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Regio and Diastereoselective Addition of Imidazoline 3-oxides to Aryl Isocyanates

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Abstract: Δ^3-Imidazoline 3-oxides **1** underwent regio and diastereoselective cycloaddition with aryl isocyanates **2** to give 5,6,7,7a-tetrahydroimidazo[1,5-b][1,2,4]oxadiazol-2(1H)-ones **3** in excellent yields. Thermally and chemically induced retro cycloaddition of compounds **3** was demonstrated.
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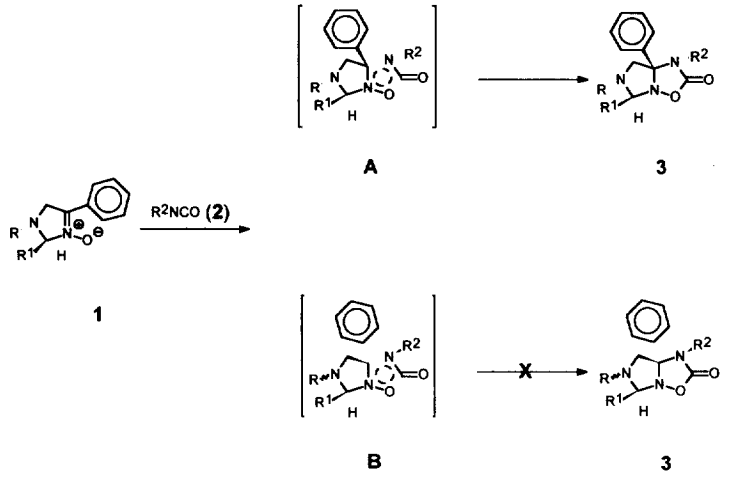
1,3-Dipolar cycloaddition reactions are excellent for the synthesis of five-membered heterocyclic rings. The commonly used 1,3-dipoles are diazoalkanes, alkyl and allyl azides, nitrile imines, nitrile ylids and nitrones.[1]

The 1,3-dipolar cycloaddition reaction of nitrones with olefins, acetylenes, isocyanates, isothiocyanates and thiocarbonyl compounds has been reported.[2-4] The 1,3-dipolar cycloaddition reaction of pyridine 1-oxide with phenyl isocyanate gave 2-anilinopyridine. The C-acylnitrone type of quinoxalin-2-one 4-oxides have also been reported to react with aryl isocyanates to give 3-arylaminoquinoxalin-2-ones via an oxadiazolone intermediate .[5]

Recently we have reported our preliminary results on the cycloaddition of imidazoline N-oxides with isocyanates.[6] We herein report in detail the synthesis of a new class of 5,6,7,7a-tetrahydroimidazo[1,5-b][1,2,4]oxadiozol-2(1H)-ones by cycloaddition of Δ^3-imidazoline 3-oxides with aryl isocyanates and thermally or chemically induced retro cycloaddition reaction of compound **3**.

Cyclic nitrones **1**, readily prepared by methods which we have already reported,[7-9] reacted with aryl isocyanates in refluxing acetonitrile or THF to give corresponding imidazooxadiazolone **3** as the sole regioisomer in excellent yields. The cycloaddition of nitrones **1f-k** to aryl isocyanates gave exclusively one diastereomer. The steric hindrance of the aryl group at C-2 on the nitrone seems to be responsible for the approach of the 2π fragment from the opposite side. The energy minimized conformations of the cis- and trans-diastereomers showed that cis should be thermodynamically more stable than the trans(trans diastereomers have about 4 kcal/mol greater E_{total}).We assume that the approach of the 2π fragment from the side opposite to the aryl group at C-2 involves lower-energy transition state and leads to the formation of cis-imidazooxadiazolone **3** (Scheme 1).



