Syntheses of Indolo[2,3-*b*]tropones and Benzo[*b*]-1-azaazulenes from 2-Hydrazinotropones[1)]

Tetsuo NOZOE,† Je-Kyun SIN,†† Kameji YAMANE,* and Kunihide FUJIMORI*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

**Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto 390*

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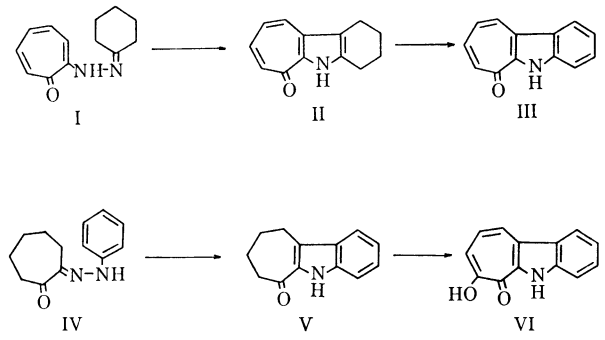
The application of Fischer's indole synthesis to cyclohexanone 2-troponylhydrazone gave 1,2,3,4-tetrahydroindolo[2,3-*b*]tropone (II), which was then dehydrogenated to indolo[2,3-*b*]tropone (III). 8-, 10-Isopropyl-, and 7-bromoindolo[2,3-*b*]tropone (XIIa—c) were also obtained by a similar method. The treatment of 2-troponylhydrazones of cycloheptanone and *N*-benzylpiperidone with dilute sulfuric acid or PPA gave 2,3-pentamethylenepyrrolo[2,3-*b*]tropone (XIII) and 2-benzyl-1,2,3,4-tetrahydrocyclohept[*b*]pyrido[3,4-*d*]pyrrol-6(5H)-one (XIV) respectively. The reaction of III with phosphoryl chloride or thionyl chloride yielded 8-chlorobenzo[*b*]-1-azaazulene (XV), which was subsequently converted into a hydrazino derivative (XVI). The oxidative decomposition of XVI with copper sulfate in acetic acid afforded benzo[*b*]-1-azaazulene (XVII).

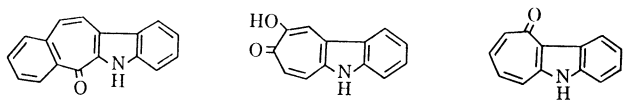
Several methods have been reported for the preparation of various indolotropones(cycloheptindolones). 1,2,3,4-Tetrahydroindolo[2,3-*b*]tropone (II) obtained by the application of Fischer's indole synthesis to cyclohexanone 2-troponylhydrazone (I) was dehydrogenated to indolo[2,3-*b*]tropone (III) and then derived to benzo[*b*]-1-azaazulene (XVII).[1)] On the other hand, indolo[3,2-*f*]tropolone (VI) was obtained by the SeO_2 oxidation of the compound V produced by the same indole synthesis from cycloheptanedione monophenylhydrazone (IV),[2)] and more recently benzoindolotropone (VII) was synthesized by similar methods.[3)]



I II III

IV V VI

Furthermore, indolo[3,2-*d*]tropolone (VIII) was obtained by the thermolysis of 5-azido-4-phenyltropolone,[4)] and compound III and its isomer (IX) were isolated from the photochemical products of acridine-10-oxide.[5)]



VII VIII IX

In this paper we wish to describe in full the experimental details of our earlier report,[1)] along with the results of a reexamination carried out recently.

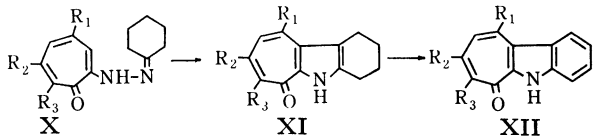
† Present address: No. 811, 2-5-1, Kamiyoga, Setagaya-ku, Tokyo 158.

†† Present address: Faculty of Science, Korean University, 1-700, Ogawa-cho, Kodaira-shi, Tokyo 187.

Results and Discussion

The heating of cyclohexanone 2-troponylhydrazone (I) with dilute sulfuric acid afforded the ring-closure product (II), which was then converted to indolo-[2,3-*b*]tropone (III) by dehydrogenation with chloranil or DDQ.

