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3-Hydroxypyrroles. I. A General Synthetic Route to 4,5-Unsubstituted Alkyl 3-Hydroxypyrrole-2-carboxylates[1]

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The synthesis of 4,5-unsubstituted alkyl 3-hydroxypyrrole-2-carboxylates was described. An equimolar mixture of glycine esters (**6**) and diethyl ethoxymethylenemalonate (**7**) gave the condensation products (**8**) with liberation of ethanol. 3-Hydroxypyrrole-2,4-dicarboxylates (**9**) were obtained by the Dieckmann condensation of **8** using alkoxide as condensing agent. Selective partial hydrolysis of pyrrole-diesters (**9**) using a large excess of alkali hydroxide afforded the 4-carboxylic acids (**10**), which readily gave alkyl 3-hydroxypyrrole-2-carboxylates (**5**) on decarboxylation in boiling β-picoline or pyridine–acetic acid in good yields.

Keywords——3-hydroxypyrrole; 4-oxo-2-pyrroline; alkyl 3-hydroxypyrrole-2-carboxylate; glycine esters; Dieckmann cyclization; amine catalysis in Dieckmann reaction; differential hydrolysis of diester; decarboxylation; intramolecular hydrogen bonding; 3-hydroxypyrrole-2,4-dicarboxylate

3-Hydroxypyrrole (**1**) is an unknown compound, and little has been reported of the chemistry of this system. However, it is found as a key skeleton in the antibiotic prodigiosins[3] (**2**), and its analogues have been the subject of studies[4] associated mainly with their tautomeric structure, 4-oxo-2-pyrroline (**3**). Pyrrolinone (**3**) is of interest as the smallest

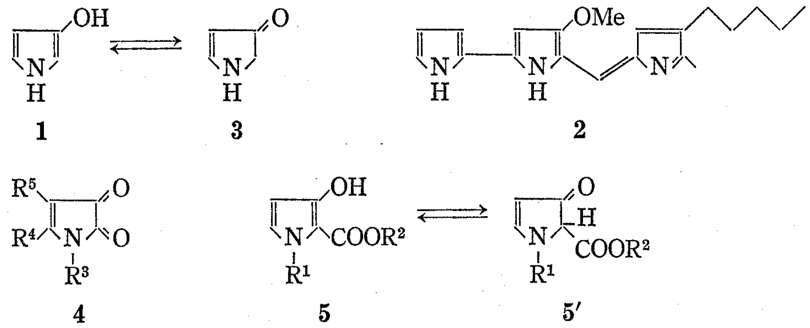

Chart 1

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[1] Preliminary communication of this paper has appeared in *Heterocycles*, **6**, 1821 (1977).

[2] Location: *133-1, Yamada-kami, Suita, Osaka 565, Japan.*

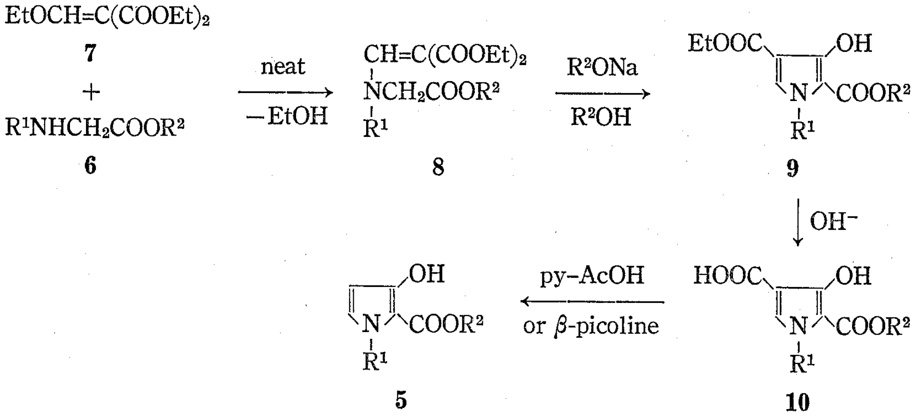
[3] *a*) H.H. Wasserman, J.E. McKeon, L.A. Smith, and P. Forgione, *J. Am. Chem. Soc.*, **82**, 506 (1960); *b*) H. Rapoport and K.G. Holden, *ibid.*, **84**, 635 (1962); *c*) B.S. Deol, J.R. Alden, J.L. Still, A.V. Robertson, and J. Winkler, *Aust. J. Chem.*, **27**, 2657 (1974).

[4] *a*) E. Benary and B. Silbermann, *Ber.*, **46**, 1363 (1913); *b*) E. Benary and R. Konrad, *Ber.*, **56B**, 44 (1923); *c*) J. Davoll, *J. Chem. Soc.*, **1953**, 3802; *d*) R. Kuhn and G. Osswald, *Chem. Ber.*, **89**, 1423 (1956); *e*) A. Treibs and A. Ohorodnik, *Ann.*, **611**, 139 (1958); *f*) *Idem, ibid.*, **611**, 149 (1958); *g*) H. Rapoport and C.D. Willson, *J. Am. Chem. Soc.*, **84**, 630 (1962); *h*) N. Yoshida, *Yakugaku Zasshi*, **86**, 158 (1966); *i*) E. Winterfeldt and H-J. Dillinger, *Chem. Ber.*, **99**, 1558 (1966); *j*) R. Chong and P.S. Clezy, *Aust. J. Chem.*, **20**, 935 (1967); *k*) S.K. Khetan and M.V. George, *Tetrahedron*, **25**, 527 (1969); *l*) R. Fuks and H.G. Viehe, *ibid.*, **25**, 5721 (1969); *m*) H.Bauer, *Ann.*, **736**, 1 (1970); *n*) I.T. Kay and N. Punja, *J. Chem. Soc.* (*C*), **1970** 2409; *o*) G. Kresze and H. Härtner, *Ann.*, **1973**, 650; *p*) E. Campaigne and G.M. Shutske, *J. Heterocycl. Chem.*, **11**, 929 (1974); *q*) S.K. Gupta, *Synthesis*, **1975**, 726.

vinylogous lactam in the field of structure-reactivity relationships. It is also expected to find practical use in the synthetic field as a five-membered azacyclic synthon because of its versatile functionalities, *i.e.*, enone, enamine and active methylene systems, concentrated in its simple molecule.

Recently, Tsuda *et al.*[5] have investigated the chemistry of 4,5-dioxo-2-pyrroline derivatives (**4**) as important synthetic intermediates for alkaloids. We set about the fundamental study of pursuing the possible applicability of 4-oxo-2-pyrroline (3-hydroxypyrrole) derivatives in the synthetic design of azacyclic molecules, and began with the synthesis of the simple derivatives of 3-hydroxypyrrole (**1**).

