5- and 2,5-Substituted 1,3-Diazaazulenes[1]

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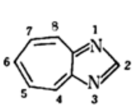
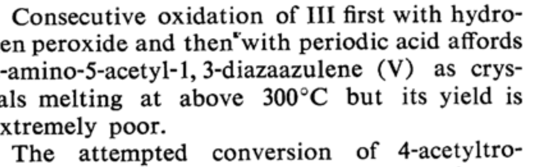
Compounds with various functional groups substituted in the 1,3-diazaazulene ring known to date are (1) 2-substituted derivatives obtained by the reaction of tropolone methyl ether and guanidine or thiourea[2], (2) 2,4-disubstituted derivatives obtained by the reaction of 2-bromo-7-methoxytropone and guanidine[3], (3) 2,6-disubstituted derivatives obtained from 5-halo- or 5-nitrotropolone methyl ether and guanidine[4], and (4) 6-substituted derivatives obtained from 2,5-diaminotropoimine and formic and acetic acids[5]. The chemical properties of these synthesized compounds have also been examined. However, 5-substituted and 2,5-disubstituted derivatives are still not known, due to the difficulty of obtaining 4-halotropolones[6] which are their direct starting material.



In the present series of work, some of these compounds were newly prepared and are described herein.

β-Dolabrin (4-isopropenyltropolone) (I)[7] is transformed to its sodium salt in ethanol and then converted to its silver salt by silver nitrate. Reaction of methyl iodide with this silver salt suspended in benzene affords a mixture of two kinds of methyl ether in the form of a yellow oil (II). Condensation of II, without separation[8], with guanidine in the presence of potassium hydroxide gives 2-amino-5-isopropenyl-1,3-diazaazulene (III) as yellow prisms, m.p. 230°C (decomp.) in a good yield. Catalytic reduction of III over palladium-carbon results in absorption of 1 mol. of hydrogen to form the known 2-amino-5-isopropyl-1,3-diazaazulene (IV)[2], by which the structure of III is confirmed.



Consecutive oxidation of III first with hydrogen peroxide and then with periodic acid affords 2-amino-5-acetyl-1,3-diazaazulene (V) as crystals melting at above 300°C but its yield is extremely poor.

The attempted conversion of 4-acetyltropolone (VI)[7], obtained by oxidation of I, to a mixture of methyl ethers VII with diazomethane and condensation of VII with guanidine to obtain V ended in failure, forming only a resinous substance. In order to protect

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[1] Paper read at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

[2] T. Nozoe, T. Mukai, K. Takase, I. Murata and K. Matsumoto, *Proc. Japan Acad.*, **29**, 452 (1953); T. Nozoe, T. Mukai and I. Murata, *J. Am. Chem. Soc.*, **76**, 3352 (1954).

[3] T. Nozoe, T. Mukai, I. Murata, M. Ishii and K. Matsumoto, unpublished data.

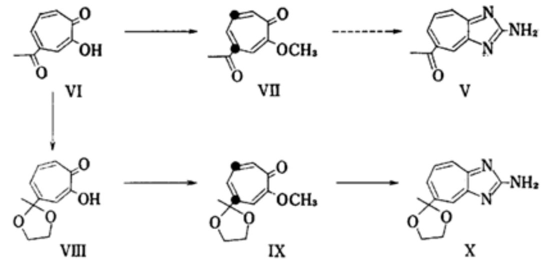
[4] T. Nozoe, T. Mukai, I. Murata and T. Asao, unpublished data. Cf. T. Nozoe, *Croatica Chem. Acta*, **29**, 215 (1957).

[5] T. Nozoe, M. Sato, S. Ito, K. Matsui and T. Matsuda, *Proc. Japan Acad.*, **29**, 565 (1953).

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

[7] T. Nozoe, K. Takase and M. Ogata, *Chem. and Ind.*, **1957**, 1070.

