Synthesis of 1-Oxaazulan-2-imine Derivatives from Tropone¹⁾

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The authors have investigated the reaction of tropones with an active methylene compound as a part of their continuing study of the chemistry of the troponoid system. A few years ago²⁾, it was found that the reaction of tropone (I) with malononitrile, in the presence of piperidine as a catalyst, afforded pale yellow crystals (II), m. p. 149°C, with a formula $C_{10}H_8ON_2$, in about 75% of yield. Since this reaction was considered to proceed by 1, 8addition mechanism^{3,4)}, the authors proposed the structure of IIa or IIb for II²⁾. A few months later, Kitahara and Doi5) suggested that IIc would be more reasonable than IIa or IIb on the basis of its ultraviolet and infrared spectra.



In the present paper, the authors wish to report the results of the reexamination of the structure of II and dehydrogenation of II, which resulted in the formation of derivatives of 1-oxaazulan-2-imine (2*H*-cyclohepta[b]furan-2-imine) in a fairly good yield.

As shown in Fig. 1, the ultraviolet spectrum of II exhibits a maximum around $320 \text{ m}\mu$, which can not be explained by IIa or IIb as pointed out by Kitahara and Doi^{5D}. In infrared spectrum of II (see experimental part), there is a sharp band at 2210 cm^{-1} for the cyano group conjugated with unsaturated bond, besides three bands at $3230 \sim 3460 \text{ cm}^{-1}$ for amino



Fig. 1. UV spectra of II in methanol and of 3-cyano-1-oxaazulan-2-imine in methanol (IV_N) , in $1 \times HCl (IV_A)$ and in $1 \times NaOH (IV_B)$.



Fig. 2. NMR spectrum of II in pyridine (60 Mc.), with tetramethylsilane as an internal reference.

group. To elucidate the structure more clearly, the nuclear magnetic resonance spectrum of II was measured in a pyridine solution (Fig. 2). The signals appear as three groups, a, b and c with an area appropriate to 2, 1 and 3 protons respectively. The doublet signal a which appears at 6.85τ with J=6.6 c. p. s. is ascribed to Ha and the multiplet signals b (centred at 4.60 τ) and c (centred at 3.71 τ) are attributed to Hb and Hc, respectively. This result is accommodated much better by the structure of 2-amino-3cyano-8H-cyclohepta-[b] furan (IId) than by IIa, II_b or IIc. The observed shift of the Ha peak to the lower field, compared with the NMR spectrum of cycloheptatriene⁶⁾, is ascribed to the paramagnetic shielding of the adjacent oxygen atom. 2-Amino-3-cyano-8H-cyclohepta [b] furan (IId) is

¹⁾ Presented at the 56 th Tohoku Local Meeting of the Chemical Society of Japan, Yamagata, June, 1962.

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²⁾ Presented at the 49th Tohoku Local Meeting of the Chemical Society of Japan, Yamagata, June, 1959.

³⁾ T. Nozoe, T. Mukai and T. Tezuka, This Bulletin, 34, 619 (1961).

⁴⁾ O. L. Chapman, D. J. Pasto and A. A. Griswold, J. Am. Chem. Soc., 84, 1213 (1962).

⁵⁾ Presented at the General Meeting of Tohoku District of the Chemical Society of Japan, Akita, October, 1959.

⁶⁾ G. Frankel, R. E. Carter, A. McLachlan and J. H. Richards, J. Am. Chem. Soc., 82, 5846 (1960).

assumed to be formed through the intermediate⁷⁾ as depicted below.



The dehydrogenation of II with tetrachloro-1, 2-benzoquinone in benzene or chloroform afforded dark red complex (III). The treatment of III with dilute hydrochloric acid gave tetrachlorocatechol and 3-cyano-1-oxaazulan-2-imine (IV) in a good yield. When II was treated with selenium dioxide, the dehydrogenation was accompanied by simultaneous hydrolysis of the cyano group at 3-position and 3-carbamoyl-1-oxaazulan-2-imine (V), m. p. 192°C (decomp.), was obtained⁸).



