

HETEROCYCLE SYNTHESSES BY DIAMINOCARBENE–PALLADIUM(II) COMPLEX INTERMEDIATES

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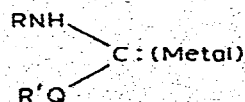
Summary

Imidazolones, dihydrooxadiazinones and tetrahydrotriazinones were synthesized by PdCl_2 catalyzed reaction of isonitriles with α -amino acid esters, with α -hydroxy acid hydrazides and with α -amino acid hydrazides, respectively. Diaminocarbene–palladium(II) complexes, which are involved as key intermediates in these heterocycle syntheses, were isolated and characterized. Diaminocarbene–palladium(II) complexes, which are prepared from $\text{PdCl}_2(\text{t-C}_4\text{H}_9\text{NC})_2$ and β -aminoalcohols, such as methyl threonate and *o*-aminophenol, were reacted with Ag_2O to afford (*N*-*t*-butylimino)oxazolidines.

There has been much interest in carbene-coordinated metal complexes from synthetic and mechanistic viewpoints [1]. Some years ago we found Group IB metal catalyzed-insertion reactions of isonitriles with amines, alcohols, thiols and phosphines, producing the corresponding formimidic acid derivatives (eq. 1) [2].



It has been now established [3] that a reaction mechanism involving aminocarbene metal complexes (I) as key intermediates is operative in the isonitrile insertion reaction.



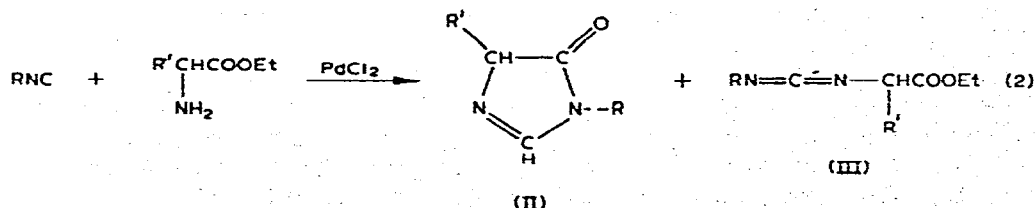
(I)

A successful extension of the isonitrile insertion reaction mentioned above is in the preparation of 5- and 6-membered heterocycles containing $-\text{N}=\text{CHNH}-$, $-\text{N}=\text{CHO}-$ and $-\text{N}=\text{CHS}-$ units. In the preceding paper [4], we described a synthesis of imidazolines, oxazolines, dihydrooxazines and thiazolines by silver(I)-catalyzed reactions of isonitriles with diamines, with aminoalcohols and with

aminothiols. In the heterocycle synthesis, PdCl_2 was found to be a much more effective catalyst than Group IB metal compounds [5]. Of interest was that an intermediate diaminocarbene-palladium(II) complex in the heterocycle synthesis was isolable [6]. This synthesis of heterocycles using PdCl_2 as catalyst is versatile and applicable to the preparation of some other heterocycles. The present paper reports the synthesis of imidazolones, iminoxazolidines, dihydrooxadiazinones and tetrahydrotriazinones by PdCl_2 -catalyzed reactions of isonitriles with α -amino acid esters, with β -aminoalcohols, with α -hydroxy acid hydrazides and with α -amino acid hydrazides, respectively. Isolation and characterization of the corresponding diaminocarbene-palladium(II) complexes which are involved as key intermediates in the heterocycle syntheses also are described.

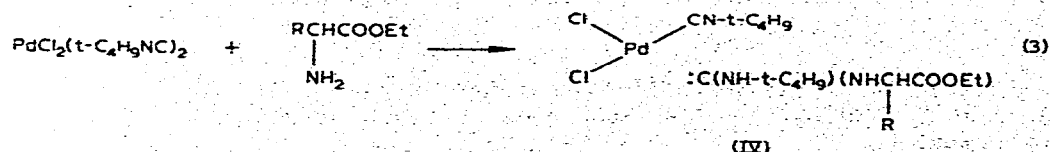
Imidazolone synthesis

An α -amino acid ester was allowed to react with an isonitrile in the presence of a catalytic amount of PdCl_2 to produce a 5-imidazolone (II) along with a small amount of a carbodiimide (III) (eq. 2).



Imidazolones also were prepared by PdCl_2 -catalyzed reaction of α -amino acid amides with isonitriles, but in low yield. Some results are summarized in Table 1.

As to the reaction mechanism, it is interesting to note that diaminocarbene-palladium(II) complexes (IV) were formed in the reaction of α -amino acid esters with $\text{PdCl}_2(\text{t-C}_4\text{H}_9\text{NC})_2$ (eq. 3).

