#### AN ABSTRACT OF THE THESIS OF

WILLIAM DIETZ TOTHEROW		for the	MASTER OF SCIENCE	
	(Name)			(Degree)
in	CHEMISTRY	prese	ented on	July 18, 1969
	(Major)			(Date)
Title:	STERIC EFFECTS	5 IN FREE	-RADIC	AL HYDROGEN ATOM
	ABSTRACTION RI	EACTIONS	5	
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A study of the relative rates of benzylic hydrogen abstractions from a series of <u>meta</u> and <u>para</u> substituted neopentylbenzenes by the bromine radical and trichloromethyl radical at  $70^{\circ}$ C has been carried out. Application of the Hammett equation yields  $\rho$  values of -0.75 for the bromine atom and -0.94 for the trichloromethyl radical. Steric hinderance in proceeding to the transition state is offered as a possible explanation for the large substituent dependence exhibited by the trichloromethyl radical. Steric Effects in Free-Radical Hydrogen Atom Abstraction Reactions

by

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A THESIS

submitted to

Oregon State University

in partial fulfillment of the requirements for the degree of

Master of Science

June 1970

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1969 18, Date thesis is presented Typed by Donna L. Olson for \_\_\_\_ William Dietz Totherow

To My Mother

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No joy in nature is so sublimely affecting as the joy of a mother at the good fortune of her child. --Richter

#### ACKNOWLEDGEMENTS

The author sincerely wishes to thank Dr. Gerald Jay Gleicher for his suggestion of this problem, and for his help, guidance and understanding throughout the course of this work. Thanks also to Mr. Victor R. Koch and Mr. Jerry D. Unruh for their operation of the nmr. And a very special thanks to my wife, Barbara, for her patience, understanding and moral support throughout the past two years. Lastly, sincere appreciation to my wife and mother who spent many hours at the tedious task of typing this manuscript.

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#### STERIC EFFECTS IN FREE-RADICAL HYDROGEN ATOM ABSTRACTION REACTIONS

#### INTRODUCTION

Steric effects have been shown to be operative in many freeradical addition reactions. For example, Osborn and co-workers have examined the steric control in the free-radical addition of carbon tetrachloride to norbornenes (34). They found that the addition of carbon tetrachloride to norbornene itself (I) yielded the trans (II) and cis (III) isomers in the ratio of 18.2:1.



It has been shown previously that with large attacking groups such as  $^{\circ}$  CCl<sub>3</sub>, initial attack occurs solely from the less hindered <u>exo</u> side (51). The direction of subsequent chlorine atom transfer is explained utilizing transition state (IV).



Transfer from the <u>exo</u> side (path A), while not completely prohibited, involves a great deal of non-bonded interaction with the trichloromethyl group already present. Transfer from the <u>endo</u> side (path B) avoids such steric interference. Similar results were obtained utilizing substituted norbornenes. When Lebel utilized HBr in the free-radical addition to the norbornene system, he found almost no evidence of steric influence on product formation (51). This result is attributed to the smaller size of the radical source, HBr, compared with the much larger CCl<sub>4</sub> species.

Martin and Koster have examined the free-radical addition of bromotrichloromethane and carbon tetrachloride to benzonorbornadiene (27). In both cases, they found initial <u>exo</u> attack by the trichloromethyl radical followed by chain transfer of the chlorine or bromine radical exclusively from the <u>endo</u> side. These results are completely analogous to those for the norbornadiene system already mentioned. It has also been demonstrated that terminal olefins undergo free-radical addition faster and give greater yields than do internal olefins (37). Again a steric explanation has been offered.

Evidence for corresponding steric effects in abstraction processes are less frequently encountered. There have been some suggestions that steric factors may control the course of a free-radical abstraction reaction. For example, although there is ample evidence for suggesting that an active methylene group is more reactive than an active methyl group (7), it has been observed that 2,4,4-trimethyl-1-pentene reacts with N-bromosuccinimide to give 2-bromomethyl-4,4-dimethyl-1-pentene (52). This product arises from bromination at the methyl position rather than at the more sterically hindered methylene site.

Meislich and co-workers have undertaken a study to determine the steric requirements of free-radical hydrogen atom abstraction using N-bromosuccinimide (29). Utilizing 1,1,1,2-tetraphenylethane and NBS, they observed the following reaction:

Product VII could have arisen only from a phenyl migration, which heretofore had not been observed in free-radical halogenation in solution (2). A benzylic radical would normally abstract a bromine atom long before a phenyl migration could occur. However, in the halogenation of VI, the bulky trityl group adjacent to the free-radical greatly retards the bromination step, so that phenyl migration

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becomes competitive. It must also be pointed out that the phenyl migration also affords a more stable free-radical. It was felt that the combination of these two effects allowed the migration to occur.

Details of hydrogen atom abstraction from alkanes have been investigated by Minisci and co-workers (4). Utilizing various dialkylamine radical cations in their reactions with methyl decanoate and n-heptane, they found that the predominant site of hydrogen abstraction was at the methylene position adjacent to the terminal methyl group. The general reaction scheme is as follows:

The isomer distributions for the two compounds described utilizing N-chlorodimethylamine as the radical source were:

 $CH_{3} - CH_{2} - CO_{2}CH_{3}$   $1.1 \quad 44.4 \quad 21.6 \quad 17.5 \quad 10.7 \quad 4.1 \quad 0.5 \quad --- \quad -- CH_{3} - CH_{2} - CH_{2} - CH_{2} - CH_{2} - CH_{2} - CH_{3}$   $1.1 \quad 55.6 \quad 29.0 \quad 14.3$ 

By increasing the effective size of the R groups attached to the dialkylamine radical cation, it was observed that reaction at the methyl position next to the terminal methyl group became increasingly more favored. The isomer distribution employing N-chlorodi-isobutylamine as the radical source is as follows:

$$CH_3 - CH_2 - CO_2CH_3$$
  
1.4 57.7 19.1 13.3 6.7 1.7 trace --- ---  
 $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$   
1.3 64.4 22.9 11.3

They concluded that the methylene position next to the methyl group was least sterically hindered, and, therefore, least affected by a large incoming radical, than were the other methylene positions in the molecule. These same investigators have employed several other very analogous systems to further support this hypothesis (30, 31, 32, 33).

Many of the principle studies involving hydrogen atom abstractions have utilized aralkyl systems. The effects of ring substitution on hydrogen abstraction from substituted toluenes using chlorine atoms (48, 41), bromine atoms (36, 49), and the trichloromethyl radical (17), have been studied extensively. In these cases the bromine atom displayed a slightly greater selectivity than the trichloromethyl radical (39, 40, 42). Hydrocarbon systems other than toluene have been examined with reference to abstraction of labile hydrogens. Martin and Gleicher utilized both the trichloromethyl radical and bromine atom in abstractions of the very labile hydrogen from a series of substituted allylbenzenes (26). Huang and Lee have examined hydrogen atom abstractions from a series of substituted ethyl benzenes (18). Employing the bromine radical they obtained a rho value of -0.69 at 80°C correlating with  $\sigma^+$ . They concluded that this polar effect was to be considered a normal substituent dependence at a secondary benzylic position when the electron donating effect of the methyl group is taken into account. In a subsequent study employing the trichloromethyl radical with the same series of substituted ethyl benzenes, they found a rho value of -0.53 correlating with  $\sigma^+$  (23). There again appears to be a slightly greater selectivity exhibited by the bromine radical than by the trichloromethyl radical in both these investigations.

In an analogous study, Gleicher has investigated hydrogen atom abstractions from a series of substituted cumenes to evaluate the polar effect at a tertiary benzylic position (11). Using N-bromosuccinimide as a source of bromine atoms, a rho value of -0.38 at 70°C correlating with  $\sigma$  is obtained. This value is not unexpected. However, when the trichloromethyl radical was used to abstract hydrogens, a rho value of -0.69 correlating with  $\sigma^+$  was found. This large and unexpected selectivity was attributed to steric effects associated with large trichloromethyl radical, not present with the bromine atom. It was felt that the large substituent dependence, along with the correlation with  $\sigma^+$ , indicated a great deal of bond breaking in the transition state. That is, since the incoming trichloromethyl radical is very large, it will be held further from the reaction center in the transition state than will the smaller bromine atom, and, therefore, there will be a larger substituent dependence than for an unhindered system. The correlation of  $\sigma^+$  with the degree of bond breaking in the transition state has already been demonstrated by Howard and Ingold for electrophilic radicals (15).

Huang and Lee have also examined hydrogen atom abstraction from benzylic positions attached to oxygen (19). Employing a series of a -substituted benzyl methyl ethers, they attempted a correlation of the relative selectivities of the trichloromethyl radical and the bromine atom. The general reaction scheme was shown to be: PhCHR·OCH<sub>3</sub> + Br· (or ·CCl<sub>3</sub>)  $\longrightarrow$  PhCR·OCH<sub>3</sub> + HBR (or CHCl<sub>3</sub>) PhCR·OCH<sub>3</sub> + Br<sub>2</sub> (or BrCCl<sub>3</sub>)  $\longrightarrow$  PhCRBr·OCH<sub>3</sub> + Br· (or ·CCl<sub>3</sub>) PhCRBr·OCH<sub>3</sub> + Br, (or ·CCl<sub>3</sub>)  $\longrightarrow$  PhCRBr·OCH<sub>3</sub> + Br· (or ·CCl<sub>3</sub>) PhCRBr·OCH<sub>3</sub> = Hr· (or ·CCl<sub>3</sub>)  $\longrightarrow$  PhCRBr·OCH<sub>3</sub> + Br· (or ·CCl<sub>3</sub>)

For the series of compounds employed, the relative selectivities for the two radicals were nearly identical even though the rho values for each system varied from about -0.12 to -0.38. That is, the rate of reaction was observed to be independent of any steric interference due to the size of the incoming radical.

An effort to examine the significance of possible steric effects in hydrogen atom abstractions from benzylic positions, suggested by the results of the cumene investigation, was deemed desirable. It was decided that a system should be constructed which would contain a maximum amount of steric bulk at the reaction site, and yet retain the same general electronic characteristics of the cumenes. Such a system would be a series of substituted 2,2,4,4-tetramethyl-3-phenylpentanes. This would be analogous to the cumene system, with the two methyl groups replaced by the very much larger tertiary butyl group. Several attempts to synthesize this molecule failed to produce the desired end product. However, a practical route was found to a series of substituted neopentylbenzenes. This is analogous to the ethylbenzene series, with the methyl group replaced by a tertiary butyl group. Although this system was not as hindered as that previously described, it can provide a very large amount of steric bulk close to the reaction site, coupled with a ready accessibility.

It has been suggested by several investigators that steric effects should reduce rather than increase the substituent dependence of free-radical hydrogen atom abstraction reactions. A result such as this would suggest just the opposite effect proposed by both the cumene series and the present study. For example, Howard and Ingold have devised a sterically hindered system in an effort to evaluate the steric requirements for free-radical hydrogen atom abstractions (16, 17). Utilizing the styrylperoxy radical in reactions with <u>meta</u>- and <u>para</u>-substituted 2,6-dialkylphenols, they obtained the results in Table I.

