

## LITERATURE CITED

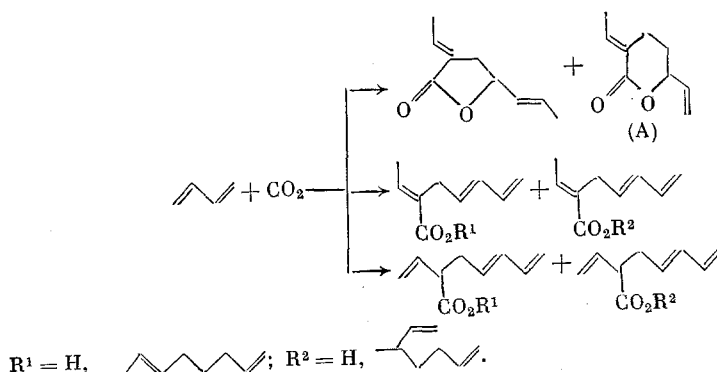
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ACTIVATION OF CO<sub>2</sub> IN REACTION WITH BUTADIENE  
 CATALYZED BY PALLADIUM COMPLEXES

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Studies on the fixation of CO<sub>2</sub> by transition-metal complexes [1-5] stimulated the development of research on the catalytic activation of CO<sub>2</sub> in reactions with monoolefins [6-7], alkynes [8, 9], allene [10], butadiene [11-17], and isoprene [18]. The reaction of CO<sub>2</sub> with butadiene [11] leads to a mixture of linear unsaturated C<sub>9</sub> acids and cyclic lactones in low yields [14]



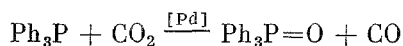
However, in the presence of Pd(acac)<sub>2</sub>-PPh<sub>3</sub> in MeCN solution, practically only the lactone (A) can be obtained in a yield of ~40% [17].

To develop highly efficient and selectively acting catalysts, capable of activating CO<sub>2</sub> under mild conditions, we studied the reaction of CO<sub>2</sub> with butadiene in a DMFA solution by the

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action of the catalytic system  $\text{Pd}(\text{acac})_2\text{-PPh}_3$ , widely used in telomerization of 1,3-dienes with  $\text{H}_2\text{O}$  [19]. From the literature data, we assumed that the low yields of the products of the reaction of  $\text{CO}_2$  with butadiene [11-17] are due to the deactivation of the Pd catalyst as the result of oxidation of  $\text{Ph}_3\text{P}$  to  $\text{Ph}_3\text{P=O}$ .



In a solution of  $(\text{Ph}_3\text{P})_3\text{PhCl}$  in boiling decalin ( $\sim 185^\circ\text{C}$ ), this reaction leads in the course of a few days to  $\text{Ph}_3\text{P=O}$  in a yield of  $\sim 60\%$  [20].

It was found by preliminary experiments that under the catalytic activation conditions of  $\text{CO}_2$  ( $70$  and  $120^\circ\text{C}$ ), the action of palladium complexes reduces  $\text{CO}_2$  to  $\text{CO}$ , and  $\text{Ph}_3\text{P}$  becomes practically quantitatively oxidized to  $\text{Ph}_3\text{P=O}$ . It is clear that under the conditions of cooligomerization of  $\text{CO}_2$  with butadiene,  $\text{Ph}_3\text{P=O}$  does not form catalytically active complexes with Pd, able to promote the formation of molecules of lactones and acids, when  $\text{Ph}_3\text{P=O}$  is used as the activating ligand, it is impossible to obtain even traces of oligomerization products of  $\text{CO}_2$  with butadiene. A similar result was obtained in the cooligomerization of butadiene with  $\text{SO}_2$  catalyzed by palladium complexes [21].

In contrast, in the reaction of  $\text{CO}_2$  ( $50$  atm) with butadiene (molar ratio  $\text{CO}_2$ :diene = 1:2) in the presence of  $\text{Pd}(\text{acac})_2$  in  $\text{PPh}_3$  in a DMFA solution ( $120^\circ\text{C}$ , 20 h), a mixture of unsaturated acids (I) and (II) and lactone (III) is formed (Table 1). In these experiments, excess butadiene converts into 1,3,7-octatriene. Increase in the proportion of  $\text{PPh}_3$  in the composition of the catalytic system leads to an appreciable increase in the selectivity of the process and to an increase in the yield of products of cooligomerization of  $\text{CO}_2$  with the diene. At ratios of  $\text{Pd}:\text{PPh}_3 = 1:20$  and  $\text{CO}_2$ :diene = 1:10, compounds (I)-(III) are exclusively formed in a total yield of 90%, based on the  $\text{CO}_2$  used.

