

CHEMISTRY

## Oxidative Methoxycarbonylation of Allene in the Presence of a Copper–Palladium Catalyst

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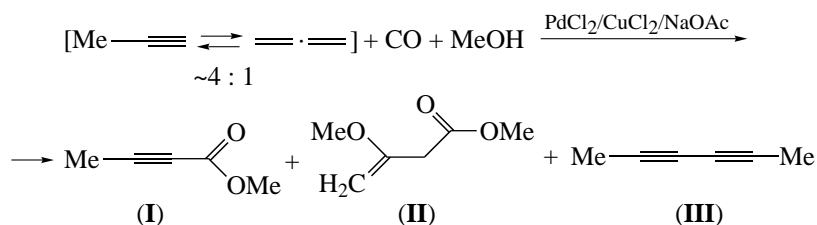
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Methoxycarbonylation of acetylene compounds on treatment with carbon monoxide in methanol in the presence of the PdCl<sub>2</sub>–CuCl<sub>2</sub>–NaOAc catalytic system has been studied in detail [1–11] and considered in reviews [12, 13]. These studies resulted in the development of a convenient method for the synthesis of methyl acetylenecarboxylates. However, no data on the direct catalyzed carbonylation of propyne or its isomer, allene, can be found in the literature.

Meanwhile, propyne is the second most readily available alkyne after acetylene, because a propyne–allene mixture is a large-scale product of the acetylene production by pyrolysis [14]. Therefore, direct synthesis of methyl 2-butynoate (**I**) from propyne, carbon monoxide, and methanol could be useful for fine organic synthesis, as regards providing it with reagents. For example, it is known that methyl 2-butynoate (**I**) was prepared [15] from 1,3-dichloro-2-butene by a

multistep procedure including consecutive alkaline hydrolysis, dehydrochlorination, oxidation, and esterification. In addition, in the presence of various catalysts, propyne readily isomerizes to allene to give a 4 : 1 equilibrium mixture (propyne is the major component). Study of methoxycarbonylation of propyne or the equilibrium propyne–allene mixture could provide important information concerning the behavior of allene in this reaction.

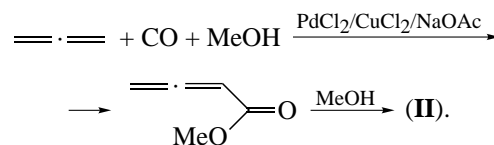
Our experiments showed that direct methoxycarbonylation of a propyne–allene mixture with carbon monoxide in methanol catalyzed by the PdCl<sub>2</sub>–CuCl<sub>2</sub>–NaOAc system (the molar ratio methanol : propyne–allene : PdCl<sub>2</sub> : CuCl<sub>2</sub> : NaOAc = 5000 : 125 : 0.6 : 70 : 70) gives, apart from the expected methyl 2-butynoate (**I**) (yield 7–10%), methyl 3-methoxy-3-butenolate (**II**) (yield 9–13%), and hexa-2,4-diyne (**III**) (yield 5–8%). The reaction was performed at 0 to 10°C for 3 h.



Scheme 1.

Since no isomerization of acetylenecarboxylates into the corresponding allenecarboxylates was observed previously in the methoxycarbonylation of alkynes under the same conditions [10, 11], it can be concluded that compound **II** is formed from allene. The methoxycarbonylation of allene does not stop at the step of formation of methyl 2,3-butadienoate (**IV**) but proceeds as the addition of methanol to this product,

giving rise to compound **II**.



Scheme 2.

Diacetylene (**III**) is the product of oxidative dimerization of methylacetylene on treatment with CuCl<sub>2</sub>:



A fundamental result of this study is the established fact that allene undergoes methoxycarbonylation in the

presence of a copper–palladium catalytic system to give an important synthon (**II**), which opens up the real prospects for the wide use of this product and for the extension of this new reaction to substituted allenes.

## EXPERIMENTAL

IR spectra were recorded as microlayers and KBr pellets on Specord IR-75 and Bruker JFS-25 spectrophotometers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker DPX-400 instrument (400 MHz) in  $\text{CDCl}_3$  using HMDS as the internal standard. Mass spectra were run on a Finnigan GCQ spectrometer with direct sample injection into the ion source. The products were separated using a PAKhV-07 preparative chromatograph with a katharometer as the detector ( $75^\circ\text{C}$ , a  $5000 \times 10$  mm column; Chromaton N-AW-HMDS as the solid support (0.2–0.25 mm); polyphenyl ether (15 wt %) as the stationary phase; helium as the carrier gas).

