The Anionoid Substitution Reaction of Diethyl 6-Bromoazulene-1, 3-dicarboxylate*

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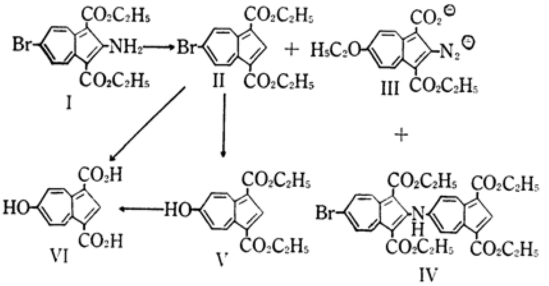
In previous papers[1-3] we have reported on the synthesis of some 5- and 6-substituted azulene derivatives from 5-aminotropolone and 4-acetyltropolone derivatives as a part of a general scheme of the synthetic study of azulenes with the functional group on a seven-membered ring. For synthesizing some 6-substituted azulenes, the present authors studied the anionoid substitution reactions of diethyl 6-bromoazulene-1, 3-dicarboxylate (II), which is the deaminated product of diethyl 2-amino-6-bromoazulene-1, 3-dicarboxylate (I);[4] this paper will describe the results.

The diazotization reaction of I was accomplished in dioxane by the use of a large excess of sulfuric acid and sodium nitrite and without cooling. The decomposition of diazonium salt to yield the corressponding deaminated product was achieved by letting the salt stand at room temperature in the presence of sodium hypophosphite. Thus, diethyl 6-bromoazulene-1, 3-dicarboxylate (II) was obtained in a 25% yield, accompanied by two by-products (III and IV), one of which, III, was a 6-ethoxyazulene derivative, being the intramolecular diazonium-salt type reported by Asao et al.[5] The other one, IV, obtained in a 2% yield, was assumed to be diethyl 2-(1, 3-diethoxycarbonylazulen-6-yl)amino-6-bromoazulene-1, 3-dicarboxylate on the basis of the infrared spectrum, the analytical values and the chemical reactivities of II, as will be described below. The ultraviolet spectrum of II is shown in Fig. 1.



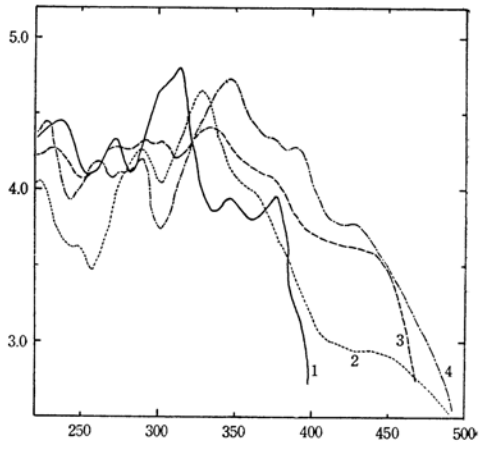


Fig. 1. Ultraviolet absorption spectra in methanol.

1 Diethyl 6-bromoazulene-1, 3-dicarboxylate (II)
2 Diethyl 6-hydroxyazulene-1, 3-dicarboxylate (V)
3 Diethyl 6-hydrazinoazulene-1, 3-dicarbox-ylate (X)
4 Diethyl 6-[di(2-hydroxyethyl)amino]-azulene-1, 3-dicarboxylate (XIV)

A mild alkaline treatment of II resulted in the replacement of the bromine atom by the hydroxyl group, thus forming diethyl 6-hydroxyazulene-1, 3-dicarboxylate (V), which, on being treated with acetic anhydride, gave an acetate with an absorption at 1764 cm^{-1} for the acetoxy group. However, under more severe conditions, not only V but also II gave 6-hydroxyazulene-1, 3-dicarboxylic acid (VI). Since the alkaline treatment of I give only 2-amino-6-bromo-1, 3-dicarboxylic acid,[4] these results show the bromine atom at the 6-position in II to be more active than in I. The treatment of II with sodium ethoxide or

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* Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[1] T. Nozoe, K. Takase and M. Tada, This Bulletin, 36, 1006 (1963).

