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Dioxopyrrolines. XXVII.[1] Syntheses of 2-Aryl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-diones

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2-Aryl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-diones (**3**) were easily prepared in good yields by condensation of the enamino-esters (**2**) with oxalyl chloride. The products were characterized by ultraviolet and infrared spectroscopy.

Keywords——Δ^2-pyrroline-4,5-dione; dioxopyrroline; enamino-ester; ethyl 3-aryl-3-aminopropenoate; 2-aryl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-dione; UV; restricted rotation

Δ^2-Pyrroline-4,5-dione (dioxopyrroline) (A) is regarded as a versatile synthon for a variety of heterocycles, since it has many reactive centers. Among ionic reactions, nucleophilic addition to C_2, C_4 and C_5, and electrophilic addition to C_3 are expected. The double bond is also prone to undergo cycloaddition reactions. For example, Diels–Alder reaction gave angularly substituted *cis*-hydroindoles (B),[2] providing the key step in our total syntheses of Amaryllidaceae[3] and Erythrina alkaloids.[4] [2+2]-Photocycloaddition gave 2-azabicyclo-[3.2.0]heptane-3,4-diones (C),[5] which were useful intermediates to other heterocycles such as azatropolones (D)[6] and dihydropyridones (E).[7] In connection with these investigations we have developed several methods for preparing various Δ^2-pyrroline-4,5-diones.[2a] In this paper we describe in detail the synthesis of *N*-substituted 2-aryl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-diones (**3**).

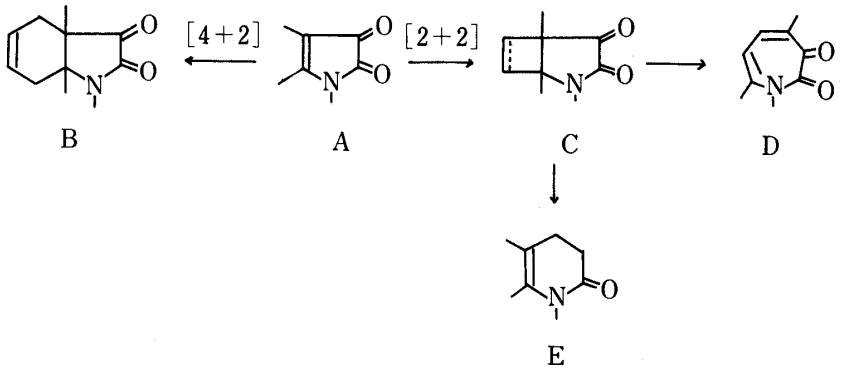

Chart 1

The synthesis of dioxopyrrolines of this type is based on the condensation of appropriate enamino-esters with oxalyl chloride. The method was originally applied to imines by Ziegler *et al.*,[8] who obtained tetrahydroisatin in acceptable yield by reaction of oxalyl chloride with cyclohexanone aniline imine. However, our re-examination of this reaction on the imines produced from aliphatic amines revealed that the yield of the desired dioxopyrroline is not

satisfactory. The simple imine (**5**), under similar conditions with oxalyl chloride, also gave the dioxopyrroline (**6**) (as the mono-hydrated form) in only 5% yield. This may be due to instability of the imines under the reaction conditions.

In contrast to imines, we found that enamines conjugated with a carbonyl group, such as enamino-esters, were far more stable under the above conditions and readily gave the dioxopyrrolines, usually in excellent yields. Enaminones also gave dioxopyrrolines in acceptable yields.[9]