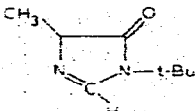
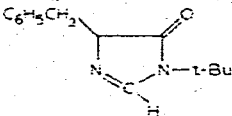
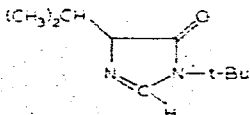
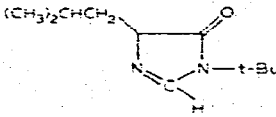
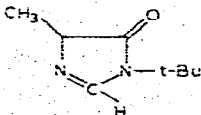


Yields (%)

- a. (R = CH_3), 65;
- b. (R = PhCH_2), 65;
- c. (R = $\text{i-C}_3\text{H}_7$), 80;
- d. (R = $\text{i-C}_4\text{H}_9$), 76

The structure of the carbene-palladium(II) complex (IV) has been established by elemental analysis, IR, NMR and molecular weight determination. The IR spectra of carbene-palladium(II) complexes (IV) exhibited strong bands at $2221\text{--}2218\text{ cm}^{-1}$ due to the *t*-butyl isocyanide ligand and at $1565\text{--}1575\text{ cm}^{-1}$, which are characteristic of coordinated diaminocarbene ligand. The *cis*-configura-

TABLE I
PREPARATION OF IMIDAZOLONE BY THE REACTION OF ISONITRILE WITH α -AMINO ACID
ESTER OR AMIDE

α -Amino acid ester or amide	Product (%)	
	Imidazolone	Carbodiimide
$\text{CH}_3\text{CHCO}_2\text{Et}$ NH_2	 (IIa)	$\text{CH}_3\text{CHCO}_2\text{Et}$ $\text{N}=\text{C}=\text{N-t-Bu}$ (IIIa)
$\text{C}_6\text{H}_5\text{CH}_2\text{CHCO}_2\text{Et}$ NH_2	 (IIb)	$\text{C}_6\text{H}_5\text{CH}_2\text{CHCO}_2\text{Et}$ $\text{N}=\text{C}=\text{N-t-Bu}$ (IIIb)
$(\text{CH}_3)_2\text{CHCHCO}_2\text{Et}$ NH_2	 (IIc)	$(\text{CH}_3)_2\text{CHCHCO}_2\text{Et}$ $\text{N}=\text{C}=\text{N-t-Bu}$ (IIIc)
$(\text{CH}_3)_2\text{CHCH}_2\text{CHCO}_2\text{Et}$ NH_2	 (IIc')	$(\text{CH}_3)_3\text{CHCH}_2\text{CHCO}_2\text{Et}$ $\text{N}=\text{C}=\text{N-t-Bu}$ (IIId)
$\text{CH}_3\text{CHCONH}_2$ NH_2	 (IIa)	

tion of IV is indicated by two bands at ca. 300 cm^{-1} assigned to $\nu(\text{Pd}-\text{Cl})$ (IVa: 320 cm^{-1} and 283 cm^{-1}). The diaminocarbene-palladium(II) complex (IV) thus obtained, which was stable at room temperature, was treated with triphenylphosphine at 80°C for 30 min to produce the corresponding imidazolone (II) and carbodiimide (III) e.g.,

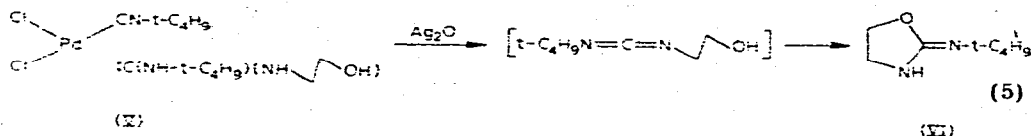


This finding suggests that diaminocarbene-palladium(II) complex (IV) may be

an intermediate in the imidazolone synthesis. The by-product carbodiimide (III) is regarded as the dehydrogenated product of diaminocarbene-palladium(II) complex (IV). Recently, we reported that carbodiimide (III) is produced in high yield and high selectivity by the oxidation of IV with Ag_2O [7].

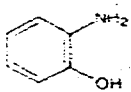
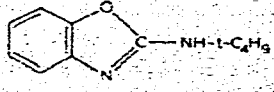
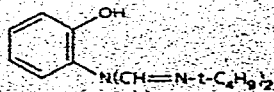
Iminooxazolidine synthesis

