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ON THE REVERSIBILITY OF HOMOLYTIC AROMATIC SUBSTITUTION III.[1]
THE VARIATION OF THE PARTIAL RATE FACTOR FOR THE PHENYLATION OF p-DICHLOROBENZENE WITH TEMPERATURE

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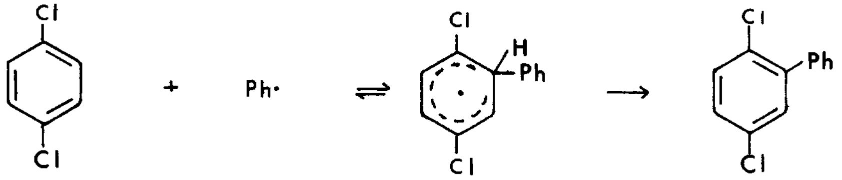
The results presented in the preceding paper[1] and elsewhere[2,3] would seem to indicate that the first step in homolytic aromatic substitution, namely formation of the σ-cyclohexadienyl radical, may be reversible particularly when the incoming radical enters ortho to a substituent. If this were so, then the partial rate factors for the phenylation of p-disubstituted benzenes (against benzene as the reference compound) might be expected to decrease with increasing temperature.



(1)

The table shows that the partial rate factor for the phenylation of p-dichlorobenzene decreases with increasing temperature. Addition of copper(II) benzoate to the reaction mixtures results in an increase in the partial rate factor at each of the temperatures employed. Copper (II) salts effect the efficient oxidation of cyclohexadienyl radicals prior to their dissociation, disproportionation or dimerization.[4] These results are thus consistent with the fact that the radical (1) is formed reversibly and that it is more prone to undergo dissociation than the unsubstituted phenylcyclohexadienyl radical.

TABLE. Partial Rate Factors for the Phenylation of p-Dichlorobenzene.

Radical Source	Temp. (°C)	Additive None	Cu(OCOPh)$_2$ [a]
PhN=NCPh$_3$	60	5.98	-
PhN=NCPh$_3$	80	2.75	-
(PhCOO)$_2$	80	2.60	4.13
(PhCOO)$_2$	100	2.43	2.62

REFERENCES

1. Part II. R. Henriquez and D. C. Nonhebel, Tetrahedron Letters, 1975, preceding paper.
2. R. Henriquez, A. R. Morgan, P. Mulholland, D. C. Nonhebel and G. G. Smith, J.C.S. Chem. Comm., 1974, 987.
3. M. Kobayashi, H. Minato and N. Kobori, Bull. Chem. Soc. Japan, **42**, 2738 (1969).
4. D. H. Hey, K. S. Y. Liang and M. J. Perkins, Tetrahedron Letters, 1967, 1477.