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The Synthesis and Electrophilic and Nucleophilic Substitution Reactions of 6-Chloro-1-azaazulan-2-ones and 2,6-Dichloro-1-azaazulenes[1]

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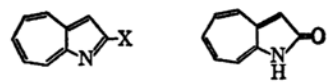
6-Chloro-1-azaazulan-2-ones and 2,6-dichloro-1-azaazulenes have been synthesized from 2-amino-5-chlorotropone. By the investigation of their electrophilic and nucleophilic substitution reactions, it is proved that the electrophilic substitutions take place at the C-3 positions of those compounds, and that the nucleophilic substitutions occur at the C-6 positions and then at the C-2 positions. The tautomerism of 6-amino-2-chloro-1-azaazulene derivatives is discussed.

1-Azaazulenes and their 2-hydroxy derivatives (1-azaazulan-2-ones) are important and interesting substances not only as non-benzenoid analogues of indoles and isomers of quinolines, but also as heterocyclic azulene-type compounds. Several derivatives of 1-azaazulene (I) and 1-azaazulan-2-one (II) have been synthesized.[3-10] The electrophilic substitution reactions of those compounds[8a,8,10a] and the nucleophilic substitution reactions of 2-chloro-1-azaazulene (III)[3b,5b,7] have been investigated. However, 1-azaazulenes and those related compounds which possess functional groups other than alkyl groups in their seven-membered ring have not been known.[11] The purpose of the present paper is to synthesize 1-azaazulenes which possess halogen atoms in their five- and seven-membered rings, and to investigate the chemical properties of these synthesized 1-azaazulenes.



(I): X=H (II) (IV)
(III): X=Cl

It has long been known that abnormal substitutions take place during the nucleophilic reactions of halo-tropolones,[12] 2-halo-tropones,[13] and tropolone arylsulfonates,[14,15] and that abnormal ring formations occurd in the cases of azulenes,[4,15] 1-azaazulan-2-ones,[6] and 1-oxaazulan-2-one (IV) derivatives[14,15] obtained from 2-halo-tropones and tropolone arylsulfonates. Therefore, a method which is known to give a normal condensation product was employed: that is, the condensation reaction of 2-aminotropone derivatives with diethyl malonate.[6]

1) Part of the D. Sc. thesis of Takashi Toda, Tohoku University, March, 1958. Presented in part at the Local Meeting of the Tohoku District of the Chemical Society of Japan, June, 1956, at Yonezawa and at the 11th General Meeting of the Chemical Society of Japan, April, 1958, at Tokyo.

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3) T. Nozoe, S. Seto, S. Matsumura and T. Terasawa, a) *Chem. Ind.*, **1954**, 1356. b) *ibid.*, **1954**, 1357.

4) a) T. Nozoe, S. Seto, S. Matsumura and T. Asano, *Proc. Japan Acad.*, **32**, 339 (1956). b) S. Matsumura, This Bulletin, **34**, 1362 (1961); **35**, 677 (1962).

5) a) T. Nozoe, Y. Kitahara and T. Arai, *Proc. Japan Acad.*, **30**, 478 (1954). b) J. Shin, D.Sc. thesis submitted to Tohoku University, March, 1958.

6) a) T. Nozoe, S. Seto and S. Nozoe, *Proc. Japan Acad.*, **32**, 472 (1956). b) S. Seto and S. Nozoe, *ibid.*, **32**, 765 (1956).

7) S. Seto and K. Suzuki, report presented at the General Local Meeting of the Tohoku District of the Chemical Society of Japan, at Hirosaki, Oct., 1956.

8) a) Y. Murase, M.Sc. thesis submitted to Tohoku University, March, 1955. b) S. Nozoe, *ibid.*, March, 1957. c) A. Sato, *ibid.*, March, 1959.

9) a) G. Sunagawa, N. Soma, H. Nakao and Y. Matsumoto, *Yakugaku Zasshi* (*J. Pharm. Soc. Japan*), **81**, 1799 (1961). b) G. Sunagawa and N. Soma, *ibid.*, **82**, 418 (1962). c) G. Sunagawa and H. Nakao, *Chem. & Pharm. Bull. Japan*, **13**, 450 (1965). d) H. Nakao, N. Soma, Y. Sato and G. Sunagawa, *ibid.*, **13**, 473 (1965). e) H. Nakao, N. Soma and G. Sunagawa, *ibid.*, **13**, 828 (1965).

10) a) T. Toda, This Bulletin, **40**, 590 (1967). b) T. Nozoe, S. Seto and T. Toda, *ibid.*, **41**, 208 (1968).

11) After this work had been completed, a few examples of the nucleophilic substitution reactions of 1-azaazulenes which possess halogen atoms in their seven-membered ring were reported by Shin (Ref. 5b) and by Sunagawa and Soma (Ref. 8a, b).

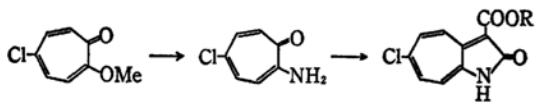
12) a) T. Nozoe and Y. Kitahara, *Proc. Japan Acad.*, **30**, 204 (1954). b) Y. Kitahara, *Sci. Repts. Tohoku Univ., Ser. I*, **39**, 258, 265, 275 (1955); **40**, 74 (1956). c) K. Doi, This Bulletin, **34**, 497 (1961). d) T. Toda, *ibid.*, **40**, 588 (1967).

13) a) S. Seto, *Sci. Repts. Tohoku Univ., Ser. I*, **38**, 377 (1953). b) T. Nozoe, S. Seto and T. Sato, *Proc. Japan Acad.*, **30**, 473 (1954). c) T. Sato, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **80**, 1056, 1167, 1171, 1340 (1959).

14) a) T. Sato, *ibid.*, **80**, 1342, 1345, 1347, 1349 (1959). b) H. Takeshita, M.Sc. essay submitted to Tohoku Univ., March, 1957.

15) a) T. Nozoe, S. Seto, K. Takase, S. Matsumura and T. Nakazawa, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 346 (1965). b) M. Kato. D.Sc. thesis submitted to Tohoku Univ., March, 1965. c) M. Kaneko, M.Sc. thesis submitted to Tohoku Univ., March, 1965.

The Synthesis and Electrophilic Substitution Reactions of 6-Chloro-1-azaazulan-2-ones and 2,6-Dichloro-1-azaazulenes. 2-Amino-5-chlorotropone (V) was prepared by the action of liquid ammonia[16,17] on 5-chlorotropolone methyl ether (VI).[18] The reaction of V with diethyl malonate in the presence of sodium ethoxide afforded ethyl 6-chloro-1-azaazulan-2-on-3-carboxylate (VII) in *ca.* a 70% yield. The UV spectrum of VII is very similar to that of ethyl 1-azaazulan-2-on-3-carboxylate (VIII). The treatment of VII with aqueous alkali did not touch the chlorine atom, but gave a free carboxylic acid (VIIa).



(VI) (V) (VII): R=Et (VIIa): R=H

The hydrolysis of VII with concentrated hydrochloric acid also gave VIIa; the following decarboxylation reaction of VIIa in quinoline or collidine resulted in only tarry substances.