As shown in Figs. 1 and 3, the ultraviolet spectra of IV and V are very similar to that of 1-oxaazulan-2-one (2H-cyclohepta [b] furan-2-one)⁹⁾. The infrared spectrum of IV shows



Fig. 3. UV spectra of 3-carbamoyl-1-oxaazulan-2-imine in methanol (V_N) in $1 \times HCl (V_A)$ in conc. H_2SO_4 (V_S) and of 3-carbamoyl-1oxaazulan-2-one in methanol (XI_N) and in conc. H_2SO_4 (XI_S) .

an absorption band at 3300 cm^{-1} for the imino group and at 2207 cm^{-1} for the conjugated cyano group. In the infrared spectrum of V, there are bands at 3310 and 3155 cm^{-1} for the imino and amino groups and at 1650 cm⁻¹ for the conjugated carbonyl group. IV and V are amphoteric substances, and soluble in both dilute acid and alkali. Passage of hydrogen chloride gas through a solution of IV in chloroform precipitated out the hydrochloride (VI) as pale yellow crystals, from which IV was regenerated by neutralization with sodium hydrogen carbonate. VI is much more stable than IV and it is possible to purify VI by sublimation under reduced pressure. Addition of sodium ethoxide to a solution of IV in chloroform gave the sodium salt VII as yellow crystals. From the fact that infrared spectrum



of VII showed two bands at 2210 and 2170 cm^{-1} for the cyano group, it is clear that the ring is opened as depicted above. The infrared spectrum of VII was similar to that of sodium troponate¹⁰ (experimental part). There are no absorption bands from 2000 to 1600 cm⁻¹, but a band at 1595 cm⁻¹. It is not clear, however, whether this band should be due to the polarized carbonyl group or carbon-carbon double bond vibration as in the case of sodium troponate¹⁰.

The ultraviolet spectra of IV in 1 N hydrochloric acid and 1 N sodium hydroxide solution are shown in Fig. 1. In an alkaline solution, the bathochromic shift ascribed to the formation of VII was observed, whereas in an acidic solution there is no remarkable shift in spite of the formation of VI.

Attempts to obtain 1-hydroxy-8, 8-dicyanoheptafulvene or its derivatives such as 1methoxy-¹¹ or 1-acetoxy-8, 8-dicyanoheptafulvene did not succeed. For example, neutralization of VII with dilute acetic acid resulted in the ring closure to give IV. Acylation of

 ⁷⁾ In the addition reaction of tropones, the adducts same type as the intermediate have been obtained by. K. Takase and M. Yasunami (unpublished data), cf. Ref. 4.
 8) Kitahara and Doi reported that dehydrogenation of II with selenium dioxide afforded 3-cyano-l-oxaazulan-2-imine, m. p. 161°C. Cf. Ref. 5.

⁹⁾ S. Seto, Sci. Repts. Tohoku Univ., Ser. I, 37, 367 (1954).

¹⁰⁾ Y. Ikegami, Kagaku-no-Ryoiki, (Extra Vol.) 38, 70, Nankodo, Tokyo (1959).

¹¹⁾ Kitahara and Doi reported that, on using acetic anhydride as condensation reagent, reaction of tropolone methyl ether with malononitrile afforded 1-methoxy-8, 8-dicyanoheptafulvene, m. p. 206°C. Presented at the 15 th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

VII with acetyl or benzoyl chloride resulted also in the ring closure giving VIII or IX, which were obtained by acylation of IV. The infrared spectrum of VIII shows a band at 2164 cm^{-1} for the cyano group and at 1666 cm⁻¹ for the carbonyl group. The latter supported the presence of the *N*-acetyl group rather than the *O*-acetyl group. The ultraviolet spectrum of VIII is shifted to a longer wavelength region than that of IV, because of the extension of the conjugate system (Fig. 4).

Previously, Nozoe and his coworkers reported that the reaction of tropolone methyl ether with ethyl cyanoacetate in the presence of sodium ethoxide afforded the azulene derivatives in a good yield¹²). However, Matsumura found that, under the same condition as above, the reaction of tropolone methyl ether and malononitrile resulted in the formation of the unknown compound, m. p. > 300°C, instead of the expected azulene derivative¹³). By comparison of the infrared spectra, it was found to be identical with VII. Furthermore, it was confirmed that, in the presence of sodium ethoxide, the reaction of VII with malononitrile did not yield the azulene derivatives, but resulted almost in the recovery of VII.

The heating of 3-cyano-1-oxaazulan-2-imine (IV) with 1 N hydrochloric acid gave 3-cyano-1-oxaazulan-2-one¹⁴⁾ (X) and 3-carbamoyl-1-oxaazulan-2-imine (V). On the other hand, X was not affected by heating with 1 N hydro-chloric acid. This fact shows that the presence of imino group in IV assists the hydrolysis of the cyano group.



