Journal of Organometallic Chemistry, 88 (1975) C41—C43

Preliminary communication

CONVERSION OF BUTADIENE INTO 2,4,6-OCTATRIENE BY Pd^0 PHOSPHINE COMPLEXES

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(Received February 6th, 1975)

Summary

CO_2 enhances the catalytic effect of tertiary phosphine—palladium complexes in the dimerization of butadiene to 1,3,7-octatriene and the subsequent isomerization to 2,4,6-octatriene.

The dimerization of butadiene to 1,3,7-octatriene catalyzed by palladium complexes is well known [1]. It was recently shown that the catalytic activity of $Pd[PPh_3]_4$ and $Pt[PPh_3]_3$ in the dimerization reaction is greatly enhanced if the reaction is carried out under CO_2 pressure [2]. We are currently studying the dimerization of butadiene catalyzed by several Pd^0 phosphine complexes [3] in the presence of CO_2 in order to gain some insight into the effects of CO_2 on the catalyst, and we have observed that the PdL_n,CO_2 system (L = tertiary phosphine) is a very effective catalyst for the transformation of butadiene to 2,4,6-octatriene*. In Table 1 the results which have been obtained with $Pd[PEt_3]_3$, $Pd[P(C_6H_{11})_3]_2$ and $Pd[PPh_3]_3$ are summarized.

Withdrawal of a small portion of the reaction mixture shortly after the end of the pressure drop due to the consumption of butadiene revealed that 1,3,7-octatriene was the main product. This shows that the reaction proceeds in two steps, the formation of 1,3,7-octatriene followed by its isomerization to 2,4,6-octatriene. The isomerization does not seem to be catalyzed by a Pd^0 species. This has been shown treating 1,3,7-octatriene with $Pd[PEt_3]_3$ both in presence and absence of CO_2. In neither case was 2,4,6-octatriene obtained, whereas the catalyst which is recovered from the $Pd[PEt_3]_3$,CO_2 and butadiene reaction, and which contains only traces of metallic palladium, is an effective catalyst in the absence of CO_2 for either dimerization of butadiene or isomerization of 1,3,7-octatriene. Since larger quantities of metal

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*In the absence of CO_2 these complexes catalyze the dimerization of butadiene to 1,3,7-octatriene but the degree of conversion is low even after long reaction times.

TABLE 1

DIMERIZATION OF BUTADIENE [a]

Catalyst (mmol)	Reaction time (h)	Conversion (%)	1,3,7-Octatriene (%)	2,4,6-Octratriene (%) [b]	Others (%) [c]
$Pd[PEt_3]_3$ (0.8)	1.25	80	95	traces	4
$Pd[PEt_3]_3$ (0.8)	3.25		traces	92 (7:7:31:55)	6
$Pd[P(C_6H_{11})_3]_2$ (0.6)	6.5	80	95	traces	4
$Pd[P(C_6H_{11})_3]_2$ (0.6)	9		traces	90 (8:8:30:53)	0
$Pd[P(C_6H_5)_3]_3$ (0.7)	12	60	82	traces	15
$Pd[P(C_6H_5)_3]_3$ (0.7)	69		9	84 (6:6:30:58)	5

[a] 200 ml autoclave, butadiene 25 g (0.46 mol), CO_2 was introduced at room temp. in the reaction vessel already charged with butadiene to a total pressure of 8-9 kg/cm^2, solvent 40 ml of benzene, temp. 110°C.

[b] B p. 84-88 °C (100 mmHg): 4 isomers were detected by GLC (0.6% diethylglycol succinate on 60/80 mesh Carbopack A, 2 mm × 2 m column, 90°C). The *trans,trans,trans* isomer was isolated by cooling the isomeric mixture at −15 °C and crystallizing the resulting white crystalline material from methanol several times [4]. The ^{1}H NMR spectra of the *t,t,t*-isomer[δ($CDCl_3$), 1.70 d (J 7 Hz, CH_3), 5.60 m - 5.95 m (CH)] and of the isomeric mixture are similar.

[c] 4-Vinylcyclohexene and other unidentified products.

were recovered from the $Pd[P(C_6H_{11})_3]_2$ and $Pd[PPh_3]_3$ runs and the PPh_3 system found to be the least active catalyst, it seems that the isomerization is not due to palladium metal.

These preliminary results suggest that CO_2, in the presence of butadiene, assists the formation of a Pd^{II} species which is active both for the dimerization of butadiene to 1,3,7-octatriene and for the isomerization of 1,3,7-octatriene to 2,4,6-octatriene.

Acknowledgment

The authors thank Mr. S. Italia for his skillful technical help.

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