Rhodium(I)-catalysed Tetramerisation of Allene

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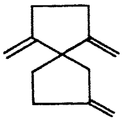
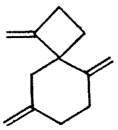
THERMAL reactions of allene give complex mixtures of dimers, trimers, and higher oligomers[1] including small amounts of spiro-compounds. Catalytic reaction with zerovalent nickel complexes, *e.g.* $Ni(CO)_2(PPh_3)_2$, gives a mixture of monocyclic trimers and tetramers.[2] We have found that halogenorhodium(I) complexes such as $Rh_2Cl_2(C_2H_4)_4$, together with 1—2 mol. of triphenylphosphine (50°; EtOH), gave allene tetramer [70—80%, $C_{12}H_{16}$, b.p. 59—60°/1 mm.; n_D^{25} 1·5055; *m/e* 160 (M^+)]; i.r. 1641 and 880 cm.$^{-1}$ (vinylidene groups). Catalytic hydrogenation of the tetramer (PtO_2; 3 mol. H_2) gave a paraffinic hydrocarbon, $C_{12}H_{22}$ [*m/e* 166 (M^+)] (this suggests a bicyclic structure for the tetramer); n.m.r. τ *ca.* 9·1 (3Me). The vinylidene groups are all unconjugated as no maleic anhydride adduct is formed and there are no i.r. peaks in the region (1580—1600 cm.$^{-1}$) expected for conjugated vinylidene groups.[3] The spiro[4,4]nonane and spiro[5,3]-nonane systems could be formed from 4 molecules of allene without skeletal rearrangement or hydrogen migration.† Hydrogen migration appears to be unlikely since no incorporation of deuterium into the tetramer was observed in EtOD, and skeletal rearrangement without hydrogen migration would be difficult. Hence there are two possible structures, (I) and (II), both consistent with the n.m.r. spectrum (100 Mc./sec.; CCl_4): τ 5·22 (m, 5H), 7·58 (m, 8H), and 8·30 (t, 2H, *J* 6 c./sec.). The spectrum in the olefinic proton region (τ 4—6) is complex and has not been assigned in detail. The absorption at τ 7·58 is also complex but may be assigned to singly allylic methylenes[1] ($C{=}C{-}CH_2{-}C$). The triplet at τ 8·30 suggests the presence of a $-CH_2-CH_2-C-$ system; the splitting must be due to coupling between the two non-equivalent methylenes, as irradiation at τ 7·58 caused decoupling. The partial structure of the tetramer is, therefore, $-C{=}C{-}CH_2{-}CH_2{-}C$. The n.m.r. spectrum further indicates the absence of doubly allylic methylenes ($C{=}C{-}CH_2{-}C{=}C$). Ozonolysis of the tetramer, followed by reduction (Zn), gave a triketone (n_D^{20} 1·4814) having ν_{max} (C=O stretch) at 1730 cm.$^{-1}$, which suggested that it was not a four-membered ring ketone. Thus the structure (I) is preferred. Jones and Lindsey[4] have prepared the same allene tetramer, by use of $RhCl(PPh_3)_3$ as catalyst in CH_2Cl_2 and have assigned it structure (I) on the basis of ozonisation and reduction to spiro[4,4]nonane.


(I)


(II)

Since a catalytic spiro-ring formation is unusual, we have examined various catalyst systems such as low-valent cobalt, rhodium, and iridium complexes. The tetramerisation was also effected with $RhX(PPh_3)_3$ (X = Cl, Br, or I) in CH_2Cl_2, the nature of the halogen ligand having little effect. In the absence of PPh_3, allene and $Rh_2Cl_2(C_2H_4)_4$ in benzene gave a monocyclic allene pentamer complex, $RhCl(C_{15}H_{20})$[5] of 1,2,4,7,8-pentamethylenecyclodecane and rhodium(I). The role of the phosphine ligand in Rh^I catalysts is very specific; no trialkyl or triarylphosphines or arsines other than triphenylphosphine were effective. Addition of π-acceptor ligands such as CO and RNC to the effective catalyst system $[Rh_2Cl_2(C_2H_4)_4-PPh_3]$ causes polymerisation rather than tetramerisation of allene. Structurally related iridium complexes such as $IrCl(PPh_3)_3$ give almost no reaction, but $CoCl(PPh_3)_3$[6] gives high polymers of allene. The most active catalyst species is probably a rhodium(I) complex of halide ion and 1 mol. of triphenylphosphine: a yellow complex of composition, $[RhCl(C_2H_4)PPh_3]_2$ [m.p. 200—220° (decomp.) in N_2,

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† A spiro[2,6]nonane skeleton is excluded because the formation of three-membered ring is unlikely and not supported by the n.m.r. spectrum.

130—150° in air; ν_{Rh-Cl} 280 cm.$^{-1}$; prepared by the reaction of $Rh_2Cl_2(C_2H_4)_4$ and PPh_3 (benzene)] was found to give ethylene upon treatment with an excess of allene, producing the tetramer even at room temperature.

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