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Effective Guanidine-Catalyzed Synthesis of Carbonate and Carbamate Derivatives from Propargyl Alcohols in Supercritical Carbon Dioxide

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Abstract: The reactions of propargyl alcohols with carbon dioxide in supercritical carbon dioxide or in acetonitrile with gaseous carbon dioxide in the presence of organic bases as catalysts have been examined. Bicyclic guanidines are effective catalysts for the formation of α-methylene cyclic carbonates under mild reaction conditions. Oxoalkyl carbonates, oxoalkyl carbamates or α-methyleneoxazolidinones are obtained in high yields and good selectivities in one-step starting from propargyl alcohols and an external nucleophile (alcohols or amines) using bicyclic guanidines as catalysts in supercritical carbon dioxide. Propargylic diols under the same reaction conditions underwent a rearrangement process instead of carbon dioxide insertion whereas in the presence of an external nucleophile the formation of oxocarbonates, oxocarbamates or cyclic carbamates was achieved in satisfactory yields.

Keywords: carbon dioxide fixation; carboxylation; homogeneous catalysis; organocatalysis; supercritical fluids

Introduction

Carbon dioxide is an easily accessible and renewable source of carbon. Indeed, the synthesis of industrially important chemicals based on carbon dioxide has attracted a growing interest. Previous works have also shown that the use of $scCO_2$ as solvent in conjunction with efficient catalysts can strongly reduce the environmental impact of many processes.[1] CO_2 is non-toxic, non-flammable, abundant and cheap. Recent comprehensive reviews from Jessop[2] and Baiker[3] list a large number of different kinds of homogeneous and heterogenous catalytic reactions, respectively, in supercritical CO_2.

Carbonates and carbamates are important targets in organic synthesis. They find wide application as solvents, as effective protecting groups for alcohols and diols involved in important syntheses of biological compounds, in the preparation of industrial products, polymers, pharmaceuticals and agrochemicals.[4] Their synthesis has been classically achieved by processes involving the use of phosgene, an highly toxic pollutant. An alternative and very attractive route to the production of these heterocyclic derivatives consists in the direct incorporation of CO_2 into an organic substrate.

Propargyl alcohols and amines can be advantageously used in combination with CO_2 as starting materials for the synthesis of functionalized cyclic carbonates and carbamates. This strategy is based on the "*in situ*" formation of propargyl carbonate $HC{\equiv}CC(R^1)OCO_2^-$ or propargyl carbamate $HC{\equiv}CC(R^1)N(R^2)CO_2^-$ anionic species. Methods based on the use of transition metals such as Ru,[5] Co,[6] Pd,[7] Cu,[8] Fe,[9] phosphines,[10] inorganic bases (K_2CO_3) in the presence of crown ethers,[11] or organic bases such as DBU coupled to Ag salts[12] have been developed for the reaction of CO_2 with propargyl alcohols. Several reaction media have been used, such as conventional polar aprotic solvents, $scCO_2$ and ionic liquids in the presence of copper metal salts.[13]

We now report a new guanidine-catalyzed one-pot synthesis of cyclic carbonates or carbamates and oxalkyl carbonates or carbamates through the direct in-

corporation of carbon dioxide into propargyl alcohols, using either $scCO_2$ as solvent and reagent or gaseous CO_2 in MeCN as the solvent.

Results and Discussion

Reactions of Propargyl Alcohols with $scCO_2$ in the Presence of Different Organic Catalytic Systems

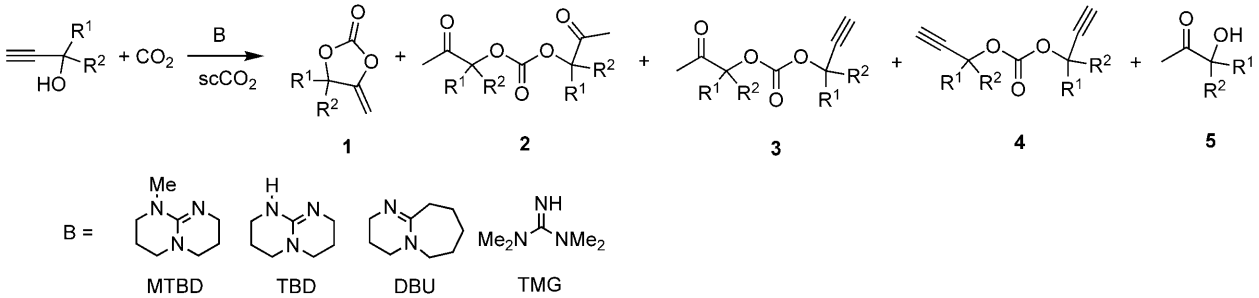
Our catalytic system is based on an organic base, in particular a guanidine derivative, whose good activity had already been shown in the formation of unsaturated oxazolidinones starting from secondary propargylic amines and CO_2, in acetonitrile or in aqueous media.[14] These previous experiments revealed the importance of the strength of the base [in fact, bases with pK_A (AN) <24 showed a low catalytic activity] and of steric effects for the success of the reaction.

The first investigations were carried out with propargyl alcohols in $scCO_2$. Typically, the substrate (5 mmol) and the catalyst (10 mol%) were charged in a stainless steel autoclave (125 mL), and liquid CO_2 (44 g) was added at room temperature in the absence of air. The resulting mixture then was magnetically stirred at 100 °C for 24 h. The reaction of different propargyl alcohols, carried out in the presence of different bases, led to the formation of a mixture of products; the results obtained are shown in Table 1 and Table 2.

The highest conversions and yields on carboxylated products **1** and **2** in the reactions of propargyl alcohols carried out in $scCO_2$ were obtained in the presence of bicyclic guanidines such as MTBD, TBD and TBD-pol as bases and catalysts (entries 1–3, 6–8). The reactions carried out with less basic systems (such as TMG, DBU, NBu_4BF_4+KF or NBu_4F) or in the absence of catalyst provided low conversions and yields of carboxylated products (entries 4, 5, 9–12).

The results of the reactions of different propargyl alcohols in $scCO_2$ in the presence of MTBD as a catalytic system are reported in Table 2. Addition of

Table 1. Reactions of 2-methyl-3-butyn-2-ol (R^1, R^2 = Me) and 1-ethynyl-1-cyclohexanol [R^1, R^2 = -$(CH_2)_5$-] in $scCO_2$ in the presence of different catalytic systems.[a]



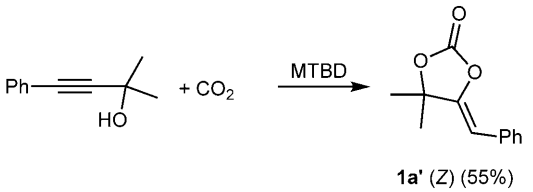
Entry	R^1	R^2	Catalyst (B)	Conversion [%][b]	Yield [%][c]					Products
					1	**2**	**3**	**4**	**5**	
1	Me	Me	MTBD[d]	99	25	60			5	**1a**, **2a**, **5a**
2	Me	Me	TBD-pol[e]	93	45	30				**1a**, **2a**
3	Me	Me	TBD[f]	91	21	52			7	**1a**, **2a**, **5a**
4	Me	Me	NBu_4BF_4+KF	21	15					**1a**
5	Me	Me	NBu_4F	14	10					**1a**
6	-$(CH_2)_5$-		MTBD[d]	97	35	38			6	**1c**, **2c**, **5c**
7	-$(CH_2)_5$-		TBD-pol[e]	93	36	36				**1c**, **2c**
8	-$(CH_2)_5$-		TBD[f]	66	8	51			4	**1c**, **2c**, **5c**
9	-$(CH_2)_5$-		DBU[g]	60	16	26				**1c**, **2c**
10	-$(CH_2)_5$-		TMG[h]	39	11	15			2	**1c**, **2c**, **5c**
11	-$(CH_2)_5$-		NBu_4F	26	21					**1c**
12	-$(CH_2)_5$-		–	14	9					**1c**

[a] *Reaction conditions:* alcohol 5.0 mmol, base 0.5 mmol, $T=100$ °C, liquid CO_2 44 g at room temperature, time 24 h.
[b] Based on starting propargylic alcohol.
[c] Determined by GLC using the internal standard method.
[d] MTBD = 1,3,4,6,7,8-hexaydro-1-methyl-2*H*-pyrimido[1,2-*a*]pyrimidine.
[e] TBD-pol = 1,3,4,6,7,8-hexaydro-2*H*-pyrimido[1,2-a]pyrimidine supported on polystyrene.
[f] TBD = 2,3,4,6,7,8-hexaydro-1*H*-pyrimido[1,2-*a*]pyrimidine.
[g] DBU = 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepine.
[h] TMG = 1,1,3,3-tetramethylguanidine.