The application of the same treatment to 4-, 6-isopropyl-, and 7-bromo-2-troponylhydrazone (Xa—c) of cyclohexanone gave compounds XIa—c, the dehydrogenation of which subsequently afforded 8-, 10-isopropyl, and 7-bromo derivatives (XIIa—c) respectively.



X XI XII

a: R_1=i-Pr, R_2=R_3=H
b: R_2=i-Pr, R_1=R_3=H
c: R_3=Br, R_1=R_2=H

The structures of these new compounds were discussed on the basis of the spectral data. The IR spectrum of II exhibited characteristic absorption bands at 3140 cm^{-1} (NH st.), 2920 cm^{-1} (CH_2 st.), and 1620 cm^{-1} (C=O or C=C conjugated). Compound III showed IR-absorption bands at 3195 cm^{-1} (NH st.) and 1614 cm^{-1} (C=O or C=C conjugated), but no paraffinic C–H streching absorption bands (Table 1).

The NMR spectrum of II exhibited signals corresponding to two methylene groups at δ 2.5—2.9 ppm (4H, m, $-CH_2-$) and δ 1.7—1.9 ppm (4H, m, $-CH_2-$), besides signals of tropone-ring protons at δ 6.76 ppm (1H, t, d, J=7.0, 2.0 Hz, H_9), δ 7.1—7.4 ppm (2H, m, $H_{7,8}$), and δ 7.49 ppm (1H, d,d, J=9.0, 1.0 Hz, H_{10}). In the NMR spectrum of III, the signals due to the methylene groups disappeared and those of aromatic protons were observed as a complex multiplet at δ 7.0—8.3 ppm. The IR and NMR spectra of XIa—c and XIIa—c supported the structure described above (Tables 1 and 2).

The bromo compound, XIIc, was obtained by treating III with NBS. It was quite stable even when

Table 1. IR spectra of II, III, XIa—c, and XIIa—c

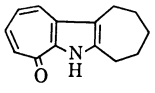
Compound	NH cm^{-1}	CH cm^{-1}	C=O conjugated and others cm^{-1} (KBr)
II	3140	2920, 2860	1620, 1591, 1545, 1520, 1495
XIa	3180	2950, 2860	1613, 1582, 1549, 1515, 1490
XIb	3140	2935, 2860	1621, 1554, 1514, 1495
XIc	3200	2940, 2850	1605, 1586, 1548, 1501, 1486
III	3195		1614, 1589, 1555, 1531, 1491
XIIa	3208		1606, 1521, 1479
XIIb	3150		1608, 1555, 1525, 1485
XIIc	3215		1600, 1552, 1482

Table 2. NMR spectra of XI and XII

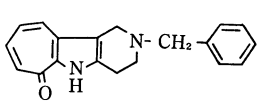
Compound	δ ppm in $CDCl_3$ (100 MHz)
XIa	1.30 (6H, d, J=7.0 Hz, $-CH_3$), 1.7—1.9 (4H, m, $-CH_2-$), 2.7—3.1 (4H, m, $=-CH_2-$), 3.76 (1H, sept., J=7.0, -CH-), 6.80 (1H, d,d, J=7.0, 2.0, H_9), 7.05 (1H, d,d, J=9.0, 2.0, H_7), 7.27 (1H, d,d, J=9.0, 7.0, H_8)
XIb	1.25 (6H, d, J=7.0, $-CH_3$), 1.7—1.9 (4H, m, $-CH_2-$), 2.6—3.0 (5H, m, $=-CH_2-$, -CH-), 6.73 (1H, d,d, J=7.0, 2.0, H_9), 7.12 (1H, d, J=2.0, H_7), 7.46 (1H, d,d, J=8.0, 1.0, H_{10})
XIIa	1.49 (6H, d, J=7.0, $-CH_3$), 4.18 (1H, sept., J=7.0, -CH-), 7.00 (1H, d,d, J=7.0, 2.0, H_9), 7.18—7.55 (4H, m, $H_{2,3,7,8}$), 7.76 (1H, d, J=6.0, H_4), 8.23 (1H, d, J=6.0, H_1)
XIIb	1.35 (6H, d, J=7.0, $-CH_3$), 2.98 (1H, sept., J=7.0, -CH-), 6.98 (1H, d,d, J=9.0, 2.0, H_9), 7.20—7.55 (4H, m, $H_{2,3,7,8}$), 7.73 (1H, d, J=7.0, H_4), 8.03 (1H, d, J=7.0, H_1), 8.05 (1H, d,d, J=9.0, 1.0, H_{10})

heated with conc. sulfuric acid, 85% phosphoric acid and when refluxed in methanol with sodium methylate. Thus, we were unable to derive indolo[3,2-*f*]tropolone (VI).