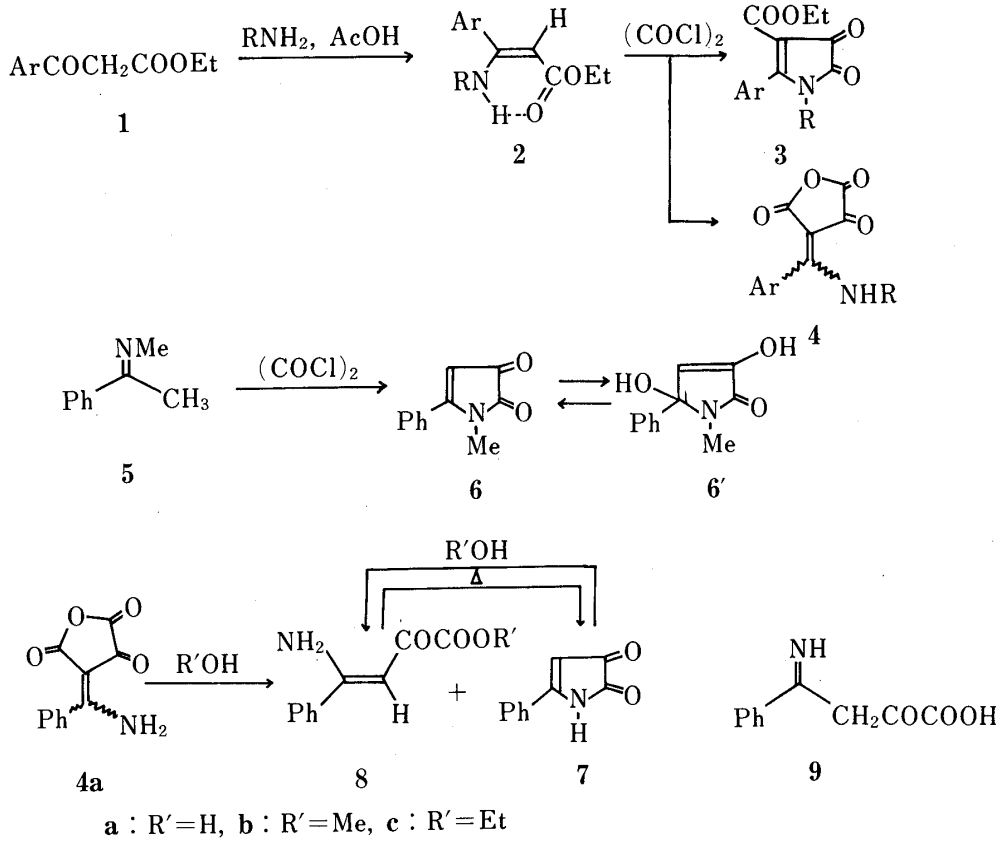

Chart 2

The enamino-esters, ethyl 3-substituted amino-3-aryl-2-propenoates (**2**), were readily prepared by heating ethyl aroyl acetates (**1**) with a 5-fold molar excess of the primary amines and acetic acid in ethanol. Acetic acid serves to prevent alkaline decomposition of the β-ketoesters, and was found to be superior to other acid catalysts such as *p*-toluenesulfonic acid[10] or phosphoric acid[11] in this enamination reaction. The enamino-esters thus obtained were purified by crystallization from an appropriate solvent, by distillation *in vacuo*, or by rapid silica gel chromatography. The enamino-(*Z*)-structure suggested by Furukawa[10] was confirmed by the presence of an olefinic proton signal in the nuclear magnetic resonance (NMR) spectra (δ 4.5—5.8) and by the deduction of intramolecular hydrogen bonding between NH and COOEt groups based on the low carbonyl frequences in the infrared (IR) spectra (see Table I).

