The Reaction of 3-(ω-Ethoxycarbonylacetyl)-2*H*-cyclohepta[*b*]-furan-2-one with Active Methylene Compounds

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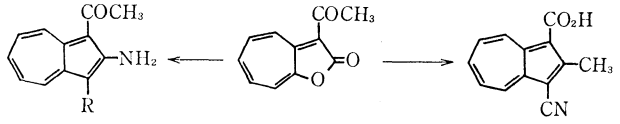
(Received December 27, 1973)

The reaction of 3-(ω-ethoxycarbonylacetyl)-2*H*-cyclohepta[*b*]furan-2-one (**4**) with malononitrile and with cyanoacetamide, in the presence of sodium ethoxide, gave 4-hydroxyazuleno[2,1-*b*]pyrid-2(1*H*)-one derivatives, (**5**) and (**9**) respectively, in good yields. On the other hand, the reaction of **4** with ethyl cyanoacetate gave 3-cyano-2-ethoxycarbonylmethylazulene-1-carboxylic acid (**12**). The structures of these products were determined on the basis of the spectral data and some chemical evidences.

It is known[1] that the reaction of 2-chloro- or 2-methoxytropones with active methylene compounds, such as malononitrile, ethyl cyanoacetate, and diethyl malonate, is a useful method for synthesizing azulene derivatives, especially those with various functional groups at the 1-, 2-, and 3-positions. In addition, it has been found[2] that 2*H*-cyclohepta[*b*]furan-2-one derivatives were the reaction intermediates in this azulene-formation reaction and that their reactions with active methylene compounds also gave azulene derivatives. Of these, the reaction of 3-acetyl-2*H*-cyclohepta-[*b*]furan-2-one (**1**) with malononitrile or cyanoacetamide gave a 1-acetyl-2-aminoazulene derivative (**2a**) or (**2b**), whereas that with ethyl cyanoacetate gave a 2-methylazulene derivative (**3**) as the major product, together with a minor amount of an 1-acetyl-2-aminoazulene derivative (**2c**).[2b] On the application of such types of reactions to 3-(ω-ethoxycarbonylacetyl)-2*H*-cyclohepta[*b*]furan-2-one (**4**),[3] we have now found that azuleno[2,1-*b*]pyridine derivatives were easily synthesized; the results will be reported in this paper.



2a: R=CN
2b: R=CONH$_2$
2c: R=CO$_2$C$_2$H$_5$

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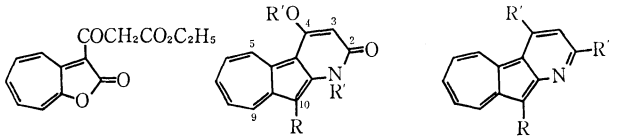
Results and Discussion

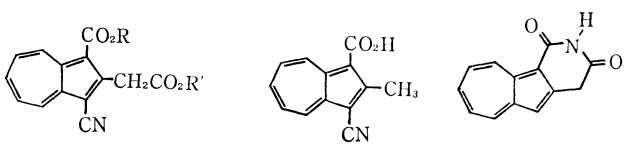
The reaction of **4** with malononitrile took place easily, in the presence of sodium ethoxide, at room temperature; an azulenic compound (**5**), $C_{14}H_8O_2N_2$, was formed in a good yield. Compound **5** is only slightly soluble in organic solvents, but it is easily soluble in aqueous alkali. The infrared spectrum of **5** in KBr exhibits absorptions at 3300—2500 (associated enolic OH), 2203 (C≡N), and 1634 and 1626 cm^{-1} (C=O). The ultraviolet absorption curve is similar to that of ethyl 2(1*H*)-oxoazuleno[2,1-*b*]pyridine-3-carboxylate,[4] as is shown in Fig. 1. The mass spectrum reveals a molecular ion peak at *m/e* 236. On the basis of these spectral data and some chemical evidence to be described below, as well as a consideration of the reaction mechanism to be described later, the structure of **5** is assumed to be 10-cyano-4-hydroxyazuleno-[2,1-*b*]pyrid-2(1*H*)-one (**5a**). As is confirmed apparently by its spectral data, **5** exists in the 2(1*H*)-pyridone form, **5a**, but not in the 2-hydroxypyridine form, **5b**. However, **5** gave both types of diacetyl derivatives, that is, *O,N*- (**6a**) and *O,O'*-diacetyl derivatives (**6b**), derived from **5a** and **5b** respectively. Thus, when heated with acetic anhydride at 130 °C, **5** gave **6a**. Its infrared spectrum exhibits absorptions at 1637 (*N*-acetyl) and 1783 cm^{-1} (*O*-acetyl), and its ultraviolet absorption curve is similar to that of **5** (Fig. 1). On the other hand, the acetylation of **5** with acetic anhydride in pyridine gave **6b**. Its infrared spectrum exhibits an absorption at 1773 cm^{-1} (*O*-acetyl), and its ultraviolet absorption curve is similar to that of ethyl 2-methoxyazuleno[2,1-*b*]pyridine-3-carboxylate[4] (Fig. 2). On methylation with diazomethane or with dimethyl sulfate, **5** gave only an azuleno[2,1-*b*]pyridone-type *O,N*-



