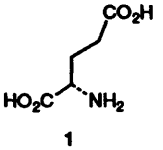
Isoxazol-5(4*H*)-ones. X-Ray Crystal Structures of a 4-Hydroxyisoxazol-5(4*H*)-one and a [4,4'-Biisoxazole]-5(4*H*),5'(4'*H*)-dione Formed by Oxygen Oxidation of 3-*tert*-Butyl-4-methylisoxazol-5(4*H*)-one

Lotte Brehm,* Jørgen S. Johansen and Povl Krogsgaard-Larsen
PharmaBiotec Research Center, Department of Organic Chemistry, The Royal Danish School of Pharmacy, DK-2100 Copenhagen, Denmark

Treatment of ethyl (*RS*)-2,4,4-trimethyl-3-oxopentanoate **4** with hydroxylamine under basic conditions gave 5-*tert*-butyl-4-methylisoxazol-3-ol **5** and a tautomeric mixture of 3-*tert*-butyl-4-methylisoxazol-5(2*H*)-one **6** and (*RS*)-3-*tert*-butyl-4-methylisoxazol-5(4*H*)-one **7**. During the attempts to crystallize the inseparable mixture of tautomers **6** and **7** two other compounds, (*RS*)-3-*tert*-butyl-4-hydroxy-4-methylisoxazol-5(4*H*)-one **8** and (*RS,RS*)-3,3'-di-*tert*-butyl-4,4'-dimethyl-[4,4'-biisoxazole]-5(4*H*),5'(4'*H*)-dione **9**, were progressively formed. The structures of compounds **8** and **9** were established by X-ray analyses. Compounds **8** and **9** are proposed to be formed by oxidation of compound **7** with oxygen, but the mechanisms underlying these two oxidative processes are unknown.

(*S*)-Glutamic acid **1** is the major excitatory amino acid (EAA) neurotransmitter in the mammalian central nervous system.[1–3] The neuroexcitatory actions of this amino acid are mediated by multiple receptors, notably the ionotropic *N*-methyl-D-aspartic acid (NMDA), the (*S*)-2-amino-3-(3-hydroxy-5-methylisoxazol-4-yl)propionic acid (AMPA), and the kainic acid receptors.[1–5] These EAA receptor subtypes are named after the respective selective agonists, NMDA, AMPA **2**, and kainic acid.



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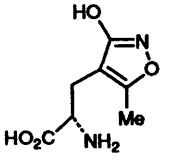

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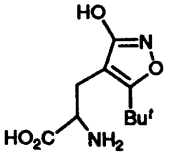

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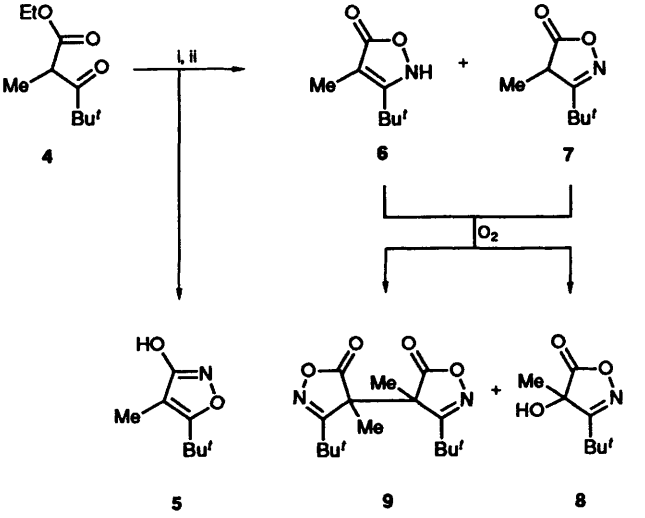
Hyperactivation of central EAA receptors appears to play an important role in the destruction of neurones in certain neurodegenerative disorders such as Alzheimer's disease and Huntington's chorea.[6] There is accumulating evidence of hypoactivity of central EAA neurotransmitter systems in schizophrenia.[7] Thus, EAA antagonists have therapeutic interest as neuroprotective agents in the former diseases, whereas EAA agonists or partial agonists may be future drugs in schizophrenia.[8] Furthermore, subtype-specific EAA receptor agonists as well as antagonists are indispensable tools for studies of EAA neurotransmitter mechanisms in the brain.

