*Synthesis and Reactions of 2, 6-Disubstituted 1, 3-Diazaazulene**

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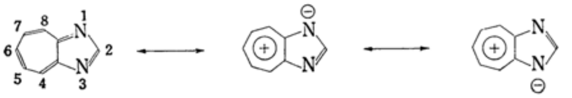
Since 1, 3-diazaazulene derivatives have been synthesized by the reaction of 2-methoxytropones with guanidine or thiourea[1-3], and also by the reaction of 2, 5-diaminotroponimine with formic or acetic acid[4], widespread theoretical interest in this series of compounds has been aroused among physical chemists, and calculations by the molecular orbital method have been carried out by Kon[5].



According to him, the electron densities of the 1- and 3-positions are much higher than those of the 2-, 4(8)-, 5(7)- and 6-positions of 1, 3-diazaazulene. In fact, as has been reported[6], 1, 3-diazaazulene has a large dipole moment, such as 4.03D in a benzene solution at 25°C. Furthermore, it has been reported that the substituents in the 2-position[2,3,7] can be easily replaced by nucleophilic reagents, as can those in the 4-[8], 5-[5] and 6-positions[10].

Since the findings concerning the electron density of 1, 3-diazaazulene as calculated by the MO method varied according to the manner of correction**, it is difficult to anticipate which substituent of the 2- or 6-position of 2, 6-disubstituted 1, 3-diazaazulene is most easily replaced by nucleophilic reagents.

The present series of experiments was undertaken to clarify this respect experimentally. First, several kinds of 2, 6-disubstituted 1, 3-diazaazulene were synthesized. By the condensation reaction with guanidine, tropolone methyl ethers with a nitro group[11], a bromine[12] or a chlorine[13] atom at the 5-position afforded 6-nitro (I), 6-bromo (II) and 6-chloro derivatives (III) of 2-amino-1, 3-diazaazulene respectively. I is soluble in an alkaline solution and shows a bathochromic shift in its ultraviolet spectrum in an alkaline medium compared with that in methanol (Fig. 1). This is due to the formation of an aci-form (Ia). The heating of 2-amino-6-nitro-1, 3-diazaazulene (I) with concentrated hydrochloric acid in a sealed tube at 130°C gives 2-amino-6-hydroxy-1, 3-diazaazulene (IV), while the more severe condition, heating at 200°C, affords 2, 6-dihydroxy-1, 3-diazaazulene (V). IV and V are soluble in acid

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* Presented at the 8th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1955.

1) T. Nozoe, T. Mukai, K. Takase, I. Murata and K. Matsumoto, *Proc. Japan Acad.*, **29**, 452 (1953).

2) T. Nozoe, T. Mukai and I. Murata, *J. Am. Chem. Soc.*, **76**, 3352 (1954).

3) T. Nozoe, T. Mukai and I. Murata, *Proc. Japan Acad.*, **30**, 482 (1954).

4) T. Nozoe, M. Sato, S. Ito, K. Matsui and T. Matsuda, ibid., **29**, 565 (1953).

5) H. Kon, *Sci. Repts., Tohoku Univ., I*, **38**, 67 (1954).

6) Y. Kurita and S. Kubo, *J. Am. Chem. Soc.*, **79**, 5460 (1957).

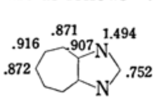
7) I. Murata, This Bulletin, **33**, 56, 1367 (1960).

8) K. Matsumoto, Master's Thesis, Tohoku Univ., 1955.

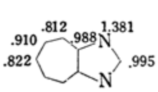
9) I. Murata, This Bulletin, **34**, 580 (1961).

10) T. Nozoe, S. Ito, K. Matsui and S. Suzuki, unpublished data.

** The calculated results by three different corrections for the hetero-atomic Coulomb integral and the induction effect are as follows[5] :



Correction I



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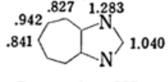


Correction III

Correction I ; $\delta\alpha$ Naza $=\beta$, no correction for induction.

