ELSEVIER

Journal of Molecular Catalysis A: Chemical 143 (1999) 297–310

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Sequential reaction of carbon dioxide and carbon monoxide with acetylenic amines in the presence of a palladium catalyst

G.P. Chiusoli [a], M. Costa [a,*], B. Gabriele [b], G. Salerno [b]

[a] *Dipartimento di Chimica Organica e Industriale, Università, Viale delle Scienze, 43100 Parma, Italy*
[b] *Dipartimento di Chimica,Università della Calabria, 87030 Arcavacata di Rende, Cosenza, Italy*

Dedicated to: Professor Peter Maitlis in recognition of his outstanding contribution to organometallic chemistry and catalysis

Received 20 May 1998; accepted 7 September 1998

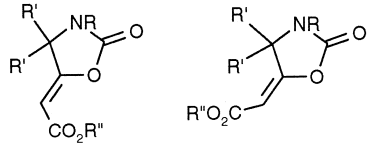
Abstract

Conditions for the sequential reaction of carbon dioxide with an acetylenic amine and carbon monoxide in the presence of a PdI_2–KI catalyst in alcohols are examined. The stereochemistry of the two 5-(alkoxycarbonyl)methylene-3,4,4-trialkyl-1,3-oxazolidin-2-one stereoisomers obtained is attributed to different pathways on the basis of experiments carried out on alkyl and benzyl esters of *N*-alkyldimethylpropynylcarbamic acid and carbon monoxide. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Carbon dioxide; Carbon monoxide; Acetylenic amines; Palladium catalyst; (Alkoxycarbonyl)methyleneoxazolidinones

1. Introduction

The present study has its origin in the observation that in the palladium-catalysed synthesis of β- and γ-lactams by oxidative carbonylation of acetylenic amines small amounts (less than 5%) of compounds **1-Z** and **1-E** (R = alkyl, benzyl) containing an additional oxygen atom were present [1]. Their formation was promoted by a little water in the reaction mixture.



1-*Z* **1-*E***

In view of the fact that carbon dioxide could originate through decarboxylation of a hydroxycarbonylpalladium species [2–4] formed in the presence of water, Eq. (1):

$$PdI_2 + CO + H_2O \overset{-HI}{\rightleftarrows} I\text{–}Pd\text{–}CO_2H \rightleftarrows [H\text{–}Pd\text{–}I] + CO_2 \quad (1)$$

* Corresponding author

1381-1169/99/$ - see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S1381-1169(98)00397-5

the formation of compounds **1** was attributed to the reaction of one molecule of carbon dioxide and one of carbon monoxide with the triple bond, according to Eq. (2)

$$\equiv\!-C(R')_2NHR + CO_2 + CO + R''OH + 1/2O_2 \overset{PdI_2-KI}{\underset{-H_2O}{\rightarrow}} \textbf{1-Z} + \textbf{1-E} \qquad (2)$$

To test this hypothesis the acetylenic secondary amine *N*-butyl-1,1-dimethylprop-2-ynamine was caused to react in methanol with carbon dioxide, carbon monoxide and air in the presence of PdI_2 and KI at 52°C for 46 h. Compounds **1** (*E*/*Z* isomers, molar ratio 3:1) were obtained in satisfactory yield.

A preliminary report has been published on this subject [5]. The present study deals with further experiments aimed at ascertaining stereochemical and mechanistic aspects.

2. Experimental

2.1. Materials and general methods

Solvents and chemicals were reagent grade and were used as received except for 1,1-dimethylprop-2-ynamine and *N*-methylprop-2-ynamine which were distilled under reduced pressure and stored over dry K_2CO_3. MeOH, EtOH and *n*-BuOH were dried over 4A molecular sieves. *N*-Butyl-1,1-dimethylprop-2-ynamine was prepared from 1,1-dimethylprop-2-ynyl acetate and *n*-butylamine according to the literature [6]. *N*-Benzyl-1,1-dimethylprop-2-ynamine and *N*-benzylprop-2-ynamine were prepared according to the conventional procedure of alkylation of primary amines with alkyl halides. Benzyl, allyl and *n*-butyl *N*-prop-2-ynylcarbamates were obtained causing prop-2-ynamine to react with the respective chloroformate according to a literature procedure [7]. *tert*-Butyl *N*-prop-2-ynylcarbamate was prepared from *N*-butyl-1,1-dimethylprop-2-ynamine and di-*tert*-butylcarbonate according to a literature method [8]. ^{1}H NMR, IR and mass spectra confirmed the assigned structures.

Melting points were determined with an Electrothermal apparatus and are uncorrected. GC analyses were performed with a Dani 3800 HR instrument fitted with a 30 m SE52 capillary column. Quantitative determinations were carried out using the internal standard method. Merck 60 F_{254} silica gel sheets (0.2 mm thick) were used for TLC analyses. Silica gel 60 (70–230 mesh ASTM) was used for preparative column chromatography.

Elemental analyses were carried out with a Carlo Erba Elemental Analyser Model EA 1108. IR spectra were obtained with a Nicolet 5PC FT-IR spectrophotometer. Mass spectra (*m*/*z*, relative intensity %) were taken with a Hewlett-Packard Mass Selective Detector 5971 Series interfaced with a Hewlett-Packard 5890 Series II GC or a Finnigan Mat SSQ710 mass spectrometer both at 70 eV ionising voltage. ^{1}H NMR data were acquired using Bruker AC300 and AMX400 spectrometers in $CDCl_3$ as solvent and with TMS as internal standard at ambient temperature. Chemical shifts and coupling constants (*J*) are given as δ values (ppm) and in Hz respectively.

2.2. General procedure for the carboxylation and alkoxycarbonylation of N-alkyl-N-prop-2-ynamines

All reactions were carried out in a 125 ml stainless steel autoclave (Parr Instruments) with magnetic stirring. In a typical experiment the autoclave was charged under air with *N*-butyl-1,1-dimethylprop-2-ynamine (0.417 g, 3 mmol), PdI_2 (0.011 g, 0.03 mmol) and KI (0.050 g, 0.3 mmol) in methanol (20 ml). The autoclave was pressurized with air (5 bar), CO (5 bar) and CO_2 (40 bar) and heated under stirring for the required time. Other conditions are indicated in Table 1. At the end of the reaction the alcohol was eliminated under vacuum, the residue was recovered with CH_2Cl_2 and filtered to remove KI and the solid catalyst (if necessary an internal standard was added) and the solution was checked by GC/MSD.

The alkoxycarbonylation reactions of carbamates were carried out similarly in autoclave in the absence of CO_2 under the conditions specified in Table 3.

2.3. Iodolactonization of n-butyl N-n-butyl-1,1-dimethylprop-2-ynylcarbamate

Into a 50 ml Schlenk-type flask equipped with a magnetic stirring bar butyl *N*-butyl-*N*-1,1-dimethylprop-2-ynylcarbamate (0.717 g, 3 mmol) was introduced under nitrogen. Iodine (0.762 g, 6 mmol) dissolved in MeOH (7.5 ml) was added. The mixture was stirred at 80°C for 40 h. After conventional work-up pure 5-(*E*)-iodomethylene-3-butyl-4,4-dimethyl-1,3-oxazolidin-2-one (**8**) was obtained as yellow oil by silica gel column chromatography using *n*-hexane-ethyl acetate 8:2 as eluent.

