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Reactions of Aromatics and Olefins Catalyzed by Homogeneous Palladium(II) Compounds Under Oxygen

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It has been found that the use of mild oxygen pressure in conjunction with homogeneous palladium(II) compounds in appropriate solvents allows olefin arylation and the oxidative coupling of olefins to proceed catalytically with respect to the metal. This is in contrast to the stringent conditions involving reoxidation catalysts, co-solvents and other adjuvants which were previously necessary to avoid quantitative reduction of palladium(II) to palladium(0) by reactions of this type. The scope and limitations of the reaction under these conditions are discussed. The new conditions allow olefin arylation to proceed normally with certain olefins, such as ethylene, which give mainly side reactions under previous conditions. Using the phenylation of styrene as a model reaction, the effects on the reaction of various parameters, such as catalyst ligands, oxygen pressure and catalyst level, were studied. Below a critical level of oxygen pressure, some catalyst reduction occurs even though catalytic yields of products may be obtained. Above this level, however, no catalyst reduction occurs and the reaction is essentially zero order with respect to oxygen.

INTRODUCTION

Chemical reactions effected by homogeneous palladium(II) species can generally be divided into two categories: (a) those which are truly catalytic with respect to palladium(II), and (b) those which reduce palladium(II) to palladium(0) unless measures are taken to prevent the reduction. The latter group of reactions can typically be made pseudocatalytic with respect to palladium(II) by using a reoxidation adjuvant such as copper(II). If reduction of the adjuvant is to be avoided, an oxygen atmosphere must also be supplied. The reactions are usually carried out in a polar solvent such as water or acetic acid and require relatively stringent conditions for successful reoxidation.

Two reactions which fall into category (b) as defined above are olefin arylation and the oxidative coupling of olefins. The former has been investigated extensively under noncatalytic conditions (*1*) and the usual attempts at catalysis by using reoxidation adjuvants have been made (*1*b, *2*). We have found that mild oxygen pressure alone is sufficient to allow these two reactions to proceed catalytically with respect to palladium(II) in appropriate solvents. The new method allows olefin arylation to proceed normally in certain cases where earlier methods suppress the reaction.

EXPERIMENTAL METHODS

Materials

Some of the palladium(II) acetate used in this study was prepared from palladium(0) powder according to the method of Wilkinson [cited in Stephenson, *et al.* (*3*)]. The remainder was commercial material (City Chemical Corp.). Palladium(II) benzoate and propionate were prepared from palladium(II) acetate using Wilkinson's method.

Styrene and vinylcyclohexane were commercial materials (Aldrich Chemical Co.). Pure grade cyclohexene and research grade ethylene were used (both from Phillips Petroleum Co.). p-Chlorostyrene was Eastman white label material.

Other materials were generally reagent grade from usual sources.

Reaction Systems

Initial runs, and all runs at greater than 300 psig, were made in a glass-lined 300 ml 316 stainless steel stirred autoclave. Later runs of up to 300 psig were carried out in magnetically stirred 3 oz tall form aerosol compatibility tubes in thermostated water baths.

In a typical olefin arylation run, aromatic and olefin were charged to the autoclave which was then flushed with oxygen. Oxygen was added to the desired pressure and maintained at this pressure throughout the reaction by addition when necessary. Heating and stirring were begun and when the reactor had stabilized at the chosen temperature, olefin addition was begun. Liquid olefins were added by pumping into the autoclave a solution of the olefin in the aromatic. Addition of the solution of known composition at the desired rate was monitored by pumping from a burette reservoir. Gaseous olefins were added by flowing a known mixture of olefin in oxygen (lean side of explosive limits) under pressure through a metal frit beneath the liquid surface in the reactor. Exit gases through the back pressure regulator were passed through a wet test meter to monitor flow rate. Amount of gaseous mixture added was determined by weight difference of the mixture cylinder. Reaction was monitored by taking periodic aliquots for analysis from the reaction during the run.

Analyses

Reaction products were examined by gas–liquid chromatography using an F&M Model 720 dual column temperature programmed gas chromatograph with a thermal conductivity detector. A 5 ft × 0.25 in. 10% UCW-98 on 60–80 mesh Chromosorb P column was used. In addition to identifying the products by GLC spiking with authentic samples, all of the major and most of the minor components of a typical run were separated by preparative GLC and were identified by nuclear magnetic resonance spectrometry and/or mass spectrometry. Quantitative GLC analyses used naphthalene as an internal standard and predetermined relative GLC detector response factors from known mixtures. This procedure gave ±5% accuracy on known mixtures.