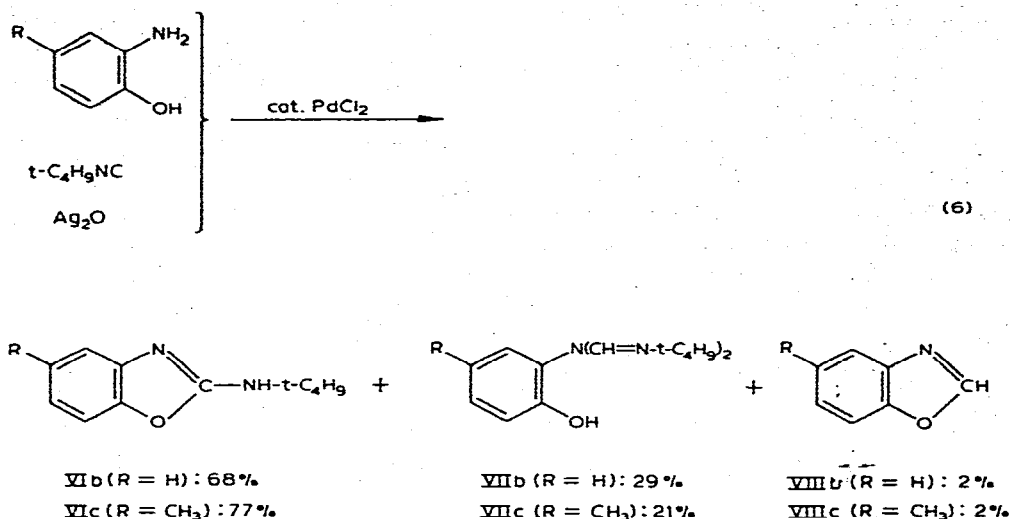
As mentioned above, N,N' -disubstituted diaminocarbene-palladium(II) complexes react with Ag_2O at room temperature to give carbodiimides in high yields. Now we have found that treatment of diaminocarbene-palladium(II) complexes (V) [8], which are prepared from $\text{PdCl}_2(\text{t-C}_4\text{H}_9\text{NC})_2$ and β -aminoalcohols such as methyl threonate and *o*-aminophenol, with Ag_2O afforded (*N*-*t*-butylimino)-oxazolidine derivatives (VI) in moderate yields with a minor by-product of diamide (eq. 5) (Table 2). The reaction may involve a carbodiimide intermediate, whose intramolecular cyclization leads to the formation of VI.



(*N*-*t*-Butylimino)benzoxazole (VIb) was prepared more conveniently by a catalytic reaction in which a heterogeneous mixture of *o*-aminophenol, *t*-butyl isocyanide, Ag_2O and a catalytic amount of PdCl_2 was heated in refluxing benzene. Two by-products, VII and VIII were formed as well (eq. 6).

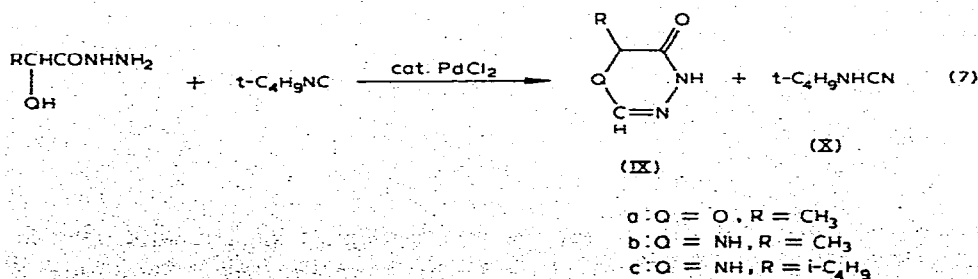
TABLE 2
PREPARATION OF (*N*-*t*-BUTYLIMINO)OXAZOLIDINE

$\text{H}_2\text{N}\backslash\text{OH}$ in V	Reaction conditions (°C, h)	Product (%)
$\begin{array}{c} \text{CH}_3\text{CH-CHCO}_2\text{CH}_3 \\ \quad \\ \text{OH} \quad \text{NH}_2 \end{array}$	80, 4	$\begin{array}{c} \text{CH}_3 \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH}_3\text{OOC} \quad \text{NH} \quad \text{C=N-t-C}_4\text{H}_9 \end{array}$ (70) (VIa)
	80, 2	 (84) (VIb)
		 (14) (VIIb)

