Nucleophilic Substitution of Chloro-Substituted Enaminones that are Derivatives of Imidazolidine Nitroxides − The Catalytic Effect of the Cyanide Ion

Galina I. Roshchupkina,[a] Tatyana V. Rybalova,[b] Yury V. Gatilov,[b] and Vladimir A. Reznikov*[b]

Keywords: Enaminones / Nitrogen heterocycles / Nitroxides / Nucleophilic substitution

The cyanide ion is a catalyst for reactions of nucleophiles with chloro-substituted enaminones derived from imidazolidine nitroxides, which result in the formation of formal nucleophilic substitution products.

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Introduction

The nucleophilic substitution reaction is one of the classic reaction types for the functionalization of organic molecules. These transformations are constantly the subjects of intense studies to elucidate mechanisms and methods for designing complex organic molecules having controlled geometries and properties. The reactivity of α-halo-substituted carbonyl compounds towards nucleophiles is well known and it is believed that the mechanism includes initial attack at the carbonyl carbon atom, subsequent epoxide ring closure, and then its ring opening under the action of another equivalent of the nucleophile.[1]

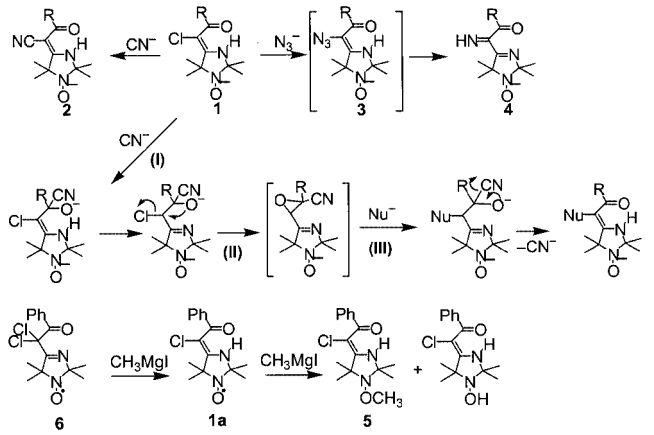
Results and Discussion

Previously, we have found that chloro-substituted enaminones **1**, which are derivatives of imidazolidine nitroxides, react unexpectedly well with cyanide ion with the formation of the formal nucleophilic substitution products, the nitriles **2**.[2] Reaction of enaminones **1** with azide ion proceeds in a similar manner, but the resulting azides **3** are unstable and are transformed spontaneously into monoimines of α-diketones (**4**).[3] A study of these reactions resulted in the conclusion that halo-substituted enaminones **1** react with these nucleophiles to form the intermediate epoxides. There are three key steps in this transformation. The first is a nucleophilic addition to the carbonyl carbon atom (**I**). Secondly, epoxide cycle formation results from an intramolecular nucleophilic substitution of chloride ion by the anionic center (**II**). It seems improbable that this step would occur without double-bond migration within the heterocycle as a result of a conjugation failure. In the case where a double-bond migration is impossible (e.g., when there is a disubstituted enamine nitrogen atom), the substitution does not proceed. Thirdly, the opening of the epoxide cycle follows by the action of one more equivalent of the nucleophile (**III**).

Nitriles **2** are of interest as paramagnetic ligands for the synthesis of coordination compounds with unusual magnetic properties.[4] Additionally, it has been shown recently that they are promising spin probes because they have pH-sensitive EPR spectra, which makes them suitable for pH measurements in molecular biophysics because their p*K* values are in the range 7−10.[5] These two applications are mostly results of introducing the nitrile group, which, on the one hand, increases the acidity of these compounds and, on the other, provides additional possibilities for participation in coordination to metal ions. We believe that enaminones of imidazolidine nitroxides having other substituents in the same position would be also of interest as paramagnetic ligands and, at first sight, there seem to be no obstacles for involving enaminones **1** in reactions with other nucleophiles.

