The Synthesis of 5- and 6-Acetylazulene Derivatives

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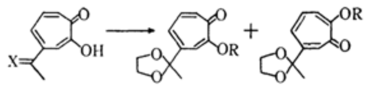
In a previous paper[1], we reported the synthesis of aminoazulenes from troponoid compounds as a part of a general scheme for the synthetic study of azulenes with the functional group on a seven-membered ring. In this paper, the synthesis of acetylazulenes is reported. The ethylene ketal (II)[2] of 4-acetyltropolone (I)[3] was converted to the corresponding methyl ethers (IIIa and IIIb) and *p*-toluenesulfonate (IVa and IVb), to which the general synthetic method[4-7] of the azulenic compound was then applied.



I : X=O IIIa : R=CH_3 IIIb : R=CH_3

II : X=$\langle^{O-}_{O-}]$ IVa : R=Ts IVb : R=Ts

The reaction of a mixture of methyl ethers (IIIa and IIIb) with ethyl cyanoacetate yielded five azulenic products (ultraviolet spectra: Fig. 1): diethyl 2-amino-5-(1, 1-ethylenedioxyethyl)azulene-1, 3-dicarboxylate (V), ethyl 2-amino-5(or 7)-(1, 1-ethylenedioxyethyl)azulene-1-carboxylate (VI), 1, 3-dicyano-5-(1, 1-ethylenedioxyethyl)-2-hydroxyazulene (VII), ethyl 3-cyano-5(or 7)-(1, 1-ethylenedioxyethyl)-2-hydroxyazulene-1-carboxylate (VIII), and ethyl 3-cyano-7(or 5)-(1, 1-ethylenedioxyethyl)-2-hydroxyazulene-1-carboxylate (IX). The structural assignment of these compounds was based on their analyses, their infrared spectra, and a consideration of the general course of the azulene synthesis[4-7], although the exact locations of the ethoxycarbonyl and cyano groups in VI, VIII and IX with respect of the ethylenedioxyethyl group are not known.

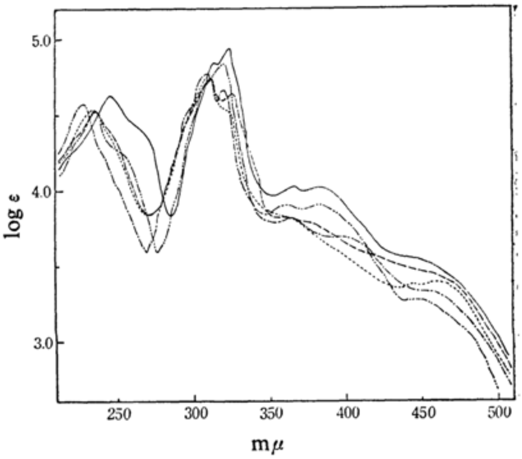


Fig. 1. Ultraviolet absorption spectra of V (——), VI (—··—), VII (—·—), VIII (— —) and IX (·······) in methanol.

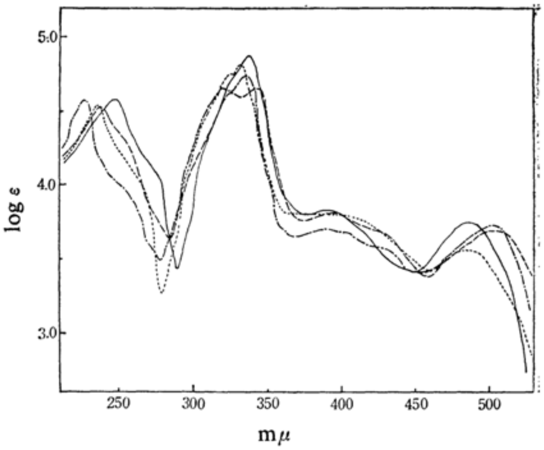


Fig. 2. Ultraviolet absorption spectra of X (——), XI (·······), XII (— —), and XIII (—··—) in methanol.

When this condensation reaction was carried out in the presence of one molar equivalent of sodium ethoxide, V was obtained as a major product, together with a small amount of VII, VIII and IX, while the reaction with two molar equivalents of sodium ethoxide did not yield V but VII as the major product, accompanied by a small amount of VI. The mild acid hydrolysis of these compounds provoked a cleavage of the ethylene ketal ring to form

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[6] T. Nozoe, S. Seto, S. Matsumura and T. Asano, *Proc. Japan Acad.*, 32, 339 (1956); H. Akino, to be published.

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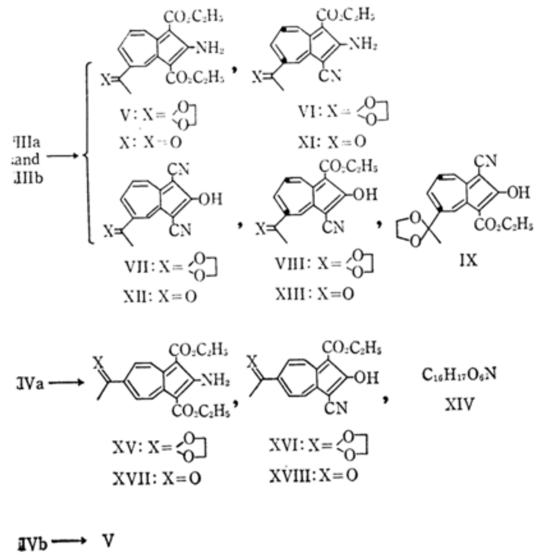
the corresponding acetyl compound; diethyl 5-acetyl-2-aminoazulene-1, 3-dicarboxylate (X) from V, ethyl 5(or 7)-acetyl-2-amino-3-cyanoazulene-1-carboxylate (XI) from VI, 5-acetyl-1, 3-dicyano-2-hydroxyazulene (XII) from VII, and ethyl 5(or 7)-acetyl-3-cyano-2-hyroxyazulene-1-carboxylate (XIII) from VIII. The ultraviolet spectra of these substances are shown in Fig. 2.