Table 2. Reactions of different propargylic alcohols in $scCO_2$ in the presence of MTBD as catalyst.[a]

Entry	R^1	R^2	Conversion [%][b]	Yield [%][c]					Products
				1	**2**	**3**	**4**	**5**	
13	Me	Me	99	25	60			5	**1a**, **2a**, **5a**
14	Me	-CH=CH_2	40	20					**1b**
15		-$(CH_2)_5$-	97	35	38			6	**1c**, **2c**, **5c**
16[d]		-$(CH_2)_5$-	97	41	30				**1c**, **2c**
17	Me	Ph	11	9					**1d**
18	Me	H	85	45		33[e]			**1e**, **3e**
19	H	H	12				3		**4f**

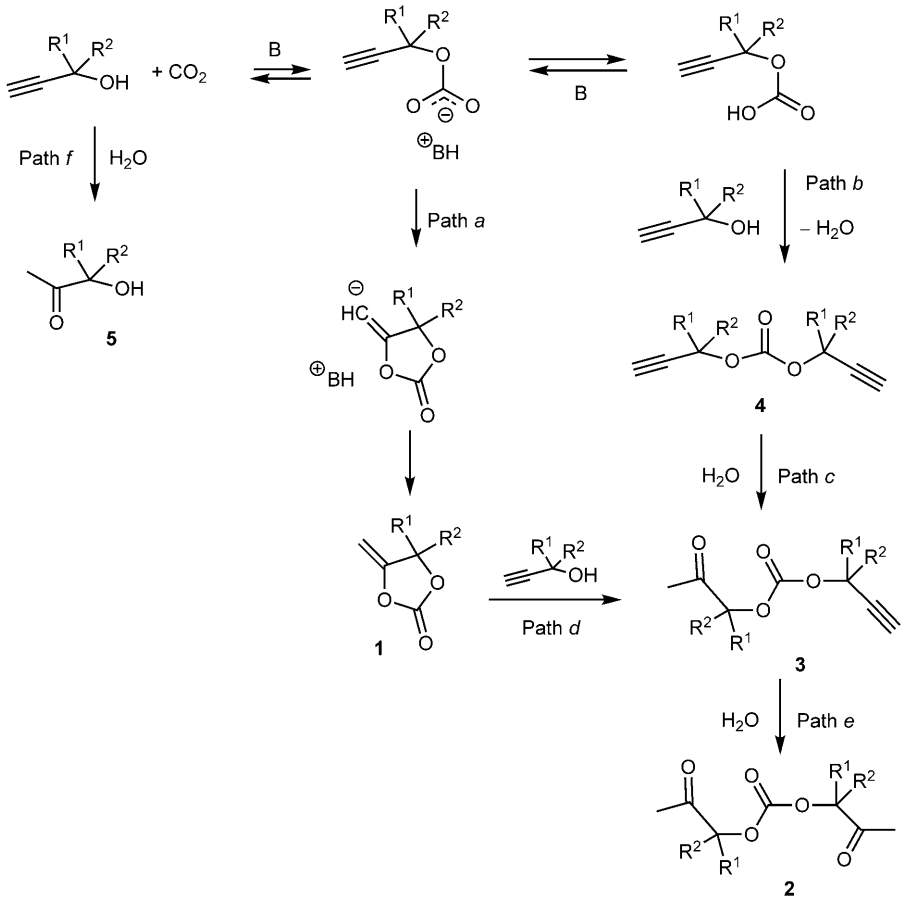
[a] *Reaction conditions:* alcohol 5.0 mmol, MTBD 0.5 mmol, $T = 100\,°C$, liquid CO_2 44 g at room temperature, time 24 h.
[b] Referred to starting alcohol.
[c] Determined by GC using the internal standard method.
[d] In $scCO_2$ (44 g) and MeCN (4 mL).
[e] Mixture of diastereoisimers in 1.2:1.0 molar ratio.



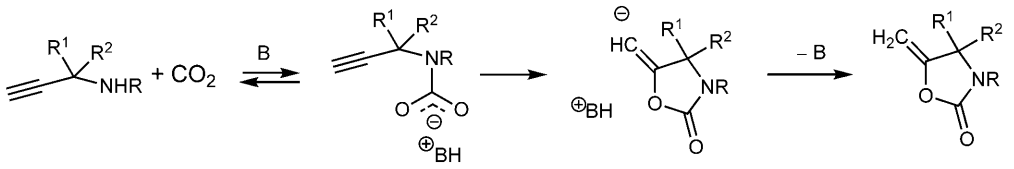
1a' (*Z*) (55%)

Scheme 1. Carboxylation of 2-methyl-4-phenylbut-3-yn-2-ol in the presence of MTBD.

CH_3CN (4 mL) increased slightly the selectivity of product **1c** compared to **2c** (entry 16). Lower yields and different selectivities were obtained with propargyl alcohols bearing different substituents from methyl or cyclohexyl groups in the α position to the triple bond. Thus vinyl and phenyl groups lowered the reactivity yielding only **1b** and **1d**, respectively (entries 14 and 17). A single methyl group led to **1e** (45%) to-



Scheme 2. Formation pathway for compounds **1**–**5**.



Scheme 3. Formation pathway for methyleneoxazolidinones.

gether with **3e** (33%), the latter being present as a mixture of diastereoisomers in a 1.2:1.0 molar ratio (entry 18), while prop-2-yn-1-ol yielded dipropargyl carbonate **4f** in very low yield (entry 19).

The formation of cyclic carbonates is not limited to terminal prop-2-ynols. In fact, under the conditions reported above, the reaction of 2-methyl-4-phenylbut-3-yn-2-ol, bearing a phenyl substituent on the triple bond, led selectively to the formation of the cyclic carbonate **1a′** (*Z*) in 55% yield (Scheme 1).[12] However, the reaction did not take place in the presence of an alkyl substituent on the triple bond, differently from the DBU-silver-catalyzed reaction.[12]

The mechanism by which carbon dioxide is introduced into propargylic alcohols to form the cyclic carbonate **1** is based on known experimental results.[15] In particular, it was previously reported that CO_2 and alkyl alcohols, in the presence of guanidines or amidines, such as 2-butyl-1,1,3,3-tetramethylguanidine (TMBG) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), led to the respective alkyl carbonate salts. In a similar manner, propargyl carbonate salts can be formed from the equilibrium between propargyl alcohols and CO_2 in the presence of guanidines, as shown in Scheme 2 (B = MTBD, TBD and DBU).[15a] The strength of the base and the pressure of CO_2 play a key role in shifting the equilibrium to the right. A 5-*endo-dig* nucleophilic attack of the oxygen atom on the internal carbon of the triple bond may then take place, followed by protonation of the resulting carbanion by the protonated base to give the cyclic carbonate **1** (Scheme 2, path *a*). On the other hand, the acyclic carbonate **4** (isolated in small amounts only when $R^1 = R^2 = H$) derives from carboxylation of the substrate followed by the attack of another molecule of the propargyl alcohol (Scheme 2, path *b*), while product **3** may derive from hydration of one the triple bonds of **4** (Scheme 2, path *c*). Alternatively, compound **3** can be formed by nucleophilic attack of the propargyl alcohol to the carbonyl of **1**, with ring opening and tautomerization (Scheme 2, path *d*). Finally, hydration of the triple bond of **3** (Scheme 2, path *e*) or of the substrate (Scheme 2, path *f*) accounts for the formation of compounds **2** and **5**, respectively. It is worth noting that, according to experimental findings, the hydration of triple bonds was promoted by guanidine only in the presence of CO_2 probably through the formation of guanidium bicarbonate species.[16]

Table 3. Catalytic reactions of propargylic alcohols with gaseous CO_2 in MeCN in the presence of TBD and MTBD as catalyst (B).[a]