**Methoxycarbonylation of the propyne–allene mixture.** Methanol (200 ml) was placed in a four-neck flask equipped with a stirrer, a thermometer, a condenser connected to a coiled trap ( $-50^\circ\text{C}$ ), and two bubblers (for the introduction of carbon monoxide and the propyne–allene mixture) and saturated with carbon monoxide ( $\sim 1.5$  l/h) at room temperature for 30 min. The temperature was decreased to  $0^\circ\text{C}$  and CO was bubbled for an additional 1 h. Without termination of CO bubbling,  $\text{CuCl}_2$  (9.38 g, 70 mmol),  $\text{NaOAc}$  (5.74 g, 70 mmol), and  $\text{PdCl}_2$  (0.106 g, 0.6 mmol) were added. Then, a 4 : 1 propyne–allene mixture (5.00 g, 125 mmol) was passed through the reaction mixture at  $0$ – $10^\circ\text{C}$  with continued feeding of CO. After 1 h, a liquid ( $\sim 2.00$  g) was collected in the coiled trap; the liquid was recycled to the reaction mixture as one portion. After stirring for 2 h with continued CO feeding and gradually raising the temperature to room temperature (the color of the solution changed from emerald green to brown), the content of the flask was diluted with cold water (1 : 1) and extracted with diethyl ether ( $5 \times 200$  ml). The ether extracts were combined, washed with water ( $4 \times 150$  ml), and dried with  $\text{MgSO}_4$ . The extractant was removed *in vacuo* to give a crude product containing methyl 2-butynoate (**I**), methyl 3-methoxy-3-butenate (**II**), and hexa-2,4-diyne (**III**), which were analyzed and separated by GLC. The weight of the crude product (averaged over three experiments) was  $1.76 \pm 0.04$  g. Composition (%): **I** ( $54 \pm 2$ ); **II** ( $23 \pm 2$ ); **III** ( $14 \pm 3$ ). The yields of the components (with allowance for the composition of the propyne–allene mixture) (%): **I** ( $9 \pm 1$ ); **II** ( $12 \pm 1$ ); **III** ( $7 \pm 1$ ).

When the amount of the propyne–allene mixture fed in the flask was increased to 8.00 g (200 mmol), the reaction under the same conditions gave 2.40 g of a crude product with the composition (%): **I** (45); **II** (20); **III** (12), which corresponds to the following yields of the components (%): **I** (7); **II** (9); **III** (5).

**Methyl 2-butynoate (I).**  $n_D^{20}$  1.4325 (lit.:  $80$ – $82^\circ\text{C}$  ( $85$  mm Hg),  $n_D^{19}$  1.4408 [15]).

For  $\text{C}_5\text{H}_6\text{O}_2$  anal. calcd. (%): C, 61.20; H, 6.17.

Found (%): C, 60.06; H, 6.38.

IR (microlayer,  $\text{cm}^{-1}$ ): 3000, 2960, 2920, 2840, 2235, 1710, 1430, 1250, 1070, 940, 810, 750, 570.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 3.74 (s, 3H,  $\text{OCH}_3$ ), 1.98 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 152.7 (C=O), 84.12 ( $\text{CH}_3$ – $\text{C}\equiv\text{C}$ ), 70.91 ( $\text{CH}_3$ – $\text{C}\equiv\text{C}$ ), 56.32 ( $\text{CH}_3$ ), 51.05 (C(O) $\text{CH}_3$ ). MS,  $m/z$  ( $I_{\text{rel}}$ , %): 98 (11), 70 (47), 68 (26), 67 (100), 66 (16), 39 (65), 38 (39), 37 (26), 32 (47), 28 (82).

**Methyl 3-methoxy-3-butenate (II).**  $n_D^{23}$  1.4280.

For  $\text{C}_6\text{H}_{10}\text{O}_3$  anal. calcd. (%): C, 55.36; H, 7.76.

Found (%): C, 55.03; H, 7.99.

IR (microlayer,  $\text{cm}^{-1}$ ): 3030, 2980, 2950, 2930, 2880, 2810, 1720, 1640, 1440, 1380, 1300, 1270, 1195, 1150, 1100, 1015, 1000, 950, 905, 850, 830, 810, 750, 680, 660.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 6.29 and 5.84 (dd, 2H, = $\text{CH}_2$ ), 4.13 (t, 2H,  $\text{CH}_2$ ), 3.77 (s, 3H,  $\text{OCH}_3$ ), 3.38 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 165.93 (C=O), 136.61 ( $\text{CH}_2=\text{C}$ ), 127.15 ( $\text{CH}_2=$ ), 70.04 ( $\text{CH}_2$ ), 58.11 (C(O) $\text{OCH}_3$ ), 52.12 ( $\text{OCH}_3$ ). MS,  $m/z$  ( $I_{\text{rel}}$ , %): 130 (10), 116 (15), 115 (100), 102 (53), 101 (80), 99 (94), 98 (72), 83 (87), 75 (71), 71 (71), 70 (58), 69 (75), 68 (30), 67 (25), 61 (25), 59 (65), 56 (37), 55 (60), 53 (24), 47 (19), 45 (73), 43 (18), 42 (38), 41 (75), 40 (60), 39 (63), 38 (25), 32 (40), 31 (27), 29 (67), 28 (75), 27 (63), 26 (24).

**Hexa-2,4-diyne.** mp  $68^\circ\text{C}$ .

For  $\text{C}_6\text{H}_6$  anal. calcd. (%): C, 92.23; H, 7.74.

Found (%): C, 91.98; H, 7.58.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.89 (s).

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