In contrast to the instability of poorly substituted 3-hydroxypyrroles, the 2-carboxy derivatives are known to be relatively stable. 3-Hydroxypyrrole-2-carboxylates (**5**) are expected to have both the pyrrole type or enamine type reactivity at the 4 and/or 5 position and the pyrrolinone (5′) type reactivity as an active methyne at the 2 position, and to be a possible substitute, for 4-oxo-2-pyrroline, with moderate stability. Therefore we have first developed a general synthetic route to 4,5-unsubstituted alkyl 3-hydroxypyrrole-2-carboxylates (**5**). A straightforward route to **5** is summarized in Chart 2.



	R^1	R^2		R^1	R^2
a	H	Et	**e**	CH_2Ph	Et
b	H	*t*-Bu	**f**	CH_2Ph	*t*-Bu
c	Me	Et	**g**	Ph	Et
d	Me	*t*-Bu	**h**	Ph	*t*-Bu

Chart 2

TABLE I. UV Spectra and Yields of **8**

Compounds	UV(EtOH)nm(ε)	Yield (%)
8a	220(14800), 278(19300)	74.3
b	221(16400), 279(29400)	90.0
c	282(21200)	63.5
d	282(18100)	21.8[a]
e	282(17600)	79.5
f	283(22500)	83.2
g	228(10700), 292(19600)	79.3
h	227(8500), 294(18700)	85.4

[a] From *t*-butyl chloroacetate.

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5) Y. Tsuda, K. Isobe, and A. Ukai, *J.C.S. Chem. Commun.*, **1971**, 1554; T. Sano and Y. Tsuda, *Heterocycles*, **4**, 1229 (1976); T. Sano, Y. Tsuda, H. Ogura, K. Furuhata, and Y. Iidaka, *ibid.*, **4**, 1233 (1976); Y. Tsuda, Y. Horiguchi, and T. Sano, *ibid.*, **4**, 1237 (1976); *idem*, *ibid.*, **4**, 1355 (1976).

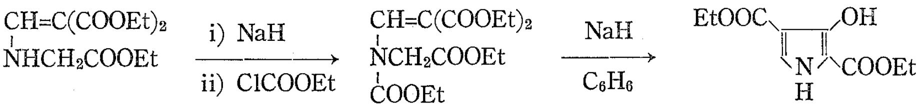
Admixture of an equimolar amount of both glycine esters (**6**) and diethyl ethoxymethylenemalonate (**7**) gave the condensation products (**8**) in good yields with liberation of ethanol (Table I). Sarcosin *t*-butyl ester (**6d**) was synthesized by the reaction of *t*-butyl chloroacetate[6] with a large excess of methylamine in ether solution (see Experimental).[7] When R^1 is small in size (H, Me), this condensation reaction is exothermic, but when R^1 is bulky (CH_2Ph, Ph), especially when R^1 is phenyl, prolonged heating is required for completion of the reaction owing to decreased nucleophilicity of the nitrogen.

The Dieckmann cyclization was performed in the alcoholic solution (R^2OH) containing sodium alcoholate. The yield is generally good, but, only in the case of **8a**, the yield is 24% at most (Table II). This was improved by use of the following reaction sequences shown in Chart 3. The enaminoester (**8a**) was converted into the N-ethoxycarbonyl derivative (**11**) in good yield by treatment with sodium hydride in benzene followed by acylation with ethyl chloroformate, and was cyclized to **9a** by use of sodium hydride in benzene in 55% overall yield. This reaction sequences does not involve the formation of isomer,[3b] and the ethoxycarbonyl group on the nitrogen atom seems to be removed after cyclization, since **8a** failed to cyclize under the condition described above (NaH/benzene).

Table II. Condensing Agents, UV Spectra and Yields of **9**

Compounds	Condensing agents and solvents	UV(EtOH)nm(ε)	Yields %
9a	EtONa/EtOH	226(29500), 258(17200)	23.7[a]
b	*t*-BuONa/*t*-BuOH	226(30800), 259(18000)	66.0
c	EtONa/EtOH	229(27400), 262(12500)	85.7
d	*t*-BuONa/*t*-BuOH	229(30700), 262(14500)	66.8
e	EtONa/EtOH	230(30200), 262(14500)	84.7
f	*t*-BuONa/*t*-BuOH	229(28300), 263(11600)	77.3
g	EtONa/EtOH	232(27800), 262(11500)	75.6
h	*t*-BuONa/*t*-BuOH	230(24000), 262(10400)	60.1

a) This yield was improved by the method *via* an alternative route.



8a **11** **9a**

Chart 3

Surprisingly, only **8c** was partially, sometimes largely, converted to the hydroxypyrrole (**9c**) during distillation of the crude product. Perhaps, this Dieckmann cyclization would be catalyzed by basic materials (*e.g.*, ethyl sarcosinate) contained in the crude mixture. The pure **8c** was not converted to **9c** on distillation, but largely converted to **9c** in boiling ethanol containing a catalytic amount of diisopropylamine after 10 hr. We investigated a Dieckmann cyclization of **8c** by use of a small amount of some weak bases in several solvents (Table III). It is obvious that **8c** was easily cyclized to **9c** by catalytic amounts of weak bases. These reaction conditions, however, require the prolonged reaction time as the scale becomes larger. Therefore, it is preferable to perform the cyclization under a usual condition (EtONa/EtOH).

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[6] R.H. Baker, "Organic Syntheses," Coll. Vol. III, ed. by E.C. Horing, John Wiley and Sons, Inc., New York, 1955, p. 144.

[7] The yield is low, and the purification procedure is troublesome. Then, the crude **6d** was used for the next condensation with **7**. The yield of **8d** given in Table I indicates the value from *t*-butyl chloroacetate.

Table III. Catalytic Dieckmann Cyclization of **8c**

Catalysts	Solvents	Results after 3 hr's refluxing
K_2CO_3	Abs. EtOH	Completion
K_2CO_3	Dry benzene	Almost recovery of the starting material
K_2CO_3	EtOH+benzene	Partial progress
K_2CO_3	Dry toluene	Partial progress
Et_3N	Abs. EtOH	Slight progress
Et_3N	Dry benzene	Slight progress
Triton B	Dry benzene	Completion
Iso-Pr_2NH	Abs. EtOH	Slight progress

Among the 3-hydroxypyrroles synthesized by us, only diethyl 3-hydroxypyrrole-2,4-dicarboxylate (**9a**) has previously been synthesized by Rapoport and Holden[3b] *via* the con densation of ethyl N-ethoxycarbonylglycinate with **7** by use of sodium in benzene. This method, however, is in low yield and troublesome to isolate the product owing to the concurrent formation of the 2-hydroxy isomer.[8]

Selective partial hydrolysis of diesters (**9**) using a large excess of alkali hydroxide afforded the 4-carboxylic acids (**10**). This selectivity of hydrolysis would result from the inaccessibility of hydroxide anion to the C-2 ester carbonyl owing to the delocalization of initially formed enolate anion to the C-2 ester carbonyl, as mentioned by Chong and Clezy[4j] to account for the failure of the attempted basic hydrolysis of a similar system.