Table 1 shows that the diene concentration has a fairly strong influence on the yield of (I)-(III). Even in experiments where the  $\text{Pd}:\text{PPh}_3$  molar ratio is 1:1 and diene: $\text{CO}_2 = 10:1$ , the yield of (I)-(III) is not less than 30%. In these experiments, the deficiency of  $\text{PPh}_3$  is most probably compensated by an excess of the diene, which is, like triphenylphosphine, a very strong  $\pi$ -donor, and coordinates with the central atom of the catalyst, promoting stabilization of the active particles in the catalyst. It should be noted that in all the experiments, the ratio of (I + II) and (III) is 80:20 on the average.

In the course of the study of the cooligomerization of butadiene with  $\text{CO}_2$ , it was found that the selectivity of the process and also the yield of the reaction products noticeably depend on the degree of purity of the initial reagents, for example, DMFA and  $\text{CO}_2$ . When DMFA and  $\text{CO}_2$  are thoroughly purified and the process is carried out in a solution of  $\text{Pd}(\text{acac})_2$  and  $\text{PPh}_3$  (1:20), at a ratio of  $\text{CO}_2$ :diene = 1:10 ( $70^\circ\text{C}$ , 20 h), compounds (I) and (II) are exclusively formed in yield of 80% (Table 2). Under the same conditions, but at a ratio of  $\text{Pd}(\text{acac})_2:\text{PPh}_3 = 1:1$ , only (III) was obtained from  $\text{CO}_2$  and butadiene in a yield of  $\sim 30\%$ .

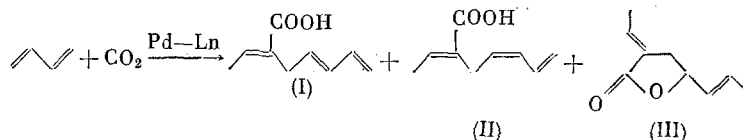
By studying the reaction of  $\text{CO}_2$  with butadiene, for the first time a preparatively convenient method could be developed for synthesizing the difficult-to-obtain 2E,5E,7- and 2E,5Z,7-octatriene-3-carboxylic acids [content of (I) not less than 80%] and 3-ethylidene-5-isopropenylbutyrolactone in high yields.

#### EXPERIMENTAL

Butadiene 99% pure was used. Carbon dioxide was purified by recondensation, by passing through  $\text{H}_2\text{SO}_4$ ,  $\text{CaCl}_2$ , and cooling with liquid  $\text{N}_2$ . Dimethylformamide was purified by distillation of water in the form of an azeotrope with benzene, then was dried over  $\text{CaH}_2$  for 24 h, and distilled over fresh  $\text{CaH}_2$  [22].

The products were analyzed on a Chrom-4 chromatograph, using a flame-ionization detector, 1.5-m column with SE-20, and helium as the carrier gas. The PMR spectra were obtained on a Tesla-487 spectrometer for solutions in  $\text{CDCl}_3$ , using HMDS as the internal standard. The  $^{13}\text{C}$  NMR spectra were recorded on a Jeol FX-900 spectrometer (22.5 MHz) with a broad band and partial suppression of protons, using  $\text{CDCl}_3$  as solvent and TMS as standard. Width of field decoupling 4000 Hz; ADC resolution 0.48 Hz. The IR spectra were run on a UR-20 spectrophotometer (in a thin layer or in mineral oil). The UV spectra were obtained on a Specord UV-VIS apparatus (alcoholic solutions). The mass spectra were run on an MKh-13-06 apparatus with an ionizing-electron energy of 70 eV, and ionization chamber temperature of  $200^\circ\text{C}$ .

TABLE 1. Influence of Ratio of Reagents and Catalyst Components on Yield of Products in Reaction of CO<sub>2</sub> with Butadiene [pCO<sub>2</sub> = 50 atm, 120°C, 20 h [Pd(acac)<sub>2</sub>]; [CO<sub>2</sub>] = 1:1000, solvent - DMFA (25 ml)]



Ratio $\text{CH}_2=\text{CH} : \text{CO}_2$ (molar)	Ratio Pd(acac) <sub>2</sub> : PPh <sub>3</sub> (molar)	Total yield of compounds (I)- (III), on CO <sub>2</sub> , %
1:1	1:1	5-7
2:1	1:1	16
10:1	1:1	30
10:1	1:5	50
10:1	1:10	80
10:1	1:20	90
5:1	1:20	80
1:1	1:20	5-7
10:1*	1:20	1-5

\*70°C.

TABLE 2. Influence of Ratio of Reagents and Catalyst Components on Yield of Products in Reactions of CO<sub>2</sub>\* with Butadiene [70°C, 20 h, [Pd(acac)<sub>2</sub>]/[CO<sub>2</sub>] = 1:1000, solvent - DMFA (25 ml)]

Ratio $\text{CH}_2=\text{CH} : \text{CO}_2$ (molar)	Ratio Pd(acac) <sub>2</sub> : PPh <sub>3</sub> (molar)	Total yield of compounds (I)-(II), %
1:1	1:20	-
2:1	1:4	30
2:1	1:20	45
10:1	1:20	80-90
10:1	1:1	-†
10:1	1:20	46 ‡

\*Purified by recondensation.

