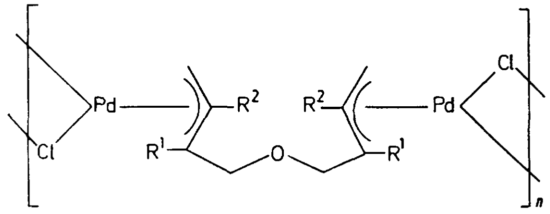
Synthesis of Butenyl Ethers: Reaction of Palladium(II) with 1,3-Dienes

By Richard V. Lawrence and John K. Ruff
(*Department of Chemistry, University of Georgia, Athens, Georgia* 30601)
and R. Craig Taylor*
(*Department of Chemistry, Oakland University, Rochester, Michigan* 48063)

Summary The reaction of tetrachloropalladate(II) or tetrabromopalladate(II) in water or aqueous acetone with 1,3-butadiene, isoprene, or 2,3-dimethyl-1,3-butadiene produces butenyl, 3-methylbutenyl, or 2,3-dimethylbutenyl ethers, respectively.

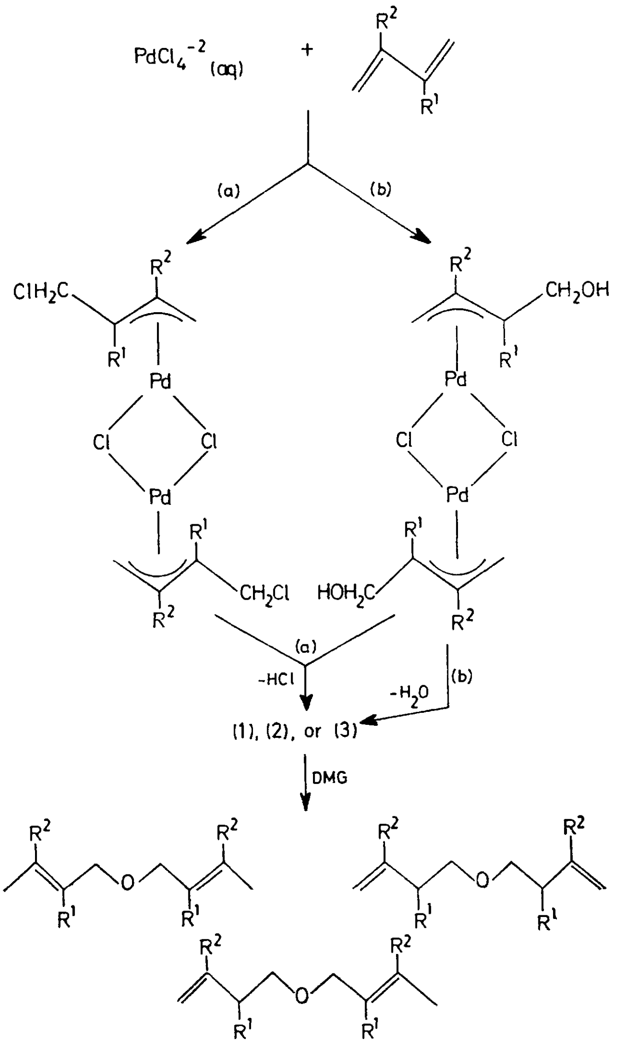
One of the most important features observed in the palladium(II)-catalysed dimerization of butadiene is the formation of telomers with various nucleophiles.[1] In particular the palladium(II) acetylacetonate–triphenylphosphine catalysed reaction of butadiene with water in the presence of CO_2 in solvents like t-butanol, acetone, and acetonitrile has been reported to yield octa-2,7-dien-1-ol as the major product together with minor amounts of octa-1,7-dien-3-ol, 1,3,7-octatriene, and octadienyl ethers.[2] During the course of our investigations of the polymerisation of various conjugated dienes catalysed by palladium(II) salts, we have obtained some results which are in striking contrast to those mentioned above. Reaction of aqueous potassium tetrachloropalladate(II) or tetrabromopalladate(II) or an aqueous acetone solution of lithium tetrachloropalladate(II) with excess 1,3-butadiene, isoprene, or 2,3-dimethyl-1,3-butadiene produced pale yellow solids which subsequent analyses indicated were polymeric, contained palladium(II), and an ether linkage. The simplest unit consistent with the results is shown in the Figure.



