Journal of Organometallic Chemistry, 54 (1973) 357–360
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CATALYSIS BY PALLADIUM SALTS

III. THE REACTION WITH ORGANIC SUBSTRATES OF *p*-BENZOQUINONE π-BONDED TO PALLADIUM(0)

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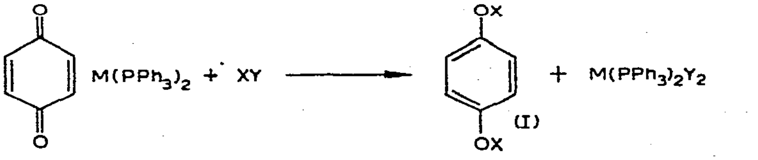
(Received October 2nd, 1972)

SUMMARY

Hydroquinone derivatives have been obtained by stoichiometric and catalytic addition of several organic reagents to *p*-benzoquinone π-bonded to triphenylphosphine Pd^0 complexes.

INTRODUCTION

A recent paper concerned with the bonding and the factors influencing the strength of the interaction between $(PPh_3)_2Pt$ and the quinone moiety, revealed that the *p*-benzoquinone π-coordinated to the metal is reduced by anhydrous hydrogen chloride to hydroquinone[1]. The reduction is facilitated by the electron back-donation to the quinone, which increases the electron density on the oxygen atoms. Activation of the hydrogen atom of hydrogen chloride seems to be necessary, and attempts to reduce coordinated *p*-benzoquinone with hydrogen, which is known to be inert towards platinum(0) triphenylphosphine complexes[2] were unsuccessful. We have found that *p*-benzoquinone π-coordinated to palladium(0) and platinum(0) triphenylphosphine complexes reacts with a variety of organic substrates, denoted XY, to give hydroquinone derivatives (Table 1) according to eqn. (1)[3].



(1)

RESULTS AND DISCUSSION

We have observed that the quinone reduction occurs very easily only with organic reagents which do not give very stable products by oxidative addition to

TABLE 1

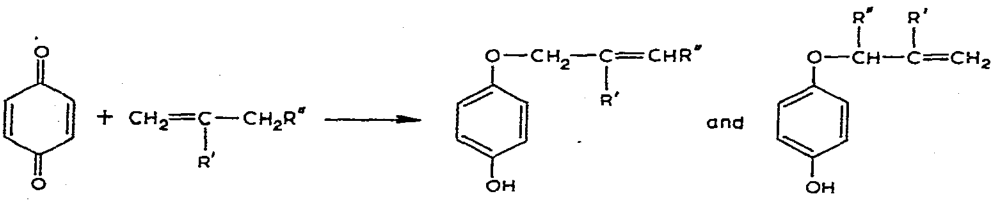
REACTION OF *p*-BENZOQUINONE COMPLEXES WITH VARIOUS ORGANIC SUBSTRATES[a]

M	*X–Y*	*Products*[b]	*Yields* (%)
Pd	CH_3I	 + L_2PdI_2	72.5
Pd	CH_3COCl	 + L_2PdCl_2	81.0
Pd	NOCl	Nitrite esters[c] + L_2PdCl_2	
Pt	CH_3COCl	 + L_2PtCl_2	82.5
Pt	C_6H_5COCl	 + L_2PtCl_2	89.0
Pd	$CH_2{=}CH{-}CH_2Cl$	$[\pi\text{-Allyl Pd(L)Cl}]_2 + C_6H_4O_2 + L$	95.0

[a] All the runs were performed in benzene at room temperature. Satisfactory analyses and spectra were obtained for all products. [b] L = triphenylphosphine. [c] This unstable compound decomposes with formation of unidentified species.

the zerovalent metal complexes. Thus allyl chloride does not react according to equation (1), as indicated in Table 1; in this case the oxidative addition of the organic substrate, which is probably the first step of reaction (1), gives a stable π-allyl compound, and the *p*-benzoquinone molecule is displaced unchanged from the coordination sphere of the metal.

Reaction (1) is stoichiometric in both the organometallic complex and the organic reagent, as indicated in Table 1. It can be carried out catalytically only when both the X and the Y group can be transferred to the *p*-benzoquinone moiety. We have found that α-olefins satisfy this condition, and react with *p*-benzoquinone with formation of alkenyl ethers, according to eqn. (2)[4].



