Homolytic Aromatic Cyclohexylation. II. The Role of π-Complex Formation[1] and Competitions for Cyclohexyl Radical

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A study of the products resulting from the reactions of cyclohexyl radicals with halogenated aromatics has been conducted, and partial rate factors and relative reactivities determined. Thermolysis at 90° of di-*tert*-butyl peroxide in excess cyclohexane and mixtures of the dihaloaromatic and benzene resulted in these values: o-$C_6H_4Br_2$ $f_x = 68$, $f_o = 31$, $f_m = 6.8$, $k_{rel} = 35$; *o*-$C_6H_4Cl_2$ $f_x = 15$, $f_o = 16$, $f_m = 5.2$, $k_{rel} = 12$; *p*-$C_6H_4Br_2$ $f_x = 13$, $f_o = 31$, $k_{rel} = 25$; *p*-$C_6H_4Cl_2$ $f_x = 7.5$, $f_o = 21$, $k_{rel} = 17$. Thermolysis in excess aromatic gave the following ones: *o*-$C_6H_4Br_2$ $f_x = 33$, $f_o = 18$, $f_m = 5.0$, $k_{rel} = 19$; *o*-$C_6H_4Cl_2$ $f_x = 6.7$, $f_o = 8.4$, $f_m = 3.4$, $k_{rel} = 6.1$; *p*-$C_6H_4Br_2$ $f_x = 6.8$, $f_o = 18$, $k_{rel} = 14$; *p*-$C_6H_4Cl_2$ $f_x = 3.5$, $f_o = 11$, $k_{rel} = 8.7$. The marked solvent effect observed in the more polar aromatic media suggested reversible formation of a π complex between cyclohexyl radical and the aromatic. Rearrangement of the π complex to a σ complex would then be the rate- and product-determining step in the homolytic cyclohexylation of aromatics. Three trends revealed by the partial rate factors and relative rates are the activation of halogen ortho to another halogen toward displacement, the enhanced reactivity of the dihaloaromatic relative to that of benzene, and the activation of hydrogen ortho to a halogen toward displacement by cyclohexyl radical. The formation of bicyclohexyl, cyclohexanol, cyclohexanone, and *tert*-butyl cyclohexyl ethers in the reaction mixture demonstrate the important competing reactions for cyclohexyl radical of combination, interaction with oxygen, and the cross combination with *tert*-butoxy radicals.

Previous studies in our laboratories[2-4] have shown that cyclohexyl radicals, generated by either photolysis or thermolysis at 105° of di-*tert*-butyl peroxide (DTBP) in cyclohexane and an aromatic, can effect aromatic substitution. The cyclohexyl radical was found to be more selective than phenyl radical in reactions with aromatic compounds, as evidenced by Hammett ρ values of +1.1 for cyclohexylation[2] as compared to +0.05 for phenylation.[5] The observation that the amount of homolytic aromatic cyclohexylation was increased by the presence of electron-withdrawing substituents on the ring and decreased by electron-donating substituents suggested that cyclohexyl radical is "nucleophilic" in its reaction with aromatics.

Appreciable displacement of halogen from mixed dihalobenzenes occurred, with halogen ortho to another halogen being especially reactive toward displacement by cyclohexyl radicals. The order of halogen reactivity observed in homolytic cyclohexylation of selected mixed dihalobenzenes was $F > I > Br > Cl$[3] as compared to $F > Cl \sim Br \sim I$ found for nucleophilic aromatic substitution.[6]

The initial study of the cyclohexylation of mixed dihalobenzenes concentrated on the products from halogen displacement. It was felt that a more detailed study of the reaction system was needed to determine the fate of the displaced halogen, to evaluate both intermolecular and intramolecular competition for cyclohexyl radicals in aromatic substitution, and to determine the nature and extent of other reactions which might compete for cyclohexyl radical to form additional products.

