The Synthesis of Azuleno[2, 1-b]pyridine Derivatives

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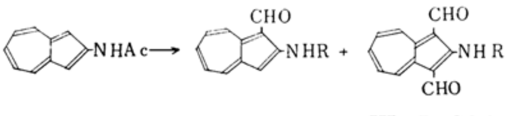
Among the azulenes fused with heterocyclic rings, azuleno[6, 5-b]furans (furo[3, 2-f]azulenes)[1], azuleno[6, 5-b]pyrroles (pyrrolo[3, 2-f]-azulenes)[1], azuleno[2, 1-b]thiophenes (thieno-[3, 2-a]azulenes)[2] and azuleno[6, 5-c]pyrazoles (pyrazolo[4, 3-f]azulenes)[3] have already been synthesized. The present writers have synthesized azuleno[2, 1-b]pyridines (pyrido[3, 2-a]-azulenes) by the application of Friedeländer's method to 2-amino-1-formylazulene (I) and its acetate (II); their results have been described briefly elsewhere[4]. In the present paper we wish to report those results in some detail.

Treatment of 2-acetamidoazulene[5] in dimethylformamide with one equivalent of phosphorus oxychloride gave an immonium salt which, without purification, was then treated with aqueous sodium carbonate to afforded 2-acetamido-1-formylazulene (II) and a small amount of 2-acetamido-1, 3-diformylazulene (III). Hydrolysis of II with alcoholic sodium hydroxide afforded 2-amino-1-formylazulene (I). Similar treatment of III afforded 2-amino-1, 3-diformylazulene (IV).

The heating of compound I with acetylacetone in the presence of a small amount of piperidine gave dark greenish brown feathery crystals (V) in about a 50% yield. V easily afforded several kinds of complexes such as hydrochloride, trinitrobenzene complex and picrate, and it gave an oxime. V also showed positive iodoform reaction. The infrared spectrum of V in Nujol showed absorption at 1665 cm^{-1} (conjugated carbonyl). These facts reveal that compound V is 3-acetyl-2-methylazuleno-[2, 1-b]pyridine, as was expected.



I : R=H   III : R=$COCH_3$
II : R=$COCH_3$ IV : R=H

A similar treatment of I with ethyl acetoacetate gave ethyl 2-methylazuleno[2, 1-b]pyridine-3-carboxylate (VI) and I with diethyl acetonedicarboxylate gave ethyl 3-ethoxycarbonylazuleno[2, 1-b]pyridine-2-acetate (VII). The compounds V, VI and VII have quite similar absorptions in the ultraviolet region (Fig. 1).

Prolonged heating of acetate II with diethyl malonate in the presence of piperidine at 50∼60°C gave dark brown needles (VIII) in a 50% yield, instead of the expected 2-acetamido-1-(β, β-diethoxycarbonyl)azulene being isolated. The ultraviolet spectrum of VIII is shown in Fig. 2. Judging from the analysis of VIII and the following experimental facts, VIII is thought to be ethyl 1, 2-dihydro-2-oxoazuleno[2, 1-b]-pyridine-3-carboxylate. Compound VIII was not affected by aqueous sodium carbonate, but it gives a brown sodium salt with aqueous sodium hydroxide from which the original substance was regenerated with acetic acid. The prolonged heating of VIII with aqueous sodium hydroxide afforded the acid IX.

When heated with phosphorus oxychloride, VIII was converted to ethyl 2-chloroazuleno-[2, 1-b]pyridine-3-carboxylate (X). The heating of X with sodium methoxide or with sodium ethoxide afforded a 2-methoxy compound XI,

