AN ABSTRACT OF THE THESIS OF

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Title: HYDROGEN ABSTRACTION FROM SUBSTITUTED

t-BUTYLBENZENES

Abstract approved: ███████████████████████
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A study of the relative rates of the alkyl hydrogen abstraction

from a series of _meta_ and _para_ substituted _t_-butylbenzenes by the

chlorine atom at 70°C has been carried out. Application of the

Hammett equation yielded a ρ value of -0.44 for the _para_ compounds.

Possible explanations for the non-linearity of the _meta_ compounds are

offered. Application of the Kirkwood-Westheimer field-effect model

for the transmission of substituent effects provides an excellent

correlation with the observed relative rate constants.

Hydrogen Abstraction from
Substituted t-Butylbenzenes
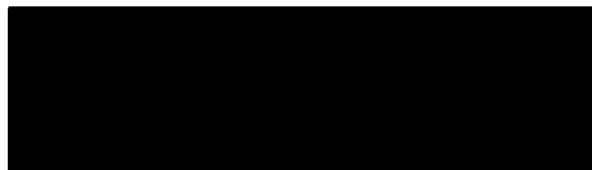
by

Robert Louis Harvey

A THESIS

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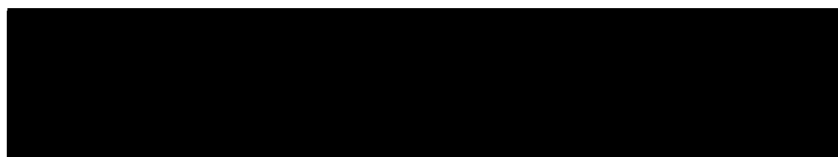the requirements for the
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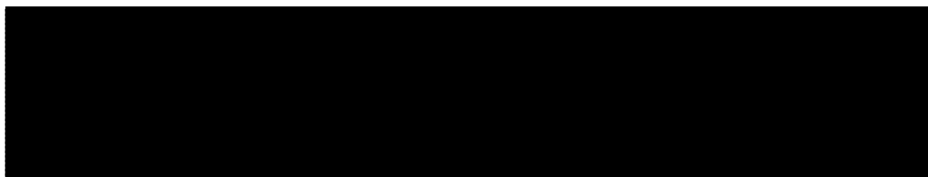
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HYDROGEN ABSTRACTION FROM SUBSTITUTED t-BUTYLBENZENES

INTRODUCTION

The research described herein attempts to correlate the electronic effect of substituents with the ease of alkyl hydrogen abstraction, a field which has been largely neglected. The t-butylbenzene system chosen for this study provides the combined utility of an abstractable primary hydrogen, purely alkyl in character, with the easy variability of substituents in the phenyl group. The presence of the insulating quaternary carbon between the ring and the reaction site should allow the examination of inductive or field effects without the interference of resonance interactions.

Several experimenters (25, 26, 64) have shown that the rates of hydrogen abstraction by chlorine atoms increase in the order primary < secondary < tertiary. This order is the reverse of carbon-hydrogen bond strengths. The same general sequence is exhibited by other free radicals (9, 78, 84, 85); i.e., the series is independent of radical type. The relative reactivities of hydrogens do vary with the selectivity of the attacking radical, however. For example, the chlorine atom is a relatively non-selective free radical, whereas the bromine atom is more selective and less reactive. The chlorine atom derived from sulfuryl chloride via benzoyl peroxide initiation

(35, 36) was chosen over the more sensitive bromine atom from

N-bromosuccinimide (NBS). This was based on a report by Boocock

and Hickinbottom (7) that treatment of t-butylbenzene with NBS in the

liquid phase results principally in nuclear bromination. Although

NBS could not be utilized in this study, Backhurst (2) has shown that

side-chain bromination of t-butylbenzene can occur in the gas phase.

The Reaction

Kharasch and Brown (35) originally proposed the following

scheme for their reaction

$$C_6H_5CO\text{-}OO\text{-}COC_6H_5 \rightarrow 2C_6H_5{}^{\cdot} + 2CO_2 \qquad \text{(Eq. 1)}$$

$$C_6H_5{}^{\cdot} + SO_2Cl_2 \rightarrow SO_2Cl^{\cdot} + C_6H_5Cl \qquad \text{(Eq. 2)}$$

$$SO_2Cl^{\cdot} \rightarrow SO_2 + Cl^{\cdot} \qquad \text{(Eq. 3)}$$

$$RH + Cl^{\cdot} \rightarrow R^{\cdot} + HCl \qquad \text{(Eq. 4)}$$

$$R^{\cdot} + SO_2Cl_2 \rightarrow RCl + SO_2Cl^{\cdot} \qquad \text{(Eq. 5)}$$
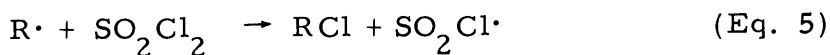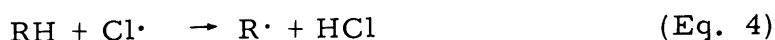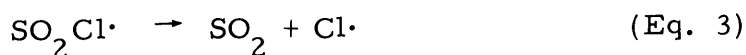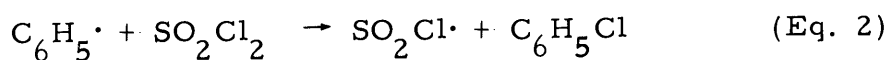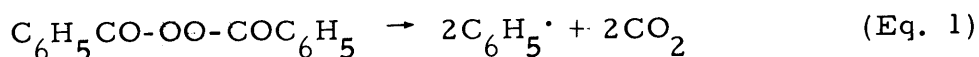
where RH is a hydrocarbon. Russell and Brown (63, 64) have pro-

posed that Eq. 3 may actually be an equilibrium which can be shifted

to the left by the accumulation of SO_2. If so, Eq. 6, below would

become operative

$$SO_2Cl^{\cdot} + RH \rightarrow R^{\cdot} + SO_2 + HCl \qquad \text{(Eq. 6)}$$
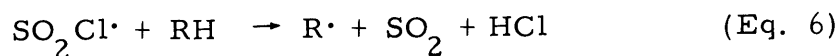
Kharasch and Read (36) demonstrated that under certain conditions

$SO_2Cl^{\cdot}$ does produce sulfonation products. The $SO_2Cl^{\cdot}$ radical would

be expected to be more selective than the chlorine atom and exhibit a

more negative ρ value than the latter (64).

Russell (61, 62) has also observed that the selectivity of chlorine

atoms is increased in aromatic solvents by the formation of π com-

plexes. Although this factor and the above consideration of $SO_2Cl\cdot$

as the abstracting agent will have to be remembered when discussing

the results of this study, they assume secondary importance relative

to the initial question of the transmission of electronic effects.

<h2 style="text-align:center">Rearrangements</h2>

Once the neophyl radical $(C_6H_5-C-(Me)_2CH_2\cdot)$ has been gener-

ated by hydrogen abstraction from t-butylbenzene, one must be con-

cerned about the possibility of three types of rearrangements. These

are outlined below in Eq. 7-9.

$$C_6H_5-C(Me)_2CH_2\cdot \begin{cases} \xrightarrow{1,3\text{ H shift}} & C_6H_5-C(Me)_2CH_2\cdot & (Eq.\ 7) \\ \xrightarrow{1,2\text{ Me shift}} & C_6H_5-\dot{C}(Me)CH_2Me & (Eq.\ 8) \\ \xrightarrow{1,2\text{ aryl shift}} & C_6H_5-CH_2\dot{C}(Me)_2 & (Eq.\ 9) \end{cases}$$
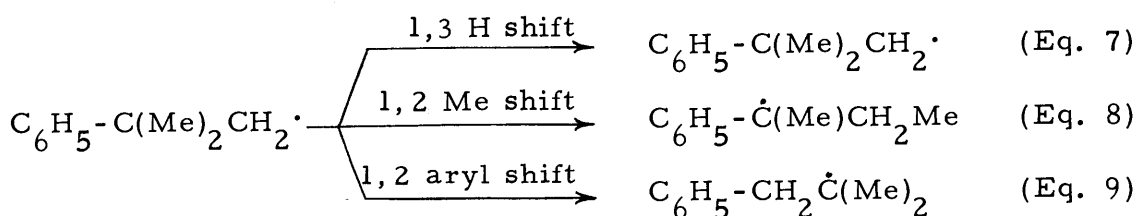
A 1,3 hydrogen shift (Eq. 7) would produce an equivalent neophyl

radical and would have no effect on the product or kinetic studies

reported here. A 1,2 methyl shift (Eq. 8) would result in a more

stable tertiary benzylic radical and might be expected to be a favor-

able process. Whitmore and his co-workers (91) found no evidence

of such rearrangement in the related neopentyl radical. Urry and

Kharasch (79) and Winstein and Seubold (95) report observing aryl

rearrangement products in Grignard reactions involving neophyl chlo-

ride. Slaugh (71) monitored a small amount of 1,2 phenyl shift in

labeled 2-phenylethyl radical; this is surprising because the shift

produces no change in radical stability. Smith and Anderson (72)

compared that same reaction to the rearrangement of 2-phenylpropyl

radical and found the latter to occur to a greater extent because of

steric and electronic effects. Rüchardt and co-workers (53-59) ex-

perimented with an assortment of substituted neophyl radicals and

concluded, among other things, that 1) there is no anchimeric assist-

ance by the phenyl group in the rate-determining step of the decom-

position of t-butyl-3-methyl-3-phenylperbutanoate (56, 57) to neophyl

radicals; 2) rearrangement is a function of the lifetime of the radical

(53); the rearrangement of substituted neophyl radicals follows

Hammett's equation with a $\rho = +1$ (54); and 3) the ability of a partic-

ular substituted phenyl group to migrate is the same regardless of

how the radical is generated (55). Seubold (70) and Winstein et al.

(94) have also shown that the tendency of an aryl group to migrate is

related to the lifetime of the neophyl radical. Seubold, in discussing

the sulfuryl chloride reaction in particular, felt that in solution the

attack of the neophyl radical on sulfuryl chloride is so rapid that it

can happen before rearrangement has time to occur. Backhurst,

Hughes, and Ingold (3) have also shown that migration occurs in the

gas phase, where radicals have an effectively longer lifetime. In summary, aryl shifts occur readily but can be minimized or eliminated by manipulation of the reaction conditions.

Previous Work

Many investigations have been made of the nature of the abstraction of hydrogen atoms bound to a carbon adjacent to a substituted phenyl ring (27, 52, 83) and hence falling under the influence of both induction and resonance. All these investigations have utilized one form or another of the Hammett equation (22, 23).

$$\log k/k_O = \sigma \rho . \qquad \text{(Eq. 10)}$$

Here k/k_O represents the relative rate of reaction of a substituted compound to some reference substrate. The substituent constant σ is a function of the nature of the substituent, and ρ, the reaction parameter, is dependent only upon the reaction and its conditions. Although originally formulated for ionic reactions, the Hammett equation has been found to be equally applicable to free radical processes. Russell (60) has suggested that ρ be interpreted as a measure of the sensitivity of the attacking radical to the polar effect of the substituent.

The radicals most frequently employed in benzylic hydrogen abstraction studies have been chlorine atom (64, 66, 81, 85), bromine atom (20, 28-30, 32, 33, 39, 43, 50, 87), trichloromethyl

radical (20, 29, 31, 43), t-butoxy radical (19, 84, 89), and phenyl

radical (9). The first two will be discussed in detail.

The reaction of substituted toluenes with chlorine atom gener-

ated from sulfuryl chloride was originally studied by van Helden and

Kooyman (78). Their work, however, and that of Walling and Miller

(85) has been superseded by that of Russell and Williamson (66), who

in 1964 explored the same system at 40° in CCl_4 (to minimize the

role of π-complexing). They found that a better correlation of data

resulted when σ^+ (10) rather than σ (41) was used to compute ρ;

the values were -0.66 ± 0.02 and -0.76 ± 0.06, respectively. All

experimenters did agree qualitatively that electron-releasing groups

facilitate and electron-withdrawing groups retard the abstraction

process. The rather low ρ value substantiates the idea that the

chlorine atom is not a very selective species. The interesting fact

that σ^+ provided the better correlation indicates that there is enough

bond-breaking in the transition state to allow polar canonical struc-

ture II in Figure 1 to contribute significantly to the stability of the

transition state. Here X = Cl, R = R' = H, and Y = a meta or para

substituent. Walling, Seymour, and Wolfstirn (88) in 1948 and Mayo

and Walling (45) in 1950 suggested the importance of structures like

II might be expected when the electron affinity (51) of the attacking

radical is high. In 1955 Russell and Brown (64) calculated that there

is only about 10% bond-breaking in the transition state of the
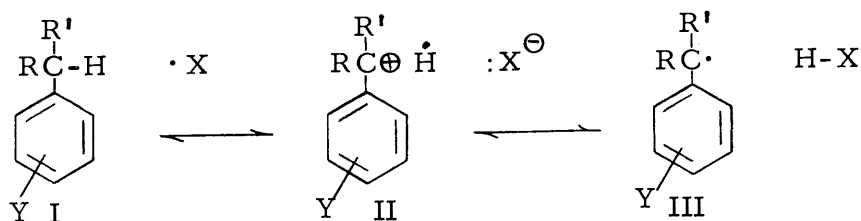
Figure 1. Transition state of free radical abstraction
of benzylic hydrogen.

abstraction of tertiary hydrogen by atomic chlorine. In light of

Russell and Williamson's later work this seems too conservative an

estimate.

The majority of the work done on benzylic hydrogen abstraction

has involved the use of atomic bromine from NBS or molecular

bromine. Kooyman, van Helden and Bickel (39) initiated the work on

substituted toluenes in 1953. Since then, Pearson and Martin (50)

found $\rho = -1.46$ (σ^+) using NBS and $\rho = -1.38$ (σ^+) using Br_2, both

at 80° in benzene solution. Ingold (32, 33) conducted similar studies

in benzene at 80° and 19° and found $\rho = 1.39$ and -1.78, respectively,

using σ^+. Walling, Rieger, and Tanner (87) found ρ to be -1.38 (σ^+)

at 80° in CCl_4. Walling and Rieger (86) studied the reaction with

several substituted N-bromosuccinimides and computed an average

ρ of -1.27 (σ^+) at 80° in CCl_4. These and other results (1) have been

taken as proof for bromine atom being the abstracting agent in NBS

brominations.