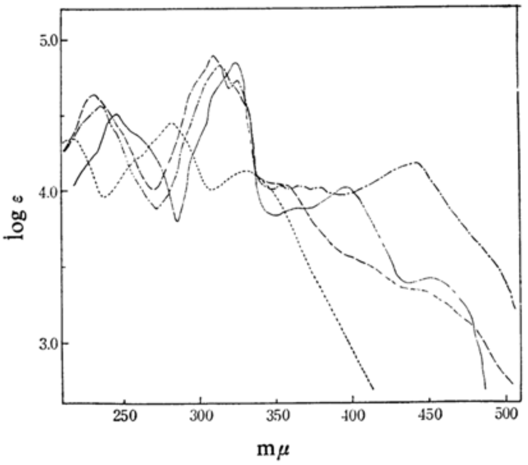
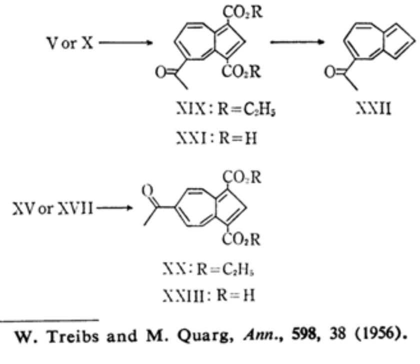


Fig. 3. Ultraviolet absorption spectra of XIV (·········), XV (——), XVI (—·—) and XVIII (—-—) in methanol.

The reaction of ethyl cyanoacetate on 4-(1, 1-ethylenedioxyethyl)-2-(*p*-tolylsulfonyloxy)tropone (IVa) gave three products, all of which were different from those obtained from IIIa and IIIb. The analyses, the ultraviolet (Fig. 3) and infrared spectra, and the general conception of the nature of the reaction suggested that the first two products were diethyl 2-amino-6-(1, 1-ethylenedioxyethyl)azulene-1, 3-dicarboxylate (XV) and ethyl 3-cyano-6-(1, 1-ethylenedioxyethyl)-2-hydroxyazulene-1-carboxylate (XVI). The third compound XIV, the main product, was assumed not to be azulenic from its ultraviolet spectrum; it has properties similar to those of the substance obtained from 5-acetamido-2-(*p*-tolylsulfonyloxy)tropone[1]. The exact structure, however, can not be drawn. The hydrolysis of ethylene ketal in XV and XVI was effected by diluted acid to give their respective acetylazulenes, XVII and XVIII.

The reaction of ethyl cyanoacetate on the isomeric *p*-toluenesulfonate (IVb), 6-(1, 1-ethylenedioxyethyl)-2-(*p*-tolylsulfonyloxy)tropone, gave the azulene (V) in a low yield, besides the recovery of the starting material. The formation of the azulene (V), the product of the reaction at C_1 and C_2, may be due to the difficulty the reagent has in approaching the 7-position of the tropone because of the presence of the side chain at the 6-position.

The removal of substituents was carried out on ethylenedioxyethylazulenes (V and XV) and acetylazulenes (X and XVII); the diazotization reaction was accomplished by means of large excess of sulfuric acid and isoamyl nitrite or sodium nitrite, the amino group being notably unreactive compared with diethyl 2-aminoazulene-1, 3-dicarboxylate[5]. The decomposition of diazonium salts to yield the corresponding deamination products was achieved by letting the salts stand at room temperature or by warming them in the presence of copper or sodium hypophosphite. In the reactions of V and XV, ethylene ketal was hydrolyzed at the same time; thus, V and X gave diethyl 5-acetylazulene-1, 3-dicarboxylate (XIX), while XV and XVII yielded diethyl 6-acetylazulene-1, 3-dicarboxylate (XX). Dicarboxylic acid XXI obtained by the alkaline hydrolysis of XIX was submitted to thermal decarboxylation to form blue-violet 5-acetylazulene (XXII) ($\nu_{C=O}$ 1664 cm^{-1}), which, though its identify has not yet been established, is probably identical with the product (m. p. 39°C) obtained by Treibs and Quarg[8] by a



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[8] W. Treibs and M. Quarg, *Ann.*, **598**, 38 (1956).

ring expansion of indane with diazoketone. The similar hydrolysis of XX to the corresponding dicarboxylic acid XXIII and subsequent thermal decarboxylation yielded a pale green oil, but its small quantity did not allow the product to be characterized.