4

5a: R=CN; R'=H
6a: R=CN; R'=COCH$_3$
7: R=CN; R'=CH$_3$
9: R=CONH$_2$; R'=H
10: R=R'=H

5b: R=CN; R'=OH
6b: R=CN; R'=OCOCH$_3$
8: R=CN; R'=Cl
11: R=H; R'=Cl



12: R=H; R'=C$_2$H$_5$
13: R=CH$_3$; R'=C$_2$H$_5$
14: R=R'=H
15: R=R'=CH$_3$

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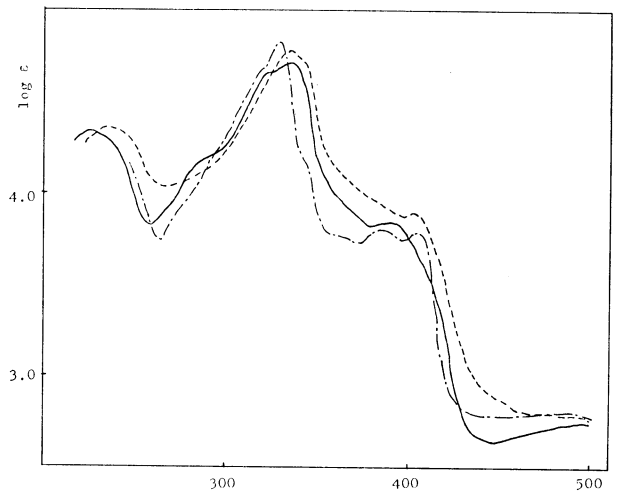


Fig. 1. The UV spectra of **5** (——), **6a** (----) and **10** (-·-·-) in methanol

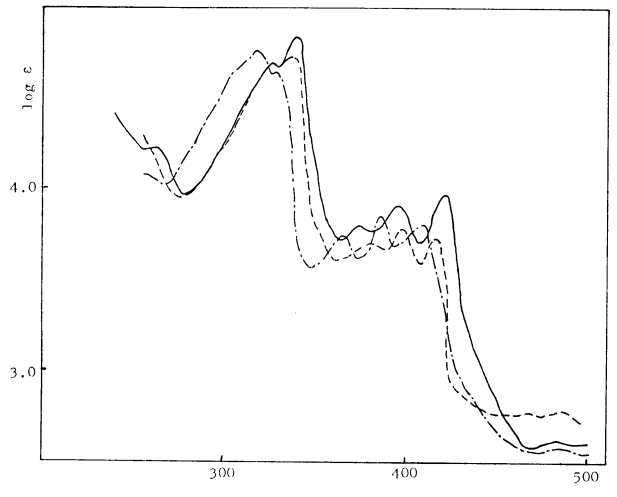


Fig. 2. The UV spectra of **6b** (——), **8** (----) and **11** (-·-·-) in methanol.

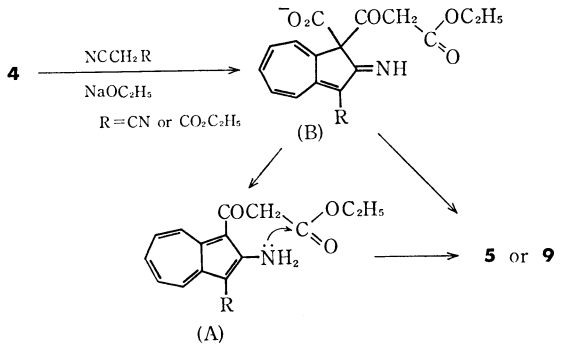
dimethyl derivative (**7**), derived from **5a**. The infrared spectrum of **7** exhibits absorptions at 2208 (C≡N) and 1656 cm^{-1} (C=O). The ultraviolet absorption curve of **7** is similar to that of **5**. On the other hand, the treatment of **5** with phosphorus oxychloride afforded an azuleno[2,1-*b*]pyridine-type dichloro compound (**8**). Its ultraviolet absorption curve is similar to that of **6b** (Fig. 2).

