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ON THE REVERSIBILITY OF HOMOLYTIC AROMATIC SUBSTITUTION

II.[1] THE PHENYLATION OF o-DICHLOROBENZENE

Roberto Henriquez and Derek C. Nonhebel*
Department of Pure and Applied Chemistry,
University of Strathclyde,
Glasgow G1 1XL
Scotland.

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The addition of aryl radicals to substituted benzenes to form σ-arylcyclohexadienyl radicals has been generally regarded as an irreversible process[2] except at high temperatures. We present here further evidence for the reversibility of the addition of phenyl radicals to benzenoid compounds from a study of the phenylation of o-dichlorobenzene.

Addition of phenyl radicals generated from dibenzoyl peroxide, to o-dichlorobenzene affords the isomeric phenyldichlorocyclohexadienyl radicals (**1** and **2**) and thence 2,3- and 3,4-dichlorobiphenyls (**3** and **4**). If, as seems reasonable on steric grounds, the radical (**1**) is thermodynamically less stable than (**2**), then the ratio of (**3**)/(**4**) obtained from the reaction might be expected to decrease with increasing temperature. This is precisely what was found (See Table).

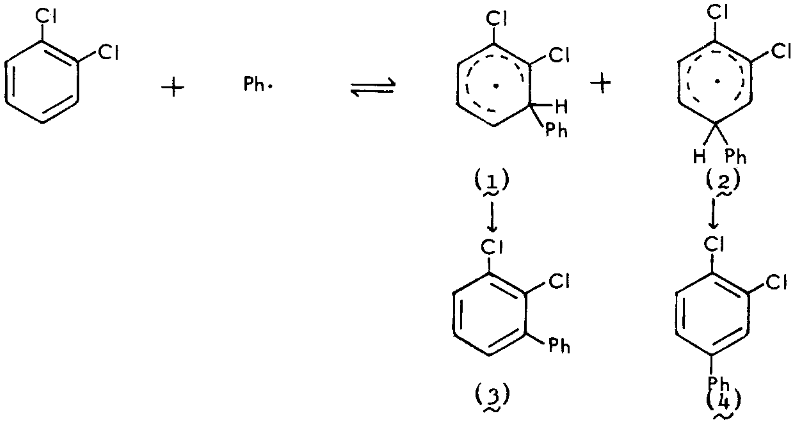

Table. Products from the Reactions of o-Dichlorobenzene (0.5 mol) and Dibenzoyl Peroxide (5 mmol)

Temp. (°C)	Additive	Products(mmol) (3)	(4)	Mole Ratio (3)/(4)
80	-	3.04	1.52	2.00
80	$Cu(OCOPh)_2$[a]	3.61	1.45	2.49
100	-	1.78	1.08	1.65
100	$Cu(OCOPh)_2$[a]	1.93	0.98	1.98
120	-	1.33	0.95	1.40
120	$Cu(OCOPh)_2$[a]	2.09	1.19	1.76

[a] 3 x 10^{-4} mole

Addition of copper(II) salts to systems undergoing homolytic aromatic substitution effects the rapid oxidation of σ-arylcyclohexadienyl radicals to biaryls thereby increasing the yield of biaryl at the expense of σ-radical dimer.[4] If the radical (1) is more prone to dissociate than (2), then addition of copper(II) benzoate might be expected to increase the ratio of (3)/(4). This was observed (see Table). The oxidation potentials of the radicals (1) and (2) would be expected to be similar and thus one cannot explain the influence of copper(II) salts on the basis that (1) would be more readily oxidized than (2).

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