(1); R^1 = R^2 = H from 1,3-butadiene
(2); R^1 = H, R^2 = Me from isoprene
(3); R^1 = R^2 = Me from 2,3-dimethyl-1,3-butadiene

Figure

In a typical preparation, an aqueous acetone solution (40 ml, 1 : 3 water–acetone by volume) containing Li_2PdCl_4-(2·95 g, 11·3 mmol) was treated with excess of isoprene (1 mol) in a sealed flask at 25 °C. A pale yellow precipitate was collected after 47 h which after drying *in vacuo* gave 0·9 g of the complex (**2**) (m.p. 148—155 °C decomp). The i.r. spectrum of (**2**) in nujol mull showed the presence of ether absorptions at 1120 and 1065 cm^{-1}, but the absence of any bands in the O–H and carbon–chlorine stretching region (676 cm^{-1}).[3] The ^{1}H n.m.r. spectrum of (**2**) in $CDCl_3$ was poorly resolved because of its low solubility. Nevertheless, the resonances at 2·08 and 2·76 p.p.m. were assigned to the methyl and terminal, anti-allylic protons, respectively. Absorptions at 3·68 and 3·60 p.p.m. were not sufficiently resolved to determine whether or not they comprised a complex coupling pattern. However, the peak positions and relative intensities suggested assigning them to the methylene and methine protons adjacent to the ether oxygen. When (**2**) was allowed to react with a 1 : 1 mole ratio of dimethylglyoxime (DMG) the major products were a mixture of 3-methylbutenyl ethers and orange di-μ-chlorobis(dimethylglyoximato)dipalladium(II). The formation of the DMG anion produces a proton which when transferred to the formally anionic π-allylic ligand yields the neutral unsaturated ether. The ^{1}H n.m.r. spectrum of the



Scheme

product indicated that both 3-methyl-2-butenyl- and 3-methyl-3-butenyl groups were present in a mole ratio of 3:1. Further separation by gas chromatography showed the product to contain three volatile components in the ratio 6·9:38·0:55·1. (Random pairing of a 3:1 mixture of two isomers gives 6·3:37·5:56·2). Although it was not possible to separate the three ethers by distillation, this procedure did remove all of the unchanged complex (**2**). Similar results were obtained for (**1**) and (**3**). In fact, the enhanced solubility of (**3**) over that of (**1**) or (**2**) made it possible to obtain a cryoscopic molecular weight in benzene (calculated for the dimer of (**3**), 928; found, 1010).

The formation of (**1**)—(**3**) presumably occurs in several steps (Scheme). The first of these is the formation of the chloro- or hydroxy-butenyl π-allylic palladium(II) complexes, (**4**) and (**5**), respectively. While there is no direct evidence for the formation of (**4**) in this work, it cannot be excluded as a possible intermediate in the formation of (**5**). Robinson and Shaw[4] reported that alcohols readily condense with (**4**) to give the corresponding 4-alkoxybutenyl complexes. Furthermore they found that such 4-alkoxybutenyl complexes undergo exchange of alkoxy groups in alcoholic HCl. If the $PdCl_4^{2-}$–isoprene–aqueous acetone mixture is extracted with $CHCl_3$ or CH_2Cl_2 prior to precipitation of (**2**), the corresponding 4-hydroxy-2-methylbutenyl complex, (**5**) ($R^1 = H$; $R^2 = Me$) can be isolated in good yield. The formation of the ether complex can proceed *via* either pathway (a) or (b) or both. This ether-producing reaction appears to be restricted to dienes in which the hydroxyalkenyl complexes initially formed are primary alcohols. Thus, while hydroxy alkenyl palladium(II) complexes can be prepared from 2,4-dimethyl-1,3-pentadiene or 2,5-dimethyl-2,4-hexadiene, the reaction of either diene with aqueous $PdCl_4^{2-}$ solutions under identical conditions to that described above does not yield alkenyl ether complexes.

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