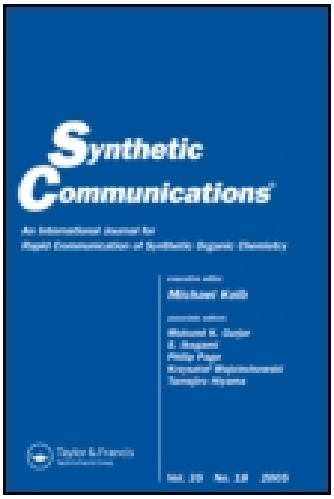


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Synthetic Access to New Carbamate and Thiocarbamate Derivatives from Pyridinecarbaldehyde Oximes and Hydroxypyridines

Ahmet Kocak [a], Gulnare Ahmetli [b], Nuriye Kocak [c], Sait Malkondu [a], Aysegul Yaylaci [a] & Sultan Kurbanli [a]

[a] Department of Chemistry, Faculty of Science, Selcuk University, Konya, Turkey

[b] Department of Chemical Engineering, Faculty of Engineering and Architecture, Selcuk University, Konya, Turkey

[c] Department of Science Education, Faculty of Education, Selcuk University, Konya, Turkey

Published online: 20 Apr 2011.

To cite this article: Ahmet Kocak, Gulnare Ahmetli, Nuriye Kocak, Sait Malkondu, Aysegul Yaylaci & Sultan Kurbanli (2011) Synthetic Access to New Carbamate and Thiocarbamate Derivatives from Pyridinecarbaldehyde Oximes and Hydroxypyridines, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:11, 1629-1637, DOI: 10.1080/00397911.2010.490627

To link to this article: http://dx.doi.org/10.1080/00397911.2010.490627

Synthetic Communications®, 41: 1629–1637, 2011

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.490627

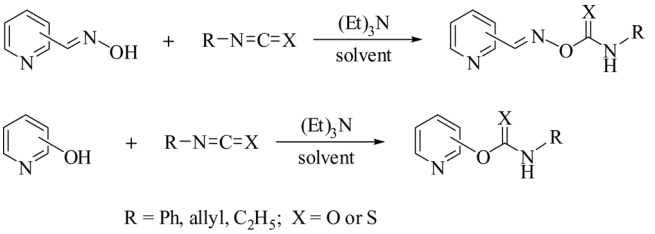
Taylor & Francis
Taylor & Francis Group

SYNTHETIC ACCESS TO NEW CARBAMATE AND THIOCARBAMATE DERIVATIVES FROM PYRIDINECARBALDEHYDE OXIMES AND HYDROXYPYRIDINES

Ahmet Kocak,[1] Gulnare Ahmetli,[2] Nuriye Kocak,[3] Sait Malkondu,[1] Aysegul Yaylaci,[1] and Sultan Kurbanli[1]

[1]*Department of Chemistry, Faculty of Science, Selcuk University, Konya, Turkey*
[2]*Department of Chemical Engineering, Faculty of Engineering and Architecture, Selcuk University, Konya, Turkey*
[3]*Department of Science Education, Faculty of Education, Selcuk University, Konya, Turkey*

GRAPHICAL ABSTRACT



Abstract *The synthesis of pyridine carbamate and thiocarbamate derivates is described. A series of oxime carbamate and thiocarbamate derivatives were synthesized by the addition of 2-, 3-, and 4-pyridinecarbaldehyde oximes to isocyanates and isothiocyanates. Furthermore, carbamate and thiocarbamate derivatives of pyridine were synthesized by the addition of 2-, 3-, and 4-hydroxy pyridine to isocyanates and isothiocyanates. Their structures were confirmed by both analytical and spectral data.*

Keywords Addition; carbamate; carbamoyl oxime; thiocarbamate

INTRODUCTION

Carbamates (urethanes) are of particular interest because of their usefulness in various industries,[1–3] such as agrochemicals,[1,2,4,5] where they are used as herbicides, fungicides, and pesticides, and in pharmaceuticals[1,2,6] as drug intermediates. Moreover, they can be used as an isocyanate source[7] for the synthesis of polyuretanes and polyureas. In addition to these, among the various

Received February 23, 2010.
Address correspondence to Sultan Kurbanli, Department of Chemistry, Faculty of Science, Selcuk University, 42075 Konya, Turkey. E-mail: skurbanli@gmail.com

amine-protecting groups, carbamates are commonly used because of their chemical stability to acids, bases, and hydrogenation.[8]

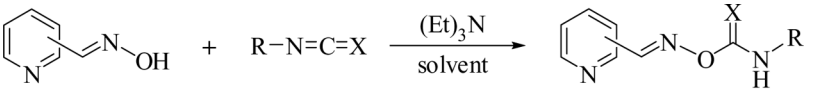
They are usually prepared by addition of an amine to a chloroformate[9] or alternately by addition of a hydroxy compound to an N-substituted carbamoyl chloride.[10] The pyridine ring system occurs in the structures of many natural products and pharmaceutical and agrochemical compounds.[11] We report herein the synthesis of a series of carbamate and thiocarbamate derivatives containing the pyridine ring system.

