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N-Chloro-*N*-alkoxyureas: synthesis, structure and properties†

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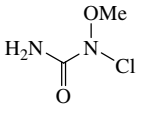
The XRD studies of *N*-chloro-*N*-alkoxyureas 1, 2 have revealed the high pyramidality of the amide nitrogen in the O–N–Cl group caused by n_O–$\sigma^*_{N–Cl}$ anomeric effect, the other sequence of this effect is anionic lability of the chlorine atom; nucleophilic substitution at the nitrogen depends on the N′-substitutent nature: chlorine atoms in ureas 1 and 5 are replaced by outer nucleophile whereas, under the same conditions, ureas 2–4 undergo cyclization into 1-alkoxybenzimidazolin-2-ones 10–12.

The pyramidality of dialkoxyamide nitrogen in ureas Me_2N-C(O)N(OR)OR′ has been demonstrated by a DNMR method ($\Delta G^{\neq}_{inv}$ = 9.8–10.5 kcal mol^{-1} at 25 °C),[2] and XRD studies in *N*-acyloxy-*N*-alkoxybenzamide,[3] *N*-acyloxy-*N*-alkoxyureas and *N*-acyloxy-*N*-alkoxycarbamates.[1] The configuration stability of nitrogen in O–N–X geminal systems [X = OC(O)R, OR, Cl] has been studied theoretically,[4,5] and for *N*-chloro-*N*-alkoxyamides it was predicted that N–C(O) and N–O rotation barriers are much higher than nitrogen inversion barriers[2,4(a)] ($\Delta G^{\neq}_{inv}$ = = 2.52 kcal mol^{-1}).[4(a)] In *N*-chloro-*N*-alkoxyureas, the N–C(O) rotation barrier was determined using the DNMR method ($\Delta G^{\neq}_{inv}$ = 19.2 kcal mol^{-1} at 25 °C).[2]

We synthesised *N*-chloro-*N*-alkoxyureas **1**–**5**‡ and studied the crystal structures of **1** and **2** (crystals were grown from CH_2Cl_2–hexane at –20 °C).§



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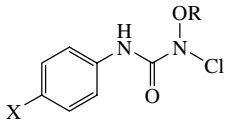
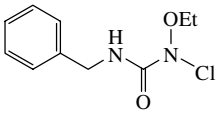


2 R = $CMe_2C(O)OMe$, X = NO_2
3 R = Et, X = NO_2
4 R = Et, X = Cl



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XRD studies of *N*-chloro-*N*-methoxyurea **1** and *N*-chloro-*N*-alkoxyurea **2** (Figures 1 and 2)§ revealed that O–N–Cl nitrogen has a pyramidal configuration [the sum of bond angles centered

† Asymmetric Nitrogen. Part 99; Geminal Systems. Part 56, for previous communications see ref. 1.

‡ N-*Chloro*-N-*methoxyurea* **1**. A mixture of a solution of Bu^{t}OCl (0.46 g, 4.24 mmol) in CH_2Cl_2 (10 ml) and *N*-methoxyurea (0.163 g, 1.81 mmol) was kept at 20 °C for 1 h; the solution obtained was filtered and concentrated *in vacuo*. The solid obtained was crystallised from CH_2Cl_2–hexane to give urea **1**, colourless crystals, mp 64–65 °C, yield 0.177 g (79%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.86 (s, 3H, OMe), 5.50 (br. s, 1H, NH), 5.89 (br. s, 1H, NH). IR (ν/cm^{-1}): 1720 (C=O). Found (%): N, 22.34; Cl, 28.31. Calc. for $C_2H_5N_2O_2Cl$ (%): N, 22.50; Cl, 28.47.