Entry	R^1	R^2	Catalyst (B)	Conversion [%][b]	Yield [%][c]					Products
					1	**2**	**3**	**4**	**5**	
1	Me	Me	MTBD	99	82	6	4		4	**1a**, **2a**, **3a**, **5a**
2[d]	Me	Me	TBD	91	12	27			35	**1a**, **2a**, **5a**
3	Me	-CH=CH_2	MTBD	76	55				8	**1b**, **5b**
4	-$(CH_2)_5$-		MTBD	75	61				5	**1c**, **5c**
5[e]	-$(CH_2)_5$-		TBD	81	12	21			29	**1c**, **2c**, **5c**
6	Me	Ph	MTBD	97	71				10	**1d**, **5d**
7	Me	H	MTBD	85	15		66[f]			**1e**, **3e**
8	H	H	MTBD	18				12		**4f**
9	Me	Et	MTBD	78	64				5	**1g**, **5g**
10	Ph	Ph	MTBD	28	14					**1h**

[a] *Reaction conditions:* alcohol 5.0 mmol, base 0.5 mmol, concentration of MTBD base 0.033 M in MeCN (15 mL), $T = 100\,°C$, CO_2 pressure 44 bar at room temperature, time 24 h.
[b] Based on starting propargylic alcohol, by GLC.
[c] Determined by GLC using the internal standard method.
[d] Formation of 2-methylbut-1-en-3-yne 16% was also observed.
[e] Formation of 1-ethynylcyclohex-1-ene 18% was also observed.
[f] Mixture of two diastereoisomers in 1.1:1.0 molar ratio determined by GLC.

Catalytic Reactions of Propargyl Alcohols with Gaseous CO_2 in MeCN as the Solvent in the Presence of TBD and MTBD

As we have seen, working in $scCO_2$ the desired cyclic carbonate **1** was usually obtained in rather low selectivity (Table 1 and Table 2). We therefore decided to investigate the reactivity of propargyl alcohols in MeCN as the solvent in the presence of gaseous CO_2 and a strong base such as MTBD. The choice of using a homogenous mixture of acetonitrile and gaseous CO_2 in the presence of a catalytic amount (10 mol%) of a substituted bicyclic guanidine, such as MTBD, was made on the basis of the good results previously obtained in the synthesis of oxazolidinones from secondary propargylic amines under similar conditions (Scheme 3).[14] In that reaction, in fact, MTBD promoted an efficient ring closure to the oxazolidinone derivative, which was rather stable under the reaction conditions and did not undergo ring opening by attack of a second molecule of alcohol to the carbonyl (Scheme 3).

Thus, various propargylic alcohols (5 mmol) were allowed to react at 100 °C with CO_2 (40 bar at room temperature for 24 h under magnetic stirring in the presence of MTBD or TBD (0.5 mmol, concentration of base 0.03 M) in MeCN. The results obtained are shown in Table 3.

The results generally show good yields in cyclic carbonates **1a–d, g** (entries 1, 3, 4, 6 and 9) whose formation is strongly influenced by the nature of the groups R^1 and R^2, the best yields and selectivity being obtained in the case of tertiary propargyl alcohols. This is clearly due to the *gem*-dialkyl effect, which tends to favour cyclization.[17] On the other hand, the reaction of an α-monosubstituted alcohol, such as but-3-yn-2-ol, mainly led to acyclic keto carbonate **3e** as a mixture of diasteroisomers (66% total yield), and to cyclic carbonate **1e**, obtained in only 15% yield (entry 7). Finally, with an α-unsubstituted substrate the reaction was very slow, and led to the formation of **4f** in low yield (12%, entry 8).

It is noteworthy that, in contrast to substituted bicyclic guanidines MTBD and TBD-pol, a bicyclic-guanidine such as TBD, in spite of its high basicity [pKa (AN) = 26.03],[18] and tetramethylguanidine (TMG) are scarcely able to promote the formation of cyclic carbonate **1** starting from tertiary propargyl alcohols (entries 2 and 5, Table 3 and entry 10, Table 1) mainly leading to the hydrated substrates **5** together with enyne derivatives. Other authors have highlighted this different behaviour in other experiments involving CO_2.[19] We have previously noticed that, in the aqueous phase, TBD favours the formation of hydrophobic sites by coordinating carbamic anions through two hydrogen bridges;[14] this causes the anion to be less active, its nucleophilicity being reduced by coordination. On the other hand substituted bicyclic guanidines as MTBD or TBD-pol coordinate the carbamate through a single hydrogen bond thus allowing a greater nucleophilicity of the anion and therefore favouring cyclization. A similar effect may also be at work in the case of the reaction between propargyl alcohol and CO_2 leading to a carbonate anion, rather than carbamate, as intermediate (Scheme 4).

Diffractometric X-ray analyses of single crystals of crystalline adducts between acetic or trifluoroacetic acid and TBD were reported[20] and confirmed the hypothesis that, with bicyclic guanidines, two simultaneous hydrogen bonds can be formed between the oxygen atoms of the carboxylate moiety and the two N–H bonds of the protonated guanidine (Figure 1).

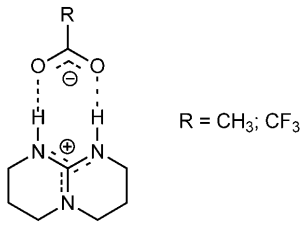
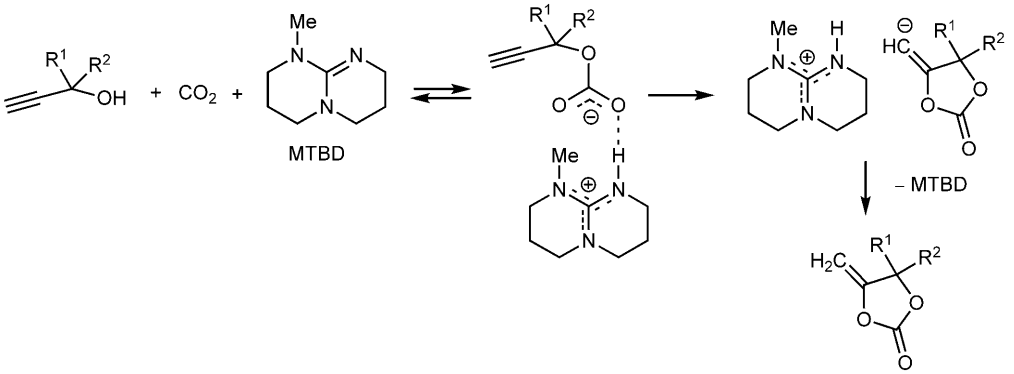
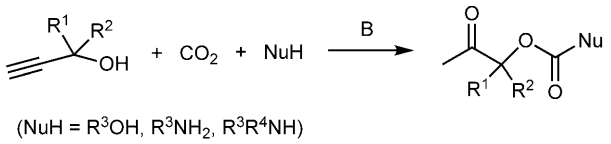


Figure 1. Acetic or trifluoroacetic acid/TBD adducts.



Scheme 4. Formation pathway for cyclic methylene carbonates.



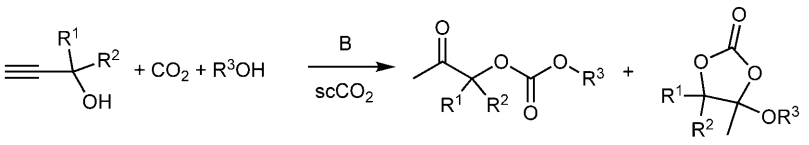
(NuH = R^3OH, R^3NH_2, R^3R^4NH)

Scheme 5. Catalytic carboxylation of propargylic alcohols in the presence of external nucleophiles.