The 2-troponylhydrazones of cycloheptanone and *N*-benzylpiperidone were also easily converted to XIII and XIV respectively by heating with dilute sulfuric acid or PPA, but the ring closure of cyclopentanone 2-troponylhydrazone did not take place under the same conditions.

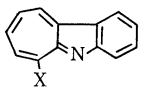


XIII

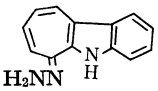


XIV

When compound III was heated with phosphoryl chloride or thionyl chloride, 8-chlorobenzo[*b*]-1-azaazulene (XV) was obtained; the original compound III had been obtained by the hydrolysis with aqueous sodium hydroxide. The reaction of XV with hydrazine hydrate gave the hydrazino derivative (XVI). The UV and visible absorption spectra suggested that XVI is probably indolo[2,3-*b*]troponehydrazone (Table 3).



XV: X=Cl
XVII: X=H



XVI

Table 3. Ultraviolet and visible absorption maxima

Compound	λ_{max} nm (log ε)
III	225 (4.40), 277 (4.40), 383 (3.81), 404 (3.89)
XVI	243 (4.39), 307 (4.06), 317 (4.06), 350 (4.17), 365 (4.08) (in CH_3OH)
XV	245 (4.41), 301 (4.51), 314 (4.62), 326 (4.55), 365 (3.78), 385 (3.79), 400 (3.38), 500 (2.74), 532 (2.74)
XVII	228 (4.34), 264 (4.14), 289 (4.54), 299 (4.56), 311 (4.62), 323 (3.50), 347 (3.66), 359 (3.70), 379 (3.68), 394 (3.22), 500 (2.58), 538 (2.57) (in cyclohexane)

By oxidative decomposition with copper sulfate in aqueous acetic acid, XVI was converted into benzo-[*b*]-1-azaazulene (XVII) as reddish-purple needles; mp 140—141 °C.

The structure was identified by a spectral comparison with an authentic sample.[2] The visible absorption spectra of XV and XVII are quite different from those of III and XVI, as is shown in Table 3.

Experimental**

All the melting points are uncorrected. The NMR spectra were obtained on a JEOL Model JMN-4H-100 spectrometer in $CDCl_3$ solution, with TMS as the internal standard.

Cyclohexanone 2-Troponylhydrazone (I). To a solution of 2-hydrazinotropone (21 g) in ethanol (210 ml), we added cyclohexanone (15 g), and the mixture was refluxed for 30 min. After cooling, the reaction mixture was diluted with water (210 ml). The separated material was collected and dried. Recrystallization from petroleum ether gave yellow needles (32 g, 96%); mp 75—76 °C. IR (KBr): 3220 (NH), 1625, and 1585 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 264 (log ε=4.31), 353 (4.24), and 415 (4.27) nm. Found: C, 71.92; H, 7.50; N, 13.08%. Calcd for $C_{13}H_{16}ON_2$: C, 72.19; H, 7.46; N, 12.95%.

1,2,3,4-Tetrahydroindolo[2,3-b]tropone (II). A mixture of I (30 g), water (500 ml), and conc. sulfuric acid (30 ml) was refluxed at 120 °C for 2 hr. After cooling, 30% aqueous sodium carbonate was added to adjust the pH value to 6 and then extracted with chloroform. The extract was dried over anhydrous sodium sulfate and condensed to dryness to give light yellow needles, which were subsequently recrystallized from benzene (15.8 g, 57%); mp 212—215 °C. UV: $\lambda_{max}^{CH_3OH}$ 237 (log ε=4.43), 293 (4.50), 360 (3.63), and 382 (3.65) nm. Found: C, 78.25; H, 6.40; N, 6.83%. Calcd for $C_{13}H_{13}ON$: C, 78.36; H, 6.58; N, 7.03%.