Homolytic cyclohexylation of *o*- and *p*-dichlorobenzene and *o*- and *p*-dibromobenzene in competition with benzene was chosen for this study, since the simple dihalobenzenes give fewer hydrogen displacement products than the corresponding mixed dihalobenzenes. Thermolysis of DTBP at 90° in cyclohexane and a mixture of the dihaloaromatic and benzene served to elucidate both intermolecular and intramolecular competition data.

Although much of the previous work[2,3] was done using excess aromatic in the reaction mixture, it was felt that excess cyclohexane should be used in the competition studies to minimize perturbation of the reaction medium as the aromatic species was varied. However, for comparison with previous results the reactions were also run in excess aromatic. The reaction products were analyzed directly by glpc.

Table I
Partial Rate Factors for Homolytic Cyclohexylation of Some Dihaloaromatics

Aromatic	Initial C_6H_{12}/aromatic	k_{rel}	f_x	f_o	f_m
o-$C_6H_4Cl_2$	5.0[a]	12	15	16	5.2
	0.5[b]	6.1	6.7	8.4	3.4
o-$C_6H_4Br_2$	5.0[c]	35	68	31	6.8
	0.5	19	33	18	5.0
p-$C_6H_4Cl_2$	5.0	17	7.5	21	
	0.5	8.7	3.5	11	
p-$C_6H_4Br_2$	5.0	25	13	31	
	0.5	14	6.8	18	

[a] Average of five separate reactions with varying amounts of benzene and *o*-dichlorobenzene. [b] Average of three reactions with varying amounts of benzene and *o*-dichlorobenzene. [c] Average of two chromatograph runs under different temperature conditions.

Results and Discussion

Part I. Solvent Effect. Partial rate factors calculated for the homolytic cyclohexylation of *o*- and *p*-dichlorobenzene and *o*- and *p*-dibromobenzene in excess cyclohexane, and in excess total aromatic, are presented in Table I. The accuracy of these data is limited by the chromatographic integration techniques used. Agreement between the two methods of manual integration employed was well within 5% of the peak area.

The most dramatic trend observed in Table I is the decrease in both intramolecular and intermolecular selectivity of the reaction when the nature of the medium is changed from excess cyclohexane to an excess of aromatics. The excess-aromatic medium has more dipolar character than the excess-aliphatic system, so that the selectivity of aromatic substitution is decreasing with an increase in the dipolar nature of the reaction system. This observation is consistent with some recent work by Davis and Ahmed in which they found a decrease in the 1-/2-selectivity of homolytic methylation of naphthalene as the solvent dielectric constant increased.[7] They argue that this implies some contribution of a charge-transfer inter-

Table II
Effect of Changing the Aromatic on the Selectivity of Homolytic Cyclohexylation

Initial C_6H_6/ o-$C_6H_4Cl_2$	k_{rel}	f_{Cl}	$f_{H\text{-}o}$	$f_{H\text{-}m}$
9.0	10	10	16	5
2.3	8	9	11	4
1.0	5	5	6	3
0.4	6	6	8	3

Table III
Competition for Cyclohexyl Radicals in Homolytic Cyclohexylation of Dihaloaromatics at 90°

Dihalobenzene	Initial C_6H_{12}/ aromatic	Aromatic substitution %[a]	Aromatic substitution Mol × 10^{-4}	Combination %[a]	Combination Mol × 10^{-4}
o-$C_6H_4Cl_2$	5.0	25	5.5	14	3.0
	0.5	46	10	1.9	0.14
p-$C_6H_4Cl_2$	5.0	44	6.0		
	0.5	45	10		
o-$C_6H_4Br_2$	5.0	20	3.3	26	4.2
	0.5	38	3.1	1.4	0.11
p-$C_6H_4Br_2$	5.0	43	11	0.9	0.23
	0.5	46	15	0.5	0.15