The crude 4-carboxylic acids (**10**) so obtained were decarboxylated into 3-hydroxypyrrole-2-carboxylates (**5**) in boiling β-picoline or pyridine–acetic acid in good yields. The latter

Table IV. Hydrolysis Reagents for **9**, Decarboxylation Solvents for **10**, Yields of **5** from **9**, and UV Spectra of **5**

Compounds	Hydrolysis reagents	Decarboxylation solvents	Yields %	UV(EtOH) nm(ε)
a	LiOH	Pyridine–AcOH	60.0	263(17000)
b	NaOH	β-Picoline	65.5	265(16300)
c	NaOH	Pyridine–AcOH	76.5	264(16700)
d	NaOH	β-Picoline	44.4	264(15200)
e	NaOH	Pyridine–AcOH	66.0	264(14900)
f	NaOH	β-Picoline	63.4	265(15900)
g	NaOH	Pyridine–AcOH	42.4	262(12500)
h	NaOH	β-Picoline	47.8	264(12500)

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8) While several methods for synthesizing 3-hydroxypyrrole derivatives have been reported,[4] most of them cannot be applied to the synthesis of 4,5-unsubstituted derivatives, except for the one by Rapoport and Holden.[3b] For example, Chong and Clezy[4j] have reported the synthesis of several 4- and/or 5-substituted 3-hydroxypyrrole-2-carboxylates (**14**) by the cyclization of enaminoesters (**13**) available from the condensation of β-keto esters (**12**) with glycine ester (**6a**), but the simplest starting material formylacetate (**12**; $R^6=R^7=H$) leading to 4,5-unsubstituted derivatives is unavailable in a free form (Chart 4).

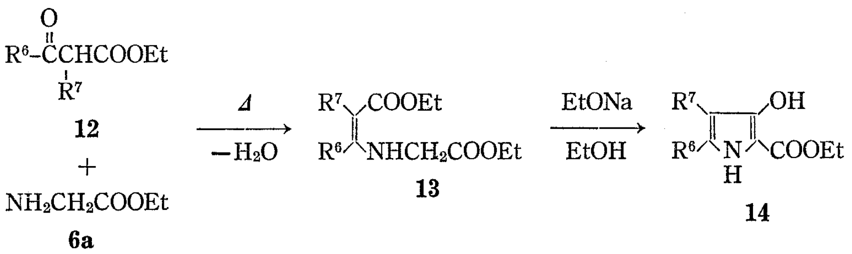

Chart 4

condition could not be used in the case of R^2=*t*-Bu (**b**, **d**, **f**, **h**). The reagents of hydrolysis and the yields of **5** from **9** are listed in Table IV.

Though each of the pyrroles (**5**) synthesized shows single hydroxyl and carbonyl band in the infrared (IR) spectrum in its crystalline state, it shows two hydroxyl and two carbonyl bands in carbon tetrachloride solution irrespectively of the concentration.9) For example, N-methyl derivative (**5c**) shows maxima at 3491, 3320 cm^{-1} as hydroxyl and 1713, 1655 cm^{-1} as ester carbonyl in solution, but, in KCl disk, 3320, 1640 cm^{-1} only. This is probably due to the two types of intramolecular hydrogen bondings; one between hydroxyl and ester-carbonyl oxygen and the other between hydroxyl and ester-alkoxy oxygen as in the case of γ-resorcylate.10) In the proton magnetic resonance (PMR) spectra of the pyrroles (**5**), a pair of doublets (when R^1=alkyl) or triplets (when R^1=H) was observed in the region: δ 5.53—5.86 (C-4 H) and 6.33—6.71 (C-5 H) with the coupling constants *ca.* 3.0 Hz, the feature being closely similar to that of known pyrroles and lacking in the absorption due to a pyrrolinone structure. The pyrrole structure of **5** is evident especially in their ultraviolet (UV) spectra where there appears one absorption maximum at 262—265 nm for the hydroxypyrrole esters (**5**).11)

Experimental

All melting points and boiling points are uncorrected. IR, Mass (MS), UV and PMR spectra were recorded on Hitachi EPI-G3, Hitachi RMU-6E, Hitachi 124 Spectrophotometer and Hitachi R-20A, respectively. In the PMR spectra, tetramethylsilane was used as an internal standard, and coupling constants (*J*) are given in Hz. All organic extracts were washed with satd. NaCl solution and dried over anhydrous magnesium sulfate before evaporation.

Ethyl N-[2,2,-Bis(ethoxycarbonyl)vinyl]glycinate12) **(8a)**——Ethyl glycinate13) (11.2 g) and diethyl ethoxymethylenemalonate14) (7) (23.8 g) were directly mixed and allowed to result in exothermic reaction with liberation of ethanol. The mixture crystallized on standing and was recrystallized from EtOH to give **8a** (22.3 g, 74.3%) as colorless plates, mp 97.5—99.0° (lit.12) 97—98°). IR ν_{max}^{KCl} cm^{-1}: 3320, 1748, 1678, 1615. MS *m/e*: 273 (M^+, 11.0%), 154 (100%). PMR ($CDCl_3$) δ: 1.28 (3H, t, *J*=7.2), 1.30 (3H, t, *J*=7.2), 1.35 (3H, t, *J*=7.2), 4.07 (2H, d, *J*=6.2, N-CH_2-), 4.18 (2H, q, *J*=7.2), 4.25 (4H, q, *J*=7.2, $O\underline{CH_2}CH_3 \times 2$), 7.90 (1H, d, *J*=14.0, N-CH=), 9.20 (1H, br, NH). *Anal.* Calcd. for $C_{12}H_{19}NO_6$: C, 52.74; H, 7.01; N, 5.13. Found: C, 52.75; H, 7.00; N, 5.32.