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The decrease in rho as the ortho-alkyl substituents increase in size is the complete reverse of that seen with the cumene series. These workers rationalize their results in terms of steric factors relating to the following three resonance forms of the transition state, suggested by Russell for this type of reaction (39).

$$(XC_{6}H_{4}O: H \cdot OOR \longleftrightarrow XC_{6}H_{4}O \cdot H: OOR \longleftrightarrow XC_{6}H_{4}O \cdot H: OOR)$$

$$I \qquad II \qquad III$$

For the unhindered system, II is at least a moderate contributor to the transition state, and the reaction exhibits a large substituent dependence as expected. However, as the large alkyl groups are introduced, the peroxy radical is prevented from approaching the phenolic hydrogen as closely as it approaches the hydrogen in the non-hindered phenol. Therefore, the transition state tends to resemble the products, structure III becomes more important and rho decreases in value.

However, several assumptions are made in this approach which may not be completely valid. First, in an effort to take into account the electron donating effects of the ortho-alkyl substituents, the rate of reaction is plotted against  $\Sigma \sigma^+$  rather than  $\sigma^+$  in obtaining the rho values. Dippy and co-workers have shown this procedure to be invalid for analogous systems (6). Secondly, the plotting of  $\Sigma \sigma^+$  rather than  $\sigma^+$  in no way affects the final calculated rho value, it merely shifts each point by a common factor. Thus, the inductive effects of the alkyl substituents are in no way taken into account.

A more likely explanation for the observed decrease in rho may be offered based upon the electron donating effects of the orthoalkyl groups. It would be expected that a smaller substituent dependence should be demonstrated by a series of molecules which already possess two other electron donating substituents.

The series of substituted neopentylbenzenes, on the other hand, requires none of the assumptions mentioned above. If steric factors are involved in free-radical hydrogen atom abstractions, as suggested by the cumene series, then the small bromine atom should produce a rho value very similar to that found by Lee for the ethylbenzene series (18). However, hydrogen atom abstraction by the much larger trichloromethyl radical at such a sterically hindered position should exhibit a much greater substituent dependence, and therefore a larger rho value, as was noted by Gleicher in the cumene series (11).

#### RESULTS

#### Synthesis of m- and p- Substituted Neopentylbenzenes

One general synthetic route was utilized in the preparation of all neopentylbenzenes with the exception of the <u>p</u>-nitro derivative. This general route is outlined as follows:



The Grignard reagent of the substituted bromobenzene was added in an inverse manner to pivoyl chloride at  $-10^{\circ}$ C, and the resulting carbonyl compound reduced utilizing the Huang-Minlon modification of the Wolf-Kishner method (46). The <u>p</u>-nitroneopentylbenzene was prepared <u>via</u> direct nitration of the parent compound (43). Details regarding the synthesis and purification of the individual compounds may be found in the experimental section.

#### Products in the Reaction of Neopentylbenzene and Bromotrichloromethane

Solutions composed of neopentylbenzene and

bromotrichloromethane were irradiated with ultra-violet light at a temperature of  $70^{\circ}$ C. Gas-liquid chromatography revealed only one product having a retention time greater than the unreacted material.

A detailed product study showed the product formed in the reaction was a -bromoneopentylbenzene. The product study also showed a molar balance within experimental error between the number of moles of neopentylbenzene consumed and the number of moles of a -bromoneopentylbenzene produced.

#### Products in the Reaction of Neopentylbenzene and N-Bromosuccinimide

Solutions composed of neopentylbenzene and N-bromosuccinimide in carbon tetrachloride were irradiated with ultra-violet light at a temperature of  $70^{\circ}$ C. Gas-liquid chromatography revealed the formation of only one product which had a retention time greater than that for the unreacted material.

A detailed product study showed this product to be a -bromoneopentylbenzene. The product study also showed a molar balance within experimental error between moles of neopentylbenzene consumed and a -bromoneopentylbenzene produced. A molar balance was also found between the moles of N-bromosuccinimide consumed, the number of moles of succinimide produced, and the number of moles of a -bromoneopentylbenzene produced.

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#### Products in the Reaction of Eight <u>m</u>- and <u>p</u>- Substituted <u>Neopentylbenzenes</u> with Bromotrichloromethane and N-Bromosuccinimide

Eight <u>m</u>- and <u>p</u>- substituted neopentylbenzenes were reacted in the manner described above. Gas-liquid chromatography revealed the formation of only one product from each of these compounds with the exception of <u>m</u>- and <u>p</u>- methylneopentylbenzenes. The reaction of these two compounds each yielded two products.

For the reaction of <u>p</u>-chloroneopentylbenzene with both bromotrichloromethane and N-bromosuccinimide, detailed product studies were performed. Analysis showed the only product formed in both reactions was a -bromo-<u>p</u>-chloroneopentylbenzene. A material balance within experimental error was found between reactants and products as previously indicated for the unsubstituted compound.

#### Reaction of <u>m</u>- and <u>p</u>- Methylneopentylbenzene

As indicated above, the <u>m</u>- and <u>p</u>- methyl substituted neopentylbenzenes gave rise to two products, as revealed by gas-liquid chromatography. The two products had very nearly identical retention times, and were assumed to be isomeric bromides formed in reaction at the benzylic positions of the two alkyl groups. As the products had such similar retention times, it was not deemed feasible to attempt a chromatographic separation. In an effort to obtain the relative amount of reaction at the secondary benzylic position, competition reactions were carried out between the parent hydrocarbon and toluene with both bromotrichloromethane and N-bromosuccinimide. It was assumed that the methyl position on toluene would be analogous to the methyl positions on the substituted neopentylbenzenes. From the relative rates of disappearance of the two compounds, the relative amount of reaction at the neopentyl position was calculated. The results of these studies are shown in Table 2.

Table 2. Relative rates of disappearance of neopentylbenzene and toluene with N-bromosuccinimide and bromotrichloromethane.

Radical	$\begin{bmatrix} k_{H} \\ k_{CH_{3}} \end{bmatrix} dis$	% rxn. at neopentyl position
• CCI <sub>3</sub>	0.27 ± 0.03	21.3 <u>+</u> 1.3
• B r	$0.46 \pm 0.02$	31.4 ± 0.8

To further substantiate these results, a mixture of the two isomers resulting from reaction of <u>m</u>-methylneopentylbenzene with both bromotrichloromethane and N-bromosuccinimide was collected using gas-liquid chromatography. A proton magnetic resonance spectrum taken of the mixture yielded two peaks indicative of tertiary butyl groups. The smaller of these was shifted about 10 cps downfield from the larger and was attributed to the product arising from bromination of the neopentyl position. This downfield shift is to be expected as a result of deshielding by the adjacent bromine atom. The larger peak is representative of bromination in the other benzylic position. The ratio of these peak areas showed reaction at the secondary benzylic position to be about 22% using N-bromosuccinimide and 19.2% for bromotrichloromethane. These results are in qualitative agreement with the direct experimental method indicated above.

#### Relative Rates of Disappearance of Substituted Neopentylbenzenes in Bromotrichloromethane

Solutions of two neopentylbenzenes and chlorobenzene as the internal standard in an excess of bromotrichloromethane were placed in ampoules containing a nitrogen enriched atmosphere. The materials were in the molar ratios of 1:1:1:25. The ampoules were sealed and placed just below the surface of an oil bath at  $70^{\circ}$ C, and irradiated with ultra-violet light for periods varying from two hours to seven hours. The reactions were terminated when they were from 9% to 90% complete, and analyzed by gas-liquid chromatography. Table 3 contains a summary of the relative rates of disappearance  $\begin{bmatrix} k_x \\ k_H \end{bmatrix}_{dis}$  of the eight substituted neopentylbenzenes.

#### Relative Rates of Disappearance of Substituted Neopentylbenzenes with N-Bromosuccinimide

Solutions of two neopentylbenzenes and chlorobenzene as the internal standard in carbon tetrachloride were placed in ampoules containing a nitrogen enriched atmosphere and N-bromosuccinimide. The materials were in the molar ratio of 1:1:1:1. The ampoules were sealed and placed just below the surface of a 70° oil bath and irradiated with ultra-violet light for periods varying from 25 minutes to 90 minutes. The reactions were terminated when they were from 5% to 80% complete. The solutions were decanted from the solid materials and analyzed by gas-liquid chromatography. Table 3 also contains a summary of the relative rates of disappearance  $\begin{bmatrix} k \\ K \\ H \end{bmatrix}$  of eight substituted neopentylbenzenes.

Table 3. Relative rates of disapperance of <u>m</u>- and <u>p</u>- substituted neopentylbenzenes with bromotrichloromethane and Nbromosuccinimide.

	Bromotrich	loromethane	N-bromosuccinimide		
Substituent	k       k       k       H	number of kinetic runs	$\begin{bmatrix} k \\ x \\ k \\ H \end{bmatrix}$	number of kinetic runs	
p-NO <sub>2</sub> -	$0.12 \pm 0.01$	5	$0.25 \pm 0.01$	4	
m-CF3-	$0.33 \pm 0.01$	5	0.40 + 0.01	4	
m-Cl-	$0.44 \pm 0.03$	5	$0.34 \pm 0.03$	5	
p-Cl-	0.71 + 0.03	5	0,75 + 0,03	5	
<u>-</u> Н-	(1.000)	-	(1.000)	-	
m-CH <sub>3</sub> -	$1.04 \pm 0.01$	5	0.99 + 0.10	4	
p-t-Butyl-	$1.12 \pm 0.02$	5	$1.51 \pm 0.05$	5	
$p - CH_2 - $	$1.96 \pm 0.18$	4	1,29 + 0.08	6	
р-СН <sub>3</sub> О-	3.52 $\frac{1}{2}$ 0.29	7	$3.16 \pm 0.17$	5	

#### DISCUSSION

#### **Product Studies**

The results obtained in analyzing the reaction of m- and psubstituted neopentylbenzenes with both bromotrichloromethane and N-bromosuccinimide indicate that, except for the methyl substituted compounds, the exclusive product is bromination in the a position. This is in agreement with results obtained previously for bromination of neopentylbenzene (43).

The above results are consistent with the free-radical mechanisms proposed by Russell (40, 42) for reaction of the trichloromethyl radical, and Pearson (36) for reaction of the bromine radical in photolytically initiated hydrogen atom abstraction reactions. For reaction with the neopentyl series, one obtains the following radical chain reaction mechanisms:

#### Abstraction by Bromine Atom



initiating



Free-energy considerations indicate that in both cases the first propagation step should be rate determining in the competitive experiments. Also, the relative kinetic results should be independent of the initiating step. Therefore, the relative rates of disapperance of the substituted neopentylbenzenes will correspond to the relative labilities of the C-H bond in the secondary benzylic position. Variations in reaction rates from one attacking radical to another will be the result of a difference in the radical selectivity.

#### Reaction of the Methylneopentylbenzenes

As noted in the result section, the reaction of both the <u>m</u>- and <u>p</u>- methylneopentylbenzenes with either bromotrichloromethane or N-bromosuccinimide yielded two products with nearly identical retention times. These products were attributed to the isomers arising from bromination at either of the two benzylic positions. To determine the relative percentage of reaction at the neopentyl position, the parent compound was reacted competitively with toluene using both radicals. In each case, neopentylbenzene reacted only about one-fourth as rapidly as toluene. Previous results indicate that a alkyl toluenes react faster than toluene itself. The present results are not in agreement with these findings. However, none of the previous investigations employed a very bulky group, such as <u>t</u>-butyl, at the reaction site.