Condensation of the enamino-esters (**2**) with oxalyl chloride in an aprotic solvent such as dry toluene, dioxane, ether or ether–dioxane gave the corresponding 2-aryl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-diones (**3**) in good yields, the results being summarized in Table II. Hydrogen chloride evolved during the reaction caused partial decomposition of **3** to increase the formation of the anhydride (**4**), which was sometimes isolated as a minor product. However, removal of hydrogen chloride with ether by distillation during the reaction avoided this

TABLE I. Physical and Spectral Properties of Enamino-esters (**2**)

	Enamino-ester (**2**) Ar	R	Yield (%)	bp or mp (°C) (Recryst. solv.)[a]	ν_{max} cm^{-1} [b]	δH in $CDCl_3$ –CH=C–N–
a	Ph	H	88	155—157 (5 mmHg)[c]	3450 3330 1660	4.90
b	Ph	Me	96	137—142 (3 mmHg)[d]	3280 1640	4.61
c	Ph	Et	85	128—129 (4 mmHg)	3260 1650	4.56
d	Ph	Iso-Pr	87	132—135 (4 mmHg)	3250 1650	4.55
e	Ph	CH_2Ph	92	74—75[e] (H–E)	3270 1660	4.68
f	Ph	CH_2COOEt	79	Oil	3270 1730 1660	4.73
g	Ph	$(CH_2)_2COOEt$	96	42—42.5 (H–E)	3270 1730 1650	4.60
h	Ph	$-CH_2CH=CH_2$	93	Oil	3280 1656	4.62
i	Ph	Ph	89	64—69[f] (H)	3250 1670	5.00
j	3,4-$(OCH_2O)C_6H_3$	H	87	45—48 (H–E)	3500 3330 1665	4.91
k	3,4-$(OCH_2O)C_6H_3$	CH_2COOEt	69	Oil	3275 1740 1650	4.73
l	4-Br–C_6H_4	H	95	56—60 (H–E)	3450 3330 1660	4.97
m	4-MeO–C_6H_4	H	62	180 (5 mmHg)	3330 1665	4.93
n	4-MeO–C_6H_4	Me	83	39—42 (H–E)	3270 1640	4.60
o	4-NO_2–C_6H_4	H	70	99—100[g] (E)	3450 3330 1660	5.03
p	4-NO_2–C_6H_4	Me	59	121—125 (E)	3270 1650	4.65

a) H, hexane; E, ether.
b) Nujol for solids, film for oils.
c) bp 141 °C (2 mmHg),[17] bp 117 °C (0.1 mmHg).[18]
d) bp 130—134 °C (2 mmHg).[19]
e) mp 68—69 °C[20] or mp 73—74 °C.[10]
f) mp 71 °C.[11]
g) mp 91 °C.[18]

undesired side reaction, thus improving the yield of the dioxopyrroline (**3**).

The dioxopyrrolines were usually obtained as orange-red crystals, and were characterized by their electronic absorptions around 400 nm due to the dioxopyrroline ring and by the high-frequency carbonyl absorptions around 1780—1760 cm^{-1} due to the five-membered ring ketone (Table III).

The anhydride (**4**), though various attempts at converting the dioxopyrroline **3a** to **4a** failed, was considered to be an acid-catalyzed decomposition product of **3**. The structure except for the stereochemistry was deduced from the following observations. The IR spectrum indicated the presence of an anhydride moiety (1840 and 1775 cm^{-1} for **4a**). A mild treatment of **4a** in ethanol with potassium hydroxide afforded, with loss of CO_2, an enamino-keto-acid (**8a**) as a major product and 2-phenyl-Δ^2-pyrroline-4,5-dione (**7**) as a minor product, which were identical with authentic samples prepared by the method reported by Mumm and Munchemeyer.[12] Similar alkaline treatment of **7** yielded **8a**, which cyclized on heating, regenerating **7**. Mumm and Munchemeyer[12] assigned the imino-keto structure (**9**) to this acid. However, the IR and ^{1}H-NMR spectra clearly indicated the enamino-(*Z*)-keto structure (**8a**). Heating of **4a** in methanol or ethanol solution provided the ester **8b** or **8c** with concomitant decarboxylation. The latter compounds were also prepared from **7** by alcoholysis. Pyrrolysis of the esters **8b** or **8c** also regenerated **7**.

