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ORGANIC SYNTHESIS BY MEANS OF NOBLE METAL COMPOUNDS. XLII[1)] REACTION OF BUTADIENE AND ALDEHYDES CATALYSED BY PALLADIUM-TRIPHENYLPHOSPHINE COMPLEXES

K. Ohno, T. Mitsuyasu, and J. Tsuji

Basic Research Laboratories, Toray Industries, Inc., Kamakura, Japan

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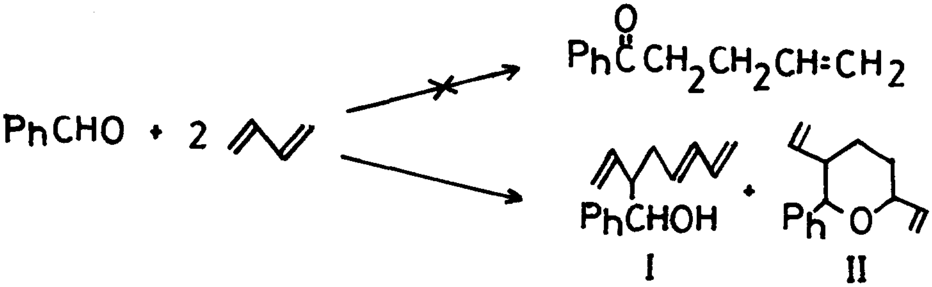
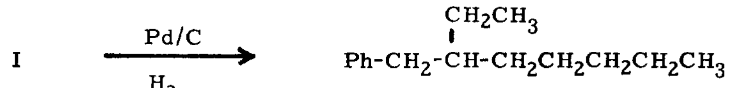
We found the palladium catalysed decarbonylation of aldehydes and proposed a mechanism involving the formation of acyl-palladium complex as an intermediate of the decarbonylation.[2)] Based on this mechanism we have attempted reactions of olefin with aldehyde, expecting insertion of olefin into the acyl-palladium bond, which might be formed by oxidative addition of aldehyde to palladium complex. In the course of this study, we tried reaction of butadiene and aldehyde and found an unexpected new reaction; namely the formation of 1- substituted 2-vinyl-4,6-heptadien-1-ol (I) and 2-substituted 3,6-divinyltetrahydropyran (II). Recent report by Haynes[3)] on the formation of divinyltetrahydropyran by reaction of formaldehyde and butadiene prompted us to report our independent and considerably different results.



Typically, benzaldehyde (11 g) and butadiene (25 ml) were allowed to react at 80° for 10 hrs in the presence of π -allylpalladium chloride (0.18 g), sodium phenoxide (0.8 g) and triphenylphosphine (0.26 g). The product was isolated by distillation (110-140°/ 4 mm, 14 g), which contained two compounds (I and II; ratio 2.6 : 1). They were seperated by column chromatography. The compound I was found to be 1-phenyl-2-vinyl-4,6-heptadien-1-ol based on the following data. Correct analysis and molecular weight determined by mass spectroscopy support the formula of $C_{15}H_{18}O$. Ir ; 3444 cm^{-1} (-OH); 1645 cm^{-1}, 995 cm^{-1} and 910 cm^{-1} (-CH•CH$_2$); 1082 cm^{-1}, 1057 cm^{-1} and 1037 cm^{-1} (-C-O). nmr (100 MHz, $CDCl_3$) : 7.4-8.0 (3H, allylic) 6.73 (1H, -OH), 5.54 (1H, PhCH-O-), 3,3 - 5.2 (8H, olefinic), 2.81 (5H, aromatic). The data coincide with the structure. Hydrogenation and hydrogenolysis of the compound I over palladium on carbon absorbed 4 moles of hydrogen to give 3-benzyloctane (III).



$$\mathrm{I} \xrightarrow[H_2]{Pd/C} \mathrm{Ph{-}CH_2{-}\underset{}{\overset{CH_2CH_3}{CH}}{-}CH_2CH_2CH_2CH_2CH_3}$$

III

The structure of II was determined as 2-phenyl-3, 6-divinyltetrahydropyran. Gas chromatogram showed the presence of four components. They are stereoisomers and three of them(II-A, B and C) were isolated in pure state by repeated column chromatography. Their structures were determined by nmr spectra shown in Table I to be 2-phenyl-trans-3, cis-6-divinyltetrahydropyran (II A), 2-phenyl-cis-3, cis-6-divinyltetrahydropyran (11-B), and 2-phenyl-cis-3, trans-6-divinyltetrahydropyran (II-C). Analyses and molecular weight determination of these isomers support the formula of $C_{15}H_{18}O$.

