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SIMPLE SYNTHESIS OF RING-FUSED PYRIDAZIN-3-ONES

Koichi Suzuki, Akihiro Senoh, and Kazunori Ueno※

OL Project, Display Development Headquarters, Canon Inc.
30-2, Shimomaruko 3-chome, Ohta-ku, Tokyo, Japan

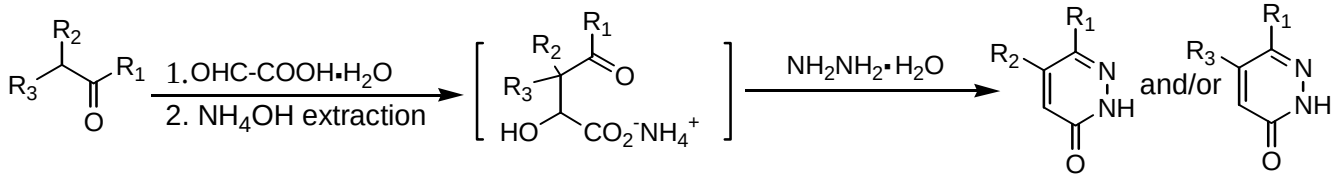
Abstract- Bicyclic and tricyclic pyridazin-3-ones, 6,7-dihydro-5*H*-cyclopenta-[*e*]-2*H*-pyridazin-3-one (**5**), 5,6,7,8-tetrahydrobenzo[*e*]-2*H*-pyridazin-3-one (**6**), 9,10-dihydronaphtho[1,2-*e*]-2*H*-pyridazin-3-one (**15**) and 9,10-dihydronaphtho-[1,2-*e*]-2-methylpyridazin-3-one (**21**) were prepared in a one-pot procedure by reacting hydrazine hydrate with a corresponding ketocarboxylic acid.

INTRODUCTION

Pyridazin-3-one and its benzoanalogue, phthalazinone are known as practical use, thermally developable photographic compounds.[1-3] These compounds work as both toner and silver carrier in the developing process, and phthalazinone is the only compound in commercial use. However, thermally developable photographic materials containing phthalazinones have the disadvantage of a short shelf-life, because phthalazinone easily sublimes. Thus, it seems worthwhile to prepare various types of ring-fused pyridazin-3-one derivatives and to evaluate their stabilities as thermally developable photographic compounds. This paper reports a convenient method of preparation for ring-fused pyridazin-3-ones by a one-pot procedure.

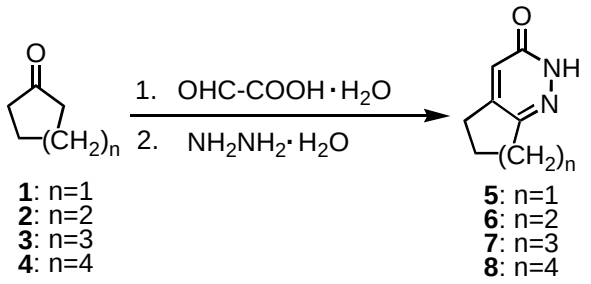
RESULTS AND DISCUSSION

There have been only a few reports on the preparation of pyridazin-3-ones.[4-15] Coates *et al*. reported a convenient method for preparing 6-substituted pyridazin-3-one through the reaction of ketones with glyoxalic acid and hydrazine monohydrate.[16] However, the experimental procedure reported there included the additional step of isolating the intermediate ketocarboxylic acid, formed by the reaction of ketone with glyoxalic acid monohydrate. The reaction mixture was extracted with aqueous ammonia, removing the intermediate as an ammonium salt; the salt was then treated with hydrazine, giving pyridazin-3-ones (Scheme 1).