[8] 2-Amino-1,3-diazaazulene hereby formed is symmetric and the same product is obtained from either of the two methyl ethers. Cf. Ref. 2.



the acetyl group, VI was reacted with ethylene glycol in dehydrated benzene to give 4-(α-ethylenedioxy)ethyltropolone (VIII)⁹⁾. Treatment of VIII with diazomethane afforded a mixture of methyl ethers IX and condensation with guanidine gave 2-amino-5-(α-etylenedioxy)-ethyl-1, 3-diazaazulene (X) as pale yellow needles, m. p. 297°C (decomp.). Treatment of X with dilute hydrochloric acid easily converted it to V. Ultraviolet absorption spectra of III, V and X are shown in Fig. 1.

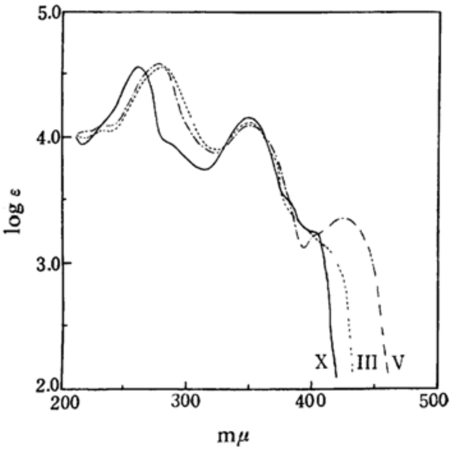
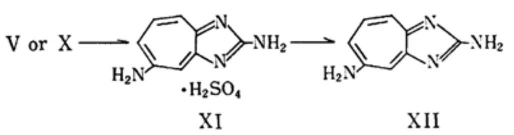


Fig. 1. Ultraviolet absorption spectra of III, V and X in methanol.

The application of the Schmidt reaction¹⁰⁾, already carried out with VI, to V gives yellow needles XI, m. p. above 300°C, which are also obtained by direct reaction of hydrazoic acid on X.

The estimation of sulfur in XI is positive and the treatment of XI with sodium hydrogen carbonate or ammonia water affords yellow prisms XII, m. p. 289°C (decomp.). From the analytical values of XII and the formation of a picrate of m. p. above 300°C, a diacetate of m. p. 285°C (decomp.), and a dibenzoate of m. p. 157°C, it is considered that XII is 2, 5-diamino-1, 3-diazaazulene¹¹⁾. Consequently, XI would be the sulfate of XII.



On the other hand, the reaction of thiourea on IX in the presence of sodium ethoxide affords 2-mercapto-5-(α-ethylenedioxy)ethyl-1,3-diazaazulene (XIII) as orange prisms, m. p. 246°C. The oxidative desulfurization of the mercapto group in XIII with hydrogen peroxide gives 5-(α-ethylenedioxy)ethyl-1, 3-diazaazulene (XIV) as yellow prisms, m. p. 153°C. The idea of the structure of these compounds is supported by the similarity of their ultraviolet absorption spectra with those of comoupnds lacking a side chain in the 5-position²⁾ and

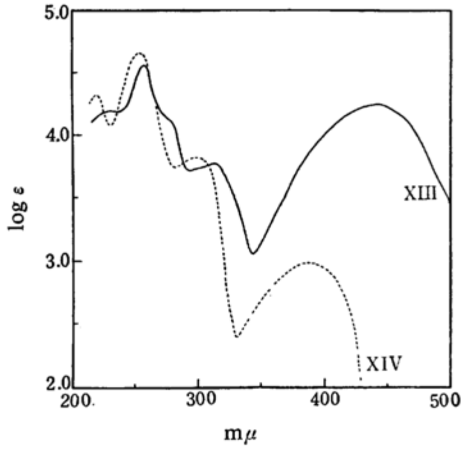


Fig. 2. Ultraviolet absorption spectra of XIII and XIV in methanol.