***t*-Butyl N-[2,2-Bis(ethoxycarbonyl)vinyl]glycinate (8b)**——Compound **8b** was prepared in a manner similar to that for **8a** starting from an equimolar amount of *t*-butyl glycinate15) and **7**. Recrystallization from ether to give **8b** (90.0%) as colorless needles, mp 96.0—96.5°. IR ν_{max}^{KCl} cm^{-1}: 3311, 1749, 1682, 1627. MS *m/e*: 301 (M^+, 14.0%), 57 (100%). PMR ($CDCl_3$) δ: 1.30 (3H, t, *J*=7.0), 1.36 (3H, t, *J*=7.0), 1.49 (9H, s) 4.00 (2H, d, *J*=6.0, N-CH_2-), 4.20 (2H, q, *J*=7.0), 4.27 (2H, q, *J*=7.0), 7.91 (1H, d, *J*=14.0, N-CH=), 9.20 (1H, br, NH). *Anal.* Calcd. for $C_{14}H_{23}NO_6$: C, 55.80; H, 7.69; N, 4.65. Found: C, 55.67; H, 7.66; N, 4.79.

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9) Pfeiffer and Bauer have reported, in the experimental part for the 4,5-disubstituted derivatives, that there appear two hydroxyl and two ester-carbonyl bands corresponding to free and intramolecularly hydrogen-bonded ones; G. Pfeiffer and H. Bauer, *Ann.*, **1976**, 383.

10) Ethyl γ-resorcylate was reported to show two kinds of intramolecularly hydrogen-bonded hydroxyl absorptions at 3461 and 3195 cm^{-1}: see C.J.W. Brooks, G. Eglinton, and J.F. Morman, *J. Chem. Soc.*, **1961**, 661.

11) Known pyrrole-2-carboxylates show two absorption maxima, *e.g.*, at 240 nm (ε=6000) and 266 nm (ε=15100) for methyl 1-methylpyrrole-2-carboxylate: see R. Andrisano and G. Pappalardo, *Gazz. Chim. Ital.*, **85**, 1430 (1955); and the simple pyrrolinone 2,3-dimethyl-4-oxo-2-pyrroline shows absorption maximum at 315 nm (ε=7000).4m)

12) Levy has reported the synthesis of **8a** from ethyl sodiodicarboxyglutaconate and ethyl glycinate hydrochloride; S.I. Levy, *J. Chem. Soc.*, **105**, 29 (1914).

13) C. Harries and M. Weiss, *Ann.*, **327**, 355 (1903); E. Fischer, *Ber.*, **34**, 433 (1901); E. Campaigne and G.M. Shutske, *J. Heterocycl. Chem.*, **11**, 929 (1974); *idem*, *ibid.*, **13**, 497 (1976).

14) W.E. Parham and L.J. Reed, "Organic Syntheses," Coll. Vol. III, ed. by E.C. Horing, John Wiley and Sons, Inc., New York, 1955, p. 395.

15) A.T. Moore and H.N. Rydon, "Organic Syntheses," Coll. Vol. V, ed. by H.E Baumgarten, John Wiley and Sons, Inc., New York, 1973, p. 586.

Ethyl N-[2,2-Bis(ethoxycarbonyl)vinyl]sarcosinate (8c)——Compound **8c** was prepared in a manner similar to that for **8a** starting from 6.93 g of ethyl sarcosinate[16] (**6c**) and 12.8 g of **7**. Distillation at 130° (0.03 mmHg) gave **8c** (10.7 g, 63.5%) as a colorless oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1750, 1690, 1610. MS *m/e*: 287 (M$^+$, 19.0%), 140 (100%). PMR (CCl_4) δ: 1.25 (3H, t, $J=7.0$), 1.28 (3H, t, $J=7.0$), 1.32 (3H, t, $J=7.0$), 2.98 (3H, s), 3.96 (2H, s), 4.10 (2H, q, $J=7.0$), 4.14 (2H, q, $J=7.0$), 4.20 (2H, q, $J=7.0$), 7.22 (1H, s). *Anal.* Calcd. for $C_{13}H_{21}NO_6$: C, 54.34; H, 7.37; N, 4.88. Found: C, 53.89; H, 7.29; N, 5.11.

***t*-Butyl Sarcosinate (6d)**——An ethereal solution (100 ml) of *t*-butyl chloroacetate[6] (5.0 g) was added to a stirred ether solution (80 ml) saturated with methylamine. After stirring overnight, the resulting precipitate was filtered off, and the filtrate was concentrated and passed through a short alumina column. The eluate was concentrated under vacuum and used for the next condensation with **7** without further purification. PMR (CCl_4) δ: 1.45 (10H), 2.35 (3H), 3.09 (2H).

***t*-Butyl N-[2,2-Bis(ethoxycarbonyl)vinyl]sarcosinate (8d)**——A mixture of the crude *t*-butyl sarcosinate (**6d**) (from 5.0 g of *t*-butyl chloroacetate) and 2.0 g of **7** was heated at 80—90° for 1 hr, and was distilled at 160° (1 mmHg) to give **8d** (2.3 g, 21.8% from *t*-butyl chloroacetate) as a colorless oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1750, 1695, 1612. MS *m/e*: 315 (M$^+$, 4.2%), 42 (100%). PMR (CCl_4) δ: 1.27 (3H, t, $J=7.0$), 1.31 (3H, t, $J=7.0$), 1.49 (9H, s), 2.98 (3H, s), 3.83 (2H, s), 4.11 (2H, q, $J=7.0$), 4.24 (2H, q, $J=7.0$), 7.20 (1H, s). *Anal.* Calcd. for $C_{15}H_{25}NO_6$: C, 57.13; H, 7.99; N, 4.44. Found: C, 56.52; H, 7.90; N, 4.71.

Ethyl N-Benzyl-N-[2,2-bis(ethoxycarbonyl)vinyl]glycinate (8e)——A mixture of ethyl N-benzylglycinate[17] (**6e**) (9.83 g) and **7** (10.9 g) was heated at 120° for 2 hr and distilled at 180° (0.006 mmHg) to give **8e** (14.6 g, 79.5%) as a pale yellow oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1760, 1708, 1695, 1606. MS *m/e*: 363 (M$^+$, 6.2%), 91 (100%). PMR (CCl_4) δ: 1.22 (3H, t, $J=7.5$), 1.23 (3H, t, $J=7.5$), 1.25 (3H, t, $J=7.5$), 3.82 (2H, s, N-CH_2-CO), 4.07 (2H, q, $J=7.5$), 4.10 (2H, q, $J=7.5$), 4.13 (2H, q, $J=7.5$), 4.51 (2H, s, N-CH_2-Ph), 7.25 (5H, s), 7.45 (1H, s). *Anal.* Calcd. for $C_{19}H_{25}NO_6$: C, 62.79; H, 6.93; N, 3.85. Found: C, 62.73; H, 6.86; N, 4.15.