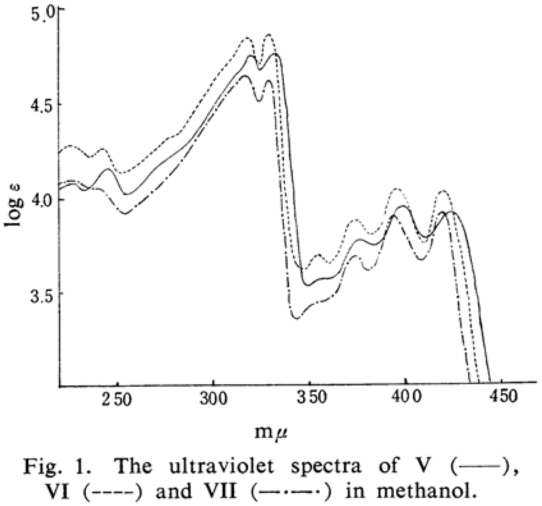


Fig. 1. The ultraviolet spectra of V (——), VI (----) and VII (—·—·) in methanol.

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[2] K. Matsui and T. Nozoe, ibid., **1960**, 1302; K, Matsui, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1517, 1520, 1522, 1665, 1667 (1961).

[3] T. Nozoe, K. Takase and M. Tada, to be published.

[4] T. Nozoe and K. Kikuchi, *Chem. & Ind.*, **1962**, 358.

[5] T. Nozoe, S. Matsumura, Y. Murase and S. Seto, ibid., **1955**, 1257,

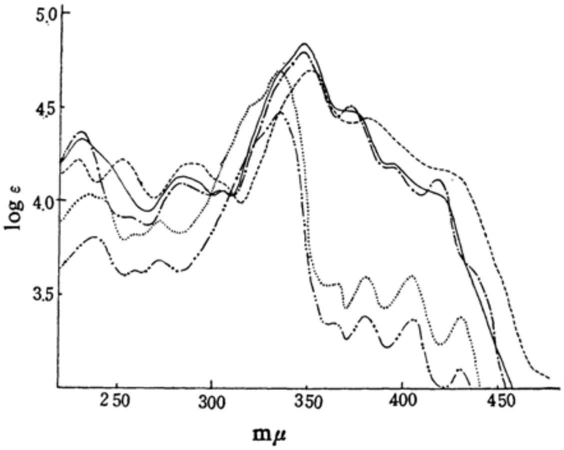
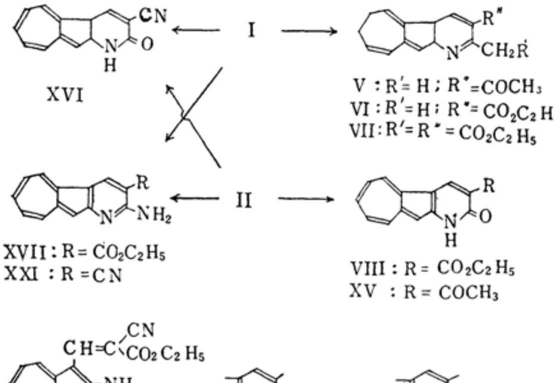


Fig. 2. The ultraviolet spectra of VIII (——), XV (----), XVI (—·—·), XI (······, log ε − 0.2) and XII (—··—, log ε − 0.4) in methanol.

or a 2-ethoxy compound XII, respectively. The ultraviolet absorption curves of XI and XII (Fig. 2) are markedly different from that of VIII but rather similar to these of V, VI and VII. The infrared spectrum of VIII in Nujol exhibits a band at 1630 cm^{-1} (pyridone carbonyl) which is absent in those of compounds XI and XII. These fact indicate that compound VIII exists in the 2-pyridone form rather than in the tautomeric 2-hydroxypyridine form VIIIa.



XVI

V : R′= H ; R″=$COCH_3$
VI : R′= H ; R″= $CO_2C_2H_5$
VII : R′= R″ = $CO_2C_2H_5$

XVII : R = $CO_2C_2H_5$
XXI : R = CN

VIII : R = $CO_2C_2H_5$
XV : R = $COCH_3$

XVIII VIIIa XVIIa

Compound X also reacted with methylamine to give a 2-methylamino compound XIII, and with dimethylamine to give a 2-dimethylamino compound XIV, but the heating of X with alcoholic ammonia resulted in the recovery of the starting material. The ultraviolet spectra of XIII and XIV are shown in Fig. 3.

