Rhodium-catalysed Synthesis of Substituted Methylene Cyclopentanes

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Summary 4,4-Disubstituted 1,6-dienes are cyclised in good yield by Wilkinson's catalyst [RhCl(PPh$_3$)$_3$], in boiling chloroform, to methylene cyclopentanes

INTRAMOLECULAR non-oxidative coupling of olefins has been observed in the rhodium trichloride-catalysed cyclisation of diallyl ether (**1a**) to (**2a**)[1] and of the corresponding nitrogen analogue (**1b**) to (**2b**)[2] Related cyclisations have also been effected and include the nickel-catalysed cyclisation of (**3**) to (**4**)[3] and more recently the palladium-catalysed cyclisation of 2-trimethylsilyloxy-1,5-dienes to cyclopentenones [*e.g.* (**5**) → (**6**)].[4]

We recently reported[5] the cyclisation of 4,4-disubstituted 1,6-dienes to cyclopentenes (**7**) → (**8**) and now report that Wilkinson's catalyst [RhCl(PPh$_3$)$_3$] also promotes cyclisation of (**7**) but the products in this case are the methylene cyclopentanes (**9**). Typically the substrate and catalyst (0·01—0·03 mol) were heated in boiling chloroform through which dry hydrogen chloride had been slowly bubbled for *ca.* 6 min before heating was commenced. Yields in general are high (Table). The n.m.r. spectra of the products were consistent with assigned structures, *e.g.* the spectrum (CDCl$_3$) of (**9a**) contained, *inter alia*, signals at τ 5·16 (m, 2H, >C:CH$_2$) and 8·90 (d, 3H, >CH*Me*). The products also showed the expected i.r. band at *ca.* 880 cm^{-1} (>C=CH$_2$). In contrast, to our previous observations on the palladium-catalysed cyclisations (**7**) → (**8**), the rhodium-catalysed processes do not occur when the double bonds are substituted. Thus (**7a**; R^1 = H, R^2 = Me), (**7a**; R^1 = R^2 = Me), (**7a**; R^1 = R^2 = Ph), and (**7a**; R^1 = H, R^2 = [CH$_2$]$_3$CH=CH$_2$) all failed to cyclise. Diallyl ethers bearing substituents on the double bonds also fail to cyclise in the presence of rhodium trichloride, in contrast to diallyl ether itself.[6]

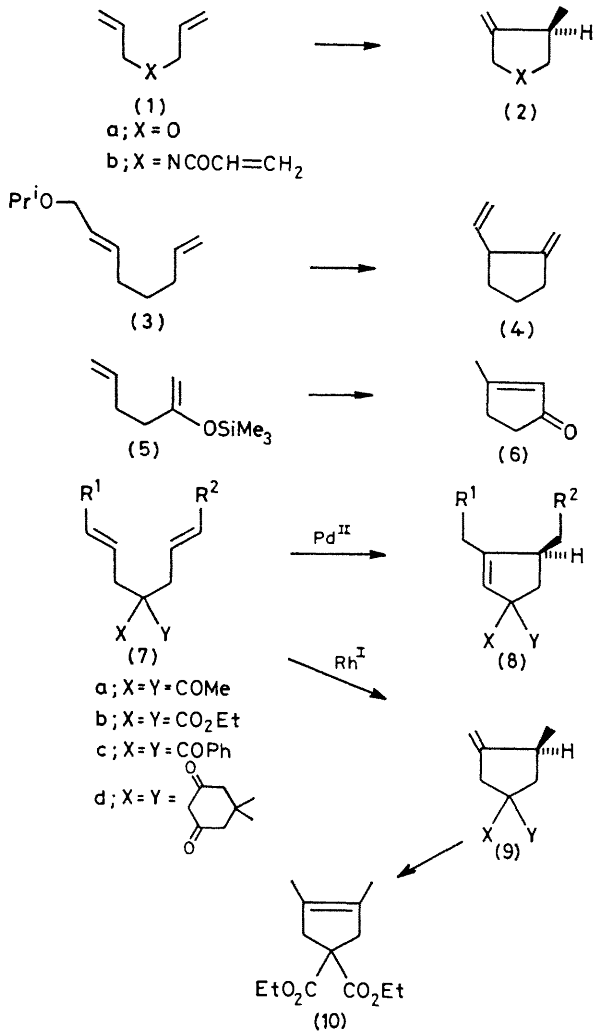

TABLE. [RhCl(PPh$_3$)$_3$-catalysed cyclisation of 1,6-dienes in boiling chloroform containing hydrogen chloride

1,6-Diene	Molar ratio of catalyst	Time (h)	Product/%[a]
(**7a**), R^1=R^2=H[b]	0·02	12	(**9a**), (96%), 87%
(**7b**), R^1=R^2=H[b]	0·01	12	(**9b**), (90%), 80%
(**7b**), R^1=R^2=H	0·01	8	(**9b**), (92%) 90%
(**7c**), R^1=R^2=H	0·01	48	(**9c**), (—) 75%
(**7d**), R^1=R^2=H	0·03	72	(**9d**), (—) 60%

[a] Isolated yields, yields in parentheses calculated from g.l.c. traces. [b] No hydrogen chloride added.

Treatment of (**9a**) with palladium acetate under the conditions necessary for the cyclisation of (**7a**; R^1 = R^2 = H) to (**8a**; R^1 = R^2 = H) did not isomerise (**9a**) to (**8a**; R^1 = R^2 = H). Treatment of (**8b**, R^1 = R^2 = H) with [RhCl(PPh$_3$)$_3$] under the conditions for the production of (**9b**) also failed to effect isomerisation to (**9b**). However treatment of (**9b**) with [RhCl(PPh$_3$)$_3$] in boiling ethanolic hydrogen chloride† for 8 h gives (**10**). The diene (**7b**; R^1 = R^2 = H) also gives (**10**) under similar conditions. In the absence of [RhCl(PPh$_3$)$_3$] (**9b**) does not isomerise to (**10**).

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† HCl gas slowly bubbled through dry ethanol for 5 min prior to the reaction.

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[3] J. Furukawa, J. Kiji, K. Yamamoto, and T. Tojo, *Tetrahedron*, 1973, 3149.

[4] Y. Ito, H. Aoyama, T. Hirao, A. Mochizuki, and T. Saegusa, *J. Amer. Chem. Soc.*, 1979, **101**, 494.

[5] R. Grigg, T. R. B. Mitchell, and A. Ramasubbu, *J.C.S. Chem. Comm.*, 1979, 669; reaction times reported in this paper are considerably shortened if the ethanol stabiliser is removed from the chloroform.

[6] R. Grigg, B. Kongkathip, and T. J. King, *J.C.S. Dalton*, 1978, 333; R. Grigg and B. Kongkathip, unpublished observations.