Journal of Organometallic Chemistry, 56 (1973) 391–394
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CATALYSIS BY PALLADIUM SALTS

V. SYNTHESIS OF ANTHRAQUINONES FROM *p*-BENZOQUINONE AND MONO-OLEFINS

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(Received December 4th, 1972)

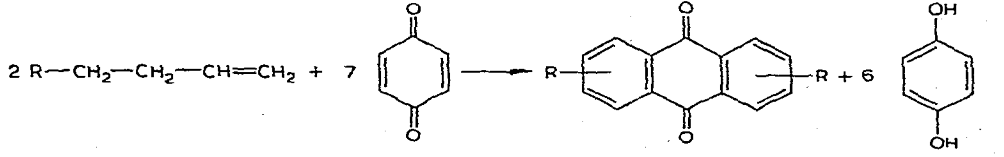
SUMMARY

Triphenylphosphinepalladium(0) complexes catalyse the formation of anthraquinone derivatives from *p*-benzoquinone and monoolefins.

RESULTS AND DISCUSSION

The dehydrogenation properties of strongly oxidising quinones such as 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) are well known and are characterised by the aromatisation of hydroaromatic compounds[1].

Recently it has been found that DDQ can abstract hydrogen from simple acyclic olefins, including tetramethylethylene, giving rise to conjugated dienes[2], and to oxidation products such as unsaturated aldehyde acetals[3] or alkenyl ethers[4] when formation of dienes is not possible. These reactions do not take place with quinones having a lower redox potential such as *p*-benzoquinone; however we have found that when catalytic amounts of zerovalent phosphine Pd^0 and Pt^0 complexes are present in the reaction medium, dehydrogenation occurs rapidly. For example, alkenyl ethers of hydroquinone were obtained in the palladium(0) catalyzed oxidation of α-olefins with *p*-benzoquinone[5]. Moreover when we tried to obtain allylic derivatives or rearrangement products by reacting *p*-benzoquinone with a linear olefin containing more than three carbon atoms in the presence of bis(triphenylphosphine)(*p*-benzoquinone)palladium(0) and water, we obtained anthraquinone and naphthoquinone derivatives. As revealed by GLC–mass spectrometric analysis, the primary reaction products are conjugated dienes which add very rapidly to the unreacted excess of quinone to give the Diels–Alder adducts, followed by facile aromatisation according to the following stoichiometry:



(1)

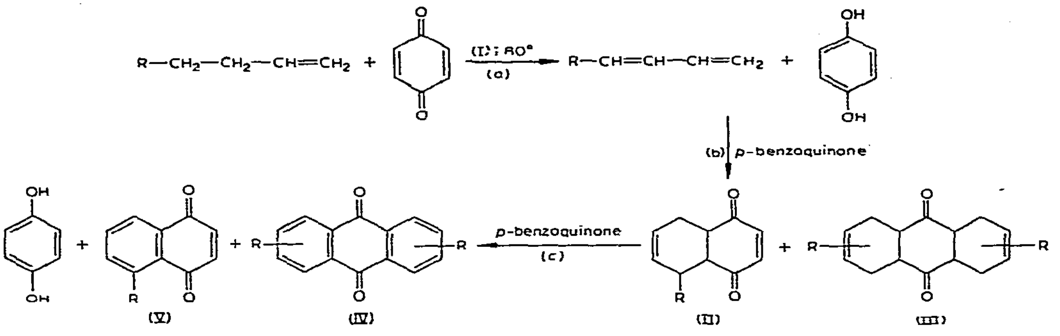
TABLE 1

SYNTHESIS OF ALKYLANTHRAQUINONES (IV)[a]