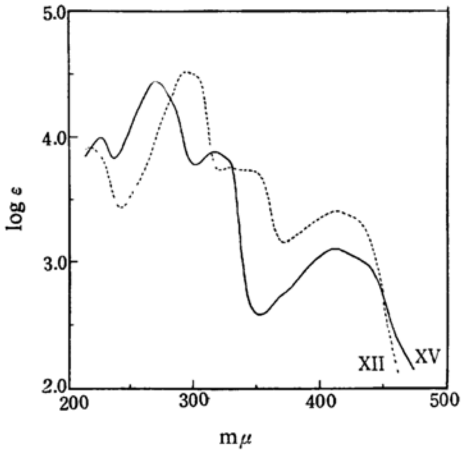


Fig. 3. Ultraviolet absorption spectra of XII and XV in methanol.

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9) I. Murata, This Bulletin, 34, 577 (1961).

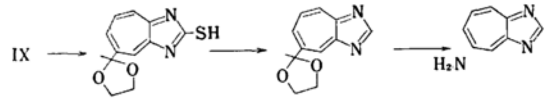
10) K. Doi, unpublished data.

11) In the Schmidt reaction of 4-acetyltropolone, the product is 4-aminotropolone and the acetylamino group is considered to have undergone hydrolysis in the intermediate stage. Cf. Ref. 10.

compounds possessing a methyl group in the 5-position[12].

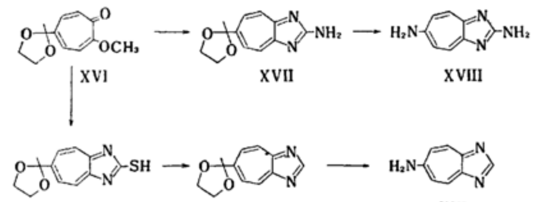
The Schmidt reaction of XIV affords yellow prisms, m. p. 214°C, though in a very poor yield. This substance forms a picrate of m. p. 244°C and its analytical values clearly indicate that it is the anticipated 5-amino-1, 3-diazaazulene (XV).

The ultraviolet spectra of 5-amino (XV) and 2, 5-diamino (XII) compounds are indicated in Fig. 3. These two compounds show corresponding absorptions but the spectrum of XII shows a fair amount of bathochromic and hyperchromic shifts from that of XV.



XIII XIV XV

The acetylamino group formed by the Schmidt reaction of α-ethylenedioxyethyl group in both XII and XV undergoes hydrolysis and is found as the free amino group in the product. In order to prove this fact in other analogous compounds, the following experiments were carried out.



XVI XVII XVIII

XIX XX XXI

Condensation of 5-(α-ethylenedioxy)ethyltropolone methyl ether (XVI)[9] with guanidine afforded XVII, m. p. 200°C, the Schmidt reaction of which gave the known 2, 6-diamino-1, 3-diazaazulene[4] (XVIII), via its sulfate of m. p. above 300°C. The condensation of XVI with thiourea to form the 2-mercapto compound XIX and the Schmidt reaction of its desulfurized product XX afforded the known 6-amino-1, 3-diazaazulene[5] (XXI). These reaction results are entirely analogous to the case of 5-substituted derivative described above.

The amino group in 2-position of XVIII submits to the diazo reaction and undergoes coupling with phenols or the Sandmeyer reaction[4]. The amino group in 2-position of 2, 5-diamino-1, 3-diazaazulene (XII) is expected to undergo diazotisation[13] but, actually, the reaction is negative.

When XII is heated with concentrated hydrochloric acid or hydrobromic acid for several hours, one of the amino groups is hydrolysed and an amino-hydroxy compound XXIII is obtained. Acid hydrolysis of XII and XXIII in a sealed tube results in the formation of 2, 5-dihydroxy-1, 3-diazaazulene (XXIV). There is no reliable proof as to which of 2- or 5-position in XXIII is a hydroxyl group but, since similar hydrolysis of XVIII affords 2-amino-6-hydroxy compound[4], it seems natural to assume that XXIII is 2-amino-5-hydroxy-1, 3-diazaazulene. The ultraviolet absorption spectra of XXIII and XXIV are shown in Fig. 4.