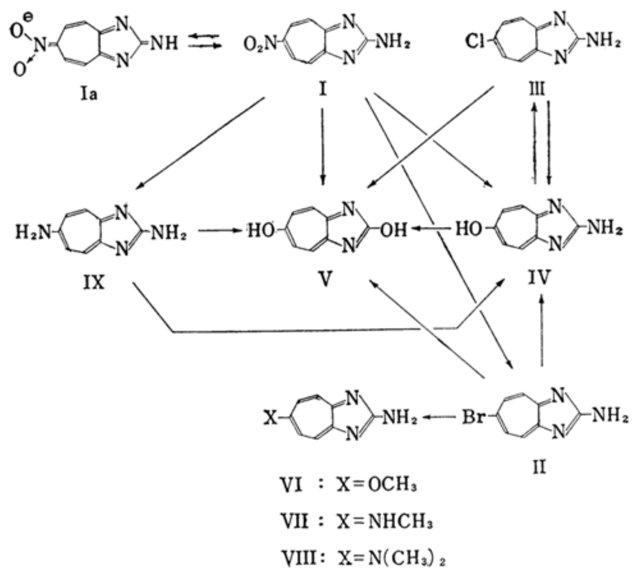
Correction II ; $\delta\alpha$ Naza $=\beta$, correction for induction effect on the two carbon atoms adjacent to an aza-nitrogen atom $=0.3\,\beta$.

Correction III ; $\delta\alpha$ Naza $=0.5\,\beta$, correction for induction effect $\fallingdotseq 1/3\cdot\delta\alpha$ Naza.

11) T. Nozoe, Y. Kitahara, T. Ando and E. Kunioka, *Proc. Japan Acad.*, **27**, 231 (1951).

12) T. Nozoe, S. Seto, T. Ikemi and T. Arai, ibid., **27**, 102 (1951).

13) T. Sato, *J, Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1171 (1959).



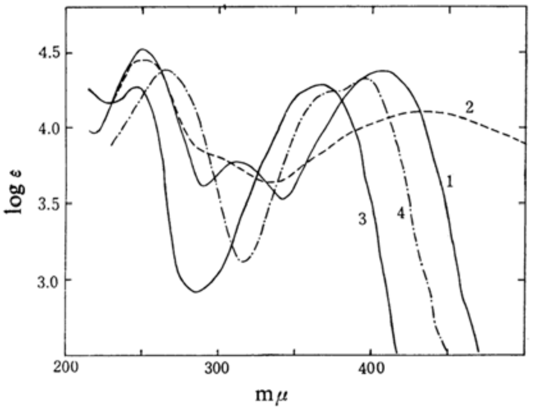


Fig. 1. Ultraviolet absorption spectra.
1, 2-Amino-6-nitro-1,3-diazaazulene (I) in methanol
2, I in 1 N NaOH
3, 2,6-Dihydroxy-1,3-diazaazulene (V) in methanol
4, V in 1 N NaOH

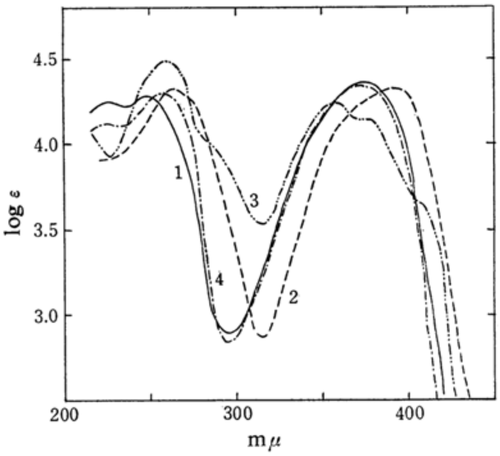


Fig. 2. Ultraviolet absorption spectra.
1, 2-Amino-6-hydroxy-1,3-diazaazulene (IV) in methanol
2, IV in 1 N NaOH
3, 2-Amino-6-methoxy-1,3-diazaazulene (VI) in methanol
4, 2-Amino-1-methylimidazolo[4, 5-d]-tropone (XV) in methanol.

and alkali, and their ultraviolet spectra shift to a longer wavelength region in an alkaline medium compared with those in methanol (Figs. 1 and 2). V does not form a picrate, but IV and the methylated compound of V do form picrates. I also gives 2-amino-6-bromo-1,3-diazaazulene (II), although the yield is rather low, on heating with acetic acid saturated with hydrogen bromide in a sealed tube. The reaction of IV and phosphoryl chloride in the presence of pyridine affords 2-amino-6-chloro-1,3-diazaazulene (III). Structural proof of both the halogenated products is given by their identification with the condensed products of 5-bromo- and 5-chloro-tropolone methyl ether and guanidine respectively. On refluxing in 6 N hydrochloric acid, II and III give a 2-amino-6-hydroxy compound IV, and heating both in concentrated hydrochloric acid in a sealed tube gives 2,6-dihydroxy-1,3-diazaazulene (V). The bromine atom of II was replaced with methoxide, methylamine and dimethylamine, giving 6-methoxy (VI), 6-methylamino (VII) and 6-dimethylamino derivatives (VIII) of 2-amino-1,3-diazaazulene respectively. VI is identical with one of the products obtained from the reaction of IV with diazomethane, as will be described later.