(*RS*)-AMPA[9,10] has been radiolabelled and is now the standard ligand for studies of AMPA receptors *in vitro*.[11,12] A number of analogues of (*RS*)-AMPA, including (*RS*)-2-amino-3-(5-*tert*-butyl-3-hydroxyisoxazol-4-yl)propionic acid (ATPA) **3**,[13] are potent and specific AMPA receptor agonists,[13,14] and have been used to characterize indirectly the topography of the AMPA receptor site. Since ATPA, in which the methyl group of (*RS*)-AMPA has been replaced by a *tert*-butyl group, is a very effective AMPA agonist, the AMPA receptor appears to contain a lipophilic cavity capable of accommodating rather bulky substituents of agonist molecules.[15,16] These aspects and the fact that ATPA, by virtue of its lipophilic character, is capable of penetrating the blood-brain barrier[4] has made this compound particularly important for pharmacological studies of the central EAA neurotransmitter system. Our drug design programme in this field includes the synthesis of analogues of ATPA, including the isoxazolin-5-one isomer of ATPA. Compound **5**, which is the key intermediate in the synthesis of ATPA, was synthesized using a modified version of the procedure described by Lauridsen *et al.*[13] The β-oxoester **4**[13] was treated with hydroxylamine under basic conditions followed by an acid catalysed cyclization reaction. Compound **5** was isolated from a complex reaction mixture, which also contained the tautomeric compounds, 3-*tert*-butyl-4-methylisoxazol-5(2*H*)-one **6** and (*RS*)-3-*tert*-butyl-4-methylisoxazol-5(4*H*)-one **7** (Scheme 1). This inseparable mixture of tautomers



Scheme 1 *Reagents:* i, NH_2OH, NaOH; ii, HCl

is a key intermediate in the planned synthesis of the above mentioned isoxazolin-5-one isomer of ATPA. In this paper we describe the structure of two oxidation products, compounds **8** and **9**, formed during the attempts to isolate and purify the mixture of the tautomers **6** and **7**.

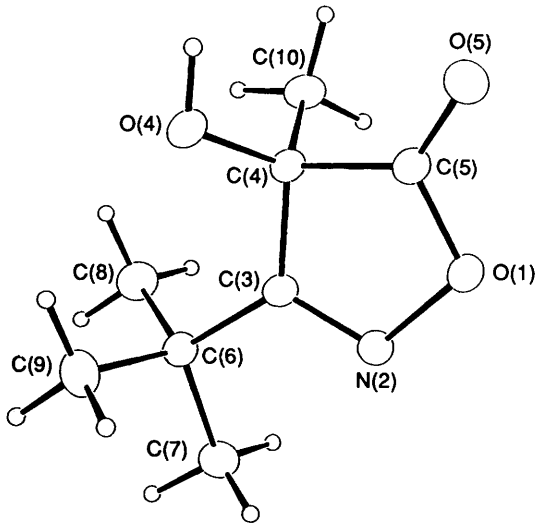


Fig. 1 Perspective drawing of compound **8** with numbering system; the thermal ellipsoids for the non-hydrogen atoms correspond to 50% probability, hydrogen atoms are represented as spheres of arbitrary radius