The alkoxycarbonylation of oxazolidinone **8** was carried out in a 45 ml stainless steel autoclave (Parr Instruments) with magnetic stirring. To compound **8** (0.309 g, 1 mmol), PdI_2 (0.006 g, 0.017 mmol) and KI (0.060 g, 0.36 mmol) dissolved in MeOH (6 ml) were added under air (1 bar). The resulting mixture was pressurized with CO (40 bar) and stirred in an oil bath at 90°C for 40 h. After conventional work-up of the crude mixture a 79% yield of **1-E** was determined by GC analysis (95% conversion of **8**).

2.4. Characterization of carbamates

2.4.1. Benzyl N-1,1-dimethylprop-2-ynylcarbamate

White solid mp 73–74°C. ^{1}H NMR ($CDCl_3$) δ 1.62 (s, 6H, 2Me), 2.33 (s, 1H, ≡CH), 4.94 (brs, 1H, NH), 5.10 (s, 2H, CH_2Ph), 7.31–7.37 (m, 5H, Ph); IR (Kbr) ν/cm^{-1} 3271 (s), 3220 (s), 3058 (m), 2932 (m), 2111 (w), 1709 (s), 1540 (s), 1455 (m), 1269 (s), 1108 (m), 1076 (s), 737 (m), 702 (m); MS *m*/*z* 217 (M^+, 1), 202 (2), 150 (4), 108 (25), 91 (100) 79 (10),65 (13). Elemental anal. Found: C, 71.81; H, 6.89; N, 6.39. $C_{13}H_{15}NO_2$ calc.: C, 71.89; H, 6.91; N, 6.45%.

2.4.2. Benzyl N-benzyl-N-1,1-dimethylprop-2-ynylcarbamate

White solid mp 56–57°C. ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 6H, 2Me), 2.39 (s, 1H, ≡CH), 4.77 (s, 2H, NCH_2), 5.13 (s, 2H, OCH_2), 7.27–7.33 (m, 5H, Ph); IR (Kbr) ν/cm^{-1} 3268 (s), 2986 (w), 2935 (w), 2110 (w), 1711 (s), 1452 (m), 1391 (m), 1363 (m), 1237 (m), 1087 (s), 1072 (s), 769 (m), 729 (s), 700 (m), 664 (s); MS *m*/*z* 307 (M^+, 1), 292 (2), 240 (5), 216 (3), 192 (3), 181 (2), 150 (12), 132 (3), 91 (100), 65 (16). Elemental anal. Found: C, 78.14; H, 6.81; N, 4.51. $C_{20}H_{21}NO_2$ calc.: C, 78.18, H, 6.84; N, 4.56%.

2.4.3. Benzyl N-butyl-N-1,1-dimethylprop-2-ynylcarbamate

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H $J = 8.5$ Hz, Me), 1.23–1.30 (m, 2H, CH_2), 1.56–1.60 (m, 2H, CH_2), 1.73 (s, 6H, 2Me), 2.43 (s, 1H, ≡CH), 3.53 (t, 2H, $J = 6.5$ Hz, NCH_2), 5.12 (s, 2H, OCH_2), 7.30–7.36 (m, 5H, Ph); IR (neat) ν/cm^{-1} 3301 (w), 3270 (m), 2960 (m), 2112 (w), 1777 (m), 1700 (s), 1457 (w), 1401 (m), 1358 (m), 1294 (m),1222 (m), 1135 (s), 1055 (w), 737 (w); MS *m*/*z* 273 (M^+, 1), 258 (4), 214 (2), 120 (2), 91 (100), 65 (11). Elemental anal. Found: C 74.68; H, 8.40; N, 5.09. $C_{17}H_{23}NO_2$ calc.: C, 74.73; H, 8.42; N, 5.13%.

2.4.4. Allyl N-butyl-N-1,1-dimethylprop-2-ynylcarbamate

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3H, $J = 7.3$ Hz, Me), 1.24–1.31 (m, 2H, CH_2), 1.53–1.63 (m, 2H, CH_2), 1.72 (s, 6H, 2Me), 2.41 (s, 1H, ≡CH), 3.50 (t, 2H, $J = 7.8$ Hz, NCH_2), 4.56 (dt, 2H, $J = 5.4$ and 1.5 Hz, OCH_2), 5.17 (ddt, 1H, $J = 10.5$, 1.7 and 1.5 Hz, =C*H*H), 5.28

(ddt, 1H, $J = 17.2$, 1.7 and 1.5 Hz, =CH*H*), 5.92 (ddt, 1H, $J = 17.2$, 10.5 and 5.4 Hz, =CH); IR (neat) ν/cm^{-1} 3308 (w), 3269 (s), 2961 (m), 2875 (w), 1700 (s), 1653 (w), 1467 (m), 1398 (m), 1377 (w), 1359 (w), 1225 (w), 1135 (m), 1057 (w); MS m/z 223 (M^+, 1), 208 (59), 180 (2), 114 (8), 108 (2), 67 (18), 57 (5). Elemental anal. Found: C, 69.91; H, 9.39; N, 6.23. $C_{13}H_{21}NO_2$ calc.: C, 69.96; H, 9.42; N, 6.28%.

2.4.5. Butyl N-butyl-N-1,1-dimethylprop-2-ynylcarbamate

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H, $J = 6.5$ Hz, Me), 0.90 (t, 3H, $J = 6.1$ Hz, Me), 1.14–1.60 (system of four multiplets, 8H, $4CH_2$), 1.69 (s, 6H, 2Me), 2.40 (s, 1H, ≡CH), 3.46 (t, 2H, $J = 7.0$ Hz, NCH_2), 4.03 (t, 2H, $J = 6.1$ Hz, OCH_2); IR (neat) ν/cm^{-1} 3310 (w), 2967 (m), 2874 (m), 1699 (s), 1463 (w), 1406 (m), 1363 (m), 1295 (w), 1251 (w), 1136 (m), 1073 (w), 936 (w); MS m/z 239 (M^+, 2), 224 (18), 196 (10), 182 (29), 168 (49), 140 (4), 130 (24), 96 (8), 74 (38), 67 (42), 57 (58), 41 (100); Elemental anal. Found: C, 70.25; H, 10.43; N, 5.81. $C_{14}H_{25}NO_2$ calc.: C, 70.29; H, 10.46; N, 5.86%.