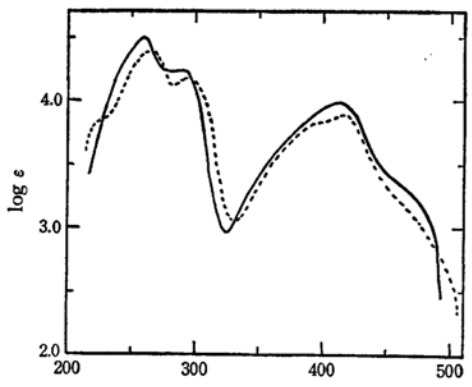


Fig. 1

—— II ---- IX

When VII was treated with concentrated hydrochloric acid in a sealed tube at about 130°C, 6-chloro-1-azaazulan-2-one (IX) was obtained by hydrolysis and by the decarboxylation of VII. On the other hand, the prolonged treatment of VII in concentrated hydrobromic acid under reflux afforded the 6-bromo derivative (X) with an exchange of halogen atoms, and the same treatment of X with concentrated hydrochloric acid gave back IX *vice versa*.

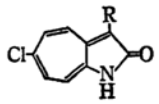
The catalytic reduction of IX and VIIa over palladized charcoal with alkali resulted in the formation of, respectively, the known 1-azaazulan-2-one (II)[3a] and its 3-carboxylic acid (VIIIa)[3a] in good yields. It is interesting and noteworthy to point out that 1-azaazulene and its derivatives, are readily reduced to give perhydro compounds by the catalytic reduction,[19] but not 1-azaazulan-2-one derivatives.

The electrophilic substitution reactions of 6-halo-1-azaazulan-2-ones were investigated.

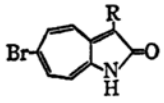
The bromination of IX in acetic acid afforded a monobromo compound (XI) in a good yield; this XI was also obtained from VIIa, with the evolution of carbon dioxide, by the same treatment. Since the bromination of 1-azaazulan-2-on-3-carboxylic acid (VIIIa) gave the 3-bromo-1-azaazulan-2-one,[3a] XI must be 3-bromo-6-chloro-1-azaazulan-2-one.

The nitration of IX and X in acetic acid with fuming nitric acid gave the corresponding nitro compounds (XII and XIII respectively). The reaction of X with *p*-tolyl diazonium chloride formed the 3-(*p*-tolyl)azo compound (XIV).

The catalytic reduction of XII and XIV over palladized charcoal gave the same 3-amino-6-chloro-1-azaazulan-2-one, which was very unstable and which could not be isolated in a free state, but which afforded a stable acetylamino derivative (XV) by the subsequent acetylation:



(IX): R=H
(XI): R=Br
(XII): R=NO_2
(XIV): R=*p*-tolylazo
(XV): R=NHAc



(X): R=H
(XIII): R=NO_2

The treatment of VII, VIIa, IX, X, and XI with acetic anhydride gave the respective corresponding acetates. The UV spectra of these acetates are similar to that of II,[3a] but not to that of I,[3b] and their IR spectra show two strong carbonyl bands, near 1720 and 1700 cm^{-1}. Therefore, they are *N*-acetyl derivatives of the original compounds. A careful examination, by means of chromatography and IR and UV spectroscopy, of the acetylation reaction mixtures and their mother layers after recrystallization did not show any evidence of the presence of *O*-acetyl derivatives.

Ethyl 2,6-dichloro-1-azaazulen-3-carboxylate (XVI) and 2,6-dichloro-1-azaazulene (XVII) were obtained by the treatment of VII and IX with phosphorus oxychloride, respectively. By the action of phosphorus tribromide, IX afforded 2,6-dibromo-1-azaazulene (XVIII), with an exchange of halogen atoms. The halogen atoms of XVII were

16) a) T. Nozoe, S. Seto, H. Takeda, S. Morosawa and K. Matsumoto, *Proc. Japan Acad.*, **27**, 556 (1951). b) *Sci. Repts. Tohoku Univ., Ser. I*, **36**, 126 (1952).
17) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **73**, 828 (1952).
18) T. Sato, *Bulletin of the Chemical Research Institute of Non-Aqueous Solutions, Tohoku Univ.*, **8**, 47 (1959).
19) Unpublished observations made in the authors' laboratory.

exchanged by the treatment of hydrogen bromide in acetic acid to give XVIII, while, *vice versa*, those of XVIII were changed to XVII with the use of hydrogen chloride.

The bromination of XVII and XVIII in acetic acid proceeded readily and gave the corresponding trihalo derivatives (XIX and XX, respectively). XIX was also obtained by the bromination of 2,6-dichloro-1-azaazulen-3-carboxylic acid, which had been prepared from VIIa with phosphorus oxychloride. However, the rate of the bromination of 2,6-dichloro-1-azaazulen-3-carboxylic acid was not as fast as in the case of VIIa. The UV spectra of the obtained 2,6-dihalo-1-azaazulenes are similar to that of 2-chloro-1-azaazulene,[3b] as is shown in Fig. 2.

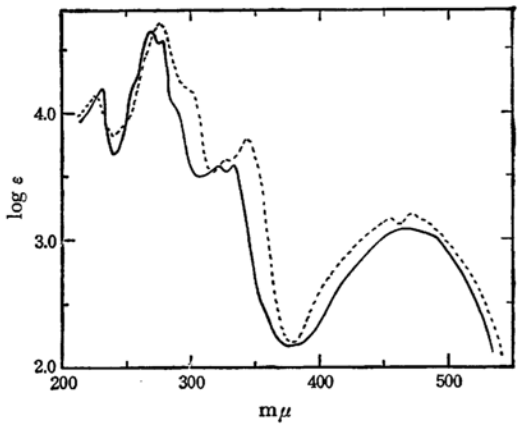


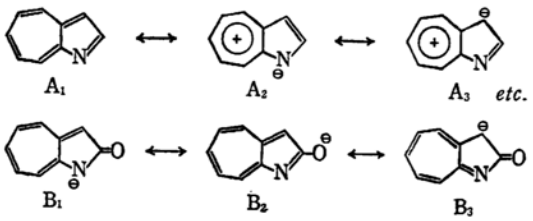
Fig. 2

—— III ---- XVII

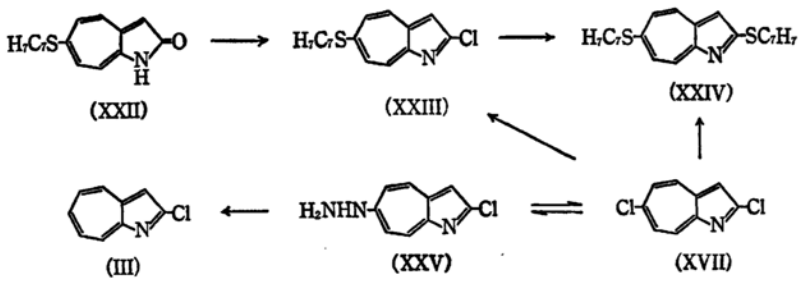
(XVI): R=COOEt (XVIII): R=H
(XVII): R=H (XX): R=Br
(XIX): R=Br
(XXI): R=COOH

The nitration and azo-coupling reactions of XVII resulted in the recovery of the starting substance.

