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Telomerization Reactions of Butadiene and CO_2 Catalyzed by Phosphine Pd(0) Complexes: (E)-2-Ethylidenehept-6-en-5-olide and Octadienyl Esters of 2-Ethylidenehepta-4,6-dienoic Acid

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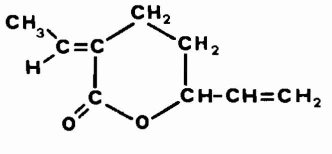
It has been recently reported that CO_2 at low pressure greatly enhances the catalytic properties of tertiary phosphine Pd(0) complexes in the dimerization reaction of butadiene and isoprene [1].

Subsequently Inoue and coworkers [2] have found that $Pd(diphos)_2$ (diphos = $Ph_2PCH_2CH_2PPh_2$) catalyzes the reaction of butadiene and CO_2 in polar and aprotic solvents to give a five membered lactone, 2-ethylidenehept-5-en-4-olide (*1*) in small yields. $Pd[PPh_3]_4$ was found to be less active than $Pd(diphos)_2$ in this reaction.

We have found that non chelating tertiary phosphine Pd(0) complexes in absence of or in apolar solvents (*e.g.* benzene) are effective catalysts for the telomerization reaction of butadiene and CO_2 to yield products different from *1*, *i.e.*, the six membered lactone (E)-2-ethylidenehept-6-en-5-olide (*2*) and the octadienyl esters of 2-ethylidenehepta-4,6-dienoic acid (*3*).



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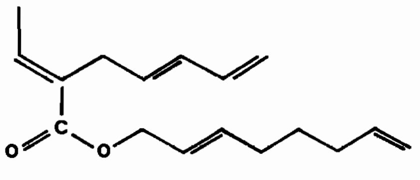
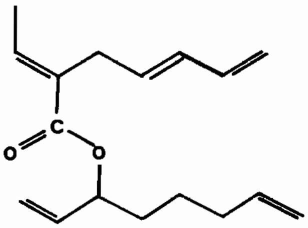


3a



3b

The structure of *2* is consistent with the spectroscopic data and elemental analysis (i.r. (liquid) $\nu C{=}O$ 1710 cm^{-1}; n.m.r. ($CDCl_3$):δ 7.08 ($CH_3CH{=}$), 5.88 ($-CH{=}CH_2$), 5.28 ($-CH{=}CH_2$), 4.77 ($-CH_2CH-$), 2.53–1.77 ($-CH_2CH_2-$), 1.77 (CH_3). The *E* stereochemistry of *2* has been demonstrated by ^{13}C n.m.r. The $^3J_{C-H}$ value (5 Hz) of the carbon of the carbonyl group and the ethylidene proton [3] compares with the value (6.78 Hz) found in crotonic acid and is smaller than that found in isocrotonic acid (14.50 Hz) [4].

The structure of esters *3* is based on the spectral data and on the identification of the saponification products of both *3* and their hydrogenated derivatives. The carboxylic acid of *3* was also isolated by Inoue [2].

Preformed Pd(0) complexes as well as mixture of $(\eta^3\text{-2-methylallylPdOAc})_2$ and the appropriate phosphorous ligand may be conveniently used in the catalytic runs.

In a typical reaction butadiene (0.31 mol), CO_2 (0.68 mol), $(C_4H_7PdOAc)_2$ (0.38 mmol) and $P(C_6H_{11})_3$ (1.54 mmol) in benzene (10 ml), H_2O (4 mmol)* were heated at 70 °C for 48 h in a high pressure reactor (80 ml).

The reaction mixture, after elimination of the solvent and small quantities of volatile components (mainly 1,3,7-octatriene) gave a yellow oil (7 g). Chromatography of the oil on a Si gel column with cyclohexane–ethylacetate gave *3* (23%) (i.r., $\nu C{=}O$ 1710 cm^{-1}) slightly impure of octadienyl esters of the 2-vinylhepta-4,6-dienoic acid (*4*) (i.r., $\nu C{=}O$ 1735 cm^{-1}) and then *2* (64%).

The ratio in which *2* and *3* are formed appears to depend on the size of the phosphine, the formation of *2* being preferred if a bulky ligand is coordinated to the metal. This is suggested by the following examples.

By using PEt_3 as the ligand (butadiene (0.31 mol), CO_2 (0.68 mol), $(C_4H_7PdOAc)_2$ (0.38 mmol) and PEt_3 (1.54 mmol) in benzene (10 ml), 60 °C, 20 h) the non volatile oily residue (7 g) is mainly constituted by *3* again impure by the octadienyl esters of acid *4*, with minute quantities of *2*. The esters of acid *4* are precursors of esters *3* as they are isomerized to *3* (3a/3b 2:1) by heating the crude reaction mixture, after elimination of the volatile components, for 6 h at 90 °C under N_2. In this thermal treatment *3* are also decomposed (35%) to the corresponding

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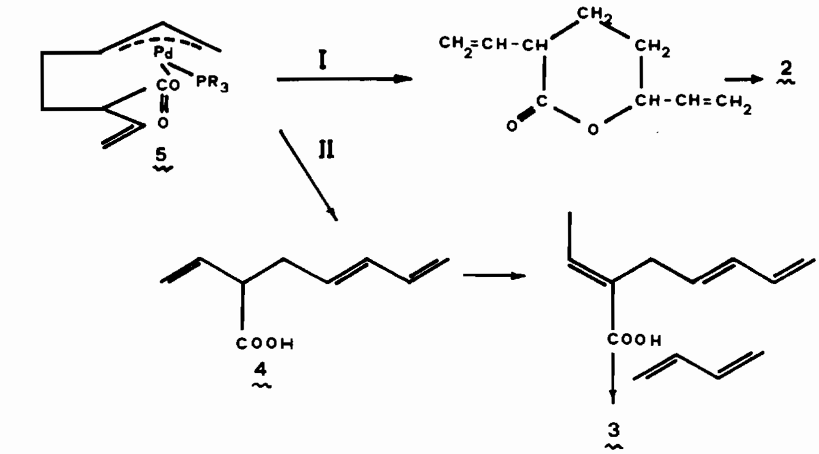
*Small quantities of water accelerate the reaction which is much slower if well dried reagents are used.



carboxylic acid and 1,3,7-octatriene through an oxidative addition of the allyl carbon oxygen bond to the phosphine Pd(0) species present in solution. Increase of the Pd/PEt_3 ratio (up to 1/5) does not change the results given above, the esters *3* being the major products formed.

On the other hand, with PPh_3 as the ligand in a 2:1 phosphine Pd ratio (butadiene (0.31 mol), CO_2 (0.70 mol), $(C_4H_7PdOAc)_2$ (0.38 mmol) and PPh_3 (1.54 mmol) in benzene (10 ml), H_2O (4 mmol), 70 °C, 24 h) the crude reaction mixture (9 g) contains 76% of octadienyl esters and 5% of the six membered lactone. However at a 1:4 Pd/PPh_3 ratio, under the same reaction conditions as above, the reaction mixture (4 g) contains esters and lactone in comparable amounts (40%).

Assuming 5 (Scheme) as the reaction intermediate* which is structurally similar to the intermediate postulated in the telomerization reaction of butadiene with organic carbonyl compounds (aldehydes, ketones) [5], it may either collapse according to route I to give the six membered lactone or to route II to give the carboxylic acid and then the corresponding octadienyl esters.

Studies are in progress in order to clarify the influence that the sterical hindrance of the ligand and the metal to ligand ratio have in the distribution of *2* and *3*.

Acknowledgments

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