

## *ipso*-SUBSTITUTION IN REACTIONS OF BENZYL RADICALS WITH DIHALOBENZENES AND 1,2,4-TRICHLOROBENZENE

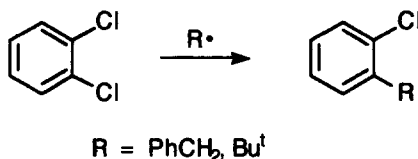
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**Abstract:** Di- and tri-halobenzenes undergo *ipso*-substitution on reaction with benzyl radicals, generated by thermolysis of dibenzyl mercury, to give halo- and dihalo-diphenylmethanes respectively. The relative reactivities of the dihalobenzenes and of 1,2,4-trichlorobenzene are consistent with the reactions proceeding via a transition state with significant charge transfer character to give cyclohexadienyl radicals.

In the course of the study of the decomposition of ketone cyclic diperoxides, the thermolyses of 3,6-dibenzyl-3,6-dimethyl- and 3,6-di-*t*-butyl-3,6-dimethyl-tetraoxa-1,2,4,5-cyclohexanes in *o*-dichlorobenzene were investigated.<sup>1</sup> *o*-Dichlorobenzene was used in the belief that it would act as an inert high boiling solvent. These reactions were found to give low yields of *o*-chlorodiphenylmethane and *o*-chloro-*t*-butylbenzene respectively, in addition to the expected products, bibenzyl, ethylbenzene and benzyl methyl ketone. It seemed probable that these products were formed as a consequence of the *ipso*-substitution of a chlorine by a benzyl and *t*-butyl radicals respectively.



There is some evidence that decomposition of these peroxides leads to excited radicals and hence the question arises as to whether these *ipso*-substituted products are derived from reactions of the excited radicals.

This paper describes an investigation of the reaction of *o*-dichlorobenzene and other dihalobenzenes with benzyl radicals generated, in the main, by decomposition of dibenzyl mercury in a large excess of the dihalobenzene. Dibenzyl mercury has been shown by Jackson to be an excellent source of benzyl radicals.<sup>2</sup> There is no doubt that these benzyl radicals are not in an excited state. The reactions were carried out in sealed tubes *in vacuo* and the products analysed by GLC (see Table 1). No traces of dichlorodiphenylmethanes, as a result of 'normal' homolytic aromatic substitution, were obtained. This reaction is reminiscent of the reactions of dihalobenzenes with cyclohexyl radicals which was shown to result in the formation of *ipso*-substituted product as well as cyclohexylated dihalobenzenes.<sup>3,4</sup> There are no reported cases of substitution of monosubstituted benzenes by benzyl radicals though anthracene has been found to react with benzyl radicals at the 9-position presumably because the intermediate cyclohexadienyl radical is considerably more stable than the analogous radical from reactions of simple benzenoid compounds.<sup>5</sup> Indeed it has been stated that substitution reactions of substituted benzenes is most unlikely to occur.<sup>2</sup> *ipso*-Substitution does not occur in reactions of phenyl radicals with *o*-dichlorobenzene.<sup>6</sup> These results suggest that there is a significant difference in mechanism in reactions of *o*-dichlorobenzene with benzyl and cyclohexyl radicals on the one hand and with methyl and phenyl radicals on the other hand.

Table. Products obtained from the Decomposition of Dibenzyl mercury (0.2 mmol) in Dihalobenzene (20 mmol).

Dihalobenzene	Mole ratio halodiphenylmethane : bibenzyl		
	Temperature of reaction		
	120°	160°	200°
<i>o</i> -Dichlorobenzene	0.106	0.104	0.075
<i>m</i> -Dichlorobenzene	-	0.031	-
<i>p</i> -Dichlorobenzene	0.070	0.045	0.028
<i>p</i> -Dibromobenzene	0.107	0.093	0.067
<i>o</i> -Chlorobromobenzene	0.125 <sup>a</sup>	0.098 <sup>a</sup>	0.059 <sup>a</sup>
<i>p</i> -Chlorobromobenzene	0.062 <sup>b</sup>	0.047 <sup>b</sup>	0.030 <sup>b</sup>
	0.069 <sup>c</sup>	0.051 <sup>c</sup>	0.040 <sup>c</sup>
<i>o</i> -Difluorobenzene	-	0.008	-
	0.029 <sup>e</sup>	0.027 <sup>e</sup>	0.017 <sup>e</sup>
<i>p</i> -Chlorofluorobenzene	0.017 <sup>f</sup>	0.010 <sup>f</sup>	0.006 <sup>f</sup>
<i>o</i> -Bromofluorobenzene	0.114 <sup>e</sup>	0.061 <sup>e</sup>	0.030 <sup>e</sup>
<i>p</i> -Bromofluorobenzene	0.023 <sup>f</sup>	0.010 <sup>f</sup>	0.009 <sup>f</sup>