Catalytic Reactions of Propargyl Alcohols with CO_2 in $scCO_2$ in the Presence of External Nucleophiles

The formation of products **2**, particularly in the case of reactions carried out in $scCO_2$, (see Table 1), prompted us to investigate the reaction of propargyl alcohols in $scCO_2$ in the presence of an external nucleophile, such as an alcohol or an amine, using an organic base as catalyst, in order to obtain, in one step, the synthesis of oxoalkyl carbonate or oxoalkyl carbamate derivatives (Scheme 5). This new, direct synthetic approach to oxoalkyl carbonates appears to be particularly attractive, considering that they are usually obtained through two-steps synthetic procedures.[21] Recently, efficient one-pot syntheses of β-oxopropyl carbamates and 4-alkylene-1,3-oxazolidin-2-ones carried out in the presence or in the absence of a catalyst starting from propargyl alcohols, primary or secondary amines and carbon dioxide have been reported.[22]

Table 4. Catalytic reactions of propargylic alcohols with CO_2 in $scCO_2$ in the presence of an alcohol or phenol as external nucleophile.[a]



6 **7**

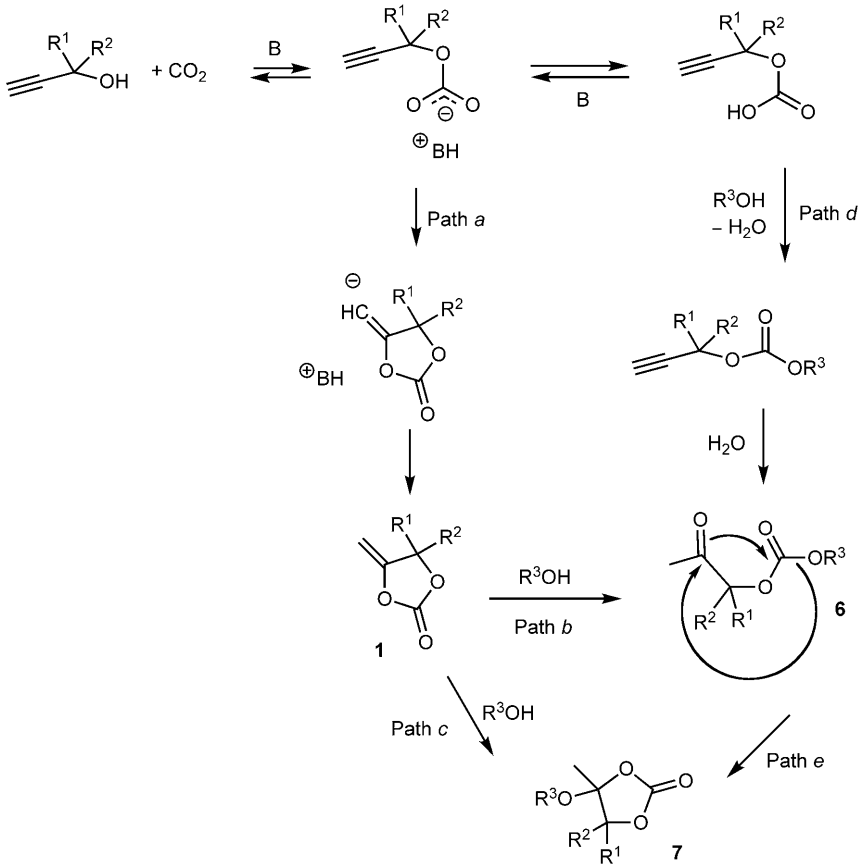
Entry	R^1	R^2	R^3OH	Catalyst (B)	Conversion [%][b]	Yield [%][c] **6**	Yield [%][c] **7**	Products
1	Me	Me	MeOH	MTBD	90	73		**6a**
2	Me	Me	*n*-BuOH	MTBD	99	81		**6b**
3	Me	Me	*n*-BuOH	TBD -pol	99	84[d]		**6b**
4	Me	Me	*n*-BuOH	TBD	87	76		**6b**
5	Me	Me	*n*-BuOH	NBu_4F	70	51		**6b**
6	Me	Me	*n*-BuOH	DBU	95	81		**6b**
7	Me	Me	butan-2-ol	MTBD	65	42		**6c**
8	Me	Me	allyl alcohol	MTBD	90		81	**7a**
9	Me	Me	propargyl alcohol	MTBD	86		68	**7b**
10	Me	Me	PhOH	MTBD	80		63	**7c**
11	-$(CH_2)_5$-		*n*-BuOH	MTBD	99	70		**6d**
12	-$(CH_2)_5$-		*n*-BuOH	TBD -pol	99	79[e]		**6d**
13[f]	-$(CH_2)_5$-		*n*-BuOH	TBD	79	65		**6d**
14	-$(CH_2)_5$-		*n*-BuOH	NBu_4F	80	62		**6d**
15	-$(CH_2)_5$-		*n*-BuOH	DBU	79	60		**6d**
16	-$(CH_2)_5$-		allyl alcohol	MTBD	83	56	18	**6e**, **7d**
17	-$(CH_2)_5$-		PhOH	MTBD	70		43	**7e**
18	-$(CH_2)_5$-		PhOH	TBD-pol	60		31	**7e**
19	Me	Ph	*n*-BuOH	MTBD	99	87		**6f**
20[g]	Me	Ph	*n*-BuOH	TBD	61	32		**6f**
21	Me	Ph	allyl alcohol	MTBD	63	22	35[h]	**6g**, **7f**
22	Me	Ph	PhOH	MTBD	99		84[i]	**7g**

[a] *Reaction conditions:* propargylic alcohol 5.0 mmol, R^3OH 5.0 mmol, base 0.5 mmol, $T = 100\,°C$, liquid CO_2 44 g at room temperature, time 24 h.
[b] Based on starting propargylic alcohol, by GLC.
[c] Determined by GLC using the internal standard method.
[d] 3 recycles.
[e] 2 recycles.
[f] 11% of the hydrated substrate was also formed.
[g] 17% of the hydrated substrate was also formed.
[h] Mixture of two diastereoisomers in 1.1:1.0 molar ratio determined by GLC.
[i] Mixture of two diastereoisomers in 2.3:1.0 molar ratio determined by GLC.

Reactions of Propargyl Alcohols with CO_2 in $scCO_2$ in the Presence of Alcohols or Phenol

We carried out several experiments using tertiary propargyl alcohols in $scCO_2$ in the presence of catalytic amounts of an organic base and an equimolar amount of an alcohol or phenol as external nucleophile. The results obtained using 2-methyl-3-butyn-2-ol, 1-ethynylcyclohexanol and 2-phenyl-3-butyn-2-ol as starting materials are shown in Table 4. As can be seen from the Table, good yields of the corresponding β-oxopropyl carbonates **6a–f** were achieved in reactions conducted using MTBD, TBD-pol, TBD, DBU and NBu_4F together with an aliphatic primary alcohol as the external nucleophile (entries 1–6, 11–15, 19, 20). Yields of products **6** decreased using a secondary alcohol, as in the case of 2-butanol (42%, entry 7). It is noteworthy that one-pot processes leading to oxopropyl carbonates starting from propargyl alcohols and CO_2 in $scCO_2$ in the presence of alcohols or phenol were never reported before. Interestingly, the reaction course changed in the case of phenol or an unsaturated alcohol, such as allyl or propargyl alcohol, which usually led to the selective formation of α-alkoxy-α-methyl cyclic carbonates **7** in low to high yields (Table 4, entries 8–10, 17, 18, 22). On the other hand, a mixture of products **6** and **7** was obtained in the reaction of ethynylcyclohexanol and 2-phenylbut-3-yn-2-ol with allyl alcohol (entries 16 and 21).

According to the literature,[21] formation of product **6** can be rationalized through a mechanism involving attack of the external nucleophile R^3OH to the carbonyl of the initially formed cyclic carbonate **1**, with ring opening and tautomerization (Scheme 6, path *a* followed by path *b*). Alternatively, the unsymmetrical acyclic carbonate **6** can be formed by the reaction between the propargyl carbonic acid and R^3OH, followed by water addition to the triple bond (Scheme 6, path *d*). On the other hand, product **7** may derive from addition of R^3OH to the vinyl ethereal bond of cyclic carbonate **1** (Scheme 6, path *c*) or by ring-chain tautomerization of **6** (Scheme 6, path *e*). Apparently, these latter pathways leading to **7** are followed only when R^3 = phenyl, allyl or propargyl. We refrain to propose a straightforward explanation for this behaviour, which would require additional investigations.



Scheme 6. Alternative pathways for the formation of compounds **6** and **7**.