The reaction of **4** with cyanoacetamide, in the presence of sodium ethoxide, gave an azulenic compound (**9**) in a good yield. The same compound was also obtained from **5** when the latter was heated in 100% phosphoric acid at 100 °C. The infrared spectrum of **9** exhibits absorptions at 3300—2500 (associated enolic OH), and 1658, 1631, and 1621 cm^{-1} (C=O), but no absorption corresponding to the cyano group. The ultraviolet absorption curve is similar to that of **5**. The mass spectrum reveals a molecular ion peak at *m/e* 254. From these findings, **9** is assigned the structure of 10-carbamoyl-4-hydroxyazuleno[2,1-*b*]pyrid-2-(1*H*)-one. When **9** was heated in 100% phosphoric acid at 130 °C, decarbamoylation took place, with the formation of 4-hydroxyazuleno[2,1-*b*]pyrid-2(1*H*)-one (**10**). The same compound, **10**, was also obtained from **5** upon heating with 100% phosphoric acid at 130 °C. The infrared spectrum of **10** exhibits absorptions at 3300—2500 (associated enolic OH) and 1618 cm^{-1} (C=O). The ultraviolet absorption curve is similar to that of **5** (Fig. 1). These spectral data have substantiated the structure of **10**. Compound **10** gave an *N*-acetyl derivative on acetylation with acetic anhydride–pyridine. Further, the treatment of **10** with phosphorus oxychloride gave 2,4-dichloroazuleno[2,1-*b*]pyridine (**11**). Its ultraviolet absorption curve is similar to that of **8** (Fig. 2).

In the reaction of **4** with ethyl cyanoacetate, an azulenic compound (**12**) was obtained in a good yield. The infrared spectrum exhibits absorptions at 3300—2500, 1656 and 920 (COOH), 2212 (C≡N), and 1742 cm^{-1} (ester C=O). The methylation of **12** with diazomethane afforded an ester (**13**), while the alkaline hydrolysis of **12**, followed by the methylation of the resulting dicarboxylic acid (**14**) with diazomethane, yielded a dimethyl ester (**15**). Further, on heating in pyridine **14** gave 3-cyano-2-methylazulene-1-carboxylic acid (**16**).[2b] On the basis of these spectral data and chemical evidence, **12** was assigned the structure of 3-cyano-2-ethoxycarbonylmethylazulene-1-carboxylic acid.

When **12** or **14** was heated with acids, such as 75% sulfuric, 85% phosphoric, or concentrated hydrobromic acid, at about 100 °C, cyclization took place, with the formation of an imide (**17**). Its infrared spectrum exhibits absorptions at 3215 (NH), 1686 and 1678 cm^{-1} (C=O), but no absorption corresponding to the cyano group. Its NMR spectrum reveals a two-proton singlet at 4.31 ppm associated with the methylene protons. The mass spectrum reveals a molecular ion peak at *m/e* 211. These spectral data have substantiated the structure of **17**. The acetylation of **17** with acetic anhydride in pyridine gave an *N*-acetyl derivative, whereas that with acetic anhydride in the presence of concentrated sulfuric acid gave an *O*-acetyl derivative.

As has been described above, it has been found that the reaction of **4** with malononitrile or cyanoacetamide yielded directly the azuleno[2,1-*b*]pyrid-2(1*H*)-one derivative, **5** or **9** respectively. On the other hand, it has been found that the reaction of **4** with ethyl cyanoacetate yielded the azulene derivative, **12**, but no azuleno[2,1-*b*]pyrid-2(1*H*)-one derivative. The forma-