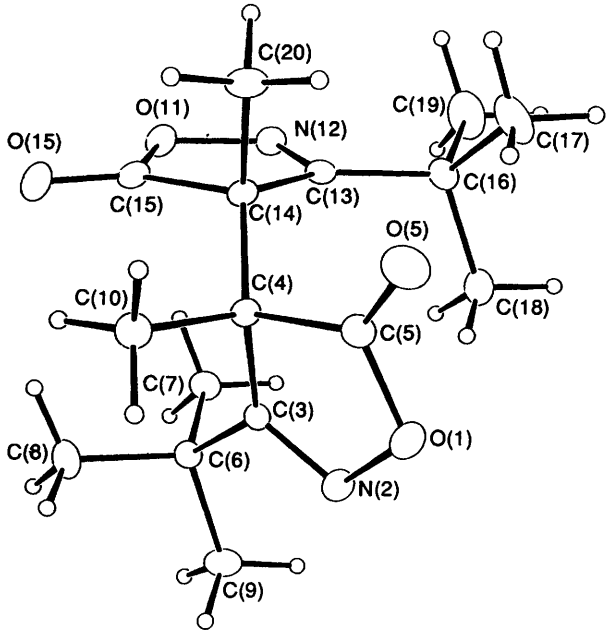


Fig. 2 Perspective drawing of compound **9** with numbering system; the thermal ellipsoids for the non-hydrogen atoms correspond to 50% probability, hydrogen atoms are represented as spheres of arbitrary radius

Results and Discussion

Compound **5**, which was synthesized in good yield (91%) from the β-oxoester **4** and hydroxylamine, was isolated from a reaction mixture, which also contained small amounts of compounds **6** and **7**.

The number of signals in the ^{1}H NMR ($CDCl_3$) spectrum of the mixture of compounds **6** and **7** suggests a tautomeric mixture of isoxazol-5(2*H*)- and isoxazol-5(4*H*)-ones (ratio, 1:4). The IR spectrum of this mixture shows carbonyl absorption bands at 1690 cm^{-1} for the isoxazol-5(2*H*)-one **6** and at 1795 cm^{-1} for the isoxazol-5(4*H*)-one **7**,[17,18] whereas the UV spectrum shows a strong absorption band of 260 nm originating in the isoxazol-5(2*H*)-one tautomeric form **6**.

During the isolation and attempted crystallization of the inseparable mixture of the tautomers **6** and **7** we observed that this mixture was very unstable and underwent transformation into two new compounds. Compound **6** and/or **7** were shown to be converted primarily into compound **8** in tetrachloromethane solution, whereas compound **9** was the major conversion product in ethyl acetate–light petroleum solution. On storage, pure tautomers **6** and **7** (oil) were transformed exclusively into compound **8**. These observations prompted us to concentrate on the isolation, purification, and structure determination of these two new compounds. Based on X-ray analyses compounds **8** and **9** were shown to be (*RS*)-3-*tert*-butyl-4-hydroxy-4-methylisoxazol-5(4*H*)-one and 3,3′-di-*tert*-butyl-4,4′-dimethyl-[4,4′-biisoxazole]-5(4*H*),5′(4′*H*)-dione, respectively.

Selected bond lengths, valency and torsion angles of compounds **8** and **9**, and dimensions of an intermolecular hydrogen bond in the crystal structure of compound **8** are given in Table 1. Perspective drawings of compounds **8** and **9** are shown in Figs. 1 and 2, respectively.

The bond lengths and angles of the two equivalent parts of compound **9** are practically equal, and agree fairly well with those found for compound **8**, except for the N–O bond [1.473(1) Å], which is significantly longer in compound **8** compared to compound **9** [1.440(1) and 1.442(1) Å] (Table 1). A search of the January 1992 version of the Cambridge Structural Database[19,20] revealed seven structure determinations with isoxazol-5(4*H*)-one fragments.[21–27] The N–O bond length in one of these compounds is found to be 1.477 Å,[25] and for the remaining compounds the N–O bond lengths are in the range 1.438–1.455 Å.

The five membered ring of compound **8** is in a shallow twist conformation ($^{C(5)}_{C(4)}$T), whereas the five membered rings of **9** are in shallow envelope conformations with C(4) or C(14) the out-of-plane atoms (Table 1). The angle between the best planes through the five membered rings of compound **9** is 101.35(4)°.