[2] T. Nozoe, K. Takase and M. Tada, ibid., 36, 1010 (1963).

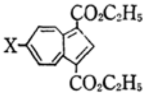
[3] T. Nozoe, K. Takase and M. Tada, ibid., 36, 1016 (1963).

[4] T. Nozoe, *Croat. Chem. Acta*, 29, 201 (1957); T. Nozoe and S. Ito, *Frotschr. Chem. org. Naturstoffe*, 19, 33 (1961); T. Nozoe, S. Seto and S. Matsumura, This Bulletin, 35, 1990 (1962); S. Matsumura, *Chem. Pharm. Bull.*, 10, 1024 (1962).

[5] T. Asao, J. Tsunetsugu and M. Kobayashi, Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

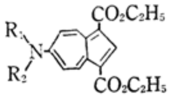
sodium hydrogen sulfide afforded diethyl 6-ethoxyazulene-1, 3-dicarboxylate (VII) or diethyl 6-mercaptoazulene-1, 3-dicarboxylate (VIII) respectively in a good yield.

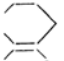
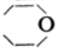
The reaction of II with liquid ammonia afforded diethyl 6-aminoazulene-1, 3-dicarboxylate (IX), which was identical with an authentic specimen synthesized from 5-amino-2-methoxytropone.¹⁾ Recently, Hafner et al.⁶⁾ reported that the reaction of 4, 8-dimethyl-6-chloroazulene with sodium azide, in the presence of dimethyl sulfoxide, afforded 4, 8-dimethyl-6-aminoazulene. In the same way, IX was also obtained from II.

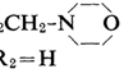


VII: $X=OC_2H_5$
VIII: $X=SH$
IX: $X=NH_2$

The bromine atom of II was easily replaced, when heated for a short period, with various amines, such as hydrazine, dimethylamine, diethylamine, ethanolamine, diethanolamine, diallylamine, ethyleneimine, pyrrolidine, piperidine, morpholine, aminopropylmorpholine and aniline, and the corresponding *N*-substituted amino derivatives of IX (X—XXI) were obtained in good yields. Under the same conditions, however, the bromine atom of 2-acetamido-6-bromoazulene (XXII)⁴⁾ was not replaced by various amines.



X: $R_1=NH_2$; $R_2=H$
XI: $R_1=R_2=CH_3$
XII: $R_1=R_2=C_2H_5$
XIII: $R_1=CH_2CH_2OH$; $R_2=H$
XIV: $R_1=R_2=CH_2CH_2OH$
XV: $R_1=R_2=CH_2CH=CH_2$
XVI: $R_1+R_2=$ 
XVII: $R_1+R_2=$ 
XVIII: $R_1+R_2=$ 
XIX: $R_1+R_2=$ 

XX: $R_1=CH_2CH_2CH_2$- ; $R_2=H$

XXI: $R_1=C_6H_5$; $R_2=H$

XXII

These facts can be understood by reference to the electrophilic nature of the seven-membered ring in azulene, enhanced by the presence of two ethoxycarbonyl groups at positions 1 and 3. This reaction path is shown in Chart I.

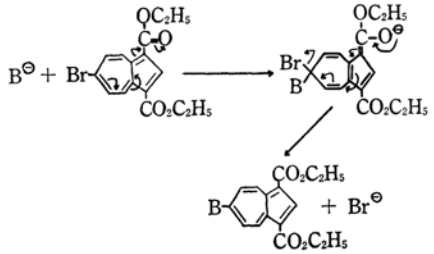
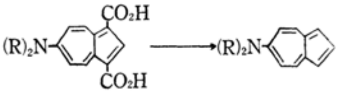


Chart I.