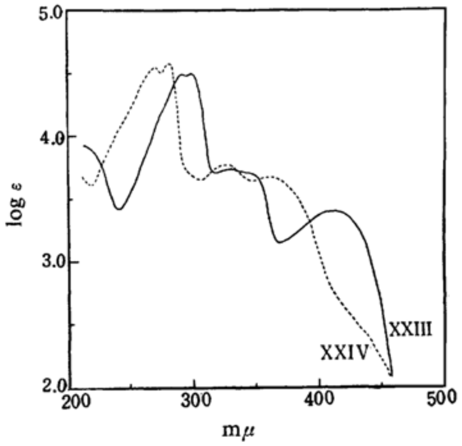
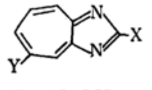


Fig. 4. Ultraviolet absorption spectra of XXIII and XXIV in methanol.

In order to obtain 2-hydroxy-5-amino-1, 3-diazaazulene (XXV), XIII was converted to XXVI with methyl iodide and the reaction of hydrazoic acid afforded 2-methylthio-5-amino-1, 3-diazaazulene (XXVII) as yellow silky needles, m. p. above 300°C. Formation of XXV by hydrolysis of the methylthio group[14] in XXVIII was not effected.



XXIII $X=NH_2$, $Y=OH$
XXIV $X=Y=OH$
XXV $X=OH$, $Y=NH_2$
XXVI $X=SCH_3$, $Y=C(OCH_2CH_2O)CH_3$
XXVII $X=SCH_3$, $Y=NH_2$

Experimental[15]

4-Isopropenyltropolone Methyl Ether (II).—A solution of I (1.62 g.) dissolved in ethanol (7 ml.)

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[12] H. Akino, K. Sato and Y. Suzuki, *Sci. Repts. Tohoku Univ.*, [1] **40**, 92 (1956).

[13] In 1, 3-diazaazulene, there is a large contribution of the polar form in which the 7-membered ring is positively charged and the 5-membered ring is negatively charged. Consequently, the 5-membered ring, i. e. 2-position, is considered to be preferentially diazotized. Cf. H. Kon, *Sci. Repts. Tohoku Univ.*, [1] **38**, 67 (1954).

[14] I. Murata, This Bulletin, 33, 1367 (1960).

[15] All melting points are uncorrected.

was added to the solution of sodium hydroxide (0.4 g.) in water (40 ml.) to form the sodium salt. A solution of silver nitrate (1.7 g.) in water (50 ml.) was added to the solution of the sodium salt while stirring with ice-cooling. The precipitate thereby formed was collected by filtration, washed thoroughly with water and ethanol, and dried over phosphorous pentoxide. Yield, 2.45 g.

This silver salt was suspended in dehydrated benzene (50 ml.) and methyl iodide (1.5 g.) was added with stirring at room temperature. After stirring the mixture for 30 min., the reaction mixture was allowed to stand over night, the silver iodide formed was filtered off, and the filtrate was concentrated under a reduced pressure from which II was obtained as an orange oil (2.3 g.).

2-Amino-5-isopropenyl-1, 3-diazaazulene (III).—II (2.3 g.) was added to the solution of potassium hydroxide (505 mg.) dissolved in ethanol (30 ml.) and added with guanidine hydrochloride (870 mg.) and the mixture was refluxed on a water bath for 1.5 hr. The crystals that precipitated out when the reaction mixture cooled and the crystals obtained by concentration of the filtrate were combined and washed with water. Crude III (1.15 g.), obtained as yellow prisms, m. p. 229~230°C (decomp.), was recrystallized from ethanol but the melting point remained unchanged.