***t*-Butyl N-Benzyl-N-[2,2-bis(ethoxycarbonyl)vinyl]glycinate (8f)**——A mixture of *t*-butyl N-benzylglycinate[18] (**6f**) (17.0 g) and **7** (16.6 g) was heated at 120° for 2 hr and allowed to crystallize on standing at room temperature. Recrystallization from *n*-hexane gave **8f** (25.0 g, 83.2%) as colorless plates, mp 70.0—72.0°. IR $\nu_{\max}^{\mathrm{KCl}}$ cm^{-1}: 1747, 1715, 1688. MS *m/e*: 391 (M$^+$, 3.8%), 91 (100%). PMR (CCl_4) δ: 1.27 (6H, t, $J=7.2$, $OCH_2\underline{CH_3}\times 2$), 1.46 (9H, s), 3.27 (2H, s, N-CH_2-CO), 4.13 (2H, q, $J=7.2$), 4.14 (2H, q, $J=7.2$), 4.52 (2H, s, N-CH_2-Ph), 7.31 (5H, s), 7.49 (1H, s). *Anal.* Calcd. for $C_{21}H_{29}NO_6$: C, 64.43; H, 7.47; N, 3.58. Found: C, 64.40; H, 7.47; N, 3.79.

Ethyl N-[2,2-Bis(ethoxycarbonyl)vinyl]-N-phenylglycinate (8 g)——A mixture of ethyl N-phenylglycinate[19] (**6 g**) (20 g) and **7** (24.1 g) was heated at 130—135° for 4 hr and distilled at 175° (0.009 mmHg) to give **8 g** (31.0 g, 79.2%) as a pale yellow oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1760, 1745, 1725, 1705, 1612. MS *m/e*: 349 (M$^+$, 47.2%), 276 (100%). PMR (CCl_4) δ: 1.20 (3H, t, $J=7.5$), 1.23 (3H, t, $J=7.5$), 1.25 (3H, t, $J=7.5$), 3.95 (2H, q, $J=7.5$), 4.10 (2H, q, $J=7.5$), 4.24 (2H, q, $J=7.5$), 4.36 (2H, s), 7.18 (5H, m), 7.51 (1H, s). *Anal.* Calcd. for $C_{18}H_{23}NO_6$: C, 61.88; H, 6.64; N, 4.01. Found: C, 62.01; H, 6.53; N, 4.37.

***t*-Butyl N-Phenylglycinate (6h)**——A mixture of *t*-butyl chloroacetate (20 g), aniline (22.4 g) and triethylamine (20 ml) was stirred for 4 days at room temperature. Dry ether (100 ml) was added to the reaction mixture, and the resulting precipitate was filtered off. The filtrate was washed with water and dried. The solvent was removed, and the residue was distilled at 119° (3 mmHg) to give **6h** (10.8 g, 38.9%) as a colorless oil. IR $\nu_{\max}^{\mathrm{film}}$ cm^{-1}: 3340, 1730, 1605. PMR ($CDCl_3$) δ: 1.49 (9H, s), 3.55 (1H, br), 3.79 (2H, s), 6.50—7.35 (5H,m).

***t*-Butyl N-[2,2-Bis(ethoxycarbonyl)vinyl]-N-phenylglycinate (8h)**——A mixture of *t*-butyl N-phenylglycinate (**6h**) (3.0 g) and **7** (3.2 g) was heated at 150° for 5 hr and distilled at 195° (0.02 mmHg) to give **8h** (4.67 g, 85.4%) as a pale yellow oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1755, 1726, 1706, 1613. MS *m/e*: 377 (M$^+$, 6.5%), 102 (100%). PMR (CCl_4) δ: 1.25 (3H, t, $J=7.0$), 1.29 (3H, t, $J=7.0$), 1.46 (9H, s), 3.99 (2H, q, $J=7.0$), 4.17 (2H, q, $J=7.0$), 4.32 (2H, s), 7.0—7.5 (5H, m), 7.59 (1H, s). *Anal.* Calcd. for $C_{20}H_{27}NO_6$: C, 63.64; H, 7.21; N, 3.71. Found: C, 63.70; H, 7.09; N, 4.25.

Ethyl N-Ethoxycarbonyl-N-[2,2-bis(ethoxycarbonyl)vinyl]glycinate (11)——To a stirred suspension of NaH (0.40 g) in dry benzene (10 ml) was added a solution of **8a** (3.0 g) in dry benzene (20 ml), and the suspension was refluxed for 2 hr. After the addition of a solution of ethyl chloroformate (2.38 g) in dry benzene (25 ml) at room temperature, the suspension was refluxed for additional 3 hr. The reaction mixture was filtered, and the filtrate was concentrated and distilled at 165° (1 mmHg) to give **11** (2.47 g, 75.7%) as a colorless oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1765, 1746, 1730, 1630. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (ε): 216 (8000), 262 (11300). MS *m/e*: 345 (M$^+$, 11.2%), 154 (100%). PMR (CCl_4) δ: 1.38 (3H, t, $J=6.0$), 1.42 (3H, t, $J=6.0$), 1.45 (6H, t, $J=6.0$,

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$OC\underline{H}_2CH_3 \times 2$), 4.19 (2H, q, $J=6.0$), 4.23 (2H, q, $J=6.0$), 4.25 (4H, q, $J=6.0$, $OC\underline{H}_2CH_3 \times 2$), 4.28 (2H, s), 8.05 (1H, s, N–CH=). *Anal.* Calcd. for $C_{15}H_{23}NO_8$: C, 52.17; H, 6.71; N, 4.06. Found: C, 51.91; H, 6.54 N, 4.29.