<sup>a</sup> *o*-chlorodiphenylmethane    <sup>c</sup> *o*-bromodiphenylmethane    <sup>b</sup> *p*-chlorodiphenylmethane

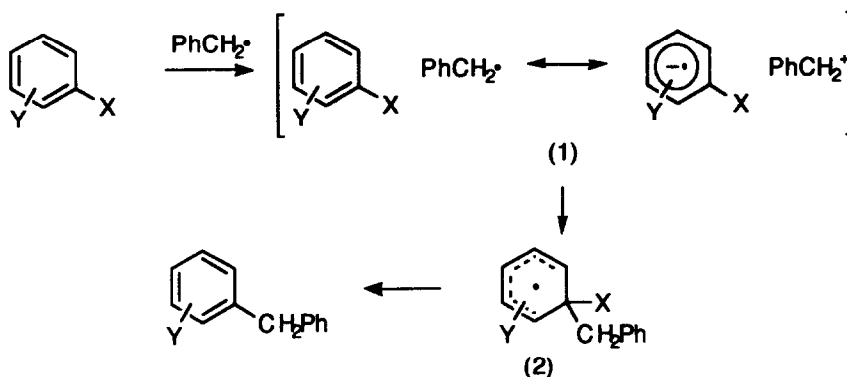
<sup>d</sup> *p*-bromodiphenylmethane    <sup>e</sup> *o*-fluorodiphenylmethane    <sup>f</sup> *p*-fluorodiphenylmethane

The *ipso*-substitution reaction of dihalobenzenes with cyclohexyl radicals has been postulated to proceed via a transition state, in which there was significant electron transfer, which then led to the  $\sigma$ -cyclohexadienyl radical. A parallel process can be considered for the reaction under study is depicted in Scheme 1. Support for the involvement of a transition state in which there is a significant degree of electron transfer comes from the observation that no *ipso*-substitution occurs in reactions of monohalobenzenes nor in reactions of dihalobenzenes with phenyl radicals.<sup>6</sup> Monohalobenzenes are less electron deficient than dihalobenzenes and hence their radical anions would be less stable than dihalobenzene radical anions. The redox potentials of halobenzenes has been shown to decrease with increasing number of halogens.<sup>7</sup> The extent electron transfer would be anticipated to be greater in the proposed transition state in reactions of nucleophilic radicals including cyclohexyl and benzyl radicals than in reactions of the electroneutral phenyl radicals. The preference for attack at the *ipso*-position in these reactions is attributed to the charge density in the halobenzene radical anion being greatest at the positions bearing the halogen atoms.<sup>7</sup>

The following conclusions can be drawn from the results presented in Table 1.

- the extent of *ipso*-substitution for the isomeric dichlorobenzenes is in the order: *ortho* > *para* > *meta*,
- the ease of replacement of halogen is in the order: bromine > chlorine > fluorine,
- the proportion of *ipso*-substitution decreases with increasing reaction temperature.

The intermediate cyclohexadienyl radicals resulting from attack at the *ortho*- and *para*- positions the unpaired electron can be delocalised by the chlorine substituents. This is not possible for the *meta*-substituted  $\sigma$ -radical. The greater extent of reaction of *o*-halobenzenes than their *para*-isomers can be attributed to relief of strain on formation of the  $\sigma$ -cyclohexadienyl radical intermediate. The *ortho*-isomers are more polar than their *meta*- and *para*-isomers and hence if a charge-transfer process were involved then the degree of substitution would be expected to be greater. The degree of *ipso*-substitution of the *ortho*-isomer was also observed to be larger in cyclohexylations of the isomeric dihalobenzenes.<sup>4,5</sup>



Scheme 1

The order of the ease of replacement of the different halogens is in line with the bond energies of carbon-halogen bonds and would suggest that the rate-limiting step of the reaction is not loss of halogen. Benzyl chloride was detected in the products from the reaction of *o*-dichlorobenzene indicating that the loss of halogen may involve abstraction by a benzyl radical from the  $\sigma$ -cyclohexadienyl radical. The ease of displacement of halogens in reactions of cyclohexyl radicals with dihalobenzenes was  $F > I > Br > Cl$ . The differing ease of displacement of halogen in reactions of cyclohexyl and benzyl radicals is interpreted in terms of a different interplay of electronic and bond energy effects in the two reactions.