†Only lactone (III) is formed, yield ~30%.

‡120°C, higher oligomers are formed.

Reaction of Triphenylphosphine with CO<sub>2</sub> in Presence of Pd(acac)<sub>2</sub>-PPh<sub>3</sub> Catalyst. A 2.6-g portion (10 mmoles) of PPh<sub>3</sub> was added to a solution of 0.157 g (0.5 mmole) of Pd(acac)<sub>2</sub> in 25 ml of absolute DMFA, and the mixture was stirred for 10-15 min, at 20°C in an Ar atmosphere. The catalyst was transferred into a steel autoclave (V = 100 ml), and CO<sub>2</sub> was pumped in (pCO<sub>2</sub> = 50 atm). The content of the autoclave were heated for 20 h at 120°C and cooled. Then, 50 ml of benzene was added to the reaction mixture, which was then washed several times with water to remove DMFA. The benzene layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was distilled off. The residue was crystallized from alcohol. Yield, 2.74 g (98%) of Ph<sub>3</sub>P=O, mp 150-151°C [21]. The CO content was determined according to [23]. At 70°C, the yield of Ph<sub>3</sub>P=O was 70%.

Reaction of Butadiene with Solid CO<sub>2</sub>. A 2.6-portion (10 mmoles) of PPh<sub>3</sub> was added to a solution of 0.157 g (0.5 mmole) of Pd(acac)<sub>2</sub> in 25 ml of absolute DMFA, and the mixture was stirred for 10-15 min in an Ar atmosphere at 20°C. The catalyst was transferred into a steel autoclave (V = 100 ml) cooled to -30 to -40°C, into which 2.2 g (0.05 mole) of solid CO<sub>2</sub>, purified as described above, was placed, and then 27 g (0.5 mole) of butadiene was added.

The contents of the autoclave were heated for 20 h at 70°C, and then cooled. The reaction mixture was diluted with 50 ml of benzene, and washed 2-3 times with H<sub>2</sub>O to remove DMFA. The benzene solution was dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed, and 1,3,7-octatriene was distilled off in a jet-pump vacuum. Yield, 6.9 g (90% based on CO<sub>2</sub> used) of a mixture of acids (I) and (II) in a 1:1 ratio. The mixture was distilled in vacuo [bp of mixture of (I) and (II) 85-90°C (1 mm)], and chromatographed through a brand L40/100 silica gel (eluent - hexane:ethyl acetate = 7:3). A mixture of acids (I) and (II) was obtained in a ratio of 80:20, from which after repeated chromatography, acid (I) was isolated in the individual state.

2E,5E,7-Octatriene-3-carboxylic Acid (I). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 900, 1005, 1635, 1680, 2400-3200. PMR spectrum ( $\delta$ , ppm): 1.84 d (3H, CH<sub>3</sub>, J = 7.5 Hz), 3.1 d (2H, CH<sub>2</sub>, J = 7 Hz), 5.0 m (2H, CH<sub>2</sub>=), 5.6-6.4 m (3H, CH=), 7.1 q (1H, CH<sub>3</sub>CH=), 11.6 s (1H, COOH). UV spectrum (EtOH):  $\lambda$  210 nm ( $\epsilon$  5000), m/z 152. <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 173.24 s (COOH), 141.52 d (C<sup>2</sup>), 136.88 (C<sup>7</sup>), 131.6, 130.42, and 130.1 d (C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>), 115.54 t (C<sup>8</sup>), 28.42 t (C<sup>4</sup>) and 14.49 q (C<sup>1</sup>).

2E,5Z,7-Octatriene-3-carboxylic Acid (II). PMR spectrum ( $\delta$ , ppm): 1.86 d (3H, CH<sub>3</sub>, J = 7.5 Hz), 3.2 d (2H, CH<sub>2</sub>, J = 7 Hz), 5.14 d (1H, cis-H, CH=CH<sub>2</sub>, J = 10.56 Hz), 5.20 d (1H, trans-H, CH=CH<sub>2</sub>, J = 16.5 Hz), 5.33 d (CH<sub>2</sub>CH= J = 7 and 10 Hz), 6.02 t (CH=CHCH=), 6.75 t (CH=CH<sub>2</sub>), 7.04 q (MeCH, J = 7.5 Hz). <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 173.24 s (COOH), 141.13 d (C<sup>2</sup>), 131.01 (C<sup>7</sup>), 129.70 and 128.72 d (C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>), 117.69 t (C<sup>8</sup>), 24.87 t (C<sup>4</sup>), 14.7 q (C<sup>1</sup>).