The electron density of the 1-azaazulene nucleus is high at 1,3-positions because of the contributions of such resonance hybrids as A_1, A_2, and A_3.[3b,20] Therefore, the electrophilic substitution reactions take place easily at the C-3 position, especially if C-2 is replaced by an electron-donating group.[3] However, if an electronegative group is introduced into them, electrophilic substitution reactions might not be easy under milder conditions, such as azo-coupling, and/or under acidic conditions, such as nitration, because protonation occurs on the nitrogen atom (or the C-3 position), and this makes for a lower electron density of the 1-azaazulene nucleus. On the other hand, 1-azaazulan-2-one derivatives possess a hydrogen which can dissociate as a proton. Therefore, II forms an anion the canonical forms of which are such as B_1, B_2, B_3, *etc.*; electrophiles can readily attack the C-3 position of this type of anion, especially under basic conditions.



The Nucleophilic Substitution Reactions of 6-Chloro-1-azaazulan-2-one and 2,6-Dichloro-1-azaazulenes. The treatment of IX with excess aqueous potassium hydroxide, sodium methoxide, liquid ammonia, sodium cyanide, *p*-toluidine, *etc.* resulted in the recovery of the starting substance. With dimethylamine in methanol, IX afforded a very small amount of orange needles, but almost all of the IX was recovered. However, 6-(*p*-tolyl)thio-1-azaazulan-2-one (XXII) was obtained in a good yield when IX was treated with the sodium salt of *p*-thiocresol in methanol. The reaction of XXII with phosphorus oxychloride gave 2-chloro-6-(*p*-tolyl)thio-1-azaazulene (XXIII), which was also obtained from XVII with one equivalent mole of *p*-thiocresol. The further treatment of XXIII with *p*-thiocresol formed 2,6-di(*p*-tolyl)thio-1-azaazulene (XXIV), which was also obtained from XVII with an excess of *p*-thiocresol.

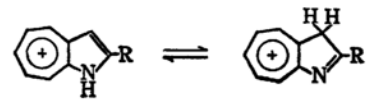


20) H. Kon, *Sci. Repts. Tohoku Univ., Ser. I*, **38**, 67 (1954).

The treatment of XVII with hydrazine hydrate in alcohol afforded a dark reddish-violet hydrazino compound (XXV) which was very unstable and which could not be isolated in a pure state. The decomposition reaction of this crude hydrazino compound with concentrated hydrochloric acid and cuprous sulfate, and with acetic acid and cuprous sulfate,[21,22] gave 2,6-dichloro-1-azaazulene, XVII, and 2-chloro-1-azaazulene, III, respectively. Therefore, the structure of XXV should be 2-chloro-6-hydrazino-1-azaazulene.

It has been predicted, on the basis of measurement of the dipole moment[23,24] and on the basis of theoretical considerations,[20,25] that the electron densities of azulenes and azaazulenes are lower in their seven-membered-ring part than in the five-membered-ring moiety. Thus, it was predicted that the nucleophilic substitution reactions of XVII would take place at the C-6 position first. The facts presented above prove this prediction from the point of view of the chemical reactivity of XVII.

On the other hand, 1-azaazulan-2-ones under the basic conditions are favoured to exist in their anion forms, such as B_1, B_2, *etc.*, as has been mentioned above. As a result of this, the nucleophilic substitution reactions of IX become difficult under the basic conditions. However, 1-azaazulenes and 1-azaazulan-2-ones can form tropyrium-type cations (C_1 and C_2) by protonation under acidic conditions. The nucleophiles readily attack such protonated species, such as in the halogen exchange reactions of IX and XVII described above. This is a phenomenon analogous to the halogen-exchange reaction of halo-tropones under acidic conditions.[26]

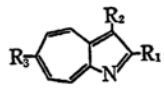


C_1 C_2

R=H or OH

The products obtained by the action of several nucleophilic reagents on XVII are shown in Table 1. The reaction of XVII with other nucleophiles than those listed in Table 1, such as sodium hydroxide, potassium cyanide, cuprous cyanide, and nitromethane, resulted in the recovery of the starting substance or did not give any clear-cut results.

TABLE 1. NUCLEOPHILIC SUBSTITUTION REACTION PRODUCTS OF XVII AND THEIR CHARACTERISTIC IR SPECTRA IN THEIR FINGER PRINT REGION



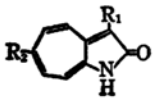
No.	R_1	R_2	R_3	Color	IR△, cm^{-1}
XVI	Cl	COOEt	Cl	Yellow	845
XVII	Cl	H	Cl	Orange-red	834
XVIII	Br	H	Br	Orange-red	831
XIX	Cl	Br	Cl	Carmine	838
XXIII	Cl	H	$SC_7H_7(p)$	Orange-red	837 (806)*
XXIV	$SC_7H_7(p)$	H	$SC_7H_7(p)$	Orange-red	838 (805)*
XXVI	Cl	H	OMe	Yellow	847
XXVII	Cl	H	OEt	Yellow	845
XXVIII	Cl	H	NH_2	Yellow-brown	840
XXIX	Cl	H	NHMe	Yellow-brown	825
XXX	Cl	H	NMe_2	Yellow-brown	825
XXXI	Cl	H	SEt	Orange	823
XXXII	Cl	H	NO_2	Violet-red	828
XXXIII	Cl	H	$CH(COOEt)_2$	Yellow-brown	840
XXXIV	Cl	H	$CH\langle^{CN}_{COOEt}$	Yellow-brown	842
XXXV	Cl	H	$NHC_7H_7(p)$	Brown-red	830 (821)*
XXXVI	Cl	H	$NHC_6H_4NO_2(p)$	Brown	828

△ KBr pellet

* Two adjacent hydrogens in phenyl group.

21) L. Gatterman and R. Holze, *Ber.*, **25**, 1074 (1892).
22) S. Seto, *Sci. Repts. Tohoku Univ., Ser. I*, **38**, 286, 295 (1953).
23) G. W. Wheland and D. E. Man, *J. Chem. Phys.*, **17**, 264 (1949).
24) Y. Kurita and M. Kubo, *J. Am. Chem. Soc.*, **79**, 5460 (1957).
25) a) A. Julg, *J. chim. phys.*, **52**, 377 (1956). b) A. Julg and P. Francois, *ibid.*, **59**, 339 (1962).
26) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **74**, 5683 (1952).

Table 2. Characteristic IR spectra of 1-azaazulan-2-ones in their finger print region



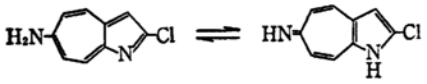
No.	R_1	R_2	Color	IR$^{\Delta}$, cm^{-1}
VII	COOEt	Cl	Yellow	850
	N-Acetate of VII		Yellow	847
VIIa	COOH	Cl	Yellow	842
	N-acetate of VIIa		Yellow	843
IX	H	Cl	Pale orange	823
	N-Acetate of IX		Yellow	822
X	H	Br	Pale orange	822
	N-Acetate of X		Yellow	820
XI	Br	Cl	Orange	841
	N-Acetate of XI		Pale orange	840
XII	NO_2	Cl	Orange	839
XV	NHAc	Cl	Orange	825
XXII	H	$SC_7H_7(p)$	Orange	825 (808)*

$^{\Delta}$ KBr pellet
* Two adjacent hydrogens in phenyl group.

