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Catalytic methoxycarbonylation of alkoxyallenes

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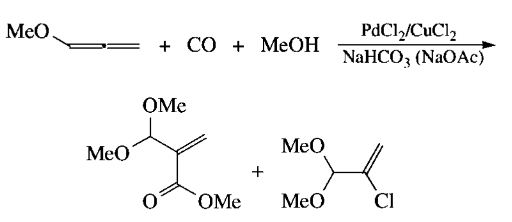
Methoxyallene reacts with carbon monoxide in the $PdCl_2$–$CuCl_2$–$NaHCO_3$ ($NaHCO_3$/NaOAc) system in MeOH to afford methyl 2-(dimethoxymethyl)acrylate and 2-chloro-3,3-dimethoxyprop-1-ene; the third product, 2-chloro-1-methoxy-2-propenyl acetate, appears when $NaHCO_3$–NaOAc is used as a buffer component.

Alkoxyallenes, which are readily available through the superbase-catalysed izomerization of propargyl ethers,[1,2] are used as versatile intermediates and building blocks in organic synthesis.[2]

Although their catalytic carbonylation may offer straightforward routes to new functionalised unsaturated compounds, this opportunity remains unexplored. This is also true for allenes. Recently,[3] we reported the reaction of allenes with carbon monoxide in the $PdCl_2$–$CuCl_2$–NaOAc ($NaHCO_3$)–MeOH system affording methyl 2-(chloromethyl)acrylate and (or) methyl 2-(methoxymethyl)acrylate.[3(b)] However, alkoxy groups adjacent to the allene system are known to drastically change its reactivity as compared to allenes.[2] Therefore, these results cannot be simply transferred to alkoxyallenes.

Here, we briefly report on the methoxycarbonylation of methoxyallene in the above catalytic system.



1 **2**

Scheme 1

Under conditions close to those for allene methoxycarbonylation,[3(b)] but at a higher temperature (–5 to 25 °C) (Table 1), methoxyallene reacts with carbon monoxide and methanol to form two products in a ratio of 1:2.8–7.3 (GLC).† The minor product, methyl 2-(dimethoxymethyl)acrylate **1**, is the product of methoxycarbonylation. Unexpectedly, the major product is 2-chloro-3,3-dimethoxyprop-1-ene **2**, which is formed without the participation of carbon monoxide (^{1}H and ^{13}C NMR and IR spectroscopy and mass spectrometry).‡

The total yield of the above products varied from 29 to 55% depending on the reaction conditions (Table 1).

A conceivable catalytic cycle leading to **1** starts with the methoxycarbonylpalladium chloride[4] attack on the central allenic carbon to give intermediate **A**, which eliminates Pd^0, thus transforming to methyl 2-[chloro(methoxy)methyl]acrylate **B** (a similar product was detected in the allene methoxycarbonylation[3(b)]) and finally to **1** (Scheme 2).

Table 1 Methoxycarbonylation of methoxyallene [$MeOCH=C=CH_2$ (20 mmol), $PdCl_2$ (0.6 mmol), $CuCl_2$ (70 mmol), $NaHCO_3$ (70 mmol), MeOH (200 ml)].[3(a)]

Entry	T/°C	t/h	Yield (%)[a]	
			1	**2**
1	–5 to 20–22	2	11	44
2	–5 to –10	2	6	44
3	10–13	2	5	24
4	25	2	8	38
5[b]	10–13	5	8	22
6[c]	–5 to 20–22	1		60
7[d]	–5 to 20–22	1		63

[a]GLC, based on methoxyallene. [b]35 mmol of $NaHCO_3$ and 35 mmol of NaOAc (instead of $NaHCO_3$), the reaction mixture contained 29% 2-chloro-1-methoxy-2-propenyl acetate **3** (yield 16%). [c]Without CO.‡ [d]Without CO and $PdCl_2$.§

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† Reaction mixtures were analysed on an LKhM-80 chromatograph with a katharometer as a detector on a column (3000×3 mm) packed with 15% Carbowax 20M on Chromaton N-AW-HMDS (0.25–0.315). Products were isolated on a PAKhV-07 GL preparative chromatograph [katharometer; helium; 75 °C; column, 5000×10 mm, packed with 15% polyphenyl ether on Chromaton N-AW-HMDS (0.2–0.25 mm)].