It was noted previously that nuclear magnetic resonance analysis of the mixed product arising from bromination in the two benzylic positions in the methyl compounds indicated a somewhat smaller amount of reaction at the neopentyl position than did direct comparison of the parent compounds. It is felt that there are two possible explanations for this. First, the nmr technique is probably subject to much greater error due to the method of collection using gas-liquid chromatography. It has also been demonstrated that the accuracy of the nmr used in this study was at best  $\pm$  5% while the accuracy of the disc integration method used in the gas-liquid chromatograph studies was well within + 2%. A second explanation may lie in the relative electron donating effects of the neopentyl group and the methyl group. If there is a slightly greater inductive effect associated with the larger neopentyl group than with the smaller methyl group, then a greater amount of reaction would be expected to take place at the primary position of the methylneopentylbenzenes.

### Correlation Using $\sigma$ and $\sigma^+$

Table 5 presents the data derived from the rate studies using both the trichloromethyl and bromine radicals. For each radical, the  $\sigma$  and  $\sigma^+$  parameters were employed to correlate the data and calculate a rho value for the reaction series. The results of these calculations are shown in Table 4. For both radicals, the better correlation was found using the  $\sigma^+$  constants. This is in keeping with most of the previous studies employing free-radical hydrogen atom abstraction from benzylic positions (11, 18, 23).

Radical	Substituent Constant	ρ	Correlation Coefficient	
Br·	σ	$-0.97 \pm 0.04$	-0.942	
Br·	σ +	-0.75 ± 0.03	-0.986	
• CC1 <sub>3</sub>	σ	$-1.24 \pm 0.05$	-0.960	
·CCI <sub>3</sub>	σ +	$-0.94 \pm 0.04$	-0.980	

Table 4. Values for hydrogen abstraction from substituted neopentylbenzenes.

#### The Magnitude of Rho

The rho value derived from the relative rates of hydrogen atom abstraction from the neopentylbenzene series using the bromine radical is -0.75 correlating with  $\sigma^+$ . The results of this study are graphically presented in Figure 1. If the 10<sup>°</sup> difference in reaction temperature is taken into consideration, this result is virtually identical to the -0.69 value found by Lee for the ethylbenzene series reacting with the bromine radical. This result was expected and is in complete agreement with all other data regarding free-radical hydrogen atom abstractions from benzylic positions.

			Reaction with Br•	Reaction with $\cdot CCl_3$
Substituent	σ	σ +	<sup>k</sup> X <sup>k</sup> H	<sup>k</sup> X <sup>k</sup> H
<u>p</u> -NO <sub>2</sub> -	0.778	0.790	0.25 ± 0.01	0.12 ± 0.01
$\underline{m}$ -CF <sub>3</sub> -	0.415	0.520	0.40 ± 0.01	$0.33 \pm 0.01$
<u>m</u> -Cl-	0.373	0.373	$0.34 \pm 0.03$	$0.44 \pm 0.03$
<u>p</u> -Cl-	0.226	0.112	0.75 <u>+</u> 0.03	0.71 <u>+</u> 0.03
Н-	0.000	0.000	1.00	1.00
$\underline{m}$ -CH <sub>3</sub> - <sup>a</sup>	-0.069	-0.069	$0.99 \pm 0.10$	$1.04 \pm 0.01$
<u>p-t-Butyl-</u>	-0.197	-0.250	1.51 <u>+</u> 0.05	$1.12 \pm 0.02$
<u>p</u> -CH <sub>3</sub> - <sup>a</sup>	-0.170	-0.306	1.29 <u>+</u> 0.08	$1.96 \pm 0.18$
<u>р</u> -СН <sub>3</sub> О-	-0.268	-0.764	3.16 ± 0.17	$3.52 \pm 0.29$

Table 5.	Relative rates of reaction of substituted neopentylbenzenes with the bromine and trichloro-
	methyl radicals at 70°C.

<sup>a</sup>Corrected for reaction at all positions.



Figure 1. Relative rates of hydrogen atom abstraction with Br.

However, the results of the reaction with the trichloromethyl radical, shown in Table 5, are not in agreement with most of the previous data. The rho value resulting from abstraction by the trichloromethyl radical is -0.94 correlating with  $\sigma^+$ , as shown in Table 4. This value is nearly twice as great as that found by Lee for the reaction of the trichloromethyl radical with the ethylbenzene series. Figure 2 graphically presents these results. It is felt that this very large substituent dependence exhibited by the trichloromethyl radical is in keeping with a transition state of fairly high energy. The most attractive explanation lies in the consideration of the specific non-bonded interactions between the <u>a</u> -<u>t</u>- butyl group and the trichloromethyl radical. Certainly, the magnitude of difference between this rho value and that obtained for the ethylbenzenes is far too great to be attributed to experimental errors.

As mentioned previously, correlation with  $\sigma^+$  has been correlated with a large amount of bond breaking in the transition state (15). In the case of the neopentyl system, reaction of both the trichloromethyl and bromine radicals correlated better with  $\sigma^+$  than  $\sigma$ . These results might therefore indicate transition states which involve a great deal of bond breaking. However, a second explanation for correlation with  $\sigma^+$  exists. That is, certain substituents have an enhanced ability to stabilize radicals (10). Support for this view can be found in the studies of polarographic reduction of



Figure 2. Relative rates of hydrogen atom abstraction with  $\cdot \text{CCl}_3.$ 

certain benzylic compounds (22, 44). However, even if this second explanation is involved, it in no way detracts from the conclusions reached above. It is the greatly enhanced selectivity of the trichloromethyl radical which is the key factor here. That is, if radical stabilization by certain substituents is operative, it will be identical for reaction with the trichloromethyl and bromine radicals, and will therefore have no effect on the overall results of the study.

#### Electron Donation by <u>t</u>-Butyl

The decrease in the magnitude of rho in proceeding from the toluene series to the ethylbenzene series was attributed to electron donation by the methyl group. As indicated by  $\sigma$  \* values, <u>t</u>-butyl is significantly more electron donating than is methyl (50). Therefore, if electronic effects alone were operative in a free-radical abstraction process, a decrease in the magnitude of rho would be expected in proceeding from ethylbenzene to neopentylbenzene. However, even for the bromine radical, the neopentyl system is somewhat more selective than is the ethylbenzene system. This result may be rationalized in terms of the large <u>t</u>-butyl group. That is, even in the case of the small bromine atom, there is a certain amount of steric hinderance in proceeding to the transition state.

The rho value found using Br. indicates that the steric and electron donating effects of the t-butyl group may be somewhat
compensatory. Therefore, if the inductive effect associated with the  $\underline{t}$ -butyl group could be reduced to that of a methyl group, an increased selectivity of the system would be expected. Thus, it is possible that the rho values derived from the neopentyl system would actually be significantly increased if the extra electron donating properties of the t-butyl group were compensated for.

## The Abstracting Species

The substituent dependence exhibited when N-bromosuccinimide and bromotrichloromethane are reacted in a free-radical process with the substituted neopentylbenzenes yields information as to the possible abstracting species.

The abstracting agent produced from N-bromosuccinimide must either be the bromine atom or succinimidyl radical. If it is, in fact, the latter, a much greater substituent dependence would be expected, since the large attacking radical would be greatly affected by the sterically hindered system. However, because of the magnitude of the rho value, it must be concluded that the abstracting species is the bromine atom.

Conversely, the abstracting species arising from bromotrichloromethane must be either  $\cdot CCl_3$  or Br.. If the bromine atom were involved in the rate determining step of the reaction, then a rho value similar to that found using NBS would be expected. However, the magnitude of the rho value indicates that only  $\cdot \text{CCl}_3$  is involved as the abstracting species.

#### EXPERIMENTAL

All of the substituted neopentylbenzenes synthesized for this study were liquids, the boiling points of which were recorded during distillation procedures for purification. NMR spectra were taken on a Varian A-60 using spectroquality carbon tetrachloride as the solvent and TMS as a reference. The elemental microanalyses reported here were performed by the Mikroanalytisches Laboratorium in Max-Planck - Institut, 433 Mulheim (Ruhr), West Germany. IR spectra were taken on a Beckman IR-8 spectrophotometer as films between sodium chloride discs. All distillations, except the one used for purification used for the p-nitro- compound, were carried out under reduced pressure using a microdistillation apparatus equipped with a 10 cm. vigreaux column. Gas-liquid chromatography analyses were carried out utilizing a Varian Aerograph 202B gas chromatograph equipped with a linear temperature programmer, thermal conductivity detectors and Sargent recorder with disc integration. A 10' x 1/4" column of 5% S.E. 30 on chromosorb G and a  $10' \ge 1/4''$  column of 5% Fluorolube GR 362 on chromosorb W were used in this investigation. Helium gas was used as the eluent.

## Purification of Bromotrichloromethane

Commercial bromotrichloromethane (Matheson Coleman &

Bell) was distilled and collected over the range of  $103.0-103.4^{\circ}C$ . Gas-liquid chromatography showed the presence of a single impurity comprising no more than 0.3% of the mixture, having the same retension time as carbon tetrachloride.

## 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  $131-132^{\circ}C$  was collected.

## Purification of N-Bromosuccinimide

Commercial N-bromosuccinimide (Matheson Coleman & Bell) which melted at 181 - 183 <sup>O</sup>C was employed without further purification.

## Purification of Diethylene Glycol

Commercial diethylene glycol (Matheson Coleman & Bell), boiling range  $128-130^{\circ}$ C at 10 mm. was used without further purification.

## Purification of Hydrazine Hydrate

Commercial hydrazine hydrate (Matheson Coleman & Bell) was

obtained and used without further purification.

## Purification of Carbon Tetrachloride

Reagent grade carbon tetrachloride (Matheson Coleman & Bell) was employed without further purification.

#### Purification of Pivalic Acid

Commercial pivalic acid (Aldrich), which had a melting range of  $35-37^{\circ}C$  was employed without further purification.

## Purification of Substituted Bromobenzenes

The following substituted bromobenzenes were obtained commercially (Colombia Organic) and used without further purification: <u>p</u>-chlorobromobenzene, <u>m</u>-trifluoromethylbromobenzene, <u>p-t</u>-butylbromobenzene, <u>m</u>-chlorobromobenzene, <u>p</u>-methylbromobenzene, <u>p</u>-methoxybromobenzene, <u>m</u>-methylbromobenzene and bromobenzene.

#### Purification of Thionyl Chloride

Commercial thionyl chloride (Matheson Coleman & Bell) was distilled once and the fraction boiling between  $77.5-78^{\circ}C$  collected.

