===

Oxidative Methoxycarbonylation of Propyne and Allene with Carbon Monoxide and Methanol in the Presence of Copper-palladium Catalyst[*]

A. G. Mal'kina, R. N. Kudyakova, V. V. Nosyreva, A. V. Afonin, and B. A. Trofimov

Faworsky Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, 664033 Russia

Abstract—A direct oxidative methoxycarbonylation of propyne with carbon monoxide in methanol medium in the presence of copper-palladium catalytic system results in methyl 2-butynoate in 18–31% yield. Depending on reaction conditions allene provides either a mixture of methyl 2-(chloromethyl)acrylate and methyl 2-(methoxymethyl)acrylate (~3–4 : 1) in overall yield 16–23%, or methyl 2-(methoxymethyl)acrylate in 19% yield.

The methyl methacrylate synthesis from propyne by a traditional scheme in the presence of homogeneous palladium catalysts is well developed [1–3]. It was indicated [2] that only propyne took part in the reaction, whereas its isomer allene deactivated the catalyst.

We recently reported [4] in short on methoxycarbonylation of a propyne-allene mixture by carbon monoxide in methanol medium in the presence of a catalytic system $PdCl_2$–$CuCl_2$–$NaOAc$. In keeping with the preliminary data the reaction gave rise to methyl 2-butynoate and methyl 3-methoxy-3-butenoate (allene methoxycarbonylation product), and also to 2,4-hexadiyne resulting from oxidative dimerization of propyne. These conditions were previously successfully applied [5–12] to oxidative methoxycarbonylation of various acetylene compounds.

Here we report on the results of a more detailed study of oxidative methoxycarbonylation of propyne and allene in the presence of the above redox system, also with the use of its modification (applying $NaHCO_3$ instead of $NaOAc$).

As was already reported [4] the direct methoxycarbonylation of propyne with carbon monoxide in the presence of $PdCl_2$–$CuCl_2$–$NaOAc$ in methanol medium at molar ratio methanol : propyne : $PdCl_2$: $CuCl_2$: NaOAc equal to 5000 : (30–50) : 0.6 : 70 : 70

_____

furnished methyl 2-butynoate (**I**) (purity 64–93%, yield 18–31% with respect to the charged propyne and 933–1550% with respect to $PdCl_2$).
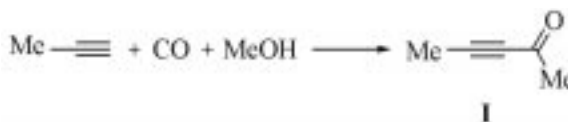
The reaction was carried out between –20 and 20°C for 4 h. Then the mixture was left overnight at room temperature (Table 1, runs nos, 1, 2) or was subjected to workup at once if it was dark-brown (Table 1, run no. 3). The physical constants and spectra (IR, ^{1}H and ^{13}C) of methyl 2-butynoate (**I**) were fully consistent with the data of [4].

In the first stage palladium chloride apparently reacts with carbon monoxide and methanol affording "methoxycarbonylpalladium chloride". Further propyne replaces the chlorine atom linked to palladium providing intermediate **II**. The latter furnishes methyl 2-butynoate (**I**) as a result of reductive elimination of Pd^o. The presumable catalytic cycle is completed by reoxidation of Pd^o into $PdCl_2$ with copper(II) chloride (Scheme 1).

The allene methoxycarbonylation is not so unambiguous. If the reaction was carried out at –60÷ –30° for 2.5–3 h (Table 2, runs nos. 1, 2) it gave a mixture of methyl 2-(chloromethyl)acrylate (**III**) and methyl 2-(methoxymethyl)acrylate (**IV**) (the latter compound was previously [4] erroneously regarded as its structural isomer methyl 3-methoxy-3-butenoate). The ratio of compounds **III** and **IV** in the

Table 1. Propyne methoxycarbonylation

Run no.	Propyne, g	Temperature, °C	Time, h	Mixture of products, g	Content of I, %	Yield I, % (to propyne charged)	Yield I, % (to PdCl$_2$)	Conversion of propyne, %
1	1.20	−30–20	4.5	0.60	93.0	19	933	100
2	1.90	−10–20	4.0	1.00	85.3	18	1417	100
3	2.00	−10	2.0	1.45	64.1	19	1550	98
		−10–20	2.0					