The formation of V instead of IV, on dehydrogenation of II with selenium dioxide as mentioned before, may be explained as the result of hydrolysis of the cyano group with selenic acid. Upon treatment of IV with acid, an increase in acid concentration suppressed the hydrolysis of the imino group of 2-position. The same tendency was also observed in the acid-hydrolysis of V. The heating of V with $1 \times hydrochloric$ acid afforded 3-carbamoyl-1oxaazulan-2-one (XI) in a good yield, whereas heating of V in concentrated sulfuric acid resulted in the recovery of V accompanied

with a small amount of XI. These facts indicated that, in an acid solution, IV and V were stabilized by the formation of the corresponding conjugate acid making the hydrolysis of the 2-imino group difficult. It is well known that the carbamoyl group of 1- or 3position of azulenes is difficult to be hydrolyzed by acid treatment¹⁵). The heating of 3-carbamoyl-1-oxaazulan-2-one (XI) with concentrated or 50% sulfuric acid or the treatment of XI with sodium nitrite in sulfuric acid resulted almost in recovery of the starting material. The ultraviolet absorption spectra of V and XI are measured in methanol and concentrated sulfuric acid (Fig. 3). There is no distinguishable shift between V and its conjugate acid (in concentrated sulfuric acid), whereas the spectrum of the conjugate acid of XI is shifted to the shorter wavelength region as compared with that of XI in methanol.

The behavior of 3-carbamoyl-1-oxaazulan-2imine (V) against alkali was studied by Nozoe and his coworkers¹⁶ who discovered that V gave 3-cyano-1-azaazulan-2-one (3-cyano-cyclohepta [b] pyrole-2(1H)-one) (XII) in a quantitative yield. To obtain X exclusively, hydrolysis of the acylated compounds VIII or IX was attempted by using acid or alkali. The heating of VIII with dilute acid resulted in the formation of V and XI via IV. The treatment of VIII with dilute alkali, even icecooling, afforded unexpected XII in a good yield the formation of which is explained as follows.



By application of the method mentioned above, it is possible to synthesize not only 1-oxaazulan-2-ones but 1-azaazulan-2-ones from the tropone derivatives.

The reaction with malononitrile was extended to other tropone derivatives. Almost in the same way as the case of II, 2-phenyltropone afforded the condensation product XIII as pale yellow crystals, m. p. 150°C, in about 80% of yield. On the basis of its ultraviolet spectrum (Fig. 4), infrared spectrum (experimental part) and analytical value, $C_{16}H_{12}ON_2$, XIII was proved to be the phenyl derivative

¹²⁾ T. Nozoe, S. Seto, S. Matsumura and T. Asano, *Proc. Japan Acad.*, 32, 339 (1956); T. Nozoe, S. Seto, S. Matsumura and Y. Murase, This Bulletin, 35, 1179 (1962).
13) S. Matumura, Private communication.

¹⁴⁾ A. Sato succeeded in the synthesis of X by dehydration of the oxime of 3-formyl-1-oxaazulan-2-one. (Unpublished work.)

¹⁵⁾ W. Schroth and W. Treibs, Ann., 643, 108 (1961); T. Asano, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959; J.

Tsunetsugu, Unpublished works.

¹⁶⁾ T. Nozoe, K. Takase and T. Nakazawa, To be published.



Fig. 4. UV spectra of VIII, XIII and 3cyano-8-phenyl-1-oxaazulan-2-imine (XIV) in methanol.



Fig. 5. NMR spectrum of XIII in acetone (60 Mc.). Tetramethylsilane as an internal reference.

of II, 2-amino-3-cyano-8-phenyl-8H-cyclohepta-[b]furan. Especially, the NMR spectrum of XIII, shown in Fig. 5, furnished the additional evidence concerning the protons of XIII. There are four groups of the absorption signal, a, c, d and e with an area appropriate about 1:4:2:5 protons respectively. The signals a (doublet at 5.13 τ , J=7.4 c. p. s.) and c (multiplet centred at 3.94τ) are ascribed to Ha and Hc of XIII and correspond to the signals a, and b and c of II (Fig. 2). The peak corresponding to b of II may be shifted to the lower field by the paramagnetic effect of the adjacent phenyl group and included to the signal c. The observed shift of Ha to the low field, compared with that of II, seemed due to the same effect of the phenyl group. The hydro-



gens of the phenyl group appear at 2.83τ and the signal d at 3.35τ seemed due to the amino group at 2-position of XIII.