After the substitution took place at C-6, no other substitution reaction occurred at C-2, even though excess reagents were used. Only a strong nucleophile such as the *p*-thiocresol anion[27] could afford the disubstituted product.

It has been shown that abnormal substitution reactions sometimes occur during the nucleophilic substitution reactions of troponoid compounds.[4,6,12-15] Therefore, the reactions described above might take place in such abnormal ways. To clarify this situation, the IR spectra of the nucleophilic substitution products were investigated. The fingerprint regions of the IR spectra of troponoid and azulenoid compounds show strong characteristic bands between 815—860 cm^{-1} and 770—820 cm^{-1} if they possess, respectively, two adjacent hydrogens and one hydrogen in their seven-membered ring.[28] The IR spectra of the 1-azaazulenes in Table 1 and of the 1-azaazulan-2-one derivatives in Table 2 show strong absorption bands between 815—850 cm^{-1}, but not between 770—820 cm^{-1} nor between 850—900 cm^{-1}. Thus, it is proved that the nucleophilic substitution reactions of XVII take place at the C-6 position in the normal way.

The IR spectrum of 6-amino-2-chloro-1-azaazulene (XXVIII) shows strong absorption bands at 1660 and 1602 cm^{-1} and bands at 3350, 3175, and 1585 cm^{-1} of a medium intensity. On the other hand, the 6-methylamino derivative (XXIX) possesses a strong band at 1598 cm^{-1} and medium bands at 3025, 1547 and 1502 cm^{-1}, while 6-dimethylamino compound (XXX) shows strong band at 1599 cm^{-1} and medium bands at 1588 and 1500 cm^{-1}. The assignment of these bands is rather difficult, because usually NH stretching appears between 3100—3500 cm^{-1}, NH deformation shows bands between 1550—1640 cm^{-1}, and the skeletal vibrations of aromatic compounds are between 1650—1480 cm^{-1}.[29] If the band of XXVIII at 1660 cm^{-1} is due to the imino C=N stretching, XXVIII has two tautomeric forms, such as D_1 and D_2. However, the UV spectra of XXVIII, XXIX



D_1 D_2

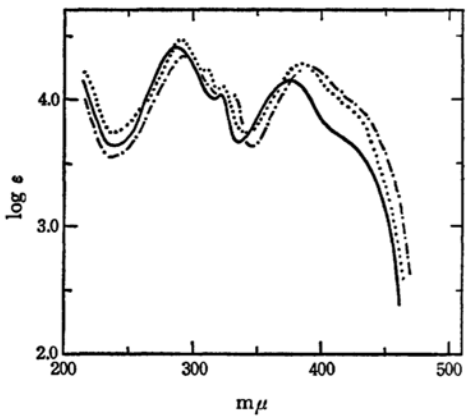
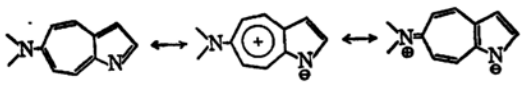


Fig. 3

—— XXVIII ---- XXIX —·—· XXX

27) L. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1952).
28) Y. Ikegami, "Kagaku no Ryoiki Special Issue, Infrared Spectra," No. 8, Nanko-Do, Tokyo (1958), p. 33.
29) L. J. Bellamy, "Infra-red Spectra of Complex Molecules," 2nd ed., Methuen, London (1958).

and XXX are very similar to each other, and XXX can not take the type-D_2 tautomeric form. Therefore, it is difficult to decide toward which form the equilibria of these compounds tend. Also, the UV and IR spectra were measured in very different states; the UV spectra were measured in highly-diluted solutions, and the IR spectra, in solid states. Therefore, the tautomeric forms may be different in the different states. As a rational explanation of those phenomena, the contribution of zwitter-ion structures, such as E_1 and E_2, to these three compounds is suggested. This would explain why the UV spectra of those three compounds, and also their IR spectra, show analogous figures.



E_1 E_2 *etc.*

Wheland has proposed the contributions of such zwitter-ion structures to 2-hydroxy- and 4-hydroxy-pyrimidines;[30] Tsubomura also pointed out the contributions of the same type of zwitter-ion structures to hydroxy- and amino-pyrimidines on the basis of a consideration of their IR and UV spectra.[31]

Experimental[32]

2-Amino-5-chlorotropone (V). In an ice-cold, sealed tube, 9.0 g of VI[18] were placed, and to this *ca.* 50 m*l* of liquid ammonia were introduced; then this mixture was allowed to stand at room temperature for 4 days. After the ammonia had then been removed, the residue was recrystallized from benzene-methanol to give 7.7 g of V, mp 157—159°C; further recrystallization from the same mixed solvents raised its mp to 159—159.5°C.

Found: C, 53.89; H, 3.45; N, 9.12%. Calcd for C_7H_6ONCl: C, 54.04; H, 3.89; N, 9.00%.

Ethyl 6-Chloro-1-azaazulan-2-on-3-carboxylate (VII). A mixture of 0.95 g of V in 5.0 m*l* of absolute alcohol and a solution of 3 m*l* of alcohol containing 0.3 g of sodium and 1.95 g of diethyl malonate in a sealed tube was heated at 100°C for 5 hr. After cooling, the alcohol was removed under reduced pressure, and water was added to the residue. The pH of the water layer was adjusted to *ca.* 4.5 with 1 N sulfuric acid, and then the precipitate formed was separated by filtration and dried in a desiccator. The recrystallization of the precipitate from ethyl acetate-alcohol gave 1.15 g of orange needles of VII; mp 227.5—228°C.

Found: C, 53.35; H, 4.52; N, 5.54%. Calcd for $C_{12}H_{10}O_3NCl \cdot H_2O$: C, 53.15; H, 4.79; N, 5.54%. λ_{max}^{MeOH} mμ (log ε; 225 (4.19), 283 (4.39) and 430 (4.18).

The mother layer of the recrystallization was chromatographed on alumina to give a further 0.12 g of VII, and 80 mg of V was recovered by the elution of the ethyl acetate.

***N*-Acetate of VII.** A solution of 40 mg of VII in 0.5 m*l* of acetic anhydride was heated for reflux for 3 hr; then, after cooling, the precipitate formed was recrystallized from benzene-cyclohexane to give 40 mg of orange-yellow micro needles of the *N*-acetate of VII, mp 181°C.

Found: N, 5.13%. Calcd for $C_{14}H_{12}O_4NCl$; N, 4.77%. IR ($CHCl_3$); 1720 and 1705 cm^{-1}.

