Base-catalysed direct introduction of carbon dioxide into acetylenic amines

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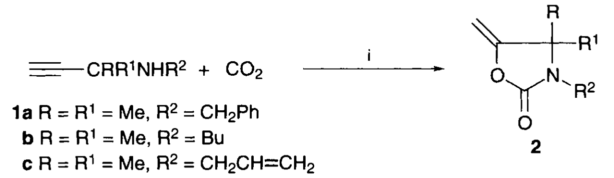
***N*-Alkylprop-2-ynylamines readily react with carbon dioxide in the presence of catalytic amounts of strong organic bases and undergo intramolecular cyclization to 5-methylene-1.3-oxazolidin-2-ones in good yields.**

Here we report the direct introduction of carbon dioxide into acetylenic amines through the formation of carbamate salts, acting catalytically in the absence of metals, based on the reaction of carbon dioxide with secondary amines to form carbamates in the presence of certain strong bases, *e.g.* 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), alkylguanidines and phosphazene bases. As the triple bond is in an appropriate position to form a lactone ring with the carbamate group, intramolecular ring closure readily occurs, Scheme 1 (R, R^1 = H, alkyl; R^2 = alkyl, allyl, benzyl; 1 bar = 10^5 Pa).

The reaction took place at room temperature and at atmospheric pressure in an aprotic polar solvent such as acetonitrile. The base can be used in catalytic amounts but has to be present in a high concentration to obtain good efficiency. Thus *N*-benzyl-*N*-(1,1-dimethylprop-2-ynyl)amine **1a** (0.415 g, 2.4 mmol) was treated with CO_2 (1 bar) in MeCN (1.2 ml) in the presence of 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) (0.036 g, 0.24 mmol) at room temperature for 24 h. Elimination of basic compounds by acid extraction gave the pure product **2a**† (0.484 g, 2.23 mmol, 93%). Only traces of the six-membered lactone resulting from ring closure on the terminal carbon of the triple bond (*N*-benzyl-3,4-dihydro-4,4-dimethyl-2*H*-1,3-oxazin-2-one) **3a**† were present. The reaction can be accelerated at higher temperature (80 °C) and pressure (5–10 bar). Thus under these conditions **1a** could be converted to **2a** in 6 h (89% yield). Using less MTBD catalyst (0.02 mol/mol substrate) a 73% yield of **2a** was obtained in 6 h at 80 °C and 10 bar of CO_2. The alkyl substituents R in the methylene group exert a favourable effect. No reaction with the unsubstituted methylene **1e** or a poor reaction with monosubstituted methylene **1d** (15% yield of **2d**) occurred at room temperature and atmospheric pressure, while 60 and 70% yields of **2e** and **2d**, respectively, were obtained at 110 °C and 10 bar of CO_2. The best yields were attained with geminal R groups; thus at 20 °C under atmospheric pressure of CO_2 **1b** and **1c** gave an 88% yield of **2b** in 6 h and 88% of **2c** in 15 h respectively. Substituents in the terminal position of the triple bond strongly decrease the yield. Thus *N*-benzyl-*N*-but-2-ynylamine in the presence of TMG (1 : 10 molar ratio with the substrate) at 140 °C and 10 bar of CO_2 for 48 h gave *N*-benzyl-5-ethylidene-1,3-oxazolidin-2-one in 18% yield. Prop-2-ynylamine did not give any oxazolidinone. No intermolecular reaction between carbamates and alkynes was observed under our conditions.



1a R = R^1 = Me, R^2 = CH_2Ph
b R = R^1 = Me, R^2 = Bu
c R = R^1 = Me, R^2 = $CH_2CH{=}CH_2$
d R = H, R^1 = Me, R^2 = Bu
e R = R^1 = H, R^2 = Me

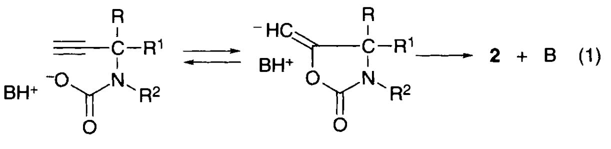
Scheme 1 *Reagents and conditions*: i, base (0.1–0.02 equiv., 0.2 mol dm^{-3}), 20 °C, 1 bar, 24 h, 75–93%

The type and strength of the base is of paramount importance to the success of the reaction. DBU, TBD, tetraalkyl- and pentaalkyl-guanidines and phosphazene bases[1] are effective. On the other side *N,N,N′,N′*-tetramethyl-1,8-naphthalendiamine (proton sponge[2]), carbodiimides and pyridine did not work; hindered amines gave very poor results.

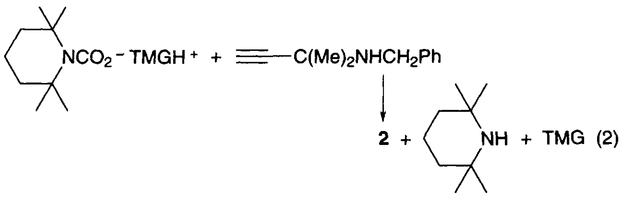
Reaction kinetics, however, do no reflect the series of the pK_A values of the superbases used. This was evidenced by carrying out the reaction at room temperature and atmospheric pressure with different bases for the same time (7 h) and under the same conditions as in the example reported above. Thus with DBU (pK_A = 24.33),[1] the conversion was 42% and the yield was 40%. These figures became 58 and 56%, respectively, with 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,2,3-diazaphosphorine (BEMP, pK_A = 27.58);[1] 20 and 18% with *N*-propyltetramethylguanidine (PTMG, pK_A = 25);[1] 13 and 12.5% with TBD (pK_A = 25.95)[1] and 90 and 89% with MTBD (pK_A = 25.44).[1] In all cases to obtain high yields and conversions at room temperature and atmospheric pressure longer times were needed than at higher temperature and pressure. For example, with DBU conversion increased from 42 to 90% and the yield increased from 40 to 86% on prolonging the reaction time to 29 h.