From these results, it is clear that the substituents in the 2- and 6-positions of 1, 3-diazaazulene suffer from the attach of nucleophilic reagents.

To establish the order of the reactivity to nucleophilic reagents of the substituents of the 2- or 6-position, however, it is neccessary to experiment by using 2, 6-disubstituted 1, 3-diazaazulene having the same substituents in the 2- and 6-positions. While any attempted synthesis of 2, 6-diamino-1, 3-diazaazulene by the reaction of II or III with ethanolic ammonia or liquid ammonia results only in the recovery of the starting material, the catalytic reduction of the 2-amino-6-nitro compound I in acetic acid using Pd-C as a catalyst is successful in giving 2, 6-diamino-1, 3-diazaazulene (IX). The heating of IX with concentrated hydrochloric acid in a sealed tube affords V, whereas the refluxing of IX in 6 N hydrochloric acid gives IV, in which the 6-amino group is only hydrolyzed.

2, 6-Dichloro-1, 3-diazaazulene (X) is obtained from 2, 6-dihydroxy-1, 3-diazaazulene (V) by treatment with phosphoryl chloride in the presence of pyridine, accompanying monochloro monohydroxy 1, 3-diazaazulene (XI). The same treatment of XI gives X. X and XI can also be converted to V by heating with concentrated hydrochloric acid, but the heating of X with 2 N acetic acid affords monochloro monohydroxy 1, 3-diazaazulene (XII), which is different from XI. Similarly, the reaction of X and methanolic ammonia gives, in a good yield, monoamino monochloro 1, 3-diazaazulene (XIII), which is different from 2-amino-6-chloro-1, 3-diazaazulene (III).

The structures of XI and XII are examined by comparing their ultraviolet spectra with those of 2-3) and 6-hydroxy-1, 3-diazaazulene10) respectively. There are some differences between the absorption curves of 2- and 6-hydroxy-1, 3-diazaazulene, as is shown in Fig. 3. The similarity of XI in the ultraviolet spectrum to that of the 2-hydroxy compound and the similarity of XII to the 6-hydroxy compound indicates that XI would be 6-chloro-2-hydroxy-1, 3-diazaazulene and XII, 2-chloro-6-hydroxy-1, 3-diazaazulene. In the same manner, XIII is ascertained to be 6-amino-2-chloro-1, 3-diazaazulene. In Fig. 4, the ultraviolet spectra of III, XIII and 2-1) and 6-amino-1, 3-diazaazulene4) are shown; the spectrum of XIII is more similar to that of the 6-amino compound than to that of the 2-amino compound. Incidentally, isomeric 2-amino-6-chloro-1, 3-diazaazulene (III) has an absorption curve similar to that of the 2-amino compound.

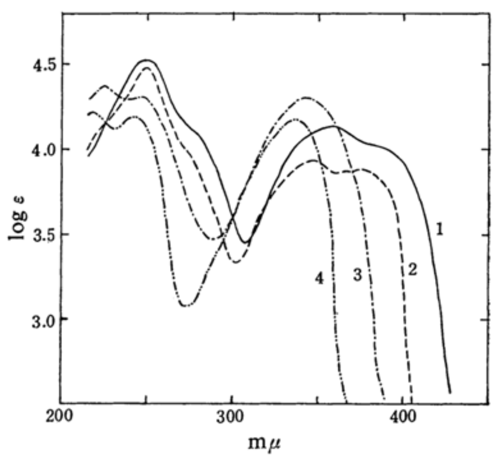
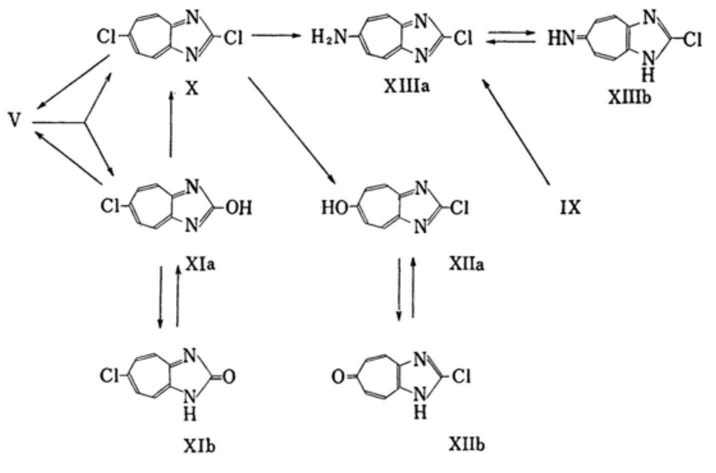