We have found, however, that, under the same conditions, enaminone **1a** is inert towards different nucleophiles, such as amines, NO_2^-, NCO^-, NCS^-, AcO^-, and [(methylsulfinyl)methyl]sodium in DMSO solutions. In the reaction of **1a** with methylmagnesium iodide in diethyl ether, only a partial reduction of the nitroxyl group and its conversion into a methoxyl group (**5**) take place with the enaminone group remaining intact. It is interesting to note that the

[a] Novosibirsk State University,
630090 Novosibirsk, Pirogova str. 2, Russian Federation
[b] N. N. Vorozhtsov Institute of Organic Chemistry, Siberian Division of the Russian Academy of Sciences,
630090 Novosibirsk, Acad. Lavrent'ev ave. 9, Russian Federation
E-mail: mslf@nioch.nsc.ru



Scheme 1

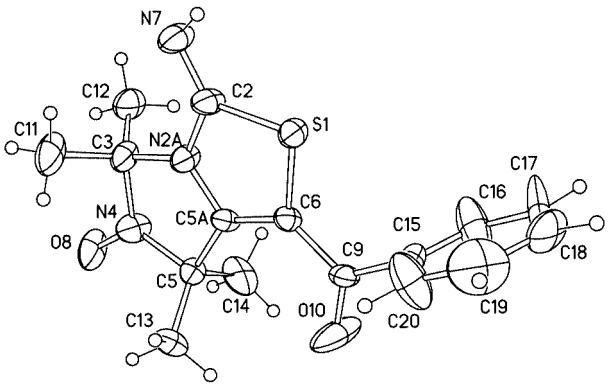


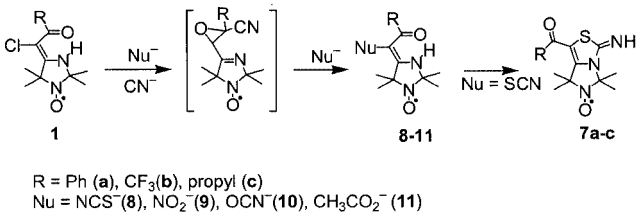
Figure 1. Crystal structure of radical **7a**; selected bond lengths [Å]: S1−C2 1.765(4), S1−C6 1.761(4), C2−N2a 1.398(5), N2a−C3 1.477(5), N2a−C5a 1.357(5), C3−N4 1.484(6), N4−C5 1.478(6), N4−O8 1.263(4), C5−C5a 1.512(5), C5a−C6 1.361(6)

reaction of the dichloro derivative **6** with excess MeMgI yields monochloro derivative **1a** along with the products described above of the further transformation of **1a**.

The reason for the inactivity of enaminones **1** towards nucleophiles that are strong bases, such as MeMgI, [(methylsulfinyl)methyl]sodium, and, probably, amines, is the readiness for deprotonation of their comparatively acidic enaminone groups, which would reduce their affinity towards nucleophiles. The inactivity of **1** in reactions with other nucleophiles can be rationalized by considering the reaction mechanism. Step **I** — the addition to the carbonyl group — should proceed more readily with hard nucleophiles and, conversely, step **III** — opening of the epoxide cycle — should be realized more easily with soft nucleophiles. Different steps of the reaction could be limiting depending on the nature of the nucleophile, but all the transformations require the nucleophile to be relatively effective in both steps **I** and **III**. Of all the nucleophiles we tested for this reaction, only the azide and cyanide ions seem to be suitable for realizing both steps.

We found out that the epoxide isolated as a reaction product of enaminone **1** (R = *tert*-butyl) with sodium cyanide undergoes spontaneous transformation to its respective nitrile **2** — even in the solid state. The transformation proceeds quantitatively and seems to be result of an autocatalytic process related to an initial liberation of a trace amount of cyanide ion that causes the reaction. Thus, we believed that the cyanide ion could be a catalyst for such transformations, particularly in the cases of soft nucleophiles. Actually, the reaction of enaminone **1a** with KNCS in the presence of a catalytic amount of sodium cyanide leads to compound **7a**. The elemental analysis data of this product corresponds to that expected for the substitution product **8a**, but, according to X-ray analysis, compound **7a** is formed as a product of a further transformation of the initially formed thiocyanate **8a**, namely a nucleophilic addition of the endocyclic nitrogen atom at the thiocyanate group, to yield a derivative of 6,7-dihydro-5*H*-imidazo[1,5-*c*][1,3]thiazole (Figure 1).