2.4.6. tert-Butyl N-butyl-N-1,1-dimethylprop-2-ynylcarbamate

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, $J = 7.3$ Hz, Me), 1.18–1.31 (m, 2H, CH_2), 1.43 (s, 9H, 3Me), 1.47–1.58 (m, 2H, CH_2), 1.66 (s, 6H, 2Me), 2.35 (s, 1H, ≡CH), 3.40 (t, 2H, $J = 7.7$ Hz, NCH_2); IR (neat) ν/cm^{-1} 3311 (w), 3270 (m), 2977 (m), 2934 (m), 2874 (m), 1696 (s), 1457 (m), 1391 (s), 1366 (s), 1304 (m), 1132 (m), 1049 (w), 774 (w); MS m/z 239 (M^+, absent), 224 (1), 183 (5), 168 (10), 140 (3), 124 (10), 96 (12), 74 (3), 67 (14), 57 (100). Elemental anal. Found: C, 70.26; H, 10.42; N, 5.82. $C_{14}H_{25}NO_2$ calc.: C, 70.29; H, 10.46; N, 5.86%.

2.4.7. Benzyl N-methyl-N-prop-2-ynylcarbamate

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 2.25 (t, 1H, $J = 3.5$ Hz, ≡CH), 2.96 (s, 3H, NMe), 4.08 (br s, 2H, CH_2), 5.15 (s, 2H, OCH_2), 7.26–7.32 (m, 5H, Ph); IR (neat) ν/cm^{-1} 3283 (m), 2955 (w), 2112 (w), 1700 (s), 1456 (m), 1402 (m), 1242 (m), 1153 (m), 769 (w), 738 (w), 699 (m); MS m/z 203 (M^+, 1), 174 (1), 158 (2), 128 (12), 112 (9), 91 (100), 77 (9), 65 (24). Elemental anal. Found C, 70.90; H, 6.37; N, 6.87. $C_{12}H_{13}NO_2$ calc.: C, 70.94; H, 6.40; N, 6.90%.

2.5. Separation of products

Pure (*Z*)- and (*E*)-[(alkoxycarbonyl)methylene]oxazolidin-2-ones **1-Z** and **1-E** (R = Bu, R′ = R″ = Me and R = CH_2Ph, R′ = R″ = Me) were isolated by silica gel column chromatography with *n*-hexane–ethyl acetate 7:3 as eluent. Product **1-Z** (R = CH_2Ph, R′ = R″ = Me) separated from the eluent mixture as pale yellow crystals which were recrystallized from *n*-hexane–toluene 1:4 mixture in monocrystalline form (mp 125–126°C). Products **1-E** (R = H, R′ = R″ = Me; R = Bu, R′ = Me, R″ = Et or Bu), **2**, **3**, **4** and **5** (R = Bu or CH_2Ph, R′ = R″ = Me) and **9** (R = Me, R′ = H, R″ = Me) were isolated by silica gel column chromatography using as eluents *n*-hexane-ethyl acetate 8:2 for **1-E**, *n*-hexane–ethyl acetate 8:2 to 6:4 for **2**–**5** and *n*-hexane–ethyl acetate 9:1 for **9**.

2.6. Characterization of products

Spectroscopic data of products **1-Z** [5] and **1-E** [5] (R = Bu, R′ = R″ = Me), **1-Z** [5] (R = CH_2Ph, R′ = R″ = Me), **2** [1] (R = CH_2Ph, R′ = R″ = Me), **4** [9] (R = CH_2Ph, R′ = Me), **4** [10] (R = Bu, R′ = Me and R = H, R′ = Me), **6** [11] and **7** [11] have been reported. New compounds were identified by elemental analyses and ^{1}H NMR, IR and mass spectroscopies.

2.6.1. (E)-5-(Methoxycarbonyl)methylene-3-benzyl-4,4-dimethyl-1,3-oxazolidin-2-one, ***1-E*** *($R = CH_2Ph$, $R' = R'' = Me$)*

Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.53 (s, 6H, 2Me), 3.64 (s, 3H, OMe), 4.41 (s, 2H, CH_2), 5.62 (s, 1H, =CH), 7.27–7.33 (m, 5H,Ph); IR (neat) ν/cm^{-1} 2882 (w), 1802 (s), 1723 (s), 1670 (s), 1401 (s), 1252 (m), 1121 (m), 1035 (s), 702 (m); MS m/z 275 (M^+, 3), 260 (6), 132 (7), 91 (100), 65 (9), 59 (3). Elemental anal. Found: C, 64.41; H, 6.16; N, 5.04. $C_{15}H_{17}NO_4$ calc.: C, 65.45; H, 6.18; N, 5.09%.

2.6.2. (E)-5-(Ethoxycarbonyl)methylene-3-butyl-4,4-dimethyl-1,3-oxazolidin-2-one, ***1-E*** *($R = Bu$, $R' = Me$, $R'' = Et$)*

Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3H, $J = 7.3$ Hz, Me), 1.20 (t, 3H, $J = 7.1$ Hz, Me), 1.31–1.40 (m, 2H, CH_2), 1.60–1.71 (m, 2H, CH_2), 1.69 (s, 6H, 2Me), 3.16 (t, 2H, $J = 7.9$ Hz, NCH_2), 4.02 (q, 2H, $J = 7.1$ Hz, CH_2), 5.61 (s, 1H, =CH); MS m/z 255 (M^+, 3), 240 (97), 210 (12), 194 (13), 184 (19), 138 (16), 83 (25), 69 (100), 59 (47), 55 (51), 41 (97). Elemental anal. Found: C, 61.14; H, 8.22; N, 5.45. $C_{13}H_{21}NO_4$ calc.: C, 61.18; H, 8.24; N, 5.49%.

2.6.3. (Z)-5-(Ethoxycarbonyl)methylene-3-butyl-4,4-dimethyl-1,3-oxazolidin-2-one, ***1-Z*** *($R = Bu$, $R' = Me$, $R'' = Et$)*

Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3H, $J = 7.3$ Hz, Me), 1.20 (t, 3H, $J = 7.1$ Hz, Me), 1.30–1.40 (m, 2H, CH_2), 1.60–1.70 (m, 2H, CH_2), 1.68 (s, 6H, 2Me), 3.17 (t, 2H, $J = 7.8$ Hz, NCH_2), 4.02 (q, 2H, $J = 7.1$ Hz, CH_2), 5.07 (s, 1H, =CH); MS m/z 255 (M^+, 4), 240 (96), 210 (12), 194 (14), 184 (16), 138 (15), 83 (21), 69 (100), 59 (48), 55 (47), 41 (93). Elemental anal. Found: C, 61.14; H, 8.21; N, 5.44. $C_{13}H_{21}NO_4$ calc.: C, 61.18; H, 8.24; N, 5.49%.

2.6.4. (E)-5-(Butoxycarbonyl)methylene-3-butyl-4,4-dimethyl-1,3-oxazolidin-2-one, ***1-E*** *($R = R' = Bu$, $R'' = Me$)*

Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3H, $J = 7.3$ Hz, Me), 0.95 (t, 3H, $J = 7.2$ Hz, Me), 1.30–1.45 (2m, 4H, $2CH_2$), 1.58–1.71 (2m, 4H, $2CH_2$), 1.69 (s, 6H, 2Me), 3.16 (t, 2H, $J = 7.9$ Hz, NCH_2), 4.09 (t, 2H, $J = 6.7$ Hz, OCH_2), 5.61 (s, 1H, =CH); MS m/z 283 (M^+, 2), 268 (94), 228 (6), 212 (47), 194 (5), 182 (13), 83 (28), 69 (41), 57 (52), 41 (100). Elemental anal. Found: C, 63.56; H, 8.80; N, 4.92. $C_{15}H_{25}NO_4$ calc.: C, 63.60; H, 8.83; N, 4.95%.