The ρ value of bromination is larger than that of chlorination

for substituted toluenes. This shows bromine atom to be a more selective abstracting agent than is chlorine atom. Application of Hammond's postulate (24) indicates that the abstraction by bromine is more endothermic than the abstraction by chlorine, and that the former transition state more closely resembles the products than does the latter. The fact that all correlations were made in terms of σ^+ indicates that canonical structure II, Figure 1 (R = R' = H, X = Br) is important in hydrogen abstraction by bromine also.

Martin and Gleicher (43, 44) have examined a series of allyl-benzenes and found the bromine atom abstraction of the allylic-benzylic hydrogen at 69.5° to give a ρ = -0.76 using σ^+. This lower ρ value was expected because the vinyl-benzyl radical is more stable than the benzyl radical because of additional resonance. This stability means that the activation energy for hydrogen abstraction is smaller for allylbenzene than for toluene, and substituent effects are felt to a lesser degree by the transition state. Huang and Lee's (30) investigation of hydrogen abstraction from substituted ethylbenzenes at 80° provided a (σ^+) ρ of -0.69. Because higher temperatures reduce the selectivity of radicals, this value would approach Martin and Gleicher's value for allylbenzenes at a temperature of 69.5°. Here again a compression of the substituent effect has occurred because the methylbenzyl radical is more stable than the benzyl radical, presumably because of electron-donation by the methyl

group. Gleicher (20) determined $\rho = -0.38$ using the standard σ

values for a series of substituted cumenes. The bond-breaking in

the transiton state of this reaction may now be so slight that struc-

ture II, Figure 1 (R = R' = CH_3, X = Br) is no longer important.

The activation energy for hydrogen abstraction and the resultant

formation of the very stable tertiary benzylic radical is now very

much smaller than the abstraction of hydrogen from toluene to form

the primary benzylic radical. Huang and Lee (28, 29) have studied

the reaction of several α-substituted benzyl methyl ethers with

bromine atoms. They found the ρ values approached zero as the

incipient radical's stability increased. All correlations were done

via σ. Their results are summarized in Table 1.

Estimation of Rho

Studies of benzylic hydrogen abstraction by chlorine atoms

have not been done on enough different systems to allow a prediction

of the ρ value for the process studied here. However, if the assump-

tion that chlorination is not qualitatively different from bromination

may be made, the extensive data for abstraction in the latter case

can be utilized to make an assessment of ρ in the following way. The

available data suggest that the substituent dependence of a benzylic

hydrogen abstraction decreases as the lability of the hydrogen atom

in the unsubstituted compound increases. A plot of the ρ value

against the logarithm of the lability of hydrogen atom in the unsub-

stituted compound relative to toluene was made. A linear correla-

tion was obtained using a least-squares calculation. The slope of the

line was -1.41 ± 0.14 with a correlation coefficient of 0.961. Table 1

lists the pertinent data. A graphical representation is shown in

Figure 2. Interpolation of Russell and Brown's (64) value for the

Table 1. Rho values and relative rates of hydrogen abstraction by
bromine atom of various α-substituted and α, α-disub-
stituted toluenes.

n	Compound	k_n/k_1	ρ	Temp.	Ref.
1	$C_6H_5CH_3$	(1.00)	-1.38^a	80°	87
2	$C_6H_5CH_2CH_3$	22.8	-0.69^a	80°	30
3	$C_6H_5CH(CH_3)_2$	50	-0.38	70°	20
4	$C_6H_5CH_2CH=CH_2$	26.2	-0.76^a	69.5°	43
5	$C_6H_5CH(OCH_3)_2$	50.6	-0.38	80°	28, 29
6	$C_6H_5CH_2OCH_3$	52.6	-0.35	80°	28, 29
7	$C_6H_5CH_2OCH_2C_6H_5$	77.5	-0.12	80°	28, 29
8	$(C_6H_5)_2CHOCH_3$	109.0	0	80°	28, 29
9	$C_6H_5C(CH_3)_3$	0.22	--	70°	64

[a] calculated using σ^+.

relative rate of hydrogen abstraction by chlorine atom of t-butyl-

benzene to toluene yielded a ρ value of -2.02. Unlike the other

systems considered, however, the radical formed from t-butylbenzene

is insulated from the substituted phenyl group by a saturated carbon
atom. This not only should preclude all resonance effects on radical
stability, but also should modify the inductive effect by some trans-
mission factor. Using the standard Branch-Calvin factor of 1/2.8
(8) to correct for this produces a ρ value of -0.72. While the
approximate nature of the above is evident, this value can be con-
sidered as a probable upper limit for the substituent effect to be
determined in this study.
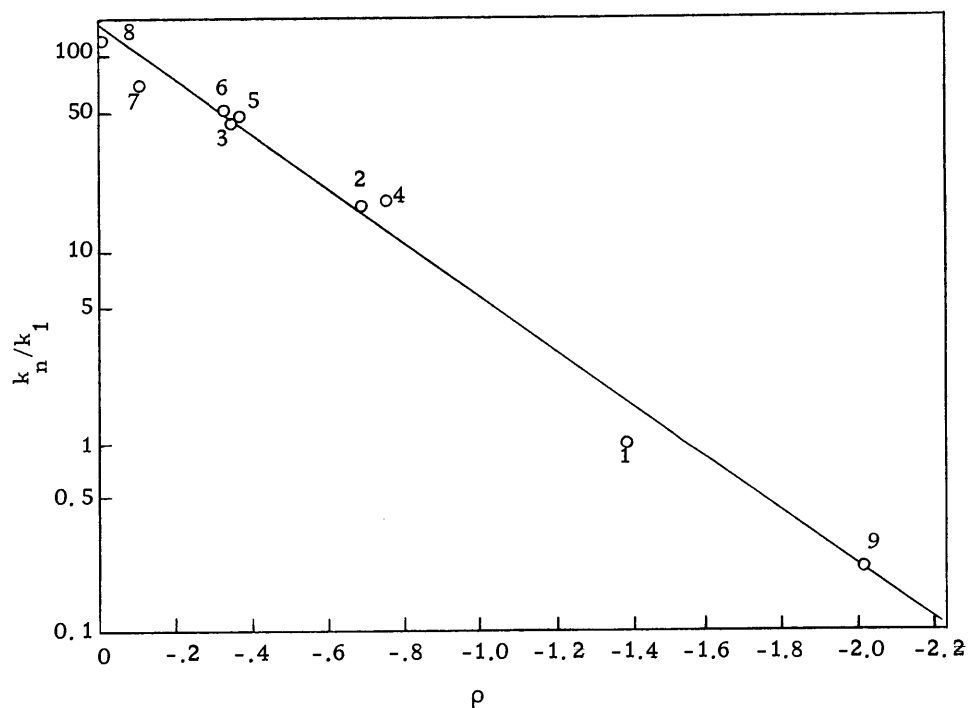
Figure 2, Log k_n/k_1 vs. Rho.

Induction

The neophyl radical produced by the loss of a hydrogen atom from t-butylbenzene should not be involved in resonance with the ring. Any effects felt by the radical should be a result of inductive interactions. Dewar and Grisdale (13) have subdivided the inductive effect into three distinct parts: a) a field effect across space; b) a σ-inductive effect, i.e., the successive polarization of σ-bonds; and c) a π-inductive effect, i.e., the successive polarization of π-bonds. They have concluded (14, 15) from studies of the ionization of naphthoic acids that the σ-inductive effect is unimportant and can be included in the field effect. Dewar and Marchand (17) arrived at the same conclusion studying fluorinated biphenyls and terphenyls. They have maintained that the π-inductive effect is also primarily a field effect (16). These ideas indicate that the main effect under consideration in this paper may be a field effect.

Kirkwood and Westheimer (37, 38) have evolved a theoretical approach to explain the manner in which polar effects are transmitted to a reaction site. They treated the reactant molecule as a cavity of low dielectric constant embedded in a solvent continuum. They considered all non-conjugative effects to be the result of an electrostatic field between the substituent dipole and the site of reaction. In the case of relative carboxylic acid dissociation

constants, the following equation was derived

$$2.303 \log \frac{K}{K_o} = \frac{e\mu \cos\zeta}{kTD_E R^2}$$

(Eq. 11)

where K/K_o is the ratio of the dissociation constant of substituted

to unsubstituted acid, e is the electronic charge on the ion, μ is the

dipole moment of the substituent, k is the Boltzman constant, D_E

is the effective dielectric constant, R is the distance from the

center of the dipole to the reaction site, and ζ is the angle between

R and the dipole axis. The values for R and ζ can be obtained only

for conformationally rigid molecules. There is uncertainty in the

meaning of D_E and in its value because it is a complex function of

the geometry of the molecule, the size of the solvent cavity, and

the ratio of external to internal dielectric constants. In 1957

Tanford (76) showed that the cavity-continuum model had a critical

dependence on the depth of the charges or dipoles below the surface

of the cavity which represented the molecule. By arbitrarily de-

fining the distance from the center of the molecule to the center of

the substituent plus 1.5 Å Tanford was able to predict relative

reactivities and equilibrium constants for uncharged substituents

with a fair degree of accuracy. A modified Kirkwood-Westheimer

approach has been applied with success to other free-radical

hydrogen abstractions (48) studies in these laboratories. It was

thought that a correlation might appear in the hydrogen abstrac-

tions from the para substituted t-butylbenzenes if a suitable rigid

geometry could be defined.

RESULTS

Synthesis of Substituted t-Butylbenzenes

Standard synthetic procedures were used to prepare ten m- and p-substituted t-butylbenzenes. Five others were obtained by purchase or as gifts. All had been previously prepared with the exception of phenyl p-t-butylbenzoate and m-phenoxy-t-butylbenzene. Details regarding the preparation and purification of these compounds are to be found in the Experimental section.

Products of the Reaction of t-Butylbenzene and Sulfuryl Chloride

Solutions composed of t-butylbenzene, chlorobenzene as an internal standard, and sulfuryl chloride were reacted in sealed tubes at 40° and 70° in the presence of catalytic amounts of benzoyl peroxide. The major products at 40° were found to be nuclear chlorination products. See the Discussion section for an explanation of this. At 70° the side-chain chlorination product accounted for more than 88% of the total products. All further product and kinetic studies were conducted at 70°. The ideal molar ratio of substituted t-butylbenzene to sulfuryl chloride for the product studies was about 4:1. This eliminated or kept to a minimum secondary reactions which were a problem when an excessive amount of sulfuryl chloride was used. If

rearrangements occurred, the products were formed in such quantities as to be undetectable by gas-liquid chromatography.

Products in the Reaction of
Fourteen Substituted t-Butylbenzenes

Twelve additional m- and p-substituted t-butylbenzenes were reacted in the manner described above. Gas-liquid chromatographic analysis revealed that seven of these (p-nitro, m-nitro, p-chloro, p-cyano, p-carbophenoxy, m-phenoxy, and p-di-t-butyl) produced only two major product types. These were believed to be eluted from the column in the order nuclear chlorination products first and side-chain chlorination product second. The identity of the side-chain product was verified in selected cases. In all cases side-chain chlorination predominated.

Para-phenoxy-t-butylbenzene gave three products and a percentage alkyl chlorination which was about 20% lower than the average of those eight listed above if the same criterion was used in calculation. This anomaly may have arisen from the presence of a rearrangement product. This is commented upon further in the Discussion section. Table 2 summarizes the results of the product studies on the nine compounds mentioned above.

The product study of p-methoxy-t-butylbenzene revealed four unidentified products. It is possible that some of these products

resulted from abstraction of a methoxy methyl hydrogen and subsequent reactions of the resulting radical. Because of structural similarities, product studies were not attempted on m-methoxy- and p-carboethoxy-t-butylbenzene. All three compounds were excluded from the kinetic studies.

Table 2. Percentages of alkyl chlorination of several t-butylbenzenes[a].

Compound	No. of Ampoules Analyzed	% Alkyl Chlorination
t-Butylbenzene	5	88.4_4
p-Nitro-t-butylbenzene	4	81.8_5
m-Nitro-t-butylbenzene	5	78.6_7
p-Di-t-butylbenzene	5	94.5_4
p-Cyano-t-butylbenzene	4	83.6_3
Phenyl p-t-Butylbenzoate	4	84.5_3
p-Phenoxy-t-butylbenzene	4	63.3_7
m-Phenoxy-t-butylbenzene	5	80.0_6
p-Chloro-t-butylbenzene	5	$100._0$

[a] Complete data for each product study are in Appendix I, Tables 8-16.

Para-bromo-t-butylbenzene reacted with sulfuryl chloride to give a red solution indicative of molecular bromine. Analysis showed the major product to be p-chloro-t-butylbenzene. Two small

unidentified products were also produced; their combined peak area was about 10% of the area of the p-chloro-t-butylbenzene. The m-bromo isomer generated three products, the largest of which had an elution time slightly less than that of p-chloro-t-butylbenzene; apparently this product was m-chloro-t-butylbenzene. The two smaller peaks were not identified. Para-iodo-t-butylbenzene and sulfuryl chloride gave a deep purple-brown solution indicative of free iodine. Six different product peaks separated on the chromatograph. The second largest peak and p-chloroneophyl chloride had identical retention times.

The anomalies displayed by the bromo- and iodo-substituted compounds caused them to be excluded from the kinetic studies.

Reaction of Chlorobenzene with Sulfuryl Chloride

Two attempts were made to react the internal standard, chlorobenzene, with sulfuryl chloride in the presence of peroxide catalyst. Gas-liquid chromatography detected no disappearance of chlorobenzene and no appearance of product peaks. This is in accordance with a statement in the literature (5) and safely allows for the use of chlorobenzene as the internal standard.

Reaction of t-Butylbenzene and Bromotrichloromethane

One attempt was made to react t-butylbenzene and

bromotrichloromethane in the presence of light at 70°. There was

no detectable disappearance of $\underline{t}$-butylbenzene.

Relative Rates of Disappearance
of Substituted $\underline{t}$-Butylbenzenes

Solutions of two $\underline{t}$-butylbenzenes, an excess of sulfuryl chloride,

and chlorobenzene were prepared and placed into ampoules con-

taining a catalytic amount of benzoyl peroxide. The ampoules were

then sealed under a reduced pressure of nitrogen and immersed in a

70° oil bath. By stopping the reaction short of completion, the two

$\underline{t}$-butylbenzenes were made to compete for the chlorine atoms. This

technique also should have minimized rearrangements, dispropor-

tionation, coupling, and other undesirable side reactions. Table 3

is a summary of the relative rates of disappearance, $(k_X/k_H)_{dis}$

of the nine t-butylbenzenes studied.

Table 3. Relative rates of disappearance of substituted
t-butylbenzenes[a, b].