The alkaline hydrolysis of X and XVII afforded dicarboxylic acid XXIV and XXV respectively, the heating of which in pyridine caused decarboxylation which produced 5-acetyl-2-aminoazulene (XXVI) and 6-acetyl-2-aminoazulene (XXVII) respectively. XXVI was also obtained by the similar decarboxylation of the dicarboxylic acid XXVIII obtained from ethylene ketal V. The ultraviolet spectra of these 5-acetyl- and 6-acetylazulene derivatives are shown in Fig. 4 and Fig. 5. When alkaline hydrolysis of V was carried out in anhydrous ethanol, monocarboxylic acid XXIX was obtained; the decarboxylation of this in pyridine yielded monoester XXX. The acid hydrolysis of XXX gave ethyl 5(or 7)-acetyl-2-aminoazulene-1-carboxylate (XXXI) (ultraviolet spectra in Fig. 6). As the position of ethoxycarbonyl which had under gone alkaline hydrolysis could not be determined, no definite conclusion can be drawn at present concerning the position of the ethoxycarbonyl group in XXX and XXXI.

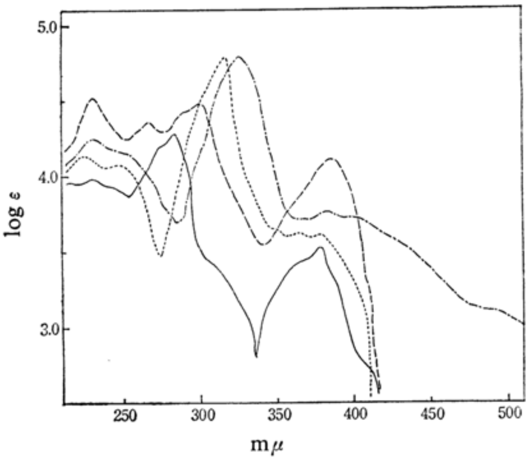


Fig. 4. Ultraviolet absorption spectra of XIX (—·—), XXII (——), XXVI (---) and acetate of XXVI (·······) in methanol.

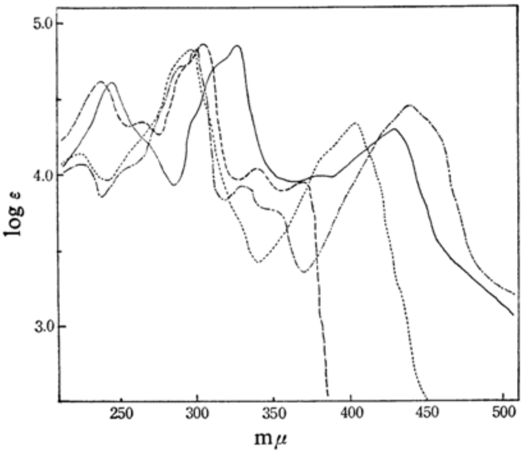


Fig. 5. Ultraviolet absorption spectra of XVII (——), XX (—·—), XXVII (·······) and acetate of XXVII (---) in methanol.

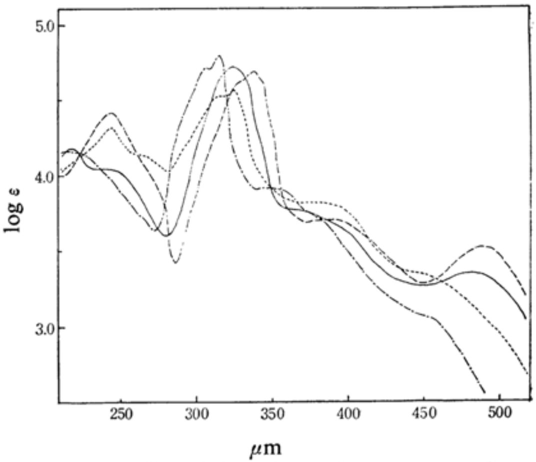
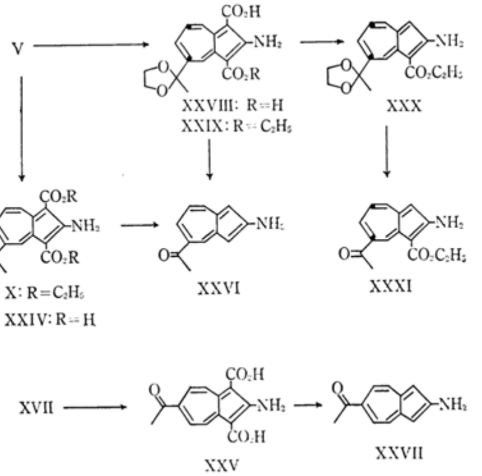


Fig. 6. Ultraviolet absorption spectra of XXIV (—·—), XXVIII (·······), XXX (---) and XXXI (——) in methanol.



The reactions of these acetylazulene derivatives with ketonic reagents are being investigated and will be reported on in the future.

Experimental[9]

The Reaction of 4-(1,1-Ethylenedioxyethyl)tropolone Methyl Ether (IIIa and IIIb) and Ethyl Cyanoacetate.—*a) With 1 mol. of Sodium Ethoxide.*—To a sodium ethoxide solution prepared from

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[9] All melting points are uncorrected. Shoulders in the UV spectral data are designated by "sh".

sodium (1.83 g., 0.036 mol.) and absolute ethanol (80 ml.), ethyl cyanoacetate (6.83 g.) was added. After this mixture had been allowed to stand for 30 min., a solution of methyl ether (a mixture of IIIa and IIIb) (6.9 g., 0.031 mol.) in absolute ethanol (30 ml.) was added, and the new mixture was allowed to stand overnight. The solvent was removed under reduced pressure, water was added, and the separated crystals (m. p. 104～109°C, 7.3 g.) were recrystallized from ethanol to afford V as yellow prisms (m. p. 112～113°C, 6.65 g.).