tion of **5** or **9** is presumed to be as follows. It had been found that, in the reaction of 3-acetyl-2*H*-cyclohepta[*b*]furan-2-one, **1**, with malononitrile or cyanoacetamide, the 1-acetyl-2-aminoazulene derivative, **2a** or **2b**, was formed *via* a dihydroazulene-type intermediate.[2b] Similarly, in the reaction of **4** with malononitrile or cyanoacetamide, an 2-amino-1-(ω-ethoxycarbonylacetyl)azulene derivative (A) should be formed at first *via* a dihydroazulene-type intermediate (B). In this case, however, cyclization between the amino and ester groups, which are present in a position favorable to lactam-formation, should occur subsequently to yield the azuleno[2,1-*b*]pyrid-2(1*H*)-one derivative, **5** or **9**. A similar cyclization should also be possible between the imino and ester groups in the intermediate (B), accompanying decarboxylation, to yield **5** or **9**. In the reaction of **4** with ethyl cyanoacetate, the azulene, **12**, is presumed to be formed through the same reaction mechanism as in the formation of 2-methylazulene derivative, **3**, in the reaction of **1** with ethyl cyanoacetate.[2b]

Experimental

All the melting points are uncorrected. The infrared spectra were taken on a Shimadzu IR-27 infracord. The ultraviolet spectra were run on a Hitachi EPS-3 spectrophotometer. The NMR spectra were determined with a Varian A-60 spectrometer. The mass spectral analyses were done on a Hitachi RMU-60 mass spectrometer.

*10-Cyano-4-hydroxyazuleno[2,1-*b*]pyrid-2(1H)-one (5).* To a solution of 1.30 g of **4** and 460 mg of malononitrile in 25 ml of anhydrous ethanol, 7.5 ml of a 1M sodium ethoxide solution was added, after which the mixture was stirred for 8 hr at room temperature. The reaction mixture was then diluted with water and acidified with 6M hydrochloric acid. The crystals thereby formed were recrystallized from dimethylformamide to give 1.23 g of **5** as reddish-violet needles; mp 354—360 °C (decomp.); UV (MeOH): λ_{max} 228 nm (log ε 4.35), 325 (4.68), 337 (4.69), 392 (3.86), and 500 (2.75).

Found: C, 71.38; H, 3.70; N, 12.04%. Calcd for $C_{14}H_8O_2N_2$: C, 71.18; H, 3.41; N, 11.86%.

*1-Acetyl-4-acetoxy-10-cyanoazuleno[2,1-*b*]pyrid-2(1H)-one (6a).* A mixture of 100 mg of **5** and 1 ml of pyridine was heated at 130 °C for 2 hr. After cooling, the addition of water to the reaction mixture yielded 90 mg of crystals. Recrystallization from dimethylformamide afforded **6a** as violet microcrystals; mp over 300 °C; IR (KBr): 2212 (C≡N), 1783, and 1637 cm^{-1} (C=O); UV (dioxane): λ_{max} 329 nm (log ε 4.75), 343 (4.85), 405 (3.94), 510 (2.16), and 554 (2.23); mass spectrum *m/e* 320 (M^+).

Found: C, 67.46; H, 3.84; N, 8.61%. Calcd for $C_{18}H_{12}O_4N_2$: C, 67.50; H, 3.78; N, 8.75%.

*2,4-Diacetoxy-10-cyanoazuleno[2,1-*b*]pyridine (6b).* A mixture of 100 mg of **5**, 0.5 ml of pyridine, and 0.5 ml of acetic anhydride was warmed in a water-bath for 1 hr. After cooling, the addition of water yielded 110 mg of crystals. Recrystallization from dimethylformamide afforded **6b** as violet micro-crystals; mp 234 °C (decomp.); IR (KBr): 2208 (C≡N) and 1773 cm^{-1} (C=O); UV (dioxane): λ_{max} 315 nm (log ε 4.66), 328 (4.74), 370 (3.71), 391 (3.82), 415 (3.84), 510 (2.45), and 543 (2.41).

Found: C, 67.66; H, 3.96; N, 8.85%. Calcd for $C_{18}H_{12}O_4N_2$: C, 67.50; H, 3.78; N, 8.75%.

*10-Cyano-4-methoxy-1-methylazuleno[2,1-*b*]pyrid-2(1H)-one (7).* a) To a solution of 100 mg of **5** in a mixture of 5 ml of ether and 1 ml of methanol, 3 ml of an ethereal solution of diazomethane was added, after which the mixture was stirred for 2 hr under ice-cooling and then allowed to stand overnight in a refrigerator. The crystals thereby formed were recrystallized from dimethylformamide, thus affording 80 mg of **7** as brownish-violet micro-crystals; mp 280—281 °C; IR (KBr): 2208 (C≡N) and 1656 cm^{-1} (C=O); UV (dioxane): λ_{max} 297 nm (log ε 4.09), 330 (4.71), 345 (4.78), and 525 (2.79); mass spectrum *m/e* 264 (M^+).