A similar reaction of compound II with ethyl acetoacetate gave brown crystals (XV) (m. p., 288°C) (decomp.), though in poor

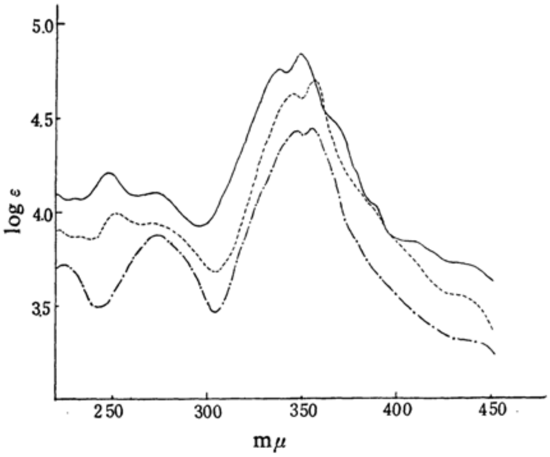
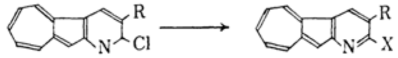


Fig. 3. The ultraviolet spectra of XVII (——), XIII (----, log ε − 0.2) and XIV (—·—·, log ε − 0.4) in methanol.

yield, compound VI not being isolated. From its analytical values and the resemblance of its ultraviolet absorption curve (Fig. 2) to that of compound VIII, XV is through to be 3-acetyl-1, 2-dihydro-2-oxoauzleno [2, 1-b] pyridine, formed by a mode of cyclization different from that of compound I and the same reagent.



X : R=$CO_2C_2H_5$
XIX : R=CN
XI : R=$CO_2C_2H_5$; X=OCH_3
XII : R=$CO_2C_2H_5$; X=OC_2H_5
XIII : R=$CO_2C_2H_5$; X=$NHCH_3$
XIV : R=$CO_2C_2H_5$; X=$N(CH_3)_2$
XX : R=CN ; X=OCH_3

The reaction of I or II with ethyl cyanoacetate was next examined. When I has heated with this reagent reddish brown needles of $C_{14}H_8O_2N_2$ (XVI) (m. p., above 29°C) and a small amount of reddish brown needles ($C_{16}H_{14}O_2N_2$) (XVIII) (m. p., 141°C) were also obtained. The ultraviolet spectrum of XVI (Fig. 2) resembles these of VIII and XV, and the infrared spectrum shows bands at 1655 cm^{-1} (pyridone carbonyl) and at 2210 cm^{-1} (cyano), indicating XVI to be 3-cyano-1, 2-dihydro-2-oxoazuleno [2, 1-b] pyridine. The infrared spectrum of XVII in Nujol shows bands at 3440, 3300 (amino) and 1680 cm^{-1} (ester carbonyl) thus XVII is thought to be ethyl 2-aminoazuleno-[2, 1-b] pyridine-3-carboxylate. XVIII, isomeric with XVII, shows a band at 2190 cm^{-1} (cyano) besides those at 3490, 3340, 3250 (amino) and 1670 cm^{-1} (ester carbonyl) in its infrared region and is thought to be 2-amino-1-(β-cyano-β-ethoxycarbonylvinyl)azulene. The reaction of II and ethyl cyanoacetate also gave XVI and XVII, with the latter predominating. The ultraviolet spectrum of XVII (Fig. 3) resembles those of XIII and XIV, indicating that XVII has the 2-aminopyridine structure rather than the tautomeric 2-pyridone imine form XVIIa.

Reaction XVI with phosphorus oxychloride gave 2-chloro compound XIX which when treated with sodium methoxide, was converted to the 2-methoxy compound XX.

Malononitrile reacted with I or II smoothly to give 2-amino-3-cyanoazuleno [2, 1-b] pyridine (XXI).