RESULTS AND DISCUSSION

In our previous studies, *O*-alkylation reaction of pyridine carbaldehyde oximes with dihalohydrins under phase-transfer conditions has been investigated,[12] and a series of pyridone derivatives has been synthesized by the reaction of hydroxy pyridines with various oxiranes.[13] As a continuation of our investigations, we report the synthesis of a series of carbamate and thiocarbamate derivatives of pyridine (Schemes 1 and 2).

The best solvents described in the literature[14–17] for this reaction, such as toluene–dimethylsulfoxide (DMSO) or tolene–dimethylformamide (DMF) mixtures, have a strong donor capacity and a good ability to establish hydrogen bonds. It is preferable to perform the reactions in solvents inert to the reactants [e.g., in diethyl ether, dioxane, tetrahydrofuran (THF), and acetonitrile]. Triethylamine was used because it has good catalytic strength.[18] The combined effect of solvent and catalyst cannot be easily predicted, as the relevant physicochemical properties of the solvent have not yet been reported.[15] The optimal conditions for oxime derivatization with phenylisocyanate are the use of acetonitrile or dichlorometane as solvents and the presence of triethylamine at room temperature.

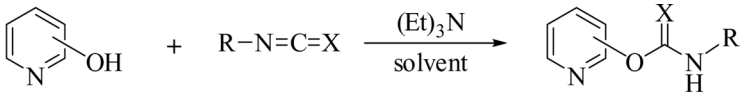
Aryl isocyanates are more reactive than alkyl isocyanates.[18–20] The use of a phenyl isocyanate instead of an alkyl or allyl isocyanate enhances carbamate formation. The results agree with the observations of Duggan[19] concerning the relative reactivity of the phenyl isocyanate and benzyl isocyanates. The derivatization took place at temperature range of 30–50 °C to avoid the decomposition of the formed carbamates, which are generally hydrolysable.[21] The product carbamates or thiocarbamates can be recovered from the product mixture using conventional techniques such as distillation, recrystallization, filtration, and the like.



1-8

1: (*E*)-2-Py, R = Ph, X = O; **2**: (*E*)-3-Py, R = Ph, X = O;
3: (*E*)-4-Py, R = Ph, X = O; **4**: (*E*)-2-Py, R = C_2H_5, X = O;
5: (*E*)-2-Py, R = Allyl, X = O; **6**: (*E*)-4-Py, R = Allyl, X = O;
7: (*E*)-2-Py, R = Allyl, X = S; **8**: (*E*)-4-Py, R = Allyl, X = S

Scheme 1. Synthesis of pyridine carbamoyl and thiocarbamoyl oximes.



9-14

9: 2-Py, R = Ph, X = O; **10**: 3-Py, R = Ph, X = O;
11: 2-Py, R = Allyl, X = O; **12**: 4-Py, R = Allyl, X = O;
13: 2-Py, R = Allyl, X = S **14:** 4-Py, R = Allyl, X = S

Scheme 2. Synthesis of pyridine carbamates and thiocarbamates.

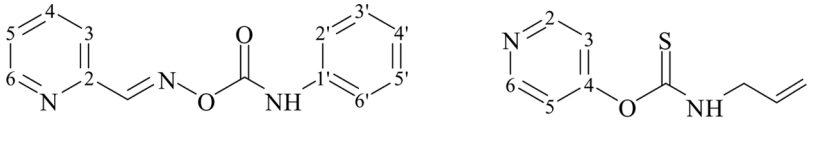
Addition of pyridine carbaldehyde oximes to isocyanates and isothiocyanates proceeds regiospecifically to afford the corresponding carbamoyl and thiocarbamoyl oxime derivatives (**1–8**) in moderate yields. The prepared pyridinecarbaldehyde oximes and the corresponding products (**1–8**) were identified as possessing the *E* configuration by correlation of ^{1}H NMR spectra. In these compounds, the chemical shift (δ 8.30–8.57) of the imine proton is downfield of the aromatic protons. If they possess the *Z* configuration, the imine proton would resonate upfield of the aromatic compounds.[22]

The structures of the carbamates and thiocarbamates were confirmed on both analytical and spectral data. The elemental analysis results agree with the theoretical values (Table 1). The Fourier transform–infrared (FT-IR) spectra of carbamates exhibited N-H stretching in the region of 3195–3220 cm^{-1}. The carbamate derivatives (**1–6** and **9–12**) showed strong C=O stretching absorptions in the region of 1700–1720 cm^{-1}, and thiocarbamate derivates (**7**, **8** and **13**, **14**) showed the presence of weak C=S stretching absorptions in the region of 1275–1295 cm^{-1}. The carbamoyl

