

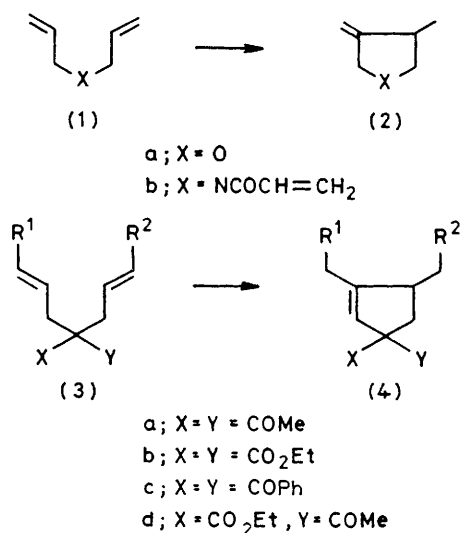
Catalytic Synthesis of Substituted Cyclopentenes

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Summary 4,4-Disubstituted 1,6-dienes undergo a palladium(II) catalysed cyclisation in boiling chloroform to give substituted cyclopentenes in good yield.

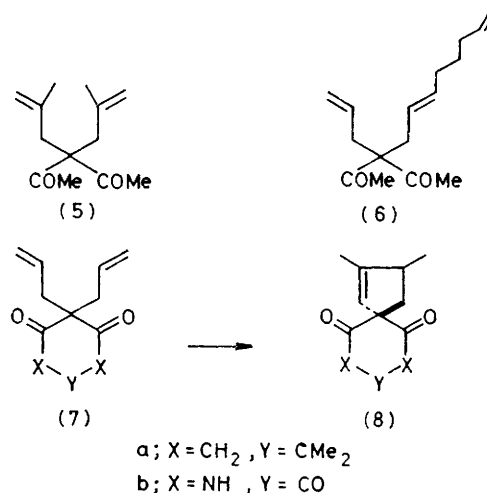
INTERMOLECULAR oxidative and non-oxidative coupling of olefins has been widely studied.^{1,2} Intramolecular analogues of these processes have been observed in the rhodium trichloride catalysed cyclisation of diallyl ether (**1a**) to

(2a)³ and of the corresponding nitrogen analogue (1b) to (2b)⁴. A related palladium chloride catalysed oxidative dimerisation of allyl alcohol is also known.⁵



We now report that the 4,4-disubstituted-1,6-dienes (3a—d, R¹ = R² = H) undergo cyclisation to the corresponding cyclopentenes (4) in boiling chloroform containing a catalytic amount of palladium acetate. Palladium chloride is also an effective catalyst and the palladium acetate catalysed reaction is accelerated if the chloroform is saturated with hydrogen chloride (reaction time 5—10 h). The cyclisation of (3d) leads to a mixture of stereoisomers in the ratio 2:1 (n.m.r.). The reaction will tolerate substituents at the terminus of the double bond. Thus (3a;

R¹ = H, R² = Me) and (3a; R¹ = R² = Me) both cyclise to the corresponding cyclopentenes (4a; R¹ = Me, R² = H, 93%) and (4a; R¹ = R² = Me, 82%). However, the dienes, (1a), (1; X = NCOMe), (3; X = Y = CN, R¹ = R² = H), (5), and (6) failed to cyclise under our conditions. A chelate action by X and Y is not important to the cyclisation since both (7a) and (7b) cyclise to (8a; 65%) and (8b; 97%).



A notable feature of the cyclisation of (3)→(4) is that it is not necessary to add an oxidant (*e.g.* Cu^{II} salts or oxygen) to make the process catalytic.

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