The Reaction of Aminotropones with Diketene. I. On the Synthesis of 3-Acetyl-1-azaazulenes and Related Reactions

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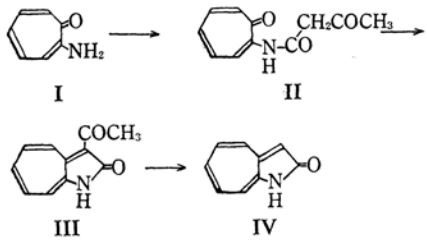
It has previously been shown that 2-aminotropones react with diethyl malonate in the presence of sodium alkoxide to afford directly 3-ethoxycarbonyl-1-azaazulan-2-ones, from which various 1-azaazulenes can be synthesized.[1-3]

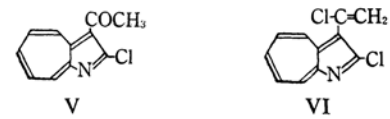
The present authors have now examined the reaction of diketene with some aminotropones and aminotropolones, and have found that the reaction products are useful for the synthesis of 3-acetyl-1-azaazulenes.

When 2-aminotropone (I) was treated with a large excess of diketene, 2-acetoacetamidotropone (II) was obtained in a good yield. The treatment of II with sodium ethoxide gave 3-acetyl-1-azaazulan-2-one (III), whose structure was confirmed from the infrared and ultraviolet absorption spectra and from the chemical evidence that III was transformed to the known 1-azaazulan-2-one (IV)[1] by the action of acid. The treatment of III with



I II III IV

phosphorus oxychloride under the usual conditions[1-3] gave two kinds of 1-azaazulene derivatives, yellow needles (V) ($C_{11}H_8ONCl$) and red prisms (VI) ($C_{11}H_7NCl_2$). The former, V, shows a strong absorption band at 1640 cm^{-1} due to a carbonyl group, while the latter shows bands at 1630 and 895 cm^{-1} due to terminal methylene moiety. The ultraviolet spectra of these products are of the 1-azaazulene type,[1-3] as is shown in Fig. 1. From these facts and from the NMR spectra, which will be described later, it was learned that V and VI were 3-acetyl-2-chloro-and 3-(α-chlorovinyl)-2-chloro-1-azaazulene respectively. It may also be observed that the vinyl derivative VI, compared with the acetyl derivative V, shows a bathochromic shift in the visible region and a hypsochromic shift in the ultraviolet region.



V VI

The NMR spectrum of V exhibits a signal for the acetyl group at 7.20τ, while that of VI shows two doublets of the AB type at 4.40 and 4.08τ, with a coupling constant of 1.2 c.p.s. due to the α-chlorovinyl group. Furthermore, a marked difference in the influence by these two substituents at the 3-position is also apparent in the chemical shifts of the protons at the 4-position of V and VI. The signals for the protons on the seven-membered ring of V consist of three parts of a multiplet with an intensity ratio of 3 : 1 : 1, centered at 2.0, 1.4 and 0.3τ respectively. The components at the abnormally low field (0.3τ) can be assigned to the H_4, because only this proton is

1) T. Nozoe, S. Seto, S. Matsumura and T. Terasawa, *Chem. & Ind.*, **1954**, 1356.
2) T. Nozoe, S. Seto and S. Nozoe, *Proc. Japan Acad.*, **32**, 172 (1956).
3) S. Seto and S. Nozoe, ibid., **32**, 756 (1956).

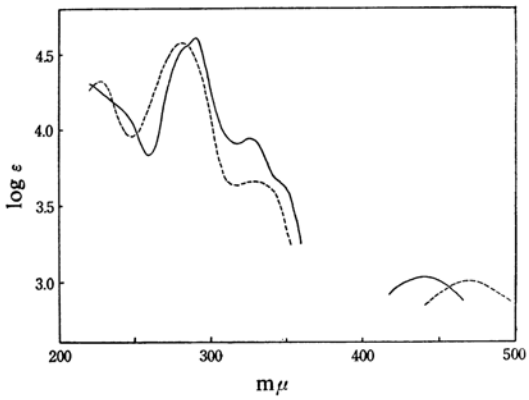


Fig. 1. UV spectra of V (——) and VI (- - -) in methanol.

situated at such a position where the magnetic anisotropy of the acetyl group can be effective. The bands at 1.4τ may be due to the H_8, the nearest proton to the nitrogen atom, since the figure of the splitting closely resembles that of the H_4, which has almost the same environment in terms of spin coupling. This assignment is also consistent with that to be expected from the order of electron density in 1-azaazulene reported by Kon.[4] Furthermore, it is also supported, as will be described later, by the analysis of the spectra of other derivative bearing substituents on the seven-membered ring. Therefore, the components at the highest field can be assigned to the three protons at the 5, 6 and 7-positions.