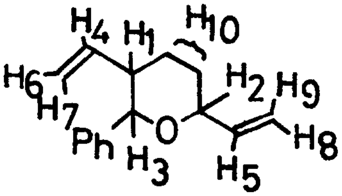
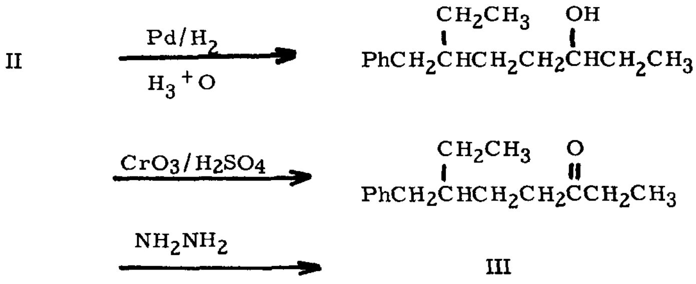


Table I

(τ value, 100 MHz, $CDCl_3$)

	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}
II-A	7.84	6.12	6.05	4.56	4.16	5.22	5.26	5.01	4.81	7.95-8.6
	$J_{1,3}$	10 cps	$J_{4,7}$	16 cps	$J_{4,6}$	8 cps	$J_{5,9}$	16 cps	$J_{5,8}$	10 cps
II-B	7.50	6.02	5.46	3.9-4.3		5.20	5.26	4.96	4.72	7.9-8.6
	$J_{1,3}$	2 cps	$J_{4,7}$	15 cps	$J_{4,6}$	8 cps	$J_{5,9}$	16 cps	$J_{5,8}$	10 cps
II-C	7.48	5.48	5.19	3.86-4.26		5.16	5.21	4.81	4.82	7.90-8.50
	$J_{1,3}$	3 cps	$J_{4,7}$	18 cps	$J_{4,6}$	8 cps	$J_{5,9}$	16 cps	$J_{5,8}$	10 cps

In order to confirm the structure chemically, the compound II was converted into III by the following steps : Hydrogenation with ring opening to give 6-benzyl-3-octanol, oxidation with CrO_3 to give 6-benzyloctanone and Wolff Kishner reduction to 3-benzyloctane (III),



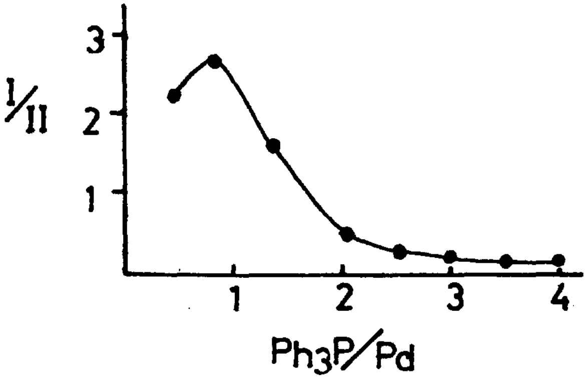
$$\mathrm{II} \xrightarrow[H_3{}^+O]{Pd/H_2} PhCH_2\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_2\overset{OH}{\overset{|}{C}}HCH_2CH_3$$

$$\xrightarrow{CrO_3/H_2SO_4} PhCH_2\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$$

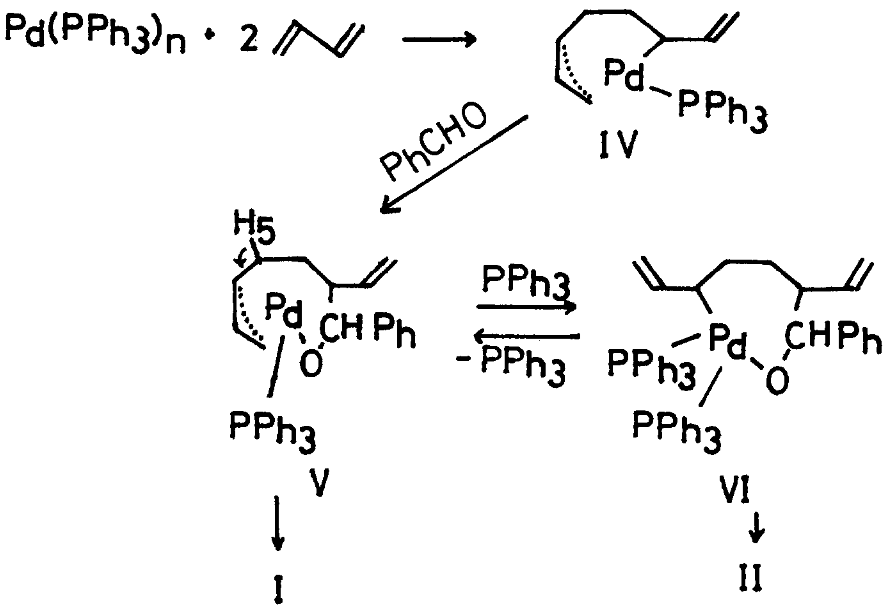
$$\xrightarrow{NH_2NH_2} \mathrm{III}$$

It was found that relative amounts of I and II can be controlled by the molar ratio of PPh_3/Pd in the catalyst. The unsaturated alcohol (I) is predominant when PPh_3/Pd is nearly one. On the other hand, the pyran (II) is obtained as a main product when PPh_3/Pd is larger than 2. The relationship is shown in Fig. 1

Fig.1



We propose the following mechanism for this reaction. At first butadiene dimerizes to give a π-allylpalladium complex (IV), which then reacts with aldehyde to give V. When one mole of phosphine is present, the complex V collapses with transfer of the hydrogen from C_5 to the oxygen to form the alcohol I. The cyclization takes place by the ligand coupling to give II when two moles of phosphine coordinate to the complex.



This unique reaction is applicable to both aliphatic and aromatic aldehydes including formaldehyde. This type of the reaction of conjugated dienes with hetro polar double bond seems to be a general reaction. As another example, we have found the cyclization reaction of isocyanate.[4)]

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