

THE DIMERIZATION OF BUTADIENE BY PALLADIUM COMPLEX CATALYSTS

S. Takahashi, T. Shibano and N. Hagihara

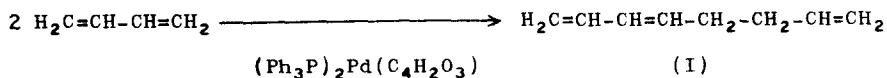
The Institute of Scientific and Industrial Research,
Osaka University, Sakai, Osaka

(Received 21 April 1967)

It has recently been reported that dimerizations of butadiene are carried out with cobalt- (1), iron- (2), nickel- (3) or rhodium- (4) containing complex catalysts to form methylheptatriene and/or n-octatriene.

In the course of an examination on reactions of dienophile coordinated palladium-phosphine complexes with butadiene, we have found that bis(triphenylphosphine)(maleic anhydride)palladium (5) catalyzed a dimerization of butadiene to form a linear butadiene dimer in good yield.

The dimerization of butadiene was performed in solvents such as benzene, tetrahydrofuran and acetone at a temperature between 100 - 120° in the presence of the catalyst. Thus, in a stainless-steel autoclave 13 g of dried butadiene, 20 ml of acetone and 219 mg (0.3 mmol) of bis(triphenylphosphine)(maleic anhydride)-palladium were heated at 115° with stirring for 7 hrs.. Gas chromatographic analysis indicated that the reaction product (I) was only one isomer of butadiene dimers (11 g, 85% yield), which was separated from solvent by fractional distillation.



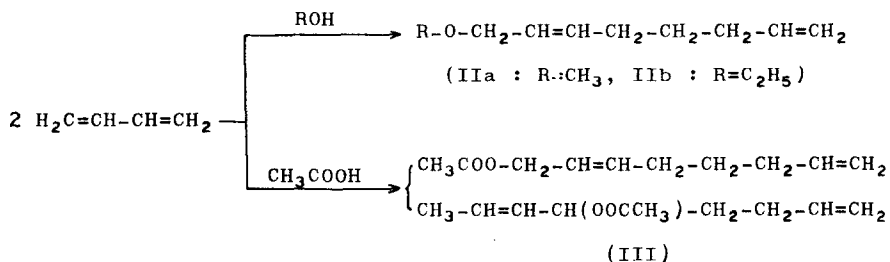
The product I, a colorless liquid of b.p. 124 - 125°, n_D^{20} 1.4682, slowly polymerized when left standing in air. Anal. Calcd. for C_8H_{12} : C, 88.82; H, 11.18; Mol. Wt., 108.2. Found: C, 88.75; H, 11.16; Mol. Wt., 111 (cryoscopic method in benzene).

The product I was confirmed to be n-octatriene by the fact that the compound I absorbed three moles of hydrogen with platinum catalyst to form n-octane.

The positions of the three double bonds in the compound I were established by the following data. The ultraviolet absorption spectrum (λ_{\max} 225 m μ (ϵ , 22000)) indicated the conjugation of two double bonds. The infrared spectrum showed the presence of terminal double bonds and conjugated double bonds. The n.m.r. spectrum showed the presence of two =CH₂, four =CH- groups and four methylene protons. Both of the i.r. and n.m.r. spectrum confirmed the absence of methyl group. The above evidence indicated that the dimer I was octatriene-1.3.7.

Physical properties of dimer I, moreover, are in well agreement with those of trans-octatriene-1.3.7 prepared by Butler and Brooks (6). When benzene or tetrahydrofuran was used as solvent, octatriene-1.3.7 was also obtained in 55 - 80% yield.

The dimerization of butadiene was also carried out in alcohols and carboxylic acid. In contrast to the reaction in acetone or benzene, the dimerization in alcohols such as methanol, ethanol and isopropylalcohol proceeded smoothly even at lower temperature (40 - 80°) to give 1-alkoxyoctadiene-2.7 and/or octatriene-1.3.7 in good yield. For instance, the reaction in methanol at 70° in the presence of bis(triphenylphosphine)(maleic anhydride)palladium catalyst proceeded much rapidly and gave a product IIa in 90% yield based on fixed butadiene. By fractional distillation the product IIa, a colorless liquid of b.p. 94 - 95° (70 mm.), n_D^{20} 1.4409, was easily separated from the reaction mixture. From the elemental analysis, molecular weight measurement and hydrogen absorption with platinum catalyst, the compound IIa was found to be a methanol-butadiene dimer 1:1 adduct which contains two double bonds. Anal. Calcd. for C₉H₁₆O : C, 77.09; H, 11.50; Mol. Wt., 140.2. Found : C, 76.63; H, 11.46; Mol. Wt., 140 (cryoscopic method in benzene).



The infrared spectrum of the compound IIa showed the presence of a terminal double bond ($991, 910 \text{ cm}^{-1}$) and an ether group (1115 cm^{-1}). The n.m.r. spectrum showed the presence of a methoxy group (6.78τ , singlet) and a partial structure, $-O-CH_2-CH=$ (6.22τ , doublet ($J=4.0 \text{ cps.}$)). Among the possible structures for the compound IIa, the proposed structure, 1-methoxyoctadiene-2.7, completely satisfied all the observations.

From the reaction in abs. ethanol, octatriene-1.3.7 and 1-ethoxyoctadiene-2.7 (IIb: b.p. $105 - 107^\circ$ (70 mm.), $n_D^{20} 1.4422$) were obtained in 50% and 33% yield, respectively. However, use of isopropylalcohol as solvent led to produce octatriene-1.3.7 in 72% yield as a main product. By the similar reaction in acetic acid at 120° , a mixture of esters (III: b.p. $72 - 82^\circ$ (6 mm.)) was obtained in about 30% yield. The formation of II or III in these systems is understood to involve the 1,4-addition of alcohol or acetic acid to conjugated diene in octatriene.

It has been also found that bis(triphenylphosphine)(p-benzoquinone)palladium (5) and tetrakis(triphenylphosphine)palladium catalyze the dimerization of butadiene to form 1-alkoxyoctadiene-2.7 and/or octatriene-1.3.7 in alcoholic media.

REFERENCES

1. S. Otsuka, T. Taketomi and T. Kikuchi, J. Chem. Soc. Japan, Ind. Chem. Sect., 66, 1094 (1963); D. W. Wittenberg, Angew. Chem., 75, 1124 (1963); S. Tanaka, K. Mabuchi and N. Shimazaki, J. Org. Chem., 29, 1626 (1964).
2. T. Saito, T. Ono, Y. Uchida and A. Misono, J. Chem. Soc. Japan, Ind. Chem. Sect., 66, 1099 (1963); H. Takahashi, S. Tai and M. Yamaguchi, J. Org. Chem., 30, 1661 (1965).
3. H. Müller, D. Wittenberg, H. Seibt and E. Scharf, Angew. Chem., 77, 318 (1965); H. Seibt and N. v. Kutepow, Belg. Patent 635483 (Chem. Abst., 61, 11891 (1964)).
4. T. Alderson, E. L. Jenner and R. V. Lindsey, Jr., J. Am. Chem. Soc., 87, 5638 (1964).
5. S. Takahashi and N. Hagihara, in preparation.
6. G. B. Butler and T. W. Brooks, J. Org. Chem., 28, 2699 (1963).