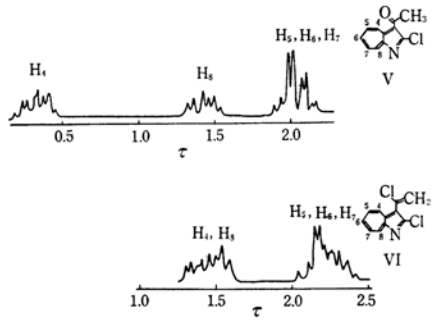
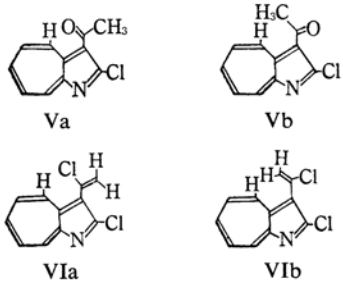


Fig. 2. NMR spectra of V and VI in $CDCl_3$.

The spectrum of VI shows two separated multiplets, centered nearly at 2.2 and 1.5τ, with an intensity ratio of 3 : 2, corresponding to the protons at the 5, 6 and 7-positions and to the protons at the 4 and 8-positions respectively.

The coplanarity of the acetyl and the α-chlorovinyl group with the azaazulene nucleus was suggested by the ultraviolet spectra, and the remarkable effect of these substituents in the NMR spectra noted above indicates that the acetyl group must have predominantly the Va, conformation which is sterically preferable to the other one, Vb. The α-chlorovinyl derivative VI also probably prefers VIa to VIb.



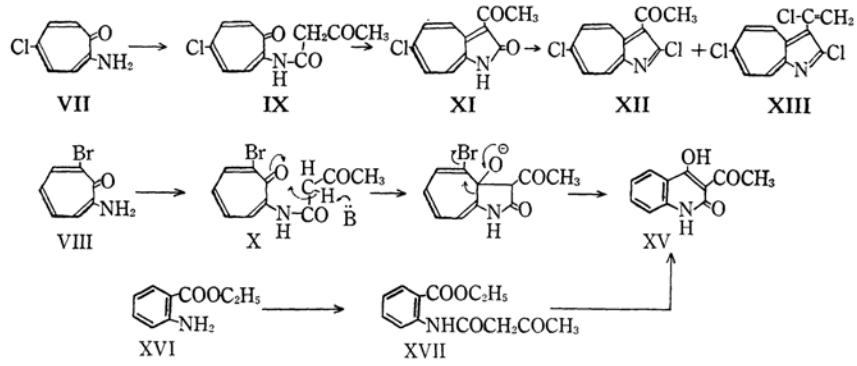
Although the mechanism of the formation of VI from III can not be understood with certainty, it is clear that VI is not produced via V, since any treatment of V with phosphorus oxychloride resulted only in the recovery of V.

2-Amino-5-chlorotropone (VII) and 2-amino-7-bromotropone (VIII) reacted with diketene under somewhat more severe conditions than in the case of I to afford the corresponding *N*-acetoacetyl derivatives, IX and X, while 2-amino-3-bromotropone was quite unreactive under the reaction conditions. The reaction of IX with sodium ethoxide gave 3-acetyl-6-chloro-1-azaazulan-2-one (XI), which in turn afforded 3-acetyl-2,6-dichloro-1-azaazulene (XII) by the action of phosphorus oxychloride as a major product. Only a small amount of red crystals that seemed to be the α-chlorovinyl derivative XIII was obtained. The structure of XII was determined by the analysis of the spectra in the same way as for V. The NMR spectrum of XII exhibits a signal for the acetyl group at 7.3τ and less complicated bands in the 2.1—0.3τ region than those of V and VI due to the ring protons. These bands can be considered to be two sets of a doublet of the AB type to a first approximation; the first doublet in the lower field (0.40τ) and the second at 1.45τ can be assigned to the H_4 and the H_8 respectively, while the signals for the H_5 and the H_7 consist of two just-overlapping doublets at 1.95τ. No splitting by spin coupling between these two protons is observed since these chemical shifts are just the same. The coupling constants, $J(H_4, H_5)$ and $J(H_7, H_8)$, are almost equal, 11.8 c. p. s.

For the sake of comparison, the spectrum of 2,6-dichloro-1-azaazulene (XIV)[5] was also determined. In this case, the signal for the H_4 is moved upfield, as compared with that

4) H. Kon, *Sci. Repts., Tohoku Univ., First Series*, 38, 67 (1954).

5) T. Toda, to be published.



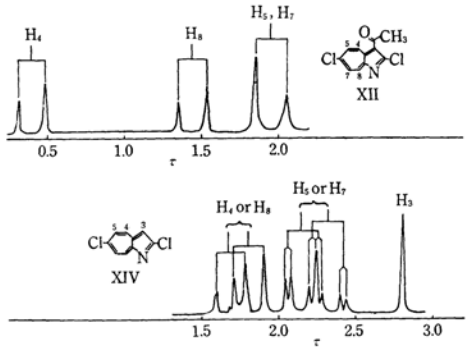


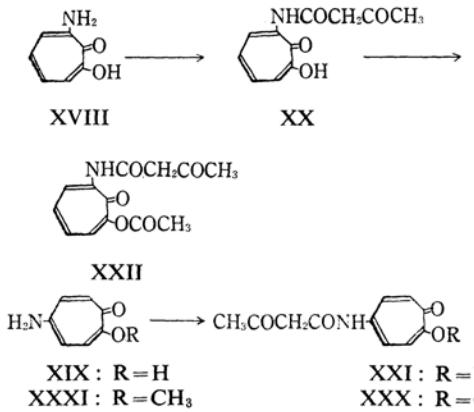
Fig. 3. NMR spectra of XII and XIV in $CDCl_3$.

of XII, and is incorporated among the signals for the H_8.