6-Chloro-1-azaazulan-2-on-3-carboxylic Acid (VIIa). A mixture of 0.25 g of VII, 1.0 g of pottassium hydroxide, 7 m*l* of water, and 20 m*l* of methanol was heated on a water bath for 2 hr. When the VII had dissolved completely, the pH of the solution was adjusted with 1 N sulfuric acid to *ca.* 3 to give the precipitate. The precipitate was separated by filtration, washed with water, and dried in a desiccator to give 0.21 g of yellow micro needles of VIIa. Recrystallization from alcohol afforded pure VIIa, mp 231—232°C (decomposed). The mother layer of the hydrolysis did not give any precipitate upon the addition of silver nitrate after the solution had been made acidic with nitric acid.

Found: C, 53.60; H, 2.72; N, 6.67%. Calcd for $C_{10}H_6O_3NCl$: C, 53.68; H, 2.70; N, 6.26%.

The *N*-acetate of VIIa was prepared by the same method as was used for the *N*-acetate of VII; yellow needles, mp 205—206°C (blacken).

Found: N, 5.31%. Calcd for $C_{12}H_8O_4NCl$: N, 5.27%. IR (KBr pellet); 1702 and 1685 cm^{-1}.

The Decarboxylated Bromination. a) *Bromination of 1-Azaazulan-2-on-3-carboxylic Acid.* The carboxylic acid (50 mg) was suspended in 1 m*l* of acetic acid and to this 50 mg of bromine was added. The acid was dissolved while carbon dioxide evolved, and the precipitate was formed after a while. The precipitate was then recrystallized twice from methanol to give 50 mg of orange needles mp 210—211°C which were found to be identical with 3-bromo-1-azaazulan-2-one by mixed-melting-point measurements.

b) *Bromination of VIIa.* VIIa (0.10 g) was treated with 80 mg of bromine in 2 m*l* of acetic acid as above to give 0.10 g of XI; orange silky needles from alcohol, mp 243—243.5°C.

Found: N, 5.62%. Calcd for $C_9H_5ONBrCl$: N, 5.41%.

N-Acetate of XI: orange-red needles, mp 190—191°C, from alcohol.

Found: N, 4.57%. Calcd for $C_{11}H_7O_2NBrCl$: N, 4.66%. IR ($CHCl_3$); 1723 and 1708 cm^{-1}.

6-Chloro-1-azaazulan-2-one (IX). A mixture of VII (0.80 g) and 8 m*l* of concentrated hydrochloric acid in a sealed tube was heated for 5 hr at 130°C. The hydrochloric acid was removed under reduced pressure, and then the residue was treated with aqueous bicarbonate to adjust its pH to *ca.* 8, washed with water, and dried in a desiccator. The precipitate was recrystallized from methanol to give yellow prisms of IX, mp 232—233°C; yield, 0.48 g.

Found: C, 59.79; H, 3.52; N, 7.49%. Calcd for C_9H_6ONCl: C, 60.19; H, 3.37; N, 7.79%. λ_{max}^{MeOH} mμ (log ε); 262 (4.38), 293 (4.15) and 410 (3.86).

N-Acetate of IX; yellow silky needles from ethyl acetate, mp 228—229°C.

Found: N, 6.42%. Calcd for $C_{11}H_8O_2NCl$: N, 6.32%. IR ($CHCl_3$); 1722 and 1705 cm^{-1}.

The Catalytic Reduction of VIIa and IX. a) In a solution of 50 mg of VIIa in 2 m*l* of 2 N sodium

30) G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley, New York (1949), p. 636.
31) H. Tsubomura, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan Pure Chem. Sect.*), **78**, 1528 (1957).
32) All melting points are uncorrected.

hydroxide, 10 mg of 5% palladium on charcoal were suspended, and then the reduction was carried out in the usual way. The catalyst was removed by filtration, and the solution was acidified with 1 N sulfuric acid to give a yellow precipitate, the recrystallization of which from alcohol afforded yellow needles of VIIIa, mp 204°C (decompose); yield, 30 mg.

Found: N, 7.05%. Calcd for $C_{10}H_7O_3N$: N, 7.41%.

b) A solution of 0.10 g of IX and 50 mg of sodium acetate in 50 m*l* of methanol was reduced by means of palladised charcoal as above to give 60 mg of orange needles, mp 164—165°C after recrystallization from ethyl acetate; this melting point was identical with that of an authentic sample of II.[3a]

3-Bromo-6-chloro-1-azaazulan-2-one (XI). A solution of 0.10 g of IX in 2 m*l* of acetic acid was treated with 90 mg of bromine and then allowed to stand overnight at room temperature. After the acetic acid had been removed, the residue was washed with aqueous sodium bicarbonate and water, and recrystallized from alcohol to give orange silky needles of XI, mp 245°C; yield, 0.12 g. This was identical with the product of the decarboxylated bromination of VIIa.

Found: C, 41.47; H, 2.19; N, 5.75%. Calcd for $C_9H_5ONBrCl$: C, 41.81; H, 1.95; N, 5.41%.

6-Chloro-3-nitro-1-azaazulan-2-one (XII). To a solution of 0.20 g of IX in 5 m*l* of acetic acid, 0.3 m*l* of fumed nitric acid was added, and then the mixture was allowed to stand overnight at room temperature. The precipitate which formed was separated by filtration, washed with water and alcohol, and then recrystallized from a large amount of alcohol-dioxane to give greenish-brown scales of XII, mp >300°C; yield, 0.18 g.

Found: C, 47.53; H, 1.99; N, 12.20%. Calcd for $C_9H_5O_3N_2Cl$: C, 47.68; H, 2.24; N, 12.47%.

6-Chloro-3-(*p*-tolyl)azo-1-azaazulan-2-one (XIV). Into a solution of 0.10 g of IX in 5 m*l* of 50% of dioxane which had been cooled in an ice bath, *p*-toluene diazonium chloride prepared from 60 mg of *p*-toluidine in the ordinary way was added, drop by drop; the pH of the solution was then adjusted to *ca.* 8.5 with 5% aqueous sodium carbonate, after which the solution was allowed to stand overnight at room temperature. The precipitate formed was separated by filtration, washed with water, and dried in a desiccator to give 0.15 g of a red-purple powder. However, the purification of this powder by means of recrystallization or chromatography failed to produce an analytically-pure substance. The UV spectrum of this shows a figure analogous to that of 3-(*p*-tolyl)azo-1-azaazulan-2-one,[3a] but it shift to a longer wavelength. λ_{max}^{MeOH} mμ (log ε); 247 (4.21), 277 (4.22), 322 (4.13) and 480 (4.16).

3-Acetylamino-6-chloro-1-azaazulan-2-one (XV). a) *The Reduction of XII.* A suspension of XII in 100 m*l* of alcohol was reduced over 10 mg of 5% palladized charcoal in the usual way. The XII dissolved gradually. After 3 mol of hydrogen had been taken up, the catalyst was removed by filtration and the alcohol was concentrated. The residue turned to a black, resinous substances upon concentration. Acetic anhydride (2 m*l*) was added to the residue and the mixture was heated on a water bath. After the acetic anhydride had been removed under reduced pressure, the residue was recrystallized from acetone-methanol to give orange micro needles of XV; mp 276—277°C; yield, 40 mg.