To date, there have been no 6,7-dihydro-5*H*-imidazo[1,5-*c*][1,3]thiazole derivatives reported in the Cambridge Structural Data Base.[6] The geometry of the thiazole ring is almost the same as that found in 3-(methoxycarbonylamino)-5-(methoxycarbonyl)-4-methyl-2-(phenylimino)-2,3-dihydrothiazole.[7] The bicyclic fragment is nearly planar within ±0.038(13) Å and forms an angle of 88.2(8)° with the plane of the phenyl ring. Infinite chains of molecules are formed in the crystal along the *a* axis by means of intermolecular N7−H···O8 hydrogen bonds [H···O8 distance, 2.19(5) Å; N7−H···O8 angle, 159(8)°].



R = Ph (**a**), CF_3(**b**), propyl (**c**)
Nu = NCS^-(**8**), NO_2^-(**9**), OCN^-(**10**), $CH_3CO_2^-$ (**11**)

Scheme 2

Reactions of enaminones **1b**,**c** with KNCS in the presence of NaCN proceed similarly with the subsequent formation of the 6,7-dihydro-5*H*-imidazo[1,5-*c*][1,3]thiazole derivatives **7b**,**c**. We note that the rate of reaction with KNCS in the presence of NaCN is noticeably lower (a few weeks at room temp.) than that with cyanide alone (2−3 h), but, nevertheless, the catalytic effect is quite appreciable, because in the absence of cyanide no product formation was observed during that period of time. The use of this approach permits the reaction of chloro-substituted enaminones **1** with other nucleophiles — NO_2^-, OCN^-, and AcO^- — to yield the subsequent substitution products, enaminones **8**−**11**.

In contrast to the cyanide ion, the azide ion does not catalyze the reaction of enaminones **1** with nucleophiles. The reasons for these phenomena may be because of the different limiting steps of the reactions with these two nucleophiles; in other words, the very short lifetime of the

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epoxide bearing the azido group substituent leads to its irreversible transformation into the imine **4**.

Conclusion

The cyanide anion catalyzes the reaction of nucleophiles with chloro-substituted enaminones of imidazolidine nitroxides. On one hand, these reactions confirm the postulated mechanism for the transformation and, on the other, provide a method for introducing different functional substituents into paramagnetic enaminones.

Experimental Section

General: IR spectra were recorded with a Bruker IFS 66 spectrometer as KBr pellets (concentration, 0.25%; thickness of pellet, 1 mm). UV spectra were measured in EtOH with a Specord M-40 spectrophotometer. ^{1}H and ^{13}C NMR spectra were run with a Bruker WP 200 SY spectrometer with 5−10% solutions in $CDCl_3$ and [D_6]DMSO using HMDS as the internal standard. High-resolution mass spectra were recorded with a Finnigan MAT 8200 mass spectrometer with direct sample injection. A Bruker P4 single-crystal diffractometer with graphite-monochromated Mo-K_α radiation was used to measure the unit cell dimensions and to collect data (θ-2θ scans, $\theta < 50°$). Melting points were measured with a Boëtius plate and are uncorrected. Thin layer chromatography was carried out with the use of Silufol UV-254 plates with chloroform and chloroform/methanol (30:1 or 20:1) as eluents. DMSO was dried with NaOH and distilled in vacuo from BaO. In all cases concentration was carried out under reduced pressure. The synthesis of the starting enaminones **1** was performed as published in ref.[2] and that of the dichloro derivative **6** as in ref.[8]

2-Chloro-2-(1-methoxy-2,2,5,5-tetramethylimidazolidin-4-ylidene)-1-phenylethanone (5): Enaminone **1a** (0.5 g, 1.7 mmol) was added portionwise to a solution of methylmagnesium iodide, prepared from Mg (0.2 g, 8.3 mmol) and CH_3I (0.53 mL, 8.5 mmol) in anhydrous diethyl ether (20 mL). The reaction mixture was stirred for 1 h under reflux, 7 h at room temp., and then was kept overnight before being treated with saturated aqueous NH_4Cl (15 mL). The organic layer was separated and aqueous phase was extracted with $CHCl_3$ (2 × 20 mL). The combined extracts were dried with $MgSO_4$ and filtered and then MnO_2 (2 g) was added to the resulting solution and the mixture stirred for 30 min at room temp. The excess oxidant was filtered off, the filtrate was concentrated, and a residue was separated on a silica gel column with $CHCl_3$ as eluent to provide sequentially the methoxy derivative **5** (0.2 g, 40%) and starting enaminone **1a** (0.3 g). M.p. of **5**: 127−129 °C (from hexane). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ = 1.48 (s, 6 H), 1.62 [br. s, 6 H, 2,5-$(CH_3)_2$], 3.70 (s, 3 H, OCH_3), 7.37 (m, 3 H), 7.57 (m, 2 H, C_6H_5) ppm. IR: $\tilde{\nu}_{max}$ = 3210 (NH), 1594, 1538 (O=C−C=C−N, C=C, C=N) cm^{-1}. UV/Vis (EtOH): λ_{max} (lg ε) = 243 (3.58), 343 (4.69) nm. $C_{16}H_{21}ClN_2O_2$ (308.8): calcd. C 62.24, H 6.81, N 9.08; found C 62.53, H 6.85, N 9.07.