The mechanisms underlying the formation of compounds **8** and **9** have, so far, not been elucidated. It does, however, seem obvious that compound **8**, and probably also **9**, are formed by oxidation of the tautomeric mixture of **6** and **7**, in particular **7**, by atmospheric oxygen, and we envisage that radical mechanisms are playing a key role in these oxidation processes. Only the racemate of compound **9** could be isolated from the reaction mixture, but we can not rule out the possibility that minor amounts of the *meso*-form of **9** are formed during the oxidation process.

Experimental

M.p.s were determined in capillary tubes and are corrected. Elemental analyses were performed by Mr. P. Hansen, Chemical Laboratory II, University of Copenhagen, Denmark. IR spectra, obtained on a Perkin-Elmer 781 Infrared Spectrophotometer, were recorded as KBr pellets (crystalline compounds) or using the liquid film technique (oils). UV spectra were recorded in methanol on a Shimadzu UV-265 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL FX 90Q spectrometer or a Bruker AC-200F spectrometer using TMS as an internal standard. *J*-values are given in Hz. TLC and gravity column chromatography were performed on silica F_{254} plates (Merck) and silica gel (Woelm, 0.063–0.200 mm), respectively. Evaporations were performed at temperatures below 50 °C, using a vacuum rotatory evaporator connected to a water aspirator. Light petroleum was the fraction boiling < 50 °C.

5-tert-*Butyl*-4-*methylisoxazol*-3-*ol* **5**,[13] (RS)-3-tert-*Butyl*-4-*hydroxy*-4-*methylisoxazol*-5(4H)-*one* **8** *and* (RS,RS)-3,3′-*Di*-tert-*butyl*-4,4′-*dimethyl*-[4,4′-*biisoxazole*]-5(4H), 5′(4′H)-*dione* **9**.—To a solution of sodium hydroxide (5.17 g, 129 mmol) in a mixture of water (5 cm^3) and methanol (100 cm^3) was added at −70 °C, drop by drop and with stirring, compound **4**[13] (22.9 g, 123 mmol). To this solution was added a filtered solution of

Table 1 Selected bond lengths, valency and torsion angles, and pseudorotation parameters for compounds **8** and **9**, and dimensions of an intermolecular hydrogen bond in the crystal structure of **8** (estimated standard deviations in parentheses)

(a) Bond lengths (Å)

	8	9		9
O(1)–N(2)	1.473(1)	1.440(1)	O(11)–N(12)	1.442(1)
N(2)–C(3)	1.280(1)	1.285(1)	N(12)–C(13)	1.285(1)
C(3)–C(4)	1.516(1)	1.533(1)	C(13)–C(14)	1.532(1)
C(4)–C(5)	1.529(1)	1.532(1)	C(14)–C(15)	1.530(1)
C(5)–O(1)	1.348(1)	1.358(1)	C(15)–O(11)	1.357(1)
C(5)–O(5)	1.204(1)	1.196(1)	C(15)–O(15)	1.202(1)
C(3)–C(6)	1.517(1)	1.532(1)	C(13)–C(16)	1.531(1)
C(6)–C(7)	1.535(1)	1.536(1)	C(16)–C(17)	1.530(1)
C(6)–C(8)	1.534(2)	1.535(1)	C(16)–C(18)	1.530(1)
C(6)–C(9)	1.538(1)	1.539(1)	C(16)–C(19)	1.539(1)
C(4)–C(10)	1.534(2)	1.565(1)	C(14)–C(20)	1.561(1)
C(4)–X[a]	1.405(1)	1.575(1)		

(b) Valency angles (°)