Scheme 1

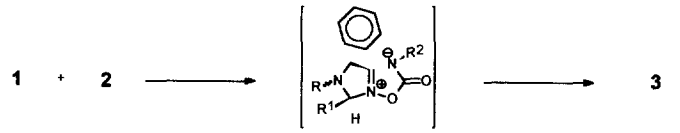
Table1. Imidazooxadiazol-2-ones

entry	yield of **3** (%)	R	R^1	R^2	mp(°C) (solvent)	IR(KBr) $cm^{-1}\nu_{C=O}$
a	100	4-$CH_3C_6H_4$	H	Ph	159-160[a]	1745
b	100	4-$MeOC_6H_4$	H	Ph	161.5[a]	1745
c	98	4-$CH_3C_6H_4$	H	4-$MeOC_6H_4$	80-81[b]	1750
d	95	4-$MeOC_6H_4$	H	4-$MeOC_6H_4$	114-115[b]	1750
e	97	4-$CH_3C_6H_4$	H	2-$MeOC_6H_4$	133-135[b]	1756
f	90	Ph	2,3$(MeO)_2C_6H_3$	Ph	159-160[c]	1775
g	93	Ph	2,3$(MeO)_2C_6H_3$	4-$MeOC_6H_4$	157-158[c]	1775
h	90	Ph	2,3$(MeO)_2C_6H_3$	2-$MeOC_6H_4$	169-170[c]	1770
i	92	4-$MeOC_6H_4$	Ph	Ph	143-144[a]	1775
j	95	4-$MeOC_6H_4$	Ph	4-$MeOC_6H_4$	153-155[b]	1775
k	97	4-MeC_6H_5	Ph	Ph	154.8-155[a]	1775

[a]=acetonitrile; [b]=ether-petroleum ether; [c]=ethanol

Two distinct mechanistic pathways may account for the formation of imidazooxadiazolones **3**. The reaction (Scheme 1; intermediate A) involves (4+2) cycloaddition of imidazoline N-oxide **1** with aryl isocyanate **2**. In this process, isocyanate **2** should react as a dipolarophile. A nucleophilic attack by imidazoline 3-oxide **1** on the

electrophilic carbon of the aryl isocyanate **2** should lead to intermediate **C** (Scheme 2) which undergoes cyclization to give **3**.



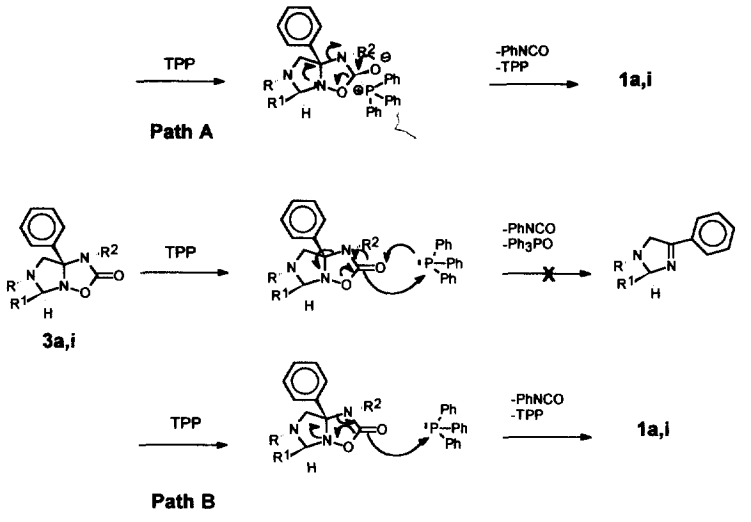
C

Scheme 2

The structures of **3** were established on the basis of their IR, ^{1}H NMR and MS spectra. Carbonyl absorptions of compounds **3a-k** are given in table 1. In the proton magnetic resonance spectra of **3a-e**, AB systems centered approximately at δ 3.85 (J_{AB}=10.85Hz) and 4.72(J_{AB}=10.24Hz) both equivalent to two protons have been assigned to protons at C-5 and C-7 respectively. In the mass spectra of **3a-e** the molecular ion peaks are absent. This is expected as the cycloadducts are thermolabile. Thus in its mass spectra, these cycloadducts underwent a retro cycloaddition as is indicated by the parent ion peaks which correspond to 1,4-diarylimidazoles formed by loss of water from **1a-e**.