N-Benzyl Compound: Light yellow needles (from *n*-hexane); mp 136.5—137.5 °C. IR (KBr): 1628, 1558, and 1518 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 237 (log ε=4.39), 296 (4.47), 369 (3.50), and 387 (3.48) nm. Found: C, 82.86; H, 6.58; N, 4.65%. Calcd for $C_{20}H_{19}ON$: C, 83.00; H, 6.63; N, 4.84%.

** The authors are grateful to the Sankyo Co., Ltd., for doing a part of the elemental analyses.

N-Benzoyl Compound: Colorless micro prisms (from benzene–cyclohexane); mp 167—168 °C. IR (KBr): 3050, 2940 (CH), 1716, and 1620 cm^{-1} (C=O). UV: $\lambda_{max}^{CH_3OH}$ 237 ($\log \varepsilon$=4.47), 290 (4.29), 360 (3.54), and 378 (3.44) nm. Found: C, 79.25; H, 5.69; N, 4.76%. Calcd for $C_{20}H_{17}O_2N$: C, 79.18; H, 5.65; N, 4.62%.

Indolo[2,3-b]tropone (III). *Method A*: Dehydrogenation with chloranil. A mixture of II (7.0 g) and chloranil (18.0 g) in xylene (115 ml) was refluxed at 160—165 °C for 24 hr. After cooling, the reaction mixture was made alkaline by adding 2 M sodium hydroxide, and the insoluble material was filtered off. After the organic layer had been dried over anhydrous sodium sulfate, the solvent was removed to give a residue. The water layer and the insoluble material were then extracted with chloroform. The extract was dried and condensed to give the residue. The combined residue was recrystallized from benzene to give III as yellow needles (3.6 g, 52%); mp 245—246 °C.

Method B: Dehydrogenation with DDQ. DDQ (2.1 g) was added to a solution of II (1.0 g) in benzene (60 ml), and the mixture was refluxed for 5 hr. After cooling, the reaction mixture was poured into 10% sodium hydroxide, and the benzene layer was isolated. The water layer was extracted with chloroform. The organic layers were dried over anhydrous sodium sulfate and condensed, and the residues were recrystallized from benzene to give III as yellow plates (0.43 g, 45%); mp 245—246 °C. The IR spectrum was identical with that of a sample prepared by Method A and the mixed melting point was not depressed. Found: C, 80.02; H, 4.65; N, 7.14%. Calcd for $C_{13}H_9ON$: C, 79.97; H, 4.67; N, 7.18%.

N-Benzoyl Compound: Yellow needles (from cyclohexane–benzene); mp 196—196.5 °C. IR (KBr): 1706 cm^{-1} (C=O). UV: $\lambda_{max}^{CH_3OH}$ 222 ($\log \varepsilon$=4.48), 275 (4.46), 310 (4.17), 382 (3.71), and 400 (3.71) nm. Found: C, 80.42; H, 4.36; N, 4.44%. Calcd for $C_{20}H_{13}O_2N$: C, 80.23; H, 4.39; N, 4.68%.

Cyclohexanone 4-Isopropyltroponyl-2-hydrazone (Xa). A mixture of 2-hydrazino-4-isopropyltropone (0.2 g) and cyclohexanone (0.1 g) in ethanol (2 ml) was refluxed for 15 min on a water bath. The solvent was then removed, and a saturated solution of picric acid in ethanol was added to the residual oil. The picrate was treated with aqueous sodium bicarbonate and the separated oil was extracted with benzene. The extract was dried and condensed to leave a residual oil. The oil solidified under reduced pressure in a vacuum desiccator. The solid was purified from ethyl ether to give a yellow powder (0.18 g, 62%); mp 104—106 °C. IR (KBr): 3255 (NH), 1592, and 1542 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 270 ($\log \varepsilon$=4.40), 353 (4.23), 412 (4.27) nm. Found: C, 74.40; H, 8.57; N, 10.91%. Calcd for $C_{16}H_{22}ON_2$: C, 74.38; H, 8.58; N, 10.85%.

Picrate: Yellow needles; mp 127—128 °C. Found: C, 54.12; H, 5.18; N, 14.35%. Calcd for $C_{22}H_{25}O_8N_5$: C, 54.20; H, 5.17; N, 14.38%.