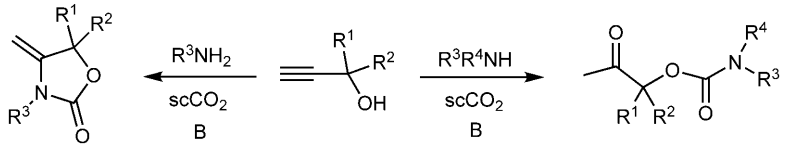
Reactions of Propargyl Alcohols with CO_2 in $scCO_2$ in the Presence of Amines as Nucleophiles

We have also studied the reactivity of propargyl alcohols with various primary and secondary amines as external nucleophiles in $scCO_2$ in presence of MTBD or TBD. The results obtained are reported in Table 5. As can be seen from the Table, primary amines selectively led to α-methyleneoxazolidinones **8**, while acyclic carbamates **9** were obtained in the case of secondary amines. Better results were consistently obtained with MTBD rather than TBD as the base. With MTBD, the yields of products **8a**, **b**, **d–i** and **9a–g** were generally high using primary alkyl-, allyl- and benzylamines or secondary alkylamines (Table 5, entries 1, 3, 5, 6, 8, 9, 11, 14, 15, 17, 20–22), while lower yields were obtained with primary aromatic amines, such as aniline (Table 5, entries 7, 13, and 19). No reaction occurred with *tert*-butylamine, probably for steric reasons (Table 5, entry 4). Guanidine-catalyzed one-pot reactions of propargyl alcohols with CO_2 in $scCO_2$ in the presence of primary and secondary amines gave yields comparable with the best of the recent literature.[8,9,13,22]

The mechanism for the formation of products **8** and **9** is similar to that already proposed for the reaction with alcohols (Scheme 6). Thus, formation of the cyclic carbonate **1** is followed by nucleophilic attack by the amine to the carbonyl to give the acyclic carbamate **9** (Scheme 7, path *a*). The latter can also be formed by the reaction between propargyl carbonic acid and the amine, followed by water addition to the triple bond (Scheme 7, path *b*). The acyclic carbonate **9** may then undergo cyclization by intramolecular attack of the amino group to the ketonic carbonyl. Clearly, this latter reaction occurs only when $R^4 = H$, and leads, after dehydration, to the formation of oxazolidinones **8** (Scheme 7, path *c*).

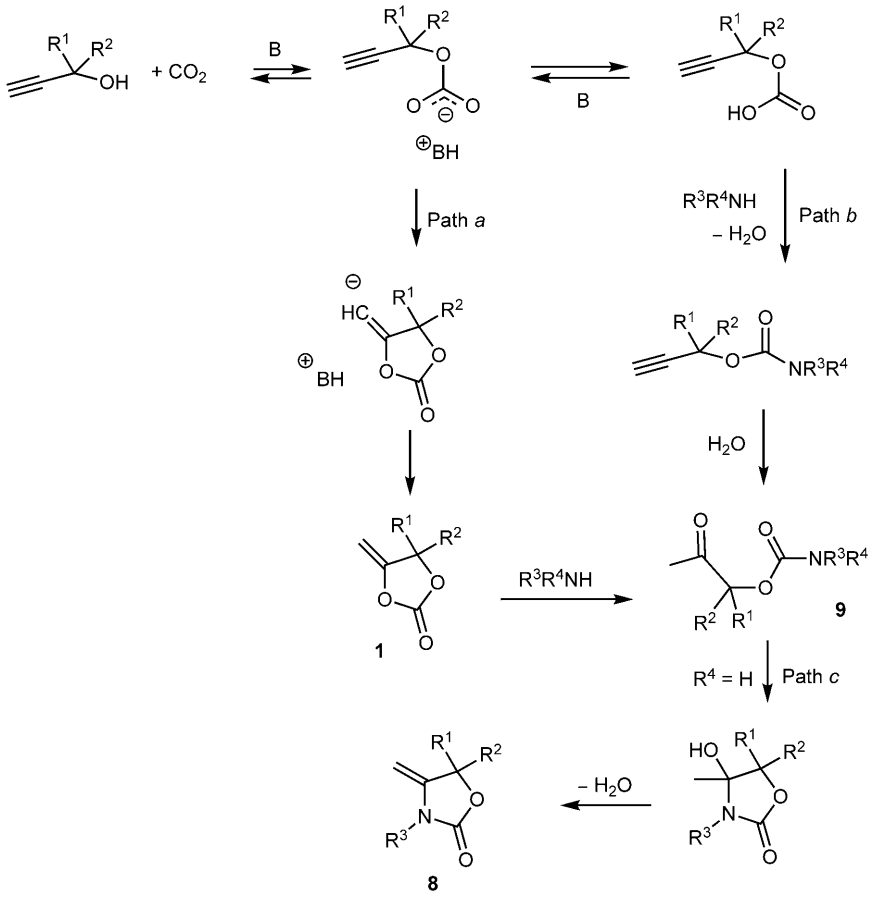
The reaction also worked well with 2-methyl-4-phenylbut-3-yn-2-ol, which, under the usual conditions with $BuNH_2$ as nucleophile and MTBD as catalyst,

Table 5. Catalytic reactions of propargylic alcohols with CO_2 in $scCO_2$ in the presence of a primary or secondary amine.[a]



Entry	R^1	R^2	R^3NH_2	Catalyst (B)	Conversion [%][b]	Yield [%][c] **8**	Yield [%][c] **9**	Products
1	Me	Me	*n*-$BuNH_2$	MTBD	90	78		**8a**
2	Me	Me	*n*-$BuNH_2$	TBD	89	78		**8a**
3	Me	Me	butan-2-amine	MTBD	92	72		**8b**
4	Me	Me	*t*-$BuNH_2$	MTBD	–	–		
5	Me	Me	allylNH_2	MTBD	91	72		**8d**
6	Me	Me	$BzNH_2$	MTBD	87	67		**8e**
7	Me	Me	$PhNH_2$	MTBD	50	38		**8f**
8	Me	Me	pyrrolidine	MTBD	96		79	**9a**
9	Me	Me	*n*-Bu_2NH	MTBD	97		79	**9b**
10	Me	Me	*n*-Bu_2NH	TBD	70		58	**9b**
11	-$(CH_2)_5$-		*n*-$BuNH_2$	MTBD	86	69		**8g**
12	-$(CH_2)_5$-		*n*-$BuNH_2$	TBD	85	65		**8g**
13	-$(CH_2)_5$-		$PhNH_2$	MTBD	51	33		**8h**
14	-$(CH_2)_5$-		pyrrolidine	MTBD	97		81	**9c**
15	-$(CH_2)_5$-		*n*-Bu_2NH	MTBD	96		82	**9d**
16	-$(CH_2)_5$-		*n*-Bu_2NH	TBD	67		48	**9d**
17	Me	Ph	*n*-$BuNH_2$	MTBD	88	72		**8i**
18	Me	Ph	*n*-$BuNH_2$	TBD	32	21		**8i**
19	Me	Ph	$PhNH_2$	MTBD	40	15		**8j**
20	Me	Ph	pyrrolidine	MTBD	96		78	**9e**
21	Me	Ph	*n*-Bu_2NH	MTBD	97		77	**9f**
22	H	H	pyrrolidine	MTBD	46		33	**9g**

[a] *Reaction conditions:* alcohol 5.0 mmol, added amine 5.0 mmol, base 0.5 mmol, $T = 100\,°C$, liquid CO_2 44 g at room temperature, time 24 h.
[b] Based on starting alcohol, by GLC.
[c] Determined by GLC using the internal standard method.

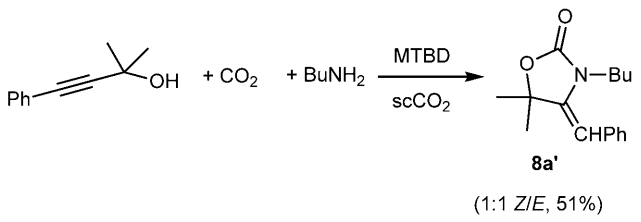


Scheme 7. Formation pathway for compounds **8** and **9**.

was converted into oxazolidinone **8a′** as a *ca.* 1:1 *Z*/*E* mixture (51% total yield, Scheme 8).

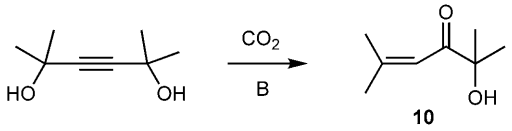
Catalytic Reactions of Propargylic Diols with CO_2 in the Presence of TBD, MTBD and DBU

In order to further extend the synthetic applicability of our methodology, the behaviour of propargylic diols with CO_2 was investigated. Thus, 2,5-dimethylhex-3-yne-2,5-diol was allowed to react in $scCO_2$ or in gaseous CO_2 in MeCN as the solvent in the presence of MTBD, TBD or DBU under the usual conditions. Surprisingly, only negligible amounts of the cyclic carbonate derivative were detected in the reaction mixture, the main reaction product being 2-hydroxy-2,5-



Scheme 8. Catalytic carboxylation of 2-methyl-4-phenylbut-3-yn-2-ol in the presence of *n*-butylamine.