The alkaline hydrolysis of the 6-dimethylamino compound (XI) and the 6-diethylamino compound (XII) gave dicarboxylic acid (XXIII) and (XXIV), both of which, when heated in pyridine, caused decarboxylation, thus giving 6-dimethylaminoazulene (XXV) and 6-diethylaminoazulene (XXVI) respectively. Compared with 6-aminoazulene,¹⁾ XXV and XXVI are more stable and do not change on being left



XXIII: $R=CH_3$ XXV: $R=CH_3$
XXIV: $R=C_2H_5$ XXVI: $R=C_2H_5$

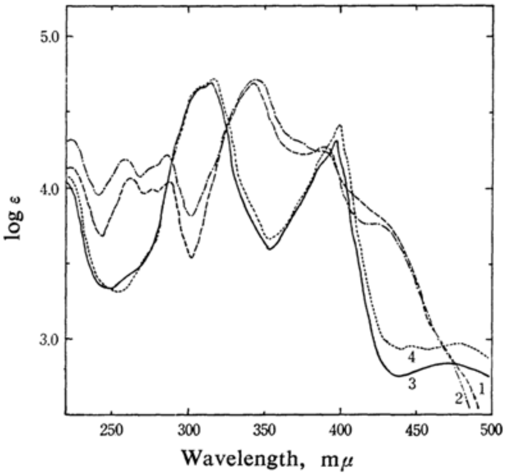


Fig. 2. Ultraviolet absorption spectra in methanol.

1 Diethyl 6-dimethylaminoazulene-1, 3-dicarboxylate (XI)
2 Diethyl 6-diethylaminoazulene-1, 3-dicarboxylate (XII)
3 6-Dimethylaminoazulene (XXV)
4 6-Diethylaminoazulene (XXVI)

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[6] K. Hafner, H. Patzelt and H. Kaiser, *Ann.*, **656**, 24 (1962).

in air for a long period of time. The ultraviolet spectra of these compounds are shown in Fig. 2.

The reactions of II with active methylene reagents are being investigated and will be reported on in the future.

Experimental[7)]

The Deamination of I. — Into a solution of I (2.0 g.) in dioxane (120 ml.) and concentrated sulfuric acid (12 ml.), a solution of sodium nitrite (1.0 g.) in water (5 ml.) was stirred at room temperature. After the solution had been stirred for 50 min., sodium hypophosphite (20 g.) was added to this diazotized solution and the mixture was vigorous stirred for 4 hr. After it had stood overnight, the solution was diluted with water (300 ml.) and extracted with benzene. The extract was washed with water, dried over anhydrous sodium sulfate, and passed through a column of alumina, and then the column was eluted with benzene. From the first effluent, crude crystals of diethyl 6-bromoazulene-1, 3-dicarboxylate (II), m. p. 198—199°C, 0.5 g.), were obtained. The recrystallization from ethanol gave purplish red micro-needles, m. p. 206—207°C.

Found: C, 54.85; H, 4.21. Calcd. for $C_{16}H_{15}O_4Br$: C, 54.70; H, 4.27%.

UV λ_{max}^{MeOH} mμ (log ε): 235 (4.45), 270 (4.30), 312 (4.80), 345 (3.95), 375 (3.95). IR (Nujol): 1684 cm^{-1}.

The second effluent gave yellow needles (200 mg.), which showed no depression of melting point on admixture with III and the infrared spectrum of which was identical with that of III.[5)]

From the third effluent, crude crystals (15 mg.) were obtained. Recrystallization from a mixture of benzene and ethanol afforded diethyl 2-(1, 3-diethoxycarbonylazulen-6-yl) amino-6-bromoazulene-1, 3-dicarboxylate (IV) as red micro-prisms, m. p. 159—160°C; 10 mg.

Found: C, 59.38; H, 4.75; N, 2.20. Calcd. for $C_{32}H_{30}O_8NBr$: C, 59.44; H, 4.54; N, 2.14%.

IR (Nujol): 3175, 1695, 1684, 1658 cm^{-1}.

Diethyl 6-Hydroxyazulene-1, 3-dicarboxylate (V). —Into a solution of potassium hydroxide (300 mg.) in 50% aqueous ethanol (8 ml.), II (100 mg.) was stirred, and then the mixture was warmed on a water bath for 5 min. This was diluted with water (25 ml.) and acidified with diluted sulfuric acid. The crystals (80 mg.) which separated were recrystallized from aqueous ethanol to give brownish yellow crystals of V (m. p. 201—201.5°C).