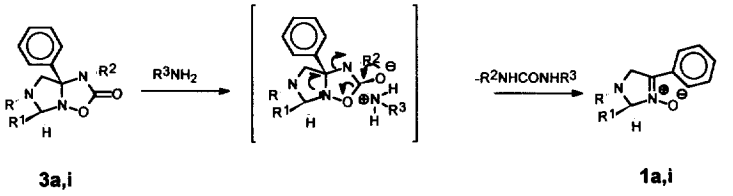
In the ^{1}H NMR spectra of **3f-k** an AB system approximately at δ 4.30 is due to the protons at C-5 and a singlet at 6.00-6.50 equivalent to one proton is assigned to proton at C-7. In the mass spectra of these compounds parent ion peaks correspond to the product of retro cyclization and in some cases to the product of retro cyclization and dehydration. NOE experiments performed for **3g** permitted a tentative assignment of the configuration of compounds **3f-k**. Irradiation of proton at C-7 led to signal enhancement for methoxy groups' protons at N-3 and C-7 aryl groups (38%, 22.7% and 31.81% respectively). Thus, the NOE results are supporting a configuration with cis oriented C-7 proton and N-3 aryl. Assuming that N-3 aryl group should be trans to the phenyl at C-4 we concluded that latter and those at C-7 should be cis to each other.

In order to induce a retro 1,3-dipolar cycloaddition reaction, compound **3i** was refluxed in THF for 24 hr but no reaction was observed. We attempted to convert compounds **3a,i** to the corresponding 3-imidazoline reacting them with TPP. We expected that the affinity of phosphorus for oxygen could provide this conversion (Scheme 3). However when **3a,i** were treated with a four fold excess of triphenylphosphine (TPP) in refluxing THF(moist) the products of the reaction were nitrones **1a,i** and aryl isocyanate which hydrolize to phenylcarbamic acid and further to aniline by loss of CO_2(aniline was detected in the reaction mixture by TLC). The probable accounts for this conversion are outlined in the scheme below. The reaction may involve a nucleophilic attack of the TPP to the oxadiazolone carbonyl (Path A) or the reaction is catalyzed by TPP which acts as a Lewis acid (Path B). Attempts to deoxygenate nitrone **1i** refluxing it in THF in the presence of two fold excess of TPP for 16hr failed. The starting nitrone was recovered unchanged.



Scheme 3

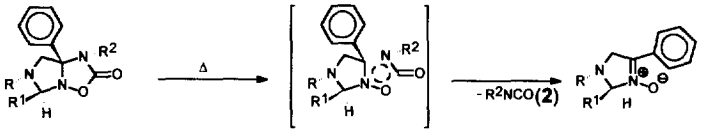
When we attempted to react compound **3i** and L-tryptophan methyl ester in refluxing THF the products isolated were again nitrone **1i** and the disubstituted urea which was synthesized separately from aryl isocyanate and tryptophan methyl ester. We repeated the reaction with aniline and the result was analogous of with tryptophan methyl ester. After 50 hrs heating compound **3i** with four fold excess of the amine the revers reaction gave the nitrone **1i** and diphenyl urea. However when we have reacted L-Tryptophan methyl ester with **3a** the product of the reaction was the imidazole corresponding to nitrone **1a**. The same imidazole was obtained from the reaction of aniline with **3a** and diphenyl urea was also isolated. We assume that in the case of **3a** where C-7 is unsubstituted the formed nitrone is probably more susceptible to dehydration.



Scheme 4

Furthermore we achieved retro-cycloaddition reactions by heating **3** in the condensed phase under vacuum (see table 2). Thermal treatment of compounds **3a-e** led exclusively to the formation of compounds **1**. In the

case of **3f** aryl isocyanate was eliminated but the formed N-oxide undergo dehydration to give corresponding imidazole. In case of **3i** where the aryl group at C-2 is unsubstituted the resulting product was nitrone **1i**.



3 A 1

Scheme 5

Table 2. Retro Cycloaddition of Compounds **3**.

Starting material	React. temp.[a]	React. time[b]	Product[d]	Yield (%)	Starting material	React. temp.	React. time	Product	Yield (%)
3a	165	20	**1a**	97	**3e**	160	15	**1a**	96
3b	165	20	**1b**	98	**3f**	160	5	**1f**[c]	0
3c	160	15	**1a**	98	**3i**	155	15	**1i**	90
3d	160	15	**1b**	95					

[a] Reaction temperatures are in °C; [b]Reaction time in min.;[c]The product of dehydration of the corresponding imidazoline N-oxide.; [d]Compounds **3a-f,i** were thermolysed at 1.3x10-3 mm Hg.

