 5.84%.

Picrate: Orange micro needles (from ethanol); mp 189 °C (decomp). Found: C, 53.75; H, 2.84; N, 11.34%. Calcd for $C_{21}H_{13}O_7N_4Cl$: C, 53.79; H, 2.78; N, 11.95%.

Hydrolysis of 5. A solution of **5** (0.3 g) in ethanol (8 ml) containing 2 M sodium hydroxide (4 ml) was refluxed for 30 min. The solvent was then removed, the residue was made acid with dil hydrochloric acid, and the solution was extracted with chloroform. The dried extract was concentrated, and the residue was recrystallized from ethanol to give colorless needles (0.11 g, 60%); mp 187—188 °C. The IR spectrum was identical with that of **7**, and the mixed melting point with the sample was not depressed.

2,8-Dichloro-3-phenyl-1-azaazulene (6). *(a)* A mixture of **5** (0.3 g) in carbon tetrachloride (210 ml), *N*-chlorosuccinimide (2.6 g), and benzoyl peroxide (0.06 g) was refluxed for 3 h. The solvent was then removed, and the residue was washed with hot water several times and extracted with benzene. The dried extract was concentrated to about 30 ml and chromatographed on silica gel. From the bright red effluent, **6** was obtained as bright red plates (2.5 g, 73%); mp 160—161 °C. Found: C, 65.76; H, 3.48; N, 5.58%.

† The authors are grateful to the Sankyo Co., Ltd., for the elemental analyses.

Calcd for $C_{15}H_9NCl_2$: C, 65.69; H, 3.28; N, 5.11%.

(b) A mixture of **7** (6.0 g) in dry benzene (300 ml) and thionyl chloride (20.0 g) was refluxed for 15 h with stirring at 80—90 °C. The solvent was then removed, and the residue was treated with a saturated solution of sodium hydrogencarbonate and extracted with benzene. The extract was dried, concentrated, and chromatographed on alumina. The red effluent gave bright red needles (1.5 g, 20%), which were subsequently recrystallized from cyclohexane. The mixed melting point with the sample obtained by Method (a) was not depressed.

(c) A mixture of **5** (6.0 g) in carbon tetrachloride (150 ml) and sulfuryl chloride (3.4 g) was refluxed for 1 h. The solvent was then removed, and the residue was treated with a saturated of sodium hydrogencarbonate and extracted with benzene. The extract was concentrated and chromatographed on alumina. From the red effluent, **6** was obtained as bright red plates (1.2 g, 35%).

From the purple effluent, a purple powder was obtained; its structure can not be clarified yet. Mp 193—195 °C. UV: $\lambda_{max}^{CHCl_3}$ 256, 302, and 514 nm. Found: C, 58.50; H, 2.64; N, 4.73; Cl, 34.39%. Calcd for $C_{15}H_8NCl_3$: C, 58.38; H, 2.61; N, 4.54; Cl, 34.37%.

(d) A mixture of **8** (0.5 g) and phosphoryl chloride (2.6 g) was heated at 105 °C for 1 h. After cooling, the reaction mixture was poured into ice water, and the solution was treated with a saturated solution of sodium carbonate and extracted with benzene. The dried extract was concentrated, and the residue was recrystallized from cyclohexane to give red plates (0.37 g, 63%). The mixed melting point with the sample obtained by Method (a) was not depressed.

(e) A mixture of **7** (0.6 g) in dry benzene (30 ml) and thionyl chloride (3.0 g) was heated under reflux for 16 h at 90—100 °C. The reaction mixture was then worked up as above (Method b). A small amount of **6** was obtained, and most of the starting material (**7**) was recovered.

(f) A mixture of **10** (0.1 g), concd hydrochloric acid (2.5 ml), and 1 M copper(II) sulfate (3 ml) was heated for a few min on a water hath. After cooling, the reaction mixture was neutralized with a 5% sodium hydrogencarbonate solution and extracted with benzene. The dried extract was concentrated and passed through a silica gel column. From the red effluent, **6** was obtained as red plates (0.06 g, 54%); mp 160—161 °C.

2-Chloro-3-phenylcyclohept[2,3-b]pyrrol-8(1H)-one (8). A mixture of **7** (1.0 g) in carbon tetrachloride (60 ml), *N*-chlorosuccinimide (0.97 g), and benzoyl peroxide (0.06 g) was refluxed for 3 h. The solvent was then removed, and the residue was treated with hot water and extracted with chloroform. The extract was washed with water, dried, and concentrated, and the residue was recrystallized from benzene to give pale yellow needles (0.52 g, 47%); mp 223—224 °C. Found: C, 70.44; H, 4.11; N, 5.58%. Calcd for $C_{15}H_{10}ONCl$: C, 70.45; H, 3.91; N, 5.48%. The spectral data are shown in Table 3.

Hydrolysis of 6. A solution of **6** (0.2 g) in ethanol (8 ml) containing 2 M sodium hydroxide (5 ml) was refluxed for 1 h on a water bath. The solvent was then removed, and the residue was made acid with dil sulfuric acid and extracted with chloroform. The dried extract was evaporated, and the residue was recrystallized from benzene to give pale yellow needles (0.18 g, 94%); mp 224—225 °C. The IR spectrum was identical with that of **8**, and the mixed melting point was not depressed.

The Reaction of 8-Chloro- and 2,8-Dichloro-3-phenyl-1-azaazulenes (5 and 6) with Nucleophilic Reagents. The mixtures obtained by the reaction of chloroazaazulenes (**5** and **6**) with nucleophilic reagents were worked up in the usual manner, and the products were purified by chromatography and recrystallization. The conditions and results are given in Tables 1 and 2.