Experimental

2-Acetamido-1-formylazulene (II) and 2-Acetamido-1, 3-diformylazulene (III). — To a solution of 800 mg. of 2-acetamidoazulene in 2.5 ml. of dimethylformamide was added a solution of 650 mg. of phosphorus oxychloride in 2.5 ml. of dimethylformamide with continuous ice cooling. After the reaction mixture had been left standing for 4 hr. at room temperature, the immonium salt that separated was collected by filtration. This salt was then dissolved in water and neutralized with dilute sodium carbonate solution, and II which crystallized out, was collected and washed with water. Yield; 595 mg; m. p., 148∼150°C.

The original filtrate was diluted with water and neutralized with a dilute sodium carbonate solution to give 290 mg. of reddish brown crystals; m. p., 135∼180°C. This solid was recrystallized from ethanol to give 70 mg. of III as brown crystals (m. p., 205∼220°C) (decomp.) and 75 mg. of II as red crystals.

II was recrystallized from a mixture of benzene and cyclohexane to give red prisms, m. p. 150∼115°C.

Found: C, 73.40; H, 5.10; N, 6.23. Calcd. for $C_{13}H_{11}O_2N$: C, 73.22; H, 5.20; N, 6.57%.

III was recrystallized from dimethylformamide to give brown feathery csystals; m. p. 225∼235°C (decomp.).

Found: C, 69.76; H, 4.57; N, 5.67. Calcd. for $C_{14}H_{11}O_3N$: C, 69.70; H, 4.59; N, 5.80%.

2-Amino-1-formylazulene (I).—To a solution of 550 mg. of compound II in 20 ml. of ethanol was added 4.5 ml. of a 2 N sodium hydroxide solution and permitted to stand for 1 hr. The acidification of the reaction mixture with acetic acid and the evaporation of the ethanol under reduced pressure gave 420 mg. of a crystalline solid; m. p, 138∼140°C. Recrystallization from a mixture of benzene and cyclohexane gave orange scales, m. p., 138∼139°C.

Found: C, 77.46; H, 5.08; N, 7.93. Calcd. for $C_{11}H_9ON$: C, 77.17; H, 5.30; N, 8.18%.

Oxime.—Brown scale ; m. p., 158∼159°C.

Found: C, 70.91; H, 5.11; N, 15.05. Calcd. for $C_{11}H_{10}ON_2$: C, 70.95; H, 5.41; N, 15.05%.

Trinitrobenzene Complex.—Red scales; m.p, 146∼147°C.

Found: C, 53.32; H, 2.95; N, 14.58. Calcd. for $C_{17}H_{12}O_7N_4$: C, 53.13; H, 3.15; N, 14.58%.

2-Amino-1, 3-diformylazulene (IV). — Treatment of 400 mg. of III similar to that given II gave 210 mg. of IV; m. p., 196∼210°C. Recrystallization from dimethylformamide gave brownish orange needles; m. p., 213∼215°C (decomp.).

Found: C, 72.52; H, 4.30; N, 6.89. Calcd. for $C_{12}H_9O_2N$: C, 72.35; H, 4.55; N, 7.03%.

3-Acetyl-2-methylazuleno[2, 1-b]pyridine (V). — A mixture of 150 mg. of I, 300 mg. of acetylacetone and a small amount of piperidine was heated on a water bath for 6 hr., and the crystals which separated out were collected by filtration. These crystals were dissolved in benzene and passed through an alumina column to give 7 mg. of V as greenish brown crystals; m. p., 143∼145°C. The original filtrate was washed with petroleum ether and the insoluble portion was dissolved in benzene, and chromatographed on an alumina column giving 35 mg. of V, m. p., 141∼143°C, and 35 mg. of I. Recrystallization from dilute ethanol gave dark greenish brown feathery crystals, m. p., 144∼145°C.

