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Regioselective Re(I)-catalyzed coupling of terminal alkynes, Et_2NH, and CO_2 leading to anti-Markovnikov adducts

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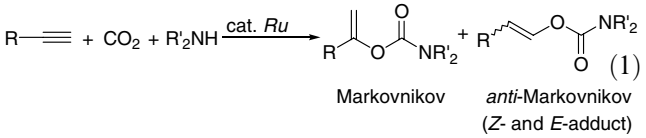
Abstract—$ReBr(CO)_5$-catalyzed addition of Et_2NH and CO_2 to terminal alkynes afforded anti-Markovnikov adducts of alkenyl carbamates in good to excellent yield and high regioselectivity.

Transition-metal-catalyzed transformation of carbon dioxide into organic substrates is an important and challenging research work in CO_2 chemistry.[1] Recently, we have reported that Re(I) complexes efficiently catalyze the coupling of CO_2 with epoxides to afford cyclic carbonates,[2] and the addition of carboxylic acids (O–H bond) to terminal alkynes giving alkenyl esters.[3] These results indicate that Re(I) is an efficient catalyst in the activation of CO_2 and O–H bond of carboxylic acid.

The synthesis of alkenyl carbamates through three-components addition of terminal alkynes, secondary amines, and CO_2, catalyzed by ruthenium complexes has been investigated in detail by Dixneuf's group and others.[4] However, in most cases, the addition reactions afforded three adducts (Eq. 1), and both yield and selectivity remain yet to be improved. Therefore, the catalytic activity of $ReBr(CO)_5$ has to be examined in the reaction of terminal alkynes with Et_2NH and CO_2. In this letter, we report a $ReBr(CO)_5$-catalyzed three-component addition, which has given anti-Markovnikov adducts in good to high yield (Eq. 2) regioselectively.



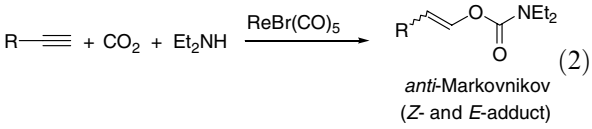


Table 1 summarize the results of $ReBr(CO)_5$-catalyzed reaction of terminal alkynes, Et_2NH, and CO_2.[5,6] The reactions were performed in a 25-mL autoclave using 2.0 mmol of alkynes, 2.5 mmol of Et_2NH, and 0.02 mmol of $ReBr(CO)_5$. CO_2 (5.0 MPa) was pressurized under atmosphere at ambient temperature. The addition reaction of phenylacetylene in *n*-heptane at 110 °C for 24 h resulted in the formation of the anti-Markovnikov addition product **2a** in 82% GC yield with a *Z* to *E* ratio of 89:11 (entry 1). In this case, only a trace amount (<1%) of the Markovnikov addition product was detectable by GC. In addition, the yield of **2a** depended on the pressure of CO_2. A low pressure of CO_2 led to a substantial decrease of yield (e.g., 4.0 MPa, 55%; 2.0 MPa, 16%). Other aromatic alkynes such as *p*-methylphenylacetylene and *p*-ethoxyphenylacetylene showed similar reactivity as phenylacetylene, which afforded the corresponding anti-Markovnikov adducts **2b** and **2c** with a majority of *Z*-adduct (entries 2 and 3).

Aliphatic alkynes also proceeded via such addition reactions to give anti-Markovnikov addition products, but in most cases with a significantly lower stereoselectivity of *Z*-adduct. The addition of 1-octyne required a prolonged reaction time to give the satisfactory yield of adducts **2d**, and the ratio of *Z*-**2d** and *E*-**2d** was

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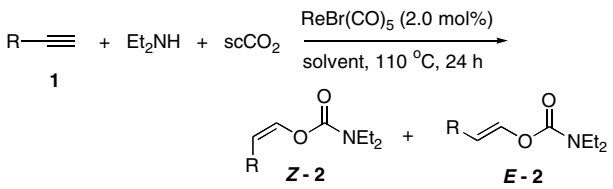
Table 1. $Re(CO)_5Br$-catalyzed three-component addition of alkyne, Et_2NH, and CO_2[a]