Although the chemical shift for each proton can not be determined, the signals at 2.1—2.5τ, which consist of a pair of a quartet, may be assigned to the H_5 and the H_7 ($J(H_4, H_5) = J(H_7, H_8) = 11.0$; $J(H_5, H_7) = 2.1$ c.p.s.) (Fig. 3). The singlet at 2.80τ must correspond to the H_3.

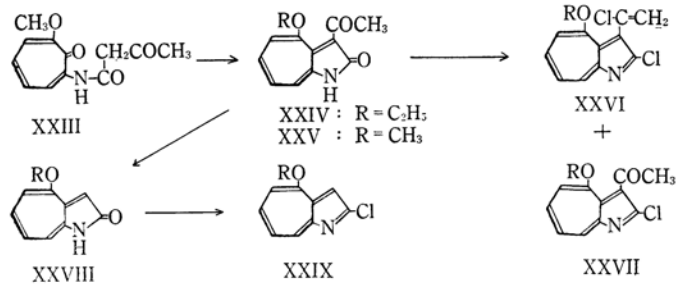
The treatment of 2-acetoacetamido-7-bromotropone (X) with alkali gave a product which was not a 1-azaazulanone derivative. This product was found to be 3-acetyl-4-hydroxycarbostyril (XV) by comparison with an authentic specimen prepared from ethyl anthranilate (XVI). It was reported that the reaction of ethyl anthranilate (XVI) with ethyl acetoacetate gave an *N*-acetoacetyl derivative (XVII) and that the heating of XVII in dry xylene in the presence of powdered sodium afforded XV.[6] The authors also found that the reaction of diketene with XVI gave the corresponding *N*-acetoacetyl derivative XVII under rather mild conditions, this could then be converted into XV in a fairly good yield, even by mild treatment with alcoholic alkali.

3-Aminotropolone (XVIII) and 5-aminotropolone (XIX) also reacted easily with diketene to afford 3-acetoacetamido- (XX) and 5-acetoacetamidotropolone (XXI) respectively. The compound XX itself did not give any cyclization product on treatment with sodium alkoxide, and the reaction of XX with acetic anhydride gave only its acetate XXII. When



a methyl ether XXIII, obtained by the reaction of XX with diazomethane was treated with sodium ethoxide, a 1-azaazulanone derivative XXIV, $C_{13}H_{13}O_3N$, was obtained. The fact that the treatment of XXII with sodium methoxide gave another 1-azaazulanone derivative XXV, $C_{12}H_{11}O_3N$, suggested that anionoid substitution by alkoxide at the 4-position of the azaazulanone ring might occur during this reaction. The existence of an ethoxy group in XXIV was verified by the NMR spectra of the 1-azaazulene derivative XXVI derived from XXIV. The treatment of XXIV with phosphorus oxychloride gave orange needlers XXVI and a small amount of yellow crystals XXVII. The latter was found from its infrared spectrum to be a likely 3-acetyl derivative. The appearance of a triplet at 8.36τ and a quartet at 5.66τ (*J*, 6.4 c. p. s.) in the NMR spectrum of XXVI indicates the presence of the ethoxy group, while two doublets at 4.61

6) K. Tomita, *J. Pharm. Soc. Japan*, **71**, 1100 (1951).



and 4.82τ (J, 0.9 c. p. s.) seem to be attributable to the two protons of the α-chlorovinyl group.

It is noteworthy that XXIV was deacetylated with surprising ease when treated with acid at room temperature to give 4-ethoxy-1-azaazulan-2-one (XXVIII). This compound was converted into 2-chloro-4-ethoxy-1-azaazulene (XXIX), whose infrared spectrum indicated the absence of an acetyl group. It was also observed that the introduction of an ethoxy group to the 4-position of both 1-azaazulan-2-one and 2-chloro-1-azaazulene causes a hypsochromic shift (about 15 mμ) of the band in the shorter-wavelength region in the ultraviolet spectrum.

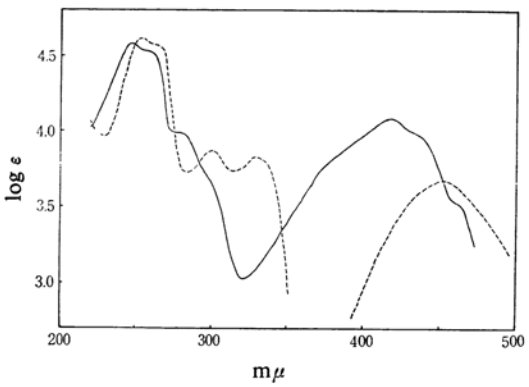
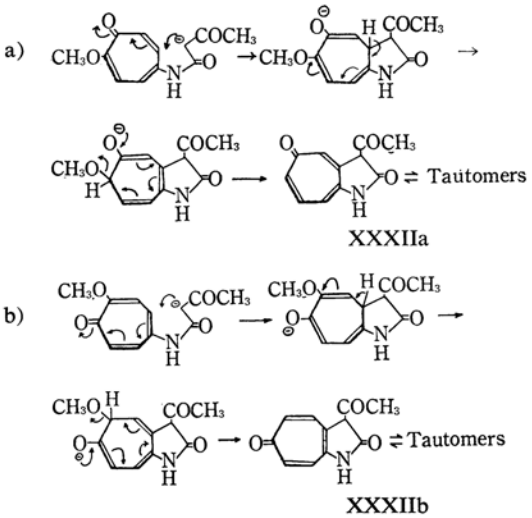


Fig. 4. UV spectra of XXVIII (——) and XXIX (- - -) in methanol.