	8	9		9
N(2)–O(1)–C(5)	108.71(7)	109.89(6)	N(12)–O(11)–C(15)	109.96(6)
O(1)–N(2)–C(3)	108.72(7)	109.60(7)	O(11)–N(12)–C(13)	109.35(7)
N(2)–C(3)–C(4)	113.10(8)	112.19(7)	N(12)–C(13)–C(14)	112.33(7)
C(4)–C(3)–C(6)	128.01(8)	132.08(7)	C(14)–C(13)–C(16)	132.10(7)
N(2)–C(3)–C(6)	118.83(9)	115.33(7)	N(12)–C(13)–C(16)	115.32(7)
C(3)–C(4)–C(5)	99.11(8)	99.28(6)	C(13)–C(14)–C(15)	99.19(6)
C(3)–C(4)–C(10)	113.58(8)	108.84(6)	C(13)–C(14)–C(20)	108.20(6)
C(3)–C(4)–X[a]	111.74(9)	120.34(6)	C(4)–C(14)–C(13)	120.80(6)
C(5)–C(4)–C(10)	106.33(9)	101.39(6)	C(15)–C(14)–C(20)	102.05(7)
C(5)–C(4)–X[a]	112.45(8)	113.02(6)	C(4)–C(14)–C(15)	112.52(6)
C(10)–C(4)–X[a]	112.74(9)	111.75(6)	C(20)–C(14)–C(4)	111.88(6)
O(1)–C(5)–C(4)	109.30(7)	108.66(7)	O(11)–C(15)–C(14)	108.71(7)
O(1)–C(5)–O(5)	121.43(9)	120.47(8)	O(11)–C(15)–O(15)	120.70(8)
C(4)–C(5)–O(5)	129.2(1)	130.57(8)	C(14)–C(15)–O(15)	130.39(8)
C(3)–C(6)–C(7)	110.06(8)	111.34(6)	C(13)–C(16)–C(17)	112.06(7)
C(3)–C(6)–C(8)	111.1(1)	110.21(7)	C(13)–C(16)–C(18)	109.46(7)
C(3)–C(6)–C(9)	107.46(8)	109.58(7)	C(13)–C(16)–C(19)	109.12(8)
C(7)–C(6)–C(8)	109.47(8)	110.04(7)	C(17)–C(16)–C(18)	110.03(9)
C(7)–C(6)–C(9)	108.8(1)	107.47(7)	C(17)–C(16)–C(19)	107.71(8)
C(8)–C(6)–C(9)	109.93(9)	108.10(7)	C(18)–C(16)–C(19)	108.38(9)

(c) Torsion angles (°)

	8	9		9
C(5)–O(1)–N(2)–C(3)	3.1(1)	−0.1(1)	C(15)–O(11)–N(12)–C(13)	−0.8(1)
O(1)–N(2)–C(3)–C(4)	4.1(1)	−3.9(1)	O(11)–N(12)–C(13)–C(14)	−3.9(1)
N(2)–C(3)–C(4)–C(5)	−8.6(1)	5.9(1)	N(12)–C(13)–C(14)–C(15)	6.32(9)
C(3)–C(4)–C(5)–O(1)	10.2(1)	−5.7(1)	C(13)–C(14)–C(15)–O(11)	−6.50(9)
C(4)–C(5)–O(1)–N(2)	−8.7(1)	4.0(1)	C(14)–C(15)–O(11)–N(12)	4.95(9)

(d) Pseudorotation parameters (°)[b]

	8	9	9
P (phase)	−1.9(4)	162.5(5)	167.5(4)
τ_m (amplitude)	10.6(1)	6.3(1)	7.0(1)
Reference bond	C(4)–C(5)	C(4)–C(5)	C(14)–C(15)

(e) Geometry of intermolecular hydrogen bond [O(4)–H(4)···O(5)][c] in compound **8**

Bond length (Å)		Angle (°)	
O(4)···O(5)	2.791(1)	O(4)–H···O(5)	163(2)°
H(4)···O(5)	1.94(2)		