Found: C, 66.84; H, 5.98. Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59%.

UV λ_{max}^{MeOH} mμ (log ε): 221 (4.07), 246.5 (3.64), 288 (4.28), 329 (4.67), 357 (4.05) sh, 433 (2.95) sh.

IR (KBr disk): 3260, 1701, 1647 cm^{-1}.

The Acetate of V.—A solution of V (50 mg.) in acetic anhydride (2 ml). was refluxed for 6 min. The residue obtained by the evaporation of the solvent was recrystallized from aqueous ethanol to give reddish orange crystals (m. p. 129—130°C; 30 mg.).

Found: C, 65.37; H, 5.55. Calcd. for $C_{18}H_{18}O_6$: C, 65.44; H, 5.49%.

IR (Nujol): 1764, 1695, 1681, 1669 cm^{-1}.

6-Hydroxyazulene-1,3-dicarboxylic Acid (VI).— To a solution of potassium hydroxide (400 mg.) in 80% aqueous ethanol (10 ml.), II (200 mg.) was added. After it had been refluxed for 3 hr., the mixture was diluted with water (30 ml.) and acidified with 6 N sulfuric acid. The separated crystals were dissolved in a diluted potassium hydroxide aqueous solution and reprecipitated with 2 N hydrochloric acid. After these crystals had been washed with water, a dark brown powder (140 mg.) of VI was obtained; m. p. 174—175°C (decomp.).

Found: C, 61.75; H, 4.11. Calcd. for $C_{12}H_8O_5$: C, 62.07; H, 3.47%.

IR (Nujol): 3125, 1653 cm^{-1}.

V (200 mg.) also gave VI (140 mg.) under the same treatment.

Diethyl 6-Ethoxyazulene-1,3-dicarboxylate (VII). —To a solution prepared from sodium (50 mg.) and absolute ethanol (12 ml.), fine powdered II (400 mg.) was added. After it had been refluxed for 10 min. on a water bath, the mixture was evaporated to dryness under reduced pressure. The residue was dissolved in benzene, and the benzene solution was passed through a column of alumina, giving orange needles (300 mg.; m. p. 129—130°C). The substance was identified with an authentic specimen[6)] of VII by a comparison of the infrared spectra.

Diethyl 6-Mercaptoazulene-1, 3-dicarboxylate (VIII).—II (50 mg.) and a 27% sodium hydrogen sulfide aqueous solution (4 ml.) were dissolved in ethanol (20 ml.). The solution was then heated on a water bath for 15 min. After it had stood overnight at room temperature, the reaction mixture was diluted with water, acidfied with 6 N sulfuric acid, and extracted with benzene. The extract was washed with water and dried over anhydrous sodium sulfate. The residue obtained by the evaporation of the solvent was recrystallized from benzene, yielding VIII (30 mg.; m. p. 222—224°C) red crystals.

Found: C, 63.45; H, 4.76. Calcd. for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30%.

IR (Nujol): 2519, 1689 cm^{-1}.

Diethyl 6-Aminoazulene-1, 3-dicarboxylate (IX). —*a) With Liquid Ammonia.*—A suspension of II (100 mg.) in liquid ammonia was allowed to stand for a week at room temperature. The residue obtained by the evaporation of the ammonia was recrystallized from ethanol to give orange scales (45 mg.), which showed no depression of melting point on admixture with an authentic specimen[1)] of IX.

b) With Sodium Azide.—A mixture of II (100 mg.) and sodium azide (0.4 g.) in dimethyl sulfoxide (5 ml.) was heated on a water bath for 15 hr. After dilution with water, this reaction mixture was extracted with ethyl acetate and the extract was passed through a column of alumina, yielding IX (30 mg.).