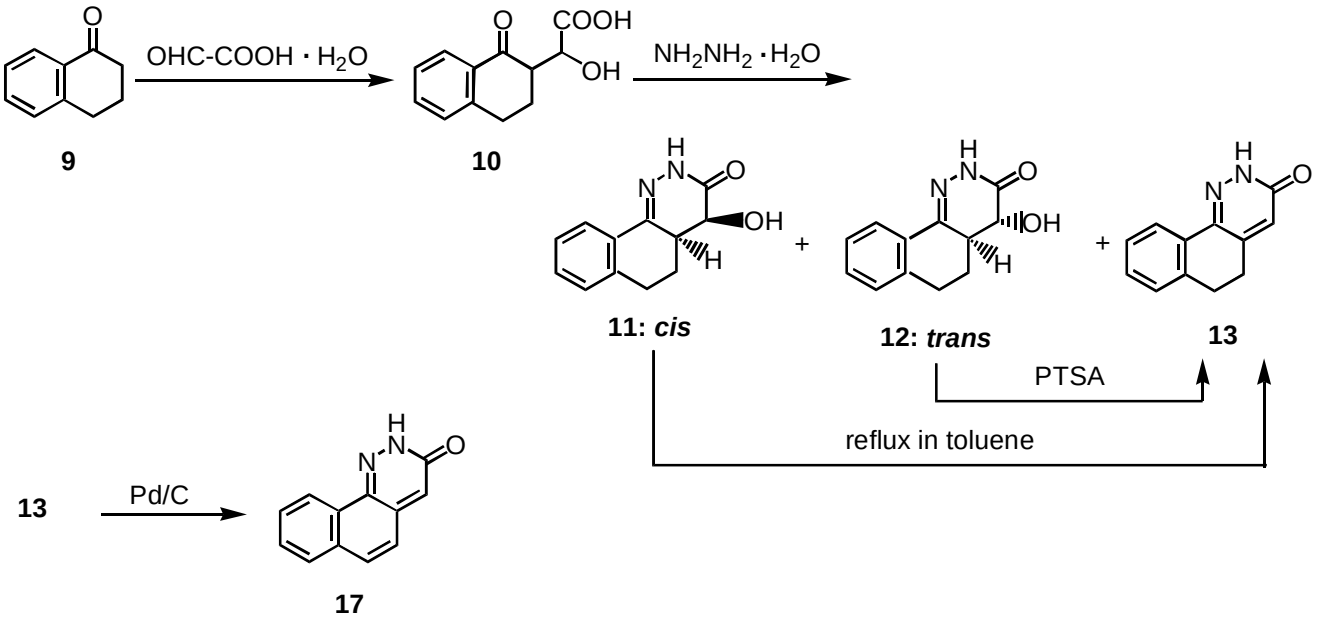
Scheme 1

In this paper, we report the preparation of ring-fused pyridazinones by the reaction of cyclic ketones with glyoxalic acid and hydrazine monohydrate through a modification of Coates' method, in which we found that the reaction proceeded *via* a one-pot procedure without requiring an isolation of the intermediate ketocarboxylic acid. By adding hydrazine hydrate into the mixture of cyclic ketones (**1-4**) and glyoxalic acid, pyridazinones (**5-8**) were obtained in high yields (Scheme 2).