Found: C, 71.54; H, 5.53; N, 23.08. Calcd. for $C_{11}H_{11}N_3$: C, 71.33; H, 5.99; N, 22.69%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 235 (4.06), 283 (4.55), 348 (4.12).

Acetate: Colorless prisms (from ethanol and dioxane), m. p. 216°C (decomp.).

Found: C, 68.71; H, 5.55; N, 18.36. Calcd. for $C_{13}H_{13}ON_3$: C, 68.70; H, 5.77; N, 18.49%.

Picrate: Yellow needles (from ethanol and dioxane), m. p. 231°C (decomp.).

Found: C, 49.16; H, 3.57; N, 20.47. Calcd. for $C_{17}H_{14}O_7N_6$: C, 49.28; H, 3.41; N, 20.29%.

Catalytic Reduction of III. — A solution of III (50 mg.) in methanol (10 ml.), added with palladium-carbon (50 mg.) was submitted to catalytic reduction at atomospheric temperature and pressure, and ca. 7 cc. of hydrogen was absorbed in 2 hr. Palladium-carbon was filtered off, the filtrate was concentrated, and the residual crystals were recrystallized from ethanol to IV (30 mg.), m. p. 293°C (decomp.). The ultraviolet and infrared spectra of IV agreed with those of the known 2-amino-5-isopropyl-1, 3-diazaazulene.

2-Amino-5-(α-ethylenedioxy)ethyl-1,3-diazaazulene (X).—A solution of potassium hydroxide (720 mg.), ethanol (30 ml.), and guanidine hydrochloride (1.21 g.), added with IX (2.65 g.), was refluxed for 2 hr. and cooled. The crystals that precipitated out and those obtained after concentration of the filtrate were combined, washed with water, and the pale yellow crystals (2.3 g.) of m. p. 297°C (decomp.) were recrystallized from ethanol to X as pale yellow needles, m. p. 297°C.

Found: C, 62.41; H, 5.71; N, 18.10. Calcd. for $C_{12}H_{13}O_2N_3$: C, 62.32; H, 5.67; N, 18.17%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 262 (4.58), 350 (4.17).

2-Amino-5-acetyl-1, 3-diazaazulene (V).—A solution of X (650 mg.) dissolved in 2 N hydrochloric acid (5 ml.) was heated on a water bath of 90°C for 20 min. The orange solution so formed was diluted with water and neutralized with sodium hydrogen carbonate by which an orange precipitate (550 mg.) of m. p. above 300°C, was obtained. Recrystallization from a mixed solvent of ethanol and dioxane afforded orange microprisms, V.

Found: C, 64.61; H, 5.18; N, 21.61. Calcd. for $C_{10}H_9ON_3$: C, 64.16; H, 4.85; N, 22.45%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 277 (4.60), 353 (4.11), 424 (3.36).

2, 5-Diamino-1, 3-diazaazulene (**XII**). — Sodium azide (0.65 g.) was added in small portions into a solution of X (2 g.) dissolved in concentrated sulfuric acid (6.5 ml.), while stirring at room temperature, and the mixture was further stirred for 2 hr. This was diluted with water (10 ml.), made slightly alkaline with 2 N sodium hydroxide, and allowed to stand in a cold place. The yellow crystals that precipitated out were collected by filtration to XI (1.7 g.) of m. p. above 300°C.

XI was dissolved in concentrated ammonia water (1.5 ml.), the solution was allowed to stand, and the pale yellow crystals (1.4 g.) that formed were recrystallized from water to XII as pale yellow prisms, m. p. 289°C (decomp.).

Found: C, 60.15; H, 4.57; N, 33.97. Calcd. for $C_8H_8N_4$: C, 59.98; H, 5.03; N, 34.98%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 292 (4.72), 343 (3.92), 415 (3.53); $\lambda_{max}^{0.1N\ HCl}$: 290 (4.62), 325 (3.96), 335 (3.97), 377 (3.63); $\lambda_{max}^{0.1N\ NaOH}$: 290 (4.75), 350 (3.97), 415 (3.48).