Compound	No. of Kinetic Runs	$(k_X/k_H)_{dis}$
m-Nitro-t-butylbenzene	4	0.212 ± 0.022
p-Nitro-t-butylbenzene	6	0.482 ± 0.041
p-Cyano-t-butylbenzene	5	0.501 ± 0.017
Phenyl p-t-Butylbenzoate	5	0.696 ± 0.068
p-Chloro-t-butylbenzene	5	0.711 ± 0.049[c]
t-Butylbenzene	--	(1.00)
p-Di-t-butylbenzene	5	1.07 ± 0.025[d]
p-Phenoxy-t-butylbenzene	5	1.22 ± 0.030
m-Phenoxy-t-butylbenzene	8	2.50 ± 0.387

a) Complete data for each kinetic run are in Appendix II, Tables
17-24.

b) Unsubstituted t-butylbenzene was the reference standard.

c) The kinetics for this compound were run in competition with
p-cyano-t-butylbenzene. The value recorded here was calcu-
lated through Eq. 15 in the Experimental section.

d) Statistically corrected.

DISCUSSION

The results obtained from gas-liquid chromatographic analyses of the reaction mixtures of several m- and p-substituted t-butyl-benzenes and sulfuryl chloride indicate that the side-chain chlorination reaction predominates over the nuclear chlorination reaction at 70°. This is consistent with the findings of other researchers (35, 7). The fact that the nuclear chlorination products are the more abundant at 40° indicates that the free radical process is probably not operating at this temperature. Two reasons for this may be advanced. First, benzoyl peroxide has a half-life of about 2000 hours at 40° (80, p. 469) making it difficult for the radical reaction to start. Sulfuryl chloride is also a source of chlorine molecules which can chlorinate an aromatic nucleus (35). If the radical process were not started, the nuclear chlorination would predominate. Secondly, Kharasch and Brown (35) noted an inhibition period of a few minutes when impure starting materials were used. They suggested that the impurities were either removed or deactivated by refluxing with sulfuryl chloride and peroxide as no diminution of the yield occurred. The temperature of 40° is 29° below the boiling point of sulfuryl chloride, so this deactivation of impurities may never occur or at least may take a very long time. Also any oxygen, a strongly inhibiting impurity (35), remaining in the ampoules in spite of the

precautions taken to exclude it, would be expected to react with the radical products of the few peroxide molecules that did manage to decompose at this temperature, hence preventing the radical mechanism from obtaining a good start. At 70° benzoyl peroxide has a half-life of only about 20 hours (80, p. 469). A sufficient number of peroxide molecules could decompose rapidly enough to destroy the oxygen and other impurities and start the chain reaction with sulfuryl chloride. In such an event, the alkyl chlorination reaction would predominate.

The Halogen Compounds

With the exception of p-chloro-t-butylbenzene, it is evident from the product studies that the halogen substituted compounds behaved anomolously with regard to the other substituted compounds. The reaction of p-bromo-t-butylbenzene with chlorine atoms resulted primarily in the replacement of bromine atom by chlorine on the aromatic nucleus. The red color of the solution showed the probable presence of molecular bromine. Eibner (18) reported in 1903 that bromobenzene and chlorine in the light produced chlorobenzene and Br_2. Miller and Walling (46) found the same reaction to have an activation energy of less than 2 kcal/mole, and to be impeded by electron-withdrawing groups in the aromatic nucleus. They proposed a mechanism involving a π-complex intermediate. Goerner and

Nametz (21) studied the peroxide-catalyzed reaction of m-and p-bromotoluenes with sulfuryl chloride. They found all the possible isomers which would result from chlorine displacement of bromine; they also detected bromobenzyl chlorides and bromides. The research reported in this paper found this type reaction to occur almost to the exclusion of the hydrogen abstraction process in the case of p-bromo-t-butylbenzene.

The meta isomer also underwent replacement of bromine by chlorine. It appeared, however, that a greater percentage of side-chain chlorination occurred than in the para compound.

Sulfuryl chloride and p-iodo-t-butylbenzene reacted to give a purple-brown colored solution which contained p-chloro-t-butylbenzene in moderate amounts and five other unidentified products. Four of these had retention times shorter than that of the starting material. The sixth and largest peak may have been p-iodoneophyl chloride. Willgerodt (89) reported that iodobenzene and chlorine produced phenyl dichloroiodide, $C_6H_5ICl_2$, which decomposed at temperatures above 120°. If a corresponding product were formed in the work reported here, it would be unlikely to survive the 300° temperature of the gas chromatograph's detectors and so would not be observed. Miller and Walling (46) reported work that showed little exchange of chlorine for iodine at room temperature. A thermal exchange, however, did occur at higher temperatures. Chlorine atom did definitely

replace the iodine on the phenyl ring in the study reported here,

although the reaction was only secondary in nature.

The Ethers

The p-methoxy-t-butylbenzene provided four products and was

therefore omitted from the kinetic studies. As has been substantiated

in the introduction, primary methyl hydrogens of the type present in

t-butylbenzene are comparatively difficult to abstract. The hydro-

gens of the methoxy substituent should be about as labile as the t-

butyl hydrogens because the resulting radical would be resonance

stabilized by the adjacent oxygen. If this abstraction were taking

place at a rate comparable to the desired abstraction, this might

explain the surplus of products. Abstractions of this nature might

also be expected to occur in the m-methoxy and p-carboethoxy sys-

tems because of structural similarities. Because of the difficulty in

identifying the resulting products and making the necessary correc-

tions for their appearance, these compounds were excluded from both

the product and kinetic studies.

Para-phenoxy-t-butylbenzene gave an alkyl to aryl chlorination

product ratio some 20% lower than the average value for the other

compounds based on the assumption that only the last peak eluted

from the column arose from hydrogen abstraction. A possible ex-

planation for this could lie in a rearrangement of the p-phenoxyneophyl

radical. The 1,2 aryl shift for the neophyl system is a well-documented one (see the Introduction). Rüchardt's ρ = +1 (53) for the phenyl migration of neophyl radicals would indicate that polar contributing structures such as II and III in Figure 3 are important to the stability of the transition state. The phenoxy substituent could allow for greater dispersal of the positive charge through additional resonance structures than the other substituents utilized. If a rearrangement did occur, it would account for the low alkyl to aryl product ratio. A more straightforward explanation for that low ratio might be based on the greater number of sites for nuclear reaction. This laboratory is planning further work on this question.
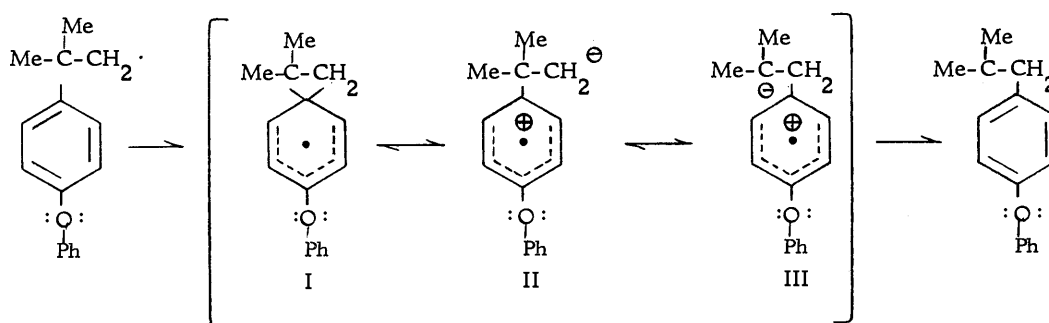
Figure 3. Transition state of 1,2 phenyl migration in
p-phenoxy-t-butylbenzene.

Kinetic Studies

Table 4 summarizes the relative rates of disappearance

$(k_X/k_H)_{dis}$ and the relative rates of alkyl hydrogen abstraction (k_X^{abs}/k_H^{abs}) for all compounds used in the kinetic studies. The σ values for the substituents are included. Inspection of Table 4 shows that inductively electron-withdrawing groups retard the reaction and electron-donating groups enhance it. Based on normal σ values three abstraction rates do not fall where they might be expected to. m-Nitro-t-butylbenzene and p-phenoxy-t-butylbenzene reacted too slowly, and m-phenoxy-t-butylbenzene reacted far too rapidly. Each of these will be considered in turn.

Meta-phenoxy-t-butylbenzene reacted about 2-1/4 times as fast as did t-butylbenzene. Because of the highly electro-negative oxygen atom, the m-phenoxy group is inductively electron-withdrawing and its presence ought to slow the alkyl hydrogen abstraction. The oxygen atom is also electron-releasing by resonance, and in reactions affected by resonance this characteristic becomes more important than the inductive one. White, Slater, and Fife (90) found that a better Hammett correlation resulted when σ_p^+ (10) rather than σ_m^+ (10) was used for meta substituents with non-bonding electrons in the Claisen rearrangement. Taft, Fox, and Lewis (75) have discussed radical stability in terms of the same kind of effect. In these examples the reaction site is directly bound to the ring, which is not the case in the t-butylbenzene system. It might be far-fetched to argue that the electron-donating resonance effect of the phenoxy

Table 4. Relative rates of hydrogen abstraction of substituted
t-butylbenzenes. σ values for the substituents.

Substituent (X)	σ^a	$(k_X/k_H)_{dis}$	k_X^{abs}/k_H^{abs}
m-Nitro	0.710	0.212	0.189
p-Nitro	0.778	0.482	0.446
p-Cyano	0.660	0.501	0.474
p-Carbo-phenoxy	0.45^b	0.696	0.665
p-Chloro	0.227	0.711	0.804
Hydrogen	0	(1.00)	(1.00)
p-t-Butyl	-0.197	1.07	1.14
p-Phenoxy	-0.320	1.22	0.874
m-Phenoxy	0.252	2.50	2.26

a) from reference 41
b) value for p-carboethoxy recorded here as the value for p-carbo-
   phenoxy is not available.

group causes enough negative charge to develop on positions ortho

and para to itself to give the phenyl ring an overall electron-donating

inductive effect. But if so, the field effect which would be felt by the

methyl protons would be a rate enhancing one. This is schematically

represented in Figure 4. The decreased reactivity of the m-nitro

derivative could not be explained by the same formalism, however,

as there is no evidence in the literature for a similar added induced

electron-withdrawing effect. Indeed, m-nitro has been typified by an

almost invariant substituent parameter for radical reactions (75).
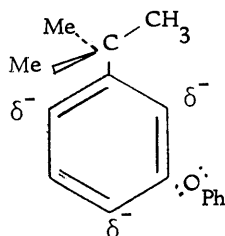
Figure 4. Inductive effect of the m-phenoxy substituent.

Dallinga and Ter Maten have examined the acid-catalyzed alkyl hydrogen-deuterium exchange of t-butylbenzenes (12). As part of a complex mechanism they suggested that the incoming deuteron complexes preferentially at a site meta to the t-butyl group or at the carbon bearing the t-butyl group. In the event that a similar mechanism may be possible for the radical system, the rate-enhancing effect of a m-phenoxy substituent is obvious if the chlorine atom complexes at the t-butyl bearing carbon atom or the carbon mutually meta to both groups and the aforementioned special resonance (75, 90) interactions are invoked. The m-nitro derivative would react very much slower than this; however, there is no obvious rationale why it should exhibit as slow a rate as it does. Besides the tenuous assumptions of the Dallinga-Ter Maten hypothesis, other specific objections may be made. If the intermediate has a structure which, for all practical purposes, is a benzenonium type radical, the rate of aromatic chlorination should be concomitant with that for side-chain chlorination. A common intermediate may be invoked for both

reactions. Dallinga and Ter Maten observed a strict parallelism

between their rates of deuterium-hydrogen exchange and transalkyla-

tion. This is not found in the radical reaction. Meta-nitro-t-butyl-

benzene showed a high percentage of ring chlorination. Meta-phenoxy-

t-butylbenzene showed a relatively low degree of ring reaction when

it is remembered that the latter compound has more than twice the

number of sites for nuclear reaction that the former has.

Some mechanistic explanation must be offered in which the

substituent effect on a neophyl radical does not also influence the rate

of ring substitution in a similar manner. An attractive one might be

a direct interaction between the substituent and the primary radical

via some field effect. Some insight into this matter may be gained

by examining the nmr spectra of the substituted-t-butylbenzenes.

Table 5 presents the chemical shifts of the methyl hydrogens of the

compounds utilized in this study. Although the data are by no means

extensive, certain inferences may be drawn. The protons in m-

phenoxy-t-butylbenzene absorb 0.03 units upfield compared with its

para isomer. The difference in chemical shift appears to be due to

the phenyl portion of the ether as a corresponding difference is ab-

sent for the meta and para methyl ethers. It is possible, therefore,

that the m-phenoxy-neophyl radical may be stabilized by direct inter-

action with the phenyl group in the substituent. Models show that

this could be particularly favorable. Assuming sp^2 hybridization

Table 5. Effect of nuclear substituents on nmr proton frequencies of methyl hydrogens in t-butylbenzene.

Substituent	meta, δ	para, δ
$-OCH_3$	1.26	1.26
$-I$	--	1.27
$-Br$	1.27	1.27
$-Cl$	--	1.28
$-H$	1.28	1.28
$-C(CH_3)_3$	--	1.30
$-CO_2C_2H_5$	--	1.30
$-OC_6H_5$	1.28	1.31
$-CN$	--	1.32
$-NO_2$	1.39	1.36
$-CO_2C_6H_5$	--	1.36

at the radical site, the p orbital is very nearly perpendicular to the plane of the phenyl group of the substituent in the most favorable conformation. The approximate distance from the radical carbon to the phenyl group is 2.9 Å. In such a favorable conformation, therefore, it would be quite plausible that the radical may be stabilized by formation of an intramolecular π-complex via overlap of the p orbital at the radical site with the aromatic system (43, 44). The m-nitro group has a similar but opposite effect. In m-nitro-t-butylbenzene

the methyl proton absorption has been shifted downfield relative to the

para isomer. This possible deshielding effect might destabilize the

primary radical formed from this system. Similar substituent effects

have been noted for substituted toluenes (34), and as might be expected,

the greatest shifts are noted for ortho substituted compounds. Because

of the anomolous behavior of these meta substituted t-butlybenzenes

it was decided to attempt an initial correlation for just the para sub-

stituted compounds.