# Preparation of Substituted Neopentylbenzenes

The parent hydrocarbon and all of the substituted compounds

except the p-nitro compound were prepared via the general synthesis which follows. The Grignard reagent of the substituted bromobenzene was prepared by adding the substituted bromobenzene dropwise over one to two hours to about 500 mls. of anhydrous ethyl ether containing a two fold molar excess of magnesium turnings. To prepare the p-methoxy compound, it was necessary to run the reaction in a 1:1 mixture of anhydrous benzene and ethyl ether. This was necessary because the Grignard reagent formed proved to be insoluble in the ether alone. After addition of the substituted bromobenzene was complete, the mixture was refluxed for two hours to insure complete reaction. While the Grignard reagent was refluxing, the acid chloride of pivalic acid was prepared. This was accomplished by adding pivalic acid to a gently refluxing solution of thionyl chloride. The compounds were in a molar ratio of 1:1.5. An infrared heat lamp was employed to maintain the pivalic acid in liquid form, so it could be added using an addition funnel. After the addition of pivalic acid was complete, refluxing was continued until HCl ceased to be literated from the reaction. The pivoyl chloride was then distilled through a 40 cm vigreaux column, and the fraction boiling between 103-105 °C collected. The pivoyl chloride was then placed in a three liter three neck flask containing one liter of anhydrous ethyl ether. The mixture was stirred and cooled to about  $-10^{\circ}$ C using a salt-ice bath. The Grignard reagent, previously prepared, was filtered

through glass wool into an addition funnel. It was then added over a period of about five hours to the solution of pivoyl chloride, which was maintained at about  $-10^{\circ}$ C. throughout the period of addition (41). The pivoyl chloride and Grignard were in a molar ratio of 1.2:1.

When the addition was complete, the reaction was hydrolyzed with 10% hydrochloric acid and the organic layer separated, washed three times with 5% sodium bicarbonate and twice with water. The resulting solution was dried over anhydrous magnesium sulfate.

The resulting compound in each case was the substituted phenyl t-butyl ketone. Each of the ketones was distilled under reduced pressure and reduced to the hydrocarbon via the Huang-Minlon modification of the Wolf-Kishner reduction (46). In this procedure, reagent grade potassium hydroxide was dissolved in about 500 mls. of hot diethylene glycol. When solution was complete, the ketone and hydrazine hydrate were introduced. The ketone, hydrazine hydrate and potassium hydroxide were in the molar ratios of 1:2:3. The mixture was refluxed at about  $100^{\circ}$ C, for one hour, after which, excess hydrazine hydrate and water were distilled off until the temperature of the mixture reached about 190°C. At this point, refluxing was continued for about five hours. The reaction was then cooled, about 500 mls. of water added and the organic layer dissolved in ethyl ether and separated. The ether solution was then washed three times with water and then dried over anhydrous

magnesium sulfate. The resulting solution contained the reduced substituted neopentylbenzene, which was purified <u>via</u> distillation under reduced pressure. The boiling points of the compounds are presented in Table 6 along with the refractive indices of all compounds and the elemental analyses of the previously unreported compounds. All compounds had purities in excess of 99% as shown by gas-liquid chromatography.

#### Preparation of <u>p</u>-Nitroneopentylbenzene

<u>p</u>-Nitroneopentylbenzene was prepared by stirring a mixture of nitric acid, sulfuric acid and neopentylbenzene overnight at  $25^{\circ}C$ , as described by Gurka (13).

#### Preparation of a -Bromoneopentylbenzene

1-Phenyl-2,2-dimethylpropanol was prepared by stirring phenyl <u>t</u>-butyl ketone with one equivalent of lithium aluminium hydride in anhydrous ethyl ether for one hour. The alcohol was then converted to the bromide by treatment with phosphorus tribromide as described by Skell and Hauser (43).

#### The Reaction of Neopentylbenzene with Bromotrichloromethane

A solution consisting of 2.99 grams (20.22 mmoles) of neopentylbenzene and 25.0 grams (126.0 mmoles) of

			23	% Carbon		on	% Hydrogen		% Other	
X	B.P., C		<sup>n</sup> D	Formula	calc.	found	calc.	found	calc.	found
Н	73-73.5	@ 22mm <sup>a</sup>	1.4868 <sup>a</sup>	C <sub>11</sub> H <sub>16</sub>						
P-CH3	66-67	@ 3.3mm	1.4879	с <sub>12</sub> н <sub>18</sub>	88.89	88.85	11.11	11.14		
<u>m</u> -CH <sub>3</sub>	64-65	@ 3.2mm	1.4878	с <sub>12</sub> н <sub>18</sub>	88.89	88.80	11.11	11.00		
₽ <u>-</u> t-C <sub>4</sub> H <sub>9</sub>	45-46	@ 0. 14mm	1.4888	C <sub>15</sub> H <sub>24</sub>	88.23	88.08	11.77	11.68		
<u>р</u> -СН <sub>3</sub> О-	49-50	@ 0.30mm	1.4991	с <sub>12</sub> н <sub>18</sub> 0	80.90	80. 74	10. 12	10. 18		
<u>р</u> -С1-	87-89	@ 9.0mm	1. 5038 <sup>b</sup>	C <sub>11</sub> H <sub>15</sub> Cl						
<u>m</u> -Cl	63.5-65	@ 1.7mm	1.5042	C <sub>11</sub> H <sub>15</sub> Cl	72.33	72.16	8.22	8.23	19.45	19.29
<u>m</u> -CF <sub>3</sub>	55-55.3	@ 3.0mm	1.4391	C <sub>12</sub> H <sub>15</sub> F <sub>3</sub>	66.67	66.51	6.94	6.84	26.99	26.24
P-NO2	94-95	@ 0.43mm <sup>c</sup>	1. 5247	C <sub>11</sub> H <sub>15</sub> NO <sub>2</sub>	<b>-</b>					

Table 6.	Physical properties of n	n- and p-	substituted	neonentvlbenzenes.
		- und P	bubblicuted j	ncopenty to enzenes.

<sup>a</sup>Literature value b. p. 185. 0-186. 5,  $n_D^{20}$  1. 4888 (29). <sup>b</sup>Literature value  $n_D^{26}$  1. 5033 (13). <sup>c</sup>Literature value m. p. 29<sup>°</sup> (13).

bromotrichloromethane was placed in a pyrex flask equipped with a condensor. The flask was then placed just below the surface of an oil bath maintained at  $70 \pm 0.5^{\circ}$ C. The solution was irradiated with a Sylvania 275-W sun lamp for a period of nine hours. At this point, approximately 68% of the neopentylbenzene had reacted, as shown by glc. The chloroform produced in the reaction, along with unreacted bromotrichloromethane were removed under vacuum. The remaining products of the reaction were separated by fractional distillation. The amount of unreacted neopentylbenzene recovered was 0.96 grams (6.52 mmoles). The only other product recovered weighed 2.93 grams and was shown to be 99% pure by glc. This material had a boiling point of 78-80°C. at 2.0 mm, which was identical to the literature value for a -bromoneopentylbenzene (43). Identical infrared spectra and refractive indices also showed this compound to be identical to a known sample of a -bromoneopentylbenzene. The weight of the a -bromoneopentylbenzene produced in the product study corresponds to 12.90 mmoles. The total amount of material recovered from the reaction accounts for 96.0% of theoretical.

<u>Refractive Indices</u>.  $n_D^{23} = 1.5138 \text{ a - bromone opentyl benzene}$ from product study.  $n_D^{23} = 1.5143$  for known sample of a -bromone opentyl benzene.

# The Reaction of Neopentylbenzene with N-Bromosuccinimide

A solution consisting of 3.20 grams (21.60 mmoles) of neopentylbenzene and 1.38 grams (7.76 mmoles) of N-bromosuccinimide in 25 mls. of carbon tetrachloride was reacted for four hours in the manner described above. At this time, all of the N-bromosuccinimide had been converted to succinimide. This point in the reaction was quite obvious, since N-bromosuccinimide, having a density greater than carbon tetrachloride remained near the bottom of the flask, while succinimide, having a density less than carbon tetrachloride floated to the surface. The reaction was merely continued until no more solid remained near the bottom of the vessel. The succinimide, which was filtered off and dried, weighed 0.75 grams (7.56 mmoles) and accounted for 97.4% of the theoretical amount based on N-bromosuccinimide originally present. Fractional distillation of the liquid phase yielded 2.04 grams (13.8 mmoles) of unreacted neopentylbenzene, and 1.61 grams (7.10 mmoles) of a bromoneopentylbenzene, which was identified as in the previous experiment. The overall material balance accounted for 96.7% of the theoretical amount.

# The Reaction of p-Chloroneopentylbenzene with N-Bromosuccinimide

A solution consisting of 3.70 grams (20.22 mmoles) of

p-chloroneopentylbenzene and 1.47 grams (8.26 mmoles) of Nbromosuccinimide in 25 mls. of carbon tetrachloride were reacted for six hours in the manner described above. The succinimide produced, which was filtered off and dried, weighed 0.80 grams (8.07 mmoles). This was 97.7% of the theoretical amount. A previous attempt at fractional distillation of the products of this reaction showed that the material which was presumed to be a -bromo-pchloroneopentylbenzene decomposed at the temperature required for distillation. To avoid this, the compound was converted to the corresponding alcohol by stirring overnight in 200 mls. of a 0.2 M solution of silver nitrate (43). Silver bromide, formed in this procedure, was filtered off, dried and weighed. The amount recovered was 1.33 grams (7.10 mmoles). The alcohol which was formed, 1-(p-chlorophenyl)-2,2-dimethylpropanol, and unreacted p-chloroneopentylbenzene were then separated by fractional distillation. The alcohol recovered weighed 1.59 grams (8.01 mmoles) and the unreacted starting material weighed 2.04 grams (11.14 mmoles). The material balance showed that these products corresponded to 94.7% of the theoretical amount based on  $\underline{p}$ -chloroneopentylbenzene originally present. A material balance was also found between the silver bromide recovered and 1-(p-chlorophenyl)-2,2-dimethylpropanol produced. The silver bromide amounted to 88.6% of the theoretical amount.

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 $1 - (\underline{p} - chlorophenyl) - 2, 2 - dimethylpropanol, a previously unreported compound, was identified. The nmr spectra in carbon tetra$  $chloride showed peaks at 0.80 <math>\delta$ , 2158  $\delta$ , 412 and 7.10  $\delta$  having areas of 9:1:1:4 respectively. The IR spectra showed a broad -OH from 3200 to 3800 cm<sup>-1</sup>, and a strong absorption at about 830 cm<sup>-1</sup>, indicating <u>p</u>-substitution. The boiling point was 70-71.5° at 0.27 mm and  $n_{D}^{23} = 1.5250$ .

<u>Analysis.</u> Calculated for  $C_{11}H_{15}C_{10}$ . C, 66.50; H, 7.56; Cl, 17.88. Found C, 66.50; H, 7.48; Cl. 17.88.

# The Reaction of <u>p</u>-Chloroneopentylbenzene with Bromotrichloromethane

A solution consisting of 3.92 grams (21.41 mmoles) of <u>p</u>chloroneopentylbenzene in 25.0 grams (126.0 mmoles) of bromotrichloromethane were reacted for 11 hours as described previously. The amount of unreacted <u>p</u>-chloroneopentylbenzene recovered was 1.69 grams (9.21 mmoles). The amount of  $1-(\underline{p}-chlorophenyl)-2$ , 2-dimethylpropanol recovered after conversion from the bromide, as described above was 2.19 grams (11.02 mmoles). The products accounted for 94.5% of the theoretical amount. The amount of silver bromide recovered from the conversion of <u>p</u>-chloro-a bromoneopentylbenzene to the corresponding alcohol was 1.86 grams (9.91 mmoles), 89.9% of the theoretical amount.