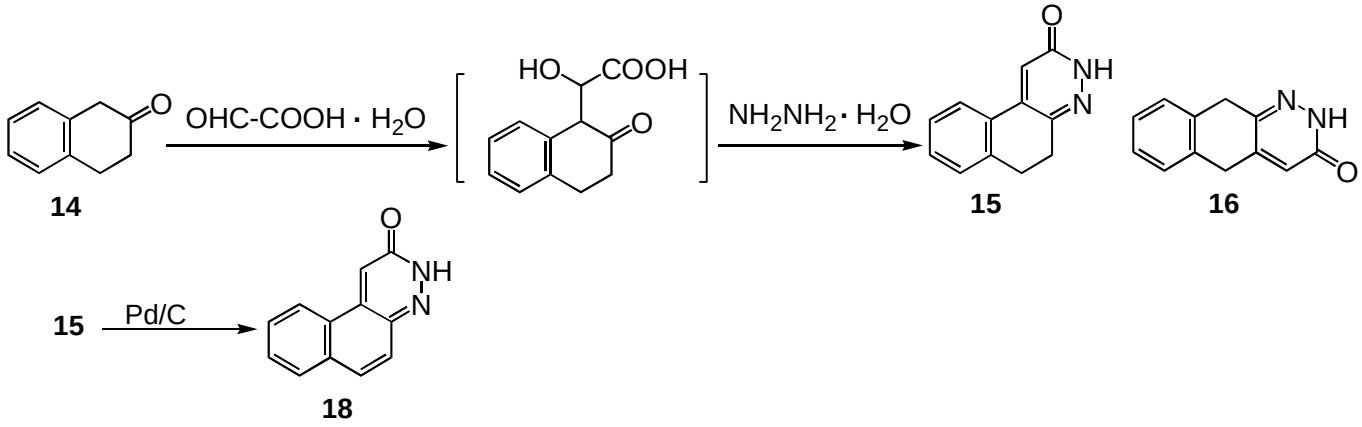
Scheme 2

Using Coates' method, treatment of α-tetralone (**9**) with glyoxalic acid without a solvent gave a keto-carboxylic acid (**10**), which crystallized out from the reaction mixture (Scheme 3). The reaction of **10** with hydrazine hydrate in ethanol under reflux for 6.5 h produced a mixture of 4-hydroxy-4,4a-*cis*-4,4a,5,6-tetrahydronaphtho[2,1-*e*]-2*H*-pyridazin-3-one (**11**) in 17.6% yield, the *trans*-isomer (**12**) in 47.2% yield and the dehydrated compound (**13**) in 6.3% yield. The stereochemistry of **11** and **12** was assigned on the basis of ^{1}H NMR spectra and a chemical conversion. The coupling constant between 4H and 4aH of the *cis*-isomer (**11**) is 4.0 Hz, while that of the *trans*-isomer(**12**) is 14.0 Hz. The *cis*-isomer (**11**) was converted to pyridazin-3-one (**13**) in toluene under reflux in 90% yield. On treatment with PTSA, the *trans*-isomer (**12**) was converted to pyridazin-3-one (**13**) in 79% yield, which was further aromatized to **17** by heating in decalin in the presence of palladium-charcoal (Scheme 3).



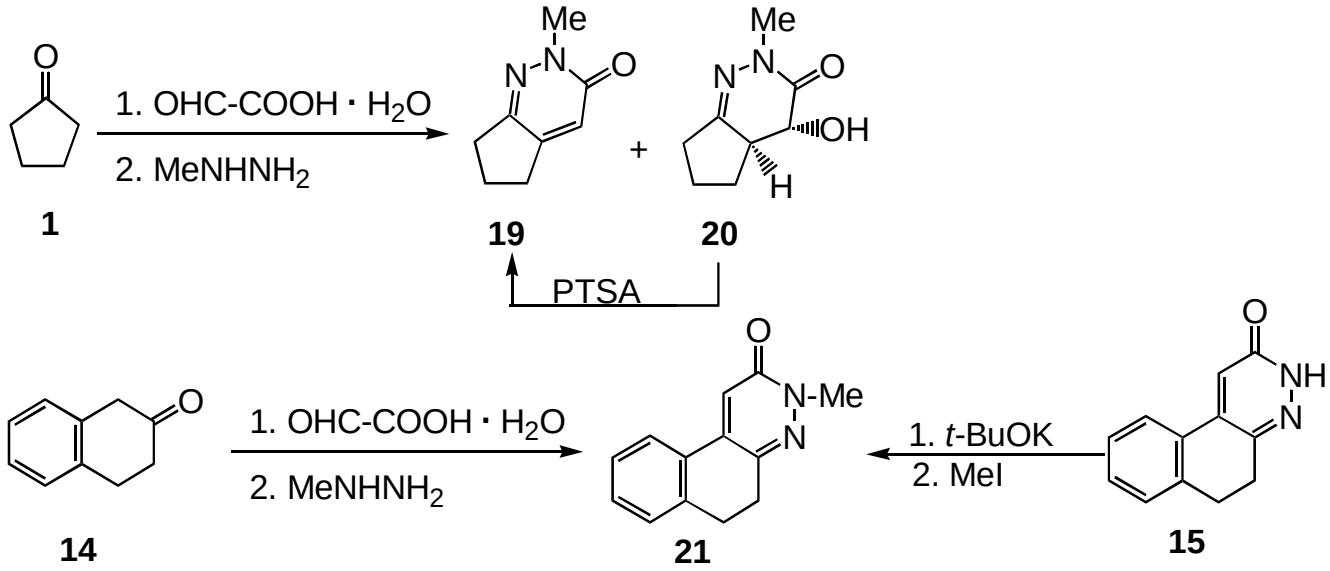
Scheme 3

In one-pot reaction of β-tetralone (**14**) with glyoxalic acid and hydrazine monohydrate (Scheme 4), **15** was obtained as a sole product and the linear isomer (**16**) was not formed. The structure of **15** was determined on the basis of NOE-experiment between the protons on 4- and 5-positions. With palladium-charcoal in decalin under reflux, **15** was transformed into **18**. Exclusive formation of **15** indicates the regiospecific attack of glyoxalic acid on the α-position of **14**.