Table 1. Physical data of the newly synthesized compounds

Compound	Yield (%)	Mp (°C) or bp (°C/mmHg)	Elemental analysis calc. (found)			
			C	H	N	S
1	75	133–135	64.72 (64.54)	4.60 (4.48)	17.42 (17.18)	—
2	61	130	64.72 (64.52)	4.60 (4.45)	17.42 (17.04)	—
3	69	120–122	64.72 (64.46)	4.60 (4.52)	17.42 (17.05)	—
4	52	88–89	55.96 (55.82)	5.74 (5.64)	21.74 (21.85)	—
5	48	140–142	58.54 (58.36)	5.37 (5.28)	15.61 (15.52)	—
6	54	192–194	58.54 (58.40)	5.37 (5.22)	15.61 (15.48)	—
7	42	Oil	54.28 (54.12)	5.01 (4.86)	18.99 (18.76)	14.49 (14.38)
8	44	Oil	54.28 (54.05)	5.01 (4.92)	18.99 (18.72)	14.49 (14.32)
9	75	126–127	67.82 (67.42)	4.71 (4.68)	13.08 (13.12)	—
10	78	130–131[a]	67.82 (67.56)	4.71 (4.60)	13.08 (12.92)	—
11	55	112–113	60.66 (60.42)	5.66 (5.54)	15.72 (15.64)	—
12	50	118–119	60.66 (60.38)	5.66 (5.44)	15.72 (15.52)	—
13	44	121–122 (1.5)	55.67 (55.54)	5.15 (5.08)	14.32 (14.18)	16.49 (16.36)
14	48	138–140 (0.5)	55.67 (55.48)	5.15 (5.04)	14.32 (14.12)	16.49 (16.42)

[a]Lit. 132 °C [23].



1 8

Figure 1. Numbering employed in NMR assignments.

and thiocarbamoyl oxime derivatives (**1–8**) exhibited strong C=N stretching bands in the region of 1660–1685 cm^{-1}.

The numbering scheme employed in NMR assignments is presented in Fig. 1. In the ^{1}H NMR spectra, chemical shifts, integrations, and splitting of products are consistent with the predicted values. In carbamoyl and thiocarbamoyl oxime derivatives (**1–8**), NH protons were observed in the region δ 6.56–6.94. These protons in compounds **9–14** were observed in the region δ 6.42–6.67. NH protons in compounds **9–14** were shifted upfield because of the lack of electron-withdrawing oxime function. The imine protons in compounds **1–8** were observed as singlets in the region δ 8.30–8.57. In the ^{13}C NMR spectra of **1–6** and **9–12**, carbonyl carbon (C=O) resonated in the region δ 164.9–168.8, whereas in compounds **7**, **8**, **13**, and **14**, thiocarbonyl carbon (C=S) resonated downfield in the region δ 181.4–184.7.

EXPERIMENTAL

All chemicals were purchased from Merck and Aldrich and were used without additional purification. Other commercial-grade solvents were distilled and then stored over molecular sieves. The melting points were determined on a Buchi capillary melting-point apparatus. The FT-IR spectra were recorded on a Pye Unicam SP 1025 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker Avance DPX 400 instrument using tetramethylsilane (TMS) as reference. The elemental compositions were determined on a Carlo Erba 1106 automatic CHN analyzer. Analytical thin-layer chromatography (TLC) was performed on Merck 60 Kieselgel F_{254} silica-gel plates; spots were visualized under ultra violet light.

Synthesis of Oximes (General Procedure)

A mixture of hydroxylamine hydrochloride (3.47 g, 0.05 mol) and Na_2CO_3 (5.3 g, 0.05 mol) in 50 mL of benzene were stirred at 60 °C for 45 min. Then 2-, 3-, or 4-pyridinecarbaldehyde (5.36 g, 0.05 mol) was added dropwise, and stirring was continued at 80 °C for 4–5 h. After completion of the reaction, the organic layer was separated from the salt by filtration and neutralized with acetic acid (2 N). The organic layer was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was dissolved in methanol or dichloromethane (DCM). The product was precipitated with petroleum ether. The precipitate was filtered, dried, and used in further reactions without purification.

Synthesis of Oxime Carbamates with Phenyl Isocyanate 1–3

A solution of phenylisocyanate (1.19 g, 0.01 mol) in DCM (10 mL) was added to a solution of (*E*)-2-, 3-, or 4-pyridinecarbaldehyde oxime (1.22 g, 0.01 mol) and triethylamine (1.0 mL, 0.01 mol) in DCM (25 mL). The mixture was stirred at 30 °C for 2–3 h. The course of the reaction was occasionally monitored by TLC. After completion of the reaction, the product was filtered and washed with water. The product was recrystallized from a mixture of methanol and CCl_4. Spectral data of **1–3** are presented.