The dehydrogenation of XIII with tetrachloro-1, 2-benzoquinone was carried out in two steps and 3-cyano-8-phenyl-1-oxaazulan-2-imine (XIV) was obtained. Application of malononitrile to XIV in the presence of *tert*-butylamine yielded 2-amino-1, 3-dicyano-4-phenylazulene (XV)¹⁷). The yield of XIV was about 50% and that of XV was about 45% from 2-phenyltropone. The structure of XV was confirmed by the independent synthesis of XV from 2-chloro-7-phenyltropone and malononitrile¹⁸).

The heating of XIV with 4 N hydrochloric acid afforded 3-cyano-8-phenyl-1-oxaazulan-2one (XVI) and 3-carbamoyl-8-phenyl-1-oxa azulan-2-imine (XVII) with the recovery of considerable amount of XIV. XVII was also obtained by the dehydrogenation of XIII with selenium dioxide. The heating of XVI in concentrated sulfuric acid gave 3-carbamoyl-8phenyl-1-oxaazulan-2-one (XVIII).

These approaches to the synthesis of the compounds from XIV to XVIII are of considerable significance from the view point of the synthetic tool for derivatives of 1-oxaazulan-2-one and azulene, not only because of the advantage of yield but the simplicity of the method.

Experimental^{19,20)}

Condensation of Tropone (I) and Malononitrile (Formation of II).—To a solution of 5 g. (0.047 mol.) of I and 3.6 g. (0.052 mol.) of malononitrile in 20 ml. of ethanol was added 0.2 ml. of piperidine. The solution turned to dark red with the heat formation and gave pale yellow prisms immediately. After standing overnight, the filtration gave 6.4 g. (75% of yield) of II as pale yellow prisms, m. p. 141~143°C, which on recrystallization from ethanol showed m. p. 149°C. IR (Nujol): 3460, 3340, 3230, 2210, 1640, 1592, 1422, 1346, 1235, 1160, 1110, 1042, 993, 850, 763, 706 and 687 cm⁻¹.

Found: C, 69.80; H, 4.36; N, 16.18. Calcd. for $C_{10}H_8ON_2$: C, 69.75; H, 4.68; N, 16.27%.

Dehydrogenation of II with Tetrachloro-1, 2benzoquinone (Formation of IV).—Addition of a solution of 1.5 g. (6.1 mmol.) of tetrachloro-1, 2benzoquinone dissolved in benzene into a solution of 1 g. (5.8 mmol.) of II in 150 ml. of benzene resulted in immediate precipitation of dark red crystals. After let to stand for 30 min. at room

¹⁷⁾ The method for synthesizing azulene derivatives from 1-oxaazulan-2-ones or 1-oxaazulan-2-imines was established by T. Nozoe, K. Takase and N. Shimazaki. Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

¹⁸⁾ H. Tsuruta, Unpublished data.

¹⁹⁾ All melting points are uncorrected.

²⁰⁾ The microanalyses were carried out by Miss A. Iwanaga and M. Suzuki of this laboratory to whom the authors are indebted.



Fig. 6. IR spectrum of VII in KBr.

temperature, 2.2 g. (90% of yield) of complex (III), m. p. 130°C (decomp.) was filtered off. Three hundred milligrams of III ware also obtained by addition of 0.3 g. of tetrachloro-1,2-benzoquinone to a solution of 0.2 g. of II in 11 ml. of chloroform. IR (Nujol): 3340, 2220, 1672, 1587, 1345, 1270, 958, 805 and 751 cm⁻¹.

Found: C, 45.60; H, 1.83; N, 6.58. Calcd. for $C_{16}H_8O_8N_2Cl_4$: C, 45.96; H, 1.93; N, 6.70%.

