Table IV. Rates and Activation Parameters for Decomposition of Peresters

t-Butyl perester	$t_{1/2}^{60°}$, min	ΔH^*, kcal	ΔS^*, cal/deg	Solvent
Peracetate[4]	5×10^5	38	17	Chlorobenzene
Perbenzoate[a]	3×10^4	33.5	7.8	p-Chlorotoluene
I	7300	28.4 ± 0.9	0.1 ± 2.3	Cumene
II	7160	29.3 ± 0.2	2.9 ± 0.6	Cumene

[a] A. T. Blomquist and A. F. Ferris, *J. Am. Chem. Soc.*, **73**, 3408 (1951).

and carbonyl in the percinnamates now requires restriction about two bonds in the transition state. This should lead to lower entropies of activation for the percinnamates, as observed.

The virtual identity of the rates and activation parameters for the *cis* and *trans* peresters clearly shows that there is no important anchimeric assistance (IV) to the dissociation of *cis* perester. 3,4-Dimethylcoumarin is formed in a product-determining step.

Several *trans*-perester decompositions were run in the presence of the stable radical, di-*t*-butyl nitroxide.[11,18] It was hoped that this would provide a measure of the yield of radicals from the perester, as well as an independent measure of the rate of decomposition.[7] Solutions of perester and di-*t*-butyl nitroxide in cumene were heated under nitrogen in sealed, degassed tubes in the cavity of an esr spectrometer.[19] The cavity was thermostated at 110 ± 2°. The disappearance of the stable radical was measured by scanning the spectrum at 2-min intervals. The change in the area under the first derivative curve was taken as a measure of the change in concentration of nitroxide. Plots of $(Z_0 - Z)$ *vs.* time were not linear, indicating other than a zero-order dependence of the rate on nitroxide concentration (Z_0 = area at time zero; Z = area at time t).

In the presence of nitroxide, the infrared rate for perester decomposition was accelerated; first-order plots were not linear. The total consumption of nitroxide was quite low as compared with the yield of radicals expected from the perester.

These observations suggest a direct reaction between the perester and nitroxide. Further, the low consumption of nitroxide indicates that it is a poor scavenger for the radicals formed from *trans* perester in cumene and/or that the scavenging products are unstable at 110° and regenerate nitroxide.

Acknowledgment. This work was supported by National Science Foundation Grant No. NSF GP 2024.

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(18) S. F. Nelson and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 143 (1966).

(19) Japan Electron Optics Laboratory Co., Ltd., Model JES 3BS-X electron spin resonance instrument. We are indebted to Dr. R. W. Kreilick for assistance with the esr measurements.

Homolytic Aromatic Cyclohexylation

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Abstract: Cyclohexyl radicals, generated by decomposition of di-*t*-butyl peroxide in the presence of cyclohexane, readily react with aromatic compounds to give substitution products. Yields of such products exceed 50% when an electron-attracting aromatic substituent is present. From the orientation and relative reactivity data resulting from attack of cyclohexyl radicals on a variety of monosubstituted benzenes, it is concluded that the nucleophilicity and selectivity increase for the radical species: phenyl < methyl < cyclohexyl. Partial rate factors for the *meta* and *para* positions have been correlated with Hammett σ parameters to give a ρ value of +1.1 for the reaction. When benzonitrile was employed as substrate, an imine was also formed from addition of cyclohexyl radicals to the cyano group and subsequent acquisition of hydrogen.

The area of homolytic aromatic arylation has been extensively investigated,[1] but among the analogous alkylation reactions only methylation has received much attention.[2,3] However, 2 decades ago it was reported[4] that p-cyclohexylbenzoic acid was among the products formed from the decomposition of benzoyl peroxide in cyclohexane. More recently Walling and Gibian[5] have shown that cyclohexyl radicals, derived from cyclohexane *via* hydrogen abstraction by triplet states of ketones, can attack benzene to ultimately yield cyclohexylbenzene. Apparently other secondary alkyl radicals are capable of this type of reaction, for lead tetraacetate decarboxylation of 2-methylbutyric acid in benzene produced unrearranged *sec*-butylbenzene among other products.[6]

Concurrently, in the course of a study involving the reactions of hydrocarbons with *t*-butoxy radicals, we observed that photolysis of di-*t*-butyl peroxide in cyclohexane gave cyclohexylbenzene along with the ex-

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(1) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford, 1960.

(2) B. Cowley, R. Norman, and W. Waters, *J. Chem. Soc.*, 1799 (1959).

(3) G. Corbett and G. Williams, *ibid.*, 3437 (1964).

(4) P. Hermans and J. Van Eyk, *J. Polymer Sci.*, **1**, 407 (1946).

(5) C. Walling and M. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965).

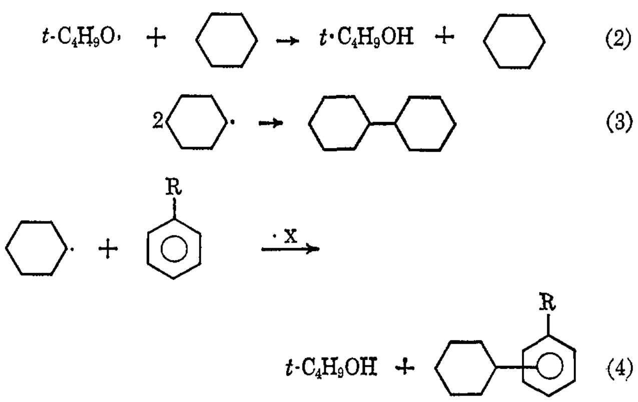
(6) J. Kochi, *ibid.*, **87**, 3609 (1965).

pected products when the reaction was conducted in benzene solution. Since little is known of the orientation resulting from alkylation of monosubstituted benzenes by secondary carbon radicals, we chose to investigate the interaction of cyclohexyl radicals, produced in the above manner, with a variety of aromatic substrates. The aromatic substituents were chosen to include both electron-attracting and electron-releasing groups, and to provide a range of inductive and resonance effects.