A plot of the relative rates of disappearance of the seven para

substituted t-butylbenzenes against the Hammett σ function shows

excellent linearity. The ρ value is -0.37 ± 0.02 with a correlation

coefficient of -0.985. The graph is shown in Figure 5. When the

corresponding relative rates of alkyl hydrogen abstraction are plotted,

however, a poorer linearity is obtained. The ρ value in this case is

-0.34 ± 0.05 with a correlation coefficient of only -0.918. This

result is somewhat misleading. When p-phenoxy-t-butylbenzene is

omitted from the correlation the ρ value becomes -0.44 ± 0.01 and the

correlation coefficient becomes -0.992. The latter graph is pre-

sented as Figure 6. The meta compounds are not correlated in any of

these three relationships. This value for ρ is only sixty percent of the

"predicted" value. Considering the very approximate nature of the

prediction, however, the two values are in reasonable accord. The

rather low ρ value probably indicates that the abstracting agent was
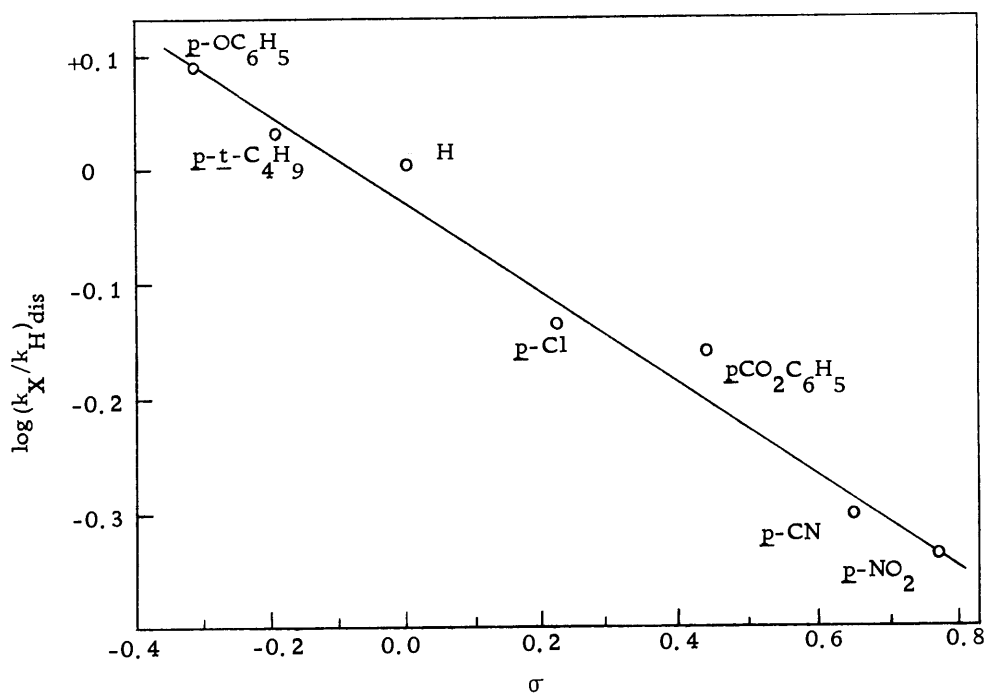
Figure 5.   Relative rates of disappearance.
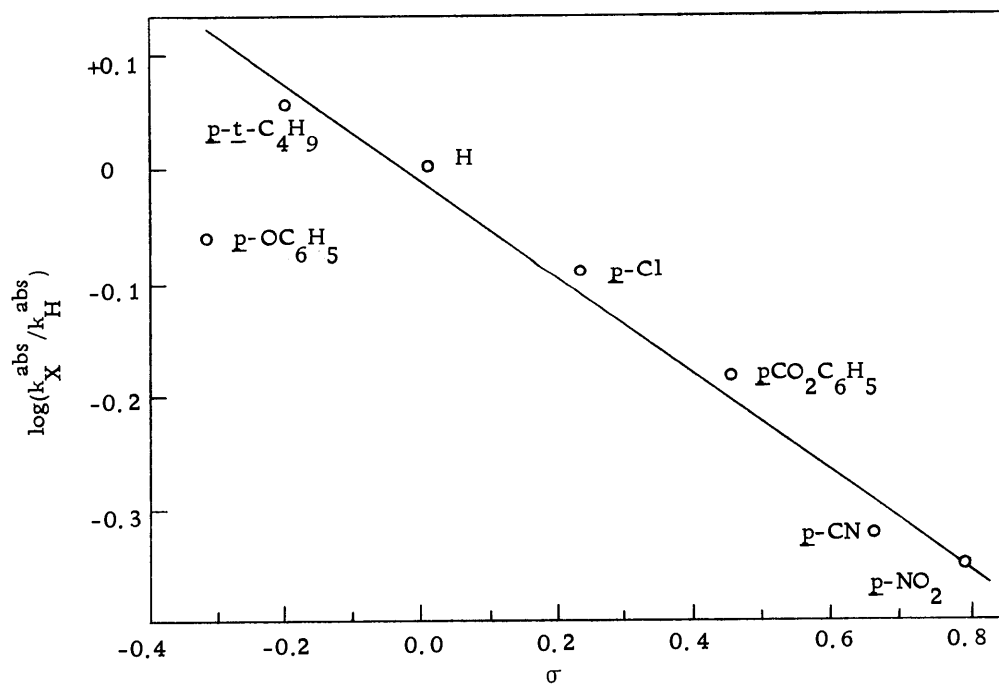
Figure 6.   Relative rates of alkyl hydrogen abstraction.

was the chlorine atom and not the more selective $SO_2Cl\cdot$ radical as has been suggested (see the Introduction). By comparison with the value for hydrogen abstraction from toluene by chlorine atoms (ρ = -0.66, ref. 66), our value confirms the expectation that the polar substituent effect is reduced by the presence of the insulating carbon atom between the reaction site and the ring. The actual reduction is probably greater than the apparent difference in the ρ values. The polar substituent effect is compressed in the toluene system because of the stability of the benzyl radical relative to the neophyl radical. The obtained result seems also to add evidence to the supposition that radicals generated β to an aromatic system are unlikely to form intramolecular complexes with the pi system of the ring because of an unfavorable geometry. Such complexes, which can be invoked to explain relatively large substituent effects in reactions which form radicals γ and δ to aromatic systems (43, 44), would also show a larger ρ value in this system.

The large deviation produced by the inclusion of p-phenoxy-t-butylbenzene in the abstraction correlation raises questions on the validity of using the basic set of σ functions. The large negative σ value for the p-phenoxy is due principally to a large resonance contribution which should not be operative in the formation of neophyl radicals. Of all the para substituents used in this study only the phenoxy group has strongly opposed inductive and mesomeric effects.

Taft has developed a σ^o function which is a measure of the inductive

portion of the electronic effect (41). Unfortunately no σ^o value has

been determined for the p-phenoxy group. The anomolous results of

the product study have the effect of lowering the relative rate of

abstraction.

Work has been in progress within this research group on corre-

lation of relative reactivities in radical reactions (48) with the

Kirkwood-Westheimer charge-dipole field effect model (37, 38).

Dr. G. J. Gleicher has calculated the relative reactivities for the

para substituted t-butylbenzenes. For radical reactions the rates

were calculated by presuming a unit of positive charge to be formed

in the transition state and determining the interactions with the dipole

of the substituent utilizing the following form of the Kirkwood-

Westheimer equation:

$$\log\left[\frac{k_X^{abs}}{k_H^{abs}}\right] = \frac{Ae}{2.3\ kT}\left\{\left[\frac{\mu\cos\Theta}{R^2 D_E}\right]_X - \left[\frac{\mu\cos\Theta}{R^2 D_E}\right]_H\right\} \quad \text{(Eq. 12)}$$

where A represents the actual fraction of positive charge to be

formed, μ is the group dipole of the substituent, Θ the angle between

the direction of the group dipole and the extension of the carbon-

substituent bond and R the distance between the center of the dipole

and the center of the carbon-hydrogen bond being broken. The

effective dielectric constant D_E is given by the relationship:

$$\frac{1}{D_E R^2} = \left\{ \frac{x}{Dbr} - \frac{2(x-\cos a)}{(1-2x\cos a+x^2)^{3/2}} - \frac{1}{x}\left[\frac{1+\frac{(x-\cos a)}{(1-2x\cos a+x^2)^{\frac{1}{2}}}}{(1-2x\cos a+x^2)^{\frac{1}{2}}+(x-\cos a)} \right] \right.$$

$$\left. + \frac{1}{x^2} \ln\left[\frac{(1-2x\cos a+x^2)^{\frac{1}{2}}+x-\cos a}{1-\cos a} \right] \right\}$$

$$+ \frac{x}{bD_i r}\left[\frac{(x-\cos a)}{(1-2x\cos a+x^2)^{3/2}} \right] + \frac{(d\cos a - r)}{D_i R^3} \qquad \text{(Eq. 13)}$$

In Eq. 13, R maintains the above definition, r is the distance from the center of the benzene ring to the midpoint of the projection of the dipole on the carbon-substituent bond extension, d is the invariant distance from the center of the molecule to the midpoint of the carbon-hydrogen bond to be broken, which, for purposes of simplification, was treated as its projection along the methyl carbon-quaternary carbon bond. The value of d is 3.846 Å. b is equal to r + 1.5 Å; this is the Tanford modification (76) which defines the actual size of the cavity in which the molecule exists, and a is the angle between r and d which has a constant value of 155° for this system. A diagram is shown in Figure 7. x is given by the expression

$$x = \left[\frac{rd}{b^2} \right]^{\frac{1}{2}} \qquad \text{(Eq. 14)}$$

and may be considered as a measure of the depth of penetration of the dipole and the removable hydrogen below the interphase of the cavity. D and D_i are respectively the dielectric constants of the solvent and the cavity. The latter was given a value of 2.2
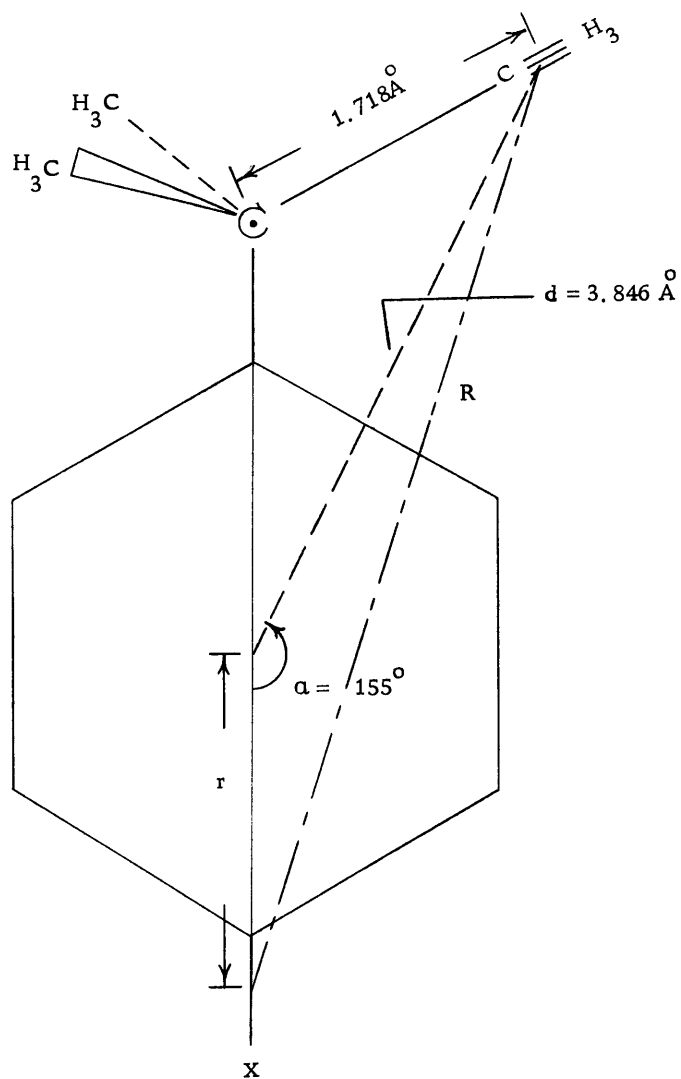
Figure 7.   Geometry of para-substituted t-butylbenzenes.

approximately equal to that of benzene. The value of D is 10, that of

sulfuryl chloride. Table 6 presents values of terms needed to evalu-

ate D_E for the para substituted t-butylbenzenes. Table 7 presents

the values of $1/R^2 D_E$ and the calculated and experimental relative

rates. A least-squares plot of the calculated relative rate constant

against their experimental counterparts yields an excellent correlation

Table 6. Values of r, R, b, and x for para substituted t-butyl-
benzenes in Å.

Substituent	r	R	b	x
t-Butyl	3.49	7.17	4.99	0.731
Hydrogen	1.94	5.67	3.44	0.790
Phenoxy	2.03	5.76	3.53	0.788
Chloro	2.25	5.97	3.75	0.781
Carbophenoxy	3.33	7.01	4.83	0.737
Cyano	3.40	7.09	4.90	0.735
Nitro	3.18	6.86	4.68	0.748

The slope is equal to 0.049 ± 0.009 and the correlation coefficient is

0.997. The graph is shown in Figure 8. The correlation is very

good and is at least suggestive that the electronic properties of the

substituents may be transmitted to the reaction site by a field effect.

The slope of this correlation is a measure of the percent of carbonium

ion character developed at the reaction site in the transition state.

Table 7. Calculated relative rates of hydrogen abstraction from para substituted t-butylbenzenes at 70° using the Kirkwood-Westheimer model.

Substituent	$\mu\cos\Theta^a$ in Debye	$\dfrac{1}{R^2 D_E} \cdot 10^3$, in Å^{-2}	$\log k_X^{abs}/k_H^{abs}$ calc.	exper.
t-Butyl	-0.50	4.01	0.8845	0.0569
Hydrogen	0.00	1.32	0.0	0.0
Phenoxy	1.16	1.76	-0.9006	-0.0585
Chloro	1.58	2.63	-1.8333	-0.0947
Carbophenoxy	1.83	4.01	-3.2374	-0.1772
Cyano	3.90	3.97	-6.8300	-0.3242
Nitro	3.98	3.98	-6.9880	-0.3527

a) Dipole moments obtained from ref. 73.

The value is 4.9 ± 0.2%, much smaller than for other systems studied in these laboratories (48). Those systems, however, were tertiary in nature and should be more capable of accomodating a portion of a positive charge than the primary radical treated here.