Found: C, 55.57; H, 3.95; H, 11.51%. Calcd for $C_{11}H_9O_2N_2Cl$: C, 55.82; H, 3.83; N, 11.84%.

b) The Reduction of XIV. From 0.10 g of XIV, 40 mg of XV were obtained by the same procedure.

6-Bromo-1-azaazulan-2-one (X). In a sealed tube, 0.10 g of IX and 2 m*l* of acetic acid which had been saturated with dry hydrogen bromide were heated for 6 hr at 100°C. The acetic acid and hydrogen bromide were removed, and then the obtained residue was washed with aqueous sodium bicarbonate and water, and dried in a desiccator. The recrystallization of this solid from methanol gave 0.11 g of orange needles of X, mp 211—212°C. The mixed melting point of X with IX was 224—226°C.

Found: C, 48.59; H, 2.51; N, 6.59%. Calcd for C_9H_6ONBr: C, 48.24; H, 2.69; N, 6.25%.

By the same treatment of X in acetic acid saturated with hydrogen chloride, IX was obtained, mp 232°C. Found: N, 7.91%.

N-Acetate of X; mp 204—205°C. IR ($CHCl_3$); 1720 and 1700 cm^{-1}.

Found: N, 4.82%. Calcd for $C_{11}H_8O_2NBr$: N, 5.21%.

6-Bromo-3-nitro-1-azaazulan-2-one (XIII). By the same treatment as in the nitration of IX, 0.10 g of X afforded 80 mg of pale-greenish-brown leaflets of XIII, mp >300°C, from a large amount of dioxane.

Found: C, 40.58; H, 2.01; N, 10.96%. Calcd for $C_9H_5O_3N_2Br$: C, 40.17; H. 1.87; N, 10.41%.

Ethyl 2,6-Dichloro-1-azaazulen-3-carboxylate (XVI). In a sealed tube, 0.10 g of VII and 1.0 m*l* of phosphorus oxychloride were heated at 100°C for 3 hr, and then the phosphorus oxychloride was removed under reduced pressure. The residue was poured into crushed ice, and the pH of the water layer was adjusted to *ca.* 8.5 with sodium bicarbonate. The precipitate formed was separated by filtration, dried in a desiccator, and recrystallized from benzene to give 90 mg of yellow needles of XVI, mp 185—186°C.

Found: C, 53.05; H, 3.69; N, 5.51%. Calcd for $C_{12}H_9O_2NCl_2$: C, 53.36; H, 3.36; N, 5.19%.

2,6-Dichloro-1-azaazulene (XVII). a) From 8.0 g of IX and 50 m*l* of phosphorus oxychloride treated as above, 7.0 g of orange red needles of XVII were obtained; mp 183°C from cyclohexane. The second crop was 0.8 g, mp 177°C.

Found: C, 53.50; H, 2,87; N, 6.91%. Calcd for $C_9H_5NCl_2$: C, 53.56; H, 2.54; N, 7.07%. λ_{max}^{MeOH} mμ (log ε); 228 (4.16), 275 (4.71), 342 (3.84), 456 (3.19) and 464 (3.20).

b) By the same treatment of 0.10 g of X with 1 m*l* of phosphorus oxychloride, 0.10 g of IX was obtained. Found: N, 7.25%.

c) XVIII (0.10 g) was treated with 5 m*l* of acetic acid, which had been saturated with hydrogen chloride, for 5 hr at 140°C in a sealed tube. After cooling, the product was treated as above to give 80 mg of XVII, mp 181—182°C. Found: N, 7.11%.

2,6-Dichloro-1-azaazulen-3-carboxylic Acid (XXI). VIIa (0.20 g) in 1 m*l* of phosphorus oxychloride was treated as above, and then the pH of the water layer was adjusted to *ca.* 5 with sodium bicarbonate. The precipitate formed and the water-layer extracts obtained by means of benzene were combined, washed with water, and recrystallized from benzene to give 0.10 g of yellow needles of XXI, which did not have

a clear melting point.

Found: C, 49.20; H, 1.88; N, 5.63%. Calcd for $C_{10}H_5O_2NCl_2$: C, 49.64; H, 2.09; N, 5.79%.

2,6-Dibromo-1-azaazulene (XVIII). a) In a sealed tube, 0.10 g of IX and 1 m*l* of phosphorus tribromide were heated at 150°C for 3 hr; after cooling, the reaction mixture was treated as in the case of XVII. The crude XVIII was chromatographed on alumina, and the benzene eluate was recrystallized from benzene-cyclohexane to give orange-red needles of XVIII, mp 202—204°C; yield, 0.10 g.

Found: C, 37.61; H, 2.12; N, 5.24%. Calcd for $C_9H_5NBr_2$: C, 37.66; H, 1.76; N, 4.88%. λ_{max}^{MeOH} mμ (log ε); 230 (4.07), 280 (4.67), 331 (3.83), 347 (3.93) and 466 (3.23).

b) XVII (0.10 g) was heated in 5 ml of acetic acid which had been saturated with hydrogen bromide, for 5 hr at 140°C, and then treated as above to give 0.12 g of XVIII, mp 202.5—203.5°C. Found: N, 5.02%.

3-Bromo-2,6-dichloro-1-azaazulene (XIX). a) A solution of 50 mg of XXI in 1 m*l* of acetic acid was treated with 40 mg of bromine at room temperature. This oily substance formed gradually solidified. The reaction mixture was then allowed to stand for 3 hr, the acetic acid was removed under reduced pressure, and the pH of the residue was adjusted to *ca.* 8.5 with aqueous sodium bicarbonate. The precipitate which formed was then washed with water and dried in a desiccator, and the benzene solution of this was chromatographed on alumina. The benzene eluate was recrystallized from benzene to give 40 mg of reddish-carmine needles of XIX, mp 208—209°C.

Found: C, 39.14; H, 1.55; N, 5.58%. Calcd for $C_9H_4NBrCl_2$: C, 39.03; H, 1.45; N, 5.06%.

b) When 60 mg of XVII in 1 m*l* of chloroform were treated with 50 mg of bromine, the reaction proceeded exothermically and the precipitate formed immediately. The precipitate was then treated as above to give 80 mg of XIX, mp 208—209°C.

2,3,6-Tribromo-1-azaazulene (XX). To a mixture of 20 mg of XVIII and 5 mg of sodium carbonate in 2 m*l* of chloroform, 10 mg of bromine were added; the mixture was then allowed to stand at room temperature for 5 hr. The chloroform was removed, and the residue was washed with water, dried in a desiccator, and recrystallized from benzene - light petroleum to give 25 mg of reddish-carmine needles of XX, mp 215—216°C.

Found: C, 29.98; H, 0.86; N, 4.16%. Calcd for $C_9H_4NBr_3$: C, 29.54; H, 1.10; N, 3.83%.

An Attempted Nitration of XVII. To a solution of 50 mg of XVII in 1 m*l* of acetic acid, 0.2 m*l* of fumed nitric acid was added, after which the mixture was allowed to stand at room temperature overnight. After the acetic acid had then been removed under reduced pressure, the pH of the residue was adjusted to *ca.* 8 with aqueous sodium bicarbonate and the precipitate thus formed was washed with water and dried. The recrystallization of the residue from cyclohexane gave 40 mg of red needles, mp 180—182°C, which did not show any depression when the needles were mixed with the starting substance. The second crop was 5 mg. When the reaction mixture was heated on a water bath, no crystalline substances were obtained, and in concentrated sulfuric acid instead of acetic acid, the starting substance was recovered.