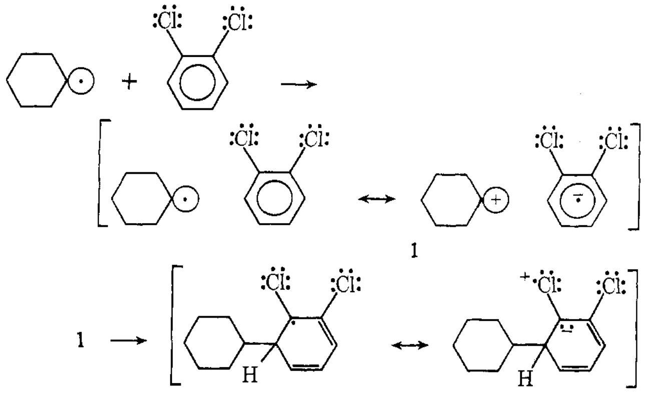
[a] Based on the total cyclohexyl reaction products found assuming that two cyclohexyl radicals are necessary to produce an aromatic substitution product and two cyclohexyl radicals are necessary for combination.

action in the transition state leading to formation of the σ complex, and stabilization of this transition state by more polar solvent would lower the activation energy for the process and cause the transition state to occur earlier along the reaction path, resulting in a decrease in selectivity.

Table II shows the results of varying the ratio of benzene to o-dichlorobenzene in a homolytic cyclohexylation in which the aromatics are in excess. The decrease in selectivity of the reaction as the amount of o-dichlorobenzene is increased is consistent with the results of Davis and Ahmed, since the dielectric constant of o-dichlorobenzene is 9.9 at 25° as compared to 2.3 for benzene.[8]

The nature of this charge transfer interaction may be the reversible formation of a π complex by donation of the odd electron of the cyclohexyl radical to the lowest antibonding π orbital of the aromatic as shown in Chart I. Such a donation would be a "nucleophilic" interaction by the cyclohexyl radical and would be aided by the presence of electron-withdrawing substituents on the ring. The rearrangement of this π complex to a σ complex would be the rate-determining and product-determining step in the aromatic substitution process.

Chart I
Formation of the π and σ Complexes for Homolytic Aromatic Cycloexylation

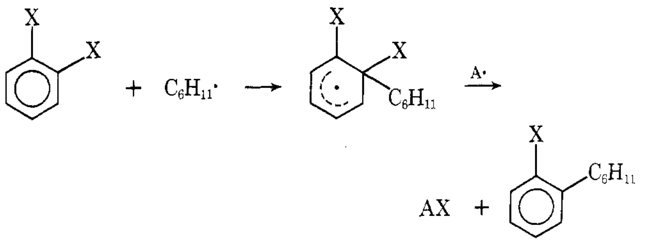


Additional evidence for π-complex formation can be found from the data in Table III. On the basis of relative rate data and partial rate factors (Table I), o-dibromobenzene is the most reactive of the aromatics toward homolytic cyclohexylation. However, the percentage of aromatic substitution for o-dibromobenzene in excess cyclohexane is much lower than the percentage for p-dibromobenzene, and for p-dichlorobenzene in the same system, as well as being much lower than for o-dibromobenzene in the excess aromatic system. Concurrently, there is a tremendous increase in the amount of bicyclohexyl formation from combination of two cyclohexyl radicals.

Suppression of the rates of combination of cyclohexyl radicals and isopropyl radicals in benzene as compared to the rates in cyclohexane has been used as evidence by Burkhart for the formation of a π complex between alkyl radical and benzene.[9] Rand and Strong uncovered direct, spectral evidence for the existence of a π complex between iodine atoms and benzene.[10] There is also a great deal of evidence available from the efforts of several groups for the effects of aromatic solvents on radical reactions which implicates the existence of π-complexed radicals.[11]

Our previous study of halogen displacement revealed that fluorine was the most readily displaced of the halogens and this evidence has been used in support of an addition-elimination mechanism shown in Chart II for the free-radical cyclohexylation of the dihaloaromatics, in which the slow step is formation of the intermediate cyclohexadienyl radical. The evidence presented above suggests that σ-complex formation is preceded by reversible π-complex formation, and that the slow step of the reaction is rearrangement of the π complex to a σ complex. The position of the transition state for this rearrangement is determined by the dipolar nature of the medium. According to the Hammond postulate,[12] in a more polar reaction system the transition state resembles the π complex more than the σ complex and bond making has not occurred to an appreciable extent, resulting in a loss in selectivity, but a greater amount of aromatic substitution. In the less polar reaction medium the transition state resembles the σ complex and bond making is more advanced, resulting in a higher energy of activation and a greater selectivity of the reaction as illustrated in Figure 1.