It should be emphasized that the conjugation of the aryl group with the dioxopyrroline ring depends largely on the bulkiness of the *N*-substituent. In the ultraviolet (UV) spectra of **3** (Ar = Ph), the intensity of a conjugated aromatic absorption band around 280 nm progressively decreases with increase of the size of the *N*-substituent from H to iso-Pr (Fig. 1). This indicates that the probability of a coplanar arrangement of the two rings decreases as the rotation of the phenyl group is increasingly restricted by steric hindrance between the phenyl group and the *N*-substituents when an *N*-substituent become bulkier.

TABLE II. Physical Properties of 2-Aryl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-diones (3)

	Pyrrolinediones (3) Ar	R	Yield (%)	mp (°)	Appearance (Recryst. solv.)[a]	Formula	Analysis (%) Calcd (Found) C	H	N
a	Ph	H	85	185—187	Orange prisms (M–B)	$C_{13}H_{11}NO_4$	63.67 (63.17	4.52 4.50	5.71 5.63)
b	Ph	Me	78	170—172	Red prisms (B)	$C_{14}H_{13}NO_4$	64.86 (64.49	5.05 5.02	5.40 5.46)
c	Ph	Et	71	91—94	Red prisms (B–H)	$C_{15}H_{15}NO_4$	65.92 (65.81	5.53 5.45	5.13 5.30)
d	Ph	Iso-Pr	70	170—171	Red prisms (B–H)	$C_{16}H_{17}NO_4$	66.88 (67.07	5.96 5.97	4.88 5.17)
e	Ph	CH_2Ph	95	133—136	Orange prisms (B–H)	$C_{20}H_{17}NO_4$	71.63 (71.46	5.11 5.09	4.18 4.07)
f	Ph	CH_2COOEt	68	122—123	Orange prisms (B–H)	$C_{17}H_{17}NO_6$	61.63 (61.48	5.17 5.15	4.23 4.17)
g	Ph	$(CH_2)_2COOEt$	70	86—87	Orange prisms (B–H)	$C_{18}H_{19}NO_6$	62.60 (62.64	5.55 5.52	4.06 3.99)
h	Ph	$CH_2CH=CH_2$	75	52.5—54	Orange prisms (B–H)	$C_{16}H_{15}NO_4$	67.36 (67.13	5.40 5.13	4.91 4.82)
i	Ph	Ph	68	199—200	Red prisms (B–H)	$C_{19}H_{15}NO_4$	71.02 (70.72	4.71 4.64	4.36 4.16)
j	3,4-$(OCH_2O)C_6H_3$	H	60	198—202	Orange prisms (M–A)	$C_{14}H_{11}NO_6$	58.13 (57.98	3.83 3.79	4.84 4.85)
k	3,4-$(OCH_2O)C_6H_3$	CH_2COOEt	38	123—124	Yellow prisms (E–B)	$C_{18}H_{17}NO_8$	57.60 (57.31	4.57 4.55	3.73 3.77)
l	4-Br–C_6H_4	H	44	204—207	Orange prisms (M–B)	$C_{13}H_{10}BrNO_4$	48.17 (48.12	3.11 3.12	4.32 4.44)
m	4-MeO–C_6H_4	H	42	150—151	Yellow prisms (M–B)	$C_{14}H_{13}NO_5$	61.09 (61.22	4.76 4.68	5.09 5.12)
n	4-MeO–C_6H_4	Me	88	92—96	Orange prisms (B–H)	$C_{15}H_{15}NO_5$	62.28 (62.29	5.23 5.23	4.84 4.94)
o	4-NO_2–C_6H_4	H	65	189—190	Orange prisms (M–B)	$C_{13}H_{10}NO_6$	53.80 (54.06	3.47 4.59	9.65 9.52)
p	4-NO_2–C_6H_4	Me	50	186—189	Red prisms (B)	$C_{14}H_{12}NO_6$	55.26 (55.30	3.98 4.06	9.21 9.14)

a) M, CH_2Cl_2; B, benzene; H, hexane; A, acetone; E, ether.