Found: C, 81.50; H, 5.17; N, 5.88. Calcd. for $C_{16}H_{13}ON$: C, 81.68; H, 5.57; N, 5.95%.

A solution of 30 mg. of V in dioxane was treated with iodine in the usual manner to give approximately 5 mg. of iodoform.

Hydrochloride.—Deep brown crystals, m. p. over 280°C.

Found: C, 66.08; H, 5.24; N, 4.37. Calcd. for $C_{16}H_{14}ONCl \cdot H_2O$: C, 66.32; H, 5.57; N, 4.83%.

Trinitrobenzene Complex. — Dark violet needles, m. p. 119.5∼121°C.

Found: N, 12.08. Calcd. for $C_{22}H_{16}O_7N_4$: N, 12.50%.

Picrate. — Yellowish brown microcrystals which showed no definite melting point (they gradually blackened around 190°C and completely carbonized 280°C).

Found: C, 57.48; H, 3.21; N, 12.04. Calcd. for $C_{22}H_{16}O_8N_4$: C, 56.90; H, 3.47; N, 12.07%.

Oxime. — Greenish brown microneedles, m. p. 250∼260°C (carbonized).

Found: C, 76.52; H, 5.44; N, 10.83. Calcd. for $C_{16}H_{14}ON_2$: C, 76.77; H, 5.64; N, 11.19%.

Ethyl 2-methylazuleno[2, 1-b]pyridine-3-carboxylate (VI).—A mixture of 150 mg. of I, 170 mg. of ethyl acetoacetate and about 30 mg. of piperidine was heated on a water bath for 7 hr. The crystals which separated were collected by filtration, dissolved in benzene and passed through an alumina column in which manner 40 mg. of VI was thereby obtained as dark violet crystal; m. p., 137∼138°C. The original filtrate was dissolved in a mixture of benzene and petroleum ether (1 : 1) and chromatographed on an alumina column giving an additional 40 mg. of VI; m. p., 137∼138°C. Recrystallization from a mixture of benzene and petroleum ether gave dark greenish violet plates; m. p., 137∼138°C.

Found: C, 77.04; H, 5.36. Calcd. for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.70%.

Hydrochloride.—Dark brown microcrystals, m. p. 217°C (decomp.).

Found: C, 60.10; H, 5.73. Calcd. for $C_{17}H_{16}O_2NCl \cdot 2H_2O$: C, 60.44; H, 5.97%.

Picrate.—Greenish brown crystals, which gradually blackened at around 215°C but which showed no definite melting point.

Found: C, 56.64; H, 3.62; N, 10.98. Calcd.

for $C_{23}H_{18}O_9N_4$: C, 55.87; H, 3.67; N, 11.23%.

Ethyl 3-Ethoxycarbonylazuleno[2, 1-b]pyridine-2-acetate (VII).—A mixture of 150 mg. of I, 300 mg. of diethyl acetonedicarboxylate and a small amount of piperidine was treated as in the case of VI. Chromatographic separation on an alumina column giving an additional 40 mg. of VI; m. p., 137~138°C. Recrystallization from a mixture of benzene and petroleum ether gave dark greenish violet plates; m. p., 137~138°C.

Found: C, 77.04; H, 5.36. Calcd. for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.70%.

Hydrochloride.—Dark brown microcrystals; m. p., 217°C (decomp.).

Found: C, 60.10; H, 5.73. Calcd. for $C_{17}H_{16}O_2NCl\cdot 2H_2O$: C, 60.44; H, 5.97%.

Picrate.—Greenish brown crystals, gradually blackened at around 215°C and showed no definite melting point.

Found: C, 56.64; H, 3.62; N, 10.98. Calcd. for $C_{23}H_{18}O_9N_4$: C, 55.87; H, 3.67; N, 11.23%.

