Journal of Organometallic Chemistry, 55 (1973) 405–407
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CATALYSIS BY PALLADIUM SALTS

IV. SELECTIVE HYDROGENATION WITH FORMIC ACID IN THE PALLADIUM CATALYSED DIMERISATION OF 1,3-BUTADIENE; SYNTHESES OF 1,7-OCTADIENE

P. ROFFIA, G. GREGORIO, F. CONTI and G. F. PREGAGLIA
Montedison S.p.A., Research Centre of Bollate, Milano (Italy)
R. UGO
Istituto di Chimica Generale, C.N.R. Centre, The University, Milano (Italy)

(Received October 2nd, 1972)

SUMMARY

Linear dimerisation of 1,3-butadiene in the presence of formic acid has been studied. 1,7-Octadiene has been obtained in good yield as the final product.

RESULTS AND DISCUSSION

We previously described the syntheses of zerovalent triphenylphosphine complexes of Pd and Pt by reduction of $(PPh_3)_2MCl_2$ (M=Pd, Pt) with alkaline metal alkoxides in the presence of excess phosphine[1,2]. We have now found that by adding an excess of 1,3-butadiene instead of phosphine ligands we can obtain a stable benzene or toluene solution, which can be freed from alkoxides by washing with water and drying over anhydrous sodium sulphate. This solution does not catalyse the dimerization of 1,3-butadiene*. However the addition of protonic substances, in 1/1 molar ratio to the palladium, produces a very active catalyst for the linear dimerization of 1,3-butadiene to 1,3,7-octatriene (I).

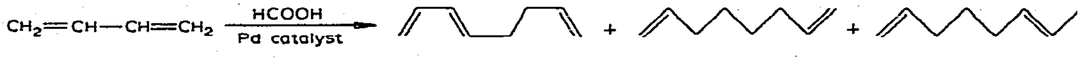
During further studies on the influence of the acidic properties of various cocatalysts on the selectivity and the activity of the linear dimerization catalyst, we noticed that formic acid shows anomalous behaviour**. It not only catalyses the dimerization reaction[6] but decomposes, and brings about hydrodimerization of 1,3-butadiene to 1,7-octadiene (II), with CO_2 evolution. The selectivity in 1,7-dienes can be as high as 80% (based on formic acid). The other hydrogenation products are 1,6-

---

* A pale yellow powder (decompn. temp. −30°) has been obtained by cooling this toluene solution at −78°, washing the precipitate with liquified n-butane, and drying on the diffusion pump at −50°[3]. This material does not contain chlorine. The NMR spectrum of a sample dissolved at −60° in $CDCl_3$ shows two broad peaks (relative intensities 1/2) centered at 4.4 and 5.1 τ, which we tentatively attribute to coordinated butadiene. Raising the temperature above 0° leads to the disappearance of the two broad signals, production of a new pattern very similar to that reported for the intermediate in nickel-catalyzed butadiene cyclic dimerizations[4].

** While this work was in progress other authors[10] reported a rather similar investigation.

octadiene (III) and a small amount of a mixture of n-butenes.



(I) (II) (III)

Typically, a benzene solution of sodium propoxide 0.5 *M* (0.7 ml) was added dropwise to a benzene suspension of $(PPh_3)_2PdCl_2$ (0.150 g) in a 1,3-butadiene atmosphere at 25°. The mixture was washed with water until the pH was 7, and was then dried over sodium sulphate. It was then maintained at 80° for 9 h in a Carius tube, after addition of 1,3-butadiene (6.5 g) and 99% formic acid (0.6 ml). The Carius tube was opened at −78° and the gas mixture collected and analysed by GLC. It contained unchanged 1,3-butadiene (1.6 g), a very small amount of 1- and 2-butenes, and carbon dioxide in an amount corresponding to complete decomposition of the formic acid taken. The final solution did not show IR absorptions in the region 1800–1600 cm^{-1} corresponding to $\nu(C{=}O)$ of carboxylic acids or its esters. The liquid reaction products were (I) (3.60 g), (II) (1.03 g), and (III) (0.12 g), these were separated by preparative GLC and characterized by IR, NMR and mass spectroscopy, and elemental analyses.

The catalytic decomposition of formic acid, followed by hydrogen transfer to unsaturated substrates, takes place also when preformed 1,3,7-octatriene (I) is added to the catalytic system instead of 1,3-butadiene. However in this case the yields and the selectivity to form (II) are lower, probably because of the concomitant decomposition of the catalytic complex with release of metallic palladium. Preformed zerovalent palladium complexes, such as $(PPh_3)_2Pd$(*p*-benzoquinone) or $(PPh_3)_4Pd$, are also active catalysts for the hydrodimerization of 1,3-butadiene. The reaction is thus thought to proceed by protonation of the zerovalent palladium species by formic acid, then reaction with the polyolefin, followed by decomposition of the intermediate formato complex and formation of a palladium hydride intermediate, by a mechanism similar to that proposed for the synthesis of an osmium dihydride[8].

The unusual selectivity of the reduction is probably due to the fact that the conjugated part of the π system of 1,3,7-octatriene inserts more easily than the terminal olefin into the Pd–H bond[11], the driving force being related to the formation of the π-allyl system[11]. Such π-allyl intermediates are probably also formed during the butadiene dimerisation, and not only from preformed 1,3,7-octatriene[9].

EXPERIMENTAL

The liquid reaction products were separated and identified by GLC using a 1500 Carbowax on Chromosorb P column 5 m length. The gaseous reaction products were separated and identified by GLC using γ-butyrolactone on Chromosorb P, column 6 m length. The carbon dioxide was also determined by a gravimetric method (as $BaCO_3$).

The IR spectra were recorded on a Perkin–Elmer 225 spectrophotometer, and the mass spectra on a Hitachi–Perkin–Elmer RMU/6 instrument; NMR spectra were recorded on a Varian HA-100 spectrometer.

All the reactions were carried out in a Carius tube in the absence of oxygen and moisture. At the end of the reaction the Carius tube was cooled to −78°, and opened at this temperature in order to avoid a loss of gaseous products.

REFERENCES

1 P. Roffia, F. Conti and G. Gregorio, *Chim. Ind.* (*Milan*), 53 (1971) 361.
2 P. Roffia, F. Conti and G. Gregorio, *Chim. Ind.* (*Milan*), 54 (1972) 317.
3 P. Roffia, F. Conti and G. Gregorio, to be published.
4 P. W. Jolly, I. Tkatchenko and G. Wilke, *Angew. Chem. Int. Ed. Engl.*, 10 (1971) 328.
5 J. M. Brown, B. T. Golding and M. J. Smith, *Chem. Commun.*, (1971) 1240.
6 P. Roffia, G. Gregorio, F. Conti and G. F. Pregaglia, *It. Pat. Appl.*, 19,592 A/71, 19,593 A/71.
7 Go Hata, K. Takahashi and A. Miyake, *J. Org. Chem.*, 36 (1971) 2116 and references therein.
8 K. R. Laing and W. R. Roper, *J. Chem. Soc. A*, (1969) 1890.
9 P. Roffia *et al.*, to be published.
10 S. Gardner and D. Wright, *Tetrahedron Lett.*, (1972) 163.
11 A. Andreetta, F. Conti and G. F. Ferrari, in R. Ugo (Ed.), *Aspects of Homogeneous Catalysis*, 1 (1971) 203.