2.6.5. (Z)-5-(Butoxycarbonyl)methylene-3-butyl-4,4-dimethyl-1,3-oxazolidin-2-one, ***1-Z*** *($R = R' = Bu$, $R'' = Me$)*

Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3H, $J = 7.3$ Hz, Me), 0.95 (t, 3H, $J = 7.2$ Hz, Me), 1.31–1.45 (2m, 4H, $2CH_2$), 1.58–1.72 (2m, 4H, $2CH_2$), 1.68 (s, 6H, 2Me), 3.17 (t, 2H, $J = 7.9$ Hz, NCH_2), 4.07 (t, 2H, $J = 6.7$ Hz, OCH_2), 5.07 (s, 1H, =CH); MS m/z 283 (M^+, 3), 268 (86), 228 (7), 212 (4), 194 (9); 182 (19), 168 (16), 69 (34), 57 (37), 41 (100). Elemental anal. Found: C, 63.55; H, 8.79; N, 4.92. $C_{15}H_{25}NO_4$ calc.: C, 63.60; H, 8.83; N, 4.95%.

2.6.6. (E)-5-(Methoxycarbonyl)methylene-4,4-dimethyl-1,3-oxazolidin-2-one, ***1-E*** *($R = H$, $R' = R'' = Me$)*

Pale yellow solid mp 95°C. ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 6H, 2Me), 3.69 (s, 3H, OMe), 5.63 (s, 1H, =CH), 5.80 (br s, 1H, NH); IR (KBr) ν/cm^{-1} 3335 (s), 2954 (m), 1797 (s), 1769 (s), 1723 (s), 1666 (s), 1440 (m), 1385 (m), 1317 (s), 1260 (m), 1195 (m), 1103 (s), 983 (m), 933 (w), 909 (w), 859 (m); MS m/z 185 (M^+, 4), 170 (6), 154 (5), 127 (5), 110 (4), 101 (100), 84 (13), 69 (18), 59 (4). Elemental anal. Found: C, 51.87; H, 5.94; N, 7.53. $C_8H_{11}NO_4$ calc.: C, 51.89; H, 5.95; N, 7.57%.

2.6.7. (Z)-3-(Methoxycarbonyl)methylene-1-butyl-4,4-dimethylazetidin-2-one, ***2*** *(R = Bu, R′ = R″ = Me)*

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3H, $J = 7.4$ Hz, Me), 1.32–1.45 (m, 2H, CH_2), 1.41 (s, 6H, 2Me), 1.55–1.62 (m, 2H, CH_2), 3.22 (t, 2H, $J = 7.4$ Hz, NCH_2), 3.80 (s, 3H, OMe), 5.69 (s, 1H, =CH); IR (neat) ν/cm^{-1} 2960 (s), 2873 (m), 1755 (s), 1725 (s), 1687 (m), 1436 (m), 1385 (m), 1280 (m), 1198 (m), 1176 (m), 1045 (w), 941 (w), 880 (w); MS m/z 225 (M^+, 1), 210 (4), 194 (7), 183 (12), 154 (100), 125 (18), 122 (21), 111 (16), 98 (13), 70 (19), 59 (66). Elemental anal. Found: C, 63.96; H, 8.42; N, 6.18. $C_{12}H_{19}NO_3$ calc.: 64.00; H, 8.44; N, 6.22%.

2.6.8. (Z)-3-(Ethoxycarbonyl)methylene-1-butyl-4,4-dimethylazetidin-2-one, ***2*** *(R = Bu, R′ = Me R″ = Et)*

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3H, $J = 7.4$ Hz, Me), 1.21 (t, 3H, $J = 7.1$ Hz, Me), 1.31–1.45 (m, 2H, CH_2), 1.41 (s, 6H, 2Me), 1.55–1.61 (m, 2H, CH_2), 3.22 (t, 2H, $J = 7.3$ Hz, NCH_2), 4.03 (q, 2H, $J = 7.1$ Hz, CH_2), 5.68 (s, 1H, =CH); IR (neat) ν/cm^{-1} 2960 s, 2872 (m), 1756 (s), 1723 (s), 1687 (m), 1435 (m), 1385 (m), 1280 (m), 1197 (m), 1175 (m), 1045 (w), 941 (w), 880 (w); MS m/z 239 (M^+, 3), 224 (5), 210 (11), 196 (16), 168 (67), 140 (24), 124 (29), 70 (56), 67 (77), 57 (28), 41 (100). Elemental anal.: C, 65.24; H, 8.77; N, 5.83: $C_{13}H_{21}NO_3$ calc.: C, 65.27; H, 8.79; N, 5.86%.

2.6.9. (Z)-3-(Butoxycarbonyl)methylene-1-butyl-4,4-dimethylazetidin-2-one, ***2*** *(R = R′ = Bu, R″ = Me)*

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3H, $J = 7.3$ Hz, Me), 0.93 (t, 3H, $J = 7.2$ Hz, Me), 1.36–1.48 (2m, 4H, $2CH_2$), 1.41 (s, 6H, 2Me), 1.53–1.74 (2m, 4H, $2CH_2$), 3.22 (t, 2H, $J = 7.3$ Hz, NCH_2), 4.19 (t, 2H, $J = 6.9$ Hz OCH_2), 5.68 (s, 1H, =CH); IR (neat) ν/cm^{-1} 2959 (s), 2925 (s), 2854 (s), 1759 (s), 1721 (s), 1684 (w), 1463 (m), 1382 (m), 1279 (m), 1179 (s); MS m/z 267 (M^+, 3), 252 (2), 225 (5), 210 (11), 196 (13), 168 (26), 140 (30), 124 (12), 63 (37), 57 (56), 41 (100). Elemental anal.: C, 67.38; H, 9.33; N, 5.20. $C_{15}H_{25}NO_3$ calc.: C, 67.42; H, 9.36; N, 5.24%.

2.6.10. 4-Methoxycarbonyl-1-butyl-5,5-dimethyl-2,5-dihydropyrrol-2-one ***3*** *(R = Bu, R′ = R′ = Me)*

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3H, $J = 7.4$ Hz, Me), 1.30–1.40 (m, 2H, CH_2), 1.46 (s, 6H, 2Me), 1.50–1.61 (m, 2H, CH_2), 3.28 (t, 2H, $J = 8.0$ Hz, NCH_2), 3.83 (s, 3H, OMe), 6.73 (s, 1H, =CH); IR (neat) ν/cm^{-1} 2960 (s), 2874 (m), 1726 (s), 1693 (s), 1619 (m), 1400 (m), 1347 (m), 1231 (s), 1060 (m), 781 (m); MS m/z 225 (M^+, 8), 224 (8), 210 (19), 183 (59), 182 (100), 168 (17), 154 (38), 153 (37), 122 (41), 59 (3). Elemental anal. Found: C, 63.95; H, 8.41; N, 6.18. $C_{12}H_{19}NO_3$ calc.: C, 64.00; H, 8.44; N, 6.22%.