As a final test of the correlation of the field effect model, it was decided to re-examine m-nitro-t-butylbenzene. Unfortunately, the structural considerations for this molecule are far more complex than for any of the para series. An essentially free rotation about the bond connecting the quaternary carbon atom in the t-butyl group with the aromatic ring can allow for an infinite number of conformers. In each of these the geometrical relationship between
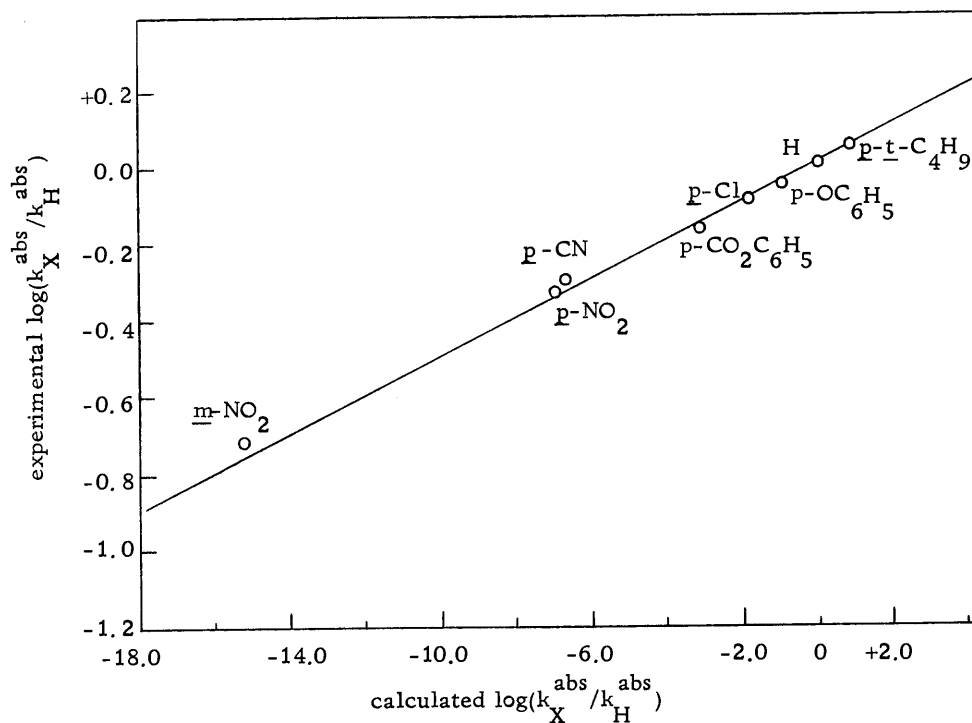
Figure 8. Experimental **vs.** calculated relative rate
constants of hydrogen abstraction.

the forming radical and the substituent will be different. To allow

for ease of calculation, therefore, a simplified model was con-

structed in which the reaction site was treated as its projection

along the aforementioned carbon-carbon bond. As should be ex-

pected, d and α, parameters which had constant value for all **para**

compounds, will differ for the **meta** series. The results of this

calculation are graphically illustrated in Figure 8. It can be seen

that the **m**-nitro compound comes very close to falling on the line

generated from the data for **para** substituents. Using the parameters

of the correlation, **m**-nitro-**t**-butylbenzene is calculated to have a

relative rate of reaction of 0.174. The value obtained experimentally

was 0.189 ± 0.021.

In summation it may be pointed out that the field effect model

seems to provide a useful rationale for the results of the experi-

ments. Of the nine compounds ultimately utilized, only one m-

phenoxy-t-butylbenzene, does not fall within the scope of this corre-

lation, and this compound may well possess the ability to form ex-

tremely stable internal complexes.

EXPERIMENTAL

Melting points were taken in unsealed capillary tubes with a
Büchi melting point apparatus. Melting and boiling points are un-
corrected. Nuclear magnetic resonance (nmr) spectra were taken on
a Varian A-60 instrument using tetramethylsilane as a reference and
spectroquality carbon tetrachloride (Matheson Coleman & Bell) as
solvent. Infrared spectra were taken on a Beckman IR-8 spectro-
photometer as films between sodium chloride discs. The elemental
microanalyses reported here were performed using the facilities of
the Department of Chemistry, Oregon State University. Gas-liquid
chromatography (GLC) analyses were carried out with a Varian
Aerograph 202B gas chromatograph equipped with a linear tempera-
ture programmer and a Sargent recorder with disc integration. A
10' x 1/4" column of 5% S. E. 30 on Chromosorb G and a 10' x 1/4"
column of 3% FFAP on Chromosorb G were used in this investigation.
Thermal conductivity detectors and helium carrier gas were em-
ployed in the gas chromatograph.

Purification of Chlorobenzene. Commercial chlorobenzene
(Matheson Coleman & Bell) was washed with dilute sulfuric acid
followed by water and dried over anhydrous magnesium sulfate.
During redistillation the fraction boiling at 131-132° was collected.

Purification of Sulfuryl Chloride. Reagent sulfuryl chloride

(Matheson Coleman & Bell) was redistilled; the colorless fraction

boiling at 69° was collected and stored in a foil-wrapped brown bottle.

Purification of Benzoyl Peroxide. Granular benzoyl peroxide

(Eastman) was used without further purification.

Purification of t-Butylbenzene. Commercial t-butylbenzene

(Aldrich) was redistilled, b. p. 165-166°. Inspection by GLC showed

less than 1% impurity.

Purification of β-Chloro-t-butylbenzene. β-Chloro-t-butyl-

benzene (neophyl chloride) (Aldrich) was purified by redistillation at

11 mm. pressure, b. p. 97.5^{o}; lit. 119-120° at 30 mm. (35). GLC

detected no impurities.

Purification of m-Bromo-t-butylbenzene. M. M. Martin kindly

supplied m-bromo-t-butylbenzene; it was fractionated twice, b. p. 97-

98° at 10 mm. , lit. 231-232° at 710 mm. (68). GLC showed a 2%

impurity.

Purification of m-Nitro-t-butylbenzene. m-Nitro-t-butylben-

zene was also supplied by M. M. Martin. It was redistilled twice at

12 mm. , b. p. 130-132°, lit. 97-99° at 2.5 mm. (11). GLC revealed

3.4% impurities.

Purification of p-Di-t-butylbenzene. Solid p-di-t-butylbenzene

was purchased from Eastman and used without further purification

when GLC revealed less than 1% impurity.

Purification of p-Bromo-t-butylbenzene. Commercial p-bromo-

butylbenzene (Columbia) was purified by distillation, b.p. 126° at 31

mm., lit. 104-106° at 14 mm. (77). GLC uncovered a 0.5% impurity

with the same retention time as t-butylbenzene.

Preparation of p-Nitro-t-butylbenzene. p-Nitro-t-butylbenzene

with an H_2SO_4-HNO_3 mixture via the method of Nelson and Brown

(47). The product was distilled three times through a 25 cm. column

packed with glass helices, b.p. 92-94° at 1 mm., lit. 135° at 10 mm.

(47). GLC showed a 2% impurity with the same retention time as m-

nitro-t-butylbenzene.

Preparation of Ethyl p-t-Butylbenzoate. The ethyl ester of p-t-

butylbenzoic acid was prepared from the acid (Matheson Coleman &

Bell, practical) and ethanol in the presence of concentrated H_2SO_4 in

an adaptation of the method described by Vogel (82). The fraction of

the product which boiled at 137-139° at 11 mm. pressure, lit. 110-

112° at 3 mm. (69) was collected. GLC revealed no detectable

impurities.

Preparation of Phenyl p-t-Butylbenzoate. The acyl chloride of p-t-butylbenzoic acid (Matheson Coleman & Bell, practical) was synthesized by refluxing the acid and thionyl chloride in benzene in a modification of Vogel's scheme (82). The distilled acid chloride, b. p. 92° at 1 mm., lit. 135° at 10 mm. (74), was shaken with phenol in 10% aqueous potassium hydroxide in another modification of Vogel's method (82). The product was distilled from the reaction mixture at 165-168° at 2 mm. pressure and solidified on standing. The ester was recrystalized from 95% ethanol; the fluffy white crystals melted at 60-61°. The infrared spectrum absorbed strongly at 1728, 1266, 1190 (doublet) and 1070 cm^{-1}. The nmr showed a methyl singlet at 1.36 δ and a complex pattern of phenyl protons from 7.0 to 8.15 δ; the areas integrated 1:1. GLC noted no detectable impurities.

Analysis. Calculated for $C_{17}H_{18}O_2$: C, 80.2; H, 7.08. Found: C, 79.6; H, 7.08.

Preparation of p-Methoxy-t-butylbenzene. The procedure described by Vogel (82) was modified to prepare the methyl ether of p-t-butylphenol (Aldrich) from the phenol and dimethyl sulfate (Matheson Coleman & Bell). The ether was distilled twice, b. p. 99-100° at 15.5 mm., lit. 221.4-222.4° at 730.5 mm. (68). GLC disclosed less than 1% impurity.

Preparation of m-Methoxy-t-butylbenzene. m-Methoxy-t-butyl-benzene was made in the same way as the para isomer above except m-t-butylphenol (Aldrich) was substituted for p-t-butylphenol. The ether boiled at 99-100° at 17.5 mm., lit. 65° at 2.5 mm. (11). GLC detected no impurities.

Preparation of p-Phenoxy-t-butylbenzene. The procedure of Sartoretto and Sowa (67) was adapted to the synthesis of p-phenoxy-t-butylbenzene. p-t-Butylphenol was converted to its potassium salt and refluxed for 26 hours with phenyl bromide in the presence of precipi-tated copper catalyst (from Vogel, 82). The ether was distilled at 0.60 mm. pressure, b.p. 115-116°., lit. 172° at 14 mm. (49). The liquid solidified on standing, was recrystallized from 95% ethanol and melted at 53-54°., lit. 54° (49).

Analysis. Calculated for $C_{16}H_{18}O$: C, 84.90; H, 8.02. Found: C, 84.66; H, 7.93.

Preparation of m-Phenoxy-t-butylbenzene. m-Phenoxy-t-butyl-benzene was prepared from m-t-butylphenol (Aldrich) as its potassium salt and phenyl bromide in the presence of precipitated copper catalyst in a variation of Sartoretto and Sowa's technique (67). Refluxing the reactants for 2-1/2 days produced a 49% yield of the ether, b.p. 145° at 6 mm. pressure; $n_D^{28} = 1.5502$. The infrared spectrum showed

strong absorptions at 1225, 928, 752, 697, and 690 cm^{-1}. The nmr

showed a methyl singlet at 1.24 δ (area 165) and a complex pattern of

phenyl protons from 6.5 to 7.5 δ (area 193). GLC showed a 2% im-

purity with the same retention time as p-phenoxy-t-butylbenzene.

Analysis. Calculated for $C_{16}H_{18}O$: C, 84.90; H, 8.02. Found:

C, 84.80; H, 7.96.

Preparation of p-Cyano-t-butylbenzene. p-Cyano-t-butylben-

zene was synthesized by converting p-t-butylbenzoic acid (Matheson

Coleman & Bell, practical) to the acid chloride with thionyl chloride;

the acid chloride was in turn changed to the amide by treatment with

concentrated ammonium hydroxide; the amide was dehydrated to the

nitrile by the action of thionyl chloride. All steps were variations of

procedures given by Vogel (82). The nitrile was distilled at 21 mm.,

the fraction boiling at 132-133°, lit. 243-245° (40), was collected.

GLC showed only a 0.4% impurity.

Preparation of p-Chloro-t-butylbenzene. Chlorobenzene was

alkylated with t-butyl chloride (Aldrich) in the presence of anhydrous

reagent ferric chloride (Matheson Coleman & Bell) according to the

scheme of Lerer and Fabre (42). The fraction of product which boiled

at 209° was used. Lit. b. p. is 112° at 30 mm. (42). The infrared

spectrum was identical to the one published by Lerer and Fabre. GLC

detected no impurities.

Preparation of p-Iodo-t-butylbenzene. t-Butylbenzene was

refluxed in the presence of iodine and concentrated nitric acid in an

adaptation of the method outlined by Vogel (82) to produce p-iodo-t-

butylbenzene, b. p. 120-130° at 12 mm. lit. 253-254° at 766 mm. (6).

GLC detected 2. 4% impurities.

Preparation of 2-Methyl-2-(p-nitrophenyl)chloropropane. Nitra-

tion of β-chloro-t-butylbenzene (Aldrich) in the manner of Nelson and

Brown (47) produced 2-methyl-2-(p-nitrophenyl)-chloropropane (p-

nitroneophyl chloride). Three recrystalizations from 95% ethanol

produced white platelets, m. p. 53-54°, lit. 60-62° (7). GLC re-

vealed no detectable impurities.

Analysis. Calculated for $C_{10}H_{12}ClNO_2$: C, 56.2; H, 5. 66;

N, 6.56. Found: C, 56.3; H, 5.97; N, 6.52.

Preparation of 2-Methyl-2-(p-chlorophenyl)chloropropane.

p-Chloro-t-butylbenzene was chlorinated with sulfuryl chloride in the

presence of benzoyl peroxide in an adaptation of the reaction of

Kharasch and Brown (35). The boiling point of the product was 74°

and 0. 35 mm. of pressure, n_D^{28} = 1.5358., Lit. b. p. is 123.5° at 10

mm., n_D^{20} = 1.5389 (54). GLC showed less than 2% impurity.

Analysis.   Calculated for $C_{10}H_{12}Cl_2$:   C, 59.11; H, 5.96.
Found: C, 58.7; H, 6.05.

Products of the Reaction of Bromotrichloromethane and t-Butyl-benzene.

An attempt was made to abstract the hydrogen atom of t-butylbenzene with the trichloromethyl radical from bromotrichloro-methane.   Because the trichloromethyl radical has nearly the same reactivity as the bromine atom (20, 29, 31, 43, 44) which will not react with t-butylbenzene in the liquid phase (7), the reaction was not expected to go.   t-Butylbenzene, chlorobenzene, and bromotrichloro-methane (Matheson Coleman & Bell, reagent) in 1:1:20 ratio were reacted photolitically in sealed, nitrogen-filled ampoules for 9 hours at 70°.   No disappearance ot t-butylbenzene occurred, although the amount of bromotrichloromethane decreased.

Procedure for Product Studies of the Reaction of Substituted t-Butylbenzenes and Sulfuryl Chloride.