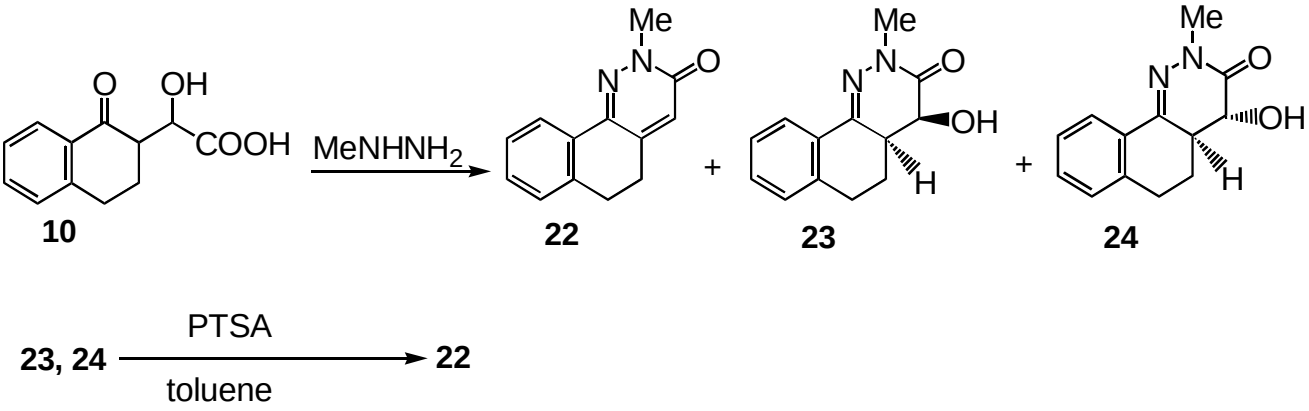
Scheme 4

The reaction of cyclopentanone with *N*-methylhydrazine and glyoxalic acid afforded the expected *N*-methyl derivatives **(19)** and a hydroxy compound (**20**) in 32 and 17% yields, respectively. Compound (**20**) was dehydrated upon treatment with PTSA to give **19**. The reaction of tetralone (**14**) with glyoxalic acid and *N*-methylhydrazine also gave **21** in 31.3% yield. Methylation of **15** under basic conditions gave **21**. In ^{1}H NMR spectra of **19** and **21**, the *N*-methyl protons on the unsaturated pyridazinone ring were observed at a lower magnetic field (3.72 ppm and 3.79 ppm respectively), compared with those on the dihydropyridazinone ring of **20** (3.37 ppm), probably because of the deshielding effect of the neighboring carbonyl group.[17]



Scheme 5

Finally, the reaction of the ketocarboxylic acid (**10**) with *N*-methylhydrazine produced the dehydrated compound (**22**) in 36% yield, together with two isomeric *N*-methylhydroxy compounds (**23**) and (**24**) in 31 and 15% yields, respectively (Scheme 6). It was confirmed that **23** and **24** gave **22** in quantitative yield by elimination of one mole of water under reflux in toluene for 30 min, respectively.



Scheme 6

EXPERIMENTAL

Melting points were determined on a Mettler FP 82 hot stage connected to Mettler FP 80 central processor and are uncorrected. IR spectra were taken with a Shimadzu IR-435 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNX-EX400 instrument. Chemical shifts were expressed in ppm downfield from tetramethylsilane as an internal standard. Mass spectra were measured with a Shimadzu GC-14A instrument. Flash column chromatography was performed by using silica gel, Fuji Silysia and Fuji Silysia FA-2 instrument.

General procedure for the preparation of 5-8

After a mixture of cycloalkanone (**1-4**) (50 mmol) and glyoxalic acid monohydrate (4.6 g, 50 mmol) was warmed at 50 ℃ for 5 h with stirring, 98% hydrazine monohydrate (3.6 g, 73 mmol) was added to the reaction mixture. The whole mixture was then stirred at 50 ℃ for 1 h. After cooling, the resulting solid was filtered and washed well with ether to give pyridazinone (**5-8**).

6,7-Dihydro-5*H*-cyclopenta[*e*]-2*H*-pyridazin-3-one (5):

This compound was obtained in 54% yield and recrystallized from acetone to give colorless prisms. mp 185-186 ℃. IR (KBr) cm^{-1}: 2700-3400 (NH), 1645 (C=O). ^{1}H NMR ($CDCl_3$) δ: 2.11 (m, 2H), 2.81 (m, 4H), 6.69 (s, 1H), 11.64 (NH, br s, 1H). Anal. Calcd for $C_7H_8N_2O$: C, 61.75 ; H, 5.92 ; N, 20.57. Found : C, 61.62 ; H, 5.83 ; N, 20.62 .