Chart II
Addition-Elimination Mechanism for Halogen Displacement by Cyclohexyl Radical



Part II. Competitions for Cyclohexyl Radical. The data in Table I also reveal three interesting characteristics of the homolytic cyclohexylation of the simple dihalobenzenes. First, in agreement with the preliminary study,[3] halogen ortho to another halogen is activated toward displacement by cyclohexyl radical. Second, the dihaloaromatics are much more reactive than benzene, with all positions being activated to varying degrees toward displacement by cyclohexyl radicals. Third, in the o-dihalobenzenes, the hydrogen which is ortho to a halogen is much more reactive toward displacement than hydrogen which is meta to the nearest halogen.

Table IV
Competition for Cyclohexyl Radicals

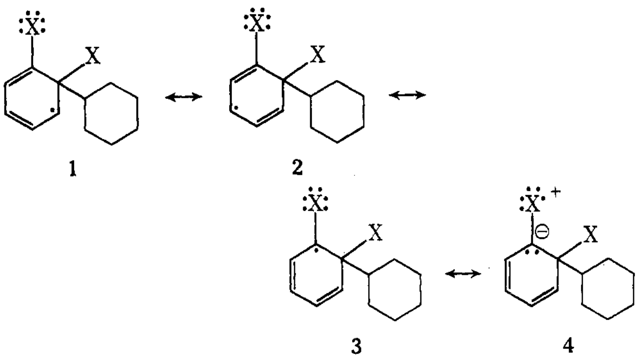
Aromatic substrate	Aromatic substitution %	Aromatic substitution Mol × 10^{-4}	Combination %	Combination Mol × 10^{-4}	Oxygenated products %	Oxygenated products Mol × 10^{-4}
$o\text{-}Cl_2C_6H_4$	24	5.5	16	3.8	15	3.6
$o\text{-}Br_2C_6H_4$	20	3.0	26	4.2	7	1.0
$p\text{-}Cl_2C_6H_4$	44	6.0			10	1.4
$p\text{-}Br_2C_6H_4$	43	11.0	0.9	0.2	3.5	0.9

Table V
Distribution of Oxygenated Products

Aromatic substrate	$C_6H_{10}O\text{-}t\text{-}Bu$ %	$C_6H_{10}O\text{-}t\text{-}Bu$ Mol × 10^{-4}	$C_6H_{10}O$ %	$C_6H_{10}O$ Mol × 10^{-4}	$C_6H_{11}OH$ %	$C_6H_{11}OH$ Mol × 10^{-4}
$o\text{-}Cl_2C_6H_4$	3	0.1	42	1.5	55	2.0
$o\text{-}Br_2C_6H_4$	1	0.01	50	0.5	50	0.5
$p\text{-}Cl_2C_6H_4$	14	0.2	50	0.7	36	0.5
$p\text{-}Br_2C_6H_4$	22	0.2	56	0.5	22	0.2