Table 2. Allene methoxycarbonylation

Run no.	Allene, g	Temperature, °C	Time, h	Content in the mixture, %[a]		Yield, % (to allene)		Yield, % (to PdCl$_2$)	
				III	IV	III	IV	III	IV
1	1.0	−60÷−30	2.5	73.5	19.3	13.1	3.7	550	150
2	1.0	−40÷−30	3.0	63.4	23.6	17.0	6.5	713	263
3[b]	3.0	−65÷−20	3.0	64.9	28.7	1.1	0.5	138	63
4[b]	1.0	−65÷−20	3.0	44.0	47.1	5.4	5.8	225	238
5	6.0	0	5.0	2.0	88.0	0.1	8.5	38	2088
6[c]	4.0	0	6.0	Traces	~100	~0	12.3		1000
7[c]	3.0	−50÷0	2.0	65.0	35.0				
			4.0	41.0	59.0	~0			
			6.0	Traces	~100		19.9		1375

[a] According to GLC data.
[b] Instead of 5.74 g (70 mmol) of NaOAc 5.88 g (70 mmol) of NaHCO$_3$ was used.
[c] Conversion of allene 50% (run no. 6) and 57% (run no. 7).

product according to GLC and ^{1}H data was ∼ 3–4:1, overall yield 16–23% (with respect to charged allene).

The ratio of products **III:IV** became 1–2:1 at replacing the buffer component of the catalytic system (NaOAc) with NaHCO$_3$ (Table 2, run nos. 3, 4) (GLC data). However it reduced the overall yield of products (Table 2, run nos. 3, 4).

However the allene methoxycarbonylation can be directed to the exclusive formation of methyl 2-(methoxymethyl)acrylate (**IV**) when the reaction is carried out at 0°C for 5–6 h (Table 2, run nos 5, 6).

According to GLC data in 2 h the reaction mixture contained 65% of methyl 2-(chloromethyl)acrylate (**III**) and 35% of methyl 2-(methoxymethyl)acrylate (**IV**). In 4 h their content became 41 and 59% respectively, and in 6 h after workup of the reaction mixture only compound **IV** was isolated in 19.9% with respect to the charged allene), and 1375% (to PdCl$_2$).

In the course of the process the color of the reaction mixture changed from emerald-green through dark green to brown and black; therewith changed the valence state of metals. If the reaction is stopped at the stage of dark-green reaction mixture, the latter contains prevailingly the intermediate methyl 2-(chloromethyl)acrylate (**III**) (Table 2, run nos. 1, 2). At the same time the black color apparently due to formation of metallic palladium means the end of reaction when the main product is methyl 2-(methoxymethyl)acrylate (**IV**) (Table 2, run nos. 6, 7).

The presumable scheme of acrylates **III** and **IV** formation apparently includes the following stages: first as in the case of methoxycarbonylation of propyne (Scheme 1) arises "methoxycarbonylpalladium chloride" that attacks allene at the *sp*-hybridized carbon providing intermediate **V**. The latter by reductive elimination of Pd^o forms methyl 2-(chloromethyl)acrylate **III** which under conditions of the reaction is converted into methyl 2-(methoxymethyl)-acrylate (**IV**) (Scheme 2).

Scheme 1.
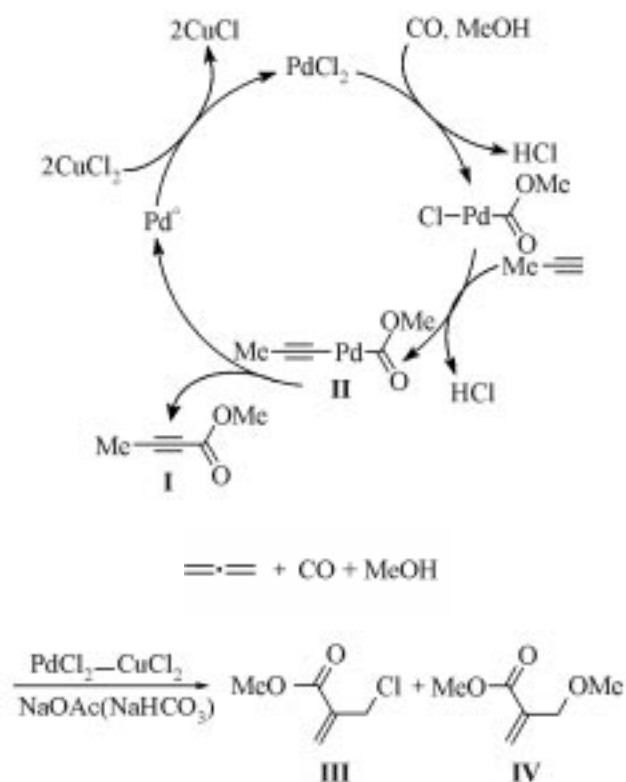
Scheme 2.
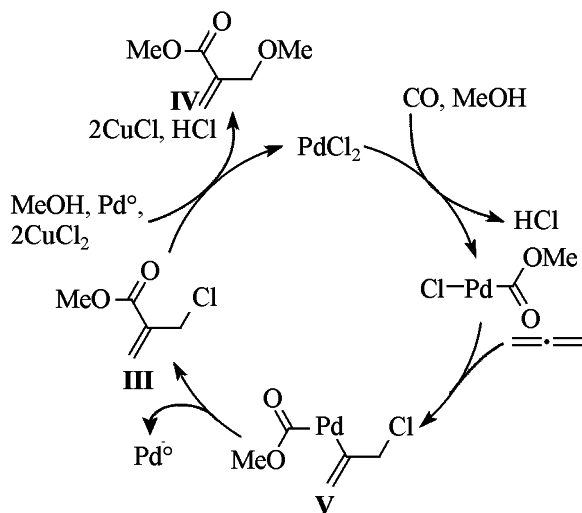
The conversion of methyl 2-(chloromethyl)acrylate (III) under the reaction conditions into methyl 2-(methoxymethyl)acrylate (IV) was confirmed by a special experiment. Thus an isolated mixture of methyl 2-(chloromethyl)acrylate (III) (65.7%) and methyl 2-(methoxymethyl)acrylate (IV) (14.2%) was subjected to methoxycarbonylation with CO in methanol in the presence of copper-palladium catalyst