Diethyl 3-Hydroxypyrrole-2,4-dicarboxylate[3b] **(9a)**——i) A sodium ethoxide solution prepared from sodium (0.5 g) and abs. EtOH (50 ml) was added to a solution of **8a** (5.0 g) in abs. EtOH (50 ml), and the mixture was refluxed for 45 min, cooled, poured into ice-water (250 ml), acidified with 20% H_2SO_4, and extracted with $CHCl_3$. The extract was washed with satd. $NaHCO_3$, and evaporated to give a crystalline product, which was purified by recrystallization from benzene–*n*-hexane and then from MeOH–H_2O to give **9a** (0.99 g, 23.7%) as colorless prisms, mp 124—125° (lit.[3b] 121°). IR ν_{max}^{KCl} cm^{-1}: 3360, 3220, 1685, 1655. MS *m/e*: 227 (M^+, 19.2%), 135 (100%). PMR ($CDCl_3$) δ: 1.30 (3H, t, $J=6.6$), 1.32 (3H, t, $J=6.6$), 4.28 (2H, q, $J=6.6$), 4.32 (2H, q, $J=6.6$), 7.22 (1H, d, $J=3.8$, ring H), 8.52 (1H, s, OH), 9.65 (1H, br, NH). *Anal.* Calcd. for $C_{10}H_{13}NO_5$: C, 52.86; H, 5.77; N, 6.17. Found: C, 52.95; H, 5.74; N, 6.31.

ii) To a stirred suspension of NaH (83 mg) in dry benzene (10 ml) was added a solution of **11** (1.0 g) in dry benzene (15 ml), and the suspension was refixxed for 4 hr with stirring. The mixture was poured into ice-water (50 ml), and shaken with benzene (50 ml). The aqueous layer was separated and washed again with benzene (20 ml). The organic layer was extracted with cold 5% NaOH (30 ml). The combined aqueous layer were acidified with 20% H_2SO_4 and extracted with $CHCl_3$. The extract was washed with satd. $NaHCO_3$. The solvent was removed, and the crystalline residue was recrystallized as in i) to give **9a** (0.41 g, 70.7%).

***t*-Butyl 4-Ethoxycarbonyl-3-hydroxypyrrole-2-carboxylate (9b)**——To a solution of **8b** (3.0 g) in abs. *t*-BuOH (40 ml) was added a solution of sodium *t*-butoxide in abs. *t*-BuOH (40 ml) prepared from 0.28 g sodium, and the mixture was refluxed for 3 hr under a Dean–Stark head packed with molecular sieves (type 4A) to exclude EtOH formed in the reaction. The mixture was poured into ice-water (100 ml), acidified with 10% H_2SO_4, and the resulting precipitate was collected, washed and dried *in vacuo*. Recrystallization from benzene gave **9b** (1.68 g, 66.0%) as colorless plates, mp 170.5—171.5°. IR ν_{max}^{KCl} cm^{-1}: 3360, 3225, 1695, 1660. MS *m/e*: 255 (M^+, 4.0%), 153 (100%). PMR ($CDCl_3$) δ: 1.38 (3H, t, $J=7.0$), 1.61 (9H, s), 4.35 (2H, q, $J=7.0$), 7.21 (1H, d, $J=4.0$, ring H), 8.35 (1H, br, OH), 9.55 (1H, br, NH). *Anal.* Calcd. for $C_{12}H_{17}NO_5$: C, 56.46; H, 6.71; N, 5.49. Found: C, 56.56; H, 6,75; N, 5.60.

Diethyl 1-Methyl-3-hydroxypyrrole-2,4-dicarboxylate (9c)——To a solution of **8c** (27.5 g) in abs. EtOH (250 ml) was added a sodium ethoxide solution prepared from sodium (3.28 g) and abs. EtOH (75 ml), and the mixture was refluxed for 1.5 hr, poured into ice-water (500 ml), acidified with 20% H_2SO_4, and extracted with benzene. The extract was washed with satd. $NaHCO_3$, evaporated, and the residue was recrystallized from cyclohexane–ether to give **9c** (19.0 g, 85.7%) as colorless leaflets, mp 56.5—57.5°. IR ν_{max}^{KCl} cm^{-1}: 3250, 3110, 1690, 1645. MS *m/e*: 241 (M^+, 31%), 122 (100%). PMR (CCl_4) δ: 1.35 (3H, t, $J=7.2$), 1.38 (3H, t, $J=7.2$), 3.80 (3H, s), 4.26 (2H, q, $J=7.2$), 4.29 (2H, q, $J=7.2$), 6.98 (1H, s, ring H), 8.45 (1H, s, OH). *Anal.* Calcd. for $C_{11}H_{15}NO_5$: C, 54.76; H, 6.27; N, 5.81. Found: C, 54.92; H, 6.31; N, 6.30

***t*-Butyl 4-Ethoxycarbonyl-1-methyl-3-hydroxypyrrole-2-carboxylate (9d)**——Compound **9d** was prepared in a manner similar to that for **9c**: **8d** (3.0 g), *t*-BuOH (15 ml), and sodium *t*-butoxide solution (sodium, 0.33 g; *t*-BuOH, 30 ml); reflux for 3 hr; extraction with benzene. After removal of the solvent, the oily residue was distilled at 155° (1 mmHg) to give **9d** (1.71 g, 66.8%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}, 3320, 1727, 1692, 1655. MS *m/e*: 269 (M^+, 9.5%), 167 (100%). PMR (CCl_4) δ: 1.35 (3H, t, $J=7.0$), 1.57 (9H,s), 3.79 (3H, s), 4.26 (2H, q, $J=7.0$), 6.96 (1H, s, ring H), 8.42 (1H, s, OH). *Anal.* Calcd. for $C_{13}H_{19}NO_5$: C, 57.98; H, 7.11; N, 5.20. Found: C, 57.52; H, 7.10; N, 5.49.

Diethyl 1-Benzyl-3-hydroxypyrrole-2,4-dicarboxylate (9e)——Compound **9e** was prepared in a manner similar to that for **9c**: **8e** (7.0 g), abs. EtOH (50 ml) and sodium ethoxide solution (sodium, 0.66 g; abs. EtOH, 15 ml); reflux for 2 hr; extraction with benzene. After removal of the solvent, the residue was distilled at 195° (0.01 mmHg) to give **9e** (5.2 g, 85.7%). The distillate crystallized on standing and was recrystallized from ether–*n*-hexane to give colorless prisms, mp 60.5—61.5°. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3250, 1680, 1650. MS *m/e*: 317 (M^+, 18.2%), 91 (100%). PMR (CCl_4) δ: 1.77 (3H, t, $J=7.0$), 1.83 (3H, t, $J=7.0$), 4.23 (2H, q, $J=7.0$), 4.26 (2H, q, $J=7.0$), 5.37 (2H, s, N-CH_2-Ph), 6.95—7.40 (6H, m, benzene and pyrrole ring H), 8.57 (1H, s). *Anal.* Calcd. for $C_{17}H_{19}NO_5$: C, 64.34; H, 6.04; N, 4.41. Found: C, 64.18; H, 6.05; N, 4.55.