EXPERIMENTAL

Melting points were taken on a Electrothermal Digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a Mattson 1000 FTIR. Proton magnetic resonance spectra were recorded on a Varian 200 MHz spectrometer. Chemical shifts are reported in delta(δ) units, using tetramethylsilane as an internal standart. Spin multiplicities are indicated by the symbols: s (singlet), d (doublet), m (multiplet). All spectra were taken in deuteriochloroform. Mass spectra were routinely recorded at 70 eV by electron impact on a Hewlett Packard GC-MS. Elemental analyses were performed in the laboratories of TUBITAK. Analytical thin layer chromatography (TLC) was done on Kieselgel 60 F_{254} (E. Merck). Visualisation was effected with UV light. Freshly prepared imidazoline 3-oxides were used after recrystallization from either ethanol or acetone. Aryl isocyanates were commercial products (Aldrich).

Preparation of imidazooxadiazol-2-ones (3). General Procedure: To a suspension of imidazoline 3-oxide **1** (2mmol) in acetonitrile (10mL) phenyl isocyanate (4mmol) was added. The mixture was refluxed at stirring for 2.5 hr. The solvent and the excess of phenyl isocyanate were removed under vacuum. The residue was triturated with petroleum ether and the formed solid was filtered. TLC controls showed the presence of almost pure **3**. Further purification was performed by recrystallization from solvents such as ethanol, acetonitrile or ether.

Imidazooxadiazol-2-one (3a). To a suspension of **1a** (0.504g, 2mmol) in acetonitrile (10mL) phenyl isocyanate (0.476g, 4mmol) was added and the mixture stirred at reflux for 2.5hr. TLC controls indicated the absence of **1a** in the mixture. The reaction was stopped and the solvent and the excess of isocyanate were removed under reduced pressure. The residue solidifies after trituration with petroleum ether. The solid was filtered and dried on air (0.740g, 100%). The melting point of the needle shaped crystals obtained after recrystallization from acetonitrile is 159-160°C. IR (KBr) $\nu_{C=O}$ 1745 cm^{-1}. ^1H NMR δ 2.28(3H,s), 3.48(1H,d,J=10.83), 4.18(1H,d,J=10.80), 4.38(1H,d,J=10.23), 5.04(1H,d,J=10.24), 6.68(2H,d,J=8.5), 6.88(2H,m), 7.10(2H,d,J=8.5), 7.30(3H,m), 7.40(5H,s); MS m/z 234 (M^+ of the corresponding 1,4-diarylimidazole).

Anal. Calcd for $C_{23}H_{21}N_3O_2$: C, 74.37; H, 5.70; N, 11.31. Found: C, 74.19; H, 5.94; N, 11.23.

The following compounds were prepared according to the procedure described for **3a**:

Imidazooxadiazol-2-one (3b). Yield quantitative. The melting point of the needle shaped crystals obtained after recrystallization from acetonitrile is 161.5°C. IR (KBr) $\nu_{C=O}$ 1745 cm^{-1}. ^1H NMR δ 3.42(1H,d,J=10.69), 3.75(3H,s), 4.12(1H,d,J=10.75), 4.32(1H,d,J=10.26), 5.00(1H,d,J=10.24), 6.75(2H,d,J=8), 6.88(2H,m),7.25-7.35(5H,m), 7.40(5H,s); MS m/z 250 (M^+ of the corresponding 1,4-diarylimidazole).

Anal. Calcd for $C_{23}H_{21}N_3O_3$: C, 71.30; H, 5.46; N, 10.85. Found: C, 71.20; H, 5.28; N, 10.50.

Imidazooxadiazol-2-one (3c). Yield 98%. The melting point of the needle shaped crystals obtained after recrystallization from ether-petroleum ether is 80-81°C. IR (KBr) $\nu_{C=O}$ 1750 cm^{-1}. ^1H NMR δ 2.30(3H,s), 3.35(1H,d,J=10.82), 3.78(3H,s), 4.20(1H,d,J=10.74), 4.36(1H,d,J=10.32), 5.08(1H,d,J=10.29), 6.15-6.32(6H,m), 7.12(2H,d,J=8.3),7.42(5H,s); MS m/z 234 (M^+ of the corresponding 1,4-diarylimidazole).

Anal. Calcd for $C_{24}H_{23}N_3O_3$: C, 71.80; H, 5.77; N, 10.47. Found: C, 71.72; H, 5.88; N, 10.30.