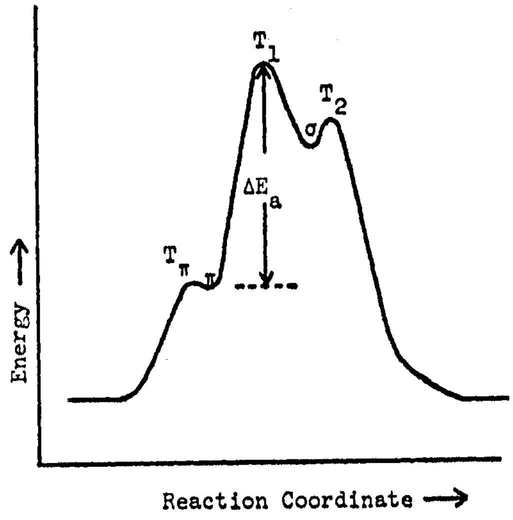
The activation of halogen toward displacement and the enhanced reactivity of the dihaloaromatics relative to that of benzene can be explained for the most part on the basis of stabilization of the various cyclohexyl–cyclohexadienyl radical intermediates which would be formed in the addition–elimination mechanism proposed for homolytic aromatic cyclohexylation (Chart II). As shown in Chart III an additional resonance structure can be drawn involving the halogen atom, for attack either ortho or para to the halogen. This could account for the enhanced reactivity of *o*- and *p*-dihalobenzenes since all positions in these molecules are either ortho or para to a halogen.

Chart III
Resonance Structures for the Intermediate Cyclohexadienyl Radical

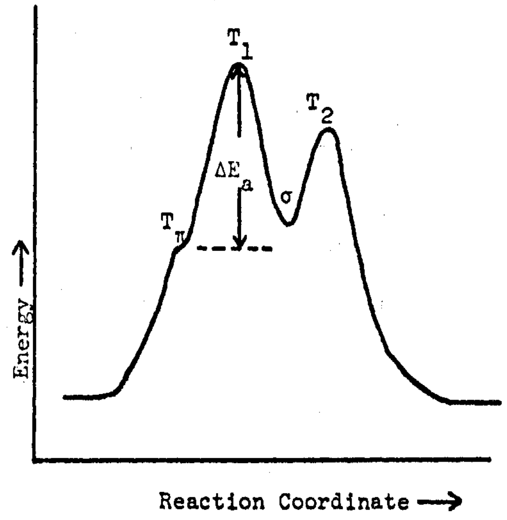


A likely driving force which supplements the resonance contribution is the relief of steric strain between two halogens in going to the intermediate σ complex for the *o*-dihalobenzenes. Bastiansen and Hassel[13] have provided evidence for the existence of this steric strain. Their calculations of the bond distances for *o*-dichloro- and *o*-dibromobenzene fit best with experimental values when they assumed that the carbon–halogen bonds were twisted 18° out of the plane of the benzene ring. The contribution of this relief of steric strain is illustrated in comparing the partial rate factors for the halogen displacement for *o*-dibromobenzene with those for *o*-dichlorobenzene and *p*-dibromobenzene. Bromine ortho to bromine is 5 times as readily displaced as bromine para to bromine, and about 4.5 times as readily displaced as chlorine ortho to chlorine.

The presence of a halogen atom on a carbon would also promote the attack of a "nucleophilic radical" at that carbon owing to its inductive electron-withdrawing effect. However, this effect would be minimized by the formation of a π complex as the initial interaction between the aromatic and the radical.



a) Later transition state



b) Earlier transition state

Figure 1. Energy profile diagrams including π-complex formation for homolytic aromatic cyclohexylation: T_π represents the transition state for π-complex formation; T_1 represents the transition state for rearrangement of the π complex to the σ complex; T_2 represents the transition state for formation of products from the σ complex; π represents the π complex; σ represents the σ complex.

Although the contribution of resonance stabilization of the intermediate σ complex is an important factor in the enhanced reactivity of the dihaloaromatics relative to that of benzene, the activation of the two different types of hydrogen in the *o*-dihalobenzenes is not equivalent. This third trend revealed in Table I indicates that hydrogen ortho to a halogen is much more reactive than hydrogen which is para to a halogen. Preference for displacement of hydrogen which is ortho to the substituent is not uncommon in homolytic aromatic substitution, as has been shown for homolytic methylation by Cowley, Norman, and Walters[14] and Corbett and Williams.[15] Hey and Williams[16] also found an ortho directing effect in their studies of homolytic arylation of substituted aromatics.