N-*Chloro*-N-*(2-methoxycarbonyl)propyl-2-oxy*-N′-*4-nitrophenylurea* **2**. The mixture of a solution of Bu^{t}OCl (0.455 g, 4.19 mmol) in CH_2Cl_2 (4 ml) and *N*-(2-methoxycarbony)propyl-2-oxy-*N′*-4-nitrophenylurea (0.0794 g, 0.267 mmol) was kept at 20 °C for 2 h; then, the solution was concentrated *in vacuo*. The white solid obtained was washed by hexane, dried *in vacuo* to give urea **2**, colourless crystals, mp 101–103 °C (CH_2Cl_2–hexane), yield 0.079 g (89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.72 (br. s, 6H, CMe_2), 3.87 (s, 3H, CO_2Me), 7.79 [d, 2H, C(2)H, C(6)H, ^3J 9 Hz], 8.25 [d, 2H, C(3)H, C(5)H, ^3J 9 Hz], 10.59 (br. s, 1H, NH). IR (ν/cm^{-1}): 1740, 1720 (C=O). Found (%): C, 43.49; H, 4.26; N, 12.85; Cl, 10.57. Calc. for $C_{12}H_{14}N_3O_6Cl$ (%): C, 43.45; H, 4.25; N, 12.67; Cl, 10.69.

N-*Chloro*-N-*ethoxy*-N′-*4-nitrophenylurea* **3** was obtained similarly to compound **2**: yield 82%, pale yellow crystals, mp 98–100 °C (CH_2Cl_2–hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.42 (t, 3H, OCH_2Me, ^3J 6.9 Hz), 4.23 (q, 2H, OCH_2Me, ^3J 6.9 Hz), 7.07 [d, 2H, C(2)H, C(6)H, ^3J 9.6 Hz], 8.26 [d, 2H, C(3)H, C(5)H, ^3J 9.6 Hz], 8.27 (br. s, 1H, NH). Found (%): C, 42.02; H, 4.01; N, 15.89; Cl, 13.45. Calc. for $C_9H_{10}N_3O_4Cl$ (%): C, 41.63; H, 3.88; N, 16.18; Cl, 13.65.

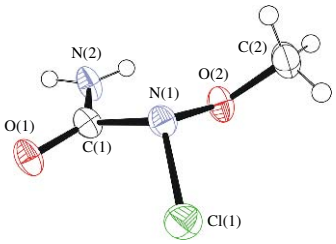


Figure 1 Molecular structure of **1**. Selected bond lengths (Å) and bond angles (°): Cl(1)–N(1) 1.7563(11), O(1)–C(1) 1.2264(15), N(1)–O(2) 1.3984(13), N(1)–C(1) 1.4429(15), N(2)–C(1) 1.3202(16); O(2)–N(1)–C(1) 109.92(8), O(2)–N(1)–Cl(1) 109.13(8), C(1)–N(1)–Cl(1) 109.96(7), N(1)–O(2)–C(2) 109.01(9).

at this nitrogen atom is 329.0(2)° for urea **1**, and 325.8(1)° for urea **2**]. Deviation of the N(1) atom from the plane of bonded atoms is 0.500(1) Å for **1** or 0.533(3) Å for **2**. This nitrogen pyramidality is a consequence of n_O–$\sigma^*_{N–Cl}$ anomeric effect dominant in *N*-chloro-*N*-alkoxyamides,[4,5] which must stabilise the sp^3 hybridization of nitrogen as predicted.[4,5]

Some elongation of the N–Cl bond in ureas **1**, **2** is observed: up to 1.757(1) Å for **1**, and 1.7572(5) Å for **2**. For comparison, the N–Cl bond lengths are 1.71–1.72 Å in 2-Cl mono-, di- and trisubstituted *N*-chloro-*N*-phenylacetamides,[6] which have almost planar configurations of the nitrogen atom. In urea **2**, some elongation of the N–O bond is observed [1.4203(7) Å] as compared to those in urea **1** [1.3984(13) Å]. It may be caused by steric hindrance in the RO substitutent. Both methyl groups at the C(8) atom have different orientations relatively to the lone electron pair (Lp) of the N(1) atom.

In *N*-chloro-*N*-alkoxyurea **2**, the carbamoyl fragment consisted of a benzene ring, both nitrogen atoms, and a carbonyl group are nearly co-planar (deviations of these atoms from the mean plane do not exceed 0.07 Å). Such a molecule conformation can be additionally stabilised by intramolecular hydrogen bonding C(3)–H(3)···O(1) (H···O 2.27 Å, C–H···O 124°). The Lp of the N(1) atom is oriented nearly perpendicular to this plane [the Lp(N1)–N(1)–C(1)–N(2) torsion angle is 74°].