Results and Discussion

Photolysis of 0.20 mole of di-*t*-butyl peroxide (DTBP) in 1.00 mole of cyclohexane and 130 ml of the appropriate aromatic compound for 24 hr resulted in partial conversion of the peroxide to *t*-butoxy radicals. The latter species mainly abstracted hydrogen from cyclohexane, forming *t*-butyl alcohol and cyclohexyl radicals, which subsequently coupled to form bicyclohexyl or attacked the aromatic solvent. Minor amounts of acetone were also produced from the β scission of the *t*-butoxy radicals.

$$(t\text{-}C_4H_9O)_2 \xrightarrow{h\nu} 2t\text{-}C_4H_9O\cdot \quad (1)$$



The reaction mixtures were analyzed quantitatively by vapor phase chromatography (vpc) for unreacted DTBP, *t*-butyl alcohol, bicyclohexyl, and cyclohexylated aromatic. Table I presents the yields of *t*-butyl alcohol based on the amount of DTBP decomposed and the yields of bicyclohexyl and cyclohexylated aromatic based on the premise that 2 moles of *t*-butyl alcohol are formed for every mole of these compounds.

Table I. Yields of Products in Homolytic Aromatic Cyclohexylation

Aromatic	Reaction temp, °C	*t*-BuOH[a]	Bicyclohexyl[b]	Arylcyclohexane[b]
C_6H_5CN	93–95	98	<1	58
C_6H_5F	79–81	92	3	54
$C_6H_5CF_3$	83–88	94	4	48
C_6H_5Cl	93–98	93 ± 3[c]	3 ± 1[c]	46 ± 3[c,d]
$C_6H_5OCH_3$	92–98	92	8	38[e]
C_6H_6	78–80	93	7	32
C_6H_5Br	98–101	90	<1	18[d]
$C_6H_5C_4H_9$-*t*	90–100	91	15	15
$C_6H_5CH_3$	84–94	96	1	11[f]

[a] % yield based on amount of peroxide decomposed. [b] % yield based on *t*-BuOH formed. [c] Average deviation for triplicate experiments. [d] Minor amounts of cyclohexylbenzene also formed. [e] 3% phenylcyclohexylmethyl ether also formed. [f] 19% phenylcyclohexylmethane and 22% bibenzyl also formed.

Reacted DTBP is nearly quantitatively accounted for as *t*-butyl alcohol in all cases. The small amount of *t*-butoxy radicals that do not abstract hydrogen undergoes the β-scission process to form acetone. No addition of *t*-butoxy radicals to aromatic systems could be detected. The combined yields of bicyclohexyl and arylcyclohexane, however, never exceed 60%, indicating that *t*-butoxy radicals abstract hydrogen from sources other than cyclohexane and the intermediate σ complex radical and/or that the σ complex radical (cyclohexadienyl-type radical) can participate in processes other than loss of hydrogen, *e.g.*, dimerization. In analogy with products reported to be present in phenylation residues,[7,8] it is likely that both of the aforementioned possibilities occur, and that the substantial amounts of residue obtained in the cyclohexylation reactions contain various biphenyl and partially hydrogenated biphenyl derivatives.[9] We do not believe that the nonquantitative yields of bicyclohexyl and arylcyclohexane result from further reactions involving these products (such as disubstitution or hydrogen abstraction), since a significant change in the ratios of starting materials in the chlorobenzene reaction (DTBP:cyclohexane:chlorobenzene varied from 1:5:5 to 1:10:20) had little effect on either the yield or isomer distribution of cyclohexylchlorobenzenes.[10] Other workers[11] have concluded that the isomeric σ complexes formed in homolytic arylation are not selectively removed by dimerization or disproportionation since the proportion of isomers actually observed is relatively insensitive to large changes in reaction conditions.

It may be seen from Table I that *t*-butylbenzene gives the highest amount of bicyclohexyl and, excepting toluene, the lowest amount of arylcyclohexane. Such results are in accord with our observation that *t*-butylbenzene is the least reactive of the aromatic compounds studied relative to benzene in homolytic aromatic substitution, apparently owing to adverse steric and inductive effects. The low yield of cyclohexyltoluene may at first glance appear anomalous, but actually homolytic aromatic cyclohexylation is a minor process in this system with the major products, phenylcyclohexylmethane and bibenzyl, being derived in whole or part from benzyl radicals. One may not have anticipated that benzyl radical products would predominate over cyclohexyl types since cyclohexane is known to be five to six times as reactive[12,13] as toluene toward hydrogen abstraction by *t*-butoxy radicals. Several workers, however, have demonstrated[13,14] that cyclohexyl radicals react with toluene as illustrated in eq 5 to produce cyclohexane and benzyl radicals. No benzyltoluenes, resulting from homolytic benzylation of toluene, could be detected in the reaction mixture.

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(7) D. DeTar and R. Long, *J. Am. Chem. Soc.*, **80**, 4742 (1958).

(8) E. Eliel, S. Meyerson, Z. Welvart, and S. Wilen, *ibid.*, **82**, 2936 (1960).

(9) In the chlorobenzene experiments the residue amounted to approximately 125 wt % of the cyclohexylchlorobenzene formed.