An Attempted Azocoupling Reaction of XVII. XVII (50 mg) was treated with 50 mg of diazotized toluidine in the ordinary way and then allowed to stand in a refrigerator overnight. The precipitate thus formed was then extracted with benzene, and the benzene layer was washed with water, dried over sodium sulfate, and chromatographed on alumina. The benzene eluate was recrystallized from cyclohexane to give 40 mg of orange-red needles, mp 182—183°C, which did not show any depression when the needles were mixed with the starting substance.

The Reaction of XVII with Hydrazine and the Decomposition of 2-Chloro-6-hydrazino-1-azaazulene. a) A solution of 0.20 g of XVII and 80 mg of hydrazine hydrate in 2 m*l* of alcohol was warmed on a water bath for 30 min. The color of the solution changed from orange to dark orange, and then gradually to dark red. The alcohol was removed under reduced pressure and extracted with ethyl acetate. The ethyl acetate extracts were washed with water and dried over sodium sulfate, and the ethyl acetate was removed under reduced pressure to give 0.16 g of a red-violet powder, which decomposed *ca.* 210°C. The powder was unstable and could not be obtained in a pure state because when it was heated in a solvent the color of the powder changed and gave tarry substances.

A solution of 0.14 g of the crude XXV in 2 m*l* of acetic acid was poured all at once into a boiling solution of 0.70 g of cuprous sulfate in 2 m*l* of water. After cooling, the pH of the solution was adjusted to *ca.* 8 with sodium bicarbonate, and the solution was extracted with benzene; the combined benzene extracts were then dried over sodium sulfate and chromatographed on alumina. The benzene eluate was recrystallized from cyclohexane to give 50 mg of orange needles, mp 72°C, which did not show any depression when the needles were mixed with 2-chloro-1-azaazulene (III); the UV spectrum of the product was identical with that of III.

b) Freshly-prepared XXV (80 mg) was dissolved in 2 m*l* of concentrated hydrochloric acid, after which the solution was poured into a boiling solution of 0.60 g of cuprous sulfate in 2 m*l* of water. After cooling, the solution was treadted as above; 20 mg of orange needles were obtained; the mp of 182°C, did not show any depression when the needles were mixed with XVII.

6-(*p*-Tolyl)thio-1-azaazulan-2-one (XXII). IX (0.18 g) was added to a solution prepared from 0.20 g of *p*-thiocresol and 0.10 g of sodium methoxide in 10 m*l* of absolute methanol, and the mixture was heated in a sealed tube for 2 hr at 100°C. The methanol was then removed under reduced pressure, and the precipitate formed was washed with water, dried in a desiccator, and recrystallized from ether-alcohol to give brownish-red prisms of XXII, mp 220—220.5°C; yield, 0.23 g.

Found: C, 71.58; H, 5.36; N, 5.49%. Calcd for $C_{16}H_{13}ONS$: C, 71.90; H, 4.90; N, 5.24%. λ_{max}^{MeOH} mμ (log ε); 221 (4.31), 261 (4.50), 329 (4.21) and 416 (4.19).

2-Chloro-6-(*p*-tolyl)thio-1-azaazulene (XXIII). a) In a sealed tube, 80 mg of XXII in 1 m*l* of phosphorus oxychloride were heated for one hour. After the reaction, the product was treated as the ordinary way. The crude substances thus obtained were recrystallised from cyclohexane-benzene to give 70 mg of orange needles of XXIII, mp 128—129°C.

Found: C, 67.55; H, 4.01; N, 5.33%. Calcd for

$C_{16}H_{12}NSCl$: C, 67.25; H, 4.23; N, 4.90%.

b) To a solution of 60 mg of *p*-thiocresol and 30 mg of sodium methoxide in 5 m*l* of absolute methanol, 0.10 g of XVII was added, and then the mixture was heated under reflux for 15 min. The solution was concentrated under reduced pressure and extracted with benzene, and the benzene extracts were washed with water, dried with water, dried over sodium sulfate, and chromatographed on alumina. The benzene eluate was then recrystallized from cyclohexane-benzene to give orange prisms of XXIII, mp 127.5—129°C; yield, 0.12 g.

2,6-Di(*p*-tolylthio)-1-azaazulene (XXIV). a) A solution of 0.10 g of XVII in 3 m*l* of absolute methanol containing 0.14 g of *p*-thiocresol and 60 mg of sodium methoxide was heated under reflux for 15 min; after reaction, this mixture was treated as above. Orange prisms of XXIV were obtained, mp 189—190°C, yield, 0.16 g.

Found: C, 73.91; H, 5.21; N, 3.91%. Calcd for $C_{23}H_{19}NS_2$: C, 73.88; H, 5.13; N, 3.75%.

b) To a solution of 50 mg of *p*-thiocresol and 20 mg of sodium methoxide in 2 m*l* of absolute methanol, 0.10 g of XXIII was added; the mixture was heated under reflux for 20 min and then treated as above to give 0.12 g of orange prisms mp 189—190°C, which did not show any depression when the prisms were mixed with the XXIV obtained above.

2-Chloro-6-methoxy-1-azaazulene (XXVI). In 2 m*l* of absolute methanol containing 30 mg of sodium, 0.10 g of XVII was heated under reflux for 30 min; after cooling, the methanol was removed under reduced pressure. The precipitate thus formed was washed with water, dried in a desiccator, and recrystallized from benzene-cyclohexane to give 80 mg of yellow needles of XXVI, mp 103—104°C.

Found: C, 61.55; H, 4.29; N, 7.37%. Calcd for $C_{10}H_8ONCl$: C, 61.56; H, 4.16; N, 7.23%. Picrate, mp 206°C. Found: N, 13.18%. Calcd for $C_{16}H_{11}O_8N_4Cl$: N, 13.25%.

2-Chloro-6-ethoxy-1-azaazulene (XXVII). XVII (0.10 g) was treated as above in 2 m*l* of absolute alcohol, containing 30 mg of sodium, to give 0.10 g of yellow needles of XXVII, mp 117—118°C, from benzene-light petroleum.

Found: N, 6.97%. Calcd for $C_{11}H_{10}ONCl$: N, 6.75%.

The Reaction of XVII with Aqueous Alkali. To a solution of 60 mg of potassium hydroxide in 1 m*l* of water, 0.20 g of XVII was added, and the mixture was heated under reflux for 2 hr. The solvent was then removed, and the residue was washed with water and dried in a desiccator to give 0.18 g of yellow needles, mp 179—181°C, which did not show any depression when the needles were mixed with the original XVII. The silver nitrate test of the aqueous layer of the reaction mixture was negative.

The Reaction of XVII with Ammonia. *a) In Methanol.* A solution of 0.10 g of XVII in 15 m*l* of methanol was saturated with ammonia gas at 0°C and then allowed to stand at room temperature for 2 days. After the solvent and ammonia had been removed, the residue was extracted with benzene and chromatographed on alumina. The benzene eluate afforded 50 mg of yellow needles, mp 181—183°C, which did not show any depression when the needles were mixed with XVII.

