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ARYLATION OF QUINONES WITH ARYL MERCURYL CHLORIDE CATALYZED BY LITHIUM PALLADIUM CHLORIDE

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ABSTRACT: Treatment of benzoquinone/naphthoquinone with aryl mercury chloride in the presence of palladium chloride and lithium chloride gives the corresponding aryl substituted benzoquinone/naphthoquinone at the quinonoid position.

Aryl substituted benzoquinones and naphthoquinones are important due to their chemotherapeutic and colouring properties. In the past various methods[1-5] have been used for their synthesis i) acid catalysed C-arylation with aryldiazonium salts ii) oxidative coupling with arenes in the presence of palladium acetate iii) C-arylation with triphenyl stilbene and iv) nucleophilic arylation with di-t-butylphenol. All these methods require acidic conditions and high temperatures which cause polymerisation of quinones and on account of this the yields are generally poor.

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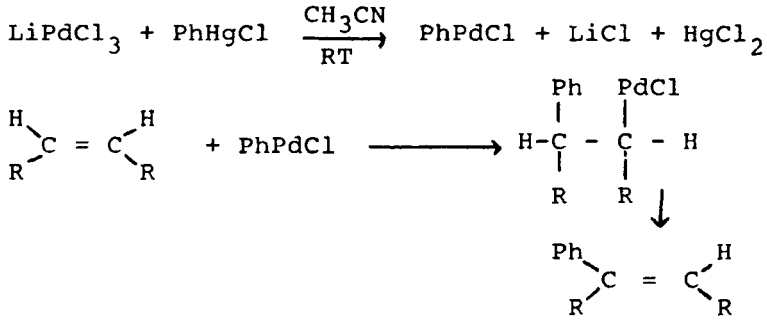
The diazonium salts do not work if an electron releasing substituent is present in the quinone ring.

R.F. Heck[6] reported the arylation of olefins by organopalladium salts. The latter has the advantage that it is soluble in the reaction medium and is produced in situ by the reaction of organo mercurial acetate with palladium acetate or chloride in polar solvents. The phenyl palladium chloride adds on the quinonoid bonds and the adduct eliminates HPdCl to give substituted quinone. The coupling of the aryl group proceeds in the manner that the aryl group goes to that carbon which is least substituted.



In order to extend the study of Heck reaction the arylation of quinonoid compound is undertaken. Various aryl mercury chlorides[7-9] have been chosen to couple with 1,4-benzoquinones and 1,4-naphthoquinones to give corresponding aryl derivatives (Table). The arylation with aryl palladium chloride in acetonitrile is

TABLE

Reaction of 1,4,-benzoquinone and 1,4-naphthoquinone with arylmercuryl chloride in the presence of palladium chloride and lithium chloride in acetonitrile.

S.No.	Aryl group in Aryl-Hg-Cl	Quinones	Reaction Time	Products formed (yields)
1.	C_6H_5	1,4-Benzoquinone	50 min.	2-Phenyl-1,4-benzoquinone (38%) + 2,6-Diphenyl-1,4-benzoquinone (20%)
2.	$4\text{-}ClC_6H_4$	- do -	1 hr 20 min.	2-(4'-Chlorophenyl)-1,4-benzoquinone (50%) + 2,6-Di (4'-chlorophenyl)-1,4-benzoquinone (20%)
3.	$2\text{-}OAcC_6H_4$	- do -	3 hr 30 min.	2-(2'-Acetoxyphenyl)-1,4-benzoquinone (55%)
4.	$4\text{-}OAcC_6H_4$	- do -	5 hr	Product not identified
5.	C_6H_5	1,4-Naphthoquinone	24 hr	2-Phenyl-1,4-naphthoquinone(50%)
6.	$4\text{-}ClC_6H_4$	- do -	24 hr	2-(4'-Chlorophenyl)-1,4-naphthoquinone (75%)
7.	$2\text{-}OAcC_6H_4$	- do -	24 hr	2-(2'-Acetoxyphenyl)-1,4-naphthoquinone (80%)
8.	$4\text{-}OAcC_6H_4$	- do -	23 hr	2-(4'-Acetoxyphenyl)-1,4-naphthoquinone (80%)

selective and the aryl group enters at the quinonoid position giving in most cases only monoaryl derivative.