Ethyl 3-Ethoxycarbonylazuleno[2, 1-b]pyridine-2-acetate (VII).—A mixture of 150 mg. of I, 300 mg. of diethyl acetonedicarboxylate and a small amount of piperidine was treated as in the case of VI. Chromatographic separation on an alumina column gave 115 mg. of VII as deep violet crystals; m. p., 107~111°C. Recrystallization from ethanol gave dark violet needles; m. p., 116~117°C.

Found: C, 71.08; H, 5.64; N, 4.08. Calcd. for $C_{20}H_{19}O_4N$: C, 71.20; H, 5.68; N, 4.15%.

Hydrochloride.—Dark violet needles; m. p., 200°C (decomp., gradually blackened around 192°C).

Found: N, 3.26. Calcd. for $C_{20}H_{20}O_4NCl\cdot H_2O$: N, 3.57%.

Picrate.—Dark reddish violet crystals; m. p., 216°C (decomp., gradually blackened around 205°C).

Found: C, 54.97; H, 3.86; N, 9.62. Calcd. for $C_{26}H_{22}O_{11}N_4$: C, 55.12; H, 3.91; N, 9.89%.

Ethyl 1, 2-Dihydro-2-oxoazuleno[2, 1-b]pyridine-3-carboxylate (VIII).—To a solution of 300 mg. of II in 6 ml. of ethanol was added 400 mg. of diethyl malonate and 200 mg. of piperidine, and the whole was heated at 50~60°C for about 30 hr. in which manner 185 mg. of VIII was obtained as brown needles, m. p. 208~215°C (decomp.). Recrystallization from dioxane raised the melting point to 212~217°C (decomp.).

Found: C, 72.14; H, 4.77; N, 5.48. Calcd. for $C_{16}H_{13}O_3N$: C, 71.90; H, 4.90; N, 5.24%.

Picrate.—Orange microcrystals; m. p., 186~188°C (decomp.).

Found: C, 54.00; H, 3.25; N, 11.00. Calcd. for $C_{22}H_{16}O_{10}N_4$: C, 53.23; H, 3.25; N, 11.29%.

The addition of a dilute sodium hydroxide solution to a solution of VIII in dimethylformamide or the heating of VIII in a sodium hydroxide solution gave a brown sodium salt, which on acidification with acetic acid gave the original material.

1, 2-Dihydro-2-oxoazuleno[2, 1-b]pyridine-3-carboxylic Acid (IX).—The heating of 70 mg. of VIII, with the addition of 1 ml. of a 1 N sodium hydroxide solution on a water bath for 1.5 hr., gave a dark greenish-brown sodium salt. Acidification with acetic acid gave 55 mg. of acid as reddish brown crystals; m. p., above 280°C. Recrystallization from dimethylformamide gave reddish brown microneedles.

Found: C, 70.71; H, 3.47; N, 6.27. Calcd. for $C_{14}H_9O_3N$: C, 70.29; H, 3.79; N, 5.86%.

Ethyl 2-Chloroazuleno[2, 1-b]pyridine-3-carboxylate (X).—A mixture of 150 mg. of VIII and 0.8 ml. of phosphorus oxychloride in a sealed tube was heated on a water bath for 1.5 hr. The crystals which separated were collected, suspended in water, treated with aqueous sodium acetate, and extracted with chloroform. The chloroform solution was washed with water and passed through an alumina column. The solvent was evaporated from the effluent, and the crystalline residue was recrystallized from a mixture of benzene and petroleum ether to give 80 mg. of dark greenish violet needles, (m. p., 155~157°C). The original filtrate was poured onto ice to decompose any excess phosphorus oxychloride, treated with aqueous sodium acetate, and extracted with chloroform. The chloroform solution was passed through an alumina column to give 25 mg. of a second crop; m. p., 150~153°C. Recrystallization from a mixture of benzene and petroleum ether gave dark violet needles; m. p., 156~157°C.

Found: C, 67.30; H, 4.06; N, 4.62. Calcd. for $C_{16}H_{12}O_2NCl$: C, 67.25; H, 4.23; N, 4.90%.