3-Ethylidene-5-propenylbutyrolactone (III). In the reaction of 27 g (0.5 mole) of butadiene and 2.2 g (0.05 mole) of solid CO<sub>2</sub> on a catalyst prepared from 0.157 g (0.5 mmole) of Pd(acac)<sub>2</sub> and 0.13 g (0.5 mmole) of PPh<sub>3</sub> in 25 ml of absolute DMFA, 2.3 g (30% based on CO<sub>2</sub> used) of (III) was obtained. The product was chromatographed through L40/100 silica gel (eluent - hexane:ethyl acetate = 7:3),  $n_D^{20}$  = 1.4960. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1755 (CO), 970, 1660 (trans-CH=CH). UV spectrum (EtOH):  $\lambda$  218 nm ( $\epsilon$  16500), m/z 152. PMR spectrum ( $\delta$ , ppm): 1.7 d (3H, CH<sub>3</sub>CH=CH, J = 6 Hz), 1.8 d (3H, CH<sub>3</sub>CH=C, J = 7 Hz), 2.5-3.1 m (2H, CH<sub>2</sub>), 4.70-5.0 m (1H, CH), 5.5-5.8 m (CHCH=, CH=CHCH<sub>3</sub>), 6.7 m (CH<sub>3</sub>CH=C), <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 170.15 (C=O), 134.91 (C<sup>9</sup>), 129.60 and 129.24 (C<sup>6</sup>, C<sup>7</sup>), 126.93 (C<sup>3</sup>), 77.38 (C<sup>5</sup>), 17.16 (C<sup>8</sup>), 15.20 (C<sup>10</sup>).

Reaction of Butadiene with Gaseous CO<sub>2</sub>. A 0.157-g portion (0.5 mmole) of Pd(acac)<sub>2</sub> and 0.52 g (2 mmoles) of PPh<sub>3</sub> were dissolved, with stirring (10-15 min at 20°C), in an Ar atmosphere in 25 ml of DMFA. The catalyst was transferred into a steel autoclave (V = 100 ml), cooled to -10 to -5°C, into which 27 g (0.5 mole) of butadiene had been placed, and then CO<sub>2</sub> was pumped in (pCO<sub>2</sub> = 50 atm) (or ~0.05 mole of CO<sub>2</sub>). The contents of the autoclave were heated for 20 h at 120°C. After the usual treatment, 0.8-1 g (13%, based on CO<sub>2</sub>) of a mixture of acids (I) and (II) and lactone (III) was obtained in a ratio of 80:20.

From 27 g (0.5 mole) of butadiene and 0.05 mole of CO<sub>2</sub> (pCO<sub>2</sub> = 50 atm) on a catalyst prepared from 0.157 g (0.5 mmole) of Pd(acac)<sub>2</sub> and 2.6 g (10 mmoles) of PPh<sub>3</sub> in 25 ml of DMFA, under the above conditions (120°C, 20 h), 6.9-7.0 (90%) of a mixture of acids (I) and (II) and lactone (III) was obtained in a ratio of 80:20.

## CONCLUSIONS

1. By using a catalyst containing palladium bis(acetylacetonate) and triphenylphosphine linear unsaturated C<sub>9</sub> acids and 3-ethylidene-5-propenylbutyrolactone can be obtained in a high yield from CO<sub>2</sub> and butadiene in dimethylformamide.

2. Under the reaction conditions, low-valence phosphonic complexes of palladium catalyze the oxidation of triphenylphosphine to triphenylphosphine oxide and the reduction of CO<sub>2</sub> to CO.

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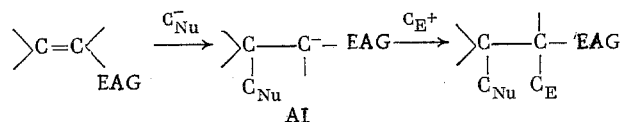
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REGIOSELECTIVE ADDITION OF C-ELECTROPHILES AND  
C-NUCLEOPHILES TO A DOUBLE BOND OF VINYLACETYLENE —  
AN EXAMPLE OF A TWO-STAGE AdE REACTION WITH  
FORMATION OF TWO NEW CARBON-CARBON BONDS

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The development of methods of chemistry of carbanions made it possible to carry out AdN reactions at multiple bonds as sequences of time-separated addition of nucleophile and electrophile. In a modern directed synthesis, this scheme is widely used, since it ensures the possibility of producing two new C-C bonds, and varying the structure of the attached C-nucleophiles (C<sub>Nu</sub>) and C-electrophiles (C<sub>E</sub>) [1]



where EAG is an electron-acceptor group.

For the synthesis, an analogous (but with a reversed sequence of stages) scheme of carrying out the AdE reaction at the multiple bonds is just as promising, but in such a

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