[a] X = O(4) for compound **8**; and C(14) for compound **9**. [b] Ref. 31. [c] Symmetry code: $1 - x, 1 - y, z$.

sodium hydroxide (10.3 g, 258 mmol) and hydroxylamine hydrochloride (17.1 g, 246 mmol) in a mixture of water (10 cm^3) and methanol (100 cm^3), cooled to −70 °C. The reaction mixture was stirred for 2 h, and during this period the temperature raised to 10 °C. Upon addition of acetone (9.0 cm^3, 123 mmol), this reaction mixture was poured into hydrochloric acid (4 mol dm^{-3}; 90 cm^3) at 80 °C, and this mixture was left with stirring at 80 °C for 30 min. The volume of the reaction

Table 2 Positional parameters for compound **8** (estimated standard deviations in parentheses)

Atom	*x*	*y*	*z*
O(1)	0.281 0(1)	0.148 92(9)	0.305 85(9)
N(2)	0.433 6(1)	−0.032 5(1)	0.340 3(1)
C(3)	0.606 7(2)	−0.012 1(1)	0.268 3(1)
C(4)	0.603 5(2)	0.187 0(1)	0.183 2(1)
O(4)	0.664 1(1)	0.223 2(1)	0.024 72(9)
C(5)	0.370 1(2)	0.276 2(1)	0.203 4(1)
O(5)	0.270 8(1)	0.434 1(1)	0.146 7(1)
C(6)	0.782 1(2)	−0.181 1(1)	0.270 5(1)
C(7)	0.734 9(2)	−0.352 6(1)	0.395 7(1)
C(8)	0.994 5(2)	−0.166 6(2)	0.304 2(1)
C(9)	0.789 7(2)	−0.196 3(2)	0.108 2(1)
C(10)	0.724 6(2)	0.256 8(1)	0.267 6(1)

Table 3 Positional parameters for compound **9** (estimated standard deviations in parentheses)

Atom	*x*	*y*	*z*
O(1)	0.295 93(8)	0.018 21(7)	0.032 01(5)
N(2)	0.308 31(9)	−0.068 65(8)	−0.036 05(5)
C(3)	0.352 53(8)	−0.173 65(9)	0.001 67(6)
C(4)	0.386 37(9)	−0.168 82(8)	0.105 48(6)
C(5)	0.334 47(9)	−0.037 37(9)	0.115 13(6)
O(5)	0.334 44(8)	0.019 92(7)	0.181 49(5)
C(6)	0.376 75(9)	−0.273 71(9)	−0.062 29(6)
C(7)	0.277 6(1)	−0.384 10(9)	−0.071 00(6)
C(8)	0.526 8(1)	−0.319 2(1)	−0.028 08(7)
C(9)	0.350 4(1)	−0.218 4(1)	−0.158 12(6)
C(10)	0.545 8(1)	−0.152 3(1)	0.149 49(6)
O(11)	0.301 09(7)	−0.487 24(7)	0.140 23(5)
N(12)	0.165 37(8)	−0.432 29(8)	0.113 83(5)
C(13)	0.176 53(9)	−0.313 11(9)	0.118 82(6)
C(14)	0.326 98(9)	−0.270 47(9)	0.156 63(6)
C(15)	0.398 5(1)	−0.396 56(9)	0.161 06(6)
O(15)	0.519 17(8)	−0.422 55(7)	0.184 73(5)
C(16)	0.040 01(9)	−0.241 7(1)	0.094 42(6)
C(17)	0.040 7(1)	−0.141 4(1)	0.164 94(8)
C(18)	0.011 0(1)	−0.182 6(1)	0.000 16(8)
C(19)	−0.077 5(1)	−0.333 2(1)	0.091 08(9)
C(20)	0.357 5(1)	−0.238 4(1)	0.259 60(6)

mixture was reduced to *ca.* 100 cm^3 by evaporation and left at 5 °C overnight. Compound **5** (16.9 g) was filtered off, and the mother liquor was extracted with dichloromethane (3 × 50 cm^3). The filtered and dried (magnesium sulfate) organic phases were evaporated and the residue subjected to gravity column chromatography (150 g of silica gel). Elution with toluene containing ethyl acetate (10–30%) and glacial acetic acid (2%) gave compound **5** (0.46 g) and a mixture of compounds **6** and **7** (0.48 g, 2%). Total amount of pure **5** (TLC): 17.36 g (91%). The IR spectrum of compound **5** was identical with that of an authentic sample.[13]