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

Diethyl 6-Hydrazinoazulene-1,3-dicarboxylate (X).—To a solution of 80% hydrazine hydrate (2 ml.) in ethanol (2 ml.), II (50 mg.) was added. The mixture was then refluxed for 10 min. on a water bath. After the addition of water (20 ml.), the precipitate thereby formed was recrystallized from ethanol to give X (30 mg.; m. p. 237°C) as brilliant yellow scales.

Found: C, 63.48; H, 6.06; N, 9.64. Calcd. for $C_{16}H_{18}O_4N_2$: C, 63.56; H, 6.00; N, 9.27%.

UV λ_{max}^{MeOH} mμ (log ε): 233 (4.26), 273 (4.28), 289.5 (4.32), 301 (4.32), 333 (4.42), 367 (4.13) sh, 420 (3.65) sh.

IR (Nujol): 3330 (broad), 1642 cm^{-1}.

Acetate of X.—Pale yellow micro-prisms (from aqueous ethanol), m. p. 232—233°C.

Found: N, 7.85. Calcd. for $C_{18}H_{20}O_5N_2$: N, 8.14%.

UV λ_{max}^{MeOH} mμ (log ε): 224 (4.33), 254 (4.02) sh, 275 (4.17) sh, 282.5 (4.23), 337 (4.73), 371 (4.32), 428 (3.68).

IR (Nujol): 3520, 3330, 3260, 1689, 1656 cm^{-1}.

Diethyl 6-Dimethylaminoazulene-1,3-dicarboxylate (XI).—To a solution of a 40% dimethylamine aqueous solution (3 ml.) in ethanol (5 ml.), II (100 mg.) was added. The mixture was refluxed for 20 min. on a water bath. After the addition of water, the precipitate thereby formed was recrystallized from ethanol to give XI (75 mg.; m. p. 161—162°C) as yellow silky needles.

Found: N, 4.22. Calcd. for $C_{18}H_{21}O_4N$: N, 4.44%.

UV λ_{max}^{MeOH} mμ (log ε): 225 (4.15), 262 (4.08), 277 (3.99), 288 (4.05), 343 (4.69), 390 (4.27).

IR (Nujol): 1669 cm^{-1}.

Diethyl 6-Diethylaminoazulene-1,3-dicarboxylate (XII).—To a solution of diethylamine (2 ml.) in ethanol (10 ml.), II (200 mg.) was added. The mixture was then refluxed for 20 min. on a water bath. After the addition of water, the crystals separated were recrystallized from aqueous ethanol to give XII (130 mg.; m. p. 171—172°C) as yellow needles.

Found: N, 3.96. Calcd. for $C_{20}H_{25}O_4N$: N, 4.08%.

UV λ_{max}^{MeOH} mμ (log ε): 225 (4.32), 260 (4.20), 279.5 (4.15) sh, 288 (4.22), 347 (4.71), 373 (4.30) sh, 390 (4.26), 423 (3.77).

IR (Nujol): 1669 cm^{-1}.

Diethyl 6-(2-Hydroxyethylamino)azulene-1,3-dicarboxylate (XIII).—To a solution of ethanolamine (2 ml.) in ethanol (8 ml.), II (50 mg.) was added. The mixture was then treated as in the case of XI to give XIII (30 mg.; m. p. 165—167°C) as yellow crystals.

Found: N, 3.86. Calcd for $C_{18}H_{21}O_5N$: N, 4.23%.

UV λ_{max}^{MeOH} mμ (log ε): 225.5 (4.17), 253.5 (4.23), 285 (4.23), 332 (4.66), 367 (4.03) sh, 424 (3.90), 476 (3.31) sh.

IR (KBr disk): 3550, 3340, 1678, 1656 cm^{-1}.

Diethyl 6-[Di(2-hydroxyethyl)]aminoazulene-1,3-dicarboxylate (XIV).—To a solution of diethanolamine (2 ml.) in ethanol (8 ml.), II (50 mg.) was added. The mixture was then treated as in the case of XII to give XIV (25 mg.; m. p. 125—126°C) as brilliant yellow needles.

Found: N, 3.55. Calcd. for $C_{20}H_{25}O_6N$: N, 3.73%.

