

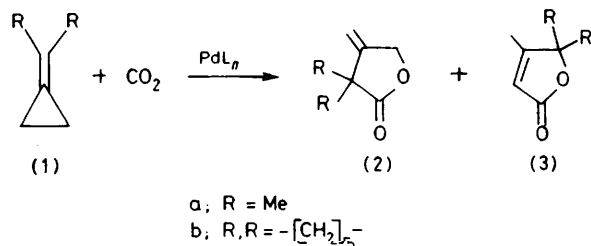
Reaction of Methylene-cyclopropanes with Carbon Dioxide Catalysed by Palladium(0) Complexes. Synthesis of Five-membered Lactones

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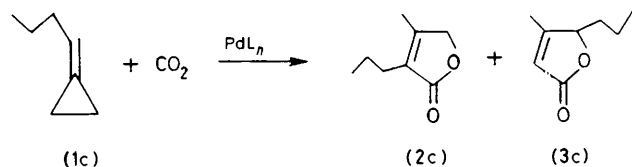
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Summary Palladium(0)-phosphine complexes catalyse the cyclodimerisation of methylenecyclopropanes and carbon dioxide with opening of the three-membered ring to give five-membered lactones.

RECENTLY much attention has been focused on the fixation of carbon dioxide. As part of a study of the catalytic fixation of CO₂ in organic compounds by transition metal complexes,¹ we have studied the reaction of methylenecyclopropanes with CO₂ catalysed by palladium(0) complexes.



When isopropylidencyclopropane (**1a**) in benzene was treated with high pressure CO₂ at 126 °C for 20 h in the presence of a catalytic amount of [Pd(dba)₂]-PPh₃ (1:4) (dba = dibenzylideneacetone), the lactone (**2a**) was formed in 69% yield [¹H n.m.r. (CCl₄) δ 1.20 (6H, s, Me), 4.75 (2H, t, -CH₂-, *J* 2.2 Hz), and 5.05 (2H, t, CH₂=, *J* 2.2 Hz); i.r. (liquid) 1780 (C=O), 1670 (C=C), 1150 (C-O), and 925 (CH₂-) cm⁻¹]. When [Pd(diphos)₂] (diphos = Ph₂PCH₂-CH₂PPh₂) was used instead of [Pd(dba)₂]-PPh₃ the lactone (**3a**), m.p. 44.5–45.5 °C (lit.² 44.5–46.5 °C), [¹H n.m.r. (CCl₄) δ 1.35 (6H, s, Me), 2.00 (3H, d, Me, *J* 1.4 Hz), and 5.55 (1H, q, -CH=, *J* 1.4 Hz); i.r. (KBr) 1750 and 1730 (branched C=O), 1640 (C=C), and 1280 (C-O) cm⁻¹] was obtained as the major product. The cyclopropane (**1b**) reacted similarly to (**1a**).



In the case of butylidencyclopropane (**1c**), three 1:1 addition products were obtained, two of which were identified as the αβ-unsaturated lactones (**2c**) and (**3c**), but the structure of the third product was not determined because of its low yield. Compound (**2c**) was separated from (**3c**) by t.l.c. on silica gel using CHCl₃ as eluant. The spectral data were as follows: (**2c**) ¹H n.m.r. (CCl₄) δ 0.87

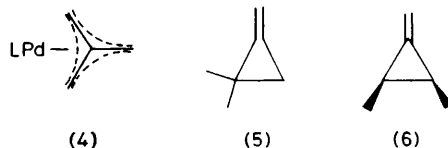
(3H, t, Me, *J* 6.1 Hz), 1.2–1.7 (2H, m, -CH₂-), 2.00 (3H, s, Me), 2.15 (2H, t, -CH₂-C=, *J* 7.0 Hz), and 4.45 (2H, s, CH₂O), i.r. (liquid) 1750 (C=O) and 1675 (C=C) cm⁻¹; (**3c**) ¹H n.m.r. (CCl₄) δ 0.91 (3H, t, Me, *J* 6.3 Hz), 1.2–1.7 (4H, m, -CH₂-), 1.96 (3H, s, Me), 4.60 (1H, br, CH), and 5.60 (1H, s, -CH=); i.r. (liquid) 1750 (C=O) and 1645 (C=C) cm⁻¹. The αβ-unsaturated lactones (**2c**) and (**3a–c**) are probably derived from the corresponding β-methylenelactones by isomerisation. Results are summarised in the Table.

TABLE. Reaction of methylenecyclopropanes with CO₂.^a

Methylenecyclopropane (mmol)	Catalyst ^a	Conversion/%	Yield of product/% ^b
			(2) (3)
(1a)	(17) A	97	69 8
	(17) B	93	Trace 48
	(16) C	26	8 Trace
	(9) D	— ^c	1 5
	(17) E	32	4 7
(1b)	(29) A	71	32 ^d Trace ^d
	(30) B	74	5 ^d 21 ^d
(1c)	(18) F	ca. 100	38 29
	(18) B	ca. 100	14 12

^a Quantities used and conditions were as follows: 0.4 mmol catalyst; 20 ml benzene; 40 atm CO₂ at 25 °C; 130 ± 8 °C; 20 h. The catalysts used were: A, [Pd(dba)₂]-PPh₃ (1:4); B, [Pd(diphos)₂]; C, [Pd(dba)₂]-P(OEt)₃ (1:4); D, [Pd(dba)₂]-PBu₃ (1:4); E, [Pd(dba)₂]-Me₂PCH₂CH₂PMe₂ (1:2); F, [Pd(PPh₃)₄]. ^b Yields were determined by g.l.c. based on the starting material. In addition to (**2**) and (**3**) isomers of the starting materials, oligomers of the starting materials, and oligomers incorporating CO₂ were formed. ^c Not determined. ^d Isolated yield.

A less basic phosphine such as PPh₃ or P(OEt)₃ has a tendency to give (**2**) rather than (**3**). The mode of CO₂ linkage to a methylenecyclopropane involves an intermediate of the type (**4**) which has been suggested for the palladium(0) catalysed cycloadditions of methylenecyclopropanes to alkenes.³



Contrary to expectation, 2,2-dimethylmethylenecyclopropane (**5**) and *cis*-2,3-dimethylmethylenecyclopropane (**6**) did not react with CO₂ under similar conditions and only the starting compounds were recovered.

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