Simamura and coworkers[5] observed that phenylation of aromatics using *N*-nitrosoacetanilides as sources of para-substituted phenyl radicals could be fit to a modified Hammett relationship. The conjugative contribution for

Table VI
Competition for Cyclohexyl Radicals in Monohalobenzenes as a Function of Temperature and Amount of O_2 Present

Monohalobenzene	Reaction temp, °C	Mol O_2 present, $\times 10^{-5}$	Aromatic substitution		Combination		Oxygenated products		% total cyclohexylated product accounted for
			%[a]	Mol $\times 10^{-4}$	%[a]	Mol $\times 10^{-4}$	%[a]	Mol $\times 10^{-4}$	
C_6H_5Cl	90	230	7.8	1.1	2.3	0.33	79	12	99
	90	0.11	28	3.5	19	2.4	6.0	0.75	
	105	4.6	34	6.6	3.6	0.64	8.7	1.0	84
	117	4.6	35	18	5.2	3.5	6.0	2.6	86
C_6H_5Br	90	230	13	1.9	1.1	0.16	65	9.8	93
	90	4.6	17	1.3	27	2.1	11	0.85	
	105	4.6	39	7.6	3.8	0.80	6.0	2.0	92
	115	4.6	36	15	7.2	2.2	5.4	2.5	92

[a] Percentages are based on the total cyclohexyl reaction products observed assuming that it takes two cyclohexyl radicals to form an aromatic substitution product and two to form a combination product.

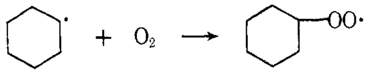
the ortho position in chlorobenzene was shown to be three times as large as that for the para position, indicating a greater resonance contribution for attack at the ortho position.

All of the factors discussed above require that the homolytic cyclohexylation of the aromatics proceeds *via* an addition–elimination mechanism as shown in Chart II. Such a mechanism is well documented for all modes of aromatic substitution, and is especially germane for homolytic aromatic substitution based on the recent demonstration by Fahrenholtz and Trozzolo through the use of CIDNP of the arylcyclohexadienyl radical intermediate for arylation.[17]

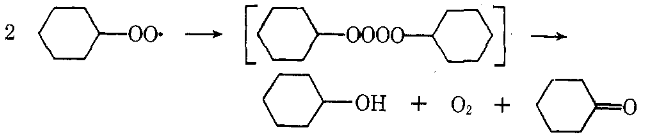
The identity of the acceptor radical, A· in Chart II, has now been established for the displacement of halogen from the dibromo- and dichlorobenzenes studied. Cyclohexyl halide completely accounts for the displaced halogen, so cyclohexyl radical is the acceptor, A·, for the halogen displaced. Direct loss of halogen atom from the σ complex would most likely lead to the production of hydrogen halide. No evidence for the presence of hydrogen halide was found in the reaction mixture.

Other reactions besides aromatic substitution occur for cyclohexyl radical in the reaction system used. Table IV lists the amounts of the other products formed. Unfortunately, the amount of combination in the cyclohexylation of *p*-dichlorobenzene could not be evaluated owing to the lack of resolution between bicyclohexyl and *p*-dichlorobenzene in the glpc for the reaction mixture.

The oxygenated products, which include cyclohexyl *tert*-butyl ether, cyclohexanone, and cyclohexanol, are particularly interesting. The amounts of these products formed are listed in Table V. Cyclohexanone and cyclohexanol most likely form as the result of the interaction of cyclohexyl radicals with molecular oxygen to give cyclohexylperoxy radicals.



The normal termination reaction for this process is the combination of two peroxy radicals with the splitting out of oxygen to give cyclohexanol and cyclohexanone.



That these two products are formed in essentially equal amounts in the *o*-dihalobenzene systems is consistent with this type of termination. However, in the *p*-dihalobenzene systems cyclohexanone forms to an appreciably greater extent than cyclohexanol. This probably results from increased formation of cyclohexyl hydroperoxide by abstraction of hydrogen by $RO_2\cdot$ from cyclohexadienyl radicals formed by addition of cyclohexyl radical at the positions ortho to the halogens. Dehydration of the hydroperoxide would produce ketone without an equivalent amount of alcohol.