(0°C, 6 h, room temperature, 12 h). As a result was isolated only methyl 2-(methoxymethyl)acrylate (IV).

Methyl 2-(methoxymethyl)acrylate (IV) was formerly prepared by methoxycarbonylation of propargyl alcohol in methanol in the presence of palladium chloride at molar ratio methanol : propargyl alcohol : $PdCl_2$ equal to $1236 : 89 : 5.6$ at heating to 100°C for 18 h [13], and also by direct methoxy-carbonylation of propyne-allene mixture (4 : 1) in the presence of copper-palladium catalyst [4], although in the latter work it was regarded as its isomer, methyl 3-methoxy-3-butenoate.

Thus the oxidative methoxycarbonylation of allene providing it will be subjected to further optimization opens a way to application in the fine organic synthesis of a highly reactive synthon, methyl 2-(methoxymethyl)acrylate, and also suggests extension of this reaction to substituted allenes.

EXPERIMENTAL

IR spectra were recorded on spectrometers Specord 75IR and Bruker JFS-25 from thin film or KBr pellets. ^{1}H and ^{13}C NMR spectra were registered on Bruker DPX-400 instrument at operating frequencies 400.13 and 100.69 MHz respectively, solvent $CDCl_3$, internal reference HMDS. Mass spectra were measured on Finnigan GCQ instrument with direct admission of a sample into the ion source.

The reaction mixtures and products were analyzed by GLC on chromatograph LKhM-80, detector katharometer, carrier gas helium, column 3000×3 mm, stationary phase 15% Carbowax 20M on Chromaton N-AW-HMDS (0.25–0.315).

Propyne was bought from Aldrich Chemical Company. Allene was prepared by procedure [14].

Methoxycarbonylation of propyne. (a) Into a four-neck flask equipped with a stirrer, thermometer, reflux condenser connected to a trap cooled to –60°C, and bubbler for carbon monoxide input was charged 200 ml of methanol, and at room temperature it was saturated with carbon monoxide for 30 min at a flow rate ~1.5 l h^{-1}. Then the content of the flask was cooled to 0°C and CO was passed for another 1 h. While the flow of CO was continued, the reaction mixture was cooled to –30°C, and 9.38 g (70 mmol) of $CuCl_2$, 5.74 g (70 mmol) of NaOAc, 0.106 g (0.6 mmol) of $PdCl_2$, and cooled to –50°C solution of 1.20g (30 mmol) of propyne dissolved in 2 ml of methanol was added thereto. Then under continuous flow of CO the reaction mixture was gradually warmed to room temperature within 4 h. Therewith

the color of the reaction mixture turned from emerald-green to dark-green. The mixture was left overnight and became dark-brown.

The reaction mixture was diluted with cold water (1:1), and the reaction products were extracted into ethyl ether (5×100 ml). The combined ether extracts were washed with water (4×30 ml) and dried on MgSO₄. The ethyl ether was removed in a vacuum, and thus 0.60 g of light-yellow liquid was obtained containing 93.6% of methyl 2-butynoate (**I**) (GLC) (0.56 g, yield 19% with respect to propyne charged, 933% with respect to PdCl$_2$) (Table 1, run no. 1).