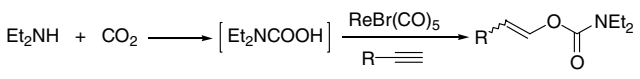
Entry	R	Solvent	Yield of **2** (%)[b]		*Z*:*E*[c]
1	Ph	*n*-Heptane	**2a**	82(71)	89:11
2	*p*-$CH_3C_6H_4$	*n*-Heptane	**2b**	83(73)	85:15
3	*p*-$C_2H_5OC_6H_4$	*n*-Heptane	**2c**	90(82)	86:14
4	*n*-C_6H_{13}	*n*-Heptane	**2d**	62	52:48
5[d]	*n*-C_6H_{13}	*n*-Heptane	**2d**	98(89)	52:48
6	$NC(CH_2)_3$	*n*-Heptane	**2e**	54	60:40
7	$NC(CH_2)_3$	Toluene	**2e**	84(53)	62:38
8	$Cl(CH_2)_3$	*n*-Heptane	**2f**	69(54)	58:42
9	*t*-C_4H_9	*n*-Heptane	**2g**	57(50)	95:5
10	$(CH_3)_2C(OH)$	Toluene	**2h**	95(83)	85:15

[a] Reactions were carried out at 110 °C for 24 h by using 2.0 mmol of **1**, 3.0 mmol of Et_2NH, and 0.04 mmol of $Re(CO)_5Br$ in a 25-mL autoclave under the initial CO_2 pressure of 5.0 MPa.
[b] Determined by GC based on **1** used. Numbers in parentheses are isolated yield.
[c] By GC of the reaction mixture.
[d] For 35 h.

52:48 (entries 4 and 5). 5-Hexynenitrile occurred the addition reaction in *n*-heptane to produce the adducts **2e** in 54% GC yield, while in toluene, the yield was increased to 84% (entries 6 and 7). In *n*-heptane, the addition reactions of 5-chloro-1-pentyne and 3,3-dimethyl-1-butyne afforded the anti-Markovnikov addition products **2f** and **2g** in 69% and 57% GC yields, respectively (entries 8 and 9). In the latter case, the high *Z* to *E* ratio (95:5) might owe to the existence of a bulky *t*-Bu group in alkyne. Similarly, in the case of 3-hydroxy-3-methyl-1-butyne used, the addition reaction produced *Z*-adduct in a good selectivity (entry 10).

It is noteworthy that under the same reaction conditions, the addition reactions did not occur with internal alkynes (e.g., 4-octyne, diphenyl acetylene). Internal alkynes were recovered completely.

In the ruthenium-catalyzed addition reactions of secondary amine and CO_2 to terminal alkyne, the vinylidene–ruthenium intermediate [Ru=C=CHR], which was formed by the reaction of ruthenium complex with terminal alkyne was postulated as the activated catalytic species.[7] On the basis of our previous work[3] and the known reaction behavior of carbon dioxide with secondary amine furnishing carbamic acid,[8] we propose the present catalytic formation of alkenyl carbamates involving firstly the formation of carbamic acid, then a subsequent addition of carbamic acid to alkynes as shown in Scheme 1.



Scheme 1. Reaction pathway via carbamic acid.

In summary, $ReBr(CO)_5$ has shown to be an efficient transition-metal catalyst to catalyze the synthesis of alkenyl carbamates via three-component addition of Et_2NH and CO_2 to terminal alkynes. The specific feature of present catalytic reaction is the high regioselectivity giving the anti-Markovnikov adducts in good to excellent yield.

Acknowledgments

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5. A typical experiment for the synthesis of Styryl *N*,*N*-diethylcarbamate **2a** (Table 1, entry 1): In a 25 mL stainless steel autoclave equipped with a magnetic stirring bar, phenyl acetylene **1a** (2.0 mmol), Et_2NH (2.5 mmol),

$ReBr(CO)_5$ (0.02 mmol), and *n*-heptane (1.0 mL) were placed under air atmosphere. CO_2 was then charged up to 5.0 MPa at ambient temperature. The mixture was heated to 110 °C in oil bath, and stirred for 24 h. After cooling, the gas was purged. The reaction mixture was diluted with toluene to 2.0 mL and mesitylene (25.8 mg) was added as internal standard. The analysis of the resulting mixture by GC revealed that **2a** (*Z*:*E* = 89:11) was formed in 85% yield. After removal of the volatiles under vacuum, the residue was purified by column chromatography (silica gel, eluted with 5% diethyl ether/hexane) to afford **2a** as colorless as oil in 71%.