(II) (III) (2)

($R' = H$; $R'' = H, CH_3, C_5H_{11}, i\text{-}C_3H_7$)

($R' = CH_3, C_6H_5$; $R'' = H$)

TABLE 2

HYDROQUINONE ETHERS OBTAINED FROM VARIOUS OLEFINS[a]

Olefin	*Solvent*	*Reaction products*	*M.p.* (°C)	*Yield* (%)[b]	*Analysis found (calcd.)* (%)	
					C	*H*
Isobutene	Dioxane	$HOC_6H_4OCH_2C(CH_3)=CH_2$	33–34	17	72.7 (73.1)	7.2 (7.31)
		$CH_2=C(CH_3)CH_2OC_6H_4OCH_2C(CH_3)=CH_2$	44	27	76.8 (77.1)	8.5 (8.25)
1-Butene	Acetonitrile	$HOC_6H_4OCH_2CH=CHCH_3$		22	[d]	
		$HOC_6H_4OCH(CH_3)CH_2=CH_3$		6	[d]	
		Diethers[c]		5	[d]	
1-Octene	Benzene	$HOC_6H_4OCH_2CH=CH(CH_2)_4CH_3$		19	[d]	
		$HOC_6H_4OCH(CH=CH_2)(CH_2)_4CH_3$		12	[d]	
		Diethers[c]		21	[d]	
4-Methyl-1-pentene	Dioxane	$HOC_6H_4OCH_2CH=CHCH(CH_3)_2$		25	[d]	
		$(CH_3)_2CHCH=CHCH_2OC_6H_4OCH_2$- $-CH=CHCH(CH_3)_2$		9	[d]	
α-Methylstyrene	α-Methylstyrene	$HOC_6H_4OCH_2C(C_6H_5)=CH_2$	60 (dec.)	22	79.2 (79.6)	6.0 (6.2)
		$CH_2=C(C_6H_5)CH_2OC_6H_4OCH_2$- $-C(C_6H_5)=CH_2$	70 (dec.)	7	84.0 (84.2)	6.1 (6.4)

[a] Bis(triphenylphosphine)(*p*-benzoquinone)palladium(0): 0.2 mmol; *p*-benzoquinone: 20 mmol; olefin: 40 mmol; solvent: 10 ml; temp.: 80°; reaction time: 6 h. [b] Yields based on *p*-benzoquinone. [c] Mixture of three isomers. [d] Oil, characterised by IR, NMR and mass spectroscopy.

In addition to the monoethers (II) and (III), which are the major products, hydroquinone and hydroquinone diethers, both arising from metathesis reactions of the hydroquinone monoethers, are formed in the reaction. All the organic products have been fully characterised by elementary analyses, GLC and spectroscopic methods (NMR, IR and mass spectroscopy) (see Table 2).

In a typical reaction, a solution of isobutene (0.021 mol) in 2.0 ml of dioxane containing *p*-benzoquinone (0.009 mol) and bis(triphenylphosphine)(*p*-benzoquinone)palladium (0.18 mmol) was kept in a Carius tube at 80° for 6 h. The mixture was then evaporated, and the resulting sticky residue extracted with warm benzene. The extract was purified from the palladium catalyst by passage through an alumina packed column. The hydroquinone 2-methylallyl ether (0.0015 mol), m.p. 33°–34° was isolated by extraction of the benzene solution with 5% NaOH followed by neutralization with HCl. The benzene solution left after the extraction with base was evaporated, and the residue crystallised from petroleum ether at low temperature. The crystalline product (0.0012 mol), m.p. 44°, was hydroquinone bis(2-methylallyl)ether.

It is noteworthy that the hydrogen abstraction does not take place in absence of metals in the case of non-activated quinones, but it was recently reported that 2,3-dichloro-5,6-dicyanobenzenequinone, which is an activated, fairly strong oxidative agent, can dehydrogenate suitable olefins, such as allylbenzene and α-methylstyrene, to form carbonyl derivatives or quinol ethers. The action of the zerovalent metal, which is known to behave as a base[1], is thus that of increasing the oxidative properties of the quinone moiety, by stabilizing its excited states[7] through occupation of π^* anti-bonding orbitals.

The formation of the reaction products (II) and (III) may be explained by assuming that there is direct attack of a coordinated semiquinone type ion on the 1- or 3-position of a π-allyl intermediate formed by metal-assisted hydrogen abstraction of a coordinated olefin, although such π-allyl species have not yet been isolated.

In conclusion we propose that the metal atom activates both the quinone and the olefin. The preference for the formation of (II) seems to be general and the ratio of (II) to (III) depends on the nature of the starting olefins and on the experimental conditions.

With 4-methyl-1-pentene we succeeded in isolating only compound (II). In this case the attack on the 3-position of an allylic intermediate is probably sterically hindered.

EXPERIMENTAL

Elementary analyses were carried out in the analytical laboratory of the Bollate Research Centre. NMR spectra were recorded with a Varian HA 100 spectrometer, and IR spectra with a Perkin–Elmer 225 spectrophotometer. Mass spectra were obtained with a Hitachi–Perkin–Elmer RMU/6 instrument.

The reaction with the XY reagent was carried out at about 60–80° ; the working up of the reaction mixture was facilitated by the low solubility of $(PPh_3)_2MY_2$ species ($M = Pt, Pd$).

In the case of reaction with olefins, different procedures were followed depending on whether the olefin employed was a liquid or a gas. In the first case, the reaction was carried out in a flask charged with the reagents and equipped with stirrer, thermometer and nitrogen inlet. In the second case, the reagents were allowed to react in a Carius tube with stirring. Working up of the reaction mixture was the same in all cases, and is as described in the main text.

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