5,6,7,8-Tetrahydrobenzo[*e*]-2*H*-pyridazin-3-one (6):

This compound was obtained in 52% yield and recrystallized from acetone to give colorless prisms. mp 197-198 ℃. IR (KBr) cm^{-1}: 3300-3400 (NH), 1658 (C=O). ^{1}H NMR($CDCl_3$) **δ**: 1.72-1.87 (m, 4H), 2.71 (m, 4H), 6.67 (s, 1H), 12.10 (NH, br s, 1H). Anal. Calcd for $C_8H_{10}ON_2$: C, 63.98; H, 6.71; N, 18.65.

Found: C, 63,87; H, 6.59; N, 18.54.

6,7,8,9-Tetrahydro-5*H*-cyclohepta[*e*]-2*H*-pyridazin-3-one (7):

This compound was obtained in 41% yield and recrystallized from acetone. mp 191-192 °C. IR (KBr) cm^{-1}: 3000-3300 (NH), 1660 (C=O). ^1H NMR ($CDCl_3$) δ: 1.70-1.80 (m, 6H), 2.63 (dd, 2H, J=10.8 and 6.4 Hz), 2.87 (dd, 2H, J=10.8 and 5.6 Hz), 6.67 (s, 1H), 11.21 (br s, NH). Anal. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.70; H, 7.18; N, 16.87.

5,6,7,8,9,10-Hexahydrocycloocta[*e*]-2*H*-pyridazin-3-one (8):

This compound was obtained in 46% yield and recrystallized from acetone. mp 214-216 °C. IR (KBr) cm^{-1}: 3200-3400 (NH), 1658 (C=O). ^1H NMR ($CDCl_3$) δ: 1.45 (m, 4H), 1.73 (m, 4H), 2.63 (t, 2H, J=6.3 Hz), 2.76 (t, 2H, J=6.3 Hz), 6.76 (s, 1H), 11.43 (NH, br s, NH). Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.39, H, 7.92, N, 15.72. Found: C, 67.31, H, 7.83, N, 15.58.

Ketocarboxylic acid (10):

A mixture of α-tetralone (**9**) (7.3 g, 50 mmol) and glyoxalic acid monohydrate (5.2 g, 56 mmol) was warmed at 50 °C for 12 h with stirring. The resulting solid was filtered, and the isolated solid was washed with ether and recrystallized from acetone to give the ketocarboxylic acid (**10**) as colorless needles (6.32 g, 71%). mp 124-126 °C. IR (KBr) cm^{-1}: 3300-3600 (OH), 1700 (C=O). ^1H NMR ($CDCl_3$) δ: 1.94-2.22 (m, 2H), 2.92-3.10 (m, 3H), 4.32 (d, 1H, J=3.0 Hz), 4.70-5.65 (br, OH, exchanged with D_2O), 7.34 (m, 2H), 7.54 (m, 1H), 7.83 (d, 1H, J=7.6 Hz). Anal. Calcd for $C_{12}H_{14}O_4$: C, 65.45; H, 5.49. Found: C, 65.39; H, 5.45.

4-Hydroxy-4,4a-*cis*-4,4a,5,6-tetrahydronaphtho[2,1-*e*]-2*H*-pyridazin-3-one (11) and 4-Hydroxy-4,4a-*trans*-4,4a,5,6-tetrahydronaphtho[2,1-*e*]-2*H*-pyridazin-3-one (12) and 5,6-dihydronaphtho[2,1-*e*]-2*H*-pyridazin-3-one (13)