Found: C, 72.55; H, 4.76; N, 10.45%. Calcd for $C_{16}H_{12}O_2N_2$: C, 72.71; H, 4.58; N, 10.60%.

b) To a solution of 100 mg of **5** dissolved in a mixture of 2 ml of 6M potassium hydroxide solution and 15 ml of water, 1 ml of dimethyl sulfate and 2 ml of 6 M potassium hydroxide solution were added, after which the mixture was stirred for 9 hr at room temperature and then allowed to stand overnight. The reaction mixture was acidified with 6 M hydrochloric acid, and the crystals thereby formed were recrystallized from dimethylformamide to afford 90 mg of **7** as brownish-violet micro-crystals; mp 280—281 °C.

*2,4-Dichloro-10-cyanoazuleno[2,1-*b*]pyrid-2(1H)-one (8).* A mixture of 150 mg of **5** and 3 ml of phosphorus oxychloride was heated under reflux. The reaction mixture was poured into ice water, and the crystals thereby formed were recrystallized from dimethylformamide, thus giving 120 mg of **8** as violet plates; mp 295 °C; IR (KBr): 2217 cm^{-1} (C≡N); UV (dioxane): λ_{max} 320 nm (log ε 4.70), 332 (4.85), 355 (4.22), 368 (3.81), 380 (3.81), 390 (4.16), 414 (4.00), 476 (2.62), 496 (2.63), 510 (2.66), 528 (2.67), and 546 (2.65); mass spectrum *m/e* 272 (100%, M^+), 274 (65%, M^++2), and 276 (10.5%, M^++4).

Found: C, 61.03; H, 2.18; N, 10.01%. Calcd for $C_{14}H_6N_2Cl_2$: C, 61.56; H, 2.22; N, 10.26%.

*10-Carbamoyl-4-hydroxyazuleno[2,1-*b*]pyrid-2(1H)-one (9).* a) To a solution of 160 mg of **4** and 65 mg of cyanoacetamide in 10 ml of anhydrous ethanol, a 2 ml portion of a 1 M sodium ethoxide solution was added, after which the mixture was stirred for 10 hr at room temperature. The reaction mixture was then diluted with water and acidified with 6 M hydrochloric acid. The crystals thereby formed were recrystallized from dimethyl sulfoxide, thus giving 120 mg of **9** as brownish-violet prisms; mp 322—324 °C (decomp.); UV (DMF): λ_{max} 325 nm (log ε 4.51), 340 (4.46), 410 (2.79), and 520 (2.74).

Found: C, 65.81; H, 4.21; N, 11.31%. Calcd for $C_{14}H_{10}O_3N_2$: C, 66.13; H, 3.96; N, 11.02%.

b) A mixture of 100 mg of **5** and 2 ml of 100% phosphoric acid was heated at 230 °C for 1 hr. Then, a similar treatment gave 90 mg of **9** as brownish-violet prisms; mp 322—324 °C (decomp.). The treatment of **5** with conc. sulfuric acid in a similar manner gave the same product.

*4-Hydroxyazuleno[2,1-*b*]pyrid-2(1H)-one (10).* A mixture of 100 mg of **5** and 2 ml of 100% phosphoric acid was heated at 130 °C for 3 hr. The reaction mixture was then cooled to room temperature and diluted with water. The crystals thereby formed were recrystallized from dimethylformamide, thus giving 80 mg of **10** as violet microcrystals; mp over 290 °C; UV (dioxane): λ_{max} 322 nm (log ε 4.75), 336 (4.76), 358 (4.08), 400 (3.78), 500 (2.60), and 540 (2.60); mass spectrum *m/e* 211 (M^+).

Found: C, 74.10; H, 4.50; N, 6.39%. Calcd for $C_{13}H_9O_2N$: C, 73.92; H, 4.30; N, 6.63%.

The treatment of 100 mg of **9** in a manner similar to that described above also gave 84 mg of **10**; mp over 290 °C.

N-Acetyl Derivative: Violet crystals from dimethylformamide; mp over 290 °C; IR (KBr): 1647 and 1613 cm^{-1};

UV (MeOH): λ_{max} 218 nm (log ε 4.32), 282 (4.21), 344 (4.81), 330 sh (4.70), 316 sh (4.35), and 410 (3.94).