2.6.11. 4-Methoxycarbonyl-1-benzyl-5,5-dimethyl-2,5-dihydropyrrol-2-one ***3*** *(R = CH_2Ph, R′ = R″ = Me)*

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.94 1.36 (s, 6H, 2Me), 3.84 (s, 3H, OMe), 4.61 (s, 2H, NCH_2), 6.83 (s, 1H, =CH), 7.27–7.31 (m, 5H, Ph; IR (neat) ν/cm^{-1} 2952 (m), 1726 (s), 1693 (s), 1497 (m), 1436 (m), 1349 (m), 1234 (m), 1059 (m), 780 (m), 715 (m); MS m/z 259 (M^+, 30), 244 (7), 227 (8), 200 (3), 168 (8), 154 (50), 126 (32), 106 (40), 91 (100), 65 (16), 41 (8). Elemental anal. Found: C, 69.46; H, 6.53; N, 5.38. $C_{15}H_{17}NO_3$ calc.: C, 69.50; H, 6.56; N, 5.41%.

2.6.12. Methyl 4-(N-butyl-N-methoxycarbonyl)-4,4-dimethyl-3-methoxycarbonylbut-2-enoate ***5*** *(R = Bu, R′ = R″ = Me)*

Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H, $J = 7.3$ Hz, Me), 1.22–1.30 (m, 2H, CH_2), 1.43–1.49 (m, 2H, CH_2), 1.63 (s, 6H, 2Me), 3.26 (t, 2H, $J = 2.3$ Hz, NCH_2), 3.62 (s, 3H, OMe), 3.67 (s, 3H, OMe), 3.78 (s, 3H, OMe), 5.82 (s, 1H, =CH); IR (neat) ν/cm^{-1} 2957 (s), 1730 (s), 1647 (m), 1436 (m), 1367 (m), 1259 (m), 1169 (m), 871 (w); MS m/z 315 (M^+, absent), 300 (1), 284 (1), 256 (10), 224 (3), 185 (10), 172 (10), 154 (30), 153 (100), 125 (18), 121 (10), 88 (32), 73 (17), 59 (27). Elemental anal. Found: C, 57.10; H, 7.91; N, 4.40. $C_{15}H_{25}NO_6$ calc.: C, 57.14; H, 7.94, N, 4.44%.

2.6.13. Methyl 4-(N-benzyl-N-methoxycarbonyl)-4,4-dimethyl-3-methoxycarbonylbut-2-enoate ***5*** *(R = CH_2Ph, R′ = R″ = Me)*

Pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 6H, 2Me), 3.65 (s, 3H, OMe), 3.69 (s, 3H, OMe), 3.75 (s, 3H, OMe), 4.41 (s, 2H, NCH_2), 5.81 (s, 1H, =CH), 7.27–7.31 (m, 5H, Ph); MS m/z 349 (M^+, 2), 318 (2), 290 (12), 186 (7), 164 (30), 154 (27), 91 (80), 77 (6), 65 (8), 59 (9). Elemental anal. Found: C, 61.85; H, 6.57; N, 3.99. $C_{18}H_{23}NO_6$ calc.: C, 61.89; H, 6.59, N, 4.01%.

2.6.14. 5-(E)-Iodomethylene-3-butyl-4,4-dimethyl-1,3-oxazolidin-2-one ***8*** *(R = Bu, R′ = Me)*

Yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3H, $J = 7.3$ Hz, Me), 1.27–1.37 (m, 2H, CH_2), 1.56–1.66 (m, 2H, CH_2), 1.63 (s, 6H, 2Me), 3.11 (t, 2H, $J = 7.8$ Hz, NCH_2), 5.64 (s, 1H, =CH); MS m/z 309 (M^+, 12), 294 (72), 238 (38), 182 (31), 163 (8), 140 (7), 123 (7), 114 (8), 55 (100), 41 (85). Elemental anal. Found C, 38.78; H, 5.15; N, 4.49. $C_{10}H_{16}INO_2$ calc.: C, 38.83; H, 5.18; N, 4.53%.

2.6.15. Methyl 4-(N-benzyloxycarbonyl-N-methyl)-3-methoxycarbonylbut-2-enoate ***9*** *(R = Me, R′ = H, R″ = CH_2Ph, R‴ = Me)*

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 2.93 (s, 3H, Me), 3.72, 3.75 (2s, 6H, 2OMe), 4.16 (bs, 2H, CH_2), 5.12 (s, 2H, OCH_2), 5.82, 5.88 (2br s 1H, =CH) (these two signals correspond to two conformers of the molecule owing to hindered rotation about the carbamic group), 7.25–7.32 (m, 5H, Ph). A. ^{1}H NMR of this compound was acquired in DMSO at room temperature giving the following signals: 2.85 (br s, 3H, Me), 3.65, 3.67 (2s, 6H, 2OMe), 4.78 (br s 2H, CH_2), 5.09 (br s, 2H, OCH_2), 6.02, 6.05 (2s, 1H, =CH), 7.28–7.35 (m, 5H, Ph). In DMSO at 60°C the =CH signals became sharper and nearer (δ 6.0207 and δ 6.0244) and merged at 90°C (δ 6.0244). IR (neat) ν/cm^{-1} 2953 (m), 1732 (s), 1708 (s), 1659 (m), 1437 (m), 1268 (s), 1172 (m), 1027 (w), 987 (w), 768 (m), 700 (m); MS m/z 321 (M^+, 1), 289 (1), 262 (2), 233 (2), 186 (11), 158 (18), 154 (8), 126 (16), 91 (100), 65 (15), 59 (7); Elemental anal. Found: C, 59.77; H, 5.89; N, 4.32. $C_{16}H_{19}NO_6$ calc.: C, 59.81; H, 5.92; N, 4.36%.

3. Results and discussion

To gain more insight into the factors influencing the formation of **1-Z** and **1-E** we caused *N*-butyl- or *N*-benzylpropynamines to react in methanol in the presence of PdI_2–KI in different molar ratio under CO, air and CO_2 with or without added water. The most significant results are summarized in Table 1.

