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THE PALLADIUM CATALYZED REACTION OF CARBON DIOXIDE WITH ALLENE

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Summary

In the presence of a bis(η^3-allyl)palladium-bisdicyclohexylphosphinoethane catalyst allene and CO_2 cooligomerize to give a mixture of esters, a lactone and polymer.

In recent years there has been considerable interest in the transition metal catalyzed cooligomerization of carbon dioxide with unsaturated organic molecules. Although the results are somewhat disappointing, successful reactions have been reported involving butadiene[1)] and alkynes[2)] and both esters and lactones have been isolated. We describe here the palladium-catalyzed cooligomerization of allene with CO_2: selected experiments are summarized in Table 1.

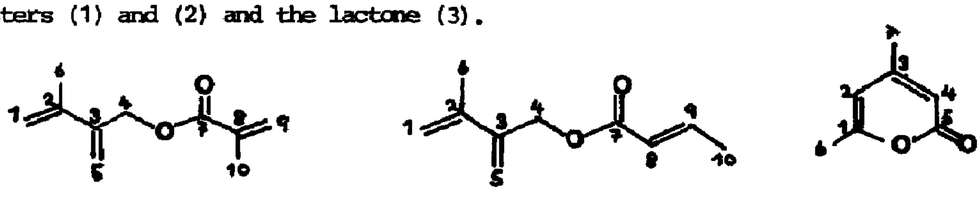
The most effective catalyst was prepared by treating $(\eta^3\text{-}C_3H_5)_2Pd$ with bis-dicyclohexylphosphinoethane. Highest yields of the cooligomerization products 1-3 (~40 %) were obtained with a reaction temperature of 110°C (expt. a). At higher or lower temperatures the yield decreased (expt. b and c); at lower temperatures, the conversion was lower while at higher temperatures the product was a carbonyl-containing polymer. The cooligomerization was less effective in the presence of other ligands (expt. d-h) or Pd(dibenzilideneacetone)$_2$ (expt. j) or when carried out in DMF (expt. i) or in the presence of water. Practically no cooligomerization was observed in the presence of $(\eta^3\text{-}C_3H_5PdCl)_2$, $(\eta^3\text{-}C_3H_5)_2Pt$, Ni(COD)$_2$ or Ni(DCPE)$_2$.

TABLE 1 THE PALLADIUM CATALYZED COOLIGOMERIZATION OF ALLENE WITH CARBON DIOXIDE [a]

Expt.	a	b	c	d	e	f	g	h	i	j	k	l
Catalyst [b]	I	I	I	I	I	I	I	I	I[c]	II	II	I[d]
	DCPE	DCPE	DCPE	DPPE	$P(C_6H_5)_3$	$P(C_6H_5)_3$	$P(C_6H_{11})_3$	$P(i\text{-}C_3H_7)_3$	DCPE	DCPE	$P(i\text{-}C_3H_7)_3$	DCPE
M : L	1:1	1:1	1:1	1:1	1:2	1:1	1:1	1:2	1:1	1:1	1:2	1:1
°C	110	120	90	110	110	110	110	112	110	110	110	110
(T, h)	48	70	72	43	28	24	42	42	24	42	42	42
Allene : CO_2	1:2.9	1:2.9	1:2.7	1:2.6	1:2.6	1:2.6	1:2.6	1:2.8	1:2.7	1:2.7	1:2.8	1:2.9
Conversion (%)	48	87	4.8	86	59.5	32.3	88.3	38.1	18.7	5.7	20.3	94.3
1 (%)	30.5	1.6	8.1	0.5	0.5	-	-	1.6	3.3	0.5	0.2	0.6
2 (%)	5.4	3.8	6.5	5.6	0.6	0.4	0.7	4.6	2.4	-	0.4	-
3 (%)	4.7	2.1	-	-	-	-	-	-	-	-	-	2.0
4 (%)	0.8	2.3	7.0	2.7	3.6	2.4	2.9	1.4	4.7	0.3	5.6	0.4
5 (%)	0.8	1.2	9.9	2.5	0.6	0.2	0.5	1.2	8.2	3.6	3.7	28.9
6 (%)	1.2	0.7	1.8	2.9	trace	0.1	0.2	12.6	4.5	1.1	16.5	6.0
7 (%)	5.8	9.0	15.8	11.6	trace	0.1	0.8	9.4	0.4	2.6	17.5	3.1
8 (%)	3.7	13.5	2.7	11.7	0.9	1.4	1.9	1.73	4.1	-	0.8	0.1
9 (%)	0.4	0.5	-	4.4	0.4	-	-	-	2.8	-	-	2.3
unident. (%)	22.3	14.6	24.4	8.5	3.0	13.2	0.7	9.8	32.7	4.2	6.7	19.5
polymer (%)	24.5	50.7	23.9	50.4	90.4	82.2	92.4	57.6	36.8	87.6	48.6	37.4