Run no. 2 was carried out under the similar conditions.

IR spectrum of methyl 2-butynoate (**I**) (thin film). cm^{-1}: 3000, 2960, 2920, 2840, 2235, 1710, 1430, 1250, 1070, 940, 810, 750, 570. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 3.74 s (3H, OCH$_3$), 1.98 s (3H, CH$_3$). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 152.7 (C=O), 84.12 (CH$_3$–$\underline{C}$≡C), 70.91 (CH$_3$–C≡$\underline{C}$), 56.32 (CH$_3$), 51.05 [C(O)$\underline{C}$H$_3$]. IR, ^{1}H and ^{13}C NMR spectra are in agreement with the corresponding data for this compound published in [4].

(b) Through a reaction mixture obtained under similar conditions containing 9.38 g (70 mmol) of CuCl$_2$, 5.74 g (70 mmol) of NaOAc, 0.106 g (0.6 mmol) of PdCl$_2$ in methanol (200 ml) saturated with CO was passed a flow of 2.0 g (50 mmol) of propyne for 45 min. After completion of passing propyne and without stopping the steam of CO the mixture was stirred at –10°C for 2 h. The reaction mixture was warmed to 20°C within 3 h (the color of solution in the course of the process changes from emerald-green through dark-green and light-green to dark brown). Then the reflux condenser was replaced by Liebig condenser with a receiver and a cooled trap. By an ordinary distillation at 59–64°C from the reaction mixture was collected in the receiver 150 ml of methanol, and in the cooled trap 1 g of propyne solution in methanol containing according to GLC 4.4% (0.04 g) of unreacted propyne. The IR spectrum of the liquid condensed in the trap contained an absorption band at 2120 cm^{-1} corresponding to the triple bond of propyne.

The bottoms after distillation were diluted with water (1:1), and after workup described under (a) procedure we obtained 1.45 g of liquid containing 64% of methyl 2-butynoate (GLC) (0.93 g, yield 19% with respect to propyne charged, 1550% with respect to PdCl$_2$) (Table 1, run no. 3).

Methoxycarbonylation of allene. (a) Into a four-neck flask equipped with a stirrer, thermometer, reflux condenser connected to a trap cooled to –50°C, and two bubbler for introduction of carbon monoxide and allene was charged 200 ml of methanol, and at 0°C it was saturated with carbon monoxide for 30 min at a flow rate ~1.5 l h^{-1}. Under uninterrupted flow of CO into the flask was placed 9.38 g (70 mmol) of CuCl$_2$, 5.74 g (70 mmol) of NaOAc, 0.106 g (0.6 mmol) of PdCl$_2$. The mixture was cooled to –60°C and at continuous flow of CO through the reaction mixture was passed 1.00 g (25 mmol) of allene within 10 min. The condensate collected in the trap was returned into the reactor. After stirring for 1 h at –40÷–35°C in continuous flow of CO the reaction mixture was slowly warmed to room temperature (the color of solution during the reaction changed from emerald-green to dark-green). Then the reaction mixture was diluted with cold water (1:1) and extracted with ethyl ether (5×100 ml). The combined extracts were washed with water (4×30 ml) and dried with MgSO$_4$. The solvent was removed in a vacuum. We obtained 0.60 g of liquid that according to GLC and ^{1}H NMR contained methyl 2-(chloromethyl)acrylate (**III**) (73.4%) and methyl 2-(methoxymethyl)acrylate (**IV**) (19.3%) (Table 2, run no. 1).

IR spectrum of the mixture (thin film), cm^{-1}: 3030, 2990, 2950, 2930, 2850, 1720, 1640, 1440, 1390, 1330, 1305, 1260, 1195, 1140, 1100, 1050, 990, 950, 915, 830, 810, 750, 680, 650.

Methyl 2-(chloromethyl)acrylate (III). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 6.36, 5.97 q (2H, =CH$_2$), 4.27 t (2H, CH$_2$), 3.80 s (3H, OCH$_3$). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 165.25 (C=O), 136.91 (CH$_2$=$\underline{C}$), 128.46 (=CH$_2$), 52.14 [C(O)–O$\underline{C}$H$_3$], 42.37 (CH$_2$Cl). Mass spectrum, *m/z* (I_{rel}, %): 134 (3), 105 (11), 103 (32), 99 (41), 75 (23), 59 (14), 49 (16), 40 (25), 39 (100), 38 (26), 37 (14).

