

New Reaction of Methylenecyclopropane with Cyclohex-2-en-1-ones Catalysed by Palladium(0) Complexes

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Summary Methylenecyclopropane and cyclohex-2-en-1-ones react in the presence of a catalyst prepared *in situ* from bis(dibenzylideneacetone)palladium(0) and a tertiary phosphine to give 2-alkylated enones.

NICKEL(0) and palladium(0) complexes are known to catalyse the codimerisation of methylenecyclopropane (**1**) with electron deficient olefins. The methylenecyclopentane derivatives thus obtained correspond formally to $[2\sigma + 2\pi]$ cycloadducts. With nickel catalysts¹ two types

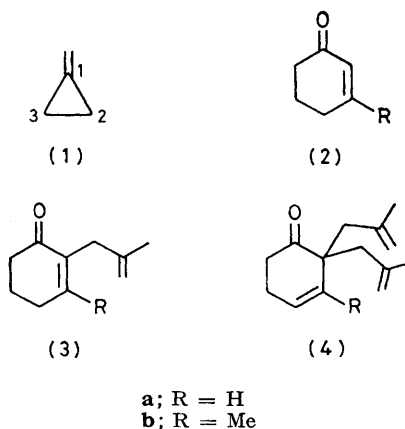
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of ring opening reactions occur, either cleavage of the C(1)–C(2) or the C(2)–C(3) bond, whereas with palladium catalysts² only the latter is observed.

Here we report a new reaction of methylenecyclopropane (1)³ with cyclohex-2-en-1-ones (2) catalysed by a palladium(0) complex. Instead of the expected cyclo-adducts this reaction leads to the 2-alkylated enones (3) and (4).

Bis(dibenzylideneacetone)palladium(0)⁴ (0.3 mmol) and methyldiphenylphosphine (0.3 mmol) were added under nitrogen to a mixture of methylenecyclopropane (1) (15 mmol) and cyclohex-2-en-1-one (2a) (15 mmol). The resulting solution was heated in a sealed glass tube at 100 °C for 20 h. The two products (3a) and (4a) were formed in 60 and 19% yield, respectively.† The spectroscopic data of purified compounds after preparative g.l.c. were in agreement with the assigned structures. The ratio, palladium:phosphine of 1:1 gave the best results. In the absence of, or with an excess of phosphine (Pd:P>2) no reactions were observed. The ratio of the products (3a):(4a) could be improved (ca. 9:1) by using an excess of cyclohex-2-en-1-one. With 3-methylcyclohex-2-en-1-one (2b) the 1:1 adduct (3b) was obtained in 81% yield together with only a small amount of a dialkylated product [*m/e* (*M*⁺)218] detected by coupled mass spectrometry–g.l.c.§

These results show that the products obtained in this new reaction result exclusively from the cleavage of the



C(2)–C(3) bond of (1). The absence of a significant amount of dialkylated product (4b) from (2b) is probably the consequence of the tetrasubstituted double bond of (3b) which hinders co-ordination to the palladium atom.

The reaction described here provides a new method of alkylating the α -vinylic position of conjugated cyclohexenones.

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† Yields were determined by g.l.c. with internal standards.

§ All compounds gave satisfactory microanalytical data.

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