Another remarkable chemical property of the dioxopyrrolines was their lability under solvolytic conditions. For example on long standing in an open vessel, the crystals gradually deteriorated with fading of the color due to uptake of a moisture. This change will be discussed in detail in the following paper.

Experimental

Unless otherwise stated, the following procedures were adopted. Melting points were taken on a Yanagimoto hot-stage mp apparatus and are uncorrected. IR spectra were taken in Nujol mulls with a Hitachi 260-10 spectrometer, and are given in cm^{-1}. UV spectra were recorded in dioxane solution with a Hitachi 200-10 spectrophotometer. ^{1}H-NMR spectra were taken in $CDCl_3$ solution with tetramethylsilane (TMS) as an internal standard on a Varian T-60 (60 MHz) or a Hitachi Perkin-Elmer (60 MHz) spectrometer.

Ethyl Aroylacetate (1)——Ethyl benzoylacetate is commercially available. Other ethyl aroylacetates, ethyl 4-bromobenzoylacetate,[13] ethyl 4-nitrobenzoylacetate,[14] ethyl 4-methoxybenzoylacetate,[15] ethyl 3,4-methylenedioxybenzoylacetate[16] were prepared from ArCOOH and ethyl acetoacetate, respectively, by the reported pro-

TABLE III. Spectral Data for 2-Aryl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-diones (**3**)

Compound	ν_{max} (Nujol) cm^{-1} C=O	UV λ_{max} (dioxane) nm ($\varepsilon \times 10^{-3}$)
3a	1780, 1735, 1660	274 (9.3), 395 (4.3)
3b	1760, 1705	285sh (6.1), 408 (4.0)
3c	1758, 1720, 1690	285sh (4.5), 408 (3.1)
3d	1760, 1735, 1675	282sh (3.9), 408 (3.3)
3e	1760, 1730, 1725	285sh (4.2), 405 (3.4)
3f	1780, 1740, 1715, 1690	280sh (4.4), 395 (3.0)
3g	1760, 1720	283sh (4.5), 395 (3.1)
3h	1760, 1721, 1680	288sh (4.4), 405 (3.2)
3i	1770, 1720	240 (13.5), 305 (5.9), 405 (3.1)
3j	1780, 1740, 1650	255 (11.4), 305sh (4.5), 350 (8.3), 403 (7.8)
3k	1770, 1720, 1680	262sh (7.5), 360 (5.7), 400 (5.7)
3l	1795, 1730, 1710	295 (12.3), 400 (4.8)
3m	1770, 1740, 1650	255 (4.3), 325 (7.4), 402 (3.9)
3n	1760, 1745, 1700, 1670	333 (8.6), 415 (4.2)
3o	1800, 1720, 1660	233 (12.6), 271 (14.1), 398 (4.2)
3p	1780, 1750, 1690	228 (15.6), 264 (12.2), 408 (2.9)

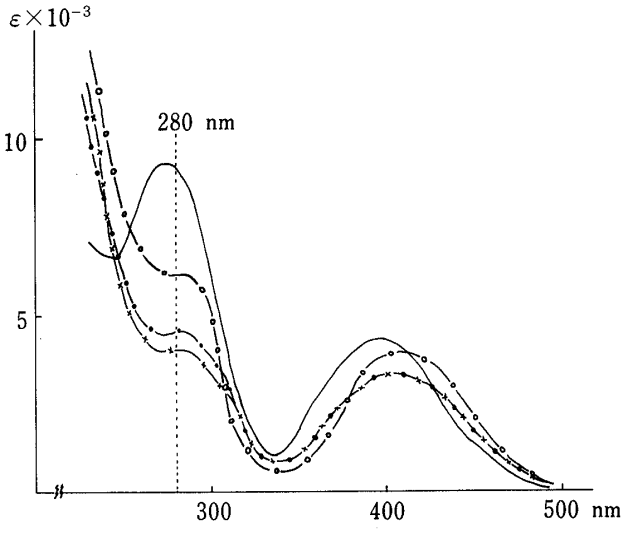

Fig. 1. UV Spectra of 3-Ethoxycarbonyl-2-phenyl-Δ^2-pyrroline-4,5-diones (**3a—d**) in Dioxane

