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RHODIUM CATALYSED [2+2+2] CYCLOADDITIONS OF ACETYLENES

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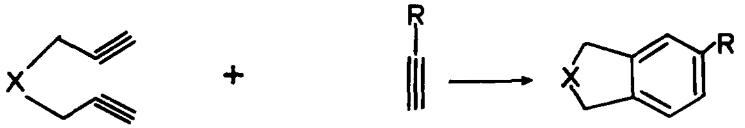
Summary. Wilkinson's catalyst $RhCl(PPh_3)_3$ is an effective catalyst (0.5 - 2 mole %) for the rapid intermolecular trimerisation of 1,6-heptadiynes with monoacetylenes under mild conditions.

The metal catalysed trimerisation of acetylenes to benzene derivatives is well known and can be achieved with many transition metal (e.g. Ni, Pd, Co, Cr, Fe) as well as Ziegler type catalysts.[1] The trimerisation can also be modified to incorporate nitriles.[2] Recently interest in these reactions has centred on their utility in steroid and alkaloid chemistry where the cobalt catalyst $CpCo(CO)_2$ has proved especially useful.[3] In contrast to cobalt, rhodium complexes are reported to generally give rise to linear dimers[4] although stoichiometric two-step trimerisations proceeding through isolable rhodacyclopentadiene intermediates have been reported.[5]

We now report a facile catalytic acetylene trimerisation using Wilkinson's catalyst $RhCl(PPh_3)_3$. Thus the diynes (1a-f) react with a 3-4 mole excess of monoacetylenes (2a-e) in ethanol at 0-79° in the presence of 0.5-2 mole % of $RhCl(PPh_3)_3$ to give benzene derivatives (3) in good yield.

The reaction shows good chemoselectivity with no detectable trimerisation of the monoacetylene (2) and usually none, or only minor amounts, of the dimer (4) arising from the diyne (1). The tendency of (2d) to undergo competing dimerisation at $\ngtr$ 25° is suppressed in reactions run at 0°. t-Butanol, tetrahydrofuran, and ethanol-chloroform mixtures are also suitable solvents for the reaction.



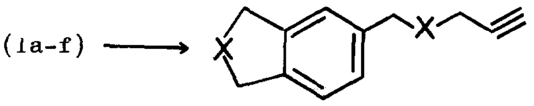
(1) a. $X=CH_2$
b. $X=O$
c. $X=SO_2$
d. X=NHCOMe
e. $X=C(COMe)_2$
f. $X=C(CO_2Et)_2$

(2) a. R=H
b. $R=n\text{-}C_3H_7$
c. $R=CH_2OH$
d. R=Ph
e. $R=SiMe_3$

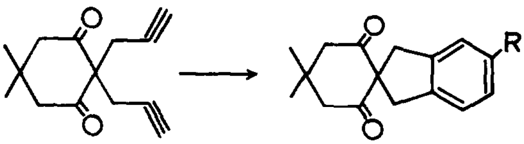
(3) a. $X=SO_2$, $R=CH_2OH$
b. $X=O$, $R=n\text{-}C_3H_7$
c. X=NHCOMe, $R=CH_2OH$
d. $X=C(COMe)_2$, R=H

The diynes (1b,c) are especially reactive. Thus (1c) and (2c) give (3a; 66%)[6] in ethanol-chloroform (1:1.5) after 10 min. at 79° [1 mole % $RhCl(PPh_3)_3$]

and (1b) and (2b) give (3b; 58%) [3h, 0^{o}, Et-OH, 0.5 mole % $RhCl(PPh_3)_3$]. Further illustrative examples include (1d) and (2c) which give (3c; 76%) and (1e) and (2a) which give (3d; 60%). In the absence of monoacetylenes the diynes (1a-f) give cyclodimers (4) in good yield, e.g. (1b) gives (4; X=O; 67%) [EtOH, 20 min., 25^{o}, 0.5 mole % $RhCl(PPh_3)_3$.

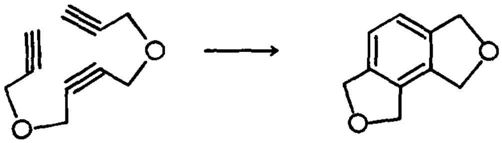


(4)



(5)

(6)
a.R=H
b.R=$(CH_2)_2C\equiv CH$



(7)

(8)

The reaction can also be used to synthesise spiro-compounds. Thus diyne (5) reacts with acetylene in ethanol [1 h, 40^{o}, 2 mole % $RhCl(PPh_3)_3$] to give (6a; 79%) and with 1,5-hexadiyne to give (6b; 59%) [40^{o}, 2 h, 1 mole % RhCl $(PPh_3)_3$]. The catalyst also promotes intramolecular [2+2+2] cyclo additions. Thus (7) cyclises to (8; 75%) in ethanol (2 h; 25^{o}) in the presence of 2 mole % $RhCl(PPh_3)_3$.

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6. All yields refer to isolated products.

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