Imidazooxadiazol-2-one (3d). Yield 95%. The melting point of the crystals obtained after recrystallization from ether-petroleum ether is 114-115°C. IR (KBr) $\nu_{C=O}$ 1750 cm^{-1}. ^1H NMR δ 3.30(1H,d,J=10.59),

3.75(3H,s), 3.78(3H,s), 4.12(1H,d,J=10.62), 4.28(1H,d,J=10.35), 5.03(1H,d,J=10.37), 6.20-6.40(8H,m), 7.40(5H,s); MS m/z 250 (M^+ of the corresponding 1,4-diarylimidazole).

Anal. Calcd for $C_{24}H_{23}N_3O_4$: C, 69.05; H, 5.55; N, 10.06. Found: C, 69.00; H, 5.54; N, 9.60.

Imidazooxadiazol-2-one (3e). Yield 97%. The melting point of the needle shaped crystals obtained after recrystallization from ether-petroleum ether is 133-135°C. IR (KBr) $\nu_{C=O}$ 1756 cm^{-1}. ^1H NMR δ 2.28(3H,s), 3.32(1H,d,J=10.48), 3.40(3H,s), 4.32(1H,d,J=10.57), 4.40(1H,d,J=11.84), 5.08(1H,d,J=9.82), 6.60-6.70(3H,m), 6.78-6.90(3H,m), 7.10(2H,d,J=8), 7.38(5H,s); MS m/z 234 (M^+ of the corresponding 1,4-diarylimidazole).

Anal. Calcd for $C_{24}H_{23}N_3O_3$: C, 71.80; H, 5.77; N, 10.47. Found: C, 71.75; H, 5.80; N, 10.35.

Imidazooxadiazol-2-one (3f). Yield 90%. The melting point of the needle shaped crystals obtained after recrystallization from ethanol is 159-160°C. IR (KBr) $\nu_{C=O}$ 1775 cm^{-1}. ^1H NMR δ 3.85(3H,s), 4.00(3H,s), 4.40(AB system,J_{AB}=11.26), 6.40(1H,s), 6.60-6.90(9H,m), 7.10-7.40(9H,m); MS m/z 356 (M^+ of the corresponding 1,2,4-diarylimidazole). Another peak correspond to m/z 374 (M^+ of the 1,2,4-triaryl-3-imidazoline 3-oxide).

Anal. Calcd for $C_{30}H_{27}N_3O_4$: C, 70.00; H, 5.51; N, 8.51. Found: C, 70.10; H, 5.55; N, 8.45.

Imidazooxadiazol-2-one (3g). Yield 93%. The melting point of the needle shaped crystals obtained after recrystallization from ethanol is 157-158°C. IR (KBr) $\nu_{C=O}$ 1775 cm^{-1}. ^1H NMR δ 3.78(3H,s), 3.85(3H,s), 4.00(3H,s), 4.35(2H,AB system,J_{AB}=11.11), 6.50(1H,s), 6.60-6.90(10H,m), 7.15-7.25(2H,m), 7.40(5H,s); MS m/z 356 (M^+ of the corresponding 1,2,4-diarylimidazole).

Anal. Calcd for $C_{31}H_{29}N_3O_5$: C, 71.11; H, 5.58; N, 8.02. Found: C, 71.10; H, 5.87; N, 7.90.

Imidazooxadiazol-2-one (3h). Yield 90%. The melting point of the crystals obtained after recrystallization from ethanol is 169-170°C. IR (KBr) $\nu_{C=O}$ 1775 cm^{-1}. ^1H NMR δ 3.78(3H,s), 3.85(3H,s), 4.00(3H,s), 4.35(2H,AB system,J_{AB}=11.11), 6.50(1H,s), 6.60-6.90(10H,m), 7.15-7.25(2H,m), 7.40(5H,s); MS m/z 356 (M^+ of the corresponding 1,2,4-diarylimidazole).

Anal. Calcd for $C_{31}H_{29}N_3O_5$: C, 71.11; H, 5.58; N, 8.02. Found: C, 71.00; H, 5.80; N, 8.10.