A solution of the ketocarboxylic acid (**10**) (1.24 g, 5.6 mmol) and 98% hydrazine hydrate (0.34 g, 6.7 mmol) in ethanol (20 mL) was heated under reflux for 5 h. The solvent was evaporated *in vacuo* and the residue purified via column chromatography, using ethyl acetate/chloroform (1/2) as an eluent to give **11** (0.23 g, 17.6%), **12** (0.62 g, 47.2%) and **13** (0.07 g, 6.3%) which were recrystallized from ethyl acetate, respectively. **11**: mp 225-226 °C. IR (KBr) cm^{-1}: 3330 (OH), 3000-3300 (NH), 1690 (C=O). ^1H NMR ($CDCl_3$) δ: 2.05 (m, 1H), 2.19 (m, 1H), 2.47 (s, OH, exchanged with D_2O), 2.87 (m, 2H), 2.99 (ddd, 1H, J=16.0, 7.2 and 4.0 Hz), 4.19 (dd, 1H, J=8.0 and 4.0 Hz), 7.19 (d, 1H, J=7.6 Hz), 7.30-7.34 (m, 2H), 8.08 (d, 1H, J=7.6 Hz), 8.54 (br s, NH). Anal. Calcd for $C_{12}H_{12}N_2O$: C, 66.65, H, 5.59, N, 12.95. Found: C, 66.73; H, 5.51; N, 12.79. **12**: mp 205-207 °C. IR (KBr) cm^{-1}: 3330 (OH), 3000-3300 (NH), 1670 (C=O). ^1H NMR ($CDCl_3$) δ: 1.73 (m, 1H), 2.57 (m, 1H), 2.77-2.87 (m, 2H), 2.96 (ddd, 1H, J=14.0, 6.8 and 3.6 Hz), 3.55 (s, OH, exchanged with D_2O), 4.03 (dd, 1H, J=14.0 and 1.2 Hz), 7.20 (d, 1H, J=7.6 Hz), 7.32-7.35 (m, 2H), 8.06 (d, 1H, J=7.6 Hz), 8.55 (br s, NH). Anal. Calcd for $C_{12}H_{12}N_2O$: C, 66.65; H, 5.59; N, 12.95. Found: C, 66.47; H, 5.71; N, 13.09. **13**: mp 181-184 °C. IR (KBr) cm^{-1}: 3000-3300 (NH), 1660 (C=O). ^1H NMR ($CDCl_3$) δ: 2.92 (m, 4H), 6.81 (s, 1H), 7.24 (m, 1H), 7.32-7.36 (m, 2H), 8.05 (m, 1H),

11.50 (br s, NH). Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.08; N, 14.13. Found: C, 72.59; H, 4.85; N, 14.01.

Compound (13) from 11:
A solution of **11** (234 mg, 1 mmol) in toluene (10 mL) was heated under reflux for 8 h. After the solvent was evaporated *in vacuo*, the residual solid was filtered and recrystallized from acetone to give **13** (211 mg, 90 % yield).

Compound (13) from 12:
A solution of **12** (234 mg, 1 mmol) and PTSA (15 mg) in toluene (10 mL) was heated under reflux for 8 h. After the solvent was evaporated *in vacuo*, the residual solid was filtered and recrystallized from acetone to give **13** (185 mg, 79 % yield).

Naphtho[2,1-*e*]-2*H*-pyridazin-3-one (17):
Compound (**13**) (200 mg, 1 mmol) and palladium-charcoal (100 mg) in decalin (20 mL) were heated under reflux for 5 h. After removing the palladium-charcoal by filtration, the solvent was evaporated and the residue was chromatographed by using chloroform as an eluent to give naphtho[1,2-*e*]-3*H*-pyridazin-3-one (**17**) (136 mg, 63 %), which was recrystallized from acetone to give yellow prisms. **17**: mp 267-269 ℃. IR (KBr) cm^{-1}: 3200-3400 (NH), 1650 (C=O). ^1H NMR ($CDCl_3$) δ: 7.07 (m, 1H), 7.14 (d, 1H, J=9.3 Hz), 7.50 (d, 1H, J=6.4 Hz), 7.57-7.66 (m, 3H), 7.64 (m, 1H), 13.47(1H, m, br s, NH). Anal. Calcd for $C_{12}H_8N_2O$: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.28; H, 4.25; N, 14.09.

9,10-Dihydronaphtho[1,2-*e*]-2*H*-pyridazin-3-one (15):
A mixture of β-tetralone (4.38 g, 30 mmol) and glyoxylic acid monohydrate (2.8 g, 30 mmol) was warmed at 50 °C for 12 h with stirring. To the reaction mixture, 98% hydrazine hydrate (1.8 g, 32 mmol) and ethanol were added and heated at reflux for 2 h. The solvent was evaporated and the residue was purified via column chromatography over silica gel by using chloroform as an eluent to afford **15** (3.8 g, 58.6 %), which was recrystallized from acetone to give colorless needles. mp 216-217 ℃. IR (KBr) cm^{-1}: 3300-3400 (NH), 1665 (C=O). ^1H NMR ($CDCl_3$) δ: 2.90 (m, 2H), 3.00 (m, 2H), 7.18 (s, 1H), 7.31 (m, 1H), 7.38 (m, 2H), 7.74 (d, 1H, J=7.8 Hz), 12.30 (1H, br s, NH). Anal. Calcd for $C_{12}H_{12}N_2O$: C, 72.71; H, 5.08; N, 14.13. Found: C, 72.81; H, 4.95; N, 14.00.