Found: C, 69.08; H, 4.91; N, 5.52%. Calcd for $C_{15}H_{11}O_3N \cdot 1/2H_2O$: C, 68.69; H, 4.61; N, 5.34%.

2,4-Dichloroazuleno[2,1-b]pyridine (11). A mixture of 150 mg of **10** and 3 ml of phosphorus oxychloride was heated under reflux for 2 hr and then poured into ice water. The crystals thereby formed were dissolved in chloroform and chromatographed on a silica gel column. The evaporation of the solvent from the effluent left green crystals. Recrystallization from benzene afforded 60 mg of **11** as green needles; mp 163—164 °C; UV (dioxane): λ_{max} 307 nm (log ε 4.68), 317 (4.75), 327 (4.64), 364 (4.75), 384 (3.86), 410 (3.57), 480 (2.23), 427 (2.46), 466 (2.54), and 616 (2.42); NMR (DMSO-d_6): δ ppm 7.2—7.8 (5H, m), 8.5 (1H, s), and 9.5 (1H, s); mass spectrum *m/e* 247 (100%, M^+), 249 (64.7%, M^++2), and 251 (10.6%, M^++4).

Found: C, 62.65; H, 2.85; N, 5.35%. Calcd for $C_{13}H_7NCl_2$: C, 62.93; H, 2.84; N, 5.65%.

3-Cyano-2-ethoxycarbonylmethylazulene-1-carboxylic Acid (12). To a solution of 520 mg of **4** and 280 mg of ethyl cyanoacetate in 30 ml of anhydrous ethanol, a 4 ml portion of a 1 M sodium ethoxide solution was added, after which the mixture was stirred for 10 hr at room temperature. After standing overnight, the mixture was diluted with water and acidified with 6 M hydrochloric acid. The crystals thereby formed were recrystallized from dioxane, thus affording 480 mg of **12** as red prisms; mp 187—188 °C; UV (MeOH): λ_{max} 233 nm (log ε 4.61), 254 sh (4.22), 262 (4.27), 292 (4.64), 303 (4.75), 340 (3.84), 370 (3.83), and 503 (2.76).

Found: C, 67.37; H, 4.68; N, 4.66%. Calcd for $C_{16}H_{13}O_4N$: C, 67.84; H, 4.63; N, 4.95%.

Methyl 4-Cyano-2-ethoxycarbonylmethylazulene-1-carboxylate (13). To a suspension of 100 mg of **12** in a mixture of 10 ml of ether and 2 ml of methanol, 2 ml of an ethereal solution of diazomethane was added, after which the mixture was stirred for 2 hr under ice-cooling. The solvent was then evaporated, and the residue was dissolved in benzene and passed through an alumina column. The evaporation of the solvent gave 100 mg of **13** as red prisms; mp 128—129 °C; IR (KBr): 2217 (C≡N), 1742, and 1692 cm^{-1} (C=O); UV (MeOH): λ_{max} 234 nm (log ε 4.54), 265 (4.33), 293 (4.61), 304 (4.71), 340 (3.79), 370 (3.81), and 503 (2.73); NMR ($CDCl_3$): δ ppm 1.8 (3H, t, J=7.5 Hz), 4.0 (3H, s), 4.25 (2H, q, J=7.5 Hz), 4.41 (2H, s), 7.6—8.1 (3H, m), 7.75 (1H, m), and 9.73 (1H, m).

Found: C, 68.43; H, 5.01; N, 4.63%. Calcd for $C_{17}H_{15}O_4N$: C, 68.67; H, 5.08; N, 4.71%.

4-Cyano-2-carboxymethylazulene-1-carboxylic Acid (14). A solution of 220 mg of **12** dissolved in a mixture of 3 ml of ethanol and 3 ml of 1 M potassium hydroxide solution was heated under reflux for 2 hr. The reaction mixture was then diluted with water and acidified with 6 M hydrochloric acid, thus affording 185 mg of crude **14**. Recrystallization from ethanol afforded red prisms; mp 208—209 °C; IR (KBr): 3300—2500, 1701, 1653 (COOH), and 2217 cm^{-1} (C≡N); UV (MeOH): λ_{max} 234 nm (log ε 4.54), 264 (4.25), 294 (4.58), 305 (4.04), 341 (3.77), 370 (3.78), and 508 (2.74).

Found: C, 65.90; H, 3.76; N, 5.32%. Calcd for $C_{14}H_9O_4N$: C, 65.88; H, 3.55; N, 5.49%.