——, R=H (**3a**); —○—, R=Me (**3b**); —●—, R=Et (**3c**); —×—, R=iso-Pr (**3d**).

cedures.

Ethyl 3-Amino-3-aryl-2-propenoate (2) (General Procedure)——A mixture of **1** (0.1 mol) and ammonium acetate (0.5 mol) (in the case of **2a**, **2j**, **2l**, **2m**, and **2o**) or a primary amine (0.5 mol) neutralized with acetic acid (0.5 mol) in ethanol (100 ml) was heated under reflux for 2—3 h. After evaporation of the solvent *in vacuo*, the residue was taken up in CH_2Cl_2, and the organic layer was washed with 5% HCl and water, then dried over Na_2SO_4, and concentrated to give the crude enamino-ester **2**, which was purified by distillation *in vacuo* (**2a**, **2b**, **2c**, **2d**, and **2m**), by recrystallization (**2e**, **2i**, **2o**, and **2p**), or by silica gel chromatography (Wakogel C-200) eluting with CH_2Cl_2 (**2f**, **2g**, **2h**, **2j**, **2k**, **2l**, and **2n**).

2-Aryl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-diones (3) (General Procedure)——Oxalyl chloride (0.1 mol) was slowly added to **2** (0.1 mol) in dry ether (50 ml) at 0 °C under stirring. After addition of dioxane (20 ml), the reaction mixture was slowly warmed to 50 °C, and ether was slowly distilled off to remove hydrogen chloride evolved during the reaction. After the evolution of hydrogen chloride had ceased, the mixture was cooled in an ice bath, and the precipitated crystals were collected by filtration. Recrystallization from an appropriate solvent gave pure pyrrolinediones **3**.

The Anhydride (4)——i) Oxalyl chloride (0.1 mol) was slowly added to **2a** (0.1 mol) in dry toluene (50 ml) at 0 °C under stirring. The mixture was warmed at 60 °C for 4 h. The precipitate formed upon cooling was collected and treated with boiling CH_2Cl_2. The CH_2Cl_2-insoluble fraction gave **4a** as a colorless amorphous powder (15% yield),

which could not be obtained in a pure form since it was barely soluble in aprotic solvents such as benzene, CH_2Cl_2, and ether, and was readily decomposed on treatment with protic solvents. IR: 1840, 1775, 1698, 1645. UV nm (ε): 258 (9800), 322 (10500). From the CH_2Cl_2-soluble fraction, **3a** was isolated in 45% yield.

ii) Similarly **2j** was treated in toluene with oxalyl chloride to afford **4j** (30%) and **3j** (20%). **4j** was barely soluble in aprotic solvents and was not obtained in a pure form. Colorless amorphous powder. IR: 1820, 1745, 1645. UV nm (ε): 253 (7600), 340 (9400).

1-Methyl-2-phenyl-Δ^2-pyrroline-4,5-dione (6)——Oxalyl chloride (5.9 g) was slowly added to the imine **5** (6.2g) (prepared from acetophenone and methylamine in the presence of $TiCl_4$) in dry toluene (10 ml) at 0 °C under stirring. Stirring was continued for a further 1 h at room temp. to give a pale yellow precipitate, which was treated with boiling CH_2Cl_2 for 2 h and filtered. The CH_2Cl_2-soluble fraction was chromatographed over silica gel to give the monohydrate of **6** (possibly **6'**; this will be fully discussed in a forthcoming paper), as colorless prisms, mp 130—140 °C (dec.) (300 mg; 5%). IR: 3350, 1730, 1700, 1670, 1650. UV nm (ε): 228 (10000), 285 (2700). Careful heating of the hydrate on a hot plate afforded **6**, as orange prisms from benzene–hexane, mp 160—163 °C. IR: 1770, 1740, 1680, 1605. UV nm (ε): 255 (3900), 285 sh (2200), 405 (650). *Anal.* Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.21; H, 4.80; N, 7.32.