6. All products **2** were isolated and gave satisfactory spectral and/or analytical data as reported below.
   Styryl *N*,*N*-diethylcarbamate **2a** (known compounds): *Z*-**2a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, 1H, $J = 7.2$ Hz), 7.28–7.20 (m, 5H), 5.53 (d, 1H, $J = 7.2$ Hz), 3.28 (q, 4H, $J = 7.2$ Hz), 1.11 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 152.7, 135.5, 128.5, 128.2, 126.7, 125.9, 109.4, 42.3, 41.7, 14.0, 13.2; GCMS *m*/*z* (% rel. inten.) 219(M^+, 16), 147(1), 119(2), 100(100), 91(32), 77(7). *E*-**2a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, 1H, $J = 12.7$ Hz), 7.20–7.10 (m, 5H), 6.20 (d, 1H, $J = 12.7$ Hz), 3.33 (q, 4H, $J = 7.2$ Hz), 1.14 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 153.2, 138.0, 134.6, 128.5, 128.2, 126.7, 112.5, 42.3, 41.7, 14.0, 13.2; GCMS *m*/*z* (% rel. inten.) 219(M^+, 15), 119(12), 118(1.5), 100(100), 91(25), 77(5).
   2-*p*-Tolylvinyl *N*,*N*-diethylcarbamate **2b**: *Z*-**2b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, 2H, $J = 7.9$ Hz), 7.16 (d, 1H, $J = 7.2$ Hz), 7.05 (d, 2H, $J = 7.9$ Hz), 5.50 (d, 1H, $J = 7.2$ Hz), 3.29 (q, 4H, $J = 7.2$ Hz), 2.26 (s, 3H), 1.13 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 152.8, 134.9, 129.3, 128.9, 128.4, 125.8, 109.3, 42.2, 41.7, 21.1, 14.0, 13.3; GCMS *m*/*z* (% rel. inten.) 233(M^+, 7), 115(6), 105(21), 100(100), 91(6), 79(9), 44(52); HRMS calcd for $C_{14}H_{19}NO_2$ 233.1416, found 233.1416. *E*-**2b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, 1H, $J = 12.7$ Hz), 6.19 (d, 1H, $J = 12.7$ Hz), 3.33 (q, 4H, $J = 7.2$ Hz), 2.24 (s, 3H), 1.14 (t, 6H, $J = 7.2$ Hz), signals of aromatic ring overlap with those of *Z*-isomer; GCMS *m*/*z* (% rel. inten.) 233(M^+, 10), 115(6), 105(20), 100(100), 91(5), 79(6), 77(13), 44(26).
   2-(4-Ethoxyphenyl)vinyl *N*,*N*-diethylcarbamate **2c**: *Z*-**2c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, 2H, $J = 8.7$ Hz), 7.18 (d, 1H, $J = 7.2$ Hz), 6.84 (d, 2H, $J = 8.7$ Hz), 5.54 (d, 1H, $J = 7.2$ Hz), 4.02 (q, 2H, $J = 6.9$ Hz), 3.37 (q, 4H, $J = 7.2$ Hz), 1.40 (t, 3H, $J = 6.9$ Hz), 1.18 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.6, 152.8, 133.9, 129.7, 127.1, 114.1, 109.0, 63.3, 42.2, 41.6, 14.8, 14.0, 13.2; GCMS *m*/*z* (% rel. inten.) 263(M^+, 33), 107(49), 101(16), 100(100), 91(7), 77(20); HRMS calcd for $C_{15}H_{21}NO_3$ 263.1520, found 263.1521. *E*-**2c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, 1H, $J = 12.7$ Hz), 6.25 (d, 1H, $J = 12.7$ Hz), 4.02 (q, 2H, $J = 6.9$ Hz), 3.42 (q, 4H, $J = 7.2$ Hz), 1.40 (t, 3H, $J = 6.9$ Hz), 1.23 (t, 6H, $J = 7.2$ Hz), signals of aromatic ring overlap with those of *Z*-isomer; GCMS *m*/*z* (% rel. inten.) 263(M^+, 13), 107(27), 101(6), 100(100), 91(4), 77(11).
   1-Octenyl *N*,*N*-diethylcarbamate **2d**: *Z*-**2d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (d, 1H, $J = 7.5$ Hz), 4.67 (dt, 1H, $J = 7.5$, 6.5 Hz), other signals overlap with those of *E*-isomer; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 153.6, 135.3, 112.5, other signals can not be assigned from the *Z*/*E* mixture's ^{13}C NMR data; GCMS *m*/*z* (% rel. inten.) 227(M^+, 2), 100(100), 72(43), 57(6), 44(15); HRMS calcd for $C_{13}H_{25}NO_2$ 227.1889, found 227.1885. *E*-**2d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (d, 1H, $J = 12.4$ Hz), 5.23 (dt, 1H, $J = 12.4$, 6.5 Hz), other signals overlap with those of *Z*-isomer; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 153.5, 136.7, 111.5; GCMS *m*/*z* (% rel. inten.) 227(M^+, 2), 100(100), 72(41), 57(5), 44(15).