Table 6. CO_2-promoted rearrangement reaction of 2,5-dimethylhex-3-yne-2,5-diol in $scCO_2$ or MeCN as the solvent in the presence of MTBD, TBD or DBU.[a]



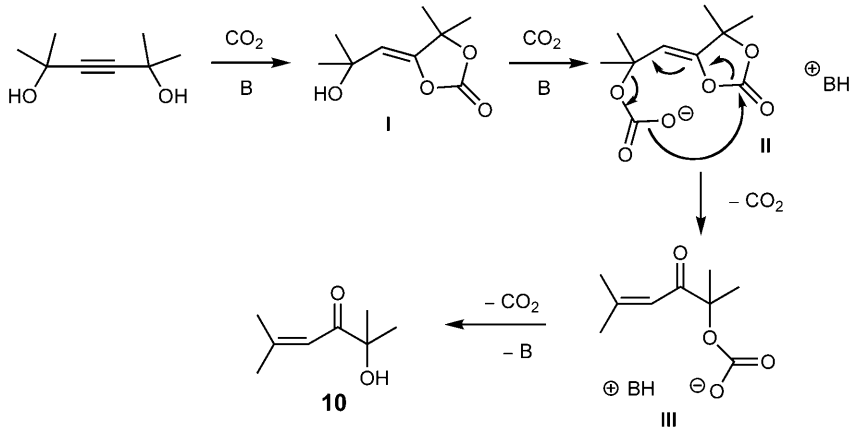
Entry	Catalyst (B)	Solvent	Conversion [%][b]	Yield [%][c] **10**
1	MTBD	$scCO_2$	96	92 (85)
2	TBD	$scCO_2$	96	92
3	DBU	$scCO_2$	90	85
4[d]	MTBD	MeCN	96	92

[a] *Reaction conditions:* in $scCO_2$: diol 5.0 mmol, catalyst (B) 0.5 mmol, CO_2 44 g, $T = 100\,°C$, time 24 h; in MeCN: diol 5.0 mmol, catalyst (B) 0.5 mmol, base 0.1 M in MeCN (5 mL), $T = 100\,°C$, time 24 h.

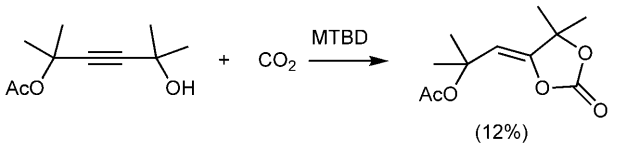
[b] Based on starting diol, by GLC.

[c] GLC yield using the internal standard method (isolated yield).

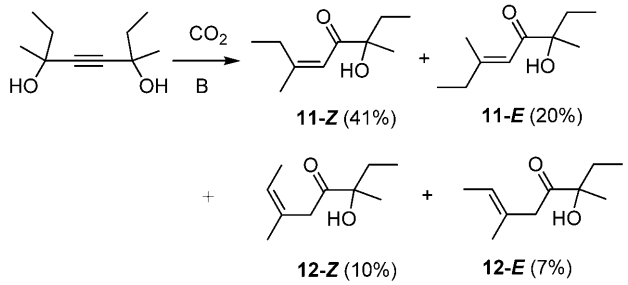
[d] 3% of cyclic hydroxy carbonate **I** was isolated.



Scheme 9. Proposed mechanism for the formation of **10**.



Scheme 10. Catalytic carboxylation of 5-hydroxy-2,5-dimethylhex-3-yn-2-yl acetate leading to a cyclic carbonate derivative.



Scheme 11. Catalytic carboxylation of 3,6-dimethyloct-4-yne-3,6-diol to **11** and **12**.

dimethylhex-4-en-3-one **10**, corresponding to a formal rearrangement of the substrate (Table 6).[6] The yield of **10** was as high as 92% when working with MTBD or TBD in $scCO_2$ (Table 6, entries 1 and 2) as well as with MTBD in MeCN under 40 bar pressure of CO_2 (entry 4), while it was slightly lower with DBU (85%, entry 3). In all cases the compound **10** was obtained with yields and selectivities considerably higher than those previously reported.[6]

The presence of CO_2 was essential for this rearrangement as proved by blank experiments. The isolation of a small amount of cyclic carbonate **I** may support the following mechanism of formation of **10** (Scheme 9): the cyclic carbonate intermediate **I** is obtained first, followed by carboxylation of the second OH group with formation of the carbonate anion **II**. Intramolecular nucleophilic attack by nucleophilic oxygen to the endocyclic carbonyl, with simultaneous ring opening and decarboxylation, affords the acyclic carbonate anion **III**, which eventually decarboxylates to give **10** (Scheme 9).

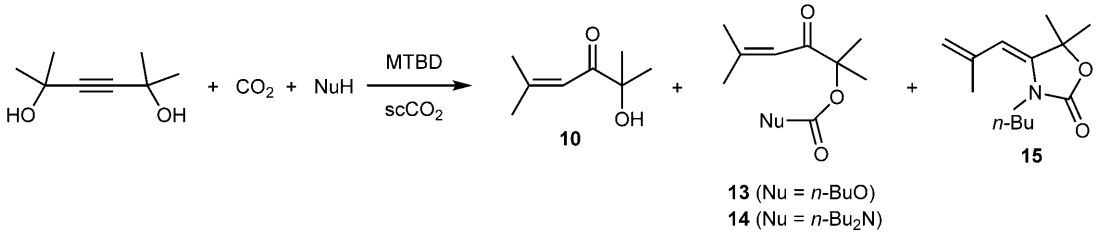
In agreement with the proposed mechanism, when the monoacetylated substrate 5-hydroxy-2,5-dimethylhex-3-yn-2-yl acetate was allowed to react under the usual conditions, it was possible to isolate the corresponding cyclic carbonate, even though in low yield (Scheme 10).

The reactivity of another propargylic diol, namely, 3,6-dimethyloct-4-yne-3,6-diol, was here tested for the first time. Under the same conditions as those reported in Table 6, entry 1, this diol was converted into the corresponding rearrangement product **11** (as a *ca.* 2:1 *Z*/*E* mixture, 61% total yield) together with product **12** ensuing from rearrangement and shift of the double bond (as a *ca.* 1.5:1.0 *Z*/*E* mixture, 17% total yield, Scheme 11)

Finally, the reactivity of propargylic diols was investigated in the presence of external nucleophilic species, such as alcohols or amines. Thus, *n*-butanol, di-*n*-butylamine or *n*-butylamine were added in equimolar amounts with respect to 2,5-dimethylhex-3-yne-2,5-diol in the presence of MTBD as catalyst in $scCO_2$. The reaction, carried out under the usual conditions, led to the formation of oxo carbonate **13**, oxo carbamate **14** or cyclic carbamate **15**, respectively, in satisfactory yields (Table 7). Rearrangement product **10** was also formed in different amounts.