UV λ_{max}^{MeOH} mμ (log ε): 226 (4.45), 260.5 (4.18), 277 (4.12), 287.5 (4.21), 346 (4.74), 377 (4.33) sh, 391 (4.28), 423 (3.79).

Diethyl 6-Diallylaminoazulene-1,3-dicarboxylate (XV).—To a solution of diallylamine (1 ml.) in ethanol (5 ml.), II (50 mg.) was added. The mixture was then refluxed for 20 min. on a water bath. After dilution with water, the reaction mixture was extracted with benzene. The extract was then washed with water and dried over anhydrous sodium sulfate. The residue obtained by the evaporation of the solvent was recrystallized from aqueous ethanol to give XV (20 mg.; m. p. 103—104°C) as brownish yellow crystals.

Found: N, 3.66. Calcd. for $C_{22}H_{25}O_4N$: N, 3.81%.

UV λ_{max}^{MeOH} mμ (log ε): 225 (4.35), 258.5 (4.17), 276.5 (4.12) sh, 286.5 (4.22), 346.5 (4.78), 376 (4.39), 389 (4.31), 425 (3.71).

Diethyl 6-Ethyleneiminoazulene-1,3-dicarboxylate (XVI).—To a solution of ethyleneimine (1 ml.) in ethanol (5 ml.), II (50 mg.) was added. The mixture was then refluxed for 10 min. on a water bath. After dilution with water, the reaction mixture was extracted with benzene, and the extract was washed with water. After it had been dried over anhydrous sodium sulfate, this was passed through a column of alumina and the column was eluted with ethyl acetate. From the first effluent, an oily substance was obtained; the yellow crystals obtained from the second effluent were recrystallized from aqueous ethanol to give XVI (15 mg.; m. p. 160—161°C) as yellow fine crystals.

Found: N, 4.56. Calcd. for $C_{18}H_{19}O_4N$: N, 4.47%.

UV λ_{max}^{MeOH} mμ (log ε): 224 (4.18), 260 (4.03), 276 (4.05) sh, 286 (4.11), 340.5 (4.69), 388 (4.15).

Diethyl 6-Pyrrolidinoazulene-1,3-dicarboxylate (XVII).—A solution of II (60 mg.) and pyrrolidine (2 ml.) in ethanol (10 ml.) was refluxed for 20 min. on a water bath and concentrated to 1/3 volume under reduced pressure. After the addition of water, the solution was extracted with ethyl acetate and the extract was washed with 2 N acetic acid and water. After the removal of the solvent, the extract gave crude crystals (35 mg.), which were recrystallized from ethanol to give XVII (25 mg.; m. p. 194—195°C (decomp.)) as dark yellow micro-prisms.

Found: C, 69.98; H, 6.49; N, 3.83. Calcd. for $C_{20}H_{23}O_4N$: C, 70.36; H, 6.79; N, 4.10%.

UV λ_{max}^{MeOH} mμ (log ε); 225 (4.30), 260 (4.22), 288 (4.20), 345 (4.77), 388 (4.34).

IR (KBr disk): 1669 cm^{-1}.

Diethyl 6-Piperidinoazulene-1,3-dicarboxylate (XVIII).—A solution of II (60 mg.) and piperidine (2 ml.) in ethanol (10 ml.) was treated as in the case of XVII to give XVIII (25 mg.; m. p. 103—103.5°C) as orange micro-needles.

Found: N, 3.56. Calcd. for $C_{21}H_{25}O_4N$: N, 3.94%.

UV $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 251 (4.22), 338 (4.63), 458 (3.96).

Diethyl 6-Morpholinoazulene-1,3-dicarboxylate (XIX).—A solution of II (60 mg.) and morpholine (2 ml.) in ethanol (10 ml.) was treated as in the case of XII to give XIX (20 mg.; m. p. 101—102°C) as brilliant yellow scales.

Found: N, 3.57. Calcd. for $C_{20}H_{23}O_5N$: N, 3.92%.

UV $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 228.5 (4.26), 263 (4.18), 287 (4.04), 345 (4.68), 396 (4.32).