Cyclohexanone 6-Isopropyltroponyl-2-hydrazone (Xb). A mixture of 2-hydrazino-6-isopropyltropone (0.3 g) and cyclohexanone (0.16 g) in ethanol (2 ml) was treated by a method similar to that used for the preparation of Xa. Yellow rhombic crystals (0.2 g, 47%); mp 76—78 °C. IR (KBr): 3276 (NH), 1590, and 1541 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 265 ($\log \varepsilon$=4.40), 353 (4.21), and 4.08 (4.27) nm. Found: C, 74.15; H, 8.51; N, 10.79%. Calcd for $C_{16}H_{22}ON_2$: C, 74.38; H, 8.58; N, 10.85%.

Picrate: Orange yellow needles; mp 146—147 °C. Found: C, 54.51; H, 4.79; N, 14.22%. Calcd for $C_{22}H_{25}O_8N_5$: C, 54.20; H, 5.17; N, 14.37%.

Alternate Method for Preparation of Xa and Xb. A mixture (3.6 g) of two isomers of hinokitiol methyl ether from the methylation of hinokitiol with diazomethane were directly treated with 85% hydrazine hydrate to give a mixture of 4- and 6-isopropyl-2-hydrazinotropones, which were then converted into the hydrazones of cyclohexanone. The resulting hydrazones (Xa and Xb) were separated in the form of picrates by fractional crystallization.

The picrates were treated with a sodium bicarbonate solution to give Xa (1.0 g) and Xb (1.6 g).

10-Isopropyl-1,2,3,4-tetrahydroindolo[2,3-b]tropone (XIa). A solution of Xa (7.2 g) in 3 M sulfuric acid (90 ml) was refluxed at 110—120 °C for 2 hr. After cooling, the reaction mixture was made slightly alkaline by adding aqueous sodium hydroxide and extracted with benzene. The extract was dried and condensed, and the residue was recrystallized from benzene to give slightly red needles (3.0 g, 45%); mp 221—222 °C. Found: C, 79.32; H, 7.77; N, 5.96%. Calcd for $C_{16}H_{19}ON$: C, 79.63; H, 7.94; N, 5.80%. UV: $\lambda_{max}^{CH_3OH}$ 243 ($\log \varepsilon$=4.51), 294 (4.47), 365 (3.77), and 383 (3.82) nm.

8-Isopropyl-1,2,3,4-tetrahydroindolo[2,3-b]tropone (XIb). A solution of X (11.9 g) in 3 M sulfuric acid (150 ml) was treated by a method to that used for the preparation of XIa. Light yellow needles (5.9 g, 53%); mp 205—206 °C. UV: $\lambda_{max}^{CH_3OH}$ 242 ($\log \varepsilon$=4.48), 292 (4.46), and 373 (3.59) nm. Found: C, 79.48; H, 7.69; N, 5.85%. Calcd for $C_{16}H_{19}ON$: 79.63; H, 7.94; N, 5.80%.

10-Isopropylindolo[2,3-b]tropone (XIIa). A mixture of XIa (1.0 g) and DDQ (2.0 g) in dry benzene (60 ml) was refluxed for 4.5 hr. The reaction mixture was then poured onto 10% sodium hydroxide and the benzene layer was isolated. The water layer was subsequently extracted with chloroform. The organic layers were washed with water, dried over anhydrous sodium sulfate, and condensed to give yellow micro prisms (0.63 g, 64%), which were then recrystallized from benzene; mp 199—201 °C. Found: C, 80.81; H, 6.44; N, 5.82%. Calcd for $C_{16}H_{15}ON$: C, 80.98; H, 6.37; N, 5.90%.

8-Isopropylindolo[2,3-b]tropone (XIIb). *Method A*: Dehydrogenation with DDQ. A mixture of XIb (1.0 g) and DDQ (2.0 g) in dry benzene (60 ml) was treated by a method similar to that used for the preparation of XIIa. Light yellow micro prisms (0.69 g, 70%); mp 222—224 °C. UV: $\lambda_{max}^{CH_3OH}$ 226 ($\log \varepsilon$=4.46), 277 (4.48), 306 (4.28), and 394 (3.87) nm. Found: C, 81.25; H, 6.30; N, 5.96%. Calcd for $C_{16}H_{15}ON$: C, 80.98; H, 6.37; N, 5.90%.