The introduction of carbon dioxide into organic substrates in general requires the use of metals except in special cases.[3] So far the catalytic addition of carbamates (obtained *in situ* from carbon dioxide and secondary amines) to triple bonds has been achieved with ruthenium complexes[4] at 110–120 °C and ring formation has also been obtained by intramolecular attack, starting from carbon dioxide and acetylenic amines both with ruthenium and copper complexes as catalysts.[5] Reactions leading to the introduction of carbon dioxide into amines through polar organometallics or ion pairs are well-known[6,7] but require further reaction with appropriate reagents (alkyl halides,[8] acyl halides,[9] epoxides,[7,10] vinyl ethers [11] or orthoformates[12] or palladium-activated alkenes[13]) to form the organic product. In this connection the use of tetraalkyl- or pentaalkyl-guanidines to form the corresponding guanidinium carboxylates has been recently shown to be particularly effective for stoichiometric alkylation to carbamic esters.

In our case the presence of a triple bond and an amino group which can react intramolecularly allows the catalytic incorporation of the intermediate carbamate into an oxazolidine ring in the absence of metals by reaction with the triple bond [eqn. (1), BH^+ = protonated base].

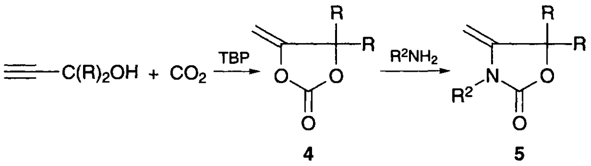


Carbon dioxide transfer to the acetylenic amine can also be effected from BH^+ carbamate of other secondary amines, *e.g.* the tetramethylguanidinium ($TMGH^+$) carbamate of tetramethylpiperidine transfers CO_2 to the acetylenic amine (in the absence of added CO_2) with formation of **2** in 83% yield at 110 °C for 24 h, [eqn. (2)].



(2)

A related reaction, involving carbon dioxide transfer to 1,1-disubstituted propynyl alcohols in the absence of metals [eqn. (3)] has been reported to occur under the catalytic action of tributylphosphine[15] (TBP). The cyclic carbonate thus formed **4** is converted into an isomer of **2** (compound **5**) by reaction with a primary amine [eqn. (3)]. The TBP-catalysed reaction,



(3)

however, does not occur with aminopropynes as in our case. By contrast the reaction described in the present paper can be extended to propynyl alcohols containing two R groups (unsubstituted propynyl alcohol is unreactive) to form cyclic carbonates as in eqn.(3). Here the reaction of 3-methylbut-1-yn-3-ol (0.983 g, 11.7 mmol) with CO_2 (20 bar) in the presence of MTBD (0.358 g, 2.34 mmol) in MeCN (23 ml) at 80 °C for 20 h leads to product **4** (2.10 g, 1.64 mmol) in 70% yield and 90% conversion.

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Footnote

† *Selected data* for: **2a** (white solid, mp 71 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 6 H, 2Me), 4.06 (d, 1 H, *J* 3.3 Hz, =CH), 4.25 (s, 2 H, CH_2), 4.43 (d, 1 H, *J* 3.3 Hz, =CH) and 7.04–7.18 (m, 5 H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.43 (2 Me), 43.93 (CH_2), 61.43 (qC), 83.99 (=CH_2), 127.59, 127.62, 128.53 (5 =CH), 131.90 (qC), 137.49 (qC) and 160.68 (CO); *m/z*: 217 (M^+, 5), 202 (16), 132 (6), 91 (100) and 65 (3); IR ν/cm^{-1} (KBr): 2910 (w), 1778 (s), 1667 (s), 1436 (m), 1410 (s), 1327 (m), 1210 (m), 1058 (s), 989 (m), 755 (m) and 702 (m). For **3a** (colourless oil); ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 6 H, 2 Me), 4.57 (s, 2 H, CH_2), 4.91 (d, 1 H, *J* 6.1 Hz, =CH), 6.27 (d, 1 H, *J* 6.1 Hz, =CH), 7.12–7.18 (m, 1 H, =CH) and 7.22–7.24 (m, 4 H, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.80 (2 Me), 46.59 (CH_2), 57.09 (qC), 111.53 (=CH), 126.58, 126.80, 128.31 (5 =CH), 136.52 (=CH), 138.51 (qC) and 151.25 (CO); *m/z*: 217 (M^+, 16), 202 (34), 133 (10), 91 (100), 85 (32) and 65 (8); IR ν/cm^{-1} (film): 2939 (w), 1704 (s), 1692 (s), 1653 (m), 1499 (m), 1434 (m), 1408 (m), 1357 (m), 1298 (m), 1242 (m), 1194 (m), 1065 (m), 1034 (m), 749 (m) and 699 (m). Elemental analyses were satisfactory for all compounds.

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