IR spectra were recorded on Specord IR-75 and Bruker IFS-25 spectrometers in microlayers. ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.69 MHz) spectra were measured on a Bruker DPX-400 instrument in $CDCl_3$; HMDS was an internal standard. MS-GLC spectra were measured on a HP5971/HP5890 spectrometer with temperature programming from 70 to 280 °C at a heating rate of 20 K min^{-1} (electron energy of 70 eV; PET-5 capillary column, 30 m). Methoxyallene was prepared by a technique described elsewhere.[1(d),(e)]

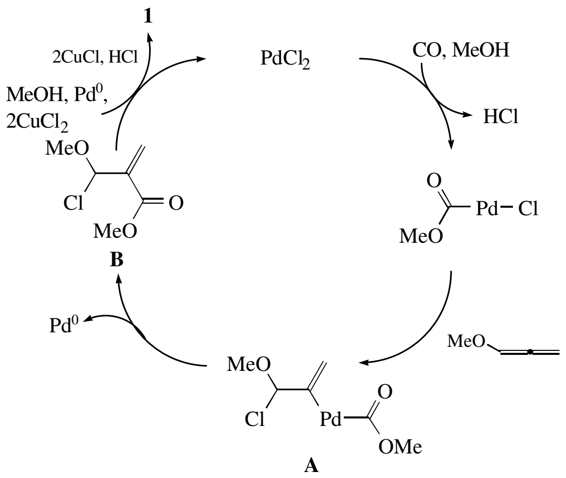
Typical procedure. 200 ml of methanol was placed in a four-neck flask equipped with a stirrer, a thermometer, a dropping funnel, a reflux condenser connected with a coil trap (–30 °C) and a bubbler (for carbon monoxide introduction), and saturated with carbon monoxide (~1.5 dm^3 h^{-1}) at 20–22 °C for 30 min and at 0 °C for 1 h. Under continuous CO bubbling, $CuCl_2$ (9.38 g, 70 mmol), $NaHCO_3$ (5.88 g, 70 mmol) and $PdCl_2$ (0.106 g, 0.6 mmol) were placed in the flask. The mixture was cooled to –5 °C, and cooled methoxyallene (1.40 g, 20 mmol) was added. After slowly heating the mixture to room temperature for 2 h with CO feeding, the mixture was diluted with cold water (1:1) and extracted with diethyl ether (5×150 ml). The extracts were washed with water (5×25 ml) and dried over K_2CO_3. The solvent was removed, and 1.57 g of a liquid consisting of acrylate **1** (0.34 g, 11%), chlorodimethoxypropene **2** (1.13 g, 44%) and 0.08 g of methoxyallene (94% conversion) was obtained (GLC) (Table 1, entry 1).

Analogously, 1.75 g of a raw product was obtained at 10–13 °C for 5 h in the presence of $CuCl_2$ (9.38 g, 70 mmol), $NaHCO_3$ (2.94 g, 35 mmol), NaOAc (2.87 g, 35 mmol) and $PdCl_2$ (0.106 g, 0.6 mmol). The product contained (GLC) acrylate **1** (0.27 g, 8%), chlorodimethoxypropene **2** (0.61 g, 22%) and 2-chloro-1-methoxy-2-propenyl acetate **3** (0.51 g, 16%) (Table 1, entry 5).

1: ^{1}H NMR ($CDCl_3$) δ: 6.35, 6.01 (2d, 1H, $=CH_2$, $^2J_{HH}$ 1.5 Hz), 5.17 (s, 1H, CH), 3.76 (s, 3H, OMe), 3.33 (s, 6H, OMe). ^{13}C NMR ($CDCl_3$) δ: 165.93 (C=O), 136.93 ($CH_2=C$), 127.23 ($=CH_2$), 99.54 (CH), 53.56 (OMe), 51.89 [C(O)O*Me*]. IR (neat, ν/cm^{-1}): 3119, 2967, 2933, 2834, 1729, 1666, 1637, 1443, 1377, 1299, 1281, 1193, 1106, 988, 905, 819, 763, 705, 678, 654, 546. MS, *m/z* (%): 159 (3), 145 $[M - Me]^+$ (64), 130 $[M - 2Me]^+$ (13), 129 $[M - OMe]^+$ (99), 113 (51), 83 (17), 75 (100), 70 (11), 69 (18), 59 (20), 55 (26), 53 (15), 47 (28), 42 (10), 39 (24), 31 (23). Found (%): C, 52.43; H, 7.92. Calc. for $C_7H_{12}O_4$ (%): C, 52.48; H, 7.56.

2: ^{1}H NMR ($CDCl_3$) δ: 5.69, 5.55 (2d, 1H, $=CH_2$, $^2J_{HH}$ 1.5 Hz), 4.80 (s, 1H, CH), 3.26 (s, 6H, OMe). ^{13}C NMR ($CDCl_3$) δ: 136.89 ($CH_2=C$), 116.34 ($=CH_2$), 101.95 [*C*$(OMe)_2$], 53.15 (OMe). IR (neat, ν/cm^{-1}): 3120, 2995, 2955, 2940, 2910, 2835, 1640, 1470, 1450, 1370, 1215, 1190, 1150, 1110, 1060, 990, 910, 770, 710, 685, 660, 550. MS, *m/z* (%): 136 $[M]^+$ (0.2), 107 $[M + 2 - OMe]^+$ (21), 105 $[M - OMe]^+$ (65), 101 $[M - Cl]^+$ (11), 75 (100), 61 (15), 55 (23), 53 (10), 47 (20), 41 (20), 39 (27), 31 (21). Found (%): C, 44.08; H, 6.73; Cl, 25.73. Calc. for $C_5H_9ClO_2$ (%): C, 43.94; H, 6.65; Cl, 25.98.