EXPERIMENTAL

Preparation of lithium palladium chloride: A mixture of lithium chloride (0.043 g, 1 m.mole) and palladium chloride (0.178 g, 1 m. mole) was stirred for 24 hr in a conical flask containing anhydrous acetonitrile (10 ml) to give lithium palladium chloride (0.1 N in CH_3CN, 1 m.mole).

Arylation of quinone: A mixture of quinone (1 m.mole) and aryl mercuryl chloride (0.8 m.mole) in acetonitrile (20 ml) was added into a suspension of lithium palladium chloride catalyst in acetonitrile (0.1 N, 10 ml) and the mixture was stirred continuously at room temperature until most of the starting material was consumed. The inorganic material was removed by filtration and the filtrate concentrated under reduced pressure. The residue was separated into components by preparative thin layer chromatography (silica G grade). The products were identified based upon their spectral characteristics.

2-Phenyl-1,4-benzoquinone: M.p. 112-14°C; IR ν_{max}(KBr): 1650, 1585 cm^{-1}; NMR ($CDCl_3$): δ 6.65(m, 3H, $C_{3,5,6}$-H), 7.35(m, Ar-H).

2,6-Diphenyl-1,4-benzoquinone: M.p. 136-8°C; IR ν_{max} (KBr): 1655, 1645, 1585 cm^{-1}: NMR ($CDCl_3$): δ 6.8(s, 2H, $C_{3,5}$-H), 7.4(m, 10H, Ar-H).

2-(4'-Chlorophenyl)-1,4-benzoquinone: M.p. 138-40°C; IR ν_{max}(KBr): 1710, 1660, 1640, 1590 cm^{-1}; NMR ($CDCl_3$): δ 6.9(s, 1H, C_3-H), 7.1-7.25(m, $C_{5,6}$-H), 7.35-7.50(m, 4H, Ar-H).

2,6-Di (4'-Chlorophenyl)-1,4-benzoquinone: M.p. 186-7°C; IR ν_{max}(KBr): 1695, 1650, 1625, 1580 cm^{-1}; NMR ($CDCl_3$): δ 6.2(m, 2H, $C_{3,5}$-H), 6.7(dd, 8H, Ar-H).

2-(2'-Acetoxyphenyl)-1,4-benzoquinone: M.p. 158-60°C; IR ν_{max}(KBr): 1710, 1655, 1620, 1580 cm^{-1}; NMR ($CDCl_3$): δ 2.05(s, 3H, $OCOCH_3$), 6.75(s, 1H, C_3-H), 6.85-6.95(m, 2H, $C_{5,6}$-H), 7.15-7.30(m, 4H, Ar-H).

2-Phenyl-1,4-naphthoquinone: M.p. 143-45°C; IR ν_{max} (KBr): 2905, 1660, 1645, 1595, 1485, 1440 cm^{-1}; NMR ($CDCl_3$): δ 7.0(s, 1H, QnH), 7.35-7.55(m, 5H, Ar-H), 7.65-7.75 and 7.95-8.15(2m, 2H each, Ar-H).

2-(4'-Chlorophenyl)-1,4-naphthoquinone: M.p. 109-11°C; IR ν_{max}(KBr): 2910, 1665, 1650, 1590, 1490, 1400 cm^{-1}; NMR ($CDCl_3$): δ 6.95(s, 1H, QnH), 7.30-7.45(m, 4H, Ar-H), 7.6-7.8 and 7.95-8.15(2m, 2H each, Ar-H).

2-(2'-Acetoxyphenyl)-1,4-naphthoquinone: M.p. 102-4°C; IR ν_{max}(KBr): 2895, 1710, 1650, 1635, 1585, 1565, 1460, 1415 cm^{-1}; NMR ($CDCl_3$): δ 2.0(s, 3H, $OCOCH_3$), 6.85(s, 1H, QnH), 7.05-7.25(m, 4H, ArH), 7.55-7.70 and 7.90-8.05(2m, 2H each ArH).

2-(4'-Acetoxyphenyl) - 1,4-naphthoquinone: B.p. not determined; IR ν_{max}(KBr): 2900, 1720, 1655, 1625, 1580, 1550, 1450, 1370 cm^{-1}; NMR ($CDCl_3$): δ 2.15(s, 3H, $-OCOCH_3$), 6.8(s, 1H, QnH), 7.1-7.25(m, 4H, Ar-H), 7.65-7.80 and 7.90-8.15(m, 2H each, Ar-H).

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