Under the same conditions, the reaction of dichloro derivative **6** with methylmagnesium iodide provided the monochloro derivative **1a**, which was isolated in 30% yield, along with the starting material **6** (50%). The formation of methoxy derivative **5** was observed chromatographically.

Radical 7a: A mixture of enaminone **1a** (0.6 g, 2 mmol), potassium isothiocyanate (0.78 g, 9 mmol), and NaCN (20 mg, 0.3 mmol) in anhydrous DMSO (20 mL) was stirred at 20 °C for 96 h and then cooled to 0 °C and poured into cold brine (30 mL). The precipitate was filtered off, washed with water, and dried. The crude product was purified chromatographically on a silica gel ($CHCl_3$/MeOH, 50:1) to give **7a** (0.5 g, 75%). M.p. 159−161 °C (from ethyl acetate/hexane). IR: $\tilde{\nu}_{max}$ = 3322, 3291, 3206 (NH), 1639, 1610, 1564 (O=C−C=C−N, C=C) cm^{-1}. UV/Vis (EtOH): λ_{max} (lg ε) = 250 (3.96), 357 (3.71) nm. $C_{16}H_{18}N_3O_2S$ (316.4): calcd. C 60.74, H 5.73, N 13.28; found C 61.29, H 5.55, N 13.23.

Crystallographic Data for Compound 7a: $C_{16}H_{18}N_3O_2S$ (316.39), crystal class orthorhombic, space group $Pna2_1$, a = 8.201(2), b = 20.042(4), c = 9.778(2) Å, V = 1607.3(5) Å^3, Z = 4, d_c = 1.308 Mg m^{-3} μ = 0.212 mm^{-1}, λ = 0.71073 Å, crystal size 0.08 × 0.15 × 2.0 mm. A correction for absorption was made by the integration method (transmission 0.9813−0.9888). The structure was solved by direct methods and refined by a full-matrix least-squares anisotropic/isotropic procedure (for hydrogen atoms) using the SHELXL-97 program. The hydrogen atom positions were located geometrically. The final indexes are wR_2 = 0.1481, S = 1.040 for all 1496 F^2 and R_1 = 0.0493 for 1019 $F_o > 4\sigma$. The absolute structure parameter (Flack parameter) is equal to 0.6(4). Atomic coordinates, thermal parameters, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Center. CCDC-194015 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

7a,b: Reactions of enaminones **1b,c** with potassium isothiocyanate were carried out as described above. **7b:** Yield = 80%. M.p. 136−138 °C (from hexane). IR: $\tilde{\nu}_{max}$ = 3429 (OH), 3296 (NH), 1683, 1644, 1613, 1585, 1556 (O=C−C=C−N, C=N, C=C) cm^{-1} UV/Vis (EtOH): λ_{max} (lg ε) = 220 (3.71), 337 (3.29) nm. $C_{11}H_{13}F_3N_3O_2S$ (308.3): calcd. C 42.85, H 4.25, N 13.63; found C 42.76, H 4.21, N 13.29. **7c:** Yield = 30%. M.p. 127−131 °C (from hexane). IR: $\tilde{\nu}_{max}$ = 3426 (OH), 3282 (NH), 1659, 1624, 1609, 1562 (O=C−C=C−N, C=N, C=C) cm^{-1}. UV/Vis (EtOH): λ_{max} (lg ε) = 335 (4.04) nm. $C_{13}H_{20}N_3O_2S$ (282.4): calcd. C 55.29, H 7.14, N 14.88; found C 54.94, H 7.05, N 14.63.