Naphtho[1,2-*e*]-2*H*-pyridazine-3-one (18):
Compound (**15**) (157 mg, 0.8 mmol) and palladium-charcoal (85 mg) in decalin (20 mL) were heated under reflux for 5 h. After removing the palladium-charcoal by filtration, the solvent was evaporated and the residue was chromatographed by using chloroform as an eluent to give naphtho[1,2-*e*]-2*H*-pyridazin-3-one **(18)** (98 mg, 51.0 %), which was recrystallized from acetone to give yellow prisms. **18**: mp 202-203 ℃. IR (KBr) cm^{-1}: 3200-3400 (NH), 1645 (C=O). ^1H NMR ($CDCl_3$) δ: 7.35 (d, 1H, J=10.0 Hz), 7.40 (d, 1H, J=10.0 Hz), 7.58 (m, 1H), 7.62 (m, 2H), 7.84 (s, 1H), 8.31 (d, 1H, J=7.8 Hz), 12.86 (1H, br s, NH), Anal. Calcd for $C_{12}H_8N_2O$: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.60; H, 4.00; N, 14.16.

6,7-Dihydro-5*H*-cyclopenta[*e*]-2-methylpyridazin-3-one (19) and 4-Hydroxy-4,4a-*trans*-4,4a,6,7-tetrahydro-5*H*-cyclopenta[*e*]-2-methylpyridazin-3-one (20):

A mixture of cyclopentanone (**1**) (4.2 g, 50 mmol) and glyoxylic acid monohydrate (4.6 g, 50 mmol) was warmed at 50 °C for 5 h with stirring. Then, to the reaction mixture, methylhydrazine (2.3 g, 50 mmol) and toluene (20mL) were added and the whole was refluxed for 1 h. The solvent was removed *in vacuo* and the residue was purified *via* column chromatography over silica gel by using chloroform as an eluent to give **19** (2.4 g, 32 %) and **20** (1.44 g, 17 %). Compounds (**19**) and (**20**) were recrystallized from acetone to give colorless prisms, respectively. **19**: mp 82-83 ℃. IR (KBr) cm^{-1}: 1645 (CO). ^1H NMR ($CDCl_3$) δ: 2.07-2.15 (m, 2H), 2.78-2.83 (m, 4H), 3.72 (s, 3H), 6.70 (s, 1H); Anal. Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65. Found: C, 64.13; H, 6.79; N, 18.56. **20**: mp 78-82 ℃. IR (KBr) cm^{-1}: 3320 (OH), 1650 (CO). ^1H NMR ($CDCl_3$) δ: 1.61-1.78 (m, 2H), 2.05 (m, 1H), 2.40-2.49 (m, 2H), 2.58-2.62 (m, 2H), 3.37 (s, 3H), 3.72 (OH, s, 1H, exchanged with D_2O), 3.87 (d, 1H, J=14.2 Hz). Anal. Calcd for $C_8H_{12}N_2O_2$: C, 57.13; H, 7.19; N, 16.66. Found: C, 57.07; H, 7.25; N, 16.57.

Dehydration reaction of 4-hydroxy-4,4a-*trans*-4,4a,6,7-tetrahydro-5*H*-cyclopenta[*e*]-2-methylpyridazin-3-one (20) to 6,7-dihydro-5*H*-cyclopenta[*e*]-2-methylpyridazin-3-one (19):

A solution of **20** (0.5 g, 3 mmol) and PTSA (20 mg) in toluene (10 mL) was heated under reflux for 1 h. The solvent was evaporated *in vacuo* and the residue was triturated with ether to give **19** (0.41 g, 91 %).