To a suspension of 1 g. of III in 20 ml. of chloroform or benzene, 40 ml. of 1 N hydrochloric acid was added and the mixture was shaken. The chloroform or benzene layer, after separation, was extracted again with 20 ml. of 1 N hydrochloric acid, washed with water and dried over sodium sulfate. Evaporation of chloroform gave 240 mg. of tetrachlorocatechol, as yellowish crystals, m. p. $185 \sim 190^{\circ}$ C. The extract with dilute hydrochloric acid was neutralized by addition of sodium hydrogen carbonate, during which orange red crystals separated out. Filtration afforded 400 mg. (90% of yield) of orange crystals (IV), m. p. 143°C (decomp.), which tended to decompose on recrystallization. Purification of IV was done through its hydrochloride as follow : Passing hydrogen chloride gas through a solution of IV in chloroform gave hydrochloride (VI) as yellow crystals, m. p. over 260°C. The hydrochloride could be sublimed at about 200°C and 3 mmHg. Addition of sodium hydrogen carbonate to an aqueous solution of VI gave 3-cyano-1-oxaazulan-2-imine (IV), m. p. 153°C (decomp.). IR (Nujol): 3300, 2207, 1676, 1598, 1498, 1271, 1106, 976, 958, 924, 875, 772, 756 and 720 cm⁻¹.

Found: C, 70.48; H, 3.34; N, 15.90. Calcd. for $C_{10}H_6ON_2$: C, 70.58; H, 3.55; N, 16.46%.

Dehydrogenation of II with Selenium Dioxide (Formation of V). — A solution of 300 mg. (1.7 mmol.) of II and 225 mg. (2.0 mmol.) of selenium dioxide in 5 ml. of methanol was refluxed for 30 min., during which dark brown precipitate separated out. After evaporation of methanol, the residue was washed well with 20 and 10 ml. of $1 \times$ hydrochloric acid. The combined washing was neutralized by adding solid sodium hydrogen carbonate and extracted with chloroform. The extract was washed with water, dried over sodium sulfate and evaporated giving 130 mg. (60% of yield) of brownish orange crystals, m. p. 182°C (decomp.). Infrared spectrum of the product was completely superposed on that of 3-carbamoyl-1-oxaazulan-2-imine (V) (see below). Sodium Salt (VII) of 1-Hydroxy-8, 8-dicyanoheptafulvene.—a) From IV.—To a solution of 100 mg. of IV in 2 ml. of chloroform was added the sodium ethoxide, prepared from 30 mg. of sodium and 2 ml. of absolute ethanol, giving 100 mg. of orange yellow crystals (VII), m. p. over 300°C.

Found : N, 13.98. Calcd. for $C_{10}H_5ON_2Na$: N, 14.58%.

b) From Tropolone Methyl Ether.—To a ethanol solution of the sodium salt of malononitrile, prepared from 40 mg. of sodium, 50 mg. of malononitrile and 2 ml. of absolute ethanol, 100 mg. of tropolone methyl ether was added. After being stirred overnight, crystals separated out. Filtration gave 120 mg. of yellow crystals, m. p. over 300°C, infrared spectrum of which was completely the same as that of VII.

c) Regeneration of IV from VII. — Under the coexistence of a chloroform layer, a solution of 200 mg. of VII in 2 ml. of water was neutralized by adding $2 \aleph$ acetic acid with vigorous stirring. The chloroform layer was separated, washed with water and dried over sodium sulfate. Evaporation of the chloroform afforded 70 mg. of orange red crystals, m. p. 145°C, (decomp.), which was identical with IV (from infrared spectrum).

VII was dissolved in dilute hydrochloric acid and the resulting solution was neutralized by addition of solid sodium hydrogen carbonate giving IV almost quantitatively.

Acylation of Sodium Salt (VII) and 3-Cyano-1oxaaulan-2-imine $(IV)^{210}$.—a) Acetylation of VII. —To a suspension of 100 mg. of VII in 2 ml. of pyridine was added 0.3 ml. of acetyl chloride under ice-cooling. The reaction mixture was allowed to stand for 60 min., poured into water and extracted with chloroform. The chloroform extract was washed with water, dried over magnesium sulfate and evaporated to 75 mg. (68% of yield) of yellow crystals, m. p. 144~146°C. Recrystallization from ethanol gave yellow needles (VIII), m. p. 146°C.

IR (Nujol): 2164, 1666, 1575, 1493, 1281, 1236, 1224, 1214, 970 and 763 cm⁻¹.

Found: C, 68.20; H, 4.05; N, 12.80. Calcd. for $C_{12}H_8O_2N_2$: C, 67.92; H, 3.80; N, 13.20%.

b) Acetylation of IV.—To a solution of 59 mg. of IV in 0.8 ml. of pyridine was added 0.3 ml. of acetyl chloride under ice-cooling. The same treatment as a) gave 60 mg. of yellow crystals, m. p.