The inseparable mixture of compounds **6** and **7** was isolated as an oil in varying amounts (2–10%) in different experiments. TLC analysis [eluent: toluene–ethyl acetate–glacial acetic acid (40:9:1); visualization: UV light and a ferric chloride spraying reagent]; λ_{max} 260 nm (log ε 3.87); ν_{max}/cm^{-1} 3090m, 2970s, 2875m, 1795s, 1690s, 1585m, 1485m and 1465m; $\delta_H(CDCl_3)$ 3.41 (0.8 H, q, *J* 8), 1.91 (0.6 H, s), 1.56 (2.4 H, d, *J* 8), 1.35 (1.8 H, s) and 1.30 (7.2 H, s).

During the attempts to crystallize the tautomeric mixture of compounds **6** and **7** (ethyl acetate–light petroleum) compound **9** precipitated. TLC analysis [eluent: toluene–ethyl acetate (4:1); visualization: UV light and a potassium permanganate spraying reagent] of the mother liquor revealed three spots (R_f 0.19, 0.44 and 0.74) representing the mixture of compounds **6** and **7**, **8**, and **9**, respectively. Light petroleum was added to the mother liquor and the mixture was left for *ca.* 14 d at 5 °C. After this period further amounts of compound **9** precipitated, and a TLC analysis of the mother liquor revealed the presence of compounds **8**, **9**, and trace amounts of the mixture of compounds **6** and **7**.

A solution of the mixture of compounds **6** and **7** in tetrachloromethane was left for *ca.* one month at 5 °C. After this period a TLC analysis revealed that the mixture of compounds **6** and **7** was transformed primarily into compound **8**. The solution was evaporated and the residue subjected to gravity column chromatography [silica gel; eluents: toluene–ethyl acetate (10–40%)] to give crystalline **8**.

During storage for two years at room temperature the mixture of compounds **6** and **7** (oil) was transformed exclusively into compound **8**.

Compound **8**. M.p. 56–58 °C (ethyl acetate–light petroleum); λ_{max} 210 nm (log ε 3.52); ν_{max}/cm^{-1} 3430s, 2995m, 2975m, 1780s, 1485m, 1470m and 1460m; $\delta_H(CDCl_3)$ 3.36 (1 H, s), 1.69 (3 H, s) and 1.36 (9 H, s) (Found: C, 56.15; H, 7.75; N, 8.1. $C_8H_{13}NO_3$ requires C, 56.11; H, 7.65; N, 8.21%).

Compound **9**. M.p. 111–113 °C (ethyl acetate–light petroleum); λ_{max} 210 nm (log ε 3.75); ν_{max}/cm^{-1} 2970m, 1775s, 1485m, 1470m and 1455m; $\delta_H(CDCl_3)$ 1.90 (6 H, s) and 1.27 (18 H, s) (Found: C, 62.4; H, 7.9; N, 9.0. $C_{16}H_{24}N_2O_4$ requires C, 62.30; H, 7.84; N, 9.12%).

X-Ray Crystallographic Analyses of Compounds **8** *and* **9**.—The colourless crystals used for the X-ray examinations were crystallized from ethyl acetate–light petroleum.