Cyclohexyl *tert*-butyl ether can be formed by the cross combination of a cyclohexyl radical with a *tert*-butoxy radical. Why appreciably more of this process occurs in the *p*-dihalobenzene system than in the *o*-dihalobenzene reaction is not clear at this time.

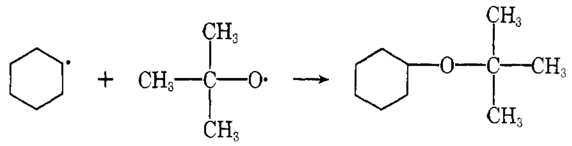


Table VI reveals information about the competition reactions for cyclohexyl radicals in reactions with monohalobenzenes, both as a function of temperature and as a function of the amount of oxygen present. Combination of two cyclohexyl radicals to form bicyclohexyl competes more favorably with aromatic cyclohexylation at 90° than at higher temperatures.

The large decrease in the amount of oxygenated products formed as the amount of oxygen present is decreased indicates that most of the oxygenated products are formed from the interaction of cyclohexyl radical and oxygen.

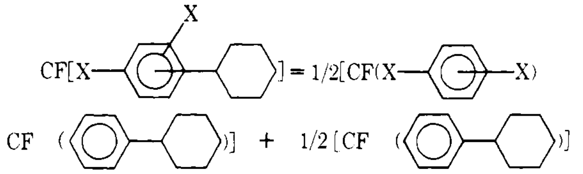
Thus, cyclohexyl radicals generated by decomposition of di-*tert*-butyl peroxide at 90° in cyclohexane and aromatics can effect aromatic substitution, combine with another cyclohexyl radical or a *tert*-butoxy radical to give bicyclohexyl or *tert*-butyl cyclohexyl ether, or interact with oxygen to ultimately yield cyclohexanol and cyclohexanone. Aromatic substitution is favored by electron-withdrawing groups which can stabilize an odd electron on the adjacent carbon, while the amount of cyclohexanol and cyclohexanone formed is dependent upon the oxygen concentration.

A marked solvent effect was observed consistent with the reversible formation of a π complex between cyclohexyl radical and the aromatic. Partial rate factors and relative rates demonstrated (1) the role of steric interaction in the displacement of halogen ortho to another halogen, (2) that the dihaloaromatics were activated toward homolytic cyclohexylation, and (3) that hydrogen ortho to a halogen is more reactive than hydrogen para to the halogen.

Experimental Section

Materials. Commercially available dihalobenzenes were used. o-Dibromobenzene was distilled at aspirator pressure (bp 103–109°) prior to use. Spectrophotometric grade benzene and cyclohexane were used and DTBP was obtained from Columbia Organics and used without further purification.

Cyclohexylation of Dihalobenzenes in Competition with Benzene in Excess Cyclohexane. A mixture of 0.032 mol of the dihalobenzene, 0.032 mol of benzene, 0.320 mol of cyclohexane, and 0.0064 mol of DTBP was weighed into a Fischer-Porter aeresol compatibility vessel. The valve was closed and the vessel was frozen in a Dry Ice–isopropyl alcohol bath. The valve was then opened to an aspirator and the vessel was pumped for 15 min, resealed, and warmed under the hot water tap until thawed. The freeze–evacuation–thaw cycle was repeated twice more and the reaction vessel was immersed in an oil bath in the dark at 90° for 8 days. The reaction vessel was then removed from the bath, cooled, opened under nitrogen, and stored in a brown bottle until analyzed by glpc. Product mixtures were analyzed on a Varian Aerograph HiFi 600D, equipped with a linear column temperature programmer and a 10.5 ft × 0.125 in. 15% Carbowax 6000-Chromosorb W column at a temperature program of 60–190° at 2°/min. (A program of 4°/min was used for the *o*-dibromobenzene reaction products.) Retention times were measured relative to the leading edge of cyclohexane, and individual peaks were identified by comparison with authentic samples. Quantization was accomplished by averaging triangulation and peak height times width at half height integrations. The areas were normalized to the total area of the on-scale peaks (all but cyclohexane). The normalized areas were then divided by molar correction factors, which were determined from known solution with benzene = 1.00, and the resulting areas were then used to determine the competitive data. Molar corrections factors (CF) for the cyclohexylated aromatics were estimated on the basis of the response of cyclohexylbenzene and the appropriate halobenzene or dihalobenzene from the following relation.