Method B: Dehydrogenation with Pd–C. A mixture of XIb (0.5 g) and 5% Pd–C (0.2 g) in *p*-cymene (5 ml) was refluxed at 198—200 °C for 48 hr. The catalyst was then removed, and the filtrate was cooled to give light yellow micro needles (0.16 g, 32%), which were then recrystallized from benzene; mp 222—224 °C.

The IR spectrum was identical with that of the sample prepared by Method A, and the mixed melting point with the sample was not depressed.

Cyclohexanone Bromotroponylhydrazone (Xc). Cyclohexanone (2.5 g) was added to a solution of 2-bromo-7-hydrazinotropone (5.0 g) in ethanol (250 ml), and the mixture was refluxed for 20 min. The solvent was then removed, and the residue was recrystallized from ethanol to give yellow prisms (6.24 g, 91%); mp 134.5—135 °C. IR (KBr): 3270 (NH), 1620, 1597 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 275 ($\log \varepsilon$=4.33), 358 (4.20), and 430 (4.28) nm. Found: C, 52.76; H, 5.14; N, 9.47%. Calcd for $C_{13}H_{15}ON_2Br$: C, 52.98; H, 5.13; N, 9.49%.

7-Bromo-1,2,3,4-tetrahydroindolo[2,3-b]tropone (XIc). *Method A*: A solution of Xc (1.0 g) in water (10 ml) and conc. sulfuric acid (0.6 ml) was refluxed at 130—140 °C for

2 hr. After cooling, 4 M sodium hydroxide was added to adjust the pH values to 5—6 and the solution was extracted with chloroform. The extract was dried and condensed to give a residue. The residue was dissolved in ethanol and treated with activated charcoal to crystallize it as yellow needles (0.44 g, 41%); mp 274—275 °C (decomp.). IR (KBr): 3200 (NH), 1605, and 1545 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 250 (log ε=4.38), 300 (4.53), 375 (3.68), and 393 (3.76) nm. Found: C, 56.27; H, 4.40; N, 4.72%. Calcd for $C_{13}H_{12}ONBr$: C, 56.13; H, 4.36; N,5.04%.

Method B: To a solution of II (0.6 g) in benzene (50 ml), *N*-bromosuccinimide (0.58 g) and benzoyl peroxide (0.06 g) were added; the mixture was then refluxed with stirring for 1 hr.

The solvent was removed, and then the residue was made alkaline by adding aqueous sodium hydroxide and extracted with benzene. The extract was dried and condensed to leave a residue. This residue was dissolved in benzene–chloroform and passed through a silica-gel column. The product obtained from the yellowish effluent was recrystallized from ethanol to give yellow needles (0.12 g, 14%); mp 274—275 °C (decomp.). The IR spectrum was identical with that of the sample obtained by means of Method A.

7-Bromoindolo[2,3-b]tropone (XIIc). *Method A*: A mixture of XIc (0.2 g) and DDQ (0.35 g) in dry benzene (20 ml) was refluxed for 5 hr. The reaction mixture was then treated by a method similar to that used for the preparation of III. Orange micro needles (0.08 g, 41%); mp 291—292 °C. IR (KBr): 3215 (NH), 1600, and 1552 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 235 (log ε=4.25), 282 (4.47), 325 (4.10), 342 (4.04), 395 (3.82), and 416 (3.87) nm. Found: C, 56.59; H, 3.04; N, 5.19%. Calcd for $C_{13}H_8ONBr$: C, 56.75; H, 2.93; N, 5.09%.

Method B: *N*-Bromosuccinimide (0.07 g) and benzoyl peroxide (0.02 g) were added to a solution of III (0.07 g) in dry benzene (15 ml), after which the mixture was refluxed for 3 hr. The solvent was then removed, and the residue was treated with boiling water to leave an insoluble solid. The solid was collected and dried.

Recrystallization from benzene gave yellow needles (0.07 g, 92%); mp 291—292 °C. The IR spectrum was identical with that of the sample obtained by means of Method A.

Attempt at the Ring Closure of Cyclopentanone 2-Troponylhydrazone. *Cyclopentanone 2-Troponylhydrazone*: A mixture of 2-hydrazinotropone (0.3 g) and cyclopentanone (0.22 g) in acetic acid (6 ml) was refluxed for 1 hr. The reaction mixture was then treated by a method similar to that used for the preparation of I.