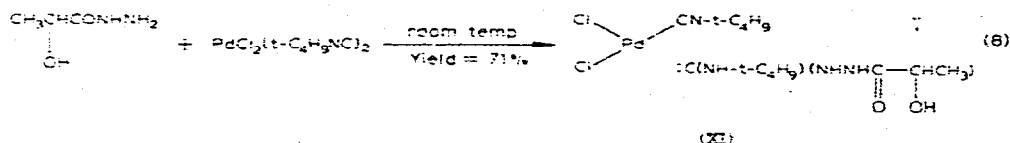


Synthesis of dihydrooxadiazinone and tetrahydrotriazinone

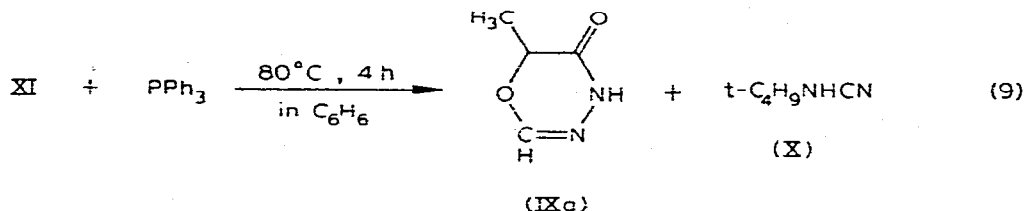
PdCl₂-catalyzed reaction of α -hydroxy acid hydrazides and α -amino acid hydrazides with alkyl isocyanides resulted in the formation of new heterocycles, 2-unsubstituted dihydrooxadiazinones and 3-unsubstituted tetrahydrotriazinones, which are otherwise unavailable (eq. 7). When lactic acid hydrazide was heated with *t*-butyl isocyanide in THF with a catalytic amount of PdCl₂ at 66°C for 5 h, 6-methyl-5,6-dihydro-4*H*-1,3,4-oxadiazin-5-one (IXa) was produced in 20% yield, together with *t*-butylcyanamide (X) (6%). Similarly, the reaction (66°C, 8 h) of alanine hydrazide and leucine hydrazide with *t*-butyl isocyanide afforded 5-methyl-tetrahydro-1,2,4-triazin-6-one (IXb) and 5-*i*-butyl-tetrahydro-1,2,4-triazin-6-one (IXc), respectively, in 70% yield.



A stoichiometric reaction of lactic acid hydrazide with PdCl₂(*t*-C₄H₉NC)₂ gave the diaminocarbene-palladium(II) complex XI (eq. 8). The IR spectrum of XI exhibited intense absorption bands at 2218 cm⁻¹ and 1560 cm⁻¹ which are assignable to the isocyanide and diaminocarbene ligands, respectively. The *cis*-configuration of complex XI was indicated by two bands at 312 cm⁻¹ and 288 cm⁻¹ assigned to ν (Pd-Cl).



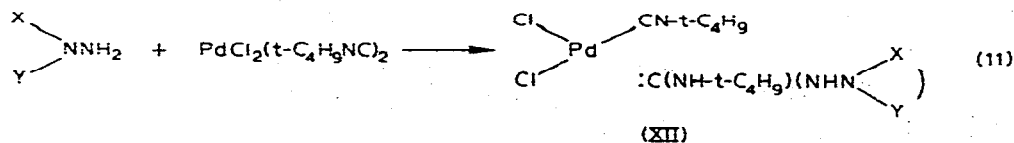
As expected, treatment of the carbene-palladium(II) complex XI with triphenylphosphine at 80°C for 4 h produced dihydrooxadiazinone (IXa) (14%) together with *t*-butylcyanamide (X) (7%) (eq. 9).



Concerning the formation of *t*-butylcyanamide, it may be noted that the reaction of a hydrazine or a hydrazone with *t*-butyl isocyanide in the presence of PdCl₂ catalyst also gave *t*-butylcyanamide. Thus, on heating a mixture of phenylhydrazine and *t*-butyl isocyanide with a catalytic amount of PdCl₂ at 80°C for 2 h, *t*-butylcyanamide was produced in 95% yield (eq. 10).



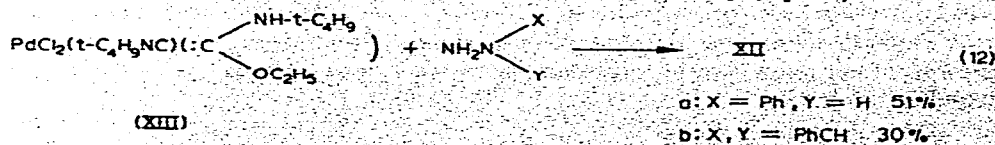
Similar treatment of dimethylhydrazine and benzaldehyde hydrazone with *t*-butyl isocyanide in the presence of PdCl₂ catalyst afforded *t*-butylcyanamide in yields of 34% (80°C, 5 h) and 13% (80°C, 6 h), respectively. It is noteworthy that diaminocarbene-palladium(II) complexes XIIa and XIIb were formed by the reaction of phenylhydrazine and benzaldehyde hydrazone with PdCl₂-(*t*-C₄H₉NC)₂ (eq. 11).