Fig. 3. Ultraviolet absorption spectra in methanol.
1, 6-Chloro-2-hydroxy-1, 3-diazaazulene (XI)
2, 2-Hydroxy-1, 3-diazaazulene
3, 2-Chloro-6-hydroxy-1, 3-diazaazulene (XII)
4, 6-Hydroxy-1, 3-diazaazulene

From this series of experiments, it is clear



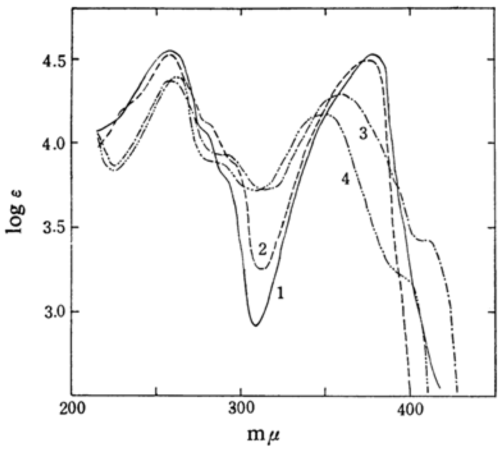


Fig. 4. Ultraviolet absorption spectra in methanol.
1, 6-Amino-2-chloro-1, 3-diazaazulene (XIII)
2, 9-Amino-1, 3-diazaazulene
3, 2-Amino-6-chloro-1, 3-diazaazulene (III)
4, 2-Amino-1, 3-diazaazulene

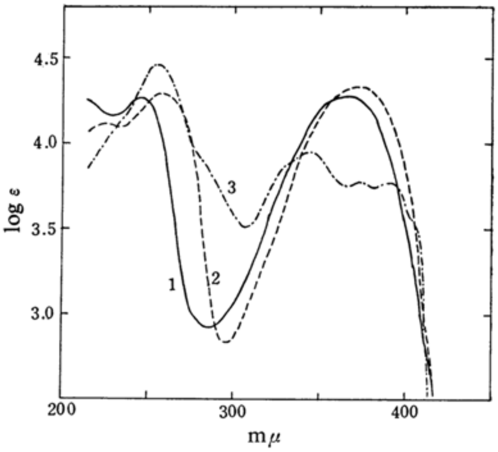
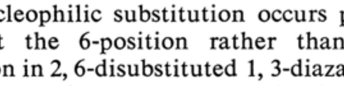


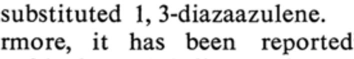
Fig. 5. Ultraviolet absorption spectra in methanol.
1, 2, 6-Dihyroxy-1, 3-diazaazulene (V)
2, 2-Amino-1-methylimidazolo[4, 5-d]-tropone (XV)
3, 1-Methylcycloheptimidazol-2-one (XVI)

that nucleophilic substitution occurs preferentially at the 6-position rather than at the 2-position in 2, 6-disubstituted 1, 3-diazaazulene. In other words, the electron density at the 6-position is less than that at the 2-position of 2, 6-disubstituted 1, 3-diazaazulene.

Furthermore, it has been reported[3,5,10,14] that 2- or 6-hydroxy-1, 3-diazaazulene are present in the so-called lactim-lactam or keto-enol tautomerisms (A and B type: X=O) and that its tautomeric equilibrium tends towards the lactam or keto form (B type: X=O). It has also been reported that there are similar tautomerisms (A and B type: X=NH) in 2- and 6-amino-1,3-diazaazulene and that the imino form (B: X=NH) is preferred to the amino form (A: X=NH). Consequently, the ultraviolet spectra of XI, XII and XIII in Figs. 3 and 4 supported that their equilibrium tends to XIb, XIIb and XIIIb rather than to XIa, XIIa and XIIIa.



