

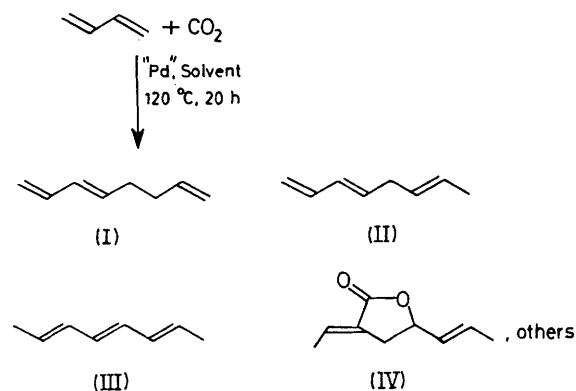
## Reaction of Carbon Dioxide with Butadiene Catalysed by Palladium Complexes. Synthesis of 2-Ethylidenehept-5-en-4-olide

By YOSHIYUKI SASAKI, YOSHIO INOUE,\* and HARUKICHI HASHIMOTO

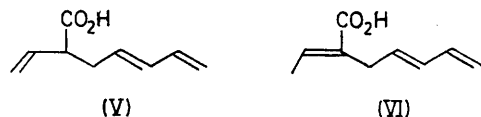
(Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Sendai 980, Japan)

**Summary** The catalytic addition of  $\text{CO}_2$  to butadiene by Pd-phosphine complexes to yield 2-ethylidenehept-5-en-4-olide was achieved in a polar, aprotic solvent such as dimethylformamide (DMF).

In the dimerisation of butadiene catalysed by transition-metal complexes  $\text{CO}_2$  can profoundly alter the properties of the catalyst.<sup>1</sup> It has been suggested that  $\text{CO}_2$  has a direct effect on the catalyst. In studying the catalytic fixation of  $\text{CO}_2$  in organic compounds, we have discovered that  $\text{CO}_2$  can react with butadiene in the presence of Pd-phosphine complexes to give a small amount of 2-ethylidenehept-5-en-4-olide (IV) together with butadiene oligomers. The structure of the product (IV) was determined by the following spectral data and elemental analysis: i.r. (liquid):



1755 (C=O), 1675, and 970  $\text{cm}^{-1}$  (*trans* CH=CH); n.m.r (CCl<sub>4</sub>):  $\delta$  1.6–1.9 (m, 6H, =CMe), 2.1–3.3 (m, 2H, CH<sub>2</sub>), 4.5–4.9 (m, 1H, HC), 5.1–6.0 (m, 2H, CH=CH), and 6.3–6.7 (m, 1H, CH=C–C=O); u.v. (EtOH): 217 nm ( $\epsilon$  16,300;  $\pi \rightarrow \pi^*$ , C=C–C=O).



Details of the reaction of CO<sub>2</sub> with butadiene in various solvents are shown in the Table. Some polar, aprotic solvents such as DMF and dimethyl sulphoxide (DMSO),

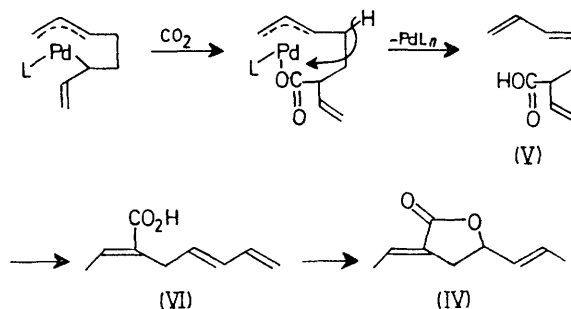
TABLE. Reaction of CO<sub>2</sub> with butadiene<sup>a</sup>.

Solvent	Product (%) <sup>b</sup>				
	(I)	(II)	(III)	(IV)	Others <sup>c</sup>
None	2.4	3.6	58.0	Trace	18.5
DMF	26.8	21.9	13.9	4.0	15.1
DMF <sup>d</sup>	32.8	20.5	7.2	12.3	9.3
DMSO	55.7	12.3	4.5	4.2	9.3
Bu <sup>t</sup> OH	44.3	17.9	6.6	0.5	15.0
Benzene	35.7	21.8	17.7	0.4	18.1
DMF <sup>e</sup>	47.5	20.3	4.5	0.7	14.5

<sup>a</sup> Solvent (10 ml), butadiene (7.3 g), CO<sub>2</sub> (50 atm), and [Pd(diphos)<sub>2</sub>] (0.2 mmol); diphos = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>; 120 °C, 20 h. <sup>b</sup> The yields, based on butadiene, were determined by g.l.c. on a FFAP column at 205 °C with He as carrier gas. The lactone (IV) was isolated by preparative g.l.c. The acids (V) and (VI) were isolated from the reaction mixture by extraction with aqueous NaOH and after acidification were purified by preparative g.l.c. <sup>c</sup> 'Others' mainly consists of butadiene trimers. <sup>d</sup> DMF (20 ml); 84 °C for 20 h then 120 °C for 20 h. <sup>e</sup> [Pd(PPh<sub>3</sub>)<sub>4</sub>] (0.2 mmol).

<sup>1</sup> J. F. Kohnle, L. H. Slauch, and K. L. Nakamaye, *J. Amer. Chem. Soc.*, 1969, **91**, 5904; K. E. Atkins, W. E. Walker, and R. M. Manyik, *Chem. Comm.*, 1971, 330; A. Musco and A. Silvani, *J. Organometallic Chem.*, 1975, **88**, C41.

are suitable for the lactone synthesis, and the diphos ligand in the Pd complex is more effective than the PPh<sub>3</sub> ligand. When this reaction was carried out below 100 °C, the organic acids (V) and (VI) were also obtained together with the lactone (IV). Both acids were easily converted into the lactone (IV) under the conditions given in the Table, indicating that these acids were the precursors of (IV).



We propose the following possible mechanism for this reaction. The formation of the  $\pi$ -allylic complex from 2 mol of butadiene and the palladium complex is followed by CO<sub>2</sub> insertion at the Pd–C bond to give the carboxylate complex, which then collapses with intramolecular transfer of hydrogen to give the acid (V). The acid isomerises easily to another acid (VI) which then is converted into the five-membered lactone (IV) by intramolecular 1,4-addition.

We thank the Ministry of Education, Japan, for partial support.

(Received, 26th April 1976; Com. 460.)