Selected Data for 1–3

(E)-2-Pyridinecarbaldehyde-N-phenylcarbamoyl oxime 1. IR spectrum, υ_{max}, cm^{-1}: 3215 (N-H), 1705 (C=O), 1670 (C=N), 965 (N-O). ^{1}H NMR spectrum, δ, ppm: 8.86 (1H, dd, H_6, $J = 4.9$, 1.8 Hz), 8.57 (1H, s, CH=N), 7.94 (1H, dt, H_4, $J = 7.7$, 1.8 Hz), 7.78 (1H, dd, H_3, $J = 8.1$, 1.6 Hz), 7.52 (2H, dd, $H_{2',6'}$, $J = 7.8$, 1.4 Hz), 7.40 (1H, dt, H_5, $J = 7.7$, 4.9 Hz), 7.32 (2H, dt, $H_{3',5'}$, $J = 7.8$, 1.4 Hz), 7.11 (1H, dt, $H_{4'}$, $J = 7.5$, 1.6 Hz), 6.92 (1H, s, NH). ^{13}C NMR spectrum, δ, ppm: 168.8 (C=O), 152.5 (C-2), 150.3 (C-6), 149.8 (CH=N), 138.3 (C-1′), 136.7 (C-4), 129.5 (C-3′,5′), 125.3 (C-4′), 124.0 (C-5), 120.2 (C-2′,6′), 119.8 (C-3).

(E)-3-Pyridinecarbaldehyde-N-phenylcarbamoyl oxime 2. IR spectrum, υ_{max}, cm^{-1}: 3195 (N-H), 1715 (C=O), 1685 (C=N), 960 (N-O). ^{1}H NMR spectrum, δ, ppm: 8.92 (1H, t, H_2, $J = 1.2$ Hz), 8.70 (1H, dd, H_6, $J = 4.7$, 1.6 Hz), 8.30 (1H, s, CH=N), 8.15 (1H, td, H_4, $J = 7.7$, 1.6 Hz), 7.56 (1H, dd, H_5, $J = 7.7$, 4.7 Hz), 7.48 (2H, dd, $H_{2',6'}$, $J = 7.7$, 1.5 Hz), 7.30 (2H, dt, $H_{3',5'}$, $J = 7.7$, 1.5 Hz), 7.07 (1H, dt, $H_{4'}$, $J = 7.4$, 1.7 Hz), 6.84 (1H, s, NH). ^{13}C NMR spectrum, δ, ppm: 166.7 (C=O), 150.3 (C-6), 147.9 (C-2), 147.4 (CH=N), 137.8 (C-1′), 133.5 (C-4), 130.2 (C-3), 129.6 (C-3′,5′), 128.0 (C-4′), 122.8 (C-5), 120.7 (C-2′,6′).

(E)-4-Pyridinecarbaldehyde-N-phenylcarbamoyl oxime 3. IR spectrum, υ_{max}, cm^{-1}: 3210 (N-H), 1710 (C=O), 1665 (C=N), 980 (N-O).^{1}H NMR spectrum, δ, ppm: 8.85 (2H, dd, $H_{2,6}$, $J = 5.2$, 0.8 Hz), 8.42 (1H, s, CH=N), 7.77 (2H, dd, $H_{3,5}$, $J = 5.2$, 0.8 Hz), 7.53 (2H, dd, $H_{2',6'}$, $J = 7.8$, 1.5 Hz), 7.34 (2H, dt, $H_{3',5'}$, $J = 7.8$, 7.5 Hz), 7.12 (1H, dt, $H_{4'}$, $J = 7.5$, 1.5 Hz), 6.90 (1H, s, NH). ^{13}C NMR spectrum, δ, ppm: 167.4 (C=O), 150.2 (C-2,6), 146.9 (CH=N), 140.3 (C-4), 138.1 (C-1′), 128.7 (C-3′,5′), 124.8 (C-4′), 120.3 (C-2′,6′), 199.5 (C-3,5).

Synthesis of Oxime Carbamates or Thiocarbamates with Alkyl Iso (or Isothio)cyanates 4–8

Triethylamine (4.1 mL, 0.04 mol) was added to a mixture of ethyl isocyanate or allyl iso (or isothio)cyanate (0.02 mol) and (*E*)-2- or 4-pyridinecarbaldehyde oxime (3.05 g, 0.025 mol) in acetonitrile (40 mL). The mixture was stirred at 45 °C for 7–9 h. The course of the reaction was occasionally monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure. Recrystallization of the black residue from a mixture of acetone and CCl_4 afforded

carbamates **4–6**. Thiocarbamate derivatives **7** and **8** were obtained oily. Spectral data of **4–8** are presented.

