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REACTION OF NORBORNENES WITH PHENYLPALLADIUM CHLORIDE[1)]

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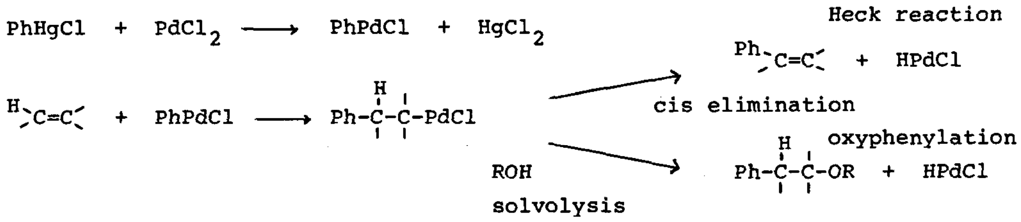
In the course of our studies on the Heck reaction of olefins with organopalladium compounds[2)], we have found an addition reaction in which a phenyl group and an anion part of protic solvents add to olefins conjugated to benzene ring (oxyphenylation)[3)]. The application of the oxyphenylation to 3,4-chromene succeeded in the synthesis of trans-isoflavan-4-ol in one step[4)].

The formation of the oxyphenylation products as well as the arylated olefins are explicable by the reaction mechanism suggested by Heck[5)]. The Heck mechanism also describes that the first step is a cis addition of the organopalladium species to the double bond and the following step is a cis elimination of hydridopalladium complex to give the substituted olefins[5)].



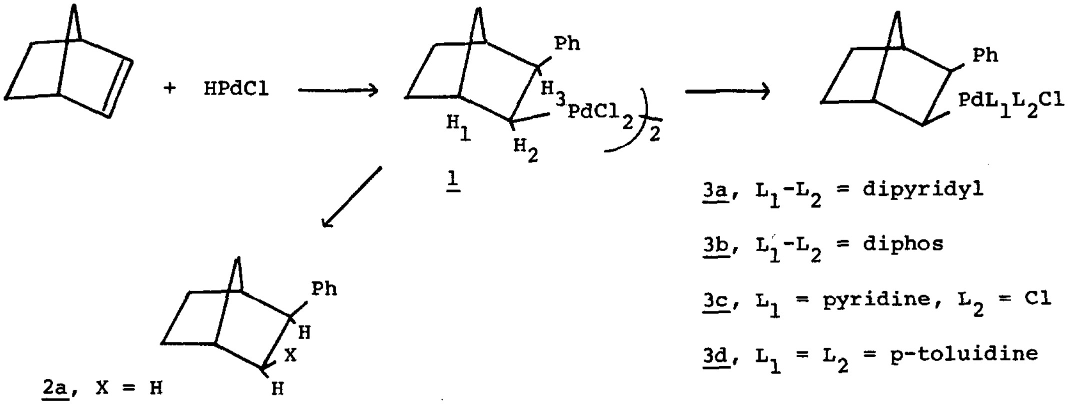
When the Heck reaction is applied to the stereochemically rigid compound which is difficult to give an olefin by the cis elimination, it is expected to isolate an intermediate complex with a carbon-palladium-σ-bond or oxyphenylation products at the expence of the arylated olefins.

We report here the isolation and characterization of a new type of complexes with the carbon-palladium-σ-bonding which are derived from the cis addition of phenylpalladium chloride on norbornenes.

To a solution of lithium palladium chloride (10 mmol) in acetonitrile, norbornene (12 mmol) and phenylmercuric chloride (10 mmol) were added and the mixture was stirred for 2 hr at room temperature. Filtration of the precipitate gave a greenish yellow complex, which were recrystallized from dichloromethane to give 1, yellow powder, mp 147-148°C (decomp.), soluble in hot chloroform but insoluble in n-hexane, benzene and ether. The complex 1 has the formula $C_{13}H_{15}PdCl_2$ (from elemental analysis). Its NMR spectrum (90 Hz, $CDCl_3$) shows signals at; 7.7-7.3 (m, 5H), 3.1-2.8 (d,d, 2H), 2.3 (s, 1H) and 1.6-1.1 (m, 6H) ppm. No signal was observed between the region of phenyl proton and of benzylic proton. Far infrared spectrum of 1 exhibits absorption peaks at 490 (C-Pd stretching) and 225 (Pd-Cl stretching trans to C-Pd bonding) cm^{-1}.