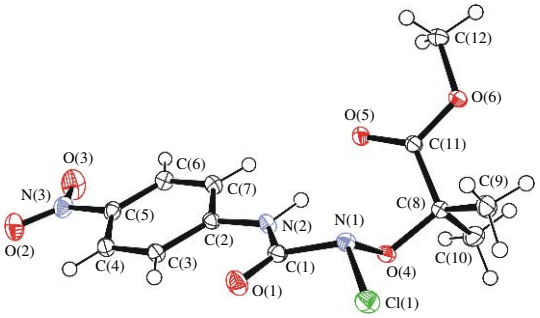


Figure 2 Molecular structure of **2**. Selected bond lengths (Å) and bond angles (°): Cl(1)–N(1) 1.7572(5), O(1)–C(1) 1.2103(7), N(1)–O(4) 1.4204(7), N(1)–C(1) 1.4719(8), N(2)–C(1) 1.1354(8), N(2)–C(2) 1.4000(8), O(2)–N(3) 1.2280(8), O(3)–N(3) 1.2323(9), O(4)–C(8) 1.4549(7), O(5)–C(11) 1.2144(7), O(6)–C(11) 1.3252(7), N(3)–C(5) 1.4618(8), C(2)–C(3) 1.4007(8), C(2)–C(7) 1.4059(8), C(3)–C(4) 1.3881(9), C(4)–C(5) 1.3866(9), C(5)–C(6) 1.3903(9), C(6)–C(7) 1.3827(9), C(8)–C(9) 1.5223(9), C(8)–C(10) 1.5290(9), C(8)–C(11) 1.5316(9); O(4)–N(1)–C(1) 108.35(5), O(4)–N(1)–Cl(1)–108.97(4), C(1)–N(1)–Cl(1) 108.51(4), N(1)–O(4)–C(8) 113.37(8), O(1)–C(1)–N(1) 121.39(6).

In both *N*-chloro-*N*-alkoxyureas **1** and **2**, N(1)–C(1) amide bonds are much longer than the N(2)–C(1) bonds [for **1**, the bond N(1)–C(1) is 1.446(3) Å, the bond N(2)–C(1) is 1.319(3) Å; for **2**, 1.4719(8) and 1.3536(8) Å, respectively]. This difference is caused by the higher conjugation of the N(2) atom with the carbonyl group.[3] Such a difference of N–C amide bonds is also observed in anomeric *N*-acetoxy-*N*-ethoxyurea.[1(b)] A broad ^{1}H NMR signal from Me_2C in urea **2**‡ evidences the pyramidality of N and a rather high nitrogen inversion barrier (*cf.* ref. 2).

Note that, in anomeric amides, the maximal pyramidality degree takes place in *N*-acyloxy-*N*-alkoxybenzamides;[3] the smallest pyramidality was observed in *N*-acyloxy-*N*-alkoxycarbamates.[1(b)] *N*-Acyloxy-*N*-alkoxyureas and *N*-chloro-*N*-alkoxyureas have an intermediate degree of pyramidality.[1(b)]

Besides the nitrogen pyramidality, the n_O-$\sigma^*_{N–Cl}$ anomeric effect causes the anionic lability of the chlorine atom, but nucleophilic substitution at the nitrogen also depends on *N′* substitutent nature: the chlorine atom in **1** is replaced by an outer nucleophile (Scheme 1).¶ Nucleophilic substitution at nitrogen in *N*-chloro-*N*-alkoxy-*N′*,*N′*-dimethylureas[5,7(a)] and *N*-chloro-

N-*Chloro*-N-*ethoxy*-N′-*4-chlorophenylurea* **4** was obtained similarly to compound **2**: yield 80%, colourless crystals, mp 73–74 °C (CH_2Cl_2–hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.41 (t, 3H, OCH_2Me, ^3J 7.2 Hz), 4.21 (q, 2H, OCH_2Me, ^3J 7.2 Hz), 7.34 [d, 2H, C(2)H, C(6)H, ^3J 8.7 Hz], 7.48 [d, 2H, C(3)H, C(5)H, ^3J 8.7 Hz], 7.97 (br. s, 1H, NH). Found (%): N, 11.52; Cl, 28.20. Calc. for $C_9H_{10}N_2O_2Cl_2$ (%): N, 11.25; Cl, 28.47.