Found: C, 64.31; H, 6.90; N, 3.82. Calcd. for $C_{20}H_{23}O_6N$: C, 64.33; H, 6.21; N, 3.75%.

λ_{max}^{MeOH} mμ (log ε): 247 (4.88), 317 (5.08), 327 (5.20), 365 (4.25), 387 (4.24), 454 (3.29). IR: (KBr disk) 3445, 3328, 1668; (Nujol) 3460, 3350, 1650 cm^{-1}.

The Picrate of V: M. p. 124.5～126°C; orange needles (from ethanol).

Found: C, 51.70; H, 4.45; N, 9.40. Calcd. for $C_{26}H_{26}O_{13}N_4$: C, 51.82; H, 4.36; N, 9.30%.

The Acetate of V: This was obtained by refluxing V in acetic anhydride for 6 hr.; m. p. 122～123°C; reddish violet needles (from ethanol).

Found: C, 63.55; H, 5.87; N, 3.23. Calcd. for $C_{22}H_{25}O_7N$: C, 63.60; H, 6.07; N, 3.37%.

IR (Nujol): 3490, 3330, 1724, 1701, 1686 cm^{-1}.

From the aqueous mother liquor, crystals (m. p. 225～230°C, 0.20 g.) were obtained after the liquor had been left standing for 3 hr. Recrystallization from benzene formed VIII as yellowish orange silky needles; m. p. 234～237°C (decomp.).

Found: C, 66.56; H, 5.41; N, 4.36. Calcd. for $C_{18}H_{17}O_5N$: C, 66.05; H, 5.24; N, 4.28%.

λ_{max}^{MeOH} mμ (log ε): 237 (4.53), 312 (4.74), 327 (4.63), 365 (3.84). IR: (KBr disk) 3060, 2208, 1647; (Nujol) 2232, 1647 cm^{-1}.

The Acetate of VIII: M. p. 148～149.5°C; pale red scales (from methanol).

Found: C, 65.02; H, 5.19; N, 3.79. Calcd. for $C_{20}H_{19}O_6N$: C, 65.03; H, 5.19; N, 3.79%.

λ_{max}^{MeOH} mμ (log ε): 233 (4.56), 260 (4.29), 303 (4.73), 368 (3.91). IR (KBr disk): 2228, 1772, 1692 cm^{-1}.

The mother liquor was washed with benzene, the water layer was acidified with 6 N sulfuric acid, and the separated crystals (m. p. 225～230°C; 0.45 g.) were recrystallized from ethanol to afford VII as brownish yellow crystals (m. p. 238.5～239°C (decomp.), 0.26 g.).

Found: C, 67.69; H, 4.23; N, 9.70. Calcd. for $C_{20}H_{23}O_6N_2$: C, 68.56; H, 4.32; N, 10.00%.

λ_{max}^{MeOH} mμ (log ε): 230 (4.58), 312 (4.76), 324 (4.65), 367 (3.80), IR (KBr disk): 3020, 2217 cm^{-1}.

The Acetate of VII: M. p. 215～216°C; pale brownish red needles (from ethyl acetate).

Found: C, 67.07; H, 4.38; N, 8.69. Calcd. for $C_{18}H_{14}O_4N_2$: C, 66.93; H, 4.07; N, 8.47%.

λ_{max}^{MeOH} mμ (log ε): 230 (4.54), 303 (4.70), 366.5 (3.79), 480 (2.83). IR (Nujol): 2217, 1783 cm^{-1}.

The filtrate was extracted with benzene, and the crystals thus obtained were recrystallized from a mixture of ethanol and water to form IX, which appeared as pale brownish yellow silky needles (m. p. 214～215°C).

Found: C, 66.23; H, 5.23; N, 4.65. Calcd. for $C_{18}H_{17}O_5N$: C, 66.05; H, 5.24; N, 4.28%.

λ_{max}^{MeOH} mμ (log ε): 236 (4.51), 312 (4.74), 325 (4.52), 453 (3.36). IR (KBr disk): 3060, 2215, 1647 cm^{-1}.

b) With 2 mol. of Sodium Ethoxide.—To a sodium ethoxide solution prepared from sodium (0.18 g., 0.0078 mol.) and absolute ethanol (6 ml.), ethyl cyanoacetate (0.84 g.) was added. After the mixture had been left standing for 30 min., a solution of methyl ether (a mixture of IIIa and IIIb) (0.75 g., 0.0034 mol.) in absolute ethanol (6 ml.) was added, and the mixture was allowed to stand overnight. The solvent was removed under reduced pressure, water was added, and the separated crystals were collected by filtration; m. p. 108～134°C; 0.21 g. Recrystallization from ethanol afforded VI as orangish yellow needles (m. p. 180～182°C, 50 mg.).

Found: C, 65.82; H, 5.51; N, 8.54. Calcd. for $C_{18}H_{18}O_4N$: C, 66.24; H, 5.56; N, 8.56%.

λ_{max}^{MeOH} mμ (log ε): 239 (4.53), 325 (4.80), 368 (3.85), 388 (3.86), 446 (3.25). IR (Nujol): 3490, 3380, 2232, 1675 cm^{-1}.

The mother liquor was washed with benzene, and the aqueous layer was acidified with 6 N sulfuric acid, from which VII (m. p. 218～223°C; 0.52 g.) was obtained.