***t*-Butyl 1-Benzyl-4-ethoxycarbonyl-3-hydroxypyrrole-2-carboxylate (9f)**——Compound **9f** was prepared in a manner similar to that for **9c**: **8f** (15.0 g), abs. *t*-BuOH (150 ml) and sodium *t*-butoxide solution (sodium, 1.33 g; abs. *t*-BuOH, 100 ml); reflux for 2.5 hr; extraction with benzene. After removal of the solvents, the residue was recrystallized from EtOH to give **9f** (10.4 g, 77.3%) as colorless needles, mp 99.0—101.0°. IR ν_{max}^{KCl} cm^{-1}: 3370, 1690, 1655. MS *m/e*: 345 (M^+, 2.2%), 91 (100%). PMR (CCl_4) δ: 1.33 (3H, t, $J=7.0$), 1.45 (9H, s), 4.25 (2H, q, $J=7.0$), 5.34 (2H, s, N-CH_2-Ph), 6.9—7.3 (6H, m, pyrrole and benzene ring H), 8.57 (1H, br). *Anal.* Calcd. for $C_{19}H_{23}NO_5$: C, 66.07; H, 6.71; N, 4.06. Found: C, 66.15; H, 6.73; N, 4.17.

Diethyl 1-Phenyl-3-hydroxypyrrole-2,4-dicaboxylate (9g)——Compound **9g** was prepared in a manner similar to that for **9c**: **8g** (23.3 g), abs. EtOH (100 ml) and sodium ethoxide solution (sodium, 2.3 g; abs. EtOH, 50 ml); reflux for 3.5 hr; extraction with benzene. After removal of the solvent, the residue was recrystallized from EtOH to give **9g** (15.3 g, 75.6%) as colorless plates, mp 90.0—91.0°. IR ν_{max}^{KCl} cm^{-1}: 3120, 1710, 1635. MS *m/e*: 303 (M^+, 37.0%), 185 (100%). PMR (CCl_4) δ: 1.09 (3H, t, $J=7.0$), 1.35 (3H, t, $J=7.0$), 4.10 (2H, q, J=7.0), 4.27 (2H, q, J=7.0), 7.15 (1H, s, pyrrole ring H), 7.30 (5H, s-like, benzene ring H), 8.72 (1H, s, OH). *Anal.* Calcd. for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.32; H, 5.63; N, 4.83.

***t*-Butyl 4-Ethoxycarbonyl-1-phenyl-3-hydroxypyrrole-2-carboxylate (9h)**——Compound **9h** was prepared in a manner similar to that for **9c**: **8h** (1.0 g), abs. *t*-BuOH (10 ml) and sodium *t*-butoxide solution (sodium, 95 mg; abs. *t*-BuOH, 15 ml); reflux for 2.5 hr; extraction with benzene. After removal of the solvent, the residue was recrystallized from EtOH to give **9h** (0.53 g, 60.1%) as colorless needles, mp 115.5—116.5°. IR $\nu_{\max}^{\text{KCl}}$ cm^{-1}: 3335, 1726, 1657. MS *m/e*: 331 (M^+, 9.8%), 77 (100%). PMR (CCl_4) δ: 1.28 (9H, s), 1.37 (3H, t, J=7.0), 4.27 (2H, q, J=7.0), 7.15 (1H, s, pyrrole ring H), 7.32 (5H, s-like, benzene ring H), 8.85 (1H, s, OH). *Anal.* Calcd. for $C_{18}H_{21}NO_5$: C, 65.24; H, 6.39; N, 4.23. Found: C, 65.27; H, 6.43; N, 4.33.

Ethyl 3-Hydroxypyrrole-2-carboxylate (5a)——To a solution of **9a** (1.39 g) in EtOH (15 ml) was added a solution of LiOH (0.74 g) in H_2O (15 ml), and the mixture was refluxed under N_2 for 3 hr. After removal of EtOH, the residue was acidified with conc. HCl to Congo red. The precipitated carboxylic acid (**10a**) was collected, washed and dried *in vacuo* (1.10 g). To a solution of the crude acid **10a** (1.10 g) in pyridine (10 ml) was added AcOH (10 ml), and the mixture was refluxed for 5 hr. The solvent was removed, and the residue was extracted with CCl_4. The extract was concentrated, and the residue was distilled at 110° (0.05 mmHg) to give **5a** (0.57 g, 60.0%) as a colorless oil, which crystallized below 30°. IR $\nu_{\max}^{\text{CCl}_4}$ cm^{-1}: 3510, 3495, 3370, 3320, 1705, 1650. MS *m/e*: 155 (M^+, 45.2%), 109 (100%). PMR (CCl_4) δ: 1.37 (3H, t, J=7.2), 4.34 (2H, q, J=7.2), 5.86 (1H, t, J=2.8, C-4 H), 6.71 (1H, t, J=2.8, C-5 H), 7.30 (1H, br, OH), 8.30 (1H, br, NH). *Anal.* Calcd. for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.25; H, 5.86; N, 9.18.

***t*-Butyl 3-Hydroxypyrrole-2-carboxylate (5b)**——A solution of NaOH (0.78 g) in EtOH (40 ml) was added to a solution of **9b** (1.0 g) in EtOH (15 ml), and the mixture was refluxed under N_2 for 1 hr. After the addition of H_2O (9 ml), the reaction mixture was refluxed for additional 4 hr. The mixture was acidified with 10% HCl to Congo red with ice-cooling, extracted with $CHCl_3$, and the extract was washed and evaporated to give a crystalline product **10b** (0.76 g). The crude acid **10b** (0.76 g) in β-picoline (20 ml) was refluxed for 5 hr, and the solution was concentrated, and the residue was distilled at 106° (1 mmHg) to give **5b** (0.47 g, 76.4%). The distillate crystallized immediately and was recrystallized from petr. ether to give colorless plates, mp 67.0—68.0°. IR $\nu_{\max}^{\text{KCl}}$ cm^{-1}: 3337, 1666, 1633; $\nu_{\max}^{\text{CCl}_4}$ cm^{-1}: 3495, 3370, 3305, 1700, 1680, 1665. MS *m/e*: 183 (M^+, 4.4%), 109 (100%). PMR (CCl_4) δ: 1.58 (9H, s), 5.73 (1H, t, J=3.0, C-4 H), 6.60 (1H, t, J=3.0, C-5 H), 7.25 (1H, br, OH), 8.55 (1H, br, NH). *Anal.* Calcd. for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 58.91; H, 7.18; N, 7.82.