N-*Chloro*-N-*ethoxy*-N′-*benzylurea* **5** was obtained similarly to compound **2**: yield 83%, colourless crystals, mp 52–54 °C (CH_2Cl_2–hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.31 (t, 3H, OCH_2Me, ^3J 7.1 Hz), 4.09 (q, 2H, OCH_2Me, ^3J 7.1 Hz), 4.51 (d, 2H, CH_2Ph, ^3J 5.4 Hz), 6.48 (br. s, 1H, NH), 7.26–7.52 (m, 5H, Ph). Found (%): Cl, 15.39. Calc. for $C_{10}H_{13}N_2O_2Cl$ (%): Cl 15.50.

§ *Crystal data for* **1**: $C_2H_5N_2O_2Cl$, orthorhombic, space group *Pbca*, a = 6.831(3), b = 10.096(6) and c = 15.994(4) Å, V = 1103.1(8) Å^3, F(000) = 512, d_{calc} = 1.5 g cm^{-3}, Z = 8, μ = 0.586 mm^{-1}.

Crystal data for **2**: $C_{12}H_{14}N_3O_6Cl$, monoclinic, space group $P2_1/n$, a = 7.9486(6), b = 11.4745(9) and c = 15.931(2) Å, β = 92.118(9)°, V = = 1451.9(3) Å^3, F(000) = 688, d_{calc} = 1.518 g cm^{-1}, Z = 4, μ = 0.297 mm^{-1}.

Data were measured using an Xcalibur 3 diffractometer (T = 100 K, graphite-monochromated MoKα radiation, ω and φ-scans, $2\theta_{max}$ = 75° for **1** and $2\theta_{max}$ = 85° for **2**). The structures were solved by a direct method using the SHELXTL PLUS program package.[9] Refinement against F^2 in an anisotropic approximation (the hydrogen atoms isotropic) by a full-matrix least-squares method for 12480 reflections was carried out to wR_2 = 0.1289 (84 parameters, R_1 = 0.0690 for 1591 reflections with $F > 4\sigma(F)$, S = 1.00) for **1** and for 10389 reflections was carried out to wR_2 = 0.086 [111 parameters, R_1 = 0.035 for 6729 reflections with $F > 4\sigma(F)$, S = 1.06] for **2**.

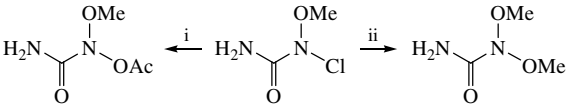
Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 606463 and 606464 for **1** and **2**, respectively. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

¶ N-*Acetoxy*-N-*methoxyurea* **6**. The mixture of a solution of *N*-chloro-*N*-methoxyurea **1** (0.100 g, 0.803 mmol) in MeCN (8 ml) and AcONa (0.165 g, 2.007 mmol) was stirred at 18–20 °C for 54 h. The solid was filtered off and washed by CH_2Cl_2. The combined filtrate was evaporated *in vacuo* yielding 0.099 g (83%) of urea **6**, colourless crystals, mp 99–100 °C (CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.21 (s, 3H, CMe), 3.90 (s, 3H, OMe), 5.56 (br. s, 1H, NH), 6.00 (br. s, 1H, NH). IR (ν/cm^{-1}): 1780, 1708 (C=O). FAB MS, m/z (%): 171 [M + Na]$^+$ (100). Found (%): C, 32.19; H, 5.54; N, 18.71. Calc. for $C_4H_8N_2O_4$ (%): C, 32.44; H, 5.44; N, 18.91.

N,N-*Dimethoxyurea* **7**. *N*-Chloro-*N*-methoxyurea **1** (0.055 g, 0.442 mmol) was added to solution of AcONa (0.045 g, 0.553 mmol) in MeOH (4 ml) at –20 °C. The reaction mixture was heated to 0 °C for 3 h and kept at 15 °C for 67 h. Then, MeOH was evaporated *in vacuo*, the solid obtained was extracted by CH_2Cl_2 (15 ml); the CH_2Cl_2 extract was evaporated *in vacuo* to yield 0.049 g (92.3%) of urea **7**, colourless crystals, mp 46–48 °C (CH_2Cl_2–hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.87 (s, 6H, OMe), 5.72 (br. s, 1H, NH), 5.97 (br. s, 1H, NH). IR (ν/cm^{-1}): 1720 (C=O). Found (%): C, 30.26; H, 6.66; N, 23.12. Calc. for $C_3H_8N_2O_3$ (%): C, 30.00; H, 6.71; N, 23.82.