Selected Data for 4–8

(E)-2-Pyridinecarbaldehyde-N-ethylcarbamoyl oxime 4. IR spectrum, υ_{max}, cm^{-1}: 3205 (N-H), 1700 (C=O), 1660 (C=N), 950 (N-O). ^1H NMR spectrum, δ, ppm: 8.82 (1H, dd, H_6, $J = 4.9$, 1.8 Hz), 8.51 (1H, s, CH=N), 7.88 (1H, dt, H_4, $J = 7.8$, 1.8 Hz), 7.75 (1H, dd, H_3, $J = 8.2$, 1.4 Hz), 7.36 (1H, dt, H_5, $J = 7.8$, 4.9 Hz), 6.94 (1H, s, NH), 3.21 (2H, q, CH_2), 1.17 (3H, t, CH_3). ^{13}C NMR spectrum, δ, ppm: 168.3 (C=O), 151.8 (C-2), 149.7 (C-6), 149.0 (CH=N), 137.1 (C-4), 124.2 (C-5), 120.1 (C-3), 36.7 (CH_2), 16.4 (CH_3).

(E)-2-Pyridinecarbaldehyde-N-allylcarbamoyl oxime 5. IR spectrum, υ_{max}, cm^{-1}: 3200 (N-H), 1720 (C=O), 1665 (C=N), 1610 (C=C), 975 (N-O). ^1H NMR spectrum, δ, ppm: 8.79 (1H, dd, H_6, $J = 5.0$, 1.7 Hz), 8.54 (1H, s, CH=N), 7.90 (1H, dt, H_4, $J = 7.8$, 1.1 Hz), 7.72 (1H, dd, H_3, $J = 8.2$, 1.7 Hz), 7.39 (1H, dt, H_5, $J = 7.8$, 5.0 Hz), 6.89 (1H, s, NH), 5.96 (1H, m, C**H**=CH_2), 5.25 (1H, dd, CH=C**H**$_2$, $J = 16.7$, 1.3 Hz), 5.13 (1H, d, CH=C**H**$_2$, $J = 9.8$), 4.15 (2H, br t, CH_2, $J = 5.6$ Hz). ^{13}C NMR spectrum, δ, ppm: 167.9 (C=O), 153.0 (C-2), 149.5 (C-6), 148.5 (CH=N), 137.0 (C-4), 133.8 (CH), 120.2 (C-3), 119.3 (C-5), 116.6 (=CH_2), 42.8 (CH_2).

(E)-4-Pyridinecarbaldehyde-N-allylcarbamoyl oxime 6. IR spectrum, υ_{max}, cm^{-1}: 3210 (N-H), 1705 (C=O), 1675 (C=N), 1615 (C=C), 965 (N-O).^1H NMR spectrum, δ, ppm: 8.88 (2H, dd, $H_{2,6}$, $J = 5.3$, 0.7 Hz), 8.45 (1H, s, CH=N), 7.76 (2H, dd, $H_{3,5}$, $J = 5.3$, 0.7 Hz), 6.87 (1H, s, NH), 5.91 (1H, m, C**H**=CH_2), 5.24 (1H, dd, CH=C**H**$_2$, $J = 16.9$, 1.4 Hz), 5.14 (1H, d, CH=C**H**$_2$, $J = 9.9$), 4.10 (2H, br t, CH_2, $J = 5.5$ Hz).^{13}C NMR spectrum, δ, ppm: 167.0 (C=O), 151.4 (C-2,6), 147.3 (CH=N), 141.5 (C-4), 134.2 (CH), 120.2 (C-3,5), 117.8 (=CH_2), 42.6 (CH_2).

(E)-2-Pyridinecarbaldehyde-N-allylthiocarbamoyl oxime 7. IR spectrum, υ_{max}, cm^{-1}: 3215 (N-H), 1680 (C=N), 1615 (C=C), 1280 (C=S), 965 (N-O). ^1H NMR spectrum, δ, ppm: 8.82 (1H, dd, H_6, $J = 4.8$, 1.8 Hz), 8.50 (1H, s, CH=N), 7.92 (1H, dt, H_4, $J = 7.7$, 1.1 Hz), 7.70 (1H, dd, H_3, $J = 8.1$, 1.6 Hz), 7.40 (1H, dt, H_5, $J = 7.7$, 4.8 Hz), 6.56 (1H, s, NH), 5.76 (1H, m, C**H**=CH_2), 5.05 (1H, dd, CH=C**H**$_2$, $J = 16.9$, 1.2 Hz), 4.90 (1H, d, CH=C**H**$_2$, $J = 9.9$), 3.82 (2H, br s, CH_2). ^{13}C NMR spectrum, δ, ppm: 183.2 (C=S), 154.4 (C-2), 152.6 (CH=N), 150.5 (C-4), 136.5 (C-4) 134.1 (CH), 119.7 (C-3), 188.2 (C-5), 115.3 (=CH_2), 43.2 (CH_2).