Orange yellow prisms (0.27 g, 61%); mp 78—79 °C. IR (KBr): 3230 (NH), 1637, and 1592 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 265 (log ε=4.34), 354 (4.26), and 418 (4.26) nm. Found: C, 70.94; H, 6.94; N, 14.02%. Calcd for $C_{12}H_{14}ON_2$: C, 71.26; H, 6.98; N, 13.85%.

When this hydrazone was heated with dilute sulfuric acid or 85% phosphoric acid, the starting material was recovered.

2,3-Pentamethylenepyrrolo[2,3-b]tropone (XIII). *Cycloheptanone 2-Troponylhydrazone*: A mixture of 2-hydrazinotropone (0.3 g) and cycloheptanone (0.3 g) in ethanol (5 ml) was refluxed for 30 min. The reaction mixture was then treated by a method similar to that used for the preparation of I.

Yellow needles (0.4 g, 79%); mp 91—92 °C. IR (KBr): 3255 (NH), 1595, and 1550 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 264 (log ε=4.35), 353 (4.25), and 415 (4.28) nm. Found: C, 73.15; H, 7.84; N, 12.21%. Calcd for $C_{14}H_{18}ON_2$: C, 73.01; H, 7.88; N, 12.17%.

Method A: Ring-closure with PPA. A solution of the hydrazone (2.0 g) described above in 105% PPA (30 ml) was heated at 150 °C for 2 hr. After cooling, the reaction mixture was diluted with water and neutralized by adding aqueous sodium bicarbonate.

The resulting precipitate was collected, dried, and recrystallized from benzene to give light yellow plates (1.1 g, 58%); mp 185—186 °C. IR (KBr): 3160 (NH), 1621, 1545, and 1525 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 235 (log ε=4.41), 295 (4.53), and 363 (3.63) nm. Found: C, 78.46; H, 7.02; N, 6.71%. Calcd for $C_{14}H_{15}ON_2$: C, 78.84; H, 7.09; N, 6.57%.

Method B: Ring-closure with dilute sulfuric acid. A solution of the hydrazone described above (0.5 g) in water (12 ml) and conc. sulfuric acid (0.8 ml) was refluxed for 1 hr. The reaction mixture was treated by a method similar to that used for the preparation of II. Light yellow plates (0.03 g, 7%); mp 185—186 °C.

The IR spectrum was identical with that of the sample prepared by means of Method A, and the mixed melting point with the sample was not depressed.

N-Benzoyl Compound: Colorless micro prisms (from cyclohexane); mp 157—158 °C. IR (KBr): 1720 cm^{-1} (C=O). UV: $\lambda_{max}^{CH_3OH}$ 237 (log ε=4.48), 288 (4.33), 360 (3.57), and 380 (3.50) nm. Found: C, 79.17; H, 5.53; N, 4.91%. Calcd for $C_{21}H_{19}O_2N$: C, 79.47; H, 6.03; N, 4.41%.

2-Benzyl-1,2,3,4-tetrahydrocyclohept[b]pyrido[3,4-d]pyrrol-6(5H)-one (XIV). *1-Benzyl-4-piperidone 2-Troponylhydrazone*: A mixture of 2-hydrazinotropone (1.5 g) and 1-benzyl-4-piperidone (2.0 g) in ethanol (5 ml) was refluxed for 2 hr. The solvent was then removed, and the residue was recrystallized from ethanol to give yellow needles (2.6 g, 77%); mp 97—98 °C. IR (KBr): 3266 (NH), 1601, and 1590 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 263 (log ε= 4.34), 354 (4.28), and 418 (4.29) nm. Found: C, 74.29; H, 6.88; N, 13.81%. Calcd for $C_{19}H_{21}ON_3$: C, 74.24; H, 6.89; N, 13.67%.