A type　B type



A type　B type

It is also interesting to discuss the tautomerism of IV, V and IX. Although 2- or 6-amino-1, 3-diazaazulene is not diazotized[1,4], 2-amino-6-hydroxy-1, 3-diazaazulene (IV) and 2, 6-diamino-1, 3-diazaazulene (IX) are diazotized. The diazonium salt of IV couples with β-naphthol to give an azo-compound XIV. IX consumes only one equivalent of nitrous acid, while the Sandmeyer reaction of its diazonium salt gives 6-amino-2-chloro-1, 3-diazaazulene (XIII). Preferential diazotization of the 2-amino group of IX is also compatible with the fact that the electron density at the 2-position is higher than at the 6-position. This means that the tautomeric equilibrium of IX seems to be tend towards IXb rather than IXa.

Methylation of 2-amino-6-hydroxy-1, 3-diazaazulene (IV) with diazomethane affords two compounds, 6-methoxy-2-amino-1, 3-diazaazulene (VI) and 2-amino-1-methylimidazolo[4, 5-d] tropone (XV), in approximately a 1 : 4 ratio. The ultraviolet spectra of IV, VI and XV are shown in Fig. 2. The spectrum of IV is very similar to that of XV or 6-hydroxy-1, 3-diazaazulene, but it is different from that of VI. The infrared spectrum of XV exhibits a carbonyl band at 1663 cm^{-1}, and that of IV, at 1660 cm^{-1}. In Fig. 5, the ultraviolet spectra of 2, 6-dihydroxy-1, 3-diazaazulene (V), XV and 1-methylcycloheptimidazol-2-one[3] (XVI) are shown. The absorption curve of V is similar to that of XV rather than to that of XVI, and the infrared spectrum of V exhibits a carbonyl band at 1686 cm^{-1}. From these facts, the tautomeric equilibrium of IV and V seems to tend towards IVb and Vb respectively rather than towards IVa and Va.

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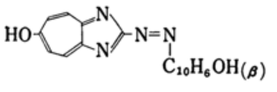
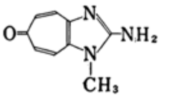
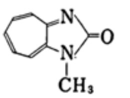
[14] I. Murata, *Sci. Rep. RITU*,. **A-12**, 271 (1960).



XIV

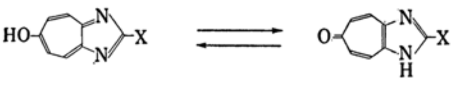


XV



XVI

IXa IXb



IVa : X=NH₂ IVb : X=NH₂

Va : X=OH Vb : X=OH

Experimental*

2-Amino-6-nitro-1, 3-diazaazulene (I). — To a suspension of 1 g. of 5-nitrotropolone methyl ether in 100 ml. of ethanol, a solution of 0.33 g. of potassium hydroxide (or 0.13 g. of sodium) and 0.56 g. of guanidine hydrochloride in 50 ml. of ethanol was added, and the mixture was refluxed for about 3 hr. The yellowish brown prisms which precipitated out were collected by filtration and recrystallized from acetic acid, giving 0.75 g. (75%) of I as yellow needles, m. p. over 300°C.

Found: C, 50.45; H, 2.92; N, 29.56. Calcd. for $C_8H_6O_2N_4$: C, 50.53; H, 3.18; N, 29.42%.

Picrate.—Organge prisms, turned to black from around 240°C.

Found: C, 39.42; H, 2.56; N, 23.82. Calcd. for $C_{14}H_9O_9N_7$: C, 39.82; H, 2.86; N, 23.39%.

2-Amino-6-bromo-1, 3-diazaazulene (II).—a) To a solution of 420 mg. of 5-bromotropolone methyl ether in 10 ml. of ethanol, a solution of 250 mg. of guanidine hydrochloride and 130 mg. of potassium hydroxide dissolved in 10 ml. of ethanol was added, and the mixture was refluxed for 2 hr. The yellow crystals which precipitated out were collected by filtration, washed with water and recrystallized from ethanol, affording 320 mg. of II as yellow prisms, which slowly changed to black from around 240°C.

Found: C, 43.28; H, 2.55; N, 18.45. Calcd. for $C_8H_6N_3Br$: C, 42.90; H, 2.70; N, 18.75%.

Picrate.—Orange yellow prisms, m. p. 262~263°C (decomp.).