(10) The yield of arylcyclohexane was 41% and the *ortho*:*meta*:*para* ratio was 52:34:14; see Table II.

(11) G. Gill and G. Williams, *J. Chem. Soc.*, 7127 (1965).

(12) R. Gilliom and B. Ward, *J. Am. Chem. Soc.*, **87**, 3944 (1965).

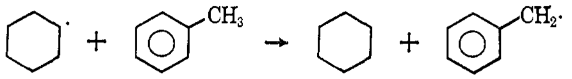
(13) P. Wagner and C. Walling, *ibid.*, **87**, 5179 (1965).

(14) J. Brook and R. Glazebrook, *Trans. Faraday Soc.*, **65**, 1014 (1960).

Table II. Orientation in Homolytic Aromatic Substitution

Aromatic	Cyclohexylation *o*	Cyclohexylation *m*	Cyclohexylation *p*	Methylation *o*	Methylation *m*	Methylation *p*	Phenylation *o*	Phenylation *m*	Phenylation *p*
C_6H_5F	61	35	4^{a}	58	37	5^{c}	54	31	$15^{f,g}$
C_6H_5Cl	54 ± 2	34 ± 2	12 ± 2^{b}	62	28	10^{c}	50	32	$18^{f,h}$
				64	25	11^{d}			
C_6H_5Br	58	32	10	55	34	11^{c}	50	33	$17^{f,i}$
				67	23	10^{d}			
$C_6H_5OCH_3$	67	28	5	74	15	11^{d}	69	18	$13^{j,k}$
							79	10	$11^{f,l}$
C_6H_5CN	52	4	44	48	9	43^{d}	60	10	$30^{f,m}$
$C_6H_5CF_3$	6	52	42	...	...	...	29	41	$30^{f,n}$
$C_6H_5CH_3$	32	43	25^{a}	59	29	12^{c}	67	19	$14^{f,o}$
				56	27	$17^{d,e}$			
$C_6H_5C_4H_9$-*t*	0	72	28	...	...	...	24	49	$27^{f,p}$
							10	63	27^{q}

[a] Vpc and infrared analysis used. [b] Represents the average deviation between triplicate experiments. [c] Photolysis of methylmercuric iodide. [d] Thermolysis of di-*t*-butyl peroxide.[2] [e] Thermolysis of acetyl peroxide: E. Eliel, K. Rabindran, and S. Wilan, *J. Org. Chem.*, **22**, 859 (1957). [f] Thermolysis of benzoyl peroxide. [g] D. Augood, J. Cadogan, D. Hey, and G. Williams, *J. Chem. Soc.*, 3412 (1953). [h] C. Shih, D. Hey, and G. Williams, *ibid.*, 2600 (1958). [i] R. Dannley, E. Gregg, R. Phelps, and C. Coleman, *J. Am. Chem. Soc.*, **76**, 445 (1954). [j] Thermolysis of N-nitrosoacetanilide. [k] T. Inukai, K. Kobayashi, and O. Shimamura, *Bull. Chem. Soc. Japan*, **35**, 1576 (1962). [l] B. Lynch and R. Moore, *Can. J. Chem.*, **48**, 1461 (1962). [m] R. Dannley and E. Gregg, *J. Am. Chem. Soc.*, **76**, 2997 (1954). [n] D. Hey, F. Saunders, and G. Williams, *J. Chem. Soc.*, 554 (1961). [o] D. Hey, B. Pengilly, and G. Williams, *ibid.*, 1463 (1956). [p] J. Cadogan, D. Hey, and G. Williams, *ibid.*, 3352 (1954). [q] Photolysis of triphenylbismuth: D. Hey, D. Singleton, and G. Williams, *ibid.*, 5612 (1963).


(5)

Small amounts of cyclohexylbenzene are produced in the reaction of cyclohexyl radicals with the halobenzenes, probably as a result of radical attack upon the 1 position of the halobenzene. This mode of reaction may be very much enhanced by higher reaction temperatures, but does not seem to depend on whether the DTBP is decomposed thermally or photolytically. For example, thermal decomposition of DTBP in cyclohexane–bromobenzene solution at 115–120° produced a statistical ratio (5:1) of cyclohexylbromobenzene to cyclohexylbenzene. Studies are in progress to further elucidate this pathway and establish the relative reactivities of the halogens.

Vacuum distillation of the reaction mixtures afforded concentrated fractions of the various arylcyclohexanes. Higher boiling fractions were obtained with *t*-butylbenzene and anisole and most probably consisted of products derived from abstraction of methyl hydrogen from these substrates to give radicals which subsequently substitute on another molecule of the substrate.[15] In fact, the infrared spectra of the higher boiling anisole fraction and independently prepared *o*-phenoxymethyanisole were almost identical. A small amount of phenyl cyclohexylmethyl ether was also detected in the anisole reaction, but no diphenoxyethane could be detected. All reaction mixtures yielded a nonvolatile residue upon distillation.

The arylcyclohexane fractions were subjected to vpc analysis to resolve the isomers. Complete resolution of cyclohexylfluorobenzenes and cyclohexyltoluenes could not be obtained by vpc techniques; therefore a quantitative infrared treatment was applied in these cases. For those arylcyclohexanes which could be separated by vpc, authentic isomer mixtures were prepared when possible by Friedel–Crafts alkylation of the appropriate aromatic, and infrared analysis of the individual peaks as they emerged from the chromatograph confirmed their isomer assignments. For the quantitative infrared analysis, isomerically pure cyclohexylfluorobenzenes and cyclohexyltoluenes were prepared by the method of Blackwell and Hickinbottom.[16] Table II reports the experimental isomer distributions for free-radical cyclohexylation under the described conditions together with available data from the literature on phenylation and methylation. Table III presents the *meta*/*para* ratios obtained from the data in Table II.