A solution of the hydrazone described above (0.3 g) in PPA (4 ml) was heated at 150 °C for 30 min. After cooling, the reaction mixture was diluted with water; aqueous potassium carbonate was then added to adjust the pH value to 8. The solution was then extracted with chloroform. The extract was dried and condensed, and the residue was recrystallized from benzene or methanol to give colorless plates (0.04 g, 14%); mp 219—220 °C. IR (KBr): 3115 (NH), 1620, 1551, and 1501 cm^{-1} (C=O or C=C conjugated). UV: $\lambda_{max}^{CH_3OH}$ 236 (log ε=4.42), 291 (4.46), 366 (3.66), and 383 (3.66) nm. Found: C, 78.77; H, 6.33; N, 9.62%. Calcd for $C_{19}H_{18}ON_2$: C, 78.59; H, 6.25; N, 9.62%.

8-Chlorobenzo[b]-1-azaazulene (XV). *Method A*: Reaction of III with thionyl chloride. To a solution of III (0.6 g) in dry benzene (20 ml), we added thionyl chloride (1.9 g); the mixture was then refluxed at 90—100 °C for 20 hr. After cooling, the reaction mixture was poured into a saturated sodium bicarbonate solution and extracted with benzene. The extract was dried and condensed to leave a residue. It was recrystallized from benzene–cyclohexane to give violet needles (0.14 g, 21%); mp 144—146 °C. IR (KBr): 3040 (CH), 1602, and 1580 cm^{-1} (conjugated C=C or C=N). NMR (in $CDCl_3$): δ 7.3—8.7 ppm (m). Found: C, 73.51; H, 3.87; N, 6.98%. Calcd for $C_{13}H_8NCl$: C, 73.10; H, 3.77; N, 6.56%.

Picrate: Orange micro prisms; mp 204 °C (decomp.). Found: C, 51.56; H, 2.50; N, 12.44%. Calcd for $C_{19}H_{11}O_7N_4Cl$: C, 51.52; H, 2.48; N, 12.66%.

Method B: Reaction of III with phosphoryl chloride. A mixture of III (1.37 g) and phosphoryl chloride (6.23 g) was heated at 105—110 °C for 1 hr. After cooling, the

reaction mixture was poured onto ice water; the solution was then made slightly alkaline by adding aqueous sodium bicarbonate.

The solution was extracted with benzene. The extract was dried over anhydrous sodium sulfate and condensed to leave a residue. The recrystallization of this residue from cyclohexane–benzene gave violet needles (1.11 g, 67%); mp 144—145 °C.

The IR spectrum was identical with that of the sample prepared by means of Method A, and the mixed melting point with the sample was not depressed.

Hydrolysis of XV. To a solution of XV (0.1 g) in ethanol (4 ml), we added 2 M sodium hydroxide (4 ml), and the mixture was refluxed for 1 hr. The ethanol was then removed, water was added, the solution was acidified with 2 M hydrochloric acid, and the separated material was collected. It was subsequently recrystallized from ethanol to give yellow needles (mp 245—246 °C). The mixed melting point with III was not depressed.

8-Hydrazinobenzo[b]*-1-azaazulene (XVI).* A solution of XV (0.1 g) in methanol (10 ml) was added, drop by drop, to a solution of 80% hydrazine hydrate (0.2 g) in methanol (10 ml), and the solution was stirred at room temperature for 3 hr. The insoluble material was removed by filtration. The filtrate was evaporated; then water was added and extracted with benzene. The extract was dried and condensed to leave a residue. It was recrystallized from benzene–cyclohexane to give reddish-violet needles (0.04 g, 43%); mp 158—159 °C. IR (KBr): 3348, 3140 (NH), 1616, 1538, and 1486 cm^{-1} (conjugated C=C or C=N). Found: C, 74.53; H, 4.97; N, 19.68%. Calcd for $C_{13}H_{11}N_3$: C, 74.62; H, 5.30; N, 20.08%.

Benzo[b]*-1-azaazulene (XVII).* A mixture of XVI (0.34 g), acetic acid (20 ml), water (20 ml), and 2M copper sulfate (34 ml) was heated for 15 min on a water bath. After cooling, the reaction mixture was made slightly alkaline by adding 2 M sodium hydroxide and the solution was extracted with chloroform. The extract was dried and condensed to leave a residue. The residue was dissolved in benzene and passed through an alumina column. The product obtained from the reddish effluent was recrystallized from cyclohexane to give reddish-violet needles (0.07 g, 24%); mp 140—141 °C.

The IR and UV spectra were identical with those of the sample prepared by Treibs' method,[2a] and the mixed melting point with the sample was not depressed.

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