²¹⁾ This part of the experiment was carried out by Mr. Haruki Tsuruta.

 $130 \sim 137^{\circ}$ C, which on recrystallization from ethanol gave VIII, m. p. 145° C.

c) Benzoylation of VII.—To a mixture of 1 g. of VII and 4 ml. of pyridine, 2 ml. of benzoyl chloride was added with stirring under ice-cooling. After being allowed to stand for 1.5 hr., the reaction mixture was poured into water giving some oil, which crystallized on standing. Filtration afforded 1.3 g. of red crystals, m. p. $110\sim130^{\circ}$ C, which on recrystallization from benzene-alcohol mixture gave brown scales (IX), m. p. 155° C. IR (Nujol): 2214, 1645, 1566, 1473, 1296, 1239, 1217, 1046, 960, 897, 715 and 698 cm⁻¹.

Found: C, 74.41; H, 3.59; N, 9.88. Calcd. for $C_{17}H_{10}O_2N_2$: C, 74.44; H, 3.68; N, 10.21%.

Hydrolysis of 3-Cyano-1-oxaazulan-2-imine (IV) with Acid. — a) With 1N Hydrochloric Acid. — A solution of 400 mg. of IV dissolved in 100 ml. of 1 N hydrochloric acid was heated on the boiling water bath for 2 hr. After being cooled, the reaction mixture was extracted with ethyl acetate. The extract was evaporated up to give 80 mg. of vellow crystals, which on recrystallization from ethyl acetate afforded 50 mg. of X, m. p. 240°C. It was shown to be identical with 3-cyano-1-oxaazulan-2-one synthesized by Sato¹⁴) by comparing infrared spectra of them and the mixed melting point determination. The acid layer was neutralized by addition of solid sodium hydrogen bicarbonate giving 160 mg. of reddish brown crystals, m. p. 186°C, (decomp.), which were obtained by filtration. The filtrate was extracted with ethyl acetate. After being dried over sodium sulfate, evaporation of the extract gave 100 mg. of brown crystals, m. p. 182°C (decomp.). The combined crystals were recrystallized from ethyl acetate to give reddish orange needles (V), m. p. 192°C (decomp.). IR (Nujol): 3310, 3155, 1650, 1595, 1500, 1408, 1302, 1271, 1143, 1125, 879, 856, 824, 784, 756, 736 and 684 cm⁻¹.

Found: C, 63.65; H, 4.01; N, 14.38. Calcd. for $C_{10}H_8O_2N_2$: C, 63.82; H, 4.29; N, 14.89%.

b) With Ethanolic 4 N Hydrochloric Acid Solution. -A solution of 200 mg. of IV in 6 ml. of concentrated hydrochloric acid and 12 ml. of ethanol was refluxed for 2 hr. on a water bath. After addition of 5 ml. of 6N sodium hydroxide, the reaction mixture was extracted with ethyl acetate. The extract was washed with water, dried over sodium sulfate and evaporated to give 15 mg. of brown crystals, m. p. 180~200°C. The aqueous layer was neutralized by adding sodium hydrogen carbonate and extracted with chloroform. The extract was dried over sodium sulfate and evaporated giving 140 mg. of reddish orange crystals, m. p. 180°C (decomp.), which was found to be V contaminated with a little amount of IV by inspection of the infrared spectrum.

Hydrolysis of 3-Carbamoyl-1-oxaazulan-2-one Imine (V) with Acid.—a) With 1 imes HydrochloricAcid.—Heating of a solution of 230 mg. of V in 20 ml. of 1 imes hydrochloric acid on a water bath afforded 110 mg. of brownish crystals, m. p. 270°C, which were filtered off after being cooled. Further heating of the filtrate on a water bath for 10 hr. gave 50 mg. of brown crystals, m. p. 275°C. The combined crystals were recrystallized from acetic acid giving yellow brown needles (XI), m. p. 275°C. IR (Nujol): 3415, 3135, 1740, 1680, 1611, 1544, 1488, 1309, 1277, 1229, 942, 882 and 795 cm⁻¹.

