Palladium-catalysed Exchange of Allylic Groups of Ethers and Esters with Active-hydrogen Compounds

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Summary The allylic groups of ethers and esters exchange with a variety of active hydrogen compounds in the presence of palladium catalysts.

IN the degradation of octa-2,7-dienyl phenyl ether to phenol and octa-1,3,7-triene with a palladium catalyst,[1] Smutny observed the formation of a small amount of 2- and 4-(octa-2,7-dienyl)phenol,[2] which is obviously not formed *via* a normal or abnormal Claisen rearrangement of the ether.

We find that the octadienyl group of octa-2,7-dienyl phenyl ether exchanges with a variety of active-hydrogen compounds in the presence of palladium catalysts, and further research has led to the finding that the allylic compounds (I) react with active-hydrogen compounds to give allylic derivatives of the active-hydrogen compounds by an intermolecular exchange of the allylic groups of (I) with the atom to which the active hydrogens are bonded.† This type of reaction applies to methanol, benzyl alcohol, phenols, carboxylic acids, primary and secondary amines, and active methylene compounds such as methyl acetoacetate.

$$R^1O\text{–}CH_2\cdot CH{=}CHR^2$$

(I) R^1 = Ph, Me, $PhCH_2$, MeCO;† R^2 = H, Me, $-CH_2\cdot CH_2\cdot CH_2\cdot CH{=}CH_2$

Allyl and substituted-allyl phenyl ethers were more reactive than the corresponding carboxylates and in the reaction of the ethers, the products were generally obtained in high yields. Bis(triphenylphosphine)palladium chloride plus sodium phenoxide, palladium acetate plus triphenylphosphine, and zerovalent palladium complexes such as tetrakis(triphenylphosphine)palladium and (maleic anhydride)bis(triphenylphosphine)palladium are effective catalysts.

The products were identified by elemental analysis, molecular-weight measurement, i.r. and n.m.r. spectroscopy and by comparison with authentic samples.[1,3-5] All the reactions were carried out at 85°. For example, the reaction of diethylamine (0·1 mole) with allyl phenyl ether

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† For R^1 = Me or $PhCH_2$, it is necessary to add phenol to obtain the migration products in fairly good yields.

(0·05 mole) at 85° for 1 hr in the presence of (maleic anhydride)bis(triphenylphosphine)palladium (0·1 mmole) gave allyldiethylamine quantitatively; b.p. 112°, n_D^{25} 1·4186; ν_{max} 1643, 994, and 914 cm^{-1} ($-CH{=}CH_2$); τ 9·0 and 7·6 (t and q, $-CH_2{\cdot}CH_3$), 7·0 (d, $-CH_2{\cdot}C{=}C$), and 4·0—5·0 (m, olefinic protons). The reaction of methyl acetoacetate (0·1 mole) with octa-2,7-dienyl phenyl ether (0·05 mole) in the presence of $PdCl_2(Ph_3P)_2$ (0·05 mmole) and sodium phenoxide (0·5 mmole) for 2 hr afforded methyl 2-acetyldeca-4,9-dienoate and methyl 2-(octa-2,7-dienyl)-2-acetyldeca-4,9-dienoate in 84 and 7% yield, respectively.

Easy fission of the allylic carbon–oxygen bond is shown by the reversibility of the reaction of octa-2,7-dienyl phenyl ether with acetic acid, which gave a 85 : 15 mixture of (II) and (III).[4] The reverse reaction using a 74 : 26 mixture of (II) and (III) results in a predominant formation of octa-2,7-dienyl phenyl ether (a ratio of the linear to the branched ether 97 : 3).

From the fact that the zero-valent palladium complexes are effective catalysts, the migration of the allylic groups seems to proceed through π-allylic intermediates (IV) which would be derived from an oxidative addition of the allylic carbon–oxygen bonds to the palladium complexes.

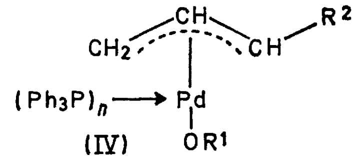
$$\mathrm{PhOCH_2{\cdot}CH{=}CH{\cdot}[CH_2]_3{\cdot}CH{=}CH_2} \underset{\mathrm{PhOH}}{\overset{\mathrm{AcOH}}{\rightleftarrows}}$$

$$\mathrm{MeCO_2{\cdot}CH_2{\cdot}CH{=}CH{\cdot}[CH_2]_3{\cdot}CH{=}CH_2}$$

(II)

$$+\ \mathrm{MeCO_2{\cdot}CH(CH{=}CH_2){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH{=}CH_2}$$

(III)



(IV)

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