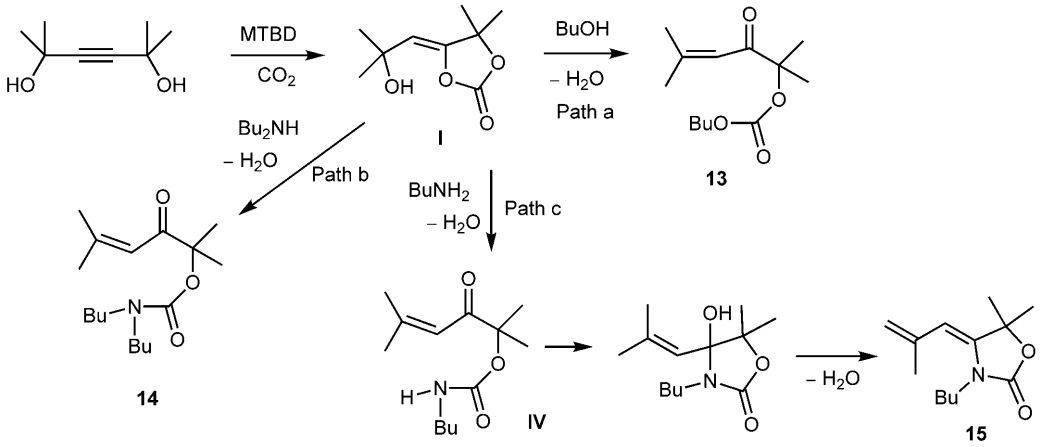
The mechanistic pathways leading to products **13**–**15** are similar to those previously described for the formation of compounds **6**, **8**, and **9** (see Scheme 6 and Scheme 7). As proved by blank experiments the product **10** is not an intermediate in these reactions. Thus, formation of oxo carbonate **13** and oxo carba-

Table 7. Catalytic reactions of 2,5-dimethylhex-3-yne-2,5-diol with an external nuclophile in $scCO_2$ in the presence of MTBD.[a]



Entry	NuH	Conversion [%][b]	Yield [%][c]			
			10	**13**	**14**	**15**
1	*n*-BuOH	96	44	44 (38)		
2	*n*-Bu_2NH	94	25		59 (50)	
3	*n*-$BuNH_2$	99	17			54 (48)

[a] *Reaction conditions:* diol 5.0 mmol, MTBD 0.5 mmol, CO_2 44 g, $T = 100\,°C$, time 24 h.
[b] Based on starting diol, by GLC.
[c] GLC yield using the internal standard method (isolated yield).



Scheme 12. Formation pathway for **13**, **14** and **15**.

mate **14** corresponds to nucleophilic attack by *n*-BuOH or *n*-Bu_2NH to the carbonyl group of the initially formed cyclic carbonate **I**, with ring opening, tautomerization and dehydration (Scheme 12, path *a* and path *b*, respectively). In a similar manner, in the case of *n*-$BuNH_2$, an oxo carbamate **IV** is formed as intermediate, which then undergoes intramolecular nucleophilic attack of the nitrogen to the oxo group followed by dehydration with shift of the double bond to give cyclic carbamate **15** (Scheme 12, path *c*).

Conclusions

Effective catalytic approaches to the preparation of cyclic and linear carbonates and carbamates have been disclosed, starting from simple and commercially available propargylic alcohols and diols, using CO_2 as carboxylating agent and guanidines, such as MTBD and TBD, as catalysts. These new methods offer significant improvements for the synthesis of very important classes of compounds with respect to the existing knwowledge. Our synthetic procedure is particularly simple and environmentally friendly, does not make use of metals and is carried out in $scCO_2$ as the solvent (alternatively, in some cases, or gaseous CO_2 has been be used in CH_3CN as solvent). It allows the direct, one-pot synthesis of cyclic carbonates and carbamates or of oxo carbonates and oxo carbamates previously obtained in two steps; this also means less purification processes and waste and a higher atom economy, a very important feature both from an economical and a practical point of view.

Experimental Section

General Remarks

Solvents and chemicals were of reagent grade and were used without further purification. MeCN was dried over 3 Å molecular sieves and stored under nitrogen. All reactions were analyzed by TLC and by GC using a 30 m SE-30 capillary column. Column chromatography was performed on silica gel 60 (70–230 mesh). Melting points were measured with an Electrothermal apparatus and are uncorrected. Electron impact mass spectra [*m/z*, relative intensity (%)] were determined with a GC-MS apparatus at 70 eV ionization energy. Infrared (IR) spectra were recorded on an FT-IR 5700 spectrophotometer. Elemental analyses were performed at our analytical laboratory. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively, using the solvent as internal standard (7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR). Chemical shifts (δ) and coupling constants (*J*) are given in ppm and in Hz, respectively. The reported configurations (*E* or *Z*) were assigned on the basis of decoupling, COSY, and NOESY correlation experiments.

General Procedure for the Catalytic Synthesis of Carbonates in $scCO_2$ (Table 1 and Table 2)

The propargyl alcohol (5.0 mmol) was transferred to a 125-mL stainless steel autoclave together with the catalyst (B, 10 mol%). The autoclave was sealed, purged at room temperature several times with CO_2 with stirring (10 bar), and eventually charged with 44 g of liquid CO_2 at room temperature (by weighing it before and after the pressurization). After stirring the mixture at 100 °C for 24 h, the autoclave was cooled, degassed, and opened. The products were recovered using 15 mL of CH_2Cl_2 and then purified by column chromatography on silica gel, using hexane-acetone from 9:1 to 7:3 as eluent.

4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one **(1a):** Yield: 262 mg (41%) (Table 1, entry 2); white solid, mp 27.5–28.3 °C. IR (KBr): ν = 2988 (m), 2939 (w), 1834 (s), 1689 (s), 1374 (m), 1316 (m), 1275 (s), 1175 (s), 1087 (s), 1036 (s), 856 (s), 770 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 6H, 2CH_3), 4.28 (d, J = 3.9 Hz, 1H, =C*H*H), 4.74 (d, J = 3.9 Hz, 1H, =CH*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.1, 149.2, 84.2, 74.0, 31.0; GC-MS: *m/z* = 128 (M^+, 2), 113 (2), 84 (8), 69 (9), 56 (72), 43 (36), 42 (47), 41 (100); anal. calcd. for $C_6H_8O_3$: C 56.24, H 6.29; found: C 56.38, H 6.33.

Di-(1,1-dimethyl-2-oxopropyl) carbonate **(2a):** Yield: 328 mg (57%) (Table 1, entry 1); yellow oil. IR (film): ν = 2987 (m), 1740 (s), 1724 (s), 1674 (m), 1653 (w), 1457 (w), 1369 (w), 1305 (s), 1150 (m), 1112 (s), 920 (w) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.53 (s, 12H, 4CH_3), 2.18 (s, 6H, 2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.0, 152.6, 85.8, 23.6, 23.2; GC-MS: *m/z* = 230 (M^+, 1), 187 (14), 147 (3), 86 (25), 85 (100), 71 (12), 57 (57), 43 (72); anal. calcd. for $C_{11}H_{18}O_5$: C 57.38, H 7.88; found: C 57.51, H 7.92.

General Procedure for the Catalytic Synthesis of Carbonates with Gaseous CO_2 in CH_3CN (Table 3)

The propargylic alcohol (5.0 mmol) was transferred to a 125-mL stainless steel autoclave together with the catalyst (B, 10 mol%) and 15 mL of CH_3CN. The autoclave was sealed, purged at room temperature several times with CO_2 with stirring (10 bar), and eventually was pressurized with 40 bar of gaseous CO_2 at room temperature. After stirring of the mixture at 100 °C for 24 h, the autoclave was cooled, degassed and opened. The products were recovered using 15 mL of CH_2Cl_2 and then purified by column chromatography on silica gel, using hexane-acetone from 9:1 to 7:3 as eluent.

4-Methylene-1,3-dioxaspiro[4.5]-decan-2-one **(1c):** Yield: 470 mg (56%) (Table 3, entry 4); colourless liquid. IR (film): ν = 2940 (s), 2864 (m), 1841 (s), 1814 (s), 1685 (s), 1450 (m), 1311 (m), 1271 (m), 1201 (m), 1129 (m), 1060 (s), 1023 (s), 852 (m), 769 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.56–1.79 (m, 6H, 3CH_2), 1.97–2.02 (m, 4H, 2CH_2), 4.27 (d, J = 3.8 Hz, 1H, =C*H*H), 4.75 (d, J = 3.8 Hz, 1H, CH*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 147.0, 90.7, 79.3, 38.1, 28.4, 19.9; GC-MS: *m/z* = 168 (M^+, 1), 99 (100), 81 (64), 79 (10), 69 (3), 55 (5), 43 (5); anal. calcd. for $C_9H_{12}O_3$: C 64.27, H 7.19; found: C 64.18, H 7.17.

4-Phenyl-4-methyl-5-methylene-1,3-dioxolan-2-one **(1d):** Yield: 646 mg (68%) (Table 3, entry 6); white solid, mp 29.7–30.9 °C. IR (KBr): ν = 2985 (m), 1820 (s), 1686 (s), 1449 (w), 1297 (w), 1225 (m), 1122 (m), 1063 (m), 1022 (s), 698 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1..96 (s, 3H, CH_3), 4.45 (d, J = 4.0 Hz, 1H, =CH*H*), 4.94 (d, J = 4.0 Hz, 1H, =C*H*H), 7.25–7.50 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.5, 148.0, 144.1, 129.5, 125.4, 90.6, 87.4, 26.9; GC-MS: *m/z* = 190 (M^+, 1), 146 (15), 131 (17), 118 (100), 117 (86), 103 (45), 91 (17), 77 (40), 63 (8), 51 (26), 43 (8); anal. calcd. for $C_{11}H_{10}O_3$: C 69.46, H 5.30; found: C 69.60, H 5.35.