Found: C, 63.73; H, 3.46; N, 7.47. Calcd. for $C_{10}H_7O_3N$: C, 63.49; H, 3.73; N, 7.41%.

b) With Sulfuric Acid.—A solution of 100 mg. of V dissolved in 0.5 ml. of sulfuric acid was heated in a closed vessel on a boiling water bath for 2 hr. The reaction mixture was poured into 10 ml. of water and extracted with chloroform continuously for 6 hr. Evaporation of the extract yielded 40 mg. of yellow brown crystals, m. p. 270°C, which on recrystallization from acetic acid gave XI, m. p. 275°C. The aqueous solution from the chloroform extraction was neutralized by addition of sodium hydrogen carbonate to give orange crystals, which were extracted with ethyl acetate. Evaporation of the extract gave 60 mg. of orange crystals, m. p. 186°C (decomp.), which was identical with the starting material V (from infrared spectrum).

The same treatment of XI as b) with concentrated sulfuric acid resulted in the recovery of XI.

Hydrolysis of the Acylated Compound (VIII and IX) of 3-Cyano-1-oxaazulan-2-imine²¹.--a) A solution of 200 mg. of VIII dissolved in a mixture of 1 ml. of concentrated hydrochloric acid and 10 ml. of methanol was refluxed for 30 min., and the methanol was evaporated under reduced pressure. The residual solution was poured into water and extracted with chloroform. The extract was washed, dried over magnesium sulfate and evaporated to 10 mg. of brown crystals, m. p. 167 \sim 242°C, which have not been examined. The acidic solution was neutralized by addition of sodium hydrogen carbonate and extracted with chloroform. The same treatment of the extract afforded 100 mg. of reddish orange crystals, m. p. 144~158°C (decomp.), which was found to be a mixture of IV and V by inspection of its infrared spectrum.

b) A solution of 200 mg. of VIII dissolved in a mixture of each 2 ml. of 2 N potassium hydroxide and methanol was refluxed for 2 hr. After being diluted with water and extracted with chloroform, the reaction mixture was neutralized to pH 3 with 2 N hydrochloric acid giving 135 mg. of yellow crystals, m. p. over 250°C. Recrystallization from dimethylformamide gave XII as yellow crystals, m. p. over 280°C, whose infrared spectrum was superimposed on that of the authentic sample¹⁶.

c) To a suspension of 300 mg. of IX in 6 ml. of methanol was added 2 ml. of 2 N potassium hydroxide and the resulting mixture was shaken with ice-cooling for 15 min. By acidification of the solution to pH 3, 145 mg. of dark orange crystals, m. p. over 280°C, were obtained by filtration. The filtration, after being evaporated and diluted with water, afforded 40 mg. of the same crystals, m. p. over 280°C. The combined crystals were identical with the authentic 3-cyano-1-azaazulan-2-one¹⁸) (from infrared spectum).

Condensation of 2-Phenyltropone and Malononitrile (Formation of XIII).—To a solution of 1 g. (5.5 mmol.) of 2-phenyltropone and 400 mg. (6 mmol.) of malononitrile in 4 ml. of absolute ethnol was added 0.2 ml. of piperidine and the reaction mixture was allowed to stand overnight at room temperature. Filtration of the crystals deposited gave 1.08 g. (80% of yield) of XIII as pale yellow needles, m. p. 150°C. IR (Nujol): 3520, 3380, 2220, 1639, 1601, 1557, 1494, 1100, 837, 789, 743, 728, 698 and 687 cm^{-1} .

Found: C, 77.38; H, 4.77; N, 11.21. Calcd. for $C_{16}H_{12}ON_2$: C, 77.40; H, 4.87; N, 11.28%.

Dehydrogenation of XIII with Tetrachloro-1, 2benzoquinone (Formation of XIV) .-- To a solution of 400 mg. (1.6 mmol.) of XIII in 20 ml. of benzene was added 480 mg. (1.9 mmol.) of tetrachloro-1,2benzoquinone and the reaction mixture was allowed to stand at room temperature for 30 min., during which reddish crystals precipitated out. Filtration afforded 850 mg. of dark orange crystals, m. p. 135°C (decomp.), which were difficult to be recrystallized from the usual solvent. The crystals obtained ware added to a mixture of 20 ml. of 2 N hydrochloric acid and 20 ml. of ethanol and the reaction mixture was shaken for 1 hr. and then poured into water. Some resinous matter with dark red separated out, from which the acidic layer was decanted. After being shaken with benzene to remove tetrachlorocatechol, the acidic solution was neutralized by addition of sodium hydrogen carbonate giving 240 mg. (60% of yield) of XIV as orange red crystals, m. p. 183°C (decomp.). IR (Nujol): 3360, 2220, 1658, 1618, 1587, 1538, 1495, 1321, 1285, 1233, 1115, 979, 912, 790, 781, 756, 717 and 692 cm⁻¹.