Picrate: Yellow needles (from ethanol), m. p. above 300°C.

Found: C, 42.46; H, 2.85; N, 24.21. Calcd. for $C_{14}H_{11}O_7N_7$: C, 43.19; H, 2.84; N, 24.26%.

Benzoate: Obtained as yellow crystals by application of benzoyl chloride in pyridine and recrystallized from dilute ethanol to yellow crystals, m. p. 157°C.

Found: C, 68.20; H, 4.80; N, 14.18. Calcd. for $C_{22}H_{16}O_2N_4 \cdot H_2O$: C, 68.38; H, 4.70; N, 14.50%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 230 (4.29), 305 (4.79), 346 (4.33), 395 (3.35).

Acetate: Obtained by refluxing in acetic anhydride for 20 min. Pale yellow needles (from dilute ethanol), m. p. 285°C (decomp.).

Found: C, 54.88; H, 5.28; N, 21.16. Calcd. for $C_{12}H_{12}O_2N_4 \cdot H_2O$: C, 54.95; H, 5.38; N, 21.37%. Ultraviolet λ_{max}^{MeOH} mμ (log ε): 224 (3.97), 288 (4.65), 344 (4.04), 395 (2.91).

2-Mercapto-5-(α-ethylenedioxy)ethyl-1, 3-diazaazulene (XIII). — A solution of sodium (120 mg.) dissolved in absolute ethanol (50 ml.), with thiourea (400 mg.) and IX (1.1 g.) added, was refluxed on a water bath for 3 hr., the ethanol was evaporated, and the residue was diluted with water (30 ml.). The precipitate formed by additional of acetic acid was collected and the orange crystals (950 mg.) of m. p. 235°C (decomp.) so obtained were recrystallized from ethanol to XIII as orange prisms, m. p. 246°C (decomp.).

Found: C, 57.88; H, 4.85; N, 11.68. Calcd. for $C_{12}H_{12}O_2N_2S$: C, 58.06; H, 4.84; N, 11.29%.

Ultraviolet $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε) : 227 (4.18), 253 (4.55), 310 (3.78), 440 (4.23).

5-(α-Ethylenedioxy)ethyl-1, 3-diazaazulene (XIV).—To a suspension of XIII (400 mg.) in water (4 ml.), 35% hydrogen peroxide (2 ml.) was added and the mixture was heated on a boiling water bath for a few minutes by which exothermic reaction occurred to form an orange solution. After cooling this mixture in ice, the mixture was made slightly alkaline with sodium hydrogen carbonate and extracted with chloroform. The chloroform residue was dissolved in benzene and passed through a column of alumina for purification by which yellow crystals (210 mg.), m. p. 152~153°C, were obtained. Recrystallization from a mixed solvent of benzene and cyclohexane afforded XIV as yellow prisms, m. p. 152~153°C.

Found: C, 66.56; H, 5.27; N, 12.87. Calcd. for $C_{12}H_{12}O_2N_2$: C, 66.65; H, 5.59; N, 12.96%. Ultraviolet $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε) : 219 (4.32), 255 (4.66), 300 (3.82), 386 (2.98).

Picrate: Yellow needles (from dilute ethanol), m. p. 181°C (decomp.).

Found: C, 48.56; H, 3.59; N, 15.80. Calcd. for $C_{18}H_{15}O_9N_5$: C, 48.54; H, 3.59; N, 15.73%.

5-Amino-1, 3-diazaazulene (XV). — Sodium azide (70 mg.) was added in small portions to a solution of XIV (220 mg.) dissolved in concentrated sulfuric acid (0.5 ml.) while stirring with cooling. After stirring for 2 hr., the mixture was diluted with water, made slightly alkaline with 2 N sodium hydroxide, and chilled. The crystalline precipitate (90 mg.) m. p. 209°C, so formed was recrystallized from water to XV as yellow prisms, m. p. 214°C.