Imidazooxadiazol-2-one (3i). Yield 92%. The melting point of the white prisms obtained after recrystallization from acetonitrile is 143-144°C. IR (KBr) $\nu_{C=O}$ 1775 cm^{-1}. ^1H NMR δ 3.72(3H,s), 4.38(2H,AB system,J_{AB}=10.99), 5.88(1H,s), 6.65(2H,d,J=8), 6.78(2H,d,J=8), 6.95(2H,m), 7.25-7.50(13H,m); MS m/z 326 (M^+ of the corresponding 1,2,4-diarylimidazole).

Anal. Calcd for $C_{29}H_{25}N_3O_5$: C, 75.14; H, 5.44; N, 9.06. Found: C, 75.10; H, 5.40; N, 9.10.

Imidazooxadiazol-2-one (3j). Yield 95%. The melting point of the white prisms after recrystallization from ether-petroleum ether is 153-155°C. IR (KBr) $\nu_{C=O}$ 1775 cm^{-1}. ^1H NMR δ 3.75(3H,s), 3.78(3H,s), 4.20(2H,AB system,J_{AB}=11.16), 6.00(1H,s), 6.60-6.85(8H,m), 7.20-7.40(10H,m); MS m/z 326 (M^+ of the corresponding 1,2,4-diarylimidazole).
Anal. Calcd for $C_{30}H_{27}N_3O_4$: C, 73.00; H, 5.51; N, 8.51. Found: C, 72.90; H, 5.60; N, 8.40.

Imidazooxadiazol-2-one (3k). Yield 97%. Recrystallized from ethanol; mp 154.8-155°C. IR (KBr) $\nu_{C=O}$ 1775 cm^{-1}. ^1H NMR δ 2.30(3H,s), 4.40(2H,ABsystem,J_{AB}=11), 5.90(1H,s), 6.70(2H,d,J=8), 6.88(2H,d,J=8), 7.20-7.50(15H,m); MS m/z 310 (M^+ of the corresponding 1,2,4-diarylimidazole).
Anal. Calcd for $C_{29}H_{25}N_3O_2$: C, 77.82; H, 5.63; N, 9.39. Found: C, 77.80; H, 5.70; N, 9.35.

Retro cycloaddition of compounds 3. General Procedure: Compound **3** (0.1mmol) was placed in a glass sample vial and heated in a vacuum oven at 155-160°C for 5-20 min under $1.3x10^{-3}$ mm Hg. Then left to cool at room temperature. The obtained **1** solidifies. The compound was triturated with 0.5mL of ethanol and collected by filtration. The identity of the obtained compounds with the authentic samples was determined comparing their mp as well as their IR spectra. (see table 2 for experimental details)

Reaction of compound 3 with TPP.

Reaction of **3a** with TPP. A solution of compound **3a** (0.185g, 0.5mmol) in THF (20mL, containing about 5% H_2O) was refluxed for 48 hrs. TLC controls showed that no conversion occurred. Then TPP (0.524g, 2mmol) was added and the mixture refluxed for another 48 hrs. The solvent was reduced to 5ml at heating and left to cool. To the formed crystalline solid ethanol was added and filtered. The solid was dissolved in ethanol at heating and filtered. The solution was left to crystallize at room temperature. The product was collected by filtration. Mp 223-224 mp of the starting N-oxide 223.5°C.
Reaction of **3i** with TPP. To a solution of compound **3i** (0.046g,0.1mmol) in THF (6mL,containing 5% water) triphenylphosphine (TPP) was added (0.104g,0.4mmol) and the mixture refluxed for 48 hrs. The solvent was evaporated under reduced pressure and the residue subjected on preparative TLC plate. The product isolated was characterized to be the corresponding **1i** by comparing their mps and IR spectra.

Reaction of compounds 3 with primary amines.

Reaction of **3a** with aniline. To a solution of compound **3a** (0.185g,0.5mmol) in 20ml of THF aniline (0.182g,2mmol) and 140mg trimethylamine hydrochloride were added in success. The reaction mixture was

refluxed for 3 days. The solvent was evaporated and the residue extracted with warm hexane (4x5mL). The combined extracts were concentrated and left to crystallize at room temperature. The white needles formed were collected by filtration. Mp 134-135°C ; mp of the authentic sample[10] 135°C. The ir spectrum of the compound was superimposed with the spectrum of authentic 1-p-tolyl-4-phenylimidazole. The remaining part of the residue was acidified with 5% HCl and extracted with ether (3x10mL). The extracts were combined and dried over anh. sodium sulfate and filtered. The solvent was evaporated and the residue crystallized from ethanol. The compound has mp 239-241°C. It's ir spectrum was compared with the spectrum of N,N'-diphenyl urea.