IR (KBr disk): 1689, 1669 cm^{-1}.

Diethyl 6-(3-Morpholinopropyl)aminoazulene-1,3-dicarboxylate (XX).—A solution of II (50 mg.) and aminopropylmorpholine (2 ml.) in ethanol (8 ml.) was refluxed for 30 min. on a water bath. After dilution with water, the solution was extracted with ethyl acetate, and the extract was washed with 2 N acetic acid and water. After it had been dried over anhydrous sodium sulfate, the extract was evaporated to dryness. The residue that was dissolved in benzene was passed through a column of alumina, and the column was eluted with benzene to give yellow crystals (25 mg.). Recrystallization from aqueous ethanol afforded reddish yellow micro-prisms (m. p. 109—110°C).

Found: N, 6.57. Calcd. for $C_{23}H_{30}O_5N_2$: N, 6.76%.

UV $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 224 (4.27), 286 (4.25), 341 (4.79), 370 (4.30)sh, 420 (3.84).

IR (KBr disk): 3380, 1678, 1664 cm^{-1}.

Diethyl 6-Anilinoazulene-1,3-dicarboxylate (XXI).—A solution of II (50 mg.) and aniline (1 ml.) in ethanol (9 ml.) was refluxed for 1.5 hr. on a water bath and then concentrated to half volume. After the addition of water (5 ml.), the precipitate thereby formed was recrystallized from ethanol to give XXI (20 mg.; m. p. 182—183°C) as reddish yellow leaflets, and II (5 mg.) was recovered.

Found: N, 3.43. Calcd. for $C_{22}H_{21}O_4N$: N, 3.85%.

UV $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 227 (4.36), 270 (4.25), 347 (4.69), 399 (4.33).

IR (KBr disk): 3310, 1689, 1658 cm^{-1}.

6-Dimethylaminoazulene-1,3-dicarboxylic Acid (XXIII).—A solution of XI (150 mg.) and potassium hydroxide (300 mg.) in 60% aqueous ethanol (10 ml.) was refluxed for 3 hr. on a water bath. The solution was then concentrated to half volume under reduced pressure, and this was diluted with water (15 ml.) and acidified with 6 N sulfuric acid. The precipitate was collected by filtration and repeatedly washed with water, by which process XXIII was obtained as a brown crystalline powder; m. p. 167—168°C (decomp.), 100 mg.

6-Diethylaminoazulene-1,3-dicarboxylic Acid (XXIV).—When XII (300 mg.) was treated as in the above experiment, XXIV was obtained as brown crystals (200 mg.; m. p. 180°C (blacken)).

6-Dimethylaminoazulene (XXV).—A solution of XXIII (100 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, the solution was passed through a column of alumina, and the column was eluted with benzene. From the effluent, orange crystals (15 mg.) were obtained, and recrystallization from benzene afforded pale red scales (m. p. 163—164.5°C) of XXV. The infrared spectrum of XXV shows no absorption for $\nu_{C=O}$ and ν_{N-H}.

Found: N, 7.86. Calcd. for $C_{12}H_{13}N$: N, 8.18%.

UV $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 307 (4.66)sh, 316(4.70), 390 (4.20)sh, 397 (4.32), 472 (2.84).

The Picrate of XXV.—Dark green micro-prisms (from ethanol); m. p. above 280°C.

Found: N, 13.60. Calcd. for $C_{18}H_{16}O_7N_4$: N, 14.00%.

6-Diethylaminoazulene (XXVI). — When a solution of XXIV (180 mg.) in pyridine (2.5 ml.) was treated as in the above experiment, XXVI (15 mg.) was obtained. Recrystallization from ethanol afforded pale red scales (m. p. 71—71.5°C). The infrared spectrum of XXVI shows no absorption for $\nu_{C=O}$ and ν_{N-H}.

Found: N, 6.61. Calcd. for $C_{14}H_{17}N$: N, 7.03%.

UV $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 309 (4.68)sh, 318 (4.72), 392 (4.26)sh, 399 (4.41), 443 (2.94), 476 (2.95).

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