Arylation of Quinones with Arenes and Palladium Acetate

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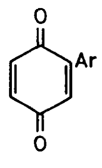
Summary Oxidation of quinones with palladium acetate in acetic acid, which contained arenes, gave arylated quinones.

The oxidative properties of quinones are well known, but little attention has been paid to the oxidation of quinones. This paper deals with the selective oxidation of quinones.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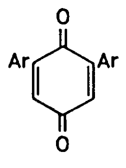
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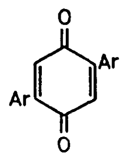
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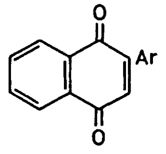
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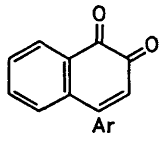
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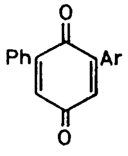
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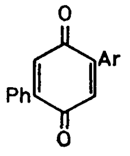
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a; Ar = Ph
b; Ar = $C_6H_3Me_2$—2,5
c; Ar = $C_6H_3Cl_2$—2,5
d; Ar = H

Arylation of quinones is an important method for the preparation of aryl-substituted quinones. However, investigation of this method has been limited to the reaction of quinones with aryldiazonium salts.[1] No report of a coupling reaction between quinones and arenes has been published except that γ-radiolysis of the 1,4-quinones in benzene was reported to afford a small amount of 2-phenyl-1,4-quinones.[2] On the other hand, arylation of olefins with palladium salts has been extensively investigated.[3] Furthermore, we have reported the arylation of *N*-acyl-pyrroles and -indoles with arenes and palladium acetate.[4] We have now found that oxidation of quinones with palladium acetate in acetic acid which contains arenes results in a coupling reaction between the quinones and arenes.

A solution of 1,4-benzoquinone (**1d**)† (4·0 mmol) and Pd(OAc)$_2$ (4·0 mmol) in acetic acid (100 ml) which contained benzene (100 ml) was stirred at 80 °C under nitrogen for 14 h. The mixture was evaporated to give an orange semicrystalline residue which was chromatographed on silica gel to give 2-phenyl-1,4-benzoquinone (**1a**), 2,6-diphenyl-1,4-benzoquinone (**2a**), and 2,5-diphenyl-1,4-benzoquinone (**3a**).

Similarly, treatment of 1,4-benzoquinone with Pd(OAc)$_2$ in AcOH–*p*-xylene gave compounds (**1b**),‡ m.p. 77—78 °C, (**2b**), m.p. 129—130 °C, and (**3b**), m.p. 184—185·5 °C [2-; 2,6-bis-; and 2,5-bis-(2,5-dimethylphenyl)-1,4-benzoquinone, respectively], and in AcOH–*p*-dichlorobenzene gave compounds (**1c**), m.p. 117—118 °C, (**2c**), m.p. 155—156 °C, and (**3c**), m.p. 223—225 °C [2-; 2,6 bis-; and 2,5-bis-(2,5-dichlorophenyl)-1,4-benzoquinone, respectively]. Treatment of 1,4-naphthoquinone (**4d**) with Pd(OAc)$_2$ in AcOH, which contained one of the above arenes, gave the corresponding compounds (**4a**), m.p. 111—112 °C, (**4b**), m.p. 83—83·5 °C, and (**4c**), m.p. 166—168 °C [2-phenyl-; 2-(2,5-dimethylphenyl)-; and 2-(2,5-dichlorophenyl)-1,4-naphthoquinone, respectively], in high yields. Furthermore, treatment of 1,2-naphthoquinone (**5d**) with Pd(OAc)$_2$ in AcOH–C_6H_6 and in AcOH–*p*-dichlorobenzene gave the compounds (**5a**), m.p. 120–121 °C (lit.,[5] m.p. 120—121 °C)§ and (**5c**), m.p. 133—134 °C [4-phenyl- and 4-(2,5-dichlorophenyl)-1,2-naphthoquinone, respectively]. These results are summarized in the Table.

The reaction is also applicable to the preparation of 1,4-benzoquinones which bear two different aryl substituents. Treatment of compound (**1a**) with Pd(OAc)$_2$ in AcOH–*p*-dichlorobenzene gave 2-(2,5-dichlorophenyl)-6-phenyl-1,4-benzoquinone (**6c**), m.p. 91—92 °C, and 2-(2,5-dichlorophenyl)-5-phenyl-1,4-benzoquinone (**7c**), m.p. 159—160 °C.

TABLE. Arylation of quinones with arenes and palladium acetate.[a]

Quinones, mmol	Pd(OAc)$_2$/mmol	AcOH/ml	Arenes, ml	Conversion (%)	Products, isolated yields (%)[b]
(**1d**), 4·0	4·0	100	C_6H_6, 100	78	(**1a**), 41; (**2a**), 12; (**3a**), 6
(**1d**), 4·0	4·0	100	*p*-$Me_2C_6H_4$, 100	80	(**1b**), 25; (**2b**), 13; (**3b**), 8
(**1d**), 4·0	4·0	120	*p*-$Cl_2C_6H_4$, 30	70	(**1c**), 50; (**2c**), 3; (**3c**), 2
(**4d**), 2·0	2·0	50	C_6H_6, 50	100	(**4a**), 85
(**4d**), 2·0	2·0	50	*p*-$Me_2C_6H_4$, 50	100	(**4b**), 78
(**4d**), 2·0	2·0	60	*p*-$Cl_2C_6H_4$, 15	100	(**4c**), 70
(**5d**), 2·0	2·0	50	C_6H_6, 50	100	(**5a**), 30
(**5d**), 2·0	2·0	60	*p*-$Cl_2C_6H_4$, 15	100	(**5c**), 27
(**1a**), 4·0	4·0	120	*p*-$Cl_2C_6H_4$, 30	88	(**6c**), 36; (**7c**), 19

[a] All reactions were performed at reflux temperature for 14 h. [b] Yields are based on amount of quinone consumed.

(*Received*, 1*st June* 1981; *Com.* 640.)

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† (**1d**) ≡ (**2d**) ≡ (**3d**).

‡ All new compounds were fully characterized by ^1H n.m.r. and i.r. spectroscopy and by elemental analysis.

§ Attempts to isolate 3-phenyl-1,2-naphthoquinone were unsuccessful (lit., m.p. 156 °C, L. F. Fieser and A. R. Bader, *J. Am. Chem. Soc.*, 1951, **73**, 681).

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[4] T. Itahara, *J. Chem. Soc., Chem Commun.*, 1981, 254.

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