Found: N, 18.58. Calcd. for $C_{14}H_9O_7N_6Br$: N, 18.54%.

b) After heating 50 mg. of I with 3 ml. of acetic acid saturated with hydrogen bromide in a sealed tube for 5 hr. at 90°C, the solid which precipitated out was dissolved in water. Neutralization of the solution with sodium hydrogen carbonate gave crystals, which were recrystallized from ethanol, giving II as yellow prisms, which slowly changed to black from around 240°C. The infrared spectrum of these crystals showed the same maxima as that of the sample obtained by method a).

2-Amino-6-chloro-1, 3-diazaazulene (III) — a) 2.5 g. of III was obtained from 2.8 g. of 5-chlorotropolone methyl ether by method a), by which II was obtained. Yellow prisms, gradually changing to black from around 247°C.

Found: C, 53.24; H, 3.68; N, 22.90. Calcd. for $C_8H_6N_3Cl$: C, 53.60; H, 3.36; N, 23.40%.

Picrate.—Yellow powder, slowly changing to black from around 280°C.

Found: N, 20.78. Calcd. for $C_{14}H_9O_7N_6Cl$: N, 20.56%.

b) A mixture of 90 mg. of 2-amino-6-hydroxy-1, 3-diazaazulene (IV), 3 ml. of phosphoryl chloride and 0.15 ml. of pyridine was heated at 105°C for 2.5 hr. while being stirred. After the excess of phosphoryl chloride had been distilled off, the residue was poured onto ice. Yellow crystals soon separated out. The crude crystals were dissolved in diluted hydrochloric acid, treated with charcoal and neutralized with sodium hydrogen carbonate, giving 60 mg. of yellow micro needles. Recrystallization of these crystals from ethanol gave II as yellow prisms, which changed to black from around 247°C.

2-Amino-6-hydroxy-1, 3-diazaazulene (IV).—After heating 0.5 g. of I with 2 ml. of concentrated hydrochloric acid in a sealed tube for 12 hr. at 130°C, the mixture was evaporated to dryness on a steam bath. The residue was dissolved in a small amount of water and treated with charcoal. Neutralization of this solution with sodium hydrogen carbonate gave 330 mg. of yellow needles. Recrystallization from water afforded IV as yellow needles, which slowly changed to black from around 240°C.

Found: C, 53.20; H, 4.72; N, 23.27. Calcd. for $C_8H_7ON_3 \cdot H_2O$: C, 53.62; H, 5.06; N, 23.45%.

Picrate. — Yellow powder, slowly changing to black from around 250°C.

Found: C, 42.71; H, 3.40. Calcd. for $C_{14}H_{10} \cdot O_8N_6$: C, 43.08; H, 2.58%.

Reaction of IV with Phenylhydrazine.—A solution of IV and phenylhydrazine in ethanol was refluxed for 5 hr. in the presence of a small amount of acetic acid. After removing the solvent, the

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* All melting points are uncorrected. The microanalyses were carried out by Mr. S. Ohyama and Miss A. Iwanaga, to whom the author's sincere gratitude is hereby extended.

residue was recrystallized from ethanol, affording red micro meedles, m. p. over 280°C.

Found: C, 67.03; H, 4.45. Calcd. for $C_{14}H_{13}N_5$: C, 66.91; H, 5.21%. Calcd. for $C_{14}H_{11}N_5$: C, 67.45; H, 4.45%.

Ultraviolet; $\lambda_{\max}^{\text{MeOH}}$ mμ (log ε): 250 (4.38), 300~315 (4.17), 416 (4.42).

2,6-Dihydroxy-1,3-diazaazulene (V).—A solution of 0.5 g. of I in 3 ml. of concentrated hydrochloric acid was heated in a sealed tube for 24 hr. at 200°C. The black material which separated out was removed by filtration, and the filtrate was evaporated to dryness. Recrystallization of the residue from water afforded 300 mg. of V as yellow needles, m. p. over 300°C.

Found: C, 52.98; H, 4.84; N, 15.74. Calcd. for $C_8H_6O_2N_2\cdot H_2O$: C, 53.33; H, 4.48; N, 15.55%.

Diacetate.—Pale yellow needles, m. p. over 300°C.

Found: N, 12.67. Calcd. for $C_{12}H_{10}O_4N_2$: N, 12.61%.

Dimethyl Derivative.—V was methylated with diazomethane in the mixture of methanol and ether, giving a dimethyl derivative as yellow needles, m. p. 254~255°C (decomp.).