The Reaction of 4-(1, 1-Ethylenedioxyethyl)-2-(*p*-tolylsulfonyloxy)tropone (IVa) and Ethyl Cyanoacetate.—To a sodium ethoxide solution prepared from sodium (0.39 g.) and absolute ethanol (40 ml.), ethyl cyanoacetate (3.5 g.) was added. After this mixture had been left standing for 30 min., a suspended solution of IVa (5.04 g.) in absolute ethanol (20 ml.) was added, the mixture was stirred for 10 hr., and then it was allowed to stand for 2 days. After removal of the solvent under reduced pressure, water was added to the residue, and the separated crystals were collected (4.25 g.). The crystals were warmed with benzene, and the insoluble part (1.85 g., m. p. 250～256°C) was recrystallized from ethanol to give pale yellow needles of XIV (m. p. 258～259°C).

Found: C, 60.56; H, 5.43; N, 4.41. Calcd. for $C_{16}H_{17}O_6N$: C, 60.18; H, 5.37; N, 4.39%.

λ_{max}^{MeOH} mμ (log ε): 222 (4.34), 288 (4.44), 335 (4.29).

The benzene soluble part was passed through a column of alumina with benzene, and the crystals obtained (m. p. 141～145°C; 1.50 g.) were recrystallized from ethanol to give XV as orangish yellow needles (m. p. 154.5～155°C; 1.15 g.).

Found: C, 64.46; H, 5.62; N, 3.66. Calcd. for $C_{20}H_{23}O_6N$: C, 64.33; H, 6.21; N, 3.75%.

λ_{max}^{MeOH} mμ (log ε): 245 (4.51), 318 (4.71), 327 (4.82), 370 (3.87), 395 (4.00), 450 (3.40). IR (Nujol): 3450, 3345, 1675, 1647 cm^{-1}.

The Picrate of XV: M. p. 137～138°C; orange needles (from ethanol).

The aqueous mother liquor was extracted with benzene to give an oily substance containing a crystalline solid which was then recrystallized from ethanol to give XVI as yellowish orange needles (30 mg.; m. p. 205～206°C).

Found: C, 66.58; H, 5.18; N, 4.40. Calcd. for $C_{18}H_{17}O_5N$: C, 66.02; H, 5.24; N, 4.28%.

$\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 234 (4.61), 313 (4.79), 327 (4.55), 360 (4.12) sh, 450 (3.18) sh. IR (Nujol): 3150, 2222, 1667 cm^{-1}.

The Reaction of 6-(1,1-Ethylenedioxyethyl)-2-*p*-tolylsulfonyloxy)tropone (IVb) and Ethyl Cyanoacetate.—A sodium ethoxide solution (30 mg. of sodium and 4 ml. of absolute ethanol), ethyl cyanoacetate (250 mg.), and a solution of IVb (360 mg.) in absolute ethanol were treated in the manner described above. After removal of the solvent, water was added and the crystals which had separated were recrystallized from ethanol to give recovered IVb (110 mg.) and the azulene derivative V (10 mg.).

The Hydrolysis of the Ethylene Ketal Group of V, VI, VII, VIII, XV and XVI.—A solution of ethylene ketal in ethanol (40 times) and 6 N sulfuric acid was refluxed for 30 min. and then allowed to cool, by which process a hydrolized compound was obtained, in a nearly quantitative yield.

a) Diethyl 5-Acetyl-2-aminoazulene-1, 3-dicarboxylate (X).—Obtained from V: M. p. 123~124°C; orange micro-prisms (from ethanol).

Found: C, 65.58; H, 5.65; N, 4.43. Calcd. for $C_{18}H_{19}O_5N$: C, 65.64; H, 5.82; N, 4.25%.

$\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 246 (4.55), 328 (4.73), 340 (4.85), 389 (3.78), 490 (3.69). IR (Nujol): 3410, 3320, 1672 cm^{-1}.

The Acetate of X: Obtained by refluxing X in acetic anhydride for 8 hr.; m. p. 161~162°C; reddish violet leaflets (from ethanol).

Found: N, 3.81. Calcd. for $C_{20}H_{21}O_6N$: N, 3.77%.

IR (Nujol): 3380, 1724, 1695, 1686 cm^{-1}.

b) Ethyl 5(or 7)-Acetyl-2-amino-3-cyanoazulene-1-carboxylate (XI).—Obtained from VI; m. p. 199~200°C; orange prisms (from ethanol).

Found: C, 67.81; H, 4.87; N, 9.92. Calcd. for $C_{16}H_{14}O_3N_2$: C, 68.07; H, 5.00; N, 9.92%.

$\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 238 (4.51), 326 (4.63), 336 (4.67), 390 (3.78), 490 (3.51). IR (Nujol): 3470, 3370, 2217, 1686, 1664 cm^{-1}.

c) 5-Acetyl-1, 3-dicyano-2-hydroxyazulene (XII).—Obtained from VII; m. p. 223~225°C; pale brown prisms (from aqueous ethanol).

Found: C, 70.48; H, 3.50; N, 11.61. Calcd. for $C_{14}H_8O_2N_2$: C, 71.18; H, 3.41; N, 11.86%.

$\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 230 (4.57), 324 (4.67), 339 (4.73), 400 (3.67), 504 (3.67). IR (KBr disk): 3010, 2218, 1672 cm^{-1}.

d) Ethyl 5(or 7)-Acetyl-3-cyano-2-hydroxyazulene-1-carboxylate (XIII).—Obtained from VIII; m. p. 204.5~206°C; dull yellowish orange leaflets (from ethanol).