A methyl ether XXX which had been prepared either by the treatment of XXI with diazomethane or by the reaction of 5-amino-2-methoxytropone (XXXI) with diketene gave yellow crystals XXXII when treated with sodium ethoxide. It is sparingly soluble in organic solvents and shows a characteristic absorption in the ultraviolet spectrum. The treatment of XXXII with acetic anhydride gave a diacetate XXXIII, which has an ultraviolet absorption curve of the 1-azaazulanone type. The infrared spectrum of XXXIII exhibits four bands for the carbonyl group, at 1755, 1710, 1700 and 1650 cm^{-1}, suggesting that XXXIII might be an *N*-acetyl-1-azaazulan-2-one derivative, bearing an acetyl group and an acetoxy group on the azaazulanone ring. This was also supported by a spectral comparison between XXXIII and the *N*-acetyl-1-azaazulan-2-one derivative XXXIV prepared from III. Two kinds of structure (XXXIIa and XXXIIb) for XXXII may be expected from a consideration of the reaction mechanism of this abnormal substitution:



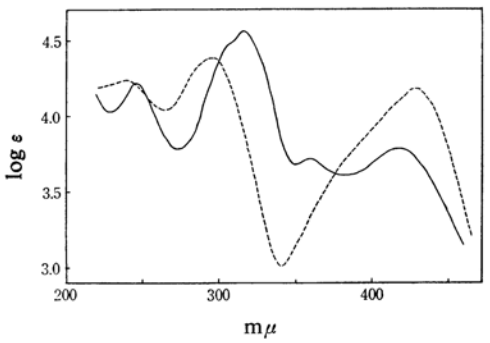
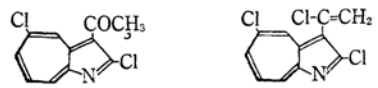


Fig. 5. UV spectra of XXXII (——) and XXXIII (- - -) in methanol.

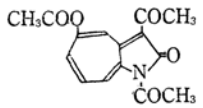
If the product XXXII had the structure XXXIIb, it would be converted into 3-acetyl-2, 6-dichloro-1-azaazulene (XII) by treatment

with phosphorus oxychloride. The treatment of XXXII, however, gave 3-acetyl- (XXXV) and 3-α-chlorovinyl derivatives (XXXVI) of 2, 5-dichloro-1-azaazulene derivatives, whose structures were strongly supported by the analysis of the NMR spectra. Consequently, XXXII must have the structure XXXIIa and XXXIII must be *N*, 3-diacetyl-5-acetoxy-1-aza-azulan-2-one.

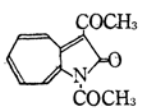


XXXV

XXXVI



XXXIII



XXXIV

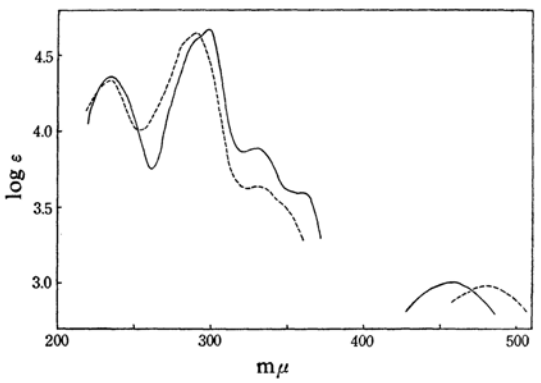
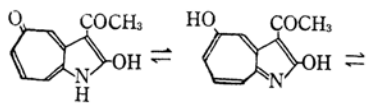
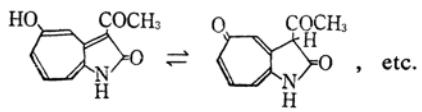


Fig. 6. UV spectra of XXXV (——) and XXXVI (- - -) in methanol.

Although the situation of the tautomerism in XXXII can not be strictly stated, the ultraviolet and infrared spectra indicate that the A form may be predominant.



(A) (B)



(C) (D)

In the NMR spectrum of XXXV the pattern arising from the protons at the 6, 7 and 8-positions of XXXV can be approximately described as an ABX system, where X corresponds to the H_8. The lower-field components must arise from the H_6, since they show additional splitting by coupling with the H_4, which corresponds to a doublet at 0.2τ (J, 2.4 c. p. s.), and the higher-field quartet can be assigned to the H_7. A first-order analysis of this spectrum gives the following values:

$J(H_6, H_7) = 10.0$, $J(H_6, H_8) = 1.5$,

$J(H_7, H_8) = 9.3$ c. p. s.