It may be seen from Table III that for aromatic substituents which are generally considered as *ortho*–*para* directors in electrophilic substitution, the *meta*:*para* ratios generally increase in the series: phenylation < methylation < cyclohexylation, with those for phenylation near the statistical value of 2.0 and those for alkylation somewhat higher. Just the reverse effect is observed in the case of the strongly electron-attracting cyano group; *i.e.*, cyclohexylation gives the lowest *meta*:*para* ratio. Thus in the cyclohexylation process the proportion of *para* substitution is increased by a group which diminishes electron density at that position and decreased by one which causes that region of the aromatic molecule to become relatively more electron rich. Such directional effects are opposite to those normally encountered in electrophilic aromatic substitution and suggest increasing nucleophilicity and selectivity of the radical attacking species in

Table III. *meta*/*para* ratios in Homolytic Aromatic Substitution

Aromatic	Cyclohexylation	Methylation	Phenylation
C_6H_5F	8.8	7.4	2.0
C_6H_5Cl	2.8	2.3, 2.8	1.8
C_6H_5Br	3.2	2.3, 3.1	2.0
$C_6H_5OCH_3$	5.6	1.4	0.9, 1.4
C_6H_5CN	0.09	0.21	0.33
$C_6H_5CF_3$	1.2	...	1.4
$C_6H_5CH_3$	1.7	1.6, 2.4	1.4
$C_6H_5C_4H_9$-*t*	2.5	...	1.8, 2.3

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(15) H. Henbest, J. Reid, and C. Stirling, *J. Chem. Soc.*, 5239 (1961).

(16) J. Blackwell and W. Hickinbottom, *ibid.*, 518 (1963).

Table IV. Relative Reactivities (*k*) and Partial Rate Factors (*f*) in Homolytic Aromatic Substitution

Aromatic	Cyclohexylation[a] k	f_o	f_m	f_p	Phenylation k	f_o	f_m	f_p
C_6H_5CN	27	42	3.3	72	3.7	6.5	1.1	6.5[1]
C_6H_5Cl	3.5[b]	5.6	3.5	2.5	1.1	1.6	1.0	1.2[d]
$C_6H_5OCH_3$	2.3	4.6	1.9	0.69	1.7	3.6	0.93	1.3[e]
$C_6H_5CF_3$	2.0	0.36	3.1	5.0	1.0	0.87	1.2	1.8[d]
C_6H_5F	1.9[c]	3.6	2.0	0.47	1.0	1.7	0.95	0.86[d]
$C_6H_5CH_3$	0.76	0.73	0.98	1.1	1.2	2.5	0.71	1.0[d]
C_6H_5-*t*-C_4H_9	0.28	0	0.60	0.47	0.64	0.46	0.94	1.0[d]

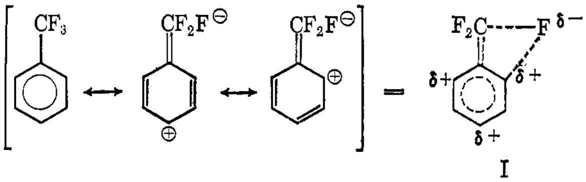
[a] Reaction temperature 90° except where noted. [b] Relative reactivity 3.8 at 32°. [c] Relative reactivity 1.8 at 32°. [d] D. Hey, S. Orman, and G. Williams, *J. Chem. Soc.*, 565 (1961). [e] See footnote *k*, Table II.

the series: phenylation < methylation < cyclohexylation.[2,16a]

The orientation observed in the cyclohexylation of the halobenzenes, anisole, and the alkylbenzenes could be rationalized solely in terms of inductive effects. Granted that the cyclohexyl radical seeks to react at relatively electropositive sites in the aromatic substrate, the halobenzenes and anisole would be expected to show *ortho* > *meta* > *para* orientation while the alkylbenzenes should demonstrate decreasing *ortho* and increasing *para* substitution. However, on this basis, benzonitrile and benzotrifluoride should give orientational trends similar to the halobenzenes, but such is not the case. Specific *para* activation produced by resonance interaction of the nitrile group with the *para* position most reasonably accounts for the large amount of *para* cyclohexylation in benzonitrile. Moreover, recent investigations of homolytic arylation[17] have shown that the influence of a substituent may be divided into resonance and inductive effects with the latter predominating only for *meta* substitution.

Attack of cyclohexyl radicals upon benzotrifluoride produces an unusual distribution of cyclohexylbenzotrifluorides. The very low amount of *ortho* substitution is in complete disagreement with the election-withdrawing nature of the trifluoromethyl group. The concepts of fluorine hyperconjugation[18] and π-inductive effects[19] both account for the preferential *para* orientation (*meta*:*para* ratio = 1.2), but neither explain the low *ortho* substitution since both predict relatively low electron density in both *ortho* and *para* positions. Recently Sheppard[20] has suggested that in certain conformations of the trifluoromethyl group of benzotrifluoride the p orbitals of the fluorines can interact with the aromatic π-electron system, especially at the *ortho* positions. The possibility that fluorine–hydrogen bonding to the *ortho* hydrogen would induce carbanion character at the *ortho* carbon was also mentioned. Either effect is consistent with the observed reduction in the amount of *ortho* substitution in our system. Still another possible explanation in the literature[21] is based on the fact that a Hammett treatment of hydrogen abstraction from alkyl side chains of substituted benzenes reveals a negative ρ,[12] implying that electron-withdrawing groups (like trifluoromethyl) hinder removal of hydrogen. Thus, the *ortho* adduct could more readily undergo side reactions such as dimerization. This interpretation, however, does not explain why fluorobenzene and benzonitrile give large amounts of *ortho* substitution.