   5-Cyano-1-pentenyl *N*,*N*-diethylcarbamate **2e**: *Z*-**2e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, 1H, $J = 7.0$ Hz), 4.66 (dt, 1H, $J = 7.0$, 6.5 Hz), 3.32 (q, 4H, $J = 7.2$ Hz), 2.40–2.24 (m, 4H), 1.76–1.70 (m, 2H), 1.15 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 152.9, 137.1, 119.5, 108.1, 42.1, 41.6, 25.0, 23.3, 16.4, 14.1, 13.3; GCMS *m*/*z* (% rel. inten.) 210(M^+, 2), 82(3), 100(100), 72(74), 57(5), 44(40); HRMS calcd for $C_{11}H_{18}N_2O_2$ 210.1372, found 210.1368. *E*-**2e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, 1H, $J = 12.4$ Hz), 5.20 (dt, 1H, $J = 12.4$, 6.5 Hz), 3.28 (q, 4H, $J = 7.2$ Hz), 2.32 (t, 2H, $J = 7.2$ Hz), 2.14 (td, 2H, $J = 7.2$, 6.5 Hz), 1.76–1.70 (m, 2H), 1.19 (t,6H, $J = 7.2$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 153.1, 138.2, 119.4, 109.4, 42.0, 41.4, 26.2, 25.5, 16.3, 14.1, 13.3; GCMS *m*/*z* (% rel. inten.) 210(M^+, 2), 100(86), 72(69), 57(6), 44(40), 29(100).
   3-Chloro-1-pentenyl *N*,*N*-diethylcarbamate **2f**: *Z*-**2f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (d, 1H, $J = 6.8$ Hz), 4.68 (dt, 1H, $J = 6.8$, 6.5 Hz), 3.50 (t, 2H, $J = 6.5$ Hz), 3.30 (q, 4H, $J = 7.2$ Hz), 2.27 (td, 2H, $J = 7.2$, 6.5 Hz), 1.85–1.80 (m, 2H), 1.12 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 153.0, 136.5, 109.1, 44.4, 42.1, 41.6, 32.0, 21.7, 14.1, 13.3; GCMS *m*/*z* (% rel. inten.) 219(M^+, 2), 100(68), 72(51); 57(8), 44(34), 29(100); HRMS calcd for $C_{10}H_{18}ClNO_2$ 219.1030, found 219.1026. *E*-**2f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (d, 1H, $J = 12.4$ Hz), 5.24 (dt, 1H, $J = 12.4$, 6.5 Hz), 3.50 (t, 2H, $J = 6.5$ Hz), 3.30 (q, 4H, $J = 7.2$ Hz), 2.14 (td, 2H, $J = 7.2$, 6.5 Hz), 1.88–1.84 (m, 2H), 1.14 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 153.3, 137.7, 110.2, 44.1, 42.0, 41.4, 32.4, 24.5, 14.1, 13.3; GCMS *m*/*z* (% rel. inten.) 219(M^+, 1), 100(44), 72(37); 57(5), 44(23), 29(100).
   3,3-Dimethyl-1-butenyl *N*,*N*-diethylcarbamate **2g**, *Z*-**2g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 (d, 1H, $J = 7.2$ Hz), 4.54 (d, 1H, $J = 7.2$ Hz), 3.27 (q, 4H, $J = 7.2$ Hz), 1.10 (t, 6H, $J = 7.2$ Hz), 1.08 (s, 9H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 153.2, 133.2, 120.3, 42.0, 41.4, 31.5, 30.5(3C), 14.1, 13.3; GCMS *m*/*z* (% rel. inten.) 199(M^+, 2), 100(85), 83(6); 72(57); 57(4), 44(33), 29(100); HRMS calcd for $C_{11}H_{21}NO_2$ 199.1572, found 199.1572.
   3-Hydroxy-3-methyl-1-butenyl *N*,*N*-diethylcarbamate **2h**, *Z*-**2h**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (d, 1H, $J = 7.2$ Hz), 4.84 (d, 1H, $J = 7.2$ Hz), 3.26 (q, 4H, $J = 7.2$ Hz), 1.86 (s, 1H), 1.37 (s, 6H), 1.09 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 153.3, 133.8, 118.2, 70.0, 42.2, 41.5, 30.3(2C), 14.1, 13.2; GCMS *m*/*z* (% rel. inten.) 201(M^+, 0.5), 158(22), 116(13), 100(100), 85(3), 72(61), 57(15), 44(22); HRMS calcd for $C_{10}H_{19}NO_3$ 201.1364, found 201.1365. *E*-**2h**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, 1H, $J = 12.7$ Hz), 5.45 (d, 1H, $J = 12.7$ Hz), 3.24 (q, 4H, $J = 7.2$ Hz), 2.27 (s, 1H), 1.30 (s, 6H), 1.07 (t, 6H, $J = 7.2$ Hz); GCMS *m*/*z* (% rel. inten.) 201(M^+, 0.5), 100(100), 72(72), 57(15), 44(23).
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