Crystal data for compound **8**. $C_8H_{13}NO_3$, M_r = 171.20. Triclinic, a = 6.6640(6), b = 8.206(2), c = 9.203(1) Å, α = 67.76(1), β = 82.76(1), γ = 72.54(1)°, V = 444.3 $Å^3$ (by least-squares refinement on diffractometer angles for 20 automatically centred reflections), λ(Cu-Kα) = 1.541 84 Å, space group $P\bar{1}$ (no. 2), Z = 2, D_c = 1.279 g cm^{-3}, $T \sim$ 110 K. Crystal dimensions 0.2 × 0.3 × 0.4 mm, μ(Cu-Kα) = 7.8 cm^{-1}.

Crystal data for compound **9**. $C_{16}H_{24}N_2O_4$, M_r = 308.38. Monoclinic, a = 10.201(3), b = 10.738(6), c = 15.450(4) Å, β = 108.17(2)°, V = 1608 $Å^3$ (by least-squares refinement on diffractometer angles for 22 automatically centred reflections), λ(Mo-Kα) = 0.710 73 Å, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), Z = 4, D_c = 1.274 g cm^{-3}. $T \sim$ 110 K. Crystal dimensions 0.3 × 0.4 × 0.7 mm, μ(Mo-Kα) = 0.86 cm^{-1}.

Data collection and processing. The diffraction data were collected on a Nonius CAD-4 diffractometer. The crystals were cooled in a stream of nitrogen gas provided by an Enraf–Nonius low-temperature device. The temperature was kept constant within 1 K during the experiments. Graphite monochromated Cu-Kα (**8**) and Mo-Kα (**9**) radiations were used. Intensities of three reflections were measured every 10^4 s to check for decay of the crystals.

Compound **8**. Intensities of one hemisphere ($1 \leqslant \theta \leqslant 75°$, $h \pm k \pm l$) were measured using the ω-2θ scan mode. Of the 1827 unique reflections, 1688 were classified as observed *i.e.* $|F_o|^2 \geqslant 5\sigma(|F_o|^2)$. No crystal decay.

Compound **9**. 8275 reflections were measured in an ω scan mode ($1 \leqslant \theta \leqslant 35°$, $hk \pm l$; $1 \leqslant \theta \leqslant 20°$, $h - k \pm l$), gave 7061 unique reflections [merging R = 0.018 on I] of which 4294 were classified as observed reflections *i.e.* $|F_o|^2 \geqslant 3[\sigma^2(|F_o|^2) + (0.04|F_o|^2)^2]^{\frac{1}{2}}$. Crystal decay, 4.1% corrected during data processing.

The $\sigma(|F_o|^2)$ were calculated from counting statistics. No absorption corrections were made.

Structure solutions and refinements. The positions of non hydrogen atoms were obtained by application of 'direct methods' (SHELX86).[28,29] The hydrogen atoms were subse-

quently located on a series of difference Fourier maps. Full-matrix least-squares calculations included an overall scale factor, atomic coordinates for all atoms, anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The quantity minimized was $\Sigma w(|F_o| - k|F_c|)^2$.

Compound **8**. $w^{-1} = [\sigma^2(|F_o|) + (0.01|F_o|)^2 + 2.5]$, R = 0.034, $R_w = 0.051$, and residual electron density in final difference Fourier map is within ± 0.26 e Å^{-3}.

Compound **9**. $w^{-1} = \sigma^2(|F_o|) + (0.02|F_o|)^2$, $R = 0.036$, $R_w = 0.045$, and residual electron density in final difference Fourier map is within $+0.43$ and -0.25 e Å^{-3}.

All calculations, except the structure solutions, were carried out by using the Enraf–Nonius Structure Determination Package.[30] Tables 2 and 3 list the final positional parameters for compounds **8** and **9**, respectively.

Supplementary Material. Hydrogen atom coordinates thermal parameters, full lists of bond lengths and angles, and selected torsion angles have been deposited at the Cambridge Crystallographic Data Centre.*

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* For details, see Instructions for Authors (1992), *J. Chem. Soc., Perkin Trans. 1*, 1992, Issue 1.

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