Ethyl 2-Methoxyazuleno[2, 1-b]pyridine-3-carboxylate (XI).—To a solution of 40 mg. of sodium in 2 ml. of methanol was added 100 mg. of X; the mixture was then heated on a water bath for 10 min., cooled, diluted with water and extracted with chloroform, The chloroform solution was washed with water and passed through an alumina column. The crystalline residue which was obtained after the evaporation of the solvent from the elute was recrystallized from a mixture of benzene and petroleum ether to give 35 mg. of XI as dark violet crystals, m. p. 161~163°C. Further recrystallization from the same solvent gave dark violet needles; m. p., 162~163°C.

Found: C, 72.17; H, 4.78; N, 5.13.Calcd. for $C_{17}H_{15}O_3N$: C, 72.58; H, 5.38; N, 4.98%.

Ethyl 2-Ethoxyazuleno[2, 1-b]pyridine-3-carboxylate (XII).—A similar treatment of 100 mg. of X with sodium ethoxide in ethanol gave 30 mg. of XII; m. p. 146~148°C. Recrystallization from ethanol gave dark greenish violet microneedles; m. p., 147.5~149°C.

Found: C, 73.37; H, 5.62; N, 4.59. Calcd. for $C_{18}H_{17}O_3N$: C, 73.20; H, 5.80; N, 4.74%.

Ethyl 2-Methylaminoazuleno[2, 1-b]pyridine-3-carboxylate (XIII).—A mixture of 50 mg. of X and 50 mg. of aqueous methylamine (40%) in 0.4 ml. of ethanol was heated on a water bath for 1 hr. in a sealed tube; it was then cooled, and the crystals which separated were collected to give 38 mg. of XIII (m. p., 146~147°C). Recrystallization from ethanol gave wine red needles.

Found: C, 72.97; H, 5.69; N, 9.61. Calcd. for $C_{17}H_{16}O_2N_2$: C, 72.83; H, 5.75; N, 9.99%.

Ethyl 2-Dimethylaminoazuleno[2, 1-b]pyridine-3-carboxylate (XIV).—The treatment of 50 mg. of X with aqueous dimethylamine (40%) in ethanol in a manner similar to that used in the case of XIII gave 48 mg. of XIV; m. p., 133∼135°C. Recrystallization from ethanol gave wine red plates; m. p., 134∼135°C.

Found: C, 73.60; H, 5.85; N, 9.12. Calcd. for $C_{18}H_{18}O_2N_2$: C, 73.45; H, 6.16; N, 9.52%.

3-Acetyl-1, 2-dihydro-2-oxoazuleno[2, 1-b]pyridine (XV).—A solution of 200 mg. of II, 200 mg. of ethyl acetoacetate and 100 mg. of piperidine in 4 ml. of ethanol was heated on a water bath for 5 hr. The crystals which separated were collected and recrystallized from ethanol to give 50 mg. of crystals; m. p., 190∼230°C. Repeated recrystallization from dimethylformamide gave brown microcrystals; m. p., 287∼288°C (decomp.).

Found: C, 75.77; H, 4.49; N, 6.16. Calcd. for $C_{15}H_{11}O_2N$: N, 75.93; H, 4.67; N, 5.90%.

The Reaction of Compound I and Ethyl Cyanoacetate.—A solution of 400 mg. of I, 400 mg. of ethyl cyanoacetate and 50 mg. of piperidine in 1 ml. of ethanol was heated on a water bath for 2 hr. On cooling of the reaction mixture gave 95 mg. of 3-cyano-1, 2-dihydro-2-oxoazuleno[2, 1]pyridine (XVI) (m. p., above 290°C) as brown crystals. Evaporation of the solvent from the filtrate, followed by the addition of a small amount of benzene separated 25 mg. of ethyl 2-aminoazuleno[2, 1-b]-pyridine-3-carboxylate (XVII) (m. p. 167∼187°C). The filtrate was passed through an alumina column giving 35 mg. of 2-amino-1-(β-cyano-β-ethoxycarbonylvinyl)azulene (XVIII) as red crystals, (m. p., 135∼139°C).