#### Procedure for Kinetic Runs Using Bromotrichloromethane

Solutions of two neopentylbenzenes, chlorobenzene and bromotrichloromethane were prepared in the approximate molar ratios of 1:1:1:25. Approximately 0.75 ml. of the solution was placed in each of several pyrex ampoules which had been purged with nitrogen. The ampoules were cooled to dry ice-acetone temperature and sealed. One ampoule was reserved for analysis of starting materials; the remainder were placed horizontally just below the surface of a mineral oil constant temperature bath maintained at  $70.0 \pm 0.5^{\circ}$ C. The samples were irradiated with ultra-violet light provided by a Sylvania 275-W sun lamp placed 20 cm. above the surface of the oil. Reaction times varied from two hours to seven hours, by which time 9% to 90% of the neopentylbenzenes had reacted. The ampoules were then cooled and opened. Analysis of the mixtures, both before and after reaction, was carried out via gas-liquid chromatography.

All determinations were run in replicate. The procedure was to have the substituted neopentylbenzene compete directly with neopentylbenzene for the abstracting radical. In the case of the <u>m</u>-trifluoromethyl derivative, it was necessary to determine its relative reactivity to <u>p</u>-chloroneopentylbenzene. The rate constants thereby obtained were converted to the desired form through the expression:

$$\begin{bmatrix} \frac{k}{\underline{m}} - CF_{3} \\ \hline \\ k_{H} \end{bmatrix} dis = \begin{bmatrix} k_{\underline{p}} - C1 \\ \hline \\ k_{H} \end{bmatrix} dis \begin{bmatrix} \frac{k}{\underline{m}} - CF_{3} \\ \hline \\ k_{\underline{p}} - C1 \end{bmatrix} dis$$

#### Procedure for Kinetic Runs Using N-Bromosuccinimide

The procedure was identical to that described above except that the solid N-bromosuccinimide was first introduced into the ampoule, followed by the solution of the two neopentylbenzenes and chlorobenzene dissolved in carbon tetrachloride. The two neopentylbenzenes, chlorobenzene and N-bromosuccinimide were in the approximate molar ratio of 1:1:1:1. The reaction times varied from 25 minutes to 90 minutes and were from 5% to 80% complete when the reactions were terminated.

# Determination of $({}^{k}X/{}^{k}H)$ dis

The ratios of relative rate constants were obtained using the usual competitive procedures (12, 20, 26). The following equation was employed:



where  $\binom{k_X}{k_H}$  dis is the relative rate constant of disappearance of the X-substituted neopentylbenzene to the unsubstituted neopentylbenzene;  $X_0$  and  $H_0$  are the number of mmoles originally present of the X-substituted neopentylbenzene and neopentylbenzene, respectively;  $H_f$  and  $X_f$  are the corresponding terms for the final number of mmoles present. The above ratios may be directly obtained from the chromatographic analysis using the following relationship:



See Appendix, Tables 1-19 for the detailed data on the kinetic studies.

# NMR Study of the Reaction Products of Bromotrichloromethane and <u>m</u>-Methylneopentylbenzene

As indicated in the results section, an attempt was made to determine the relative amount of reaction at the primary and secondary benzylic positions of <u>m</u>-methylneopentylbenzene. Solutions consisting of bromotrichloromethane and <u>m</u>-methylneopentylbenzene in a molar ratio of 25:1 were placed in sealed ampoules and reacted as described previously. The two brominated products which had nearly identical retention times were collected using gas-liquid chromatography and an nmr spectrum taken of the mixture. The nmr showed peaks at 0.88  $\delta$ , 1.05  $\delta$ , 2.43  $\delta$ , 4.35  $\delta$  and 7.10  $\delta$ (broad). The peak at 0.88  $\delta$  corresponded to the <u>t</u>-butyl-group of the <u>m</u>-methylneopentylbenzene brominated in the primary position. The peak at 1.05 corresponds to the <u>t</u>-butyl-group of the compound brominated in the secondary position. This downfield shift of 0.17 cps. is expected as a result of deshielding by the nearby bromine atom. The relative areas underneath the two <u>t</u>-butyl-groups should be indicative of the relative amount of each compound in the mixture. This method indicated that bromination in the secondary position

## <u>NMR Study of the Reaction Products of</u> N-Bromosuccinimide and <u>m</u>-methylneopentylbenzene

This study was carried out as described above except that Nbromosuccinimide was used in place of bromotrichloromethane, and carbon tetrachloride was used as the solvent. N-bromosuccinimide and <u>m</u>-methylneopentylbenzene were in the approximate molar ratio of 1:1. The nmr spectrum indicated reaction at the secondary benzylic position occurred to an extent of 23%.

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APPENDIX

 

 Table 1. Relative rates of disappearance of p-nitroneopentylbenzene and neopentylbenzene in bromotrichloromethane.

Conditions: 7 hrs. at  $70^{\circ}$ C. Mmoles  $C_6H_5Cl$ : 1.93  $NO_2(C_6H_4)C_5H_{11} - p$ -nitroneopentylbenzene  $(C_6H_5)C_5H_{11} - neopentylbenzene$ 

Run	Compound	Mmoles	Mmoles	Mmoles	% rxn.	<sup>k</sup> p-NO <sub>2</sub>
		(initial)	(final)	(used)		k H
1	NO <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.08	1.87	0.21	9.93	0. 130
	$(C_{6}^{H}H_{5})C_{5}^{H}H_{11}$	3.19	1.41	1.78	55,9	
	BrCC1 <sub>3</sub>	26.71	24.53	2.18		
	CHCl <sub>3</sub>	0.00	1.74	1.74		
2	$NO_{2}(C_{6}H_{4})C_{5}H_{11}$	2.08	1.84	0.24	11.3	0.110
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	3.19	1.10	2.09	65.6	
	BrCC1 <sub>3</sub>	26.71	24.25	2.46		
	CHCl <sub>3</sub>	0.00	2.11	2.11		
3	$NO_{2}(C_{6}H_{4})C_{5}H_{11}$	2.08	1.86	0.22	10.6	0. 115
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	3.19	1.22	1.97	61.7	
	BrCCl <sub>3</sub>	26.71	24.34	2.37		
	CHC1 <sub>3</sub>	0.00	1.76	1.76		
4	NO <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.08	1.76	0.32	15.2	0. 130
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	3.19	0.89	2.30	72.2	
	BrCC1 <sub>3</sub>	26.71	24.08	2.63		
	CHC1 <sub>3</sub>	0.00	2.04	2:04		
5	$NO_{2}(C_{6}H_{4})C_{5}H_{11}$	2.08	1.84	0.24	11.3	0.097
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	3.19	0.68	2.51	78.8	
	BrCCl	26.71	23.59	3.12		
	CHC13	0.00	2.46	2.46		
	Average	<sup>k</sup> ₽-NO <sub>2</sub> k H	$= 0.12 \pm 0$	. 01		

Table 2. Relative rates of disappearance of <u>p</u>-chloroneopentylbenzene and <u>m</u>-trifluoromethylneopentylbenzene in bromotrichloromethane.

> Conditions: 4 hrs. at 70°C. Mmoles  $C_6H_5Cl: 1.11$   $(CF_3) C_6H_4 (C_5H_{11}) - \underline{m}$ -trifluoromethylneopentylbenzene  $ClC_6H_4 (C_5H_{11}) - \underline{p}$ -chloroneopentylbenzene

Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	<sup>k</sup> <u>m</u> -CF <sub>3</sub> <sup>k</sup> p-C1
1	ClC <sub>6</sub> H <sub>4</sub> (C <sub>5</sub> H <sub>11</sub> )	1.85	0.70	1.15	62.2	0.313
	$(CF_{3})C_{6}H_{4}(C_{5}H_{11})$	1.93	1.43	0,60	31.1	
	BrCCl <sub>3</sub>	25.40	24.08	1.32		
	HCC1 <sub>3</sub>	0.00	1.89	1.89		
2	ClC <sub>6</sub> H <sub>4</sub> (C <sub>5</sub> H <sub>11</sub> )	1.85	1.03	0.82	44.3	0.316
	$(CF_{3})C_{6}H_{4}(C_{5}H_{11})$	1,93	1.61	0,32	16.6	
	BrCC1 <sub>3</sub>	25.40	24.39	1.01		
	HCC1 <sub>3</sub>	0.00	1. 12	1.12		
3	$ClC_{6}H_{4}(C_{5}H_{11})$	1.85	1.28	0.57	30.7	0.334
	$(CF_3)C_6H_4(C_5H_{11})$	1,93	1.71	0.22	11.4	
	BrCC1 <sub>3</sub>	25.40	24.61	0,79		
	HCC1 <sub>3</sub>	0.00	0.54	0.54		
4	ClC <sub>6</sub> H <sub>4</sub> (C <sub>5</sub> H <sub>11</sub> )	1,85	1.11	0,74	40.0	0.351
	$(CF_{3})C_{6}H_{4}(C_{5}H_{11})$	1,93	1,61	0, 32	16.6	
	BrCCl <sub>3</sub>	25.40	24.39	1,11		
	HCCl <sub>3</sub>	0.00	0, 83	0.83		
5	ClC <sub>6</sub> H <sub>4</sub> (C <sub>5</sub> H <sub>11</sub> )	1.85	0.54	1,31	70.7	0.343
	(CF <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> (C <sub>5</sub> H <sub>11</sub> )	1.93	1,27	0,66	34.2	
	BrCC1 <sub>3</sub>	25.40	24,62	1.78		
	HCC1 <sub>3</sub>	0.00	2.18	2.18		
	Average	k m-CF <sub>3</sub> k p-Cl	- = 0.33 + 0	0.01		

Table 3. Relative rates of disapperance of neopentylbenzene and  $\underline{m}$ -chloroneopentylbenzene in bromotrichloromethane.

Conditions: 5-1/2 hrs at 70°C. Mmoles  $C_{6}H_{5}Cl$ : 1.64  $C_{6}H_{5}(C_{5}H_{11})$  -- neopentylbenzene  $ClC_{6}H_{4}(C_{5}H_{11})$  -- <u>m</u>-chloroneopentylbenzene

Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	<u>m</u> -Cl k H
$ClC_{6}H_{4}(C_{5}H_{11})$	1.94	1.09	0.85	43.8	0.463
$C_{6}H_{5}(C_{5}H_{11})$	2.04	0. 58	1.46	71.6	
BrCC1 <sub>3</sub>	26.80	24.79	2.01		
HCCI3	0.00	2.13	2.13		
$ClC_{6}H_{4}(C_{5}H_{11})$	1.94	0. 57	1.37	70. 6	0.477
C <sub>6</sub> H <sub>5</sub> (C <sub>5</sub> H <sub>11</sub> )	2.04	0.15	1.89	92.6	
BrCCl <sub>3</sub>	26.80	23.49	3.31		
HCCI <sub>3</sub>	0.00	3,15	3.15		
CIC <sub>6</sub> H <sub>4</sub> (C <sub>5</sub> H <sub>11</sub> )	1.94	1.12	0.82	42.3	0.412
C_H_(C_H_1)	2.04	0. 53	1.51	74.0	
BrCC1 <sub>3</sub>	28.80	24.27	2.53		
нссі3	0.00	2.65	2.65		
$CIC_{6}H_{4}(C_{5}H_{11})$	1.94	0.74	1.20	61.9	0. 448
C <sub>6</sub> H <sub>5</sub> (C <sub>5</sub> H <sub>11</sub> )	2.04	0.24	1.80	88.2	
BrCC1 <sub>3</sub>	26.80	23.48	3.32		
HCC13	0.00	3.48	3.48		
ClC <sub>6</sub> H <sub>4</sub> (C <sub>5</sub> H <sub>11</sub> )	1.94	1.50	0.44	22.6	0.414
C <sub>6</sub> H <sub>5</sub> (C <sub>5</sub> H <sub>11</sub> )	2.04	1.09	0.95	46.5	
BrCC1 <sub>3</sub>	26.80	25.59	1.21		
HCCI <sub>3</sub>	0.00	1.31	1.31		
-	k <u>m</u> -Cl				
Average	k H	$- = 0.44 \pm$	0.03		
	Compound $ClC_{6}H_{4}(C_{5}H_{11})$ $C_{6}H_{5}(C_{5}H_{11})$ $BrCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $C_{6}H_{5}(C_{5}H_{11})$ $BrCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $BrCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $BrCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $BrCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $BrCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $BrCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $BrCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $BrCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $BrCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $BrCCl_{3}$ $HCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $BrCCl_{3}$ $HCCl_{3}$ $ClC_{6}H_{4}(C_{5}H_{11})$ $BrCCl_{3}$ $HCCl_{$	$\begin{array}{c} \mbox{Compound} & \mbox{Mmoles} \\ (initial) \\ \label{eq:compound} & \mbox{Initial} \\ \mbox{Cl}_6^{\rm H}_4^{\rm (C}_5^{\rm H}_{11}) & \mbox{I.94} \\ \mbox{C}_6^{\rm H}_5^{\rm (C}_5^{\rm H}_{11}) & \mbox{I.94} \\ \mbox{BrCCl}_3 & \mbox{0.00} \\ \mbox{Cl}_6^{\rm H}_4^{\rm (C}_5^{\rm H}_{11}) & \mbox{I.94} \\ \mbox{C}_6^{\rm H}_5^{\rm (C}_5^{\rm H}_{11}) & \mbox{I.94} \\ \mbox{C}_{6}^{\rm H}_5^{\rm (C}_5^{\rm H}_{11}) & \mbox{I.94} \\ \mbox{BrCCl}_3 & \mbox{0.00} \\ \mbox{Cl}_6^{\rm H}_4^{\rm (C}_5^{\rm H}_{11}) & \mbox{I.94} \\ \mbox{C}_{6}^{\rm H}_5^{\rm (C}_5^{\rm H}_{11}) & \mbox{I.94} \\ \mbox{C}_{6}^{\rm H}_5^{\rm (C}_5^{\rm H}_{11}) & \mbox{I.94} \\ \mbox{C}_{6}^{\rm H}_5^{\rm (C}_5^{\rm H}_{11}) & \mbox{I.94} \\ \mbox{BrCCl}_3 & \mbox{0.00} \\ \mbox{Cl}_6^{\rm H}_4^{\rm (C}_5^{\rm H}_{11}) & \mbox{I.94} \\ \mbox{BrCCl}_3 & \mbox{0.00} \\ \mbox{Cl}_6^{\rm H}_5^{\rm (C}_5^{\rm H}_{11}) & \mbox{I.94} \\ \mbox{BrCCl}_3 & \mbox{0.00} \\ \mbox{HCCl}_3 & $	$\begin{array}{c c} Compound & Mmoles \\ (initial) & (final) \\ \hline \\ ClC_6H_4(C_5H_{11}) & 1.94 & 1.09 \\ C_6H_5(C_5H_{11}) & 2.04 & 0.58 \\ \hline \\ BrCCl_3 & 26.80 & 24.79 \\ HCCl_3 & 0.00 & 2.13 \\ \hline \\ ClC_6H_4(C_5H_{11}) & 1.94 & 0.57 \\ C_6H_5(C_5H_{11}) & 2.04 & 0.15 \\ \hline \\ BrCCl_3 & 26.80 & 23.49 \\ HCCl_3 & 0.00 & 3.15 \\ \hline \\ ClC_6H_4(C_5H_{11}) & 1.94 & 1.12 \\ C_6H_5(C_5H_{11}) & 2.04 & 0.53 \\ \hline \\ BrCCl_3 & 28.80 & 24.27 \\ HCCl_3 & 0.00 & 2.65 \\ \hline \\ ClC_6H_4(C_5H_{11}) & 1.94 & 0.74 \\ \hline \\ C_6H_5(C_5H_{11}) & 2.04 & 0.24 \\ \hline \\ BrCCl_3 & 26.80 & 23.48 \\ HCCl_3 & 0.00 & 3.48 \\ \hline \\ ClC_6H_4(C_5H_{11}) & 1.94 & 1.50 \\ \hline \\ C_6H_5(C_5H_{11}) & 2.04 & 1.09 \\ \hline \\ BrCCl_3 & 0.00 & 3.48 \\ \hline \\ ClC_6H_4(C_5H_{11}) & 1.94 & 1.50 \\ \hline \\ C_6H_5(C_5H_{11}) & 2.04 & 1.09 \\ \hline \\ BrCCl_3 & 0.00 & 1.31 \\ \hline \\ Average & \frac{k_{m}-Cl}{k_{H}} = 0.44 \pm \frac{k_{m}}{k_{H}} = 0.44 \pm \frac{k_{m}}{k_{H}} \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table 4. Relative rates of disapperance of neopentylbenzene and p-chloroneopentylbenzene in bromotrichloromethane.

Conditions: 4-1/2 hrs. at  $70^{\circ}$ C. Mmoles  $C_{6}H_{5}$ Cl: 0.95  $C_{6}H_{5}(C_{5}H_{11})$  -- neopentylbenzene  $ClC_{5}H_{4}(C_{5}H_{11})$  -- p- chloroneopentylbenzene

Run	Compound	) Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	k p-Cl k H
1	ClC <sub>5</sub> H <sub>4</sub> (C <sub>5</sub> H <sub>11</sub> )	2.51	1.04	1.46	37.1	0.673
	$C_{6}H_{5}(C_{5}H_{11})$	2.32	1.46	0.86	58.4	
	BrCC1 <sub>3</sub>	25.13	20.00	5. 13		
	HCC13	0.00	2.00	2.00		
2	ClC <sub>5</sub> H <sub>4</sub> (C <sub>5</sub> H <sub>11</sub> )	2.51	1.89	0.72	28.7	0.672
	C <sub>6</sub> H <sub>5</sub> (C <sub>5</sub> H <sub>11</sub> )	2.32	1.52	.80	34.5	
	BrCC1 <sub>3</sub>	25.13	20.89 -	4.24		
	HCCI3	0,00	1.26	1.26		
3	ClC5H4(C5H11)	2.51	0. 58	1.93	77.5	0.747
	C <sub>6</sub> H <sub>5</sub> (C <sub>5</sub> H <sub>11</sub> )	2.32	0.43	1.89	81.0	
	BrCCl <sub>3</sub>	25.13	19.21	5.92		
	HCC13	0.00	3.47	3.47		
4	ClC5 <sup>H</sup> 4(C5 <sup>H</sup> 11)	2.51	0.95	1.56	62.2	0.702
	C <sub>6</sub> H <sub>5</sub> (C <sub>5</sub> H <sub>11</sub> )	2.32	0.58	1.74	75.0	
	BrCCI <sub>3</sub>	25.13	20.36	4.77		
	HCC1 <sub>3</sub>	0.00	2.89	2.89		
5	CIC <sub>5</sub> H <sub>4</sub> (C <sub>5</sub> H <sub>11</sub> )	2.51	0.85	1.66	66.1	0.762
	C <sub>6</sub> H <sub>5</sub> (C <sub>5</sub> H <sub>11</sub> )	2.32	0, 59	1.73	74.5	
	BrCC1 <sub>3</sub>	25.13	20.11	5.02		
	HCC1 <sub>3</sub>	0.00	3.11	3.11		
	Average		= 0.71 <u>+</u> (	). 03		

Table 5. Relative rates of disappearance of <u>m</u>-methylneopentylbenzene and neopentylbenzene in bromotrichloromethane.

Conditions: 3 hrs. at  $70^{\circ}$ C. Mmoles  $C_6H_5Cl$ : 1.92  $CH_3(C_6H_4)C_5H_{11} \rightarrow m$  - methylneopentylbenzene  $(C_6H_5)C_5H_{11} \rightarrow neopentylbenzene$ 

_	Compound		Mmoloo Mmolo	_		<sup>k</sup> <u>m</u> -CH <sub>3</sub>	
Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	k H	
1	CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	3.78	1,35	2.43	64.2	5.284	
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.18	1,81	0.37	16.9		
	BrCC1 <sub>3</sub>	25.20	22, 14	3.06			
	CHCI <sub>3</sub>	0.00	2.74	2.74			
2	CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	3.78	2.01	1.77	46.8	5.680	
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.18	2.03	0.15	6,74		
	BrCCl <sub>3</sub>	25.20	23.09	2.11			
	CHCI3	0, 00	1.47	1.47			
3	CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	3,78	1.79	1,99	52.6	4.875	
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2,18	1,91	0,27	12.4		
	BrCC1 <sub>3</sub>	25,20	22.71	2.49			
	CHC13	0,00	2,02	2.02			
4	CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	3.78	1,75	2.03	53,8	4.947	
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.18	1.86	0, 32	14.6		
	BrCC1 <sub>3</sub>	25.20	22.61	2.59			
	CHCI3	0.00	2.16	2.16			
5	CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	3.78	2.05	1.73	45.7	4.553	
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.18	1,94	0.24	11.2		
	BrCC1 <sub>3</sub>	25.20	22.88	2.32			
	СНСІЗ	0,00	1,85	1.85			
	Average	k m-CH <sub>3</sub> k H	- = 4.86 -	0.35			

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Table 6. Relative rates of disapperance of neopentylbenzene and <u>p-t-butylneopentylbenzene</u> in bromotrichloromethane.

Conditions: 4-1/2 hrs. at 70°C. Mmoles  $C_6H_5C1$ : 1.54  $C_6H_5(C_5H_{11})$  -- neopentylbenzene  $(C_4H_9)C_6H_4(C_5H_{11})$  -- <u>p-t</u>-butylneopentylbenzene

Run	Compound	Mmoles	Mmoles	Mmelee	0/	k <b><u>p-t</u>-bu</b>
		(initial)	(final)	(used)	% rxn.	к Н
1	$(C_4H_9)C_6H_4(C_5H_{11})$	2.02	0.61	1.41	65.7	1.11
	C <sub>6</sub> H <sub>5</sub> (C <sub>5</sub> H <sub>11</sub> )	2.14	0.81	1.33	<b>62.</b> 0	
	BrCC1 <sub>3</sub>	25.80	23.29	2.51		
	HCC1 <sub>3</sub>	0,00	2.65	2.65		
2	$({}^{C}_{4}{}^{H}_{9}){}^{C}_{6}{}^{H}_{4}({}^{C}_{5}{}^{H}_{11})$	2.02	1.14	0.88	43.6	1.15
	C <sub>6</sub> <sup>H</sup> 5 <sup>(C</sup> 5 <sup>H</sup> 11)	2.14	1.02	1. 12	52.5	
	BrCC1 <sub>3</sub>	25.80	23.57	2.23		
	HCCI <sub>3</sub>	0.00	2.18	2.18		
3	$({}^{C}{}_{4}{}^{H}{}_{9}){}^{C}{}_{6}{}^{H}{}_{4}({}^{C}{}_{5}{}^{H}{}_{11})$	2.02	1. 07	0.95	47.1	1, 13
	C <sub>6</sub> H <sub>5</sub> (C <sub>5</sub> H <sub>11</sub> )	2.14	1.07	1.07	49.8	
	BrCC1 <sub>3</sub>	25.80	23.79	2.01		
	HCC1 <sub>3</sub>	0.00	2.14	2.14		
4	$({}^{C}_{4}{}^{H}_{9}){}^{C}_{6}{}^{H}_{4}({}^{C}_{5}{}^{H}_{11})$	2.02	0, 86	1.16	57.2	1.14
	C <sub>6</sub> <sup>H</sup> 5(C <sub>5</sub> <sup>H</sup> 11)	2.14	1.00	1. 14	53.4	
	BrCCI <sub>3</sub>	25, 80	23.44	2.36		
	HCC1 <sub>3</sub>	0.00	2.45	2.45		
5	$({}^{C}{}_{4}{}^{H}{}_{9}){}^{C}{}_{6}{}^{H}{}_{4}({}^{C}{}_{5}{}^{H}{}_{11})$	2.02	1.09	0.93	45.8	1.07
	°6 <sup>H</sup> 5 <sup>(°5<sup>H</sup>11)</sup>	2.14	0.97	1.17	54.6	
	BrCCl <sub>3</sub>	25.80	23.87	1.93		
	HCC1 3	0,00	1.99	1.99		
	Average	k <u>p-t</u> -bu k H	- = 1.12	+ 0.02		

 Table 7. Relative rates of disapperance of p-methylneopentylbenzene and: neopentylbenzene in bromotrichloromethane.

