

Reversibility of Homolytic Aromatic Substitution: the Reaction of *p*-Xylene with Phenyl Radicals

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Summary The increase in the ratio of 4,4'-dimethylbibenzyl to 2,5-dimethylbiphenyl formed in the reaction of phenyl radicals with *p*-xylene with increasing temperature is interpreted as indicating that the formation of 1-phenyl-2,5-dimethylcyclohexadienyl radicals (**1**) is reversible.

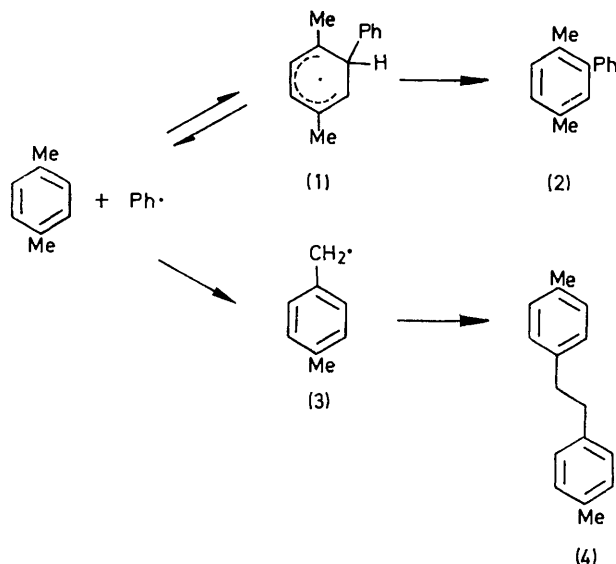
THE addition of aryl radicals to aromatic systems to form arylcyclohexadienyl radicals has generally been regarded as an irreversible process on the basis of the absence of significant isotope effect for the phenylation of benzene.¹⁻³ Thermochemical data appertaining to reactions of radicals with olefinic and aromatic compounds likewise indicated that phenylation is irreversible below 200 °C.⁴

Recent results, however, show that at high temperatures (210 °C) phenylcyclohexadienyl radicals do undergo fragmentation though this probably did not occur at moderate

temperatures.⁵ In contrast, a Japanese report suggests that arylcyclohexadienyl radicals are formed reversibly in the addition of phenyl radicals to substituted benzenes at 20 °C.⁶ We present further evidence in support of the reversibility of phenylation at moderate temperatures from a study of the reaction of phenyl radicals with *p*-xylene.

Phenyl radicals, generated by thermolysis of dibenzoyl peroxide, react with *p*-xylene both by addition to form the 1-phenyl-2,5-dimethylcyclohexadienyl radical (**1**) and thence 2,5-dimethylbiphenyl (**2**), and by abstraction of a benzylic hydrogen to afford the 4-methylbenzyl radical (**3**) and thence 4,4'-dimethylbibenzyl (**4**) (see Scheme). The relative proportions of these products is temperature dependent, more of the bibenzyl (**4**) being obtained at higher temperatures (see Table). The benzylic radical (**3**) would also be formed by hydrogen abstraction by benzyloxyl radicals. This latter reaction would be less important at

higher temperatures owing to decarboxylation of the benzyloxy radical and hence one might expect the ratio of (4)/(2) to decrease rather than increase with increasing temperature. We interpret this effect as indicating that the formation of (1) is reversible whereas (3) is generated in an irreversible reaction. Consequently more of the bibenzyl will be obtained at higher temperatures. The ratio of (4):(2) is also decreased by the addition of small quantities of



copper(II) benzoate or nitrobenzene to the reaction mixtures. Both these additives effect the rapid oxidation of σ -cyclohexadienyl radicals^{7,8} and hence a decrease in the ratio of (4):(2) is consistent with the proposed scheme. However, it is also true that the increase in the yield of (2) in the presence of additives could arise from an increase in the number of σ -radicals which are oxidized to biaryl at the expense of the yield of the dimeric product.

A possible interpretation of the difference between our conclusions and those of other workers is that the cyclo-

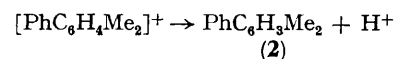
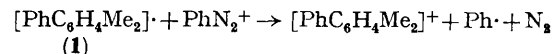
hexadienyl radical (1) has an *ortho*-substituent and is consequently more prone to undergo dissociation than the unsubstituted phenyl cyclohexadienyl radical. Further studies are in hand to assess whether the degree of reversibility in homolytic aromatic substitution is greater when the resultant arylcyclohexadienyl radical has a substituent *ortho* to the incoming aryl group than in the absence of an *ortho* substituent.

TABLE. Products from the reaction of *p*-xylene (0.5 mol) and dibenzoyl peroxide (5 mmol)

Temp/%	Additive	Products (mmol)		Mole ratio (4)/(2)
		(2)	(4)	
80	—	1.58	1.59	1.00
80	Cu(OcOPh) ₂ ^a	1.75	1.62	0.91
80	PhNO ₂ ^b	1.53	1.26	0.83
100	—	1.63	1.85	1.13
100	Cu(OcOPh) ₂ ^a	2.19	1.63	0.74
100	PhNO ₂ ^b	1.66	1.63	0.98
120	—	1.55	1.76	1.15
120	Cu(OcOPh) ₂ ^a	2.20	1.99	0.90
120	PhNO ₂ ^b	1.81	1.57	0.87
135	—	1.50	1.84	1.23

^a 3×10^{-4} mol. ^b 6×10^{-4} mol.

Phenylation of *p*-xylene under Gomberg conditions gave almost exclusively 2,5-dimethylbiphenyl with less than 1% of 4,4'-dimethylbibenzyl (4). The absence of this latter suggests that the radical (1) is formed preferentially at low temperatures and that it is rapidly oxidized before dissociation occurs. This supports Cadogan's interpretation of the mechanism of the Gomberg reaction in which the intermediate phenylcyclohexadienyl radical is rapidly oxidized by the diazonium cation in an electron-transfer process.⁹ The absence of side-chain attack in Gomberg



reactions involving substituted toluenes appears to be fairly general.¹⁰

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