[a] in toluene; [b] I = $(\eta^3\text{-}C_3H_5)_2Pd$, II = (benzilidineacetone)$_2$Pd, DCPE = $(C_6H_{11})_2PC_2H_4P(C_6H_{11})_2$, DPPE = $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$;
[c] in DMF; [d] reaction with $CH_3C{:}CH$

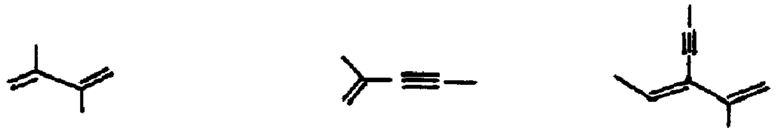
The cooligomerization products were isolated by preparative gas chromatography and identified by a combination of MS, IR, Raman, ^{1}H- and ^{13}C-NMR spectroscopy as the esters (1) and (2) and the lactone (3).



1 2 3

Product (3) is reminiscent of the lactones formed in the cyclo-cooligomerization of CO_2 with alkynes[2] and suggests that the allene might be initially isomerized to propyne. That the main reaction products (1) and (2) are formed in this way is ruled out by an experiment involving propyne (expt. 1) in which only traces of cooligomers are formed. Spectroscopic data for (1), (2) and (3) are given below.

The cooligomerization reaction is invariable accompanied by the formation of oligomers and polymer. Six of these oligomers have been isolated and identified (4-9).



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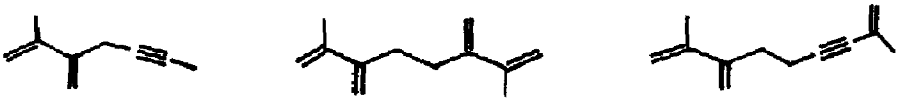
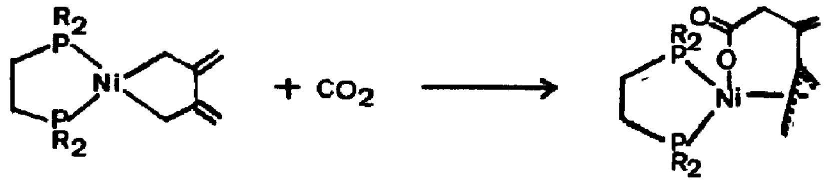


7 8 9

The mechanism of the cooligomerization reaction is not known. By analogy to related nickel-catalyzed reactions, it seems plausible that condensation of allene at the metal leads to the generation of metallacyclic systems which react further with insertion of CO_2 into the M-C bond. For example, the nickelacyclopentane species (10)[5] has been shown to react with CO_2 to give the nickel-carboxylate (11)[6]. The formation of esters and linear oligomers in the reaction discussed here implies a hydrogen-transfer step which presumably proceeds through the intermediacy of a palladium-hydride species.



10 , R=C_6H_{11} 11

Compound (1): $\nu_{C:O}$ 1725, $\nu_{C:C}$ 1637 cm^{-1} (R); δC_1 113.5, δC_2 140.8, δC_3 142.9, δC_4 65.0, δC_5 114.6, δC_6 20.9, δC_7 166.3, δC_8 136.9, δC_9 125.1, δC_{10} 18.35, δC^1H_2 5.15, 4.90, δC^4H_2 4.77, δC^5H_2 5.15, 4.98, δC^6H_3 1.76, δC^9H_2 5.30, 6.07, $\delta C^{10}H_3$ 1.82.

Compound (2): $\nu_{C:O}$ 1743, $\nu_{C:C}$ 1664, 1639 cm^{-1} (R); δC_1 114.6, δC_2 140.8, δC_3 143.1, δC_4 64.5, δC_5 113.5, δC_6 20.9, δC_7 165.4, δC_8 123.1, δC_9 144.4, δC_{10} 17.5; δC^1H_2 4.90, 5.19, δC^4H_2 4.82, δC^5H_2 5.13, 5.02, δC^6H_3 1.84, δC^8H 4.25, δC^9H 6.87, $\delta C^{10}H_3$ 1.40.

Compound (3): δC_1 161.1, δC_2 110.7, δC_3 155.1, δC_4 105.6, δC_5 161.7, δC_6 20.7, δC_7 19.3; δC^2H 5.25, δC^4H 5.66, δC^6H_3 1.73, δC^7H_3 1.60.

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