Conditions:

Mmoles  $C_6H_5Cl$ : 1.51  $CH_3(C_6H_4)C_5H_{11} \rightarrow p-methylneopentylbenzene$  $(C_6H_5)C_5H_{11} \rightarrow neopentylbenzene$ 

Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	<mark>к</mark> Н
1	CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	3.96	1.37	2.59	65.4	8.513
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	1.84	1.63	0.21	11.4	
	BrCC1	25.27	22.26	3.01		
	CHC13	0.00	2.54	2.54		
2	CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	3.96	1.43	2.53	63.9	9.854
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	1.84	1.66	0.18	9.78	
	BrCCl <sub>3</sub>	25.27	22.13	3. 14		
	CHCl <sub>3</sub>	0.00	2.51	2.51		
3	CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	3,96	1.08	2.88	72.7	9.223
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	1.84	1.59	0,25	13.6	
	BrCC1	25.27	21.97	3.30		
	CHC13	0.00	2.97	2.97		
4	CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	3.96	1.08	2,88	72.7	9.241
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	1.84	1.60	0.24	13.0	
	BrCC1 <sub>3</sub>	25.27	21.79	3.48		
	CHCI3	0.00	3.03	3.03		
	Average	<mark>k</mark>	- = 9.20	<u>+</u> 0. 48		

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Table 8. Relative rates of disappearance of p-methoxyneopentylbenzene and neopentylbenzene in<br/>bromotrichloromethane. Run A.

Conditions: 2-1/2 hrs. at  $70^{\circ}$ C. Mmoles  $C_6^{H} Cl: 1.76$   $CH_3^{O}(C_6^{H} A)C_5^{H} - p$ -methoxyneopentylbenzene  $(C_6^{H} 5)C_5^{H} 11$  -- neopentylbenzene

				Mmoles		<sup>k</sup> р-СН <sub>3</sub> О	
Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	k <sub>H</sub>	
1	CH <sub>3</sub> Q(C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.34	1.96	0.38	16.3	3.30	
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.73	2.67	0.06	2.33		
	BrCCl <sub>3</sub>	24.70	24.16	0.54			
	CHC13	0.0	0,23	0.23			
2	CH <sub>3</sub> O(C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.34	1.05	1.29	55.1	3.97	
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.73	2.13	0.60	21.9		
	BrCCl <sub>3</sub>	24.70	22.63	2.07			
	CHC1 <sub>3</sub>	0.00	1.78	1.78			
3	сн <sub>3</sub> 0(с <sub>6</sub> н <sub>4</sub> )с <sub>5</sub> н <sub>11</sub>	2.34	1.53	0.81	34.7	3.23	
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.73	2.44	0.29	10.7		
	BrCC1 <sub>3</sub>	24.70	23.48	1.22			
	CHCl <sub>3</sub>	0.00	0, 79	0.79			
4	CH <sub>3</sub> O(C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.34	0.76	1.58	67.4	4.13	
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.73	2.31	0.42	15.3		
	BrCC1 <sub>3</sub>	24.70	27.57	2.13			
	CHC1 <sub>3</sub>	0.00	1.86	1.86			
5	CH <sub>3</sub> Q(C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.34	1,30	1.04	<b>44.4</b>	3.49	
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.73	2.38	0.35	13.0		
	BrCC1 <sub>3</sub>	24.70	23.21	1.49			
	CHC13	0.00	1.32	1.32			

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Table 9. Relative rates of disapperance of p-methoxyneopentylbenzene and neopentylbenzene in<br/>bromotrichloromethane. Run B.

Conditions: 2 hrs at  $70^{\circ}$ C. Mmoles  $C_6H_5Cl$ : 2.35  $CH_3O(C_6H_4)C_5H_{11} \rightarrow p-$  methoxyneopentylbenzene  $(C_6H_5)C_5H_{11} \rightarrow neopentylbenzene$ 

Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	к
1	CH <sub>3</sub> Q(C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.52	0. 54	1,98	78.6	3.08
	$(C_{6}^{H})C_{5}^{H}$	2.45	1.54	0.91	37.1	
	BrCC1 <sub>3</sub>	26.20	27.77	3,43		
	снсіз	0.00	2.77	2.77		
2	CH <sub>3</sub> O(C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.52	2.01	0.51	20.1	3.45
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.45	2.37	0.08	3.10	
	BrCCl <sub>3</sub>	26.20	25.52	0.48		
	СНСІ3	0,00	0.53	0.53		
	Average	-	$\frac{{}^{k}_{p}-CH_{3}O}{{}^{k}_{H}} =$	3.52 ± 0.29	(Run A + R	un B)

Table 10. Relative rates of disappearance of toluene and neopentylbenzene in bromotrichloromethane. Conditions: 3 hrs. at 70°C.

Mmoles  $C_{6}H_{5}Cl$ : 1.56  $C_{6}H_{5}(CH_{3})$  -- toluene  $C_{6}H_{5}(C_{5}H_{11})$  -- neopentylbenzene

Run	Compound	Mmoles	<b>Mmoles</b>	Mmoles	% rxn.	H
- <u>-</u>		(initial)	(final)	(used)		-CH <sub>3</sub>
1	C_H_(CH_3)	2.14	1.03	1.11	51.9	0.294
	C <sub>6</sub> H <sub>5</sub> (C <sub>5</sub> H <sub>11</sub> )	2,03	1.64	0.39	19.2	
	BrCC1 <sub>3</sub>	26.13	24.59	1.54		
	нссі	0.00	1.47	1.47		
2	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )	2.14	0. 19	1.95	91.1	0.231
	$C_{6}^{H} C_{5}^{(C_{11})}$	2.03	1.16	0.97	47.8	
	BrCC1 <sub>3</sub>	26.13	23.39	2.74		
	HCC1 <sub>3</sub>	0.00	3.15	3.15		
3	C_H_(CH_3)	2.14	0.91	1.23	57.5	0. 179
	C <sub>6</sub> H <sub>5</sub> (C <sub>5</sub> H <sub>11</sub> )	2.03	1.81	0.22	12.3	
	BrCC1 <sub>3</sub>	26.13	24.58	1.55		
	HCC1 <sub>3</sub>	0.00	1.40	1.40		
4	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )	2.14	0.07	2.07	96.7	0.285
	$C_{6}^{H} (C_{5}^{H} (11))$	2,03	0.77	1.26	62.1	
	BrCC1 <sub>3</sub>	26.13	21.61	4.52		
	HCC13	0.00	3.85	3.85		
	Average	<u>– H</u> – CH <sub>3</sub>	- = 0.27	<u>+</u> 0.03		

Table 11. Relative rates of disapperance of <u>p</u>- nitroneopentylbenzene and neopentylbenzene with Nbromosuccinimide.

> Conditions: 45 min. at  $70^{\circ}$ C. Mmoles C<sub>6</sub>H<sub>5</sub>Cl: 2.48 Mmoles N-bromosuccinimide: 1.97 NO (C H )C H

 $NO_2(C_6H_4)C_5H_{11} - p$ - nitroneopentylbenzene  $(C_6H_5)C_5H_{11}$  -- neopentylbenzene

Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	<sup>k</sup> p- NO <sub>2</sub> k
1	NO <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub> (C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	1.78 3.42	1. 59 2. 18	0. 19 1. 24	10.6 36.4	0.251
2	<sup>NO</sup> 2 <sup>(C6H4)C5H11</sup> (C6H5)C5H11	1.78 3.42	1.54 1.95	0.24 1.47	13.5 42.9	0.244
3	${}^{NO}_{2}({}^{C}_{6}{}^{H}_{4}){}^{C}_{5}{}^{H}_{11}$	1.78 3.42	1,61 2,30	0.17 1.10	9.60 32.1	0.250
4	${}^{NO_2(C_6H_4)C_5H_{11}} (C_6H_5)C_5H_{11}$	1.78 3.42	1,51 1,86	0.27 1.56	15.4 45.7	0.265
	Average	<sup>k</sup> p-NO <sub>2</sub> k H	- = 0.25	+ 0.01		

Table 12. Relative rates of disapperance of  $\underline{m}$  - trifluoromethylneopentylbenzene and  $\underline{p}$  - chloroneopentylbenzene with N-bromosuccinimide.

> Conditions: 1-1/2 hrs. at 70°C. Mmoles  $C_6H_5Cl$ : 2.49 Mmoles N-Bromosuccinimide: 1.97  $CF_3(C_6H_4)C_5H_{11} - \underline{m}$  -trifluoromethylneopentylbenzene  $Cl(C_6H_4)C_5H_{11} - \underline{p}$ -chloroneopentylbenzene

Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	k p-CF3 k p-C1
1	CF <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.09	1.08	1.01	48.5	0.405
	C1(C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	1.93	0.37	1.56	81.0	
2	CF <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.09	1, 15	0.94	44.8	0.388
	C1(C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	1.93	0.43	1.50	77.6	
3	CF <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.09	1.08	1.01	48.5	0, 381
	CI (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	1.93	0.33	1.60	32.8	
4	CF <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.09	0.98	1.11	53.0	0.414
	Cl (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	1.93	0.32	1.61	83.6	
	Average	<u>k</u> CF <sub>3</sub> k	- = 0.40	<u>+</u> 0.01		

Table 13. Relative rates of disapperance of <u>m</u>-chloroneopentylbenzene and neopentylbenzene with N-bromosuccinimide.