$H_4 = 0.2$, $H_8 = 1.5$, $H_6 = 1.9$, $H_7 = 2.2\tau$

The spectrum of XXXVI also displays almost the same pattern for the protons at the 6, 7 and 8-positions, but the doublet due to the H_4 is moved upfield (1.3τ). The signal for the acetyl group of XXXV appears at 7.2τ, and the signals for the α-chlorovinyl group in XXXVI represent an AB system at 4.0 and 4.4τ (J, 1.5 c. p. s.). A schematical illustration of these spectra is given in Fig. 7.

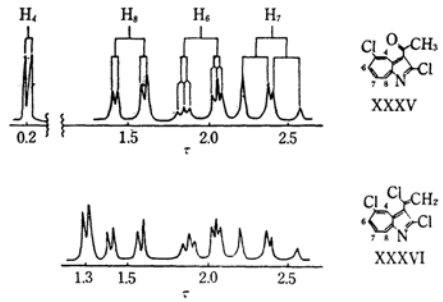


Fig. 7. NMR spectra of XXXV and XXXVI in $CDCl_3$.

The only structures for XXXV and XXXVI that can account for these spectra are 3-acetyl-2, 5-dichloro-1-azaazulene and 2, 5-dichloro-3-(α-chlorovinyl)-1-azaazulene respectively.

Additional work is in progress to make a further extension of these reactions; it will be reported on in the near future.

Experimental*

2-Acetoacetamidotropone (II).—A solution of 2-aminotropone (2 g.) in diketene (10 ml.) was heated on a water bath for 2 hr.; the complete evaporation of the excess diketene then left colorless crystals, which were collected and recrystallized from methanol to give colorless needels, m. p. 118—121°C. Yield, 3.1 g.

Found: C, 64.12; H, 5.62; N, 6.33. Calcd. for $C_{11}H_{11}O_3N$: C, 64.38; H, 5.40; N, 6.83%.

* All melting points are uncorrected. The microanalyses were carried out by Misses Yôkô Endo and Yukiko Endo of this Institute, to whom the authors are indebted. The measurements of the ultraviolet and infrared spectra were made, respectively, with a Hitachi EPU-2A type spectrophotometer and with a Hitachi EPI Model S-2 spectrophotometer. The NMR spectra were measured with a Varian 4301 high resolution NMR spectrometer.

3-Acetyl-1-azaazulan-2-one (III). — A mixture of II (1 g.) and sodium (0.4 g.) in absolute ethanol (50 ml.) was refluxed for 1.5 hr., and then the ethanol was distilled off. When the residual crystals were dissolved in water and neutralized with diluted hydrochloric acid, yellow crystals precipitated; these were collected and recrystallized from ethanol to give yellow needles, m. p. 265—270°C. Yield, 650 mg.

Found: C, 70.90; H, 4.68; N, 7.85. Calcd. for $C_{11}H_9O_2N$: C, 70.58; H, 4.85; N, 7.48%.

The Deacetylation of III. — After 50 mg. of III had been heated in hydrobromic acid (1 ml.) at 100°C for 2 hr., the solution was neutralized with sodium carbonate and extracted with ethyl acetate to give yellow needles (25 mg.) of IV.

3-Acetyl-2-chloro-1-azaazulene (V) and 2-Chloro-3-(α-chlorovinyl)-1-azaazulene (VI). — A mixture of III (200 mg.) and phosphorus oxychloride (6 ml.) was heated at 85°C for 15 min. After the excess phosphorus oxychloride had been removed under reduced pressure, cracked ice was added to the residue. The solution was then neutralized with sodium bicarbonate and extracted with benzene. The deep yellow crystals obtained by the evaporation of the solvent were chromatographed on an alumina colum, after which elution with benzene-petroleum ether gave red prisms of VI and yellow needles of V. The respective recrystallizations from benzene-petroleum ether afforded red prisms of VI (35 mg.), m. p. 76—77°C and yellow needles of V (140 mg.), m. p. 159—160°C.

V: λ_{max}^{MeOH} mμ (log ε): 291 (4.62), 326 (3.95), 440 (3.03).

Found: C, 64.26; H, 3.89; N, 6.67. Calcd. for $C_{11}H_8ONCl$: C, 64.24; H, 3.92; N, 6.81%.

VI: λ_{max}^{MeOH} mμ (log ε): 228 (4.32), 281 (4.58), 330 (3.66), 470 (2.99).

Found: C, 59.35; H, 3.16; N, 6.71. Calcd. for $C_{11}H_7NCl_2$: C, 58.96; H, 3.15; N, 6.25%

2-Acetoacetamido-5-chlorotropone (IX).—A solution of VII (270 mg.) in diketene (8 ml.) was heated at 100—120°C for 2 hr. The evaporation of the excess diketene left brownish yellow crystals, which were collected and recrystallized from acetone to afford pale yellow needles, m. p. 145°C. Yield, 325 mg.

Found: C, 55.36; H, 3.87; N, 6.15. Calcd. for $C_{11}H_{10}O_3NCl$: C, 55.10; H, 4.21; N, 5.85%.