XVI was recrystallized from dimethylformamide to give reddish brown needles; m. p., above 290°C.

Found: C, 76.17; H, 3.74; N, 12.63. Calcd. for $C_{14}H_8ON_2$: C, 76.36; H, 3.66; N, 12.72%.

XVII was recrystallized from *n*-butanol to give reddish brown needles; m. p., 189∼190°C.

Found: C, 72.52; H, 4.99; N, 10.46. Calcd. for $C_{16}H_{14}O_2N_2$: C, 72.16; H, 5.30; N, 10.52%.

XVIII was recrystallized from ethanol to give red prisms; m. p., 139.5∼141°C.

Found: C, 71.96; H, 5.02; N, 10.58. Calcd. for $C_{15}H_{14}O_2N_2$: C, 72.16; H, 5.30; N, 10.52%.

The Reaction of Compound II and Ethyl Cyanoacetate.—A similar treatment of 300 mg. of II with ethyl cyanoacetate gave 305 mg. of brownish purple crystals (m. p., 190∼230°C). The sparingly soluble portion of these crystals in chloroform afforded 75 mg. of XVI (m. p. over 290°C), while the easily soluble part gave 170 mg. of XVII (m. p., 188∼189°C).

2-Chloro-3-cyanoazuleno[2, 1-b]pyridine (XIX).—A mixture of 90 mg. of XVI and 0.5 ml of phosphorus oxychloride in a sealed tube was heated on a water bath for 1.5 hr.; it was then cooled, and the crystals which separated were collected by filtration. Treatment of these crystals with a dilute sodium carbonate solution afforded 72 mg. of dark violet crystals (m. p., 256∼261°C). Recrystallization from dimethylformamide gave dark greenish violet needles; m. p., 264∼265°C.

Found: C, 70.24; H, 2.78; N, 11.60. Calcd. for $C_{14}H_7N_2Cl$: C, 70.45; H, 2.96; N, 11.74%.

3-Cyano-2-methoxyazuleno[2, 1-b]pyridine (XX).—To a solution of 20 mg. of sodium in 0.6 ml. of methanol was added 40 mg. of XIX; the solution was then heated on a water bath for 20 min. The crystals which were obtained were then dissolved in chloroform, passed through an alumina column, and the solvent was evaporated from the effluent. The residue was recrystallized from a mixture of ethanol and *n*-butanol to give 25 mg. of brownish violet needles; m. p., 229∼230°C.

Found: C, 76.86; H, 4.17; N, 11.80. Calcd. for $C_{15}H_{10}ON_2$: C, 76.91; H, 4.30; N, 11.96%.

2-Amino-3-cyanoazuleno[2, 1-b]pyridine (XXI).—a) A solution of 70 mg. of I, 70 mg. of malononitrile and a small amount of piperidine in 0.3 ml. of ethanol was heated for 1 hr. on a water bath, and the resulting crystals (80 mg., m. p. 245∼268°C) were recrystallized from dimethylformamide to give brownish violet needles (m. p., 266∼268°C) (decomp.).

Found: C, 77.03; H, 3.92; N, 18.61. Calcd. for $C_{14}H_9N_3$: C, 76.69; H, 4.14; N, 19.17%.

Hydrochloride.—Reddish orange microneedles, m. p. over 280°C.

Found: C, 61.62; H, 4.09. Calcd. for $C_{14}H_{10}N_3Cl \cdot H_2O$: C, 61.43; H, 4.42%.

b) The treatment of a solution of 100 mg. of II, 50 mg. of malononitrile and 30 mg. of piperidine in 1 ml. of ethanol in a manner similar to that used in the case of a) afforded 75 mg. of XXI; m. p., 260∼265°C. (decomp.). Recrystallization from dimethylformamide raised the melting point 266∼268°C (decomp.); these crystals were shown to be identical with those obtained by a).

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