Radical 9a: A mixture of enaminone **1a** (0.3 g, 1 mmol), $NaNO_2$ (0.14 g, 2 mmol), and NaCN (10 mg, 0.15 mmol) in anhydrous DMSO (10 mL) was stirred at 20 °C for 96 h and then cooled to 0 °C and poured into cold brine (30 mL). The precipitate was filtered off, washed with water, and dried. The mixture of unchanged **1a** (25 mg, 8%) and nitro derivative **9a** (0.12 g, 40%) was separated chromatographically on silica gel with $CHCl_3$/MeOH (50:1) as eluent. M.p. 180−184 °C (ethyl acetate/hexane). IR: $\tilde{\nu}_{max}$ = 3425 (OH), 3221 (NH), 1675, 1602, 1588 (O=C, C=C) cm^{-1}. UV/Vis (EtOH): λ_{max} (lg ε) = 254 (4.31), 336 (4.18) nm. $C_{15}H_{18}N_3O_4$ (304.3): calcd. C 59.20, H 5.96, N 13.81; found C 59.55, H 6.03, N 13.58.

Radical 10a. Method A: A mixture of enaminone **1a** (0.6 g, 2 mmol), potassium cyanate (0.83 g, 10 mmol), and NaCN (20 mg, 0.3 mmol) in anhydrous DMSO (15 mL) was stirred at 20 °C for 2 weeks and the poured into ice-cold brine (40 mL). The resulting mixture was extracted with chloroform (3 × 20 mL) and the combined extracts were washed with brine (3 × 10 mL) and water (3 × 10 mL) and then dried ($MgSO_4$). The residue obtained after re-

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moval of the solvent was purified chromatographically on silica gel ($CHCl_3$/MeOH, 50:1) to give **10a** (0.31 g, 50%). **Method B:** A mixture of enaminone **1a** (0.2 g, 0.68 mmol), potassium cyanate (0.28 g, 3.4 mmol), and NaCN (10 mg, 0.15 mmol) in anhydrous DMSO (10 mL) was heated to 110 °C with stirring for 30 min and then kept at this temperature for 30 min. After cooling, the reaction mixture was treated as described above to yield **10a** (0.12 g, 60%). M.p. 192−195 °C (ethyl acetate/hexane). IR: $\tilde{\nu}_{max}$ = 3203 (NH), 1707, 1644, 1597, 1573 (O=C, C=C) cm^{-1}. UV/Vis (EtOH): λ_{max} (lg ε) = 251 (3.83), 323 (3.97) nm. MS: calcd. for $C_{16}H_{18}N_3O_3$ *m*/*z* = 300.13524; found *m*/*z* = 300.13481.

10c: Reaction of enaminone **1c** with potassium cyanate was carried out in the same manner as described for enaminone **1a** to yield **10c** (15%). IR: $\tilde{\nu}_{max}$ = 3366 (OH), 3164 (NH), 1702, 1674, 1624 (O=C, C=C) cm^{-1} UV/Vis (EtOH): λ_{max} (lg ε) = 214 (3.98), 298 (4.74) nm. MS: calcd. for $C_{13}H_{20}N_3O_3$ *m*/*z* = 266.15046; found *m*/*z* = 266.15044.

Radical 11a: A mixture of enaminone **1a** (1.0 g, 3.4 mmol), anhydrous sodium acetate (0.84 g, 10 mmol), and NaCN (20 mg, 0.3 mmol) in anhydrous DMSO (15 mL) was stirred at 20 °C for 16 d. The reaction mixture was poured into cold brine (30 mL) and the precipitate was filtered off, washed with brine and water, and then dried on air. The crude acetate was dissolved in chloroform (20 mL) and filtered through silica gel (5 cm) with chloroform as eluent to give **11a** (0.9 g, 80%). M.p. 155−157 °C (ethyl acetate/hexane). IR: $\tilde{\nu}_{max}$ = 3262 (NH), 1759 (O=C−O), 1627, 1580, 1547 (O=C, C=C) cm^{-1}. UV/Vis (EtOH): λ_{max} (lg ε) = 242 (3.85), 332 (4.45) nm. $C_{17}H_{21}N_2O_4$ (317.4): calcd. C 64.34, H 6.67, N 8.83; found C 64.45, H 6.76, N 8.82.