Conditions: 40 min. at  $70^{\circ}$ C. Mmoles C<sub>6</sub>H<sub>5</sub>Cl: 1.52 Mmoles N-bromosuccinimide: 2.08 Cl (C<sub>6</sub>H<sub>4</sub>)C<sub>5</sub>H<sub>11</sub> -- <u>m</u>-chloroneopentylbenzene (C<sub>6</sub>H<sub>5</sub>)C<sub>5</sub>H<sub>11</sub> -- neopentylbenzene

Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	km-Cl kH
1	Cl (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.18	1.72	0,46	21.0	0, 361
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.10	1.07	1.03	49.0	
2	Cl (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.18	1.74	0.44	20.0	0.337
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.10	1.07	1.03	49.0	
3	Cl (C6H4)C5H11	2.18	1.84	0.34	15.0	0.227
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.10	1.28	0.82	39.1	
4	Cl (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.18	1,53	0.65	30.0	0.389
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.10	0, 87	1.23	58.7	
5	Cl (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	2.18	1.57	0,61	28.0	0.352
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.10	0.98	1.12	53.3	
	Average	k H H	= 0.34 .±	0. 03		
Table 14. Relative rates of disappearance of <u>p</u>-chloroneopentylbenzene and neopentylbenzene with N-bromosuccinimide.

Conditions: 40 min. at 70°C. Mmoles  $C_{6}H_{5}Cl$ : 2.84 Mmoles N-bromosuccinimide: 2.13  $Cl(C_{6}H_{4})C_{5}H_{11} - p$  - chloroneopentylbenzene  $(C_{6}H_{5})C_{5}H_{11}$  -- neopentylbenzene

Run	Compound	Mmoles	Mmoles	Mmóles	% rvn	<sup>k</sup> <u>p</u> -Cl
	pound	(initial)	(final)	(used)	<i>7</i> 0 TXII.	H H
1	Cl (C H )C H 5 11	1.97	1.32	0.65	33.0	0.734
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.10	0.88	1.22	58.0	
2	Cl (C H <sub>6</sub> H)C H <sub>11</sub>	1.97	1.18	0.79	40.2	0, 780
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.10	1.09	1.01	48.0	
3	Cl (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	1.97	1.71	0.26	13.4	0.755
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.10	1.72	0.38	18.0	
4	Cl (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	1.97	1.26	0.71	36.0	0.714
	(C <sub>6</sub> <sup>H</sup> 5)C <sub>5</sub> <sup>H</sup> 11	2.10	1, 13	0.97	46.0	
5	Cl (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	1.97	1.73	0.24	12.4	0.713
	(C <sub>6</sub> <sup>H</sup> 5)C <sub>5</sub> <sup>H</sup> 11	2.10	1.74	0.36	17.0	
	Average	kp-Cl k H	= 0.75 <u>+</u>	0. 03		

Table 15. Relative rates of disappearance of <u>m</u>-methylneopentylbenzene and neopentylbenzene with N-bromosuccinimide.

Conditions: 1 hr. at 70°C.

Mmoles C<sub>6</sub>H<sub>5</sub>Cl: 2.37

Mmoles N-bromosuccinimide: 2.02

 $CH_3(C_6H_4)C_5H_{11} - \underline{m}$ -methylneopentylbenzene  $(C_6H_5)C_5H_{11} - neopentylbenzene$ 

Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	<u><u>m</u>-CH<sub>3</sub> <u>k</u> H</u>
1	<sup>CH</sup> <sub>3</sub> (C <sub>6</sub> <sup>H</sup> <sub>4</sub> )C <sub>5</sub> <sup>H</sup> <sub>11</sub> (C <sub>6</sub> <sup>H</sup> <sub>5</sub> )C <sub>5</sub> <sup>H</sup> <sub>11</sub>	4.48 2.01	2.26 1.06	1.82 0.35	40.6 17.4	3.42
2	<sup>CH</sup> <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub> (C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	4.48 2.01	2.47 1.59	2.01 0.42	48.8 20.7	2.85
3	<sup>CH</sup> <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub> (C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	4.48 2.01	2.89 1.76	1.59 0.25	35.5 12.4	2.91
4	CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub> (C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	4.48 2.01	2.78 1.76	1.70 0.25	37.9 12.4	3.37
	Average	<sup>k</sup> <u>m</u> -СН <sub>3</sub> к	- = 3.14	<u>+</u> 0.28		

Table 16. Relative rates of disappearance of <u>p-t-butylneopentylbenzene</u> and neopentylbenzene with N-bromosuccinimide.

Conditions: 1 hr. at  $70^{\circ}$ C. Mmoles  $C_6H_5CI$ : 2.05 Mmoles N-bromosuccinimide: 2.08  $C_4H_9(C_6H_4)C_5H_{11} - p-t-butylneopentylbenzene$  $(C_6H_5)C_5H_{11} - neopentylbenzene$ 

Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	k <u>p-t</u> -bu k H
1	C_H_(C_H_)C_H_1	1.98	1.09	0.89	44.7	1.62
	$(C_{6}^{H}_{5})C_{5}^{H}_{11}$	2.32	1.61	0.71	30.6	
2	C <sub>4</sub> H <sub>0</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	1.98	0.70	1.28	64.8	1.50
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.32	1,15	1, 17	50.6	
3	C <sub>4</sub> H <sub>0</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	1,98	0.66	1.32	66.7	1.52
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.32	1.20	1.12	48.2	7
4	C <sub>4</sub> H <sub>0</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	1.98	1.15	0.83	42.1	1.47
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.32	1.60	0.72	31.2	
5	$C_{A}H_{9}(C_{6}H_{4})C_{5}H_{11}$	1.98	0.77	1.21	61.0	1.44
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.32	1.06	1.26	54.1	
		k p-t-bu				

Average  $\frac{p-t-bu}{k} = 1.51 \pm 0.05$ 

Table 17. Relative rates of disappearance of <u>p</u>-methylneopentylbenzene and neopentylbenzene with N-bromosuccinimide.

Conditions: 1 hr., 25 min. at  $70^{\circ}$ C.

Mmoles C<sub>6</sub>H<sub>5</sub>Cl: 3.21

Mmoles N-bromosuccinimide: 2.53

 $CH_{3}(C_{6}H_{4})C_{5}H_{11}$  -- <u>p</u>-methylneopentylbenzene

 $(C_{6}H_{5})C_{5}H_{11}$  -- neopentylbenzene

Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	<sup>k</sup> <u>р</u> -СН <sub>3</sub> k H
1	<sup>CH</sup> <sub>3</sub> (C <sub>6</sub> <sup>H</sup> <sub>4</sub> )C <sub>5</sub> <sup>H</sup> <sub>11</sub> (C <sub>6</sub> <sup>H</sup> <sub>5</sub> )C <sub>5</sub> <sup>H</sup> <sub>11</sub>	2.89 1.93	0.99 1.63	1.90 0.30	65.9 15.7	4. 29
2	CH <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub> (C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.89 1.93	0.85 1.63	2.04 0.30	70.5 15.7	3.97
3	<sup>CH</sup> <sub>3</sub> (C <sub>6</sub> <sup>H</sup> <sub>4</sub> )C <sub>5</sub> <sup>H</sup> <sub>11</sub> (C <sub>6</sub> <sup>H</sup> <sub>5</sub> )C <sub>5</sub> <sup>H</sup> <sub>11</sub>	2.89 1.93	0. 39 1. 14	2.50 0.79	86.4 41.0	3.81
4	$CH_3(C_6H_4)C_5H_{11}$ $(C_6H_5)C_5H_{11}$	2.89 1.93	1.04 1.53	1.85 0.40	63.9 20.5	4.59
5	$^{\text{CH}}_{3}({}^{\text{C}}_{6}{}^{\text{H}}_{4}){}^{\text{C}}_{5}{}^{\text{H}}_{11}$ $({}^{\text{C}}_{6}{}^{\text{H}}_{5}){}^{\text{C}}_{5}{}^{\text{H}}_{11}$	2.89 1.93	1.26 1.56	1.63 0.37	56.4 19.3	3.89
6	<sup>сн</sup> <sub>3</sub> (с <sub>6</sub> <sup>н</sup> <sub>4</sub> )с <sub>5</sub> <sup>н</sup> <sub>11</sub> (с <sub>6</sub> <sup>н</sup> <sub>5</sub> )с <sub>5</sub> <sup>н</sup> <sub>11</sub>	2.89 1.93	0.63 1.35	2.26 0.58	78.2 30.1	3.78
	Average	<mark>е-сн</mark> 3	= 4.10 +	0.26		

 Table 18. Relative rates of disappearance of <u>p</u>-methoxyneopentylbenzene and neopentylbenzene with N-bromosuccinimide.

Conditions: 1/2 hr. at  $70^{\circ}$ C. Mmoles  $C_6H_5$ Cl: 1.40 Mmoles N-bromosuccinimide: 2.02  $CH_3Q(C_6H_4)C_5H_{11} - p$ -methoxyneopentylbenzene  $(C_6H_5)C_5H_{11}$  -- neopentylbenzene

Run	Compound	Mmoles	Mmoles	Mmoles	% rxn.	<sup>k</sup> р-СН <sub>3</sub> О
		(initial)	(final)	(used)		<sup>к</sup> н
1	CH <sub>3</sub> O(C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	0.97	0.39	0.58	59.7	3.40
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	1.09	0.86	0.23	21.1	
2	CH <sub>3</sub> O (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	0.97	0. 50	0.47	48.3	3.27
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	1.09	0.91	0.18	16.5	
3	CH30 (C6H4)C5H11	0.97	0.47	0.50	51.5	2.84
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	1.09	0.87	0.22	20.2	
4	CH <sub>3</sub> O (C <sub>6</sub> H <sub>4</sub> )C <sub>5</sub> H <sub>11</sub>	0.97	0.37	0.60	61.8	<b>2.</b> 97
	(C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	1.09	0, 83	0.26	23.9	
5	CH_0 (C_H_)C_H	0.97	0.30	0.67	69.0	3.32
	$(C_{6}^{H} + 5)C_{5}^{H} + 11$	1,09	0.80	0.29	27.5	
	Average	<sup>k</sup> р-СН <sub>3</sub> О- к <sub>Н</sub>	= 3.16	<u>+</u> 0.17		

Table 19. Relative rates of disappearance of toluene and neopentylbenzene with N-bromosuccinimide.

> Conditions: 25 min. at  $70^{\circ}$ C. Mmoles C<sub>6</sub>H<sub>5</sub>Cl: 2.60 Mmoles N-bromosuccinimide: 2.02 C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> -- toluene (C<sub>6</sub>H<sub>5</sub>)C<sub>5</sub>H<sub>11</sub> -- neopentylbenzene

Run	Compound	Mmoles (initial)	Mmoles (final)	Mmoles (used)	% rxn.	<sup>k</sup> H <sup>k</sup> -СН <sub>3</sub>
1	<sup>С</sup> <sub>6</sub> <sup>Н</sup> 5 <sup>СН</sup> 3 (С <sub>6</sub> <sup>Н</sup> 5)С5 <sup>Н</sup> 11	2.03 2.04	1.12 1.57	0.91 0.47	44.7 22.9	0.452
2	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.03 2.0 <del>4</del>	0.89 1.36	1.14 0.68	56.3 33.5	0 <b>. 4</b> 90
3	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>11</sub>	2.03 2.04	1.26 1.64	0.77 0.40	37.9 19.4	0. 461
4	$C_{6}^{H_{5}}CH_{3}$ $(C_{6}^{H_{5}})C_{5}^{H_{11}}$	2.03 2.0 <del>4</del>	1.28 1.68	0.75 0.36	36.8 17.6	0.427

Average 
$$\frac{\frac{k}{H}}{\frac{k}{-CH}} = 0.46 \pm 0.02$$