Found: N, 14.74. Calcd. for $C_{10}H_{10}O_2N_2$: N, 14.68%.

Picrate of Dimethyl Derivative.—Yellow needles, m. p. 240~241°C (decomp.).

Found: N, 16.70. Calcd. for $C_{16}H_{13}O_9N_5$: N, 16.63%.

2-Amino-6-methoxy-1,3-diazaazulene (VI).—A mixture of 150 mg. of II and 80 mg. of sodium methoxide in 20 ml. of absolute methanol was refluxed for 6 hr. After the mixture had been cooled, 50 mg. of II was recovered by filtration, was and the filtrate passed through an alumina column. Crystals obtained from the effluent were recrystallized from ethanol, giving VI as yellow needles, m. p. 237~238°C (decomp.).

Found: C, 61.68; H, 5.24; N, 23.90. Calcd. for $C_9H_9ON_3$: C, 61.70; H, 5.18; N, 23.99%.

Picrate.—Yellow powder, m. p. 266~267°C. (decomp.).

Found: N, 20.22. Calcd. for $C_{15}H_{12}O_8N_6$: N, 20.79%.

2-Amino-6-methylamino-1,3-diazaazulene (VII). After heating a mixture of 100 mg. of II, 40 mg. of methylamine hydrochloride, 30 mg. of sodium methoxide and 1.5 ml. of absolute methanol in a sealed tube at 160°C for 6 hr., an orange solid was obtained by evaporating the solvent. This solid was dissolved in methanol and passed through a column of ion-exchange resin (Amberite IRA-410). 40 mg. of VII was obtained as orange yellow prisms, m. p. 264~265°C (decomp.) (from ethanol).

Found: C, 56.24; H, 6.24; N, 29.31. Calcd. for $C_9H_{10}N_4\cdot H_2O$: C, 56.23; H, 6.29; N, 29.15%.

2-Amino-6-dimethylamino-1,3-diazaazulene(VIII). —The reaction of II with dimethylamine gave VIII as orange yellow prisms, which slowly changed to black from around 240°C (from water).

Found: C, 63.28; H, 6.20; N, 29.89. Calcd. for $C_{10}H_{12}N_4$: C, 63.81; H, 6.43; N, 29.77%.

2,6-Diamino-1,3-diazaazulene (IX).—A solution of 500 mg. of I dissolved in 20 ml. of acetic acid was submitted to hydrogenation in the presence of 200 mg. of 5% Pd-C. 180 ml. of hydrogen was absorbed. The solvent was distilled off under reduced pressure, and the resulting reddish crystalline was dissolved in ethanol and passed through a column of ion-exchange resin (Amberlite IR-4B). The ethanol was evaporated off from the elute, and the residue was sublimed under reduced pressure. Recrystallization of the sublimate from water afforded 170 mg. of IX as yellow silky needles, m. p. over 300°C.

Found: C, 59.99; H, 5.05; N, 34.56. Calcd. for $C_8H_8N_4$: C, 59.98; H, 5.03; N, 34.98%.

Bis-picrate.—Yellow powder, m. p. over 300°C.

Found: N, 22.71. Calcd. for $C_{20}H_{14}O_{14}N_{10}$: N, 22.65%.

Dihydrochloride.—Pale yellow prisms, m.p. over 300°C.

Found: N, 24.26. Calcd. for $C_8H_8N_4\cdot 2HCl$: N, 24.04%.

2,6-Dichloro-1,3-diazaazulene (X) **and 6-Chioro-2-hydroxy-1,3-diazaazulene** (XI).—A mixture of 270 mg. of V, 7 ml. of phosphoryl chloride and 0.9 ml. of pyridine was stirred for 3 hr. at 110°C. The excess of phosphoryl chloride was distilled off under reduced pressure, and the residue was poured onto ice. The solution was adjusted to a slightly acidic state with sodium hydrogencarbonate and extracted with chloroform. The chloroform was then removed, the residue was redissolved in benzene, and the benzene solution was passed through an alumina column. The benzene was distilled off from the eluate, and the residue was recrystallized from benzene, affording 110 mg. of 2,6-dichloro-1,3-diazaazulene (X) as colorless needles, m. p. 226~227°C (decomp.).

Found: C, 48,97; H, 2.36; N, 14.38. Calcd. for $C_8H_4N_2Cl_2$: C, 48.27; H, 2.03; N, 14.08%.