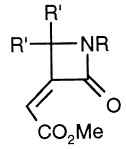
Table 1
Yields of oxazolidinones **1-Z** and **1-E** from *N*-substituted-1,1-dimethylprop-2-ynamines, CO, CO_2, MeOH and air, according to Eq. (2) [100:1 molar ratio of amine to catalyst (PdI_2 + KI in excess), amine conc. 0.15 M]

Run	Amine R	Air (bar)	CO (bar)	CO_2 (bar)	MeOH (ml)	H_2O (ml)	Temp (°C)	Time (h)	KI/Pd molar ratio	Conv. (%)[a]	Yield (%)[a]						
											1-Z	**1-E**	**(1-Z + 1-E)**	**2**	**3**	**4**	**5**
1	Bu	6	18		20		75	30	15	87	3	1	4	48	22	1	2
2	Bu	7	15		20	2	75	25	15	88	9	3	12	32	7	11	6
3	Bu	7	15	23	15	5	75	45	15	91	20	10	34	22	3	16	4
4	Bz	7	17	36	25	5	75	42	15	90	16	9	25	21	2	14	7
5	Bu	7	15	44	20		75	25	15	91	38	13	51	13	1	17	7
6	Bu	5	5	40	20		75	24	15	91	36	11	47	14	1	21	4
7	Bu	5	5	40	20		60	41	15	91	40	12	52	6	1	20	4
8	Bu	5	5	40	20		50	46	10	96	53	17	70	4	1	2	9
9	Bu	5	5	40	20		50	65	10	98	62	21	83	3	1	2	7
10	Bu	5	5		20		50	46	10	54	2	1	3	21	6	3	3
11	Bu	5	5		20	5	50	46	10	69	13	4	17	22	4	10	5
12	Bz	5	5	40	20		53	63	10	98	59	30	89	1		3	5

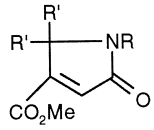
[a]GLC yields, referred to the starting amine.

The best results were obtained at 40–45 bar of CO_2, 5 bar of CO and 5 bar of air with KI/Pd molar ratio of 10 at 50–55°C for 50–65 h (runs 8, 9, 12). A partial pressure of carbon monoxide as high as 15 bar, temperatures of about 75°C (runs 5, 6) and the presence of water (runs 3, 4) led to a decrease of the yields of isomers **1**. The best conditions found allow the initial carboxylation step to proceed promptly due to the high CO_2 partial pressure without hindering the subsequent oxidative alkoxycarbonylation step which can take place at low CO partial pressure as well. Under these conditions the use of CO in the absence of CO_2 led to a 3% yield of **1** (R = Bu, R′, R″ = Me) (run 10) which increased to 17% (**1-Z**:**1-E** = 3) in the presence of 15% water in the reaction mixture (run 11). The addition of water led to an improvement of the yields of isomers **1** at low partial pressure of CO_2 or in its absence. In the absence of added water, that resulting from the reaction did not generate sufficient CO_2 from CO and the yield dropped to 4%, other by-products becoming predominant (compare runs 1 and 2).

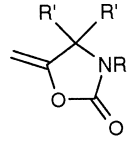
The main by-products of the reactions with CO and CO_2 shown in Table 1 were oxazolidinone **4**, β-lactam **2**(*Z*), γ-lactam **3** and compound **5**(*Z*) derived from trimethoxycarbonylation at the nitrogen and triple bond carbons of the starting propynamine.



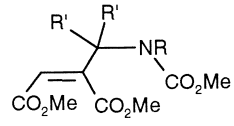
2



3



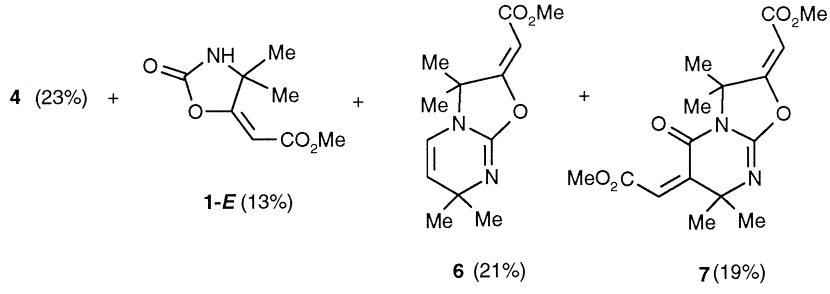
4



5

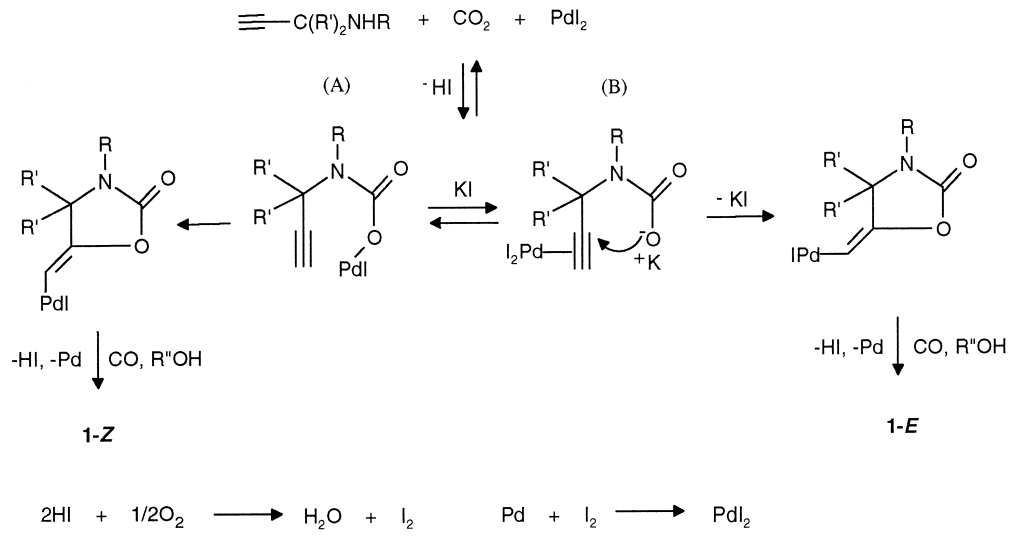
Using alcohols with longer chains as solvents the formation of β-lactams increased, thus the reaction carried out in ethanol or in *n*-butanol under the best conditions reported above gave the following yields respectively: oxazolidinone **4** (R = Bu) 7% and 5%, β-lactam **2** (R = Bu) 20% and 32%, oxazolidinones **1-Z** (R = Bu) 37% and 17% and **1-E** (R = Bu) 21% and 27%. This may be attributed to the lower solubility of carbon dioxide in these solvents than in methanol, which favours the carbonylation reaction.

Extension of the reaction to primary amines under the same conditions (Eq. (3)) led to a limited amount of the carboxylation and carboxylation–alkoxycarbonylation products **4** (R = H, R′ = Me) and **1-E** (R = H, R′ = Me) and a mixture of four products of oxidative carbonylation of *N*,*N*-bis-1,1-dimethylpropynylurea (about 50% yield, products **6** and **7**, already found by us in the reaction of dialkynylureas with CO [11], being the most abundant). The latter is formed in situ by oxidative carbonylation of the primary propynamine.



(3)

A catalytic system based on Pd–C + KI has been shown to be able to replace the PdI_2 + KI system with the same results, the former being oxidized to the latter in methanol in the presence of oxygen.



Scheme 1.

Further experiments were carried out to clarify the course of the reaction leading to **1-Z** and **1-E** (Scheme 1, unreactive ligands are omitted for simplicity in this and the following schemes). Formation of **1-Z** and **1-E** was attributed to different reaction pathways, the former (A) implying cis attack of palladium carbamate on the triple bond, the latter (B) trans attack of the carbamate anion on the palladium-coordinated triple bond.