RESULTS AND DISCUSSION

The oxidative coupling of benzene to styrene was used as a model reaction throughout much of this study. With this system there are three competitive reactions occurring under catalytic olefin arylation conditions. In addition to olefin arylation, oxidative olefin–olefin coupling to produce 1,4-diphenyl-1,3-butadiene and oxidation of styrene to acetophenone and benzaldehyde also occur. The degree to which each reaction takes place depends upon reaction conditions. In general, the formation of once arylated olefin is favored by the maintenance of a relatively low concentration of olefin in a large excess of aromatic under just sufficient oxygen pressure to maintain catalyst activity. At higher olefin concentrations olefin–olefin coupling becomes increasingly important while at higher oxygen pressures relatively more olefin is converted to oxygenated species. Depending upon the relative arylation rates of the reactant and product olefins, the relative concentrations of these compounds in the reaction medium is also important. As the concentration of product olefin builds up and/or the reactant olefin is depleted during reaction, formation of multiarylated olefin by arylation of the product olefin becomes increasingly important. These effects are illustrated graphically in Fig. 1. In the model phenylation of styrene, the rate of styrene phenylation is sufficiently high relative to the rate of stilbene phenylation that multiphenylation to produce tri- and tetraphenylethylene

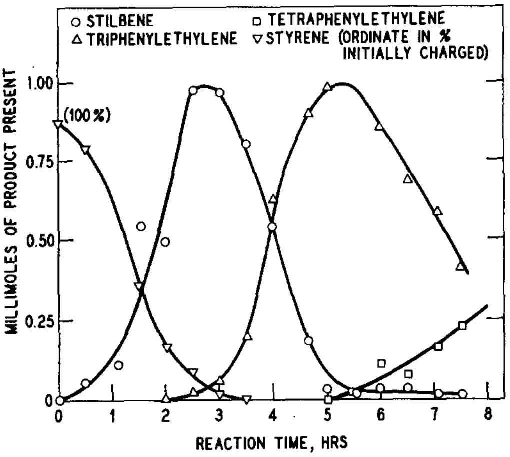

Fig. 1. Product distribution vs reaction time with all styrene charged initially.

is practically negligible unless the styrene concentration is allowed to reach essentially zero. This is avoided by slow, continuous styrene addition throughout a run. The relative rates of phenylation of ethylene and styrene are comparable, however, resulting in the formation of both styrene and stilbene from ethylene by this route.

For olefin arylation, the novel catalytic conditions described here appear to be applicable to most any combination of aromatic and olefin, with certain qualifications: (a) the aromatic and olefin must each bear at least one hydrogen and these positions must not be excessively sterically hindered, (b) functional groups which deactivate the catalyst (e.g., amines) must be avoided, (c) double bond isomerization and aromatization both occur to varying extents, where possible, (d) the palladium(II) catalyst employed must be labile and soluble in the system. Table 1 lists several aromatic–olefin pairs which have been successfully catalytically coupled under these conditions. All runs in Table 1 were under identical conditions. The cyclohexene run produced a mixture of phenylcyclohexene isomers, with the 1- and 4-isomers being identified by GLC mass spectrometry combination analysis. Biphenyl was also produced in this run. Subsequent investigation established that the biphenyl arose through aromatization of phenylcyclohexenes rather than from oxidative coupling of benzene.* Since the biphenyl yield was not included in the yield value reported in Table 1, this value is misleadingly low relative to the others in terms of the amount of oxidative coupling which has occurred. The run with chlorobenzene produced a mixture of *ortho-*, *meta-* and *para*-chlorostilbene.

Oxygen Pressure

Using the model phenylation of styrene with palladium(II) acetate and a reaction temperature of 80°C, catalytic yields of stilbene can be obtained under even as low as 50 psig oxygen. In order to completely avoid catalyst reduction, however, pressures of oxygen in the 125–150 psig range are required. Above this critical lower limit of oxygen pressure to avoid catalyst reduction, the phenylation of styrene is essentially zero order with respect to oxygen, with only small increases in stilbene yield being observed with increasing oxygen pressure. Styrene conversion increases with increasing oxygen pressure, but this is due to increased oxidation of styrene to benzaldehyde and acetophenone. These effects are shown in reactions 1–4 of Table 2.