a: X = Ph, Y = H 89%

b: X, Y = PhCH 55%

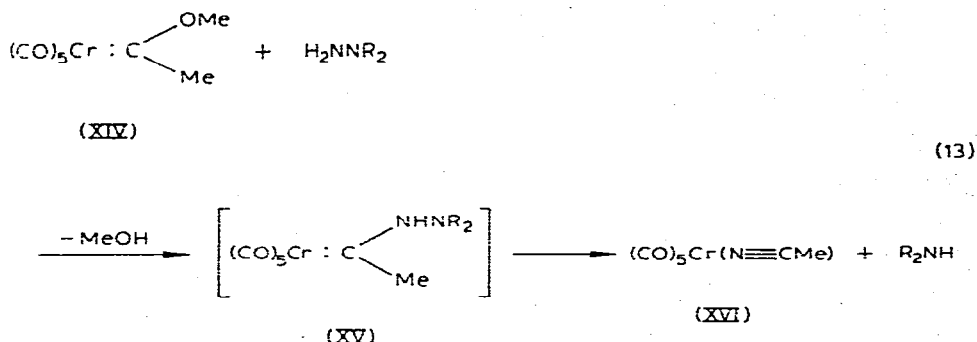
The structure of complex XII was convincingly confirmed by elemental analysis, IR (XIIa: 2219, 1565, 317, 289 cm⁻¹), NMR and molecular weight determination. The complexes XIIa and XIIb were prepared independently by the reaction of the [(*t*-butylamino)(ethoxy)carbene]palladium(II) complex XIII with phenylhydrazine and with benzaldehyde hydrazone, respectively (eq. 12).



a: X = Ph, Y = H 51%

b: X, Y = PhCH 30%

Treatment of complexes XIIa and XIIb with triphenylphosphine at 80°C gave t-butylcyanamide in 73% and 10% yields, respectively. The findings are closely related to Fischer's observation [9] that methylmethoxycarbenechromium pentacarbonyl reacted with hydrazine to yield the acetonitrile-pentacarbonyl chromium(0) complex XVI. The formation of XVI was explained by a mechanism involving a hydrazinomethylcarbene complex intermediate (XV), which was not isolable (eq. 13).



Experimental

General procedure for imidazolone synthesis

A mixture of α -amino acid ethyl ester (5 mmol) and t-butyl isocyanide (6 mmol) in benzene (2 ml) was heated at reflux with a catalytic amount of PdCl_2 (0.25 mmol) for 7 h with stirring under nitrogen. Distillation of the mixture gave 1-t-butyl-4-alkyl-5-imidazolone (II) and a small amount of carbodiimide (III). Analytically pure samples of II and III were obtained by preparative GLC. The imidazolones II were identified by comparison of their spectra with those of the respective authentic samples, which were prepared by the reported procedures [10,11]. Carbodiimides III were identified by elemental analysis, IR and NMR [7].

IIIa: Anal. Found: C, 60.41; H, 9.14; N, 14.33. $\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_2$ calcd.: C, 60.58; H, 9.15; N, 14.13%. IR (neat) 2110, 1740 cm^{-1} ; NMR (CDCl_3 with TMS) δ 1.27 (t, $J = 7.2$ Hz, 3H), 1.29 (s, 9H), 1.32 (d, $J = 7.2$ Hz, 3H), 3.96 (q, $J = 7.2$ Hz, 2H), 4.18 (q, $J = 7.2$ Hz, 2H). m/e 198 (M^+).

IIIb: IR (neat) 2120, 1740 cm^{-1} ; NMR (CDCl_3 with TMS) δ 1.16 (t, $J = 6.6$ Hz, 3H), 1.19 (s, 9H), 3.01 (m, 2H), 4.08 (t, $J = 7.2$ Hz, 1H), 4.13 (q, $J = 6.6$ Hz, 2H), 7.20 (s, 5H). m/e 274 (M^+).

IIIc: IR (neat) 2120, 1743 cm^{-1} ; NMR (CDCl_3 with TMS) δ 0.92 (d, $J = 6.0$ Hz, 3H), 0.95 (d, $J = 6.0$ Hz, 3H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.30 (s, 9H), 1.4–2.4 (m, 1H), 3.67 (d, $J = 6.0$ Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H). m/e 226 (M^+).

IIId: IR (neat) 2120, 1745 cm^{-1} ; NMR (CDCl_3 with TMS) δ 0.85 (d, $J = 5.4$ Hz, 3H), 0.87 (d, $J = 5.4$ Hz, 3H), 1.20 (t, $J = 6.6$ Hz, 3H), 1.23 (s, 9H), 1.3–1.7 (m, 3H), 3.73 (m, 1H), 4.03 (q, $J = 6.6$ Hz, 2H). m/e 240 (M^+).

1-t-Butyl-4-methyl-5-imidazolone (IIa) was also synthesized by heating at reflux a mixture of α -alanine amide (5 mmol), t-butyl isocyanide (6 mmol), and PdCl_2 (0.25 mmol) in THF (3 ml) for 2 h under nitrogen.

General procedure for preparation of diaminocarbene—palladium(II) complex (IV)

A mixture of PdCl_2 (5 mmol) and *t*-butyl isocyanide (10 mmol) in CHCl_3 (20 ml) was stirred at room temperature under nitrogen until a clear solution was obtained. Then, the α -amino acid ethyl ester (5 mmol) was added in small portions to the solution and the mixture was stirred at room temperature for 90 h. The reaction mixture, after being treated with Norit, was concentrated and triturated with ether to precipitate the diaminocarbene—palladium(II) complex (IV). The latter was identified by elemental analysis, IR, NMR and molecular weight determination (vapor pressure osmometer in DMF).