Reaction of **3i** with aniline. To a solution of compound **3i** (0.046g,0.1mmol) in dry THF (6mL) aniline was added (0.040g,0.43mmol) and the mixture stirred at reflux for 50hrs. The solvent was evaporated and the residue extracted twice with warm hexane (2x3mL). The remaining mixture was separated by means of preparative TLC. One of the compounds recrystallized from ethanol has mp 187-188°C lit[9] mp of the corresponding imidazoline 3-oxide is 187-188°C. IR spectrum of the compound was identical to those of starting **1i**. The second one (N,N'-diphenyl urea) was recristallized from chloroform, mp 239-241°C.

Reaction of **3a** with L-tryptophane methyl ester. To a solution of **3a** (0.037g,0.1mmol) in THF (5mL) triethylamine (0.0100g,0.1mmol) and tryptophane methyl ester hydrochloride were added and the reaction mixture stirred at reflux for 72hrs. The solvent was evaporated on a rotary-evaporator and the residue extracted with warm hexane (4x5mL). The combined extracts were reduced to 7mL and left to crystallize at room temperature. The first formed crystals were filtered (10mg,27%)and proven to be unreacted **3a**. The filtrate was left overnight at room temperature. The formed colourless crystals were filtered (11mg,47%). The presence of N-phenyl-N-(β-indolyl-α-methoxycarbonyl)ethyl urea in the reaction mixture was detected by means of qualitative TLC using a standart obtained according to the procedure described below.

Reaction of **3i** with L-tryptophane methyl ester. To a solution of **3i** (0.046g,0.1mmol) in THF (10mL) tryptophane methyl ester hydrochloride (0.0254g,0.1mmol) and equimolar amount of triethylamine were added successively and the reaction mixture stirred at reflux for 48hrs. The solvent was evaporated and the mixture subjected on a preparative TLC plate. Compound **1i** was isolated in 60% yield. (The identity of the compound was proven by comparison with the starting **1i**) The corresponding urea was isolated and its mp and IR spectrum were compared with the mp and spectrum of the compound obtained from the reaction of tryptophane methyl ester with phenyl isocyanate.

Preparation of N-phenyl-N'-(β-indolyl-α-methoxycarbonyl)ethyl urea. To a solution of tryptophan methyl ester hydrochloride (0.254g,1mmol) in chloroform (10mL) triethylamine (0.101g,1mmol) was added and the reaction mixture stirred at room temperature for 15min. Phenyl isocyanate (0.119g,1mmol) was dropped to the mixture and the stirring continued for 4hrs. Water was added to the mixture and the layers separated on a

separation funnel. The organic phase was dried over anh. Na_2SO_4 and filtered. The solvent was evaporated on a rotary-evaporator and the residue triturated with ether. The white solid was collected by filtration. Yield 85%. Mp163-164°C. IR (KBr) ν_{NH} 3438; 3352; 3309. $\nu_{C=O}$ 1731ester; 1640 urea.

REFERENCES AND NOTES

1. Norman, R.O.C. *Principles of Organic Synthesis*; Chapman and Hall: London, **1978**; pp.296-299.
2. Padwa, A.; *Angew. Chem.* **1976**, 88, 131-144 and references cited therein.
3. Oppolzer, W. *Angew. Chem.* **1977**, 89, 10-24.
4. Beckmann, E. *Ber.*, **1890**, 23, 3331-3341, ibid. **1894**, 27, 1957-1959.
5. Kurasawa, Y.; Takada, A.; Kim, H.S. *J. Heterocyclic Chem.* **1995**, 32, 1085-1114.
6. Coşkun, N. *Tetrahedron Lett.* **1997**, 38, 2299-2302.
7. Coşkun,N.;Sümengen,D. *Synth. Commun.* **1993**, 23, 1699-1706.
8. Coşkun, N.; Asutay, O.; Sümengen, D. *Chim. Acta Turc.* **1996**, 24, 165-167.
9. Coşkun, N.; Asutay, O. *Chim. Acta Turc.* In press.
10. The corresponding imidazole was obtained by vacuum dehydration of the corresponding imidazoline 3-oxide (our unpublished results).

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