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 catalysts[1] two types

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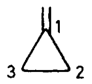
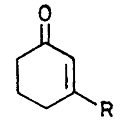
of ring opening reactions occur, either cleavage of the C(1)–C(2) or the C(2)–C(3) bond, whereas with palladium catalysts[2] only the latter is observed.

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 cycloadducts this reaction leads to the 2-alkylated enones (**3**) and (**4**).

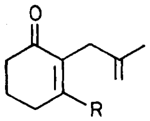
Bis(dibenzylideneacetone)palladium(0)[4] (0·3 mmol) and methyldiphenylphosphine (0·3 mmol) were added under nitrogen to a mixture of methylenecyclopropane (**1**) (15 mmol) and cyclohex-2-en-1-one (**2a**) (15 mmol). The resulting solution was heated in a sealed glass tube at 100 °C for 20 h. The two 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.§



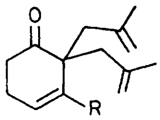
(1)



(2)



(3)



(4)

a; R = H
b; R = Me

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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