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PRELIMINARY NOTE

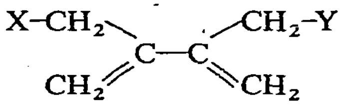
Dimerization and polymerization of allene by a homogeneous palladium catalyst

Two groups of workers[1,2] have recently reported the reaction of palladium halide complexes with allene to form π-allylpalladium complexes. It has now been found that solutions of palladium salts of weakly coordinating anions such as acetate, nitrate, or perchlorate in glacial acetic acid will catalyze the reaction of allene to give unsaturated acetic esters. The reaction will consume about 50 moles of allene per mole of palladium salt at 50° and 1 atm allene pressure in 7 hours.

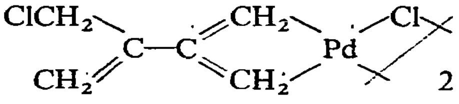
A variety of products are formed, but about 80% of reacted allene can be accounted for by the formation of allyl acetate, 2,3-dimethylbuta-1,3-diene, 3-methyl-2-hydroxymethylbuta-1,3-diene acetate Ia and 2,3-dihydroxymethylbuta-1,3-diene diacetate Ib in the approximate ratio 7 : 19 : 100 : 14. Propene has also been demonstrated to be a product of the reaction. Allyl acetate and 3-methyl-2-hydroxymethylbuta-1,3-diene acetate are formed from the addition of one molecule of acetic acid to respectively one and two molecules of allene. The formation of propene and 2,3-dimethylbutadiene requires reduction of allene, and 2,3-dihydroxymethylbuta-1,3-diene diacetate is the oxidized adduct of two molecules of allene and two acetate ions. Palladium apparently acts as an oxidation–reduction catalyst through a palladium(0) or palladium hydride intermediate. Under the conditions of the reaction, no allyl acetate is formed in the absence of palladium, so allyl acetate forms through a palladium catalyzed reaction.

Products were characterized by IR and NMR analysis. Allyl acetate and 2,3-dimethylbutadiene were shown to have the same GLC retention time as authentic samples, and 2,3-dihydroxymethylbuta-1,3-diene diacetate had m.p. 43°, lit. m.p. 43–44°.

One of the interesting aspects of the reaction is that carbon–carbon bonds are formed between the internal carbon atoms of allene and carbon–oxygen bonds are formed to the terminal allene carbon atoms. A somewhat analogous situation was found[1] for the reaction of allene with dichlorobis(benzonitrile)palladium(II) in benzonitrile solution which gave complex II. It is probable that an acetate complex similar to II is an intermediate in the formation of 2-methyl-3-hydroxymethylbuta-1,3-diene acetate. The instability[3] of π-allylpalladium acetate complexes in comparison to the chloride bridged complexes is apparently the reason that the reaction with acetate anion is catalytic while the reaction with palladium halide complexes



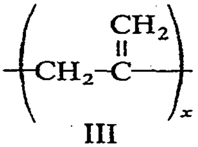
Ia X = H, Y = OAc
Ib X = Y = OAc

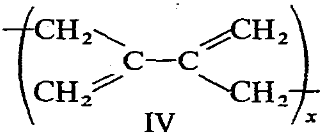


II

yields stable π-allylpalladium chloride compounds. Halide and pseudohalide ions have been shown to poison the catalytic reaction.

If the reaction system is changed by addition of a 1 : 1 mole ratio of triphenylphosphine to palladium, allene is absorbed at an increased rate; but only very small concentrations of the previously described products are found. A solid precipitates from these solutions which is quite soluble in nonpolar solvents and insoluble in polar solvents such as acetic acid and methanol. This solid has been identified as a polymer resulting from head to head polymerization of allene and has a molecular weight of 1000 to 2000.


III


IV

The 1,2-polymer of allene has been previously reported[4], and has the repeating unit III. This structure for 1,2-polyallene is supported by its infrared spectrum which has bands at 897, 1426, and 1636 cm^{-1} assigned respectively to the vinylidene out of plane deformation, the CH_2 bending deformation, and the C=C stretch. Polyallene from the palladium–phosphine catalyzed reaction in glacial acetic acid has a vinylidene out of plane deformation at 896 cm^{-1}, a CH_2 bending deformation at 1465 cm^{-1}, and the C=C stretch at 1596 cm^{-1}. The C=C frequency of 1596 cm^{-1} is significantly lower than the 1636 cm^{-1} reported for 1,2-polyallene, and it supports structure IV. 1,2-Polyallene III is reported to have NMR peaks of equal integral value at δ −2.69 and −4.95 ppm. Head to head polyallene IV has a peak at δ −2.37 ppm for the aliphatic protons and two peaks of equal size at δ −4.96 and −5.08 ppm for the olefinic protons. The olefinic double peak appears to have low shoulders on both sides. The shoulders could be due to minor amounts of other olefinic structures, or the appearance of shoulders could indicate a spin system more complex than AB. The integral value for the aliphatic protons is equal to the sum of the peaks for the olefinic protons. A double peak for the olefinic protons demonstrates that the olefinic protons are nonequivalent and is consistent only with structure IV.

Perhaps the most convincing evidence for structure IV is the reaction of the polymer with maleic anhydride at room temperature in benzene to give a Diels–Alder adduct. The infrared spectrum of this material was similar to the spectrum of the Diels–Alder adduct of maleic anhydride and butadiene. Presence of anhydride groups was demonstrated by the appearance of strong carbonyl bands at 1770 and 1840 cm^{-1} in addition to two other bands at 1240 and 935 cm^{-1}. The infrared spectrum did not contain much information on the aliphatic portion of the adduct, and insolubility prevented an NMR investigation. Found: C, 65.2; H, 5.1; calcd. for $C_{10}H_{10}O_3$ C, 67.4; H, 5.6.

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