Found: C, 67.25; H, 4.54; N, 5.10. Calcd. for $C_{16}H_{13}O_4N$: C, 67.84; H, 4.63; N, 4.95%.

$\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 235 (4.48), 320 (4.56), 341 (4.63), 380 (3.73), 504 (3.67). IR (KBr disk): 2980, 2220, 1690 cm^{-1}.

The Acetate of XIII: Obtained by refluxing XIII in acetic anhydride; m. p. 169~170°C; brilliant red needles (from ethanol).

Found: C, 66.63; H, 4.61; N, 4.30. Calcd. for $C_{18}H_{15}O_5N$: C, 66.45; H, 4.65; N, 4.31%.

IR (Nujol): 2212, 1779, 1684 cm^{-1}.

e) Diethyl 6-Acetyl-2-aminoazulene-1, 3-dicarboxylate (XVII).—Obtained from XV; m. p. 139~140°C; orange needles (from ethanol).

Found: C, 65.89; H, 5.80; N, 4.38. Calcd. for $C_{18}H_{19}O_5N$: C, 65.64; H, 5.82; N, 4.25%.

$\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 248 (4.60), 330 (4.84), 380 (3.98), 432 (4.30). IR (Nujol): 3510, 3340, 1692, 1669, 1656 cm^{-1}.

f) Ethyl 6-Acetyl-3-cyano-2-hydroxyazulene-1-carboxylate (XVIII).—Obtained from XVI; m. p. 196.5~198°C; pale red granules (from ethanol).

Found: C, 67.84; H, 4.52; N, 4.50. Calcd. for $C_{16}H_{13}O_4N$: C, 67.84; H, 4.63; N, 4.95%.

$\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 240 (4.54), 318 (4.80), 330 (4.66), 357 (3.96), 375 (3.98), 440 (4.12). IR (Nujol): 3200, 2217, 1695, 1667 cm^{-1}.

Diethyl 5-Acetylazulene-1,3-dicarboxylate (XIX). —*a) The Deamination of V in Ethanol.*—To a solution of V (0.50 g.) in 50% aqueous ethanol (25 ml.), concentrated sulfuric acid (4.7 ml.) was added; isoamyl nitrite (2.4 g.) was then added into this mixture with stirring at room temperature. After having been stirred for 4 hr. and having been left standing overnight, the mixture was diluted with water and extracted with benzene. The benzene extract was passed through a column of alumina; from the first effluent, crude crystals of XIX (m. p. 106~109°C; 280 mg.) were obtained. Recrystallization from ethanol formed red needles (m. p. 116.5~117°C).

Found: C, 68.66; H, 5.75. Calcd. for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77%.

$\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 235 (4.54), 272 (4.36), 305 (4.48), 324 (3.94) sh, 395 (4.11), 508 (2.68). IR (Nujol): 1689 cm^{-1}.

From the second effluent, X (20 mg.) was obtained.

When sodium hypophosphite was used on the decomposition of the diazotized solution, XIX (60 mg.) was obtained from V (100 mg.).

b) The Deamination of V in Dioxane.—To a solution of V (100 mg.) in dioxane (3 ml.) and concentrated sulfuric acid (0.4 ml.), a solution of sodium nitrite (50 mg.) in water (0.2 ml.) was dropped in. After this mixture had been stirred for 30 min., active copper powder (100 mg.) was added, and the mixture was warmed on a water bath. The mixture was treated in the above-mentioned method to give XIX (35 mg.).

c) The Deamination of X.—A solution of X (100 mg.) in 50% aqueous ethanol (5 ml.) and concentrated sulfuric acid (4.5 ml.) was diazotized and treated as in a); XIX (30 mg.) was thus obtained.

Diethyl 6-Acetylazulene-1, 3-dicarboxylate (XX). —*a) The Deamination of XV in Ethanol.*—To a solution of XV (100 mg.) in 60% aqueous ethanol (5 ml.), concentrated sulfuric acid (0.6 ml.) was added, and to this mixture, isoamyl nitrite (0.44 g.) was added with stirring at room temperature. After having been stirred for 2 hr. and having been standing overnight, the reaction mixture was diluted with water (20 ml.) and extracted with benzene. The benzene extract was passed through a column of alumina, and from the first effluent, crude crystals of XX (m. p. 105~106°C; 60 mg.) were obtained. Recrystallization from ethanol formed deep violet blue scales (m. p. 129~130°C).

Found: C, 68.61; H, 5.79. Calcd. for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77%.

λ_{max}^{MeOH} mμ (log ε): 242 (4.62), 270 (4.26), 310 (4.77), 345 (3.93), 375 (2.82), 527 (2.49). IR (Nujol): 1686 cm^{-1}.

b) The Deamination of XV in Dioxane.—Into a solution of XV (200 mg.) in dioxane (6 ml.) and concentrated sulfuric acid (0.4 ml.), a solution of sodium nitrite (50 mg.) in water (2 ml.) was dropped. After this mixture had been stirred for 30 min., active copper powder (100 mg.) and a solution of sodium hypophosphite (0.8 g) in water (93 ml.) were added. After having been stirred an additional for 2 hr., the reaction mixture was treated as in a) From the first effluent, XX (60 mg.) was obtained; from the second effluent, XVII (60 mg.) was obtained.

c) The Deamination of XVII.—XVII (90 mg.) was diazotized and treated as in a); XX (30 mg.) was obtained.