IVa: Anal. Found: C, 38.88; H, 6.62; N, 9.15; Cl, 15.23. $\text{C}_{15}\text{H}_{29}\text{N}_3\text{O}_2\text{Cl}_2\text{Pd}$ calcd.: C, 39.11; H, 6.34; N, 9.12; Cl, 15.39%. IR (KBr) 3440, 3240, 3075, 2221, 1748, 1575, 320, 283 cm^{-1} ; NMR (CDCl_3 with TMS) δ 1.30 (t, $J = 7.2$ Hz, 3H), 1.4–1.5 (m, 3H), 1.5–1.7 (m, 18H), 4.20 (broad q, 2H), 5.6 (broad m, 1H).

IVb: Anal. Found: C, 46.39; H, 6.08; N, 7.72; Cl, 13.76. $\text{C}_{21}\text{H}_{33}\text{N}_3\text{O}_2\text{Cl}_2\text{Pd}$ calcd.: C, 46.98; H, 6.20; N, 7.83; Cl, 13.21%. IR (KBr) 3400, 3230, 3070, 2218, 1745, 1575 cm^{-1} ; NMR (CDCl_3 with TMS) δ 1.18 (t, $J = 7.2$ Hz, 3H), 1.3–1.5 (m, 18H), 1.7 (m, 2H), 3.5 (m, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 7.20 (s, 5H).

IVc: Anal. Found: C, 41.59; H, 6.69; N, 8.52; Cl, 14.34. $\text{C}_{17}\text{H}_{33}\text{N}_3\text{O}_2\text{Cl}_2\text{Pd}$ calcd.: C, 41.77; H, 6.80; N, 8.60; Cl, 14.51%. IR (KBr) 3450, 3240, 3075, 2220, 1743, 1565, 322, 276 cm^{-1} ; NMR (CD_3OD) δ 1.13 (m, 6H), 1.42 (m, 3H), 1.5–1.8 (m, 18H), 1.8–2.6 (m, 1H), 4.30 (broad q, 2H), 5.43 (m, 1H). Mol. wt.: Found 468; calcd. 489 (monomeric).

IVd: Anal. Found: C, 42.99; H, 7.32; N, 8.40; Cl, 14.39. $\text{C}_{18}\text{H}_{35}\text{N}_3\text{O}_2\text{Cl}_2\text{Pd}$ calcd.: C, 43.00; H, 7.02; N, 8.36; Cl, 14.10%. IR (KBr) 3430, 3245, 3075, 2220, 1748, 1575 cm^{-1} ; NMR (CDCl_3 with TMS) δ 1.0 (m, 6H), 1.32 (broad t, 3H), 1.4–1.8 (m, 18H), 1.6–2.6 (m, 3H), 4.24 (broad q, 2H), 5.5 (m, 1H).

Treatment of IVa with triphenylphosphine

A mixture of IVa (0.1 mmol) and $\text{P}(\text{C}_6\text{H}_5)_3$ (0.2 mmol) in benzene (0.5 ml) was heated at reflux for 30 min under nitrogen. The reaction mixture was filtered and the solvent was distilled in vacuo to produce the corresponding imidazolone (IIa) (18%) and carbodiimide (IIIa) (27%). Yields were determined by GLC.

Preparation of iminoxazolidine by the reaction of diaminocarbene—palladium(II) complex (V) with Ag_2O

A heterogeneous mixture of diaminocarbene—palladium(II) complex (V) (0.2 mmol), prepared by the reported method [8], and Ag_2O (0.3 mmol) in benzene (2 ml) was stirred at 80°C for 2–4 h under nitrogen. The reaction mixture was filtered to remove insoluble inorganic material and the solvent was distilled in vacuo. For example, VIb (84%) and diamide (VIIb) (14%) were prepared by the reaction of Vb with Ag_2O for 4 h at 80°C . Yields were determined by GLC.

VIa: Anal. Found: C, 56.19; H, 8.24; N, 12.81. $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_2$ calcd.: C, 56.05; H, 8.47; N, 13.08%. IR (neat) 3360, 1735, 1655 cm^{-1} ; NMR (CDCl_3 with TMS) δ 1.31 (s, 9H), 1.38 (d, $J = 6.0$ Hz, 3H), 3.71 (s, 3H), 4.13 (d, $J = 6.0$ Hz, 1H), 4.3 (broad s, 1H), 4.60 (q, $J = 6.0$ Hz, 1H).

VIIb: Anal. Found: C, 69.68; H, 7.51; N, 14.95. $C_{11}H_{14}N_2O$ calcd.: C, 69.44; H, 7.42; N, 14.73%. IR (neat) 1640, 1580 cm^{-1} ; NMR ($CDCl_3$ with TMS) δ 1.45 (s, 9H), 5.6 (broad s, 1H), 6.8–7.5 (m, 4H). m/e 190 (M^+).