Found: C, 77.58; H, 3.90; N, 10.94. Calcd. for $C_{16}H_{10}ON_2$: C, 78.03; H, 4.09; N, 11.38%.

Synthesis of 2-Amino-1,3-dicyano-4-phenylazulene (XV) from 3-Cyano-8-phenyl-1-oxaazulan-2-imine (XIV).—A solution of 50 mg. (0.2 mmol.) of XIV and 30 mg. (0.45 mmol.) of malononitrile in 6 ml. of absolute ethanol was stirred overnight in the presence of 60 mg. of *tert*-butylamine giving yellow crystals. Filtration afforded 50 mg. (90% of yield) of yellow crystals (XV), m. p. 296°C, which showed no depression on admixture with the authentic sample synthesized from 2-chloro-7-phenyltropone and malononitrile¹⁸). The infrared spectrum of XV was superimposed on that of the authentic sample¹⁵.

Hydrolysis of 3-Cyano-8-phenyl-1-oxaazulan-2imine (XIV) with Acid.—A solution of 400 mg. of XIV dissolved in 35 ml. of $4 \times hydrochloric$ acid was heated on a water bath for 3 hr. and on being cooled dark yellow needles crystallized out. Filtration afforded 150 mg. of yellow needles, m. p. 255°C, which on recrystallization from dimethylformamide gave needles (XVI), m. p. 265°C. IR (Nujol): 2215, 1755, 1613, 1582, 1488, 1312, 1282, 1230, 961, 930, 905, 795, 768, 732 and 699 cm⁻¹. $\lambda_{\text{Max}}^{\text{MeOH}} m \mu$ (log ε): 223 (4.40), 255 (4.26), 310 (4.20) and 414 (4.39).

Found: C, 77.25; H, 3.65; N, 5.80. Calcd. for $C_{16}H_9O_2N$: C, 77.72; H, 3.67; N, 5.67%.

The filtrate of XVI was neutralized by addition of solid sodium hydrogen carbonate giving 200 mg. of orange crystals, m. p. 173°C, which were obtained by filtration. The crystals obtained were dissolved in benzene and chromatographed through a column containing 6 g. of alumina. After evaporation, the elute with ether gave 20 mg. of reddish crystals (XIV), m. p. 172~173°C (decomp.), and the elute with ethyl acetate gave 50 mg. of reddish orange crystals (XVII), m. p. 184~185°C (decomp.). IR (Nujol): 3345, 3165, 1660, 1585, 1497, 1357, 1304, 1282, 1107, 1092, 930, 795, 769, 751, 726, 694 and 674 cm⁻¹. λ_{MeOH}^{MeOH} m μ (log ε): 238 (4.46), 290 (4.18) and 422 (4.38).

Found: C, 72.79; H, 4.46; N, 10.22. Calcd. for $C_{16}H_{12}O_2N_2$: C, 72.71; H, 4.58; N, 10.60%.

Hydrolysis of 3-Cyano-8-phenyl-1-oxaazulan-2one (XVI) with Sulfuric Acid.—One hundred milligrams of XVI ware dissolved in 0.5 ml. of concentrated sulfuric acid and the solution was heated in a closed vessel in the boiling water bath for 1 hr. The solution was poured into 3 ml. of water to give brownish crystals. Filtration afforded 110 mg. of crystals, m. p. 233~236°C, which on recrystallization from benzene gave yellow crystals (XVIII), m. p. 258~260°C. IR (Nujol): 3400, 3145, 1724, 1672, 1603, 1580, 1490, 1277, 1259, 1217, 804, 781, 754, 735 and 698 cm⁻¹. $\lambda_{Max}^{MeeH} m\mu$ (log ε): 223 (4.37), 253 (4.23), 304 (4.16) and 415 (4.35).

Found: C, 72.49; H, 4.32; N, 4.92. Calcd. for $C_{16}H_{11}O_3N$: C, 72.44; H, 4.18; N, 5.28%.

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