5-Acetylazulene-1, 3-dicarboxylic Acid (XXI).—To a solution of potassium hydroxide (140 mg.) in 70% aqueous ethanol (5 ml.), XX (200 mg.) was added, and the mixture was refluxed for 4 hr. After it had cooled the solution was acidified with 6 N sulfuric acid to give XXI (140 mg.) as dark brown crystals (m. p. above 270°C; sparingly soluble in organic solvents).

5-Acetylazulene (XXII).—The decarboxylation of XXI was carried out under reduced pressure (15 mmHg) at 280~300°C, yielding a violet oil which was then passed through a column of alumina with petroleum ether (b. p. 40~60°C) to give a violet blue oil (XXII). IR (Nujol): 1664 cm^{-1}.

λ_{max}^{MeOH} mμ (log ε): 220 (3.97), 235 (3.98), 392 (4.25), 370 (3.40), 383 (3.50), 564, 584 sh, 612, 670 sh.

6-Acetylazulene-1, 3-dicarboxylic Acid (XXIII).—When XX (150 mg.) was treated as in the above experiment, XXIII (100 mg.) (brown crystals; m. p. above 260°C; sparingly soluble in organic solvents) was obtained. IR (Nujol): 1704 cm^{-1}.

5-Acetyl-2-aminoazulene-1, 3-dicarboxylic Acid (XXIV).—To a solution of potassium hydroxide (100 mg.) in 85% aqueous ethanol (3 ml.), X (100 mg.) was added, and the mixture was refluxed for 5 hr. After the solution had cooled, it was acidified with 6 N sulfuric acid to give XXIV (70 mg.) as a black crystalline powder (m. p. 203~204.5°C (decomp.); sparingly soluble in organic solvents).

Found: C, 60.78; H, 4.04; N, 4.75. Calcd. for $C_{14}H_{11}O_5N$: C, 61.54; H, 4.06; N, 5.13%.

λ_{max}^{MeOH} mμ (log ε): 243 (4.45), 339 (4.75), 385 (3.76), 494 (3.61). IR (KBr disk): 3439, 3325, 1657 cm^{-1}.

6-Acetyl-2-aminoazulene-1, 3-dicarboylic Acid (XXV).—When XVII (180 mg.) was treated as in the above experiment, XXV (130 mg.), (reddish brown crystals; m. p. 265°C (decomp.); sparingly soluble in organic solvents) was obtained.

λ_{max}^{MeOH} mμ (log ε): 246 (4.43), 329 (4.67), 378 (3.86), 434 (4.17). IR (Nujol): 3540, 3340, 1661 cm^{-1}.

2-Amino-5-(1, 1-ethylenedioxyethyl)azulene-1 ,3-dicarboxylic Acid (XXVIII).—To a solution of potassium hydroxide (0.80 g.) in ethanol (6 ml.), V (1.00 g.) was added, and the mixture was refluxed for 4 hr. After the mixture had cooled, it was diluted with water and acidified with 6 N sulfuric acid to give XXVIII (0.71 g.) (dull yellowish orange crystals,; m. p. 174~175°C (decomp.); sparingly soluble in organic solvents).

Found: C, 61.71; H, 4.97; N, 4.73. Calcd. for $C_{16}H_{15}O_6N$: C, 60.56; H, 4.77; N, 4.41%.

λ_{max}^{MeOH} mμ (log ε): 345 (4.34), 315 (4.57), 326 (4.62), 380 (3.86) sh. IR (Nujol): 3430, 3340, 1658, 1642 cm^{-1}.

5-Acetyl-2-aminoazulene (XXVI).—*a) From XXIV.*—A solution of XXIV (300 mg.) in pyridine (2 ml.) was heated at 125~130°C to effect decarboxylation. The residue produced by the evaporation of the excess pyridine was dissolved in benzene, and the solution was passed through a column of alumina to give XXVI (m. p. 162~163°C; 130 mg.). Recrystallization from ethanol formed deep violet leaflets (m. p. 167~167.5°C; 110 mg.).

Found: C, 78.05; H, 5.93; N, 7.47. Calcd. for $C_{12}H_{11}ON$: C, 77.81; H, 5.99; N, 7.56%.

λ_{max}^{MeOH} mμ (log ε): 227 (4.25), 322 (4.79), 384 (3.75) 395 (3.72), 490 (3.11) sh. IR: (KBr disk) 3457, 3343, 3238, 1638, 1628; (Nujol) 3460, 3360, 3270, 1645, 1629 cm^{-1}.

Picrate: M. p. 166.5~167.5°C; brownish violet needles (from ethanol).

Found: C, 52.11; H, 5.54; N, 13.21. Calcd. for $C_{18}H_{14}O_8N_4$: C, 52.18; H, 5.77; N, 13.52%.

Acetate: M. p. 176~177°C; deep reddish violet needles (from ethanol).

Found: C, 74.42; H, 5.54; N, 6.16. Calcd. for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77; N, 6.16%.

λ_{max}^{MeOH} mμ (log ε): 224 (4.11), 250 (4.05), 315 (4.75), 380 (3.59). IR (Nujol): 3380, 1689, 1661 cm^{-1}.

b) From XXVIII.—When XXVIII (400 mg.) was dissolved in pyridine (2 ml.) and treated as in a), XXVI (80 mg.) was obtained.

6-Acetyl-2-aminoazulene (XXVII).—When a solution of XXV (150 mg.) in pyridine (2 ml.) was treated as in the above experiment, XXVII (m. p. 167~168°C; 20 mg.) was obtained. Recrystallization from ethanol formed brilliant brownish yellow scales (m. p. 168.5~169.5°C; 15 mg.).