Structures of compounds synthesized were confirmed by ^1H and ^{13}C NMR spectroscopy of diamagnetic analogs, namely the 1-hydroxy derivatives that were obtained by catalytic reduction with hydrogen in the presence of Pd/C (20 °C, 1 h). All hydroxyamino derivatives were found to be oxidized quantitatively to the starting nitroxides.

7a (NOH): ^1H NMR ([D_6]DMSO, 200.13 MHz): δ = 1.42 [s, 6 H, 5,5-$(CH_3)_2$], 1.51 [s, 6 H, 2,2-$(CH_3)_2$], 7.50 (m, 2 H), 7.57 (m, 1 H), 7.66 (m, 2 H) ppm. ^{13}C NMR ([D_6]DMSO, 50.32 MHz): δ = 22.2 [5,5-$(CH_3)_2$], 22.9 [2,2-$(CH_3)_2$], 64.4 (C-5), 81.4 (C-2), 101.7 (C=*C*S), 127.3, 128.3, 131.8, 139.6 (Ph), 154.6, 155.6 (C-4, SC=N), 184.4 (C=O) ppm.

9 (NOH): ^1H NMR ($CDCl_3$, 200.13 MHz): δ = 1.19 (s, 6 H), 1.52 [s, 6 H, 2,5-$(CH_3)_2$], 5.5 (broad s, 1 H, OH), 7.47 (m, 3 H), 7.80 (broad s, 2 H, Ph), 10.21 (broad s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ = 23.3 [5,5-$(CH_3)_2$], 25.7 [2,2-$(CH_3)_2$], 69.2 (C-5), 80.4 (C-2), 117.3 (=CNO_2), 128.3, 129.2, 132.8, 137.7 (Ph), 163.3 (C-4), 188.0 (C=O) ppm.

10a (NOH): ^1H NMR ($CDCl_3$, 200.13 MHz): δ = 1.36 [s, 6 H, 5,5-$(CH_3)_2$], 1.58 [s, 6 H, 2,2-$(CH_3)_2$], 6.9 (broad s, 1 H, OH), 7.40 (m, 2 H), 7.48 (m, 1 H), 7, 62 (m, 2 H, Ph), 9.31 (broad s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ = 23.0 [5,5-$(CH_3)_2$], 23.7 [2,2-$(CH_3)_2$], 64.1 (C-5), 80.1 (C-2), 113.2 (=C-O), 127.6, 128.2, 131.8, 138.0 (Ph), 140.0 (OCN), 148.3 (C-4), 183.2 (C=O) ppm.

10c (NOH): ^1H NMR ([D_6]DMSO, 200.13 MHz): δ = 0.87 (t, *J* = 7 Hz, C*H*$_3$CH$_2$), 1.33 (s, 6 H, 5,5-$(CH_3)_2$], 1.41 (s, 6 H, 2,2-$(CH_3)_2$], 1.53 (m, $CH_3CH_2CH_2$), *C*H_2CO signal masked by solvent signal, 8.12 (br. s, 1 H, OH), 10.54 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D_6]DMSO, 50.32 MHz): δ = 13.1, 16.8 (C_3H_7, *C*H_2CO signal masked by solvent signal), 23.0 [5,5-$(CH_3)_2$], 23.6 [2,2-$(CH_3)_2$], 62.6 (C-5), 78.6 (C-2), 113.1 (=C−O), 138.3 (OCN), 147.7 (C-4), 187.9 (C=O) ppm.

11a (NOH): ^1H NMR ($CDCl_3$, 200.13 MHz): δ = 1.45 [s, 12 H, 2,5-$(CH_3)_2$], 1.91 (s, 3H, C*H*$_3$CO), 5.5 (br. s, 1 H, OH), 7.35 (m, 3 H), 7.61 (m, 2 H, Ph), 10.30 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ = 20.2 (CH_3CO), 23.1 [5,5-$(CH_3)_2$], 26.4 [2,2-$(CH_3)_2$], 67.8 (C-5), 79.6 (C-2), 118.3 (=C−O), 126.8, 127.3, 129.5, 138.7 (Ph), 159.8 (C-4), 170.0 (COO), 188.2 (Ph*C*O) ppm.

Acknowledgments

We are indebted to the Russian Foundation for Basic Research for covering the license fee of the Cambridge Structural Database (Project 99-07-90133).

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Received December 29, 2002

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