9,10-Dihydronaphtho[1,2-*e*]-2-methylpyridazin-3-one (21):

A mixture of β-tetralone (**14**) (4.38 g, 30 mmol) and glyoxylic acid monohydrate (2.8 g, 30 mmol) was warmed at 50 ℃ for 12 h with stirring. To the reaction mixture, *N*-methylhydrazine (1.47 g, 32 mmol) and ethanol (20 mL) were added and the whole was heated under reflux for 2 h. The solvent was evaporated and the residue was chromatographed over silica gel with chloroform to afford **21** (2.33 g, 31.3 %). Compound (**21**) was recrystallized from benzene-hexane to give colorless needles. **21**: mp 215-217 ℃. IR (KBr) cm^{-1}: 1655 (CO). ^1H NMR ($CDCl_3$) δ: 2.89 (m, 2H), 3.00 (m, 2H), 3.79 (s, 3H), 7.19 (s, 1H), 7.29 (m, 1H), 7.38 (m, 2H), 7.71 (m, 1H). Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.51; H, 5.67; N, 13.31.

Methylation of 15

To a suspension of **15** (198 mg, 1 mmol) and *t*-BuOK (137 mg, 1.1 mmol) in THF (20 mL), MeI (160 mg, 1.1 mmol) in THF (5 mL) was added dropwise under stirring. After stirring at rt for 15 h, the reaction mixture was poured into water (100 mL) and extracted twice with chloroform (25 mL). The chloroform layer was dried over $MgSO_4$ and then evaporated *in vacuo* to give **21** (158 mg, 74.5 %).

5,6-Dihydronaphtho[2,1-*e*]-2-methylpyridazin-3-one (22), 4-Hydroxy-4,4a-*cis*-4,4a,5,6-tetrahydronaphtho[2,1-*e*]-2-methylpyridazin-3-one (23) and 4-Hydroxy-4,4a-*trans*-4,4a,5,6-tetrahydronaphtho[2,1-*e*]-2-methylpyridazin-3-one (24):

A solution of ketocarboxylic acid (**10**) (0.63 g, 2.8 mmol) and *N*-methylhydrazine (0.12 g, 3.0 mmol) in

ethanol (20 mL) was heated under reflux for 6 h. The solvent was removed *in vacuo* and the residue was chromatographed over silica gel with chloroform to give **22** (198.6 mg, 36 %), **23** (200 mg, 31 %) and **24** (96.6 mg, 15 %), which were recrystallized from acetone, respectively. **22**: mp 210-211 ℃. IR (KBr) cm^{-1}: 1660 (CO). ^1H NMR ($CDCl_3$) δ: 2.89 (m, 4H), 3.86 (s, 3H), 6.78 (s, 1H), 7.22 (m, 1H), 7.31-7.36 (m, 2H), 8.05 (m, 1H). Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70 ; N, 13.20. Found: C, 73.10; H, 5.80; N, 12.90. **23**: mp 172-173 ℃. IR (KBr): 3340 (OH), 1640 (CO). ^1H NMR ($CDCl_3$) δ: 2.03 (m, 1H), 2.20 (m, 1H), 2.75 (br, OH, exchanged with D_2O), 2.83 (m, 2H), 2.97 (ddd, 1H, J=16.0, 8.0 and 4.0 Hz), 3.50 (s, 3H), 4.17 (d, 1H, J=4.0 Hz), 7.18 (d, 1H, J=7.6 Hz), 7.24-7.33 (m, 2H), 8.15 (d, 1H, J=7.6 Hz). Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.12; N, 13.90. Found: C, 67.80; H, 6.10; N, 11.90. **24**: mp 167-168 ℃. IR (KBr): 3340 (OH), 1660 (CO). ^1H NMR ($CDCl_3$) δ: 1.72 (m, 1H), 2.54 (m, 1H), 2.78 (m, 2H), 2.94 (ddd, 1H, J=14.4, 6.8 and 3.6 Hz), 3.50 (s, 3H), 3.54 (br, OH, exchanged with D_2O), 3.95 (d, 1H, J=14.4 Hz), 7.19 (d, 1H, J=7.6 Hz), 7.24-7.34 (m, 2H), 8.12 (d, 1H, J=7.6 Hz). Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.12; N, 13.90. Found: C, 67.60; H, 6.10; N, 12.10.

Compound (22) from 23 and 24

A solution of **23** (50 mg, 0.22 mmol) and PTSA (10 mg) in toluene (5.0 mL) was heated under reflux for 30 min. The resulted solid (40 mg, 91.8%) after removing the solvent *in vacuo* was identified with **22** by comparison with the IR and ^1H NMR spectra. Under the same reaction condition, **24** (50 mg, 0.22 mmol) gave **22** (43 mg, 98.7%).

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