After the chloroform extraction, the water layer was adjusted to a slightly alkaline state with sodium hydrogen carbonate, affording yellow needles. Recrystallization of the crystals from water gave 80 mg. of 6-chloro-2-hydroxy-1,3-diazaazulene (XI), which gradually changed to black from around 240°C.

Found: C, 53.12; H, 3.21; N, 15.71. Calcd. for $C_8H_5ON_2Cl$: C, 53.21; H, 2.79; N, 15.51%.

2-Chloro-6-hydroxy-1,3-diazaazulene (XII).—A mixture of 50 mg. of X, 4 ml. of 2 N acetic acid and 1 ml. of ethanol was refluxed for 1.5 hr. Thirty milligrams of colorless needles were obtained by cooling the reaction mixture in an ice box. Recrystallization of the crystals from water gave XII as colorless needles, m. p. 237~237.5°C (decomp.).

Found: C, 52.79; H, 3.21; N, 15.52. Calcd. for $C_8H_5ON_2Cl$: C, 53.21; H, 2.79; N, 15.51%.

6-Amino-2-chloro-1,3-diazaazulene (XIII).—a) The heating of 40 mg. of X in 2 ml. of methanol saturated with ammonia in a sealed tube at 100°C for 1 hr. afforded 35 mg. of yellow crystals. The crystals were dissolved in dilute hydrochloric acid and neutralized with a sodium hydrogencarbonate solution, giving XIII as yellow needles, m. p. over 300°C.

Found: C, 53.46; H, 3.34; N, 23.47. Calcd. for $C_8H_6N_3Cl$: C, 53.60; H, 3.36; N, 23.40%.

b) Fifty milligrams of IX dissolved in 0.6 ml. of acetic acid was diazotized with sodium nitrate, and the reaction mixture was poured into a solution of 50 mg. of cuprous chloride in 0.3 ml. of concentrated hydrochloric acid. The mixture was adjusted to a slightly alkaline state with sodium hydrogencarbonate, affording a brown solid. The solid was extracted with ethanol continuously, and yellow crystals were obtained. Recrystallization of the crystals from ethanol gave yellow needles, m. p. over 290°C. The ultraviolet and infrared spectra of these crystals completely agreed with those of XIII obtained by procedure a).

6-Hydroxy-2-(2-hydroxy-1-naphthyl)-azo-1, 3-diazaazulene (XIV).—One hundred milligrams of IV dissolved in 2 ml. of 6 N hydrochloric acid were diazotized with a solution of 50 mg. of sodium nitrate dissolved in 0.4 ml. of water. The reaction mixture was slowly poured into a solution of 90 mg. of β-naphthol dissolved in 3 ml. of a 3 N sodium hydroxide solution. The color of the mixture immediately turned to violet, and a deep-colored solid was salted out. The solid was then dissolved in water and neutralized with dilute hydrochloric acid, giving 60 mg. of violet crystals. Recrystallization of these crystals from pyridine afforded XIV as brownish violet needles, m. p. over 300°C.

Found: C, 68.13; H, 3.70. Calcd. for $C_{18}H_{12}$·O_2N_4: C, 68.35; H, 3.82%.

Ultraviolet: $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 225 (4.71), 290 (4.20), 355 (418), 510 (4.59).

Reaction of IV with Diazomethane.—To a solution of 300 mg. of IV dissolved in 6 ml. of methanol, 25 ml. of diazomethane ether solution prepared from 2.5 g. of *N*-nitrosomethylurea was added and left to stand overnight. The crystals which precipitated out were filtered and washed with benzene, affording 190 mg. of crystals. Recrystallization of the crude crystals from ethanol afforded XV as yellow prisms, which gradually changed to black from around 290°C.

Found: C, 55.92; H, 5.73; N, 21.37. Calcd. for $C_9H_9ON_3 \cdot H_2O$: C, 55.95; H, 5.74; N, 21.75%.

Picrate.—Yellow needles, gradually changing to black from around 240°C.

Found: C, 44.78; H, 2.74; N, 21.18. Calcd. for $C_{15}H_{12}O_8N_6$: C, 44.56; H, 2.99; N, 20.79%.

The solvent was distilled off from the original reaction filtrate, and the residue was dissolved in benzene and passed through an alumina column. Benzene was removed from the eluate, leaving 50 mg. of crystals. Recrystallization of these crystals from ethanol afforded yellow needles, m. p. 236°C (decomp.), which showed no depression of melting point on admixture with VI.

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