Olefin	*Yield* (%)	*Elemental analysis found (calcd.)(%)*		*IR* (cm^{-1})[c]	*NMR* (τ *ppm*)[d]
		C	*H*		
cis-2-Pentene	73	81.6	5.2	1660 [ν(C=O)], 1600, 1580 [ν(C=C)]	2.0–2.5 (m, 6H, aromatic hydrogens)
		(81.3)[e]	(5.08)[e]	1330, 1275, 1260 [δ(C=O)]	7.4 (s, 6H, two CH_3)
1-Hexene	75	81.9	6.3	3060 [ν(C=H) aromatics]	2.0–2.5 (m, 6H, aromatic hydrogens)
		(81.8)[f]	(6.03)[f]	1660 [ν(C=O)]	7.9 (q, 4H, two CH_2)
				1583, 1570 [ν(C=C)]	8.7 (t, 6H, two CH_3)
				1330, 1280, 1265 [δ(C=O)]	
1-Octene	69	82.2	7.7	3085 [ν(C–H) aromatics]	2.0–2.5 (m, 6H, aromatic hydrogens)
		(82.5)[g]	(7.5)[g]	1658 [ν(C=O)]	7.9 (t, 4H, two CH_2)
				1580, 1566 [ν(C=C)]	8.5 (m, 8H, four CH_2)
				1318, 1295, 1265 [δ(C=O)]	9.1 (t, 6H, two CH_3)

[a] All runs were performed in dioxane solution at 80°C (under a small positive pressure in the case of *cis*-2-pentene and 1-hexene). Molar concentration ratios of catalyst/*p*-benzoquinone/olefin/water equals 0.02/2/3/4. Reaction time 6 h; *p*-benzoquinone conversion 100%. [b] Yields based upon the reacted *p*-benzoquinone according to the equation (1). The conjugated 1,3-dienes which arose from the dehydrogenation of the initial olefin were detected in the final solution, and accounted for about 10% of the reacted *p*-benzoquinone. [c] Spectra recorded in nujol mull. [d] Spectra recorded in $CDCl_3$. [e] $C_{16}H_{12}O_2$. [f] $C_{18}H_{16}O_2$. [g] $C_{22}H_{24}O_2$.

We now provide evidence that the reaction proceeds via successive steps (a), (b), (c), as reported in the following general scheme:



where R = H ; $-CH_3$; $-C_2H_5$; $-C_4H_9$; (I) = $(PPh_3)_2$(p-benzoquinone) palladium

An equimolecular mixture of compounds (IV) having the alkyl substituents in 1,5- or 1,8-positions may be generally separated by thin-layer chromatography (TLC). Compounds (II) and (III) which are considered as intermediate species formed through step (b) have not been isolated when the *p*-benzoquinone/olefin ratio was equal to or lower than one. With higher ratios the aromatic compound (IV) formed by the dehydrogenation reaction (c) was the main product together with small amount of (V).

Table 1 lists the main reaction products as characterised by elemental and spectroscopic analysis. With *cis*-2-pentene as reacting olefin we have observed the formation of a small amount of a mixture of products which can not be related directly to the initial olefin. As a result of mass spectral analysis we have discovered small amounts of Diels–Alder adducts where the residues R are quite different from those expected in the light of the initial olefins. For instance, with *cis*-2-pentene, peaks of mass 296, 328, 342 have been detected which correspond to the partially aromatized anthraquinones carrying C_3, C_4 and C_5 alkyl substituents respectively. We thus conclude that a finite disproportionation of the initial internal olefin occurs under our conditions and is the only reaction which can account for the results. Although olefin metathesis is usually catalysed in the homogeneous phase by Mo, W and Re complexes[8], some authors have briefly reported that palladium catalysts may also display a certain activity[9].

EXPERIMENTAL

In a typical reaction, a solution of 1-octene (0.02 moles), *p*-benzoquinone (0.03 moles), dioxane (10 ml), water (0.05 moles) were reacted in the presence of (I) (0.20 mmoles) at 80° for 6 h under N_2. From the reaction mixture a main yellow product (0.85 g) was isolated by preparative TLC and has been completely characterized as compound (IV), where $R=C_4H_9$. A small amount of (V) and other not completely aromatized intermediates (II) and (III) has been qualitatively detected by mass spectroscopy but not separated nor isolated. Zerovalent palladium complexes are active catalysts for this reaction; however, $Pd(PPh_3)_2Cl_2$ can be activated by addition of alkoxides in non-polar solvents[7]. The corresponding Pt^0 complexes are much less catalytically active.

All the elementary analyses were carried out in the analytical laboratory of Bollate Research Centre. NMR spectra were recorded using a Varian HA 100 spectrometer and mass spectra were obtained using a Hitachi–Perkin–Elmer RMU/6 instrument. IR spectra were obtained on a Perkin–Elmer 225 Spectrophotometer. All reagents used were research-grade.

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