Cyclohexylation of Dihalobenzene in Competition with Benzene with Aromatic in Excess. The same procedure was used as in excess cyclohexane, but with the following amounts of reagents: 0.064 mol of dihalobenzene, 0.064 mol of benzene, 0.064 mol of cyclohexane, and 0.0064 mol of DTBP, as compared to 0.032 mol of the dihalobenzene, 0.032 mol of benzene, 0.320 mol of cyclohexane, and 0.0064 mol of DTBP, in excess cyclohexane.

The production of hydrogen halide was tested by opening the sealed tubes into a silver nitrate trap with an aspirator pulling on the other side of the trap. No precipitate formed in the silver nitrate solution, indicating that no hydrogen halide was produced in the reaction.

Synthesis of Authentic Cyclohexylated Aromatics. Both monohalo- and dihalocyclohexylbenzenes were synthesized by Friedel-Crafts cyclohexylation of the appropriate aromatic using cyclohexylchloride and aluminum chloride according to the method of Mayes and Turner.[18] The isomeric products were separated by preparative glpc on a Matronic 500 dual column instrument equipped with a 15 ft × 0.25 in. Carbowax 6000–Chromosorb W column. Sufficient quantities of each isomer could be isolated by this method for ir and retention time analysis. Infrared analysis was performed on a Beckman IR-8 spectrometer.

Synthesis of *tert*-Butyl Cyclohexyl Ether. The method of Lawesson and Yang was used.[19] Crude product was isolated by vacuum distillation (62–67°, aspirator pressure) and purified by preparative glpc on a 15 ft × 0.25 in. 15% Carbowax W column with column temperature 86°, injection point temperature 152°, detector temperature 140°, and carrier gas pressure 30 psi.

Other Authentics. Cyclohexanone and cyclohexanol were purchased from Matheson Coleman and Bell. Bicyclohexyl was obtained from Eastman Organics. All were used without purification.

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Registry No.—*o*-$C_6H_4Cl_2$, 95-50-1; *o*-$C_6H_4Br_2$, 583-53-9; *p*-$C_6H_4Cl_2$, 106-46-7; *p*-$C_6H_4Br_2$, 106-37-6; C_6H_{12}, 110-82-7; C_6H_5Cl, 108-90-7; C_6H_5Br, 108-86-1.

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Stable Carbocations. CLXVIII.[1] Protonation and Cleavage of Dialkyl Pyrocarbonates in FSO_3H-SbF_5 (Magic Acid)-SO_2 Solution

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The protonation and cleavage reactions of dimethyl, diethyl, di-*n*-propyl, and diisopropyl pyrocarbonate in FSO_3H-SbF_5 (magic acid) solution have been studied by pmr and cmr spectroscopy. Cleveage products formed are protonated alkyl hydrogen carbonates, alkyl fluorosulfonates, and carbon dioxide. Di-*n*-propyl and diisopropyl pyrocarbonate give, in addition, a mixture of hexyl cations. In all cases small amounts of protonated carbonic acid and protonated alcohol were also formed. The mechanism of the cleavage reactions is discussed based on experimental data. Cmr parameters of dialkyl pyrocarbonates are also reported.

In the course of our investigation of heteroatom-substituted carbenium ions,[4] we have observed in FSO_3H-SbF_5 (magic acid) solution, by nmr spectroscopy, mono- ($R = R' = H$), di- ($R = H$), and trialkoxycarbenium ions, including the parent ion ($R = R' = R'' = H$).

Mono- and dialkoxycarbenium ions are formed by the