(E)-4-Pyridinecarbaldehyde-N-allylthiocarbamoyl oxime 8. IR spectrum, υ_{max}, cm^{-1}: 3210 (N-H), 1675 (C=N), 1620 (C=C), 1295 (C=S), 945 (N-O).^1H NMR spectrum, δ, ppm: 8.69 (2H, dd, $H_{2,6}$, $J = 5.2$, 0.9 Hz), 8.37 (1H, s, CH=N), 7.75 (2H, dd, $H_{3,5}$, $J = 5.2$, 0.9 Hz), 6.61 (1H, s, NH), 5.86 (1H, m, C**H**=CH_2), 5.25 (1H, dd, CH=C**H**$_2$, $J = 16.5$, 1.4 Hz), 5.17 (1H, d, CH=C**H**$_2$, $J = 9.4$), 4.04 (2H, br s, CH_2).^{13}C NMR spectrum, δ, ppm: 184.5 (C=S), 152.0 (C-2,6), 146.7 (CH=N), 140.8 (C-4), 139.3 (CH), 121.7 (C-3,5), 115.0 (=CH_2), 43.9 (CH_2).

Synthesis of Pyridine Carbamates with Phenyl Isocyanate 9 and 10

Triethylamine (10.1 mL, 0.1 mol) was added to a mixture of 2- or 3-hydroxypyridine (9.51 g, 0.1 mol) and phenylisocyanate (11.91 g, 0.1 mol) in a mixture of DCM and DMSO (1:1, 60 mL). The mixture was stirred at 35 °C for 3–4 h. After completion of the reaction, the solvents were removed under reduced pressure. The residue was recrystallized from a mixture of acetonitrile and tetrahydrofurane. Spectral data of **9** and **10** are presented.

Selected Data for 9 and 10

O-2-Pyridyl-N-phenylcarbamate 9. IR spectrum, υ_{max}, cm^{-1}: 3215 (N-H), 1715 (C=O), 955 (N-O).^{1}H NMR spectrum, δ, ppm: 8.29 (1H, dd, H_6, $J = 4.8$, 2.1 Hz), 7.57 (1H, dt, H_4, $J = 8.0$, 0.9 Hz), 7.51 (1H, dd, H_3, $J = 8.0$, 1.8 Hz), 7.36 (2H, dd, $H_{2',6'}$, $J = 7.9$, 1.8 Hz), 7.26 (2H, dt, $H_{3',5'}$, $J = 7.9$, 1.8 Hz), 7.18 (1H, dt, H_5, $J = 7.4$, 4.8 Hz), 7.01 (1H, dt, $H_{4'}$, $J = 7.4$, 1.9 Hz), 6.67 (1H, s, NH). ^{13}C NMR spectrum, δ, ppm: 166.4 (C-2), 165.7 (C=O), 141.1 (C-6), 138.2 (C-1′), 135.3 (C-4), 128.9 (C-3′,5′), 128.0 (C-4′), 122.4 (C-2′,6′), 114.7 (C-3), 112.5 (C-5).

O-3-Pyridyl-N-phenylcarbamate 10. IR spectrum, υ_{max}, cm^{-1}: 3210 (N-H), 1705 (C=O), 960 (N-O).^{1}H NMR spectrum, δ, ppm: 8.47 (1H, t, H_2, $J = 1.3$ Hz), 8.34 (1H, dd, H_6, $J = 4.9$, 1.6 Hz), 7.77 (1H, td, H_4, $J = 7.9$, 1.6 Hz), 7.27 (2H, dd, $H_{2',6'}$, $J = 7.7$, 1.5 Hz), 7.17 (1H, dd, H_5, $J = 7.9$, 4.9 Hz), 7.03 (2H, dt, $H_{3',5'}$, $J = 7.7$, 1.5 Hz), 6.88 (1H, dt, $H_{4'}$, $J = 7.4$, 1.6 Hz), 6.64 (1H, s, NH).^{13}C NMR spectrum, δ, ppm: 164.9 (C=O), 156.1 (C-3), 140.2 (C-6), 137.8 (C-1′), 136.2 (C-2), 130.1 (C-3′,5′), 125.9 (C-4′), 125.4 (C-5), 125.0 (C-4), 121.6 (C-2′,6′).

Synthesis of Pyridine Carbamates or Thiocarbamates with Ally Iso (or Isothio)cyanate 11–14

A solution of 2- or 4-hydroxypyridine (1.90 g, 0.02 mol) in acetone (20 mL) was added to a mixture of allyl iso (or isothio)cyanate (0.02 mol) and triethylamine (2.02 mL, 0.02 mol) in acetone (20 mL). The mixture was stirred at 50 °C for 8–10 h. After completion of the reaction, the products were purified according to the procedure for **9**. Spectral data of **11–14** are presented.