Isomerization of **1-Z** to **1-E** and vice versa did not occur appreciably under the reaction conditions as checked in two series of control experiments. Thus product **1-Z** (R = Bu) dissolved in dry methanol (conc. = 0.7 M) was stirred at 52°C for 24 h in the presence of PdI_2 + KI (10 mol per mol of Pd, **1-Z**:Pd = 33:1 molar ratio). No isomerization was observed even adding CO (16 bar), air (6 bar) and phenylacetylene (conc. = 0.2 M) as in the usual carbonylation conditions of the triple bond [12].

Isomerization of the vinylpalladium precursors of **1** shown in Scheme 1 also seems not likely because an excess of KI displaces the equilibrium between palladium carbamate and potassium carbamate and leads to a decrease of the **1-Z**:**1-E** ratio from 3.2 to 1.7 as shown in Table 2 on passing from 10 to 100 KI:Pd molar ratio.

The molar ratio of the two isomers **1-Z** and **1-E** does not depend even on the reaction time, their ratio being practically unchanged at low conversion. The catalytic cycle is completed by the oxidation of palladium by iodine formed in situ by the action of air on the hydrogen iodide generated in the alkoxycarbonylation step.

Table 2
Influence of KI/Pd molar ratio on **1-Z**/**1-E** molar ratio

KI/Pd molar ratio	**1-Z**/**1-E** molar ratio
10	3.20
28	2.35
100	1.70

N-Butyl-1,1-dimethylprop-2-ynamine (conc. 0.15 M) in MeOH, CO_2 (40 bar), CO (5 bar), air (5 bar), 10% Pd–C + KI, amine:Pd molar ratio = 100 at 50°C for 45 h.

Table 3
Cyclization-oxidative carbonylation of R′O(CO)NRC(Me)$_2$C≡CH in MeOH (0.15 M) in the presence of Pd–C (10%) +10 KI (substrate:Pd molar ratio = 100) at 52°C, CO (16 bar), air (6 bar)

Substrate		Time (h)	Conversion (%)[a]	Yield (%)[a]	
R″	R			**1-Z**	**1-E**
PhCH$_2$	H	46	63	–	36
PhCH$_2$	*n*-Bu	64	87	traces	69
PhCH$_2$	PhCH$_2$	61	85	< 1	64
PhCH$_2$	*n*-Bu	66	33[b]	< 0.5	21
CH$_2$=CHCH$_2$	*n*-Bu	63	96	50	25
tert-Bu	*n*-Bu	44	98	-	94
n-Bu	*n*-Bu	45	88	< 1	85

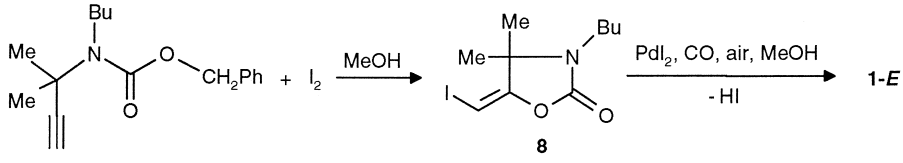
[a]GLC yields, referred to the starting carbamate.
[b]Reaction carried out in n-butanol as solvent.

Evidence for the involvement of pathway (B) in the proposed reaction mechanism is offered by the cyclization-oxidative alkoxycarbonylation of some esters of *N*-alkyldimethylpropynylcarbamates R″O(CO)N(R)C(Me)$_2$C≡CH in methanol in the presence of PdI$_2$ or 10% Pd–C and KI as catalytic system. Results are reported in Table 3.

The results show that all the tested carbamates, except the allylic one, which gave a substantial amount of **1-Z**, led to isomer **1-E** almost exclusively.

The acetylenic carbamate apparently effects a nucleophilic attack of the anionic oxygen on the palladium-activated triple bond with concomitant heterolytic splitting of the OR′ bond leading to **1-E** according to Scheme 2 (corresponding stereochemically to path B of Scheme 1).

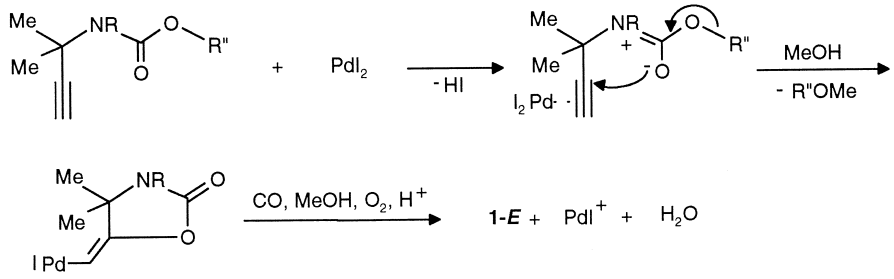
This behaviour has been reported in iodolactonization reactions [13,14]. We observed that 5-*E*-iodomethylene-3-butyl-4,4-dimethyl-1,3-oxazolidin-2-one (66% yield) was formed simply by addition of iodine to the starting *n*-butyl *N*-*n*-butyl-*N*-1,1-dimethylprop-2-ynylcarbamate in methanol at 80°C for 40 h under stirring. Carbonylation of this compound in methanol under CO (16 bar) and air (5 bar) at 90°C for 48 h in the presence of PdI$_2$–KI as catalytic system, gave isomer **1-E** stereospecifically in 79% yield (R = *n*-Bu), Eq. (4).



(4)

In our case the presence of iodine is not critical both in the palladium-catalysed reaction of *N*-benzyl-1,1-dimethylprop-2-ynamine with CO, CO$_2$ and air and in that of benzyl *N*-benzyl-*N*-(1,1-dimethylprop-2-ynyl)carbamate with CO and air. In fact using PdCl$_2$ (in stoichiometric amount) and Na$_2$CO$_3$ the former gave the same product distribution of **1-Z** and **1-E** (2:1 molar ratio of **1-Z**:**1-E**) observed with PdI$_2$ although in lower yield (33%), other compounds (**2** and **3**) being formed as by-products; the latter gave product **1-E** selectively in 27% yield. The fate of the R′ species was followed with the benzyl group. which mainly formed benzyl methyl ether as expected for a cationic species along with benzyl methyl carbonate and oxidation products such as benzaldehyde and its dimethyl acetal.

The involvement of pathway A emerges from the reaction with allyl carbamate, which gave a mixture of **1-Z** and **1-E** in 75% yield (2:1 molar ratio) along with a decarboxylation product. The



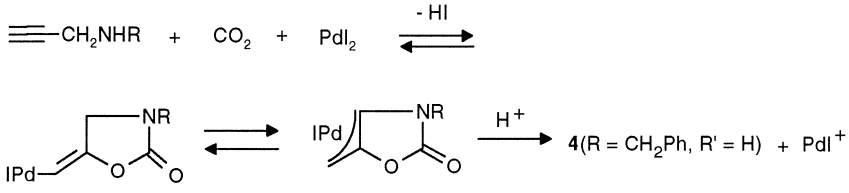
Scheme 2.

intermediacy of an allyl palladium(IV) complex which could result from the reaction of the allyl carbamate with PdI_2 (as $[PdI_4]^{2-}$) may explain the formation of product **1-Z** according to Scheme 3.