Found: C, 77.89; H, 6.02; N, 7.50. Calcd. for $C_{12}H_{11}ON$: C, 77.81; H, 5.99; N, 7.56%.

λ_{max}^{MeOH} mμ (log ε): 225 (4.06), 290 (4.69), 301 (4.79), 335 (3.90), 340 (3.74) sh, 440 (4.43). IR (Nujol): 3460, 3340, 3270, 1642 cm^{-1}.

Picrate: M. p. above 270°C; fine black crystals (from ethanol).

Found: N, 12.00. Calcd. for $C_{18}H_{14}O_8N_4$-C_2H_5OH; N, 12.17%.

Acetate; M. p. 198~199°C; blacklish green micro-prisms (from methanol).

Found: C, 73.65; H, 5.97; N, 6.11. Calcd. for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77; N, 6.16%.

λ_{max}^{MeOH} mμ (log ε): 220 (4.12), 297 (4.83), 404 (4.33). IR (Nujol): 3340, 1704, 1675, 1661 cm^{-1}.

2-Amino-5-(1,1-ethylenedioxyethyl)azulene-1,3-dicarboxylic Acid Monoethyl Ester (XXIX).—To a solution of potassium hydroxide (140 mg.) in ethanol (5 ml.), V (400 mg.) was added, and the mixture was refluxed for 4 hr. After it had cooled, the solution was acidified with 6 N sulfuric acid to give XXIX (350 mg.) as brownish yellow crystals (m. p. 161∼164°C (decomp.); sparingly soluble in organic solvents).

Found: C, 62.61; H, 5.44; N, 4.22. Calcd. for $C_{18}H_{19}O_6N$: C, 62.60; H, 5.55; N, 4.06%.

$\lambda_{\max}^{\text{MeOH}}$ mμ (log ε): 245.5 (4.49), 316 (4.70), 327 (4.80), 370 (3.85), 454 (3.43). IR (KBr disk): 3448, 3327, 1662 cm^{-1}.

p-Bromophenacyl Ester of XXIX.—In a solution of sodium hydroxide (200 mg.) in water (20 ml.), XXIX (100 mg.) was dissolved, and the solution was weakly acidified with 2 N hydrochloric acid. To this solution, a solution of *p*-bromophenacyl bromide (350 mg.) in ethanol (20 ml.) was added, and the mixture was refluxed for 2 hr. The reaction mixture was diluted with water (5 ml.), and the precipitate thereby formed was collected by filtration. Crude crystals of the ester of XXIX (m. p. 186∼190°C; 100 mg.) were recrystallized from ethanol to form a pale brown crystalline powder (m. p. 214∼215°C, 50 mg.).

Found: C, 58.40; H, 4.17; N, 3.06. Calcd. for $C_{26}H_{24}O_7NBr$: C, 57.57; H, 4.46; N, 2.58%.

Ethyl 2-Amino-5(or 7)-(1,1-ethylenedioxyethyl)-azulene-1-carboxylate (XXX).—A solution of XXIX (260 mg.) in pyridine (1.5 ml.) was heated at 130∼140°C to effect decarboxylation. The residue produced by evaporation of the excess pyridine was dissolved in benzene, and the solution was passed through a column of alumina. A reddish crude substance obtained from the effluent was recrystallized from ethanol to give reddish orange prisms (m. p. 144∼145°C; 60 mg.).

Found: C, 67.74; H, 6.31; N, 4.65. Calcd. for $C_{17}H_{19}O_4N$: C, 67.76; H, 6.36; N, 4.65%.

$\lambda_{\max}^{\text{MeOH}}$ mμ (log ε): 216 (4.26), 306 (4.77), 316 (4.86), 357 (4.00), 380 (3.80) sh. IR (KBr disk): 3541, 3344, 3287, 1663 cm^{-1}.

Picrate: M. p. 138.5∼139.5°C; orange prisms (from ethanol).

Acetate: M. p. 164∼165°C; violet red micro-prisms (from ethanol).

Found: C, 66.53; H, 5.99; N, 3.95. Calcd. for $C_{19}H_{21}O_5N$: C, 66.46; H, 6.16; N, 4.08%,

$\lambda_{\max}^{\text{MeOH}}$ mμ (log ε): 244 (4.28), 306 (4.84), 316 (4.96), 356 (3.95), 370 (3.97). IR (Nujol): 3500, 1689, 1650 cm^{-1}.

Ethyl 5(or 7)-Acetyl-2-aminoazulene-1-carboxylate (XXXI).—A solution of XXX (50 mg.) in ethanol (2 ml.) and 6 N sulfuric acid (0.02 ml.) was refluxed for 20 min. The reaction mixture was diluted with water (3 ml.) to form XXXI (m. p. 130∼132°C; 45 mg.), which was then recrystallized from ethanol to give brownish orange micro-prisms (m. p. 131∼132°C; 40 mg.).

Found: C, 69.59; H, 5.49; N, 5.28. Calcd. for $C_{15}H_{15}O_3N$: C, 70.02; H, 5.88; N, 5.44%.

$\lambda_{\max}^{\text{MeOH}}$ mμ (log ε): 220 (4.22), 246 (4.10), 331 (4.73), 490 (3.41). IR: (KBr disk) 3313, 3254, 1664, 1612; (Nujol) 3380, 3280, 1656, 1603 cm^{-1}.

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