We feel that the evidence for fluorine hyperconjugation is convincing and that this model should be the basis for our interpretation of the data. As shown in eq 6, a partial loosening of the C–F bond effects a partial negative charge on fluorine and partial positive charges in the *ortho* and *para* positions of the ring.



(6)

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Accepting Sheppard's calculations regarding the proximity of fluorine and the *ortho* positions, a simple polar or field effect should be important. Not only will the electronegative fluorine tend to neutralize the favorable positive charge in the *ortho* position, but it also would tend to repulse an incoming nucleophilic cyclohexyl radical. A simple steric effect of the CF_3 group cannot be invoked since the methyl group allows more than five times as much *ortho* substitution even though both substituents are of comparable size.

The reactivities of the arenes relative to benzene toward substitution by cyclohexyl radicals were determined by a competitive technique. The appropriate arene–benzene mixture was allowed to compete for the cyclohexyl radical in each case, and the reaction mixture analyzed directly by vpc for the relative amounts of arylcyclohexane and cyclohexylbenzene formed. These compounds were taken as indicative of the relative amounts of attack by cyclohexyl radicals upon the aromatic nuclei of arene and benzene. Having obtained the relative reactivity (*k*) of a particular monosubstituted benzene in this manner, the partial rate factors (*f*) for the *ortho*, *meta*, and *para* positions were calculated employing the data in Table II. Table IV contains the relative reactivities and partial rate factors for cyclohexylation along with literature data of phenylation.

The data shown in Table IV may be rationalized in terms of the nucleophilicity of the cyclohexyl radical

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(16a) NOTE ADDED IN PROOF. A. Stefani, G. Chuang, and J. Hataway, Abstracts of Papers, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 12–16, 1966, have shown that the cyclopropyl radical is relatively nucleophilic compared to either the methyl or trifluoromethyl radical by studying the rates of addition of these species to a series of olefins.

(17) R. Ito, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

(18) J. D. Roberts, R. Webb, and E. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

(19) M. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962.

(20) W. Sheppard, *J. Am. Chem. Soc.*, **87**, 2410 (1965).

(21) C. Rondestvedt and H. Blanchard, *J. Org. Chem.*, **21**, 229 (1956).

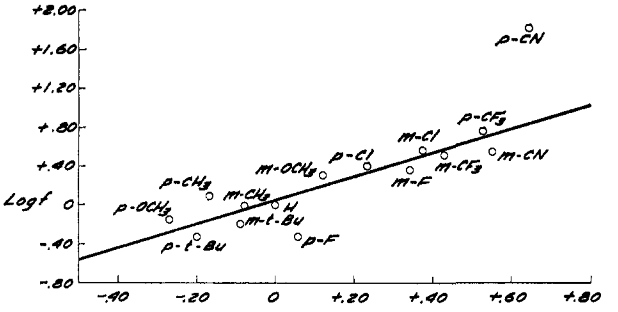

Figure 1. Hammett correlation for homolytic aromatic cyclohexylation.

and the preference of the latter species for regions of relatively low electron density. Again it may be seen that the cyclohexylation process is more selective than phenylation. The relative reactivities for phenylation vary by less than a factor of 6 over the range of substrates listed, while those for cyclohexylation differ by almost a factor of 100. Both methyl and *t*-butyl substituents cause an over-all deactivation of the aromatic nucleus toward cyclohexylation due to unfavorable inductive and steric effects. The importance of the spatial limitation is particularly illustrated by the lack of substitution at the *ortho* positions of *t*-butylbenzene.

The partial rate factors for both *meta* and *para* cyclohexylation may be correlated with available σ-substituent parameters according to the Hammett relationship, as illustrated in Figure 1. A least-squares analysis of this plot (excluding *p*-F and *p*-CN) yields a line of slope $+1.1$ with a standard deviation of 0.10 log unit. A similar correlation has recently been shown to exist for the *meta* rate factors in arylation with a ρ value of $+0.05$ for the phenyl radical.[17] The higher positive value of the ρ for the cyclohexylation process further emphasizes the nucleophilicity associated with the attacking species and reflects a greater amount of bond making in the transition state. Inspection of Figure 1 reveals that the *p*-fluoro and *p*-cyano points deviate significantly from the plot, indicating that the existing σ values reflect neither the ability of the *p*-cyano group to stabilize the transition state for homolytic cyclohexylation (which probably resembles the intermediate radical σ complex) nor the destabilizing effect of the *p*-fluoro group. Such deviations are understandable since the σ values originate from the ionization constants of substituted benzoic acids and do not necessarily reflect the ability of a substituent to stabilize an odd electron.

It is interesting that a better correlation is obtained with σ rather than σ^+ values since many radical reactions do follow the σ^+ values. For example, the formation of substituted benzylic radicals by abstraction of hydrogen by bromine and chlorine atoms, trichloromethyl radicals, and peroxy radicals all give a better Hammett correlation with σ^+ values.[22] However, these radicals are relatively electronegative and probably enhance the contribution of polar structures to the stabilization of the transition state. Howard and Ingold,[23] in discussing the factors affecting ρ in radical reactions, point out that radicals with a low electron affinity (*e.g.*, alkyl radicals) could be expected to follow σ rather than σ^+ values. Our observations lend further support to this hypothesis and the σ correlation indicates that, among the structures which could contribute to the transition state, polar structures should be relatively unimportant.