Alkali Treatment of 4a——A suspension of **4a** (1.4 g) in ethanol (100 ml) was treated with 10% KOH (10 ml) at 0 °C for 30 min. After acidification with 5% HCl to pH 3, the mixture was extracted with CH_2Cl_2 and the extract was washed with H_2O, dried over Na_2SO_4, and concentrated to give a crystalline residue. Several crystallizations of this product from CH_2Cl_2 gave **8a** (900 mg; 73%) from the readily soluble fraction as pale yellow needles, mp 157—159 °C (lit.,[12] 161 °C). IR: 3270, 3200, 3100, 1720, 1600. UV λ_{max}^{EtOH} nm (ε): 243 (7800), 342 (17000). *Anal.* Calcd for $C_{10}H_9NO_3$: C, 62.82; H, 4.75; N, 7.33. Found: C, 62.65; H, 4.70; N, 7.45. The less soluble fraction gave **7** (100 mg; 8%), orange prisms, mp 220—224 °C (lit.,[12] mp 210 °C). IR: 3170, 1780, 1690. UV nm (ε): 270 (14000), 405 (3600). ^{1}H-NMR δ: 5.8 (1H, s, –CH=), 7.4—8.0 (5H, m, PhH). *Anal.* Calcd for $C_{10}H_7NO_2$: C, 69.36; H, 4.07; N, 8.09. Found: C, 69.21; H, 4.02; N, 8.01. Careful sublimation of **8a** at 150 °C/1 mmHg afforded **7** as orange prisms, mp 220—222 °C.

Alcoholysis of 4a——i) A solution of **4a** (410 mg) in methanol (30 ml) was heated under reflux for 11 h. Evaporation of the solvent gave a yellowish oil, which was crystallized from Et_2O–CH_2Cl_2 to yield the methyl ester **8b** (293 mg; 81%), as colorless prisms, mp 102—104 °C. IR: 3250, 3100, 1730, 1620. UV λ_{max}^{EtOH} nm (ε): 354 (19000), 253 (7000). ^{1}H-NMR δ: 3.88 (3H, s), 6.33 (1H, s, –CH), 7.5—7.8 (5H, m, PhH). *Anal.* Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.29; H, 5.44; N, 6.74.

ii) Similarly, the ethyl ester **8c** was obtained in a yield of 80%, as colorless prisms from Et_2O–hexane, mp 100—101 °C. IR: 3200, 3100, 1730, 1610. UV λ_{max}^{EtOH} nm (ε): 353 (16400), 254 (6300). ^{1}H-NMR δ: 1.37 (3H, t, J=7 Hz) and 4.33 (2H, q, J=7 Hz, $COOCH_2CH_3$), 6.30 (1H, s, –CH=), 7.5—8.8 (5H, m, PhH). *Anal.* Calcd for $C_{12}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.87; N, 6.22; N, 6.82.

Methanolysis of 2-Phenyl-Δ^2-pyrroline-4,5-dione (7)——A methanolic solution of **7** (467 mg) was heated under reflux for 8 h. After evaporation of the solvent, the residue was crystallized from Et_2O–CH_2Cl_2 to yield **8b** (489 mg; 88%), mp 102—104 °C, which was identical with the sample obtained from **4a**. Careful sublimation of **8b** at 140 °C/1 mmHg afforded **7**, as orange prisms, mp 220—222 °C.

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