2-Acetoacetamido-7-bromotropone (X). — A solution of VIII (150 mg.) in diketene (1.5 ml.) was heated at 95—98°C for 4 hr. After the evaporation of the excess diketene, the crystals were recrystallized from methanol to give colorless needles, m. p. 114—115°C. Yield, 130 mg.

Found: C, 46.76; H, 3.36; N, 5.23. Calcd. for $C_{11}H_{10}O_3NBr$: C, 46.40; H, 3.89; N, 4.93%.

3-Acetyl-6-chloro-1-azaazulan-2-one (XI).—When IX (115 mg.) was added to a sodium ethoxide solution (sodium, 80 mg.; absolute ethanol, 20 ml.), orange crystals appeared immediately. While the mixture was then refluxed for 2 hr., however, the crystals dissolved gradually. After the removal of the solvent, the residue was acidified with 6 N sulfuric acid and adjusted to pH 2; the yellow crystals which had been deposited were collected and recrystallized from methanol to give yellow needles, m. p. 278°C (decomp.). Yield, 185 mg.

Found: C, 59.11; H, 3.44; N, 6.40. Calcd. for $C_{11}H_8O_2NCl$: C, 59.59; H, 3.64; N, 3.22%.

3-Acetyl-2, 6-dichloro-1-azaazulene (XII). — A mixture of XI (115 mg.) and phosphorus oxychloride (8 ml.) was warmed at 80°C for 2 hr. After the evaporation of the excess phosphorus oxychloride under reduced pressure, the residue was neutralized with an aqueous sodium bicarbonate solution, adjusted to pH 8, and extracted with ethyl acetate. The solution, after being dried on sodium sulfate, was passed through an alumina column. Elution with benzene gave yellow needles of XII. Recrystallization from benzene gave yellow needles, m. p. 183°C (decomp.). Yield, 100 mg. λ_{max}^{MeOH} mμ (log ε): 298 (4.65), 340 (4.04), 450 (3.07).

Found: C, 55.05; H, 2.64; N, 5.97. Calcd. for $C_{11}H_7ONCl_2$: C, 55.00; H, 2.92; N, 5.84%.

Red crystals of XIII were also obtained from the effluent, but in a very poor yield.

The Reaction of X with Alkali. — A solution of X (20 mg.) in an alcoholic potassium hydroxide solution (potassium hydroxide, 70 mg.; ethanol, 1 ml.; water, 2 drops) was warmed on a water bath for 30 min. The acidification of the solution with diluted hydrochloric acid caused colorless crystals to precipitate; they were collected and recrystallized from ethanol to give colorless needles, m. p. 246—247°C. This substance was found to be identical with 3-acetyl-4-hydroxycarbostyril (XV) by comparison with an authentic sample.

Ethyl 2-Acetoacetamidobenzoate (XVII). — A mixture of ethyl anthranilate (1 g.) and diketene (2.5 ml.) was warmed at 70—80°C for 1.5 hr. After the complete removal of the excess diketene, the resultant oily residue was dissolved in ether and the solution was shaken with diluted hydrochloric acid to remove any unreacted starting material. The concentration of the ether solution gave colorless crystals, which were recrystallized from petroleum ether to yield granular crystals, m. p. 163—165°C. Yield, 1 g.

3-Acetyl-4-hydroxycarbostyril (XV).—A solution of XVII (20 mg.) in an alcoholic potassium hydroxide solution (potassium hydroxide, 70 mg; ethanol, 1 ml.; water, 2 drops) was warmed on a water bath for 30 min. After the evaporation of the ethanol, the solution was acidified with diluted hydrochloric acid. The colorless precipitate which was thus deposited was collected and recrystallized from ethanol to afford colorless needles, m. p. 244—247°C. Yield, 10 mg. This product was found, by a comparison of their infrared spectra, to be identical with an authentic sample prepared by Tomita's method.[6]

3-Acetoacetamidotropolone (XX). — A mixture of XVIII (500 mg.) and diketene (2.5 ml.) was heated on a water bath for 2 hr. After the removal of the excess diketene under reduced pressure, the residual crystals were recrystallized from methanol to afford colorless needles, m. p. 93—95°C. Yield, 680 mg. IR 3180, 1700, 1680 cm^{-1} (KBr).

Found: C, 59.31; H, 5.17; N, 6.42. Calcd. for $C_{11}H_{11}O_4N$: C, 59.72; H, 5.01; N, 6.33%.

5-Acetoacetamidotropolone (XXI). — A mixture

of 5-aminotropolone (4 g.) and diketene (20 ml.) was heated at 80°C for 2 hr. The colorless crystals that separated when the mixture was cooled to room temperature were collected and washed with ether. Recrystallization from acetone-methanol afforded colorless needles (4.16 g.), m. p. 138—139°C.

Found: C, 59.49; H, 4.72; N, 6.45. Calcd. for $C_{11}H_{11}O_4N$: C, 59.72; H, 5.01; N, 6.33%.