It has been shown that the relative electronegativities of radicals increase in the series: cyclohexyl < methyl < phenyl;[24] thus nucleophilicities would be in the reverse order. Following this reasoning, a tertiary alkyl radical should be still more nucleophilic than the secondary cyclohexyl radical and thus lead to even higher *meta:para* ratios with electron-releasing substituents. To test this hypothesis, *t*-butyl peroxypivalate, a source of *t*-butyl radicals,[25] was thermally decomposed in chlorobenzene. However, no *t*-butylchlorobenzene could be detected; rather disproportionation of *t*-butyl radicals to isobutylene and isobutane occurred. Davies and Waring[26] have recently reported that apocamphane-1-carboxylic acid reacts with lead tetraacetate in refluxing benzene to give 1-phenylapocamphane in 56% yield by a free-radical mechanism. However, a tertiary bridgehead radical would be expected to be of higher energy than an aliphatic tertiary radical because of the rigidity of the bicyclic system, which also blocks disproportionation.

Use of benzonitrile as a substrate for homolytic aromatic substitution provides the additional possibility of radical addition to the side chain. Under the photolytic conditions of the cyclohexylation process, only trace amounts of 1-phenyl-1-cyclohexylmethylenimine were observed, but thermal decomposition of DTBP in a cyclohexane–benzonitrile system at 110° for 3 days produced substantial amounts of the imine (one-third that of the nuclear substitution product) and an over-all yield of 40% of cyclohexylbenzonitriles, as compared with a 58% yield of the same product in the photolytic reaction. Although an independently prepared sample of the imine evidenced considerable absorption in the ultraviolet (ϵ_{240} ~12,000) and decomposed over 50% upon photolysis in cyclohexane solution under simulated reaction conditions, the lower yield of product substituted on the aromatic nucleus, the higher reaction temperature, and the longer reaction time of the thermal reaction suggest that addition of cyclohexyl radicals to the cyano group requires a higher activation energy than nuclear substitution.

The direction of radical addition to the cyano dipole is also of interest. As already mentioned, cyclohexyl radicals added exclusively to the positively polarized carbon end of the nitrile functionality, for no N-benzylidenecyclohexylamine could be found. However, phenyl radicals generated in benzonitrile by thermal decomposition of benzoyl peroxide also added exclusively at this position to produce 1,1-diphenylmethylenimine. Since the isomer distribution data of Table II indicate that phenyl and cyclohexyl radicals are much different in nucleophilic character, their direction of addition to the nitrile group must be determined

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(23) J. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

(24) H. Pritchard and H. Skinner, *Chem. Rev.*, **55**, 745 (1955).

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by the differences in energy of the possible products. The intermediate radical addition product, whatever its nature may be, must acquire hydrogen from some source to yield the observed imine. The nitrogen-centered imino radical, like alkoxy radicals, should be more efficient in this respect than the alternative benzylic radical.

Since benzonitrile has an unusually high methyl radical affinity[27] consistent with addition of methyl radicals to the cyano group, other workers[2] have searched for products of such addition but none could be detected.

Finally, then, the type of homolytic aromatic alkylation reported herein may be of some synthetic usefulness, especially for alkyl derivatives of electron-deficient aromatics. Yields of such types as cyclohexylbenzonitriles and cyclohexylbenzotrifluorides exceeded 50% and these compounds would not be readily accessible by electrophilic alkylation. It is worthy of note that yields of arylcyclohexanes are greatest for electron-deficient aromatics, in qualitative agreement with the proposed nucleophilicity of the cyclohexyl radical and the relative reactivities shown in Table IV.

Experimental Section

Infrared spectra of arylcyclohexanes were recorded on a Beckman IR8 spectrophotometer. Vapor phase chromatography was performed on an instrument constructed in our own shop using the following columns: 12 ft × $^1/_4$ in. 20% silicone grease on Chromosorb P (column A); 6 ft × $^1/_4$ in. 30% Carbowax 6000 on Chromosorb W (column B); 12 ft × $^1/_4$ in. 30% Carbowax 6000 on Chromosorb W (column C). Final isomer distributions were determined using the Aerograph Hy-Fi Model 600 D chromatograph equipped with a 10 ft × $^1/_8$ in. 10% Apiezon L on 60–80 mesh acid-washed Chromosorb P column (column D) at 20 psi nitrogen pressure. The relative reactivities were determined on a 10 ft × $^1/_8$ in. 5% Carbowax 6000 on 60–80 mesh Chromosorb W (column E) at 150° and 15 psi, except for the fluorobenzene runs where a 15 ft × $^1/_8$ in. 20% diethylene glycol succinate on 60–80 mesh Chromosorb P (column F) at 150° and 20 psi was used.

Materials. Commercially available aromatic compounds were used and redistilled when necessary. The cyclohexane was Eastman spectroquality grade. Di-*t*-butyl peroxide (DTBP) and *t*-butyl peroxypivalate were obtained from Lucidol Division, Wallace and Tiernan, Inc.

Photolysis of DTBP in Cyclohexane–Aromatic System. General Procedure. The photolysis apparatus consisted of a Pyrex outer vessel equipped with thermometer, nitrogen inlet, and condenser connected to a bubbler, and a Pyrex inner jacket which supported the General Electric H100A4 Hg lamp. The outer glass jacket of the Hg lamp had to be removed to allow insertion of the lamp in the apparatus. Cyclohexane (84.0 g, 1.00 mole), DTBP (29.2 g, 0.20 mole), and 130 ml of the appropriate aromatic were added, and the system was flushed with nitrogen at room temperature for 1 hr. The nitrogen was then shut off and the mixture was photolyzed for 24 hr at the reflux temperature of the mixture. Heat for the reflux was supplied by the lamp itself and a proper reflux rate was maintained by passing a stream of air over the ultraviolet source. The reaction mixture was magnetically agitated during the photolysis.