Found: N, 28.81. Calcd. for $C_8H_7N_3$: N, 28.95%. Ultraviolet $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε) : 227 (4.00), 269 (4.45), 315 (3.89), 411 (3.11).

Picrate: Yellow prisms (from dilute ethanol), m. p. 244°C (decomp.).

Found: C, 44.94; H, 2.65; N, 21.89. Calcd. for $C_{14}H_{10}O_7N_6$: C, 44.92; H, 2.69; N, 22.46%.

2-Amino-6-(α-ethylenedioxy)ethyl-1, 3-diazaazulene (XVII).—A solution of potassium hydroxide (100 mg.) dissolved in ethanol (10 ml.), with guanidine hydrochloride (170 mg.) and XVI (400 mg.) added, was refluxed for 2 hr., the potassium chloride that precipitated out on cooling was removed by filtration, and the ethanol was evaporated. The crude crystals (290 mg.) of m. p. 190~191°C so obtained were recrystallized from water to XVII as yellow needles, m. p. 199~200°C.

Found: C, 59.74; H, 5.65; N, 17.41. Calcd. for $C_{12}H_{13}O_2N_3\cdot 1/2H_2O$: C, 59.99; H, 5.87; N, 17.49%. Ultraviolet $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε) : 258 (4.54), 353 (4.25), 385 (infl.).

Picrate: Yellow scales (from dilute ethanol), m. p. 244°C (decomp.).

Found: C, 46.24; H, 2.93; N, 18.21. Calcd. for $C_{18}H_{16}O_9N_6$: C, 46.96; H, 3.50; N, 18.26%.

2, 6-Diamino-1, 3-diazaazulene (XVIII).—Sodium azide (25 mg.) was added in small portions to a solution of XVII (70 mg.) dissolved in concentrated sulfuric acid (0.3 ml.) while stirring at room temperature and the mixture was stirred for 2 hr. This was diluted with water, made slightly alkaline with 2 N sodium hydroxide, and the crystals (60 mg.) of m. p. above 300°C so obtained were treated with concentrated ammonia water. Recrystallization from water gave yellow silky needles, m. p. above 300°C, whose ultraviolet and infrared spectra were in complete agreement with those of the known 2,6-diamino-1, 3-diazaazulene.

2-Mercapto-6-(α-ethylenedioxy)ethyl-1, 3-diazaazulene (XIX). — A solution of sodium (76 mg.) dissolved in absolute ethanol (30 ml.) and containing thiourea (255 mg.), with XVI (730 mg.) added, was refluxed for 3 hr., the ethanol was evaporated, and the residue was diluted with water. Acidification with acetic acid produced a precipitate which was recrystallized from dilute ethanol to 520 mg. of XIX as orange silky needles, m. p. 277°C (decomp.).

Found: C, 58.17; H, 5.04; N, 11.05. Calcd. for $C_{12}H_{12}O_2N_2S$: C, 58.06; H, 4.84; N, 11.29%. Ultraviolet $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε) : 230 (4.30), 251 (4.64), 305 (3.84), 440 (4.37).

6-(α-Ethylenedioxy)ethyl-1, 3-diazaazulene (XX). To a suspension of XIX (400 mg.) in water (6 ml.), 35% hydrogen peroxide (2 ml.) was added and the mixture was heated on a water bath for a few minutes, by which the reaction proceeded with effervescence and a clear solution was produced. The mixture was made slightly alkaline with sodium hydrogen carbonate and extracted with chloroform. The crude crystals (270 mg.) of m. p. 161~162°C (decomp.) so obtained were recrystallized from benzene to XX as yellow needles, m. p. 166.5~167.5°C (decomp.).