The ethyl acetate eluate afforded 20 mg of yellow needles, mp 102°C, which did not show any depression when the needles were mixed with XXVI.

b) XVII (0.70 g) was dissolved in 50 m*l* of liquid ammonia which had been cooled in a sodium chloride-ice bath, and then the mixture was allowed to stand at room temperature for 4 days. After the ammonia had been removed the residue was washed with water, dried in a desiccator, and fractionally-recrystallized from benzene and acetone. From the benzene-soluble part, 0.15 g of XVII was recovered, and from the acetone-soluble part, 0.35 g of orange brown prisms of XXVIII, mp 218—220°C, was obtained.

Found: C, 54.60; H, 4.69; N, 13.83%. Calcd for $C_9H_7N_2Cl\cdot H_2O$: C, 54.97; H, 4.61; N, 14.25%.

2-Chloro-6-methylamino-1-azaazulene (XXIX). A solution of 0.10 g of XVII, 70 mg of methylamine hydrochloride, and 50 mg of sodium carbonate in 2 m*l* of methanol was heated in a sealed tube at 100°C for one hr, and then the methanol was removed. The residue was washed with water and recrystallized from acetone-methanol to give 70 mg of yellow-brown micro prisms of XXIX, mp 224—225°C.

Found: C, 62.05; H, 4.38; N, 14.11%. Calcd for $C_9H_7N_2Cl$: C, 62.34; H, 4.71; N, 14.54%.

2-Chloro-6-dimethylamino-1-azaazulene (XXX). A solution of 0.20 g of XVII and 0.5 m*l* of 40% of aqueous dimethylamine in 4 m*l* of methanol was heated under reflux for one hour, and then treated as above to give 0.19 g of pale brown XXX, mp 158—162°C. Recrystallization from benzene raised its mp to 194—195°C; yellow brown scales; yield, 0.16 g.

Found: C, 64.15; H, 5.32; N, 13.43%. Calcd for $C_{11}H_{11}N_2Cl$: C, 63.89; H, 5.36, N, 13.56%.

2-Chloro-6-ethylthio-1-azaazulene (XXXI). A solution of 0.10 g of XVII, 60 mg of sodium methoxide, and 70 mg of ethyl mercaptan in 2 m*l* of absolute methanol was heated under reflux for 15 min, and then the methanol was removed. The residue was dissolved in benzene, washed with water, dried over sodium sulfate, and chromatographed on alumina. The benzene eluate gave 90 mg of orange prisms of XXXI, mp 94°C, from benzene.

Found: C, 58.73; H, 4.46; N, 6.46%. Calcd for $C_{11}H_{10}NSCl$: C, 59.05; H, 4.51; N, 6.26%.

2-Chloro-6-nitro-1-azaazulene (XXXII). A solution of 0.10 g of XVII and 70 mg of sodium nitrite in 3 m*l* of methanol was heated under reflux for 2 hr, concentrated, and extracted with ethyl acetate. The combined ethyl acetate extracts were washed with water, dried over sodium sulfate, and chromatographed on alumina. The ethyl acetate eluate was then recrystallized from the same solvent to give silky, reddish-violet needles of XXXII, mp 220°C (decomp.); yield, 60 mg.

Found: C, 51.37; H, 2.57; N, 12.86%. Calcd for $C_9H_5O_2N_2Cl$: C, 51.82; H, 2.42; N, 13.43%.

Diethyl (2-Chloro-1-azaazulen-6-yl)malonate (XXXIII). To a solution of 50 mg of sodium in 3 m*l* of diethyl malonate, 0.20 g of XVII was added; the mixture was heated at 50°C for one hour, and then the diethyl malonate was removed under reduced pressure. The residue was poured into crushed ice, and the pH of the solution was adjusted to *ca.* 8 by the addition of acetic acid; this giving a precipitate. The precipitate was separated by filtration, washed with water, dried in a desiccator, and extracted with benzene. The benzene

extracts gave 20 mg of the starting substances. The benzene-insoluble solid was dissolved to ethyl acetate and chromatographed on alumina. The ethyl acetate eluate gave a resinous substance. The repeated recrystallization of this from ethyl acetate gave brown micro needles, mp 255°C (decomp. and gradually blacken about 220°C); yield, 40 mg.

Found: N, 3.97%. Calcd for $C_{16}H_{16}O_4NCl$: N, 4.35%.

When the reaction was carried out at room temperature, 90% of XVII was recovered, and the treatment of XVII in absolute methanol with diethyl malonate and sodium methoxide under reflux resulted in a 15% recovery of the XVII, a 20% recovery of the XXVI, and some intractable tar.

Ethyl 1-Cyano-1-(2-chloro-1-azaazulen-6-yl)acetate (XXXIV). To a solution which had been prepared from 0.24 g of ethyl cyanoacetate and 50 mg of sodium in 5 m*l* of benzene, 0.20 g of XVII was added, after which the mixture was heated at 70°C for 5 hr. After cooling, the reaction mixture was poured into crushed ice, and the pH of the water layer was adjusted to *ca.* 6.5 with acetic acid. The reaction mixture was then separated into a benzene-soluble part and an insoluble precipitate. The benzene layer afforded 0.10 g of the recovered XVII after concentration. The precipitate (0.10 g) was dissolved in ethyl acetate - alcohol (10: 1) and chromatographed on alumina three times. The recrystallization of the ethyl acetate - alcohol eluate gave 40 mg of yellow-brown micro prisms of XXXIV, mp 260°C (decomp., blacken *ca.* 200°C).

Found: C, 61.64; H, 4.15; N, 9.99%. Calcd for $C_{14}H_{11}O_2N_2Cl$: C, 61.21; H, 4.40; N, 10.19%.

2-Chloro-6-(*p*-tolyl)amino-1-azaazulene (XXXV). A solution of 50 mg of XVIII and 50 mg of *p*-toluidine in 3 m*l* of methanol was heated under reflux for one hour and then concentrated under reduced pressure; the precipitate thus formed was washed with aqueous sodium bicarbonate and then water. After having been dried in a desiccator, this was dissolved in benzene, and the benzene solution was chromatographed on alumina. The benzene eluate was recrystallized from cyclohexane -benzene to give 70 mg of reddish-brown micro prisms of XXXV, mp 200—201°C.

Found: N, 10.24%. Calcd for $C_{16}H_{13}N_2Cl$: N, 10.42%.

2-Chloro-6-(*p*-nitrophenyl)amino-1-azaazulene (XXXVI). A solution of 50 mg of XVII and 70 mg of *p*-nitroaniline in 4 m*l* of methanol was heated under reflux for one hour after which the methanol was removed under reduced pressure. The residue was washed with aqueous sodium bicarbonate and water, and recrystallized from acetone - methanol to give 60 mg of brown micro needles of XXXVI, mp 241—242°C.

Found: N, 14.07%. Calcd for $C_{15}H_{10}O_2N_3Cl$: N, 14.02%.

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