Methyl 2-(methoxymethyl)acrylate (IV). ^{1}H NMR spectrum (CDCl$_3$) δ, ppm: 6.29, 5.84 q (2H, =CH$_2$), 4.13 t (2H, CH$_2$), 3.77 s (3H, OCH$_3$), 3.38 s (3H, OCH$_3$). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 165.93 (C=O), 136.61 (CH$_2$=$\underline{C}$), 127.15 (=CH$_2$), 70.40 (CH$_2$), 58.11 (O$\underline{C}$H$_3$), 51.42 [C(O)O$\underline{C}$H$_3$]. Mass spectrum, *m/z* (I_{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).

(b) In the same way but at 0°C within 6 h was obtained 0.80 g (12.3%) of methyl 2-(methoxy-methyl)acrylate (**IV**) (Table 2, run no. 6). In the course of the synthesis the unreacted allene (2.0 g) was collected in the cooled trap. IR, ^{1}H and ^{13}C NMR spectra of methyl 2-(methoxymethyl)acrylate (**IV**) are in agreement with the corresponding published data [4, 13].

(c) Into 200 ml of methanol at 0°C was passed a flow of carbon monoxide at a rate ~1.5 l h^{-1} for 30 min. Under uninterrupted flow of CO into the flask was placed 9.38 g (70 mmol) of CuCl$_2$, 5.74 g (70 mmol) of NaOAc, 0.106 g (0.6 mmol) of PdCl$_2$, and 1.60 g of a mixture containing 1.05 g (65.7%) of methyl 2-(chloromethyl)acrylate (**III**) and 0.23 g (14.2%) of methyl 2-(methoxymethyl)acrylate (**IV**). The reaction mixture was stirred at this temperature under constant CO flow for 6 h while the color of the reaction mixture changed from emerald-green to dark-green. The temperature was slowly raised to ambient, and the reaction mixture was left standing for 12 h (the solution turned dark brown and then black). The workup as in procedure (a) furnished 0.35 g of a product containing according to GLC 79.3% (0.28 g) of methyl 2-(methoxymethyl) acrylate (**IV**).

REFERENCES

1. Europe Patent, 696474, 1996. *Chem. Abstr.,* 1996, vol. 124, 233398e.
2. Keijsper, J., Arnoldy, P., Doyle, M.J., and Drent, E., *Rec. Trav. Chim. Pays-Bas,* 1996, vol. 115, pp. 248–255.
3. Haehn, PC., Haidegger, E., and Schodel, N., *Hydrocarbon Engineering,* 1997, no. 1, pp. 41–48.
4. Trofimov, B.A., Kudyakova, R.N., Mal'kina, A.G., Nosyreva, V.V., Kalinina, N.A., and Albanov, A.I., *DAN,* 2001, vol. 378, no. 1, pp. 61–63.
5. Tsuji, M., Takahashi, M., and Takahashi, T., *Tetrahedron Lett.,* 1980, vol. 21, no. 9, pp. 849–850.
6. Trofimov, B.A., Skvortsov, Yu.M., Mal'kina, A.G., and Gritsa, A.I., *Zh. Org. Khim.,* 1985, vol. 21, no. 9, p. 2020.
7. Trofimov, B.A., Gritsa, A.I., Istomina, S.N., Mal'kina, A.G., and Skvortsov, Yu.M., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1986, no. 10, pp. 2336–2339.
8. Gritsa, A.I., Istomina, S.N., and Trofimov, B.A., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1988, no. 8, pp. 1738–1742.
9. Vasilevsky, S.F., Trofimov, B.A., Mal'kina, A.G., and Brandsma, L., *Synthetic Commun.,* 1994, vol. 24, no. 1, pp. 85–88.
10. Trofimov, B.A., Mal'kina, A.G., Gritsa, A.I., Skvortsov, Yu.M., Stankevich, V.K., and Sokolyanskaya, L.V., *Zh. Org. Khim.,* 1996, vol. 66, no. 1, pp. 106–109.
11. Trofimov, B.A., Mal'kina, A.G., and Skvortsov, Yu.M., *Zh. Org. Khim.,* 1993, vol. 29, no. 6, pp. 1268–1291.
12. Trofimov, B.A. and Mal'kina, A.G., *Heterocycles,* 1999, vol. 51, no. 10, pp. 2485–2522.
13. Nogi, T. and Tsuji, J., *Tetrahedron,* 1969, vol. 25, pp. 4099–4108.
14. Brandsma, L. and Verkruijsse, H.D., *Sinthesis of Acetylenes, Allenes and Cumulenes,* Elsevier: Amsterdam, 1981.