A solution of the t-butylbenzene, sulfuryl chloride, and chlorobenzene (as the internal standard) was prepared in the approximate molar ratio of 4:2:1, respectively.   In the cases of p-di-t-butylbenzene, phenyl p-t-butylbenzoate, and p-phenoxy-t-butylbenzene the amount of chlorobenzene had to be increased by a factor of about four in order to effect solution.   Approximately 0.5 ml. of this solution together with 4-5 mg. (0.20 mmole) of benzoyl chloride was intro-duced into several constricted Pyrex culture tubes.   A portion of the

solution was placed in a tube without peroxide to be used for analysis

of starting material. The tubes were then evacuated at aspirator

pressure and dry ice-acetone temperature and flushed with dried nitro-

gen. This process was repeated five times and on the sixth evacuation,

the tubes were sealed. The ampoule without the peroxide was stored

in the dry ice-acetone bath, the others being suspended in a controlled

temperature mineral oil bath at $70.0 \pm 0.5^{\circ}$. Reaction time varied

from 1-1/2 to 15 hours, after which time the reaction was quenched.

The ampoules were then opened and analyzed via gas-liquid chroma-

tography. The reactions were from 7 to 33% complete, computed in

terms of disappearance of the t-butylbenzene substrate. The small

amounts of reaction and small amounts of sulfuryl chloride kept

secondary reactions to a minimum. The ratio of the peak area of the

alkyl chlorination product to the area(s) of the nuclear chlorination

product(s) was assumed to be equal to the ratio of the number of

mmoles of those products. This assumption was checked for the

products of the unsubstituted t-butylbenzene reaction and found to be

very nearly true. The percentage of alkyl chlorination was then

calculated from these ratios.

Products of the Reaction of Chlorobenzene and Sulfuryl Chloride.

Two attempts were made to react chlorobenzene and sulfuryl chloride

(6:2) with peroxide catalyst. Ten ampoules were filled and sealed in

the usual way but without any t-butylbenzene present. Five ampoules were heated at 70° for 1/4 hour and five for 2 hours. No peaks other than the sulfuryl chloride and chlorobenzene peaks appeared on the gas-liquid chromatographic analysis chart.

Products of the Reaction of t-Butylbenzene and Sulfuryl Chloride. Chlorination of t-butylbenzene was first attempted at 40°. GLC showed two product peaks, the first of which was the larger and had a retention time identical to that of p-chloro-t-butylbenzene[1]. The smaller second peak corresponded to neophyl chloride. The fact that the nuclear chlorination reaction predominated at this temperature led us to try the reaction at 70°. At 70° the side-chain chlorination was definitely in excess of the nuclear substitution reaction. The reasons for this phenomenon are presented in the Discussion section. Secondary reactions of monochlorinated species were found to occur readily in excess sulfuryl chloride. To reduce these reactions the amount of sulfuryl chloride was adjusted to the values recorded above. At 70° the major product of the reaction between t-butylbenzene and sulfuryl chloride was neophyl chloride. The ratio of this product to nuclear chlorination products was 7.53 ± 0.84.

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[1] The S. E. 30 column did not separate the m- and p-isomers. The FFAP split this peak into a doublet, the p-isomer eluting slightly later than the m-isomer.

Products of the Reaction of p-Nitro-t-butylbenzene and Sulfuryl

Chloride. Kharasch and Brown (35) reported that o- and p-nitro-

toluenes did not react with sulfuryl chloride because of the chain

breaking properties of the nitro group. This researcher did not find

this to be true of p- (or m-) nitro-t-butylbenzene. GLC resolved two

product peaks, the second one being the larger. This peak had an

elution time identical to that of an authentic sample of 2-methyl-2-

(p-nitrophenyl)chloropropane. The small peak then was assumed to

be the nuclear chlorinated product(s). The reaction was found to be

extremely slow, being only 9% complete after 15 hours. The alkyl

to aryl ratio of chlorination products was 4.51 ± 0.36.

Products of the Reaction of m-Nitro-t-butylbenzene and Sulfuryl

Chloride. The gas-liquid chromatograph of the reaction mixture of

m-nitro-t-butylbenzene disclosed four product peaks. The largest

one had the longest retention period and was assumed to be the side-

chain chlorination product. The three smaller peaks must have been

the nuclear chlorination products. The ratio of the former to the

latter was 3.69 ± 0.13.

Products of the Reaction of p-Cyano-t-butylbenzene and Sulfuryl

Chloride. Chlorination of p-cyano-t-butylbenzene produced two

product peaks. The more tenacious of the two was also the larger and

so was surmised to be 2-methyl-2-(p-cyanophenyl)chloropropane.

The ratio of the large to small peak was 5.11 ± 0.165.

Products of the Reaction of p-Di-t-butylbenzene and Sulfuryl

Chloride. The chlorination of p-di-t-butylbenzene produced one very

large and one very small product peak. The larger one possessed the

longer elution period and was presumably the alkyl chlorination

product. The ratio of alkyl to aryl products was large, 17.3 ± 1.05.

This is not surprising for two reasons. First, there are twice as

many equivalent alkyl protons available for abstraction than with any

other material, and secondly, the bulky t-butyl groups would make

nuclear substitution difficult.

Products in the Reaction of p-Chloro-t-butylbenzene and Sulfuryl

Chloride. p-Chloro-t-butylbenzene was unusual in that it produced

essentially 100% side chain chlorination. The single product peak's

retention time was identical to that of an authentic sample p-chloro-

neophyl chloride. Two extremely minor peaks with shorter retention

times appeared but were negligible.

Products of the Reaction of p-Bromo-t-butylbenzene and

Sulfuryl Chloride. The reaction mixture of p-bromo-t-butylbenzene

became a deep red and was decolorized by cyclohexene, indicating the

presence of molecular bromine. GLC displayed a very large peak

whose retention time was the same as that of p-chloro-t-butylbenzene.

Two smaller peaks appeared with retention times longer than that of

p-bromo-t-butylbenzene. The second was about twice as large as the

first; together they did not comprise 10% of the area of the p-chloro-

t-butylbenzene. p-Chloroneophyl chloride had an elution period

different from either of them; they were probably nuclear and side-

chain chlorination products of the original substrate. The fact that

they were so minor led us to omit this compound from the kinetic

studies.

Products of the Reaction of m-Bromo-t-butylbenzene and

Sulfuryl Chloride. After reaction with sulfuryl chloride, the m-

bromo-t-butylbenzene reaction mixture became a deep gold color

which was not decolorized by cyclohexene. GLC revealed three

product peaks. The largest of these was apparently m-chloro-t-butyl-

benzene as it had a retention time very slightly less than that of p-

chloro-t-butylbenzene; it was relatively smaller than its para isomer

in the p-bromo-t-butylbenzene reaction, comprising about 50% of the

sum of the areas of all three peaks. The second and third peaks had

elution times longer than that of p-chloroneophyl chloride. The sec-

ond of the pair was about twice the size of the first, so they were

probably alkyl and aryl chlorination products of the original substrate.

Again no kinetic runs were made because of the predominance of the

displacement reaction.

Products of the Reaction of p-Iodo-t-butylbenzene and Sulfuryl

Chloride. p-Iodo-t-butylbenzene reacted with chlorine atoms to give

a deep purple-brown solution indicative of free iodine. Six products

appeared on the chromatograph. Five products comprised about 50%

of the total area of the six peaks. The largest of these five was p-

chloro-t-butylbenzene on the basis of retention times. The sixth peak

was the largest, had the longest elution period and was not p-chloro-

neophyl chloride. This peak was probably the alkyl chlorination

product. No kinetic study was done on p-iodo-t-butylbenzene because

of the uncertainties of this product study.

Products of the Reaction of p-Methoxy-t-butylbenzene and

Sulfuryl Chloride. This reaction produced at least four products[2],

one of which had a retention time shorter than that of p-methoxy-t-

butylbenzene and amounted to about 25% of the total product peak areas.

It was not known why so many products formed; a possible explanation

is that a methoxy methyl hydrogen was abstracted and unknown

products resulted. Whatever the problem, it would be expected to

occur in the m-methoxy-t-butylbenzene and ethyl p-t-butylbenzoate

systems for similar reasons. These latter two compounds were ex-

cluded from product and kinetic studies, and p-methoxy-t-butylbenzene

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[2] Possibly five as the largest product peak showed a significant
shoulder.

was excluded from the kinetic study.

Products of the Reaction of p-Phenoxy-t-butylbenzene and

Sulfuryl Chloride.   The p-phenoxy-t-butylbenzene yielded four prod-

ucts.   The largest had the longest retention time and was presumed to

be the alkyl chlorination isomer.   The comparatively small ratio of

alkyl to aryl chlorination, 1.73 ± 0.09, may have been the result of a

1,2 aryl shift, or of the availability of so many sites for nuclear

chlorination.

Products of the Reaction of m-Phenoxy-t-butylbenzene and

Sulfuryl Chloride.   Three products resulted from the chlorination of

m-phenoxy-t-butylbenzene.   The first two peaks were very much

smaller than the third; the former were assumed to be nuclear chlor-

ination products.   The ratio was 4.02 ± 0.24, alkyl to aryl chlorina-

tion.

Products of the Reaction of Phenyl p-t-Butylbenzoate and

Sulfuryl Chloride.   The phenyl ester of p-t- butylbenzoic acid gave

only two chlorination products via analysis by GLC.   The second peak

was larger than the first and was supposed to be the side-chain chlori-

nation product.   The alkyl to aryl chlorination ratio was 5.56 ± 0.63.

The detailed information on each product study may be found in

the Appendix I, Tables 8-16.

Procedure for the Determination of Relative Rates of Disappear-
ance of Substituted t-Butylbenzenes. Solutions of two t-butylbenzenes,
sulfuryl chloride, and chlorobenzene were prepared in the approxi-
mate molar ratio of 1:1:3:1. Ampoules containing a small amount of
benzoyl peroxide were filled, sealed, and reacted in the same way as
described previously for the product studies. Reaction times, how-
ever, were shortened to from 10 minutes to 4 hours at $70.0 \pm 0.5^{\circ}$.
All determinations were run in replicate. The procedure was to have
the substituted t-butylbenzene compete directly with t-butylbenzene for
the abstracting radical. In the case of p-chloro-t-butylbenzene it was
necessary to determine its relative reactivity to p-cyano-t-butylben-
zene. The relative rate constants thereby attained were converted to
the desired form by use of the expression

$$\left[\frac{k_{p-Cl}}{k_H} \right]_{dis} = \left[\frac{k_{p-Cl}}{k_{p-CN}} \right]_{dis} \cdot \left[\frac{k_{p-CN}}{k_H} \right]_{dis} \qquad (Eq.\ 15)$$

Determination of $(k_X/k_H)_{dis}$. The ratios of relative rate con-
stants of disappearance were obtained using the usual competitive pro-
cedures (20, 31, 43). The following equation was used:

$$\left[\frac{k_X}{k_H} \right]_{dis} = \frac{\log(X_o/X_f)}{\log(H_o/H_f)} \qquad (Eq.\ 16)$$

where $(k_X/k_H)_{dis}$ is the relative rate constant of disappearance of the
X-substituted t-butylbenzene to the unsubstituted t-butylbenzene; X_o

and H_o are the number of mmoles originally present of the X-substituted t-butylbenzene and t-butylbenzene, respectively; and X_f and H_f are the corresponding terms for the final number of mmoles present. The above ratios were obtained directly from the chromatographic analysis by using the following equation:

$$\frac{X_o}{X_f} = \frac{\left[\dfrac{\text{area under X peak}}{\text{area under } C_6H_5Cl \text{ peak}}\right] \text{ initially}}{\left[\dfrac{\text{area under H peak}}{\text{area under } C_6H_5Cl \text{ peak}}\right] \text{ finally}} \qquad \text{(Eq. 17)}$$

See Appendix II, Tables 17-24 for the detailed data on the kinetic studies.

Determination of k_X^{abs}/k_H^{abs}. The relative rate constant of alkyl hydrogen abstraction, k_X^{abs}/k_H^{abs}, of the X-substituted t-butylbenzene to t-butylbenzene was then computed using the following relationship:

$$\frac{k_X^{abs}}{k_H^{abs}} = \left[\frac{k_X}{k_H}\right]_{dis} \cdot \left[\frac{\% \text{ side-chain chlorination of } X\text{-}t\text{-butylbenzene}}{\% \text{ side-chain chlorination of } t\text{-butylbenzene}}\right]$$

$$\text{(Eq. 18)}$$

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APPENDIX

APPENDIX I
PRODUCT STUDIES

Table 8. Product study of the chlorination of t-butylbenzene by
sulfuryl chloride.

Conditions: 1-1/2 hours at 70°C.

Mmoles SO_2Cl_2: 2.5

Mmoles C_6H_5Cl: 7.10

Mmoles peroxide: 0.02

$C_6H_5(C_4H_9)$ -- t-butylbenzene

$C_6H_5(C_4H_8Cl)$ -- side-chain chlorination product

$ClC_6H_4(C_4H_9)$ --nuclear chlorination products

Run	Compound	Mmoles initial	Mmoles final	% rx.	Side-chain nuclear
	$C_6H_5(C_4H_9)$	10.06	8.24	18.1	
	$C_6H_5(C_4H_8Cl)$	0	1.57		
	$ClC_6H_4(C_4H_9)$	0	0.217		7.24
2	$C_6H_5(C_4H_9)$	10.06	8.39	16.6	
	$C_6H_5(C_4H_8Cl)$	0	1.88		
	$ClC_6H_4(C_4H_9)$	0	0.192		8.80
3	$C_6H_5(C_4H_9)$	10.06	8.26	17.9	
	$C_6H_5(C_4H_8Cl)$	0	1.48		
	$ClC_6H_4(C_4H_9)$	0	0.238		6.22
4	$C_6H_5(C_4H_9)$	10.06	7.73	23.1	
	$C_6H_5(C_4H_8Cl)$	0	1.81		
	$ClC_6H_4(C_4H_9)$	0	0.235		7.70

Table 8. continued

Run	Compound	Mmoles initial	Mmoles final	% rx.	Side-chain nuclear
5	$C_6H_5(C_4H_9)$	10.06	7.25	27.9	
	$C_6H_5(C_4H_8Cl)$	0	1.87		
	$ClC_6H_4(C_4H_9)$	0	0.225		8.31
Average					7.65 ± 0.74
% Alkyl Chlorination					88.4$_4$

Table 9: Product study of the chlorination of p-nitro-t-butylbenzene by sulfuryl chloride.