Reaction Time

In order to establish that there is not only no catalyst reduction but also no catalyst deactivation during reaction, a study was made of catalyst productivity as a function of reaction time. As long as the critical lower limit of oxygen pressure for catalyst maintenance is exceeded, catalyst activity appears to remain constant with time. This is illustrated in Fig. 2 where stilbene yield is plotted against reaction time for a typical styrene phenylation run. The rate of stilbene production is essentially constant after the first 1.5 hr. The initial upswing in stilbene production

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* Although the catalytic oxidative coupling of aromatics to biaryls using homogeneous palladium(II) compounds has recently been reported (*4*), olefin arylation appears to be the strongly preferred reaction in the presence of olefin, since no biaryls arising from aryl–aryl coupling were detected in any of the runs in this study.

TABLE 1

CATALYTICALLY COUPLED AROMATIC-OLEFIN PAIRS

Olefin	Aromatic	Product	Yield (%)[a]
Vinylcyclohexane	Benzene	β-Cyclohexylstyrene	177
Cyclohexene	Benzene	Phenylcyclohexenes	114
Styrene	Chlorobenzene	Chlorostilbenes	108
p-Chlorostyrene	Benzene	*p*-Chlorostilbene	214
Styrene	Benzene	Stilbene	248

[a] Yield = [moles of product/moles of monomeric Pd(II) catalyst] × 100% × A where A = moles of monomeric palladium(II) catalyst required to produce 1 mole of product under noncatalytic conditions. (A = 1 for monoarylation, 2 for diarylation, etc.)

evident in the left half of the plot is due to initial buildup in styrene concentration. The run was made with no styrene initially present but with styrene added continuously at a constant rate throughout the run.

Catalyst Level

Reactions 5–7 of Table 2 illustrate the effect of catalyst concentration on the catalytic phenylation of styrene. At low catalyst levels the rate of reaction is dependent upon catalyst concentration. Between 0.12 and 0.50 wt % catalyst level, however, the reaction becomes pseudo-zero order with respect to catalyst. This can be seen by comparing values in the "stilbene yield" column at 0.5 and 1.0 wt % catalyst levels. Doubling the catalyst level has not, within the limits of experimental error, changed the amount of stilbene produced.

Reaction Temperature

Most runs were made at 80°C. Reaction occurs, although very slowly, even at room temperature. At temperatures above 80°C

TABLE 2

Run no.	Olefin	Oxygen pressure (psig)	Temp (°C)	Catalyst		Styrene		Stilbene yield (%)[a]	Selectivity to stilbene (%)
				Level (%)	Reduction	Conversion (%)	Yield[a]		
1	Styrene	50	80	0.58	33	40.0	—	172	14.6
2		100	80	0.58	5	61.0	—	261	14.5
3		200	80	0.58	0	67.2	—	281	14.2
4		300	80	0.58	0	74.3	—	314	14.4
5		300	80	0.12	0	20.5	—	2.82[b]	19.5
6		300	80	0.50	0	63.0	—	15.3[b]	38.0
7		300	80	1.0	0	63.2	—	14.7[b]	29.0
8		300	76	0.63	0	35	—	480	54
9[c]		300	100	0.55	0	62.1	—	1100	20
10	Ethylene	300	80	0.11	0	2.3[d] 0.1[e]	648	39	95[f]
11		300	100	0.11	0	5.0[d] 1.7[e]	580	192	75[f]

[a] Yield as defined in Table 1.

[b] Yield (mmoles).

[c] Rate of styrene addition in run 9 was 4 times that in run 8.

[d] Ethylene conversion to styrene.

[e] Ethylene conversion to stilbene.

[f] Relative selectivity to styrene.

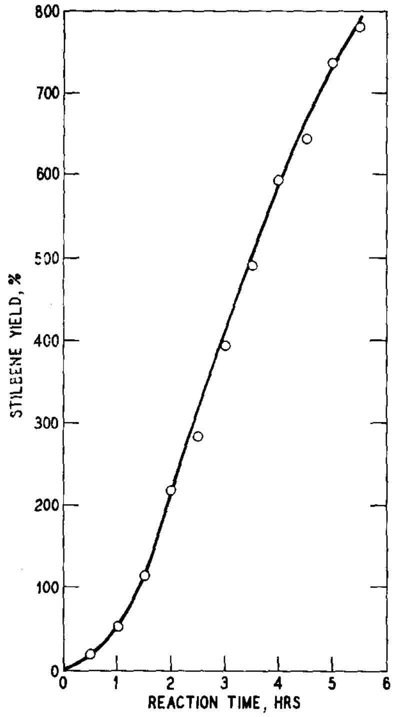

FIG. 2. Stilbene yield vs reaction time with continuous styrene addition.