Relative Rate Studies. A mixture of 42.0 g of cyclohexane (0.50 mole) and 7.3 g of DTBP (0.05 mole) was photolyzed for 24 hr at the reflux temperature (near 90°) in 2.20 moles of mixed aromatic solvent. Two runs were conducted for each system employing an equimolar mixture of benzene and arene in one case and a 2:1 ratio of benzene:arene in the other. The reaction mixtures were analyzed directly for the relative amounts of arylcyclohexane and cyclohexylbenzene by vpc using either column E or F. An average result was taken for the two runs for each arene. The resulting values of k in Table IV are accurate to ±1 in the second significant figure.

Determination of Product Yields. Unreacted DTBP and *t*-butyl alcohol were determind by vpc analysis using column A at 100°. Toluene or ethylbenzene were employed as internal standards and added to the reaction following its completion. Bicyclohexyl and arylcyclohexane were analyzed on column B at 175° with *o*-dichlorobenzene or 1,2,4-trichlorobenzene added as internal standard. Wherever possible the gas chromatograph was calibrated for area response differences between internal standard and reaction products.

Synthesis of Arylcyclohexanes *via* Electrophilic Substitution. Generally the aromatic (excepting benzotrifluoride and benzonitrile) was alkylated with cyclohexene (6:1 mole ratio) and either concentrated H_2SO_4 (amount equal in weight to cyclohexene) or $AlCl_3$ (amount equimolar to cyclohexene) as catalyst at ice-bath temperatures. The yield of arylcyclohexane obtained by distillation ranged from 45 to 55% depending on the substrate, and boiling points were in a range consistent with those reported in the literature.[16]

Synthesis of Cyclohexylbenzonitriles. The cyclohexylbenzonitriles were prepared from the cyclohexylbromobenzenes, by the method of Friedman and Shechter.[28] A mixture of 44 g (0.18 mole) of cyclohexylbromobenzene (mixture of isomers) and 19.7 g (0.22 mole) of CuCN in 30 ml of DMF was refluxed for 17 hr, after which the reaction mixture was treated with aqueous ethylenediamine producing an intense blue color. Extraction with benzene and ether followed by drying and distilling the brown organic layer produced a 60% yield of the desired nitrile isomerides (bp 110–135° at 0.4–0.6 mm). A boiling point for the *para* isomer (123° at 0.5 mm) has been reported.[29]

Determination of Isomer Distributions by Vpc Analysis. A portion of each reaction mixture was distilled through a mini-lab apparatus under reduced pressure to obtain concentrated fractions of the various arylcyclohexanes. Such a distillation was shown not to alter the isomer distribution but served to make further analyses more convenient and allow some estimation of the amount of residue (nonvolatile products) formed. Preliminary isomer ratios and infrared spectra of pure isomers were obtained by subjecting these distillates to vpc analysis using column C at 175°. Such spectra agreed in all cases with those obtained from similar vpc analysis of the independently synthesized arylcyclohexanes. Final isomer distributions as reported in Table II were determined using column D in conjunction with the Aerograph Hy-Fi. Peak areas of isomers were taken as indicative of the amount of each isomer present. Table V reports retention times of the arylcyclohexanes under these conditions.

Table V. Retention Times (min) of Arylcyclohexanes[a]

Aromatic	Column temp, °C	*o*	*m*	*p*
Fluorobenzene	140	45	50	50
Chlorobenzene	175	43	53	56
Bromobenzene	175	63	81	88
Anisole	165	60	82	90[b]
Benzonitrile	195	35	53	58[c]
Benzotrifluoride	150	23	27	33
Toluene	150	57	57	62[d]
t-Butylbenzene	175	. .	62	86

[a] Column D; nitrogen pressure, 20 psi. [b] Bicyclohexyl, 26 min; and phenylcyclohexylmethyl ether, 75 min. [c] 1-Phenyl-1-cyclohexylmethylenimine, 38 min. [d] Bicyclohexyl, 35 min; phenylcyclohexylmethane, 54 min; bibenzyl, 95 min.

Determination of Isomer Distributions by Quantitative Infrared Analysis. The cyclohexylfluorobenzenes and cyclohexyltoluenes were analyzed in this manner. Isomerically pure reference compounds were prepared by the method of Blackwell and Hickinbottom.[16]

Columns C and D separated *o*-cyclohexylfluorobenzene from the *meta* and *para* isomers. The infrared absorbance ratios of various known mixtures of the authentic *meta* and *para* isomers were measured using the 815-cm^{-1} peak for the *para* isomer and the 770- and 688-cm^{-1} peaks for the *meta* isomer. From such data and

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[27] W. Hellman, A. Rembaum, and M. Szwarc, *J. Chem. Soc.*, 1127 (1957).

[28] L. Friedman and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961).

[29] O. Neunhoeffer, *J. Prakt. Chem.*, **133**, 95 (1932).

the *meta*/*para* absorbance ratio obtained by trapping the unresolved vpc peak, the ratio of these isomers could be determined.

Since no separation of cyclohexyltoluenes was possible on the $^1/_4$-in. columns listed, Beer's law plots were constructed for all three isomers, employing bands at 755 (*ortho*), 778 (*meta*), and 809 cm^{-1} (*para*). Such plots were linear over the concentration range studied (<0.05 *M* in CS_2). Fortunately column C separated the cyclohexyltoluenes from phenylcyclohexylmethane and bibenzyl; hence this peak was trapped in its entirety, and from the absorbances at the wave numbers previously mentioned, actual amounts of each isomer could be calculated. The isomer distribution so determined agreed with a partial isomer distribution obtained from column D which separated *o*- and *m*-cyclohexyltoluene as a combined peak from the *para* isomer in the ratio 75:25.