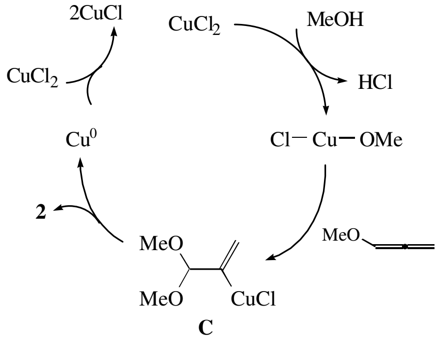
3: ^{1}H NMR ($CDCl_3$) δ: 6.08 (s, 1H, CH), 5.69, 5.49 (2d, 1H, $=CH_2$, $^2J_{HH}$ 1.5 Hz), 3.48 (s, 3H, OMe), 2.15 (s, 3H, Me). ^{13}C NMR ($CDCl_3$) δ: 186.62 (C=O), 133.09 ($CH_2=C$), 116.31 ($=CH_2$), 101.92 (CH), 33.07 (OMe), 16.35 (Me). IR (neat, ν/cm^{-1}): 3122, 2982, 2934, 2901, 1744, 1713, 1669, 1638, 1479, 1373, 1294, 1234, 1178, 1109, 1012, 989, 963, 914, 743, 686, 628, 602, 584, 530, 480, 464. MS, *m/z* (%): 129 $[M - Cl]^+$ (31), 122 $[M + 1 - COMe]^+$ (12), 121 $[M - COMe]^+$ (6), 107 $[M + 2 - OCOMe]^+$ (22), 105 $[M - OCOMe]^+$ (67), 89 (16), 61 (16), 55 (11), 43 (100), 39 (10). Found (%): C, 46.76; H, 6.48; Cl, 18.52 (purity 83%). Calc. for $C_6H_9ClO_3$ (%): C, 43.78; H, 5.51; Cl, 21.54.



Scheme 2

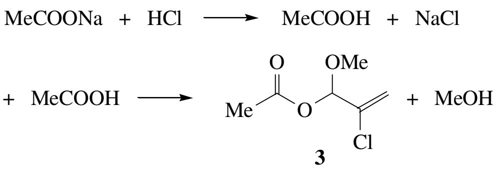
The formation of 2-chloro-3,3-dimethoxyprop-1-ene **2** is assumed to follow Scheme 3, where methoxycopper chloride attacks methoxyallene to afford intermediate **C**, which further affords **2** as a result of the Cu^0 reductive elimination, thus indicating a higher reactivity of methoxyallene towards the non-palladium components of the catalytic system.

Indeed, without CO, chlorodimethoxypropene **2** is formed in 60% yield (Table 1, entry 6)[‡] and without CO and PdCl$_2$ (Table 1, entry 7)[§] the yield of **2** is 63% thus being consistent with Scheme 3.



Scheme 3

The use of an equimolar NaHCO$_3$/NaOAc mixture as a buffer (Table 1, entry 5) did not influence the yields of acrylate **1** and chlorodimethoxypropene **2**. However, a new product, 2-chloro-1-methoxy-2-propenyl acetate **3** was detected in the reaction mixture (IR, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry; yield, 16%; concentration in the mixture, 29%).[†] The formation of **3** likely results from exchange of the methoxy group of chlorodimethoxypropene **2** for the acetoxy group (Scheme 4).



Scheme 4

Thus, the above reactions contribute to a better undestanding of the alkoxyallene reactivity towards transition metals. After an optimization, these reactions may become facile straightforward sources of products **1**–**3** and their homologues, which are potent building blocks for fine organic synthesis.

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[‡] Methanol (200 ml) was placed in a flask and cooled to –5 °C. Then, CuCl$_2$ (9.38 g, 70 mmol), NaHCO$_3$ (5.88 g, 70 mmol), PdCl$_2$ (0.106 g, 0.6 mmol) and methoxyallene (1.40 g, 20 mmol) were added. After stirring for 1 h at –5 °C and slowly heating to room temperature, the mixture in the flask was diluted with cold water (1:1) and extracted with diethyl ether (5×150 ml). The extracts were washed with water (5×25 ml) and dried over K$_2$CO$_3$. The solvent was carefully removed, and the residue contained 1.36 g (GLC) of **2** and 0.24 g of methoxyallene (yield of **2** 60%, the methoxyallene conversion 83%). By distillation of the residue in a vacuum, 0.97 g (43%) of **2** was isolated, bp 57–58 °C (50 Torr), n_D^{20} 1.4285 (Table 1, entry 6).

[§] Under the above conditions with the same charges and PdCl$_2$ excluded the residue contained 1.52 g of **2** and 0.15 g of methoxyallene (63% yield, 89% conversion) was obtained. The vacuum distillation gave 1.00 g of **2** (41%) (Table 1, entry 7).