Selected Data for 11–14

O-2-Pyridyl-N-allylcarbamate 11. IR spectrum, υ_{max}, cm^{-1}: 3205 (N-H), 1715 (C=O), 1615 (C=C), 965 (N-O). ^{1}H NMR spectrum, δ, ppm: 8.31 (1H, dd, H_6, $J = 4.6$, 2.0 Hz), 7.55 (1H, dt, H_4, $J = 8.0$, 1.0 Hz), 7.43 (1H, dd, H_3, $J = 8.0$, 1.7 Hz), 7.18 (1H, ddt, H_5, $J = 7.4$, 4.6 Hz), 6.58 (1H, s, NH), 5.81 (1H, m, C**H**=CH_2), 5.16 (1H, dd, CH=C**H**$_2$, $J = 17.0$, 1.5 Hz), 5.01 (1H, d, CH=C**H**$_2$, $J = 10.1$), 3.99 (2H, br t, CH_2, $J = 5.3$ Hz).^{13}C NMR spectrum, δ, ppm: 166.8 (C-2), 165.0 (C=O), 140.7 (C-6), 135.3 (C-4), 134.1 (CH), 117.2 (=CH_2), 115.0 (C-3), 113.6 (C-5), 43.9 (CH_2).

O-4-Pyridyl-N-allylcarbamate 12. IR spectrum, υ_{max}, cm^{-1}: 3215 (N-H), 1710 (C=O), 1610 (C=C), 970 (N-O).^{1}H NMR spectrum, δ, ppm: 8.41 (2H, dd, $H_{2,6}$, $J = 5.5$, 0.8 Hz), 7.52 (2H, dd, $H_{3,5}$, $J = 5.5$, 0.8 Hz), 6.63 (1H, s, NH), 5.88 (1H, m, C**H**=CH_2), 5.31 (1H, dd, CH=C**H**$_2$, $J = 17.3$, 1.5 Hz), 5.09 (1H, d, CH=C**H**$_2$, $J = 9.7$), 3.97 (2H, br t, CH_2, $J = 5.8$ Hz).^{13}C NMR spectrum, δ, ppm: 181.4 (C-4), 165.3 (C=O), 139.9 (C-2,6), 134.5 (CH), 117.6 (C-3,5), 116.2 (=CH_2), 43.4 (CH_2).

O-2-Pyridyl-N-allylthiocarbamate 13. IR spectrum, υ_{max}, cm^{-1}: 3220 (N-H), 1605 (C=C), 1275 (C=S), 975 (N-O). ^{1}H NMR spectrum, δ, ppm: 8.27 (1H, dd, H_6, $J = 4.7$, 2.2 Hz), 7.57 (1H, dt, H_4, $J = 8.1$, 0.9 Hz), 7.41 (1H, dd, H_3, $J = 8.1$, 1.8 Hz), 7.20 (1H, dt, H_5, $J = 7.4$, 4.7 Hz), 6.48 (1H, s, NH), 5.65 (1H, m, C**H**=CH_2), 5.03 (1H, dd, CH=C**H**$_2$, $J = 16.6$, 1.5 Hz), 4. 87 (1H, d, CH=C**H**$_2$, $J = 9.5$), 3.79 (2H, br s, CH_2).^{13}C NMR spectrum, δ, ppm: 184.7 (C=S), 165.9 (C-2), 140.9 (C-6), 136.5 (C-4), 135.2 (CH), 115.3 (=CH_2), 114.7 (C-3), 113.0 (C-5), 43.2 (CH_2).

O-4-Pyridyl-N-allylthiocarbamate 14. IR spectrum, υ_{max}, cm^{-1}: 3210 (N-H), 1600 (C=C), 1280 (C=S), 985 (N-O). ^{1}H NMR spectrum, δ, ppm: 8.23 (2H, dd, $H_{2,6}$, $J = 5.4$, 0.6 Hz), 7.47 (2H, dd, $H_{3,5}$, $J = 5.4$, 0.6 Hz), 6.42 (1H, s, NH), 5.57 (1H, m, C**H**=CH_2), 4.93 (1H, dd, CH=C**H**$_2$, $J = 16.6$, 1.5 Hz), 4.72 (1H, d, CH=C**H**$_2$, $J = 9.4$), 3.80 (2H, br s, CH_2).^{13}C NMR spectrum, δ, ppm: 184.7 (C=S), 182.2 (C-4), 140.3 (C-2,6), 133.6 (CH), 116.5 (C-3,5), 115.8 (=CH_2), 44.1 (CH_2).

ACKNOWLEDGMENT

We thank the Research Foundation of Selcuk University (SUBAP, Grant No. 07201010) for financial support of this work.