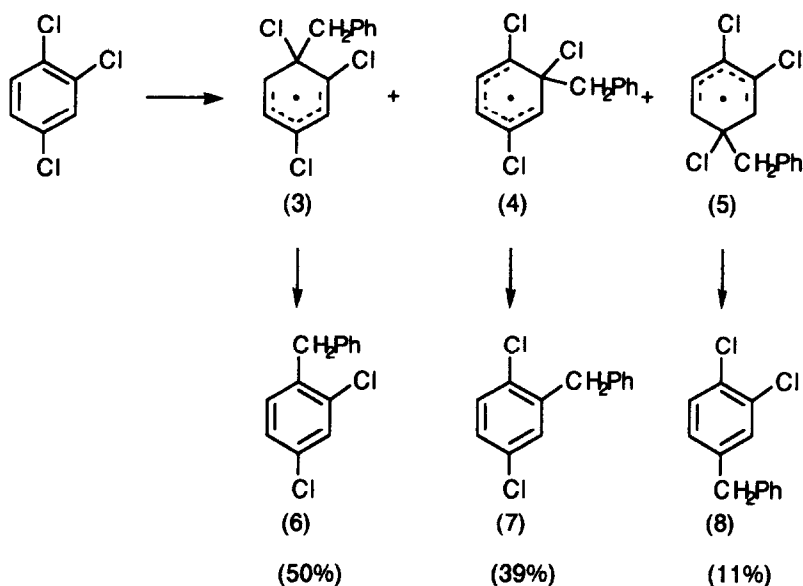
We have previously proposed that the formation of cyclohexadienyl radicals in normal homolytic aromatic substitutions is a reversible process.<sup>5,8</sup> That less *ipso*-substitution occurs at higher temperatures is consistent with the formation of the radical (2) also being reversible.

*ipso*-Substitution of *o*- and *p*-dichlorobenzenes was also observed when a mixture of dihalobenzene (0.05 mol), toluene (0.2 mol) and di-*t*-butyl peroxide (0.01 mol) was heated at 110°C in a nitrogen atmosphere for 5 days. Reaction of toluene with *t*-butoxyl radicals provides an alternative source of benzyl radicals which reacted with the dihalobenzene.<sup>9</sup>

We have also examined the reaction of benzyl radicals with 1,2,4-trichlorobenzene with a view to investigating the regioselectivity of reaction. The relative yields of 2,4-, 2,5- and 3,4-dichlorodiphenylmethanes (6, 7 and 8) were found to be 50%, 39% and 11%, i.e. the relative reactivities at the 1-, 2- and 4-positions were 4.7 : 3.7 : 1 respectively. The cyclohexadienyl radical (3) is predicted to be the more stable than the isomeric radicals (4 and 5) as it will be stabilised by the resonance interaction of two chlorines while the other radicals would only be stabilised by a single chlorine.

The results again show that the extent of *ipso*-substitution is greater when the chlorine substituted is *ortho* to a second chlorine, i.e. the extent of reaction at C-2 is greater than at C-4 though nominally the stabilities of the cyclohexadienyl radicals leading to these two products should be similar in that they are respectively stabilised by one *ortho*- and one *para*-chlorine. This can be attributed to the relief of strain on formation of the  $\sigma$ -cyclohexadienyl radical intermediates as was suggested above to account for the degree of *ipso*-substitution being greater in reactions of *o*-dichlorobenzene than *p*-dichlorobenzene.

The relative proportions of *ipso*-substitution : dibenzyl formation for 1,2,4-trichlorobenzene at 160° is 1 : 4 while for *o*-dichlorobenzene it was 1 : 9.6 demonstrating that the extent of *ipso*-substitution is increased by the number of electronegative substituents supporting the postulate that the transition state for the reaction has significant charge-transfer character.



Scheme 2

It is worth noting that there are significant differences between *ipso*-substitutions of dihalobenzenes with cyclohexyl and benzyl radicals and of di- and tri-nitrobenzenes with adamantyl radicals, generated by oxidation of adamantanecarboxylic acid with peroxydisulphate.<sup>10</sup> In the latter reactions, displacement of a nitro group *ortho* to another group did not take place. Nevertheless a similar mechanism involving partial electron transfer in the transition state was proposed.

## EXPERIMENTAL

GLC analyses were carried out on a Perkin Elmer F11 gas chromatograph fitted with a flame ionisation detector using a column filled with 5% Apiezon on siliconised celite at 170°. Yields of products were determined using phenyl benzoate as an internal standard.

**Materials.** Dibenzyl mercury was prepared by reaction of benzylmagnesium chloride with mercury(II) chloride as colourless crystals, m.p. 109–110°C (lit.<sup>11</sup> 110°).

The halodiphenylmethanes were obtained by reduction of the corresponding benzophenones using the Wolff-Kishner reduction (for *o*- and *m*-chlorodiphenylmethanes), Clemmensen reduction (for *p*-chlorodiphenylmethane) or by reduction with red phosphorus and hydriodic acid (for the remaining halodiphenylmethanes).

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