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Reactions of Butadiene and Acetone Catalyzed by Pd(0) Phosphine Complexes

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Pd(0) complexes containing PPh_3 are known to catalyze the addition of active hydrogen containing molecules (*e.g.* alcohols, carboxilic acids, amine) to butadience dimer to yield mainly 1-substituted-2-7-octadiences.[1] We have recently made[2] a series of tertiary phosphine Pd(0) complexes PdL_n (n = 2, 3, 4), the coordination number being a function of the sterical hindrance of the phosphine. It is known that phosphine ligand size and basicity play an important role in homogeneous catalytic reactions. Examples are the hydrogenation catalytic properties of tris-(tertiary phosphine)chlororhodium,[3] the Ni catalyzed cyclodimerization of butadiene and dimerization of propylene.[4] Thus, it appeared interesting to us to investigate the catalytic activity of the PdL_n complexes in telomerization reactions of butadiene in order to compare their catalytic properties with those of systems containing PPh_3 as the phosphorous ligand.

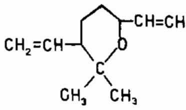
Preliminary results have shown that trialkylphosphine Pd(0) complexes may catalyze reactions which are barely catalyzed by the PPh_3 analogs and the products formed within the same reagent system may differ substantially according to the steric requirements of the ligand.

We have found that $Pd[PEt_3]_3$ and $Pd[P(cyclohexyl)_3]_2$ catalyze the addition of acetone to butadience dimer to yield compounds *1* - *4*, whereas PPh_3-based catalysts have been reported to be not active for this reaction.[5] Contrariwise PPh_3–Pd systems catalyze the addition of aldehydes to butadiene, alkylphosphine Pd complexes being less active.[5]

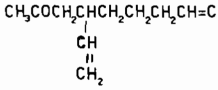
In a typical reaction butadiene (2.2 mol), acetone (4.3 mol) and water (1 mol) were reacted in presence of $Pd[PEt_3]_3$ (4 mmol) for 24 h at 80 °C. Fractional distillation of the reaction mixture afforded 1,3,7-octatriene (25 g), 2-dimethyl-3,6-divinyltetrahydropyran (*1*) (16 g), a mixture of methylnona-3,8-dienyl ketone (*2*) and methyl-2-vinyl-hepta-6-enyl ketone (*3*) (*ca.* 10:1; 20 g) and higher boiling oligomers. Compounds *2* and *3* were isolated by preparative glc.

$CH_3COCH_2CH_2CH{=}CHCH_2CH_2CH_2CH{=}CH_2$

2

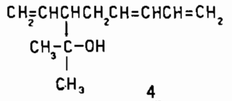


1



$CH_3COCH_2\underset{\underset{CH_2}{\overset{\|}{CH}}}{C}HCH_2CH_2CH_2CH{=}CH_2$

3



$CH_2{=}CH\underset{CH_3-\underset{CH_3}{C}-OH}{CH}CH_2CH{=}CHCH{=}CH_2$

4

The structure of *1* is consistent with the mass spectrum fragmentation pattern (M^+ 166), i.r. spectrum [cm^{-1}, 1640, 990, 910 (=CH and =CH_2), 1120, 1070 (C–O–C)]. The pmr spectrum of *1* shows four methyl resonances clearly indicating that both *cis* and *trans* isomers of *1* (*ca.* 1:3) are present. Due to overlapping signals the stereochemistry of the two isomers has not yet been elucidated [δ, 1.08 *s*, 1.17 *s* (major isomer), 1.05 *s* (minor isomer) (6H, CH_3); 1.5 *m* (4H, CH_2); 2.0 *m* (1H, –C–CH); 3.9 *m* (1H, –O–CH); 4.8 - 5.2 (4H, =CH_2); 5.4 - 6.2 (2H, =CH)].

The structures of *2* and *3* (M^+ 166) follow from their spectral properties. *2*, i.r. spectrum (cm^{-1}), 1720 (ketone carbonyl), 1640, 990, 910 (terminal olefin), 968 (*trans* double bond); pmr spectrum (δ), 1.4 *m* (2H, aliphatic CH_2), 1.8 - 2.2 (4H, allylic CH_2), 2.0 *s* (3H, –$COCH_2$), 2.35 *d* (2H, –$COCH_2$), 4.9 *m* (2H, =CH_2), 5.2 - 5.8 (3H, =CH). The i.r. band at 968 cm^{-1} indicates that *2* has prevalently *trans* structure. *3*, i.r. spectrum (cm^{-1}), 1720 (ketone carbonyl), 1640, 995, 910 (terminal olefin); pmr spectrum (δ), 1.35 *m* (4H, aliphatic CH_2), 1.9 - 2.1 (2H, allylic CH_2), 1.95 *s* (3H, –$COCH_3$), 2.3 - 2.6 (3H, –$COCH_2$ and –C–CH), 4.8 - 5.0 (4H, =CH_2), 5.4 - 5.8 (2H, =CH).

If $Pd[P(cyclohexyl)_3]_2$ (1.7 mmol) is used as the catalyst (butadiene 1 mol, acetone 2 mol, water 0.5 mol, 24h, 80 °C) 1,3,7-octatriene (21 g) and 2-methyl-3-vinyl-octa-5,7-dien-2-ol (*4*) (14 g), are the major products. The structure of *4* is consistent with the mass spectrum fragmentation pattern (M^+ 166), i.r. spectrum (cm^{-1}, 1640, 1600, 1000, 910), pmr spectrum [δ, 1.10 *s*, 1.14 *s* (3H each, CH_3); 2.0 *m* (2H, allylic CH_2); 2.5 *m* (1H, C–CH–); 3.10 *s* (1H, OH) 4.7 - 5.1 (4H, =CH_2); 5.3 - 6.8 (4H, =CH)]. The ^{13}C spectrum shows that *4* is a mixture of *cis* and *trans* isomers (*ca.* 2:1 in favour of the *cis* isomer) as proved by the allylic CH_2 resonances [δ from TMS, 27.4 (*cis* isomer), 32.5 (*trans* isomer)].

If Pd$[PPh_3]_3$ is used as the catalyst the reaction is sluggish and compounds *1* - *4* are formed in very low yields.

The presence of water in the reaction mixture is essential for the formation of compounds other than octatriene with both Pd$[P(cyclohexyl)_3]_2$ and Pd$[PEt_3]_3$ catalysts.*

The formation of pyran *1* and tertiary alcohol *4* may be explained with a mechanism similar to that proposed by Tsuji[5] in the reaction of aldehydes with butadiene in the presence of Pd–PPh_3 complexes. The formation of ketones *2* and *3* might be tentatively explained assuming the formation of a CH_3COCH_2–Pd complex catalyzed by water, which is active for olefin insertion.**

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*Trace quantities of octa-2,7-dien-1-ol and octa-1,7-dien-3-ol were detected by glc.[6]

**Bennet *et al.*[7] have recently reported that addition of acetone to PtC_6H_8(diphos) to yield $PtCH_2COCH_3(C_6H_9)$-(diphos) is catalyzed by water through the probable intermediate $PtOH(C_6H_9)$(diphos).