These results clearly suggest that the stereochemistry of **1-Z** and **1-E** depends on whether a nucleophilic attack on the triple bond precedes the palladium-catalysed carbonylation or a palladium carbamate first forms and controls the double insertion of the triple bond and carbon monoxide. Examples of both types of attack are reported in the literature for different cases [1,15]. The reactions of carbamic esters thus account for the stereochemistry observed in reaction 2.

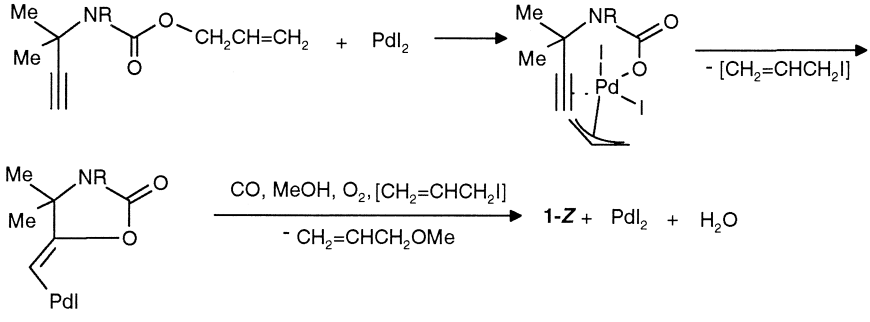
It is to be pointed out that the carboxylation–alkoxycarbonylation reported here represents the first catalytic reaction in which carbon dioxide and carbon monoxide are introduced in sequence in an organic substrate. A stoichiometric reaction in two steps was described by Carmona et al. [16] in the formation of an anhydride from a metallacyclic complex, CO and CO_2.

As previously mentioned carbon dioxide reacted with acetylenic amines not containing geminal substituents R′ in the presence or absence of carbon monoxide and in the presence of air to give compound **4** [5] formally according to Eq. (5).



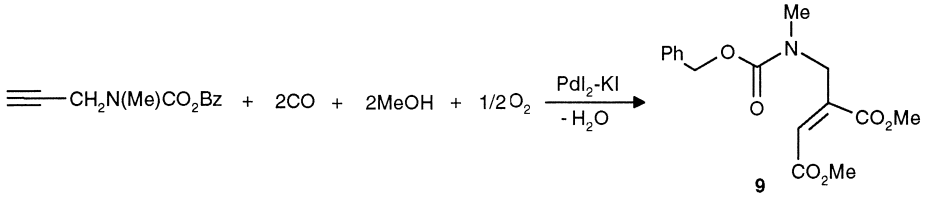
(5)

The mechanism must involve the same carbamic species shown in Scheme 1 (although not included in Eq. (5), air has a beneficial effect in displacing the equilibrium towards carbamate formation). This time, however, the vinylpalladium species formed by cyclization is cleaved by



Scheme 3.

protonation because of the formation of an allylic species which does not react with CO readily. Compound **4** was previously obtained also by direct incorporation of CO_2 under the catalytic action of organic superbases in aprotic solvents [9,10]. We also caused a propynylcarbamate, not containing geminal substituents R′, to react with CO and air under the same conditions adopted for the experiments of Table 3. Benzyl *N*-methyl-*N*-prop-2-ynylcarbamate, however, did not give compound **4** (R = Me, R′ = H) but another compound (**9**) resulting from cis dialkoxycarbonylation of the triple bond (Eq. (6)).



(6)

We attribute this behaviour to the fact that, in the absence of geminal groups in the methylene carbon, ring closure becomes more difficult and a competitive reaction such as (6) can prevail.

Summing up, carbon dioxide or the mixture of carbon dioxide and carbon monoxide can be introduced into an acetylenic amine in methanol under the catalytic action of palladium iodide in the presence of oxygen. Temperatures around 50°C and a high CO_2 to CO ratio are required. When carried out with carbamic esters and CO the reaction gives rise to the same products obtained from CO_2 and CO. In particular **1-E** is formed from alkyl or benzyl carbamates through nucleophilic attack of the ester oxygen on the triple bond, followed by trans alkoxycarbonylation, while the **1-Z–1-E** mixture results from allyl carbamate both through the above process and through formation of a palladium carbamate, followed by alkoxycarbonylation via cis insertion of carbon monoxide.

Acknowledgements

We thank Ministero Università, Ricerca Scientifica e Tecnologica (MURST) and CNR, Progetto Strategico and Progetto Tecnologie Chimiche Innovative for financial support. The facilities of Centro Interfacoltà di Misure of the Univerity of Parma have been utilized for NMR determinations.

References

[1] A. Bonardi, M. Costa, B. Gabriele, G. Salerno, G.P. Chiusoli, Tetrahedron Lett. 36 (1995) 7495.
[2] E. Drent, P.H.M. Budzelaar, Chem. Rev. 96 (1996) 663.
[3] B. Gabriele, G. Salerno, M. Costa, G.P. Chiusoli, J. Mol. Catal. 111 (1996) 43.
[4] V.N. Zudin, G.N. Ll'inich, V.A. Likholobov, Y.I. Yermakov, J. Chem. Soc., Chem. Commun. (1984) 545.
[5] A. Bacchi, G.P. Chiusoli, M. Costa, B. Gabriele, C. Righi, G. Salerno, Chem. Commun. (1997) 1209.
[6] Y. Imada, M. Yuasa, I. Nakamura, S.I. Murahashi, J. Org. Chem. 59 (1994) 2282.
[7] H.E. Carter, R.L. Frank, H.W. Johnston, Org. Syntheses, Coll. 3 (1955) 167.
[8] E. Ponnusamy, U. Fotadar, A. Spisni, D. Fiat, Synthesis, (1986) 48.
[9] M. Costa, G.P. Chiusoli, M. Rizzardi, Chem. Commun. (1996) 1699.
[10] M. Costa, G.P. Chiusoli, D. Taffurelli, G. Dalmonego, J. Chem. Soc., Perkin Trans. 1 (1998) 1541.
[11] A. Bacchi, G.P. Chiusoli, M. Costa, C. Sani, B. Gabriele, G. Salerno, J. Organomet. Chem. 562 (1998) 35.

[12] B. Gabriele, M. Costa, G. Salerno, G.P. Chiusoli, J. Chem. Soc., Perkin Trans. 1 (1994) 83.
[13] S. Takano, S. Hatakeyama, Heterocycles 19 (1982) 1243.
[14] S. Kobayashi, T. Isobe, M. Ohno, Tetrahedron Lett. 25 (1984) 5079.
[15] M.F. Semmelhack, C. Kim, N. Zhang, C. Bodurov, M. Sanner, W. Dobler, M. Meier, Pure Appl. Chem. 62 (1990) 2035, and references cited therein.
[16] E. Carmona, E. Gutierrez-Puebla, J.M. Marin, A. Monge, M. Paneque, M.L. Poveda, C. Ruiz, J. Am. Chem. Soc. 111 (1989) 2883.