Conditions: 15 hours at 70°C

Mmoles SO$_2$Cl$_2$:   1.65

Mmoles C$_6$H$_5$Cl: 4.98

Mmoles peroxide: 0.02

NO$_2$C$_6$H$_4$(C$_4$H$_9$) -- p-nitro-t-butylbenzene

NO$_2$C$_6$H$_4$(C$_4$H$_8$Cl) -- side-chain chlorination product

NO$_2$C$_6$H$_3$Cl(C$_4$H$_9$) -- nuclear chlorination products

Run	Compound	Mmoles initial	Mmoles final	% rx.	Side-chain / nuclear
1	NO$_2$C$_6$H$_4$(C$_4$H$_9$)	5.95	5.40	9.2	
	NO$_2$C$_6$H$_4$(C$_4$H$_8$Cl)	0	0.535		
	NO$_2$C$_6$H$_3$Cl(C$_4$H$_9$)	0	0.105		5.09
2	NO$_2$C$_6$H$_4$(C$_4$H$_9$)	5.95	5.14	13.6	
	NO$_2$C$_6$H$_4$(C$_4$H$_8$Cl)	0	0.663		
	NO$_2$C$_6$H$_3$Cl(C$_4$H$_9$)	0	0.147		4.30
3	NO$_2$C$_6$H$_4$(C$_4$H$_9$)	5.95	5.39	9.4	
	NO$_2$C$_6$H$_4$(C$_4$H$_8$Cl)	0	0.425		
	NO$_2$C$_6$H$_3$Cl(C$_4$H$_9$)	0	0.0913		4.66
4	NO$_2$C$_6$H$_4$(C$_4$H$_9$)	5.95	5.42	8.9	
	NO$_2$C$_6$H$_4$(C$_4$H$_8$Cl)	0	0.439		
	NO$_2$C$_6$H$_3$Cl(C$_4$H$_9$)	0	0.121		4.00
Average					4.51 ± 0.363
% Alkyl Chlorination					81.8$_5$

Table 10. Product study of the chlorination of $\underline{m}$-nitro-$\underline{t}$-butyl-benzene by sulfuryl chloride.

Conditions: 2-1/2 hours at $70^{\circ}C$.

Mmoles SO_2Cl_2: 1.31

Mmoles C_6H_5Cl: 5.17

Mmoles peroxide: 0.02

$NO_2C_6H_4(C_4H_9)$ -- $\underline{m}$-nitro-$\underline{t}$-butylbenzene

$NO_2C_6H_4(C_4H_8Cl)$ -- side-chain chlorination product

$NO_2C_6H_3Cl(C_4H_9)$ -- nuclear chlorination products

Run	Compound	Mmoles initial	Mmoles final	% rx.	Side-chain / nuclear
1	$NO_2C_6H_4(C_4H_9)$	5.04	4.25	15.7	
	$NO_2C_6H_4(C_4H_8Cl)$	0	0.856		
	$NO_2C_6H_3Cl(C_4H_9)$	0	0.227		3.78
2	$NO_2C_6H_4(C_4H_9)$	5.04	3.92	22.2	
	$NO_2C_6H_4(C_4H_8Cl)$	0	0.770		
	$NO_2C_6H_3Cl(C_4H_9)$	0	0.207		3.72
3	$NO_2C_6H_4(C_4H_9)$	5.04	4.34	13.9	
	$NO_2C_6H_4(C_4H_8Cl)$	0	0.696		
	$NO_2C_6H_3Cl(C_4H_9)$	0	0.177		3.93
4	$NO_2C_6H_4(C_4H_9)$	5.04	3.89	22.8	
	$NO_2C_6H_4(C_4H_8Cl)$	0	0.869		
	$NO_2C_6H_3Cl(C_4H_9)$	0	0.241		3.61
5	$NO_2C_6H_4(C_4H_9)$	5.04	3.88	23.0	
	$NO_2C_6H_4(C_4H_8Cl)$	0	0.752		
	$NO_2C_6H_3Cl(C_4H_9)$	0	0.219		3.43
Average					3.69 ± 0.14
% Alkyl Chlorination					78.6_7

Table 11. Product study of the chlorination of p-di-t-butylbenzene by sulfuryl chloride.

Conditions: 1-1/2 hours at 70°C

Mmoles SO_2Cl_2: 2.03

Mmoles C_6H_5Cl: 37.3

Mmoles peroxide: 0.02

$C_6H_4(C_4H_9)_2$ -- p-di-t-butylbenzene

$C_6H_4(C_8H_{17}Cl)$ -- side-chain chlorination product

$C_6H_3Cl(C_4H_9)_2$ -- nuclear chlorination products

Run	Compound	Mmoles initial	Mmoles final	% rx.	Side-chain nuclear
1	$C_6H_4(C_4H_9)_2$	8.10	6.37	21.4	
	$C_6H_4(C_8H_{17}Cl)$	0	1.18		
	$C_6H_3Cl(C_4H_9)_2$	0	0.0600		19.7
2	$C_6H_4(C_4H_9)_2$	8.10	6.38	21.2	
	$C_6H_4(C_8H_{17}Cl)$	0	1.41		
	$C_6H_3Cl(C_4H_9)_2$	0	0.0960		14.7
3	$C_6H_4(C_4H_9)_2$	8.10	6.55	19.1	
	$C_6H_4(C_8H_{17}Cl)$	0	1.51		
	$C_6H_3Cl(C_4H_9)_2$	0	0.088		17.1
4	$C_6H_4(C_4H_9)_2$	8.10	6.43	20.6	
	$C_6H_4(C_8H_{17}Cl)$	0	1.52		
	$C_6H_3Cl(C_4H_9)_2$	0	0.0888		17.1
5	$C_6H_4(C_4H_9)_2$	8.10	6.70	17.3	
	$C_6H_4(C_8H_{17}Cl)$	0	1.52		
	$C_6H_3Cl(C_4H_9)_2$	0	0.084		18.1
Average					17.3 ± 1.04
% Alkyl Chlorination					94.5$_4$

Table 12.   Product study of the chlorination of p-cyano-t-butylben-
zene by sulfuryl chloride.

Conditions: 1-1/2 hours at 70°C.

Mmoles SO_2Cl_2:   2.13

Mmoles C_6H_5Cl: 1.98

Mmoles peroxide: 0.02

$CNC_6H_4(C_4H_9)$ -- p-cyano-t-butylbenzene

$CNC_6H_4(C_4H_8Cl)$ -- side-chain chlorination product

$CNC_6H_3Cl(C_4H_9)$ -- nuclear chlorination products

Run	Compound	Mmoles initial	Mmoles final	% rx.	Side-chain / nuclear
1	$CNC_6H_4(C_4H_9)$	8.01	6.31	21.2	
	$CNC_6H_4(C_4H_8Cl)$	0	1.43		
	$CNC_6H_3Cl(C_4H_9)$	0	0.274		5.22
2	$CNC_6H_4(C_4H_9)$	8.01	6.01	25.0	
	$CNC_6H_4(C_4H_8Cl)$	0	1.61		
	$CNC_6H_3Cl(C_4H_9)$	0	0.337		4.78
3	$CNC_6H_4(C_4H_9)$	8.01	6.11	23.7	
	$CNC_6H_4(C_4H_8Cl)$	0	1.50		
	$CNC_6H_3Cl(C_4H_9)$	0	0.289		5.19
4	$CNC_6H_4(C_4H_9)$	8.01	6.17	23.0	
	$CNC_6H_4(C_4H_8Cl)$	0	1.67		
	$CNC_6H_3Cl(C_4H_9)$	0	0.318		5.25

Average 5.11 ± 0.165

% Alkyl Chlorination 83.6_3

Table 13. Product study of the chlorination of phenyl p-t-butylbenzoate by sulfuryl chloride.

Conditions: 2 hours at 70°C.

Mmoles SO_2Cl_2: 0.584

Mmoles C_6H_5Cl: 6.48

Mmoles peroxide: 0.01

$PhOOCC_6H_4(C_4H_9)$ -- phenyl p-t-butylbenzoate

$PhOOCC_6H_4(C_4H_8Cl)$ -- side-chain chlorination product

$PhOOCC_6H_3Cl(C_4H_9)$ -- nuclear chlorination products

Run	Compound	Mmoles initial	Mmoles final	% rx.	Side-chain nuclear
1	$PhOOCC_6H_4(C_4H_9)$	1.98	1.36	31.3	
	$PhOOCC_6H_4(C_4H_8Cl)$	0	0.458		
	$PhOOCC_6H_3Cl(C_4H_9)$	0	0.0802		5.71
2	$PhOOCC_6H_4(C_4H_9)$	1.98	1.37	30.8	
	$PhOOCC_6H_4(C_4H_8Cl)$	0	0.584		
	$PhOOCC_6H_3Cl(C_4H_9)$	0	0.0902		6.48
3	$PhOOCC_6H_4(C_4H_9)$	1.98	1.42	28.3	
	$PhOOCC_6H_4(C_4H_8Cl)$	0	0.478		
	$PhOOCC_6H_3Cl(C_4H_9)$	0	0.104		4.61
4	$PhOOCC_6H_4(C_4H_9)$	1.98	1.35	31.8	
	$PhOOCC_6H_4(C_4H_8Cl)$	0	0.541		
	$PhOOCC_6H_3Cl(C_4H_9)$	0	0.107		5.06

Average 5.47 ± 0.038

% Alkyl Chlorination 84.5_3

Table 14. Product study of the chlorination of p-phenoxy-t-butyl-
benzene by sulfuryl chloride.

Conditions: 11 hours at 70°C.

Mmoles SO_2Cl_2:   0.93

Mmoles C_6H_5Cl: 10.1

Mmoles peroxide: 0.02

$PhOC_6H_4(C_4H_9)$ -- p-phenoxy-t-butylbenzene

$PhOC_6H_4(C_4H_8Cl)$ -- side-chain chlorination product

$PhOC_6H_3Cl(C_4H_9)$ -- nuclear chlorination products

Run	Compound	Mmoles initial	Mmoles final	% rx.	Side-chain nuclear
1	$PhOC_6H_4(C_4H_9)$	2.04	1.57	23.0	
	$PhOC_6H_4(C_4H_8Cl)$[a]	0	0.305		
	$PhOC_6H_3Cl(C_4H_9)$	0	0;177		1.72
2	$PhOC_6H_4(C_4H_9)$	2.04	1.57	23.2	
	$PhOC_6H_4(C_4H_8Cl)$	0	0;323		
	$PhOC_6H_3Cl(C_4H_9)$	0	0.207		1.56
3	$PhOC_6H_4(C_4H_9)$	2.04	1.56	23.6	
	$PhOC_6H_4(C_4H_8Cl)$	0	0;305		
	$PhOC_6H_3Cl)C_4H_9)$	0	0.174		1.75
4	$PhOC_6H_4(C_4H_9)$	2.04	1.54	24.3	
	$PhOC_6H_4(C_4H_8Cl)$	0	0.280		
	$PhOC_6H_3Cl(C_4H_9)$	0	0.147		1.90

Average   1.73 ± 0.0925

% Alkyl Chlorination   63.3$_7$

a) Based on the assumption that only the last peak eluted on the
chromatograph corresponded to side-chain chlorination.

Table 15. Product study of the chlorination of p-chloro-t-butylben-
zene by sulfuryl chloride.

Conditions: 5 hours at 70°C

Mmoles SO$_2$Cl$_2$: 2.03

Mmoles C$_6$H$_5$Cl: 4.13

Mmoles peroxide: 0.02

ClC$_6$H$_4$(C$_4$H$_9$) -- p-chloro-t-butylbenzene

ClC$_6$H$_4$(C$_4$H$_8$Cl) -- side-chain chlorination product

Cl$_2$C$_6$H$_3$(C$_4$H$_9$) -- nuclear chlorination products

Run	Compound	Mmoles initial	Mmoles final	% rx.	Side-chain nuclear
1	ClC$_6$H$_4$(C$_4$H$_9$)	6.22	4.14	33.4	
	ClC$_6$H$_4$(C$_4$H$_8$Cl)	0	2.1		
	Cl$_2$C$_6$H$_3$(C$_4$H$_9$)	0	negligible		v. large
2	ClC$_6$H$_4$(C$_4$H$_9$)	6.22	4.18	32.8	
	ClC$_6$H$_4$(C$_4$H$_8$Cl)	0	2.0		
	Cl$_2$C$_6$H$_3$(C$_4$H$_9$)	0	negligible		v. large
3	ClC$_6$H$_4$(C$_4$H$_9$)	6.22	4.25	31.7	
	ClC$_6$H$_4$(C$_4$H$_8$Cl)	0	2.0		
	Cl$_2$C$_6$H$_3$(C$_4$H$_9$)	0	negligible		v. large
4	ClC$_6$H$_4$(C$_4$H$_9$)	6.22	4.28	31.2	
	ClC$_6$H$_4$(C$_4$H$_8$Cl)	0	2.0		
	Cl$_2$C$_6$H$_3$(C$_4$H$_9$)	0	negligible		v. large
5	ClC$_6$H$_4$(C$_4$H$_9$)	6.22	4.14	33.4	
	ClC$_6$H$_4$(C$_4$H$_8$Cl)	0	2.1		
	Cl$_2$C$_6$H$_3$(C$_4$H$_9$)	0	negligible		v. large
Average					v. large
% Alkyl Chlorination					100.0

Table 16. Product study of the chlorination of $\underline{m}$-phenoxy-$\underline{t}$-butylbenzene by sulfuryl chloride.

Conditions: 12 hours at 70°C.

Mmoles SO_2Cl_2: 1.66

Mmoles C_6H_5Cl: 4.03

Mmoles peroxide: 0.02

$PhOC_6H_4(C_4H_9)$ -- $\underline{m}$-phenoxy-$\underline{t}$-butylbenzene

$PhOC_6H_4(C_4H_8Cl)$ -- side-chain chlorination product

$PhOC_6H_3Cl(C_4H_9)$ -- nuclear chlorination products

Run	Compound	Mmoles initial	Mmoles final	% rx.	Side-chain / nuclear
1	$PhOC_6H_4(C_4H_9)$	4.05	3.37	16.7	
	$PhOC_6H_4(C_4H_8Cl)$	0	0.434		
	$PhOC_6H_3Cl(C_4H_9)$	0	0.107		4.04
2	$PhOC_6H_4(C_4H_9)$	4.05	3.77	7.1	
	$PhOC_6H_4(C_4H_8Cl)$	0	0.405		
	$PhOC_6H_3Cl(C_4H_9)$	0	0.108		3.75
3	$PhOC_6H_4(C_4H_9)$	4.05	3.50	13.6	
	$PhOC_6H_4(C_4H_8Cl)$	0	0.456		
	$PhOC_6H_3Cl(C_4H_9)$	0	0.113		4.04
4	$PhOC_6H_4(C_4H_9)$	4.05	3.47	14.5	
	$PhOC_6H_4(C_4H_8Cl)$	0	0.487		
	$PhOC_6H_3Cl(C_4H_9)$	0	0.132		3.69
5	$PhOC_6H_4(C_4H_9)$	4.05	3.39	16.3	
	$PhOC_6H_4(C_4H_8Cl)$	0	0.436		
	$PhOC_6H_5Cl(C_4H_9)$	0	0.0957		4.56

Average 4.02 ± 0.236

% Alkyl Chlorination 80.0_6

APPENDIX II
KINETIC STUDIES

Table 17. Relative rates of disappearance of p-nitro-t-butylbenzene to t-butylbenzene.