REFERENCES

1. Dibenedetto, A.; Narracci, M.; Aresta, M.; Fragale C. Reaction of silyl-mono and diamines with carbon dioxide: Evidence of formation of inter- and intramolecular ammonium carbamates and their conversion into organic carbamates of industrial interest by *trans*-esterification of carbonates under carbon dioxide catalysis. *Green Chem.* **2002**, *4*, 439–443.
2. Gupte, S. P.; Shivarkar, A. B.; Chaudhari, R. V. Carbamate synthesis by solid-base catalyzed reaction of disubstituted ureas and carbonates. *Chem. Commun.* **2001**, *24*, 2620–2621.
3. Mindl, J.; Hrabik, O.; Sterba, V.; Kavalek, J. Cyclization of substituted phenyl N-(2--hydroxybenzyl)carbamates in aprotic solvents: Synthesis of 4H-1,3-benzoxazin-2(3H)-ones. *Collect. Czech. Chem. Commun.* **2000**, *65*, 1262–1272.
4. Motolcsy, G.; Nadasy, M.; Andriska, V. *Pesticide Chemistry*; Academiai Kiado: Budapest, 1988.
5. Thompson, A. Pest control on field vegetables threatened by the loss of organophosphorus (OP) and carbamate insecticides? *Pesticide Outlook* **2002**, *13*, 84–86.
6. Martin, L. L.; Davis, L.; Klein, J. T.; Nemoto, P.; Olsen, G. E.; Bores, G. M.; Camacho, F.; Petko, W. W.; Rush, D. K.; Selk, D.; Smith, C. P.; Vargas, H. M.; Winslow, J. T.;

Effland, R. C.; Fink, D. M. Synthesis and preliminary structure–activity relationships of 1-[(3-fluoro-4-pyridinyl)amino]-3-methyl-1H-indol-5-yl methyl carbamate (P10358), a novel acetylcholinesterase inhibitor. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 157–162.
7. Ozaki, S. Recent advances in isocyanate chemistry. *Chem. Rev.* **1972**, *72*, 457–496.
8. Greene, W. T.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; Wiley: New York, 1991.
9. Matyner, M.; Kurkjz, R. P.; Cotter, R. The chemistry of chloroformates: Reactions of chloroformates with nitrogen compounds. *Chem. Rev.* **1964**, *64*, 656–664.
10. Barton, D.; Ollis, W. D. Derivatives of carbon dioxide. In *Comprehensive Organic Chemistry*; Pergamon Press: Oxford, 1979, vol. 2, pp. 1083–1090.
11. Bakke, J. M. Nitropyridines: Synhtesis and reactions. *Pure Appl. Chem.* **2003**, *75*, 1403–1415.
12. Kocak, A.; Kurbanli, S.; Malkondu, S. *O*-Alkylation of pyridine aldo- and ketoximes with dihalohydrins under phase-transfer conditions. *Synth. Commun.* **2007**, *37*, 1155–1165.
13. Kocak, A.; Kurbanli, S.; Malkondu, S. Synthetic access to new pyridone derivatives through the alkylation reactions of hydroxypyridines with epoxides. *Synth. Commun.* **2007**, *37*, 3697–3708.
14. Baker, J. W.; Gaunt, J. The mechanism of the reaction of the aryl isocyanates with alcohols and amines, part V: Kinetic investigation of the reaction between phenylisocyanate and methyl and ethyl alcohols in benzene solution. *J. Chem. Soc.* **1949**, *19*, 27–31.
15. Chang, M. C.; Chen, S. A. Kinetics and mechanism of urethane reactions: Phenyls isocyanate–alcohol systems. *J. Polym. Sci. Part A: Polym. Chem.* **1987**, *25*, 2543–2559.
16. Kocovsky, P. Carbamates: A method of synthesis and some synthetic applications. *Tetrahedron Lett.* **1986**, *27*, 5521–5524.
17. Loev, B.; Kormendy, M. F. An improved synhtesis of carbamates. *J. Org. Chem.* **1963**, *28*, 3421–3426.
18. Saunders, J. H.; Frisch, K. C. *Polyurethanes Chemistry and Technology, Part I: Chemistry, High Polymers*; John Wiley and Sons: New York, 1962.
19. Duggan, M. E.; Imagire, J. S. Copper(I) chloride–catalyzed addition of alcohols to alkyl isocyanates: A mild and expedient method for alkyl carbarnate formation. *Synthesis* **1988**, *2*, 131–132.
20. Trost, B. M.; Sudhakar, A. R. Cis hydroxyamination equivalent: Application to the synthesis of (−)-acosamine. *J. Am. Chem. Soc.* **1987**, *109*, 3792–3794.
21. Christenson, I. Alkaline hydrolysis of some carbamic acid esters. *Acta Chem. Scand.* **1964**, *18*, 904–922.
22. Dalton, D. R.; Foley, H. R. O-Carbamoyloximes. *J. Org. Chem.* **1973**, *38*, 4200–4203.
23. Haworth, R. D.; Lamberton, A. H.; Woodcock, D. 44. Investigations on the influence of chemical constitution upon toxicity, part I: Compounds related to "doryl." *J. Chem. Soc.* **1947**, 176–182.