The Acetate (XXII) of XX. — A solution of XX (50 mg.) in acetic anhydride (0.4 ml.) was heated at 120°C for 4 hr., and then the excess acetic anhydride was removed under reduced pressure. The recrystallization of the residue from methanol gave colorless scales, m. p. 146—148°C. Yield, 30 mg. IR 3270, 1750, 1690 cm^{-1} (KBr).

Found: C, 59.49; H, 4.83; N, 6.37. Calcd. for $C_{13}H_{13}O_5N$: C, 59.31; H, 4.98; N, 5.32%.

The Methyl Ether (XXIII) of XX. — To a suspension of XX (630 mg.) in a mixture of ether (18 ml.) and methanol (3 ml.), ethereal diazomethane was added until the evolution of nitrogen ceased. The end point of the reaction was determined by a coloration test with ferric chloride. During this reaction, the crystals (XX) dissolved gradually and colorless needles newly appeared. The needles were collected and recrystallized from ethanol to give colorless needles, m. p. 163—166°C. Yield, 360 mg. IR 3240, 1710, 1675 cm^{-1} (KBr).

Found: N, 6.18. Calcd. for $C_{12}H_{13}O_4N$: N, 5.96%.

3-Acetyl-4-ethoxy-1-azaazulan-2-one (XXIV). — A suspension of XXIII (100 mg.) in a sodium ethoxide solution (sodium, 40 mg.; ethanol, 4 ml.) was refluxed for 4 hr., and then the yellow solution thus obtained was concentrated under reduced pressure. When the residue was dissolved in water (2 ml.) and neutralized with diluted hydrochloric acid, yellow crystals separated. The recrystallization of the crystals from methanol yielded yellow needles, m. p. 220—225°C. Yield, 70 mg. λ_{max}^{MeOH} mμ (log ε): 252 (4.57), 440 (4.14). IR 1690, 1630 cm^{-1} (KBr).

Found: C, 68.14; H, 6.14; N, 5.72. Calcd. for $C_{13}H_{13}O_3N$: C, 67.52; H, 5.67; N, 6.06%.

3-Acetyl-4-methoxy-1-azaazulan-2-one (XXV). — A suspension of XXIII (50 mg.) in a sodium methoxide solution (sodium, 20 mg.; absolute methanol, 3 ml.) was refluxed for 3.5 hr. After the evaporation of the solvent, the residue was neutralized with dilute hydrochloric acid and extracted with ethyl acetate. The removal of the sovlent left yellow crystals, which were then collected and recrystallized from methanol to give yellow needles, m. p. 200—220°C (decomp.). Yield, 20 mg. IR 1690, 1625 cm^{-1} (KBr).

Found: C, 65.82; H, 4.85; N, 6.65. Calcd. for $C_{12}H_{11}O_3N$: C, 66.35; H, 5.10; N, 6.45%.

2-Chloro-3-(α-chlorovinyl)-4-ethoxy-1-azaazulene (XXVI). — A mixture of XXIV (100 mg.) and phosphorus oxychloride (3 ml.) was heated at 95—98°C for 1 hr., after which the excess phosphorus oxychloride was removed under reduced pressure. To the residue, ice-cooled water was added, and the solution was neutralized with sodium bicarbonate, adjusted to pH 8, and extracted with benzene. The crystals obtained from the extract were chromatographed on an alumina column, and elution with benzene afforded orange crystals. Recrystallization from benzene-petroleum ether gave orange needles, m. p. 109—111°C. Yield, 95 mg. λ_{max}^{MeOH} mμ (log ε): 253 (4.52), 270 (4.51), 304 (399), 332 (3.93), 455 (3.64). IR 1640, 885 cm^{-1} (KBr).

Found: C, 58.51; H, 3.48; N, 5.25. Calcd. for $C_{13}H_{11}ONCl_2$: C, 58.23; H, 4.14; N, 5.22%.

4-Ethoxy-1-azaazulan-2-one (XXVIII). — When a solution of XXIV (100 mg.) in concentrated hydrochloric acid (1 ml.) was allowed to stand at room temperature, yellow crystals began to separate out in a few minutes. After it had been allowed to stand for 1 hr., the mixture was neutralized with a sodium bicarbonate solution and the crystals were collected. Recrystallization from methanol gave yellow needles, m. p. 180—183°C. Yield, 80 mg. λ_{max}^{MeOH} mμ (log ε): 246 (4.58), 417 (4.09). IR 1670 cm^{-1} (broad) (KBr).

Found: C, 69.66; H, 5.65; N, 7.44. Calcd. for $C_{11}H_{11}O_2N$: C, 69.82; H, 5.86; N, 7.40%.

2-Chloro-4-ethoxy-1-azaazulene (XXIX). — A mixture of XXVIII (40 mg.) and phosphorus oxychloride (1.5 ml.) was heated at 90—95°C for 1 hr. The evaporation of the excess phosphorus oxychloride left a dark red residue, which was then dissolved in cold water (5 ml.) and neutralized with sodium bicarbonate. The precipitate which was thus deposited was collected and chromatographed on an alumina column. Elution with benzene gave orange crystals. Recrystallization from benzene-petroleum ether afforded orange needles, m. p. 120—122°C. Yield, 30 mg. λ_{max}^{MeOH} mμ (log ε): 252 (4.62), 300 (3.88), 328 (3.84), 452 (3.69).