N-*Acetoxy*-N-*ethoxy*-N′-*benzylurea* **8** was obtained similarly to compound **6**, yield 95%, colourless crystals, mp 51–53 °C (CH_2Cl_2–hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.29 (t, 3H, OCH_2Me, ^3J 7 Hz), 2.19 (s, 3H, CMe), 4.13 (q, 2H, OCH_2Me, ^3J 7 Hz), 4.48 (d, 2H, CH_2Ph, ^3J 5.7 Hz), 6.43 (br. s, 1H, NH), 7.26–7.40 (m, 5H, Ph). IR (ν/cm^{-1}): 1798, 1727 (C=O). Found (%): C, 56.93; H, 6.45; N, 11.05. Calc. for $C_{12}H_{16}N_2O_4$ (%): C, 57.13; H, 6.39; N, 11.10.

N-*Ethoxy*-N-*methoxy*-N′-*benzylurea* **9** was obtained similarly to compound **7**: yield 89%, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.30 (t, 3H, $NOCH_2Me$, ^3J 7.2 Hz), 3.83 (s, 3H, NOMe), 4.12 (q, 2H, $NOCH_2$Me, ^3J 7.2 Hz), 4.54 (d, 2H, CH_2Ph, ^3J 5.7 Hz), 6.40 (br. s, 1H, NH), 7.25–7.40 (m, 5H, Ph). IR (ν/cm^{-1}): 1735 (C=O). Found (%): C, 58.70; H, 7.04; N, 12.67. Calc. for $C_{11}H_{16}N_2O_3$ (%): C, 58.91; H, 7.19; N, 12.49.

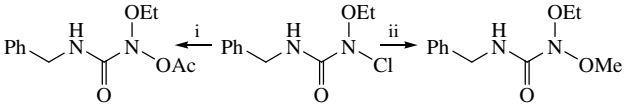


6 (71%) **1** **7** (95%)

Scheme 1 *Reagents and conditions*: i, AcONa, MeCN, room temperature; ii, MeOH, AcONa, room temperature.

N-alkoxy-*N*′-methylureas[5,7(b)] was found to proceed in the same manner.

Similarly, the nucleophilic substitution in compound **5** under the action of AcONa in MeCN yields *N*-acetoxy-*N*-ethoxyurea **8**, and its methanolysis leads to *N*,*N*-dialkoxyurea **9** (Scheme 2).

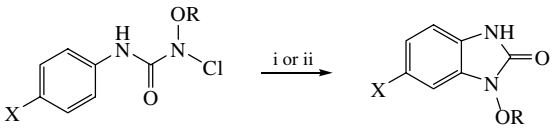


8 (95%) **5** **9** (89%)

Scheme 2 *Reagents and conditions*: i, AcONa, MeCN, room temperature, 38 h; ii, MeOH, AcONa, room temperature, 50 h.

However, in the case of *N*-chloro-*N*-alkoxy-*N*′-arylureas **2**–**4**, under the same conditions, the intramolecular nucleophilic substitution takes place, and 1-alkoxybenzimidazolin-2-ones **10**–**12** are obtained in high yields (Scheme 3). Earlier, such a cyclization of *N*-chloro-*N*-alkoxy-*N*′-arylureas in the presence of strong bases (NaH, Bu^{t}OK) has been reported.[8(a)] A like oxidative cyclization of *N*-benzyloxy-*N*′-arylureas under the action of $Pb(OAc)_4$ is also known.[8(b)] It may be supposed that *N*′-aryl ring possessing an electron-withdrawing substitutent became an intramolecular nucleophile in the presence of weak bases.