Found: C, 66.86; H, 5.07; N, 12.72. Calcd. for $C_{12}H_{12}O_2N_2$: C, 66.65; H, 5.59; N, 12.96%. Ultraviolet $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε) : 218 (4.16), 253 (4.56), 314 (3.88), 385 (2.99).

6-Amino-1, 3-diazaazulene (XXI).—Sodium azide (65 mg.) was added to a solution of XX (190 mg.) dissolved in concentrated sulfuric acid (0.5 ml.) while chilling in ice and the mixture was stirred for 2 hr. at room temperature. This was diluted with 2 ml. of water, neutralized to pH 5 with 2 N sodium hydroxide; an ethanol solution of picric acid was added. The precipitate formed was collected by filtration and a picrate (220 mg.) of m. p. 245°C (decomp.) was obtained. Repeated recrystallization from dilute ethanol afforded yellow needles, m. p. 282°C (decomp.), undepressed on admixture with the known 6-amino-1, 3-diazaazulene picrate.

Found: C, 44.57; H, 2.79; N, 22.49. Calcd. for $C_{14}H_{10}O_7N_6$: C, 44.92; H, 2.69; N, 22.46%.

2-Amino-5-hydroxy-1, 3-diazaazulene (XXIII). — A mixture of XII (200 mg.) and 6 N hydrochloric acid (2 ml.) was refluxed in an oil bath for 6 hr. and hydrochloric acid was evaporated to dryness. The residue was neutrallized with a saturated solution of sodium hydrogen carbonate and the yellow crystals (120 mg.) of m. p. 226°C (decomp.) so obtained were recrystallized from water to XXIII as pale yellow prisms, m. p. 249°C (decomp.).

Found: N, 25.85. Calcd. for $C_8H_7ON_3$: N, 26.07%.

2, 5-Dihydroxy-1, 3-diazaazulene (XXIV).—A mixture of XII (200 mg.) and concentrated hydrochloric acid (2 ml.) was heated in a sealed tube at 170~180°C for 6 hr. Treatment as in the case of XXIII afforded crystals (160 mg.) of m. p. above 290°C which were recrystallized from water to yellow microneedles, m. p. above 290°C.

Found: N, 17.56. Calcd. for $C_8H_6O_2N_2$: N, 17.28%. Ultraviolet $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 270 (4.54), 280 (4.57), 330 (3.76), 363 (3.67).

2-Methylthio-5-(α-ethylenedioxy)ethyl-1, 3-diazaazule (XXVI).—To a solution of potassium hydroxide (55 mg.) dissolved in absolute methanol (10 ml.), XIII (250 mg.) was added, followed by methyl iodide (170 mg.), and the mixture was refluxed gently on a water bath. After 45 min., methanol was evaporated and the residual crystals (250 mg.), m. p. 123~125°C, were recrystallized from cyclohexane to pale yellow needles, m. p. 128~129°C.

Found: C, 59.82; H, 5.16; N, 11.62. Calcd. for $C_{13}H_{14}O_2N_2S$: C, 59.53; H, 5.38; N, 10.68%. Ultraviolet $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 241 (4.42), 274 (4.35), 363 (4.25).

2-Methylthio-5-amino-1, 3-diazaazulene (XXVII).—Sodium azide (80 mg.) was added at room temperature to a solution of XXVI (260 mg.) dissolved in concentrated sulfuric acid, covered with chloroform, and the mixture was stirred for 3 hr. at room temperature. The mixture was diluted with water (2 ml.), neutrallized with 2 N sodium hydroxide, and the orange precipitate so produced was recrystallized from 50% ethanol, with treatment with activated carbon, to yellow silky needles, m. p. above 290°C.

Found: C, 47.98; H, 5.67; N, 18.40. Calcd. for $C_9H_9N_3S\cdot 2H_2O$: C, 47.57; H, 5.77; N, 18.40%. Ultraviolet $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 225 (4.08), 311 (4.68), 359 (4.05), 458 (3.50).

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