Methyl 4-Cyano-2-methoxycarbonylmethylazulene-1-carboxylate (15). To a suspension of 130 mg of **14** in a mixture of 3 ml of ether and 3 ml of methanol, 10 ml of an ethereal solution of diazomethane was added, after which the mixture was stirred for 2 hr under ice-cooling. The subsequent evaporation of the solvent left a crystalline material, which was dissolved in benzene and passed through a short column of alumina. The evaporation of the solvent from the effluent gave 110 mg of **15** as red needles; mp 138—139 °C; IR (KBr): 2212 (C≡N), 1736, and 1686 cm^{-1} (C=O); UV (MeOH): λ_{max} 234 nm (log ε 4.57), 264 (4.35), 293 sh (4.60), 304 (4.72), 340 (3.86), 369 (3.87), and 503 (2.92); NMR ($CDCl_3$): δ ppm 3.75 (3H, s), 3.98 (3H, s), 4.41 (2H, s), 7.6—8.1 (3H, m), 8.75 (1H, m), and 9.73 (1H, m).

Found: C, 67.84; H, 4.97; N, 4.73%. Calcd for $C_{16}H_{13}O_4N$: C, 67.84; H, 4.63; N, 4.95%.

3-Cyano-2-methylazulene-1-carboxylic Acid (16). A mixture of 100 mg of **14** and 1.5 ml of pyridine was heated at 130 °C for 2 hr. The reaction mixture was then diluted with water and acidified with 6 M hydrochloric acid, thus affording 76 mg of crude **16**; mp 272—273 °C. Recrystallization from dimethylformamide gave orange red needles; mp 273 °C. This was identified with an authentic sample[2b] by a mixed-melting-point determination and by an infrared spectral comparison.

1,2,3,4-Tetrahydroazuleno[1,2-c]pyridine-2,4-dione (17). A mixture of 100 mg of **12** and 2 ml of conc. sulfuric acid was heated at 100 °C for 30 min. The reaction mixture was then allowed to cool and poured into ice water, thus giving 65 mg of **17** as violet crystals; mp 226—230 °C. Recrystallization from dimethylformamide afforded violet columns; 232 °C (decomp.); UV (dioxane): λ_{max} 296 nm (log ε 4.71), 308 (4.82), 359 (3.79), 367 (3.77), 377 (4.02), 490 sh (2.57), 520 (2.68), 550 (2.60), and 600 (2.13); NMR (DMSO-d_6): δ ppm 4.31 (2H, s), 6.98 (1H, S s), 7.4—8.1 (3H, m), 8.67 (1H, m), 9.58 (1H, m), and 10.8 (1H, bs).

Found: C, 73.73; H, 4.57; N, 6.56%. Calcd for $C_{13}H_9O_2N$: C, 73.92; H, 4.30; N, 6.63%.

The treatment of 100 mg of **12** with conc. hydrobromic (3 ml) or 85% phosphoric acid (2 ml) in a manner similar to that described above also gave **17** (mp 232 °C) in yields of 65 mg and 65 mg respectively.

N-*Acetyl Derivative*: Violet columns (from dimethylformamide); mp 275 °C (decomp.); IR (KBr): 1634 cm^{-1} (C=O); UV (dioxane): λ_{max} 310 nm (log ε 4.65), 338 (4.90), 360 (4.59), 400 (4.46), 528 (2.76), 548 (2.82), and 594 (2.44); mass spectrum *m/e* 253 (M^+).

Found: C, 71.40; H, 4.73; N, 5.74%. Calcd for $C_{15}H_{11}O_3N$: C, 71.14; H, 4.37; N, 5.53%.

O-*Acetyl Derivative*: Violet needles (from ethanol); mp 168—170 °C; IR (KBr): 1786 and 1626 cm^{-1} (C=O); UV (dioxane): λ_{max} 296 nm (log ε 4.62), 307 (4.73), 329 (4.15), 360 (4.01), 378 (4.01), 522 (2.97), 556 (2.90), and 604 (2.61); mass spectrum *m/e* 253 (1.5%, M^+) and 211 (100%).

Found: C, 71.38; H, 4.62; N, 5.80%. Calcd for $C_{15}H_{11}O_3N$: C, 71.14; H, 4.37; N, 5.53%.

This work was financially supported by grants from the Ministry of Education of Japan and the Sankyo Co., Ltd., to which the authors' thanks are due.

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