Thus, with the help of XRD data, the nitrogen pyramidality in O–N–Cl geminal systems of *N*-chloro-*N*-alkoxyureas has been established. This fact and the anionic lability of the chlorine atom prove the n_O–$\sigma_{N–Cl}$ anomeric effect domination in *N*-chloro-*N*-alkoxyureas, which can be regarded as a novel kind of anomeric amides. The course of nucleophilic substitution at the nitrogen atom was found to depend on the nature of N′-substitutent.



2–**4** **10**–**12**

2, **10** X = NO_2, R = Me_2CCO_2Me, yield 94%
3, **11** X = NO_2, R = Et, yield (i) 94%, (ii) 61%
4, **12** X = Cl, R = Et, yield 76%

Scheme 3 *Reagents and conditions*: i, AcONa, MeCN, room temperature; ii, AcONa, MeOH, room temperature.

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1-[(2′-Methoxycarbonyl)propyl-2′-oxy]-6-nitrobenzimidazolin-2-one **10** was obtained similarly to compound **12**: yield 94%, pale yellow crystals, mp 189–190 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.76 (s, 6H, Me_2C), 3.87 (s, 3H, OMe), 7.19 [d, 1H, C(4)H, ^3J 8.7 Hz], 8.11 [dd, C(5)H, ^3J 8.7 Hz, ^4J 2.1 Hz], 8.16 [d, 1H, C(7)H, ^4J 2.1 Hz], 10.35 (br. s, 1H, NH). IR (ν/cm^{-1}): 1740, 1720 (C=O). Found (%): C, 48.59; H, 4.50; N, 13.93. Calc. for $C_{12}H_{13}N_3O_6$ (%): C, 48.82; H, 4.44; N, 14.23.

1-Ethoxy-6-nitrobenzimidazolin-2-one **11** was obtained similarly to compound **12**: yield 71%, white crystals, mp 211–212 °C. ^{1}H NMR (300 MHz, [$^2H_6$]DMSO) δ: 1.33 (t, 3H, NOCH$_2$*Me*, ^3J 6.9 Hz), 4.30 (q, 3H, NOC*H*$_2$Me, ^3J 6.9 Hz), 7.21 [d, 1H, C(4)H, ^3J 8.4 Hz], 7.94 [d, 1H, C(7)H, ^4J 2.1 Hz], 8.02 [dd, 1H, C(5)H, ^3J 8.4 Hz, ^4J 2.1 Hz], 11.85 (br. s, 1H, NH). IR (ν/cm^{-1}): 1740 (C=O). EI MS, *m*/*z* (%): 223 [M]$^+$ (43.6), 195 [M – CO]$^+$ (100). Found (%): C, 48.21; H, 4.35; N, 18.53. Calc. for $C_9H_9N_3O_4$ (%): C, 48.43; H, 4.06; N, 18.82.

1-Ethoxy-6-chlorobenzimidazolin-2-one **12**. The mixture of solution of *N*-chloro-*N*-ethoxyurea **4** (0.153 g, 0.613 mmol) in MeCN (12 ml) and AcONa (0.125 g, 1.534 mmol) was stirred at 22–25 °C for 20 h, then CH_2Cl_2 (10 ml) was added; the solid was filtered off; the filtrate was evaporated *in vacuo*; the residue was extracted by CH_2Cl_2. The CH_2Cl_2 extract evaporation *in vacuo* followed by crystallization from Pr^i_2O afforded 0.087 g (76%) of benzimidazolinone **12**, white crystals, mp 170–171 °C (Pr^i_2O). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.46 (t, 3H, NOCH$_2$*Me*, ^3J 7.5 Hz), 4.36 (q, 3H, NOC*H*$_2$Me, ^3J 7.5 Hz), 7.02 [d, 1H, C(4)H, ^3J 8.4 Hz], 7.08 [d, 1H, C(5)H, ^3J 8.4 Hz], 7.13 [s, 1H, C(7)H], 9.74 (br. s, 1H, NH). IR (ν/cm^{-1}): 1740 (C=O). EI MS, *m*/*z* (%): 214 M$^+$ (22.0), 212 M$^+$ (58.9). Found (%): C, 50.88; H, 4.37; N, 13.08. Calc. for $C_9H_9ClN_2O_2$ (%): C, 50.84; H, 4.27; N, 13.17.

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