General Procedure for the Catalytic Synthesis of Carbonates and Carbamates in $scCO_2$ in the Presence of an External Nucleophile (Table 4 and Table 5)

The propargylic alcohol (5.0 mmol) was transferred to a 125-mL stainless steel autoclave together with the catalyst (10 mol%) and an alcohol or an amine (5.0 mmol), acting as external nucleophile. The autoclave was sealed, purged at room temperature several times with CO_2 with stirring (10 bar), and eventually charged with 44 g of liquid CO_2 at room temperature (by weighing it before and after the pressurization). After stirring of the mixture at 100 °C for 24 h, the autoclave was cooled, degassed and opened. The products were recovered using 15 mL of CH_2Cl_2 and then purified by column chromatography on silica gel, using hexane-acetone from 9:1 to 7:3 as eluent.

Methyl 2-methyl-3-oxobutan-2-yl carbonate **(6a):** Yield: 536 mg (67%) (Table 4, entry 1); colourless liquid. IR (film): ν = 2992 (s), 2960 (s), 2856 (m), 1809 (s), 1747 (s), 1725 (s), 1639 (w), 1443 (s), 1384 (s), 1368 (s), 1292 (s), 1157 (m), 1124 (m), 1028 (m), 947 (s), 860 (s), 795 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37 (s, 6H, 2CH_3), 2.03 (s, 3H, CH_3CO), 3.64 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.2, 154.2, 85.2, 54.6, 23.2, 22.9; GC-MS: *m/z* = 160 (M^+, 4), 117 (50), 85 (15), 73 (100), 59 (34), 57 (35), 43 (92), 41 (24); anal. calcd. for $C_7H_{12}O_4$: C 52.49, H 7.55; found: C 52.32, H 7.46.

3-n-Butyl-5,5-dimethyl-4-methyleneoxazolidin-2-one **(8a):** Yield: 695 mg (76%) (Table 5, entry 1); colourless

liquid. IR (film): $\nu = 2935$ (s), 2874 (m), 1816 (w), 1739 (s), 1446 (s), 1412 (s), 1273 (m), 1202 (m), 1089 (s), 1035 (w), 934 (w), 773 (m), 736 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.87$ (t, $J = 3.6$ Hz, 3H, CH_3), 1.21–1.35 (m, 2H, CH_2CH_3), 1.42 (s, 6H, CH_3), 1.47–1.57 (m, 2H, $CH_2CH_2CH_2$), 3.37 (t, $J = 7.2$ Hz, 2H, NCH_2), 3.93 (d, $J = 2.8$ Hz, 1H, =CHH), 4.02 (d, $J = 2.8$ Hz, 1H, =CHH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 155.5$, 150.8, 81.8, 79.0, 41.0, 28.2, 27.8, 19.8, 13.6; GC-MS: $m/z = 183$ (M^+, 21), 168 (15), 141 (30), 128 (73), 112 (10), 97 (58), 96 (84), 84 (41), 82 (57), 68 (28), 67 (23), 57 (35), 56 (30), 43 (29), 41 (100); anal. calcd. for $C_{10}H_{17}NO_2$: C 65.54, H 9.35; found: C 65.50, H 9.33.

General Procedure for the CO_2-Promoted Rearrangement Reaction of Propargylic Diols in $scCO_2$ (Table 6, entries 1–3 and Scheme 11)

The propargylic diol (5.0 mmol) was transferred to a 125-mL stainless steel autoclave together with a catalytic amount (10 mol%) of base (MTBD, TBD or DBU). The autoclave was sealed, purged at room temperature several times with CO_2 with stirring (10 bar), and eventually charged with 44 g of liquid CO_2 at room temperature (by weighing it before and after the pressurization). After stirring of the mixture at 100 °C for 24 h, the autoclave was cooled, degassed and opened. The products were recovered using 15 mL of CH_2Cl_2 and then purified by column chromatography on silica gel, using hexane-acetone from 9:1 to 7:3 as eluent.

General Procedure for the CO_2-Promoted Rearrangement Reaction of 2,5-Dimethylhex-3-yne-2,5-diol in MeCN (Table 6, entry 4)

The 2,5-dimethylhex-3-yne-2,5-diol (710 mg, 5.0 mmol) was transferred to a 125-mL stainless steel autoclave together with MTBD (77 mg, 0.5 mmol) and 15 mL of MeCN. The autoclave was sealed, purged at room temperature several times with CO_2 with stirring (10 bar), and eventually was pressurized with 40 bar of gaseous CO_2 at room temperature. After stirring of the mixture at 100 °C for 24 h, the autoclave was cooled, degassed and opened. The products were recovered using 15 mL of CH_2Cl_2 and then purified by column chromatography on silica gel, using hexane-acetone from 9:1 to 7:3 as eluent.

2-Hydroxy-2,5-dimethylhex-4-en-3-one **(10):** Yield: 603 mg (85%) (Table 6, entry 1); colourless oil. IR (film): $\nu = 3449$ (s), 2976 (s), 2934 (m), 1816 (w), 1678 (s), 1445 (m), 1366 (m), 1162 (m), 1104 (m), 1037 (m), 971 (m), 818 (w) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.34$ (s, 6H, 2 CH_3), 1.95 (d, $J = 1.4$ Hz, 3H, CH=C(CH_3)CH_3), 2.19 (d, $J = 1.4$ Hz, 3H, CH=C(CH_3)CH_3), 4.15 (s, br, 1H, OH), 6.23 (m, 1H, C*H*=C(CH_3)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 203.1$, 160.1, 117.4, 75.2, 28.1, 26.6, 21.2; GC-MS: $m/z = 142$ (M^+, 1), 127 (2), 114 (3), 83 (41), 69 (6), 60 (5), 59 (100), 55 (18), 43 (28), 41 (10); anal. calcd. for $C_8H_{14}O_2$: C 67.57, H 9.92; found: C 67.38, H 9.87.

General Procedure for the Reactions of 2,5-Dimethylhex-3-yne-2,5-diol with a Nucleophilic Species in $scCO_2$ (Table 7)

The 2,5-dimethylhex-3-yne-2,5-diol (710 mg, 5.0 mmol) was transferred to a 125-mL stainless steel autoclave together with the catalyst MTBD (77 mg, 0.5 mmol) and an alcohol or an amine (5.0 mmol), acting as external nucleophile. The autoclave was sealed, purged at room temperature several times with CO_2 with stirring (10 bar), and eventually charged with 44 g of liquid CO_2 at room temperature (by weighing it before and after the pressurization). After being stirred at 100 °C for 24 h, the autoclave was cooled, degassed and opened. The products were recovered using 15 mL of CH_2Cl_2 and then were purified by column chromatography on silica gel using hexane-acetone from 9:1 to 7:3.

3-n-Butyl-5,5-dimethyl-4-(2-methylallylidene)oxazolidin-2-one **(15):** Yield: 535 mg (48%) (Table 7, entry 3); yellow oil. IR (film): $\nu = 3085$ (w), 2962 (s), 2935 (s), 2874 (s), 1766 (s), 1673 (s), 1416 (s), 1208 (m), 1103 (m), 961 (m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.93$ (t, $J = 5.4$ Hz, 3H, CH_2CH_3), 1.22–1.34 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.57 (s, 6H, 2 CH_3), 1.81 (s, 3H, $CH_2=CCH_3$), 3.42 (t, $J = 5.4$ Hz, 2H, NCH_2), 4.83 (s, 1H, C=CH*H*), 4.98 (br s, 2H, C=C*H*C, C=C*H*H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.1$, 142.3, 139.3, 115.1, 101.1, 82.3, 40.6, 28.0, 27.3, 24.6, 19.6, 13.5; GC-MS: $m/z = 223$ (M^+, 30), 208 (23), 180 (16), 164 (27), 150 (18), 136 (100), 122 (20), 108 (32), 81 (25), 41(25); anal. calcd. for $C_{13}H_{21}NO_2$: C 69.92, H 9.48; found: C 70.11, H 9.54.

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