The Dimerization of Butadiene in Methanol by a Palladium Complex Catalyst

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(Received July 29, 1967)

In a previous work[1] we have reported how palladium complexes catalyzed a dimerization of butadiene to form a linear dimer. The dimerization of butadiene in benzene, tetrahydrofuran, or acetone gave octatriene-1.3.7, while the reactions in alcohols proceeded more smoothly to give 1-alkoxyoctadiene-2.7 and/or octatriene-1.3.7, depending on the nature of the alcohols employed. We now wish to report in detail on studies of the products derived from the dimerization reaction in methanol. It was found that the dimerization of butadiene in methanol at 70°C in the presence of bis(triphenylphosphine)(maleic anhydride)palladium gave 1-methoxyoctadiene-2.7 (85%), plus small amounts of octatriene-1.3.7 (3%) and an isomer (I) (5%) of methoxyoctadiene. When tetrakis(triphenylphosphine)platinum was used as the catalyst, the reaction proceeded slowly, but the proportion of the isomer I in the products was relatively greater. The pure isomer I was isolated from this reaction mixture by preparative gas chromatography. The isomer I is a colorless liquid with a bp of 145—146°C, n_D^{20} 1.4321. (Found: C, 77.17; H, 11.51%. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%.) The infrared spectrum of the compound I showed the presence of terminal double bonds (994, 923, 910 cm^{-1}) and an ether group (1101 cm^{-1}). The NMR spectrum showed the presence of a methoxy group (6.88 τ), two $=CH_2$ and two $=CH-$ groups, and a partial structure, $=CH-CH(OCH_3)-CH_2-$. These spectra indicate that the compound I is 3-methoxyoctadiene-1.7, $H_2C=CH-CH(OCH_3)-CH_2-CH_2-$

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[1] S. Takahashi, T. Shibano and N. Hagihara, *Tetrahedron Letters,* **1967**, 2451.

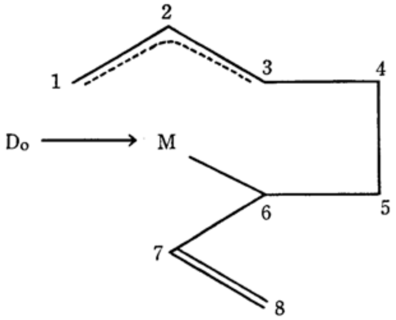
CH_2–CH=CH_2.*[1]

It is obvious that the formation of octatriene-1.3.7 in this catalytic dimerization in aprotic solvents involves hydrogen migration. Accordingly, the increasing rate of the reaction in protic solvents suggests the participation of the proton of the solvent. Because of our interest in the mechanism, therefore, the dimerization was carried out in CH_3OD. The main product, II (bp 164°C, n_D^{20} 1.4416), was recognized as monodeuterio-1-methoxyoctadiene-2.7 on the basis of its infrared (ν_{C-D} 2145 cm^{-1}) and NMR spectra. The position of the deuterium in the compound II could not be determined simply because the signals of the protons on C^4 and C^6 completely overlapped in its NMR spectrum. In order to distinguish them, the terminal double bond in the compound II was hydrogenated with $Ru(Ph_3P)_3Cl_2$ catalyst[2] in benzene-ethanol. It was confirmed that the compound II was 1-methoxy-6-deuteriooctadiene-2.7 because the hydrogenated product, III (bp 85—86°C/37 mmHg, n_D^{20} 1.4298), was found to be 1-methoxy-6-deuteriooctene-2 on the basis of a comparison of its NMR spectrum with that of 1-methoxyoctene-2 (bp 82—83°C/33 mmHg, n_D^{20} 1.4307).

$$2H_2C{=}CH{-}CH{=}CH_2 + CH_3OD \rightarrow CH_3{-}O{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CHD{-}CH{=}CH_2 \quad \text{(II)}$$

$$\xrightarrow{H_2} CH_3{-}O{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CHD{-}CH_2{-}CH_3 \quad \text{(III)}$$

These results suggest the presence of a π-allyl intermediate (IV) similar to that proposed by Wilke *et al.*,[3] although attempts to isolate the intermediate have thus far been unsuccessful. Thus, octatriene-1.3.7 may be produced through a reaction course which involves the $C^4 \rightarrow C^6$ migration of hydrogen, and two isomers of the methanol adduct, through the two different modes of the addition of methanol to the intermediate (1, 6 addition and 3, 6 addition).



(IV) M=Pt or Pd

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*[1] The isomer of the acetic acid adduct, which was characterized as 4-acetoxyoctadiene-2.7 in our previous paper,[1] may really have the 3-acetoxyoctadiene-1.7 structure, similar to that of the isomer of the methanol adduct.

[2] P. S. Hallman, D. Evans, J. A. Osborn and G. Wilkinson, *Chem. Commn.*, **1967**, 305.

[3] G. Wilke, B. Bogdanović, P. Hardt, P. Heimbach, W. Kiem, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter and H. Zimmermann, *Angew. Chem.*, **78**, 157 (1966).