Preparation of Anisole Derivatives. 1,2-Diphenoxyethane was obtained as a white solid (mp 96–97°; lit.[30] 97–98°) from the condensation of phenol with ethylene bromide under basic conditions. Phenyl cyclohexylmethyl ether (bp 139–141° at 10 mm) was prepared by a similar condensation of phenol with cyclohexylmethyl bromide.

Preparation of Toluene Derivatives. Phenylcyclohexylmethane (bp 71–73° at 0.5 mm) was formed in very low yield (~1%) by the action of benzyl chloride upon an ethereal solution of cyclohexyl Grignard reagent. A benzyltoluene mixture (bp 107–110° at 0.3 mm) was produced in 50% yield by the reaction of toluene with benzyl chloride and $AlCl_3$. Bibenzyl was commercially available.

Thermal Decomposition of DTBP in Cyclohexane–Benzonitrile Solution. DTBP (7.3 g, 0.05 mole), cyclohexane (21.0 g, 0.25 mole), and benzonitrile (103.0 g, 1.00 mole) were placed in a three-neck 300-ml flask equipped with thermometer, magnetic stirring bar, nitrogen inlet, condenser, and bubbler. The system was flushed with N_2 for 30 min and then refluxed for 70 hr. The reaction mixture was analyzed as in the photolytic case. Duplicate experiments gave *ortho*:*meta*:*para* ratios of 49:3:48 and 49:4:47.

Synthesis and Photolysis of 1-Phenyl-1-cyclohexylmethylenimine. To an ethereal solution of 0.40 mole of cyclohexylmagnesium chloride was added an equimolar amount of benzonitrile dropwise. Following this addition the reaction was hydrolyzed with ice and HCl while keeping the mixture near pH 7 to avoid hydrolysis and/or hydrochloride formation of the imine. The ether layer was removed, washed with water, dried with Na_2SO_4, and filtered. Distillation gave a 35% yield of the imine (bp 114–119° at 0.4 mm) which gradually crystallized to a pale yellow solid (mp 52–53°). The infrared spectrum showed a strong absorption at 1670 cm^{-1} in the region where a C=N stretching vibration should appear, and the ultraviolet spectrum (in cyclohexane) showed maxima at 240 mμ (ϵ 11,800), 275 (660), 288 (410), and 325 (60). A solution of 9.3 g of the imine (0.05 mole) in cyclohexane was photolyzed for 24 hr. Only 3.9 g of the imine (42%) was recovered by distillation. No attempts were made to identify the products of this photolysis. That this imine, and not N-benzylidenecyclohexylamine, was indeed formed in the thermal decomposition of DTBP in the cyclohexane–benzonitrile system was demonstrated by vpc peak enrichment and comparison of infrared spectra.

Decomposition of Benzoyl Peroxide in Benzonitrile. A solution of 12.1 g of benzoyl peroxide (0.05 mole) in 103.0 g of benzonitrile (1.00 mole) was heated at 90–110° for 3 hr, during which time CO_2 evolution was observed. Analysis of the reaction mixture on column D showed an appreciable amount of 1,1-diphenylmethylenimine but no N-benzylideneaniline. The imine was synthesized as previously described (bp 123–125° at 1 mm) (lit.[31] 127° at 3.5 mm) while the Schiff base was formed from benzaldehyde and aniline. The expected cyanobiphenyls were also present and the *ortho* isomer appeared as a shoulder on the *larger* imine peak.

Decomposition of *t*-Butyl Peroxypivalate in Chlorobenzene. The perester is supplied as a 75% solution in mineral spirits and known as Lupersol 11. An amount of this solution containing 0.10 mole of perester was thermally decomposed at 60° in 200 ml of chlorobenzene for 25 hr (5 half-lives) under an inert atmosphere. No *t*-butylchlorobenzenes were detected from this reaction.

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Radical-Ionic Reaction Mechanisms. Homolysis of the Carbonium Ion *t*-Butyl Tropeniumperacetate[1,2]

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Abstract: Calculations of delocalization energies of certain radical cations and their precursors indicate that such species should sometimes form under ordinary ionic reaction conditions. One such system has been studied. The carbonium ion *t*-butyl tropeniumperacetate fluoroborate decomposes in acetonitrile 2700 times faster than does *t*-butyl phenylperacetate in the same solvent. The ratio of *t*-butyl alcohol to acetone produced in this decomposition and the induced decomposition at high concentrations indicate homolytic decomposition. This rate comparison implies that a tropeniumyl group stabilizes the methyl radical much more than does a phenyl group. Such a finding is at variance with the predictions of polar effects on free-radical reactions but accords with our predictions based on molecular orbital calculations of the stabilities of benzyl and tropeniumylmethyl radicals.

Resonance stabilization of carbonium ions and free radicals is well known.[3a] Furthermore, free radicals are stabilized by delocalization into either electron-rich or electron-deficient π systems. For example, both the tri-*p*-anisylmethyl and tri-(*p*-nitrophenyl)methyl radicals are more stable than the triphenylmethyl radical.[3b] Calculations on methyl or benzyl radicals indicate that either CH_2^+ or CH_2^- should stabilize these radicals.[4] Thus substitution

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[2] (a) Abstracted from the Ph.D. Thesis of G. R. Jurch, Jr., University of California, San Diego, 1965; (b) National Defense and Education Act Predoctoral Fellow, 1961–1964.

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