Conditions: 1-1/2 hours at 70°C.

Mmoles SO_2Cl_2: 6.06

Mmoles C_6H_5Cl: 1.93

Mmoles peroxide: 0.02

$C_6H_5(C_4H_9)$ -- t-butylbenzene

$NO_2C_6H_4(C_4H_9)$ -- p-nitro-t-butylbenzene

Run	Compound	Mmoles initial	Mmoles final	% rx.	$\left[\dfrac{k_{p\text{-}NO_2}}{k_H}\right]_{dis}$
1	$C_6H_5(C_4H_9)$	2.99	1.64	45.0	
	$NO_2C_6H_4(C_4H_9)$	1.99	1.46	26.7	0.519
2	$C_6H_5(C_4H_9)$	2.99	1.53	48.9	
	$NO_2C_6H_4(C_4H_9)$	1.99	1.46	26.5	0.461
3	$C_6H_5(C_4H_9)$	2.99	1.28	57.2	
	$NO_2C_6H_4(C_4H_9)$	1.99	1.39	30.4	0.427
4	$C_6H_5(C_4H_9)$	2.99	1.39	53.4	
	$NO_2C_6H_4(C_4H_9)$	1.99	1.36	31.7	0.497
5	$C_6H_5(C_4H_9)$	2.92	1.71	41.4	
	$NO_2C_6H_4(C_4H_9)$	2.02	1.50	25.6	0.553
6	$C_6H_5(C_4H_9)$	2.92	1.931	33.9	
	$NO_2C_6H_4(C_4H_9)$	2.02	1.688	16.4	0.435

Average $\left[\dfrac{k_{p\text{-}NO_2}}{k_H}\right]_{dis}$ = 0.482 ± 0.041

Table 18. Relative rates of disappearance of $\underline{m}$-nitro-$\underline{t}$-butylbenzene to $\underline{t}$-butylbenzene.

Conditions: 4 hours at 70°C.

Mmoles SO_2Cl_2: 7.64

Mmoles C_6H_5Cl: 2.99

Mmoles peroxide: 0.02

$C_6H_5(C_4H_9)$ -- $\underline{t}$-butylbenzene

$NO_2C_6H_4(C_4H_9)$ -- $\underline{m}$-nitro-$\underline{t}$-butylbenzene

Run	Compound	Mmoles initial	Mmoles final	% rx.	$\left[\dfrac{k_{\underline{m}-NO_2}}{k_H}\right]_{dis}$
1	$C_6H_5(C_4H_9)$	3.09	0.700	77.3	
	$NO_2C_6H_4(C_4H_9)$	2.12	1.58	25.3	0.196
2	$C_6H_5(C_4H_9)$	3.09	0.685	77.8	
	$NO_2C_6H_4(C_4H_9)$	2.12	1.53	28.0	0.203
3	$C_6H_5(C_4H_9)$	3.09	0.771	75.0	
	$NO_2C_6H_4(C_4H_9)$	2.12	1.49	29.8	0.255
4	$C_6H_5(C_4H_9)$	3.09	1.63	74.0	
	$NO_2C_6H_4(C_4H_9)$	2.12	0.804	22.9	0.193

Average $\left[\dfrac{k_{\underline{m}-NO_2}}{k_H}\right]_{dis}$ = 0.212 ± 0.0217

Table 19. Relative rates of disappearance of p-di-t-butylbenzene to t-butylbenzene.

Conditions: 10 minutes at 70°C.

Mmoles SO_2Cl_2: 5.55

Mmoles C_6H_5Cl: 2.56

Mmoles peroxide: 0.02

$C_6H_5(C_4H_9)$ -- t-butylbenzene

$C_6H_4(C_4H_9)_2$ -- p-di-t-butylbenzene

Run	Compound	Mmoles initial	Mmoles final	% rx.	$\left[\dfrac{k_{p-di}}{k_H}\right]_{dis}$
1	$C_6H_5(C_4H_9)$	2.48	1.72	30.5	
	$C_6H_4(C_4H_9)_2$	2.45	1.16	52.5	2.08
2	$C_6H_5(C_4H_9)$	2.48	1.46	41.1	
	$C_6H_4(C_4H_9)_2$	2.45	0.785	67.9	2.15
3	$C_6H_5(C_4H_9)$	2.48	1.39	44.0	
	$C_6H_4(C_4H_9)_2$	2.45	0.700	71.4	2.16
4	$C_6H_5(C_4H_9)$	2.48	1.54	37.7	
	$C_6H_4(C_4H_9)_2$	2.45	0.853	65.2	2.23
5	$C_6H_5(C_4H_9)$	2.48	1.78	28.0	
	$C_6H_4(C_4H_9)_2$	2.45	0.967	60.5	2.07

Average $\left[k_{p-di}/k_H\right]_{dis}$ = 2.14 ± 0.05

Average $\left[\dfrac{k_{p-di}}{k_H}\right]_{dis}$ Corrected statistically = 1.07 ± 0.025

Table 20. Relative rates of disappearance of p-cyano-t-butyl-
benzene to t-butylbenzene.

Conditions: 1/6 hour at $70^{\circ}C$.

Mmoles SO_2Cl_2: 5.45

Mmoles C_6H_5Cl: 2.54

Mmoles peroxide: 0.02

$C_6H_5(C_4H_9)$ -- t-butylbenzene

$CNC_6H_4(C_4H_9)$ -- p-cyano-t-butylbenzene

Run	Compound	Mmoles initial	Mmoles final	% rx.	$\left[\dfrac{k_{p\text{-}CN}}{k_H}\right]_{dis}$
1	$C_6H_5(C_4H_9)$	2.48	0.930	62.5	
	$CNC_6H_4(C_4H_9)$	2.52	1.57	37.6	0.461
2	$C_6H_5(C_4H_9)$	2.48	0.870	64.9	
	$CNC_6H_4(C_4H_9)$	2.52	1.48	41.1	0.505
3	$C_6H_5(C_4H_9)$	2.48	1.05	57.7	
	$CNC_6H_4(C_4H_9)$	2.52	1.64	35.0	0.502
4	$C_6H_5(C_4H_9)$	2.48	0.951	61.7	
	$CNC_6H_4(C_4H_9)$	2.52	1.50	40.3	0.539
5	$C_6H_5(C_4H_9)$	2.48	1.11	55.4	
	$CNC_6H_4(C_4H_9)$	2.52	1.68	33.2	0.499

Average $\left[\dfrac{k_{p\text{-}CN}}{k_H}\right]_{dis}$ = 0.501 ± 0.017

Table 21. Relative rates of disappearance of phenyl p-t-butylbenzoate to t-butylbenzene.

Conditions: 1/4 hour at 70°C

Mmoles SO_2Cl_2: 4.95

Mmoles C_6H_5Cl: 2.15

Mmoles peroxide: 0.02

$C_6H_5(C_4H_9)$ -- t-butylbenzene

$PhOOC_6H_4(C_4H_9)$ -- phenyl p-t-butylbenzoate

Run	Compound	Mmoles initial	Mmoles final	% rx.	$\left[\dfrac{k_{p-COOPh}}{k_H}\right]_{dis}$
1	$C_6H_5(C_4H_9)$	2.50	1.15	54.1	
	$p\text{-}C_6H_5OOCC_6H_4(C_4H_9)$	1.48	0.859	41.9	0.699
2	$C_6H_5(C_4H_9)$	2.50	0.919	63.2	
	$p\text{-}C_6H_5OOCC_6H_4(C_4H_9)$	1.48	0.702	52.5	0.746
3	$C_6H_5(C_4H_9)$	2.50	0.800	68.0	
	$p\text{-}C_6H_5OOCC_6H_4(C_4H_9)$	1.48	0.653	55.9	0.645
4	$C_6H_5(C_4H_9)$	2.50	0.916	63.4	
	$p\text{-}C_6H_5OOCC_6H_4(C_4H_9)$	1.48	0.701	52.7	0.813
5	$C_6H_5(C_4H_9)$	2.50	0.900	64.0	
	$p\text{-}C_6H_5OOCC_6H_4(C_4H_9)$	1.48	0.819	44.6	0.578

Average $\left[\dfrac{k_{p-COOPh}}{k_H}\right]_{dis}$ = 0.696 ± 0.068

Table 22. Relative rates of disappearance of p-phenoxy-t-butylbenzene to t-butylbenzene.

Conditions: 1/2 hour at 70°C.

Mmoles SO_2Cl_2: 4.19

Mmoles C_6H_5Cl: 2.62

Mmoles peroxide: 0.02

$C_6H_5(C_4H_9)$ -- t-butylbenzene

$PhOC_6H_4(C_4H_9)$ -- p-phenoxy-t-butylbenzene

Run	Compound	Mmoles initial	Mmoles final	% rx.	$\left[\dfrac{k_{p\text{-}PhO}}{k_H}\right]_{dis}$
1	$C_6H_5(C_4H_9)$	2.11	1.48	30.0	
	$p\text{-}C_6H_5(C_6H_4(C_4H_9)$	1.09	0.719	34.1	1.16
2	$C_6H_5(C_4H_9)$	2.11	1.15	45.4	
	$p\text{-}C_6H_5OC_6H_4(C_4H_9)$	1.09	0.523	51.0	1.21
3	$C_6H_5(C_4H_9)$	2.11	1.20	43.4	
	$p\text{-}C_6H_5OC_6H_4(C_4H_9)$	1.09	0.544	50.1	1.22
4	$C_6H_5(C_4H_9)$	2.11	1.27	39.9	
	$p\text{-}C_6H_5OC_6H_4(C_4H_9)$	1.09	0.566	48.1	1.28
5	$C_6H_5(C_4H_9)$	2.11	1.13	46.4	
	$p\text{-}C_6H_5OC_6H_4(C_4H_9)$	1.09	0.500	54.1	1.24

$$\text{Average}\left[\frac{k_{p\text{-}PhO}}{k_H}\right]_{dis} = 1.22 \pm 0.030$$

Table 23. Relative rates of disappearance of m-phenoxy-t-butyl-benzene to t-butylbenzene.

Conditions: 1-1/2 hours at 70°C.

Mmoles SO_2Cl_2: 4.17

Mmoles C_6H_5Cl: 2.06

Mmoles peroxide: 0.02

$C_6H_5(C_4H_9)$ -- t-butylbenzene

$C_6H_5OC_6H_4(C_4H_9)$ -- m-phenoxy-t-butylbenzene

Run	Compound	Mmoles initial	Mmoles final	% rx.	$\left[\dfrac{k_{m-PhO}}{k_H}\right]_{dis}$
1	$C_6H_5(C_4H_9)$	2.00	1.46	26.9	
	$C_6H_5OC_6H_4(C_4H_9)$	1.06	0.504	52.5	2.38
2	$C_6H_5(C_4H_9)$	2.00	1.26	37.1	
	$C_6H_5OC_6H_4(C_4H_9)$	1.06	0.358	66.2	2.35
3	$C_6H_5(C_4H_9)$	2.00	1.19	40.6	
	$C_6H_5OC_6H_4(C_4H_9)$	1.06	0.390	63.2	1.92
4	$C_6H_5(C_4H_9)$	2.00	1.26	36.9	
	$C_6H_5OC_6H_4(C_4H_9)$	1.06	0.247	76.7	3.17
5*	$C_6H_5(C_4H_9)$	2.00	1.41	29.5	
	$C_6H_5OC_6H_4(C_4H_9)$	1.04	0.419	59.7	2.58
6*	$C_6H_5(C_4H_9)$	2.00	1.47	36.6	
	$C_6H_5OC_6H_4(C_4H_9)$	1.04	0.386	62.9	3.18
7*	$C_6H_5(C_4H_9)$	2.00	1.30	35.2	
	$C_6H_5OC_6H_4(C_4H_9)$	1.04	0.542	47.9	2.55

Table 23. continued

Run	Compound	Mmoles initial	Mmoles final	% rx.	$\left[\dfrac{k_{m-PhO}}{k_H}\right]_{dis}$
8*	$C_6H_5(C_4H_9)$	2.00	1.30	35.2	
	$C_6H_5OC_6H_4(C_4H_9)$	1.04	0.542	47.9	2.55

* Runs 5-8 heated for 1 hour at 70°C. Mmoles SO_2Cl_2: 4.22;
Mmoles C_6H_5Cl: 2.01.

Average $\left[\dfrac{k_{m-PhO}}{k_H}\right]_{dis}$ = 2.50 ± 0.387

Table 24. Relative rates of disappearance of p-chloro-t-butylbenzene to p-cyano-t-butylbenzene.

Conditions: 1-1/2 hours at 70°C.

Mmoles SO_2Cl_2: 5.26

Mmoles C_6H_5Cl: 1.98

Mmoles peroxide: 0.02

$CNC_6H_4(C_4H_9)$ -- p-cyano-t-butylbenzene

$ClC_6H_4(C_4H_9)$ -- p-chloro-t-butylbenzene

Run	Compound	Mmoles initial	Mmoles final	% rx.	$\left[\dfrac{k_{Cl}}{k_{CN}}\right]$ dis
1	$CNC_6H_4(C_4H_9)$	3.19	0.913	7.14	
	$ClC_6H_4(C_4H_9)$	1.51	0.247	83.6	1.45
2	$CNC_6H_4(C_4H_9)$	3.19	1.03	67.6	
	$ClC_6H_4(C_4H_9)$	1.51	0.306	79.7	1.42
3	$CNC_6H_4(C_4H_9)$	3.19	0.846	73.5	
	$ClC_6H_4(C_4H_9)$	1.51	0.222	85.3	1.44
4	$CNC_6H_4(C_4H_9)$	3.19	1.01	68.5	
	$ClC_6H_4(C_4H_9)$	1.51	0.309	79.6	1.38

Average $\left[\dfrac{k_{Cl}}{k_{CN}}\right]_{dis} = 1.42 \pm 0.02$

$\left[\dfrac{k_{Cl}}{k_{H}}\right]_{dis} = 0.711 \pm 0.049$ using Eq. 15.