Ethyl 1-Methyl-3-hydroxypyrrole-2-carboxylate (5c)——To a solution of **9c** (1.0 g) in EtOH (10 ml) was added a solution of NaOH (0.83 g) in EtOH (30 ml), and the mixture was refluxed for 3 hr under N_2. Water (10 ml) was added, and the mixture was refluxed for additional 3 hr. After removal of EtOH, cold water (20 ml) was added, and the resulting mixture was acidified with conc. HCl to Congo red. The precipitate (**10c**) was collected, washed and dried *in vacuo* (0.79 g). The crude acid **10c** (0.79 g) gave **5c** (0.54 g, 76.5%) as a colorless oil on a treatment similar to that for **5a**; reflux for 3 hr; distillation at 110° (1 mmHg). The distillate crystallized on standing, and was recrystallized from cyclohexane to give colorless plates, mp 40.0—41.0°. IR $\nu_{\max}^{\text{KCl}}$ cm^{-1}: 3220, 1640, $\nu_{\max}^{\text{CCl}_4}$ cm^{-1}: 3491, 3320, 1713, 1655. MS *m/e*: 169 (M^+, 51.4%), 123 (100%). PMR (CCl_4) δ: 1.38 (3H, t, J=7.2), 3.72 (3H, s), 4.33 (2H, q, J=7.2), 5.58 (1H, d, J=3.0, C-4 H), 6.42 (1H, d, J=3.0, C-5 H), 7.75 (1H, br). *Anal.* Calcd. for $C_8H_{11}NO_3$: C, 56.79; H, 6.55; N, 8.28. Found: C, 56.69; H, 6.55; N, 8.47.

***t*-Butyl 1-Methyl-3-hydroxypyrrole-2-carboxylate (5d)**——The compound **9d** (1.53 g) gave **5d** (0.53 g, 44.4%) as a colorless oil (bp 110°/1 mmHg) *via* the carboxylic acid **10d** (1.0 g) by hydrolysis (NaOH, 1.53 g; 3 hr's reflux) and subsequent decarboxylation (5 hr's reflux in β-picoline) in a manner similar to that for **5a**. IR $\nu_{\max}^{\text{CCl}_4}$ cm^{-1}: 3475, 3280, 1708, 1650. MS *m/e*: 197 (M^+, 4.4%), 123 (100%). PMR (CCl_4) δ: 1.57 (9H, s), 3.68 (3H, s), 5.53 (1H, d, J=3.0, C-4 H), 6.33 (1H, d, J=3.0, C-5 H), 7.85 (1H, br). *Anal.* Calcd. for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.67; N, 7.10. Found: C, 60.78; H, 7.68; N, 7.18.

Ethyl 1-Benzyl-3-hydroxypyrrole-2-carboxylate (5e)——Compound **5e** was obtained from **9e** (15.0 g) *via* the carboxylic acid **10e** (13.2 g) by hydrolysis (NaOH, 11.4 g; 3 hr's reflux) and decarboxylation (4 hr's reflux in pyridine–acetic acid) in a manner similar to that for **5a**. bp 160° (1 mmHg). The distillate crystallized immediately and was recrystallized from EtOH to give colorless plates (7.65 g, 66.0%), mp 77.0—78.0°. IR $\nu_{\max}^{\text{KCl}}$ cm^{-1}: 3335, 1655: $\nu_{\max}^{\text{CCl}_4}$ cm^{-1}: 3490, 3300, 1710, 1656. MS *m/e*: 245 (M^+, 30.0%), 91 (100%). PMR (CCl_4) δ: 1.20 (3H, t, J=7.2), 4.11 (2H, q, J=7.2), 5.22 (2H, s, N-CH_2-Ph), 5.70 (1H, d, J=3.0, C-4 H), 6.55 (1H, d, J=3.0, C-5 H), 6.85—7.30 (5H, m), 7.97 (1H, br). *Anal.* Calcd. for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.62; H, 6.15; N, 6.10.

***t*-Butyl 1-Benzyl-3-hydroxypyrrole-2-carboxylate (5f)**——Compound **5f** was obtained in a manner similar to that for **5a** from **9f** (5.0 g) *via* the carboxylic acid **10f** (4.5 g) by hydrolysis (NaOH, 2.9 g; 5 hr's reflux) and decarboxylation (5 hr's reflux in β-picoline). bp 165° (1.5 mmHg), 2.52 g (63.4%). The crystallized distillate was recrystallized from MeOH to give colorless leaflets, mp 63.0—64.0°. IR $\nu_{\max}^{\text{KCl}}$ cm^{-1}: 3300, 1645; $\nu_{\max}^{\text{CCl}_4}$ cm^{-1}: 3480, 3280, 1706, 1652. MS *m/e*: 273 (M^+, 2.8%), 91 (100%). PMR (CCl_4) δ: 1.38 (9H, s), 5.22 (2H, s, N-CH_2-Ph), 5.68 (1H, d, J=2.8, C-4 H), 6.49 (1H, d, J=2.8, C-5 H), 6.8—7.3 (5H, m), 8.20 (1H, br). *Anal.* Calcd. for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.13. Found: C, 70.20; H, 7.04; N, 5.32.

Ethyl 1-Phenyl-3-hydroxypyrrole-2-carboxylate (5g)——Compound **5g** was prepared in a manner similar to that for **5a** from **9g** (6.06 g) *via* the carboxylic acid **10g** (4.6 g) by hydrolysis (NaOH, 5.6 g; 7 hr's reflux) and decarboxylation (8 hr's reflux in pyridine–acetic acid). bp 160° (1 mmHg). A pale yellow oil (1.90 g, 50.7%). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3450, 3320, 1710, 1653, 1600. MS *m/e*: 231 (M$^+$, 50%), 185 (100%). PMR (CCl_4) δ: 1.02 (3H, t, J=7.0), 4.09 (2H, q, J=7.0), 5.85 (1H, d, J=3.0, C-4 H), 6.62 (1H, d, J=3.0, C-5 H), 7.25 (5H, m), 8.50 (1H, br). *Anal.* Calcd. for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.41; H, 5.65; N, 6.41.

***t*-Butyl 1-Phenyl-3-hydroxypyrrole-2-carboxylate (5h)**——Compound **5h** was prepared in a manner similar to that for **5a** from **9h** (0.98 g) *via* the carboxylic acid **10h** (0.87 g) by hydrolysis (NaOH, 0.59 g; 8.5 hr's reflux) and decarboxylation (7.5 hr's reflux in β-picoline containing one drop of piperidine). bp 120° (0.02 mmHg). A pale yellow oil (0.37 g, 49.1%). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3280, 1720, 1652, 1600. MS *m/e*: 259 (M$^+$, 4.7%), 185 (100%). PMR (CCl_4) δ: 1.22 (9H, s), 5.79 (1H, d, J=3.0, C-4 H), 6.51 (1H, d, J=3.0, C-5 H), 6.95—7.55 (5H, m), 8.35 (1H, br). *Anal.* Calcd. for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.45; H, 6.83; N, 5.68.