VIIb: IR (neat) 3375, 1658, 1613, 1580 cm^{-1} ; NMR ($CDCl_3$ with TMS) δ 1.36 (s, 9H) 1.47 (s, 9H), 6.4–7.3 (m, 6H). m/e 275 (M^+).

PdCl₂ catalyzed reaction of o-aminophenol and t-butyl isocyanide with Ag₂O

A heterogeneous mixture of *o*-aminophenol (5 mmol), *t*-butyl isocyanide (6 mmol) and Ag_2O (5 mmol) in benzene (10 ml) with a catalytic amount of $PdCl_2$ (0.5 mmol) and molecular sieves (3A 1/16, 1.5 g) was stirred at 70°C for 2 h under nitrogen. The reaction mixture was filtered to remove inorganic material and then distilled in vacuo to give aminobenzoxazole (VIb and VIc) with a small amount of diamide (VIIb and VIIc) and benzoxazole (VIIIb and VIIIc). Yields were determined by GLC.

VIc: Anal. Found: C, 70.21; H, 7.92; N, 13.49. $C_{12}H_{16}N_2O$ calcd.: C, 70.56; H, 7.90; N, 13.72%. IR (neat) 1655, 1590 cm^{-1} ; NMR ($CDCl_3$ with TMS) δ 1.46 (s, 9H), 2.33 (s, 3H), 6.5–7.2 (m, 3 + 1H). m/e 204 (M^+).

VIIc: Anal. Found: C, 70.31; H, 9.16; N, 14.33. $C_{17}H_{27}N_3O$ calcd.: C, 70.55; H, 9.40; N, 14.52%. IR (neat) 3350, 1670, 1670, 1620 cm^{-1} ; NMR ($CDCl_3$ with TMS) δ 1.33 (s, 9H), 1.45 (s, 9H), 2.36 (s, 3H), 6.2–7.2 (m, 5H). m/e 289 (M^+).

Preparation of dihydrooxadiazinone (IXa)

A mixture of lactic hydrazide [12] (5 mmol) and *t*-butyl isocyanide (5 mmol) in tetrahydrofuran (5 ml) with a catalytic amount of $PdCl_2$ (0.5 mmol) was refluxed for 5 h with stirring under nitrogen. Distillation of the mixture in vacuo gave 6-methyl-5,6-dihydro-4*H*-1,3,4-oxadiazin-5-one (IXa) (20%) and *t*-butylcyanamide (X) (6%). Yields were determined by GLC.

IXa: Anal. Found: C, 42.59; H, 5.54; N, 24.11. $C_4H_6N_2O_2$ calcd.: C, 42.10; H, 5.30; N, 24.55%. IR (neat) 1680 cm^{-1} ; NMR ($CDCl_3$ with TMS) δ 1.53 (d, $J = 6.3$ Hz, 3H), 4.76 (q, $J = 6.3$ Hz, 1H), 6.77 (s, 1H), 7.8–8.7 (broad s, 1H). m/e 114 (M^+).

Preparation of tetrahydrotriazinone (IXb and IXc)

A mixture of α -amino acid hydrazide [13] (5 mmol) and *t*-butyl isocyanide (5 mmol) in tetrahydrofuran (5 ml) with a catalytic amount of $PdCl_2$ (0.5 mmol) was refluxed for 8 h with stirring under nitrogen. Distillation of the mixture in vacuo gave the tetrahydrotriazinone. In this case *t*-butylcyanamide was produced in trace amount. Yields were determined by GLC.

IXb: Anal. Found: C, 42.77; H, 6.47; N, 37.27. $C_4H_7N_3O$ calcd.: C, 42.47; H, 6.24; N, 37.15%. IR (KBr) 3225, 3030, 1665, 1635 cm^{-1} ; NMR (DMSO- d_6) δ 1.20 (d, $J = 6.6$ Hz, 3H), 3.85 (q, $J = 6.6$ Hz, 1H), 6.77 (d, $J = 3.6$ Hz, 1H), 6.9 (broad s, 1H) 9.9 (broad s, 1H). m/e 113 (M^+).

IXc: IR (KBr) 3240, 3025, 1660, 1625 cm^{-1} ; NMR (DMSO- d_6) δ 0.82 (d, $J = 5.4$ Hz, 3H), 0.84 (d, $J = 5.4$ Hz, 3H), 1.2–1.9 (m, 3H), 3.73 (t, $J = 6.6$ Hz, 1H), 6.68 (d, $J = 3.6$ Hz, 1H), 6.95 (broad s, 1H), 9.88 (broad s, 1H). m/e 155 (M^+).