Found: C, 63.99; H, 4.51; N, 6.99. Calcd. for $C_{11}H_{10}ONCl$: C, 63.62; H, 4.85; N, 6.75%.

Methyl Ether (XXX) of XXI. — a) To a suspension of XXI (3.5 g.) in methanol (40 ml.), ethereal diazomethane was added until a portion of the mixture no longer showed coloration with ferric chloride. The colorless crystals that appeared were collected and recrystallized from acetone to give colorless crystals, m. p. 164°C (decomp.). Yield, 2.4 g.

Found: C, 61.06; H, 5.52; N, 5.79. Calcd. for $C_{12}H_{13}O_4N$: C, 61.27; H, 5.57; N, 5.96%.

b) To a solution of 5-aminotropolone (100 mg.) in methanol, ethereal diazomethane was added until a portion of the solution no longer colored with ferric chloride. After the evaporation of the solvent, the addition of a small amount of acetone brought the residue to crystallization. The crystals were collected and recrystallized from acetone to give yellow crystals of 110 mg. of 5-amino-2-methoxytropone (XXXI), m. p. 95—105°C. A mixture of XXXI (110 mg.) and diketene was warmed at 60°C for 20 min., and the crystals that separated out on cooling were collected and recrystallized from acetone to afford colorless crystals of XXX. Yield, 80 mg.

3-Acetyl-2-hydroxycyclohepta[b]pyrrol(1*H*)-5-one (XXXII). — After a suspension of XXX (1.5 g.) in a solution of sodium ethoxide (sodium, 600 mg.; absolute ethanol, 84 ml.) was refluxed for 3 hr., the solvent was removed. The residue was then

dissolved in 20 ml. of water, acidified with diluted sulfuric acid, and adjusted to pH 4, and the yellow crystals that separated were collected. Recrystallization from methanol gave yellow crystals, m. p. >300°C. Yield, 800 mg. λ_{max}^{MeOH} mμ (log ε): 245 (4.21), 316 (4.56), 360 (3.71), 418 (3.78).

Found: C, 63.47; H, 4.70; N, 6.62. Calcd. for $C_{11}H_9O_3N$: C, 65.02; H, 4.46; N, 6.89%.

***N*, 3-Diacetyl-5-acetoxy-1-azaazulan-2-one (XXXIII).**—A mixture of XXXII (40 mg.), pyridine (0.7 ml.) and acetic anhydride (1 ml.) was warmed at 80—90°C for 10 min. The yellow needles that separated out on cooling were collected and recrystallized from benzene to give yellow needles, m. p. 177—179°C. Yield, 25 mg. λ_{max}^{MeOH} mμ (log ε): 245 (4.21), 316 (4.56), 360 (3.71), 418 (3.78).

Found: C, 62.84; H, 4.73; N, 5.59. Calcd. for $C_{15}H_{13}O_5N$: C, 62.71; H, 4.56; N, 4.88%.

***N*, 3-Diacetyl-1-azaazulan-2-one (XXXIV).** — A mixture of III (50 mg.), acetic anhydride (1.5 ml.) and pyridine (1 drop) was heated on a water bath for 10 min. After the mixture had then been cooled to room temperature, the yellow needles that separated out were collected and recrystallized from benzene to give yellow needles, m. p. 190—191°C. Yield, 30 mg. IR 1710, 1695, 1640 cm^{-1} (KBr).

Found: C, 68.23; H, 4.77; N, 6.56. Calcd. for $C_{13}H_{11}O_3N$: C, 68.11; H, 4.84; N, 6.11%.

3-Acetyl-2,5-dichloro-1-azaazulene (XXXV) and 2,5-Dichloro-3-(α-chlorovinyl)-1-azaazulene (XXXVI). — A mixture of XXXII (200 mg.) and phosphorus oxychloride (15 ml.) was heated at 80°C for 2 hr., after which the excess phosphorus oxychloride was removed under reduced pressure. The residue was dissolved in water, and the pH was adjusted to 8 with sodium bicarbonate. The extraction of the solution with ethyl acetate afforded orange crystals of a mixture of XXXV and XXXVI. The mixture was chromatographed on an alumina column, and elution with benzene-petroleum ether gave red plates (XXXVI) and yellow needles (XXXV). Recrystallizations from benzene (for XXXV) and benzene-petroleum ether (for XXXVI) gave yellow needles of XXXV, m. p. 179—180°C (35 mg.) and red plates of XXXVI, m. p. 127—128°C (50 mg.).

XXXV: λ_{max}^{MeOH} mμ (log ε): 235 (4.36), 298 (4.69), 332 (3.88), 460 (3.00).

Found: C, 55.06; H, 3.14; N, 6.01. Calcd. for $C_{11}H_7ONCl_2$: C, 55.00; H, 2.94; N, 5.84%.

XXXVI: λ_{max}^{MeOH} mμ (log ε): 234 (4.34), 290 (4.66), 330 (3.64), 480 (2.97).

Found: C, 51.36; H, 2.61; N, 5.81. Calcd. for $C_{11}H_6NCl_3$: C, 51.08; H, 2.34; N, 5.42%.

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