The Reaction of 8-Chloro-3-phenyl-1-azaazulene (5) with Hydrazine Hydrate.[3] A solution of 80% hydrazine hydrate (4.0 g) in methanol (100 ml) was added, drop by drop, to a solution of **5** (1.0 g) in methanol (100 ml), after which the solution was stirred at room temperature for 2 h. The reddish purple crystals which precipitated out were collected and recrystallized from cyclohexane–benzene to give *N,N'*-bis(3-phenyl-1-azaazulen-8-yl)hydrazine as reddish purple micro prisms (0.55 g); mp 277—278 °C.

On the other hand, the solvent was removed from the filtrate of the reaction mixture, water was added, and the solution was extracted with benzene. The extract was dried, the solvent was removed, and the residue was recrystallized from cyclohexane to afford 8-hydrazino-3-phenyl-1-azaazulene (**14 1**) (0.40 g).

3-Phenyl-1-azaazulene (2). A mixture of 8-hydrazino-3-phenyl-1-azaazulene (0.2 g), acetic acid (5 ml), water (5 ml), and a 10% copper(II) sulfate solution was heated for a few min on a water bath. After cooling, the reaction mixture was made slightly alkaline with 2 M sodium hydroxide and the solution was extracted with ether. The dried extract was concentrated to leave a reddish purple oil. The residual oil was purified by distillation under reduced pressure (bp 90 °C/0.01 Torr). *Picrate*: Orange needles, mp 236 °C (decomp.). The results are given in Table 1.

2-Chloro-3-phenyl-1-azaazulene (11). A mixture of **10** (0.7 g), acetic acid (28 ml), 1 M copper(II) sulfate (56 ml), and water (28 ml) was heated for 15 min on a water bath. After cooling, the reaction mixture was made slightly alkaline with 2 M sodium hydroxide and extracted with chloroform. The dried extract was concentrated and chromatographed on silica gel. From the red effluent, a red oil was obtained and subsequently distilled under reduced pressure (bp 100 °C/1 Torr) (0.37 g). The results are given in Table 2.

2-Chloro-8-bromo-3-phenyl-1-azaazulene (15n). A mixture of **10** (0.12 g), 48% hydrobromic acid (8 ml), and 1 M copper(II) sulfate (9.6 ml) was heated for a few min on a water bath. After cooling, the reaction mixture was treated with a 5% sodium hydrogencarbonate solution and extracted with chloroform. The dried extract was concentrated and chromatographed on silica gel. The product obtained from the red effluent was recrystallized from cyclohexane to give red plates (0.04 g). The results are given in Table 2.

1,2-Dihydro-3-phenyl-1-azaazulen-2-one (12). *(a)* A mixture of **11** (0.37 g) in ethanol (15 ml) and 2 M sodium hydroxide (30 ml) was refluxed for 5 h on a water bath. After cooling, the reaction mixture was made slightly acid with a dil sulfuric acid solution and extracted with benzene. The dried extract was then concentrated, and the residue was recrystallized from benzene to give micro prisms (0.04 g, 12%); mp 264—265 °C. IR(KBr): 1638 cm^{-1} (C=O). UV λ_{max}^{MeOH} 235($\log \varepsilon = 4.34$), 283(4.41), 420(4.00)nm. Found: C, 81.33; H, 5.00; N, 6.13%. Calcd for $C_{15}H_{11}ON$: C, 81.43; H, 5.01; N, 6.33%.

(b) To a sodium ethoxide solution prepared from sodium metal (1.25 g) and absolute ethanol (30 ml), aminotropone (3.0 g) and methyl phenylacetate (7.4 g) were added, after which the mixture was heated in a sealed tube at 130 °C for 5 h. The reaction mixture was concentrated, made acid with 2 M hydrochloric acid, and then extracted with benzene. The benzene layer was dried over anhydrous sodium sulfate and the benzene was removed. From the residual oily product, a small amount of **12** (0.14 g, 3%) was obtained,

with the recovery of the starting material. The mixed melting point with the sample obtained by Method (a) was not depressed.

*2,8-Di(p-tolylthio)-3-phenyl-1-azaazulene (**16**).* *(a)* To a sodium methoxide solution prepared from sodium metal (0.37 g) and absolute methanol (7 ml), *p*-thiocresol (0.2 g) and **6** (0.2 g) were added, and then the mixture was heated under reflux for 15 min. The reaction mixture was concentrated under reduced pressure and extracted with benzene, and the benzene extracts were washed with water, dried over anhydrous sodium sulfate, and chromatographed on alumina. The product obtained from the benzene effluent was recrystallized from cyclohexane to give red prisms (0.12 g, 39%); mp 209—210 °C. Found: C, 77.46; H, 5.16; N, 3.12; S, 14.26%. Calcd for $C_{29}H_{23}NS_2$: C, 77.10; H, 5.19; N, 3.04; S, 13.97%.

(b) A mixture of **6** (0.2 g) and *p*-thiocresol (0.18 g) in dimethyl sulfoxide (10 ml) was stirred for 15 h at room temperature. The reaction mixture was diluted with water, made alkaline with aqueous sodium carbonate, and extracted with benzene. The benzene extracts were dried over anhydrous sodium sulfate and chromatographed on alumina. The product obtained from the benzene effluent was recrystallized from cyclohexane to give red prisms (0.13 g, 42%); mp 209—210 °C. The IR spectrum was identical with that of the sample obtained by Method (a), and the mixed melting point was not depressed.

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