Preparation of carbene-palladium(II) complex (XI)

A mixture of PdCl_2 (5 mmol) and *t*-butyl isocyanide (10 mmol) in CHCl_3 (20 ml) was stirred at room temperature under nitrogen until a clear solution was obtained. Then lactic hydrazide (5 mmol) was added in small portions and the solution was stirred at room temperature for 24 h. The reaction mixture, after being treated with Norit, was concentrated and triturated with ether to precipitate the carbene-palladium(II) complex (XI) (71%).

XI: Anal. Found: C, 34.16; H, 6.17; N, 12.35; Cl, 15.19. $\text{C}_{13}\text{H}_{26}\text{N}_4\text{O}_2\text{Cl}_2\text{Pd}$ calcd.: C, 34.88; H, 5.85; N, 12.51; Cl, 15.84%. IR (KBr) 3220, 2218, 1685, 1560, 312, 288 cm^{-1} ; NMR (CDCl_3 with TMS) δ 1.3–1.6 (m, 12H), 4.3–4.6 (m, 1H). Mol. wt.: Found, 466; calcd., 447 (monomeric).

Treatment of XI with triphenylphosphine

A mixture of XI (0.1 mmol) and $\text{P}(\text{C}_6\text{H}_5)_3$ (0.2 mmol) in benzene (0.5 ml) was heated at reflux for 4 h under nitrogen. The reaction mixture was filtered off. Dihydrooxadiazinone (IXa) (14%) and *t*-butylcyanamide (X) (7%) were found (GLC) in the filtrate.

General procedure for t-butylcyanamide synthesis from hydrazine or hydrazone

A mixture of *t*-butyl isocyanide (6 mmol) and the hydrazine or hydrazone (5 mmol) in benzene (5 ml) was heated at reflux with stirring under nitrogen with a catalytic amount of PdCl_2 (0.5 mmol) for 2–6 h. For example, a mixture of *t*-butyl isocyanide and phenylhydrazine was refluxed with a catalytic amount of PdCl_2 for 2 h at 80°C. The reaction mixture was distilled in vacuo to give *t*-butylcyanamide (95%) and an equivalent amount of aniline. Yields were determined by GLC.

General procedure for preparation of carbene-palladium(II) complex (XII)

A mixture of PdCl_2 (5 mmol) and *t*-butyl isocyanide (10 mmol) in CHCl_3 (20 ml) was stirred at room temperature under nitrogen until a clear solution was obtained. Then the hydrazine or hydrazone (5 mmol) was added in small portions and the solution was stirred at room temperature for 24 h. The reaction mixture, after being treated with Norit, was concentrated and triturated with ether to precipitate carbene-palladium(II) complex (XII) (XIIa, 89%, XIIb, 55%).

XIIa: Anal. Found: C, 42.42; H, 5.76; N, 12.50; Cl, 15.88. $\text{C}_{18}\text{H}_{26}\text{N}_4\text{Cl}_2\text{Pd}$ calcd.: C, 42.54; H, 5.80; N, 12.40; Cl, 15.70%. IR (KBr) 3440, 3200, 2219, 1600, 1565, 317, 289 cm^{-1} ; NMR (CDCl_3 with TMS) 1.4–1.8 (m, 18H), 6.80 (m, 5H). Mol. wt.: Found, 417; calcd., 451 (monomeric).

XIIb: Anal. Found: C, 43.42; H, 5.91; N, 11.97; Cl, 15.66. $\text{C}_{17}\text{H}_{26}\text{N}_4\text{Cl}_2\text{Pd}$ calcd.: C, 44.03; H, 5.65; N, 12.08; Cl, 15.29%. IR (KBr) 3440, 3300, 3230, 2219, 1607, 1550 cm^{-1} ; NMR (CDCl_3 with TMS) δ 1.4–1.8 (m, 18H), 7.2–8.0 (m, 6H). Mol. wt.: Found, 419; calcd., 463 (monomeric).

Treatment of XII with triphenylphosphine

A mixture of XIIa (0.1 mmol) and $\text{P}(\text{C}_6\text{H}_5)_3$ (0.2 mmol) in benzene (0.5 ml) was refluxed for 3 h under nitrogen. The reaction mixture was filtered producing the corresponding *t*-butylcyanamide (73%). The yield was determined by GLC. Treatment of XIIb with $\text{P}(\text{C}_6\text{H}_5)_3$ was carried out for 6 h in a similar manner as that used for XIIa to give *t*-butylcyanamide (10%).

Preparation of carbene-palladium(II) complex (XII) by the reaction of [(t-butylamino)(ethoxy)carbene] palladium(II) complex with hydrazine or hydrazone

Phenylhydrazine or benzaldehyde hydrazone was added in small portions to the solution of [(t-butylamino)(ethoxy)carbene] palladium(II) complex, prepared by the method of the previous paper [8], at 0°C and the resulting solution was stirred for 1 h at 0°C, and 1 h at room temperature under nitrogen. The reaction mixture was triturated with ether-n-hexane (10 : 1) to precipitate the complex (XII).

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