reaction rate is increased, but selectivity to arylated olefin is decreased as increased relative amounts of oxygenated species and olefin–olefin coupled products are produced at the higher temperatures. This is illustrated in Table 2 which compares identical reactions (runs 8 and 9) at 76 and 100°C. The higher styrene addition rate at 100°C was necessary to avoid depletion of the olefin during reaction due to the increased reaction rate. Runs 10 and 11 of Table 2 compare the phenylation of ethylene at 80 and 100°C. Although ethylene conversion and total phenylation increases at the higher temperature, selectivity to styrene decreases as an increased relative amount of stilbene is produced.

Catalyst Ligands

Palladium(II) catalyst solubility is a necessary prerequisite for an effective olefin arylation catalyst, but it is not a sufficient condition. The present study has indicated that, in a series of palladium(II) compounds, the more tightly bound complexes such as palladium(II) acetylacetonate, although quite soluble in the reaction medium, are ineffective as catalysts for oxidative coupling under the conditions of these experiments. These effects are illustrated in Table 3. The pK_a of the corresponding acid is listed in the table as a rough measure of the relative bond strengths between the metal and the ligand. If it is assumed that in a series of anions, the stronger (more dissociated) the corresponding acid the more loosely bound the anion will be in a palladium(II) complex, it can be seen that the more loosely bound palladium(II) compounds make the best olefin arylation catalysts. Thus, in this series of compounds, palladium(II) benzoate (the salt of the strongest acid) is the best olefin arylation catalyst in terms of both absolute yield of, and selectivity to, arylated olefin.

TABLE 3
EFFECT OF CATALYST LIGANDS

Catalyst	Stilbene yield (%)[a]	Selectivity to stilbene (%)	pK_a of corresponding acid
$Pd(OBz)_2$	730	47	4.19
$Pd(OAc)_2$	613	38	4.75
$Pd(OPr)_2$	370	—	4.89
$Pd(ac.ac)_2$	0	0	—

[a] Yield as defined in Table 1.

Olefin–Olefin Coupling

If it is desired to oxidatively couple olefins to butadiene derivatives using palladium(II) catalysts, unreactive aromatic or nonaromatic solvents must be used if olefin arylation is to be avoided as a side reaction. We have found that solvents such as chloroform may be used. Even though catalytic yields of coupled products are obtained, some catalyst reduction has been apparent in most of our runs, however. As an example, the reaction of 10.0 g of styrene and 1.0 g of palladium(II) acetate in 100 ml of chloroform under 300 psig oxygen at 60°C for 5 hr produces a 187% yield (as defined in Table 1) of 1,4-diphenyl-1,3-butadiene with some palladium(0) formation being evident. The diphenylbutadiene was established, by preparative GLC and nmr analysis, to be 64% *cis,trans*-isomer and 36% *trans,trans*-isomer.

Oxidized Products

The formation of acetophenone and benzaldehyde in the catalytic oxidative coupling of benzene and styrene with palladium(II) compounds is not due to a Wacker-type mechanism catalyzed by the palladium(II) compound and involving reaction between the olefin and water in (or produced during) the reaction. This was demonstrated by careful runs in the presence of various water scavengers, such as anhydrides and molecular sieves, and runs involving continuous azeotropic water removal, which failed to alter the ratio of oxygenated to coupled products.

A direct olefin oxidation mechanism involving activation of oxygen through coordination with the metal catalyst is indicated, and evidence for this exists in the literature. Metal–oxygen complexes are now well known and characterized, such as the iridium–oxygen complexes prepared by Vaska (*5*). Metal–oxygen intermediates have recently been invoked to explain olefin oxidations catalyzed by iridium (*6*), rhodium (*7*) and palladium (*6*). The especially mild carbon–carbon double bond cleavage has been explained in terms of oxygen activation through coordination to the metal (*6*). A transition metal complex containing both coordinated oxygen and coordinated olefin has recently been isolated and characterized and is mentioned as a model compound for an intermediate in the homogenous oxidation of olefins by nonradical mechanisms (*8*).

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