Reduction of 1 with sodium borohydride or lithium aluminum hydride gave a colorless oil 2a, bp 128-132°C/15 mmHg, which was identified as exo-2-phenylnorbornane by the comparison of gas chromatography and NMR datum of 2a with those of the authentic sample[7)]. The doublet of a benzylic hydrogen (J= 8 Hz)[8)] in the NMR spectrum of the deuterated hydrocarbon 2b prepapred from 1 by reduction with lithium aluminum deuteride suggests the cis relationship between the phenyl group and the palladium atom, because the retention of configuration is known in the hydride reduction of a carbon-palladium-σ-bond[9)].

Treatment of 1 with dipyridyl or bisdiphenylphosphinoethane (diphos) gave the stable complexes; 3a, yellow powder, 167-168°C (decomp.) and 3b, colorless needles, 177-178°C (decomp.), respectively. Pyridine complex 3c, yellow powder, mp 135°C and p-toluidine complex 3d, colorless powder, 177-178°C (decomp.) were also obtained. The attempted preparation of triphenylphosphine complex was unsuccessful.



1

3a, L_1-L_2 = dipyridyl

3b, L_1-L_2 = diphos

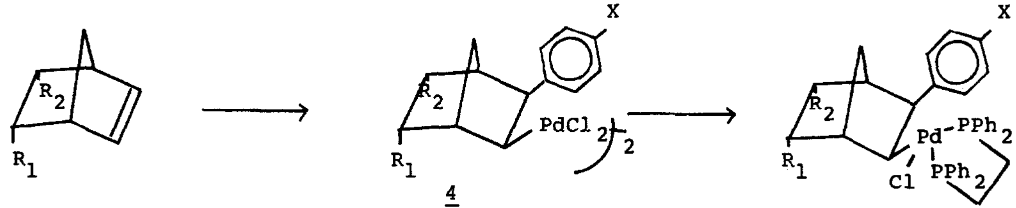
3c, L_1 = pyridine, L_2 = Cl

3d, L_1 = L_2 = p-toluidine

2a, X = H

2b, X = D

In the reaction of norbornene with p-chlorophenyl- and p-anisylmercuric chloride, the corresponding complexes were obtained as yellow powder, 4a, 157-158°C (decomp.) and 4b, 187°C (decomp.). They gave the stable colorless diphos complexes, 5a, 176-177°C (decomp.) and 5b, 173°C (decomp.) respectively. In a similar manner as above, the reaction of 5-bicyclo[2.2.1]heptene-2,3-endo-dicarboxylic acid 6a and its anhydride 6b with phenylmercuric chloride formed the corresponding complexes, 4c, yellow powder, 143-145°C (decomp.) and 4d, green powder, 215-216°C (decomp.), respectively. Stable diphos complexes 5c, 159-160°C (decomp.) and 5d, 215-216°C (decomp.) were obtained from 4c and 4d respectively.



1, $R_1 = R_2 = H$

6a, $R_1 = R_2 = CO_2H$

6b, $R_1-R_2 = (CO)_2O$

4

a, $R_1 = R_2 = H$, $X = Cl$

b, $R_1 = R_2 = H$, $X = OMe$

c, $R_1 = R_2 = CO_2H$, $X = H$

d, $R_1-R_2 = (CO)_2O$, $X = H$

5

Only one example of other norbornyl complex with a carbon-palladium-σ-bond was given by the addition reaction of norbornene with π-allyl palladium species[10].

Also, the mechanism of the Heck reaction is based on the assumption that the reaction proceeds via the carbon-palladium-σ-complex intermediate. However, any complex showing the cis addition reaction of phenylpalladium species on the first step of the Heck reaction has never been isolated.

The trans configuration of benzylic hydrogen H_3 and palladium atom in the complex 1 makes it difficult to eliminate hydridopalladium chloride from 1.

It is also impossible to give 3-phenyl-1-norbornene by the elimination of hydrogen H_1 and palladium chloride from 1. The replacement of palladium chloride with an anion of protic solvent (oxyphenylation) is more favorable than the elimination of hydridopalladium (the Heck reaction). Thus, we were interested in the solvolysis of 1.

Refluxing of 1 in 50% aqueous dioxane, DMSO and formic acid gave unexpected major product, 2-phenylnorbornane 2a in all three cases, the yields of which were 56, 65 and nealy 100% respectively, accompanied by complicated distribution of various other products. The yield of 2-phenylnorbornene was a few per cent at most. 7-syn-Phenyl-2-exo-norbornanol, mp 89-90°C, was isolated as a oxyphenylation product, the structure of which was confirmed by its NMR spectrum with a coincidence with the authentic datum11). However, the yields were only 8 and 2% in the reaction of 1 in a aqueous solution of dioxane and DMSO, respectively.

Acknowledgement

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